Rencontres des Chimistes Théoriciens du Grand Est 2022

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Communications orales

Computational design of molecular systems for nano-thermoelectric applications

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The ongoing research in nanotechnology is facing similar energy control issues than at the micro and macroscale. Among the different issues to be solved, one important problem concerns the wasted energy generated by in-use over-heating, notably by the resistance of the nano-components of a nano-unit against the electrical current flow.(1) A straightforward approach that naturally comes to mind to prevent such potential deleterious effect is to exploit thermoelectric effects at the nanoscale. In that context, we are currently investigating molecular junctions as potential candidates to solve this issue by combining computational and experimental tools.(2) This requires reviewing the present rationalization of the experimental measurements and approximations done at the quantum chemical levels. On the basis, we are evaluating organometallic wires which are fulfilling part of the features which should enhance thermoelectric properties compare to the current identified systems.(3)

(1) a) HOMO Level Pinning in Molecular Junctions: Joint Theoretical and Experimental Evidences. S. Rodríguez González, Z. Xie, O. Galangau, P. Selvanathan, L. Norel, C. Van Dyck, K. Costuas, C. D. Frisbie, S. Rigaut, J. Cornil, *J. Phys. Chem. Lett.*, **2018**, *9*, 2394–2403; DOI: 10.1021/acs.jpclett.8b00575. b) On the reliability of acquiring molecular junction parameters by Lorentzian fitting of I/V curves. V. Delmas, V. Dies-Cabanes, C. van Dyck, E. Scheer, K. Costuas, J. Cornil, *Phys. Chem. Chem. Phys.*, **2020**, 22, 26702–26706; DOI: 10.1039/D0CP05372D. c) Electronic transport through single-molecule oligophenyl-diethynyl junctions with direct gold - carbon bonds formed at low temperature G. Mitra, V. Delmas, H. Al Sabea, L. Norel, O. Galangau, S. Rigaut, J. Cornil, K. Costuas, E. Scheer *Nanoscale Adv.*, **2022**, 4, 457–466; DOI: 10.1039/d1na00650a

(2) Photo-modulable Molecular Transport Junctions based on Organometallic Molecular Wires. F. Meng, Y.-M. Hervault, L. Norel, K. Costuas, C. Van Dyck, V. Geskin, J. Cornil, H. H. Hng, S. Rigaut, X. Chen, *Chem. Sci.*, **2012**, *3*, 3113-3118. DOI: 10.1039/c2sc20323e

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*Intervenant

Representation of a molecular-electronic transition: reduced-density-matrix theory meets matrix perturbation theory

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During this talk I would like first to revisit the foundations of the natural-orbital representation of molecular-electronic transitions in order to prove the non-universality of the commonly admitted interpretation of the so-called natural transition orbitals. This part of the speech, related to qualitative analysis frameworks, will also lead us to the conclusion that there is no universal departure/arrival natural-orbital representation of molecular-electronic transitions. We will eventually show that without the disambiguation preliminarily introduced, the most widely used excited-state quantum-chemical calculation method - namely, time-dependent density-functional response theory - would yield electronic-transition pictures that would be either incomplete, equivocal, or arbitrary. The second part of the talk will be devoted to the study of the consequences of introducing a post-linear-response treatment of light-induced electronic-structure reorganization: orbital relaxation. In this context, results from matrix perturbation theory will be explicitly used to derive boundary values for the exact quantity of electronic charge transferred during a molecular-electronic transition.

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[*]Intervenant

Ortho-métallation de s-aryltétrazine par activation de liaisons C–H : étude mêlant théorie et expériences

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Parmi les classes d'hétérocycles aromatiques, les s-aryltétrazines sont des motifs moléculaires incorporant quatre atomes d'azote que l'on retrouve dans de nombreux domaines d'applications comme dans la photochimie, les matériaux énergétiques ou bien encore dans le domaine médical.(1)

Toutefois, leurs modes de synthèse reposent encore principalement sur celles développées par Pinner ou de Stollé présentant de fortes limitations en termes de tolérance de groupements fonctionnels et des rendements faibles pour des tétrazines hautement fonctionnalisées malgré les avancées de nombreuses équipes de recherche.(2) Récemment, l'équipe du Pr. J.-C. Hierso a développé une approche innovante basée sur l'utilisation catalytique de métaux de transition pour l'activation puis la fonctionnalisation de liaisons C–H en position *ortho* du cœur tétrazine.(3),(4) L'étape clé de cette stratégie est l'obtention d'un intermédiaire *ortho*-métallé qui permettra l'introduction de la nouvelle fonctionnalisation à l'issue du cycle catalytique (Figure 1). Pour mieux appréhender la formation de l'intermédiaire clef et avoir une compréhension fine de cette étape pour divers métaux de transition, l'approche théorique peut s'avérer pertinente.

Dans ce contexte, mon travail de thèse combine des études théoriques et expérimentales pour mieux comprendre la formation de ces métallacycles, étape élémentaire et limitante du cycle catalytique. En s'appuyant sur les différents résultats expérimentaux obtenus lors de la synthèse des divers complexes (conditions expérimentales, structures RX ou bien encore données cinétiques), je présenterais les calculs de profil d'énergie et les structures des intermédiaires clefs. Et enfin Je montrerais comment le dialogue théorie/expérience permet d'élucider la structure et la stéréochimie des complexes intermédiaires métallacycles impliqués dans la réactivité des *s*-aryltétrazines.

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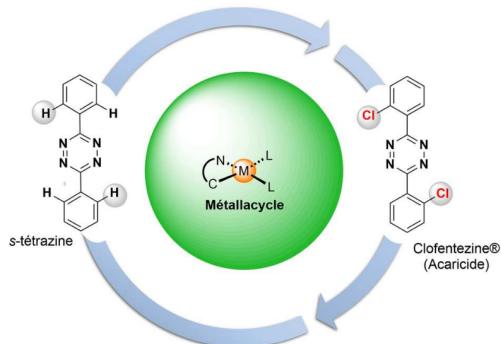
Figure 1 : Fonctionnalisations catalysées des s-*aryltétrazines* via *la formation d'un métallacycle.*

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Emergence of Spinmerism from Model Hamiltonian View

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Spin-crossover metal ions and organic radicals can be combined to generate original spin states zoologies. From a model Hamiltonian first restricted to exchange interactions between a commutable spin unit (SM = 0 or 1), and two radicals (s1 = s2 = 1/2), the spin states of the system can exhibit a mixture of SM = 0 and SM = 1 local spin states. It is shown that this mixing reaches a maximum for 2KM = K1 + K2, where KM, K1 and K2 are the intra-metal and metal-ligand direct exchange integrals. Then, the spin states energies are corrected using second-order perturbation theory to account for the ligand-to-metal charge transfers (LMCT) and MLCT. Whilst the here-depicted regimes might not be immediately achievable, our conclusions promote an original manifestation of intrication with potential application in qubits.

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*Intervenant

Quantum embedding by means of the Block-Householder transformation

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Quantum embedding has emerged over the last two decades as a viable strategy for modelling strong electron correlation in large molecules and extended systems. The purpose of an embedding procedure is to replace the original full-size problem, for which an accurate solution to the Schrödinger equation is out of reach, by one or several simpler problems that preserve only a fragment of the original system. The fragment, which can be a single atomic site (often referred to as impurity) in a lattice, is embedded into a formal bath that is supposed to mimic the effects of the impurity's environment. In this presentation, I will introduce a recently developed quantum embedding based on the (one-electron reduced) density matrix which is revisited by means of the unitary Block-Householder transformation.

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*Intervenant

Local potential functional embedding theory: On the way from lattice models to quantum chemistry

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Calculation of the electronic structure of molecules is an important part of chemistry because it enables us to calculate and predict many different properties of molecules and reactions. Two different approaches are popular in quantum chemistry: First are wave function theories. They can offer high accuracy but have high computational cost. The second approach is the Kohn-Sham density functional theory (KS-DFT) (1) which gives solutions with a single configuration and can treat larger systems but can't accurately treat strongly correlated systems. Another way to solve the Schrodinger equation for large systems are embedding theories. They split the big system into smaller fragments. With this approach, the electronic structure of only one fragment per time is calculated but since interactions between fragments are cut, an orbital called bath orbital is added to each fragment. The Schrodinger equation is solved for the "fragment + bath" system (so-called cluster) (2, 3). The bath ensures that local properties of the true fragment (like the density) can be reproduced by the embedded one. It actually plays the role of an electronic reservoir. Then embedding theories try to combine solutions of smaller systems in order to approximate the energy of the full system. An in-principle exact embedding approach called Local Potential Functional Embedding Theory (LPFET) where DMET is combined with KS-DFT has been derived recently (4) within the homogeneous Hubbard model. What makes LPFET different from regular KS-DFT is that approximation to the Hartree exchange-correlation energy/potential is calculated through an exact diagonalization of the cluster's Hamiltonian. The cluster is constructed within the (one-electron) orbital space with the help of a unitary transformation (called Householder transformation (5)). In our work, we managed to extend this method to small heterogeneous Hubbard molecules and we will present preliminary results. This extension of LPFET theory to Hubbard molecules is an important step toward its application to quantum chemistry.

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Strain and support effect on γ-Fe$_2$O$_3$(111)

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Generating hydrogen from water and sunlight using photoelectrolysis can be a vital alternative for new energy applications. But, weak reactivity and low efficiency remain major hurdles for large-scale implementation of water-photoelectrolysis. A great number of metal oxides have been screened, and maghemite has shown some promising properties. However, the understanding of the properties and stability of maghemite surfaces in the literature remains inadequate. In this project, we have first considered different possible surface terminations of pure maghemite (111). Among them, some of the best competing surfaces are further investigated for the effect of strain, interaction with Pt(001), and other electronic properties of γ-Fe$_2$O$_3$. We compare the thermodynamic stability of various terminations with and without compressive strain. Electronic properties of some key surfaces have been analyzed and the impact of the Pt(001) surface has been considered.

Nine different possible terminations of eighteen layers slabs of γ-Fe$_2$O$_3$ have been investigated. Geometry optimizations reveal that oxygen terminations are significantly less stable than iron ones. In some cases, the most stable surfaces have opposite directions of magnetic moment with respect to their bulk counterpart, specially those which are present on the surface. Although, the whole system still remains ferrimagnetic. To achieve the epitaxial relation between γ-Fe$_2$O$_3$(111) and Pt(001) surface, we performed a 30-degree rotation onto γ-Fe$_2$O$_3$ surface along with a 5x3 supercell for Pt(001). This transformation provides the smallest possible compressive strain of 4.64% along x and 0.86% along the y-direction. Preliminary stage calculations suggest that the effect of strain destabilizes the surface but does not change the relative order of stabilization among iron/oxygen termination. The strain energy was observed to be 24 - 38 meV/ Å 2 weakest for oxygen termination. We compare the electronic and structural properties of constrained and unconstrained γFe$_2$O$_3$(111) which are crucial to understand the epitaxial growth of γFe$_2$O$_3$ on Pt(001) surface. Finally, we investigate the effect of Pt-support along with constrain on the stability of different terminations of γFe$_2$O$_3$(111). For the Fe-terminated surface, we obtained interaction energy of -113 meV/Å^2 and a corresponding strain energy of 32 meV/ Å 2 . Therefore, the formation of this heterostructure is favorable with the adhesion energy of -81 meV/ Å^2 . As a perspective, we plan to investigate the water dissociation and adsorption of key species such as OH, O, and H on the most stable surface termination of γFe$_2$O$_3$(111) on Pt(001) support.

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*Intervenant

Cracking of alkenes catalyzed by zeolites: from ab initio molecular dynamics to machine learning perturbation theory

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Cracking and isomerization reactions via cationic intermediates are building blocks of many chemical transformations for valorization of long chain paraffins coming from plastic waste, vegetable oils, Fischer-Tropsch process or crude oils.

We have performed the first characterization of the transition state of a type B1 cracking reaction (from secondary to tertiary cations), starting from C_7 alkenes in acidic chabazite at T = 500 K by enhanced *ab initio* molecular dynamics, at the PBE+D2 level of theory. A free energy barrier of $\Delta A\ddagger = 60.1$ kJ/mol was found, starting from a π-complex (the relevant kinetic intermediate).[1] The complexity of the system may require more accurate levels of theory that are computationally more expensive. Higher levels of theory have been made affordable by the application of Machine Learning Perturbation Theory (MLPT)[2,3] which make possible the first calculation of a free energy barrier at the RPA level of theory. Low variations of the free energy barrier are found for GGA functionals while the barrier computed at the RPA level is in excellent agreement with the experimental one (Fig 1.b Current efforts are devoted to the investigation of the effect of the level of theory for isomerization reaction barriers.
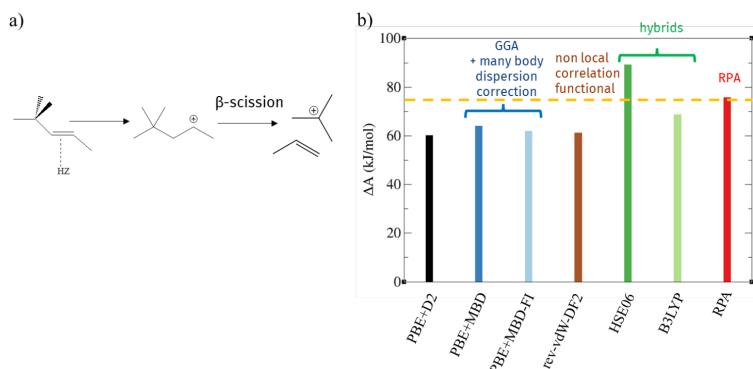
Fig. 1. a) Mechanism of the B1 cracking reaction. b) Correction by MLPT of the free energy of activation at different levels of theory. The orange dashed line represents the estimate from experiments and kinetic modeling.[4]

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*Intervenant

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Catalytic upgrading of biomass using metallic clusters supported on amorphous silica surfaces

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Hydrocarbons derived from lignocellulosic biomass have gathered an increasing interest for fuel production. The bio-oils obtained by the pyrolysis of lignin contain a large number of phenolic compounds (45 wt.%), and it can be upgraded by HydroDeOxygenation (HDO) process. It has been shown experimentally that Fe@silica are active and selective in HDO. In this work, we have evaluated through DFT calculations the performance of M13@silica (M = Fe, Co, Ni, Cu) in the HDO reaction of phenol (1,4). We have selected amorphous silica surfaces (2) with a silanol density of 2 and 3.3 OH/nm2 as they can selectively achieve the adsorption of phenol. The grafting mechanisms of M13 clusters have been investigated (3), showing a strong interaction between transition metals and the silanol groups, accompanied with a large charge transfer, making it very stable and promising for a large range of applications. The inhibitory effect of CO and water molecules on the adsorption of oxygenated compounds is negligible for Fe13@silica, Co13@silica and Ni13@silica catalysts, while for Cu13@silica, both CO and H2O are expected to be major inhibitors of the HDO process. Therefore, silica-supported transition-metal (Fe, Co, Ni) clusters appear as suitable candidates for the HDO process. Investigation of the direct deoxygenation pathways of phenolic compounds on these systems is under progress. We will show that dihydrogen is activated on the M13 clusters while phenol is adsorbed at the M13/silica interface, through a π-interaction between the aromatic ring (which is deformed) and the M13 and hydrogen bonding with the silanol.

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*Intervenant

Cages moléculaires actives en catalyse supramoléculaire : Synthèse, études théoriques et réactivité

Laurie Zujew * [1], Stéphanie Durot , Christophe Gourlaouen [1]

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La valorisation du dioxyde de carbone comme synthon en chimie est un enjeu pour l'industrie pour réduire sont empreinte carbone. Un exemple est la réaction entre le CO2 et les époxydes permettant la formation de carbonates cycliques en présence de catalyseur. Les cages moléculaires incorporant des metalloporphyrines se sont révélées performantes à la fois pour la reconnaissance moléculaire et pour la catalyse supramoleculaire, le Laboratoire de Synthèse des Assemblages Moléculaires Multifonctionnels (LSAMM) associé au Laboratoire de Chimie Quantique (LCQ) ont décidé de développer de nouvelles structures pour la catalyse de cette réaction. Des cages composées de deux porphyrines reliées par des chaines flexibles possédant des triazoles comme sites de coordination périphériques ont ete synthétisées avec succès au LSAMM et elles ont montré une forte activité catalytique pour la formation de carbonates cycliques. Néanmoins, la nécessité d'utilisation d'un co-catalyseur associée aux conditions de réaction (120°C – 20 bars de CO2) afin d'obtenir le produit ont poussé les deux laboratoires à concevoir de nouvelles cages afin d'améliorer ces résultats. Les travaux exposés ici consistent donc à concevoir de nouveaux nanoréacteurs optimisés grâce aux calculs théoriques et à synthétiser les architectures tridimensionnelles afin d'étudier leurs propriétés en catalyse.

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*Intervenant

Modelisation by DFT of the carbonylation of an epoxydes catalysed by a bi-porphirinic cages

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Nowadays in the perspectives of biomimicry, molecular cage regain interest. The catalytic activity of the bisCo(III) porphyrin molecular cage consisting in two free-base porphyrins connected by flexible linkers (CoCl)2-1 was studied in the synthesis of cyclic carbonates from CO2 and propylene oxide (PO)) with pyridine and DMAP as cocatalyst(1). However, during investigation the rate of the CO2 consumption was subject to some matters. In addition, the molecular cage was shown to be a catalyst of high yield for the studied reactions even without the planned co-catalyst, adding some questions on possible other co-catalysts(2). Moreover, it was shown that the bi-cage was more efficient to convert the epoxides compared to CoCl-TPP(3). To get more knowledges about the exact processes, quantum modelling calculations were performed to explore the paths of this reaction catalysed by pyridine, chloride or even triazoles present in the linkers of the cages. Molecular dynamics were also performed to observe the conformation evolution of the porphyrin. To do these simulations, we had to deal with the absence of parmaters for Co3+. The first DFT computations shown the necessity of a catalyst for this reaction as well such as DMAP but not pyridine. These computations were also made on porphyrin model and the best paths for each catalyst were computed. The dynamics was started with Co(III) substitutes and explored the conformational flexibility of the cage to validate the hypothesis made for the QM calculations. The understanding of the reactional mechanism and the role played by the different reactants pave the way for the design of a new catalyst.

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*Intervenant

Synthèse et analyse de nouveaux récepteurs pour la reconnaissance ionique

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Les noyaux acridiniums sont des petites briques de base qui sont robustes et qui ont des propriétés commutables aussi bien chimiquement, électrochimiquement que photochimiquement.(1) Les fragments acridiniums sont également des unités pi-étendues et électro-déficientes (présence d'une charge positive) qui ont été incorporés dans notre laboratoire dans des récepteurs supramoléculaires (pinces, macrocycles ou encore cages).(2)

Ici, nous nous proposons d'explorer plus profondément la chimie des acridiniums via la synthèse de pince inverse. Ces structures vont pouvoir induire des assemblagess hôte-invités avec des espèces ioniques, grâce à des interactions electrostatiques de type liaisons chalcogènes. Dans un premier temps, des calculs théoriques ont permis de réaliser l'optimisation géométriques de ces molécules, de prévisualiser et de mettre en évidence les interactions électrostatiques désirées. En s'appuyant ensuite sur la chimie précédemment développée, nous sommes parvenus à la synthèse de deux nouveaux types de récepteurs capables d'interagir avec des espèces anioniques et cationiques ainsi que de se complexer avec des macrocycles tels que des cyclodextrines.

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*Intervenant

Quantum dynamics of the two dimensional diffusion of adsorbates on metallic surfaces.

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We aim at investigating the diffusion of adsorbates on a metallic surface with entirely quantum calculations. We want to see which quantum phenomena are likely to occur during diffusion. The Multiconfigurational Time Dependent Hartree (MCTDH) method will be used to obtain the quantum dynamics from the first principle calculations. In the long term we want to see how our result can be used to extract observable quantities such as the intermediate scattering function (ISF) and the dynamical structure factor (DSF) already seen in the previous project (1,2), with the aim to correctly interpret and rationalize the experimental data.

One of the systems to be studied is dihydrogen on the surface of palladium atoms Pd(111). In order to study the quantum dynamics of this system, it is essential to start by computing its eigenenergies and eigenstates, which will allow us to verify how realistic the approach is. During the RCTGE 2022 meeting, a theoretical study of the vibrational spectrum of the H2/Pd(111) system will be presented as well as other results obtained so far.

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[*]Intervenant

Multi-scale simulations of biological systems

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In this talk we present multi-scale simulations of proteins at mesoscale. In particular we will focus on cell-like crowded conditions and on the problem of protein mobility and stability in such environments. We will discuss examples relating to health such as the cell-death problem, the misfolding and aggregation of proteins involved in Alzheimer and ALS. We will also show how the same framework can used to investigate processes beyond the molecular scale, e.g. motion of epithelial cilia, flow of interstitial fluid in brain and others.

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[*]Intervenant

Solvation Properties of Hydrophobic Deep Eutectic Solvents investigated via Molecular Dynamics.

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Deep eutectic solvents (DES) are defined as mixtures of pure compounds, usually a Lewis or Brønsted acid or base, for which the eutectic point temperature is significantly below that of an ideal liquid mixture. Recently DES has become a promising alternative to ionic liquids (ILs) in the development of sustainable solvents. The former has been reported to possess many of the physico-chemical properties of ILs, such as a low vapor pressure, relatively wide liquid range, and non-flammability, without necessarily having their drawbacks(1). The most notable difference to ILs is certainly the fact that they are much easier to prepare leading to significant lower production costs(2). Additionally, many of the numerous constituents currently used to prepare DES can be bio-sourced and are biodegradable which is not generally the case for ILs(3). Recent reports show the high capability of using hydrophobic DES as an extraction phase for (poly)phenol molecules from an aqueous solution(4, 5, 6).

Molecular dynamics (MD) simulations are a valuable tool to get structural and dynamical properties of liquids, on their solvation properties as well as on liquid-liquid interfaces. Herein we have investigated the solvation of benzene-diol molecules (hydroquinone, resorcinol, catechol) using MD in different menthol:thymol mixtures, in which the molar fraction of thymol has been varied from 0 (pure menthol) to 1 (pure thymol) by steps of 0.1. Benzene-diol has been chosen as a simple model for (poly)phenols. A snapshot of a typical simulation box, composed of 1 solute molecule and 1000 solvent molecules, is given in Figure 1. Particular care is used to describe the H-Bonds between the various solute and the solvent molecules. Analysis reveals that the strongest interaction between solute and solvent are seen in menthol rich mixtures as a result of H-Bonds between the slightly acidic -OH group of the solute (H-Bond donor) and the somewhat basic -OH group of the menthol molecule (H-Bond acceptor). These results indicate that DES mixtures may be fine-tuned to optimize their solvation properties.

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Chimie, modèles : une expérience pédagogique en Licence et en Master à Nancy

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Dans l'enseignement de la chimie théorique et computationnelle sur le site de Nancy, nous explorons des modes pédagogiques non conventionnels. Nous n'avons pas un vivier d'étudiants qui s'orientent vers la modélisation (dans la période 2009-2022, seuls deux étudiants de notre Master ont effectué un stage M2, puis une thèse, en chimie théorique). Or, certain.e.s étudiant.e.s souhaitent se former dans ce domaine (l'option RFCT en M2 a toujours ouvert, depuis 2016). En Licence, l'enseignement de la chimie computationnelle était traditionnellement discontinu (atomistique en L1, puis de la chimie orbitalaire en L3) avec une focalisation exclusive sur la chimie quantique. Depuis quelques années, avec une forte implication dans les groupes de travail pour la Licence et le Master de Chimie, nous faisons évoluer une partie de nos enseignements. Deux UE en option (L1 PC et L3 Chimie) sont proposées pour découvrir la visualisation des molécules et les outils de calcul et de simulation par une approche ludique. En M1, des EC interdisciplinaires sont construites avec les collègues expérimentateurs. Des chercheurs CNRS, des professeurs invités participent désormais aux modules de l'option RFCT en M2, qui est mutualisée avec l'ED C2MP. Je vous présenterai des exemples concrets des formations que nous avons montées dans notre composante, en discutant comment ce type de travail peut modifier notre relation avec les étudiants, et les outils que nous avons développés et parfois exportés dans un contexte de médiation scientifique.

[*]Intervenant

Supramolecular study of Enzyme-Assisted Self-Assembly (EASA) of oligopeptides : A joined theorical and experimental approach

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Enzyme-Assisted Self-Assembly (EASA) is a tool to control both the localization of the self-assembly process and its evolution over time. The enzyme, which is the trigger, transforms a precursor compound (generally a peptide) in a hydrogelator. When the enzyme is immobilized on a surface, it directs the formation of a micrometer thick hydrogel. This has been illustrated from planar surfaces, nanoparticles or porous materials. However, many questions about the mechanism of this process have not yet been addressed, limiting further investigations and applications: how the kinetic of the enzymatic transformation is correlated to the kinetic of the self-assembly? Does the self-assembly start from the enzyme? Are the enzyme entrapped in the self-assembled nanofibrous network ? What is its dynamic in the resulting supramolecular hydrogels ? What is the molecular structure of the resulting self-assembly? How the enzymes are interacting with it ?

To answer these questions, a pluridisciplinar investigation is required, going from physico-chemistry, material science and simulation.

My two host laboratories are currently focusing on the phosphorylated Fmoc-FFpY tripeptide which in presence of alkaline phosphatase (AP) lead to the formation of the hydrogelator Fmoc-FFY able to self-assemble in a hydrogel. Thus, this chemical system involves three partners: the precursor Fmoc-FFpY, hydrogelator Fmoc-FFY and the enzyme, AP. The key challenge is to apprehend the relationship between them in a dynamic and static states to access the mechanism of self-assembly, the localization of the enzyme and the architecture of the nanostructure. In order to do so three techniques can be used. The first one is the circular dichroism (CD) which can provide informations about the supramolecular (chiral) organization of the self-assembly, and the kinetic of formation as well. The second method is an empirical Bayesian approach where fibers observed by cryo-TEM can be reconstructed in 3D in order to gain access to a density map of the architecture which can display the spatial organization of Fmoc-FFY almost at the molecular scale and the location (or not) of enzymes. The last approach is based on molecular dynamics. The simulation will allow to understand the conformation at a molecular state, the first stage of

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[*]Intervenant

assembly, to calculate interactions energy and estimate stability of those architectures over time. At the end all scales of the self-assembly mechanism are studied: molecular, supramolecular and microscopic scales. First results about these three axes will be given during my presentation.

Record power conversion efficiencies for Iron sensitized solar cells from rational molecular and electrolyte engineering

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Iron complex dyes bearing N-heterocyclic carbene (NHC) ligands have emerged during the last years as an earth abundant, low-cost, and non-toxic alternative to the traditional noble metal complexes used as sensitizers, which currently hold the record efficiencies in the Dye Sensitized Solar Cells (DSSCs) field. Unfortunately, despite their long-excited state lifetimes allow to reach high quantum injection yields, the first power conversion efficiencies (PCEs) displayed by NHC iron complex DSSCs were found very low (0.13%). In this context, here we will present the recent steps forward the development of more efficient iron complex dyes sensitizers by following different methodologies. These strategies are based on the chemical design rules aimed to improve the dye-to-TiO2 electron injection, as well as on the optimization of electrolyte composition and cell fabrication. Our results have demonstrated that, combining a rational molecular design driven by reliable Time-dependent Density Functional Theory (TD-DFT) calculations of the dye-sensitized TiO2 interface (see Figure 1), with the electrolyte and device optimization derived from an accurate experimental characterization of the efficiency of the interfacial electron transfer processes; one can effectively boost the performances of NHC iron complex DSSCs.(1),(2) As a result, we have been able to reach a record PCE of 1.83%,(2) which has never recorded for iron complex sensitized solar cells.

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*Intervenant

Quantum computing for photochemistry

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In quantum computing, solving the electronic structure problem is considered as the "killer application" for near term quantum computers. To treat this problem, a great focus has been paid to hybrid-classical-quantum algorithms such as the well-known "Variational-Quantum-Eigensolver" (VQE). While VQE has been proficiently applied to find electronic eigenstates/energies of various small molecules, using this approach on more complex systems is still a genuine challenge especially when peculiar spectral features such as conical intersections are present.

In nature, conical intersections play a keyrole in many prominent reactions. For instance, in the process of vision: the retinal molecule is known to undergo a photoisomerisation mediated by a non-radiative relaxation through a conical intersection. In such a situation, characterizing the phenomenon requires to precisely describe the shape of the conical intersection, with both qualitative and quantitative high-level treatments. This makes it a difficult target to current quantum algorithms, such as VQE.

Motivated by this problem, we recently introduced a new quantum algorithm called the "State-Averaged Orbital-Optimized VQE" (SA-OO-VQE) designed to treat on an equal footing degenerate states on near term quantum computers. In this talk, we introduce the theory of SA-OO-VQE and illustrate how it works on the formaldimine molecule (a minimal model for the retinal with a similar conical intersection). Furthermore, we will introduce new extensions to the SA-OO-VQE algorithm recently developed to estimate nuclear gradients and non-adiabatic couplings out of the quantum algorithm. We show that SA-OO-VQE is able to qualitatively and quantitatively reproduce the molecule's conical intersection. We will also show that the algorithm can be used in a geometry optimization process to find the minimal energy conical intersection of the molecule.

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*Intervenant

Quantum non-adiabatic dynamical studies of the photoisomerization of molecular switches

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Photoinduced non-adiabatic processes are playing a key role in photophysics and photo-chemistry and are ubiquitous in molecular systems. They allow efficient ultrafast radiationless relaxation processes and are involved in several biological systems such as the photoisomerization of the retinal in the first step of the vision. Therefore, the understanding of the reaction mechanism through simulations are of high interest in the design of molecular switches towards photo-controllable (bio)materials. Nevertheless, such process involving pathways through conical intersections are requiring strong inter-state electronic couplings to be considered within quantum dynamical simulations. A large amount of work has already been dedicated to the development of dynamical methods and of retinal chromophore minimal models to try to establish a correlation between quantum yields of the photoisomerization, mechanism of the reaction and the involvement of several specific modes of the models. Here we further study the correlation between the torsional angles and other degrees of freedom. A minimal retinal model developed by Marsili et al. (1) was used as a starting point to perform quantum dynamical calculations using MCTDH software.

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*Intervenant

A theoretical study of the electronic spectrum of 2,2'-bipyridine-3,3'-diol: from polar solvents to confinement in a nanocavity

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Since the 1980's, the absorption and fluorescence properties of 2,2'-bipyridine-3,3'-diol (BP(OH)2) have motivated theoretical and experimental studies.1 In particular, an intramolecular double proton transfer is frequently observed in solution after electronic excitation, leading to a di-zwitterion. The band positions of the absorption and fluorescence spectra are affected by the solvent polarity and its capability to establish an intermolecular hydrogen bond with the solute. In addition, some interesting features appear when $BP(OH)_2$ is nanoconfined in molecular cavities, such as cyclodextrins, depending on the cavity size.2

We propose to adapt and apply a successful strategy that we recently developed, based on an integrated multilevel approach providing an ad-hoc intramolecular force field for the chromophore ground and excited states to be used in classical molecular dynamics simulations. Such simulations are coupled with TD-DFT calculations of the optical properties of the chromophore in its local environment.3 We are particularly interested in assessing our method to treat nanoconfinement effects. As a matter of fact, confinement can lead to significant modifications of the dynamical, optical, and physicochemical properties of confined species, which can be exploited for a wide range of applications.4

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*Intervenant

Ab initio calculations on assymetric isotoplogues of species such as X2

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We will discuss preliminary *ab initio* calculations on simple diatomic molecules in the perspective of simulating their high resolution spectra. In particular, we will focus on key hyperfine parameters (nuclear quandupole moment, spin-rotation) associated with the determination of the potential energy curves. Furthermore, the calculation of the line intensity is required (dipole electric moment). Nevertheless, the dipole moment of assymetric isotoplogues of species such as X2 is null in the Born-Oppenheimer approximation which requires to use of diagonal corrections to this approximation. From these perspectives, we use the package CFOUR (Coupled-Cluster techniques for Computational Chemistry). Our preliminary results will be discussed in the light of available experimental data and/or previous calculations.

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*Intervenant

Reactivity of 2-Methoxy-5-Nitrothiophene Substituted : Kinetic Investigation and Theoretical Approach

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The second-order rate constants have been measured for reactions of 2-methoxy-3-X-5-nitrothiophenes **1a-e** (X = NO_2, CN, $COCH_3$, CO_2CH_3 and $CONH_2$) with secondary cyclic amines in CH3CH solution at 20 ∘C to determine experimentaly the eleophilicities E of thiophenes according to the linear free energy relationship:

log k (20 °C) = s (E + N).

A theoretical protocol has been then developed for the first time to predict the electrophilic parameters E of thiophenes **1a-g** in methanolic solution and it ended by a good correlation between the experimental and theoretical electrophilic parameters E of our thiophenes.

Key words: Kinetics, SNAr Mechanism, Mary's Equation, Electrophilicity parameters, Thiophenes, Density Functional Theory (DFT).

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*Intervenant

Theoretical Study of N-rich scaffold for optoelectronic devices

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The chemistry around s-tetrazines has been evolving quickly during the last decade.(1) Its range of applications increased as well, going from the development of more useful building blocks by C–H activation developed by our group, to the "click" chemistry to develop medical agents.(2) However, far from their interests as platform for syntheses, s-tetrazines also present photophysical properties that may be interesting, when optimized, to develop new optoelectronic devices such as Organic Light Emitting Devices (OLED)(1) and Thermally-Activated Delayed Fluorescence (TADF) for Light-Emitting Devices.(3)

In that sense, the objective here is to propose relevant molecules that may be suitable for photophysical applications, using theoretical tools and quantum approaches (such as DFT and Time Dependent DFT). To do this, we had to survey which computational approach (functional, basis set...) would provide the best agreement with experimental UV-vis spectra, and so the most realistic results.

In this communication, I will present our survey of different compounds all based on s-tetrazines, with its core considered as an acceptor and substituents as donor (Figure 1). We quantify our results by looking at multiple properties like ΔE_{ST}, charge transfer nature and UV spectra that may present the compounds.
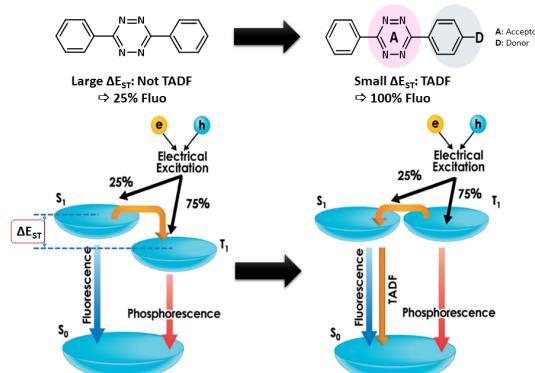
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Identification of proteinogenic amino acids from peptide translocation through MoS2 solid-state nanopores assisted by machine learning

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Solid-state nanopores made of two-dimensional materials such as molybdenum disulfide have emerged as a prominent technique for detection and sequencing of biomolecules, which present an essential role in life and healthcare. Measurement of fluctuations in ionic current when charged biomolecules, initially immersed in an electrolyte, translocate through nanometer-sized channel in response to an external voltage applied across the membrane contain information about biomolecule properties. By analyzing the features of ionic current amplitude and duration, one can extract crucial information about the biomolecule, including its sequence. We performed all-atom classical Molecular Dynamics (MD) simulations to study the translocation of peptides through MoS2 nanopores. First, the ionic current time series was extracted from MD for twelve different amino acids (R, K, E, D, F, M, V, P, S, C, Y, G) belonging to different families. We applied a two-threshold method to extract peptide-induced blockade events and we implemented clustering of the data using the Gaussian Mixture Model (unsupervised Machine Learning) to characterize 2D probability distributions of ionic current amplitude and duration obtained from structural breaks of peptide-induced blockade events. We demonstrated that each amino acid presents a diversity of ionic current fingerprints, however, by applying Machine learning algorithm, both similarities and differences among the distributions were characterized. Finally, the supervised approach was proposed to identify residue motifs inside the pore, implementing the eXtreme Gradient Boosting (XGBoost) and Random Forest classifiers to current time-series. Adding the duration and ionic current average from structural breaks as input variables greatly improve the performance of the models. These promising findings may offer a route toward identification of a single amino acid using MoS2 solid-state nanopores.

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*Intervenant

Affiches

Genesis of MoS2 from model-Mo-oxide precursors supported on gamma-alumina

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The molecular-scale understanding of MoS_2 genesis from Mo-oxide precursors by sulfo-reduction supported on alumina is highly challenging with a strong impact on the activation process of heterogeneous industrial catalysts. By means of density functional theory (DFT), we quantify the activation free energies of the elementary steps involved in the sulfo-reduction mechanisms of Mo-trioxide oligomers and the stability of the corresponding Mo-oxysulfide intermediates supported on the γ-alumina (100) surface. The Gibbs free energy profiles highlight the chemical reactivity of various oxygen sites involved in the O/S exchange mechanism and reveal the interfacial oxygen atoms (Mo-O-Al) are the most challenging sites to be exchanged with S. We quantitatively compare the two main paths proposed experimentally: the one involving Mo-oxysulfide and Mo-trisulfide intermediates and the second one involving only Mo-oxysulfide (Figure-1). While O/S exchange requires moderate activation energies, the rate-determining steps correspond to S- and O-removal on small MonO3n-xSx or MonS3n ($n \leq 3$) oligomeric intermediates. To overcome these high-energy steps, the small Mo-trisulfide (MonS3n) oligomers are proposed to be fast diffusing surface species and form larger MoS3 clusters. A reconstruction from chain to triangular Mo3S9 conformer also facilitates this phase transformation resulting in a triangular MoS3 phase. These large MoS3-species will eventually be transformed into the targeted MoS2 phase using hydrogen.

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*Intervenant

Influence of non-covalent interactions on Cobaltacycles reactivity analyzed by DFT-D

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Recently cobaltacycles have been of interest in chemical synthesis as they were able to catalyze the C-H bond functionalization of the cycling organic ligand in Cp*Co(III) complexes, such as Cp*Co(κN,κC-*phpy*)X (where *phpy* is 2-phenylpyridine and X is a X ligand), through a reductive elimination.(1,2,3) This reaction is induced by the preliminary oxidation of the Co(III) complex into a Co(IV) one. We recently evidenced that the intermediate Co(IV) 2-phenylpyridine complex can either undergo the wanted reductive elimination of X-*phpy* or a cyclocondensation of the Cp* ligand on the *phpy* ligand,(4) thus raising the question of the recyclability of the catalyst. Our laboratory research projects have been centered on the role of noncovalent interactions (NCIs) in the reactivity of coordination complexes for nearly two decades, and we believe that some kind of "coding" of the reactivity might lie in the NCIs.(5) We applied the newly developed Independent Gradient Model (IGM)(6,7) in order to quantify and qualify the NCIs in Cp*Co(κN,κC-phpy)X (where X is a X ligand) complexes. A database of different quantified interactions was elaborated in order to establish a correlation between the quantified NCIs and experimental and/or computational results. This database was obtained after evaluation at the DFT-D level of a reasonable sample of different cobaltacycles by changing only the nature of the X ligand. Our results suggest that there might be a correlation between the IGM data and the reactivity of the complex. In this way, those methods can show potential for more reactivity analysis and prediction at a routine scale as they are not computationally expensive.

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[*]Intervenant

Free-energy landscape analysis of protein-ligand binding: the case of human Glutathione Transferase A1

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Glutathione Transferases (GSTs) are a superfamily of enzymes present in a wide range of prokaryotes and eukaryotes. This superfamily regroups different enzyme families, which have in common to catalyze the nucleophilic addition of the thiol group of reduced glutathione (GSH) onto electrophilic and hydrophobic substrates, forming GSH conjugates. The conjugation reaction occurs spontaneously but the enzyme accelerates it dramatically. This conjugation protects cells against damages caused by both exogenous and endogenous harmful molecules (1). With some exceptions, GSTs are catalytically active as homodimers. GST monomers are in general constitued of 200 to 250 residues and are organized into two subdomains. The typically 80-residue-long N-terminal subdomain (I), made of α-helix and β-sheets contains an active site where GSH is hosted in catalytic conformation and which is termed G site. Residues forming the G site are generally conserved among GSTs. The second subdomain (II) is all-helical, hydrophobic and contains the H site which binds the substrate. Together with the G site, the combined architecture of GST monomers is adapted to bind GSH to hydrophobic substrates. Contrary to the G site, the residues of the H site vary from one GST to the others, resulting in H sites of different structures able to recognize different substrates.
In the present work, we performed all-atom Molecular Dynamics simulations in explicit solvent of human GSTA1-1 in its APO state, bound to GSH ligand and finally bound to glutathione-conjugated dinitro-benzene GDNB conjugate. From MD, two probes were analyzed i) to decipher the local conformational changes induced by the presence of ligand or ligand plus substrate in the G site and ii) to "map" the communication pathways involved in the process. These two local probes are, first, coarse-grained angles (CGA), named q and g, representing the local conformation of the protein main chain and, second, c dihedral angles representing the local conformation of the amino-acid side chains (2). Finally, from local probe time series, free-energy profiles of each probe along the amino-acid sequence of three different protein states (APO, GSH-bound and GDN-bound states) were computed and compared using similarity indices. This methodology, already applied successfully by our group to chaperone proteins (3), allowed us to extract key residues involved in protein-ligand binding and to compare them with experimental data.

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*Intervenant

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Curvature and Torsion of Protein Main Chain as Local Order Parameters of Protein conformational ensemble

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We consider local order parameters of protein conformational ensembles (folded, unfolded, disordered), defined by the local curvature and torsion of the protein main chain. Because chemical shifts (CS's) measured by NMR spectroscopy are extremely sensitive to the local atomic environment, CS has served as a local probe of thermal unfolding of proteins by varying the position of the atomic isotope along the amino acid sequence. The variation of the CS of each $C\alpha$ atom along the sequence as a function of the temperature defines a local heat-induced denaturation curve. We demonstrate that these local heat- induced denaturation curves mirror the local protein nativeness defined by the free energy landscape of the local curvature and torsion of the protein main chain described by the $C\alpha$–$C\alpha$ virtual bonds. Comparison between microsecond molecular dynamics (MD) simulations and CS data of the gpW protein demonstrates that some local native states defined by the local curvature and torsion of the main chain, mainly located in secondary structures, are coupled to each other whereas others, mainly located in flexible protein segments, are not. Consequently, CS's of some residues are faithful reporters of global protein unfolding, with heat-induced denaturation curves like the average global one, whereas other residues remain silent about the protein unfolded state. For the latter, the local deformation of the protein main chain, characterized by its local curvature and torsion, is not cooperatively coupled to global unfolding. Order parameters based on the curvature and torsion of the protein main chain are also relevant to decipher the differences between the conformational ensembles of wild-type and mutants of intrinsically disordered proteins, as illustrated by millisecond time-scale MD simulations of alpha-synuclein monomer and dimers and its mutants (A53T, E46K and A30P) involved in the Parkinson disease. Pre-fibrillar alpha-synuclein dimers are identified which might represent toxic intermediates of amyloids.

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*Intervenant

Maladie de Parkinson : vers la conception in silico d'un médicament.

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La maladie de Parkinson est due à la formation d'un agrégat de la protéine α-synucléine (αSYN). Cet agrégat est caractérisé par un empilement des chaînes protéiques et par une dimérisation de ces empilements. La prise en compte et la compréhension du processus d'assemblage supramoléculaire de cet édifice est nécessaire à la conception d'un médicament efficace. Une des stratégies envisagées est d'empêcher la formation de ces agrégats et notamment ce dimère d'empilements. Pour cela, nous proposons la synthèse de petites molécules organiques qui vont pouvoir (1) s'auto-assembler sous forme de nanotube organique via un réseau de liaison hydrogène et (2) interagir avec l'assemblage supramoléculaire que constitue αSYN. Les études in silico représentent un atout considérable dans ce projet. Grâce à une approche multi-échelle combinant dynamique moléculaire classique et chimie quantique, nous allons pouvoir caractériser les différents assemblages et leurs interactions.

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*Intervenant

UV Spectrum and Photodecomposition of Peroxynitrous Acid (HOONO)

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Peroxynitrous acid HOONO was first observed in an Argon matrix. It is an unstable species and has not been seen in the gas phase at ambient pressure and temperature because of its short lifetime of a few milliseconds.

As is well known, the reaction of HO_2 and NO is a major producer of the OH radical (HO_2+NO→OH+NO2), which is considered the oxidative 'work horse' in the atmosphere. On other hand, OH is removed through the reaction (OH+NO_2+M→HNO_3+M) yielding nitric acid and, to a less extent (about 15%), peroxynitrous acid (OH+NO_2+M→HOONO+M). HOONO desintegrates readily through thermolysis and photo-decomposition. The mechanisms are not well understood. In this work, we investigate the photochemical decomposition.

The energies and structures of various conformers of peroxynitrous acid have been calculated at the CCSD(T)/AVTZ level of theory. Three configurations were found, denoted cis-cis, which is the most stable, cis-perp and trans-perp. The UV spectra are computed by DFT (M06-2X/AVTZ) using the NEWTON-X package. The principal peak does not coincide with the vertical excitation energy which can be explained as due to the slow motion of the ONOO and the NOOH torsional modes. The decay pathways of HOONO were determined using the steepest descent method. Three channels were found for the two stable conformers cis-cis and trans-perp.

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