

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	<b>Introduction</b>	<i>Gilles Grégoire (CPPS)</i>	
9h30-10h10	<b>Keynote 1:</b> Marie-Aline Martin	<b>ISMO</b>	<i>Prix CPPS 2020 Rotational Spectroscopy of astrophysical molecules</i>
10h10-10h30	O1: Claire de March	<b>ICSN</b>	<i>Structural elucidation and molecular mechanisms of mammalian odorant receptors</i>
10h30-11h00	<i>Pause café</i>		
11h00-11h40	<b>Keynote 2:</b> Michel Sliwa	<b>LASIRE – Université de Lille</b>	<i>Mechanism of photo-switchable proteins revealed by the synergy of time-resolved optical spectroscopy and crystallography</i>
11h40-12h00	O2: Emiline Boyer	<b>ICP</b>	<i>Immobilization effect on optical properties of quantum dots transferred from solution to surfaces probed by nonlinear optical spectroscopy</i>
12h00-12h20	O3 : Lou Barreau	<b>ISMO</b>	<i>Xanthone excited-state dynamics measured with time-resolved photoionization spectroscopy</i>
12h30-15h00	<i>Repas / Séance Posters : Hall LPS</i>		
15h00-15h40	<b>Keynote 3:</b> Julia Contreras	<b>LCT – Sorbonne Univ.</b>	<i>From quantum topology to properties. A focus on superconductivity</i>
15h40-16h00	O4: Wahid Ullah	<b>ICP</b>	<i>Optically-active graphdiyne oxide quantum dots as photosensitizers for enhanced photocatalytic hydrogen generation</i>
16h-16h20	O5: Luan Juppet	<b>ISMO</b>	<i>IR - Millimeter-wave double resonance for precision molecular spectroscopy</i>
16h40-17h00	O6: Marine Fournier	<b>SOLEIL</b>	<i>Photoelectron spectroscopy of solvated uracil and bromouracil molecules</i>
17h00	<i>Prix meilleure affiche "jeune"</i>		

## K1: Rotational Spectroscopy of Astrophysical Molecules

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The identification of new molecules in the interstellar medium (ISM) is often intrinsically linked to their prior study in the laboratory, especially at centimeter to submillimeter wavelengths where the recorded spectra act as identity cards. Yet, current astronomical surveys, using instruments as ALMA or the GBT, display a wealth of transitions that cannot be assigned to any known molecule. Laboratory data, in particular rest frequencies in the range where these instruments operate, is thus more than ever needed.

From an Earth-experimentalist point of view, the candidates for interstellar detection can be sorted into two groups: stable and reactive species. The recent interstellar detection of the first PAHs-type molecules (e.g., benzonitrile, cyanonaphthalenes, and indene), after decades of unsuccessful searches, has brought the first group of molecules back into light and stresses the need for new laboratory data on related relatively large compounds. As for the second group, although reactive species represent a significant amount of the known interstellar species (more than 50%), the astronomical detection of relatively large ones remains hindered by the lack of available laboratory data. Even for already known reactive species, such laboratory data are often limited to the centimeter and millimeter-wave region ( $f < 300\text{-}400$  GHz), while observatories such as ALMA can operate up to about 1 THz. Reactive species are often challenging to produce and characterize in the laboratory compared to their stable, frequently commercially available, counterparts. New laboratory data on a wide range of both stable and reactive species is thus more than ever needed.

In our group, we are exploiting chirped-pulse millimeter-wave and frequency-multiplication-based (sub)millimeter spectroscopy to record the rotational spectrum of known or postulated astronomical species and provide accurate rest frequencies for astronomical searches up to the terahertz domain. In this talk, I will present an overview of our experimental capabilities illustrated by results on several stable and reactive species of astrophysical importance.

## **O1: Structural elucidation and molecular mechanisms of mammalian odorant receptors**

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Odor perception is based on odorant receptors (ORs), which belong to the large family of G protein-coupled receptors and more particularly to the rhodopsin-like family, also called class A. The vast majority of odorant receptors show poor cell surface expression in non-olfactory cells due to retention of the endoplasmic reticulum (ER), hindering their structural elucidation and functional study. Here, we study at the molecular level the expression mechanisms of this sub-family of G protein-coupled receptors. In this project, we use the diversity of the odorant receptor repertoire to create new optimized synthetic receptors based on their consensus sequences. Using these consensus ORs cases, we study the role of amino acids in their expression through molecular modeling, site-directed mutagenesis, and flow cytometry. Their functionality is also assessed by *in vitro* assays. We then developed a protocol to produce and purify the most promising ORs which allow us to obtain the first structural elucidation of a mammalian OR. This research is crucial, not only to understand the strategy of our brain to perceive its olfactory environment but also to identify general mechanisms governing the function of ORs.

## **K2: Mechanism of photo-switchable proteins revealed by the synergy of time-resolved optical spectroscopy and crystallography.**

Michel Sliwa<sup>1</sup>, Xingjie Fu<sup>1</sup>, Cédric Mittelheisser<sup>1</sup>, Stanislaw Nizinski<sup>1</sup>, Lucas Martinez Uriarte<sup>1</sup>, Jacques-Philippe Colletier<sup>2</sup>, Martin Weik<sup>2</sup>

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Among photo-active biological systems, photo-switchable proteins are key elements in important biological functions such as vision, photoprotection and photosynthesis. They can also be used in different applications such as optogenetics and super-resolution bio-imaging. Their intrinsic properties of using light in an efficient way are characterized by photo-switching dynamics that takes place on a broad time-scale, ranging from hundreds of femtoseconds to a few milliseconds. It involves several excited states and ground state intermediates, and a complex interplay between the chromophore and the protein. Even though photo-physical parameters (switching / fluorescence quantum yields...) are crucial for their used in advanced bio-imaging applications, the switching mechanism that controls these parameters is still a matter of debate. Indeed, mechanistic details, in particular on the ultra-fast photochemical time scale, remain unclear. Another challenge in deducing the photo-switching mechanism is to create a uniform picture explaining both single pulse excitation experiments used in the study of ultrafast photo-dynamics, and *in vivo* continuous light irradiation condition for bio-imaging. I will discuss here how the synergy of time resolved optical spectroscopy and serial femtosecond crystallography allows us to reveal the photo-mechanism for photo-switchable fluorescent proteins [1-5] and orange carotenoid protein [6-9]. Crucial parameters in the photo-switching dynamics were unveiled to rationally tailor the development of efficient new photo-active proteins for bio-imaging and optogenetics.

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**Acknowledgement:** We thank all our colleagues that are co-authors of the papers cited.

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## O2: Immobilization effect on optical properties of quantum dots transferred from solution to surfaces probed by nonlinear optical spectroscopy

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Quantum dots (QD) constitute a novel generation of fluorescent probes due to their confined size in the 1-10 nm range. In this field, nanosensors sensitivity is of pivotal importance to target biomolecules. We focus here on the optimize grafting of organic ligand-coated CdTe and CdSe/ZnS core-shell type QDs monolayers on glass surfaces to address the environmental problem and cost of nanosensors.<sup>1</sup> QD monolayers samples are pre-characterized by UV-VIS absorption and (Time-resolved) fluorescence emission, evidencing the success of transferring the QD optoelectronic properties from colloidal solution to amine-terminated aliphatic organosilane monolayer-modified glass samples. Moreover, from time-resolved fluorescence spectroscopy, the effect of chemical structure of monolayers are seen from a fast-quenching phenomenon in relation to colloidal QD solution. Afterwards, an advanced surface-specific spectroscopic tool, non-linear optical Two-Colour IR-Visible Sum-Frequency Generation spectroscopy (2C-SFG), is used to probe and evidences the dipolar coupling between QD excitons and their molecular surroundings,<sup>2</sup> which improves the nanosensor's detection threshold. This electro-optical coupling (inorganic-organic charge transfer) is modelled through quantum chemical calculations dedicated to spectroscopy. A calculation strategy is optimized in order to properly reproduce the electronic structure of nanostructured systems at semi-empirical and DFT level. Due to the relatively large size of our system, different ones, smaller than ours are modelized, in order to identify possible size effect. The types of interaction involved are characterized using electronic density analysis tools. Semi-empirical methods are used and calibrated in order to perform atomistic simulations on a larger scale to take into account the effects of the chemical environment (solvent, ligands).

### Acknowledgements

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### O3: Xanthone excited-state dynamics measured with time-resolved photoionization spectroscopy

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Xanthone is a prototypical molecule for photochemistry in the triplet state due to its triplet yield close to unity [1] and its fast (ps) intersystem crossing in solution [2]. However, the mechanisms at play in the isolated molecule after photoexcitation to the second singlet excited state  $S_2$  are still under debate [3-4]. Here, we investigate the femtosecond time-resolved dynamics in gas-phase Xanthone after excitation at various wavelengths within the  $S_2$  band (310-330 nm). Photoelectron spectroscopy in a Velocity Map Imaging Spectrometer and Time-of-Flight Mass Spectrometry are performed after multiphoton ionization at 800 nm or single-photon ionization at 266 nm. The experimental results are compared to recent wavepacket dynamics simulations [4].

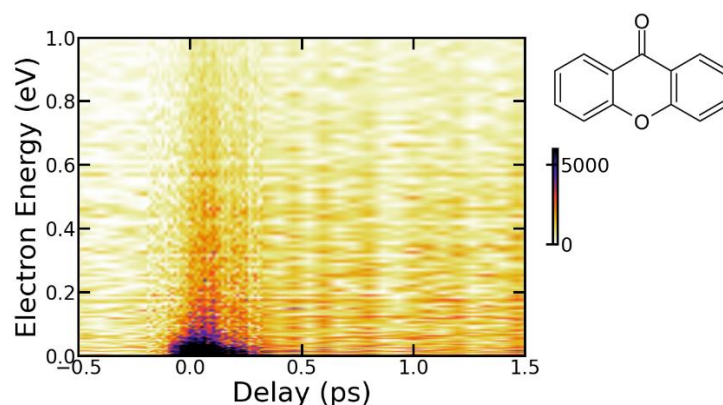


Figure: Time-resolved photoelectron spectrum of Xanthone after excitation at 322 nm and single-photon ionization at 266 nm.

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### **K3: From quantum topology to properties. A focus on superconductivity**

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A room temperature superconductor is probably the most desired system in solid state physics. So far, the greatest advances, cuprates, pnictides and number of others were obtained in a serendipitous way. As there is no clear theory for these superconductors, it is difficult to predict where progress will be made. In contrast the Bardeen-Cooper-Schrieffer (BCS) theory gives a clear guide for achieving high  $T_c$ , and hydrogen seems to be a main clue. Within this approach, the recently reported superconductivity at 190 K in compressed H<sub>2</sub>S [1] has been arguably the biggest discovery in the field since the superconducting cuprates nearly 30 years ago.

However, a microscopic understanding of why this particular material features such a strong coupling is still missing. We have recently shown that the underlying chemical structure and bonding need to be characterized for a good comprehension of the chemical composition-superconductivity relation.

We have constructed simple metal and BCS models showing that the Electron Localization Function [2] can be used to define a quantity called the networking value, which should provide insight into the superconducting activity.

By analyzing through DFT calculations the structural and electronic properties of nearly 200 compounds predicted to be superconductors in the literature, we have shown that the networking value correlates well with the predicted critical temperature, much better than any other descriptor analyzed thus far. And this, for all bonding types [3].

The discovery of the positive correlation between superconductivity and the bonding network offers the possibility of screening easily hydrogen-based compounds and, at the same time, sets clear paths for chemically engineering better superconductors.

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## O4: Optically-active graphdiyne oxide quantum dots as photosensitizers for enhanced photocatalytic hydrogen generation

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Graphdiyne (GDY) is an emerging two-dimensional carbon material with unique configurations comprising of both sp and sp<sup>2</sup>-hybridized carbon atoms that form an extensive network of benzene rings interconnected by diacetylenic linkages.[1] The GDY structure is chemically stable and offers uniform pore size and distribution, rich in  $\pi$ -conjugated electrons, superior electronic properties, tunable band gap and electron donor/acceptor properties enabling applications ranging from energy harvesting and storage to sensing, medical uses or water purification.[2]

Although, pristine GDY is a rigid structure but thanks to the availability of mixed hybridized carbon atoms that can be modify (chemical doping and oxidation) to make the materials processable for the device use.[3] Titanium dioxide (TiO<sub>2</sub>) is one of the earliest known and most studied photocatalyst used for photocatalytic degradation of pollutants and photocatalytic water splitting.[4] TiO<sub>2</sub> is low cost, non-toxic and shows good photostability but its efficiency is relatively low due to its large band gap of about 3.18 eV and fast electron-hole pair recombination, which hampered its ability to photocatalytic activity. To reduce the band gap energy and prolong the electron-hole recombination life, TiO<sub>2</sub> is usually reacted with other metals, metals oxide, organic compounds, and carbon materials.[5] Nevertheless, the high cost of metallic based materials limits their use in commercial applications while the coupling to novel carbon materials seems a more promising path.

In this work, we synthesized highly fluorescent graphdiyne quantum dots (GDYO-QDs) and coupled to commercial TiO<sub>2</sub>-P25 as a co-catalyst for photocatalytic H<sub>2</sub> generation. Different ratios were tested, and optimal conditions were determined to obtain very high amount of H<sub>2</sub> (ca. 2240  $\mu$ mol/g for TiO<sub>2</sub> with 1% GDY-QDs compared to 98  $\mu$ mol/g for TiO<sub>2</sub> alone) under UV-visible light. More importantly, the hybridization of QDs-GDY demonstrated good activity and stability under visible light. The hybrid photocatalyst was characterized by variable technics, such as TEM, UVvis spectroscopy, time resolved photoluminescence spectroscopy to shed light on the synergetic effect and role of QDs-GDY as metal-free co-catalyst.

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## O5: IR – Millimeter-wave double resonance for precision molecular spectroscopy

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Metrology-grade spectroscopic measurements of molecules are of high importance for numerous applications such as testing fundamental physics [1], molecular physics [2], and astrophysics [3]. In this context, we tested the well-established double resonance technique [4-7] using both infrared and millimeter wave transitions to provide high resolution and frequency metrology dataset. The hyperfine components of rotational transitions involving both the ground and the  $\nu_2=1$  vibrational state of ammonia as well as the  $\nu_2=1$  vibrational state of  $D_2O$  have been investigated through IR-THz Doppler-free and cross-over-free double resonance spectroscopy. Spectra were obtained using both a free running external cavity quantum cascade laser (QCL installed at SOLEIL synchrotron) as well as a sub-Hz QCL [8] (installed at LPL Villetaneuse) frequency-stabilised on the REFIMEV signal [9].

The lasers have been used to optically pump the molecules inducing a velocity class selection. We will present the major interests of this approach for precision spectroscopy and the current limitations we meet.

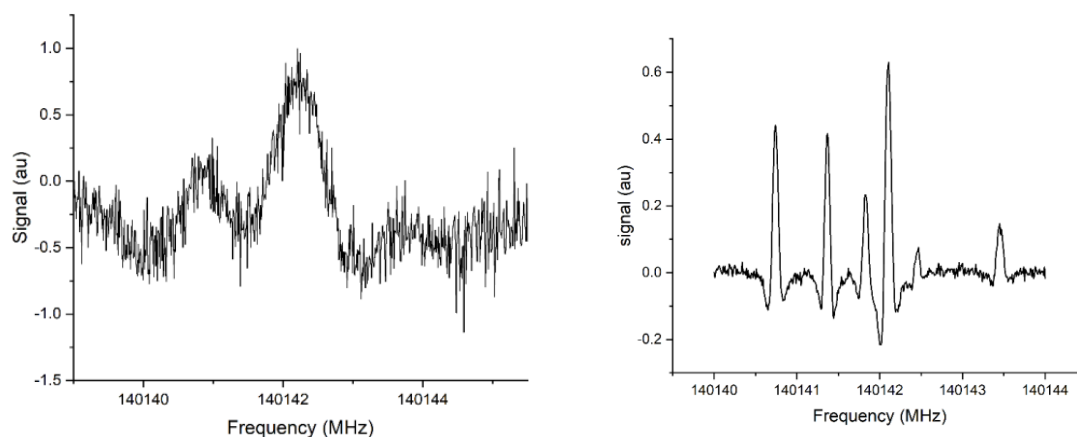


Figure 1: Hyperfine structure of a rotation-inversion transition within  $\nu_2=1$  vibrational state of ammonia. a) Without the IR pump and b) with resonant IR pumping

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## O6: Photoelectron spectroscopy of solvated uracil and bromouracil molecules

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The knowledge of the electronic structure and the ionization energy are shaping the behaviours of molecules. Our study aimed to determine the influence of solvation on the electronic structure of uracil, a RNA nucleobases and one of its derivatives, the 5-bromouracil. For this soft X-rays electron spectroscopy has been used. The measurements have been performed using synchrotron radiation (synchrotron SOLEIL) and an under-vacuum liquid jet, coupled with an electron spectrometer, available on PLEIADES beamline<sup>1</sup>. With this configuration, it is possible to probe about three molecular layers at the surface of the liquid, which means that our measurements are very surface-sensitive. The 1s electronic core level of carbon and nitrogen have been probed in two different pH conditions (basic and neutral). The recorded photoelectrons spectra of solvated uracil in neutral condition are closely similar to the ones obtained on water-uracil clusters<sup>2</sup>. The comparison between photoelectrons spectra at each pH condition reveals some binding energies differences of the peaks in the photoelectron spectra that could illustrate a modification of the chemical environment. Additionally, information on the Lowest Unoccupied Molecular Orbital (LUMO) electronic level has also been retrieved. A tentative of deciphering the different de-excitation pathways following a photoexcitation of a 1s electron, from carbon or nitrogen, to the LUMO, highlighted the complexity to interpret such data obtained in liquid phase.

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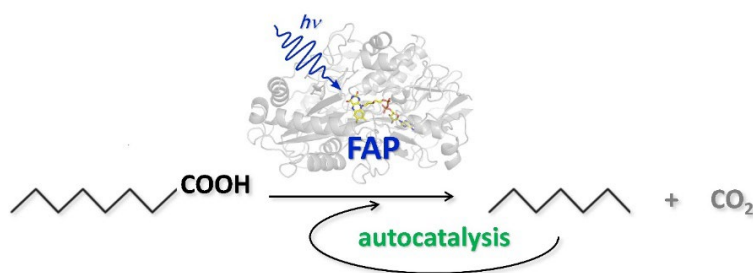
## Poster

### Autocatalytic Effect Boosts the Production of Medium-chain Hydrocarbons by Fatty Acid Photodecarboxylase

Poutoum P. Samire<sup>1,2</sup>, Bo Zhuang<sup>2,3</sup>, Bertrand Légeret<sup>1</sup>, Ángel Baca-Porcel<sup>1</sup>, Gilles Peltier<sup>1</sup>, Damien Sorigué<sup>1</sup>, Alexey Aleksandrov<sup>3</sup>, Frédéric Beisson<sup>1</sup>, Pavel Müller<sup>2</sup>

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Ongoing climate change and geopolitical tensions are driving the search for renewable, carbon-neutral and local alternatives to fossil fuels. Photocatalytic conversion of fatty acids to hydrocarbons by Fatty Acid Photodecarboxylase (FAP)<sup>[1, 2]</sup> represents a promising route to green fuels. However, the alleged low activity of FAP on C2-C12 fatty acids seemed to preclude the use for synthesis of gasoline-range hydrocarbons. We reveal<sup>[3]</sup> that *Chlorella variabilis* FAP (CvFAP) *in vitro* can convert octanoic acid four times faster than hexadecanoic acid, its best substrate reported to date. We also show that *in vivo* this translates into a CvFAP-based production rate over ten-fold higher for *n*-heptane than for *n*-pentadecane. Time-resolved spectroscopy and molecular modeling provide evidence that the high catalytic activity of FAP on octanoic acid is in part due to an autocatalytic effect of its *n*-heptane product. These results should guide future FAP improvement strategies and represent an important step towards a bio-based and light-driven production of gasoline-like hydrocarbons.



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## Photoionization spectroscopic studies of silane derivative radicals at SOLEIL synchrotron

**Ning Chen, Linh Le Hai, Séverine Boyé-Péronne and Bérenger Gans**

Chemically similar to carbon, silicon is believed to be an element that exists abundantly in interstellar space [1]. Even though most silicon is in the form of silicate grains, the chemistry of the remaining silicon (estimated at around 1% of total silicon [2][3]) is very poorly known. All species containing silicon are, therefore, potentially very interesting to better understand the chemistry of silicon. In this poster, we present experimental results concerning the photoionization spectroscopy of a variety of silicon-bearing radicals ( $\text{Si}_x\text{H}_y$ ) and silicon- and carbon-bearing radicals ( $\text{Si}_x\text{C}_y\text{H}_z$ ) which had been scarcely studied up to now because of their instability. The production of these radicals is achieved by using a flow-tube reactor coupled with a microwave discharge that generates fluorine atoms. The  $\text{SiH}_4$  precursor or  $\text{SiH}_4/\text{CH}_4$  mixture undergoes H-abstraction reaction with F atoms (and potentially other chemical reactions) to obtain silane  $\text{Si}_x\text{H}_y$  or silicon- and carbon-bearing radicals  $\text{Si}_x\text{C}_y\text{H}_z$ . The coupling of this radical source with a double-imaging photoelectron/photoion coincidence ( $i^2\text{PEPICO}$ ) spectrometer and the DESIRS beamline at SOLEIL allowed us to acquire the ion yield and mass-selected photoelectron spectra for a series of radicals. Photoionization energies have been derived from the spectra. In addition, using *ab initio* calculations and Franck-Condon simulations, several photoionization transitions have been assigned and interesting phenomena like the observation of spin-forbidden transitions or rich autoionization structures have been described.

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## Photoionization spectroscopy using a broadly-tunable VUV laser

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### *Abstract*

In order to study the photoionization spectroscopy of different reactive species, the VULCAIM setup has been developed in ISMO in 2019 [1-2]. It couples a tunable pulsed vacuum-ultraviolet (VUV) laser with a photoion/photoelectron spectrometer. The VUV radiation is generated from a fixed UV laser radiation ( $\nu_{UV}$ ) and a tunable visible laser ( $\nu_{VIS}$ ), by inducing four-wave mixing ( $2\nu_{UV} \pm \nu_{VIS}$ ) in a supersonic jet of the rare gas.

High-resolution VUV radiation ( $\leq 0.1 \text{ cm}^{-1}$  at  $80000 \text{ cm}^{-1}$ ) can be produced with this configuration when using a tunable dye laser equipped with a double grating system. However, the VUV tunability range is limited to less than  $1000 \text{ cm}^{-1}$  for each dye solution. In many studies, it can be useful as a first step to scan the VUV photon energy over a broad range to search for interesting photoionization transitions of a targeted species. For this reason, the VULCAIM setup has been very recently equipped with an optical parametric oscillator (OPO) laser as an alternative to the tunable dye laser. This new configuration allows to produce a VUV laser which can be tuned over more than  $24000 \text{ cm}^{-1}$ , with a spectral resolution of about  $3 \text{ cm}^{-1}$ . A mass-analyzed threshold ionization (MATI) spectrum of  $\text{NO}^+$  over the  $74200 - 83900 \text{ cm}^{-1}$  spectral range has been recorded as a single spectrum using this broadly-tunable VUV laser to demonstrate the capabilities of this new configuration in photoionization. Photoionization studies of  $\text{CH}_3$  radical produced by a pyrolysis source have also been performed with this VUV laser.

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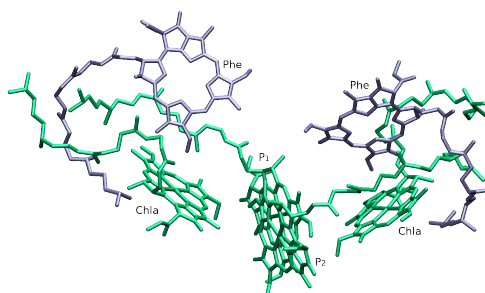
## DFT Studies of phytol chain in chlorophyll type molecules

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Plants contain chlorophyll-type molecules, which play a vital role in photosynthesis for several reasons. Among the numerous molecules involved, chlorophylls are particularly crucial. Photosynthesis, a well-known process, involves two distinct photosystems: Photosystem I (PSI) and Photosystem II (PSII). PSI acts as the catalyst in this reaction, utilizing light to transfer electrons from plastocyanin to ferredoxin.



This study represents the beginning of an ongoing research project. It comprises two parts: a dynamics<sup>1,2</sup> component and an addition of a methanol molecule component. The dynamics aspect occurs in collaboration with experimental chemists who employ a mass spectrum to investigate on chlorophyll a, we want to study the behavior of the phytol tail in gas phase. Within the same collaborative context, the second part focuses on the addition of methanol, which serves as a solvent in our coworkers' electrospray.

The objective is to observe the motion of the phytol chain in the gas phase and determine the specific site of attachment for methanol, to end, see a proton migration and conclude if its preferred or not.

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# Quantifying Non-Thermal Desorption from NH<sub>3</sub> Ices: A Comparative Study of Photon and Electron Irradiation in the Valence- and Core-Shell Energy Ranges

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The relative abundances of gaseous and solid nitrogen in the interstellar medium remain controversial.[1,2] Besides the difficulty in observing N and N<sub>2</sub>, the quantities of nitrogen returning to the gas phase by photo-processing of the ice mantles are not well constrained. In star-forming regions, NH<sub>3</sub> containing ices are exposed to UV and X-Ray photons.[3,4] This leads to non-thermal photodesorption induced by the primary radiation or by exothermic photochemistry (recombination of the secondary species created in the ice mantles).

In order to quantify the non-thermal desorption of N containing molecules and to have a deeper understanding of the complex surface chemistry in ice mantles, we have conducted comparative measurements of photon- and electron-induced desorption (PSD and ESD) from condensed NH<sub>3</sub>. Two setups were used for these experiments, the SPICES setup of the LERMA group, and the E/SOLID setup housed at ISMO. In both systems NH<sub>3</sub> ices are formed by cryogenic deposition (50-100 molecular layers), and the desorption of neutral species is measured by mass spectrometry. Thermal desorption experiments (TPD) were used to calibrate the desorption signal, the ice thickness and for the analysis the processed ice layers. The SPICES setup was coupled to two SOLEIL synchrotron beamlines: (i) DESIRS, valence-shell range (6-12 eV) and (ii) SEXTANTS, core-shell range (395-420 eV, N-K edge). The twin electron irradiation experiments were performed using the E/SOLID setup, in the low-energy range as well as at 385 eV, in order to mimic the secondary Auger electrons known to be major vectors of chemical changes and desorption in X-ray irradiations at the N-K edge.[5,6]

Desorption yields are compared for photon and electron irradiation either as a function of the incident energy in the low-dose regime (spectroscopic study), or as a function of the cumulated dose at a fixed irradiation energy (kinetic study). In the valence-shell range, NH<sub>3</sub> and N<sub>2</sub> are the major desorbing species, with an apparent energy threshold at ~6 eV, showing that both direct and indirect desorption occurs. Different mechanisms at play will be discussed. In the core-shell range, again NH<sub>3</sub> and N<sub>2</sub> are the major desorption products. The remarkable matching between the photo-desorption yields in the ionization continuum and the ESD yields at 385 eV confirms the key role of the Auger electrons in the photodesorption process.

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# Mesoporous g-C<sub>3</sub>N<sub>4</sub>, TiO<sub>2</sub> and g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> photonic films with a chiral nematic structure: slow photonic effect inducing improved H<sub>2</sub> generation

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**Abstract:** Energy crises have flashed in the last few decades. Photocatalysis is a promising green and sustainable process for converting solar light energy into chemical energy. Various semiconductors, including graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and titanium dioxide (TiO<sub>2</sub>), have attracted attention as promising photocatalysts due to their unique properties. However, a common challenge among all photocatalysts is their limited photocatalytic activity, which can be attributed to high recombination of photogenerated charges and a low absorption factor. Extensive research has been dedicated to exploring new chemical and physical strategies to enhance the light harvesting capabilities of photocatalysts.

Photonic structures, engineered to manipulate the propagation of light and utilizing phenomena such as the slow photon effect, are employed to enhance light harvesting capabilities. This work proposes the fabrication of three different bioinspired photonic crystal systems: SiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>, SiO<sub>2</sub>/TiO<sub>2</sub>, and SiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> films with a chiral-nematic structure. The fabrication method combines soft chemistry (sol-gel chemistry) with biotemplate nanomaterials, specifically cellulose nanocrystals (CNCs), see figure 1. The resulting films exhibit iridescent colors and Bragg peak reflection, which can be controlled by adjusting the sol formulation. Characterization techniques such as UV-vis spectroscopy, scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and X-ray photoelectron spectroscopy (XPS) were used to analyze the films. The photocatalytic activity was evaluated for H<sub>2</sub> generation under Mercury lamp illumination. The results demonstrate that the structure can be controlled by the adjusting the sol formulation, thereby influencing the optical properties and the position of the Bragg peak reflection. It was observed that adjusting the Bragg position directly affects the photocatalytic performance of the photocatalyst, exploiting the slow photon effect.

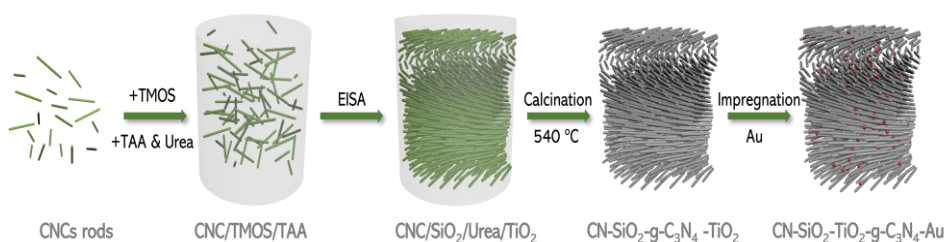


Figure 1. Synthetic route for the Au-SiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub>/TiO<sub>2</sub> with chiral nematic structure derived from cellulose nanocrystals as a biotemplate and TMOS, urea and TAA as precursors.

**Acknowledgements:** Masa Johar acknowledges all collaborators: François Brisset for SEM analysis, Diana Dragoe for XPS analysis, and Marie-Claire Schanne-Klein for the access to the polarized microscope, as well as Campus France and An-Najah National University for their joint scholarship.

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# Singlet exciton fission mechanisms in carotenoids

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Carotenoids are tetraterpenoid derivatives that presents in a wide range of organisms. Their conjugated polyene chain is responsible for their specific photophysical properties. To understand the photophysics of aggregate carotenoids we studied lycopene, a carotenoid with eleven conjugated double bonds that is found in aggregated form in tomatoes chromoplast. We generated artificial lycopene aggregates, which display significant absorption difference from monomers (Figure 1). A large blue shifted peak at 355 nm indicates the formation of H-aggregates (so-called card pack aggregates). This spectral shift might be attributed to exciton interactions. This kind of aggregation may be responsible the peak at 570 nm. Absorption at 514 nm could be related either another lycopene assembly or a lycopene monomer in suspension. Resonance Raman analysis confirmed that lycopene species absorbing at 355, 514, and 570 nm are different. Transmission electronic microscopy images shows the formation of few different types of crystals with longitudinal of 2  $\mu\text{m}$  and diameter of 50-200 nm. Ultrafast transient absorption spectroscopy revealed the presence of long-lived excited states. The datasets for 355, 515, and 570 nm excitations, obtained by fs-TA analysis shows the different evolution in short period of time (less than 60 ps). The energy deactivation pathway are excitation dependent because of the different lycopene association. The results of TA analysis in ns-to- $\mu\text{s}$  range confirmed the presence of long-living triplet states. At longer times, the energy pathways unifies. Further study of singlet fission mechanisms in lycopene aggregates will allows us to create a model to describe properly the early times energy transfer mechanisms.

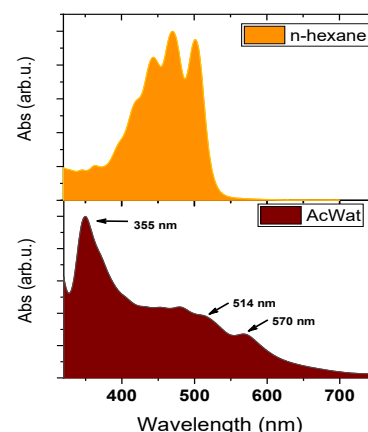


Fig. 1 Room temperature absorption spectrum of monomeric lycopene in n-hexane and lycopene crystalloids in acetone water 1:1 suspension.

## Artificial strong metal-support interaction on plasmonic core-shell nanostructures for photo(electro)catalytic reaction

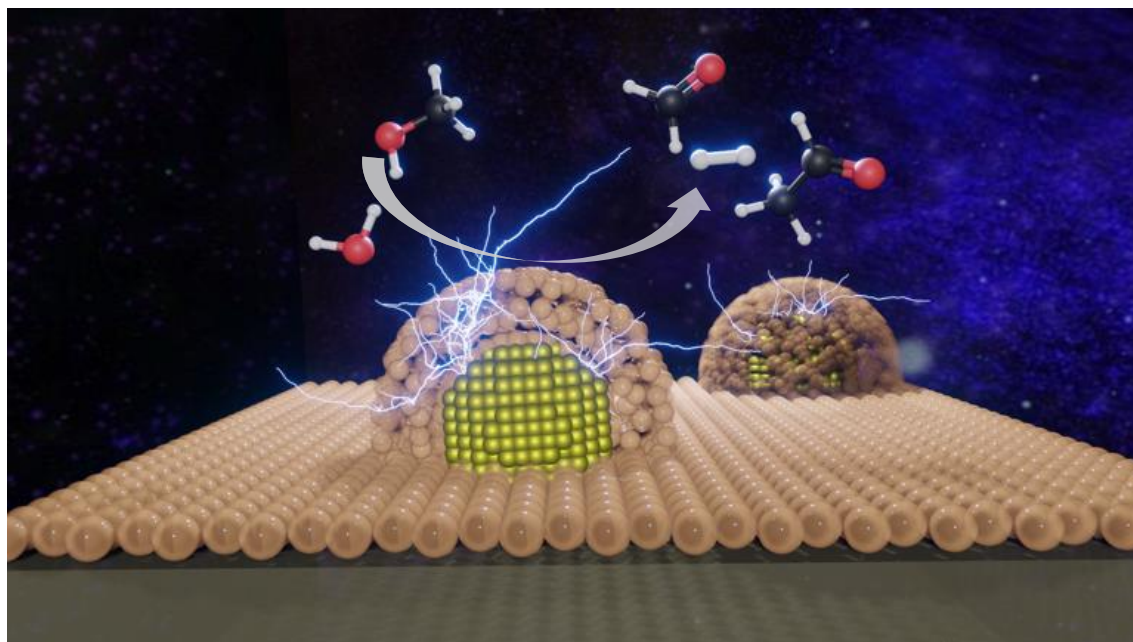
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Photocatalysts mediated by metal nanoparticles have offered a huge contribution to photon-to-hydrogen conversion. Few studies, however, have mentioned encapsulation resulting from “strong metal-support interaction” (SMSI) in the context of photocatalysis. Therefore, further investigations should be performed to understand the effect of photocatalyst designs, the intrinsic activities of metallic nanoparticles, to name but a few, in photocatalytic redox reactions. From a perspective of reaching optimal photon-to-hydrogen conversion yield when anatase TiO<sub>2</sub> is coupled with plasmonic gold nanoparticles (NPs), two key factors are of pivotal importance: i) the efficiency of electron transfer among active sites and ii) the available reactive surface. In this study, we accomplish the construction of *artificial* SMSI-like nanostructures through a soft-chemistry process whereby a thin TiO<sub>2</sub> overlayer covers Au NPs highly dispersed on the surface of SiO<sub>2</sub> nanospheres. Comprehensive characterizations involving spectroscopy, microscopy, and electrochemistry evidenced that the synergetic metal-support interactions offer significant effect on the electronic properties, guarantee efficient photogenerated electron transfer and plasmonic charge carrier injection through SMSI region. In addition, we proposed a schematic mechanism to pinpoint the selectivity towards photo-redox pathways in regard to photocatalyst configuration that produce hydrogen and value-added compounds – formaldehyde and acetaldehyde – on account of C-H activation and C-C coupling.



# Quand les solutés structurent le solvant : interactions sucre – eau en phase gazeuse.

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La liaison hydrogène est au centre des interactions entre les biomolécules et leur environnement, principalement composé d'eau et d'autres biomolécules. Les sucres appartiennent à l'une des classes les plus importantes de biomolécules. Ces molécules particulièrement flexibles codent des informations moléculaires par leur composition chimique ET leurs préférences conformationnelles, étroitement liées à leur environnement direct et local. Cette grande flexibilité et diversité conformationnelle leur font jouer un rôle central dans les processus de reconnaissance moléculaire.

Grâce à des expériences de spectroscopie vibrationnelle à double résonance sélective en conformation et résolue en masse, nous pouvons identifier les choix conformationnels de sucres isolés et l'effet d'un nombre contrôlé de molécules en interaction.(1) Jusqu'à présent, dans le cas des études d'interaction sucre-eau, nous avons principalement étudié l'effet d'un nombre limité et contrôlé de molécules d'eau sur la conformation des sucres.(2)

Nous présenterons des résultats très récents mettant en évidence le comportement symbiotique de l'influence des molécules de solvant sur les sucres et des sucres sur le solvant. Cela repose sur l'identification de structures d'agrégats hydratés de sucres où les molécules d'eau et les OH du sucre créent les mêmes réseaux de liaisons H que ceux qui ont été identifiés pour les oligomères d'eau (voir figure). Ces résultats font écho au concept selon lequel le sucre peut être considéré comme des « oligomères d'eau pré-organisés » (3) ayant la capacité de façonner et affecter son propre environnement.

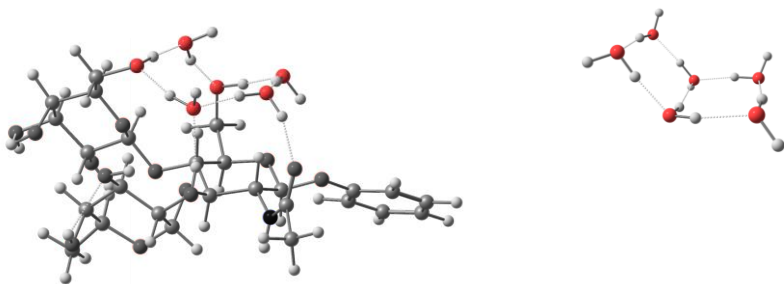


Figure 1. Comparaison de la conformation "libre" de l'hexamère de l'eau (4, à droite) et de la conformation « empilée » du trisaccharide Lewis X en interaction avec quatre molécules d'eau (à gauche).

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## Solvation effect observed on a molecule deposited on an argon cluster

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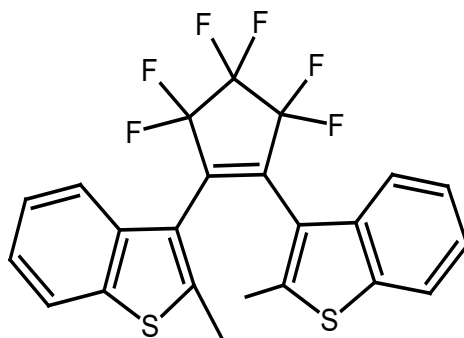
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Real-time dynamics of the electronically-excited open-ring isomer of 1,2-bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene (BTF6) and 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (PTF6) photochromic molecules was investigated using a set-up that associates a molecular beam, femtosecond lasers and a velocity map imager. The molecules were either free in the gas phase or bound to an argon cluster. The free molecule dynamics was found to follow a three wavepacket model. One describes the parallel conformer (P) of these molecules. The other two wavepackets describe the reactive antiparallel conformer (AP). They are formed by an early splitting of the wavepacket that was launched initially by the pump laser. All the channels were identified. When BTF6 and PTF6 molecules are bound to an argon cluster, the same three wavepacket model applies. We will present the effect of the argon cluster on the relaxation dynamics.

**BTF6**



**SUB-MILLIMETER SPECTROSCOPY OF RELATIVELY  
LARGE RADICAL SPECIES. EXPERIMENTAL  
IMPROVEMENT AND FIRST RESULTS ON VINOXY,  
ACETYL, AND ACETONYL RADICALS.**

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Molecular radicals are key species for chemical reactions occurring in combustion processes as well as in atmospheric and astrophysical environments<sup>1</sup>. However, the characterization of “large” radicals (defined here as containing more than 5 atoms) using high-resolution gas phase absorption spectroscopic techniques remains tedious and requires the development of specific experimental setups to increase the sensitivity of the spectrometers. To this end, we associated a frequency multiplication chain spectrometer, allowing high-resolution spectral acquisition in the 75-900 GHz range, with a relatively specific technique of radical synthesis based on H abstraction on a given precursor by reaction with F atoms in a flow cell<sup>2,3</sup>. Since paramagnetic species (e.g., radicals) are sensitive to the magnetic field, an alternative magnetic field was generated in the cell allowing the use of Zeeman Modulation<sup>4</sup> (ZM) as well as Faraday Rotation Modulation<sup>5</sup> (FRM) techniques to record broadband and “radical-only” spectra. Using these techniques, the spectra of the vinoxy radical (CH<sub>2</sub>CHO), the acetyl radical (CH<sub>3</sub>CO), and the acetonyl radical (CH<sub>3</sub>COCH<sub>2</sub>) have been recorded. I will present these instrumental developments as well as the associated preliminary spectroscopic results.

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## Studying the vibrational structure of molecules by photodetachment: a new spectroscopic method

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Chlorophylls and Pheophytins play critical roles as essential pigments in the intricate process of photosynthesis. Chlorophyll stands out as an exceptionally efficient antenna for absorbing sunlight. Following absorption, this energy is subsequently transferred to an arrangement of four Chlorophylls and two Pheophytins within the Photosystem II (PSII) reaction center. The high efficiency observed in the initial charge transfer step is believed to arise from a resonance between the vibrational modes of Chlorophyll and the energy gap separating the excitonic and charge transfer pairs. However, the detailed vibronic structure of both Chlorophyll and its dimeric form remains largely elusive. Consequently, our research endeavors to elucidate the vibronic structure of neutral Chlorophyll 'a'. To accomplish this, we employ an innovative spectroscopic technique, namely the photodetachment of an electron from a cooled dipole bound anion. In order to detach this electron, we excite the anion by a photon with energy greater than the detachment threshold. This generates an electron and a neutral species. The excess energy (photon energy minus detachment threshold energy) is distributed between the electron and the neutral species (**Figure 1 below**). By measuring the kinetic energy of the ejected electron after photoexcitation, we investigate the vibronic properties of both the anionic and neutral species. Notably, this spectroscopic method allows us to access the vibrational modes of the neutral species in the absence of any perturbations, thus enabling a direct comparison with high-level quantum calculations.

Our poster showcases the outcomes of our research, starting with the initial validation of our experimental setup using the 4-fluorophenolate anion. We then step up into the investigation of the properties of the chlorophyll family, while also optimizing the experimental conditions in the gas phase through LCQ spectral analyses. Finally, we present our experiments conducted on pheophytin 'a', which include action spectra, photoelectrons imaging, and other relevant results, all carried out using our setup.

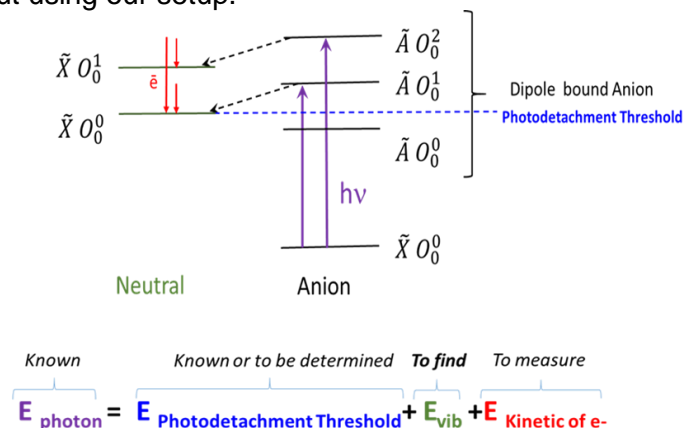


Figure 1 : Energy diagram representing the principle of photodetachment

## Development of integrative methods for the structure elucidation of protein-ligand complexes combining experimental and computational data

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In the field of structural biology, the elucidation of the interactions between proteins and ligands is a crucial step in understanding their functional properties. The use of computational modelling tools[1], such as Autodock, Autodock Vina and Dock6 between others, has greatly aided in this effort, allowing for the prediction of ligand binding sites of the protein-ligand complexes. However, the accuracy of these predictions can be limited [2].

In this study, we aim to achieve a more accurate match between experimental data and computational models by using a range of data that we integrate with a program called CNS when the acquisition of precise and high quality data from X-Ray crystallography, Cryo-EM and NMR is not possible. We emulate different scenarios, from almost perfect amount and quality of information to sparse data with added noise and by using raw experimental data such as the chemical shifts with and without assignment from NMR, deuterium/proton exchange with NMR or MS, mutagenesis and more.

Our goal is bidirectional, for one side to improve the reliability and predictive power of computational modelling approaches in protein-ligand elucidation, but also limit the amount of experimental data needed to achieved a high quality complex structure.

### References

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- [2] S. F. Sousa, P. A. Fernandes, and M. J. Ramos, "Protein–ligand docking: Current status and future challenges," *Proteins Struct. Funct. Bioinforma.*, vol. 65, no. 1, pp. 15–26, 2006, doi: 10.1002/prot.21082.

## **Etude biochimique et photophysique de Protéines Fluorescentes Jaunes (YFPs)**

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Les Protéines Fluorescentes (FPs) sont des outils incontournables de la recherche biologique et biomédicale. Utilisées comme rapporteur fluorescent, elles permettent la compréhension des processus biologiques à l'échelle moléculaire. Leur particularité tient du fait que leur chromophore est formé par la cyclisation autocatalytique de 3 acides-aminés adjacents, ce n'est pas un groupe prosthétique. Les propriétés de la FP dépendent fortement de l'environnement protéique du chromophore.

La compréhension de la relation structure-fonction-dynamique de ces protéines est primordiale pour optimiser leurs performances en fluorescence et notamment leur photostabilité. Le photoblanchiment (diminution progressive et irréversible de la fluorescence des FPs à la suite d'une irradiation prolongée) est une déficience qui restreint l'étude de certains phénomènes biologiques qui durent plusieurs minutes voire plusieurs heures.

L'équipe Photobiologie de l'ICP s'intéresse à la compréhension des mécanismes impliqués dans la photostabilité des FPs et plus particulièrement des Protéines Fluorescentes jaunes (YFPs), comme la Citrine ou la EYFP. La littérature a permis d'identifier les positions 69 et 145 comme jouant un rôle dans la photostabilité de ces FPs. [1]

Trois nouvelles YFPs ont donc été produites en mutant ces positions, le but étant de générer des YFPs plus photostables que la Citrine (protéine très utilisée mais très peu photostable) tout en conservant, voire en améliorant, ses propriétés photophysiques (propriétés d'absorption et d'émission, brillance, rendement quantique, etc) et biochimiques (pK<sub>1/2</sub> et sensibilité aux chlorures).

L'objet de cette étude est de caractériser d'un point de vue photophysique et biochimique ces trois nouvelles YFPs et de mieux comprendre la relation structure-propriétés de ces protéines très étudiées dans l'équipe.

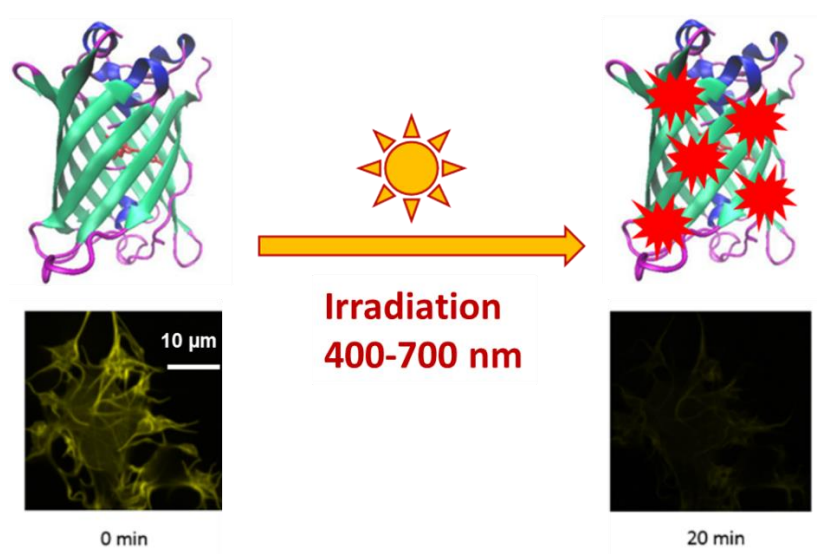
[1] M. D. Wiens et al, *Integrative Biology*, **10**, 419–428 (2018)



## Photobleaching of yellow fluorescent proteins: Investigation on the nature of the photoproducts

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Fluorescent proteins (FPs) are genetically encoded fluorescent probes that have become invaluable in bioscience/biophotonics as they allow the understanding of biological processes at the molecular level to get wonderful insights into living machines at work. The accurate monitoring of the biochemical events deeply depends on the FPs long term photostability, a poorly studied parameter until now. The improvement of this photostability is a major challenge that requires a thorough understanding of the mechanisms involved in photobleaching. Here, we report the first results of a study aimed at understand the effect of punctual and targeted mutations on positions 69 and 145 on the mechanisms involved in the photobleaching of five yellow-emitting FP [1].

Two experimental approaches have been used so far on these five FPs. On the one hand, the analysis of the evolution of the absorption spectra over the irradiation time allowed to know which residues can have the biggest influence on the photostability of the protein. On the other hand, analysis of the photoproducts by UV-vis spectroscopy, gel SDS PAGE and mass spectrometry provided initial information on the chemical nature of the generated photoproducts for each FP.

### Références

[1] Wien et al. *Integr. Biol.*, **10**, 419 (2018)