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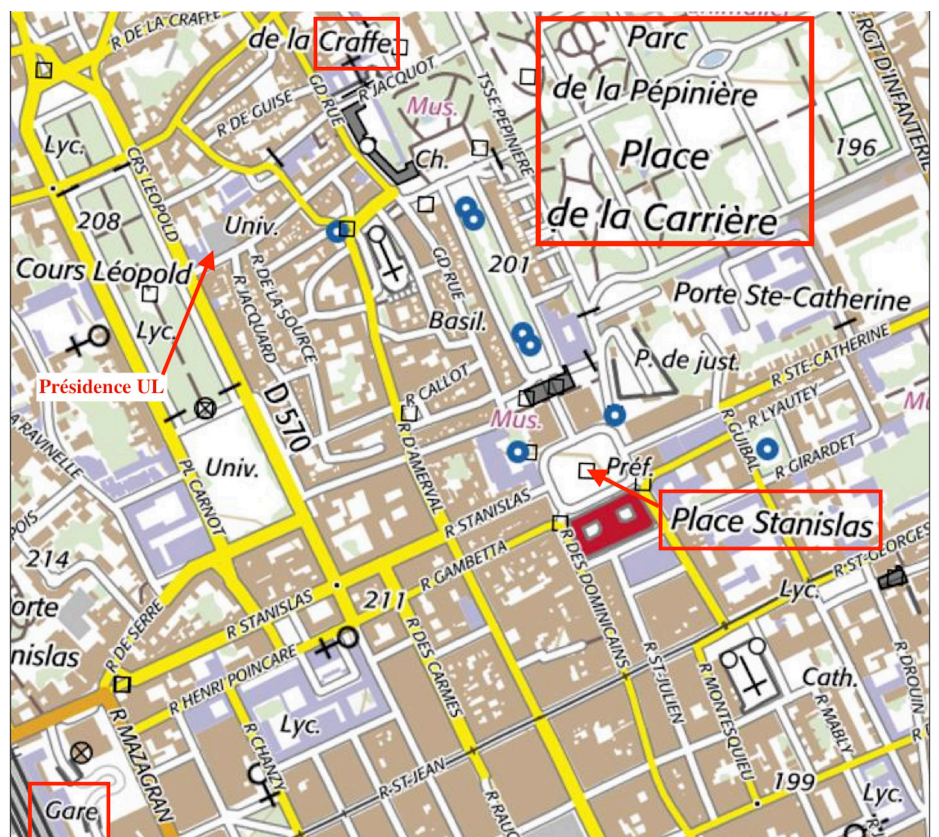
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Invited lectures

Chemical Catalysis and Motion. Role of the Environment

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Conformational motions and chemical reactions are intrinsically coupled in biological catalysis. On one side, loop motions are often needed to bind of the substrate in the active site, to release the product and or to bring together reaction fragments in many enzymes. On the other side, ATP hydrolysis is often used as a source of chemical energy to fuel directed motions in biomolecular machines through conformational changes in the biocatalysts. Here we will first present a computational study of the mechanism for the opening/closing conformational change of the WPD-loop in two Tyrosine Phosphatases, PTP1B and YopH We use our Adaptive String Method to obtain the Minimum Free Energy Paths associated to these loop conformational changes in a space spanned by a selection of few torsions and distances. According to our findings the loop transition between the closed and open conformations can be described as a combination of a diffusive displacement over a flat free energy landscape and a torsional rearrangement that requires the crossing of a free energy barrier mostly associated to a single peptide bond. This picture can be useful to rationalize loop motions in enzymes. We will then explore ATP hydrolysis in a biomolecular motor, the NS3 Zika helicase, an enzyme with two active sites to carry out ATPase activity and the translocation motion along a nucleic acid strand. We will show how the conformational change of a conserved loop placed in between the two active sites is sensitive to the chemical reaction and then provide the link between reactivity and motion in this biological motor. This description about loop conformational changes can be extended to other enzymatic systems and biomolecular machines and can be useful to rationalize the behavior of loops in enzymatic reactions.

Hydrogen-Bond Asymmetry of Water: Anti-Correlated Hydrogen-Bonds of D₂O evidenced by 2D-IR spectroscopy

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Liquid water is traditionally viewed to form a distorted tetrahedral hydrogen-bond (H-bond) network. Yet, this rather symmetric structure has been challenged by x-ray [1] and computer simulation [2] studies. These studies have revealed a highly asymmetric H-bond geometry resulting in chain- or ring-like configurations, relevant to understanding the various anomalies of water [2]. Here, we characterize the inherent H-bond structure of water by studying water diluted in dimethylformamide with two-dimensional infrared (2D-IR) spectroscopy. We characterize the distribution of local H-bonds via coupling and broadening of the OD stretching vibrations of HOD and D₂O. Experiments on the coupled OD stretch oscillators of D₂O – the asymmetric and symmetric vibrational modes – reveal a markedly narrower inhomogeneous linewidth for the coupled modes as compared to the uncoupled vibration of HOD. Frequency maps obtained from density functional theory calculations show that these differing linewidths can be explained by anti-correlated H-bond strengths of water. This anti-correlation is confirmed by the cross-peaks in the 2D-IR spectra, yet, our results indicate that this anti-correlation is rather short-lived (~200 fs) and a mere result of the H-bond potential energy landscape. In fact, experiments on urea dissolved in dimethylsulfoxide provide evidence for a similar asymmetry of urea's N-H H-bonds. As such, our results suggest that asymmetric H-bonding is an inherent feature of XH₂ groups (X=N,O), but the structural consequences are rapidly smeared out at ambient conditions.

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Molecular level characterization of multiphase processes relevant to the atmosphere

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Aerosols and clouds are known to play important roles in the atmosphere regulation, but the scientific understanding of the associated processes is incomplete, leading to major uncertainties in climate predictions. An important contributor to the poor understanding is a lack of molecular level descriptions of heterogeneous chemical reactions and physical transformations that occur in the atmosphere's complex multiphase environment.

Significant progress has been achieved in the past decades, showing the importance of the atomistic approach to fully understand the catalytic processes in this chemically rich environment. One of the major challenges for modeling these aspects at the molecular level is being able to describe precisely both the reaction mechanism and the explicit environment. A second difficulty is to establish a direct comparison with experimental data in particular due to timescales and size discrepancies. This talk will show different applications based on nanoscale molecular simulations (Classical Molecular Dynamics, full Quantum and QM/MM approaches). Comparisons with experiments will be also addressed.

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Oral communications

Dielectric response of interfacial or confined water

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We study the dielectric response of highly polar liquids such as water at an interface or in confinement between two walls using a classical density functional theory approach. In the longitudinal polarisation case where a perturbing field is applied perpendicularly to the walls, we show that the notion of local dielectric constant, although ill-defined at a microscopic level, makes sense when a coarse-graining over the typical size of a particle is introduced. The approach makes it possible to study the effective dielectric response of thin liquid films of various thicknesses in connection to recent experiments. We argue that the observed properties as function of slab dimension, in particular the very low dielectric constants of the order of 2-3 measured for thin slabs of ~ 1 nm thickness do not highlight any special property of water but can be recovered for a generic polar solvent having similar particle size and the same high dielectric constant. We discuss the notion the interfacial dielectric constant at a proper molecular level.

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How the acidity of aqueous droplets and films is controlled by the air-water interface

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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 experiments [3,4] have reported a mapping of acidity within droplets, but the results remain contrasted and a molecular understanding of the interface’s 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 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 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. We will show why, unexpectedly, small water droplets are basic even though the interface stabilises hydronium cations. We have extended this model to describe how general acid-base equilibria are modified in these closed interfacial systems and discuss some examples of atmospheric and general interest.

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Topological graphs and algorithmic graph theory in molecular dynamics simulations

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Algorithmic graph theory, a branch of AI, is powerful for the analysis of structures and their conformational dynamics in molecular dynamics simulations. In particular, a 2D-graph encodes topological properties of matter through vertices and edges that report on the specific (pairwise) interactions between the vertices. At the molecular level of representation, the vertices are usually associated to atoms while the edges report on the interactions between the atoms, e.g. chemical bonds and intermolecular interactions. Modelling the interactions between the atoms of a molecule by a 2D-graph is nowadays well established, examples include the classification of similar molecules according to their topology, the prediction of patterns in biological molecules, the prediction of the 3D structure of small molecules, etc. Molecular graphs are also commonly used in supervised machine learning algorithms, especially for neural network schemes. In this presentation, we will review the methods based on graph theory that our group has developed in recent years. We will focus on the 2D-MolGraphs developed for interpreting and post-processing molecular dynamics (MD) trajectories generated at the atomistic level of representation. I will show how these graphs provide a direct and fast methodology for the identification of 3D-structures over time, with an easy identification through graphs of transitions of the interconversions between the conformations. We will present the versatility and transferability of our topological 2D- MolGraphs with applications that range from gas phase molecules to condensed matter, typically for inhomogeneous aqueous solid interfaces. We will also show our current development of a coarse grained topological 2D graph based on H-bonded rings/cycles and their polymorphism for biological molecules. Also, applications of these graphs to chemical reactivity will be shown. We will be presenting some of the other challenges that we have started to tackle with the help of graphs. This is a collaborative work with Dr Sana Bougueroua (Research Engineer, Université Paris-Saclay, Univ Evry), Prof Dominique Barth (Université Paris-Saclay, Univ Versailles), PhD Ylène Aboufath (Université Paris-Saclay, Univ Versailles).

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Liquid-liquid Extraction of Strontium(II) by a Crown Ether: the effects of Acidity and Concentration on Interface Crossing investigated by PMF Simulations.

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We report molecular dynamics and potential of mean force "PMF" calculations of the free energy profiles for transferring the [Sr⊂ DC18C6, (NO₃)₂] complex from water to "oil" (chloroform). In particular we analyze the effects of acidity and concentration on the partitioning and interfacial behavior of the [Sr⊂ DC18C6,(NO₃)₂] complex, comparing different systems, where the water phase is either "pH neutral" or acidic (5M nitric acid), and where the solute is either "diluted" (1 complex per box) or more "concentrated" (from 5 to 27 complexes per box). In all cases, complexes are found to adsorb at the water / oil interface, but the free energy of transfer ΔG_t (wat → oil) from "bulk" water to "bulk" oil is markedly pH and concentration dependent. As the water phase gets acidified, at the different concentrations, ΔG_t (wat → oil) changes from positive values (4.1 to 2.8 kcal/mol) to negative values (-1.6 to -3.1 kcal/mol), following experimental observations. Nitric acid HNO₃ thus promotes strontium extraction by solvating the nitrate ligands of the complexes in the organic phase. By definition, surface activity implies accumulation at the interface and this feature is shown to promote extraction: increasing the concentration decreases ΔG_t (itf → oil), by ca. 2 kcal/mol for both pH neutral system and acidic systems. These features are crucial for understanding the assisted ion transfer process at the nanoscopic level and reconcile the apparent conflict between computational predictions that the complexed cation is "trapped at the interface", and the observed extraction from acidic water solutions.

Second harmonic scattering of highly concentrated electrolyte: measurement of the screening length.

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Recently, a new optical type of measurement has shown promising results for water/electrolytes organization [1-2]. The technique is based on the nonlinear optical process of second harmonic scattering (SHS), a nonlinear optical phenomenon involving the conversion of two photons at the fundamental frequency ω into one photon at the harmonic frequency 2ω . In water, this incoherent second order process is due to orientational fluctuations of the non-centrosymmetric H₂O molecules. However, when molecules are correlated in orientation, the scattered photons emitted by each individual molecule interfere and the scattering pattern is modified. Though tiny, this modification can be detected and attributed to orientational correlations and can be connected to rotational invariant of the g-orientational pair correlation function derived with integral equation. With this method, we explore the water organization in the highly concentrated regime of LiCl and NaCl solution. First, we show that the water organization reports the salt correlation function. Then, the SHS intensity, resolved in polarization, allows us to measure the screening length (or Debye Length) in the highly concentrated regime. We show that the decrease of the screening length depends on the inverse of the Debye length to the power one, instead of the power three, known as the “underscreening” regime. So, we show that SHS could be a powerful technique, fully optical, to investigate correlation length in bulky systems.

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Simulating divalent ions-rich systems: challenges and hopes

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Ca²⁺ and Mg²⁺ cations play a central role in a number of fundamental biological processes, from calcium signaling to Mg²⁺-dependent activity of ribozymes. Molecular level understanding of these key processes requires to characterize the interaction between biomolecules and divalent cations, which is both an experimental and computational challenge. Indeed, only limited reference experimental data are available, and standard biomolecular simulations with divalent cations using non-polarizable force fields suffer from severe overbinding artifacts, in addition to challenging sampling problems.

We develop a scaled charge description [1,2] of ions and charged biomolecular groups, which takes into account electronic polarization in a mean-field way. This approach is demonstrated on small model systems [3], where simulation results can be directly compared to experimental data and to explicitly polarizable force fields. We show that it successfully improves ion-binding properties to typical biomolecular groups, and present our current efforts to extend it to polyphosphate species (e.g. ATP) and DNA/RNA. This method thus opens the way to large-scale, accurate, and computationally cheap simulations of divalent cation containing (bio)systems.

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On analytical theories for conductivity and self-diffusion in concentrated electrolytes

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Describing analytically the transport properties of electrolytes, such as their conductivity or the self-diffusion of the ions, has been a central challenge of chemical physics for almost a century. In recent years, this question has regained some interest in light of Stochastic Density Field Theory (SDFT) -- an analytical framework that allows the approximate determination of density correlations in fluctuating systems. In spite of the success of this theory to describe dilute electrolytes, its extension to concentrated solutions raises a number of technical difficulties, and requires simplified descriptions of the short-range repulsion between the ions. In this article, we discuss recent approximations that were proposed to compute the conductivity of electrolytes, in particular truncations of Coulomb interactions at short distances. We extend them to another observable (the self-diffusion coefficient of the ions) and compare them to earlier analytical approaches, such as the mean spherical approximation and mode-coupling theory. We show how the treatment of hydrodynamic effects in SDFT can be improved, that the choice of the modified Coulomb interactions significantly affects the determination of the properties of the electrolytes, and that comparison with other theories provides a guide to extend SDFT approaches in this context.

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Electrochemistry at the interface formed between two immiscible aqueous electrolyte solutions

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Electrochemistry at the interface between two immiscible electrolyte solutions (ITIES) allows the investigation of ion transfer processes from one liquid phase to another. The distribution of ions on either side of such an electrified interface will depend on the applied potential difference, the ion hydrophilicity / lipophilicity and its charge. Since the 1970s, various biphasic systems have been studied: aqueous | oil,[1] aqueous | ionic liquid,[2] and oil | ionic liquid.[3] However, the interfacial electrochemistry of aqueous biphasic systems (ABS) remains yet to be undertaken. ABS can be obtained by mixing a pair of solutes (e.g. polymer–polymer, polymer–salt or salt–salt) which, under carefully selected conditions like concentration or temperature, can form two immiscible aqueous phases, each of them rich in one of the solutes.[4]

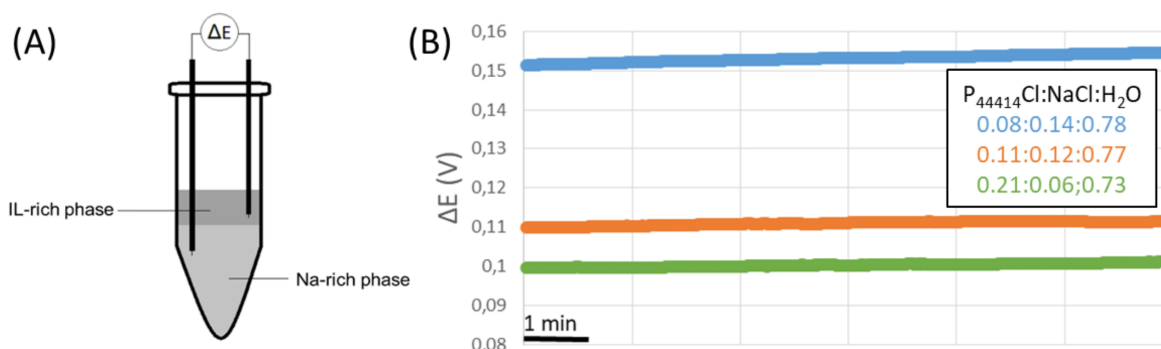


Fig 1: (A) Schematic representation of the experimental set-up; (B) Interfacial open circuit potential of aqueous biphasic systems for various initial relative mass composition of the ternary system P₄₄₄₁₄Cl: NaCl:H₂O.

After a brief introduction of the fundamental and practical aspects of electrochemistry at the ITIES, we will report the study of the ABS based on tributyl(tetradecyl)phosphonium chloride (P_{4,4,4,14}Cl) and NaCl using interfacial electrochemical techniques. At first, we investigated the interfacial behavior of cation as $P_{4,4,4,14}^+$ at the aqueous | oil interface by cyclic voltammetry. Open circuit potential at the interface formed between two immiscible aqueous electrolyte solutions will be measured for various initial chemical composition (Figure 1). These preliminary experiments aim at establishing a correlation between the potential values measured and the chemical composition of the ABS.

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Kinetic and mechanistic study of the reactions of NO₃ radical with two unsaturated aldehydes: 2- and 3-methyl-2-butenals

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Rate constants for the gas-phase reactions of NO₃ radical with a series of branched and linear unsaturated aldehydes, 2-butenal (also called crotonaldehyde), 2-methyl-2-butenal (or 2-methyl-crotonaldehyde) and 3-methyl-2-butenal (or 3-methyl-crotonaldehyde), have been determined by experimental and theoretical studies. Experiments were performed in simulation chamber at 295 ± 3 K and atmospheric pressure. Rate constants were determined using both absolute and relative rate methods. Experimental results were found to be in good agreement leading to the following rate constants (in cm³ molecule⁻¹ s⁻¹): k(2-butenal+NO₃) = (4.6 ± 1.3) × 10⁻¹⁵; k(2-methyl-2-butenal+NO₃) = (14.0 ± 2.8) × 10⁻¹⁵; k(3-methyl-2-butenal+NO₃) = (19.1 ± 4.1) × 10⁻¹⁵. Theoretical calculations were also performed using the DFT-BH&HLYP/6-311++G(d,p) method and lead to rate constants in agreement with experiments and allow to explore mechanisms for abstraction and addition pathways. This work has been recently published on November 9, 2022 (see Ref.¹).

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Determination of Total Vapor Pressure and Surface Tension of Deep Eutectic Solvents (DESS) and Conventional Green Solvents

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Biogas is a very interesting source of renewable energy. In addition to the main compounds, CH₄ (35–75%) and CO₂ (25–60%), biogas also contains many impurities, including numerous volatile organic compounds (VOCs). The upgrading of biogas to biomethane requires the removal of these impurities. Physical absorption is considered to be an appropriate method that meets the standard of green technology and engineering. Absorbents perform a crucial function by removing impurities from the biogas, but most current absorbents are often toxic and non-biodegradable. Deep eutectic solvents (DESS) are presented as a promising solution to the challenges of VOCs absorption and biogas upgrading [1–3]. DESS are liquid mixtures of two or more environmentally friendly, readily available compounds with tunable and attractive properties (*i.e.*, they are tunable, non-toxic and biodegradable). In addition, they are assumed to be non-volatile [4]. However, there is a lack of research studies on this topic in the literature. Therefore, the aim of this study is to report the first total vapor pressure measurements of several classes of DESS (*i.e.*, hydrophobic and cyclodextrin-based DESS) as well as conventional green solvents (propylene glycol, glycerol) [5]. Isothermal vapor-liquid equilibria of DES/VOC mixtures were also investigated. Finally, the surface tension and contact angle of the solvents on different material surfaces were determined. Taken together, these results will help to understand the obtained vapor-liquid partition coefficients and to select the most suitable DES for biogas upgrading. They will also be useful to optimize the absorber design process.

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Solvent influence on the *ortho*-metallation of *s*-tetrazine

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Among aromatic heterocycles, *s*-aryltetrazines are molecular motifs incorporating four nitrogen atoms found in various application areas such as photochemistry, energetic materials, and even in the medical field.[1] However, their synthesis methods still rely primarily on those developed by Pinner or Stollé, which have significant limitations in terms of functional group tolerance and low yields for highly functionalized tetrazines, despite the advances of numerous research teams.[2]

Recently, we have developed an innovative approach based on the catalytic use of transition metals for the activation and functionalization of C-H bonds in the *ortho* position of the tetrazine core.[3],[4] The key step of this strategy is the formation of an *ortho*-metallated intermediate that allows the introduction of the new functionalization at the end of the catalytic cycle (Figure 1). To better understand the formation of the key intermediate and gain a detailed understanding of this step for various transition metals, we have combined an experimental and a theoretical study.

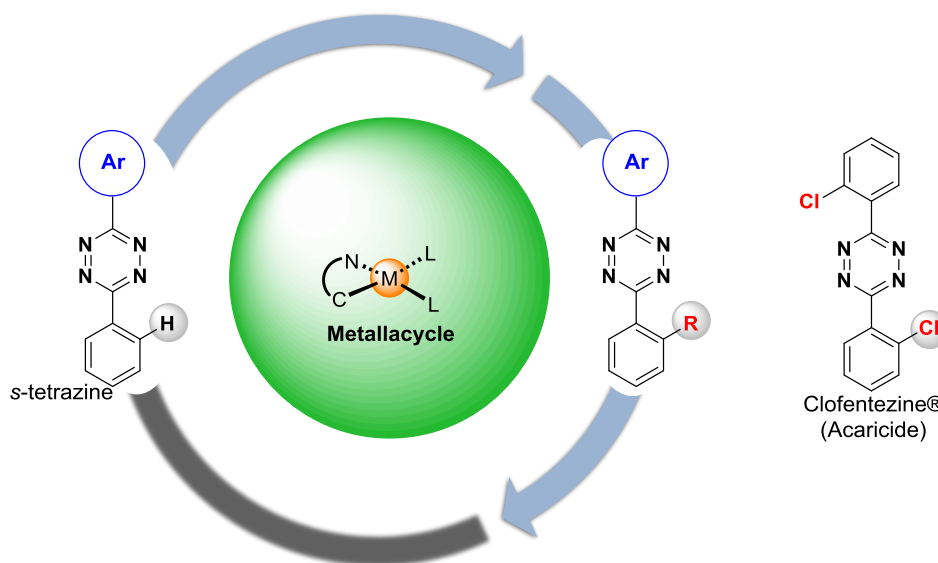


Figure 1 : Catalyzed Functionalization of *s*-Aryltetrazines through the Formation of an *Ortho*-Metallacycle.

Based on the various experimental results obtained during the synthesis of various complexes (experimental conditions, X-ray structures, as well as kinetic data), we will present the influence of different parameters such as the nature of the metal, the solvent or the nature of the aromatic moiety.

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Molecular dynamics investigation of the influence of surfactants with differently charged headgroups on the surface propensity of bromide

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In the atmospheric environment, both organic and inorganic compounds are present and have a strong influence on the chemical composition of the troposphere. Enriched with surface-active organic compounds, ocean surface water and sea mist spray play a crucial role in modulating halide ion distribution at air/liquid interfaces [1,2]. For instance, the abundance of bromide (Br⁻) ions at the interface is implicated in halogen activation processes relevant for the ozone budget in the troposphere [3]. In this context, we evaluate the surface affinity of cationic hexylammonium, neutral hexylamine, and anionic propylsulfate at the air/liquid interface, and the effect of these ionic surfactants on the abundance of bromide at interfaces. Inspired by liquid jet X-ray Photoelectron Spectroscopy (XPS) experiments, we conducted Molecular Dynamics (MD) simulations and we were able to speculate about the distribution of these species between bulk and surface area in aqueous systems. Here, the results are in good agreement with the experimental ones, which clearly advocate that those organic molecules dislike the bulk and prefer to reside near the free surface; indicating the effect of salting out. In contrast, both solutions containing hexylammonium and hexylamine show an enhancement of the surfactant bromide concentration while the propylsulfate solution do not alter the bromide concentration. In parallel, these trends persist even in the presence of NaCl. These results demonstrate that molecular level properties bring valuable insights on the interfacial behavior of organic and inorganic species on water films, that can be transposed to aerosol particles.

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Exploring the Interactive Mechanisms of Bioglasses through an Advanced Multiscale Technique during the Initial Immersion Stages

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In the course of the last years, mesoporous bioactive glasses (MBGs) are increasingly used in the medical field, particularly for bone reparation and regeneration due to their biocompatibility and unique bioactive properties. Their bioactive properties are often determined by their ability to form and develop a bone-like apatite layer consisting of crystalline carbonate hydroxyapatite (HCA) on their surface when exposed to bodily fluids [1-2]. We present a comparative study of the bioactive properties of two MBGs: 58S (60% SiO₂, 36% CaO, 4% P₂O₅ (mol. %)) and 70S30C (70% SiO₂, 30% CaO (mol. %)) prepared by optimized sol-gel method [3]. For the study of their interactive mechanisms, we used two different physiological media, namely c-SBF (*classic Simulated Body Fluid*) and m-SBF (*modified Simulated Body Fluid*) with various interaction times. X-ray total scattering coupled with Pair Distribution Function (PDF) analysis, complemented by Raman spectroscopy and scanning electron microscopy, were used to monitor the formation and development of distinct species that form on the surface of bioglasses from the first hours of immersion in SBFs. The obtained results indicate the presence of different interaction mechanism between MBGs and physiological fluids, leading to the formation of additional phases like amorphous calcium phosphate and calcite, which evolve and can transform to HCA, depending on the soaking time, the MBG composition, as well as on the type of SBF.

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Self-assembling of biomolecules For the development of emergent biomaterials

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Nanostructures based on the self-assembly of biological molecules have interesting physicochemical properties, which can be exploited to develop new materials. Different strategies are developed to induce the formation of ordered architectures and control their structure and morphology [1]. In this context, globular proteins, lipids and short peptides raise much interest due to their capability to form versatile supramolecular architectures [2,3]. Here we present as a first topic a multi-length scale spectroscopic study of lysozyme self-assembly. The present work unifies molecular scale information from FTIR with the structural information in the nanoscale obtained by SAXS [4,5]. Molecular interactions influence the size and the morphology of the formed aggregates, and the macroscopic viscoelastic properties. The latter information is obtained by Transient Grating spectroscopy [6]. A strong relation between the macroscopic, mesoscopic, and molecular properties of lysozyme self-assembly have revealed. This information can improve the preparation of protein-based hydrogel. The second biologic system is monolinolein lipid that mixed with water can self- assemble leading to the formation of lipidic mesophases. Here we focus on the structural and molecular characterization of the system during the phase transitions from double gyroid (Ia3d) to double diamond (Pn3m) cubic phases and from the latter to the reverse hexagonal (HII) phase by combining FTIR and SAXS [7]. Our results suggest that a larger fraction of water is hydrogen-bonded to the headgroup of lipids in the HII phase at higher temperature than in the cubic phase at lower temperature via H-bonds [7]. These lipidic mesophases can continue to exist even with excess of water revealing their great potentiality to be used as a drug delivery system. The third studied system is the short peptide diphenylalanine (FF), that is one of the most suitable building blocks, due to its ability to form extended ordered architectures with a wide morphological differentiation [8,9]. Here we investigate how FF self-assembly properties can be modulated acting on the interaction between the aromatic sides and their microenvironment through the acetonitrile/water ratio. Our measurements revealed a hierarchical aggregation where morphologies can be tuned by changing the AcN content. The strong morphological tunability of this system makes it interesting for the development of new generation photovoltaic cells.

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Posters

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

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Quantum dots (QD) constitute a novel generation of fluorescent probes due to their confined size in the 1-10 nm range. In this field, nanosensors sensitivity is of pivotal importance to target biomolecules. We focus here on the optimize grafting of organic ligand-coated CdTe and CdSe/ZnS core-shell type QDs monolayers on glass surfaces to address the environmental problem and cost of nanosensors.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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Porous hydrogels for metal ions scavenging from wastewater

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Hydrogels are soft materials formed by polymeric networks that can absorb significant amounts of water while remaining insoluble in water due to chemical or physical cross-linking. Over the past few decades, hydrogels have become a subject of growing research interest because of their unique properties, including their ability to swell, flexibility, biocompatibility, and non-toxicity. [1,2] The application of these hydrophilic structures for wastewater treatment is a relatively new development, prompted by the alarming rise of toxic pollutants like heavy metals in the environment. Chemical precipitation, ion exchange resins, and filtration techniques have been used in the past few years for water remediation, however their costs in terms of production, disposal, and environmental impact are still too high. Adsorption has proven to be an alternative for water treatment due to its effectiveness and low economical impact. In this study we investigate the properties of adsorption efficiency and selectivity of two different kind of hydrogels in the recovery heavy metal ions from aqueous solution. The tests have been carried out by treating mixed noble metal ion solutions (containing gold, ruthenium, iridium, palladium, platinum and rhodium with concentrations of 10 ppm each), which closely mimic the realistic condition of an industrial waste. The hydrogels examined in this study are 3 mm beads based on Sodium Alginate and CarboxyMethyl Cellulose [3,4], and 5 mm in diameter and 3 mm thick dry discs based on Acrylamide and Acrylic Acid, main monomer and co-monomer respectively. [5] The investigation includes an analysis of properties such as swelling degree, gel fraction, and internal structure, which are crucial to understand the mechanisms underlying the interactions between hydrogel and metal ion solutions.

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Hydrated Excess Proton Dynamics

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The dynamics of a hydrated excess proton plays a central role in a broad range of chemical processes, from acid-base chemistry to biochemical reactions and energy production in fuel cells. However, despite decades of intensive experimental and theoretical investigations, its mechanism still has not been fully elucidated. Using recent developments in machine learning [1], we trained a deep neural-network potential on high-level electronic structure calculations to obtain an accurate but computationally inexpensive reactive force-field for a hydrated excess proton and combined this description with ring-polymer molecular dynamics to account for nuclear quantum effects. We then performed extensive molecular dynamics simulations of a hydrated excess proton in different conditions, including bulk water and heavy water at several temperatures, at the air-water interface and in a water cluster dissolved in acetonitrile. These simulations are analyzed to determine the proton transfer mechanism, how it is affected by the hydrogen-bonding environment, by isotopic substitution and by temperature, and how it impacts proton mobility. We show how our results provide a molecular interpretation to a series of recent experimental results on hydrated excess proton dynamics [2-5].

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Classical density functional theory coupled to integral equations: application to supercritical CO₂

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The challenges posed by global warming are prompting manufacturers to turn to more environmentally-friendly solvents as an alternative to conventional solvents, such as organic compounds. Since their discovery, supercritical fluids have proved to be good candidates for developing green chemistry [1]. They have interesting solvation properties. The most used is supercritical CO₂ (scCO₂) because it is easy to reach its critical point ($T_c = 304$ K and $P_c = 73$ atm) and because it is non-toxic, non-flammable and abundant. It is used in a wide range of industries including pharmaceuticals, oil, cosmetics and food [2]. However, its solvating power remains limited, particularly when it comes to solubilising polar solutes. Hence the need to add a cosolvent (e.g., a polar solvent), increase the concentration of the solute or modify the thermodynamic parameters to maximise its solubility [3]. One of the challenges associated with scCO₂ is determining its solubility quickly and efficiently. Several methods are used to determine the solubility of scCO₂, including parameterised equations of state, which require experimental data, and molecular dynamics (MD) simulations. Although these methods have made it possible to obtain solubility information for a few solutes and thermodynamic conditions, they remain costly (in terms of data or calculation time), limiting their use for predictions. The aim of this study is to develop a fast and efficient method for determining the solubility of various solutes under different thermodynamic conditions. We are using a new approach, integral equations coupled to classical density functional theory (like electronic DFT, but here it is the molecular density that we are trying to minimise), which has proved its effectiveness in studies of the water molecule [4]. In this way, we can determine the structure and free energy 10000 times faster than molecular dynamics. We will present the first results for various solutes and several thermodynamic conditions.

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Impact of supercritical CO₂ on C-Phycocyanin protein in presence of polyethylene glycol

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Amid worldwide economic and environmental challenges, the urge to find sustainable processes and new sources of proteins has positioned supercritical CO₂ (ScCO₂) as an interesting alternative solvent in chemical engineering and food science [1]. Its solvation properties may indeed be tuned by changes in thermodynamic parameters such as temperature ($T > 31^{\circ}\text{C}$) and pressure ($P > 74$ bar) and/or by the addition of co-solvents such as water or ethanol. However, the use of ScCO₂ as an extraction solvent in complex matrices remains essentially empirical, given the poor knowledge on its solvation properties at molecular scale in crowded environments. Molecular interactions and excluded volume effects in biological matrices induce macromolecular crowding, which may stabilize and protect the native structure of proteins under high-temperature and/or high-pressure conditions [2], [3], [4]. However, much less is known on how such interactions evolve in ScCO₂ solvent. For this purpose, we considered a simplified model composed of a globular protein, C-Phycocyanin (CPC), which may serve as a pigment in food applications, and a polymer, polyethylene glycol (PEG) that mimics the macromolecular crowding found in complex food matrices.

Preliminary experiments show no significant changes in the density and in the viscosity of PEG solutions following a 10-minutes exposure to ScCO₂ at 60°C and 40 MPa, thereby suggesting no significant impact of ScCO₂ on the specific volume and on the conformation of the polymer. Similar measurements on CPC and CPC-PEG solutions will follow. In-situ small-angle neutron scattering (SANS) and X-ray scattering (SAXS) measurements as well as molecular dynamics (MD) simulations are also planned to further understand the molecular interactions between CPC, PEG, and ScCO₂. The ultimate goal of this study is to provide a better understanding on the influence of ScCO₂ on the structure of CPC in a crowded environment.

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Conformational space of the translocation domain of botulinum toxin: atomistic modeling and filament description of the helix bundle

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The botulinum neurotoxins (BoNTs), among the most powerful toxic compounds found in nature, are formed of various domains [1]. The underlying toxicity mechanism is based on a sequence of molecular events, in particular the translocation of the catalytic domain through the membrane of a neurotransmitter vesicle into the cytosol of the neuron. A recent structural study [2] of the isolated translocation domain of BoNT suggests a model for the interaction of this domain with the membrane, based on the transition of the α helical switch towards a β hairpin. The present work investigates this proposition and the consequences for the interaction between toxin and membrane using atomistic simulations in conjunction with the mesoscopic *Twister* model [3].

The various conformational mobilities of the translocation domain observed according to the starting conformation, protonation and solvent type, as well as the effect of the membrane examined in an implicit way by comparing water and water-ethanol solvents leads to the conclusion that the protruding switch hairpin is essential for the interaction between the protein and the membrane and that its appearance modifies the internal dynamics and the effect of hydrophobicity on the whole protein. In addition, the central two α helices, helix1 and helix2, forming two coiled-coil motifs, are analyzed in the framework of the *Twister* model, in which the deformation of the membrane by the protein is caused by the presence of local torques due to the asymmetry of the hydrophobic residues on helices. Different torque distributions are observed depending on the α or β conformation of the switch and permit to propose an origin for the mechanism opening the membrane.

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Electrical Fluctuations next to an electrode to probe the properties of interfacial electrolytes

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The fluctuations of physical quantities are often considered as noise that should be minimized with respect to a signal. In electrochemical processes, the charge exchange between electrode and electrolyte promotes chemical changes at the interface, and such interfacial electron transfer reactions serve as the foundation for important technologies that combine electrical and chemical energy. In this context, we use molecular simulations to investigate the link between solvent polarization fluctuations around a solute near an electrode and electron transfer kinetics (Marcus theory) and how these fluctuations are reflected in the charge fluctuation of the electrode^{1,2,3}.

It has also been observed that the metallicity of the electrode, which reflects its electronic structure, affects the electron transfer kinetics⁴. This metallic character can be captured in a simplified description via the so-called Thomas-Fermi screening length within the electrode^{5,6}. This quantity can further be introduced in molecular simulations in the constant-potential ensemble⁷, which allowed in particular to uncover its role on the interfacial thermodynamics via the charge distribution within the electrode⁸.

In order to understand the charge distribution induced on the surface by a single ion as a function of its distance from the electrode⁹, we use classical molecular simulations of an ion in vacuum or water next to a graphite electrode with a tunable metallicity. Based on the 2D and radial distributions of the induced charge, we discuss the effects of the ion-surface distance and of the screening both in the metal (Thomas-Fermi length) and the solvent (described in the continuum picture by its permittivity). By comparing the simulation results with analytical predictions, we analyze the effect of the atomic structure of the electrode. Finally, we also compare analytically and numerically the case of a single ion and that of a periodic lattice of ions, since molecular simulations are done under periodic boundary conditions.

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Chemical kinetics in water microdroplets and the role of aqueous interfaces

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Water microdroplets have unique properties as reaction media that are not yet well understood. Indeed, the rate of many reactions is accelerated, sometimes by several orders of magnitude compared to conventional processes in solution, and some reactions that are highly unfavorable under usual conditions occur spontaneously there. The role of the air-water interface is thought to play a key role, sometimes associated to the presence of strong electric fields (Figure 1). The study of interfacial effects on chemical reactions is an emerging topic with many ramifications, ranging from environmental and atmospheric sciences to biochemistry and organic synthesis. This presentation will summarize our recent advances on this subject from the point of view of theoretical chemistry and the use of combined QM/MM molecular dynamics simulations [1-3].

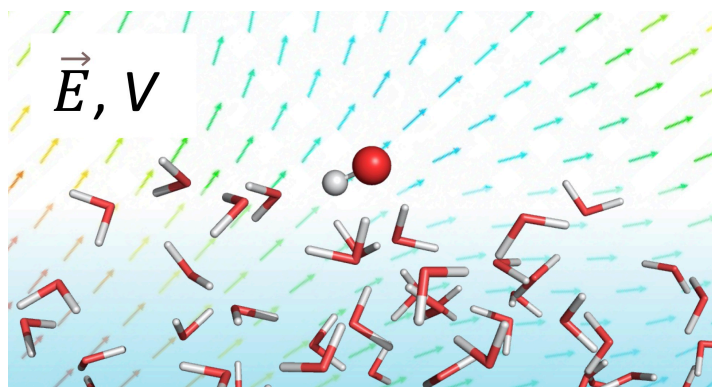


Figure 1. Schematic illustration of interfacial electric fields from Ref. [3], in which their influence on chemical reactivity has been analyzed.

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Pure predictions of solvation energies of molecular and radical species from a group-contribution model associating a cubic EoS and COSMO-RS through an EoS/gE approach

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Equations-of-state (EoS) with advanced mixing rule have proven to be an accurate approach for the estimation of solvation energies. In this sort of model, a cubic equation-of-state is combined with an excess Gibbs energy model (g^E). We showed that the UMR-PRU (Universal Mixing Rule Peng-Robinson UNIFAC) EoS allows a good representation of non-ideal and strongly asymmetric mixtures. Despite the good performance of UNIFAC in this mixing rule, some drawbacks can be pointed out: (1) many interaction parameters between existing groups are still missing; (2) the need for a large amount of experimental data to fit the interaction parameters between groups; (3) the current available parameters are usually not fitted to represent experimental data at very low concentrations, i.e., fail at infinite dilution; and (4) such model cannot deal with unusual chemical species, such as free radicals. Although rarely considered, these latter species are present in many types of reactions and in particular, combustion or polymerization. In the present case, our goal is to develop a software capable of generating liquid-phase detailed kinetic models for fuel systems in which auto-oxidation (i.e., a free radical-based mechanism involving thousands of reactions and chemical species) takes place. The reaction rates in liquid phase will be deduced from the ones in the gas phase by means of the free energy of solvation (infinitely diluted) correction ($\Delta\bar{g}_{liq}^{i,\infty}$). To overcome the shortcomings of UNIFAC, we considered COSMO-RS as a g^E model, which have the advantage of only requiring pure compound information as input (density charge distribution of molecules, and their surface and volume). These pure compound data are obtained from quantum calculations that may take minutes or hours per molecule. For this reason, we established a group contribution method for a fast computation of those COSMO inputs. This change in the g^E model facilitates the acquisition of the required inputs, and enables the simulation of a much wider range of systems. For stable molecules, the accuracy of this new model was evaluated based on the extensive COMPSOL database containing around 70,000 experimental binary data of $\Delta\bar{g}_{liq}^{i,\infty}$. The absolute average deviation (AAD) obtained was close to 0.30 kcal/mol when quantum-calculated inputs were used. When COSMO-RS inputs are calculated from the group contribution concept, the AAD increases to 0.50 kcal/mol. With respect to free radicals, since there are no experimental data available for $\Delta\bar{g}_{liq}^{i,\infty}$, a pseudo-experimental database comprising around 100 free radicals in 80 different solvents was generated with the software COSMOTerm. A good correlation was found between the results calculated by the proposed EoS and the pseudo-experimental data (AAD \approx 0.30 kcal/mol). Satisfactory results can also be obtained for phase equilibrium calculations.

Quadrupolar Li⁺ NMR relaxation investigation of water-in-salt aqueous LITFSI solutions through classical molecular dynamics simulations and ab initio computations

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In lithium-ion batteries, organic electrolytes were commonly used thanks to their high electrochemical stability window ($\approx 4\text{-}5$ V). However, due to the risk of high flammability and volatility of this kind of electrolyte, the aqueous electrolytes that are safer and more environmentally friendly have become interesting as an alternative. Unfortunately, water's narrow electrochemical stability window (1.23 V) limits the application of aqueous electrolytes for lithium-ion batteries. It led to the development of a new aqueous electrolyte named water-in-salt, with the example made by Suo and workers [1] extending the electrochemical stability window to ≈ 3.0 V. This water-in-salt (WIS) electrolyte is composed of lithium bis(trifluoromethanesulfonyl)imide (LITFSI) in aqueous solutions. Many investigations were made on this system [2], and here, we theoretically investigate the lithium ion's nuclear magnetic resonance (NMR) relaxation. Nuclear magnetic resonance relaxometry is a powerful technique for gathering dynamic information. However, interpreting the measurements in terms of microscopic motion poses a significant challenge. For nuclei with spins $I > 1/2$, NMR relaxation is mainly governed by the coupling between the nuclear quadrupole and the electric field gradient (EFG) fluctuations arising from the dynamics of solvent molecules and ions around the nucleus. Using the methodology that proved successful for aqueous electrolytes [3, 4, 5], we investigate LiTFSI WIS electrolyte using a combination of ab initio calculations to consider electron cloud effects through the Sternheimer approximation and classical molecular dynamics simulations to explore long-term fluctuations by determining the effective correlation time obtained from the EFG autocorrelation function. This approach allows us to obtain relaxation rates across various concentrations that will be compared with experiments and will give information on the system's dynamical properties.

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