# EMLG-JMLG
# Annual Meeting 2024

## Structure and Dynamics of Hydrogen-Bonded Systems

Trieste, 8-13 September 2024

Elettra Sincrotrone Trieste

# Book of Abstracts

## Welcome by EMLG-JMLG 2024 chairs

We are delighted to gather the Molecular Liquids community in Trieste from **8** to **13 September 2024** for the annual joint meeting of the European Molecular Liquids Group (EMLG) and Japanese Molecular Liquids Group (JMLG). The EMLG-JMLG group is a network of researchers interested in the study of the structure, dynamics and interactions of molecules in liquid systems by experimental, theoretical and simulation techniques. The European group was founded in 1981 and was joined by the Japanese group in 1996. International conferences were organized since 1982 in different countries, with topics covering molecular aspects of fluids in Physics, Chemistry and Biology. The main aim of these interdisciplinary conferences was to bring together scientists working on the field, to favour international cooperation and information exchange between researchers and students.

The EMLG-JMLG 2024 conference will take place at the Budinich Lecture Hall of The Abdus Salam International Centre for Theoretical Physics (ICTP) in Trieste (Italy) from September 8 to 13, 2024.

The EMLG-JMLG 2024 annual meeting will focus on the most recent experimental, theoretical and computational findings concerning the **structure and dynamics of hydrogen bonded systems**. These encompass water and water mixtures, ionic liquids, deep eutectic solvents, biomolecules, biomolecular condensates, biological membranes, aqueous interfaces. Additionally, the conference will address traditional topics within the realm of the physical chemistry of molecular liquids including, pure liquids and mixtures, supercritical fluids, glassy systems, soft matter and colloids, bio-based solvents, and more. Particular attention will be paid to the use of synchrotron-based techniques for the study of liquid systems and soft matter. The EMLG-JMLG 2024 annual meeting is organized with the support of Elettra Sincrotrone Trieste, a multidisciplinary research centre of excellence, open to the international research community, specialized in generating high quality synchrotron and free-electron laser light and applying it in materials and life sciences.

We are looking forward to meeting you in Trieste!

**Marco Paolantoni**
*University of Perugia*

**Barbara Rossi**
*Elettra Sincrotrone Trieste*

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## About Trieste

Trieste lies in the northernmost part of the high Adriatic in northeastern Italy, at the head of the Gulf of Trieste, on a narrow strip of Italian territory lying near the border with Slovenia.

It is the capital of the autonomous region of Friuli Venezia Giulia. Thanks to its deep-water port, Trieste is a maritime gateway for northern Italy, Germany, Austria and Central Europe.

It is also an important research location in Europe because of the numerous international organizations and institutions hosted in its territory.

Trieste is a beautiful and cultural city, whose cosmopolitan character can be found in the characteristic mixture of languages, peoples and religions. For centuries it acted as a bridge between Central Europe with the Mediterranean Sea being at the intersection of Latin, Slavic and Germanic cultures. The heart of the city is Piazza Unità d'Italia, which is the Europe's largest sea-front square, surrounded by monumental building, whose view can be spectacularly appreciated when walking on Molo Audace, a pier which extends for 200 meters in the sea.

In the vicinity one can admire the beautiful Canal Grande and the Greek Orthodox Church of San Nicolò. In the distance, the white profi le of Miramare castle looks over the gulf.

It was the romantic residence of Maximilian and Charlotte of Habsburg and now offers the public a chance to see the collection of original furnishings and to enjoy a walk in the park.

Admiring the sunset over the sea in Trieste is an exquisite experience, where the golden hues dance upon the waves, creating a breathtaking symphony of colors and emotions.

## The Abdus Salam International Centre for Theoretical Physics

For more than 50 years, the Abdus Salam International Centre for Theoretical Physics (ICTP) has been a driving force behind global efforts to advance scientific expertise in the developing world. Founded in 1964 by the late Nobel Laureate Abdus Salam, ICTP is a unique institution that explores fundamental scientific questions at the highest level, promotes active engagement with scientists in developing countries, and advances international cooperation through science. ICTP alumni serve as professors at major universities, chairpersons of academic departments, directors of research centres and ministers of science and technology in nations throughout the developing world. Many of them have been recognized in their own countries and internationally for their contributions to science and science policy. The impact of ICTP extends well beyond the Centre's facilities to virtually every corner of the Earth.

# Abstracts

## Exploring Water Structure at Charged Interfaces

Paul S. Cremer

*Department of Chemistry, Penn State University, USA*

Numerous examples of charged interfaces in aqueous solutions are found in natural and synthetic systems. Examples include lipid bilayers, micelles, macromolecules, and double-stranded DNA. Many of these interfaces are negatively charged with five functional groups playing very significant roles: sulfate, sulfonate, phosphate, phosphonate, and carboxylate. Metal cations in the aqueous solution form a double layer near these surfaces and can interact directly with the anionic functional groups via contact ion pairing (CIP) and solvent shared ion pair (SIP) formation. Cation binding often follows a Hofmeister series and the nature of the anionic headgroup as well as the supramolecular arrangement of the negative charges can play a decisive role in determining binding order as well as whether a metal cation will form CIPs or SIPs. Of course, H-bonding is one of the most important factors in determining the specific structure of ion pairing. This is because the separated hydrated ions have chemically specific H-bonding structures that must be disrupted in order for CIP and even SIP pairing to occur. Moreover, water molecules expelled from the hydration shell of each ion are free to go off into the bulk aqueous solution and form new water-water H-bonding interactions. The type of binding and the set of rules that govern ion pair formation will be discussed in this talk. Specifically, both thermodynamic and spectroscopic data for monovalent and divalent metal cation binding will be presented.

Oral contribution

Monday 9th
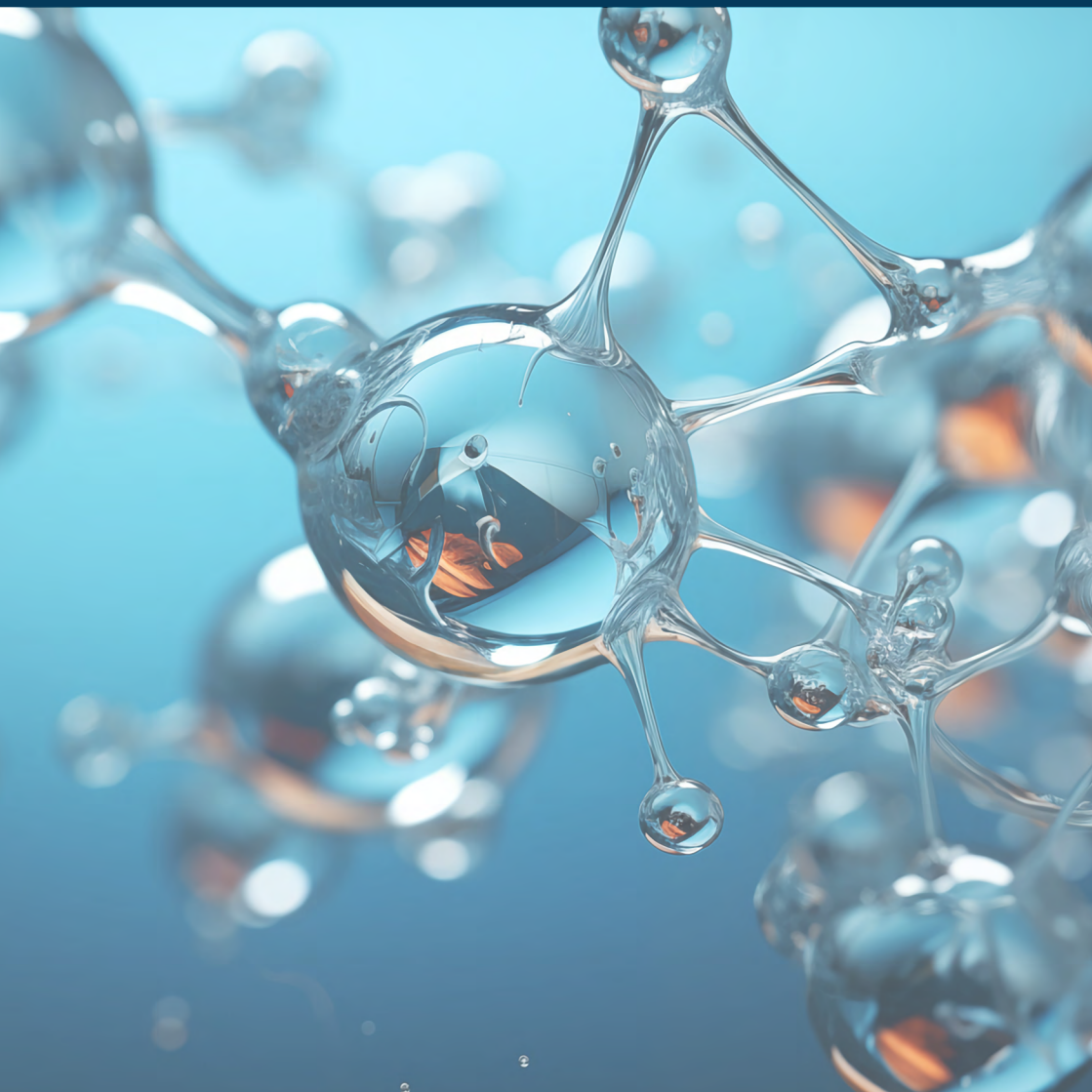
# Structure of water at planar and curved hydrophobic and hydrophilic surfaces: Direct comparison using the α-shape analysis

Ivo Nezbeda, Jiri Skvara, Milan Predota
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The structural and dynamic properties of water can be strongly influenced by the surface geometry and their interactions. There are two issues to be addressed: (i) the property of the surface and (ii) the effect of curvature.

In this work, molecular dynamics simulation was used to study the behaviour of the SPC/E water at both hydrophilic and hydrophobic spherical surfaces including the limiting case of a planar surface. These surfaces were simulated using the coarse-grained spherical graphite particles of different radii.

To study the effect of the sphere diameter on the local structural arrangement, interfacial water molecules as well as three successive molecular layers were identified and their properties were compared with a reference planar wall system represented by the 9-3 Lennard-Jones potential. The molecular layers were identified using our implementation of the α-shape algorithm known as the Universal Scheme for Triangulated Interfaces.

The most important/interesting result is found for the hydrophilic surface when the molecules in the first spherical layer form a 2-dimensional layer with saturated H-bonds so that with respect to other layers this innermost layer represents a simple structureless wall.

Oral contribution

Monday 9th

# Violation of the structure-making/breaking concept of aqueous alkali metal chloride solutions in the gigapascal pressure range

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Takanori Hattori[3], Takeshi Yamada[4]

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The static structure and dynamic properties of ion solvation at the molecular level are essential for understanding physicochemical properties and chemical processes' underlying mechanisms in geology, biology, and environmental science. The nature of ion solvation depends on the charge and size of ions. It is discussed based on the structure-making/breaking concept, the Kosmotope/Chastrope effect, and the Hofmeister sequence under ambient conditions. In this study, we perform neutron diffraction combined with empirical potential structure refinement modeling, quasielastic neutron scattering, and molecular dynamics simulation on a series of aqueous alkali metal chloride solutions at 0.1 MPa and 1 GPa at 298 K. Under ambient conditions, Li+ and Na+ have distinct solvation shells extended to the third neighbor, whereas K+, Rb+, and Cs+ have a broad first solvation shell only. The self-diffusion coefficient of solvation water around Li+ and Na+ is lower, but that of Rb+ and Cs+ is larger than that of pure water. Upon compression to the gigapascal pressure range, K+, Rb+, and Cs+ solvation shells are developed to the third neighbor shell. The self-diffusion coefficients of these ions become smaller than that of pure water. These findings in the static structure and dynamic properties demonstrate that K+, Rb+, and Cs+ behave as structure-making ions at high pressures. This transformation is caused by the structural change of solvent water from the tetrahedral network structure to the densely packed arrangement in the gigapascal pressure range. The present results hint at understanding geological processes in the Earth's upper mantle, pressure-induced protein folding, and the formation of salty ice in planetary science.

**References**

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**Oral contribution**

**Monday 9th**

# Surface affinity of simple ions in aqueous solutions

Pal Jedlovszky

*Eszterhazy Karoly Catholic University, Hungary*

Salts of simple ions, such as alkali halides are long known to be effectively repelled from the surface of water, as they increase the surface tension of their solution. In spite of this long-standing notion, it was shown two decades ago both experimentally and by simulations that large, polarizable simple anions, such as I-, are accumulated at the surface of their aqueous solutions. However, the seeming contradiction between the surface accumulation of such ions and the increase of the surface tension by their salts has to be resolved.

We perform a set of MD simulations of the aqueous solutions of alkali Cl- and Na+ halide salts using both nonpolarizable and polarizable models, and analyze the properties of the liquid surface using the ITIM method [1]. This way, we can see the variation of structural [2], dynamical [3], and dipolar [4] characteristics of the particles pertaining to the subsequent molecular layers beneath the surface; and calculate profiles of various quantities along the surface normal relative to the intrinsic, capillary wave-corrugated surface rather than to the average Gibbs dividing surface. The intrinsic treatment provided us with unprecedented details of the liquid surface, and revealed, that the surface layer, containing I+ ions in excess concentration, is followed by layers of its depletion, resulting in a net negative surface excess, in line with the increase of the surface tension. The surface charge imposed by the surface accumulation of the I- ions is compensated by a diffuse layer of the cations, giving rise to an electric double layer structure that is compatible with the Gouy-Chapman theory.

We find that the negative surface excess and surface tension increase of the I- salts is caused by the overcompensation of its surface accumulation by the effective repulsion of the small alkali cations from the surface. This finding raises the question whether the combination of I- with a large enough simple cation results in a surface active simple salt. We address this issue in two ways. First, we show by simulation that the fictitious salt in which the cation is identical, apart from its charge, with I-, is indeed surface active [5]. Second, we demonstrate by a combined experimental and simulation study that tetramethylammonium iodide, consisting of a quasi-spherical quasi-simple cation, is indeed mildly surface active [6].

**References**

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**Invited talk**

**Monday 9th**

# Widom Line in Supercritical Water in Terms of Changes in Local Structure

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Performing molecular dynamics simulations with the TIP4P/2005 water model along 9 isobars (from 175 bar to 375 bar) in the temperature range between 300K and 1100K., we have found that the loci of the extrema in the rate of change of specific structural properties can be used to define purely structure-based Widom lines. We have examined several parameters that describe the local structure of water, such as tetrahedral arrangement, nearest neighbor distance, local density around the molecules, and the size of the largest dense domain (see Figure 1). The last two parameters were determined using Voronoi polyhedral and Density-based Spatial Clustering of Applications with Noise methods, respectively. By analyzing the moments of the associated distributions, we show that along a given isobar, the temperature at which we observe a maximum in the fluctuation, the rate of change of the average values, or in the skewness values, unambiguously determine the Widom line that is in agreement with the experimentally detected, thermodynamic response function-based ones.

**References**

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# Hydrogen-Bonding Contributions to the Dipole Moment of Supercritical Water

Zoe Macpherson[1], Cecilia Barrera[1], Jose Gomes[2], Miguel Jorge[1], Leo Lue[1]

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Supercritical water shows great promise as a new green solvent, with applications in hydrogen generation from biomass and in wastewater treatment. These applications depend crucially on the ability to tune the solvation environment provided by water by manipulating the thermodynamic conditions. In water, the solvation environment is mainly a consequence of the electrostatic, hydrogen bonding, and dispersion interactions between molecules. In the liquid state, a continuous network of hydrogen bonds dominates the fluid structure, but as supercritical conditions are approached and superseded, this network becomes increasingly disrupted. The dipole moment characterizes the electrostatic interactions in the system, and plays a significant role in determining the thermophysical properties of a fluid, particularly its solvation properties and dielectric constant. In the gas phase, water molecules have a dipole moment of 1.85 D; however, in condensed phases, surrounding molecules polarize one another, significantly increasing their dipole moments. Despite its fundamental and practical importance, it remains very challenging to experimentally measure and even theoretically predict the molecular dipole moment in condensed phases, particularly for supercritical states where spacial correlations between molecules are long-ranged. Recently, we developed the Self-Consistent Electrostatic Embedding (SCEE) method, which is able to accurately estimate the molecular dipole moment in condensed phases with relatively low computational expense. In this approach, classical MD simulations are used to explore phase space in combination with high-level QM/MM methods to compute the electronic properties. We have previously demonstrated its ability to determine the dipole moment of water at ambient conditions, obtaining a value of ~2.8 D.1 This is in excellent agreement with previous ab initio MD calculations and experiment. In this work, we apply SCEE to examine the molecular dipole moment of water across a broad range of conditions, covering the liquid, vapor and supercritical regions. We investigate the fluid structure and molecular polarization of water, decoupling local and mean-field polarization contributions and providing a clear link between hydrogen bonding and induced dipole moment. We also show that this new physical insight is generalizable to a variety of other compounds, including alcohols and ketones.2,3 Finally, we present preliminary work on estimating the static dielectric constant and dielectric response by applying post facto polarization corrections based on the induced dipoles to the predictions of MD simulations4.

**References**
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# Theoretical investigation of dielectric properties of ice

Zahra Tohidi Nafe, Ádám Madarász

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Although the dielectric properties of ice Ih have been investigated extensively in the past decades both theoretically and experimentally, still there is no consensus whether the dielectric constants ($\varepsilon$) are the same in different directions in the ice crystal [1-5]. Additionally, certain data suggest variations in the static dielectric constants between ordinary and deuterated ice, with the latter demonstrating higher values.
In this study, we present a comprehensive investigation employing combined theoretical methods to explore the dielectric properties of ice Ih. We utilized Neural Network Potentials (NNP) alongside the Amobea14 force field for optimizations and molecular dynamics (MD) simulations. Our findings indicate that the Amobea14 force field accurately reproduces the energies predicted by NNP, which were trained using Density Functional Theory (DFT) methods.
To calculate the dipole moments both non-polarizable and polarizable force fields were tested. Additionally, we employed the Generalized Smoothed Trajectory Analysis (GSTA) method to assess nuclear quantum effects (NQE) on the dielectric constant of ice Ih.
Several thousand independent proton-disordered configurations were generated by the GenIce program. With this large number of configurations, we were able to calculate the difference in dipole moments in different directions with small uncertainty. Moreover, the impact of the size of the simulation box on the $\varepsilon$ of ice Ih was investigated.
In summary, our study shows that it is crucial to use a large number of independent configurations and polarizable force field to explore the dielectric properties of ice Ih. Also, it is not enough to use only optimized structures, but molecular dynamics simulations need to be performed, because the dipole moments change significantly with simulation temperature.

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# Picosecond time-resolved spectroscopic investigations of the Morin and morin-cation complexes fluorescence: towards new techniques for detecting metal pollutants in water

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Investigations on morin and metallic cations:morin time-resolved spectroscopic characterization will be presented. We explore, here [2], for the first time metallic cations:morin complexes with Ca(II), Zn(II) and Al(III) in MeOH by steady-state and picosecond time-resolved fluorescence techniques. We evidenced that the metallic cations:morin complexes could exhibit typical pico- and nanosecond time-resolved signatures. We observed that for the metallic cations, with the lowest complexation efficiency, we still see traces of the emission of the morin:solvent complex that we evidenced in our former article[1]. Therefore, supported by steady-state and time-resolved spectroscopies, we present an argued assignment of the time-components extracted from the fluorescence decays to the main species present in solution. We investigated with more accuracy and sensitivity (by time-resolved fluorescence) the presence of cation in aqueous solutions than it was already performed in literature.

In this work, we tried to answer a problematic for which discrepancies and no precise answers has never been given: is it possible to identify the various cation:morin complexes as well as the different free morin species in solution by time-resolved fluorescence? What kind of new insights on complexes metallic cation:morin's photodeactivation can be extracted from time-correlated single photon counting with a 32-picosecond time-resolution? Do the time-resolved emission spectra (TRES) help us to assign to metallic cation:morin complexes their own time-component?

We hope that this work will stimulate the development of new methods for the detection of metallic cations in water including time-resolved fluorescence techniques.

**References**

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# Emu neutron backscattering spectrometer: capabilities and applications

Nicolas R de Souza, Alice Klapproth

Australian Centre for Neutron Scattering (ANSTO)

The Australian Centre for Neutron Scattering operates a suite of fifteen neutron instruments distributed around the thermal- and cold-sources of the OPAL nuclear reactor, ANSTO, Australia. Two of the cold instruments are optimized for quasielastic neutron scattering (QENS) measurements.

This presentation will highlight the scientific capabilities of the Emu backscattering spectrometer enabling access to microscopic, molecular dynamics up to about 2 ns time scale, as manifest in the momentum transfer range of 0.27 to 1.8 $Å^{-1}$. Investigations of diffusive processes in organic materials make up the bulk of applications with that technique, while spectroscopy of low-lying excitations such as quantum rotational tunneling is also possible. The technique affords great sensitivity to hydrogenous species including H relaxation processes. In favorable cases, sensitivity to weaker scattering elements such as e.g. D, Na, O, … is achieved [1].

The most-requested sample environment is a 1.5…750K cryofurnace in optional combination with other sample conditioning schemes such as gas delivery, pressure, light irradiation, electrical field, … Other sample environment equipment may be requested or jointly developed. Beamtime allocation is merit-based.

Applications to various areas will be presented to highlight the versatility of the spectrometer in investigations of liquid dynamics in bulk and heterogeneous phases, from simple fluids to polymers and biophysics, from the fundamental to the applied domains [2-5]. In addition to fully-fledged QENS studies, elastic- and inelastic- fixed window scans add relevance to backscattering spectroscopy, as further illustrated by a handful of recent high impact studies [4]. The typical combination of data from Emu and other neutron spectrometers, and other techniques will be discussed.

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## On the mechanism of excess proton transport in water

Damien Laage, Axel Gomez, Ward Thompson
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The transport of excess protons in water is central to acid-base chemistry, energy production, and biochemical processes. However, elucidating its molecular mechanism remains challenging due to the ultrafast proton dynamics. While pioneering molecular simulations had proposed a mechanism, the latter was recently questioned by nonlinear vibrational spectroscopy measurements. We have performed neural-network potential-based ring-polymer molecular dynamics simulations and vibrational spectra calculations to characterize the molecular mechanism of proton transport and identify its rate-limiting step. We have determined that excess proton transfer in water involves successive intermediates where the proton is localized and hydrated by distinct and stable Eigen-like and Zundel-like hydrogen- bond configurations, whose spectral properties are in agreement with the nonlinear vibrational spectroscopy observations. The proposed mechanism, supported by simulations, thus provides a molecular picture consistent with the latest experimental characterizations of proton dynamics. Our results show that proton transport in water is controlled by sequential exchanges between stable hydrogen bonds around the proton-donating and accepting water molecules.

## Hydrogen bonding between water molecules and sugars probed in the gas phase

Pierre Çarçabal
*CNRS ISMO, France*

Hydrogen bonding is at the centre of the interplay between biomolecules and their environment, mostly composed of water and other biomolecules. Sugars belong to one of the most important class of biomolecules and they are key actors of a variety of biological processes, including vital molecular recognition mediated by non-covalent interactions. These especially flexible molecules encode molecular information through their chemical composition AND their conformational preferences, closely related to the direct and local environment in which they are embedded.

Using mass resolved, conformer selective double resonance vibrational spectroscopy with systematic use of isotopic substitution, we can interrogate the conformational choices of isolated sugars and the effect of a controlled number of surrounding molecules. So far, in the case of sugar-water interaction studies, we have mostly focused on the effect of water on the sugar conformer.

We will present most recent results evidencing the symbiotic structuring behaviour of solvent molecules on sugars, and in return of sugars on the solvent. This relies on the identification of hydrated clusters of sugars structures where the OHs of the sugar and water molecules create the same H bond networks than those that have been long studied for water oligomers. These findings echoes to the concept that sugars can be seen as "pre-organized water oligomers" with the ability of shaping and affecting its own environment. This unique property of sugars could be the fundamental key to understand the basis of their central role in molecular recognition.

Oral contribution

Monday 9th

Oral contribution

Monday 9th

*Oral contribution*

*Monday 9th*

# Effects of Fluorocarbon Chain Length on the Adsorption of Perfluoroalkyl Substances on Nanoplastic Particles

Katalin Bere, Bálint Bakk, István Szilágyi

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Due to human and industrial activities nanoplastics (NPLs) and per- and polyfluorinated substances (PFASs) are recognized as one of the most hazardous emerging contaminants of the nature. Owing to their colloidal size distribution these particles can easily enter to living organisms, where they can exert their harmful effects. Their migration properties are largely affected by the parameters of the solid-liquid interface and strongly influenced by the chemical composition of the media. The presence of PFASs may lead an interaction with NPLs which causes the formation of adducts with unknown colloidal properties and health effects.

In this project, aggregation and adsorption processes of oppositely charged NPLs with different fluoroalkyl chain length-PFASs were examined in the presence of mono-and multivalent electrolytes. The interparticle forces and the colloidal stabilities were followed by light scattering techniques.

The results of the zeta potential measurements were shed light, that in case of positively charged NPLs, the length of the carbon chain greatly affected the affinity of PFASs to the surface of the particles. During the adsorption, charge neutralization and reversal were detected at appropriate concentrations and the affinity of PFASs to the NPLs surface followed the C4 < C6 < C8 order. Paralell to this, at high positive and high negative potentials stable systems were observed while at the isoelectric point (IEP), destabilization processes were took place. In the IEP where the charge reversal was detected, the particles underwent rapid aggregation processes, which indicated by large hydrodynamic radii values, respectively.

In contrast, in case of negatively charged particles significant changes were not experienced by varying the chain length.

In addition, the effects of the ionic valence of salt components were played a significant role for both particle types. Owing to the salt components, the electrical double layer of the particles was shrank and the extent of the shrinking followed the Na+< Ca2+ < La3+ order. The destabilization impact was the most significant in case of trivalent ions which led the formation of unstable particle dispersions at relatively low salt levels.

Based on these results, one can conclude that the interaction between NPLs and PFASs are highly possible in nature and greatly affected by the presence of the different dissolved electrolytes. These findings can serve as a good basis for predicting transport of PFASs by NPLs in aqueous compartments in environmental samples.

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*Oral contribution*

*Monday 9th*

# Theoretical study on solvent dependency of photophysical properties

Masahiro Higashi

*Nagoya University*

The photophysical properties of molecules in solutions are affected by the solvents. However, it is often difficult to explain the molecular mechanism. We have been studying such solvent dependency of photophysical properties by combining quantum chemical calculations and appropriate solvent models. In this presentation, we will talk about our recent progress. For example, we investigated solvent dependency of excited-state intramolecular proton transfer (ESIPT) in 2-(2′-hydroxyphenyl)-benzothiazole [1]. It was found that the hydrogen-bond acceptability of solvent plays important roles in ESIPT. We also investigated solvent and anion dependency of fluorescence quenching of a phospholium cation [2]. The charge-transfer state of the cation-anion complex was found to be responsible for the dependency. Furthermore, we will talk about solvent dependency of fluorescence spectrum of pyrene-MoS2 nanosheet system [3]. It was demonstrated that the interaction of MoS2 vacant orbitals with the locally excited state of pyrene forms charge-transfer excited states, exhibiting the solvent dependency of fluorescence energy.

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Oral contribution

Monday 9th

# Molecular dynamics investigation of interfacial properties of pharmaceutical molecules: curcumin on vacuo and sCO2 interfaces.

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Recent investigations into the mechanisms of transformation between polymorph form of an active pharmaceutical ingredient (API) revealed the importance of the structural and dynamical properties at the interface.[1] For instance it was shown, that during the melt-recrystallization process, the distribution of conformations occurring at the interface, controls the changes between its polymorphic forms.[2]

In this work, molecular dynamic simulations are used to analyze the correlation between the conformation changes at Curcumin-Vacuum and Curcumin-supercritical $CO_2$ interfaces, driven by increasing the temperature beyond the melting one. Indeed, Curcumin has attracted considerable amount of attention in biomedical literature due to potential benefits that include anti-inflamatory, anti-carcinogenic and anti-oxidant activities. Several polymorphic forms[3] of curcumin have been described, but not yet studied theoretically.

For this purpose we developed new force field parameters to reproduce the experimental melting temperature and to capture the changes between the various conformations (the rotation barriers) of Curcumin, namely those present in its three polymorphic forms. During the increase of the temperature, Curcumin molecules at the polymorph I-vacuum interface were identified using the ITIM algorithm.[4] This makes it possible to analyze the structural changes at the interface, namely the distribution of conformations, nearest neighbor distribution, Voronoi polyhedra parameters and local densities.

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Oral contribution

Monday 9th

# Hydrogen absorption in ionic liquids

Luis Miguel Varela Cabo, Alejandro Rivera-Pousa, Martín Otero-Lema, Raúl Lois-Cuns, Pablo Martínez-Crespo, Hadrián Montes-Campos, Trinidad Méndez-Morales

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We report density functional theory and classical molecular dynamics simulations to investigate the molecular mechanisms governing hydrogen solvation in different ionic liquids. The structural analysis in bulk systems [1] reveal that under high temperature and pressure conditions weak interactions between hydrogen and the ionic liquids take place, with a slight preference of this gas to be placed at the apolar domains. Moreover, gas uptake mechanism of hydrogen molecules nanoconfined inside carbon nanotubes (from 6 Å to 12.24 Å) filled with an ionic liquid (ethylammonium nitrate and 1-ethyl-3-methylimidazolium tetrafluoroborate) are considered to study their effect on the gas capture capacity and on the location of gas molecules within the nanotubes, and compared to those of nitrogen. Our results [2] show that nitrogen absorption ability is, in general, greater than that of hydrogen, with the aprotic ionic liquid being more efficient for gas confinement, since hydrogen storage is mainly governed by the amount of accessible free volume but nitrogen solvation energetics must be also considered.

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# Water structures in BMIMBF4 aqueous solutions: an insight on H-bond interactions

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Room temperature ionic liquids (RTILs) have garnered significant attention in various fields due to their unique properties, such as thermal stability, low toxicity, solvation capacity, low vapor pressure, and remarkable electrical conductivity. RTILs can form well-defined nanostructures owing to the polar and non-polar domains created by their constituent ions [1]. It is well-established that these nanostructures can be influenced by the presence of water [2]. Numerous studies have investigated local nanostructure and water cluster formation as a function of water concentration considering aqueous RTILs solutions [2-6]. Despite this, the specific structuring of hydrogen bonds interactions in these systems has not yet been clarified at the molecular level. Imidazole-based ionic liquids have been utilized as models for this type of investigation, in particular with 1-butyl-3 methylimidazolium tetrafluoroborate (BMIMBF4). Raman and IR spectroscopies are highly sensitive to hydrogen bond interactions, making them valuable tools for studying the hydration properties of BMIMBF4, as suggested by numerous studies in literature [7-10]. However, a clear experimental understanding of the hydration mechanism across a wide concentration range is still lacking. In our study, we aim to conduct a qualitative and quantitative analysis of the hydration properties of BMIMBF4/water mixtures over a wide concentration range, which has never been considered from a spectroscopic perspective. To achieve this, we employ a methodology inspired by the Raman-MCR technique based on spectral subtraction that have already proved very effective to trace hydration shell spectra from UV-Raman spectra of BMIMBF4/water mixtures in a diluted regime ($x_{BMIMBF4} < 0.5$) [3]. In this case, we considered a comparative analysis extracting UV-Raman and ATR-IR SC spectra from BMIMBF4/water mixtures from a diluted to concentrated regime ($x_{BMIMBF4} > 0.9$) .We propose this method also as a useful way to obtain reliable quantitative information about the hydration features of the systems considered, including, hydration numbers and aggregation properties. This research elucidates molecular properties of RTILs, aiding their applications.

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# Pillared graphene oxide frameworks for the adsorption and separation of dimethylsulfoxide-water mixtures

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Potential applications of previously synthesized pillared graphene oxide frameworks with phenyldiboronic acid linkers in the field of adsorption and separation of polar protic and aprotic liquid solvents have been systematically explored using Grand Canonical Monte Carlo simulations. Particular attention was initially paid to the adsorption of pure liquid water, methanol and dimethylsulfoxide. The results obtained a significant increase of the isosteric heat of adsorption at low uptake in the case of dimethylsulfoxide, indicating that pillared graphene oxide frameworks could be used in the separation of dimethylsulfoxide-water liquid mixtures. Systematic Grand Canonical Monte Carlo simulations were then subsequently performed for representative dimethylsulfoxide-water mixtures, revealing that these materials could indeed have potential applications in the separation of these mixed liquid solvents. Molecular dynamics simulations of representative bulk and confined dimethylsulfoxide-water mixtures further revealed a substantial slowing down of the dynamics under confinement, particularly in the case of hydrogen bonds formed between water and dimethylsulfoxide.

## The mutual interplay between structure and dynamics of hydrogen bonds at organic and inorganic interfaces

Giancarlo Franzese

*Universitat de Barcelona, Spain*

We will present our recent results about how different interfaces affect the structure and dynamics of water hydrogen bonds and how, in turns, these affect the properties of the interfaces. We will explore concepts such as bound and unbound hydration water and their relation with phenomena that relevant in biology and nanotechnology.

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## Raman and Infrared Imaging of Biological Systems at the Nanoscale

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Transthyretin (TTR) amyloidosis is a progressive disease characterized by an abrupt aggregation of misfolded protein in multiple organs and tissues TTR is a tetrameric protein expressed in the liver and choroid plexus. Protein misfolding triggers mono-merization of TTR tetramers. Next, monomers assemble forming oligomers and fibrils. Although the secondary structure of TTR fibrils is well understood, there is very little if anything is known about the structural organization of TTR oligomers. To end this, we used nano-infrared spectroscopy, also known as atomic force microscopy infra-red (AFM-IR) spectroscopy. This emerging technique can be used to determine the secondary structure of individual amyloid oligomers and fibrils. Using AFM-IR, we examined the secondary structure of TTR oligomers formed at the early (3–6 h), middle (9–12 h), and late (28 h) of protein aggregation. We found that aggregating, TTR formed oligomers (Type 1) that were dominated by $\alpha$-helix (40%) and $\beta$-sheet (30%) together with unordered protein (30%). Our results showed that fibril formation was triggered by another type of TTR oligomers (Type 2) that appeared at 9 h. These new oligomers were primarily composed of parallel $\beta$-sheet (55%), with a small amount of antiparallel $\beta$-sheet, $\alpha$-helix, and unordered protein. We also found that Type 1 oligomers were not toxic to cells, whereas TTR fibrils formed at the late stages of protein aggregation were highly cytotoxic. These results show the complexity of protein aggregation and highlight the drastic difference in the protein oligomers that can be formed during such processes.

# Aggregation of whey proteins in mixed solutions

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Soft materials, formed through various thermal treatments [1] and utilizing different protein mixtures, can exhibit diverse physical and viscoelastic characteristics. Whey proteins, known for their nutritional value and functional properties such as gelation, emulsion, or foam formation [2], are commonly used in food formulations. The predominant globular proteins in whey are β-lactoglobulin (BLG) and albumin (BSA), often employed as models due to their cost-effectiveness and propensity to aggregate under various environmental conditions. This study aims to provide molecular and structural insights into the aggregation processes of BLG [3] and BSA whey proteins in both diluted and crowded solutions. Aqueous protein solutions with low pH are examined at different BLG-BSA molar ratios, in a diluted regime to induce fibril formation, and in a crowded regime to facilitate the development of hydrogel networks. A multi-technique spectroscopic approach is used to probe the co-aggregation process at different length scales, as shown in Figure 1. Molecular-scale information is obtained through FTIR, CD, and UVRR spectroscopies, while structural details at the nanoscale are derived from the SAXS technique. The structure of nanoaggregates is influenced by molecular interactions, with branching determining the viscoelastic properties of the system [4]. These properties are further characterized using HD-TG non-linear spectroscopy.

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# Viruses in aqueous media as colloidal systems: particle's hydrodynamic diameter and zeta-potential, surface charge, and solution stability

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MS2 and PCV2 viruses were investigated in aqueous solutions. MS2 is an icosahedral bacteriophage infecting Gram-negative bacteria and consisting of a protein outer layer (capsid) and encapsulated 3569 nucleotides long single-stranded RNA genome. PCV are non-enveloped single-stranded DNA viruses infecting pigs, PSV2 being structurally the smallest known non-satellite virus.

Our aim was to (i) investigate the capsid surface of the viruses measuring their hydrodynamic diameter and zeta-potential, the charge distribution on the surface, and local electrostatic potential, (ii) analyze the colloidal stability of MS2 in the presence of surfactants and inorganic salts, and (iii) study surface properties of MS2 and PCV2 suggesting ways of their disintegration.

We measured the hydrodynamic diameter and the zeta-potential of MS2 phage particles and PCV2 empty capsids to be 30 nm and -34 mV, and 22 nm and -41 mV respectively, using dynamic light scattering method and electrophoresis. The MS2 and PCV2 capsid surfaces were also examined using a series of acid-base indicator dyes of various charge type, size, and structure. Their spectral and acid-base properties (pKa) are very sensitive to microenvironment in aqueous solution including containing nanoparticles. The values were found to be -50 mV or +10 mV, and -91 or +14 mV (+-2 mV), depending on the molecular probes and implying the 'mosaic' pattern of the charge distribution on the surfaces. The value is concluded to be a reliable indicator of the dispersion stability and the key to effective virus aggregation or/and disassembly through the reduction of their values with coagulants.

We investigated MS2 aqueous solution stability influenced by inorganic electrolytes and colloidal surfactants at physiological condition. It was found that the zet-potential is reduced from -35 mV to -10 mV in the presence of 0.01 M CaCl2, 0.1 M NaCl, and higher electrolytes concentrations, producing MS2 aggregates of ~600-900 nm size, but individual ~30 nm particles were also recorded.

Adding cationic, anionic, and non-ionic colloidal surfactants below and above critical micelle concentration (cmc) to MS2 solutions showed the following. The zeta-potential was reduced upon the addition of cationic surfactant and even the surface recharge took place from -25 mV to +35 mV below and above cmc respectively, while MS2 virus aggregation was very clear above cmc of CTAB. The addition of anionic surfactants as monomers or in the form of micelles did not show MS2 aggregation, dispersion, or disassembly. The presence of non-ionic micelles increased phage aggregation and reduced the zeta-potential value. Thus, the 2 : 1 electrolyte at low concentrations or cationic and non-ionic micelles destabilize MS2 particles in aqueous solution.

Our data can be used for developing disinfection strategies by destabilizing the solution or disintegrating the virus particles.

# Deep UV Raman spectroscopy for probing active eukaryotic viruses

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Deep Ultraviolet Resonance Raman Spectroscopy (DUVRR) is an emerging and powerful analytical tool that can be used for detection and characterization of biological samples in a label-free and real time approach. The excitation in the Deep UV provides specific resonance enhancement of biological moieties, especially protein, DNA and RNA structures (1, 2), allowing to efficiently isolate and detect biological Raman markers in the spectra. It is well known that DUV radiation is a genotoxic agent. Prolonged UV light exposition induces damage to the genomes of viruses, breaking bonds and forming photodimeric lesions in RNA (1-3). These damages prevent both transcription and replication which leads to viral inactivation. Even though the effects of UV radiation on DNA of microorganisms have been well-recorded, its impact on RNA and RNA modifications is less known. A sample that is prone to such a damage are viruses, and with the SARS-COV-2 (RNA virus) outbreak, the need of fast tools for viral characterization and classification became even more necessary.

In this work, we will show how to obtain stable, high quality and information-rich DUVRR spectra of active Vesicular Stomatitis Virus (VSV) without affecting its viability, RNA and protein integrity. By opportunely tuning the excitation wavelength, we can detect and assign in the vibrational spectra specific markers of lipid, protein and RNA components useful to elucidate biochemical characteristics of active VSV virus. In addition, we can study the effect of antivirals and DUV irradiation in the mechanism of inactivation of VSV viruses in order to find the most promising antivirals and damaging wavelength for the active VSV virus, respectively. These information can further be exploited to build effective countermeasure tools for pathogenic viruses.

# Computational Modelling of Hydrogen Bonds in Ionic Liquids

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Hydrogen bonding is one of the prevalent factors in the properties of Ionic liquids (ILs), and specially protic ionic liquids. This review explores how molecular dynamics (MD) simulations, coupled with machine learning (ML) potentials, can illuminate these hidden interactions.

In this presentation we will show first some results using traditional force fields will be shown as well as their predictive power for hydrogen bonds of different strength and their caveats. Afterwards the focus will shift to ML potentials, where we will show how it can be a powerful tool for overcoming these limitations. By learning from high-fidelity data, such as quantum mechanical calculations, ML potentials can capture the nuances of H-bonding in ILs with improved accuracy and efficiency. We will show also how these potentials are even capable of prediction proton transfer between different species in the liquid phase.

In summary, this review will examine the specific advantages of using ML potentials in MD simulations of ILs. It will explore how these simulations can provide insights into H-bond lifetimes, dynamics, and their influence on material properties.

Oral contribution

Tuesday 10th

# Spectroscopic evidence for doubly hydrogen-bonded cationic dimers in the solid, liquid and the gaseous phases of carboxyl-functionalized ionic liquids

Ralf Ludwig

*University of Rostock*

Intermolecular interactions determine whether matter sticks together, gases condense into liquids, or liquids freeze into solids. The most prominent example is hydrogen bonding in water, responsible for the anomalous properties in the liquid phase and the polymorphism in ice. The physical properties are also exceptional for ionic liquids (ILs), wherein a delicate balance of Coulomb interactions, hydrogen bonds and dispersion interactions results in a broad liquid range or the vaporisation of ILs as ion pairs. In this study we show that strong, local and directional hydrogen bonds govern the structures and arrangements in the solid, liquid and the gaseous phase of carboxyl-functionalized ILs. For that purpose we explored the H-bonded motifs by X-ray diffraction and attenuated total reflection (ATR) infrared (IR) spectroscopy in the solid state, by ATR and transmission IR spectroscopy in the liquid phase and by cryogenic ion vibrational predissociation spectroscopy (CIVPS) in the gaseous phase at low temperature. The analysis of the CO stretching bands reveal doubly hydrogen bonded cationic dimers (c=c), resembling the archetype H-bond motif known for carboxylic acids. The like-charge doubly hydrogen bonded ion pairs are present in the crystal structure of the IL, survive phase transition into the liquid state and are still present in the gaseous phase even in (2,1) complexes wherein one counterion is removed and repulsive Coulomb interaction increased. The interpretation of the vibrational spectra is supported by quantum chemical methods. These observations have implications on the fundamental nature of the hydrogen bond between ions of like charge.

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Oral contribution

Tuesday 10th

# Non-vehicular proton transport mechanism through rational design of a fluorine-free protic ionic liquid

Stefano Nejrotti[1], Claudia Barolo[1], Matteo Bonomo[1], Alessandro Mariani[2,3,4], Stefano Passerini[3,4], Hanno Maria Schütz[3,4]

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Protic ionic liquids (PILs) have gathered growing interest for energy-related applications in the field of electrochemistry, thanks to their high ionic conductivities and their viable preparation.[1] Notably, in some cases superionicity has been achieved through partial decoupling of the charge transport from a purely vehicular mechanism, since the proton, as a charge carrier, can have access to unique diffusion patterns. Here, we propose N,N-diethyl-3-sulfopropan-1-ammonium hydrogen methanedisulfonate [DESPA][HMDS] as a novel PIL whose rational design aims at achieving fast proton transfer through an intrinsic mechanism, thanks to the presence of sulfonic acid functionalities, of almost equivalent proton affinity, both in the anion and cation structure. The synthesis and characterization of the PIL was carried out, revealing superionic features at high temperatures, as indicated by the positive deviation from the ideal behaviour in the Walden plot, and by a inverse Haven ratio up to 1.55. To elucidate the nature of such superionicity, the PIL was studied by diffusional NMR, displaying an unprecedented two- to three-fold increase in the mobility of the exchangeable proton, compared to that of the anion and the cation. Again, this feature is observed at high temperatures (> 373 K), and points towards the presence of a non-vehicular Grotthuss(-like) proton transport mechanism in our PIL. Moreover, the molecular structure of [DESPA][HMDS] was designed to be fluorine-free, as perfluoroalkyl substances (PFASs), often employed in the formation of superionic PILs,[2,3] constitute a growing concern in terms of health and environment, and might be subjected to a phase-out by the European Union in the coming years.[4]

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Oral contribution

Tuesday 10th

# Ionic transport mechanism in mixtures of protic ionic liquids

Martín Otero-Lema[1], Raul Lois-Cuns[1], Hadrian Montes-Campos[1], Trinidad Méndez-Morales[1], Oscar Cabeza[2], Luis Miguel Varela[1]

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Protic ionic liquids (PILs) exhibit unique transport properties governed by their extensive hydrogen-bonding networks. In this study, we employ computational techniques, specifically polarizable molecular dynamics simulations, to investigate the charge conduction mechanisms in mixtures of PILs with different solvents. Our simulations reveal that the coordination between ions and solvent molecules – mediated through hydrogen bonding - critically influence ionic conductivity, with certain solvents exhibiting anomalous conductivity behavior that does not fit current theories such as the random alloy model [1]. This computational approach provides new insights into the molecular interactions within these mixtures, paving the way for the rational design of new PIL-based systems with enhanced transport properties for applications in electrochemical devices.

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Oral contribution

Tuesday 10th

# Influence of Water on the Transport Properties of Ternary Mixtures with Triglyme and [Li][NTf$_2$]

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In the engineering of energy storage devices, lithium batteries offer the biggest opportunities regarding energy densities but their electrolytes often have undesirable properties like, for example, a high combustibility [1]. Therefore, possible alternatives to conventional electrolytes are searched for.

Recent studies have shown that by mixing salts consisting of lithium cations and weakly coordinating anions such as NTf$_2^-$ with triglyme, so called pseudo-ionic liquids can be formed for certain mixing ratios [2].

Molecular dynamics simulations revealed that by adding triglyme to [Li][NTf$_2$], the lithium salt changes from contact ion pairs to solvent-separated ion pairs. The lithium cations are coordinated by the oxygen atoms of the triglyme molecules and in consequence, the interaction between anions and cations is weakened leading to improved transport properties of the system.

Hereby, the structural motifs of the cation-triglyme clusters depend almost entirely on the mixing ratio of the two components. For the equimolar mixture, every cation is, on average, enclosed by one triglyme molecule forming a complex with its four oxygen atoms. If the mole fraction of triglyme is further increased, the one-fold triglyme-coordinated state of the cations changes to a two-fold coordination state where two triglyme molecules surround lithium in a double-helical-like manner.

If small amounts of water are additionally added to the different mixtures of [Li][NTf$_2$] and triglyme, the transport properties such as self-diffusion and viscosity can be further increased. The water molecules intercalate between the cation and the outer oxygen atoms of the coordinating triglyme molecule. The water molecules form coordinative bonds with the cation as well as hydrogen bonds with the detached triglyme oxygen atoms and anions. By this, the water molecules are shielded from each other and should therefore behave chemically different than bulk-phase water. Here, a comparison can be made to water-in-salt electrolytes [3]. At a certain threshold of water content in the ternary mixtures, water starts forming clusters again. At this point, the advantage of adding water diminishes due to the smaller electrochemical window of bulk water [3].

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# Hydrogen bonding in ionic liquids and derivated materials

Anna Martinelli
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Protic ionic liquids are a peculiar class of materials that, similarly to the more conventional family of aprotic ionic liquids, have a low melting point, a high ionic density and a relatively high ionic conductivity. In addition, however, they form extended hydrogen bonded networks by virtue of having exchangeable protons in their chemical structure, typically on the cation.

Protic ionic liquids are obtained by a 'simple' neutralization reaction by which a proton is transferred from an acid (AH) to a base (B), resulting in a protonated cation (BH+) and an anion (A-). The degree of completaion of this reaction depends on the pKa of the reagents, which also has an impact on the strength of hydrogen bonding between BH+ and A-. Hydrogen bonds add as an attractive force to the already complex set of coulombic and van der Waals interactions. Understanding the correlation between strength/nature of hydrogen bonds and other physicochemical properties such as glass transition temperature, diffusivity and conductivity is of fundamental interest, but is also crucial to orient the design of energy relevant devices like fuel cells, batteries and capacitors.

In this contribution, I will present some work performed in my research group in the context of protic ionic liquids, which is mainly experimental and which, along with the case of pure ionic liquids, also encompasses ionic liquid mixtures (mixed anion effects, addition of a base) and ionic liquids confined in mesoporous domains. The experimental methods primarily used include vibrational spectroscopy (Raman and infrared), NMR spectroscopy (diffusion NMR, relaxation NMR, solid-state, etc), calorimetric methods (DSC and TGA) and impedance spectroscopy, with the support in specific studies from MD simulations and DFT calculations.

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# Aqueous Nanoscale Systems

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Water is the most important liquid for life. It is intimately linked to our well-being. Without water, cell membranes cannot function. Charges and charged groups cannot be dissolved, self-assembly cannot occur, and proteins cannot fold. Apart from the intimate link with life, water also shapes the earth and our climate. Our landscape is formed by slow eroding/dissolving processes of rocks in river and sea water; aerosols and rain drops provide a means of transport of water. Because of the complexity of liquid water and aqueous interfaces, the relationship between the unique properties of water and its molecular structure has not been solved.

Techniques that can provide femtosecond structural information over multiple length scales can help. For this purpose, we developed nonlinear light scattering [1] and imaging tools [2] to access molecular structural information of aqueous solutions and interfaces. With our new approaches we have found nanoscale ordering in dilute salt solutions [3], and probed the structure of aqueous nanoscale interfaces relevant for chemistry and biology: emulsions [4], lipid droplets [5], liposomes [6], water droplets [7] and oxides [8]. We solved the mysteries behind the Jones-Ray effect [3] and the origin of charge on neutral oil droplets in water, which underlies hydrophobicity [9]. The optical properties of water can also be used to determine the electrical potential (voltage) of interfaces. This unique spatiotemporally resolved hydration readout is useful for obtaining new insights relevant for chemistry [2], biophysics [10], neurology [11] and catalysis [12]. This presentation will highlight some of our recent findings.

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# How to model divalent ions?

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When it comes to modeling divalent ions, I am full of questions, but have few answers. There are a couple of physical facts that make ions like $Ca^{2+}$ complicated, such as strong electrostatic interactions with other ions and water molecules, polarization, and charge transfer. By giving an account of these, we are well into the realm of quantum mechanics. So, if we rephrase the question of the title as "How do we model divalent ions with classical mechanics?", the answer becomes even more complicated. Polarization can be taken into account with polarizable force fields (FF), but these are expensive. So if we rephrase our question again as "How do we model divalent ions with classical non-polarizable force fields?", the answer becomes really challenging. Here, we try to pose further questions to get closer to an answer.

A few problems that we need to avoid if want to find the appropriate model are the following (using $CaCl_2$ as a case study).

1. We want to avoid too strong association of $Ca^{2+}$ and $Cl^-$, namely, we want to avoid ion complexation. This means that we want to avoid too high peaks in the $Ca^{2+}$ - $Cl^-$ radial distribution functions (RDF).

2. We want to avoid too strong association of $Ca^{++}$ with surrounding water, namely, we want to avoid too rigid hydration shells that prevent ions from appropriate association.

3. We want to avoid non-ergodicity, namely, we want to avoid too deep depletion zones between the first and second peaks in RDFs. The presence of those depletion zones would prevent traffic of particles between the shells, namely, transitions between states.

We discuss FFs with explicit water and show that scaling of the ionic charges to take into account polarization is needed to avoid the problems listed above. Full charges make the electrostatic interactions too strong, so the system falls on either side of the free energy Himalaya. By reducing the charge, those problems can still be present, but they can be minimized by using the ionic diameter (the distance parameter of the Lennard-Jones potential) to optimize the system to get sensible RDFs and agreement with experimental data for neutron scattering, viscosity, diffusion constants, and conductance.

The other possibility for modeling divalent ions is to smear water into a continuum and make it implicit. That may seem like a harsh, outdated approximation, but here we also have the parameter with which we can tune the strength of electrostatic forces: the dielectric constant. While the ionic charge needs to be reduced in explicit-water FFs, the dielectric constant needs to be reduced in implicit-water models to suppress the screening of the ion-ion interactions. Ionic diameters can be used for fine tuning here as well. Experimental phenomena such as charge inversion and the non-monotonic behavior of the activity coefficient can be reproduced with simple, but appropriately scaled reduced models.

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# Molecular modeling of alkali halides using phase-transferable models: aqueous solutions, crystalline hydrates, molten salts, and noncovalent bonds

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Alkali halides are most commonly found in aqueous solutions whose behavior is largely determined by hydrogen (generally noncovalent) water-water, water-ion, and ion-ion bonds. Computer simulations of these substances require accurate interaction models that can correctly capture not only the interactions themselves, but also the balance between them. This is particularly important for correctly predicting phase equilibria between aqueous solutions, crystalline hydrates, anhydrous crystals, and molten salts.

In our recent work, we have refined the AH-BK3 polarizable models [1], resulting in a set of force fields [2, 3] that provide good predictions for almost all properties of aqueous solutions, anhydrous crystals, their solubility, and the structures of 16 different crystalline hydrates [4].

Here, using these force fields:

1. We study [5] the structure of solutions of 14 salts at normal temperatures and all possible concentrations, including supersaturated states. We identify noncovalent bonds in the systems using a general method based on spatial distribution functions. We show that larger ions readily lose water molecules from their hydration shells with increasing concentration, while small ions maintain their hydration shells almost completely unchanged. The loss of water from the hydration shells is compensated by the formation of contact ion pairs. However, this compensation is not always perfect, as small ions do not allow sufficient ion pair formation, and the loss of hydration of large counterions leads to an overall decrease in the number of bonds.

2. We study the concentration dependence of aqueous salt solutions at low temperatures around the maximum density. The predictions of the polarizable models are comparable to those of the Madrid/2019 models [6], and their deviations from experiments are rather due to inaccuracies of the water molecule in the case of both models, TIP4P/2005 and BK3.

3. We study the volumetric and thermochemical properties of anhydrous crystals and molten salts at high temperatures, including the formation enthalpies and Gibbs energies used to determine melting temperatures.

4. We study different cesium halide crystal structures and show that our force fields predict their stability and polymorphism well.

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# Interfacial Inversion, Interference and IR Absorption in Vibrational Sum Frequency Scattering Experiments

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Molecular interfacial structure greatly determines the properties of nano- and microscale systems. Vibrational sum frequency scattering (SFS) spectroscopy is a unique interface-selective tool to measure the interfacial vibrational spectrum of sub-micron to micron scale objects dispersed in liquid and solid media. The interfacial structure is extracted from the interfacial susceptibility, a physical property derived from the intensity. Here, we describe the effect of infrared absorption that occurs in a bulk medium that is spectroscopically complex and use the results to investigate the effect of interfacial inversion, interfacial interference, and interfacial interference combined with absorption. We use the same three chemicals to do so, hexadecane oil, water, and a neutral Span80 surfactant. For all cases, the effective surface susceptibility can be retrieved from the intensity. We further find that inverting the phases results in different interfacial structures (even though they are composed of the same three chemicals) and explain this in terms of the different interactions that are necessary to stabilize the drops (steric stabilization for water drops in oil vs. charge stabilization for oil drops in water). Interfacial interference can be used to estimate the surface density of the different compounds.

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# Highly Conductive Deep Eutectic Solvents Using Iodine

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Eutectic effect is observed in metallic alloy systems. This also occurs in molecular and ionic systems. If a mixture system becomes the liquid state at ambient temperatures by a large eutectic effect, it is referred to as deep eutectic solvent (DES). The great advantages of DES are its easy preparation, often just mixing (or with mild heat), and environmentally friendly nature, when the components are appropriately chosen. Accordingly, DES is getting more attention recently [1].

Typical DESs are composed of hydrogen-bonding donor and acceptor (often salt). Since the intermolecular interaction in DESs is essentially strong, the viscosity is high. As a result, the electrical conductivity of typical DESs is not much high. Recently, we have demonstrated that some imidazolium iodides and ammonium iodides easily become DESs by mixing with iodine, and they possess very high electrical conductivities [2,3]. For example, 1:2.5 mixture of methylammonium iodide and iodine showed approximately 100 mS cm-1 at 298 K [3]. The electrical conductivity of the DES composed of 1-ethyl-3-methylimidazolium iodide and iodine with the molar ratio of 1:4 was also very high (~70 mS cm-1 at 298 K). Notably, they are much higher than common DESs and ionic liquids. Also note that the conductivity of the DES of 1-ethyl-3-methylimidazolium iodide and iodine is even higher than that of a similar ionic liquid (1-butyl-3-methylimidazolium iodide) and iodine mixture with the same molar ratio. The viscosities of DESs were not high (typical cases are 10-20 cP) compared to ionic liquids. The results of the Walden plot showed that most DESs studied here were a good conductor compared to the ideal diffusion system. The Raman spectra of some DESs showed clear intramolecular vibrational bands of polyiodides, such as $I_3^-$, $I_4^{2-}$, and $I_5^-$. Considering the presence of polyiodides in the DESs, the high electrical conductivity can be attributed to the Grotthuss mechanism. We are now carrying out studying the other halides (chlorides and bromides) and the water effect, as well as measuring the thermal behavior [4]. We will discuss the new results, too.

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# Hydrogen bonding in ionic liquids: A 1H and 19F NMR relaxometry study

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Due to its central role in influencing the thermodynamical, structural and dynamical properties in ionic liquids, there is a strong scientific interest in a detailed description of hydrogen bonding in this substance class.[1] We studied two different ionic liquids: Firstly, triethylammonum bis(trifluoromethylsulfonyl)imide ([$N_{222}H$][$NTf_2$]), which is known for the formation of strong hydrogen bonds between cations and anions and secondly the phosphonium analogue triethylphosphonium bis(trifluoromethylsulfonyl)imide ([$P_{222}H$][$NTf_2$]), forming comparatively weaker hydrogen bonds. Structurally these two ionic liquids differ only slightly in the central atom of the cation. However, the dynamical properties are strongly affected by the different hydrogen bond strength. In this work we measured frequency- and temperature-dependent 1H and 19F relaxation rates by using fast-field-cycling NMR relaxometry (FFC NMR), which provides access to translational and rotational correlation times as well as self-diffusion coefficients. Since the protons are only located on the cations and the fluorine nuclei only on the anion we obtain these properties ion-specific. Molecular dynamics (MD) simulations are used to validate our results. Both approaches, FFC NMR and MD simulations, show higher rotational correlation times and lower self-diffusion coefficients for [$N_{222}H$][$NTf_2$] indicating a stronger hydrogen bond.

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# Extraction of Ni(II) Ion from an Aqueous Solution by Functionalized Ionic Liquids

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Room-temperature ionic liquids attract attention from various fields, such as secondary batteries, organic syntheses, and drug delivery systems, because of their unique properties of electroconductivity, negligible volatility, nonflammability, and low toxicity. Especially, ionic liquids have several advantages in solvent extraction. One of them is their low volatility. Human being and nature are exposed to vapor of organic solvents like chloroform and carbon tetrachloride in conventional solvent extraction. The other is the high polarity of ionic liquids consisting of cations and anions. Therefore, ionic liquids may accept highly charged species, such as metal ion complexes. This is the most striking benefit of ionic liquids as extraction solvents. In conventional solvent extraction, which uses low polar solvents, the metal ion complexes have to be reformed to an uncharged species by association with appropriate anions. However, normal ionic liquids, such as imidazolium and bis(trifluoromethylsulfonyl)amide systems, cannot strongly capture metal ions due to the low basicity of the cations and anions. Thus, ionic liquids need to be modified to have a high coordination ability.

We synthesized four functionalized ionic liquids (FILs) by modifying the hydroxy, carboxy, ester, and hydrazide groups on the cation's alkyl chain of 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, C8mimTFSA. First, the coordination ability of the FILs for Ni(II) ion was explored in non-functionalized C8mimTFSA by the Job's method with ultraviolet-visible spectroscopy. Ni(II) ion was chosen as a representative metal ion due to its structural and valence stability. Second, the immiscibility of the FILs with water was assessed to extract metal ions from aqueous phase to FIL phase. Finally, extraction of Ni(II) ion was tried at an ambient temperature. Additionally, infrared spectroscopy was applied to the Ni(II)-FIL solutions to clarify the coordination structure of Ni(II)-FIL complexes. As expected, charged complexes could be extracted from the aqueous phase into the FIL phase. In the presentation, the coordination and extraction abilities of the four FILs will be discussed on the molecular scale according to the above experimental results.

# The bottom up approach: frequency dependent relaxation rates from md simulations

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By using Fast Field Cycling (FFC) NMR spectroscopy, dynamical processes can be studied over many orders of magnitude. However, interpreting FFC-NMR data often requires motional models that often use simplified analytical forms of the relevant time correlation functions. Here we propose a novel approach for computing the inter- and intramolecular contributions to the magnetic dipolar relaxation from molecular dynamics (MD) simulations, enabling us to predict NMR relaxation rates addressing the full FFC frequency range, covering many orders of magnitude, while also avoiding influences due to limitations in system size and the accessible time interval. Our approach is based on combining the analytical theory of Hwang and Freed (HF) [1] for the long-range intermolecular contribution of the magnetic dipole-dipole correlation function with MD simulations [2].

We show that the correlation functions due to the HF-theory do asymptotically converge with our MD simulation results at long times. Here we apply this approach to compute the inter and intramolecular NMR relaxation of 19F nuclei in the ionic liquid n-pentyl- pyridinium bis-(trifluoromethyl-sulfonyl)imide (C5Py-NTf2 ) to study the dynamic of the NTf2 anion. Thus, we are able to study both the influence of the translational dynamics and the rotational dynamics of the anions. Moreover, by using our MD simulation based approach, we are able to disentangle the different contributions to the intramolecular 19F NMR relaxation rate due to the complex intramolecular dynamics of the anion.

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# Sustainable PET solvation in eutectic solvents

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PET (polyethylene terephthalate) is a widely distributed polymer, comprising 8% of the total global plastic production. PET-based products are ubiquitous in modern life, ranging from packaging to, electronica and medical devices. However, it strongly contributes to environmental pollution if not properly disposed of or recycled. In fact, improperly discarded PET items can end up in landfills, waterways, and oceans, where they can harm wildlife and ecosystems. On the other hand, proper recycling of PET reduces the demand for new plastic production and helps mitigate environmental impacts.

Here we show experimental and computational results on our investigation on PET solvation in two different natural mono-terpenoids and their mixture. Such solvents represent a valid and sustainable option for efficient recycling of commercial PET. [1] We probed the performance of carvacrol (CARV) [2] and thymol (THYM), two structural isomers, and their 1:1 mixture in a commercial PET solubilization, achieving a remarkable >10 wt% solubilization at 150°C without inducing the plastic degradation.

We explored the conformation of polymer coil in the three solvents using Dynamic Light Scattering (DLS) and Small Angle X-ray Scattering (SAXS) experiments, highlighting different degrees of solvation capability of the terpenoids and their mixture. Furthermore, Molecular Dynamics (MD) simulations of the same systems allowed obtaining an atomistic description of the solvation mechanism of thymol and carvacrol towards PET. This approach shows that the PET's high solubility in these media is driven by thymol's hydrogen bonding interactions with PET oxygens and carvacrol's π-π interactions with the PET aromatic rings. This work represents a significant advancement in the comprehension of PET dissolution utilizing a natural ES based on monoterpenoids, paving the way for sustainable PET recycling.

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## The role of hydrogen-bonds in the formation and structural properties of deep eutectic solvents

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Deep eutectic solvents (DESs) are currently ruling the research topic about advanced processing media as a more sustainable alternative to traditional solvents owing to their simple preparation, versatility, and environmentally benign pedigree. DESs also belong to the "designer" solvents category, meaning that their chemical-physical properties can be tuned to meet specific requirements through a judicious choice of the precursors and their relative composition. Aside from practical significance, the scientific debate about the fundamental definition of these systems is still going on. At present, DESs are defined as mixtures of two or more compounds showing a melting point depression that is deeper than the ideally predicted one for a defined composition. This unusual thermal behavior seems to rely on the hydrogen-bond (H-bond) network established between the parent compounds. However, alternative interactions concurring as a driving force for the melting point depression have been also demonstrated, and thus this definition seems to start crackling. On the other hand, the achievement of a clearer predictive understanding of the structure–property relationship necessary to design new task-specific DESs is a legitimate goal.

In this contribution, I will show you the results from our work where we tackled some of these unanswered questions through an in-depth structural investigation of different types of DESs. This includes both salt-based DESs belonging to the so-called type "I – IV" categories, and the more recently developed "type V" ones, which are formed by neutral molecular species like terpenes and phenolic compounds. [1,2] Attention will be given also to the structural modification induced by the addition of a co-solvent (e.g., water, methanol, ethanol) to the DES phase. [3] To this purpose, we resorted to a combined approach among different techniques, including synchrotron radiation X-ray absorption and scattering, Raman/IR spectroscopies, differential scanning calorimetry, and molecular dynamics simulations. The combined experimental and theoretical outcome was able to elucidate the complex nature of interactions able to shape the structural arrangement of these H-bonded systems.

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## Investigation of Hydrogen Bonding using the Attenuated Total Reflectance Spectroscopy in the Ultraviolet Region

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The lone pair electrons of a hydrogen bond acceptor are the electrons that are "covalent" in the hydrogen bond. Therefore, electronic transitions caused by lone pair electrons can serve as probes directly affected by changes in hydrogen bonding. Spectroscopic studies using X-ray Photoelectron Spectroscopy (XPS) and other techniques have been conducted to investigate these transitions. On the other hand, electronic transitions due to lone pair electrons are also observed in the far-ultraviolet (FUV) region, where transitions near the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) are observed.

We have developed an attenuated total reflectance spectrometer in the FUV region (ATR-FUV) and pioneered a technology to easily observe FUV spectra in solutions. For example, the far-UV spectrum of liquid water has recently been observed as a transmission spectrum, but even prior to that, we observed the FUV spectra of liquid $H_2O$ and $D_2O$ using ATR-FUV. Furthermore, due to its simplicity, this measurement method has allowed us to observe and report on a wide variety of aqueous solutions.

As a result, it was revealed that the A-X transition of water in the FUV spectrum changes very sensitively depending on the coordination experienced by the lone pair electron of water. For instance, ATR-FUV spectra of super concentrated aqueous solutions, such as Water-in-Salt (WIS) and Hydrated Melt (HM) using a lithium salt, were measured. The effects of anions and cations on the ATR-FUV spectra were examined. The findings indicate that the transition energy of the A-X transition of water in HM and WIS increased by nearly 10 nm (equivalent to an energy shift of over 0.3 eV) compared to a typical aqueous electrolyte. It was also discovered that the transition energy of water varies depending on the environment of the non-bonding electron, which is either directly linked with or influenced by hydrogen bonding with other water molecules, or directly associated with $Li^+$.

## Multiscale probing of interactions in aqueous ionic solutions

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Solutions of charged atoms/molecules in water are an essential ingredient of many diverse aspects of life and relevant to technology: The bodily fluids (blood and cellular fluid are prime examples), but also are the key contents of batteries. Ionic solutions are commonly described as homogeneous mixtures in which ions are statistically distributed. However, Kirkwood showed nearly a century ago that this simple description is incomplete for the relevant concentration range and that the structure of electrolyte solutions is far more complex. Disentangling the structural complexity of water, ions and (macro)molecules and their respective interactions requires structural information on multiple length scales, from the single water molecule to the nano- and microscale. Here, we present a combination of linear and nonlinear light scattering approaches combined with vibrational spectroscopy that can be used to map both short – and long-range interactions as well as collective effects pertaining to all molecular actors. Our findings can shed new light on a variety of biological and technological processes.

## The birth and evolution of solvated electrons in water

Fabio Novelli

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The photo-induced radiolysis of water is an elementary reaction in biology and chemistry, forming solvated electrons, OH radicals, and hydronium cations on fast time scales. Here, we use a novel Optical-Pump Terahertz-Probe (OPTP) spectroscopy set-up to trigger the photo-ionization of water molecules with optical laser pulses at ~400 nm and then time-resolve the transient solvent response with broadband terahertz fields with a ~90 fs time resolution.

When pure water is photoionized, we observe three distinct spectral responses in the OPTP experiments[1]. The first is a positive broadband mode that can be attributed to an initial diffuse, delocalized electron with a radius of $(22 \pm 1)$ Å, which is short lived (< 200 fs) because the absorption is blue-shifting outside of the THz range. The second emerging spectroscopic signature with a lifetime of ca. 150 ps is attributed to an inter-molecular mode associated with a mass rearrangement of solvent molecules due to charge separation of radicals and hydronium cations. After ~0.2 ps we observe a long-lasting THz signature with depleted intensity at 110 cm-1 that is well reproduced by ab initio molecular dynamics. We interpret this negative band at 110 cm-1 as the solvent cage characterized by a weakening of the hydrogen bond network in the first and second hydration shell of the cavity occupied by the localized electron.

The dissolution in water of iodide anions (I-) increases the number of photo-generated electrons. In particular, we showed in a separate publication[2] that a 9M water solution of sodium iodide displays a large (-20%) and fast (~70 fs) OPTP signal. As the optical properties of the liquid are modulated on a timescale that is shorter than the duration of the THz optical cycle, the THz fields transmitted by such concentrated, salty liquid solutions are upshifted in frequency from ~1 to ~3 THz, with an efficiency of about 4%. This technique could be used to tailor THz fields at low frequency and, in the long term, it could open the door to "water electronics." An advantage is fast decay time of the THz photo-switch, ~70 fs, which could be used at a fast rate or, equivalently, have a large bandwidth than typical semiconducting devices.

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## Structure and optical properties of water: a study on aqueous solutions and ice

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Water is a unique solvent which plays a fundamental role in biochemical and industrial processes, and more in general in life as we know it. Many of the peculiar properties of water arise from its ability to form hydrogen-bonded networks. [1] However, despite the significant efforts, both the electronic structure and optical properties of water have still not been fully elucidated. In recent years, several theoretical works have focused on investigating the ground state and optical absorption of liquid water and ice, whereas less effort has been dedicated to emission properties. [2-4] While the luminescence of UV-excited ice has been studied over the last few decades, [5, 6] more recent experiments have shown an anomalous intrinsic fluorescence of HCl and NaOH aqueous solutions. [7] In this context, our goal is to study UV absorption and emission of crystalline ice and HCl and NaOH concentrated aqueous solutions at a quantum-chemical level. All our UV-optical spectra have been computed using the WEST code [8] which allows us to work within periodic boundary conditions, hence, to model the bulk properties of the system of interest. This leads to a more accurate description of the water-based systems, whose properties are often computed using cluster models due to the limiting computational cost. The method here employed then allows us to calculate absorption and emission spectra, studying the nature of the transitions and their relation with specific structural and electronic properties of the system.

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## Molecular basis for acidic proteomes in halophilic proteins

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Proteins of obligatory halophilic organisms - which accumulate KCl in their cytoplasm up to multimolar concentrations - remain folded and functional despite these hard conditions. This ability is thought to emerge from their unusual amino acid composition: among other differences, halophilic proteins are much richer in acidic amino acids than their non-halophilic (also called mesophilic) counterparts: they have a typical net charge of $-8*e*$ or $-10*e*$, rather than the $-3*e*$ or $-4*e*$ found in mesophilic proteins. We have used molecular dynamics simulations with classical, atomistic force fields to investigate how the excess acidic amino acids enable halophilic proteins to remain folded and functional at high KCl concentrations. Simulations of 5 pairs of halophilic and mesophilic proteins, with different sizes, net charges and degrees of halophilicity have revealed that the solvation shell composition of proteins varies systematically with the surface density of acidic amino acids making up proteins. Contrary to expectations, however, that composition is robust to changes in electrolyte concentration for *all* proteins investigated, suggesting that an excess of acidic amino acids is not necessary to keep proteins hydrated in solvents with low water activity as previously thought. Free energy calculations further revealed that spatially close acidic amino acids on proteins can, at high salt concentration, interact with cations in solution to form cooperative, stabilizing interactions. These interactions do not rely on rigid relative orientations of their side chains, and may occur also in unfolded but collapsed protein configurations. Because the ensemble of collapsed but unfolded protein configurations is much smaller than the total unfolded configuration ensemble, the net effect of the cooperative interactions should stabilize the folded protein configuration, however. Simulations also revealed that, contrary to expectations, the more intense hydrophobic effect at high salt concentration has little impact on protein dynamics. Rather, salt concentration impacts protein dynamics non-linearly, through electrostatic interactions: flexible regions rich in like-charges might experience lower amplitude motions at higher salt concentration, whereas the opposite may occur for flexible protein regions rich in unlike-charges , because of enhanced electrostatic screening at high salt concentrations. These results have implications for the rational design of enzymes to produce molecules, to reduce $CO2$, or to produce $H2$ in saline solutions, thus reducing usage of scarce fresh water resources.

Oral contribution

Thursday 12th

# Solvent Vibrations Reflecting Telomere G-Quadruplex Rearrangements during Thermal Unfolding

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G-quadruplexes (G4s) are non-canonical four-stranded DNA helical structures formed through the stacking of four in-plane Hoogsteen-paired guanine bases [1,2]. Their location in the human genome is often related to cancer biology and genome activities like transcription, replication, genome stability, and epigenetic regulation [3, 4].
In general, not much is known about the hydration layer around G4. Most of the work has been performed in crowded conditions, where it seems that their pronounced polymorphism is strictly regulated by their hydration [5–7]. Water molecules can go in both the medium and the narrow grooves; however, recent research suggested that the latter can accommodate extended filiform networks of water molecules, called spines [8]. Antiparallel and hybrid topologies are indeed more prone to host stable water spine structures. In diluted conditions, many factors affect the G4 structure because each state is separated by small energy barriers, therefore it is intriguing to investigate the relation between solvation and G4 conformations. We exploited UV Resonance Raman scattering to simultaneously explore the vibrational behaviour of a human telomeric G4 and its aqueous solvent as the biomolecule undergoes thermal unfolding [9]. We found that the OH stretching band, related to the local hydrogen-bonded network of a water molecule, was in strict relation with the vibrational features of the G4 structure as a function of temperature. In particular, the modifications to the tetrahedral ordering of the water network were strongly coupled to the G4 rearrangements, showing changes in temperature that mirrored the DNA multi-step melting process. The comparison between circular dichroism and Raman results supported this view.
The present findings provide novel insights into the impact of the molecular environment on G4 conformation. Improving current knowledge on the solvent structural properties will also contribute to a better understanding of the role played by water arrangement in the complexation of G4s with ligands.

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Oral contribution

Thursday 12th

# Data Driven Discovery of the Origins of UV-Absorption in Alpha-3C Protein

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Ultraviolet absorption in protein have typically been associated to the presence of aromatic groups. However, recent studies have demonstrated that proteins lacking aromatic groups can also exhibit absorption in this region of electromagnetic spectrum. One of the recently studied synthetic non-aromatic protein, α3C, has been experimentally observed to exhibit absorption in the ultraviolet and visible range, with an absorption tail ranging from 250 – 800 nm. Motivated by these results and previous theoretical studies on amino acid dimers in vacuum, we decided to explore these absorption properties using a novel approach. In this work, following the classical molecular dynamics simulation of α3C in an aqueous solution, we applied unsupervised machine learning techniques to identify and cluster emergent atomic environments from the simulation configurations. We identified three distinct major clusters and investigated their absorption properties separately using density functional tight binding (DFTB) combined with the quantum mechanics/molecular mechanics (QM/MM) method.

Oral contribution

Thursday 12th

# Hydration shell structure of ordered and disordered proteins

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It is well known that many properties of protein molecules (catalytic activity, binding to other molecules, dynamical properties, folding etc...) are fundamentally influenced by their solvent layer: by the properties of water molecules and the H-bonded network they form around the macromolecule. It is commonly assumed that at least one hydration layer of is necessary for the protein to be functional and for enzymes to be catalitically active. However, the effect of the properties and extent of the H-bonded network further from the surface of the biopolymer is still a controversial issue. In the present paper we investigate this question in part using the structural descriptors known from water structure analysis (local structural index, tetrahedrality, Tanaka order paremeter, ring formation.) In our study we analyse in detail the first hydration layer, which is known to have a non-homogeneous structure. Here we also pay particular attention to the amino acid composition and the existence of different secondary structural forms such as helices, sheets and turns. Our investigations are carried out for both a classical, ordered (lysosime) and for an intrinsically disordered protein (HMG-I, hgh mobility group). We characterize the lifetime of water molecules in the hydration layer using a lifetime distribution function, taking into account that molecules can move in and out of the layer. The dynamical properties of water molecules, which are known to undergo significant changes (slowing down), are analysed using orientation correlation functions and displacement/time distribution functions. The well-defined clusters present in the H-bonding network for both protein and surface water molecules are analysed using the well known louvain method from network theory.

Oral contribution

Thursday 12th

# Dynamics of Hydrated Soft Matters Studied by Broadband Dielectric Spectroscopy and Molecular Dynamics Simulations

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We have been studying temperature dependence of dielectric response of aqueous solutions and hydrated soft matters such as proteins and lipid bilayers from the sub-GHz to THz frequency range. The broad frequency range is covered by several spectrometers. A vector network analyzer is used for the sub-GHz to 20 GHz region, and two time-domain spectrometers covers sub-THz region (30 GHz to 300 GHz) and THz region (0.2 THz to 2.0 THz). When it is necessary, we use a FTIR spectrometer for the far-IR region (50 cm-1 to 700 cm-1). Temperatures for the measurement can be controlled for all the spectrometers from -40°C to room temperature. This allows us to observe temperature dependence of the complex dielectric spectra for the almost entire spectral region. By using this system we measured temperature dependent dielectric response of the dehydrated and hydrated states of various soft matters such as globule protein, membrane protein, and lipid bilayer. Generally, there is a low-frequency vibrational modes due to the global motions of the soft matters in the THz frequency region, which does not show large temperature dependence. In the GHz region a spectral component due to the relaxation dynamics of the hydration water molecules is observed, and this spectrum shifts to the higher frequency side when temperature increases. At around -40°C the low-frequency relaxation component and the high-frequency vibrational component overlaps, which causes sudden increase in the intensity of the absorption spectrum in the THz region.

Furthermore, we performed molecular dynamics simulations for hydrated globule proteins to interpret these experimental observations. The decomposed total dipole moments into protein, hydration water, and their cross correlation contributions enables us to describe the dielectric relaxation processes independently. Furthermore, these contributions are divided into the local contributions in terms of the residue and the backbone components in lysozymes. The whole line shapes of the spectra were well reproduced in the range from 0.1 GHz to 2.0 THz.

*Oral contribution*

*Thursday 12th*

## Exploring 2-propanol and its fluorinated derivatives using femtosecond optical Kerr effect spectroscopy and theoretical chemistry methods

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2-Propanol (IP) is a commonly used organic solvent for cleaning optics and electronic contacts, in DNA extraction, and as a sanitizer (70% solution in water) due to its antiseptic properties. Fluorinated alcohols, such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), are frequently employed as co-solvents having a significant impact on the structural and dynamic properties of proteins and peptides in aqueous solutions. In contrary to IP and HFIP, the less studied 1,1,1-trifluoro-2-propanol (TFIP) is a chiral molecule and exhibits some peculiar behavior when mixed with water. While IP and HFIP mix with water at any ratio, TFIP shows phase separation for some concentrations, which was previously attributed to low affinity between CH3 and CF3 groups, hindering micelle-like assembly formation [1]. Here, we employ femtosecond optical Kerr effect spectroscopy combined with molecular dynamics simulations and quantum-mechanical calculations to investigate the vibrational, translational, and rotational dynamics as well as the local structure of IP, TFIP, and HFIP molecules. For TFIP we present results for pure enantiomer and a racemic mixture.

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*Oral contribution*

*Thursday 12th*

## Microscopic dynamics of liquid glycerol in ambient conditions: new insights

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The molecular dynamics simulation of ambient condition glycerol are used to calculate the time dependent atom-atom van Hove correlation functions $G_{ab}(r,t)$, as well as the corresponding intermediate scattering functions $F_{ab}(k,t)$ and the dynamical structure factors $S_{ab}(k,\omega)$, both for the self and distinct contributions. Their study reveals the microscopic origin of the high viscosity of this liquid [1]. In particular it is found that room temperature glycerol behaves as a supercooled liquid [2], with the typical power law decay of the relaxation times. Interestingly, it is also found that the charge order decay at short range is significantly faster than that found in water and other associated liquids. The puzzling contrast between very fast short time dynamics and slow long time dynamics is traced back to the nature of the charge order with multiple H-bonding possibilities on the same molecule. This order leads to a stretched exponential decay over the entire time range, characterized by a rapid reorganization of the short range molecular order and slow long time dynamics. This behavior persists across different force fields, suggesting that the mechanisms described are genuine to the real glycerol.

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# Co-localized infrared/Raman spectroscopic investigation of water/H2/N2/CO2 mixtures at high pressure and temperature

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Understanding the mutual solubility of water with multi-component gas mixture ($CO_2$, $N_2$, $H_2$) at high pressures and temperatures is of great interest in various fields such as gas storage in deep aquifers [1], hydrogenation processes for biomass valorization [2] and for the understanding of the chemistry in hydrothermal vents.[3] Until now, phase behavior,[4] spectroscopic studies [5] and atomic scale insights [6] of water-$CO_2$ binary mixtures have been performed for a deeper molecular level understanding of their thermophysical properties. It was found that the increase with temperature of the $CO_2$-water mutual solubility with a complete miscibility reached at temperature close to the critical temperature of water was related to a progressive breakdown in the hydrogen bond network of water leading to a predominant number of $H_2O$ molecules existing as monomers at the highest temperatures. However, little to none is known about the phase behaviour of more complex systems such as ternary and quaternary mixtures.[1] In this context, we propose a novel co-localized Infrared/Raman spectroscopic approach to investigate the mutual solubility of water with $CO_2$, $N_2$ and $H_2$. The simultaneous recording of IR and Raman spectra using a single high-pressure cell allows several benefits by saving time and resources, and allowing a direct correlation between IR and Raman data, and thus allowing quantitative analysis from Raman data. Thus, we have investigated the gas and the liquid phase of the binary, ternary and quaternary mixtures of water-$CO_2$-$N_2$-$H_2$ in order to characterise the evolution of the local order in both phases as a function of temperature in the range 40-320°C at a constant pressure P=20 MPa. In particular, the effect of $H_2$ and $N_2$ on the thermophysical properties of the $CO_2$/water mixtures will be presented.

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# Dynamic Monte Carlo method enhanced by machine learning model to understand mass transport in heterogeneous medium

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Molecular diffusion in heterogeneous media is a ubiquitous phenomenon observed in a wide variety of physical, chemical, and biological systems. Understanding these phenomena requires detailed insight into the diffusion mechanism in heterogeneous systems. The timescale of mass transport in the heterogeneous systems is typically longer than that of all-atom molecular dynamics (MD) calculations. Thus, the ability of MD simulations to directly address these phenomena is limited. One approach to overcome this difficulty is to construct and evaluate coarse-grained dynamics of the transported molecules using dynamic Monte Carlo (MC) method [1]. Using this methodology, we have successfully investigated the transport of the hydrogen gas molecules in the polymer electrolyte membranes [2,3]. The input for this dynamic Monte Carlo method is the free energy landscape and position-dependent diffusion constant of the transported molecules. The free energy landscape can be evaluated rigorously via many conventional methods of MD calculations. To evaluate the position-dependent diffusion constant of the light molecule like hydrogen molecules, we developed new method using flat-bottom potential [4].

Although the free energy landscape and position-dependent diffusion constant can be rigorously evaluated via MD calculations, such calculations are computationally expensive. This cost is the barrier to broader application of the dynamic MC method to the variety of the large-scale systems. Hence, we are motivated to reduce the cost by using a surrogate model to predict these two quantities via a machine learning (ML) model. The ML model is expected to replace some of the computationally demanding MD calculations of the free-energy landscape and position-dependent diffusion constant. For this end, we used a support vector regression with the smooth overlap of atomic position (SOAP) kernel. In an application to the hydrogen molecules in the polymer electrolyte membranes, the trained model with appropriate hyperparameters predicted these quantities with an *R*$^2$ value higher than 0.8. Using these two quantities, we evaluated the global diffusion constants and found a good agreement with the reference value. Therefore, we concluded that the combination of the dynamic MC method and ML model is a promising approach to understand the mass transport in heterogeneous systems.

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Oral contribution

Thursday 12th

# Understanding the Molecular Structure of Choline Geranate (CAGE): Insights from Molecular Dynamics Simulations

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Choline and geranate-based (CAGE) solvents have recently emerged as promising candidates for oral and transdermal drug delivery systems owing to their biocompatible and antibacterial attributes.

Previous investigations have provided insights into CAGE, including the effect of different choline and geranate ratios on physicochemical properties [1], the influence of water [2], and structural evaluations using experimental techniques [3]. However, there remain gaps in the structural details and a lack of systematic theoretical research to address , among others, the reliability of the force-fields available or the nature of the interaction between -COOH and -COO of geranic acid and geranate [4].

In this study, CAGE in 1:1 and 1:2 choline/geranate ratios with an 8% water content was analyzed by employing classical molecular dynamics (MD) simulations alongside Density Functional Theory (DFT)-based molecular dynamics. Three distinct transferable force-fields were employed for CAGE, including non-polarizable CL&P, AMBER, and polarizable CL&Pol force fields, while non-polarizable TIP4P and polarizable SWM4-NDP models were utilized for water.

Segregation between polar and non-polar domains is observed in both CAGE1:1 and CAGE1:2, and the polar components (water, the -OH of choline, the -COOH of geranic acid, and the -COO of geranate) establish an intricate hydrogen-bond network. Specifically, in CAGE1:1, hydrogen-bond interactions are found between each oxygen of the -COO of geranate and one choline and one water molecule on average, each of which simultaneously interacts with another geranate. In CAGE1:2, additionally, geranic acid's -COOH group forms hydrogen bonds with the -COO of geranate, as well as with the oxygen of a water molecule, which in turn interacts with another geranic acid. The overall description of the structure is consistent across all three force-fields, with slight discrepancies between CL&Pol and CL&P. However, AMBER exhibits appreciable differences in the distribution of water around geranate and the interaction between geranic acid and geranate.

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Oral contribution

Thursday 12th

# Properties of binary organogels comprising phenol and anionic surfactant investigated by sound damping and dielectric relaxation measurements

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We study audible sound absorption and dielectric relaxation measurements, where binary organogels comprising phenol and a surfactant (AOT). We have found that collective motions of organogel higher structures, or the fibrous network, are responsible for characteristic audio and dielectric relaxations.

Organogels are applying to be a host material in which optical devices, such as emitters, are dispersed. Gels can easily form a shape we want, which works as an advantage of the material design. In the previous paper by an present author and others [1, 2], we have studied organogel availability and properties comprising phenols (p-chlorophenol and derivatives) and a surfactant AOT (bis(2-ethylhexyl) sulfosuccinate). As a higher-order structure of the organogel, we found a fibrous network with dimensions where length and diameter are 20μm and 1μm, respectively. This network is put out from self-assembly of the binary gelators. We have reported on the microscopic structure, rheology, and transparency of these gels [1, 2]. We talk about in this conference audible-zone sound and dielectric relaxation measurements, for better understanding of organogel applications.

The gelators (phenol and AOT) and solvents (m-xylene, 2,2,4-trimethylpentane, and cyclohexane) were used. The 0.2 mol dm–3 solutions of each gelator were mixed to obtain an organogel spontaneously. In the audio measurements, the organogel material is filled in a poly(urethane) tube, where the sound damping with and without organogels was recorded.

Our dielectric measurements use 3-terminal electrode containing a main electrode that is sandwiched by two guard electrodes. The dielectric spectra were acquired using an Alpha A analyzer (Novocontrol). The frequency and temperature were swept between 10 mHz–10 MHz and 223 K–298 K, respectively.

Results from audible sound damping indicate that the organogel in alkane (2,2,4-trimethylpentane) absorbs 20 dB at 7,000 Hz, whereas 15 dB at 3,000 Hz. Dielectric relaxation measurements reveal that the real and imaginary parts of relaxation depend on temperature, where characteristic relaxation modes in frequency appear at around 1—1,000 Hz. We will understand sound damping and dielectric relaxation in relation with organogel higher-order structures.

# Small-angle neutron scattering and Raman spectroscopy studies of solvation behavior in aqueous solutions of alcohols, amines and ionic liquids

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Solvation behavior of various types of small organic molecules are studied by scattering and spectroscopic techniques, aiming to reveal their structural organization and eventual self-assembly in aqueous solutions, and the closely related vibrational dynamical signatures of the surrounding water network. Prototypical series of methylimidazolium - based ionic liquids, and methyl-substituted urea solutions were investigated by UV Raman spectroscopy and small-angle neutron scattering. Selected Raman signals in different wavenumber ranges show the local organization of cation-anion pairs as a function of the increasing amount of water in a wide range of concentrations. The high-frequency range of Raman spectra was analyzed by a differential method to extract the solute-correlated (SC) spectra from the OH stretching profile of water, which emphasize the molecular structuring of the interfacial water in the hydration shells around the selected anions.

The neutron scattering data show the water – IL segregation at nanometer length scale and obey the Ornstein-Zernike form of statistical concentration fluctuations. Raman data indicate that the organization of the interfacial water differs markedly for different solutions, and reflect the specific anion–water interactions. In particular, in the case of [BMIM][BF4], which forms weaker hydrogen bonds with water, the aggregation properties depend strongly on concentration, and correlate with the local changes in the interfacial water. On the other hand, stronger water–anion hydrogen bonds and more persistent hydration layers were observed for [BMIM][TfO], which likely suppress aggregation of the IL.

While the studied aqueous solutions of methylimidazolium ILs, alcohols, amides and heterocyclic amines all show strong concentration fluctuations, the structure of aqueous solutions of linear alkylamines exhibit qualitatively different behavior, characterized by appearance of a strong and concentration-dependent pre-peak feature at small scattering angles, which is interpreted as the signature of a locally ordered microheterogeneous structure of polar and apolar domains, in a manner of charge ordering in ionic systems [2].

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# Chemical Continuum: Overcoming Discrete Notions Underlying Fluctuations in Water

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Is Liquid Water really a tale of two liquids? Is the structure of the excess proton in water an Eigen or Zundel species? Can molecules dissolved in water be rigidly classified into hydrophobic or hydrophilic? Discrete or binary classifications are at the heart of the interpretation of phenomena associated with understanding the properties of aqueous solutions. In this discussion, I will share three stories that have recently emerged from our group that will attempt to challenge some of these ideas.

One of the most well studied and common interpretations of water's anomalous properties is the existence of two liquids namely the low-density liquid (LDL) and high-density liquid (HDL). Similarly, two-state models (Eigen or Zundel) are central to acid-base chemistry which is at the heart of characterizations of proton transfer in liquid water. Here, I will illustrate some recent work leveraging unsupervised learning techniques to highlight how chemical discreteness limits our interpretations of fluctuations of the hydrogen-bond network in these contexts.

A critical first step in solvation theory is the creation of a cavity. The thermodynamics associated with this process is at the heart of hydrophobicity and its two-length scale cross over. I will share some recent data-driven approaches that will illustrate how shape and geometry affects the crossover in hydrophobicity.

In the final part of my talk, I will discuss some recent findings on how oily (non-polar) molecules can pick up polar traits due to subtle quantum mechanical effects. We believe that this feature is central to an ongoing raging debate in the field on the origin of the negative charge at hydrophobic surfaces which we attribute to the coupling between the hydrogen-bond network topology and charge transfer.

# Thermodynamics of hydrogen bonding liquids using the van der Waals concept

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In 1983, summarizing their developments of perturbation theory, Chandler at al [1] declared that for systems with electrostatic interactions, and for hydrogen bonding substances in particular, the so-called van der Waals picture of liquids breaks down. The strength of attractive forces, that became competitive with typical repulsions, was recognized as the main reason for such a failure.

In this presentation we argue that the recently proposed approach [2, 3] by suggesting to consider all short-range attraction forces be responsible for changes of excluded volume in the system, results in the first-order perturbation theory that performs extremely accurately over a wide range of thermodynamic conditions. To illustrate, the proposed theory first is applied to Lennard-Jones-like Yukawa fluid – the case, when all calculations can be reduced to the closed analytical description using existing MSA solutions [4]. An extension of this approach to complex systems, like ionic and associating fluids, is discussed. The importance of excluded volume phenomenon in a particular case of hydrogen bonding substance such as water is illustrated as well.

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# Ag+ ion coordination in molecular solvents: a complex case study

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Knowledge of the solvation structure of a metal cation in aqueous and organic media can disclose a fundamental understanding of its dissolution, transport, and thermodynamic properties. As far as the Ag+ ion is concerned, its coordination chemistry has been the subject of a debate spanning at least the last four decades. This is well testified by the proliferation of coordination models for Ag+ solvates presented so far, ranging from common tetrahedral or octahedral to more exotic trigonal bipyramidal or linearly distorted tetrahedral geometries, through both experimental and theoretical investigations.[1–3] This complexity derives from the peculiar electronic properties of the Ag+ center, for which the relativistic effects cannot be neglected and have a pivotal role in shaping this peculiar coordination chemistry. In this way, this ion poses a hard test bench challenging the state-of-the-art techniques and data analysis methods for the determination of metal ions coordination in solution.

In this research, we carried out a re-evaluation of the Ag+ ion coordination in aqueous solution and organic media through both synchrotron radiation spectroscopic techniques and simulation methods. The conjunction of extended X-ray absorption fine structure (EXAFS) and X-ray absorption near-edge structure (XANES) data analysis, aided by ab initio molecular dynamics, allowed us to overcome the previous discrepancies present in the literature. A complex picture of the Ag+ ion hydration was obtained, where two first-shell water molecules coordinate with a linear geometry, while the hydration sphere is completed by two more distant intra-shell water molecules to form a "2+2" model.[4] A similar picture is obtained in methanol solution, despite half the hydrogen-bonding (H-bonding) capability of this solvent molecule compared to water. Differently, a regular tetrahedral coordination was unambiguously determined in the aprotic dimethyl sulfoxide with advanced theoretical models in the framework of the finite differences method for the analysis of the XANES data. The coordination thus results in being highly influenced by the balance between the ion-solvent and solvent-solvent interactions, the latter being constituted by the H-bonded network among first- and outer-sphere solvent molecules.

Altogether these data show how the Ag+ solvation is far from being described with simple limit geometries. We expect our results to provide corroborated fundamental knowledge for future investigations involving solutions of Ag+ salts, which largely depend on structural insights such as those provided in this work.

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# Evidence of ferroelectric features in low-density supercooled water from ab initio deep neural-network simulations

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Water's peculiar behaviour and its anomalies have fascinated scientists for decades, posing intriguing questions about the nature of this essential substance.

In particular, over the last decade an increasing body of evidence has emerged, supporting the existence of a metastable liquid-liquid critical point in supercooled water, whereby two distinct liquid phases of different densities coexist. This talk delves into our recent research on the liquid-liquid transition in deeply supercooled water, utilizing cutting-edge deep neural-network (DNN) potentials. We explore the complex interplay between density and polarization fluctuations that govern the transitions between the low-density (LDL) and high-density (HDL) liquid phases. Our findings reveal unexpected dynamics in the LDL phase, including spontaneous polarization and collective reorientational angular jumps of water molecules within the hydrogen-bond network. These discoveries offer fresh insights into the mechanisms underlying water's anomalies and provide a deeper understanding of its fundamental properties. The talk will highlight the significance of electronic polarization and its role in shaping the dynamics of supercooled water, paving the way for future experimental and theoretical investigations in this exciting field.

Cesare Malosso, Natalia Manko, Maria Grazia Izzo, Stefano Baroni, Ali Hassanali: "Evidence of ferroelectric features in low-density supercooled water from ab initio deep neural-network simulations", 2024; [http://arxiv.org/abs/2404.08338 arXiv:2404.08338].

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# Investigation of polymer networks using atomistic simulations

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In the last years, a growing interest in hydrogel and microgel polymer networks has been developed, favored by the significant advances in chemical and *in silico* synthesis. They can be formed through the cross-linking of hydrophilic polymer chains within an aqueous micro-environment. Depending on the nature of the constituent polymer, the mechanism of cross-linking may proceed through the formation of reversible/irreversible bonds, leading to the formation of physical/chemical polymer networks. In this talk I will provide two examples of investigations of chemical and physical polymer networks using atomistic simulations.

In the first part, I will focus on chemical polymer networks, i.e. microgels based on the thermo-responsive polymer poly(N-isopropylacrylamide) (PNIPAM), which are usually investigated for the volume phase transition, a sharp change of the network size because of a temperature variation, that finds a great variety of applications. I will discuss the importance of water for a reliable *in silico* description of a polymeric aqueous solution [1,2]. Then, I will highlight how microgels show very interesting features even at low temperature. By comparing atomistic molecular dynamics simulations with neutron scattering experiments, I will provide evidence that PNIPAM microgels can undergo a dynamical transition akin to that observed in proteins [3,4], in which water plays a driving role [5].

In the second part, I will focus on an example of physical polymer network made of gellan, an anionic polysaccharide. Recently it was shown that gellan microgels are promising materials for paper artworks restoration [6] and thus, understanding the mechanism of gelation is important to optimize the preparation process. Here, il will discuss a molecular investigation of the aggregation mechanism of gellan carried out using atomistic simulations based on a newly developed gellan force field. By analyzing the solution behavior of a suspension of gellan chains in aqueous solution as a function of the polymer concentration, I will provide evidence of the occurrence of a two-step aggregation process [7].

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Oral contribution

Friday 13<sup>th</sup>

# Sticky-MARTINI – A Reactive Coarse-Grained Model for Self-Assembly

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Reflecting recent developments in computer hardware and algorithms, computer simulations have been increasingly employed, with remarkable success, to study the phase behaviour and synthesis mechanisms of porous materials. The main challenge, however, is that such processes involve multiple physical phenomena – self-assembly, chemical reactions, phase separation, electrostatic interactions, hydrogen bonding – taking place over a wide range of time and length scales. In particular, the ability to simultaneously describe mesoscale self-assembly processes and chemical reactions has remained an elusive goal. Typically, highly coarse-grained (CG) classical models are required to describe mesophase self-assembly [1], while describing chemical reactions usually relies on computationally expensive and/or parameter-rich approaches such as Quantum Mechanical calculations, kinetic Monte Carlo or reactive force fields that are restricted to small system sizes and short times [2]. In this work, we bridge this gap and propose a new molecular modelling paradigm to describe silica polymerization reactions in aqueous solutions at conditions that are representative of realistic experimental processes like biosilicification or porous silica synthesis – i.e. at close to ambient temperatures and over a wide range of pH. The key innovation is to describe the Si-O-Si chemical bond formation and breakage process through a continuous potential with a balance between attractive and repulsive interactions between suitably placed virtual sites and "sticky" particles – hence the name "Sticky-MARTINI" [3]. The simplicity of the model, its applicability in standard parallelized molecular dynamics codes, and its compatibility with the widely used MARTINI coarse-grained force field [4] allows for the study of systems containing millions of atoms over microsecond time scales using an explicit solvent formalism. As proof-of-concept, we demonstrate the suitability of the new model in describing a surfactant micelle encapsulation process.

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Oral contribution

Friday 13<sup>th</sup>

# Multiscale Hybrid Model for Liquids: Coupling Molecular Dynamics with Hydrodynamics in Simulations

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Molecular simulation of biological systems can, at least theoretically, be done at the appropriate spatial scale, yet achieving relevant temporal scales remains a significant challenge, even theoretically. A considerable amount of computational resources is dedicated to simulating the liquids surrounding biomolecules. One cost-effective strategy involves transitioning from an atomistic to a continuum representation of liquids, particularly in areas far from the biomolecules where atomic details are less critical.
Our hybrid model is designed to facilitate a seamless transition between atomistic Molecular Dynamics (MD) and coarser Fluctuating Hydrodynamics (HD) within a unified framework [1]. This model integrates hybrid particles that contain weighted contributions from both MD and HD phases, enabling simulations across diverse temporal and spatial scales. In the atomistic limit, each hybrid particle represents a single atom; in the hydrodynamic limit, it represents a piece of the continuum.
A variety of constraint procedures exist for such couplings, with the variational principle approach being particularly favored due to its clear physical justification. In our model, we apply a constraints to the momentum of hybrid particles to ensure momentum conservation within the system [2]. We employ Gauss' principle, which is renowned for minimizing the magnitude of constraint forces, to derive the equations of motion. Though less popular than Hamilton's principle, Gauss' principle stands out as a true minimization principle and is applicable to any form of constraint, including non-holonomic constraints, which are of particular interest for our model.
The GROMACS software was modified to implement our theoreticl approach for liquid argon and water. The results confirmed that, at the hydrodynamic scale, the standard deviation of density within our hybrid system matches closely with the theoretical predictions of pure hydrodynamics, validating our model's effectiveness in accurately capturing the dynamics of hybrid systems.

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## Stress fluctuations and adiabatic speed of sound in liquids: A simple way to estimate $C_s$ from simulations

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Sound propagation and its different mechanisms in liquids and solids are of paramount importance for fundamental many-particle effects in condensed matter, as well as for technologies based on vibrational properties of crystals and disordered systems. One of the fundamental quantities in dynamics of the liquid state, the adiabatic speed of sound $C_s$, is difficult to predict from computer simulations, especially in simulations where the electronic structure is explicitly solved during the simulation, like the density functional theory-based molecular dynamics (DFTbMD).

Here we derive an expression for the instantaneous correlator of fluctuations of the longitudinal component of stress tensor, which contains $C_s$ along with others quantities easy accessible via computer simulations. We demonstrate the applicability and efficiency of the method using molecular dynamical simulations in the case of Lennard-Jones and soft-sphere simple fluids, Kr-Ar liquid mixture in a simulation with effective pair interactions as well as in liquid Sb, fluid Hg and molten NaCl with DFTbMD simulations.

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## Beyond Local Structures in Critical Supercooled Water through Unsupervised Learning

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The presence of a second critical point in water has been a topic of intense investigation for the last few decades. The molecular origins underlying this phenomenon are typically rationalized in terms of the competition between local high-density (HD) and low-density (LD) structures. Their identification often requires designing parameters that are subject to human intervention. Herein, we use unsupervised learning to discover structures in atomistic simulations of water close to the liquid–liquid critical point (LLCP). Encoding the information on the environment using local descriptors, we do not find evidence for two distinct thermodynamic structures. In contrast, when we deploy *nonlocal* descriptors that probe instead heterogeneities on the nanometer length scale, this leads to the emergence of LD and HD domains rationalizing the microscopic origins of the density fluctuations close to criticality.

# Charge order and the absence of scattering pre-peak in alkylamines

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In contrast to alkanols which show prominent scattering pre-peaks in x-ray and neutron diffusion experiment [1,2], alkylamines do not have such pre-peaks, except for a weak one for propylamine [3]. Since both liquids are hydrogen bonding liquids, one expect the formation of clusters, hence scattering pre-peaks. Indeed, molecular dynamics simulation show the existence of such clusters, and more importantly the order parameters of disordered liquids, which are the atom-atom pair correlation functions and the associated structure factors, have strong similarities with those in alkanols, which make the absence of pre-peak even more puzzling. The analysis partial scattering contributions form the amine head groups and the alkyl tails reveal how the cross contributions tend to exactly cancel the added contributions of the two former. The study of the charge ordering between the differently charged groups through the order parameters, allow to trace back this behaviour to that of the water-like topology of the amine head group, coupled to the topological constraints posed by the alkyl tail. This analysis indicates that systems with strong micro-heterogeneity, such as those encountered in soft matter or biological liquids, may or may not exhibit scattering pre-peak depending on the nature of the charge order resulting from the topology of the distribution of the charges and that of the molecules which carry them. Interestingly, the differences between the force field models are found to be more important than in alkanols.

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# Exploring the Complexity of Hydrogen-Bonded Liquids Through Voronoi Entropy

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In hydrogen-bonded liquids, molecules in close proximity align to form hydrogen bonds which contribute to their short-range order. This configuration creates chains or clusters of molecules joined by hydrogen bonds over a small spatial range of a few molecular diameters. This short-range order has a significant effect on the macroscopic characteristics of hydrogen-bonded liquids, including conductivity, viscosity, and various thermodynamic properties[1–3]. Voronoi entropy (SVor) is calculated for the 2D representation of the molecules[4] or for any seeds or points in a 2D plane[5] to find the orderliness of those 2D planes from the Voronoi polygons. In general, SVor is calculated for the 2D planes where the real structure of the molecules is lost. In this work, SVor is calculated for the 3D Voronoi polyhedrons (VPs) constructed from the simulated liquids using molecular dynamics simulation. VPs are constructed by joining points in space with their closest neighbors. Every point in a region is closer to its center than it is to any other point and it separates space into distinct regions. VPs are generated using VOROTIS software. Hydrogen-bonded liquids such as water, acetone and aniline and their binary mixtures with 8 primary alcohols (R = 1 to 8 in R-OH, R - CRH2R+1) are modeled. Each binary mixture is simulated using 1000 molecules by changing their concentrations from ratio 1:9 to 9:1. The orderliness of these binary mixtures and their pure forms are calculated. The change in orderliness as the concentration changes and the effect of alkyl chain lengths are studied using SVor. The SVor calculated shows water molecules have the lowest value and aniline molecules with the highest value. The lowest values mean more ordered and the highest values mean less ordered. The orderliness decreases as the alkyl chain length of the molecules increases.

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# Exploring Hydrogen Bonding structures in Aqueous Solutions of Imidazolium-based Protic Ionic Liquids through UV Resonance Raman Spectroscopy

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Understanding the complex interplay between hydration and hydrogen bonding in Protic Ionic Liquids (PILs) is crucial for elucidating their physicochemical properties. In this study, we investigate this complex relationship by examining the high-frequency range (2800–3800 cm-1) of UV Resonance Raman (UVRR) spectra. Despite significant overlap between C–H and OH Raman signals, a novel spectral analysis method, solute-correlated (SC) spectra extraction, enables the separation of bulk and hydration water contributions.

The SC spectra reveal distinct Raman bands corresponding to CH stretching modes of the methyl and imidazole groups, alongside OH stretching bands indicative of hydration water. Analysis of SC spectra for various PILs ([MIM][X], where X = $NO_3^-$, $TfO^-$, $HSO_4^-$, and $Cl^-$) demonstrates notable changes in hydrogen bonding configurations, especially evident in the behavior of [MIM][Cl].

Notably, [MIM][Cl] shows pronounced sensitivity to concentration changes, suggesting efficient competition between chloride ions and water molecules for hydrogen-bond sites. The observed shift in CH stretching bands with increasing PIL concentration indicates stronger double-ionic cation–anion hydrogen bonds compared to cation-water bonds.

Moreover, analysis of OH stretching bands in SC spectra reveals the diminishing strength of water-anion hydrogen bonds in the order: [Cl] ~ [$HSO_4$] > [$NO_3$] > [TfO], reflecting trends observed in double-ionic cation–anion bonds. The concentration-dependent modulation of water-anion hydrogen bonds suggests a dynamic interaction between PIL aggregation and hydration.

Further insights into the hydration properties of PILs are gained by estimating hydration numbers, which show the predominance of solvent-separated ion pairs (SSIPs) and solvent-shared ion pairs (SSIPs) at lower concentrations. Notably, [MIM][Cl] exhibits the highest aggregation tendency, attributed to its unique H-bond acceptor capabilities and molecular symmetry.

Overall, our findings provide valuable insights into the complex hydrogen bonding structure and hydration behavior in imidazolium-based PILs, shedding light on their structural properties and potential applications.

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# Photophysics of the indoline derivative photosensitizer D205: investigation on the influence of the binary mixture 1-butanol/acetonitrile

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The efficiency of Dye-Sensitized Solar Cells (DSSCs) is determined to a large extent by the characterization of the photophysics of the dye. Indeed, the properties of the solvent such as hydrogen bond donor or acceptor ability, the polarity, the viscosity, and the possibility to interact through stacking, strongly influence the processes occurring in the excited state (non-radiative processes) [1]. As a consequence, the rationalization of the effect of the solvent on the photophysics of dyes (in general and dyes used in solar cells in particular) is a subject of active research [2].

This work aims to clearly understand the photophysics of D205 in the mixture between 1-butanol (BuOH) and acetonitrile (ACN). These solvents help to rationalize the effect of hydrogen bonds and dipole-dipole interactions on the photophysics of the dye. To achieve this objective, in this study, techniques such as steady-state spectroscopy (UV-Vis, fluorescence and Raman), as well as time-resolved spectroscopy (Time-correlated Single Photon Counting and femtosecond Transient Absorption), were utilized to elucidate the photophysical properties of D205 in this mixture.

Hydrogen bonding capacity and polarity, in particular, induced a red shift in the absorption maxima (from 524 nm to 531 nm) and a blue shift in the fluorescence maxima (from 650 nm to 633 nm). Furthermore, an increase in the fraction of BuOH also correlated with a decrease in quantum yield, suggesting competition between dipole-dipole interactions and H-bond formation. Time-resolved spectroscopy consistently showed an increase in fluorescence lifetimes ($\tau$ACNfluo = 514 ps and $\tau$BuOHfluo = 698ps) and excited state relaxation times ($\tau$ACN1 = 282 ps and $\tau$BuOH1 = 655 ps) with increasing BuOH content, a trend also found in the knrad constant, suggesting that non-radiative pathways dominate the relaxation process. The study's findings highlight the intricate interplay between D205-BuOH H-bonding and D205-BuOH dipole-dipole interactions, elucidating the fluorescence quenching dynamics involved.

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# Posters

## Accumulation of ions in confined geometries (slits, pores, cavities) with dielectric constant different from that of the bulk

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We study the partitioning of ions from a bulk electrolyte into confined geometries such as slits, pores, and cavities. These geometries have different dimensionalities depending on in how many dimensions they are confined and in how many dimensions they are homogeneous. Slits are confined in one dimension (planar symmetry), pores are confined in two dimensions (cylindrical symmetry), while cavities are confined in all the three dimensions (spherical symmetry). The walls confining these inhomogeneous electrolytes can carry surface charges, so electrical double layers are formed inside these confined systems.

We allow the confined systems to have dielectric constant that is different from the bulk. That introduces a solvation energy penalty when we bring the confined system into equilibrium with the bulk. Such an equilibrium may be called Donnan equilibrium because the electrostatic features of the two systems are different. They can be different because of the different dielectric constants, because of the charged confinement of the inhomogeneous system, or, as in the classical case, because of a semipermeable membrane that selectively do not let some ionic species through. Because of this electrostatic imbalance, an electrostatic Donnan potential occurs between the two systems that is needed to assure charge neutrality in the confined system.

We use implicit-solvent electrolyte models (charged hard spheres in a continuum dielectric) and study them with the Donnan Grand Canonical Monte Carlo (D-GCMC) method [1] using individual ion insertions/deletions. In this method, the solvation penalty and the Donnan potential are built into the chemical potential. The selectivity of the confined system and the degree of coion exclusion are basic features of such confined electrolyte systems that have basic relevance in applications such as energy storage and energy conversion. We study how these features are influenced by the basic system parameters such as (1) system geometry (dimensionality), (2) pore dielectric constant, (3) pore size, (4) surface charge density on the pore wall, and (5) electrolyte concentration.
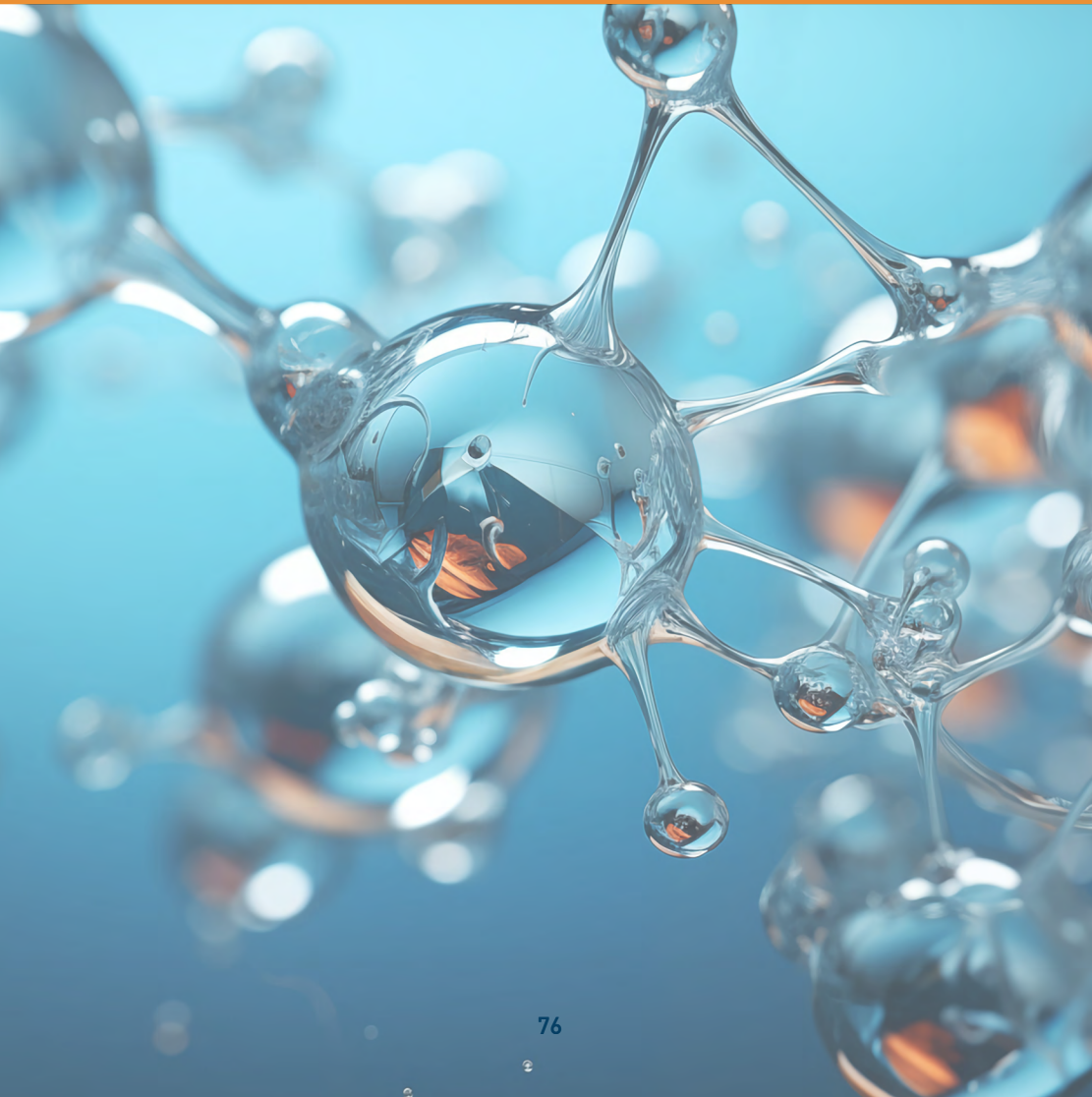
## Harnessing non-linear optical properties of ionic liquids: a computational approach

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Over the past three decades, the quest for materials with non-linear optical properties (NLOPs) has been ongoing. Recent advancements have been driven by the potential applications of these materials in sensors and optoelectronic devices. Quantitative chemical calculations play a crucial role in unraveling the intricate factors governing the magnitude and nature of NLOPs, shedding light on environmental and experimental influences. Ionic liquids, in particular, have garnered significant attention due to their easily manipulable physical and chemical attributes, allowing for the creation of tuneable materials that can either exhibit NLOPs themselves or enhance those of solutes. Moreover, NLOP-based techniques provide insights into the structural complexities of ionic liquids [1], often characterised by nanoheterogeneous structures and intricate H-bond networks. Exploring all these possibilities can be boosted by reliable theoretical predictions of the NLOPs of ionic liquids, providing guidance into ionic liquids with desired properties and the identification of targeted structural motifs.
Investigating ionic liquids poses unique challenges for theoretical chemistry tools. Dynamic studies are essential to account for the inherent fluctuations in their structures, while modelling systems must encompass large-scale configurations, including several ion pairs, to accurately capture strong, long-range Coulomb interactions. This complexity must also be taken into account when estimating theoretically the NLOPs of a given ionic liquid, and has hardly been considered in the literature [2]. In this work, we explore the impact of structure fluctuation over time and the inclusion of multiple ion pairs on the estimation of NLOPs of the butyl-methylimidazolium chloride, [BMIM][Cl]. Specifically, we focus on the first and second hyperpolarizabilities and the depolarisation ratio, considering various levels of theory. We delineate the criteria necessary for a robust model system to provide reliable predictions and offer insights into the behaviour of these properties in response to changes in geometry and modelling approaches, both in model system size and theoretical level. Our findings lay the groundwork for reliable predictions of NLOPs in non-conventional solvents, providing essential guidance for exploring their diverse applications, ranging from tailored material design with desired optical properties to the elucidation of ionic liquid structure.

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## Python-based software for the spectral modeling of femtosecond transient absorption data

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The investigation of the organic photosensitizers is one of the keys to increasing the efficiency of Dye-Sensitized Solar Cells (DSSCs). The pump-probe technique serves as an excellent tool for examining the electron transfer dynamics of dyes; however, the spectroscopy data acquired necessitates processing through specialized programs [1,2].
This work aims to optimize the program code, increasing its readability and testing the efficiency of data processing on well-known objects. The result of this work is a Python-based toolbox designed for this purpose. Our developed program features several key enhancements and additions compared to existing packages. Firstly, it includes advanced global analysis of time-resolved spectroscopic data, along with the capability to perform group velocity dispersion (GVD) correction. The graphical user interface is provided to ease the learning curve for global fitting.
Featuring a user-friendly graphical interface, the toolbox streamlines the application of various reaction models to the data, enabling the generation of coupled differential equations. It allows the analysis of any time-dependent dataset to extract time-independent correlations of observables using GVD-modified Gaussian and exponential functions. Additionally, the toolbox boasts specific functionalities, such as removing the pump-probe signal without harming the sample signal, removing bad single spectra, and taking into account Raman signals. The advantages and effectiveness of this software are demonstrated through the processing of transient absorption data of well-known indoline dye D205 in various solvents, including acetonitrile (ACN), dimethyl sulfoxide (DMSO), methanol (MeOH), and 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF4). The longest-time components tau1 (tau1 (DMSO) = 419.2 ps, tau1 (ACN) = 340.5 ps, tau1 (MeOH) = 124.4 ps, tau1 (BmimBF4) = 988.9 ps) correspond to the relaxation of the excited state to the ground state and correlate well with the literature values.

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# Thermodynamics of Mixing of Acetonitrile with Water

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The volume, energy, entropy, and Helmholtz free energy of mixing of models of ace-tontrile with water is investigated by extensive computer simulations and thermody-namic integration. To check the force field dependence of the results, all calculations are repeated with two commonly used water models, namely SPC/E and TIP4P. The combination of the OPLS_UA model of ACN and the SPC/E, TIP/4P water models results in positive values indicating the demixing of the mixture. Whereas, the other combinations gives negative values free energy of mixture throughout the composition range, indicating that the mixture is thermodynamically more stable than the two sep-arate pure liquids in the entire composition. Of note is that the calculated values are in the range of RT indicating that the driving for mixing or demixing is weak. The D values are always greater than 0 over in the entire composition range, indicating full miscibility of the ACN mixture with water for these combinations.

# Terahertz spectroscopy of thick and diluted water solutions

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When measuring the absorption of electromagnetic radiation by a sample in transmis-sion geometry, the optimal material thickness is often on the order of one penetration depth, i.e., the thickness of the sample should be comparable to the inverse of its absorption coefficient over the probed frequency range. However, when measuring refraction properties, the amount of temporal delay accumulated by the transmitted field is proportional to the thickness of the sample: the thicker the sample, the larger the acquired phase. These different optimal thicknesses constrain the simultaneous detection of refractive and absorptive properties.

This work focuses on one important substance in particular: liquid water and some of its diluted salt solutions. Water absorbs strongly at terahertz (THz) frequencies via the inter-molecular modes of hydrogen-bonded water molecules. For example, Figure 1 of Ref.[1] shows cartoons of the different modes of liquid water in the THz range. Below 1 THz, the dielectric response is dominated by the Debye-like reorientation of the collective dipole of H-bonded water molecules. Intermolecular translations or "net-work stretching" modes are centered at ca. 6 THz, while librational modes are found between ~10 THz and ~30 THz. The absorption coefficient of water roughly increases with THz frequency and reaches several thousand inverse centimeters, corresponding to penetration depths of a few microns.

The dissolution of salts affects the dielectric function of liquid water and makes the mi-croscopic understanding of the underlying molecular dynamics more difficult. Typical time-domain spectroscopy (THz-TDS) on liquid water is performed in transmission for samples as thick as ~100 microns. We demonstrated before[2] that intense THz-TDS can probe 5x thicker samples, ~500 microns colloidal aqueous solutions of gold na-noparticles. This idea was recently extended to the study of the dielectric function of dilute aqueous solutions and demonstrated for a typical salt, Sodium Chloride. While most previous reports of successful THz-TDS measurements on NaCl solutions are at concentrations of about one Molar (1 M), in ref.[3] it was shown that it is possible to quantify the tiny change in the index of refraction of a water-based sample upon dissolving a hundred times less solute (10 mM).

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# Pre-resonance effects in deep UV Raman spectra of normal and deuterated water

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Raman spectroscopy has a longstanding tradition in investigating the structure of water by observing changes in vibrational behavior, typically by focusing the attention on the OH or OD stretching band of Raman spectra. Indeed, this broad signal, observed in the high frequency range of Raman spectra of water, is particularly sensitive to the effect of various physical and chemical stimuli, such as temperature, pressure, isotopic composition, and added species in solution. In this work, we have investigated the shape of the OH/OD stretching Raman band of water as a function of the excitation wavelength in the deep UV region, i.e. between 200 and 266 nm. While the integrated Raman intensity of the OH stretching band is known to undergo a significant enhancement for excitations below 300 nm, not much attention was paid to the evolution of the band shape. Our Raman spectra collected using different excitation wavelengths display distinct changes in the Raman profile of the OH stretching band moving from visible excitation wavelength (532 nm) to deep UV (200 nm). By analyzing the spectral profiles, we highlighted selective pre-resonance effects in the high wavenumber component of the OH/OD stretching band, associated to water molecules with distorted hydrogen bonds (weakly H-bonded water; high-density liquid, HDL in the literature) relative to that of water molecules with strong hydrogen bonds (strongly H-bonded water; low-density liquid, LDL in the literature) [1]. A van't Hoff treatment of the temperature-dependent Raman spectra provides an estimate of the thermal energy associated to the change from ordered (ice-like) to disordered configurations that agrees with values obtained by related methods based on a two-state model of water [2]. Overall, these findings suggest the possibility of exploiting the signal enhancement that occurs in the deep UV region to investigate H-bonding properties in aqueous media. Since the enhancement is related to the H-bonding state of water molecules, in principle, the Raman signal arising from water molecules specifically affected by the solute could be selectively enhanced by using deep UV excitation.

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# Calcium versus potassium selectivity in a nanopore: enhancing charge inversion by localized charged groups and decreased dielectric constant

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The Anomalous Mole Fraction Effect (AMFE) in negatively charged pores is a signature of the selectivity of $Ca^{2+}$ over monovalent cations ($K^+$). Increasing the mole fraction of $Ca^{2+}$ in the $KCl/CaCl_2$ mixture, the total conductance first declines as $Ca^{2+}$ ions replace $K^+$ ions inside the pore. Then it increases as $Ca^{2+}$ becomes the main charge carrier with increasing bulk $Ca^{2+}$ concentration. While the AMFE was first pointed out in calcium selective ion channels [1], it was shown that it is also present in synthetic nanopores [2]. Here we use the Local Equilibrium Monte Carlo method coupled to the Nernst-Planck transport equation [3] to study a simple model of a finite nanopore in a membrane with ions being explicitly modeled as charged hard spheres and water as an implicit continuum. At the negatively charged pore wall, charge inversion occurs that has a considerable effect on the bahavior of ions in the pore. We showed that charge iversion is enhanced if we localize the pore charges instead of smearing them as a continuous surface charge [4]. This model is in agreement with the fact that the pore charge is present in localized $COO^-$ groups on the wall of a PET nanopore. In effect, $Ca^{2+}$ ions overcharge the pore wall at which the $K^+$ ions have a disadvantage in the $K^+$ vs. $Ca^{2+}$ competition because the overcharged pore wall does not attract them so strongly. Here, we examine various models of the charged groups on the wall. Also, we apply the Donnan Grand Canonical Monte Carlo method [5] to study the effect of decreasing the dielectric constant in the pore.

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**P 08**

## Hydrogen Bonding Properties of Model Carbohydrates in Water

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The solvation properties of sugars dissolved in water have already been already extensively studied and documented, [1] due to their relevance in a wide range of applications, particularly those involving living organisms. Sugars serve not only as a source of energy and carbon, [2] but are also involved in the regulation of metabolic pathways. [3] Additionally, specific sugar molecules have shown bioprotective properties, [4,5,6] which enable them to prevent the inactivation and denaturation of macromolecules in specific microorganisms. This protective function is achieved by inducing a "quiescent" state in these species when exposed to adverse external conditions or stress. [7] To better comprehend these phenomena, it is necessary to clarify the interplay between the water and sugar molecules in solutions. The literature presents contradictory opinions regarding the effect of sugars on the bonding network of water. In particular, two questions need to be answered: 1) has the sugar a strengthening or weakening effect on the H-bond network compared to pure water [8] and 2) do different sugars manifest distinct solvation effects? [9]
To address these questions, an experimental approach based on infrared (IR) spectroscopy was employed to investigate the structural properties of aqueous solutions of glucose and trehalose, which represent a mono- and a disaccharide, respectively. The behavior of the O-H stretching and H-O-H bending features was observed as a function of the sugar content. Higher sugar concentrations in solution corresponded to an increased average strength of the H-bonds. Additionally, the results suggest that the solvation properties of glucose and trehalose are remarkably similar, despite their structural differences.

**P 09**

## High-Pressure Effects on Cellulose Dissolution Behavior into Ionic Liquid Analized using Molecular Dynamics Simulation

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Cellulose is expected to be utilized for a wide range of applications in human health and environmentally friendly products [1]. The first step in converting cellulose into products is to dissolve cellulose into solvent, such as Ionic Liquids (ILs). Generally, the dissolution is achieved through high temperatures, which incurs a high energy cost and degradation of cellulose. On the other hand, pressure application has a lot of advantages; for example, it does not destroy covalent bonds, requires relatively low energy, and sometimes can enhance the solubility. Therefore, it is important to examine the effect of pressure on the solubility of cellulose into IL; however, it is difficult to investigate it experimentally. Therefore, we investigated the high-pressure effects on cellulose dissolution behavior (cellulose dissolution rate and cellulose solubility) in IL using Molecular Dynamics (MD) simulation.
All-atom MD simulations were performed using Gromacs 5.0.7. The solvent system consisted of 1-Butyl-3-methylimidazolium acetate ([BMIm][OAc]) and the co-solvent dimethyl sulfoxide (DMSO).
Cellulose dissolution rate. The system consisted of cellulose crystals ($I\beta$, 36 chains, DP 8) surrounded by 1390 IL and 1212 DMSO. The dissolution process was simulated under NPT ensemble for 500 ns at 500 K and various pressures (0.1-1000 MPa).
Cellulose solubility. A single cellulose chain (DP 8) was simulated under NVT ensemble for 20 ns. The solvent (300 IL, 500 DMSO) and the solution (1 chain, 300 IL, 500 DMSO) were simulated under NPT ensemble for 50 ns, and 200 ns, respectively at 400 K and various pressures (0.1-1000 MPa). Finally, the solvation free energies were calculated using Energy Representation Module.
Cellulose dissolution rate under high pressure. Cellulose dissolution under various pressure (0.1-1000 MPa) were simulated. The results indicate that the dissolution rate decreases exponentially with increasing pressure. Examination of the self-diffusion coefficients of the solvent molecules revealed a decrease exponentially with increasing pressure. It is suggested that the reduced translational motion of solvent molecules contributes to the decrease in the dissolution rate of the cellulose crystal. Additionally, the strengthening of inter-chain interactions of cellulose due to increased pressure could be another contributing factor.
Cellulose solubility under high pressure. The decrease of solvation free energy is known to increase the solubility, and the solvation free energy and the natural logarithm of the solubility are proportional. The result shows the solvation free energy decreased almost linearly with increasing pressure, from -189 kcal/mol under atmospheric pressure to -215 kcal/mol at 1000 MPa. This suggests that the solubility of cellulose in IL increases with increasing pressure exponentially.

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**P 10**

## A Study on Analytical Expression of Solvent Free Energy Considering Structural Fluctuations of Solute in Integral Equation Theory

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Solvation effect plays important roles in chemical reactions and protein functions. Integral equation theory for molecular liquids is a powerful method for efficiently calculating the magnitude of solvation effects because it provides analytical formulae for solvation free energy. However, in the conventional integral equation theory, the structure of solute is fixed at a specific configuration, which could be problematic, especially for large solutes. For example, proteins in physiological environment are constantly fluctuating due to thermal motion. Molecular dynamics simulation is a straightforward and most widely used method for calculating solvation considering structural fluctuations of solutes. However, molecular dynamics simulation often suffers from statistical sampling of large systems. Therefore, a new calculation tool to calculate solvation effect considering structural fluctuations is desirable and such calculation methods have been developed. For example, Yokogawa et al. extended integral equation to efficiently calculate intramolecular conformational distribution [1], and it was extended to treat binary solute-solvent system by Matsumura and Sato [2]. In this study, we directly derived an analytical formula for the solvation free energy that incorporates the structural fluctuation of solute into the integral equation theory. The analytical formula was obtained by combining the reference interaction site model (RISM) equation where the intramolecular correlation function of solute sites is treated as a Gaussian chain, and the charging formula for excess chemical potential [3]. Since the obtained analytical formula is composed of convolution integrals used in the conventional integral equation theory, it can be efficiently calculated using the fast Fourier transform at almost the same cost as the conventional method. This analytical formula enables the integration equation theory to consider the effects of structural fluctuations of solutes. Numerical calculation results for simple molecules will be reported in the presentation.

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**P 11**

## Molecular Dynamics Simulation of Enantiomer Separation Under a Rotating Electric Field in a Chiral Liquid

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Separation of enantiomers is a physicochemical problem of fundamental and practical interest for example in pharmaceutical industry because a drug is often a particular enantiomer of a chiral molecule. Separation or selective synthesis of enantiomers can be achieved using a chiral substrate but this technique is system-dependent because a universal chiral matrix does not exist. Enantiomeric separation can be also obtained by shear flow or local vorticity (1-3) or by rotating electric field. This last approach had been theoretically proposed long time ago (4) and experimentally applied only decades later (5). In this work, we present results of molecular dynamics (MD) simulations of racemic chiral liquids under rotating electric field aiming to detect the enantiomeric separation. Two molecular models have been tested: a realistic model of bromochlorofluoromethane and a fictional model composed of a chain of four atoms bearing a dipole. For this second system, the flow of R and S enantiomers in opposite directions has been clearly observed and analyzed as a function of the rotational velocity of the electric field.

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# Exploring Proton Dynamics in Confinement: A Study of Photoacids in Reverse Micelles

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Confined water is known to have a different hydrogen bond network structure than water in the bulk. Given that proton transfer proceeds through the hydrogen bond network, known proton transfer mechanisms for water in the bulk cannot be assumed to hold under confinement.[1,2] We use a combination of molecular dynamics simulations using classical, atomistic force fields, as well as using quantum mechanics-molecular dynamics (QM/MM) ensemble simulations to investigate proton transfer in confinement, using as model system a single photoacid molecule (HPTS) confined within a reverse micelle (RM). The RM is formed by the negatively charged surfactant AOT in water and oil. The MD simulations revealed that HPTS, which has net charge -3e, does not preferentially stay at the center of the micelle as naively expected. Rather, the photoacidic OH group often forms strong hydrogen bond with surfactant sulfonate groups, which anchor it to the RM surfactant-water interface. Only in 1/3 of the observed configurations does the photoacidic OH group hydrogen bond to water, while still remaining near that interface. Several snapshots demonstrating this interaction - favorable for deprotonation - were selected for further analysis using quantum mechanics-molecular dynamics (QM/MM) ensemble simulations of the excited state, to model the initial stages of proton transfer following photoacid excitation. Additional ground state QM/MM simulations revealed that, after deprotonation, the proton remains at the RM interface and associates transiently with the sulfonate headgroups of AOT, after which reprotonates water molecules. In MD simulations of RMs containing a deprotonated HPTS + hydronium simulated at the classical level we also observe the hydronium ion remains at the surfactant-water interface, whereas the photoacid rapidly moves towards the center of the RM. These simulations thus suggest that proton recombination will be affected by confinement in a manner not easily predictable, because of the competition between the proton affinity by the surfactant-water interface and the movement of photoacid away from that interface (which disfavor protonation relative to what happens in an unconfined solvent) and the confined nature of the system, which limits the distance between HPTS and proton (and thus favors protonation). This study not only advances our understanding of proton dynamics in confined environments but also underscores the significant implications for both biological functions and technological applications where such dynamics play a critical role.

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# Computer Simulation Investigation of the Molecular Scale Structure and Dynamics of the Free Surface of Imidazolium-Based Ionic Liquids

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The structure and dynamics of the surface of four imidazolium-based room temperature ionic liquids are investigated by intrinsic surface analysis methods at both the molecular and atomic levels. This combination has provided us with unprecedented details of the surface of the ionic liquids considered, and enabled us to understand the spatial arrangement of the particles at these surfaces.

We see no evidence to support the electric double layer-like scenario at the liquid surface, nor for their self-association at the surface of the liquid (i.e., the 'chessboard' scenario). Although we have seen a large excess of cations in the surface layer and an excess of anions in the subsequent one when looking at the surface in the resolution of entire ions, the liquid surface has been shown to carry, in fact, a small negative surface charge. This seeming contradiction is resolved considering that the surface is dominated by the uncharged alkyl chains and those largely obscure the cation groups to which they are bound, while the smaller and more mobile anions can more easily access the free surface in a larger extent than the positively charged groups of the cations, giving thus rise to the observed excess negative surface charge.

The single particle dynamics at the liquid surface has been found to be, in general, two to three orders of magnitude slower than that in conventional molecular liquids due to the much stronger inter-particle interactions acting here. In particular, lateral diffusion is found to be a generally slower process than the exchange of the ions between the subsequent subsurface layers. Consequently, ions are unable to engage in significant lateral diffusion during their residence in a given subsurface layer. The only exception to this is the case of the $bmim^+$ cations in the first layer at the liquid surface, due to their approximately one order of magnitude longer residence times.

# Low dielectric constant of nanoconfined water

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The relative out-of-plane dielectric constant of nanoconfined water was shown to be as low as 2.1 for thicknesses below 1 nm by Fumagalli et al. (Science, 2018). This study motivated numerous theoretical investigations aiming to explain this surprising behavior. It is unexpected because such a low measured value is even lower than the high-frequency dielectric constant of ice.

In this work, we demonstrate that both experimental and theoretical studies suffer from intrinsic arbitrariness due to the ill-defined concept of a macroscopic dielectric constant in a microscopic 2D limit. We propose that the two-dimensional transverse polarizability is the natural choice to characterize the response of a nanoconfined dielectric in a capacitor. This polarizability can also be connected to the actual experimental measurements of differential capacitance, providing a clear method for comparing both experimental and theoretical results. This approach eliminates the need for intermediate arbitrary choices required for the computation of the dielectric constant.

# Ordering properties and phase behaviour of anisotropic hard particles in quasi-one-dimensional channels

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Systems of two- and three-dimensional hard anisotropic particles are serving as typical examples of entropy driven phase transitions. The behaviour of these systems is even more interesting under strong confinement. Even new structures emerge with the positional restriction such as the hexatic, tetratic and helical arrangements. Moreover, disordered structures can emerge, and the question of jamming and glassy behaviour is in focus, too. Therefore there is a growing experimental and theoretical interest to study and understand the ordering behaviour of anisotropic hard particles under strong confinement. This is also due to the progress made in the experimental realization of such nanoconfined systems where almost two- and even one-dimensional restrictions can be achieved. This can be done with confining the particles between two parallel plates and with absorption of the particles into tubular nanopores.

To understand the nature of ordering in confinement, simple models must be introduced, which can be studied with theoretical methods exactly. We studied the systems of hard disks, squares, rectangles and also mixtures of these particles confined into a two-dimensional channel, furthermore spheres and cylinders confined into a narrow hard cylindrical pore. We study the cases when the pore is very narrow, only nearest and next-nearest neighbour interactions are allowed between the particles. In spite of these restrictions, in some studied cases the particles can pass each other, therefore the systems are definitely different from the strictly one dimensional ones. Our aim is to demonstrate the capability of the transfer operator theory in the highly confined regime. Exact density profiles, equations of state and correlation functions can be derived even for mixtures and even for such cases when the particles can form two parallel layers in the channel.

Using the exact theory we can prove that genuine phase transition is ruled out in every studied case. However, interesting structural transitions take place with increasing density, such as orientational and [1,2] positional [3] ordering, and layer formation. The transition between these structures is smooth without any non-analytic behaviour in the thermodynamic quantities, however, the structural change can be happen very suddenly accompanied by a sharp and high compressibility and heat capacity peaks. Even critical behaviour can be observed at the infinitely large pressure limit.

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# Hydroxymethylfurfural solubility and solvation in eutectic solvents: an experimental and theoretical study

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5-hydroxymethylfurfural (HMF) is an aromatic furan derivative that can be synthesized in a sustainable way, starting from different kind of raw biomasses. It is highly versatile, serving as a precursor for biofuels, biopolymers, and various solvents. During its synthesis, separating it from an aqueous phase is essential. Deep Eutectic Solvents (DES) emerge as promising green solvents for sustainable extractions in this context.
Here we present results concerning the microscopic structural arrangement of liquid HMF, obtained through the synergy of classical Molecular Dynamics (MD) simulation and Wide-Angle X-ray Scattering (WAXS) experiments.
Moreover the solubility of HMF in diverse DES is reported, aiming at extracting thermodynamic parameters for such a process.
We also show results from computational description of HMF solvation structural features in selected promising DES.
The role of pi-pi stacking and hydrogen bonding interactions in driving these correlations is highlighted and some indication for optimization of HMF solvation are presented.
This work is supported in the framework of Project SEED4GREEN 20223W4RT9_PE5_PRIN2022.

# Effect of temperature and hydrostatic pressure on physicochemical properties during preparation of cellulose hydrogels using ionic liquid/dimethyl sulfoxide solution

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Cellulose hydrogels (CHGs) are gels that form a three-dimensional network structure with a cellulose backbone and contain large amounts of water in the gaps. Therefore, CHGs are expected to be applied to a wide range of human body and environment-friendly products such as wound dressings[1], contact lenses[2], and plastic substitute materials[3]. Therefore, a wide range of physicochemical properties CHGs are required depending on the type of application. It is known that the gel properties can be controlled by changing the preparation conditions such as temperature, pressure, solvent composition, and so on.
In this study, the effects of CHGs preparation conditions on gel properties (shrinkage rate, water content, mechanical strength, and crystallinity) were examined when the gelation temperature (5-60 °C) and hydrostatic pressure (0.1-250 MPa) were varied two-dimensionally.
First, a cellulose solution was prepared by adding cellulose (the weight ratio between the cellulose and 60 wt% [BMIm][OAc]/ DMSO was 1:10). Next, the cellulose solution was poured in a mold, placed in water for water displacement to prepare CHGs. During the water displacement, temperature (5-60 °C) and hydrostatic pressure (0.1-250 MPa) were varied two-dimensionally in a systematic manner. Finally, the shrinkage rate, water content, mechanical strength (compressive modulus), and crystallinity of the prepared CHGs were evaluated.
Temperature dependence of gel properties: Both compressive modulus and crystallinity decreased with increasing temperature and showed a two-state transition corresponding to the gelation temperature increase regardless of the hydrostatic pressure (0.1, 100, 250 MPa) during gelation. The strong correlation between the compressive modulus and crystallinity suggests that the crystalline state of the cellulose backbone, which forms the three-dimensional network structure, strongly affected the elastic modulus.
Hydrostatic pressure dependence of gel properties: The compressive modulus increased with increasing hydrostatic pressure at fixed temperatures of 5 °C and 35 °C, however at 60 °C, it either did not change or showed a slight increase with the increase of hydrostatic pressure. The crystallinity did not vary or tended to increase slightly with increasing hydrostatic pressure, regardless of the gelation temperature. Since no correlation between the compressive modulus and crystallinity was observed, the possible reason for the change in compressive modulus corresponding to the hydrostatic pressure is that thickness and microstructure of the cellulose backbone, were changed due to the hydrostatic pressure and influenced the compressive modulus. Therefore, in the future, we plan to observe the microstructure of the gels using scanning electron microscopy and other techniques.

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# Effects of different polymer types on the sensor performance of ionic liquid coated hetero-core optical fiber surface plasmon resonance sensors for CO2 detection

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CO2 sensors are used in various fields. Compared with the conventional CO2 sensor such as the non-dispersive infrared CO2 sensor, optical fiber sensors have advantages such as no electrical contacts at the sensing part. The hetero-core structured optical fiber, which can be applied as the promising optical fiber sensor, is fabricated by inserting optical fibers with different core diameters and fusing them [1]. By coating a thin film of a noble metal such as Au around the cladding of the hetero-core part, a hetero-core optical fiber SPR sensor can be easily fabricated, and it also shows high sensitivity to changes in the refractive index. The measurement principle of the sensor is based on the phenomenon that the attenuation peak of the reflected light by SPR shifts by the change in the refractive index of the surrounding environment [2]. Whilst it is known that some ionic liquids (ILs) and polymers selectively absorb CO2. Therefore, if the mixed film of CO2 absorbing IL and polymer is coated on a hetero-core optical fiber SPR sensor, it could work as an optical fiber SPR CO2 sensor.

The purpose of this study is to evaluate the response characteristics of the fabricated CO2 sensor by coating two kinds of mixed IL-polymer film on the hetero-core optical fiber SPR sensor using one IL and two different polymers. The polymer used in this study were, polyethersulfone (PES) and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), both of which have CO2 adsorption characteristics. As an IL, 1-ethyl-3-methylimidazolium tetrafluoroborate was used. We experimentally evaluated the performance of the fabricated sensors with two kinds of mixed films of IL-PES and IL-PVDF-HFP.

Hetero-core fiber optic sensors consist of two different fibers of multi-mode transmission fiber with 50 μm core diameter and inserted single-mode fiber segment with 3 μm core diameter. It was coated with a gold film. For the preparation of IL solution, IL was mixed with each polymer and dimethylacetamide in a certain proportion. The prepared IL solution was dip-coated onto the sensor part. The sensor was then dried in a dryer.

The sensitivity, response time for fabricated hetero-core fiber optic CO2 sensor were evaluated using an LED light source of 650 nm and optical power meter under alternating dry CO2/Air flow. We experimentally obtained the sensitivity, response, times of -0.022 and 0.466 dB, 36 and 3 min for the sensors using PES and PVDF-HFP, respectively. The sensitivity of the CO2 sensor with PVDF-HFP was 21 times higher than that of the CO2 sensor with PES. The response time was also much shorter for the sensor with PVDF-HFP than that for the sensor with PES.

We have successfully demonstrated that the IL-PVDF-HFP mixed film sensor has superior performance in both sensitivity and responsiveness as compared to the IL-PES mixed film sensor.

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# Molecular simulations of alkali metal halide using phase-transferable models: crystalline hydrates

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In addition to hydrogen bonds in solutions, similar bonds also occur in solid materials, specifically ice and crystalline hydrates, which contain water molecules together with electrolyte ions in their structure, e.g. $NaCl \cdot 2H_2O$, $LiCl \cdot 5H_2O$, $LiI \cdot 3H_2O$, or $KF \cdot 4H_2O$. Molecular modeling of these systems and phenomena requires sufficiently accurate models. In our research group, we develop phase-transferable polarizable models that can accurately predict the properties of solutions and anhydrous crystals [1].

This study systematically investigates the ability of these force fields to describe the behavior of all experimentally known alkali halide hydrates [2], focusing on the stability and parameters of their crystal lattices compared to other models. We demonstrate that other force fields often struggle to accurately model hydrates containing $Li^+$ cations, while our polarizable force fields show promising results in modeling most hydrates, except $LiCl \cdot H_2O$. Moreover, we refine our force fields to successfully model $LiCl \cdot H_2O$ and elucidate the positions of $Li^+$ cations in the beta phases of $LiBr \cdot H_2O$ and $LiI \cdot H_2O$. Our study also presents a novel simulation methodology suitable for complex polarizable models and nonorthorhombic crystal lattices, based on simulations of finite crystals in vacuum. Furthermore, our models hold the potential to predict the behavior of hyperhydrates [3] that are found on the icy moons like Europa or Titan.

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## Modelling bi-specific antibodies in aqueous solution

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We present theoretical results for physico-chemical properties of system of molecules modeling bi-specific antibodies, such as, dual-variable-domain monoclonal antibodies (DVD-Ig) and Fabs-In-Tandem Immunoglobulin (FIT-Ig) [1]. These molecules are representatives of the engineered proteins that combine the function and specificity of two monoclonal antibodies. Individual molecules are here depicted as an assembly of nine (or in case of the Fit-Ig eleven) hard spheres, organized to resemble the Y-shaped object. The effects of the increased size, asymmetry, and flexibility of individual molecules on measurable properties of such systems of molecules are investigated. We examined the liquid-liquid phase separation, the second virial coefficient , and viscosity under various experimental conditions. The calculations are compared with the data for regular monoclonal antibodies and discussed in view of the experimental results for DVD-Ig solutions available in literature.

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## Hydrogen bonding between ions of like charge in carboxyl-functionalized ionic liquids characterized by NMR deuteron quadrupole coupling constants

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In a recent study we presented deuteron quadrupole coupling constants (DQCC) for hydroxyl-functionalized ionic liquids (ILs) [1] and showed that the unusual hydrogen bonds between two cations (c-c) are present alongside the regular Coulomb-enhanced hydrogen bonds between cation and anion (c-a). With cooling, the (c-c) hydrogen bonds persist, resulting in supercooling and glass formation.

Here, we extended our investigations to carboxyl-functionalized ILs in the crystalline or glassy states consisting of two types of hydrogen bonding: A doubly hydrogen bonded cyclic cationic dimer (c=c), that resembles the archetype H-bond motif known for carboxylic acids in the gaseous phase [2] and a linear (c-c-a) cluster species, with a remaining single cationic hydrogen bond and an additional hydrogen bond between cation and anion at higher temperatures. We measure these sensitive probes of hydrogen bonding by means of solid-state NMR spectroscopy. The DQCCs of (c=c) cationic hydrogen bonds and (c-c-a) cluster species are compared to those of salt bridges in supramolecular complexes and those present in molecular liquids. At low temperature, the (c=c) cationic species successfully compete with the (c-c-a) ion pairs and dominate the cluster populations. We show that cationic cluster formation prevents these ILs from freezing.

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# Molecular dynamics study of the effect of a strong electric field on an oligo(oxyethylene) chain in solutions

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The polymer materials subjected to an electric field display microscopic changes in structure, which is of interest for wide range of applications including the electrospinning technology [1]. In this contribution, we study the structural properties of oligo(oxyethylene) of different chain lengths in water and methanol under an external electric field using extensive molecular dynamics simulations. We analyze the size and anisotropy of shape of oligomer chain by end-to-end distance, radius of gyration, and quantities derived from the gyration tensor. We calculate the distributions of dihedral angles and cosine of the angles of the monomer units and the dipole moments of the chain and solvents relative to the electric field direction. In order to quantify the helicity of the chain, we count the monomer units predefined helical patterns. Our results show that the originally isotropic chain in both solvents becomes an increasingly anisotropic and adopts oblate shape with increasing field intensity, but in water this feature is diminished with increasing chain length. The population of the gauche conformation increases significantly with increasing field intensity. In methanol, the monomer units of the chain orient perpendicular to the field whereas, in water, we observe a shift to smaller angles. The dipole moments of the chain and solvents increasingly point in field direction.

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# Chelation of heavy metals by ethylenediaminetetraacetic acid in aqueous solution

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Contamination of soils and aquatic environments with heavy metal ions poses a significant risk to human health due to their extreme toxicity even at low concentrations [1]. Ethylenediaminetetraacetic acid (EDTA) is a chelating agent that efficiently binds to heavy metal ions, forming stable complexes. Consequently, various EDTA-based adsorbents are employed for water purification and medical treatment [2]. In this study, we gain insigh into the mechanisms and conditions that lead to the stable complex formation of EDTA with heavy metal ions such as Hg, Pb, Zn, and Cd in water. We apply classical molecular dynamics simulations and quantum density functional theory to determine the detailed structure of the ion-EDTA complexes formed at different levels of EDTA deprotonation, which depends on pH of aqueous environment. Additionally, we examine the role of hydrogen bonds between EDTA and water molecules and estimate the adsorption energy of the considered ions captured by EDTA molecule.

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# Antioxidative Activity of Mostly Hydrophilic, Plant-Based Substances for the Stabilization of Various Oils

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Most oils containing triglycerides, methyl esters, omega-3 oils are prone to rapid oxidation making problems for their usage in industry [1,2]. The vast majority of research [3] focuses on one single type of oil (e.g., biodiesel). Nowadays, the comparison of different oils as lubricant oils, biofuels, edible oils, vegetable oils, cosmetic oils, insulating oils, processing oils is favourable. Polyphenolic acids and vitamins could stabilize such systems [4], enhance solubility and show advances because of customizable hydrotropic properties [5].  Also, they possible could dissolve protein aggregates that occur in many diseases because of coop up nerve cells or overfill the space between neurons. In this work, the effect of natural, mostly hydrophilic, antioxidants on the stabilization of vegetable oil (peanut oil) and processing oils (Polyalphaolefin PAO 6, Priolube 1973) is investigated.  The substances analyzed – benzoic acid derivatives: syringic acid, gallic acid, gallic acid esters as EtGall, ProGall, isoamylgallate, laurylgallate; hydrocynnamic acid derivatives: ferulic acid, p-coumaric acid; rosmarinic acid and carnosic acid; tocopheroles: α-tocopherole; stilbenes: resveratrol; flavonoles: quercetin. With the use of Rapid Small Oxidation Tests the relevant systems of surfactant-free microemulsions were analyzed. The fatty acid oxidation taking place in the sample chamber leads to a decrease in pressure until a threshold value of $\Delta P = -10\%$ is exceeded, thus completing the measurement. The measurements are done at oxygen pressure of 700 kPa. The concentration and temperature dependence of the oxidative stability index (OSI) in the range 110-160°C have been investigated in peanut oil.  The comparison of OSI values has been done in unified temperature and concentration scale. The best stabilizers has been shown to be rosmarinic and gallic acids as well as gallates (100-170 % increase in relative OSI in oil, 100-300 % in lubricant). For the gallates, in peanut oil as well as in lubricant: the greater the number of C atoms of carbon radical of the gallic acid ester, the worse the stabilization of the gallic acid ester against oxidation. Compared to carnosic acid, rosmarinic acid is more than three times as effective both in peanut oil, and in Priolube. OSI has been found to depend linearly on bond-dissociation enthalpies BDE of the phenolic O-H bond and the number of radicals captured per molecule of antioxidant σ. The differences in the antioxidative activity of polyphenols have been analyzed.

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# CERIC: an open offer of complementary techniques for materials characterization

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Scientific problems have become more and more complex in the latest years, and facing them requires an ever-increasing number of instrumental and analytical techniques, as well as a multi-disciplinary approach. Such complexity requires the availability of expertise as well as open access to a wide range of probing techniques and many different complementary instruments. The CERIC-ERIC research infrastructure was developed to face this challenge and to make a wide variety of instruments available through open access as well as the management of the acquired data.

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Thanks to the complementary investigation techniques made available by CERIC - including synchrotron radiation, neutron radiation, microscopic techniques, ion-beam analysis methods and nuclear magnetic resonance - it is possible to study organic and non-organic liquid samples at a level of atomic detail, thereby characterizing (bio) materials for a wide variety of applications.

# Solvation shell composition in aqueous ternary systems

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Through atomistic molecular dynamics simulations and IR spectroscopy combined with IR solvation shell spectroscopy, we investigated how solutes perturb molecular structures and local thermodynamics of binary solvents in their proximity by probing tert-butyl alcohol (TBA; solute) in water ($H_2O$; solvent) and 1-propanol (PRO; cosolvent) mixtures of composition spanning from pure propanol to pure water and 10% v/v steps in-between. TBA exhibits a weak propensity for hydrophobic aggregation, through both direct and solvent-shared contacts, for all solvent compositions, as expected. Counterintuitively, this propensity depends non-monotonically on solvent composition, with the highest association constant estimated from simulation (6.6 $M^{-1}$ occurring for solutions with small but not zero amounts of PRO. This result indicates an active contribution of the cosolvent to the solvophobic effect driving TBA – TBA aggregation. The composition of the solvent mixture near the hydrophilic (OH) part of the solutes varies similarly to that of the bulk solvent. In contrast, the solvent mixture near the methyl groups of TBA varies non-linearly with the composition of the solvent mixture in the bulk, with the solvation shell composition remaining largely consistent in propanol-rich bulk solvent mixtures but sensitive to variations in water-rich ones. IR solvation shell experiments focused on the analysis of the non hydrogen-bonded (or dangling) OH stretching feature centred at 3660 $cm^{-1}$. Quantitative analyses revealed consistent low presence of dangling OH up to 50% of water volume, after which a higher and similarly steady plateau is reached. This trend was confirmed in our simulations, lending confidence to the models used. Notably, other experimental attributes of the same feature exhibit a non monotonic trend at solvent compositions either side of 50% v/v water, above which the frequency is increasingly redshifted as the water content grows; the amplitude follows the opposite trend reaching its maximum in water-rich mixtures. The frequency shift correlates with the variation in composition of the solvation shell of the $CH_3$ groups of TBA seen in simulations, while the amplitude trends resemble those of the constant of association determined by simulations. This study quantitatively shows, for the first time through experiment and simulation, that small amounts of cosolvent can enhance the aggregation of small solutes in water, and correlates that observation to the nonlinear variation of the solvation shell composition of solutes with changes in bulk solvent.

# Multi-wavelengths Resonance Raman spectroscopy for discrimination and detection of degradation in extra-virgin olive oils

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Olive oil is a fundamental component of the Mediterranean diet and it is characterized by nutritional properties giving significant health benefits. In particular extra-virgin oils (EVOs) are obtained using cold pressing techniques avoiding any thermal or chemical treatments that may compromise their high-quality and the specific biochemical features. Adulteration is a chronic critical issue of olive oils since several mislabelling or mixed extra-virgin olive oils and seed oils are fraudulently sold. Another critical point concerns the influence of the storage conditions on the EVOs quality. Inappropriate settings for storage such as too high temperature or prolonged light and oxygen exposure can reduce the quality by inducing a series of chemical reactions (rancidity, oxidation and decomposition) that significantly change the physical-chemical properties of these substances. In this sense, incorrect storage can so dramatically change the quality of olive oils that they can no longer be classified as EVOs.

In recent years several techniques emerged for the detection of oil qualities and adulteration. Among them, the one gaining popularity are the ones which combines sensitivity, quickness, easiness of use and cost effectiveness. Here we propose a multi-wavelengths resonance Raman spectroscopy approach, with excitation in the visible and deep UV range, as a quick and sensitive method for the detection of olive oils quality. In our study we have investigated freshly produced samples of EVOs obtained in farm mills located in Italy, Croatia and Slovenia. A wide range of storage conditions have been simulated in our study, including warehouses, sheds, refrigerated cool rooms as well as other less suitable storage. By the comparison between the resonance Raman spectra, we have identified some band that are markers particularly sensitive to the unsaturation degree and content of carotenoids in the oils. To promote the automatic recognition of oil quality and conservation history, we plan to train an artificial intelligence using the multi wavelengths Raman spectra.

This proof-of-concept study opens the possibility to deploy an innovative spectroscopic approach to enable fast, simple and confirmatory diagnostics of quality in extra-virgin olive oils.

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## Deep UV Raman spectroscopy for probing eukaryotic cells and virus-infected cells

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Deep UV Resonance Raman (DUVRR) spectroscopy is a potent analytical technique that can be used to selectively detect and characterize different types of biological samples in real time and label-free approach.1 Selection of excitation wavelengths in the Deep UV can selectively enhance specific molecular groups in biological molecules, particularly protein, genome structures and lipids. This permits to efficiently isolate and detect biological Raman markers in the spectra2,3.

DUVRR spectroscopy have been proved as an asset in different types of investigation studies like bacteria identification4, malignant biological specimens5, studying protein structure6, and also for examining protein folding7 and fibrillation8.

In this work, we will show how to obtain stable, high quality and information-rich DUVRR spectra of active and pfa fixed Vero cells grown by using different experimental procedures. With evaluation of best grown procedure, we infected cells with the Vesicular Stomatitis Virus (VSV), that is a non-pathogenic virus, for humans, that serves as useful model for most recent viral outbreaks. The Vero E6 cells were infected with VSV virus and UVRR cell spectra collected as a function of time, to assess which conditions will provide us best spectra to distinguish virus-infected from non-infected cells. After choosing the best time point of infection, we will evaluate same conditions trough comparison with the visible Raman spectra, for further evaluation of spectral markers and changes. The results will be discussed in a way how the combination of chemometric approaches for DUVRR data analysis may provide robust classification models to diagnostic and prognostic purposes.

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## Low-Frequency Spectra of Amide Based Deep Eutectic Solvents

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Deep Eutectic solvents (DESs) are generally composed of hydrogen bonding acceptor (HBA) and hydrogen bonding donor (HBD) (solids in typical) and liquid state at room temperature. Recently, DESs based on Li salt and amide mixtures are gaining much research interest in electrochemistry [1]. For example, amide-based DESs show a clear nanoscopic heterogeneous structure, and their intermolecular interactions such as hydrogen bonding play a crucial role in the electrical conductivity of these systems [2]. Here, we have studied the low-frequency spectra of some amide-based DESs using femtosecond Raman-induced Kerr effect spectroscopy (fs-RIKES) to gain insights into the intermolecular interaction and solution structure.

Lithium bis(trifluoromethanesulfonyl)amide (LiNTf2) was chosen as HBA and five amides namely acetamide, propanamide, butyramide, N-methylacetamide, and urea were chosen as HBDs. The DESs were prepared by mixing dried Li-salt and amides at 1:3 molar ratio in a glove box under nitrogen atmosphere. A laboratory-built fs-RIKES based on a titanium sapphire laser was used for the intermolecular vibrational dynamics [3]. The scans were performed with a time resolution of 3300 points at 0.5 µm/step for a short time window of 11 ps at 298 K. The physical properties such as density, surface tension, and viscosity were also measured at 298 K.

The obtained Kerr transients of samples were normalized at t = 0 which is attributed to the electronic response. A biexponential function was used to fit the overdamped relaxations over 2 ps. The Kerr transients were then converted to low-frequency spectra using a standard Fourier-transform deconvolution analysis reported previously [4]. The low-frequency spectra of different DES systems showed differences in line shapes as well as peak frequency with different amides. For example, the line shape of LiNTf2/N-methylacetamide was trapezoidal and that of the other DESs was bimodal. The peak frequency in the higher frequency bands of LiNTf2/urea and LiNTf2/acetamide are peak 71.0 and 69.2 cm-1, respectively, which are higher than LiNTf2/ propanamide and LiNTf2/butyramide (~60 cm-1). This indicates that the strength of intermolecular interactions in the urea and acetamide DES systems is stronger than the propanamide and butyramide DESs. This difference in the strength of intermolecular interaction also affects the physical properties, as well. The LiNTf2/urea showed the highest density, surface tension, and viscosity (1.614 g cm-3, 41.6 mN m-1, and 2690 cP) among the five DES systems. The lowest surface tension was observed in the butyramide DES (30.4 mN m-1) and the lowest viscosity was found in the propanamide DES (132 cP).

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