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Abstract book

Content

Nanoparticles growth mechanisms, morphology and electronic properties

Magali Benoit *† 1

1 Surfaces, Interfaces et Nano-Objets – Centre d'élaboration de matériaux et d'études structurales – France

The Surface, Interface and Nano-object (SINanO) group at CEMES (Toulouse) conducts a multidisciplinary research (physics, chemistry, biology) devoted to the growth and the study of the structural, physical and chemical properties of i) surfaces and interfaces, ii) nanoobjects and iii) their interactions with atoms or molecules (adsorption, self-organization, ligand-driven growth and functionalization). Our research is fundamental, but often addresses functional devices or materials that aim to become functional, such as lasers, devices for spintronics or nanoparticles for hyperthermia or antibiotic therapy, for example. An originality of the SINanO group is to combine experimental and theoretical approaches on a large number of topics.

In this context, I will present examples of coupled experimental/theoretical studies carried out in our group on the growth mechanisms of metallic nanoparticles, as well as on the relative stability of their different morphologies and on the effect of the environment on their properties (1-5). I will also discuss how machine learning approaches can be used in these investigations (6,7).

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*Intervenant
†Auteur correspondant: mbenoit@cemes.fr

Mesoscopic simulations of coatings using the electrophoretic process in aqueous suspensions

Mélina Noblesse * [1,2], Lisa Pin [1], Eric Bouillon [1], Sandrine Duluard [2],
Céline Merlet [2], Florence Ansart [2]

[1] Safran Ceramics [Mérignac] – Safran Ceramics [Mérignac] – France
[2] Centre interuniversitaire de recherche et d'ingénierie des matériaux – CNRS (UMR 5085), Université Toulouse III - Paul Sabatier, Institut National Polytechnique (Toulouse) – France

The carbon footprint caused by industrial processes, technological developments and population growth has only increased over the last decades. In the aeronautical sector, improving the performance of turbomachines is a major challenge in the face of growing environmental constraints, as this sector is known for its strong environmental impact linked to the emission of greenhouse gases, including carbon dioxide (1). One of the solutions explored by engine manufacturers to improve the performance of turbomachines is the replacement of the primary material by a ceramic matrix composite made of silicon carbide SiC/SiC. This solution would make it possible to respond to various aspects identified by the sector: lightening of structures, improvement of the primary cycle (in temperature and pressure) and increase in propulsive efficiency. Despite the stabilization of thermomechanical performance compared to nickel-based superalloys, silicon carbide presents an increased sensitivity to water vapor at high temperatures, raising the necessity of protecting it for example through coatings.

Electrophoretic deposition (EPD) is a process that has been used for many years in the field of wet deposition techniques, ensuring low temperature shaping, a deposit with controlled stoichiometry, as well as the development ofeasier coatings on parts with complex geometry, which is easier thancompared with dry processes. In Tthis process consists of two steps: the first is thecharged particles migrationof particles under the application of an electric field, and the second is the coagulation and deposition on the chosen substrate. Electrophoretic deposition is mainly used in the presence of organic solvents because of their wide electrochemical stability window, the absence of electrochemical reactionand the absence of heating at the electrodes (3). However, these solvents canoften present constraints related to their volatility and toxicology which need to be controlled. Using water as a solvent would reduce, or even suppress, environmental and toxicological constraints. HoweverNevertheless, two consequences are observed at the electrodes due to the water electrolysis: a local variation of pH that which can destabilize the suspension, and the formation of bubbles at the electrodes which can create porosity and deteriorate the coating. In addition, only few studies exist on the understanding of relationships between the process parameters, the structure and properties of the resulting coating.

This talk will detail the strategy we follow to simulate coatings using the electrophoretic processdeposition of mullite particles in aqueous suspensions. This work is based on the work of B.Gieraet al. (4) whichstudied coatings using EPD infocused on polystyrene in organic suspensions. The method used to study this process is theWe use Brownian Mmolecular Ddynamics simulations which allow us to vary (BMD). The material studied is mullite (reference material) resulting from the first generation of Environmental Barrier Coatings (EBC) in suspension with

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*Intervenant

water.Ttwo categories of parameters can be studied through these simulations. There are the: i) suspension parameters such as particle size, mass fraction, density or zeta potential. Finally, there are the and ii) process parameters such as the applied voltageelectric field. The characteristicsWe then characterizeconcerning the mass fraction, the coating thickness with time, and the particles packing compacity, the the porosity and the microstructure of the simulated deposits coatings which will be compared to the experimentally obtained coatingal results.

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Molecular simulations study of the adsorption dynamics of ions on carbon electrodes

Nicolas Gaudy * [1], Céline Merlet[†] [1], Mathieu Salanne[‡] [2]

[1] Centre interuniversitaire de recherche et d'ingénierie des matériaux – CNRS (UMR 5085), Université Toulouse III - Paul Sabatier, Institut National Polytechnique (Toulouse) – France
[2] PHENIX – Laboratoire de PHysico-chimie des Electrolytes et Nanosystèmes InterfaciauX (PHENIX UMR 7195, UPMC-CNRS), Université Pierre et Marie Curie, 4 place Jussieu, 75252 Paris – France

Molecular dynamics simulations are a method of choice to study, at microscopic scales, the adsorption processes of ions from an electrolyte onto the electrodes of capacitive storage systems such as supercapacitors. Here, we use all-atom molecular dynamics simulations to model a pure ionic liquid electrolyte [EMIM][TFSI] in contact with graphite electrodes. When applying a potential difference between the two carbon electrodes, a migration of counter ions is observed, ultimately leading to a compensation of the charges carried by the electrode atoms. The adsorption dynamics depend on several parameters (electrostatics interactions, coordination number, viscosity of the electrolyte, size of the ions etc.) and influence the power of these capacitive systems. In order to improve the performance of supercapacitors, it is then important to describe and understand the interfacial properties at a molecular scale. Here, thanks to molecular simulations, we have access to the adsorption rate of ions, to their reorientation, to the variation of charge of the electrode atoms during adsorption etc. This allows us to study in detail the mechanisms governing the electrolyte-electrode interface during the charging of supercapacitors.

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[*]Intervenant
[†]Auteur correspondant: celine.merlet@univ-tlse3.fr
[‡]Auteur correspondant: mathieu.salanne@sorbonne-universite.fr

Dynamics of hydrogen adsorption and dissociation on nitrogen covered tungsten surface

Norhan Omar [*][†] [1], Oihana Galparsoro [2], Cédric Crespos [1], Lionel Truflandier [1], Pascal Larregaray [1]

[1] Institut des Sciences Moléculaires – Université de Bordeaux (Bordeaux, France) – France
[2] Donostia International Physics Center (Donostia, Espagne) – Espagne

The reactivity of surface processes is influenced by various parameters, notably the type of the molecules interacting with it and its intrinsic characteristics. For instance, as tungsten is a metallic surface, which makes it reactive to adsorbents, its reactivity varies considerably between a clean tungsten surface and one covered with impurities, the type and quantity of which, have substantial impact on the processes involved.

In a previous study conducted by our research team, theoretical analysis of the dynamics of the hydrogen (H_2) dissociation on the clean tungsten surface W(110) and on an oxygen (O)-covered surface was performed (1,2). The approach revealed a significant decrease in the adsorption and dissociation of H_2 molecules in the presence of oxygen on the surface compared to a clean tungsten surface, resulting in a reduced sticking coefficient in agreement with experiment.

We here investigate the impact of nitrogen (N) covering the W(110) surface on the dynamics of H_2 dissociation. The Pfnür team experimentally examined the chemisorption of N_2 on the W(110) surface back in 1986, observing a surface reconstruction (3). Our goal is to investigate more in the details the influence of the surface reconstruction on the H_2 dissociation process. We therefore examine H_2 dissociation on two distinct tungsten surfaces, both coated with nitrogen. The first surface involved nitrogen adsorption on the W(110) surface, while the second surface involved nitrogen in-Plane tungsten, as experimentally observed by the Pfnür research group. This reconstruction numerically led to a significant increase in H_2 dissociation compared to other W(110) surfaces covered either with oxygen or nitrogen adsorbed on the surface. Consequently, the sticking coefficient of H_2 is considerably increased, even at low collision energies as experimentally (4) suggested in polycrystalline tungsten.

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[*]Intervenant
[†]Auteur correspondant: norhan.omar@u-bordeaux.fr

Theory of Spin Crossover Molecules on Metal Surfaces : the effect of Ligand doping

Rémi Pasquier * [1]

[1] Institut de Physique et Chimie des Matériaux de Strasbourg – université de Strasbourg, Centre National de la Recherche Scientifique, Matériaux et Nanosciences Grand-Est, Réseau nanophotonique et optique – France

We will present here several results of our study of the simulation of spin-crossover molecules adsorbed on metallic surfaces. We will focus on our study of the effects of doping the $Fe(phen)_2(NCS)_2$ molecule on the energetics of the spin-transition phenomenon. We show that the molecule undergoes a switch from the original low spin state to the high spin state, caused by a significant amount of electron redistribution in the molecule as we will demonstrate using several tools such as Bader charge analysis. We also compute STM images and show that they allow one to discriminate between the fluorinated and unfluorinated systems. This theoretical prediction is awaiting future experimental confirmation.

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*Intervenant

A system-bath model to investigate the interaction of a molecule with its environment

Loïse Attal *† [1], Cyril Falvo [1,2], Florent Calvo [2], Pascal Parneix [1]

[1] Institut des Sciences Moléculaires d'Orsay – Université Paris-Saclay, Centre National de la Recherche Scientifique – France
[2] Laboratoire Interdisciplinaire de Physique [Saint Martin d'Hères] – Centre National de la Recherche Scientifique, Université Grenoble Alpes, Centre National de la Recherche Scientifique : UMR5588 – France

Addressing the dynamics of molecular systems coupled to an environment is a challenging task, especially when considering finite-size environments that can be affected by their interactions with the smaller system. In such cases, the usual open quantum system methods and approximations might fail as they assume that the environment (or "bath") is infinite, always at thermodynamical equilibrium, and not perturbed by the system (1). In particular, they do not take into account the fact that finite environments can be heated by the excitation of the system and evolve out of equilibrium. For example, such situations may occur when studying molecules in clusters or matrices (2), or when probing small molecules trapped in fullerenes (3).

In this context, we are developing a new theoretical model based on a system-bath approach where we consider a one-dimensional system (*e.g.* one vibrational mode) interacting with a large harmonic bath (_ ˜100-1000 modes). The system and its coupling to individual bath modes are treated as rigorously as possible but the bath part of the Hamiltonian is simplified with its modes being replaced by a ladder of effective quantum energy states which describes the energy stored in the bath. This model allows us to study the relaxation dynamics of the system at finite temperature and to analyze the response of the bath to the system's excitation. In this contribution, we will present the first results obtained by using this method on a system taken from (4), where an O-H stretching mode interacts with a "surface" modeled by a set of 40 to 600 harmonic oscillators.

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*Intervenant
†Auteur correspondant: loise.attal@universite-paris-saclay.fr

Theories and simulations of ultrafast processes in molecules

Federica Agostini [*][†] [1]

[1] Université Paris-Saclay, CNRS, Institut de Chimie Physique UMR8000, 91405 Orsay, France – CNRS : UMR8000 – France

In this talk I will present various methodologies to simulate the excited-state dynamics in molecules, underlying ultrafast processes typically encountered in photochemistry. I will focus in particular on trajectory-based techniques, comparing those derived from the exact factorization (1), and thus based on coupled trajectories (2, 3), with those based on independent trajectories, as the well known Ehrenfest method and surface hopping.

After presenting the theory, I will give an overview on several applications ranging from isolated molecular models (4) and molecules (5, 6) undergoing ultrafast internal conversions and intersystem crossings (7), to systems in the presence of external time-dependent fields (8, 9).

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[*]Intervenant

[†]Auteur correspondant:

Non-adiabatic dynamics with trajectory surface hopping: benchmarking electronic structure methods on azomethane photoisomerization

Thomas Papineau [*][†] [1], Denis Jacquemin [1,2], Morgane Vacher[‡] [1]

[1] Chimie Et Interdisciplinarité : Synthèse, Analyse, Modélisation – Institut de Chimie du CNRS, Centre National de la Recherche Scientifique, Nantes université - UFR des Sciences et des Techniques – France
[2] Institut Universitaire de France – Ministère de l'Education nationale, de l'Enseignement supérieur et de la Recherche

Mixed quantum-classical non-adiabatic dynamics allows to obtain theoretical insights into ultrafast phenomena that occur at the femtosecond scale. The most popular approach is trajectory surface hopping (TSH), which requires an electronic structure method for describing quantum mechanically the electrons. The most suited electronic structure methods for describing a photochemical reaction are multi-configurational. Because these are computationally expensive, TSH studies are often limited to small molecular systems and/or short simulation time.
In this presentation, I will explore a panel of other popular electronic structure methods and assess their suitability for TSH. Most of the electronic structure methods commonly available in quantum chemistry software are mono-configurational (*i.e.*, they use a single Slater determinant). Because of this, they are expected to give an incorrect description in regions of strong non-adiabatic couplings, such as the so-called conical intersections that can be encountered during electronic deexcitation.

This presentation focuses on the azomethane molecule (H3C-N=N-CH3), which is known for undergoing a fast *cis*-to-*trans* photoisomerization upon light excitation. This molecule provides an interesting model for studying the behavior of the different methods in terms of both the excited states population decay and the geometrical changes undergone during isomerization.
A highly accurate XMS-CASPT2 reference dynamic is compared to various post-Hartree-Fock methods (namely MS-CASPT2, CASSCF, CC2, ADC(2), and CIS), as well as several functionals used in TD-DFT and its Tamm-Dancoff approximation. The different relaxation pathways are identified, and the ability of the different methods to quantitatively reproduce them will be discussed.

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[*]Intervenant
[†]Auteur correspondant: thomas.papineau@univ-nantes.fr
[‡]Auteur correspondant: morgane.vacher@univ-nantes.fr

Dissociation and isomerization upon ionisation of ethylene: a non-adiabatic dynamics perspective

Lina Fransen [* 1], Morgane Vacher[† 1]

[1] Chimie Et Interdisciplinarité : Synthèse, Analyse, Modélisation – Centre National de la Recherche Scientifique, Nantes université - UFR des Sciences et des Techniques – France

Ionised ethylene $C_2H_2^+$ can dissociate via H^- and H_2-loss, where the latter has been hypothesized to be preceded by isomerization to the ethylidene form (1). Being the smallest pi radical system, $C_2H_2^+$ has been studied extensively theoretically and experimentally. Yet key questions regarding its photodynamics remain unanswered. What are the dissociation and isomerization mechanisms and their respective time scales? What factors govern the competition between isomerization, H^- and H_2-loss? In this contribution, we aim to shed light on these questions using a semiclassical non-adiabatic dynamics method, namely surface hopping. We simulate the dynamics of ethylene following ionisation and excitation to the four lowest-energy cationic states. The electronic structure is treated at the CASSCF level, using an active space comprising all valence electrons. The large active space allows us to - in contrast to previous dynamics studies - observe a significant number of dissociation events and reproduce the experimentally observed pathways (ethylene-ethylidene isomerization, H-loss and H_2-loss). The electronic relaxation is ultrafast; regardless of the initial electronic state, more than 50% of the population decays within 50 fs to the cationic ground state, where most dissociation and isomerization events take place. Multiple conical intersections at planar and twisted geometries act as funnels between the low-lying cationic states, and their implications on the photochemistry have previously been hypothesized (2). Our simulation results allow us to test these hypotheses. The simulations suggest that H_2-loss occurs mainly from the ethylidene isomer CH_3CH^+. The time scale of ethylene-ethylidene isomerization has previously been extracted from indirect experimental measurements in which neutral ethylene was ionised and excited by an extreme-ultraviolet attosecond pulse train (pump) and the ensuing relaxation dynamics were monitored at varying time delays with intense near-infrared light (probe) (3, 4). We find an order-of-magnitude discrepancy between the experimentally inferred and the simulated isomerization time scales and suggest an explanation for this difference.

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[*]Intervenant
[†]Auteur correspondant: morgane.vacher@univ-nantes.fr

An exact factorization perspective on dynamics around conical intersections: On the nature of topological and geometric phases in molecules

Lea Ibele [*][†] [1], Federica Agostini [1]

[1] Institut de Chimie Physique – CNRS, Université Paris Sud, Université Paris Saclay – France

The exact factorization of the electron-nuclear wavefunction proposes to represent the dynamics of a molecule in the excited state as a single time-dependent nuclear wavefunction, evolving under the action of a single time-dependent potential energy surface and a single time-dependent vector potential (1). Concepts, such as conical intersections and transition dipole moment, do not exist in this formalism. In this work, I will discuss processes in the vincinity of a conical intersection within the standard Born-Oppenheimer representation and the exact factorization picture (2,3). We compare the influence of the conical intersections on the dynamics of the wavepacket when passing around the conical intersection (4). The observable nature of topological phases related to conical intersections in molecules is addressed, highlighting numerically the fundamental difference between topological and geometric phases. Such topological phases should be ubiquitous in molecular physics, but their elusive character has made them a topic of extensive discussion in recent years. Topological phases are related to the adiabatic representation of the electrons and are, thus, not observable. In contrast, geometric phases naturally arise from the coupled electron-nuclear dynamics and are robust physical observables.

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[*]Intervenant

[†]Auteur correspondant: lea-maria.ibele@universite-paris-saclay.fr

Quantum Dynamics around PPE's conical intersections for spectroscopic and real-time studies

Joachim Galiana *† [1], Benjamin Lasorne‡

[1] Institut Charles Gerhardt Montpellier – Chimie Physique Théorique & Modélisation, Centre National de la Recherche Scientifique, Université de Montpellier, Ecole Nationale Supérieure de Chimie de Montpellier – France

In this presentation, we discuss the use of non-adiabatic quantum dynamics for the study of different poly(phenylene)ethynylenes (PPEs), building blocks of light-harvesting dendrimers. PPEs exhibit strongly non-adiabatically coupled electronic excited states. Because of this and of the presence of conical intersections in the potential energy surfaces (PESs) of the molecules, the Born-Oppenheimer approximation breaks down, which requires molecular dynamics to take into account the coupling between the electronic excited states. We propose linear and quadratic vibronic coupling (L/QVC) diabatic model Hamiltonians for reproducing the PESs of the simple PPEs. Next, we use this diabatic potential and inter-state couplings to run quantum dynamics calculations using the Multi Configuration Time-Dependent Hartree (MCTDH) formalism. Here, quantum dynamics calculations serve different purposes depending on the molecule studied, such as spectroscopic studies (absorption and emission spectra calculations in the UV-visible domain) or real-time dynamics (excitation-energy transfer and population transfers).

The first building block of interest is the symmetrical meta-substituted phenylene (m22, Fig. 1, upper left). The absorption spectra of m22 and its localized fragment (p2, Fig. 1, upper right) are analogous, with similar vibrational structure, which have been measured(1) and reproduced numerically(2,3). However, their emission spectra are different, with m22 exhibiting an unusual Stokes shift of about 2000 cm^{-1}. In a recent work(4), we identified this Stokes-shifted spectrum as a contribution resulting from the strong inter-state coupling in the first two electronic excited states (Fig. 2). We hereby provide a reasonable explanation for the unusual Stokes shift in the stationary spectroscopy experiments.

The second building block of interest in an asymmetrical meta-substituted PPE (m23, Fig. 1, bottom) and its symmetrical counterpart with two p2 branches, for which excitation-energy transfer (EET) occurs thanks to different branch lengths hence a significant energy gradient. Using analogous Hamiltonian models, we are able to reproduce the expected ultra-fast ($\sim$ 25 fs) EET from an excitation on the shortest branch to the longest branch.

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*Intervenant

†Auteur correspondant: joachim.galiana@umontpellier.fr

‡Auteur correspondant: benjamin.lasorne@umontpellier.fr

Deciphering the Secrets of Madder Molecules through Computational Chemistry

Linh Tran * [1,2], Romain Berraud-Pache [2], Maguy Jaber [2]

[1] Sorbonne Université - UFR d'Ingénierie – Sorbonne Université – France
[2] Laboratoire d'Archéologie Moléculaire et Structurale – Université Pierre et Marie Curie - Paris 6, Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique, CNRS UMR 8220, 4 place Jussieu, 75005, Paris – France

The captivating diversity and remarkable colour properties of natural dyes, used for paintings, textiles, statues, and other objects of cultural heritage, have long fascinated researchers, especially chemists. Among them, one of the most renowned dye plant in Europe, and particularly in South of France is Madder. Madder is the origin of the famous "Adrianople red" (or red Turkish) giving a bright red on cotton, in a long and tedious recipe. Its dyes are extracted from its roots, with Alizarin and Purpurin being the most important (1). Prior to the advent of computational chemistry, even though researchers worked diligently, deciphering the experimental spectroscopic properties of Madder's colorants posed a persistent challenge. This was primarily due to the extraction difficulty, impurities, the instability of some compounds, and their high price. Now, we can overcome this challenge with a new approach. Thanks to the application of computational spectroscopy techniques (2), we can reproduce, understand and predict the spectra of compounds that were previously unknown or inaccessible experimentally.

In this investigation, we have studied several Madder's dyes at the Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT) level. We have designed a computational workflow to predict their UV-Vis and NMR spectra. Nevertheless, their spectroscopic properties are influenced by external factors like pH, solvent effects, or metallic cations (1). We have focused on the impact of solvation models such as implicit, explicit, or multilevel techniques (Quantum Mechanic/Molecular Mechanic QM/MM). We have also considered the possible deprotonated forms of the dyes for different pH. For UV-Vis spectrum calculations, on top of the vertical excitation energies, we have also taken into account the vibrational effects, using Vertical Gradient or Adiabatic Hessian approximation. The workflow has been validated for Alizarin and Purpurin, and extended to other molecules inaccessible experimentally. Our analysis emphasizes the importance of considering the solute-solvent interactions to reproduce the experimental measurements. These results will serve as a new database to help understand complex experimental data, particularly in the field of cultural heritage. These findings can also establish a groundwork for exploring more complex systems, such as pigments or dyeing processes, involving the interaction between a metallic cation, notably Aluminium, and a colorant like Alizarin or Purpurin(1). This investigation will help gain insight into the correlation between structural properties with functional performance. It will provide assistance to conservators and historians in their efforts to safeguard the preservation of cultural heritage objects. Furthermore, it can help researchers increase natural dye's performance.

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*Intervenant

Simulation of the equilibrium and the transport of ions at the liquid-liquid interface

Lara Ziberna * [1], Philippe Guilbaud [2], Magali Duvail [1]

[1] Institut de Chimie Séparative de Marcoule – Commissariat à l'énergie atomique et aux énergies alternatives, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique, Université de Montpellier, Ecole Nationale Supérieure de Chimie de Montpellier – France
[2] CEA-Direction des Energies (ex-Direction de l'Energie Nucléaire) – Commissariat à l'énergie atomique et aux énergies alternatives, CEA, DES, ISEC, DMRC, Univ Montpellier, Marcoule, France – France

Lanthanide ions recycling has grown in importance in recent years as the demand for these elements has increased, and the rate of extraction from rare metals has decreased (1). One of the approaches for recycling metals is liquid-liquid extraction, which separates solutes based on the difference in their solubility between two liquids. In the nuclear industry, many processes based on liquid-liquid extraction are employed for recycling nuclear fuel, where lanthanide ions are separated from nuclear waste. DIAMEX (DIAMide Extraction) process is one such technique (2), where the reference molecule for separation of smaller lanthanides between two liquid phases is N-N'-DiMethyl-N-N'dioctyl-2-hexylethoxymalonamide (DMDOHEMA) (3).

In our research, we use classical Molecular Dynamics (MD) to investigate the structural properties of the liquid-liquid interface between aqueous and organic phases with amphiphilic extractant (DMDOHEMA or DMDBTDMA). The main objective is to characterize and describe the species distribution at the interface and in the bulk. First, we examined how the initial box configuration impacts the formation of the interface, as well as how the ratio between the two phases affects the shape and structure of the interface in comparison with experimental and theoretical data. Further, we characterize and describe the distribution of extractant at the interface and in the bulk organic phase at various extractant concentrations, comparing the behavior of two different extractants. We will also investigate the distribution of extractants, salts and micelles formed in the system during extraction.

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*Intervenant

Molecular prediction of lanthanide cation transfer for liquid-liquid extraction

Erwann Guillam [*][†] [1], Magali Duvail [1], Jean-François Dufrêche [1]

[1] Institut de Chimie Séparative de Marcoule – Commissariat à l'énergie atomique et aux énergies alternatives, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique, Université de Montpellier, Ecole Nationale Supérieure de Chimie de Montpellier – France

Liquid-liquid extraction is a key hydrometallurgical process used to selectively separate the lanthanide cations, such as in the SANEX process (Selective ActiNide EXtraction) (1) developed by CEA for the recycling of spent nuclear fuels. In this process, the lanthanide cations are transferred from an acid-enriched aqueous phase to an organic phase containing malonamide extractants, like DMDOHEMA, diluted in a mixture of alkanes. This ion transfer between the two phases is governed by the Gibbs energy of transfer which is measured experimentally by the distribution coefficients of the ions (2).

This work deals with the prediction of the Gibbs energies of transfer of lanthanide cations using Steered Molecular Dynamics (SMD), an out-of-equilibrium simulation technique for Molecular Dynamics. The SMD methodology uses a moving biasing harmonic potential to steer the lanthanide cations from the aqueous phase to the organic phase, allowing for accurate sampling of the free energy landscape of the interface (3,4).

We simulated water–octanol interfaces as a model system for liquid-liquid extraction. In nuclear hydrometallurgy, octanol (octan-1-ol) is used as a phase modifier to prevent the formation of a heavy organic third phase associated with criticality risks. Calculating the molecular orientation revealed that the octanol molecules at the interface organize themselves in a rigid bilayer structure, as previously observed (5), preventing the water transfer toward octanol. SMD simulations will be used to determine the Gibbs energy barrier of this interface, allowing the calculation of the water solubility in octanol.

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[*]Intervenant
[†]Auteur correspondant: erwann.guillam@cea.fr

Aggregation Phenomenon and Effects of Trapped Compounds in Complex Mixture by Molecular Dynamics Simulations.

Luis Acevedo Fernandez * [1,2], Jimmy Castillo[†][1], Germain Vallverdu[‡][2]

[1] Universidad Central de Venezuela – Venezuela
[2] Institut des sciences analytiques et de physico-chimie pour l'environnement et les materiaux – Université de Pau et des Pays de l'Adour, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France

Complex mixtures are challenging systems for both experimental and theoretical investigations. To go further in the understanding of the molecular behavior of such systems at the atomic scale, computational approaches such as molecular dynamics simulations are powerful methodologies that can be implemented in a synergetic way along with experimental techniques. Crude oil and new feedstock systems are arguably good examples of complex mixtures. Particularly, asphaltenes, the heavy-weight fraction of crude oil that is insoluble in n-alkane but soluble in aromatics solvents, has been intensively investigated over the last years (1-3)

Experimental data indicates that asphaltenes have the ability to adsorb and occlude other oil fractions, namely resins, biomarkers, radicals, and even metals. For a thorough comprehension of asphaltene aggregation phenomenon, it is crucial to consider the presence of these so-called trapped compounds. Nevertheless, there is a notable lack of research from a computational point of view regarding this aspect. Hence, our investigations aim to propose computational strategies designed to provide not only an in-depth description of the aggregates structure and the aggregation mechanism, but also a more precise perspective on the influence of these trapped compounds on the aggregation phenomenon and the type of interactions involved. Within this framework, we implemented all-atoms molecular dynamic simulations and developed a methodology using an annealing procedure to generate ensembles of aggregates with the required sizes and several compositions that include trapped compounds. The structure and stability of these aggregates were then analyzed and compared with experimental data. The results show a tendency for most of these trapped compounds to be adsorbed on the surface of the aggregates, while a small fraction is being "occluded".

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[*]Intervenant
[†]Auteur correspondant: jimmy.castillo@ciens.ucv.ve
[‡]Auteur correspondant: germain.vallverdu@univ-pau.fr

Mechanism of excess proton transport in water revealed by neural network-based path integral molecular dynamics simulations

Axel Gomez [*][†] [1], Ward H. Thompson [2], Damien Laage[‡] [1]

[1] PASTEUR – Department of Chemistry, École Normale Supérieure, PSL University, Sorbonne Unversity, CNRS, 75005 Paris – France
[2] Department of Chemistry, University of Kansas, Lawrence, KS 66045 – États-Unis

Proton transport in water is central to acid-base chemistry, energy production, and biochemical processes. However, while the anomalously fast diffusion is known to arise from the Grotthuss shuttling mechanism involving successive proton transfers, the details of its molecular mechanism remain ill-characterized. Recent vibrational spectroscopy studies have shown that the mechanism proposed by early molecular simulations is not consistent with experimental structural dynamics. Using state-of-the-art machine learning-based molecular dynamics simulations,(1) we address this fundamental question and present the first molecular mechanism for excess proton transfer in bulk water that is consistent with all available experimental data. This new simulation technique combines a high-level description of the electronic structure with explicit nuclear quantum effects via ring-polymer molecular dynamics, and its outstanding computational efficiency gives access to long molecular dynamics trajectories that allow obtaining converged free energies. The proposed stepwise mechanism consists of stable intermediates in which the excess proton is localized. Hydrogen bond exchanges play a major role in this process. The resulting picture is in very good agreement with experimental observations, in particular with recent nonlinear vibrational spectroscopy experiments,(2,3) which were compared with the calculation of vibrational energy levels of the proton transfer mode. The mechanism is further confirmed by a temperature dependence study and an investigation of the kinetic isotope effects of proton transport. Our work opens the way to understanding proton transfer-driven reactions in much more complex environments.

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[*]Intervenant
[†]Auteur correspondant: axel.gomez@ens.psl.eu
[‡]Auteur correspondant: damien.laage@ens.psl.eu

Exploring protein-protein interaction networks in 3D under the lens of coevolution

Raphaël Guerois [*][†] [1]

[1] Institut de Biologie Intégrative de la Cellule – Commissariat à l'énergie atomique et aux énergies alternatives, Université Paris-Saclay, Centre National de la Recherche Scientifique, Commissariat à l'énergie atomique et aux énergies alternatives : DRF/I2BC, Centre National de la Recherche Scientifique : UMR9198 – France

Predicting protein-protein interactions and characterizing their structural organization provides essential information to elucidate the molecular mechanisms underlying cross-talk between cellular pathways. Exploiting coevolution information has emerged over the last years as a major strategy for predicting the mode of recognition between proteins. Our recent methodological developments (1, 2) have provided key insights to unravel the regulatory subtleties that might exist between pairs of interacting proteins (3, 4). The advent of machine learning in the field, culminating in the Alphafold2 (5) breakthrough, is pushing the boundaries from analyses of binary to multiple interactions (6-8). We will discuss the evolution of this avalanche of modelled data, the confidence with which it can be used, and the challenges ahead for a better understanding of the fine mechanisms of protein regulation.

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[*]Intervenant
[†]Auteur correspondant: Raphael.GUEROIS@cea.fr

Agnostic exploration of a new pathway for prebiotic glycine synthesis by ab initio and machine learning molecular dynamic

Léon Huet * [1], Timothée Devergne , Fabio Pietrucci , Rodolphe Vuilleumier , A. Marco Saitta

[1] Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC) – Institut de minéralogie, de physique des matériaux et de cosmochimie, CNRS : UMR7590, Université Paris VI - Pierre et Marie Curie, Muséum National d'Histoire Naturelle (MNHN) – 4, place Jussieu - Tour 23 - Barre 22-23, 4e étage - 75252 Paris Cedex 5, France

In contemporary prebiotic chemistry, advanced modeling protocols are indispensable. They underpin experimental progress and explore novel compounds and mechanisms. The synthesis of prebiotic amino acids is a central inquiry. Historically, the Strecker mechanism was the accepted pathway, but recent investigations, including meteorite analysis, have raised doubts. We've developed an ab initio methodology, using a combination of DFT and machine learning potential, that critically evaluates established synthesis pathways, such as Strecker, and proposes alternatives. Applied to glycine synthesis, it confirmed Strecker and revealed a new pathway. This new path beckons exploration of uncharted energy landscapes, reducing reliance on human interpretation.

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*Intervenant

Free-energy Landscapes of an Intrinsically Disordered Protein: alpha-synuclein

Adrien Guzzo [1], Patrice Delarue [1], Adrien Nicolaï [1], Gia Maisuradze [2], Patrick Senet [*][†] [1,2]

[1] Laboratoire Interdisciplinaire Carnot de Bourgogne – Université de Bourgogne, CNRS : UMR6303 – France
[2] Cornell University – États-Unis

Due to the lack of a folded structure, the computation and analysis of the near random configurational space of intrinsically disordered proteins (IDPs) is challenging. Here we focus on the case of alpha-synuclein (a-syn). The a-syn monomer is an IDP in solution and is prone to aggregate in large beta-sheet structures in the brain, fibrils, which are the hallmark of the Parkinson disease. The central hydrophobic region of a-syn (residues 61-95), called NAC, is necessary for the aggregation. Missense mutations (A30P, A53P, and E46K) in the N-terminal region are associated with familial forms of this neuropathy. How these single amino-acid substitutions in the N-terminal region modify the conformations of wild-type (WT) a-syn is unclear.

Here, using coarse-grained MD simulations, we sampled the conformational space of wild-type and family mutants of a-syn monomers and dimers for an effective time scale of 29.7 ms. A 2-D (effective) free-energy landscape of the monomers and dimers as function of the number of residues in alpha-helix and beta-sheet was computed for wild-type and mutated proteins from MD trajectories. The density of states reveals an unexpected two-phase characteristic with a homogeneous phase (state B, b-sheets) and a heterogeneous phase (state HB, mixture of a-helices and b-sheets) for the monomers. Free-energy landscape of global topological descriptors extracted from a graph representation of the monomers reveal sub-populations of monomers which are not visible in other probability distributions of global structural parameters as the gyration radius.

The (effective) free-energy landscape of inter- and intra-molecular contacts of the dimers show striking differences among the mutants. Most of the dimers form disordered aggregates and a minority (9-15 %) aggregate as pre-fibrillar dimers. Differences in the nucleation of dimers are observed among the mutants. Native fibril contacts between the two monomers are present in the NAC domain for WT, A30P and A53T and in the N-domain for A53T and E46K. Structural properties of pre-fibrillar dimers simulated agree with rupture-force Atomic Force Microscopy and single-molecule Förster Resonance Energy Transfer available data. This suggests that the pre-fibrillar dimers might correspond to the smallest toxic oligomers. Present results indicate that even the elementary a-syn aggregation step, the dimerization, is a complicated phenomenon, mutant dependent, and which does not only involve the NAC region, and which cannot be understood in a single free-energy landscape representation.

[*]Intervenant
[†]Auteur correspondant: psenet@u-bourgogne.fr

A New Neural Network Interatomic Potential for the Simulation of the Thermal and Mechanical Properties of Silica Zeolites

Luca Brugnoli * [1], Francois-Xavier Coudert[†] [1]

[1] PSL Research University, Chimie ParisTech – CNRS, Institut de Recherche de Chimie Paris, 75005, Paris, France

Pure silica zeolites are a well-known class of nanoporous materials with several technological and industrial applications, such as molecular sieves, as well as in adsorption and catalysis(1). They are metastable phases of SiO_2, whose structure is arranged in a network of corner-sharing SiO_4 tetrahedra. Although limited to these building blocks, up to 255 different topologies are currently recognized(2), which could lead to potentially hundreds of thousands of distinct structures(3). Significant progress has been made in elucidating their structure–property relationships (4,5), but several phenomena, including diffusion, thermal behaviour, and specific non-linear responses, remain inadequately explored. The development of force fields through machine learning, based on a training set derived from first-principles methods, enables the achievement of quantum-level accuracy while retaining the computational efficiency characteristic of classical methods. Utilizing a training set composed of trajectories, energies, and forces derived from ab initio molecular dynamics simulations (AIMD) of 11 zeolite frameworks under different strain conditions, an E(3)-equivariant interatomic potential (IP) was trained using NequIP, a deep-learning neural kernel. The resultant IP revealed a Mean Absolute Error (MAE) of 0.76 Kcal mol^{-1} Å^{-1} for forces and 0.014 Kcal mol-1 per atom for energy. Furthermore, when subjected to external, previously unseen zeolite frameworks, the IP retained similar accuracy. The developed IP was then tested on the thermal and mechanical properties of selected frameworks. Through (N, P, T) MD simulations at different temperatures, thermal expansion was investigated, showing good agreement with the experimental trends of both positive and negative thermal expansion characteristic of the selected frameworks. Similarly, (N, P, T) MD simulations at 600 K and varying pressures were employed to characterize the mechanical properties and amorphization process of zeolite crystals, reproducing the experimental trend for the onset pressure of amorphization. Despite some found limitations, such as the overestimation of thermal expansion at low temperatures and the impossibility of simulating amorphization at high degrees of compression-conditions that fall outside the scope of the utilized training set-the IP developed here offers a promising direction for the development of other deep-learning-based IPs and holds wide-ranging implications for the nanoporous material modelling community.

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*Intervenant
[†]Auteur correspondant: fx.coudert@himieparistech.psl.eu

Study of photophysical properties of azaBODIPY compounds through vibronic calculations

Ludmilla Verrieux * [1], Arnaud Fihey [1] , Boris Le Guennic [1]

[1] Institut des Sciences Chimiques de Rennes – Université de Rennes, Institut National des Sciences Appliquées - Rennes, Ecole Nationale Supérieure de Chimie de Rennes, Centre National de la Recherche Scientifique – France

AzaBODIPY (Figure **1.A**) are a class of fluorophore which have experienced exponential growth in wide range of applications and are today promising candidates for medical imaging and fluorescence guided surgery.(1) In this context their experimental development is based on optimizing the nature of the ligands and replacing the boron center with another metal atom (aza-M-DIPY, M = metal),(2) in order to shift the absorption and emission wavelengths further in the NIR region, and increase their fluorescence quantum yield. To establish such structure-properties relationships, their vertical photophysical properties can be accurately computed with TD-DFT. Taking into account vibrational contribution and non-radiative mechanisms is necessary to achieve a more correct description of the photophysical properties.(3) In this contribution we show how the use of TD-DFT coupled with vibronic models(4) can help rationalizing the spectra band structure (Figure **1**) and guide the design of more efficient aza-M-DIPY emitters by computing their fluorescence quantum yield.

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*Intervenant

Spin–vibronic mechanism at work in a luminescent square-planar cyclometalated tridentate Pt(II) complex: absorption and ultrafast photophysics

Souvik Mandal * [1], Chantal Daniel

[1] post doctoral researcher – UNIVERSITY STRASBOURG – France

The absorption spectrum of (Pt(dpybMe)Cl) (dpyb = 2,6-di-(2-pyridyl)benzene), representative of luminescent halide-substituted tridentate cyclometalated square planar Pt(II) neutral complexes, has been revisited by means of non-adiabatic wavepacket quantum dynamics. The early photophysics has been investigated on the basis of four singlet and five triplet excited states, namely nineteen "spin–orbit states", coupled with both vibronic and spin–orbit couplings, and includes eighteen normal modes. It is shown that in-plane scissoring and rocking normal modes of the cyclometalated tridentate ligand are responsible for the vibronic structure observed at around 400 nm in the experimental spectrum of the complex. The ultrafast decay of (Pt(dpybMe)Cl), within 1 ps, follows a spin–vibronic mechanism governed by excited state electronic characters, spin–orbit, and active tuning mode interplay. Both spin–orbit coupling and Pt(II) coordination sphere stretching modes and in-plane scissoring/rocking of the cyclometalated ligand activate the ultrafast decay within 20 fs of absorption. At longer time-scales (> 100 fs) an asynchronous stretching of the Pt–C and Pt–N bonds activates the depopulation of the upper "reservoir" electronic states to populate the two lowest luminescent T1 and T2 electronic states. The in-plane rocking motion of the ligand controls the T1/T2 population exchange which is equilibrated at about 1 ps. Stabilization of the upper non-radiative metal-centered (MC) states by out-of-plane ligand distortion of low frequency is not competitive with the ultrafast spin–vibronic mechanism discovered here for (Pt(dpybMe)Cl). Modifying the Pt–C covalent bond position and rigidifying the cyclometalated ligand will have a dramatic influence on the spin–vibronic mechanism and consequently on the luminescence properties of this class of molecules.

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*Intervenant

Joint Experimental and Theoretical investigation of excited state vibrational coherences in Mn Single Molecule Magnets

Julien Eng * [1], Kyle Barlow [2], Euan Brechin [2], J. Olof Johansson [2], Thomas Penfold [1]

[1] Chemistry, SNES - Newcastle University – Newcastle University Newcastle upon Tyne, NE1 7RU, Royaume-Uni
[2] EaStCHEM School of Chemistry, University of Edinburgh – Royaume-Uni

Single molecule magnets (SMM) are typically large poly-metallic molecules with two degenerate magnetic ground states that retain magnetisation under a so-called "blocking temperature". In d-metal molecules, the blocking temperature is very low, rendering most industrial applications impossible. The lowest blocking temperature is observed in the Mn12 complex that retains magnetisation for months below 2K(1). Magnetic recording using femtosecond laser pulses has recently been achieved in some dielectric media, showing potential for ultrafast data storage applications(2). Light control of magnetisation represents a great challenge in the field of data storage as it opens the way for larger and more compact storage arrays. Yet, SMMs remain largely unexplored using ultrafast techniques.

In this work(3), we investigate the photophysics and excited-state relaxation of a trinuclear μ3-oxo-bridged Mn(III) SMM, whose magnetic anisotropy is closely related to the Jahn–Teller distortion. Ultrafast transient absorption spectroscopy in solution reveals oscillations superimposed on the decay traces due to a vibrational wavepacket. A joint experimental and theoretical study on Mn monomers allows to shine light on the origin of the vibrational coherences observed experimentally on the larger Mn3 complex. It is shown to emanate from the μ3-oxo-bridge effectively constraining the wavepacket motions along the Jahn-Teller axis. Our results provide new possibilities for optical control of the magnetisation in SMMs and open up new molecular-design challenges to control the wavepacket behaviour in the excited state of SMMs.

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*Intervenant

Modifications of Tanabe-Sugano d6 diagram induced by radical ligand field: ab initio inspection of a Fe(II)-verdazyl molecular complex

Pablo Roseiro * [1], Saad Yalouz [1], David J.r. Brook [2], Nadia Ben Amor [3], Vincent Robert [1]

[1] Laboratoire de Chimie Quantique de Strasbourg – Université de Strasbourg, CNRS – France
[2] Department of Chemistry – États-Unis
[3] Laboratoire de Chimie et Physique Quantiques – Université Toulouse III - Paul Sabatier, UMR5626 – France

Quantum entanglement between the spin states of a metal centre and radical ligands is suggested in an iron(II) $(Fe(dipyvd)_2)^{2+}$ compound (dipyvd = 1-isopropyl-3,5-dipyridil-6-oxoverdazyl). Wavefunction *ab initio* (Difference Dedicated Configuration Interaction, DDCI) inspections were carried out to stress the versatility of local spin states. We named this phenomenon *excited state spinmerism*, in reference to our previous work where we introduced the concept of spinmerism as an extension of mesomerism to spin degrees of freedom. The construction of localized molecular orbitals allows for a reading of the wavefunctions and projections onto the local spin states. The low-energy spectrum is well-depicted by a Heisenberg picture. A 60 cm^{-1} ferromagnetic interaction is calculated between the radical ligands with the Stotal = 0 and 1 states largely dominated by a local low-spin SFe = 0. In contrast, the higher-lying Stotal = 2 states are superpositions of the local SFe = 1 (17%, 62%) and SFe = 2 (72%, 21%) spin states. Such mixing extends the traditional picture of a high-field d6 Tanabe-Sugano diagram. Even in the absence of spin-orbit coupling, the avoided crossing between different local spin states is triggered by the field generated by radical ligands. This puzzling scenario emerges from versatile local spin states in compounds which extend the traditional views in molecular magnetism.

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*Intervenant

Reference Energies for Valence Ionizations and Satellite Transitions

Antoine Marie * [1], Pierre-Francois Loos [1]

[1] Groupe Méthodes et outils de la chimie quantique (LCPQ) – Laboratoire de Chimie et Physique Quantiques Laboratoire – France

Direct and inverse photoemission spectroscopies are important tools to analyze the structure of molecules and materials. The theoretical prediction of these spectra can be a useful complementary tool to understand and assign the peaks observed in experimental spectra. While exact theoretical spectra will always be out of reach for realistic systems, benchmark of near-exact values for small systems are really valuable to the theoretical chemist who need to design new affordable and accurate methods. There are several benchmarks of principal ionization potential and a few for valence ionizations but there are currently no benchmarks of satellite transition energies in molecules (to the best of our knowledge). The satellite peaks in a photoemission spectrum correspond to a simultaneous ionization of an electron and excitation of another one (or more) In this work, we compute near-exact values, using the selected configuration interaction method, of satellite transition energies of some small organic molecules. In addition, we gauge the performance of the hierarchy of truncated coupled-cluster methods up to CCSDTQ, as well as their CCn approximations. Finally, the performance of several common Green's function-based methods are reported as well. These results highlight again the need to develop beyond-GW methods.

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*Intervenant

The QuantNBody package : a numerical platform for methodology development in quantum chemistry

Saad Yalouz [*][†] [1]

[1] Laboratoire de Chimie Quantique, Institut de Chimie, CNRS/Université de Strasbourg, 4 rue Blaise Pascal, 67000 Strasbourg, France – Université de Strasbourg, CNRS – France

The manipulation of many-body operators in the language of second quantization is a crucial step for accessing the properties of model or ab initio systems in quantum chemistry and physics. From a numerical point of view, this requires developing codes to represent quantum operators in a given quantum many-body basis (e.g., Hamiltonians, excitation operators). In a great majority of cases, this aspect is kept as a "blackbox" to spare the users from cumbersome numerical parts and to facilitate the use of already implemented methods. Nevertheless, this type of implementation can appear as a real problem for researchers in need of reliable numerical tools to quickly develop and test new methodologies based on second quantization algebra. The "QuantNBody" package (1) was designed to answer this problem: it is a user-friendly numerical toolbox to facilitate the creation and implementation of methods in quantum chemistry.

In this talk, I will present the QuantNBody package and its philosophy. In a first part, I will discuss how the package works and I will give some examples of its use/application (2, 3). Second, I will focus on a specific example of method built with this tool for excited states calculation: the so-called Orthogonally Constrained Orbital Optimization method (4). This approach focuses on the description of excited states within their respective optimal orbital basis with specific constraints introduced to preserve the orthogonality with other multi-reference states.

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[*]Intervenant

[†]Auteur correspondant:

Divide and Conquer embedding approach for electronic structure calculation.

Quentin Marecat * [1], Emmanuel Fromager [2], Matthieu Saubanère [1]

[1] Institut Charles Gerhardt Montpellier - Institut de Chimie Moléculaire et des Matériaux de Montpellier, Centre National de la Recherche Scientifique, Université de Montpellier – France
[2] Université de Strasbourg – Université de Strasbourg, CNRS – France

In this talk, I present an innovative self-consistent Divide and Conquer (DaC) algorithm for investigating the electronic structure of strongly correlated materials without calculating explicitly the N-particle many-body wave function (1). Following the concept of density matrix embedding theory, the strategy consist in dividing the system into clusters, for witch an effective Schrödinger equation can be solved with high-level methods such as full CI (2). More precisely, we design a unitary transformation of the one body reduced density matrix (1RDM) to perform the division into cluster, providing an accurate (1RDM-functional) effective Hamiltonian. In addition, a reconstruction scheme for the full-system 1RDM (and additionally 2RDM), based on the Virial conditions is introduced, leading to a self-consistency iterative process that closed the DaC loop.

The effectiveness of the approach is illustrated through a case study involving a simple quantum chemistry Hamiltonian with the 14 orbitals Hydrogen ring, offering comparisons against established state-of-the-art DMET methods (3).

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*Intervenant

A new variational density matrix formalism for correlated systems

Matthieu Vladaj * [1], Quentin Marecat [1], Bruno Senjean[†] [1], Matthieu Saubanère[‡] [1]

[1] Institut Charles Gerhardt Montpellier - Institut de Chimie Moléculaire et des Matériaux de Montpellier, Centre National de la Recherche Scientifique, Université de Montpellier, Ecole Nationale Supérieure de Chimie de Montpellier, Centre National de la Recherche Scientifique : UMR5253 – France

Over the last few decades, density functional theory (DFT) has played a major role in the study of the physico-chemical properties of molecules and materials. Its low numerical cost, compared with wavefunction-based methods, has made DFT a major area of research in theoretical chemistry, allowing the emergence of numerous exchange-correlation functionals.

However, many of these functionals fail to reach chemical accuracy, especially when static correlation is a major contributor to the ground-state energy. In this context, the one-particle Reduced Density-Matrix Functional Theory (1-RDMFT) is more and more regarded as a viable alternative to DFT: with only a small increase in computational cost by replacing the density by the density-matrix as the fundamental variable, it allows, by construction, the kinetic and exchange contributions to be represented analytically.

Unfortunately, the conditions of representability, i.e. the conditions ensuring that the matrix represents a physical system, are not generally known. As a result, the variational constrained equations leading to the ground state energy, and so, to the molecular properties of the system, are much more complex to solve. We propose to adress the afordmentionned challenges by introducing a new formalism, namely the Density-matrix Interpolation Variational Ansatz (DIVA). This new formalism, based on the convexity of the reprentability domain, allows to 1) simplify the resolution of ground state energy using a "by construction" representable density-matrix and 2) to develop a new class of ground-state energy functionals

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[*]Intervenant

[†]Auteur correspondant: bruno.senjean@umontpellier.fr

[‡]Auteur correspondant: matthieu.saubanere@umontpellier.fr

One dimensional model for relativistic quantum chemistry

Timothee Audinet * [1], Julien Toulouse[†]

[1] Laboratoire de chimie théorique – Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique – France

Relativistic effects account for gold's color, mercury's liquid state at room temperature and are responsible for the efficiency of lead-acid batteries in cars. Relativistic electronic-structure computational methods are routinely applied on molecular systems, however most of those methods are based on the no-pair approximation, neglecting the effects of the negative energy solutions of the Dirac equation on the system. Hence, the next challenge is to go beyond this approximation. Such description is needed to recover some properties, even in very simple systems, e.g. the Lamb shift in the Hydrogen atom. In this presentation we will be interested in a one-dimensional model of relativistic hydrogen-like atom in which we are able to make accurate calculations. After calculating the spectrum of the 1D Dirac operator in first quantization, we develop an effective Hamiltonian in second quantization. Within this framework we are able to calculate the effects of the negative energy solutions, such as the vacuum polarization and the Lamb shift.

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[*]Intervenant

[†]Auteur correspondant: toulouse@lct.jussieu.fr

DFTB molecular dynamics for a quantitatively accurate description of the experimental absorption bands of solvated organic switches.

Benjamin Ludwig * [1], Adèle Laurent , Arnaud Fihey

[1] Modélisation Et Spectroscopie – Chimie Et Interdisciplinarité : Synthèse, Analyse, Modélisation – France

Density Functional Tight Binding (DFTB) (1), (2) is a quite recent computational tool that has been rapidly gaining popularity among quantum chemists. Its ability to accurately model the electronic structure of chemical systems while maintaining high levels of computational efficiency allows the simulations of large systems at a full quantum level of theory. Several results published recently have shown its accuracy for the modelling of organic photo-active (3)–(5) species as well as bio-molecules (6). From this kind of fast quantum chemical calculation, emerged new tools for the theoretician chemist such as Quantum Molecular Dynamics simulation with thousands of atoms with a reasonable computational cost. This type of simulation allows the study of dynamical solute-solvent interactions as well as the influence of the photochrome conformational motion on its absorption properties. Our philosophy with this approach is to have a computational methodology related to those used experimentally, that is to say that the absorption spectrum is a result of the dynamics of the system and the existence of several conformations at room temperature contributing to a single measure. Herein we present our results and details of the methodology for the simulation of Azobenzenes (AZB) derivatives in explicit solvents. A series of 13 AZB derivatives has been selected from the experimental litterature and their photo-chemical properties have been computed at Density Functional Theory (DFT) and DFTB levels. We found a satisfying agreement between DFTB, DFT and experimental reference results. Moreover, the statistical approach following DFTB Molecular Dynamics simulations permits to reproduce the broadening of excitation peaks seen experimentally and furthermore give insights on which geometrical properties of the molecule is inducing those changes.

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*Intervenant

Molecular insight into the photonastic phenomenon: study of the coupling between the photochemical reaction and the intramolecular relaxation of the polymer

Marta Serrano Martínez * [1,2], Orlando Villegas [1,2], Nicolas Pineau [3,4], Claire Lemarchand [3,4], Aurelie Perrier[†] [2]

[1] Institute of Chemistry for Life and Health Sciences – Ecole Nationale Supérieure de Chimie de Paris - Chimie ParisTech-PSL, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France
[2] Laboratoire Interdisciplinaire des Energies de Demain – Centre National de la Recherche Scientifique, Université Paris Cité – France
[3] DAM Île-de-France – Direction des Applications Militaires – France
[4] Laboratoire Matière sous Conditions Extrêmes – DAM Île-de-France, Université Paris-Saclay – France

Photonastic materials perform light-induced movements, transforming light energy into mechanical energy, akin to the motions observed in plants and flowers. This project focuses on bio-inspired polymeric photoactuators with applications in microfluidics, biomedics, soft robotics, and motors. A polymer thin film containing photoactive molecules, particularly photochromes, can exhibit significant shape changes upon light excitation. By employing computational chemistry and particularly molecular dynamics (MD) simulations, we investigate the molecular processes governing the macroscopic behavior of these systems, which in our case consists of a derivative of azobenzene (AZ) embebbed in a polybutadiene matrix. Our aim is to propose a strategy to investigate the coupling between the photochemical reaction and the intramolecular relaxation of the polymer. In a previous study, we assumed that these processes occurred simultaneously (J. Chem. Theory Comput. 2020, 16, 7017). However, subsequent results indicate that the intramolecular relaxation time is considerably shorter than the estimated photo-induced reaction time. To improve the description of the system, a purely classical molecular mechanics model of AZ photoswitches in both their ground and first excited states (S0 and S1) is considered. The photoreaction is modelled by switching between these two potential energy surfaces (PES). During MD simulations, we will mimic electronic excitations and decay by switching between the S0 and S1 force fields along the photoreaction coordinate, while allowing the polymer chains to rearrange concomitantly. Through this molecular-scale study, we aim to deepen our understanding of the photonastic phenomena and the mechanical response of the polymer-photochrome system.

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*Intervenant
[†]Auteur correspondant: aurelie.perrier@chimieparistech.psl.eu

Computational Analysis of Structural Changes in Photoswitchable Systems using Molecular Simulations

Orlando Villegas * [1,2], Marta Serrano Martínez [1,2], Nicolas Pineau [3,4], Aurelie Perrier [2], Claire Lemarchand[†] [3,4]

[1] Institute of Chemistry for Life and Health Sciences – Ecole Nationale Supérieure de Chimie de Paris - Chimie ParisTech-PSL, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France
[2] Laboratoire Interdisciplinaire des Energies de Demain – Centre National de la Recherche Scientifique, Université Paris Cité – France
[3] Direction des Applications Militaires – Commissariat à l'énergie atomique et aux énergies alternatives – France
[4] Laboratoire Matière sous Conditions Extrêmes – DAM Île-de-France, Université Paris-Saclay – France

Photonastic materials exhibit the remarkable ability to convert light into mechanical energy through macroscopic transformations. This phenomenon is usually associated with plants and flowers whose petals open in the daylight and close in the evening due to a cascade of light-triggered reactions, resulting in a change of hydrostatic or Turgor pressure within the plant cells. Based on this concept, various bio-inspired polymeric photoactuators devices have been recently proposed and, notably, a polymeric material incorporating a 4,4'-dihydroxyazobenzene photoswitch within a chitosan matrix demonstrated intriguing macroscopic bending upon exposure to 355 nm irradiation (*Chinese J. Polym. Sci.* **2020**, 39. 417). The observed photonastic behavior of this system further demonstrated its high efficiency in converting light into mechanical work. In this context, computational chemistry can play a crucial role in understanding and optimizing the conversion of solar energy into mechanical energy. It can indeed offer valuable information on the molecular and supramolecular processes at the origin of this photonastic phenomenon. To achieve this, we propose a model system consisting of a 4,4'-dihydroxyazobenzene photoswitch embedded within a model polybutadiene matrix. Through the implementation of molecular dynamics (MD) simulations and time-dependent density functional theory (TD-DFT) calculations. We will discuss (i) the influence of the polymer matrix on the properties of the cis and trans azobenzene isomers and (ii) the effect of the photochromic reaction on the surrounding polymer environment.

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[*]Intervenant
[†]Auteur correspondant: claire.lemarchand@cea.fr

Effect of inorganic ligands on Pa5+ and PaO3+ relative stabilities: A computational study

Tamara Shaaban [*][†] [1], Valérie Vallet[‡] [1], Florent Réal[§] [1]

[1] Laboratoire de Physique des Lasers, Atomes et Molécules - UMR 8523 – Université de Lille, Centre National de la Recherche Scientifique, Université de Lille : UMR8523, Centre National de la Recherche Scientifique : UMR8523 – France

A better understanding of the physical and chemical properties of actinide complexes in the solvated phase, i.e., their speciation, the nature of chemical bonds between actinides and their environment, their thermodynamic and spectroscopic properties, can have direct implications on societal and industrial applications. A key parameter is thus the coordination mechanism with ligands that acts strongly on many properties such as thermodynamics, optical or magnetism ones. The unique coordination and properties of f-elements with ligands (1) attracted the attention of many experimental and theoretical researchers. Among the actinides, protactinium (Z=91) keeps on being specific because, depending on its oxidation state it can behave as "f element" (Pa(VI)) or "d element" (Pa(V)). In solution, Pa(V) is dominating because Pa(IV) is unstable and can be directly oxidized to Pa(V) unless a strong reducing agent is present (2). Pa(V) can exist in solution as Pa^{5+} and in some specific solutions it will form PaO^{3+} (3), but apparently it does not form the actinyl moiety PaO_2^+ which is not the case of their heavier neighbours uranium, neptunium and plutonium. However, experimental characterization of Pa(V) and Pa(IV) is challenging because they have high tendency towards hydrolysis, polymerization and sorption on any solid.

In this work, with the use of the state-of-the-art quantum calculations, we investigate the two possible forms of Pa(V), namely PaO^{3+} and Pa^{5+} and the influence of coordinated ligands in order to determine the suitable experimental conditions to tune their relative stability. For that we consider two different stoichiometrically equivalent complexes $PaO(OH)_2(X)(H_2O)$ and $Pa(OH)_4(X)$ where $X = OH^-$ (see Fig. 1), F-, Cl-, Br-, I-, NO_3^-, SCN^-, $C_2O_4^{2-}$ and SO_4^{2-} and compare their relative stabilities.

Figure 1: Perspectives of Pa(OH)5 and PaO(OH)3(H2O) in water (protactinium in green, oxygen in red, hydrogen in white)

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[*]Intervenant

[†]Auteur correspondant: tamara.shaaban@univ-lille.fr

[‡]Auteur correspondant: valerie.vallet@univ-lille.fr

[§]Auteur correspondant: florent.real@univ-lille.fr

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Computing RedOx Properties in Solution

Maxime Labat * [1,2], Emmanuel Giner [2], Mathieu Salanne [1], Guillaume Jeanmairet[†] [1]

[1] PHysicochimie des Electrolytes et Nanosystèmes InterfaciauX – Sorbonne Université – France
[2] Laboratoire de chimie théorique – Sorbonne Université – France

Solvation effects have a significant impact on chemical reactions, and many molecular properties are influenced by the choice of solvent. However, precise quantum chemistry (QM) calculations are most often done either in vacuum neglecting the role of the solvent or using a continuum solvent model ignoring its molecular nature. An ingenious and commonly used approach to overcome this problem is the QM/MM partitioning of the system. The part considered essential for describing the chemistry is treated at the QM level, while the rest is described by classical molecular mechanics (MM). This thesis aims to develop an innovative hybrid method QM/MM that maintains a comparable accuracy to molecular simulation methods generally used but with significantly lower computational cost.

Our MM part consists solely of the solvent which is represented by classical force fields. The originality of our method lies in the use of a theory derived from the physics of liquids, the Molecular Density Functional Theory (MDFT). In MDFT, solvent molecules are treated as rigid molecules represented by a density field that depends on both position and orientation. To account for the interaction experienced by the solvent due to the solute, the solute is represented by an external potential, which is treated as a perturbation. There exists a functional of the solvent density that reaches its minimum for the equilibrium density. At its minimum, the functional equals the solvation free energy. Thus, MDFT is particularly suitable for capturing solvent effects, as both the solvent free energy and the solvent structure can be easily calculated through numerically efficient functional minimization.

On the other hand, our QM part focuses solely on the solute. We will study open-shell systems or strongly correlated that require a good description of electronic correlation. We have chosen a configuration interaction-based method since it provides an excellent description of electronic interactions by considering a large number of electronic configurations for a system. Specifically, we employ the Selcted Configuration Interaction (SCI) method. This method sorts the determinants based on their perturbative contribution, selects only the most important ones, and re-diagonalizes the Hamiltonian using this reduced basis. Therefore, the solute energy can be obtained rapidly with excellent precision.

To combine the MDFT and SCI methods, we follow the following procedure. First, we calculate the solute energy and its electrostatic potential at the QM level. This potential serves as the perturbing potential in the MDFT calculation. Next, we minimize the functional to obtain the solvation structure and free energy. By analyzing the equilibrium density, we can compute the inhomogeneous charge density of the solvent and its corresponding electrostatic potential. This potential is then added to the electronic Hamiltonian of the solute, and we calculate a new solute energy (tackling the presence of the solvent), using the CIPSI method. This approach is

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[*]Intervenant
[†]Auteur correspondant: guillaume.jeanmairet@sorbonne-universite.fr

self-consistent and involves iterative steps until both the solute energy and solvation free energy converge.

To assess our framework, we primarily focused on water (QM) in water (MM). This systems isinteresting because it requires an accurate description of solute electronic structure, and of solvent polarization. We lookeed at three chemical properties: the solvent charge density, the QM and MM energies convergences and the radial distribution function of the solute. We observed that the results are not yet fully quantitative compared to experimental data, but the most important features are qualitatively captured. Therefore, it is crucial to develop a better method to describe the repulsive solute-solvent interactions in order to investigate such highly polarized systems.

For the future, we want to stufy more revelant solutes for an application in energy storage; the hydroquinone and benzoquinone, a famous redox couple; and the nitroxides radicales. Morever, we wants to build an interface with pi-SCF because it would allow us to optimized the solute geometrie and use the so-called Couple Cluster methods for the QM part.

Some thoughts on the quantum mechanical definition of the Mean Square Displacement

Roberto Marquardt * [1]

[1] Laboratoire de Chimie Quantique – CNRS, Université de Strasbourg – France

The mean square displacement (MSD) has been a notorious quantity ever since the observation by Robert Brown in 1827 (1) of the eponymic motion of colloidal particles. While the theoretical understanding of the MSD in terms of diffusion has been established from classical statistical mechanics at the beginning of the 20th century (2,3), the quantum mechanical approach bears some interesting questions.

In this talk we address the definition of the MSD related to the quantum correlation function of the position operator (4) and a more recently proposed definition based on thermal wave packets (5). As an example, the quantum mechanical MSD will be evaluated for thermalized CO molecules adsorbed on a Cu(100) substrate (6).

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*Intervenant

Computation of exchange couplings in photogenerated excited states in DFT-KS

Grégoire David * [1], Boris Le Guennic

[1] Institut des Sciences Chimiques de Rennes (ISCR) – Université de Rennes 1, Institut des Sciences Chimiques de Rennes, UMR CNRS 6226, 35043 Rennes Cedex – France

Optically excited states of three-spin molecules have recently attracted much attention to manipulate magnetooptical properties, with possible application in spintronics or quantum technologies. They consist of a stable radical linked to a chromophore, which once excited, creates a three-spin system magnetically coupled. However, unlike exchange couplings in ground states, little is known about them in excited states, and their study is challenging from both experimental and theoretical points of view.

Determination of magnetic exchange couplings usually resorts to DFT with the computation of high spin and broken symmetry determinants, which are ground states of their given spin symmetry. This strategy cannot be directly applied to excited states due to the inherent variational collapse, and the first computations in this context are based on time-consuming wave-function-based methods or Spin Flip TD-DFT.(1,2)

In this communication, I will show how the recently developed decomposition/recomposition method offers an affordable and unequivocal strategy to compute exchange couplings in excited states. This method allows decomposing magnetic exchange couplings in their three main physical contributions (the direct exchange, the kinetic exchange and the spin polarisation contribution), which once summed up, offers a rigorous evaluation of the coupling. (3,4) This strategy is based on a selective relaxation of the orbitals involved in the different mechanisms, and these controlled relaxations prevent the question of variational collapse. The method is applied to study couplings in a series of radical-based molecules recently synthesised by Stein *et al.*.(5)

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*Intervenant

Optimized excitonic transport mediated by local energy defects: survival of optimization laws in the presence of dephasing

Lucie Pepe * [1], Saad Yalouz * [†] , Vincent Pouthier

[1] Laboratoire de Chimie Quantique – CNRS, Université de Strasbourg – France

In an extended star with peripheral defects and a core occupied by a trap, it has been shown that exciton-mediated energy transport from the periphery to the core can be optimized (S. Yalouz et al. Phys. Rev. E **106**, 064313 (2022)). If the defects are judiciously chosen, the exciton dynamics is isomorphic to that of an asymmetric chain and a speedup of the excitonic propagation is observed. Here, we extend this previous work by considering that the exciton in both an extended star and an asymmetric chain, is perturbed by the presence of a dephasing environment. Simulating the dynamics using a Lindblad master equation, two questions are addressed: how does the environment affect the energy transport on these two networks? And, do the two systems still behave equivalently in the presence of dephasing? Our results reveal that the time-scale for the exciton dynamics strongly depends on the nature of the network. But quite surprisingly, the two networks behave similarly regarding the survival of their optimization law. In both cases, the energy transport can be improved using the same original optimal tuning of energy defects as long as the dephasing remains weak. However, for moderate/strong dephasing, the optimization law is lost due to quantum Zeno effect.

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*Intervenant
†Auteur correspondant: yalouzsaad@gmail.com

How the pH of aqueous droplets and its size dependence are controlled by the air-water interface acidity

Miguel De La Puente * [1], Damien Laage[†] [1]

[1] PASTEUR, Département de Chimie, École Normale Supérieure, PSL, Sorbonne Université, CNRS – Ecole Normale Supérieure de Paris - ENS Paris – France

The air-water interface exhibits a unique chemical reactivity that is completely different from that in the bulk and that is central to fields ranging from "on-droplet" catalysis to atmospheric chemistry.(1) One of the most fundamental properties altered by the air-water interface is acidity. However, defining and measuring acidity in micro-droplets is extremely challenging, since factors ranging from system size to spatial resolution can critically impact such measurements.(2) Recent innovative experiments (3,4) have reported a mapping of acidity within droplets, but the results remain contrasted and a molecular understanding of the interface impact on acidity is needed.

Molecular dynamics (MD) simulations are a precious tool to obtain a molecular- level picture of acidity in interfacial systems. However, the computational cost of typical reactive simulations traditionally imposes a compromise either on the accuracy of the electronic structure descriptions or on the statistical sampling, which are both required to provide a quantitative measure of acidity. Here, we overcome these limitations by employing deep neural network potentials(5) trained to reproduce potential energy surfaces of hybrid DFT quality at a fraction of the computational cost, which we combine with path-integral MD to account for nuclear quantum effects.(6)

We performed reactive simulations of the water self-dissociation equilibrium and calculated the hydronium and hydroxide self-ion stabilities near the air-water interface. We then combined these results with an analytical model to determine the pH and self-ion concentration profiles within nano- and micro-droplets and to assess the impact of system size and interfacial depth on these key quantities.

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*Intervenant
[†]Auteur correspondant: damien.laage@ens.fr

Quantum embedding strategy for describing multiple electronic states

Filip Cernatic * [1], Saad Yalouz[†]

[1] Laboratoire de Chimie Quantique, Institut de Chimie de Strasbourg – université de Strasbourg, CNRS : UMR7177 – France

In recent years, quantum embedding theory, which focuses on modelling molecules and materials with strong local correlation, has attracted increasing attention. The essence of the theory can be broken down into two basic steps: dividing a many-electron system into single- or multiple-impurity fragments, and embedding each fragment in a small number of bath orbitals spanning the rest of the system. Although the bath subspace can be constructed in a variety of ways, one strategy is to use the one-electron reduced density matrix (1RDM)(1-4) Current literature on embedding based on 1RDM mostly focuses on specific (ground(1-4) or excited(5)) electronic states. In our work, we propose an extension toward embedding of multiple states by introducing **ensemble embedding** – a strategy, suitable for the weighted average of ground and excited state 1RDMs(6). We show an example of how to build single-impurity embedding for targeting the singlet ground and first excited states, and present results of applications on *ab initio* and model systems.

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[*]Intervenant
[†]Auteur correspondant: yalouzsaad@gmail.com

Exploring Surface Terminations and Reactivity in Epitaxially Grown Maghemite on Pt Substrates through First Principles

Amit Sahu * [1], Celine Dupont[†] [1]

[1] Laboratoire Interdisciplinaire Carnot de Bourgogne [Dijon] – Université de Bourgogne, Université de Technologie de Belfort-Montbeliard, Centre National de la Recherche Scientifique, Centre National de la Recherche Scientifique : UMRCNRS 6303, Centre National de la Recherche Scientifique : UMR6303 – France

Transitioning to sustainable energy sources like solar and wind power offers a promising solution to climate change, but the issue of efficient energy storage remains a significant hurdle. Hydrogen emerges as a potential game-changer, serving both as an energy carrier and storage medium, attainable through the process of photoelectrolysis. However, the efficiency of this process relies on identifying effective catalysts, which has proven elusive thus far, especially concerning metal oxides. Iron-based oxides, particularly maghemite, have attracted considerable attention due to their favorable attributes, including stability and non-toxicity, but a comprehensive understanding is still lacking. Thanks to a DFT+U approach, we investigate two distinct maghemite surface terminations, (001) and (111), epitaxially grown on a Pt substrate. Additionally, the impact of the computational model (tetragonal vs. cubic) on surface termination stability is examined. Besides, the surface reactivity towards water would also be compared.

The comparative stability of various termination combinations is explored, with a focus on the (001) termination, leading to the identification of four stable systems. Among these, AB, featuring Fe_{Th} and Fe_{Oh} terminations, exhibits the highest stability. Conversely, the (111) termination presents three stable terminations, with AD1 emerging as the most stable. The influence of heterostructures formed by combining strained maghemite surfaces with a Pt(001) substrate is investigated, revealing the dominance of (111) surfaces over (001) in these configurations.

Furthermore, we analyze the stability and electronic behavior of (001) and (111) surfaces derived from cubic and tetragonal maghemite models, highlighting the impact of surface vacancies and layer thickness on stability and rearrangements. In particular, the presence of vacancies affects surface destabilization, with notable inner layer distortion observed in smaller systems. The investigation of water adsorption on these surfaces reveals that the Fe_{Th} site consistently exhibits stronger adsorption compared to Fe_{Oh}, suggesting that water molecules are likely to preferentially adhere to the Fe_2O_3 surface's tetrahedral sites. This research represents a critical step toward understanding the reactivity and stability of maghemite surfaces and their potential in catalysis and energy applications.

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*Intervenant

[†]Auteur correspondant: celine.dupont@u-bourgogne.fr

State-specific coupled-cluster methods for excited states

Yann Damour *† 1, Fabris Kossoski 1, Anthony Scemama 1, Pierre-Francois Loos 1

1 Laboratoire de Chimie et Physique Quantiques – Laboratoire de Chimie et Physique Quantiques (LCPQ) – UMR5626 – France – France

Over the past few years, a major effort has been put to attain accurate descriptions of excited states in molecules, particularly vertical excitation energies from the ground state. The well-established Density Functional Theory (DFT) offers a pathway to access excited states by employing time-dependent DFT, which uses linear-response theory on top of a ground-state computation. A similar concept is embraced in the single-reference coupled-cluster (CC) theory, where ground-state amplitudes serve for excited-state calculations. However, this approach inherently biases excitation energies towards the ground state. To address this issue, there are two viable alternatives. Firstly, one can employ state-averaged methods, in which the choice of orbitals is made such that they are neither particularly favorable nor unfavorable for different states. Secondly, in state-specific methods, a dedicated set of orbitals is optimized for each state of interest. While these techniques are commonplace within configuration-interaction methods, integrating them into CC theory can be somewhat intricate. Nonetheless, recent investigations have unveiled promising outcomes with a state-specific method called ΔCC(1,2). In this approach, calculations are executed based on a closed-shell doubly-excited Slater determinant, allowing access to doubly excited states-an area where low-order CC methods often fall short in accuracy. Regrettably, this concept generally cannot be applied to open-shell excited states due to to their multireference character. Thus, one way to deal with it consists on using multi-reference coupled-cluster (MRCC) methods but they are generally cumbersome. Luckily, open-shell singlet and triplet excited states are generally aptly described by two spin-flipped Slater determinants, constituting a minimalist MRCC approach known as the two-determinants CC(3-5) (TD-CC). In contrast to more complex MRCC methodologies, the TD-CC equations can be derived in a straightforward manner. In this presentation, we will provide a concise overview of the ΔCC and TD-CC methods before investigating into their respective performances across various types of excited states.

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*Intervenant
†Auteur correspondant: ydamour@irsamc.ups-tlse.fr

Recent developments in molecular excited-state dynamics with the exact factorization

Eduarda Sangiogo Gil [*][†] [1], Federica Agostini[‡] [1]

[1] Université Paris-Saclay – Institut de Chimie Physique, Université Paris-Saclay, CNRS – France

In this presentation, I will discuss recent developments in the field of molecular excited-state dynamics. In particular, I will present the first implementation of coupled-trajectory Tully surface hopping (CT-TSH), derived from the exact factorization, suitable for applications to molecular systems. CT-TSH has been combined with the semiempirical FOMO-CI electronic structure method to investigate the photoisomerization dynamics of trans-azobenzene. This study shows that CT-TSH can capture correctly decoherence effects in this system, yielding consistent electronic and nuclear dynamics in agreement with (standard) decoherence-corrected TSH. In CT-TSH the electronic coefficients' evolution is directly influenced by the coupling of trajectories, resulting in the improvement of internal consistency if compared to standard TSH. In addition, the exact factorization is currently being extended to treat systems of photons, electrons, and nuclei, aiming to investigate the effects of strong light-matter coupling (at the full quantum mechanical level).

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[*]Intervenant

[†]Auteur correspondant: eduarda.sangiogo-gil@universite-paris-saclay.fr

[‡]Auteur correspondant: federica.agostini@universite-paris-saclay.fr

A comparison of the shock properties of three polymer melts : a molecular dynamics study

Claire Lemarchand * [1,2]

[1] Direction des Applications Militaires – Commissariat à l'énergie atomique et aux énergies alternatives – France
[2] Laboratoire Matière sous Conditions Extrêmes – DAM Île-de-France, Université Paris-Saclay – France

Understanding the behavior of polymers under shock loading is essential for many of their industrial applications such as car equipment, sport gear, and plastic bonded expolsives. In this work, we use molecular dynamics to perform direct shock simulations in three polymer melts, polybutadiene, polystyrene and phenoxyresin. These polymers have different glass transition temperatures and different chemical structures, but all three of them are linear homopolymers exisitng in an amorphous glassy state. After assessing that the density, structural properties and Hugoniot locus of the three polymer melts compare satisfactorily to previous experimental and numerical data, we take advantage of the detailed description provided by the molecular dynamics simulations to compare their shock properties. In particular, the shear stress relaxation behind the shock front is studied in all three polymers. The distribution of the shock energy into kinetic, intermolecular and intramolecular potential energy is also calculated.

*Intervenant

Spectroscopic properties in Vibrational Strong Coupling in Disordered matter from Path - Integral simulations

Jaime De La Fuente Diez [*][†] [1], Riccardo Spezia[‡] [2], Rodolphe Vuilleumier[§] [3]

[1] École normale supérieure - Paris – Université Paris sciences et lettres – France
[2] CNRS – Centre National de la Recherche Scientifique – France
[3] Sorbonne Université – Sorbonne Universités, UPMC, CNRS – France

Vibrational Strong Coupling (VSC) is a phenomenon that occurs when one of the harmonics of an optical cavity is coupled resonantly to a vibrational transition of a molecular system, creating a pair of hybrid light-matter states. This can be clearly visualized in vibrational spectroscopy: what before coupling was a molecular transition, turns into a pair of peaks symmetrically displaced from the molecular transition (1). These peaks are called the polaritons. Also, there are states, known as the dark states, that remain inactive in IR, but are thought to have a key role in the phenomena that have been experimentally associated with VSC. Experimentally, it has been shown that VSC can not only affect the spectroscopy of molecular systems, but has an impact on the kinetics and thermodynamics of chemical processes. Studies by Ebbesen and coworkers have revealed that reaction rates can be modified by VSC (2, 3, 4), as well as thermodynamics (5).

In this context, the proposed oral communication will present a series of studies done on a simplified system, consisting of a set of 1-dimensional morse oscillators, parametrized to resemble a water-like OH stretching, and a harmonic mode that couples to all of them, which in turn represents a cavity mode that can be made resonant to the former. In this setup, Path-Integral Monte Carlo simulations can be performed, which provide the IR spectroscopy of the system, showing the appearance of the polariton states. Also, this setup allows access to the composition of the polaritons and dark states, allowing us to look into the set of both polaritonic and dark states, and analyze their constitution and degree of delocalization. A crucial part of this work is the discussion of the effect of frequency disorder, a distribution of frequencies in the matter modes, in this model, how it impacts the previously mentioned parameters, as well as the spectroscopy. Finally, the influence of different hamiltonians for the system, particularly the Pauli - Fierz and the Tavis Cummings hamiltonians has also been explored.

We find that, when anharmonic potentials are used to describe matter, quantum nuclear effects have to be taken into account to introduce the red shift of the mode frequencies with regard to its harmonic equivalents. With regard to the spectroscopy, our method correctly produces 2 bright modes, the polaritons, and a set of IR-inactive modes, the dark states. The polaritons are active because the cavity induces all the modes to oscillate in phase in them, while they are kept at random in the dark modes, which have no cavity contribution. The compositions of the polaritons are further analyzed, showing that the modes closest in frequency participate the most in them. Regarding delocalization, the polaritons are fully delocalized, as can be expected

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[*]Intervenant
[†]Auteur correspondant: fuentediezjaime@gmail.com
[‡]Auteur correspondant: riccardo.spezia@sorbonne-universite.fr
[§]Auteur correspondant: rodolphe.vuilleumier@ens.psl.eu

from hybrid light-matter states, while the dark states, while more localized, present a certain delocalization that persists within moderate disorder. This delocalization can be attributed to the participation of a few modes close in frequency to the eigenstate, and could be an important factor in energy redistribution inside the system.

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Physical properties of 2D multilayered perovskites and 2D/3D bilayers

Jacky Even* [1], Claudine Katan [†‡] [2]

[1] Institut des Fonctions Optiques pour les Technologies de l'informatiON – Institut National des Sciences Appliquées - Rennes, Centre National de la Recherche Scientifique – France

[2] Institut des Sciences Chimiques de Rennes (ISCR) – Universite de Rennes 1, CNRS : UMR6226 – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

2D multilayered metal halide perovskites share similarities with 3D perovskites including direct electronic band gap, sizeable optical absorption, small effective masses, Rashba-like effects (1). They exhibit other attractive features related to tunable quantum and dielectric confinements, strong lattice anisotropy, more complex combinations of atomic orbitals and lattice dynamics, extensive chemical engineering possibilities, including chiral cations (1,2). This will be illustrated by recent combined experimental and theoretical studies on excitons, formation of edge states, hot carrier effects and carrier localization (2-7). Moreover, combined in 2D/3D bilayer structures using new versatile growth methods, excellent solar cell device stability has been demonstrated (8). The difference of performances between n-i-p or p-i-n device architecture can be rationalized based on band alignment calculations (9,10). Noteworthy, the concept of lattice mismatch provides guidance for choosing the 2D and 3D materials to combine (1,11).

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*Auteur correspondant: jacky.even@insa-rennes.fr

†Intervenant

‡Auteur correspondant: claudine.katan@univ-rennes1.fr

Investigation of a germanium induced $\sqrt{109}$ x $\sqrt{109}$ reconstruction on Ag(111): germanene or not germanene ?

Marie-Christine Hanf * [1], Kai Zhang [2], Romain Bernard [2], Yves Borensztein [2], Hervé Cruguel [2], Andrea Resta [3], Yves Garreau [3], Alina Vlad [3], Alessandro Coati [3], Davide Sciacca [4], Bruno Grandidier [4], Mickael Derivaz [1], Carmelo Pirri [1], Philippe Sonnet [1], Régis Stephan [1], Geoffroy Prevot [2]

[1] IS2M – Université de Haute Alsace - Mulhouse, Université de Strasbourg, CNRS – France
[2] Institut des NanoSciences de Paris, INSP, F-75005 Paris – CNRS : UMRSorbonneUniversité – France
[3] Synchrotron SOLEIL, 91192 Gif-sur-Yvette – Syncrtotron Soleil – France
[4] Université Polytechnique Hauts-de-France, Junia-ISEN – CNRS Université Lille – France

Germanene, a Ge monolayer exhibiting a honeycomb lattice, has been the topic of numerous studies in the last years, since astonishing electronic properties are expected such as the presence of a Dirac cone or large carrier mobility. However, unlike graphene, germanene must be grown on a substrate, and the atomic structure of the obtained layer depends on the chosen substrate.

Here the Ge monolayer results of the evaporation of Ge in ultra-high vacuum onto a Ag(111) substrate kept at 445K. Scanning tunneling microsopy measurements indicate the presence of a $\sqrt{109}$ x $\sqrt{109}$ reconstruction with respect to the Ag(111) surface lattice, and surface X-ray diffraction (SXRD) measurements point to the formation of a germanium layer containing substitutional Ag atoms. Different configurations (varying the Ag/Ge fraction and the overlayer atomic density) have been tested by fitting simulated structure factors to the SXRD experimental ones, and by density functional theory (DFT) simulations. It appears that the best fit (according to SXRD) and the most stable model (resulting from DFT) correspond to a Ge-Ag layer with $Ge_{98}Ag_{6}$ composition. The local density of state image is in very good agreement with the scanning tunneling microscopy measurements. DFT calculations show that the Ge98Ag6 overlayer grown on pure Ag(111) is not characterized by a honeycomb lattice, but that the atoms are arranged in hexagons, pentagons and heptagons.

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*Intervenant

Exact Excited-State Functionals of the Asymmetric Hubbard Dimer

Sara Giarrusso *† 1,2, Pierre-Francois Loos * ‡ 2

1 Université Paris-Saclay, CNRS, Institut de Chimie Physique UMR8000, 91405, Orsay – CNRS, Univ. Paris-Sud, Université Paris-Saclay, C2N – Orsay, 91405 Orsay cedex, France – France
2 Laboratoire de Chimie et Physique Quantiques (UMR 5626), Université de Toulouse, CNRS, UPS, France – Université de Toulouse Paul Sabatier – France

The exact functionals associated with the (singlet) ground and the two singlet excited states of the asymmetric Hubbard dimer at half-filling are calculated using both Levy's constrained search and Lieb's convex formulation. While the ground-state functional is, as commonly known, a convex function with respect to the density (or, more precisely, the site occupation), the functional associated with the (highest) doubly-excited state is found to be concave. Also, we find that, because the density of the first excited state is non-invertible, its "functional" is a partial, multi-valued function composed of one concave and one convex branch that correspond to two separate domains of the external potential. Remarkably, it is found that, although the one-to-one mapping between density and external potential may not apply (as in the case of the first excited state), each state-specific energy and corresponding universal functional are "functions" whose derivatives are each other's inverse, just as in the ground state formalism.

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*Intervenant
†Auteur correspondant: sara.giarrusso@irsamc.ups-tlse.fr
‡Auteur correspondant: loos@irsamc.ups-tlse.fr

DFT calculation for heteroleptic silver-rich 8-electron superatoms

Hao Liang * [1]

[1] ISCR – Université de Rennes I – France

The heteroleptic silver-rich nanoclusters, $(Au@Au_4Ag_{12}(dtp)_7(PPh_3)_4)^{2+}$ (dtp = dithiophosphate; M17) and $(Pt@Au_4Ag_11(dtp)_7(PPh_3)_4)$(M16), were recently synthesized via a galvanic replacement reaction leading to an alteration of the cluster nuclearity and geometry. DFT calculations show that the two clusters are 8-electron superatoms(1-4) with 1S2 1P6 configuration. The metal framework of M17 contains an $(Au@(Au_4Ag_8))^{5+}$ centered icosahedron with four additional Ag+ peripheral atoms while that of M16 contains a $(Pt@(Au_4Ag_8))^{4+}$ centered icosahedron with three additional Ag^+ outer atoms. Calculations indicate that the outer additional silver atoms are locally stable (nearly) planar tricoordinated 16-electron Ag(I) centers, interacting only very weakly with the icosahedral metals. The two clusters shows large HOMO-LUMO gaps, consistent with their stability. The experimental absorption spectra are well-reproduced by TD-DFT calculations, where the low- energy bands at 441 nm (M17) and 420 and 543 nm (M16) correspond to 1P → 1D transitions. Our results contribute understanding how to stabilize new heteroleptic nanoclusters.

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*Intervenant

^{25}Mg and ^{67}Zn NMR study of Mg$_x$Zn$_{(1-x)}$O solid solutions: observing correlated disorder

Aël Cador [*] [1], Claire Roiland [1], Laurent Le Pollès[†] [1], Régis Gautier[‡] [1]

[1] Ecole Nationale Supérieure de Chimie de Rennes – ISCR UMR CNRS 6226 – France

Solid solutions of MgO and ZnO have attracted attention due to their potential applications in ultraviolet optoelectronic devices(1). A first characterization of these solutions by NMR spectroscopy has already been carried out by Cadars et al.(2) but showed synthesis problems and low sensibility. Here, we report recent characterizations by NMR spectroscopy which show that even at low substitution rates, the spectra change substantially from pure MgO or ZnO. While they show some degree of disorder, they do not correspond to the spectra obtained with the Szjzek model(3) which is characteristic of disordered, isotropic materials.

These experimental studies have been complemented by DFT calculations. Due to the large number of possible structures in such solutions, the structures have been sampled using the Supercell program(4), which can generate all possible structures for a given supercell size and stoichiometry, merge the symmetry-equivalent structures and perform a random sampling among them. The simulated spectra of samples of the larger supercells match with the experiment, and some structure-property relationships have been proposed.

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[*]Intervenant

[†]Auteur correspondant: laurent.le-polles@ensc-rennes.fr

[‡]Auteur correspondant: regis.gautier@ensc-rennes.fr

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

Emeline Boyer [* 1], Carine Clavaguéra [1], Lich Pham Ba [1], Audrey Gayral [1], Thomas Noblet [2], Laurent Dreesen [2], Christophe Humbert [1]

[1] Institut de Chimie Physique , Université Paris-Saclay, CNRS, Bâtiment 349, 15 avenue Jean Perrin, 91405 Orsay, France – Institut de Chimie du CNRS, Université Paris-Saclay, Centre National de la Recherche Scientifique – France
[2] 2GRASP-Biophotonics, CESAM, University of Liège, Institute of Physics, Allée du 6 Août, 4000 Liège, Belgium – Belgique

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 coreshell type QDs monolayers on glass surfaces to address the environmental problem and cost of nanosensors(1). 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(2), 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).

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[*]Intervenant

Dynamics of hydrogen interaction on tungsten surfaces

Laura Viaud [*][†] [1], Pascal Larregaray[‡] [1], Cédric Crespos[§] [1], Laurent Bonnet[¶]
[1]

[1] Institut des Sciences Moléculaires – Université Sciences et Technologies - Bordeaux 1, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France

Because of its fundamental role in natural and technological processes, surface reactivity has been intensively studied both experimentally and theoretically for decades. Currently, understanding the interaction of hydrogen with the surface of tungsten is a major challenge for nuclear fusion technologies (1). Therefore we studied the collision dynamics of hydrogen on tungsten via classical and quantum molecular dynamics approaches, using a multidimensional Potential Energy Surface (PES) interpolated from Density Functional Theory (DFT) energies based on the vdW-DF2 functional (2). In particular, we focus on the sticking probability, which has been previously measured experimentally (3). Preliminary results show a considerable improvement concerning the quantitative agreement between theory and experiment with respect to previous works (4) using the PW91 functional (5), pointing out the decisive role of the density functional on the sticking dynamics.

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[*]Intervenant
[†]Auteur correspondant: laura.viaud@u-bordeaux.fr
[‡]Auteur correspondant: pascal.larregaray@u-bordeaux.fr
[§]Auteur correspondant: cedric.crespos@u-bordeaux.fr
[¶]Auteur correspondant: laurent.bonnet@u-bordeaux.fr

Supramolecular auto-assembly of small peptides. Studies by molecular dynamics.

Tetiana Dorosh [*][†] [1], Rachel Schurhammer[‡] [1], Alain Chaumont[§] [1]

[1] Chimie de la matière complexe – université de Strasbourg, Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France

Spontaneous formation from individual components-molecules into an organised structure is called molecular self-assembly, usually based on molecules' local interactions of molecules1. Different driving forces and environmental details lead to various possible applications of auto-assembly, such as bioimaging2, drug delivery3,4, and protein delivery5. Understanding the molecular interactions during hydrogel formation will help predict their optimal use based on their properties and interactions with other materials.

In our project, MA-hR10(Fig.1) is a fully charged polyelectrolyte with oligopeptide sidechains exhibiting reversible UCST behaviour. In the experimental part, systems consisting of MA-hR10 and counterions TFA- went through a temperature cycle from 7°C to 20°C and back to 7°C with filtration to obtain approximately the same size of micelles. We simulated systems with different containments (10-20) of peptide and its derivative R10 - pure and impure systems at two temperatures (279.15 K and 333.15K in order to understand the behaviour of these systems better. At 279.15 K, the main interactions occur between (i) Gdm+ and Gdm+, Gdm+ and (ii) O- of TFA- (NH• • •O) and (iii) Gdm+ with COO-TERM (NH• • •O), which led to the formation of aggregate, dimers and trimers (Fig.2.a). With increasing temperature, the structure of these aggregates changed during the simulation and became more spheric for both pure and impure systems (i.e. with R10) (Fig.2.b).

These results indicate that these chemical systems respond to temperature changes via a modification of the aggregate structure.

Figure 1. Molecular structure representation of MA-hR10 peptide.

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[*]Intervenant

[†]Auteur correspondant: tetiana.dorosh@etu.unistra.fr

[‡]Auteur correspondant: rschurhammer@unistra.fr

[§]Auteur correspondant: chaumont@unistra.fr

UV-spectrum and photo-decomposition of peroxynitrous acid in the troposphere

Wiem Chebbi [*] [1]

[1] Groupe de spectrométrie moléculaire et atmosphérique – Université de Reims Champagne-Ardenne : UMR7331, Centre National de la Recherche Scientifique : UMR7331, Université de Reims Champagne-Ardenne, Centre National de la Recherche Scientifique – France

Crutzen (1) suggested that nitrogen oxides arriving in the stratosphere due to anthropogenic activities contribute to the catalytic conversion of ozone into dioxygen, thus damaging the stratospheric ozone layer. The nitrogen oxides can be removed partially from this cycle by recombination with the hydroxyl radical. Whereas the formation of nitric acid ($HO + NO_2 + M \rightarrow HONO_2 + M$) neutralises NO_2 and is indeed its predominant sink pathway in the troposphere, the alternative reaction leading to peroxynitrous acid ($HO + NO_2 + M \rightarrow HOONO$) is reversible and thus will not terminate the harmful catalytic reaction cycles. Peroxynitrous acid HOONO was first observed in an Argon matrix (2). It has not been seen in the gas phase at ambient pressure and temperature because of its short lifetime of a few seconds (3). HOONO disintegrates readily through thermolysis and photo-decomposition. The mechanisms are not well understood.

In this work, we investigate the photochemical decomposition and the non-adiabatic decay dynamics of the molecule. We have calculated the UV spectra for the two most stable conformers, namely the cis-cis and trans-perp conformers, using various theoretical methods. Our aim was to investigate the experimental UV spectrum (4) by identifying the observed signals and to calculate the photolysis rate constant based on the obtained cross-section data. Upon UV excitation, the molecule will break up to yield either $HO_2 + NO$ or $NO_2 + OH$. The corresponding photolysis rate constant was obtained in the present work for the first time. We show that under the conditions in the upper troposphere, photo-decomposition is faster than thermal decomposition by two orders of magnitude. This rate constant will be needed for atmospheric modelling.

The trajectory surface hopping (TSH) algorithm was used to describe the non-adiabatic decay processes of the photo-excited molecule. The calculations were carried out using the NEWTON-X package (5), which is interfaced with the MOLPRO and GAUSSIAN quantum chemistry programs.

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[*]Intervenant

ESIPT-capable zinc(II) complexes with 1-hydroxy-1H-imidazole-based ligands: molecular design and anomalous anti-Kasha emission

Nikita A. Shekhovtsov *[†] [1], Elena B. Nikolaenkova [2], Victor F. Plyusnin [3], Sofia N. Vorobyova [1], Alexey S. Berezin [1], Christophe Gourlaouen [4], Alexsei Ya. Tikhonov [2], Mark B. Bushuev[‡] [1]

[1] Nikolaev Institute of Inorganic Chemistry, Siberian Branch of Russian Academy of Sciences, 3, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia – Russie
[2] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Acad. Lavrentiev Ave., Novosibirsk, 630090, Russia – Russie
[3] Voevodsky Institute of Chemical Kinetics and Combustion, Siberian Branch of Russian Academy of Sciences, 3, Institutskaya str., Novosibirsk, 630090, Russia – Russie
[4] Laboratoire de Chimie Quantique, Institut de Chimie, UMR 7177 CNRS-Université de Strasbourg, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France – - – France

Compounds with strong intramolecular hydrogen bonds of the O–H⋯Y and N–H⋯Y types (Y = O, NR) tend to exhibit photoinduced proton transfer reactions. The excitation of such compounds in their most stable form leads to the electron density redistribution followed by the excited state intramolecular proton transfer (ESIPT) yielding the tautomeric form. The emission of ESIPT-fluorophores is known to be extremely sensitive to various external and internal stimuli and can be fine-tuned through substitution in the proton-donating and proton-accepting moieties. In addition, ESIPT-dyes may demonstrate rare and non-trivial photophysical properties such as excitation wavelength dependent emission, dual and multiple fluorescence. These features, coupled with high emission efficiency, make ESIPT-fluorophores an appealing platform for a plethora of practical applications, *e.g.* in the design of novel sensors and components for organic light-emitting diodes (OLEDs), in bioimaging and in analytical chemistry.

Although the molecules of ESIPT-emitters can bind metal ions (which is used for the detection of metals), this phenomenon is typically coupled with their deprotonation and the disappearance of ESIPT in metal complex molecules. Nevertheless, the purposeful design of specific sites for metal coordination paves the way toward metal ion binding without deprotonation. Compared to conventional and purely organic ESIPT-fluorophores, the study of ESIPT-capable metal complexes is an emerging area of research. To date, there are fewer than 20 references dealing with the synthesis and investigation of such complexes.

Herein we report a series of rationally designed 1-hydroxy-1*H*-imidazole-based ESIPT-dyes HLn. Due to the spatial separation of metal binding and ESIPT sites, these compounds can coordinate metal ions without being deprotonated. The reactions of ZnX2 (X = Cl, Br, I) with HLn afford ESIPT-capable (Zn(HLn)X2) complexes. Comparative experimental and theoretical studies showed that the coordination of metal ion significantly alters the photophysical and photochemical properties of the studied compounds. According to TDDFT calculations, the complexes

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*Intervenant
[†]Auteur correspondant: nikita.shekhovtsov.niic@gmail.com
[‡]Auteur correspondant: bushuev@niic.nsc.ru

(Zn(HLn)X2) demonstrate Kasha-like S1 → S0 fluorescence with the Stokes shift of 100 nm, whereas the ligands HLn exhibit anomalous anti-Kasha S2 → S0 fluorescence with extraordinarily small Stokes shifts of 50 nm. Such non-trivial emission behavior of HLn is attributed to (i) the dark nature of the S1 state and the bright nature of the S2 state, (ii) the large S1–S2 energy gap, which slows down the rate of S2 → S1 internal conversion, in accordance with the energy gap law, (iii) the efficient non-radiative deactivation of the S1 state via an energetically achievable S0/S1 conical intersection. The findings from this study contribute to the development of fine-tuning principles of the luminescence of both purely organic ESIPT-emitters and ESIPT-capable metal complexes.

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UNDERSTANDING THE MANY-BODY ELECTRONIC STRUCTURE THE NITROGEN-VACANCY CENTER IN DIAMOND

Alan Custodio Dos Reis Souza * [1], Mariya Romanova [2], Michele Casula [3], Jelena Sjakste [1], Nathalie Vast [1]

[1] École Polytechnique – CNRS UMR 7642, CEA-DRF-IRAMIS, LSI – France
[2] CEA – DES, IRESNE, DEC, Cadarache, Saint-Paul-Lez-Durance – France
[3] Sorbonne Université – CNRS, MNHN, IRD – France

Understanding the electronic structure and exited states of the negatively charged nitrogen vacancy center (NV-) in diamond is of fundamental interest for the fast advance of its quantum technological applications, spamming from qubits to superconductivity sensing. The nature of the ground (3A2 triplet) state and of photoluminescence signals were first identified using optically detected magnetic resonance, showing one visible emission at 1.94 eV and one singlet-singlet infrared transition at 1.19 eV. However, the symmetry character and the position of the singlet states with respect to the ground state are unknown experimentally and still under debate. In the present work, we combine from-first-principle generalized DFT calculations in combination with an in-house extended Hubbard model to describe the defect many-body energy states. Using the HSE06 exchange-correlation potential, we performed density functional theory calculations of the ground state and of some excited states total energies with the ΔSCF method, which we used as input data to fit our extended Hubbard model. We find that the explicit inclusion of the Hund interaction in the Hamiltonian is necessary to properly describe the correlated singlet-singlet transitions, while the triplet states are properly described by the DFT-HSE06. Moreover, we discuss the link between the Hund interaction term and the spin-spin interaction term in this correlated system. Our results show the significance of electronic correlations in the description of the optical and non-radiative excitations of the NV- center in diamond, a crucial outcome for developing the use of solid-state spin defects in technological quantum applications.

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*Intervenant

Modeling of bimetallic nanoparticles synthesized through radiolysis with theoretical chemistry and automated learning.

Raphaël Vangheluwe * [1], Carine Clavaguéra [1], Van-Oanh Nguyen-Thi [1], Dominik Domin [1]

[1] Institut de Chimie Physique – Institut de Chimie du CNRS, Université Paris-Saclay, Centre National de la Recherche Scientifique – France

High proton metal nanoparticles (NP) see a lot of developments and interests as radiosensitizers for radiotherapy. A new bimetallic Bi:Pt NP (d ≈ 5nm) coated in PEG-based ligands was developed at ISMO, Paris Saclay using radiolysis. But what effects does the synthesis method have on the organization and surface of the NP, and how is the latter going to interact with its environment? In addition, we investigated the possibility of adapting a small-scale, low-cost machine learning tool to fill in the gap by the lack of force field parameters for molecular dynamics. We investigated the structure of the bimetallic core using semi-empirical methods and molecular DFT on a selection of core-shell and alloy initial structures (d ≤ 1nm). We also added PEG ligands around the optimized core to observe their interactions with the latter.

The ChIMES model (Chebyshev interaction model for efficient simulation) can design machine-learned force fields for the system to run in molecular dynamics and has been used in simulations for molten carbon (1) and ambient water (2) We used the data generated by all these DFT calculations to train the ChIMES machine-learned force fields and to bridge the gap between the empirical size of the NPs and the models used.

We thus observed the explosion of core-shell structures and the relative stability of the alloy. We confirmed that the ligands are attached to the Pt atoms present on the surface. We designed three different data training sets for the machine learning procedure, each providing us with a better understanding of the tool, and leading us to obtain confident preliminary results as to the applicability of ChIMES to this metallic system.

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*Intervenant

Energy Redistribution upon Hydrogen Atom Scattering off Hydrogen-Covered W(100) Surfaces

Raidel Martin Barrios *† [1], Oihana Galparsoro [2], Aliezer Martinez-Mesa [3],
Llinersy Uranga-Piña [3], Cédric Crespos [1], Pascal Larregaray [1]

[1] Institut des Sciences Moléculaires – Université Montesquieu - Bordeaux 4, Université Sciences et Technologies - Bordeaux 1, École Nationale Supérieure de Chimie et de Physique de Bordeaux (ENSCPB), Institut de Chimie du CNRS, Centre National de la Recherche Scientifique – France
[2] Donostia International Physics Center – Espagne
[3] Dynamical processes in Atomic and Molecular Systems (DynAMoS), Faculty of Physics, University of Havana, Havana 10400, Cuba. – Cuba

Recent experiments have shown that translational energy loss is mainly mediated by electron–hole pair excitations, for hydrogen atoms impinging on clean metallic surfaces (1). Inspired by these studies, quasi-classical trajectory simulations are performed to investigate the energy transfer after scattering of hydrogen atoms off clean and hydrogen-covered tungsten (100) surfaces. The present theoretical approach examines the coverage effect of the preadsorbed hydrogen atoms, as was done for the case of the tungsten (110) surface (2). Dispersion can be rationalized in terms of three different dynamical mechanisms, the contribution of which changes with coating. These allow, in particular, to understand why the shape of the energy loss spectra depends critically on whether the scattering is analyzed in the whole space or at a specular angle.

Figure 1: *Position of adsorbed H atoms (red points) on W(100) at* Θ= 1 ML (left) and Θ= 2 ML (right). *Blue circles show the position of the second layer tungsten atoms.*

Figure 1: *Energy loss spectra for scattered atoms at specular angle, at* Θ= 0 ML (blue), Θ= 1 ML (orange) *and* Θ= 2 ML (green). The distribution is normalized to the total number of trajectories. The black dots represent the average energy loss for each case.

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*Intervenant
†Auteur correspondant: raidel.martin-barrios@u-bordeaux.fr

Red-emitting tetraphenylethylene derivative with aggregation-induced enhanced emission for luminescent solar concentrators: A combined experimental and density functional theory study

Qinfang Wang [*][†] [1], A. Ottochian [1], Ilaria Ciofini [1], Carlo Adamo [1], A. Pucci [2]

[1] École nationale supérieure de chimie de Paris, Centre national de la recherche scientifique, Institute of Chemistry for Life and Health Sciences, PSL Research University, Paris, France – PSL Research University – France
[2] Department of Chemistry and Industrial Chemistry, University of Pisa, Pisa, Italy 3 Institut Universitaire de France, Paris, France – Italie

Relying on the molecular dynamics (MD) and the time-dependent density functional theory (TD-DFT), this research is to firstly, build a dye-polymer blend system; secondly, model the mechanical process on the polymer matrix; finally, study the electron properties or optical properties, especially the fluorescence behaviour of the central dyes. Thanks to the embedded system, the physical mechanical reaction on the polymer matrix can be conducted to the central dyes. In the last step, we extract the dyes from the snapshots in the last 100ps to do the TD-DFT calculations. What's more, for the crystalline configurations, one central dimer is considered as the key region and the neighbour molecules are considered as the charge region in background charge calculations to avoid an extremely long calculation of the crystalline structures. In this work, a new methodology is presented to explain the mechanochromic process. Two embedded AIEgens who experience the mechanochromism, which indicates that during the mechanochromic process, the rotational and flapping groups in TPE-MRh and TPE-BPAN make the dimers experience a complex movement, including shearing, bending approaching and disassembling, which may both affect the intermolecular and intramolecular interaction. Compared with compression deformation, the tension deformation can result in a higher MSD. The absorption spectrums and exciton binding energies of TPE-MRh dimer show that the presence of force can hinder the intermolecular CT during the excitation. While for TPE-BPAN dimer, the CT during excitation can be supressed (enhanced) by compression (tension) force. The TPE-BPAN dimer can be disassembled by tension force.

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[*]Intervenant
[†]Auteur correspondant:

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