Journée de la fédération CPPS - Mercredi 5 Juin 2024

CPPS
Fédération de Chimie Physique de Paris-Saclay

Toutes les communications orales ont lieu dans l'amphithéâtre Blandin du LPS, Bât 510.

Les pauses café, le buffet de midi et la séance poster ont lieu dans le Hall du bâtiment.

Programme

8h45-9h15	Accueil des participants		
9h15-9h30	**Introduction**	*Gilles Grégoire (CPPS)*	
9h30-10h10	**Keynote 1:** Morgane Vacher	**CEISAM, Nantes**	*Ultrafast photo-induced dynamics in molecules*
10h10-10h30	O1: Sergey Denisov	**ICP**	*Dynamics of electron-metal contact pair solvation in aqueous salt solutions*
10h30-11h00	*Pause café*		
11h00-11h40	**Keynote 2**: Gustavo Pino	**Université Nationale de Cordoba (Argentine)**	*Spectroscopy of Cold Anions: Dipole-Bound-States (DBS) and Core-Excited Dipole-Bound-States (CE-DBS)*
11h40-12h00	O2: Mariah Harris	**ISMO/PPSM**	*An Optical Biosensor for the Detection of Bacteria*
12h00-12h20	O3 : Antoine Vite	**ICP**	*Investigation of fossilization processes through IR spectro-imaging: Amber study at sub-micro scale*
12h30-15h00	*Buffet* *Séance Posters Hall LPS*		
15h00-15h40	**Keynote 3:** Frédéric Foucher	**CEMHTI, Orléans**	*Exobiologie : de l'origine de la vie à la recherche de vie extraterrestre*
15h40-16h00	O4: Franco Molina	**ISMO**	*Selective Tautomer Production and Cryogenic Ion Spectroscopy of Nucleobases Radical Cations*
16h-16h20	O5: Théo Béguin	**ICP**	*Describing the photochemical reactions involved in the photobleaching of a fluorescent protein: How to go from a global view to the identification of reactive sites*
16h20-16h40	O6 : Suman Sarkar	**Lumin**	*Formation and dynamics of molecular aggregates of the C96tBu8 GQD on the 3D perovskite MAPbBr3 surface*
16h40	*Fin*		

K1: Ultrafast photo-induced dynamics in molecules

Morgane Vacher

Nantes Université, CNRS, CEISAM, UMR 6230, Nantes, France

A key complement to experiments in the laboratory, providing great details of a dynamical molecular process, is computer simulations. For instance, non-adiabatic dynamics simulations are often key to the understanding of the mechanism, rate and yield of photochemical reactions. In this talk, I will present simulations of photochemical and attochemical reactions, i.e., coupled electron-nuclear dynamics induced by ultrashort light pulses [1,2]. In the first part, I will discuss the dynamics induced in ethylene following ionization by an extreme ultraviolet attosecond pulse train. Our simulations provide information about the mechanisms and timescales of dissociation and isomerization induced reactions [3]. Further, combining experiment and theory, we have found that isotope labelling can be an efficient tool in attochemistry to identify the relevant nuclear coordinates and electronic states controlling the relaxation dynamics [4]. In the second part of my talk, I will focus on coupled electron-nuclear dynamics upon ionization to different electronic wavepackets of (deuterated) benzene and fluoro-benzene molecules [5]. In fluoro-benzene, our calculations unravel both inter-state and intra-state quantum interferences that leave clear signatures of attochemistry and charge-directed reactivity in the shape of the autocorrelation function. The latter are in agreement with experimental high harmonic spectroscopy measurements of benzenes and fluoro-benzene. In the last part, I will present an example of recent experimental and theoretical results on the photo-induced dynamics of an iron photosensitizer. Coherent structural dynamics in the excited state of an iron photosensitizer was observed through oscillations in the intensity of Kα x-ray emission spectroscopy (XES). Using multiconfigurational wavefunction calculations, we explain and discuss the origin of the unexpected sensitivity of (semi)core-to-core transitions to structural dynamics [6,7,8].

[1] I. C. D. Merritt, D. Jacquemin, M. Vacher, *J. Phys. Chem. Lett.* **12**, 8404-8015 (2021).
[2] A. Ferté and M. Vacher. In Chemical Modelling: Volume 17 (2022), Editors: Hilke Bahmann and Jean-Christophe Tremblay.
[3] L. Fransén, T. Tran, S. Nandi, M. Vacher, *J. Phys. Chem. A* **128**, 1457-1465 (2024).
[4] M. Vacher, A. Boyer, V. Loriot, F. Lépine, Saikat Nandi, *J. Phys. Chem. A* **126**, 5692-5701 (2022).
[5] T. Tran, A. Ferté, M. Vacher, *J. Phys. Chem. Lett.* **15**, 3646-3652 (2024).
[6] K. Kunnus, M. Vacher et al., *Nature Comm.* **11**, 634 (2020).
[7] M. Vacher, K. Kunnus, M. G. Delcey. Kelly Gaffney, M. Lundberg, *Struct. Dyn.* **7**, 044102 (2020).
[8] J. Rogvall, R. Singh, M. Vacher, M. Lundberg, *Phys. Chem. Chem. Phys.* **25**, 10447-10459 (2023).

O1: DYNAMICS OF ELECTRON-METAL CONTACT PAIR SOLVATION IN AQUEOUS SALT SOLUTIONS

S. A. Denisov[1], D. Dobrovolskii[1], M. Mostafavi[1]

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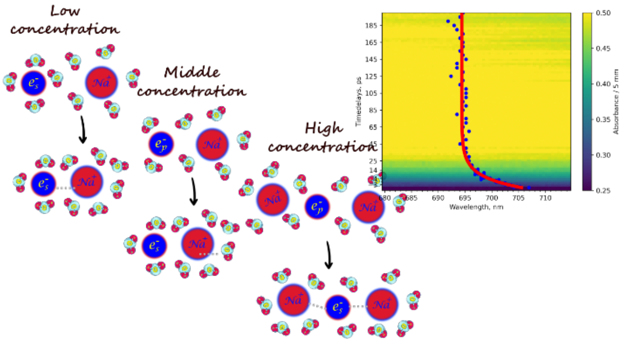
When an excess electron is introduced into liquid water, it forms a hydrated electron (e_S^-), a key entity in radiation chemistry, though a complete theoretical framework for its properties is still lacking.



Following the identification of e_S^-, studies examined how dissolved inorganic salts affect their optical absorption spectrum.[1] An increase in salt concentration typically shifts the e_S^- absorption spectrum toward higher energies.[1] Kreitus et al.[2] further investigated these shifts in aqueous LiCl solutions, known for their solubility and inertness, across a 0-15, M concentration range at 294 K in water and heady water. Mostafavi et al.[3] expanded on this by exploring how chloride and perchlorate salts with various metal cations affect e_S^-'s absorption in water. They noted that the blue shift in the spectrum varies with the cation size and the salt's dissociation degree, with incomplete dissociation partially screening the cation charge.

In this study, the dynamics of metal cation-electron pairs solvation were investigated in different metal salt water solutions. The influence of the nature of metal cations was investigated by means of electron pulse radiolysis. These dynamics of electron-metal contact pair solvation were observed for the first time experimentally. The solvation dynamics of electrons in water, which takes less than 1 ps, can be slowed down at least 10 times. We discuss a descriptive mechanism of such solvation in the presence of metal cations.

[1] M. Anbar et al., *J. Phys. Chem.*, **1965**, *69*, 1244.
[2] I. V. Kreitus, *J. Phys. Chem.*, 1**985**, *89*, 1987.
[3] J. Bonin et al., *Rad. Phys. Chem.*, **2005**, *74*, 288.

K2: Spectroscopy of Cold Anions: Dipole-Bound-States (DBS) and Core-Excited Dipole-Bound-States (CE-DBS)

R. A. Jara-Toro,[1] M. I. Taccone,[2] J. Dezalay,[3] G. von Helden,[2] J. A. Noble[3] and G. A. Pino[1]*

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Analogous to the Rydberg states in neutral molecules, valence-bound states (VBSs) of anions containing polar neutral cores with a large enough dipole moment (⍰ ≥ 2.5 Debye) can support diffuse dipole-bound states (DBSs) below the detachment threshold.[1-3] Electronically excited states of neutral polar molecules or radicals can also bind an electron to form core-excited dipole-bound states (CE-DBEs). However, since the dipole-bound electron is a quasi-free electron, CE-DBSs are very difficult to observe since they lie above the electron detachment threshold.

The development of very sophisticated techniques such as pump-probe spectroscopies and velocity mapping imaging (VMI) to study electron detachment processes coupled with methodologies to cool down the ions have allowed access to a deeper knowledge on the properties of DBSs.[3]

In recent years, we have study the Photo Detachment Spectroscopy (PDS) of cryostatically cooled closed-shell aromatic anions by detecting of the neutral radical or the neutral fragments as a function of the photon excitation energy.[4,5]

In this talk, I will present a study of the PDS of the acetylacetonate ($C_5H_7O_2^-$) anion for which two DBSs were identified. One of them lies close to the electron detachment threshold (D_0-DBS), and surprisingly, the other (D_1-DBS) one was found 1 eV above this energy. The electron detachment from the (D_1-DBS) takes place after internal conversion (IC) to the (D_0-DBS), being this one the time limiting step process.

1) Lykke, K. R.; Mead, R. D.; Lineberger, W. C. Observation of Dipole-Bound States of Negative Ions. *Phys. Rev. Lett.* 1984, *52*, 2221−2224.

2) Pino, T.; Tulej, M.; Guthe, F.; Pachkov, M.; Maier, J. P. Photodetachment Spectroscopy of the $C_{2n}H^-$ (n = 2−4) Anions in the Vicinity of Their Electron Detachment Threshold. *J. Chem. Phys.* 2002, *116*, 6126−6131.

3) Zhang, Y. R.; Yuan, D. F.; Wang, L. S. Probing Dipole-Bound States Using Photodetachment Spectroscopy and Resonant Photoelectron Imaging of Cryogenically Cooled Anions. *J. Phys. Chem. Lett.* 2023, *14*, 7368−7381.

4) Pino, G. A.; Jara-Toro, R. A.; Aranguren, J. P.; Dedonder-Lardeux, C.; Jouvet, C. Dissociative Photodetachment vs. Photodissociation of Aromatic Carboxylates: The Benzoate and Naphthoate Anions. *Phys. Chem. Chem. Phys.* 2019, *21*, 1797-1804.

5) Noble, J. A.; Aranguren-Abrate, J. P.; Dedonder, C.; Jouvet, C.; Pino, G. A. Photodetachment of Deprotonated Aromatic Amino Acids: Stability of the dehydrogenated radical depends on deprotonation site. *Phys. Chem. Chem. Phys.*, 2019, *21*, 23346-23354.

O2: An Optical Biosensor for the Detection of Bacteria

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Throughout human history, bacterial infections have posed significant challenges to public health.[1] With the discovery of antimicrobial agents and antibiotics to combat bacterial infections came the ability of bacteria to become resistant to these drugs due to genetic mutations and overuse.[1,2] As the current antimicrobial medicines are becoming ineffective, there is an urgent need for new medicines and an urgent push to improve early detection of bacterial infections. Currently, effective bacterial detection methods require the ability to identify pathogenic bacteria with sensitivity and specificity but such methods can be expensive and time consuming. [3,4] To overcome the current limitations of existing detection techniques, biosensors utilizing nanoparticles (NPs) and fluorescence have emerged as alternatives by offering detection in faster and more efficient ways. In the present work, we create an optical biosensor by utilizing fluorescent organic NPs as the sensing element, a pH sensor, and fluorescence as the reader device. Fluorescent organic NPs allow for great photostability, easy cellular uptake, and can be turned within the visible range making them valuable for biosensing applications.[5] We found that the photophysical properties of the individual compounds in varying pH buffers remained consistent when they become bound together in solution by copper-free click chemistry, with the NPs not responsive to the pH change while the sensor displayed increased fluorescence intensity in acidic media. When immobilized onto a glass surface, the photophysical properties and pH sensing capabilities were retained. By plotting the intensity ratio of the pH sensor over the intensity of the NPs, a pKa of the luminescent surface was determined to be 5.96 ± 0.15, which is within the physiological range for bacteria detection. Lastly, when primarily tested with bacteria, the NPs, pH sensor, and grafted solution display no toxic effects to their growth, leading to promise for future tests. In conclusion, there is potential in our optical biosensor for detecting bacteria by sensing pH. Next steps include measuring bacterial growth concomitant with pH and photophysical measurements.

(1) Debabov, D. *Appl. Biochem. Microbiol.* **2013**, *49* (8), 665–671.
(2) Reygaert, W. C. *AIMS Microbiol.* **2018**, *4* (3), 482–501.
(3) Váradi, L.; Luo, J. L.; Hibbs, D. E.; Perry, J. D.; Anderson, R. J.; Orenga, S.; Groundwater, P. W. *Chem. Soc. Rev.* **2017**, *46* (16), 4818–4832.
(4) Castillo-Henríquez, L.; Brenes-Acuña, M.; Castro-Rojas, A.; Cordero-Salmerón, R.; Lopretti-Correa, M.; Vega-Baudrit, J. R. *Sensors* **2020**, *20* (23), 6926.
(5) Wani, W. A.; Shahid, M.; Hussain, A.; AlAjmi, M. F. SpringerBriefs in Materials; Springer: Singapore, 2018.

O3: Investigation of fossilization processes through IR spectro-imaging: Amber study at sub-micro scale

Antoine Vite

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Les fossiles sont des matériaux résultant de la préservation d'organismes anciens. Ils nous transmettent des informations sur la diversité et le fonctionnement des écosystèmes passés par le biais de la fossilisation. Cependant les fossiles sont des objets complexes et leur formation n'est pas toujours bien comprise. La démocratisation de nouvelles techniques de spectro-imagerie capables d'atteindre des résolutions latérales de l'ordre de la dizaine de nanomètre comme l'AFM-IR (Atomic Force Microscopy - InfraRed) ouvre un nouveau champ d'investigation des anciennes formes de vie et des conditions de fossilisation.

La fossilisation est un phénomène rare qui a lieu sous des conditions physico-chimiques particulière. Les processus qui la gouvernent dépendent à la fois des caractéristiques propres de l'organisme (anatomie, composition chimique) et des conditions environnementales dans lesquelles il a lieu. Il en résulte des états de préservation variant considérablement d'un site à l'autre.

Le cas de l'ambre est particulièrement remarquable puisqu'elle est connue pour préserver des tissus mous en trois dimensions. Cependant les mécanismes contrôlant une telle qualité de préservation restent encore mal compris, car ils mettent en jeu des interactions de long terme entre la matrice et l'inclusion fossile.

Le travail présenté ici a pour but de caractériser l'interface entre le fossile et la matrice ambre en tant que zone critique du processus de fossilisation. L'interface est en effet une zone de contact pouvant constituer une surface d'échange ou une barrière, mais cette interaction longue de plusieurs millions d'années est encore très mal comprise. La spectroscopie infrarouge est idéale pour analyser la chimie de l'ambre, puisqu'il s'agit d'une roche organique constituée d'un ensemble complexe de polymères. L'utilisation des techniques O-PTIR (Optical-PhotoThermal IR) et AFM-IR permettent de sonder l'interface à des résolutions spatiales micrométrique et sub-micrométrique, nous offrant ainsi la possibilité d'analyser chimiquement les processus de fossilisation dans l'ambre, et cela à des échelles jusqu'ici inatteignables.

K3: Exobiologie : de l’origine de la vie à la recherche de vie extraterrestre

Frédéric Foucher

CEMHTI, CNRS, Université d’Orléans. Orléans

L’exobiologie s’intéresse à l’origine de la vie et à son évolution sur Terre comme ailleurs dans l’univers. Cette thématique de recherche couvre différents domaines dont l’astrochimie (avec l’étude de la formation et de la stabilité de molécules organiques dans l’espace), la chimie prébiotique (i.e. l’étude des réactions chimiques ayant conduit à l’apparition de la vie sur Terre), et la recherche de vie extraterrestre.

Historiquement, des recherches en exobiologie ont été conduites dès la fin des années 60 au CNRS d’Orléans sous l’impulsion d’André Brack qui fondera par la suite (en 1982) le groupe d’exobiologie au Centre de Biophysique Moléculaire. L’originalité des travaux réalisés sur Orléans repose principalement sur une approche transdisciplinaire, mêlant chimie, physique, géologie et biologie. Le groupe est notamment connu pour son implication dans la mission européenne ExoMars, depuis sa genèse à la fin des années 90, et pour ses travaux en micropaléontologie.

Lors de cette conférence, Frédéric Foucher présentera le domaine de l’exobiologie et exposera une partie des travaux réalisés sur Orléans. En particulier, il présentera le réacteur hydrothermal développé suite au Défi Origines 2021-2022 de la Mission pour les Initiatives Transverses et Interdisciplinaires (MITI) du CNRS, et permettant de réaliser des expériences de chimie prébiotique dans des conditions simulant l’environnement de la Terre primitive (ou de Mars). Il présentera également les travaux réalisés sur l’étude de la stabilité de biosignatures à la surface de Mars.

O4: Selective Tautomer Production and Cryogenic Ion Spectroscopy of Nucleobases Radical Cations

F. L. Molina,[1] *M. Broquier,*[1] *S. Soorkia,*[1] *G. Grégoire*[1] *and Gustavo A. Pino*[2]

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[2] University National of Cordoba, CONICET, Corboba, Argentina

The structure of molecules can be elucidated using cryogenic ion spectroscopy. Cooling enables high-precision IR and UV spectra to be recorded, making it possible to apply IR-UV double resonance methods to determine molecule structures by comparison with quantum chemical calculations

We have introduced a novel approach for the isomer-selective generation of radical cations ($R^{+\bullet}$) of nucleobases, Cytosine (C), Uracil (U) and Thymine (T), through the photodissociation of cryogenically cooled silver complexes (NB-Ag+) precursors. It is based on a charge transfer state in the NB-Ag+ complex that lies in the vicinity of the locally excited $\pi - \pi^*$ state and leads to the photochemical production of the radical cation of NB.[1]

The UV-PD spectra of $R^{+\bullet}$ show a broad band in the 15000-20000 cm-1 region and a well-resolved vibronic transitions in the 24000-28000 cm-1 region. Different tautomers were identified using IR-UV and UV-UV Hole-Burning spectroscopy.

The notable outcome is the lack of isomerization during the photodissociation of the silver complex leading to the formation of the DNA radical cations even when the nascent DNA radical is not the lowest energy tautomer. Finally, TD-DFT calculations faithfully reproduce the electronic excitation spectra of highly excited states (D0-D4 transitions), both for the adiabatic energies and vibronic spectra.[2,3]

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2) Franco L. Molina, Jordan Dezalay, Satchin Soorkia, Michel Broquier, Majdi Hochlaf, Gustavo Ariel Pino, Gilles Grégoire. Phys. Chem. Chem. Phys. 2022, 24, 25182.
3) Franco L. Molina, Michel Broquier, Satchin Soorkia, Gilles Grégoire, Gustavo Ariel Pino. J. Phys. Chem. A, **128**, 3596 (2024)

O5: Describing the photochemical reactions involved in the photobleaching of a fluorescent protein: How to go from a global view to the identification of reactive sites

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Fluorescent proteins (FPs) are genetically encoded fluorescent probes that have become invaluable in bioscience and biophotonics as they allow the understanding of biological processes at the molecular level in living cells. Unfortunately, the accurate monitoring of biochemical events is often limited by photobleaching, a gradual loss of fluorescence of FPs under light excitation, which affect both time and spatial resolution during image recording. Consequently, the improvement of FPs' photostability is a major challenge that requires a thorough understanding of the mechanisms involved in photobleaching1. Some photochemical reactions and the residues involved have already been reported2, but there is currently no systematic approach to get the full spectrum of potential photoproducts and their corresponding residues. This represents a crucial prerequisite for developing a rational mutagenesis strategy. This challenge arises from the diversity of photoreactions that a given FP can undergo, and which can deeply depend on the experimental conditions3. In addition, the kinetics and the proportions of those photoreactions may also vary from a FP to another2.

Here, we report a whole analytical workflow combining biochemistry, UV-visible spectroscopy, mass spectrometry and kinetic modelling aiming to (1) describe the photochemical reactions (2) identify the residues involved in the photobleaching of YFPs, a family of FPs widely used in fluorescence microscopy and still in active development. First, we built a custom setup that allow both irradiation of aqueous solution of YFP with controlled irradiation densities and monitoring of absorption and fluorescence emission spectra over the time. From these experiments, we can extract the kinetic parameters of photobleaching and assess their changes under the modification of certain experimental conditions (e.g. nature of the YFP, concentration, light power, molecular oxygen presence…). In a second step, the detailed analysis of the photobleached samples by mass spectrometry (MS and MS/MS) provided insights into the chemical nature of the generated photoproducts.

This workflow confirms the presence of a diversity of photoproducts for EYFP, Citrine and some of their variants at position 69 and 145 and highlights significant disparities in kinetics and relative quantities of those identified photoproducts. However, two main different reactional pathways have been identified. The first one is heavily oxygen dependent and results in multiple oxidations of the FP, concomitant with the protonation of its chromophore. According to mass spectrometry analysis (MS/MS), the oxidations are mainly localized around the chromophore pocket, likely induced by the photosensitization of the chromophore with molecular oxygen, triggering various reactions on the surrounding residues. The second pathway lead to cleavage of the peptidic chain near the chromophore, leading to a non-absorbing state. These results are consistent with previous observations in the literature on individual fluorescent proteins of different colors sharing the same chromophore but possessing distinct protein sequences3,4, thereby demonstrating the relevance of the workflow for obtaining a comprehensive understanding of photobleaching for YFPs and for other FPs in the future.

1. Cranfill et al., Quantitative assessment of fluorescent proteins, Nat Methods, 2016, 13, 557-562.
2. Acharya et al., Photoinduced Chemistry in Fluorescent Proteins: Curse or Blessing ?, Chem. Rev., 2017, 117, 758-795.
3. Duan et al., Structural Evidence for a Two-Regime Photobleaching Mechanism in a Reversibly Switchable Fluorescent Protein, J. Am. Chem. Soc., 2013, 135, 15841-15850.
4. Heickemer & Langosch., Site-Specific Fragmentation of Green Fluorescent Protein Induced by Blue Light, Biochemistry, 2021, 13, 557-562.

O6: Formation and dynamics of molecular aggregates of the C96tBu8 GQD on the 3D perovskite MAPbBr3 surface

Suman Sarkar,[1] Hugo Levy-Falk,[1] Huynh Thanh,[1] Elsa Cassette,[1] Loïc Rondin, Daniel Medina-Lopez,[2] Emmanuelle Deleporte,[1] Stéphane Campidelli,[2] Jean-Sébastien Lauret[1]

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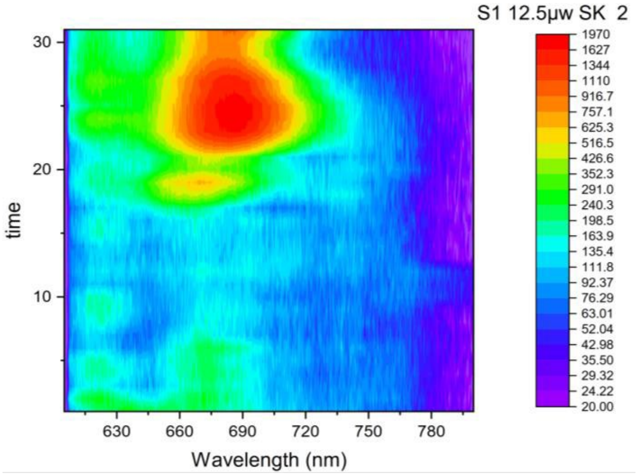
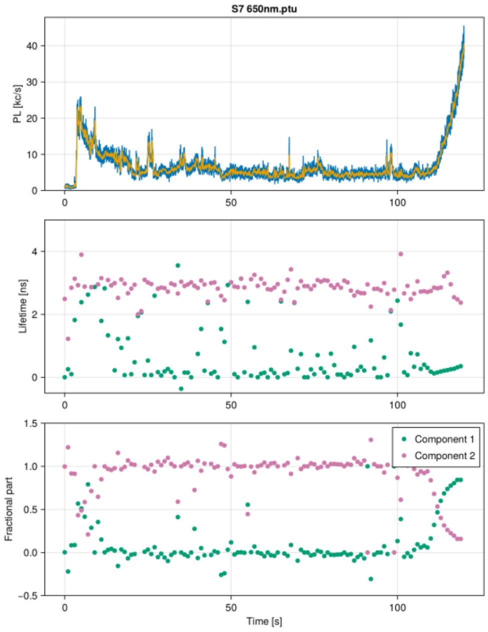
Bottom-up synthesized C96tBU8 graphene quantum dot1 shows stable and strongly polarized emission in single-molecule spectroscopy. On the other hand, the lead-halide perovskite MAPbBr3 crystal has interesting optical properties with the advantage of the ease of making a single crystal with a ligand-free surface.

The band structure of the MAPbBr3 can allow the energy and/or charge transfer with the GQD. In this talk, we will present our spectroscopic investigation on the coupled system with confocal microscopy and time-resolved measurements. We will show the molecule forms an aggregate2 state on the surface. The dipolar alignment of the molecule gives a red shift and intense photoluminescence. This organized aggregate state shows a shorter lifetime of a few hundred picoseconds compared to the single molecule lifetime of a few nanoseconds.





1. Levy-Falk, H., Capelle, O., Liu, T., Medina-Lopez, D., Deleporte, E., Campidelli, S., Rondin, L. and Lauret, J. (2023), Investigation of Rod-Shaped Single-Graphene Quantum Dot. Phys. Status Solidi B, 260: 2300310.

2. Expanded Theory of H- and J-Molecular Aggregates: The Effects of Vibronic Coupling and Intermolecular Charge Transfer Nicholas

Poster List:

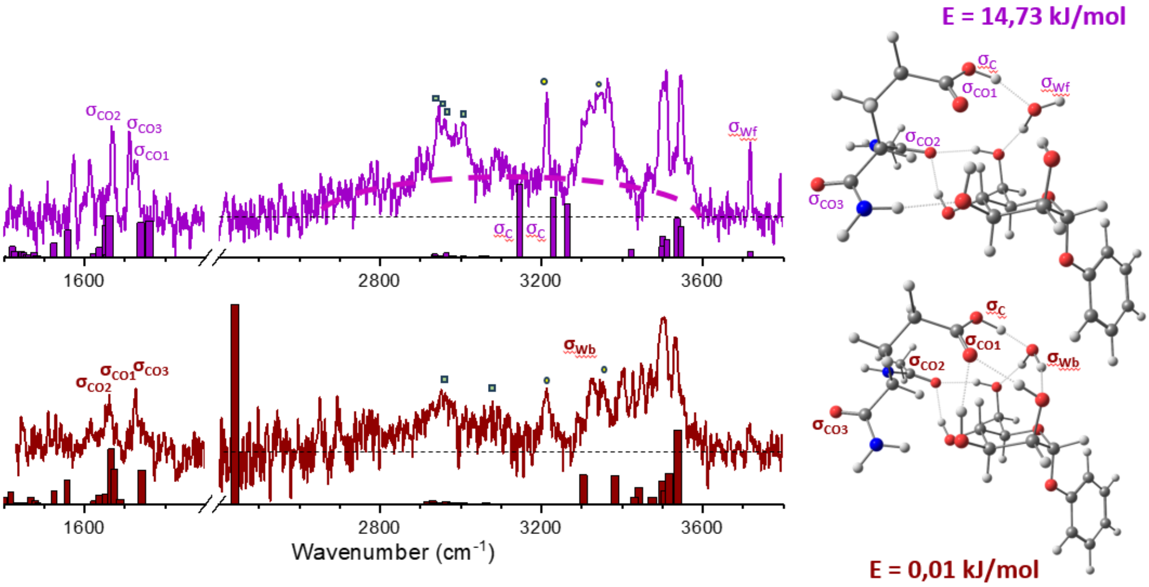
Sugar Peptide Water interactions studied with laser spectroscopy

Arsène KOSSOV, Ander CAMIRUAGA, Pierre ÇARÇABAL

Institut des Sciences Moléculaires d’Orsay, Université Paris-Saclay, CNRS, Orsay, France

Sugars are a family of biomolecules that plays numerous roles in biological processes of living organisms such as energy transfer, or structural roles. Among those roles stands molecular recognition, allowed by the flexible structures adopted by sugars that can reorient themselves and non-covalently bond to other molecules thanks to an extended hydrogen bonding network. Some sugars can then be selectively recognized by some proteins which plays a key role in the immune system and some diseases. It is then interesting and important to understand the structural properties of this key-lock association and the role of water that can strongly influence those structures.

We studied in environment-free conditions the association of a functionalized mannose molecule with a functionalized glutamic acid that reproduces a peptide bond. With double resonance laser spectroscopy in the far-IR and mid-IR range, we compared the structure of this dimer with a micro-hydrated one to which one water molecule was added. The resulting spectra are selective in mass and conformer specific. By comparing those spectra to a theoretical study conducted at the B3LYP-D3/def2-TZVPP level of theory of the density functional theory, we obtained a correct match for the two most stable structures observed for the dimer and for the mono-hydrated dimer. The water molecule appears to be inserted between the mannose and the glutamic acid in two different ways leading to a complete reorganization of the hydrogen bonding network, with some very explicit differences in vibration signatures.



Suivi du photoblanchiment de protéines fluorescentes à l'aide d'un montage d'irradiation : contrôle des conditions expérimentales.

R. Dauverné ; T. Béguin ; M. Erard ; H. Pasquier

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Les protéines fluorescentes (FP) sont des sondes fluorescentes codées génétiquement qui sont devenues inestimables pour les biosciences et la biophotonique. En effet, elles permettent de comprendre les processus biologiques au niveau moléculaire dans les cellules vivantes. Malheureusement, le suivi précis des événements biochimiques étudiés est souvent limité par leur photoblanchiment, une perte progressive de leur capacité à émettre des photons de fluorescence suite à une excitation lumineuse prolongée. Cette perte irréversible de l'intensité de fluorescence affecte la résolution temporelle et spatiale lors d'expériences d'imagerie cellulaire. L'étude du phénomène de photoblanchiment, résultat de réactions photochimiques irréversibles, nécessite une caractérisation rigoureuse des sources lumineuses qui en sont à l'origine ainsi qu'une étude approfondie des paramètres expérimentaux pouvant affecter sa cinétique.

Le travail présenté ici décrit la façon dont ces deux derniers points ont été appliqués à la caractérisation d'un système d'irradiation « fait maison » ainsi qu'à l'étude du photoblanchiment et de la photoconversion de plusieurs FP. Cette caractérisation implique des mesures d'actinométrie[1] permettant de mesurer la puissance surfacique (irradiance) réelle reçue par les échantillons lors des irradiations effectuées sur notre dispositif expérimental. Elle nécessite également l'étude approfondie de l'impact de divers paramètres expérimentaux sur la cinétique de photoblanchiment, tels que la concentration, le volume, l'agitation et la puissance de la lumière d'irradiation utilisée.

1- A. Lahlou ; Fluorescence to measure light intensity ; *Nature Methods* **volume 20**, pages 1930–1938 (2023) ; https://doi.org/10.1038/s41592-023-02063-y

Ultrafast Exciton Dynamics in 2D van der Waals Nanostructures: Probing the Hot Exciton Relaxation of Size-Controlled & Well-Dispersed Graphene Nanoflakes

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Graphene nanostructures, such as graphene quantum dots (G-QDs), graphene nanoribbons (G-NRs) and carbon nanotubes (C-NTs), combine the unique mechanical and electronical transport properties of sp^2-hybridized carbon materials and the optical properties of direct semiconductors provided by the optical gap resulting from the reduction of dimensionally. Among them, the recent developments within the well-known synthesis of G-QDs though bottom-up approach [1] have led to exceptionally well-controlled nanostructures in terms of size, shape and dispersion [2]. The resulting graphene nanoflakes provide tunable emission in the red range, with fluorescence quantum yield close to 1. Furthermore, these nanostructures have revealed to be promising stable emitters of single photons, as shown in our laboratory [2-5].

Here we use transient absorption of 30 fs temporal resolution with polarization-controlled configuration to probe the hot exciton relaxation (internal conversion, $S_n \rightarrow S_1$) in rectangular G-QDs of various lateral lengths. The nanoflakes are composed of exactly 96, 114 and 132 conjugated carbons (respectively 2.30, 2.71 and 3.11 nm). While the ultrafast electronic dynamics in graphene nanostructures are often being blurred by large broadband photo-induced absorption signals [6-8] (in particular involving triplet states, $T_1 \rightarrow T_n$), here the suppressed aggregation in the studied graphene nanoflakes allows a clear observation and identification of the discrete ground state bleaching and photo-induced emission signals.

We selectively excite the different samples at the second optically active electronic transition and, thought the appearance of a photo-induced emission signal at the energy corresponding to the bandedge and red-shifted vibrational replica (*i.e.* at the position of the steady-state photoluminescence peaks), the dynamics of relaxation were unveiled. The resulting relaxation times range from 100 fs to 175 fs. These results allowed to discuss the mechanism of relaxation, with the effect of the length of the graphene nanoflakes and of the fluence excitation [Quistrebert *et al.*, in preparation].

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Study of the vibrational structure of chlorophyll family molecules through photodetachment of cold anions

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Photosynthesis, a highly efficient process, converts carbon dioxide and water into oxygen and sugar using sunlight. Chlorophyll molecules and their dimers play key roles in various steps of photosynthesis, especially in the initial charge separation process, known for its high quantum yield. The efficiency of the charge separation mechanism may be due to a resonance between vibrational modes of chlorophyll 'a' and the energy gap separating its neutral and ionic pairs. However, the precise vibrational structure of these molecules remains unknown. Our goal is to investigate the vibrational and vibronic structures of chlorophyll and its derivatives. To achieve this goal, we conduct electron photodetachment spectroscopy from cooled anions. The properties of the neutral are characterized by measuring the kinetic energy of the ejected electron after photoexcitation. This new spectroscopy enables access to the vibrational modes of the chlorophyll cycle in the absence of solvent.

During this presentation, we will show our initial results concerning pheophytin-a, a chlorophyll where the magnesium atom is replaced by two hydrogens on the nitrogen of its macrocycle. We have measured the photodetachment thresholds of a series of model molecules of pheophytin, pheophorbide, and Methyl pheophorbide (Figure 1). These latter two molecules are identical to a pheophytin where the Phytyl chain C20H39 has been replaced by a hydrogen atom or a methyl group, respectively. These comparisons allowed us to correlate the values of the photodetachment energies with the deprotonation sites of the molecule. Additionally, we will present some relevant vibrations of pheophorbide and compare them with theoretical simulations.

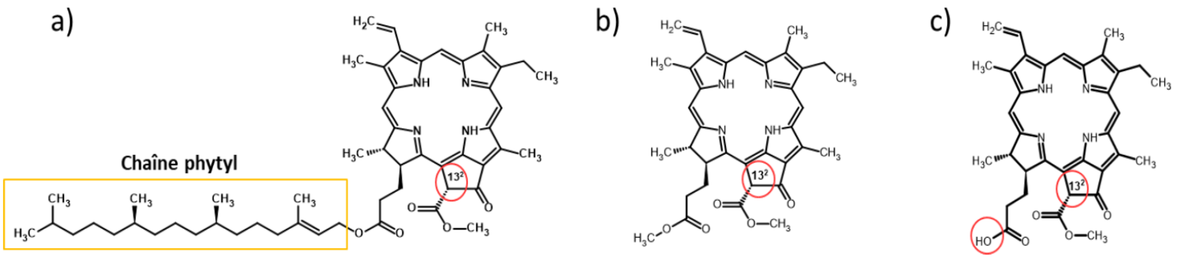

Figure 1 Developed formula of neutral compounds a) Pheophytin b) Methyl Pheophorbide c) Pheophorbide. The most probable deprotonation sites are encircled in red.

Substitution effect on electronic-excited photochemistry of meta-Nitrophenolate compounds: study by cold ion photodissociation and photoelectron spectroscopy

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Nitroaromatic compounds are employed in phototherapy due to their ability to photorelease nitric oxide (NO), which has several favorable physiological effects in pathological treatment. In this context, the light is used as a trigger to release NO, providing control in the concentration and spatiotemporal resolution.[1]
Model compounds are the NitroPhenolates (NP-), considered as donor-acceptor (O--NO2) chromophores with a charge-transfer (CT) excitation in the visible region (lowest $\pi\pi^*$ transition) which eventually photorelease NO.2 Gas-phase action spectroscopy of NP- shows that o-, p- and m- substitution affects the donor-acceptor coupling tunning the absorption band, i.e., locating the m-NP- absorption near the biological transparency window (600-850 nm).[2]
Therefore, we select a set of mNP- derivatives, including a third substituent, -CH3 or -NH2, in the o- or p-position of the phenolate group to evaluate how it affects the electronic donor-acceptor coupling and the NO yield, expecting that the steric effect improves the NO release. The comparative study uses photodissociation (PDS) and photoelectron (PES) spectroscopy under cryogenic conditions.
The Electron Affinity (EA) energy, determined by PES, is founded in the visible region for all the compounds and decreased by the inclusion of -CH3 and -NH2 groups. The photodissociation spectra have been recorded below and above the EA. The spectra were assigned to the lowest $\pi\pi^*$ transition by comparison with electronic excited states calculations and Franck-Condon simulations. Furthermore, resonances were found near the EA for the substituted compounds while for the mNP- a UV band is observed above its EA. The presence of electronic excitations below and above the EA suggests a competition between valence and non-valence excited states that are involved in the photofragmentation process.[3]

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GRAPHENE QUANTUM DOTS IN A MOLECULAR CRYSTAL

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Graphene quantum dots (GQDs) synthesized by bottom-up chemistry are a tunable bandgap-material and promise applications in optoelectronic, biosensing, and quantum technologies [1-2]. The recent investigations on the intrinsic properties of these GQDs classify them as a stable and bright single photon source at room temperature [3-7]. Moreover, temperature dependent PL study of GQDs' embedded in a polystyrene matrix shows the reduction of the spectral linewidth down to ~2.3 meV at low temperature compared to the room temperature value of ~80 meV [6]. Despite this reduction, the linewidth is still few orders of magnitude higher than the radiative limit that is estimated to be of ~1 µeV [8]. This broadening is mostly due to the coupling of the electronic states of the GQD with the vibration modes of the host matrix. Therefore, changing the matrix is mandatory to reach this theoretical limit. In this presentation, I will report on a study of the photophysics of the C114-tBu10 GQD embedded in a molecular crystal made of C78 dendrimers [1]. I will describe the synthesis and characterization of these original molecular crystals and the protocol to embed the GQDs. Finally, I will show photoluminescence studies of GQDs down to the single crystal.

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Nanoparticles combined with particle therapy for the treatment of tumors

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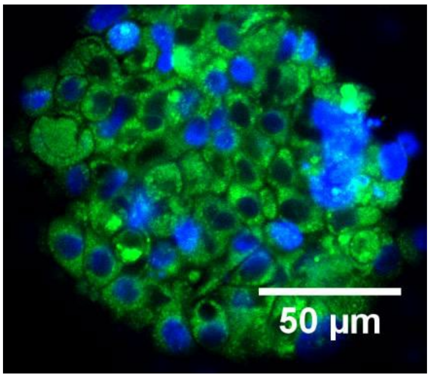
Radiotherapy is one of the main treatments for cancer. The challenge is to increase the radiation damage on tumor whilst preserving healthy tissue. Particle therapy, which uses ion beams, offers an alternative method whose ballistic properties are used to improve targeting of the radiation action into the tumor.

The objective of this work is to enhance particle therapy's performance in sterilizing radioresistant tumors and reducing side effects on healthy tissues by adding nanoparticles (NPs) that can amplify the effects of ionizing radiation [1].

Our group's innovative experimental work aims to evaluate the effectiveness of combining nanoparticles with ion beams. These experiments are being conducted for the first time on a 3D cell model which is a tumor-like model named "spheroid" that mimics the geometric (3D) and environmental (nutrient and oxygen gradients) conditions of a tumor [2].

We optimized the production of spheroids using cell lines from different cancers: Hela for cervical cancer, BxPC3 for pancreatic cancer, and U-87 for glioma. The characterization of the internalization and localization of metallic NPs in these 3D cell models is ongoing (see the figure on the right for a BxPC3 spheroid: Platinum NPs (in green) internalized in the cytoplasm of spheroid cells after 15 hours of NPs incubation (cell nuclei in blue)).



The ion irradiations will be conducted in Japan, a world leader in particle therapy with which our team has a long-term collaboration. These experiments, which will focus on the comparative efficacy of metallic nanoparticles (Platinum, Bismuth/Platinum, or Gadolinium) combined with Carbon or Helium ion beams, will be conducted for the first time on the optimized 3D cell models (Hela, BxPC3, and U-87).

The efficacy of the irradiation protocols is quantified by measuring cell survival using clonogenic survival assays.

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Non-adiabatic electronic relaxation of tetracene from its brightest singlet state

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Polycyclic aromatic hydrocarbons are at the core of the development of organic photovoltaics, for that they can potentially produce multiple charge carrier from a single absorbed photon in a process known as singlet fission [1]. The ultrafast excitation dynamics of PAH following the absorption of a photon in the visible to the UV range provides a fundamental understanding of the underlying molecular energetics, and shed light on the role of the non-adiabatic couplings in the electronic relaxation.
We present a femtosecond time-resolved photoion and photoelectron study of the free tetracene molecule excited into its brightest singlet state, followed by a fast electronic relaxation onto lower lying singlet states. Along with the excitation in higher lying states, inherent effects such as the production of thermal electrons [3] and the correlation to different cationic states, makes such studies challenging. Our experimental and theoretical results suggest that these difficulties might have been overcome [4].
This experimental work is in addition supported by molecular dynamic simulations of the non-adiabatic relaxations in polyacenes which were realized independently - and prior to – our results [5].

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Structural and magnetic properties of the iron based superconductor BaFe2S3

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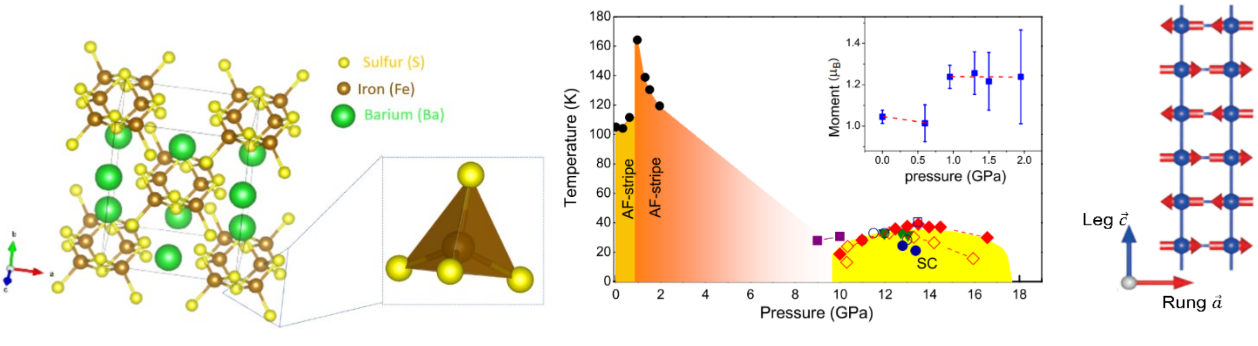
The discovery of iron-based superconductors had a huge impact on condensed-matter physics and led to extensive studies. Recently, a family of quasi-1D Fe-based spin ladders (Fig. 1a), BaFe2X3 (X=Se, S), has been found to present superconductivity (SC) : a SC dome between 10-17 GPa and Tc between 11 and 26 K has been evidenced [1,2]. The (Pressure, Temperature) phase diagram also presents a magnetic order at ambient pressure below TN≈120 K (X=S) or 250 K (X=Se), which can compete or coexist with the SC state (Fig. 1b). The interest of this series of compounds is its low dimensionality which contrast with usual 2D superconductors (iron-based, cuprates and recently nickelates) and simplify the theoretical approaches. The crystal structure of these compounds consists of Fe^{2+} ladders, formed by edge-sharing FeS4 tetrahedron separated by Ba ions (Fig. 1a). There are two ladders by unit cell. The symmetry between ladders in the unit cell is lower for BaFe2Se3 (Pm space group [3]) than for BaFe2S3 (Cmcm space group). The magnetic structure stabilized below TN is characterized by an unusual block-type AFM order with a q_b=(½ ½ ½) propagation wave vector for the Se compound [3,4] while a standard stripe-like order with a q_s=(½ ½ 0) is stabilized for the S member [5]. This difference in magnetic ordering for systems with such comparable structures remains to be understood.

To help us understand this difference, my group started to investigate the X=Se sample, both the structural [4], dynamical [6], and magnetic [7,8] point of view at ambient pressure, and later under pressure [9]. They have also performed inelastic neutron scattering one BaFe2Se3 single crystal (1g) to measure the spin dynamics [10]. By comparing the dispersion to spin-wave calculation, they extracted a set of magnetic exchange interaction. The purely antiferromagnetic Heisenberg model obtained show a strong second neighbor interaction within the ladder, resulting in a strong frustration. This strong frustration is at the origin of the exotic block-like magnetic order present in this member.



(a) (b) (c)

Fig 1 : (a) BaFe_2 S_3 atomic structure (Cmcm) with a zoom in the edge-shared FeSe4 tetrahedra. (b) : BaFe_2 S_3 (Pressure,Temperature) phase diagram. (c) : Spins directions in the ladder for BaFe_2 S_3

Sample and preliminary work

Single crystals of BaFe2S3 are grown by our collegues at SPEC (CEA) that I have fully characterized (EDX, XRD, SEM, SQUID, resistivity, heat capacity…). The total crystal mass is 1g. We have also performed single crystal X-ray diffraction at synchrotron SOLEIL (CRISTAL beamline) to confirm the high quality of the crystal (see reciprocal space reconstruction on Fig. 2a). Recently we also performed powder neutron diffraction on D1B to establish the pressure-temperature phase diagram, confirming the magnetic structure with a propagation vector of q_s=(½ ½ 0) at ambient pressure (Fig. 2b).

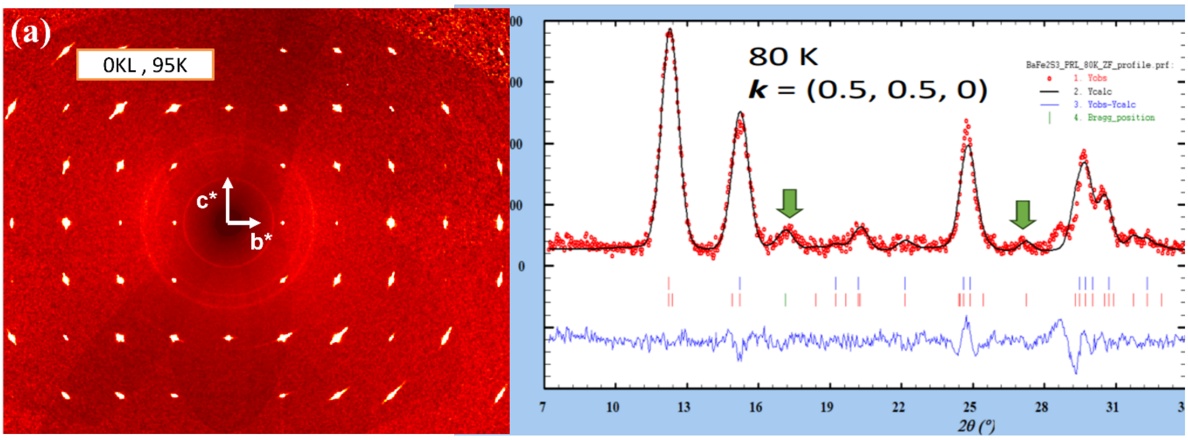


Fig 2 : (a) BaFe2S3 reciprocal lattice reconstruction of (0KL) plane. (Cristal Beamline (synchrotron Soleil)) (b) : Powder neutron diffraction showing the emergence of a magnetic peak at 80K (bellow TN) with a q=(½ ½ 0) (D1B Beam line ILL).

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