

# Advanced Optical Spectroscopies in Paris-Saclay

## Probing dynamics and conformation

### Orsay, November 29-30<sup>th</sup> 2017

		WEDNESDAY November 29th	THURSDAY November 30th		
		09:00-09:15	BREAKFAST	09:00-09:15	
S1: Biomolecules		09:15-09:35	OPENING: Pascale CHANGENET-BARRET (LOB)	09:15-09:45	S5: Theory
		09:35-10:20	KEYNOTE: Rien van GRONDELLE (VU University Amsterdam)	09:45-10:05	
		10:20-10:50	INVITED: Pavel MULLER (I2BC)	10:05-10:25	S6: Fluo
		10:50-11:10	Lipsa NAG (LOB)	10:25-10:50	
		11:10-11:30	MORNING BREAK	10:50-11:10	
S2: Chirality 1		11:30-12:15	KEYNOTE: Thomas BAUMERT (Kassel University)	11:30-12:15	S7: Chirality 2
		12:15-12:45	INVITED: François HACHE (LOB)	12:15-12:45	
		12:45-13:05	Lara MARTINEZ (University of Napoli)	12:45-13:05	
		13:05-13:25	Frédéric GOBEAUX (LIONS/NIMBE)	13:05-13:25	
		13:25 - 14:35	LUNCH  Buffet at Bures University Restaurant	13:25 - 14:35	
S3: Fs spectro		14:35-15:20	KEYNOTE: Tobias BRIXNER (University of Wurzburg)	14:35-15:20	S8: VIS FWM
		15:20-15:40	Johanna BRAZARD (IPCMS)	15:20-15:40	
		15:40-16:00	AFTERNOON BREAK	15:40-16:00	
S4: Proteins		16:00-16:30	INVITED: Michel NEGRERIE (LOB)	16:00-16:30	S9: IR FWM
		16:30-17:00	INVITED: Frank WIEN (SOLEIL)	16:30-16:50	
		17:00 - 18:30	POSTER SESSION & COCKTAIL	16:50-17:00	
			CLOSING: Thomas GUSTAVSSON (LIDYL)		

**ORGANIZING COMMITTEE:** Elsa CASSETTE (LIDYL, chair), Pascale CHANGENET-BARRET (LOB, chair); Laura BACIOU (LCP), Thomas GUSTAVSSON (LIDYL), Manuel JOFFRE (LOB), Sylvie JUBERA (LIDYL, website), Aurélien de la LANDE (LCP), David LAUVERGNAT (LCP), Laurent NAHON (Soleil), Robert PANSU (ENS Paris-Saclay), Lionel POISSON (LIDYL), Bruno ROBERT (SB2SM), Anne ZEHNACKER-RENTIEN (ISMO)

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# Site Map

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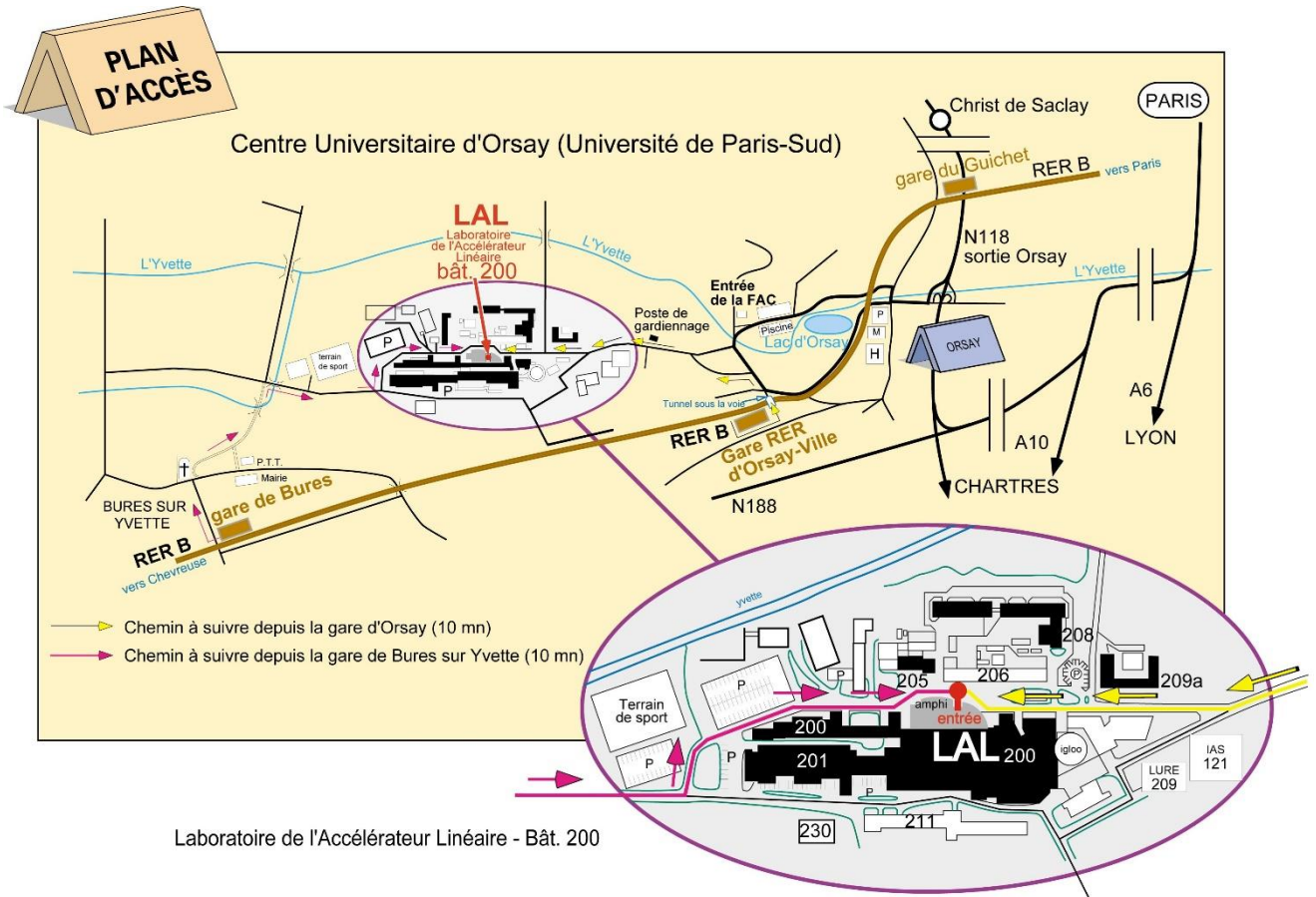
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*Stop: Orsay-ville*



# Wednesday, November 29th, 2017

**9h15-9h35** : *Opening: Pascale Changenet-Barret et Thomas Gustavsson*

**9h35-11h10**: *Biomolecules, chairman Bruno Robert*

9h35-10h20: *Rienk van Grondelle*

10h20-10h50: *Pavel Muller*

10h50-11h10: *Lipsa Nag*

**11h10-11h30**: *Coffee break*

**11h30-13h25**: *Chirality, chairwoman Anne Zehnacker Rentien*

11h30-12h15: *Thomas Baumert*

12h15-12h45: *François Hache*

12h45-13h05 : *Lara Martinez*

13h05-13h25 : *Frédéric Gobeaux*

**13h25-14h35**: *Lunch at Bures University Restaurant*

**14h35-15h40**: *Femtosecond Spectroscopy, chairwoman Elsa Cassette*

14h35-15h20: *Tobias Brixner*

15h20-15h40: *Johanna Brazard*

**15h40-16h00**: *Coffee break*

**16h00-17h00**: *Proteins, chairwoman Laura Baciou*

16h00-16h30: *Michel Négrerie*

16h30-17h00: *Frank Wien*

**17h00-18h30**: *Poster Session and Cocktail*

# **Keynote lecture**

**Rienk van Grondelle**

## Invited lecture:

# “Classical” Transient Absorption Spectroscopy Extended to Sub-nanosecond Timescales

*Pavel MÜLLER & Klaus BRETTEL*

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Transient Absorption Spectroscopy (TAS) is a powerful tool to study dynamics of photoreactions on time scales ranging from femtoseconds to seconds. Typically, processes slower than ~10 nanoseconds are probed by a “classical” method but processes on the femto- and picosecond timescales have to be examined by more sophisticated “pump-probe” techniques. The major shortcoming of the pump-probe techniques is their poor signal-to-noise ratio. In order to extract reaction kinetics, high sample concentrations and extensive signal averaging (typically >10<sup>5</sup> laser shots) are required. Indeed, the latter can lead to deterioration of sensitive samples and the situation becomes even more complicated when the photoreaction of interest is an irreversible process with high yield, in which case the problems can only be overcome by using immense sample volumes. Remarkably, some biologically relevant processes are indeed irreversible, have high quantum yields and occur on a picosecond timescale, which is not accessible to commercial classical TAS setups. It was therefore desirable to extend the time window of the more sensitive and less invasive classical technique to shorter timescales.

Our group has developed a real-time transient absorption setup with ~300 ps time resolution and high sensitivity.<sup>[1]</sup> The improved time resolution is assured by a detection system based on a photodiode with 200 ps rise time, and low-noise sources of monitoring light: cw-lasers with stable outputs at 15 discrete wavelengths in the visible, as well as in near UV and near IR regions. The setup can resolve absorption changes as small as a few mOD in a single-flash experiment. Sensitive samples are protected against excessive monitoring light by a combined system of shutters, attenuation filters and a beam chopper.

Using this setup, we could for instance resolve the kinetics of light-induced splitting of the cyclobutane pyrimidine dimer (CPD) catalyzed by a class I DNA photolyase<sup>[2]</sup> or an unusually fast deprotonation of a tryptophan cation radical during photoactivation of a class II DNA photolyase (*under review*), which are both processes occurring within a few hundreds of picoseconds. We have used our TAS setup also for elucidation of photoactivation of a plant photoreceptor cryptochrome,<sup>[3]</sup> of a bacterial CPD class I photolyase<sup>[4]</sup> or of an animal (6-4)photolyase<sup>[5]</sup> (repairing pyrimidine(6-4)pyrimidone lesions in DNA). Most recently, we have used it to clarify the mechanism of light-induced production of alkanes/-enes from fatty acids by a newly discovered enzyme called *Fatty Acid Photodecarboxylase*<sup>[6]</sup> (decarboxylation of the fatty acid occurs in ~300 ps).

- [1] M. Byrdin, V. Thiagarajan, S. Villette, A. Espagne, K. Brettel, *Rev. Sci. Instrum.* **2009**, *80*, 043102.
- [2] V. Thiagarajan, M. Byrdin, A. P. M. Eker, P. Müller, K. Brettel, *Proc. Natl. Acad. Sci. USA* **2011**, *108*, 9402-9407.
- [3] P. Müller, J.-P. Bouly, K. Hitomi, V. Balland, E. D. Getzoff, T. Ritz, K. Brettel, *Sci. Rep.* **2014**, *4*, 5175.
- [4] P. Müller, K. Brettel, L. Grama, M. Nyitrai, A. Lukacs, *Chem. Phys. Chem.* **2016**, *17*, 1329-1340.
- [5] P. Müller, J. Yamamoto, R. Martin, S. Iwai, K. Brettel, *Chem. Commun.* **2015**, *51*, 15502-15505.
- [6] D. Sorigué, B. Légeret, S. Cuiñé, S. Blangy, S. Moulin, E. Billon, P. Richaud, S. Brugière, Y. Couté, D. Nurizzo, P. Müller, K. Brettel, D. Pignol, P. Arnoux, Y. Li-Beisson, G. Peltier, F. Beisson, *Science* **2017**, *357*, 903-907.

# Oral Communication:

## Ultrafast Electron Transfer and Identification of the TyrOH<sup>•+</sup> Radical Cation in the Flavoenzyme TrmFO

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Charge transfer reactions are ubiquitous in protein biochemistry and lie at the core of understanding functional dynamics of proteins. In most cases, they involve the participation of specialized cofactor molecules within the protein. However, in numerous cases the amino acid residues, which make up the protein structure, have also been shown to be involved in forming reaction intermediates— particularly the residues of tyrosine (TyrOH) and tryptophan (TrpH). In order to fully comprehend charge transfer reactions, it is imperative to be able to identify the short-lived intermediates involving the amino acid residues formed as a result.

So far tryptophanyl radicals had been observed both in their protonated cation form (TrpH<sup>•+</sup>) and in their unprotonated neutral form (Trp<sup>•</sup>)<sup>1</sup>. However, tyrosyl radicals had only been observed in their unprotonated (TyrO<sup>•</sup>)<sup>2</sup> form as its protonated form, presumably highly unstable due to the extremely low pKa, remained unseen.

In flavoproteins, photoreduction of excited flavin by electron transfer from nearby tyrosine or tryptophan residues is an efficient fluorescence quenching mechanism. The flavoprotein TrmFO is found in many bacteria: it is implicated in the post-transcriptional formation of m5U54 in tRNAs and is required for structural stabilization of these crucial RNA molecules. In our studies, we used a genetically modified form of TrmFO as a suitable model system to characterize for the first time the protonated tyrosyl radical TyrOH<sup>•+</sup> through ultrafast fluorescence and absorption spectroscopies. It is seen to have a distinct visible absorption band, forming in ~1 ps and decaying in ~3 ps.

Our results<sup>3</sup> have made it possible to disentangle photoproduct states in flavoproteins complex situations which are often encountered. Moreover, they imply that TyrOH oxidation does not necessarily induce its concerted deprotonation. The results will be universally important for understanding redox chains relying on tyrosyl intermediates.

1. Aubert, C., Mathis, P., Eker, A. P. & Brettel, K. Intraprotein electron transfer between tyrosine and tryptophan in DNA photolyase from *Anacystis nidulans*. *Proc. Natl. Acad. Sci.* 96, 5423–5427 (1999).
2. Gräslund, A., Sahlin, M. & Sjöberg, B.-M. The tyrosyl free radical in ribonucleotide reductase. *Environ. Health Perspect.* 64, 139 (1985).
3. Nag, L., Sournia, P., Myllykallio, H., Liebl, U. & Vos, M. H. Identification of the TyrOH<sup>•+</sup> Radical Cation in the Flavoenzyme TrmFO. *J. Am. Chem. Soc.* 139, 11500–11505 (2017).



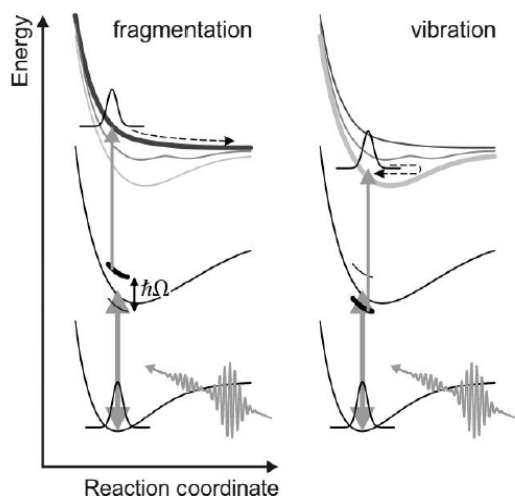
# Keynote Lecture:

## Coherent control of bound electrons in molecules and ionization of chiral molecules with femtosecond techniques

Thomas Baumert

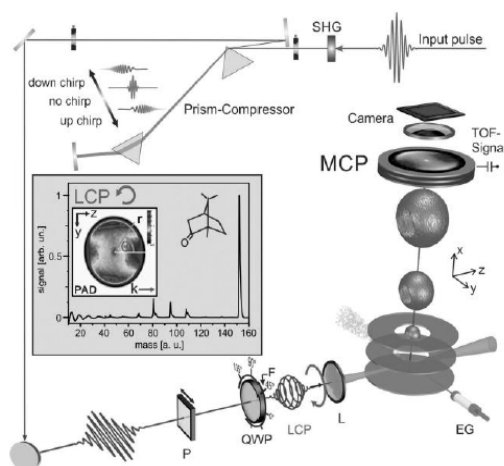
Institut für Physik and CINSaT, Universität Kassel, Heinrich-Plett-Str. 40, 34132 Kassel, Germany

Two current gas phase experiments from our laboratories will be addressed:



i) The direct manipulation of charge oscillations has emerged as a new perspective in chemical reaction control. We demonstrate that the electron dynamics of a molecule is efficiently steered by controlling the interplay of a driving femtosecond laser pulse with the photoinduced charge oscillation. These oscillations have a typical Bohr period of around 1 fs for valence electrons; therefore, control has to be exerted on a shorter time scale. Specifically, we show how precision pulse shaping is used to manipulate the coupled electron and nuclear dynamics in order to address different bound electronic target states in a molecule. We present a strong-field coherent control mechanism which is understood in terms of a simple classical picture and at the same time verified by solving the time-dependent Schrödinger equation. This mechanism is universally applicable and opens a wide spectrum of applications in the reaction control of complex systems.

see for example our recent review: "Ultrafast and Efficient Control of Coherent Electron Dynamics via SPODS" T. Bayer, M. Wollenhaupt, H. Braum and T. Baumert; *Advances in Chemical Physics*, Editors: P. Brumer, S. A. Rice and A. R. Dinner, John Wiley & Sons, Inc., 2016, Chapter 6, 235 - 282 (and references therein)



ii) The photo electron circular dichroism (PECD) is a striking forward / backward electron emission with respect to the light propagation of a light beam ionizing randomly oriented chiral molecules. We extended PECD to the resonance enhanced multi photon ionization (REMPI) regime with femtosecond laser pulses and studied PECD as a function of absorbed photons, intensity and excitation wavelength. As the effect is in the ten percent regime, sub one percent sensitivity to enantiomeric excess was demonstrated. The PECD sensitivity should allow to study and control the coupled electron nuclear motion in chiral potentials.

see for example our latest publication: "Intermediate state dependence of the photoelectron circular dichroism of fenchone observed via femtosecond resonance-enhanced multi-photon ionization" A. Kastner, T. Ring, B. C. Krüger, G. Barratt Park, T. Schäfer, A. Senftleben and T. Baumert; *The Journal of Chemical Physics*, 2017, 147, 013926 (9 pp) (and references therein)

# Invited Lecture:

## Multiscale conformational dynamics probed by time-resolved circular dichroism

Marco Schmid, Pascale Changenet-Barret, François Hache  
*Laboratoire d'Optique et Biosciences*  
*Ecole polytechnique, CNRS, INSERM, Université Paris-Saclay*  
*francois.hache@polytechnique.edu*

Conformation changes are of paramount importance in many chemical or biological processes and it is important to be able to follow their dynamics. These changes can be very local ones or concern the collective behavior of many atoms. The relevant timescales can therefore span several order of magnitudes, from picoseconds to seconds. In order to address these questions, we have devised complementary set-ups to measure time-resolved absorption and circular dichroism (CD) in the ultraviolet. A first one based on a sub-picosecond pump-probe experiment is applied to the study of internal molecular motion after photoexcitation in binaphthol derivatives. We observe a picosecond dynamics that we attribute to the change of the dihedral angle. A comparison of several derivatives allows us to emphasize the crucial role of the hydrogen bond in this dynamics. A second experimental set-up combining cw CD detection with a T-jump experiment allows us to investigate the folding/unfolding dynamics of DNA G-quadruplexes on millisecond timescales, providing new information on the energy landscape involved in the process.

*Time-resolved circular dichroism : what can we learn on conformational changes ?*  
F. Hache, Display and Imaging **3-4**, 197-209 (2015).

*Application of time-resolved circular dichroism to the study of conformational changes in photochemical and photobiological processes (Invited feature article)*  
F. Hache, J. Photochem. Photobiol. A **204**, 137 (2009)

*Measurement of circular dichroism dynamics in a nanosecond temperature-jump experiment*  
M. T. Khuc, L. Mendonça, S. Sharma, X. Solinas, M. Volk and F. Hache, Rev. Sci. Instrum. **82**, 054302 (8p) (2011).

# Oral Communication:

## Computed spectral properties as a tool for characterization of DNA's photophysics and photochemistry.

L. Martínez-Fernández,<sup>1,2</sup> and R. Improta<sup>1,2</sup>

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2. LIDYL, CEA, CNRS, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France

DNA exhibits a extremely complex photophysical behavior, which is characterized by different time components usually attributed to the presence of multiple decay channels involving excited states of different nature.[1] Elucidating, then, their main deactivation mechanisms is not an easy task even for single nucleobases. [2]

We studied DNA characterizing their excited potential energy surface (PESs). [2] Different spectral properties are then computed at main points of their PES and compared with time resolved experiments (TIR, TAS, CD) in order to identify the most likely relaxation mechanisms.[2-5] We focus on the computation of CD spectra, which are very valuable tools to study the interaction between the excited states of the different bases.

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# Oral Communication:

## *In Situ* SRCD Study of a Functional Amyloid Assembly into Fibrillar Gel

Frédéric Gobeaux<sup>1,\*</sup> & Frank Wien<sup>2</sup>

<sup>1</sup> LIONS - NIMBE CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France [\\*frederic.gobeaux@cea.fr](mailto:frederic.gobeaux@cea.fr)

<sup>2</sup>SOLEIL Synchrotron, Saint Aubin, France

It is now well established that under certain conditions, proteins and peptides can form amyloid fibrils outside pathological context to fulfill a beneficial role<sup>1,2</sup>; in particular, peptide hormones form reversible amyloid aggregates for storage purpose.<sup>3</sup> Although the interactions driving the assembly of reversible functional amyloids are similar to those of pathological amyloids (i.e. a balance between hydrogen bonds, hydrophobic and electrostatic interactions), the mechanisms and dynamics of assembly of functional amyloids have been less thoroughly studied and it is not clear in which respect they may differ. Indeed, while the formation of pathological amyloids is kinetically controlled, the formation of reversible functional amyloids is clearly resulting from thermodynamic equilibriums.

Here, we present the self-assembly properties of Atosiban-acetate, a peptide drug that is an oxytocin antagonist which is used to delay premature labor.

In a first section, we define the physical-chemical formation conditions of the Atosiban fibrillar gels and characterize their structure with complementary techniques such as Transmission Electron Microscopy, Small Angle X-Ray Scattering, Fourier-Transform Infrared spectroscopy and Synchrotron Radiation Circular Dichroism (SRCD). We show that they exhibit all the typical features of amyloid fibrils. The second section is devoted to the kinetics of assembly of these fibrils with both intrinsic and ThT-induced fluorescence and particularly SRCD monitoring. As shown by Bartolini et al.,<sup>4</sup> circular dichroism is a particularly suitable technique to follow amyloid assembly in that it allows characterizing both monomeric and aggregated form of the peptide. Here, thank to synchrotron radiations, we are able to characterize dense gels (up to 10%w/w) that are highly absorbent because of the high proportion of aromatic residues with only small volumes (about 3  $\mu$ L). The conversion of Atosiban monomers into  $\beta$ -sheet exhibits a typical sigmoidal shape with barely a lag phase and the role of the tyrosine group is highlighted.

- (1) Fowler, D. M.; Koulov, A. V.; Balch, W. E.; Kelly, J. W. Functional Amyloid – from Bacteria to Humans. Trends Biochem. Sci. 2007, 32 (5), 217–224.
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# Keynote Lecture:

## Incoherent Detection and Chiral Sensitivity for Time-Resolved Coherent Spectroscopy in all Environments

Tobias Brixner

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This presentation describes new method developments in our group directed at 1) coherent two-dimensional (2D) spectroscopy using incoherent observables and 2) chirally sensitive time-resolved spectroscopy.

Concerning topic 1, we are interested in comparative investigations of quantum systems in all states of matter, i.e., gases, liquids, solids, and surfaces. For that purpose and in contrast to most conventional 2D approaches we do not measure the coherently emitted electric field within a four-wave mixing process but rather employ incoherent observables (ion mass spectra, fluorescence, and photoelectrons). We extract coherent information using “phase cycling” with collinear pulse sequences from a femtosecond pulse shaper. Specifically, we realized “coherent 2D mass spectroscopy” via Fourier transformation of ion yields in a time-of-flight mass spectrometer to provide 2D spectra simultaneously for all mass peaks. As an example, we find 2D Fano lineshapes disclosing the major ionization pathways in NO<sub>2</sub> [to be published]. Second, we have realized rapid-scan coherent 2D spectroscopy via fluorescence detection using a DAZZLER pulse shaper [1]. Recently, we combined this with ultrabroadband excitation using a hollow-core fiber [2] to implement two-quantum 2D spectroscopy as well as new variants such as one-quantum-two-quantum correlations [to be published]. Extending this idea towards 2D spectroscopy with spatial resolution is achieved in a confocal microscope setup (NA = 1.4), revealing varying response functions in structured hexadecafluorinated zinc phthalocyanine (F<sub>16</sub>ZnPc) films [to be published]. Lastly, spatial resolution down to 5 nm in 2D spectroscopy can be achieved in a combination with time-resolved photoemission electron microscopy (PEEM) [3,4]. Recent examples include a nanoengineered plasmonic system that displays long-range (over distances of twice the wavelength) coherent energy transfer [5].

Concerning topic 2, we have developed an optical setup for creating “laser-pulse enantiomers”, i.e., precise mirror images of any (even broadband, polarization-shaped) electric input field [6]. The setup outperforms achromatic waveplates and allows a shot-to-shot switching between different helicities. This can be used for broadband time-resolved circular dichroism (TRCD) spectroscopy [to be published] and in the future also for chiral quantum control. In addition, we show that coherent control using polarization shaping can be used to optimally enhance TRCD signals in the near-field of plasmonic nanostructures [7]. It is derived that the optimal pulses for maximum chirality response are not circularly polarized but have a more complex structure.

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# Oral Communication:

## Vibrational Coherence Spectroscopy to probe conical intersection

Johanna Brazard<sup>1,2</sup>, Laurie A. Bizimana<sup>1</sup>, William P. Carbery<sup>1</sup>, Tobias Gellen<sup>1</sup>, Daniel B. Turner<sup>1</sup>

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Conical intersections are molecular configurations at which Born-Oppenheimer approximation is not valid anymore and thus potential-energy surfaces are degenerated.<sup>1</sup> Despite their importance and predicted ubiquity,<sup>2</sup> conical intersections have been experimentally detected in only a few molecules. Those studies have revealed a vibrationally coherent photoreaction where the coherent movement of a wavepacket from one electronic surface to another signifies passage through a conical intersection.<sup>4</sup>

Vibrational Coherence Spectroscopy (VCS) consists of performing transient absorption experiments with sub-10 fs and spectrally broadband pulses. VCS allows detecting the electronic population kinetics and the vibrational dynamics along the photoreaction, in the form of overlapping oscillatory signals.<sup>5,6</sup>

We studied the ultrafast photophysics of a highly fluorescent oxazine molecule, cresyl violet perchlorate (CV), by VCS with sub-8fs pulses.<sup>5</sup> The signature of a conical intersection, in a mode at 593 cm<sup>-1</sup>, was unraveled by applying coherent wavepacket evolution analysis to the transient absorption data of CV. This strongly Raman-active mode is associated with an in-plane vibrational mode of the aromatic oxazine ring.

**Funding:** New York University (start-up funding), National Science Foundation (Graduate Research Fellowship for L.A.B.).

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# Invited Lecture:

## Structural and allosteric transitions of NO-sensor proteins probed from picosecond to second

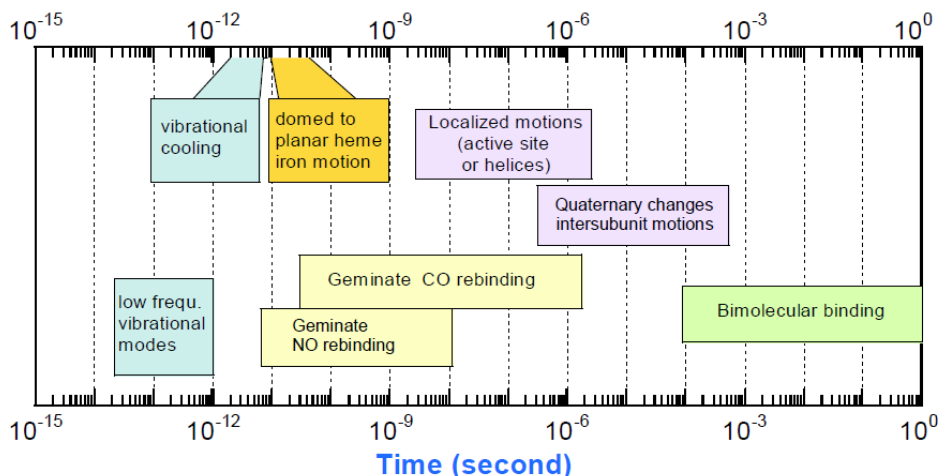
Michel Négrerie

Laboratoire d'Optique et Biosciences

Unité Inserm 1182, UMR 7645

Ecole Polytechnique

Nitric oxide (NO) sensors are diverse heme-proteins present in both mammal and bacteria cells. The binding of NO to or the release of NO from the central iron induces a coordination switch which triggers localized and global structural changes in the protein. Whereas motions of side-chains in the NO binding site take place in the picosecond time range following ligand binding or release, allosteric transitions occur in the microsecond time scale. I will present an overview of how these structural transitions in several NO binding proteins are detected in a broad time range, from picosecond to second, by time-resolved absorption spectroscopy. Then I will show how the motion of the central iron of the heme, induced by NO binding, is measured by time-resolved Raman spectroscopy.



S. G. Kruglik, B.-K. Yoo, J.-C. Lambry, J.-L. Martin & M. Négrerie. Structural changes and picosecond to second dynamics of cytochrome *c* in interaction with nitric oxide in ferrous and ferric redox states.

(2017) *Physical Chemistry Chemical Physics* **19**, 21317–21334.

C. R. Andrew, O. N. Petrova, I. Lamarre, J.-C. Lambry, F. Rappaport & M. Négrerie. The dynamics behind the affinity: controlling heme-gas affinity via geminate recombination and heme propionate conformation in the NO-carrier cytochrome *c*'.

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# Invited Lecture:

## **Synchrotron Radiation Circular Dichroism @ DISCO**

Molecular Biology & Biophysics at Synchrotron SOLEIL

*Frank Wien* DISCO Beamline Synchrotron SOLEIL

*Veronique Arluison* Laboratoire Léon Brillouin /CEA

Contact : [frank.wien@synchrotron-soleil.fr](mailto:frank.wien@synchrotron-soleil.fr)

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The DISCO beamline at SOLEIL Synchrotron covers the VUV to visible spectral range (1). Three endstations, include Deep UV imaging, Atmospheric Pressure Photoionisation and Synchrotron Radiation Circular Dichroism (SRCD). The latter will be addressed specifically in this presentation with respect to conformational changes and dynamics observed in biological samples such as proteins and nucleotides.

On the publicly accessible SRCD endstation, users explore the circular and linear absorptions down to 120nm for films and down to 170nm in solutions, with continuous high photon flux ( $10^{11}$  photon/s), improved signal to noise ratios and short acquisition times.

Examples will be given of the benefits of accessing higher electronic transitions, such as the charge transfer regions for proteins. It turns out that the extension of the spectral band down to 170nm yields more information, which has improved the secondary structure-conformation determination for proteins, specifically for beta sheet rich proteins. BestSel also a publicly accessible algorithm allows now the distinction between parallel and anti-parallel beta-sheets based on CD spectra (2).

In addition, other examples of SRCD from protein DNA complexes will be shown. In a multidisciplinary approach between the Laboratoire Léon Brillouin (LLB) and the Synchrotron SOLEIL, investigations of protein-mediated bridging of bacterial DNA have been successfully carried out. We will demonstrate DNA structuring by a bacterial protein called Hfq, which forms amyloid structures (3).

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2. Micsonai, A., **Wien, F.**, Kernya, L., Lee, Y. H., Goto, Y., Refregiers, M., and Kardos, J. (2015) *Proc Natl Acad Sci U S A* **112**, E3095-3103i
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# Thursday, November 30th, 2017

**9h15-9h45:** *Theory*, chairman *David Lauvergnat*

9h15-9h45: *Cyril Falvo*

9h45-10h05: *Marie-Pierre Gageot*

10h05-10h25: *Valérie Brenner*

**10h25-11h10:** *Fluorescence*, chairman *Klaus Brettel*

10h25-10h50: *Valentin Maffeis*

10h50-11h10: *Zhengyu Zhang*

**11h10-11h30:** *Coffee break*

**11h30-13h25:** *Chirality2*, chairman *Laurent Nahon*

11h30-12h15: *Valérie Blanchet*

12h15-12h45: *Thierry Ruchon*

12h45-13h05 : *Rim Hadidi*

13h05-13h25 : *Jing Tian*

**13h25-14h35:** *Lunch at Bures University Restaurant*

**14h35-15h40:** *Visible Four-wave Mixing*, chairman *Manuel Joffre*

14h35-15h20: *Jennifer Ogilvie*

15h20-15h40: *Daniel Finkelstein-Shapiro*

**15h40-16h00:** *Coffee break*

**16h00-17h00:** *IR Four-wave Mixing*, chairman *Manuel Joffre*

16h00-16h30: *Wutharath Chin*

16h30-16h50: *Adeline Bonvalet*

**16h50-17h00:** *Closing: Thomas Gustavsson*

## Invited Lecture:

### Ultrafast Dynamics of Carboxy-Hemoglobin: Two-dimensional Infrared Spectroscopy Experiments and Simulations

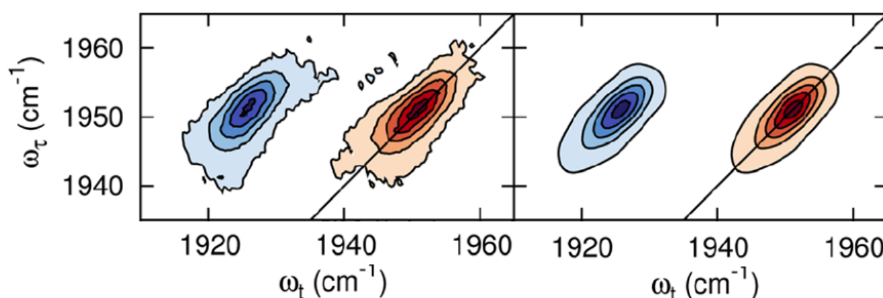
Cyril Falvo<sup>1</sup>, Louis Daniault<sup>2</sup>, Thibault Vieille<sup>2</sup>, Vincent Kemlin<sup>2</sup>, Jean-Christophe Lambry<sup>2</sup>, Christoph Meier<sup>3</sup>, Marten Vos<sup>2</sup>, Adeline Bonvalet<sup>2</sup>, and Manuel Joffre<sup>2</sup>

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<sup>2</sup>*Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, INSERM, Université Paris-Saclay, 91128 Palaiseau, France*

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Understanding the structure and dynamics of proteins is an important research challenge that needs to be addressed in order to understand their physiological function. The development of two-dimensional IR spectroscopy (2D-IR) in the past decade has allowed for the study of the real-time dynamics of proteins from femtosecond to picosecond timescales [1]. Hemoproteins are important in physiology because they are responsible for transport and storage of oxygen. Hemoproteins-CO complex have been widely studied in the past, both experimentally and theoretically as a probe of the Hemoproteins dynamics. In particular, it is known that carboxy-myoglobin (MbCO) exhibits complex dynamics with inter-conversion between different sub-states [2]. Fewer spectroscopic studies have been performed to resolve the dynamics of the carboxy-hemoglobin (HbCO), which is known to have different dynamics than the more frequently studied MbCO [3].



**Fig. 1** Experimental (left) and simulated (right) 2D-IR spectrum of HbCO obtained for a waiting time  $T = 0.5$  ps.

Here, we present simulations of the 2D-IR spectroscopy of HbCO at equilibrium compared with experimental measurements. The simulations are based on a semi-classical model. The model describes directly the fluctuations of the potential energy surface (PES) originating from the electrostatic environment and the heme group, and was previously used to simulate vibrational ladder climbing and coherent control experiments [6,7,8]. The agreement between theory and experiment (see Fig. 1) is achieved without using any adjustable parameters, which demonstrates the ability of our model to describe the internal protein dynamics [9]. Our simulations show the strong effect of the distal histidine through a hydrogen bond, which is responsible for the slow decay of the frequency-frequency correlation function.

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# Oral Communication:

## Modélisation DFT-MD des spectroscopies non-linéaires SFG aux interfaces solide/eau liquide et air/eau liquide

Marie-Pierre Gaijeot

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Nous exposerons nos travaux récents portant sur les simulations ab initio de dynamique moléculaire dans la représentation DFT (DFT-MD/AIMD) d'interfaces chargées inhomogènes oxydes/eau liquide et air/eau liquide et la modélisation des spectres non-linéaires SFG (Sum Frequency Generation) à ces interfaces.

Les simulations DFT-MD permettent de comprendre l'organisation complexe de l'eau liquide à ces interfaces et la dynamique sous-jacente. Nous avons en particulier démontré l'existence d'un réseau de liaisons hydrogène à 2D parallèle à la surface entre l'air et l'eau liquide, et montré comment ce réseau évolue avec la présence d'électrolytes (à diverses concentrations). Voir la référence J. Phys. Chem. Letters 8 :3133, 2017. Nous démontrons également que ce réseau 2D est présent à d'autres interfaces.

Les simulations DFT-MD permettent d'extraire les spectres non-linéaires SFG de ces interfaces, tenant ainsi compte des anharmonicités vibrationnelles, des couplages de modes et de la température, à comparer aux expériences. L'intérêt de la spectroscopie théorique est de faire le lien directement entre signatures spectrales et compréhension moléculaire de ces bandes. Nous avons en particulier mis en place des méthodes d'analyses spectrales qui donnent une interprétation des signatures vibrationnelles dépendant de deux domaines interfaciaux, i.e. BIL (Binding Interfacial Layer) et DL (Diffuse Layer). Nous démontrons sur une très grande série d'interfaces chargées que ces deux domaines sont les seuls donnant des signaux actifs SFG. Nous présenterons comment extraire ces domaines à partir des simulations et les renseignements moléculaires extraits, notamment l'épaisseur des couches effectivement interrogées en SFG.

**Acknowledgment:** Travaux en collaborative avec Prof. Y. Ron Shen, University of California at Berkeley, USA, Dr E. Backus au Max Planck Institute de Mainz en Allemagne via l'ANR-DFG DYNWIN. Travaux réalisés avec PhD/Post-Docs : S. Pezzotti, D. Galimberti, L. Potier, F. Siro-Brigiano, M. Pfeiffer-Laplaud.

# Oral Communication:

## Nonradiative deactivation in model proteins chains: a synergetic experiment-theory approach

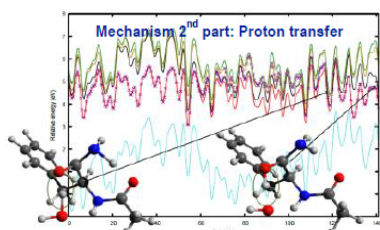
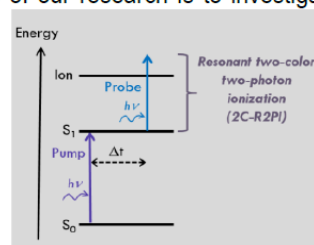
T. Very,<sup>1,2\*</sup> S. Hoyau,<sup>2</sup> N. Ben Amor,<sup>2</sup> E. Gloaguen,<sup>1</sup> B. Tardivel,<sup>1</sup> M. Mons<sup>1</sup> and V. Brenner<sup>1</sup>

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Following UV absorption, many **biomolecular systems** are endowed with mechanisms of **excited-states deactivation** that ensure their **photochemical stability**. One of the major goals of our research is to investigate **conformer-selective dynamics of bio-relevant** molecular systems by a **synergetic experiment-theory** approach which consist in:

i) **An experimental characterization** of both the **lifetimes, in nano-, pico- and femtosecond conformer-selective** experiments, and the **nature of the electronic states** formed. Pump-probe **diagnostic techniques** are used and allow us to identify the relaxation pathways followed by the different conformers of the biomolecular system formed in the experiment.



ii) **An innovative multi-step multi-level computational strategy** to both **characterize the low-lying relevant excited states** and **model efficiently their potential energy surfaces**. First, **nonadiabatic dynamics simulations** based on TDDFT (NA-TDDFT) provide hints about the critical motions that drive the deactivation. The corresponding paths are then **investigated at a better level** with two classes of methods; the **standard approximate coupled cluster singles and doubles method (CC2)** or **multireference methods (CASPT2 and MRCI)**.

**Developed** on small capped peptide models,<sup>1,2</sup> this approach is now applied to **microsolvated capped peptides** as well as **capped dipeptides**.<sup>3-6</sup> We will show on a few examples how this approach allows us to document the **basic physical phenomena** controlling the **lifetime** of excited states of such systems, highlighting the **link between electronic dynamics and structure**.

**Keywords:** Photochemistry of biomolecules, Excited states computations, Conformer-selective spectroscopies, Nonadiabatic dynamics, Size-extensive CC and MRCI linear scaling methods.

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- (6) Ben Amor, N.; Hoyau, S.; Maynaud, D.; Brenner, V. *to be submitted*.

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# Invited Lecture:

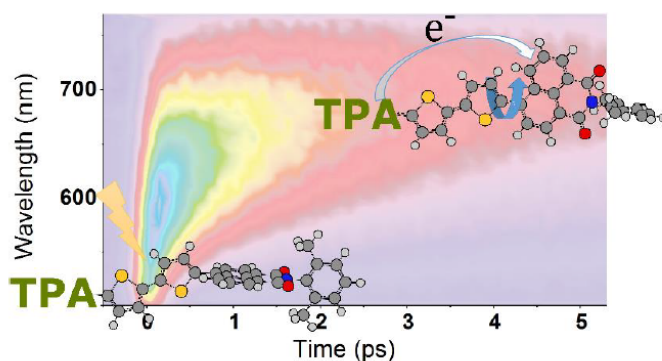
## Push-Pull dyes for Grätzel cells: a time resolved fluorescence study using upconversion in non-transparent systems

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Ultrafast charge dynamics occurring at the dye/mesoporous metal oxide interface in Dye-Sensitized Solar Cells (DSSCs) are still investigated, particularly in p-type cells. Understanding how the molecular structure impacts the dynamics will lead to the improvement of the overall efficiency by using kinetics-tailored dyes. Time-resolved optical spectroscopy techniques have been intensively used to investigate charge transfer, injection and recombination in these systems. Transient absorption spectroscopy, the major technique used to study DSSCs, is not well adapted to quasi opaque system.<sup>1</sup> As a consequence, very thin and, therefore, transparent samples are often used as model systems. In addition, in a complete cell, the sheer number of excited species and the multiplicity of relaxation paths lead to complex dynamics.

With this in mind, we have undertaken the study of these dynamics using time resolved fluorescence in order to: 1) limit the complexity of the signal obtained and 2) work in a reflection mode allowing complete cell studies. This approach also enables potentiostatic control of the system which has recently resulted in new insights in the charge dynamics of DSSCs.<sup>2</sup> In parallel, we have investigated photodynamics of push-pull dyes in solution from the fs to the ns timescale using two different detection techniques: fluorescence upconversion (FU) and time-correlated single photon counting (TCSPC). Depending on the dye and the solvent used, we found that the evolution from the excitation of the first  $\pi\pi^*$  state towards an intramolecular charge transfer state (ICT) is not a straight-forward process and may involve several excited states.



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# Oral Communication:

## Laser Induced Nucleation of an Aggregation Induced Emission (AIE) Molecule in a Microfluidic System by Fluorescence Lifetime Video (FLIM)

**Zhengyu Zhang**<sup>1,2\*</sup>, Valérie Génot<sup>1</sup>, Jean Frédéric Audibert<sup>1</sup>, Yury Prokazov<sup>3</sup>, Evgeny Turbin<sup>3</sup>, Werner Zuschratter<sup>3</sup>, Guillaume Tresset, Brigitte Pansu, Thomas Rodet<sup>1</sup>, Anne

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Polymorphism control of organic molecules has been under keen investigation for decades. Nucleation is the first step to control the polymorphs of crystals. Despite the Classic Nucleation Theory has been well developed and widely applied since 1950s, it has purposely avoided the difficulty of the structure of the nuclei. This thus needs further experimental investigations. So far, however, observation of nucleation encountered great difficulties, mainly because it is a small, random and rare event.<sup>[1, 2]</sup> The aim of this research is to develop a novel approach to control crystallization and probe the structure and kinetics of nucleation by fluorescence.

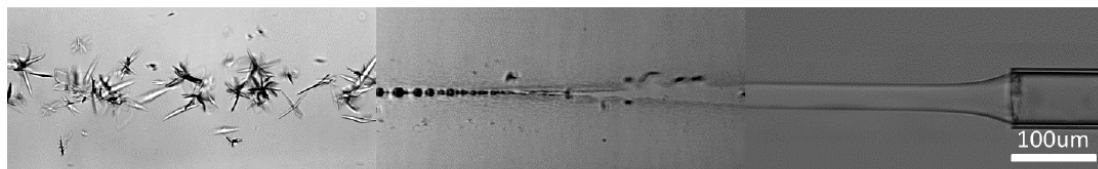


Figure 1. Crystallization of DBDCS in the microfluidic system.

Therefore, a new microfluidic system was built (Fig. 1) to control the crystallization of DBDCS, a molecule that is not fluorescent in solution, but becomes fluorescent after aggregation. A UV laser is focused at different places along the flow through a microscope, enabling an in-situ detection of nucleation by FLIM. The transit time of a particle moving flow through the field of view, depending on the velocity, is usually less than 40ms, wherein we can record its intensity, lifetime and shape. From the number of crystals detected at different positions of the same flow for the same duration, we can measure the nucleation rate. From their average sizes, we can deduce the growth rate. From their lifetimes, we can identify one of the four polymorphs. Real-time FLIM video of the moving particles were recorded for the first time. But the nucleation remains random over a time period of 100ms (200 $\mu$ m).

We can induce, localize and synchronize the nucleation by a laser. Thus, we can now probe the nucleus, nanoseconds after his formation.

The DBDCS/good solvent/bad solvent ternary phase diagram is explored to find characteristic phenomena. Two types of crystallization processes have been observed: nucleation in the mixed solvents or liquid-liquid phase separation followed by droplet formation and crystallization in the droplets. Three polymorphs are produced.

**Funding:** École Doctorale INTERFACES grant of Université Paris-Saclay

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# Keynote Lecture:

## Time-resolved chirality : three different approaches.

S. Beaulieu, A. Comby, A Clergerie, J. Caillat, D. Descamps, N. Dudovich, B. Fabre, G. A. Garcia, R. Geneaux, A. G. Harvey, Z. Massin, L. Nahon, A. F. Ordonez, S. Petit, B. Pons, G. Porat, O. Smirnova, T. Ruchon, R. Taieb, Y. Mairesse, V. Blanchet

CELIA – Univ. de Bordeaux, Univ. Sorbonnes – LCPMR, Synchrotron SOLEIL, Weizmann Institute, MBI, LIDYL – CEA Saclay

In the photoionization of randomly-oriented pure enantiomers by circular polarization light, an asymmetry of the emitted photoelectron is observed along the photon propagation axis. This forward/backward asymmetry can reach several percentage and reverses with the handedness of the enantiomer or the helicity of the light polarization.[1] We have performed the first (to our knowledge) experimental investigation on femtosecond-dependent chiral dynamics in gas phase. The molecular dynamics investigated are vibronic coupling from Rydberg states in Fenchone and Camphor ( $C_{10}H_{16}O$ )[2,3] The time-resolved approach opens new horizons and questions on what are the most important dynamical aspects of the scattering of an electron in chiral potential that is as well evolving.[4]

Acknowledgments: This work was financially supported by Agence Nationale de la Recherche (ANR) (ANR-14-CE32-0014 MISFITS); Labex LAPHIA and Université of Bordeaux, ERC Exciters

siteweb : [harmodyn.celia.u-bordeaux.fr](http://harmodyn.celia.u-bordeaux.fr)

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# Invited Lecture:

## Synthesis, Characterization and Control of extreme ultraviolet attosecond light springs

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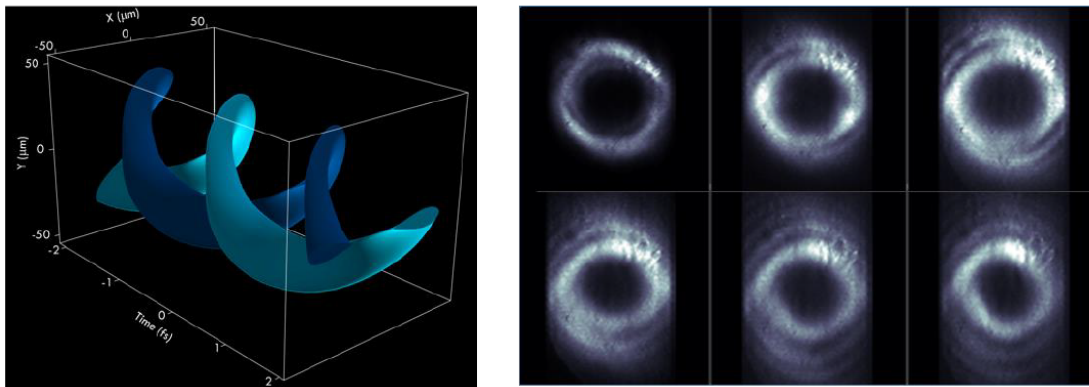
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The generation of beams carrying orbital angular momentum (OAM) has recently been extended to the extreme ultra violet (XUV) range [1-3]. In practice, an intense infrared femtosecond beam carrying OAM is focused into a gas target to drive photon up-conversion in the XUV through high harmonic generation (HHG). In this communication, we will report on HHG driven with an 800 nm beam carrying 1 to 3 units of OAM in different targets (Argon, Neon). In the far-field, we observe that the harmonic beam profile is donut-shaped and that the radius of the ring does not depend on the harmonic order. We show that this is consistent with a linear increase of the OAM with harmonic order, using an analytical analysis and a full 4-dimensional numerical experiment simulating HHG.

We also measured the attosecond synchronization of the HHG comb implementing the RABBITT [1] technique for the first time with XUV beams carrying OAM. By matching the phase fronts of the harmonics and the dressing field, we demonstrate in an original way that there is a difference of two units in the OAM carried by two consecutive odd harmonic orders. This confirms the linear increase of OAM with harmonic order, the slope being determined by the OAM of the driver. Additionally, this measurement allows us to reconstruct the attosecond shape of the emission, as shown in Figure 1.



**Fig. 1.** (left) Experimental reconstruction of the attosecond structure resulting from the coherent superposition of high harmonic orders carrying a topological charge linearly increasing with harmonic order. (right) Spatial profile of the 11<sup>th</sup> harmonic for different weights of the first and second trajectories.

We then demonstrate control over the OAM in the XUV by setting the OAM of the driving IR field to 2 and 3. The ring radius of the XUV beam is still constant with harmonic order but increases with the driver topological charge. Finally, we demonstrated control of the radial index content of harmonics beams carrying OAM, by adjusting the respective contributions of the quantum trajectories during the HHG process [3].

Our results open new perspectives for the synthesis of attosecond electronic springs through photoionization and investigate predicted but never observed helicoidal dichroisms.

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# Oral Communication:

## PECD of chiral amino-acids: case of Proline

Rim Hadidi, Dusan Bozanic, Gustavo Garcia and Laurent Nahon

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In a bottom-up approach of biomolecular complexity, the studies of photoelectron circular dichroism (PECD) may shed light on the electronic and molecular structures of elementary bricks of life such as amino-acids in the gas phase. This chiroptical effect manifests itself as a forward/backward asymmetry in the photoelectron angular distribution (PAD) with respect to the light's propagation axis when using circularly polarized light to ionize pure enantiomers. PECD is very sensitive to the long range molecular potential and thus is able to provide structural information (such as conformers, isomers, clusters...) including of course absolute configuration [1]. In addition PECD has been proposed as an astrophysical symmetry breaking effect with a potential link with the origin of homochirality of life [2].

After the study of the simplest chiral amino-acid, alanine [2][3], we extend here our studies to a peculiar amino-acid proline (Pro) which is the only naturally occurring amino-acid containing a pyrrolidine (secondary amine) side chain. This provides proline-rich proteins with specific structural properties. As other fragile biomolecules, our challenge was to bring free Pro into the gas phase, and to do so we have been using two complementary vaporization methods in order to study its PECD over a large VUV range (8 -17 eV) using the double imaging electron/ion coincidence (i<sup>2</sup>PEPICO) spectrometer DELICIOUS3: the first technique is aerosol thermodesorption (TD) producing only intact free molecules without any thermal degradation [4]; the second one is the resistive heating (RH) in an oven coupled to an adiabatic expansion which offers high mass resolution, crisper electron images and the ability to use ion imaging.

Several temperatures were used to vary the conformer population of the nascent Pro in order to perform a comprehensive conformer analysis of the PECD with the help of ongoing CMS-X $\alpha$  calculations [3]. Our future numerical simulations will also highlight the observed marked conformer-specific fragmentation as well and the conformer population effect on PECD.

Related ongoing PECD studies include the case of Pro-containing dipeptides, aromatic amino-acids and homochiral nanoparticles.

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# Oral Communication:

## Study of writing laser polarization dependence of femtosecond laser induced circular optical properties in silica glass

J. Tian<sup>1</sup>, M. Lancry<sup>1</sup>, E. Garcia-Caurel<sup>2</sup>, R. Ossikovski<sup>2</sup> and B. Pommellec<sup>1</sup>

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From a practical point of view, femtosecond IR lasers can now generate pulses with ultra-high intensity of tera-( $10^{12}$ ) or even peta-( $10^{15}$ ) W/cm<sup>2</sup>. This kind of laser leads to radically different laser-matter interaction from that achieved with a conventional laser. Highly non-linear multiphoton processes are observed, so even transparent material can absorb this light when the intensity is high enough. This allows 3D direct writing when the beam is strongly focused into transparent materials, particularly silica-based glasses. The mechanism of interaction of the femtosecond laser light with dielectric materials is not fully understood but one recognized specificity due to the very small pulse duration is that the action of the light on electrons and ions is decoupled. Then, by choosing the correct configuration of the beam (laser polarization, intensity, and phase distribution) for controlling the ponderomotive force, we can imagine forcing the electrons to move to one side of the beam, creating an inhomogeneous plasma. This may be the clue to an innovative aspect in materials science. Many recent works on pure silica have been conducted, and several properties have been demonstrated in this glass: average index changes, linear birefringence LB and linear dichroism LD. We recently revealed a chiral mechanical structure by measuring the surface topography of laser tracks written in opposite directions that could lead to circular properties. Taylor et al. reported highly ordered « chiral-like » nanostructures using circular polarized laser light but no circular optical properties. We recently report on the creation of circular optical properties and non-reversible measurements according to the probe face. Here it is shown that by controlling the laser-writing configuration, we can create a quite high ellipticity of 40deg/mm @550nm revealing the creation of a large circular dichroism (CD), and strong optical rotation of 103deg/mm @550nm which revealed by circular birefringence (CB), a useful range for potential applications. As the writing polarization is adjustable from 0 to 360°, the ellipticity maximum appear for linear polarization oriented at +/-45° of the scanning direction.

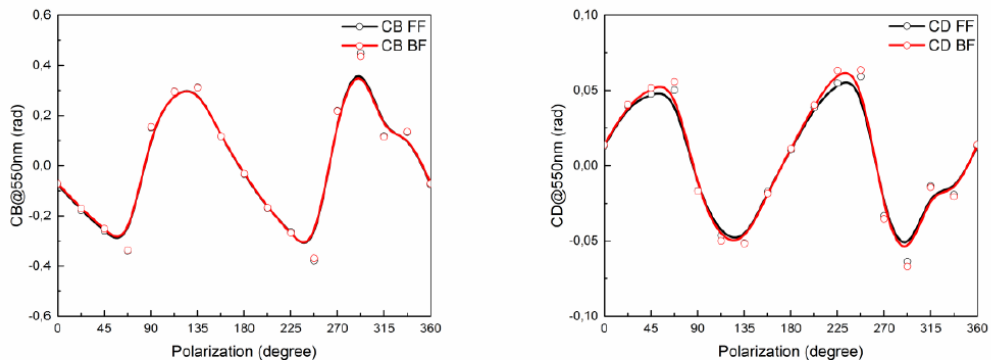


Fig. 1. Circular Birefringence (CB) and Circular Dichroism (CD) according fs-laser writing polarization for both face (FF) and the back face (BF). Laser writing conditions: 1030 nm, 250 fs, 100 kHz, 0.6 NA, writing speed: 1mm/s, 1.5  $\mu$ J/pulse

# Keynote Lecture:

## MULTIDIMENSIONAL SPECTROSCOPIC STUDIES OF COHERENCE IN PHOTOSYNTHETIC SYSTEMS

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In photosynthesis, the primary ultrafast processes involve solar energy harvesting by photosynthetic antennae, followed by energy transfer to reaction centers for conversion into stable charge separation. The photosystem II reaction center (PSII RC) of higher plants, and the bacterial reaction center (BRC) of purple photosynthetic bacteria possess similar structures, exhibiting two-fold symmetry with electron transfer occurring along a single branch. Coherent dynamics in photosynthetic systems were first reported by Vos et al. in the BRC<sup>1</sup> and have recently been reported in 2D electronic spectroscopy (2DES) studies of the PSII RC as well<sup>2,3</sup>. Multidimensional spectroscopies provide rich information about coherent processes and excitonic structure. We present a comparative 2DES study of the PSII RC and BRC and their monomer pigments. By comparing the frequencies and 2D distributions of the coherent dynamics in the monomers and RCs we motivate the assignment of the physical origin (vibrational, vibronic or electronic) of the coherences and aim to better understand their possible functional significance.

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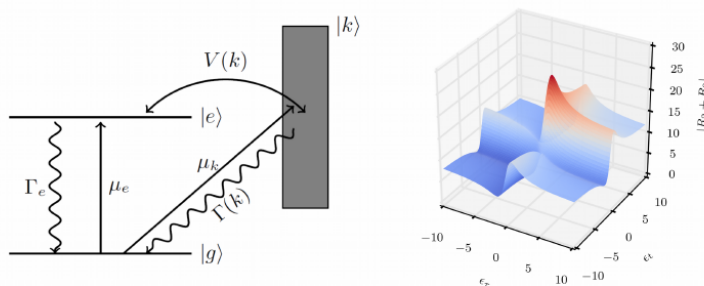
# Oral Communication:

## Two-Dimensional Spectroscopy of Fano Models

D. Finkelstein-Shapiro<sup>1\*</sup>

<sup>1</sup>*Chemical Physics, Lund University, Sweden*

The Fano model and its distinctive asymmetric lineshape have enjoyed tremendous success in explaining spectra in a number of areas ranging from atomic physics to mesoscopic systems. It arises from the interference between two excitation pathways in a two-level system coupled to a continuum (Figure 1). The open questions surrounding the dissipative processes in these structures makes them natural candidates for four-wave mixing experiments. Here, we present the theory of Fano interferences in nonlinear spectroscopy. We give an overview of the basic physics that can be extracted from the measurements and outline the advantages of using the most complete form of four-wave mixing experiments, two dimensional spectroscopy, in unearthing interferences in heterogeneous systems and eliciting coupling through the continuum. We open on the outstanding problems of the theory.



*Figure 1. Left: Fano model with radiative transitions ( $\mu$ ), electronic couplings ( $V$ ) and dissipative pathways ( $\Gamma$ ). Right: surface plot of the two-dimensional electronic spectroscopy signal showing the asymmetric profile.*

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# Invited Lecture:

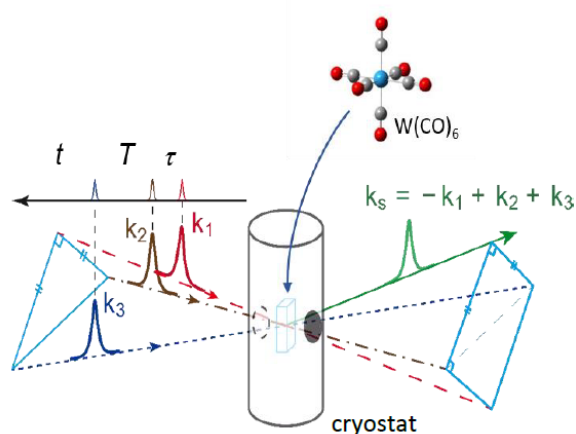
## How to use IR photon echo at low temperature to probe lattice properties.

Wutharath Chin<sup>1</sup>, Raphaël Thon<sup>2</sup>, Didier Chamma<sup>1</sup>, Jean-Pierre Galaup<sup>3</sup>, Claudine Crépin<sup>1</sup>

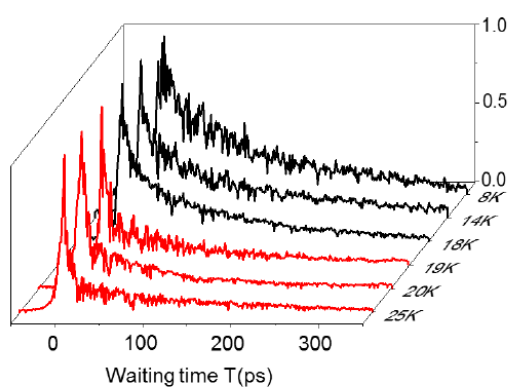
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Scheme of IR photon echo:  $k_1$ ,  $k_2$ ,  $k_3$  pulses interact with  $W(CO)_6$  trapped in cryogenic matrix and create  $k_s$  photon echo signal.



Photon echo signals showing the population time of  $W(CO)_6$  trapped in methane from 8 K to 25 K (phase I and phase II in red and black).

The advent of ultrafast laser sources in the infrared (IR) domain has enabled the study of numerous and diverse molecular systems through nonlinear four-wave mixing techniques. Time-resolved IR photon echo is one such technique that gives access to relaxation processes. Population dynamics and vibrational coherence thereby inform on the interactions between the system under interest and its surrounding medium.

The vibrational dynamics of  $W(CO)_6$  complex has been studied in several cold crystalline solids ( $\sim 20$  K) with IR photon echo. The CO stretch vibration has not only been used to determine the effect of the medium on the dynamics<sup>1</sup> but also to probe the properties of the surrounding lattice. Of particular interest is the case of molecular lattice: the orientational fluctuations in solid methane which presents a phase transition near 20 K strongly perturb  $W(CO)_6$  vibrational relaxation<sup>2</sup> while coupling between the CO vibration with a librational mode of the lattice has been evidenced in solid nitrogen<sup>3</sup>.

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# Oral Communication:

## Three-dimensional mid-infrared spectroscopy in carboxy-hemoglobin using an acousto-optic programmable dispersive filter

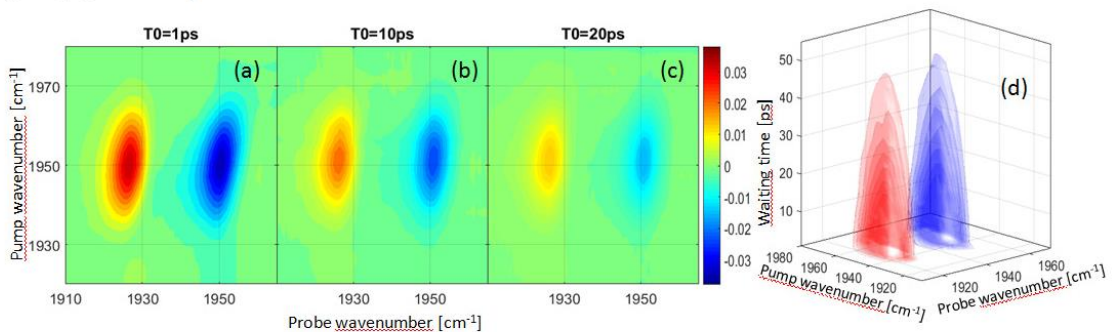
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A great variety of experimental methods have been developed in order to implement multidimensional spectroscopy using femtosecond optical pulses. Among these methods, the use of a pulse-shaping device for generating the appropriate pulse sequence is attractive as it greatly simplifies the experimental setup and makes interferometric stability straightforward. In combination with the pump-probe geometry [1], this approach to multidimensional spectroscopy has been previously demonstrated in the mid-infrared [2] and visible [3] spectral domains.

In this work, we demonstrate the use of a Calomel acousto-optic programmable dispersive filter (AOPDF) [4] for measuring the 2DIR spectrum of carboxyhemoglobin. In contrast with previously-reported mid-IR pulse shapers relying on a zero dispersion line [5], the AOPDF is a highly-compact device which can be readily inserted in the pump beam of an existing pump-probe experiment.



**Fig. 1** Sequence of 2DIR spectra measured for a waiting time equal to (a) 1 ps, (b) 10 ps, and (c) 20 ps. (d) 3DIR signal measured as a function of probe wavenumber, pump wavenumber, and waiting time shown as a series of seven isosurfaces associated with a threshold differential signal varying from 0.04 to 0.16 by steps of 0.02.

The measurement is performed in frequency domain, with the AOPDF delivering narrow pump pulses of varying center frequency with a  $0-\pi$  phase-cycling sequence, completing the acquisition of a 2DIR slice in 84 laser shots. The data is then averaged and the waiting time is scanned from 0 to 55 ps using a translation stage. Fig. 1 shows the resulting experimental data, evidencing the decay of the 2DIR spectrum as a function of the waiting time.

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# Poster Session: PO1

## **Ro-vibrational cooling of molecules. Toward slowing neutral molecule through ionization process**

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Laser techniques applied to precision spectroscopy or to the control of internal and external degrees of freedom have considerably improved our knowledge on molecular physics. One of the greatest challenge of modern physical chemistry is to push forward the limits of electromagnetic and laser techniques to manipulate and probe molecules at low temperatures where molecular interactions are dominated by pure quantum phenomena.

Direct optical cooling of external degrees of freedom for molecules needs closed transitions and has been successfully demonstrated for molecules with suitable vibrational structure. In this context, we have developed an original technique that enables us to manipulate the internal degrees of freedom of diatomic molecules in order to increase the brightness in a particular ro-vibrational level. Then, we aim to propose a new kind of universal solution to produce cold sample of molecules at rest.

# Poster Session: PO2

## Spectroscopie électronique d'action d'ions isolés en phase gazeuse

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L'ionisation par électronébulisation (ou *electrospray ionization* - ESI) s'est imposée comme une méthode incontournable en spectrométrie de masse. L'ESI permet de placer en phase gazeuse presque tout type d'espèce moléculaire, même les plus fragiles et les plus lourds assemblages non covalents. Cette méthode produit, à partir d'échantillons en solution, des distributions d'états de charge à la fois pour des anions et des cations si plusieurs sites de déprotonation ou de protonation sont présents sur les molécules. L'association de l'ESI avec la spectrométrie de masse offre la possibilité unique d'accéder à des objets ioniques en phase gazeuse, sélectionnés en masse et en charge.

Néanmoins, ce type d'expérience n'est pas trivial, car il implique de confiner des densités d'ions suffisamment grandes en interaction avec de hauts flux de photons. Jusqu'à récemment, les sources de rayonnement se limitaient aux lasers dans l'infrarouge [1] dans le visible et proche UV [2] et dans le VUV [3]. Le rayonnement synchrotron possède des propriétés de brillance et d'accordabilité en longueur d'onde fortes intéressantes et qui sont utilisées depuis les années 80 en spectroscopie ionique sur des cibles atomiques ou moléculaires de petite taille [4].

Le couplage d'ion piège ionique radiofréquence avec une ligne lumière du synchrotron SOLEIL a été réalisé [5]. Nous montrerons comment ce type de montage peut donner accès à des informations spectroscopiques et photochimiques des ions ainsi que les applications possibles.

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# Poster Session: PO3

## Time-Resolved Spectroscopy of Thioflavin T and its Building Blocks

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Thioflavin T (ThT) is a benzothiazole (BTA) salt linked to N,N-dimethylaniline (DMA). ThT is a widely used marker for studies on protein aggregation and amyloid fibril formation.<sup>[1]</sup> The freely rotatable bond between the BTA and DMA moieties governs the dynamics of ThT, the associated rotation is the main (non-radiative) depopulation channel of the excited state whose lifetime is around 1 ps.<sup>[2,3]</sup> The fluorescence of ThT exhibits a pronounced dependence on excitation wavelength, attributed to the ground-state's pre-rotation angle.<sup>[4]</sup> This suggests that the excited pre-rotated molecule is inhibited from deactivating by further rotation.

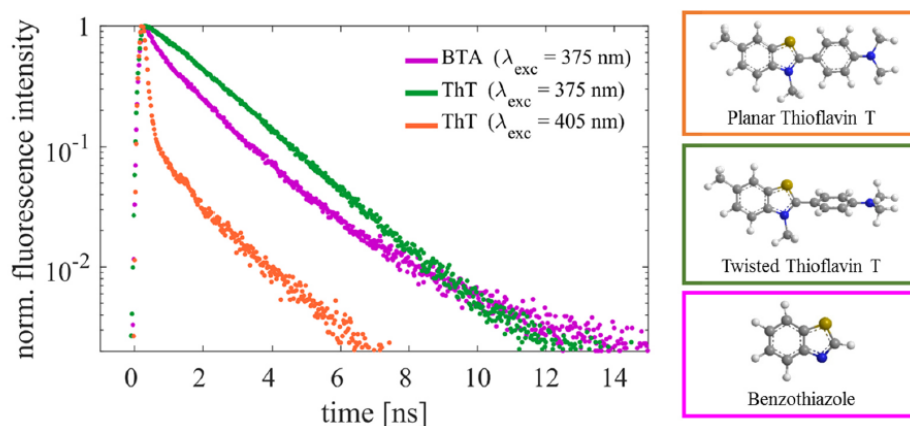


Figure 1. Time-resolved fluorescence at 450 nm for ThT (excited at 405 nm) and its building block BTA (excited at 375 nm) in ethanol.

To test whether pre-rotated molecules exhibit a prolonged excited-state lifetime, we perform time-resolved spectroscopy via fluorescence upconversion, TCSPC and ultrafast transient absorption for ThT and its building blocks. With near-UV excitation, the lifetime is prolonged from  $\approx 1$  ps to 1.3 ns. A comparison of the data for ThT and BTA unveils that the ThT dynamics solely originate from a pre-rotated subensemble for which the two building blocks are spectroscopically independent and no excited-state depopulation through rotation occurs (Fig. 1). Analogous conclusions can be drawn with the DMA building block only. Hence, our studies provide a time-domain corroboration of the pre-rotation model.<sup>[4]</sup>

**Funding:** Deutsche Forschungsgemeinschaft via Cluster of Excellence RESOLV (EXC 1069)

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# Poster Session: PO4

## Dynamics of Carrier relaxation in wide band gap materials.

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**Abstract:** Understanding the dynamics of excited carriers in wide band gap materials is a requirement to describe a broad range of physical mechanisms such as scintillator response, radiation induced damage of crystals, or laser-induced breakdown. The difficulty arises from the competition between all the different relaxation channels: electron-phonon collisions, impact ionization, exciton and transient or permanent defects formation. Since all these processes mutually interact and mainly occur during the laser pulse, complementary techniques must be used. Thus we will show results obtained with various time resolved techniques: Fourier-transform interferometry, absorption, reflectivity, luminescence; digital holography.

All the following processes could be observed: coherent phonon excitation, multiphoton excitation, transient defect formation and exciton self-trapping, carrier recombination, interaction between free or self-trapped exciton occurring at high excitation density, and finally impact ionization, using an original double pump scheme.

These observations are made in materials which are extremely important for numerous applications, namely silica ( $\text{SiO}_2$ ) and sapphire ( $\text{Al}_2\text{O}_3$ ).

# Poster Session: PO5

## Gold Nanoparticles for Physics, Chemistry, Biology and Medicine

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Our research activities concentrate on the synthesis and assembly of gold nanoparticles (NPs) of **high quality** to provide **original materials** for plasmonics, plasmon-driven chemistry, sensing and medicine through collaborations. (Gold-NP/chromophore) nanohybrids are linked to the chemical industry, the renewable energy and new technologies for health. In the long term, they should be able to impact key areas such as photovoltaics, water electrolysis, H<sub>2</sub> dissociation, oxidation/reduction of CO<sub>2</sub> or cancer therapy via the generation of reactive oxygen species (R. O. S).

**The excitation of the Localized Surface Plasmon Resonances (LSPR) of plasmonic nanoparticles (NPs) by short laser pulses sets off a cascade of complex transient phenomena.** The phenomena of exaltation and confinement of the electromagnetic field at the surface of the NPs has been the subject of numerous studies over the last twenty years. These nanoparticles (NPs) are also able to inject hot electrons (or hot holes) to a nearby chromophore, when certain conditions are fulfilled. In 2014 and 2015, the discovery of a new injection mechanism, known as "**direct**" **charge injection** from NP to molecule or semiconductor, explained why a large number of charged species have been observed under certain conditions. Following this, **hot-carriers** have become a "**flagship**" in nanosciences and a new keyword "plasmon-driven chemistry" has appeared. Surface plasmon decay either through light absorption or light scattering. Light absorption leads to the formation of these hot carriers and then to heat and/or light emission. The previously cited direct injection mechanism is competitive with these two relaxation pathways when the energy levels of the NP and of the molecule and the spatial overlap are optimized.

**In short**, the understanding and the characterization of the complex transient mechanisms involved at the *nanoparticle/chromophore* interface, requires the combination of predictive theoretical models and **ultra-fast spectroscopic techniques**. Plasmonic NPs do behave like **nanosources of light, heat and hot carriers** and their **morphology** (size, shape and aspect ratio) is at the center of these **competitive relaxation processes**.

1- Near-Field Localization of Single Au Cubes, a Predictive Group Theory Scheme. Sarra Mitiche, [Sylvie Marguet](#), Fabrice Charra, Ludovic Douillard, *J. Phys. Chem. C*, 121, 2017, 4517

2- Fano Transparency in Rounded Nanocube Dimers Induced by Gap Plasmon Coupling. M. Pellarin, J. Ramade, J. Michael Rye, C. Bonnet, M. Broyer, M. A. Lebeault, J. Lermé, [S. Marguet](#), J. Navarro, and E. Cottancin, *ACS Nano*, 12, 2016, 11266

3- Two-photon luminescence of single colloidal gold nanorods: revealing the origin of plasmon relaxation in small nanocrystals. C. Molinaro, Y. El Harfouch, E. Palleau, F. Eloi, [S. Marguet](#), L. Douillard, F. Charra, C. Fiorini-Debuisschert, *J. Phys. Chem. C*, 40, 2016, 23136

4- Engineering the emission of light from a scanning tunneling microscope using the plasmonic modes of a nanoparticle. E. Le Moal, [S. Marguet](#), D. Cannesson, B. Rogez, E. Boer-Duchemin, G. Dujardin, T.V. Teperik, D.C. Marinica, A.G. Borisov *Physical Review B* 93, 2016, 035418

5- An Electrically Excited Nanoscale Light Source with Active Angular Control of the Emitted Light. E. Le Moal, [S. Marguet](#), B. Rogez, S. Mukherjee, P. Dos Santos, E. Boer-Duchemin, G. Comtet, G. Dujardin, *Nano Letters*, 13, 2013, 4198

6- Mapping the Electromagnetic Near-Field Enhancements of Gold Nanocubes. C. Deeb, X. Zhou, R. Miller, S. K. Gray, [S. Marguet](#), J. Plain, G.P. Wiederrecht, R. Bachelot, *J. Phys. Chem. C*, 116, 2012, 24734

7- Spatial Confinement of Electromagnetic Hot and Cold Spots in Gold Nanocubes. M. Haggui, M. Dridi, J. Plain, [S. Marguet](#), H. Perez, G. C. Schatz, G. P. Wiederrecht, S. K. Gray, R. Bachelot, *ACS Nano*, 2, 2012, 1299

# Poster Session: PO6

## Combining attosecond extreme ultraviolet pulses and shaped near infrared pulses: Multidimensional four wave mixing spectroscopy

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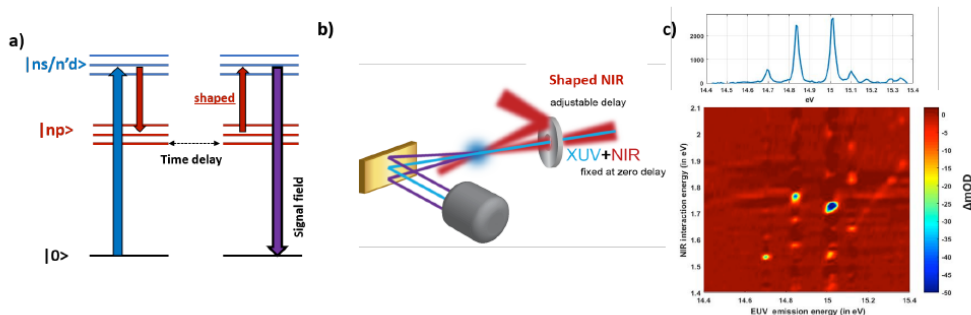
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With the emergence of isolated XUV attosecond pulses, bandwidths as large as 40 eV are now commonly used in many laboratories. Dynamics following excitation with those pulses will arise from all accessible excited states, complicating the retrieval of state-specific time evolution. In optical multidimensional spectroscopy, correlations between excitation and probe frequencies are obtained using four wave mixing (FWM) formalism to identify the signal dependence on the incident field spectral phases, amplitudes and k vectors. Our laboratory has recently shown that FWM signal is generated using the combination of an attosecond pulse centered at 15 eV and two 5 fs NIR pulses centered at 750 nm.<sup>1</sup> The goal is to develop a two-dimensional extreme ultraviolet (XUV) technique using the signal field dependence on the NIR pulse phases and amplitudes. To that effect a spatial light modulator based pulse shaper is implemented to control the emitted XUV and gain spectral information on the NIR transition in play. Interactions involved in the FWM scheme are indicated in **figure 1a**). The coincident XUV and NIR pulses create a wavepacket in the 4p Rydberg dark states of Argon via the bright ns/n'd Rydberg states between 14.4 and 15.4 eV. At a later time delay, a noncollinear shaped NIR pulse couples the 4p dark states wavepacket back to the ns/n'd states manifold, which subsequently emit the signal field. The experimental beam geometry is shown in **figure 1b**). The first NIR and the XUV are collinear while the shaped NIR is noncollinear. The emitted field shown in violet is spatially separated from the other beams. The pulse shaper is used to extract the second interaction frequency by modulating the amplitude and phase of a tunable single frequency of the NIR pulse spectrum. The emitted frequency is correlated with the NIR transition frequency and the 2D spectrum obtained, shown in the **figure 1c**).



**Figure 1:** a) Energy level diagram. b) Beam geometry. The blue beam represents the incident EUV pulse and the violet beams the emitted EUV fields. c) XUV emitted field spectrum and 2D NIR-XUV spectrum.

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# Poster Session: P07

## TRCD measurements combined with the T-Jump technique to investigate folding/unfolding dynamics of Guanine quadruplexes.

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The combination of time-resolved circular dichroism spectroscopy (TRCD) and the temperature jump method (T-Jump) enables us to temporally measure temperature-induced folding/unfolding dynamics of biomolecules, namely proteins [1] but also DNA substructures. One type of the latter is investigated during my thesis: the so-called guanine quadruplexes (G4). Guanine-rich sequences are prevalent in many important regions, such as telomeres and regulatory regions of many oncogenes [2].

Consequently, the underlying folding mechanism is important in order to get better knowledge about the role of G4 *in vivo*. Recent works have tried to answer this question [3], but it is still highly debated. Therefore, we performed experiments with the aforementioned methods in order to improve the understanding of the folding mechanism.

During my work, we have studied some telomeric G4, as well as TBA G4 with its truncated triplex-forming sequence. The latter could be a possible intermediate in G4 folding [4]. Finally, a derivative of an oncogenic promoter sequence c-MYC has been studied, too.

In summary, this ensemble of results have deepen the insight into G4 folding mechanism and are in agreement with theoretical investigations [3].

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## Poster Session: PO8

### Effect of Trifluoromethylation on optoelectronic and electrical studies of anthracene-based semiconducting polyethers AnBPA and AnBPAF using DFT and TDDFT methods

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#### Abstract

The electronic structures and charge transport properties of two anthracene-based polymers, anthracene/bisphenol A (AnBPA) and anthracene/fluorinated bisphenol A (AnBPAF), were investigated by using density functional theory (DFT) and were compared to experimental results. The polyethers were studied in gas phase and in chloroform solvent. The effect of the trifluoromethyls substituents on gap energies and charge mobilities were explored based on TDDFT and Marcus theories, respectively. We study the molecular geometries of ground states, the frontier molecular orbitals, the electronic energy levels, the absorption, and charge-transport properties (reorganization energy and charge transfer integral). Calculated absorption results in gas and solution phases were in agreement with experimental values. Then, the calculated charge transport properties show that the hole mobility of AnBPA was high as compared with the AnBPAF polymer.

#### Keywords:

Anthracene derivatives, Trifluoromethylation, TDDFT, Absorption, Charge-transport.

## Poster Session: PO9

# Ultrafast Multi-excitonic Dynamics in Hybrid Materials for Solar Energy Conversion

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Solar energy conversion into electricity is an old but still intense current research topic. Despite silicon solar cells are dominating the solar cell market, several alternative solar cell technologies are continuously proposed. For example, novel material based Solar cells like Dye-Sensitized Solar Cells (DSSC), Organic Solar Cells (OPVs), Quantum Dot-Sensitized Solar Cells (QDSC) and more recently Perovskite Solar Cells (PSC) are the focus of considerable research development. Among them, the hybrid organic/inorganic perovskite solar cells are probably one the most promising candidates as their power conversion efficiency (PCE) has quickly risen from 3.8% to 22.1% over the past seven years.<sup>1</sup>

In another hand, new generation solar cells are deployed to exploit non-conventional energy conversion strategies, for example allowing to overcome the thermodynamic Shockley –Queisser (SQ) limit (maximum PCE = 33.7 % in single-junction solar cell). However, decreasing the fabrication cost remains a major challenge for these newest generation solar cells.

One strategy to overcome SQ in photovoltaic devices is to go beyond the “one photon gives one electron” limit.<sup>2</sup> For instance, *Singlet Fission (SF)* in OPVs is a process where the photo-generated spin-singlet excited state is converted in to two spin-triplet states. Similarly, in QDSC, *multiple exciton generation (MEG)* process involves the conversion of high photon energy into multiple excitons or electron-hole pairs. In both *SF* and *MEG* cases, the multiplication of the charge carrier process prevents for losing the excess energy through heat. This increase the overall current of the cell and the PCE is estimated to over 44%. However, whereas *SF* can be very efficient in certain systems, resulting triplets with very limited diffusion length are difficult to use in practice. Per opposition, *MEG* results in bright states but was only observed in confined system with a reduced efficiency and always indirectly, ie, through the observation of the resulting Auger recombination occurring at much longer time scale (100s of ps). The implications for photovoltaics requires a greater understanding of the underlying factors that govern MEG efficiency which so far remain unclear.

Advanced time-resolved spectroscopic techniques with high temporal resolution should play an important role in the mechanism elucidation by studying the process in real time and before the system has time to relax. Accordingly, the aim of this PhD project is to study ultrafast excitonic dynamics in hybrid halide perovskites nanostructures with different composition, size and morphologies as Colloidal Quantum Dots (0D) and Nanoplatelets (2D), using Transient Absorption Spectroscopy with high sensitivity and temporal resolution (< 100 fs) and UV/visible two-dimensional electronic spectroscopy with a resolution of about 10 fs<sup>3</sup> in complementary with Fluorescence Up-Conversion Technique<sup>4</sup>.

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