X CONGRESS

DIVISION OF THEORETICAL AND COMPUTATIONAL CHEMISTRY

BOOK OF ABSTRACTS

September 14-16, 2026
Department of Chemistry
Sapienza University of Rome

Monday, September 14, 2026

Time	Session	Speaker / Content
13:00-14:00	Registration	
14:00-14:15	Opening Ceremony	Committee
	Chair	Mariagrazia Fortino
14:15-14:45	Invited Lecture	Mauro Stener (UniTS)
14:45-15:00	Oral Communication	Daniele Fazzi (UniBo)
15:00-15:10	Oral Communication	Alberto Zoccante (UPO)
15:10-15:20	Oral Communication	Francesca Argentieri (UniTS)
15:20-15:30	Oral Communication	Pierraffaele Barretta (UMG)
15:30-15:40	Oral Communication	Silvia Pezzola (UniRoma2)
15:40-15:50	Oral Communication	Vincenzo Vigna (CNR-ITM)
15:50-16:30	Coffee Break	
	Chair	Giovanni Di Liberto
16:30-16:45	Oral Communication	Emanuele Coccia (UniTS)
16:45-17:15	Invited Lecture	Riccardo Spezia (Sorbonne, France)
17:15-17:30	Oral Communication	Michele Ceotto (UniMi)
17:30-17:40	Oral Communication	Luca Melega (UniPi)
17:40-17:50	Oral Communication	Sara Balocco (SSM)
17:50-18:00	Oral Communication	Michael Zambrano (UniNA)
18:00-18:10	Oral Communication	Marco Bertani (UniMoRe)
18:10-18:20	Oral Communication	Giuseppe Amante (SSM)
18:20-20:00	Poster Session	Poster

Tuesday, September 15, 2026

Time	Session	Speaker / Content
	Chair	**Isabella Daidone**
09:00-09:30	**Invited Lecture**	**Volker Deringer (University of Oxford)**
09:30-09:45	**Oral Communication**	Alfonso Pedone (UniMoRe)
09:45-10:00	**Oral Communication**	Giovanni Maria Piccini (UniMoRe)
10:00-10:15	**Oral Communication**	Francesca Fasulo (UniNA)
10:15-10:25	**Oral Communication**	Roberto Paciotti (UniCh)
10:25-11:00	**Coffee Break**	
	Chair	**Marco D'Abramo**
11:00-11:10	**Oral Communication**	Marina Macchiagodena (UniFi)
11:10-11:20	**Oral Communication**	Ester Salvi (UPO)
11:20-11:30	**Oral Communication**	Daniele Bondi (UniBo)
11:30-11:40	**Oral Communication**	Alberto Barlini (SNS)
11:40-11:50	**Oral Communication**	Giacomo Londi (UniPi)
11:50-12:00	**Oral Communication**	Pietro Maria Curzietti (SNS)
12:00-12:30	**Invited Lecture**	**Francesco Zerbetto (UniBo)**
12:30-14:30	**Lunch + Poster Session**	
	Chair	**Valentina Migliorati**
14:30-15:00	**Invited Lecture**	**Marta Corno (UniTo)**
15:00-15:15	**Oral Communication**	Giacomo Melani (Eni)
15:15-15:30	**Oral Communication**	Roberto Amabile (Ruhr-Universität Bochum, Germany)
15:30-15:40	**Oral Communication**	Marco Marchetta (UniTS)
15:40-16:10	**Invited Lecture**	**Nadia Rega (SSM)**
16:10-16:50	**Coffee Break**	
	Chair	**Michele Pavone**
16:50-17:00	**Award Ceremony**	
17:00-17:15	**Roetti Award Talk**	Giovanni Bistoni (UniPg)
17:15-17:30	**Scrocco Award Talk**	Fortuna Ponte (UniCal)
17:30-17:45	**Del Re Award Talk**	Davide Mitoli (UniTo)
17:45-18:30	**Division Assembly**	
20:30	**Social Dinner**	

Wednesday, September 16, 2026

Time	Session	Speaker / Content
	Chair	Greta Donati
09:00-09:30	Invited Lecture	Dimitrios A. Pantazis (MPI, Germany)
09:30-10:00	Invited Lecture	Stefano Corni (UniPd)
10:00-10:10	Oral Communication	Francesco Gambuli (SSM)
10:10-10:20	Oral Communication	Rachele Zunino (UniNA)
10:20-10:30	Oral Communication	Eduarda Sangiogo (UniPi)
10:30-11:00	Coffee Break	
	Chair	Massimiliano Aschi
11:00-11:30	Invited Lecture	Gloria Mazzone (UniCal)
11:30-11:40	Oral Communication	Clara Saetta (UniMiB)
11:40-11:50	Oral Communication	Yolanda Rusconi (SSM)
11:50-12:00	Oral Communication	Matilde Benassi (UniMoRe)
12:00-12:10	Oral Communication	Marco Tommaso Barreca (UniPr)
12:10-12:20	Oral Communication	Matteo Rinaldi (SNS)
12:20-12:30	Oral Communication	Silvia Alessandrini (UniBo)
12:30-12:45	Oral Communication	Vincenzo Barone
12:45-13:00	Closing Remarks	

Oral Communications

Alessandrini, Silvia

Automatic exploration of the reaction between oxirane and the CH radical

Silvia Alessandrini [1], Moritz Bensberg [2], Cristina Puzzarini [1], Markus Reiher [2]

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Quantum chemistry offers a powerful route to elucidate reaction pathways and kinetics of radical-molecule systems relevant to the interstellar medium, but the exhaustive exploration of reactive networks remains a challenging task due to the high dimensionality and complexity of potential energy surfaces (PESs).

I will discuss an automated reactive PES exploration workflow applied to the oxirane (C2H4O) + methylidyne (CH) radical reaction, a prototype system that represents a challenging test case for automated network exploration. Indeed, the CH radical is a highly reactive species, with an unpaired electron, and an accessible quartet state. This peculiarity allows both addition and abstraction reactions to occur even under interstellar conditions. On the other hand, oxirane represents an unstable cyclic species offering different reactive sites to the radical. Thus, the reaction is expected to lead to several open-channels that challenge automatization.

The exploration is carried out using the NT2 algorithm as implemented in Chemoton, which requires only the reactants as input. Furthermore, the interface of Chemoton with Molassembler allows the direct characterization of all the newly discovered structures using molecular graphs and local geometry at the individual atoms, that permitting the differentiation of enantiomers.

The approach required about 17927 NT2 calculations, and discovered about 818 reactions and 212 compounds. Overall, the extensive network was confirmed with more than 60 exothermic channels lying below the energy of the reactants. Among products, 26 C3H4O isomers are found on the reactive PES (H atom as co-product), together with 23 isomers having the C3H3O formula (H2 as co-product). However, the most exothermic product is CO plus the C2H3 radical. Kinetic simulations based on the computed energies indicate that the dominant product at interstellar temperatures is the HCO radical and ethene (C2H4), with s-trans-propenal (acrolein) and 2H-oxetene being also formed in a non-negligible amount. Overall, the results underline the importance of automated computational exploration of reactive PESs for reliable astrochemical modeling and motivate systematic application of such workflows to other systems relevant for interstellar chemistry.

Amabile, Roberto

Graph decoration of periodic nets: counting admissible Metal-Organic Frameworks up to symmetry

Roberto Amabile
Ruhr-Universität Bochum

Metal-Organic Frameworks (MOFs) are a well-known class of nanostructured materials with tunable porous structure. Reticular chemistry – a branch that combines topology with crystallography – sits at the foundation of the deliberate, "rational" design strategies for new materials. The connectivity of MOFs is well understood when the discretised molecular blocks map in one and only one way onto the elements of an ideal graph – its nodes and edges – representing the inter-block connectivity – the net.

However, since blocks are not ideal spheres (for nodes) or cylinders (for edges), they can map onto graph elements in several symmetry-related ways. A rectangular block, for instance, sits in a square pocket in two highly-symmetric orientations.

This work addresses such local and global arrangements, collectively called a graph decoration, from the graph perspective: how to decorate a net, how to count its decorations up to symmetry, and how to decide whether admissible decorations exist. The work also shows how to enumerate the decorations constrained by chemical intuition expressed as forbidden local patterns and with an exhaustive treatment cast as a satisfiability problem.

ARGENTIERI, FRANCESCA

Toward An Efficient TDDFT Algorithm For Linear And Non-linear Optical Spectroscopies

Francesca Argentieri, Prof. Daniele Toffoli, Prof. Mauro Stener
Department of Chemical and Pharmaceutical Sciences, University of Trieste, Italy

Metal nanoclusters, in particular ligand-protected gold clusters, are challenging systems for the theoretical simulation of optical spectra because of their large electronic structure and dense excited-state manifolds[1,2]. In this work, we present ongoing developments toward a more efficient protocol, by combining polTDDFT[2], which uses a compact representation of the excited states, with the physical interpretation provided by the sum-over-states (SOS) expressions for Magnetic Circular Dichroism (MCD), Two-Photon-Absorption (TPA), and Two-Photon Circular Dichroism (TPCD) properties.

The first application concerns MCD spectra, focusing on the Faraday B term, which is the relevant contribution for closed-shell, nondegenerate systems[3,4]. The implementation is validated on molecular benchmarks and then extended toward gold nanoclusters, where MCD can provide detailed information on electronic transitions that are difficult to appreciate from absorption spectra alone [5].

As a further development, we explore TPA properties within the SOS framework[6,7]. Preliminary applications to model systems and to Au-based nanoclusters suggest that this approach may offer a unified and computationally efficient route to simulate one-photon absorption, MCD, and TPA spectra in complex nanostructured systems.

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Balocco, Sara

LOCAL A-SITE CONTROL OF OXYGEN VACANCY FORMATION AND MIGRATION IN Sr2Fe1.5Mo0.5O6−δ: A FIRST-PRINCIPLES STUDY

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Solid oxide fuel cells (SOFCs) and their reversible counterparts, solid oxide electrolyzer cells (SOECs), offer efficient routes for clean energy conversion, water splitting and hydrogen storage [1]. However, fast oxygen-ion and electron transport in state-of-the-art solid-state electrolytes and electrodes typically requires high operating temperatures, which compromise device durability and lead to slow start-up. Lowering the operating temperature therefore demands advanced electrode materials, particularly mixed ionic–electronic conductors (MIECs) [2].

Among these materials, perovskite oxides have emerged as promising electrodes for both the oxygen evolution and oxygen reduction reactions (OER/ORR), although their efficiencies toward these two opposite processes often differ substantially. Sr2Fe1.5Mo0.5O6−δ (SFMO) has attracted considerable interest as a potentially bifunctional electrode material because of its high electronic conductivity, redox-active B-site cations (Fe/Mo), and ability to accommodate oxygen vacancies [3 –6]. Following previous works focused on the role of cations at the B-site on oxide diffusion [3 –5], we investigate in this study the impact of cationic substitution at the A-site on oxygen vacancy formation and migration in SFMO via DFT+U-based first-principles calculations. Partial substitution of A-site cation of the parent material (Sr) with smaller (Ca) and larger (Ba) cations, both individually and in mixed Ca/Ba compositions, allowed us to probe the role of lattice strain while preserving the Fe–O–Fe framework involved in oxygen transport.

We find that Ca/Ba co-doping promotes oxygen-vacancy formation, whereas migration barriers are governed by the local A-site environment. Ca-containing environments facilitate oxygen migration, while Ba-rich environments hinder diffusion by generating less favorable transition-state geometries, consistent with the larger ionic radius of Ba^{2+}. As a result, low Ca/Ba co-doping emerges as the best compromise between vacancy formation and oxygen mobility. The same structural picture is reflected at SFMO (001) surface, where the effect of nearby A-site cations on vacancy formation is rationalized through comparison with tensile and compressive strain, supporting a primarily lattice-driven origin of the doping effect. Overall, our results reveal trends relevant to the optimization of SFMO as a bifunctional electrode material for low-temperature solid oxide technologies.

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Barlini, Alberto

Response Properties in Complex Environments with Multilevel Density Functional Theory

Alberto Barlini (a), Tommaso Giovannini (b)
(a) Scuola Normale Superiore,
(b) Università degli Studi di Roma Tor Vergata

Molecular response properties describe how molecular systems interact with external perturbations and are therefore central to the interpretation and prediction of photoinduced phenomena. However, the accurate simulation of such properties in complex environments remains challenging, because the molecular response is strongly affected by the interactions of the cromophore with the environment [1,2].

Here, we present a quantum embedding strategy for the calculation of molecular response properties in

complex environments [3]. The approach is based on a multilevel density functional theory (MLDFT) formulation [4,5], extended to response theory through a coupled-perturbed Kohn–Sham (CPKS) framework. The method combines Kohn–Sham fragment-localized molecular orbitals (KS-FLMOs) [6,7] with a polarizable molecular mechanics layer, effectively accounting for mutual polarization effects between the chromophore and its environment. The approach is general [3] and can be applied to any response properties, both linear and nonlinear. Our results demonstrate that multilevel polarizable embedding represents a versatile approach for the simulation of molecular response properties in complex media, with potential extensions toward spectroscopic observables and light-driven processes in heterogeneous environments.

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Barone, Vincenzo

Relazioni struttura-proprietà: possibili ambiguità dell'accordo tra teoria ed esperimento

Vincenzo Barone
INSTM

Le relazioni struttura-proprietà sono spesso interpretate come se un accordo stretto tra esperimento e teoria identificasse automaticamente la struttura molecolare rilevante. Mostriamo che questa inferenza può fallire anche ad alta accuratezza, perché l'osservabile misurata sonda in realtà una struttura di riferimento efficace, mediata vibrazionalmente, mediata per tunnelling o sopra barriera. La spettroscopia rotazionale in fase gassosa fornisce il banco di prova più pulito, poiché le costanti misurate dipendono quasi esclusivamente dalla struttura. Un confronto imparziale tra l'esperimento e le osservabili ottenute aggiungendo correzioni vibrazionali alle grandezze di equilibrio calcolate elimina ogni falso accordo generato dalla compensazione tra errori di struttura elettronica e media vibrazionale trascurata, e rende le incongruenze risolte isotopicamente diagnostiche dal punto di vista fisico.

In questo quadro, il livello di struttura elettronica adeguato per le molecole covalenti può risultare insufficiente per i sistemi con legami a idrogeno, siano essi intra- o intermolecolari. Tuttavia, in diversi casi aumentare il livello della teoria di struttura elettronica da solo non è sufficiente. Ad esempio, il conformero II della glicina e il complesso acido formico-acqua sono più coerenti con strutture di riferimento efficaci sopra barriera, mentre la malonaldeide e il dimero dell'acido formico richiedono strutture mediate per tunnelling. La stessa logica si estende a sistemi più grandi, nei quali il corannulene valida il quadro intramolecolare e il complesso corannulene-acqua localizza la discrepanza residua nella separazione intermolecolare. Quando la determinazione strutturale si avvicina all'accuratezza spettroscopica, l'accordo non è più sufficiente: occorre anche identificare la struttura di riferimento fisicamente rilevante.

Barreca, Marco Tommaso

Light-Controlled Qubit Coupling in Organic Diradicals Linked by an MR-TADF Emitter

Marco Tommaso Barreca, Francesco Di Maiolo

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Optically addressable high-spin states in organic systems represent an attractive platform for the optical control of magnetic interactions in molecular spin-qubit architectures.[1,3,4] While metal-free organic diradicals offer high chemical tunability, realizing externally controllable spin-spin interactions while preserving individual qubit addressability remains a fundamental challenge for implementing dynamic quantum operations.[1-4]

In this talk, we present a comprehensive theoretical study of two multiresonant thermally activated delayed fluorescence (MR-TADF)-bridged organic diradicals incorporating stable 1,2,3,5-dithiadiazolyl (DTDA) radical units.[5] Using high-level multireference ab initio electronic structure methods, namely CASSCF/QD-NEVPT2 and CASSCF/XMS-PDFT, we show that both architectures preserve a disjoint ground-state electronic structure with effectively degenerate singlet and triplet manifolds, indicating fully decoupled radical spins in the ground state. Upon photoexcitation of the MR-TADF bridge, the population of the bridge-centered LUMO triggers an exchange interaction that activates electronic communication between the two DTDA fragments, stabilizing a low-lying metastable quintet state (Q0) through the coupling between the bridge-centered triplet excitation and the radical spins.[5]

Notably, we show that thermally accessible torsional fluctuations around the bonds connecting the MR-TADF core to the radical units break molecular planarity, lifting the symmetry constraints that suppress spin mixing in fully planar configurations. This dynamic structural distortion activates spin-orbit coupling channels that efficiently mediate intersystem crossing, driving a robust population transfer from the low-lying triplet states to the target quintet manifold with rates reaching the order of 10^7 s^{-1}.

This study highlights MR-TADF emitter-linked diradicals as a promising, metal-free paradigm for accessing long-lived photoexcited high-spin states, opening a viable route toward the light-controlled activation of magnetic interactions between otherwise non-interacting molecular qubits.

[1] S. M. Kopp et al. JACS 146 (2024) 27935–27945
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[3] L. Savi et al. JCTC 22 (2026) 1465–1475
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Barretta, Pierraffaele

Tuning the Circular Dichroism of Chiral 2D Halide Perovskites via Halide Mixing and Metal Substitution

Pierraffaele Barretta, Mariagrazia Fortino, Alice Sardina, Ruggiero Sala, Giulia Grancini, Adriana Pietropaolo
Università Magna Graecia di Catanzaro

Chiral hybrid organic-inorganic perovskites (HOIPs) have emerged as prominent class of materials in optoelectronics, semiconductors and photovoltaic applications including solar cells[1,2]. These properties arise from the interplay between the organic cations and the inorganic metal-halide framework[3]. Herein, we investigate the effect of halide mixing and metal substitution on the circular dichroism (CD) response of chiral 2D-HOIPs based on methylbenzylammonium (MBA). Pb-based, Sn-based and mixed Pb/Sn perovskites with a fixed halide composition of 75% iodide and 25% bromide were synthesized, and the CD spectra of the R and S enantiomers were experimentally measured. A systematic red-shift in CD response is observed from 440 nm (pure-tin) to 470 nm (mixed Pb/Sn) and 500 nm (pure-lead), accompanied by a marked increase in signal intensity and a monosignate lineshape in the pure-lead systems, while mixed compositions exhibit broader spectral profiles. To rationalize these observations, a combined theoretical approach based on ab initio molecular dynamics and time-dependent density functional theory was employed to simulate CD spectra and analyze structural fluctuations[4]. The computed spectra reproduce the main experimental trends, including the relative CD intensities and enantiomeric sign inversion. Analysis of the AIMD trajectories reveals distinct differences in the structural flexibility of equatorial metal-halide bonds between Pb-based and Sn-based HOIPs. These results highlight the key role of metal-halide bonding dynamics in modulating chirality transfer and chiroptical activity in HOIPs, providing insights for the design of lead-reduced chiral perovskites with tailored optical properties.

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Benassi, Matilde

Modelling the structure and properties of NaPSiS glassy electrolytes via Machine Learning Potentials

Matilde Benassi, Marco Bertani, Alfonso Pedone
Università degli Studi di Modena e Reggio Emilia

Sodium solid-state electrolytes are very promising for large-scale energy storage, and sodium thiophosphate glasses stand out for their high ionic conductivity. Experimental studies show that doping with silicon (NaPSiS) improves their stability, but the exact relationship between composition, structure, and properties is still not well understood. Molecular Dynamics simulations could help investigate these systems, but classical potentials lack accuracy, while ab initio methods are too expensive for large systems. To solve this problem, Machine Learning Interatomic Potentials (MLIPs) offer a great alternative.

In this work, we developed MLIPs for NaPSiS systems to investigate the Mixed Glass Former Effect. The studied systems follow the formula y Na2S + (1-y) [x SiS2 + (1-x) PS5/2] with x = 0.5 or 0.67 and y ranging from 0.0 to 1.0, for which experimental data are available [1]. We compared the structural features obtained using both MACE foundation models (MP0, MATPES, and MH-1 [2]) and our fine-tuned models, focusing on the effect of the dataset on the results. Then, we analyzed sodium diffusion, highlighting the structural motifs that promote or hinder sodium ion mobility, providing new insights into the composition–structure–conductivity relationship in sodium-based solid electrolytes.

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Bertani, Marco

Atomistic Mechanisms of Na-Ion Mobility in NaPSO Glass Electrolytes From Ab-Initio Dynamics to Machine-Learning Simulations

Marco Bertani, Alfonso Pedone
Università di Modena e Reggio Emilia

The transition toward large-scale electrification requires energy-storage technologies that are not only high-performance but also sustainable and ethically responsible. While lithium-ion batteries currently dominate the market, their dependence on flammable liquid electrolytes and geographically constrained lithium resources raises concerns about long-term safety, cost, and supply security. Sodium-based all-solid-state batteries (AS3Bs) provide a compelling alternative thanks to the abundance of sodium and the intrinsic safety of solid electrolytes. Among the various candidates, sulfide-based glassy electrolytes—particularly NaPS compositions—exhibit high ionic conductivity and compositional tunability, but their strong moisture sensitivity limits practical use. Mixed oxysulfide glasses (NaPSO) mitigate this issue by incorporating oxygen, improving chemical robustness while retaining favorable transport properties.

Despite extensive experimental characterization, a detailed atomistic picture linking NaPSO structure to Na-ion mobility remains incomplete, especially regarding the non-monotonic conductivity trends observed upon S→O substitution. In this work, we combine ab-initio molecular dynamics (AIMD) with machine-learning interatomic potentials (MLIPs) based on the MACE framework to bridge this gap. AIMD simulations provide a physically grounded description of short-range order and local chemical environments, which we also use to validate a MLIP capable of accessing nanosecond timescales and statistically meaningful diffusion events.

Our analysis shows that Na-ion mobility is tightly controlled by the local structural environment. Oxygen-rich coordination, higher phosphate polymerization, and reduced Na–Na proximity suppress hopping events, whereas sulfur coordination, increased free volume, and the presence of nearby Na ions promote faster diffusion pathways. By applying Principal Component Analysis to chemically informed descriptors, we uncover clear structural signatures that distinguish highly mobile from weakly mobile Na species.

These results demonstrate that structure–mobility relationships exist in NaPSO glasses. This opens the door to future data-driven prediction of ionic mobility directly from local structure, enabling rational design of next-generation oxysulfide glass electrolytes.

Bistoni, Giovanni

New Quantum Chemistry Methods and Analysis Tools for Chemical Insight: Recent Developments in and beyond ORCA

Giovanni Bistoni
Università degli studi di Perugia

This presentation provides an overview of new quantum chemistry methods and analysis tools developed by our group, mostly implemented in ORCA, to interpret molecular interactions, chemical bonding, and electronic-structure effects. The main goal of these developments is to transform quantum chemical calculations into clear chemical insight, helping to rationalize why molecules interact, how bonds are formed, and which factors control stability and reactivity.

The talk introduces new approaches for studying noncovalent and intramolecular interactions,[1,2] including improved strategies for analyzing systems in which covalent bonds connect different molecular fragments.[3] It also presents atom-based analysis tools that help identify which parts of a molecule contribute most to key stabilizing or destabilizing effects.[4] Illustrative applications are shown in areas such as asymmetric catalysis, biological recognition, biomolecular interactions, and molecular complexes.

Finally, the presentation discusses how machine learning models,[5] inspired by these analysis tools, can be used to improve the accuracy and practical usefulness of density functional theory calculations. Together, these methods and tools contribute to the broader goal of computational chemistry: connecting electronic-structure theory with chemical intuition to better understand and predict molecular behavior.

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Bondi, Daniele

Integrating Computational Methods and Artificial Intelligence for Inverse Molecular Design of Novel Purine Derivatives Using PROTEUS

Daniele Bondi[1], Francesco Calcagno[2,3], Fabrizia Negri[1,3], Ivan Rivalta[2,3]

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The problem of inverse molecular design has become central to chemical research. It involves searching for molecules with specific target properties, an exceptionally difficult task due to complex structure-property relationships and the sheer size of chemical spaces to investigate, which makes brute-force computational studies impractical. Machine learning (ML) has recently emerged as a powerful solution to this challenge.

In this work, we focus on 2-aminopurine (2-AP), a purine isomer of adenine with numerous technological applications in nucleic acid research. Unlike native DNA and RNA bases, 2-AP exhibits strong fluorescence and an isolated absorption band around 300 nm. Substituting adenine with 2-AP thus enables the spectroscopic investigation of biological macromolecules. Through functionalization, the UV absorption wavelength of 2-AP can be tuned for novel applications. Here, an absorption energy target of 343 nm (3.61 eV), corresponding to a widely used laser wavelength, was selected for an inverse molecular design study using PROTEUS, a reinforcement learning-based software.1 PROTEUS explores chemical space by generating molecular candidates encoded as SELFIES strings and iteratively self-trains through their evaluation via a chemical reward function.

This AI-driven analysis focused on 2-AP derivatives bearing different substituents at the C6 position. Prior to the inverse molecular design study, a conventional computational investigation was carried out on prototypical purine molecules using conformational analysis, ground-state optimization, and TDDFT calculations to elucidate the effect of substituents on the first excited-state absorption energy. Building on these insights, the PROTEUS framework was then employed to efficiently explore large chemical spaces without exhaustive combinatorial screening. Ultimately, PROTEUS identified numerous 2-AP derivatives exhibiting absorption energies close to the target value of 3.61 eV.

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Ceotto, Michele

Semiclassical Methods for Quantum Adiabatic and Non-adiabatic Nuclear Dynamics

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Università degli Studi di Milano

In this presentation we show how quantum mechanical effects, such as electronic transitions, can be reproduced with semiclassical molecular dynamics.

To reach this goal we employ two approaches: one is to look at the non-adiabatic coupled Schroedinger differential equations, and the other is to approximate the Path Integral expression for the non-adiabatic quantum propagator.

Both differential and integral quantum dynamics expressions are formulated in semiclassical approximation. This approximation is performed on the exact quantum expression in a consistent way and without any specific recipe.

For each semiclassical method we perform simulations in the diabatic framework and focus on testing the ability to reproduce nuclear quantum effects in non-adiabatic coupling regime. These effects can be detected either by looking at vibronic spectra or at population transfers between electronic states. The derivation, the accuracy, and the advantages versus the disadvantages of these semiclassical formulations are presented.

In conclusions, the main goal of this presentation is to show how classical mechanics can be employed to “democratically” and accurately reproduce pure electronic and nuclear quantum effects such as those ones involved in quantum nuclear molecular dynamics beyond the Born-Oppenheimer approximation.

Coccia, Emanuele

Simulating closed- and open-quantum photoinduced electron dynamics for X-ray spectroscopies

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Dipartimento di Scienze Chimiche e Farmaceutiche, Universita' di Trieste

We present a real-time method based on the propagation of the time-dependent Schrödinger equation in the space of electronic states to compute X-ray linear absorption (XAS) and circular dichroism (XCD) spectra of molecules from the ground or a valence excited state. Applications to gas-phase thymine and methyloxirane are presented. Moreover, stochastic Schrödinger equation has been used to simulate time-resolved XAS in thymine for its ultrafast internal conversion.

Corni, Stefano

Strong coupling between plasmonic and molecular excitations: insights from multiscale modeling

S. Corni

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Nanoparticles featuring free electrons (such as metal or doped semiconductor nanoparticles) can sustain localized surface plasmons (LSPs), collective excitations of such free electrons that are characterized by high oscillator strength, resonance frequency tunability, and by the capability of amplifying the intensity of the exciting electromagnetic field in a nanometric spatial region close to the nanoparticle [1]. An excited molecule placed in such a region would be electromagnetically coupled to the nanoparticle excitations, may decay to the ground state by transferring the molecular excitation to a LSP, than in turn may decay re-exciting the molecule, and so on in a back and forth energy exchange process. When the coupling is sufficiently strong (i.e., the exchange process is faster than the intrinsic decay rate of both the molecule and the LSP), the picture rather becomes that of a quantum hybridization between the LSP and the molecular excited state, giving rise to mixed excitations (partly molecular and partly plasmonic) called plexcitons [2]. Plexcitons can modify how the energy flows between different molecules on the nanoparticle, or between different electronic states of the same molecule [3]. In principle, the creation of the hybrid state can also modify the photochemical reactivity of the original molecule [4]. During the years we have developed a multiscale approach able to describe strong coupling between LSPs and molecules [5], that exploit a continuum model description of the nanoparticle and a quantum chemical description (DFT/TDDFT and Couple Cluster) of the molecule. The approach will be briefly introduced and some recent results will be presented.

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Corno, Marta

Multiscale Computational Modeling of Drug Delivery Systems: From Mesoporous Silica to Cyclodextrin-Based Nanocarriers

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Drug delivery systems based on inorganic and supramolecular carriers have attracted increasing interest due to their ability to enhance the solubility, stability, bioavailability, and controlled release of pharmaceutical compounds. In this framework, computational chemistry represents a powerful tool for unveiling the molecular mechanisms governing host–guest recognition, adsorption, encapsulation, and release processes at the atomic scale.

This contribution provides an overview of the multiscale computational studies carried out on different classes of drug delivery systems, ranging from mesoporous silica materials to cyclodextrin-based supramolecular carriers. Early investigations focused on the adsorption and interaction of bioactive molecules on silica-based systems, highlighting the role of surface chemistry and intermolecular interactions in modulating drug–carrier affinity. More recently, particular attention has been devoted to cyclodextrin inclusion complexes involving native α-, β-, and γ-cyclodextrins, as well as methylated and hydroxypropyl derivatives.1

The presented studies combine quantum mechanical calculations, conformational exploration, and spectroscopic simulations to characterize the stability, geometry, and vibrational properties of host–guest complexes. Different pharmaceutical and bioactive molecules, including melatonin,2 curcumin, vemurafenib, caffeine, nitrazepam,3 and 4-methylumbelliferone, have been investigated as representative case studies. Particular emphasis will be placed on the analysis of binding energy redistribution, non-covalent interactions, solvent effects, and the relationship between molecular structure and encapsulation capability.

Finally, the contribution will discuss current efforts toward the modelling of increasingly realistic supramolecular architectures, including functionalized cyclodextrins and preliminary nanosponge models,4 with the aim of bridging the gap between idealized host–guest systems and complex nanocarriers employed in real drug delivery applications. Perspectives and challenges in the computational design of advanced nanocarriers for pharmaceutical applications will also be addressed.

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Curzietti, Pietro Maria

Quantum chemical insights into the adsorption of polycyclic aromatic hydrocarbons on the epsomite [010] surface

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Epsomite ($MgSO_4 \cdot 7H_2O$) is a hydrated magnesium sulphate of astrobiological interest, as Mg-rich sulphate deposits explored by the Mars2020 Perseverance mission at Jezero crater represent targets for preservation and detectability of molecular biosignatures. In this work, a slab model of the [010] epsomite surface has been worked out by means of periodic Density Functional Theory (DFT) calculations using the CRYSTAL software.The model surface has been subsequently applied to study the adsorption mechanism of hydroxylated polycyclic aromatic hydrocarbons (PAHs) of interest in the context of the Perseverance rover measurements performed within the Mars 2020 mission. Adsorption has been simulated by considering configurations driven by either interaction with under-coordinated Mg^{2+} cations or hydrogen bonding involving exposed water molecules or sulfate groups. Different orientations of the PAHs have been considered, according to the electrostatic features of the interacting moieties. Efforts have been devoted to understanding the character of the Mg-O bond and to elucidating the role of dispersion forces in driving the adsorption process and their interplay with more directional H-bond interactions. The results show that thin, non-stoichiometric slab models, worked out to reduce computational demands, do not reconstruct with respect to thicker ones and do not suffer from spurious

dipole moments. Orthogonally oriented adsorbates represent the least stable configurations, while oblique ad-structures evolve toward parallel or quasi-parallel arrangements after optimization. Electron density and charge displacement analyses reveal that the Mg-O interaction exhibits a closed-shell character, as also confirmed by a topological Bader analysis5. Molecule-surface interactions involving Mg^{2+} coordination with adsorbate's oxygen atoms appear to be energetically favoured, when dispersion is included. Dispersion interactions significantly affect the adsorption mechanism and, for 1,3-dihydroxynaphthalene the average molecule-surface hydrogen-bond energy has been found to be inversely correlated with the relative amount of dispersion to the interaction energy, highlighting the competitive interplay between these contributions.

Deringer, Volker

Invited Lecture

University of Oxford

Abstract not included.

Fasulo, Francesca

Atomistic Insights into Structures and Dynamics of Electrolytes/Sodium Metal Interfaces

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Sodium metal batteries (SMBs) are viable alternative to lithium-based energy storage technologies due to the high abundance and low cost of sodium. However, the practical deployment of Na metal anodes is severely hindered by interfacial instability with the electrolyte, which leads to uncontrolled solid electrolyte interphase (SEI) formation and rapid performance degradation [1,2]. A detailed atomic-scale understanding of SEI formation mechanisms is therefore crucial for the rational design of stable electrolyte systems.

In this work, we present a comparative atomistic investigation of SEI formation at the Na metal interface with two representative electrolyte systems: an ionic-liquid electrolyte (IL: NaFSI/PyrFSI) [3] and a polymer-based electrolyte, [Poly(ethylene oxide)Na][FSI] (PEO:Na) [4]. To overcome the limitations of first-principles simulations in accessing relevant model sizes and time scales, we develop a machine-learning interatomic potential (MLIP) via the MACE framework [5], trained on density functional theory reference data.

Large-scale molecular dynamics simulations reveal the decomposition of FSI at Na interface in both the electrolyte systems. However, the resulting SEI compositions and morphologies differ markedly, with strongly electrolyte-dependent kinetics and pathways. RTIL environments promote rapid fluorine release, laterally uniform NaF-rich passivation layers, whereas PEO-based electrolytes favor slower and stepwise decomposition with thicker or less cohesive interphases depending on the initial salt concentration. These results provide new atomistic insights into electrolyte-dependent SEI formation in sodium metal batteries and highlight the potential of MLIP atomistic simulations as predictive tool for electrolyte/electrode interfaces.

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Fazzi, Daniele

Modelling Static and Dynamic Disorder Effects in Organic Mixed Ionic-Electronic Conductors

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The diffusion of ions and electronic charges (hole/electron) in Organic Mixed Ionic-Electronic conductors (OMIECs) is profoundly affected by disorder effects.[1] The latter encompass structural, energetic and thermal fluctuations, spanning a wide range of spatial and time domains.

In this contribution, I report our recent findings in modelling disorder effects for two orthogonal classes of OMIECs, namely non-conjugated polymers and conjugated small-molecule systems. For both classes, the bulk structural properties are investigated by deriving a set of order parameters and auto-correlation functions, to provide detailed atomistic insights into both short- and long-range length scales, as well as to disclose the dynamic effects via molecular dynamics simulations.

For non-conjugated polymers, we introduce a novel strategy to evaluate both static and dynamic disorder effects in the description of the coupled electronic and ionic transport mechanisms.[2] For conjugated small-molecule systems,[3] we simulate realistic operational environments, namely the introduction of water in the crystal structures. Under confinement, water changes its structure and dynamics, displaying new static and dynamic properties with respect to the bulk, ultimately impacting the transport phenomena governing the OMIECs device performance.[4]

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Enantioselective Binding of Ruthenium Polypyridyl Complexes to G-Quadruplex DNA: A Computational Study for Cancer Therapy

Fortuna Ponte, Emilia Sicilia
Università della Calabria

Transition metal complexes containing ions such as Pt(II), Pt(IV), Os(II), Re(I), Ir(III), and Ru(II) have emerged as promising candidates for both conventional anticancer therapy and phototherapeutic applications, owing to their highly tunable photophysical, photochemical, and redox properties. Among these systems, Ru(II)-based complexes, particularly Ru(II) polypyridyl derivatives, have attracted significant attention because of their remarkable chemical stability, lower toxicity relative to platinum-based chemotherapeutics, and unique mechanisms of action. In this work, the attention will be focused on ruthenium-based complexes capable of inducing apoptosis in cancer cells through non-conventional pathways. These compounds have generated considerable interest due to their pronounced selectivity toward G-quadruplex DNA structures over canonical DNA structures. Starting from the study reported by Hall and co-workers (DOI: 10.1002/anie.201814502), which provided the first crystallographic evidence of the interaction between a mononuclear ruthenium polypyridyl complex and G-quadruplex DNA, the aim of the present work was to carry out a comprehensive computational investigation of the two ruthenium stereoisomers Λ-$[Ru(TAP)_2(11\text{-}CN\text{-}dppz)]^{2+}$ (L-Ru) and Δ-$[Ru(TAP)_2(11\text{-}CN\text{-}dppz)]^{2+}$ (D-Ru), where with TAP is indicated the ligand 1,4,5,8-tetraazaphenanthrene, while the dppz is the dipyridophenazine ligand. The primary objective of this project is to elucidate, through theoretical and computational chemistry approaches, the anticancer activity of these two ruthenium complexes capable of triggering apoptosis in cancer cells via unconventional mechanisms of action. In this work Molecular Dynamics (MD) simulations were carried out to investigate the binding mode of these ruthenium complexes with G-quadruplex structures. A detailed analysis of the interactions established with canonical DNA duplex, d(TCGGCGCCGA) structure was also performed to compare the two DNA assemblies. Furthermore, the photophysical properties of both Ru complexes were investigated through Density Functional Theory (DFT) and its time-dependent extension (TD-DFT), with the aim of evaluating their ability to generate oxidative stress through the production of reactive oxygen species (ROS).

Gambuli, Francesco

Divergent Structural Dynamics of Pathogenic and Disease-Resistant Human Prion Proteins at Microsecond Timescale

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Prion diseases (PrDs) represent a class of fatal neurodegenerative disorders dictated by the post-translational conversion of the cellular prion protein (PrPC) into a pathogenic, β-sheet-rich misfolded form (PrPSc). [1,2] Identifying the early-stage molecular determinants driving this conformational transition, along with the structural divergence introduced by single-point mutations, still remains a pivotal challenge.

In this study, we examine the structural dynamics of wild-type human PrP (wt-PrP), two pathogenic mutants associated with Gerstmann-Sträussler-Scheinker disease (P102L and G131V), [3] and the naturally occurring disease-resistant variant (G127V) [4] via extensive all-atom molecular dynamics (MD) simulations on the microsecond timescale.

The microsecond-long MD simulations combined with several post-processing analyses (quantitative characterizations of secondary structure elements and specific interaction pathways among residues), allowed us to exhaustively monitor both the amino acids side chains dynamics and larger sizescale dynamics such as the secondary structure elements.

We systematically investigated both the globular C-terminal domain and the intrinsically flexible N-terminal domain. We found that the dynamics of both domains are affected by the mutants, with G131V importantly impacting the globular domain. Overall, our results unveil, from a molecular perspective, the completely different behavior of the G127V with respect to the G131V mutation, providing an atomistic insight on the disease-resistant and pathogenic effect, respectively. Overall, in this puzzling scenario, our results shed light on the C-terminal domain and N-terminal domain dynamics of wt-, pathogenic and disease-resistant PrPs. [5]

Our results are also in agreement with experimental findings [6] and provide a molecular picture for understanding structural events that can be propaedeutic to misfolding processes.

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The catalytic cycle of a fatty acid photodecarboxylase from a multiscale QM/MM approach

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Fatty acid photodecarboxylases from Chlorella variabilis (CvFAPs) are rare photoenzymes that catalyze light-driven, redox-neutral decarboxylation of fatty acids into C1-shortened hydrocarbons,[1,2] although several key steps of their catalytic mechanism remain unclear.

Here, we use a multiscale computational approach combining classical MD and QM/MM MD simulations to characterize the full catalytic cycle. We first investigate the protein-driven forward electron transfer (fET) from the fatty acid substrate to photoexcited flavin cofactor. Our results reveal that fET triggers active-site rearrangements, including reorganization of a nearby water molecule into a hydrogen bond with the flavin and migration of the substrate carboxylate away from the cofactor, collectively enabling a downhill electron transfer on the hundreds of picoseconds timescale. Subsequent QM/MM MD simulations show that the resulting fatty acid radical undergoes rapid decarboxylation within a few picoseconds, overcoming a small activation barrier.[3] We then examine the termination step, finding that the alkyl radical is mainly quenched via proton transfer from a conserved arginine (scenario B), while bicarbonate formation involving water is only rarely observed (scenario A), suggesting a minor role at room temperature.[4] Finally, excited-state QM/MM calculations indicate that different active-site configurations reproduce similar red shifts in flavin absorption, consistent with transient FADRS species.[2,5]

Overall, this work provides a coherent molecular picture of CvFAP catalysis, highlighting the interplay between active-site electrostatics and water dynamics.

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Macchiagodena, Marina

Relative Binding Free Energies via a Lennard-Jones Reference

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In the last decades, accurate in silico prediction of protein-drug binding affinities has been a critical part of hit-to-lead efforts in drug discovery. Several computational methodologies, based on molecular dynamics (MD) simulations with explicit solvent, have been devised to improve the calculation of absolute binding free energy in drug-receptor systems (Cournia, Z. et al., J. Chem. Inf. Model., 2017, 57 (12), 2911-2937).

One of the most used MD-based methods for free energy determination is the so-called alchemical approach (Gao, J. et al., Science, 1989, 244, 1069–1072), in which the free energy change between two states is obtained using a stratification of nonphysical intermediate states.

In this context, the Dual-Topology (DT) scheme for Relative Binding Free Energy (RBFE) calculations between dissimilar molecules is used. The method is based on the production of a swarm of concurrent nonequilibrium (NE) alchemical simulations that are started from end-state canonical configurations sampled using the Hamiltonian Replica Exchange Method (HREM). To eliminate the requirement of chemical similarity between ligands, we have introduced a universal Lennard-Jones (LJ) blob reference state. The application to 16 MCL-1 ligands achieved accurate results comparable to experimental findings. The method is now applied using homogeneous CPU-based architectures or hybrid CPU/GPU architectures since the algorithm has been adapted for two of the most widely used software packages for high-performance molecular dynamics, GROMACS (Abraham, M. J. et al., SoftwareX, 2015, 1, 19-25) and ORAC (Marsili, S. et al., J.Comput. Chem., 2010, 31, 1106-1116).

Marchetta, Marco

Dynamical symmetries and selection rules in high-harmonic generation spectroscopy of nonlinear molecules

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High-harmonic generation (HHG) is a highly nonlinear process that arises from the interaction of matter with intense nonresonant laser pulses [1]. HHG provides a powerful tool for investigating electron dynamics [2]; furthermore, the HHG spectrum encodes information about the system electronic structure [3]. We have computed HHG spectra of H2O and NH3, interacting with linearly polarised pulses in different orientations [4] and the HHG spectra of CH4 interacting with a bicromatic (ω/2ω) bicircular pulse. All the calculations have been carried out using the real-time time-dependent configuration interaction with single excitations (RT-TD-CIS) method [5] coupled with a Gaussian basis set. The selection rules in the HHG spectra, as computed with RT-TD-CIS, are interpreted in the framework of dynamical symmetries (DSs). These symmetries emerge as a combination of the temporal properties of the driving pulse and the spatial characteristics of the molecular electronic Hamiltonian and of the pulse [6,7]. These symmetries can also be broken if the molecule is not in its equilibrium geometry; this results in the progressive appearance of the subset of harmonics forbidden at the equilibrium geometry, whose intensities increase with the asymmetry. This is shown by considering the asymmetric stretching of the CH4 molecule.

Moreover, multiple-orbital effects have been observed and analyzed [8,9]. The findings underscore the pivotal role of DSs in shaping the HHG response, highlighting their ability to bridge the complex interactions between molecular structure, electronic transitions, and the pulse. We show that Gaussian-based RT-TD-CIS is a reliable tool to study the HHG spectra of aligned nonlinear molecules, and the role of ionisation/recombination channels in the dynamics.

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Harnessing Ruthenium Complexes for Phototherapies: A Computational Perspective

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Light-activated medical treatments are gaining increasing prominence in cancer therapy because of their high selectivity, which helps reduce the adverse side effects typically associated with conventional chemotherapy. Among these approaches, photodynamic therapy (PDT) and photoactivated chemotherapy (PACT) are emerging as complementary strategies for the selective destruction of neoplastic tissues through direct cellular damage. Both techniques rely on the irradiation of otherwise inert compounds, promoting the population of excited states of the drug. In PDT, these excited states generate cytotoxic species such as singlet oxygen ($^1O_2$) and other reactive oxygen species (ROS), whereas in PACT they trigger the release or formation of the active therapeutic species. Metal-based compounds have been extensively investigated for these applications and, compared with purely organic chromophores, offer the advantage of accessing a rich manifold of excited states that are particularly relevant for phototherapeutic activity. In particular, ruthenium polypyridyl complexes have recently attracted considerable attention as a new generation of phototherapeutic agents.

In this context, density functional theory (DFT) and time-dependent DFT (TDDFT) simulations have proven to be powerful tools for accurately predicting key photophysical and photochemical properties of metal-based photosensitizers [1–10]. These computational approaches contribute to elucidating the underlying photochemical pathways and provide valuable insights for the rational design of new ruthenium-based drugs with enhanced therapeutic performance.

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Melani, Giacomo

Taking care of complexity: A pragmatic view on computational modeling in catalysis and materials science

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Computational modeling is a central tool in materials science, yet its industrial relevance requires going beyond idealized reaction pathways on pristine surfaces. Real catalysts operate under harsh conditions, where local chemistry is tightly coupled to macroscopic reactor environments. The key challenge for computational catalysis is therefore not simply to perform larger or longer simulations, but to ensure that these calculations capture realistic complexity without compromising quantum–chemical accuracy. In this work, we argue for a transition from static representations to an operando view of catalytic materials in sustainable technologies. We discuss strategies to incorporate dynamic effects, the role of machine–learning interatomic potentials in bridging quantum and mesoscale descriptions, and the design of high–throughput workflows that genuinely support decision–making. Our central message is that catalysts should no longer be treated as rigid structures, but as dynamic, adaptive systems characterized by thermal fluctuations, transient reactive interfaces, and evolving surface chemistry. From an industrial standpoint, success lies not in identifying a single minimum–energy pathway, but in developing robust computational frameworks capable of guiding screening and process decisions under realistic operating conditions.

Melega, Luca

Cholesky decomposition implementation of molecular structure and properties at the Coupled Cluster level

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In recent years, rank-reducing techniques have seen a surge of interest by the quantum chemistry community, due to them being able to mitigate the intensive computational cost associated with electronic structure methods, thus extending their applicability to larger molecular systems. In that regard, we exploit the Cholesky decomposition (CD) of the electron repulsion integrals (ERI) tensor [1], reducing the impact of its manipulation on the cost of quantum chemical calculations. CD is not only able to compress the information stored within the ERI tensor, making it possible to manipulate it without recomputing or reading the integrals from disk, but also affords a strict control over the accuracy of their representation, since the approximation error is bound to be lower than the predetermined threshold used for the decomposition. Here we applied the CD of ERIs and their derivatives to the computation of analytical geometrical gradients at the Coupled Cluster (CC) level of theory [2,3]. We present an efficient and parallelized implementation of CD, using a two-step algorithm [4] that can fully exploit Abelian point-group symmetry [5] and compute not only the Cholesky vectors, but also their derivatives with respect to nuclear displacements, also fully exploiting point-group symmetry. We use the Cholesky vectors and their derivatives to achieve an efficient and parallel implementation of the CC density matrices and for the intermediates in the Z-vector equations, along with their contractions with Cholesky decomposed differentiated integrals, yielding optimized molecular structures at the CCSD level [6]. The capabilities of our new implementation are tested on a range of systems, for which we compute the energy and molecular structures. Lastly, our implementation of CD-CCSD perturbed amplitude equations, inspired by the one developed by Gauss and Stanton [7], with the objective of computing CC second-order properties such as electric polarizabilities and NMR nuclear shieldings, will be analyzed.

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Paciotti, Roberto

QM Characterization of an Unprecedented Halogen Bond: An FMO Study of Human Carbonic Anhydrase II Inhibition by Bithionol.

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Halogenated ligands offer promising drug design strategies through halogen bond (X-bond) formation with key target residues. Here, we computationally investigate the complex between human carbonic anhydrase II (hCA II) and the organochlorine compound bithionol, which inhibits the enzyme by targeting the His64 side chain via a novel nitrogen-halogen bond [1]. Using Non-Covalent Interaction (NCI) analysis [2] and the Fragment Molecular Orbital (FMO) method [3], we characterized this peculiar binding mode. Molecular Electrostatic Potential (MEP) calculations mapped a pronounced σ-hole [4] on the bithionol chlorine atom directed toward His64. FMO single-point calculations (M06-2X/6-31G*//PCM[1]) quantified the pair interaction energy (PIE) of the His64-bithionol X-bond at -2.9 kcal/mol, alongside a weaker X-bond with Phe20 (-1.2 kcal/mol). Furthermore, Pair Interaction Energy Decomposition Analysis (PIEDA) [5] revealed that dispersion forces account for 59% of the total attractive energy. FMO fragment analysis demonstrated a marked binding asymmetry: one phenolic ring drives the X-bonds, while the other maximizes contacts within a deep hydrophobic cavity. These insights provide a robust structural rationale for designing asymmetric hCA II inhibitors based on halogenated scaffolds.

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Metallocofactor Plasticity in Biological Water Oxidation

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Life relies almost entirely on the ability of photosynthetic organisms to use sunlight for powering the synthesis of complex chemicals. Photosystem II (PSII) is the enzyme responsible for the initial conversion of excitation energy into the flow of electrons that sustains all subsequent redox processes in photosynthesis. PSII is also responsible for catalysing the all-important 4-electron oxidation of water, the only source of dioxygen in Earth's atmosphere. Water oxidation is catalysed by a manganese-containing multinuclear metallocofactor (Mn4CaOx) that is unique in biology, the oxygen-evolving complex (OEC). Its detailed geometric and electronic structure description is essential for understanding its function. Parallel to the slow progress of crystallographic studies, the combination of quantum chemistry and spectroscopy play a leading role in uncovering fundamental principles and previously unsuspected phenomena. A key concept that emerges from studies that focus on magnetic and spectroscopic properties of the OEC is the inherent plasticity of the metallocofactor, an aspect which remains inaccessible to conventional structural studies. Depending on the catalytic state, this manifests as Jahn–Teller orientational isomerism, valence tautomerism, and substrate-binding equilibria. Crucially, our research indicates that this plasticity is of fundamental mechanistic significance in biological water oxidation, being employed to control access to active species, to gate catalytic progression, and to direct reactivity. The polymorphism of the catalyst and the use of minority species at crucial catalytic points illuminates unexpected evolutionary optimizations in biological water oxidation, but also raises important questions for design strategies in bioinspired approaches.

Pedone, Alfonso

Challenges in Atomistic Simulations of Glasses and Amorphous Materials

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Atomistic simulations have become indispensable tools for understanding the structure, dynamics, and properties of glasses and amorphous materials. Nevertheless, several fundamental challenges still limit their predictive power, transferability, and direct connection with experiments. In this lecture, three interconnected issues will be discussed: the generation of realistic glass structures, the development and validation of reliable interatomic potentials, and the prediction of structural and functional properties using both classical and machine-learning-based approaches. Particular emphasis will be placed on the complexity of reproducing the potential energy surface of disordered materials, the role of thermal history and quenching protocols, and the critical importance of training datasets in machine-learning interatomic potentials (MLIPs).

Recent examples from our research activities on oxide, sulfide, and oxysulfide glasses for energy applications will be presented, highlighting current limitations in reproducing medium-range order, and properties.[1,2] The lecture will also briefly discuss recent efforts on the prediction of crystallization in aluminosilicate glasses using machine learning combined with atomistic structural descriptors,[3] the simulation of nanoindentation experiments to investigate deformation mechanisms in glasses,[4] and the prediction of solid-state NMR shielding parameters through first-principles and machine-learning-assisted approaches.[5] The lecture will conclude with a discussion of open challenges and future perspectives for integrating atomistic simulations, machine learning, and experimental validation in glass science.

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Piccini, GiovanniMaria

Beyond Intuition: Dynamic Data-Driven Exploration of Catalytic Reactivity with Chemical Accuracy

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Free energy sampling of complex catalytic processes requires identifying not only reactants and products, but also a multitude of intermediates and short-lived metastable states. This remains a fundamental challenge in computational chemistry, particularly in systems where traditional approaches rely on chemical intuition or inefficient exploration of reaction space.

Loxodynamics[1] is a machine learning–driven method for automated reaction discovery based on biased molecular dynamics. By exploiting local asymmetries in configuration space, it enables efficient exploration of low-energy pathways without prior knowledge of the reaction network. The approach combines dimensionality reduction with an iterative sampling strategy to reconstruct free energy surfaces at finite temperature and identify relevant metastable states and transition pathways.

Here, we apply this framework to the study of proton transfer dynamics in catalytic systems under operando conditions. In particular, we investigate reactions such as alcohol dehydration[1], acetalization, and aromatic alkylation in zeolites[2], where proton transfer plays a central role in determining reactivity and selectivity. These systems provide a stringent test for both reaction discovery and the accurate description of proton dynamics in confined environments.

To further improve predictive accuracy, we introduce a perturbative QM/QM MetaFEP scheme[2], enabling the estimation of free energy profiles at coupled-cluster level beyond density functional theory. This approach allows for a quantitatively reliable description of proton transfer processes and reactive intermediates in realistic catalytic systems.

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Following Ultrafast Molecular Relaxation Through Transient Vibrational Signatures

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Scuola Superiore Meridionale

Vibrational spectroscopy has become a central tool for probing the ultrafast structural evolution of photoexcited molecular systems. Techniques such as femtosecond stimulated Raman, transient infrared, and two-dimensional infrared spectroscopy provide access to the time-dependent evolution of molecular geometries, intermolecular interactions, and energy redistribution pathways. Extracting mechanistic information from these experiments, however, requires theoretical approaches capable of connecting spectral signatures to the underlying electronic and nuclear dynamics while explicitly accounting for environmental effects.

In this talk, I will present a multiscale computational framework combining electronic structure calculations, excited-state ab initio molecular dynamics, hybrid QM/MM methodologies, and advanced non-periodic descriptions of solvation. This strategy enables a molecular-level characterization of ultrafast relaxation processes and reveals how specific vibrational coordinates drive photochemical and photophysical transformations.

Time-dependent vibrational analyses based on wavelet methodologies provide a direct view of mode activation, coupling, and anharmonicity along the dynamics. We will show how these approaches can be extended well beyond the Franck–Condon region, allowing transient vibrational signatures to be tracked throughout the relaxation pathway and correlated with evolving molecular structure. Attention will be placed on the interpretation of nonlinear vibrational spectroscopies, including multidimensional approaches, where mode coupling, spectral diffusion, and solvent fluctuations encode key information on reaction mechanisms and energy flow.

Applications will be discussed for molecular rotors, π-stacked charge-transfer complexes, photoacids, and protein–DNA cross-linking models. I will conclude by outlining ongoing methodological developments and future perspectives for the computational interpretation of increasingly complex ultrafast vibrational spectroscopies.

Rinaldi, Matteo

Multiscale DMRG/Fluctuating Charges Framework for Modeling Electronic Excitation Energies in Solution

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The investigation of electronic transitions in solution is a useful tool to gather information on systems involved in relevant biological or chemical processes. However, solvated systems are composed of a very large number of atoms; therefore, from a computational point of view, a reasonable way to address this is to resort to multiscale modeling.[1,2]Among these methods, hybrid Quantum Mechanics /Molecular Mechanics (QM/MM) methods have proven to be particularly successful[3,4] since they are capable of describing specific solute-solvent interactions, such as hydrogen bonding patterns, which can play a role in shaping spectroscopic signals.[5]

Many interesting solvated systems contain a solute with a complex electronic structure that needs to be described by an accurate multiconfigurational QM approach, such as conjugated systems, chromophores in photosensitive proteins or transition metal enzymes. To this purpose, we present a QM/MM strategy based on the coupling of the Density Matrix Renormalization Group (DMRG)[6,7] method to the Fluctuating Charges (FQ) force field (DMRG/FQ).[9] This is based on the framework of our recent CASSCF/FQ[8] method and permits treating large solute molecules using active spaces of more than 20 electrons in 20 orbitals.

The resulting DMRG/FQ method is then applied to the calculation of electronic excitation energies and solvatochromic shifts of a set of molecules in solution, benchmarked against experimental data, which paves the way for future applications on biological systems.

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Rusconi, Yolanda

Investigating the Interplay between Enantiomorphic-Site and Chain-End Control in the Ring-Opening Polymerization of β-Lactones through DFT calculations

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Understanding the molecular origins of stereocontrol in ring-opening polymerization (ROP) remains a fundamental challenge in catalyst design for the synthesis of polymers with the desired properties.[1,2] In this work, we report a novel chiral "sandwich" β-diketiminate zinc catalyst, rac-(4-MeBDI*)ZnOiPr, that polymerizes rac-trans-3,4-dimethylpropiolactone (trans-DMPL) to produce isotactic trans-polyhydroxymethylbutyrate (trans-PHMB), with a %mm = 73-75%.[3] Density functional theory (DFT) calculations combined with activation strain model (ASM)[4] and buried volume (%VBur)[5] analyses provide an elucidation of the stereoselective polymerization mechanism operated by this system.

Computational investigation, paired with a detailed NRM analysis, reveals that stereocontrol does not originate from a purely chain-end-control (CEC) or enantiomorphic-site-control (ESC) mechanism. Instead, this catalytic system operates through a novel chirality-assisted chain-end control (CACEC), in which the conjunction of catalyst and propagating chain chirality act in synergy, determining monomer insertion selectivity. DFT calculations show that the Δ catalyst enantiomer bearing an RR chain-end (Δ-RR) exhibit a strong preference for isotactic enchainment, with a calculated free-energy difference of 1.3 kcal·mol-1 between competing insertion pathways, corresponding to ~90% selectivity for incorporation of second RR monomer unit. In contrast, the Δ-SS species, coordinated to a SS chain-end, is essentially unselective, in accordance with the NMR evidence. Analysis of the stereodetermining transition states reveals that stereocontrol arises from the interplay of chain positioning within the catalytic pocket, monomer distortion, and steric interactions with the ligand framework. ASM analysis demonstrates that increased deformation of the incoming monomer is the principal source of destabilization in the disfavored pathways. %VBur analysis further highlights how the asymmetric steric environment generated by the catalyst preferentially accommodates the RR chain-end, resulting in lower activation barriers and enhanced activity. These findings provide a detailed molecular-level framework for understanding stereocontrol in chiral lactone polymerization catalysts, key to design more selective ROP systems.

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Saetta, Clara

Nature and pH-dependent Surface Chemistry of TiN in Aqueous Environment from Ab-Initio and Machine Learning Accelerated Simulations

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The nature of surfaces in aqueous environment has crucial implications in a broad series of important processes important in catalysis and materials chemistry. Titanium Nitride (TiN) is a widely applied system. The atomistic nature of its interface with water and its pH-dependent surface chemistry are rather unexplored. In this presentation, we used density functional theory calculations in conjunction with ab initio and machine learning molecular dynamics to investigate the nature of TiN in aqueous environment. We focused on the stable (100) TiN surface. Then, we adopted the grand canonical formulation of species in solution to study di acid-base equilibrium constants on the surface and we calculated the pH at the point of zero charge (pHPZC), close to 3. We validated the predicted pHPZC with experimental measurements on commercial TiN. We also predicted the dissociation free energy of water at 298 K which is ~0.5 eV, comparable to other materials such as TiO2. The results of this study provide an atomistic description of the nature of TiN/H2O interface. They provide some information on relevant aspects for materials chemistry and catalysis applications of TiN.

Salvi, Ester

TDDFT Nonadiabatic Couplings in Solution : the VEM-UD State-Specific Polarization Approach

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Nonadiabatic coupling matrix elements (NACMEs) are crucial quantities in the description of photophysical and photochemical processes, determining internal conversion rates, surface-hopping dynamics, and the optimization of conical intersections. While analytic NACME formulations within time-dependent density functional theory (TDDFT)[1] are well established for gas-phase systems, their extension to simulations in the condensed phase remains limited.[2] Existing implementations are built on a linear-response (LR) treatment of the solvent reaction field, providing a partial description of excited-state dispersion while fully excluding the state-specific polarization effects.[3]

In this work, we present an analytic formulation of derivative couplings within TDDFT that explicitly incorporates state-specific (SS) polarization effects through the Vertical Excitation Model (VEM), [4] in its unrelaxed-density (VEM-UD) flavor.[5] The implementation, carried out in a development version of the Gaussian software package, was validated against numerical finite-difference calculations.

Applications across a diverse set of molecular systems demonstrate that state-specific solvent polarization consistently affects the computed NACMEs and internal conversion rates, an effect that is missed by standard LR-PCM treatments. In several cases, the inclusion of SS polarization through VEM-UD brings the computed rates into closer agreement with experimental observations or reference values from higher-level theoretical methods.

Overall, the new VEM-UD framework represents a significant advancement for simulations of nonadiabatic processes in solution, with direct relevance in the application to systems of increasing complexity, from small photochemical benchmarks to TADF emitters and substrates with singlet–triplet inversion.[6]

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Sangiogo Gil, Eduarda

Simulating the excited-state dynamics of a fatty acid photodecarboxylase

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Fatty Acid Photodecarboxylase (FAP) is a photoenzyme that catalyzes the light-driven decarboxylation of fatty acids. This photochemical reaction involves a complex interplay of excited-state electron transfer, radical formation, and environmental effects provided by the protein matrix. The reaction is initialized by a photoinduced electron transfer from the fatty acid substrate to the flavin cofactor upon blue-light absorption, leading to the formation of reactive biradical intermediates. Understanding these early photochemical events is fundamental for the rational design of new photoenzymes and photocatalytic systems.

In this work, we employ excited-state dynamics simulations based on trajectory surface hopping within a semiempirical framework to investigate the initial stages of the FAP reaction mechanism, from photoexcitation to biradical formation. Particular emphasis is placed on the challenges associated with describing the complex electronic structure, the nonadiabatic processes occurring within the timescale on the order of hundreds of picoseconds, and the influence of the enzymatic environment. We discuss the computational methodologies, descriptors, and protocols developed to address these challenges and enable efficient simulations. Our results provide mechanistic insight into the early excited-state dynamics of FAP and offer guidance for the future design and optimization of photoactive biocatalysts.

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Kuquinones derivatives as new potent modulator of mTorc1 activity

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Kuquinone (KuQ) derivatives [1], such as 1-ethyl-KuQ [1] and 1-methyl-KuQ [2], are well known for their photocatalytic properties [3]. Cell viability assays have shown that KuQs reduce cancer cell growth by 50% (IC50) at concentrations in the mM range, while their toxicity toward fibroblasts is negligible [1–2]. Despite their low solubility, KuQs also inhibit Topoisomerase I in vitro at mM-range concentrations [4]. The main limitations of KuQs are therefore: i) very poor solubility, and ii) biological activity confined to the mM range.

To address these limitations, novel KuQ-based compounds were designed by functionalizing the KuQ core with polar moieties inspired by naturally occurring polyphenols. In silico approaches, spanning quantum-mechanical (QM) and molecular dynamics (MD) methods, were employed to predict key molecular properties, including the partition coefficient (LogP), ADME profile (absorption, distribution, metabolism, excretion), and compliance with Lipinski's rule of five.

Among the potential biological targets, mTORC1 was selected as the most promising candidate, given its central role in cellular regulation across both physiological and pathological conditions [5]. Docking studies were therefore performed on mTORC1, comparing the KuQ derivatives with rifampicin, a well-established mTORC1 inhibitor [5]. The results show that KuQ derivatives exhibit higher docking scores and greater stability within the active site compared to rifampicin ($\Delta G_{KuQ} = -10.8$ kcal/mol vs. $\Delta G_{rifampicin} = -9.2$ kcal/mol).

Finally, cellular toxicity and modulation of the mTORC1 effector pathway were evaluated in hepatocellular carcinoma cells through cell-viability assays and Western blot analysis.

Spezia, Riccardo

Simulating Collision-Induced Dissociation with Reaction Dynamics: From Electronic Structure to Machine Learning

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Understanding the products and reaction mechanisms obtained in tandem mass spectrometry is of critical importance across a wide range of fields, from fundamental research to applications such as proteomics and metabolomics. Computational methods can play a key role in predicting the spectra of unknown molecules, as well as in obtaining quantitative information, such as bond dissociation energies.

Over the past few years, we have developed a reaction dynamics-based approach to study the fragmentation spectra and mechanisms of complex organic and biological molecules, with a particular focus on peptides and metabolites. In particular, we have successfully reproduced experimental spectra and proposed reaction mechanisms that are difficult to deduce from experiments alone.

These simulations are typically performed using electronic structure theory, ranging from MP2 and DFT for smaller systems to semi-empirical Hamiltonians and DFTB for larger ones. However, to accurately simulate the physical process, it is necessary to run multiple trajectories (from 100 to 1000 or more, depending on the system). This requirement limits the time length of each trajectory to a few picoseconds, making a direct comparison with experimental conditions, where the time scales are much longer, complicated.

The recent advent of machine learning methods opens an intriguing possibility: achieving DFT-level accuracy while enabling simulations on nanosecond time scales. Here, we will show how this approach can enhance our understanding of the fragmentation mechanisms of a simple model system, such as protonated urea.

Stener, Mauro

New TDDFT Algorithms, Protocols and Analysis Tools for the Study of Optical Properties and Plasmons of Large Metal Clusters

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A recent algorithm to solve the TDDFT equations in the space of the density fitting auxiliary basis set has been developed and implemented in ADF/AMS [1]. The TDDFT equations are recast to a non-homogeneous linear system, whose size is much smaller than in Casida formulation, allowing to calculate a wide portion of the absorption spectrum for large systems. The method extracts the spectrum from the imaginary part of the polarizability at any given photon energy, avoiding the bottleneck of Davidson diagonalization. The new algorithm also benefits from a recent very efficient extension to hybrid and range-separated functionals [2,3] and is supported by many analysis tools. Recent applications to ligand protected [4], chiral metal clusters [5,6] and plasmonic systems [7] will show the potentiality of the method. A fascinating and surprising effect is the dichroism of plasmon resonances: in some instances the dichroism is suppressed, in other we observe transfer of dichroism form a chiral fragment to a non-chiral metallic system. .We will discuss some 'tools' to enhance the dichroism of plasmon resonances, via structural deformation [8], alloying [7], and changing the ligand coverage [9].

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Vigna, Vincenzo

RAGMODEX: A Retrieval-Augmented and Explainable AI Framework for Reliable QSAR Modeling and Molecular Design

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Machine Learning (ML) has become a central tool in molecular discovery and Quantitative Structure-Activity Relationship (QSAR) modeling, yet model interpretability and reliability remain major barriers to practical adoption. This work introduces RAGMODEX (Retrieval-Augmented Generation for Molecular Design and Explainable AI), an open-source and model-agnostic platform designed to improve the transparency and trustworthiness of AI-assisted molecular design workflows. The framework addresses two common but frequently underestimated limitations of QSAR modeling. First, it improves explainability by resolving ambiguities introduced by bit collisions in folded molecular fingerprints, enabling more reliable SHAP-based attribution through systematic reconstruction of the chemical substructures contributing to each fingerprint feature. Second, RAGMODEX incorporates applicability domain analysis and chemical-space-aware validation strategies to identify cases in which predictive performance may be artificially inflated by scaffold-related structural similarity between training and test compounds. By integrating retrieval-augmented generation (RAG), explainable AI, and guided molecular optimization into a unified environment, the platform enables informed interpretation of predictions while supporting iterative molecular design. Its application to GLUT-1 inhibitor discovery highlights the utility of the framework for interpretable and reliability-aware QSAR modeling.

Zambrano Angulo, Michael Alejandro

First-Principles Study of Hole Injection at Multi-Cation Perovskite/HTL Interfaces

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Lead halide perovskites (LHPs) have emerged as leading materials for next-generation optoelectronic devices due to their tunable band gaps, long carrier diffusion lengths, and outstanding defect tolerance. Compositional engineering through the incorporation of multiple A-site cations, such as methylammonium (MA^+), formamidinium (FA^+), and cesium (Cs^+), has enabled simultaneous improvements in power-conversion efficiency, thermal stability, and environmental resilience[1,2]. Nevertheless, device performance remains strongly governed by interfacial phenomena, where energy-level alignment, interfacial coupling, and charge-transfer kinetics at the perovskite/charge-transport-layer boundary critically determine carrier extraction efficiency and operational stability.

Here, density functional theory (DFT) calculations combined with electronic-coupling and charge-transfer analyses are employed to investigate interfaces formed between representative hole transport layers (HTLs) and lead halide perovskite surfaces with di-cation and triple-cation compositions. The results reveal that FA^+ and Cs^+ incorporation strengthens interfacial adhesion and modifies the local electronic environment, promoting thermodynamically favourable hole transfer across all investigated heterostructures. Enhanced driving forces are identified for di-cation systems and PbX2-terminated surfaces, indicating a strong dependence of charge-transfer efficiency on both composition and surface termination.

The calculated electronic couplings predict ultrafast hole injection dynamics on the femtosecond timescale, highlighting the highly efficient carrier extraction capability of these interfaces. Notably, cesium exhibits a dual functionality: beyond improving structural stability, it acts as an interfacial anchoring center that facilitates efficient hole-transport pathways. These findings provide a microscopic understanding of charge-transfer mechanisms in modern LHP/HTL heterostructures and establish practical design guidelines for optimizing perovskite optoelectronic devices through compositional engineering, surface termination control, and interface tailoring.

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Zerbetto, Francesco

Brownian motion is the true anomality

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Chemical kinetics governs the way a system approaches equilibrium, but what governs chemical kinetics? The short answer is molecular motion. At (very) long times, and in the absence of constrains, the motion is Brownian. At (very) short times, any kick triggers a momentarily ballistic response. And in between? It depends on the type of molecule, the external forces, and ultimately the working conditions. A comprehensive framework is emerging that links the analysis of the molecular motions to environmental noises that differ from white. The model is general and has applications that extend to volcanic emissions, stock exchange fluctuations and cancer tissue identification.

Zoccante, Alberto

PoLA:Characterization of the porosity of materials and prediction of gas adsorption with a minimum wall distande descriptor

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Nanoporous materials (either crystalline or amorphous) are of great interest for several applications from gas separation and storage to catalysis. An accurate description of their textural properties is of paramount importance for understanding their properties, as well as for the design of new materials, however widely used methods as the DFT fitting of adsorption isotherms and BET model for the specific surfaces are not always effective to correlate textural and adsorption properties.

We propose a new approach, based on the Porosity Local Analysis (PoLA), to describe the porous volume distribution and the active surface, applicable to atomistic models as well as to real materials, and able to predict the gas uptake of various adsorbates.

The PoLA algorithm characterizes the porous nature of each volume element inside the material using the minimum distance from opposite walls. The result is the distribution of the volumes characterised by the minimum distances V(minD), which describes in detail the porous nature of all the points inside the material. This description is physically more accurate than the ones based on pre-defined pores of a specific shape, particularly for amorphous materials.

Being the V(MinD) related to the adsorbate/adsorbent interaction potentials, it is also related to the adsorption isotherms and can be used to predict the uptake of various gases, as N2 or H2.

We demonstrate this correlation using a dataset of (amorphous) porous carbons and (crystalline and defective) zeolites, based on atomistic models and Grand Canonical Monte Carlo (GCMC) simulations of nitrogen and hydrogen adsorptions.

A machine Learning algorithm based on a Neural Network trained on the model dataset (PoLA textures and gas adsorption isotherms) allows to extend the analysis to experimental isotherms, estimating the Porous Volume Distribution associated with the real samples. The same algorithm is also able to predict the adsorption of H2 and other gases.

Zunino, Rachele

QM/MM Investigation of O2 Binding in Arthropod Hemocyanin: Molecular Insights Across Arthropod Lineages

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Hemocyanin (Hc) is a copper-containing protein responsible for the reversible binding and transport of molecular oxygen in arthropods and mollusks.1-3 Beyond its respiratory function, Hc is also involved in several immune-related and redox processes, highlighting its multifunctional biological role.4 The active site of Hc consists of a type-3 dicopper center in which each copper ion is coordinated by three histidine residues. Oxygen binding occurs through reversible coordination of O2 between the two copper atoms and is accompanied by significant structural rearrangements of the active site.5,6

Although the structure and oxygen-binding mechanism of Hc have been extensively investigated experimentally, computational studies have so far mainly focused on the hemocyanin of Limulus polyphemus.7,8 As a result, the molecular factors governing oxygen affinity across different arthropod lineages, particularly in relation to the evolutionary transition from marine to terrestrial environments, still require deeper investigation.

Herein, we present a comparative computational investigation of O2 binding in Hcs from representative arthropod species. Molecular dynamics simulations combined with QM/MM calculations were employed to characterize both the deoxy and oxy states of the binuclear copper active site. Our results reveal substantial variability in O2 binding energetics across species, with oxygenation consistently associated with contraction of the Cu–Cu distance and formation of a peroxide-like O2 adduct. Detailed analyses indicate that second-sphere interactions, including hydrogen-bonding networks and local solvent organization, play a crucial role in modulating oxygen affinity and stabilizing the oxygenated state.

Overall, these findings provide new atomistic insights into the structure–function relationships of arthropod Hcs and contribute to a broader understanding of the molecular mechanisms underlying the evolutionary adaptation of respiratory proteins.

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Poster Communications

P01 Azzali, Alessandro

Machine learning interatomic potential design to exploring new sulfide solid state electrolytes

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All-solid state batteries (ASSBs) are excellent alternative to liquid Li-ion technology. ASSBs have several advantages [1-3], such as greater stability, better safety, and higher energy density. But they also have some intrinsic, still unsolved, problems: lower ion mobility, caused by their solid nature, interface stability and production costs. Glassy-ceramic Lithium thiophosphates, LPS (xLi2S-(1-x)P2S5) and LPSO, LPS oxygen doped, are among the most promising electrolytes materials, and by tuning their composition is possible to optimize their performance and achieve high ion conductivities, at least 10-3 S/cm to be competitive with liquid electrolytes. This is an extremely difficult task because the complicated anionic environment greatly affects the electrochemical properties, and we not yet know deeply why. As result the optimization of the composition process, to get the best electrolyte, requires laborious trial-and-error laboratory procedures. We can help make this process much quicker by using molecular modelling. Typically, computational approaches to electrochemistry involve ab-initio molecular dynamics (AIMD) methods, which despite their accuracy, are very slow and computationally intensive, compared to classical molecular dynamics (MD), which instead relies on parametric force fields (FF). Classical MD calculations on LPS and LPSO are, at the moment, difficult to perform because they require the development of a suitable FF whose analytical form is complicated because of the different states of chemical coordination that Li+ assumes in the amorphous solid. Nevertheless, it is important for the electrochemical community to have access to a quick and efficient way to model electrolytes such as LPS and LPSO.

To leverage the advantages of both methods we used deep learning molecular dynamics [2-5] and generated a new deep learning force field (DLFF). The deep neural network has been trained using our ab-initio data, this way the DLFF has the high accuracy [6-8] of the ab-initio level chosen for the training set and, being parametric, a high efficiency (classical MD level). Using this DLFF, we have performed fast and accurate simulations on model systems beyond the actual limits of AIMD in size and time scales. This way we determined the electrochemical properties of different compositions of LPS and LPSO in a quick and accurate way, which was rarely achieved before. This approach is to make this technology competitive in a large-scale industrial environment.

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P02 Baldinelli, Lorenzo

Disentangling Interaction Networks in Complex Modular Systems for Rational Design

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In this talk, we discuss how the modular architecture of complex molecular systems can be leveraged to understand and control chemical function through the systematic analysis of noncovalent interaction networks.[1] Transition-metal complexes and ion-pair catalytic assemblies exemplify this principle: their function emerges from the collective interplay of interactions distributed across metal centers, ligands, counteranions, and extended environments. Resolving this interplay computationally opens direct routes to rational design.

Two case studies illustrate this from opposite ends of the design space. In asymmetric counteranion-directed photoredox catalysis, [2] the confined chiral environment of an IDPi counteranion organizes a radical cation–styrene reactive couple through a network of short-range aryl–aryl interactions and long-range dispersion forces. Atomic decomposition of London dispersion (ADLD) and molecular dispersion potential (MDP) analyses reveal how stereoselectivity emerges from spatially localized, atom-resolved noncovalent contacts within the catalytic pocket, making the interaction network predictive of experimental trends across substrate substitution. In Cr(IV) molecular qubits embedded in crystalline host matrices, [3] matrix composition alone reshapes the spin structure through geometric distortions and inhomogeneous electrostatic fields. A multistep protocol combining periodic DFT and SA-CASSCF/NEVPT2 calculations reproduces zero-field splitting parameters and spin coherence times with quantitative accuracy, establishing matrix engineering as a precise design handle.

Across both systems, the same logic holds: modular complexity encodes function in interaction networks, and interaction-resolved computational frameworks provide the means to decode and exploit it.

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P03 Bertagnin, Luca

Quantum Inspired Neural Network potentials and Simulations for metabolomics

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The objective of this research is to build, train, and utilize a machine-learned interatomic potential (MLIP), also referred to as a neural network potential (NNP), tailored for the fragmentation dynamics of molecular ions relevant to tandem mass spectrometry (MS/MS). The model is trained on data computed at the density functional theory (DFT) level. The use of chemical dynamics trajectories to predict MS/MS spectra has proven to be a powerful approach over the past 15–20 years, initially developed by Hase and Spezia. Spectral libraries used for identification of compounds often suffer from limited reliability due to variations in instruments and experimental conditions. This project aims to address this limitation through simulation, enabling the construction of a fully in silico metabolomics database.

Direct DFT-based dynamics simulations remain computationally prohibitive for large-scale applications. Therefore, quantum chemical calculations are used to generate training data for the MLIP, with the objective of reducing computational cost by several orders of magnitude while maintaining limited loss of accuracy. This constitutes an innovative strategy that enhances MS/MS spectral prediction, allows greater flexibility in simulating experimental conditions through longer trajectory times, and provides a new computational tool to support spectral analysis.

The project is currently in the NNP development phase. The starting infrastructure is derived from the FeNNoL library[1], a Python framework for building, training, and deploying neural network potentials for molecular simulations. Within this framework, trained force fields are defined as “models.” Initial tests were performed using a smaller model; however, its reactivity during trajectories was unsatisfactory. Consequently, a larger model was trained on a dataset that more accurately represents the chemical space of interest, particularly with respect to reactive events. This resulted in a more accurate model, termed fennix-bio1L-lr-omolBio.

Building on this foundation, we now fine tune and validate the model using protonated urea trajectories generated with our in-house code MARS[2] (Molecular trAjectories for Reactive Simulations). The fragmentation of protonated urea was deeply studied by both experiments and simulations by Spezia and co-workers in the past[3] and it constitutes a solid reference.

The method can be quickly applied to the fragmentation of other molecules of metabolic interest, like uracil or methyl-guanine, also investigated previously in the group with standard methods. This stage is intended to validate the methodology before extending it to larger systems, further refining training and improving reliability. The long-term objective is full integration of the model into MARS to facilitate routine use.

Subsequently, we plan to construct an in silico database through targeted model fine-tuning for specific molecular classes of interest, including nucleic acids and steroids.

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P04 Bonardi, Alessandro

Iron Phthalocyanine Electrocatalysis in Aqueous Media: Is Water Simply a Solvent?

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Accurate modeling of redox processes in single-atom catalysts (SACs) represents one of the central challenges in computational electrocatalysis, as this class of catalysts is becoming increasingly relevant and the description of the behaviour of transition metals like iron is not trivial. [1] Iron phthalocyanine (FePc) is extensively used as a molecular model for Fe-based SACs anchored on nitrogen-doped carbon supports, including nitrogen-doped graphene. [2] Despite experimental evidence consistently pointing toward a Fe(II)/Fe(III) redox transition under oxidative conditions, standard density functional theory (DFT) calculations frequently fail to capture this behaviour, with the oxidation incorrectly predicted to involve the ligand rather than the metal centre. [3] In this work, we examine the origin of this discrepancy through a systematic set of DFT calculations making use of hybrid functionals and explicit solvation models. Our results demonstrate that the divergence between theory and experiment stems from an inadequate description of the iron coordination environment, as the introduction of one or two axial water ligands leads to a pronounced redistribution of the relative energies of the Fe-centred and ligand-centred orbitals. This rearrangement of molecular orbitals recovers the correct prediction of metal-centred oxidation. Furthermore, a simplified, yet physically sound, model of the iron coordinating site yields computed redox potentials in agreement with experimental values to within 0.1-0.2 V. These findings highlight the critical role of water, not simply as a bulk dielectric medium, but as an explicit ligand capable of tuning the electronic structure and, consequently, the reactivity of the active site. The implications extend well beyond FePc to a broad range of Fe-based SACs, indicating that any reliable computational investigation must explicitly account for solvent coordination effects, especially in the case of SACs, as their behaviour lies at the crossroads between materials and coordination compounds. This work provides practical guidelines for enhancing the predictive accuracy of quantum chemical models in electrocatalysis, with two key conclusions: 1) the redox properties of transition metal complexes and graphene-supported SACs are strongly sensitive to the coordination environment, including explicit solvent molecules; and 2) faithful modelling of such systems requires the inclusion of coordinated water to correctly describe their redox behaviour.

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P05 Borzelli, Federica

Computational modeling of 3-methylindole fluorescence decay kinetics

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Tryptophan fluorescence is a widely used intrinsic probe of protein structure and dynamics. However, interpreting its fluorescence decay remains challenging, since the stability of the chromophore's excited states, relaxation pathways, and radiative properties are very sensitive to protein conformations.

In this context, we adopted the Molecular Dynamics–Perturbed Matrix Method (MD-PMM) [1] to describe both the fluorescence emission spectrum and the excited-state relaxation kinetics of 3-methylindole (3MI) in water. This strategy has already proven effective in predicting the photophysical properties of indole in water [2]. Here, we extend this approach to 3MI, a closer analogue of the tryptophan chromophore which may serve as a suitable quantum center for this amino acid. Characterizing the excited-state kinetics of 3MI in aqueous solution thus provides a key benchmark before extending the model to protein environments.

High-level quantum-mechanical calculations indicated that the relevant excited states of 3MI are two bright states, denoted by analogy with tryptophan as La and Lb, together with the dark πσ* state. Starting from MD simulations in water in the corresponding state-specific ensembles, we employed the MD-PMM framework to compute the fluorescence emission spectrum and to evaluate the kinetic constants governing interconversion among excited states. This allowed us to derive a kinetic scheme for the excited-state relaxation of 3MI in water. The predicted spectrum, relaxation constants, fluorescence lifetime, and quantum yield show good agreement with available experimental data [3].

These encouraging results support the use of 3MI as a quantum center for future, more accurate predictions of tryptophan fluorescence spectra and decay kinetics in protein environments.

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P06 Cascone, Luca

Theoretical and Computational Investigation of Solvent-Assisted Proton-Coupled Electron Transfer in Oligopeptides

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Theoretical and computational studies can provide valuable insight into proton-coupled electron transfer (PCET) processes by enabling the characterization of the thermodynamic and kinetic factors governing the reaction pathways [1,2]. In particular, density functional theory (DFT) calculations allow the investigation of redox and protonation states, reduction potentials, pK_a values, reorganization energies, and reaction driving forces, thus helping to elucidate the interplay between proton and electron motion in complex molecular systems.

In this contribution, several case studies of PCET processes in oligopeptides characterized by different secondary structures and donor–acceptor arrangements [3] will be presented. Through a computational multiscale approach, alternative reaction pathways will be analyzed, including both concerted and stepwise mechanisms, as well as competing processes that may affect charge-transfer efficiency. Particular attention will be devoted to the role of the solvent in modulating the thermodynamics and kinetics of the reaction, highlighting how specific solute–solvent interactions can influence the preferred PCET pathway. The impact of the methodological description of the solvent environment on the accuracy of the results will also be discussed through a comparison between implicit and explicit solvent models, with the aim of assessing their strengths, limitations, and applicability in the study of PCET processes in peptide-based systems.

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P07 Ciattaglia, Giulia

Thermodynamic characterization of non-covalent host–guest inclusion complexes through molecular dynamics simulations

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β-Cyclodextrin (β-CD) is a cyclic oligosaccharide that is widely used in pharmaceuticals and environmental applications thanks to its low toxicity and its ability to form inclusion complexes with hydrophobic molecules [1]. In this study, we examine the host–guest interactions between β-CD and environmentally relevant contaminants — specifically, the E and Z isomers of dimethomorph (DMM) [2] and a fluorinated bisphenol A derivative (FBPA) [3] — using molecular dynamics simulations. To characterise the temperature dependence of the binding process, we employed a statistical-mechanical model [4] capable of reconstructing the thermodynamic properties of non-covalent host–guest complexes from simulations performed along an isobar. The model accurately reproduces the binding thermodynamics over the investigated temperature range. Our results reveal stable and reversible inclusion complexes for all guest molecules. For DMM, β-CD interacts primarily with the aromatic moieties. The Z isomer displays a single predominant binding mode, while the E isomer exhibits multiple stable inclusion geometries. A stable host–guest association is also observed for FBPA. These findings provide molecular-level insights into cyclodextrin-based recognition processes and support the development of materials for capturing and removing pollutants. Future work will extend this approach to cyclodextrin-based nanosponges to explore the impact of the cross-linked network on guest encapsulation.

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P08 Corapi, Chiara

Modelling Ground and Excited State Properties of Mechano-Luminochromic Copper-Halide based Systems

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Mechano-luminochromic copper halide-based materials, including Hybrid Coordination Polymers (HCPs) and cluster-based systems, represent a promising class of functional materials for stress and impact sensing through optical responses.[1] Among these, HCPs featuring a copper iodide-based ladder structure functionalized with 3-Bromopyridine (i.e., [(CuI)3-BrPy]n) show remarkable mechano-luminochromic behaviour under UV irradiation, shifting the emission from blue to green upon mechanical grinding.[2] In addition to these extended polymeric frameworks, cubane-type copper iodide clusters have emerged as an alternative class of mechano-luminochromic systems with similarly tunable emission properties.[3]

The atomistic origins of such mechano-induced red-shift are still unclear. To address this issue, we performed first-principles calculations at the density functional theory (DFT) and time-dependent (TD-DFT) level, by computing ground and excited-state properties of [(CuI)3- BrPy]n and various cubane clusters (i.e., [(CuI)4L4] where L=py, 4-Phpy, 2-Mepy), while exploring different exchange-correlation functional, effective core potentials and basis sets.

Concerning the polymeric system, our first-principles calculations show a direct correlation between the Cu-Cu/Cu-I distances with respect to low-lying singlet and triplet excited states. Notably, the Cu-Cu distances are crucial coordinates governing the excited state potential energy profiles, leading to a complex photochemical scenario involving intersystem crossing, phosphorescence as well as thermal activated delayed fluorescence (TADF) mechanisms.

By comparing our DFT/TD-DFT calculations with experimental data (e.g., X-Ray Diffraction, Raman, temperature-dependent steady and time-dependent photoluminescence), a mechanism underlying the mechano-luminochromic behaviour of [(CuI)3-BrPy]n has been formulated. When ground, the emission of [(CuI)3-BrPy]n is assigned to a mixed halide-to-ligand/metal- to-ligand charge transfer triplet excited state (3XMLCT), whereas a TADF mechanism is predominant in the pristine material at room temperature.

Our findings provide a robust framework for understanding the mechano-luminochromic behaviour of Cu-I-based compounds, allowing for a rational design of piezochromic coatings with tailored sensitivity for force and impact sensing applications.

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P09 D'Ambrosio, Francesca

Unraveling Structure–Property Relationships in Carbon Nanodots: a Computational Challenge

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Carbon nanodots (CNDs) are sub-nanometric carbon-based nanoparticles exhibiting intense and tunable photoluminescence, low toxicity, and high chemical versatility, which have paved the way for applications in biomedicine, sensing, catalysis, and optoelectronics [1,2]. Since their discovery in 2004, extensive experimental efforts have been devoted to understanding the origin of their optical properties. However, a comprehensive atomic-level description of carbon nanodots and their structure-property relationships remains elusive due to their intrinsic structural complexity [3,4].

CNDs are commonly described as quasi-spherical nanoparticles composed of a partially amorphous carbonaceous core, in which sp^2-ordered domains coexist with disordered sp^3 regions, surrounded by a heterogeneous and chemically rich surface functionalization. Their final structure depends heavily on synthesis conditions, precursor chemistry, and degree of carbonization, resulting in significant differences in size, morphology, and optical response. Therefore, any realistic theoretical model must capture the complex interplay of these factors, which poses a significant challenge for the computational modeling of CNDs [4].

Early theoretical approaches often relied on small aromatic molecules or polycyclic aromatic hydrocarbons (PAHs) as simplified models, or on polymer-like and random-network representations of the amorphous carbon core [5,6]. While these strategies have provided valuable insights, they only partially capture the intrinsic disorder and structural diversity of experimentally synthesized CNDs.

In this contribution, we present a multiscale computational strategy that employs progressively larger carbon clusters (CCs) as effective structural motifs to model the unsaturated and amorphous regions of the carbon nanodot core. This approach combines the GOAT-EXPLORE algorithm, for the sampling of low-energy isomers of CCs, with TD-DFT calculations for the determination of their optical properties [7]. In parallel, we are exploring the extension of the model through Monte Carlo–based approaches to broaden the accessible configurational space and move toward more statistically representative descriptions.

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P10 D'Amore, Maddalena

Quantum Mechanical models for complex semiconductor surfaces. Can we solve the paradoxa of Si (111)-7x7 Surface?

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Accurate Density Functional calculations of Si (111)-7x7 surfaces employing different exchange correlation functionals and using different bottom terminations of slab models are reported. The DAS (dimer adatom stacking fault) model structure [1], [2] is the most accepted one for Si (111)-7x7 but it fails in predicting some experimental electron and structural features: the adatom heights and insulating surface bands at low temperatures.

These paradoxa of DAS were afforded and partly fixed by new minima we identified, thus revealing the sensitivity of the DAS structure to subtle surface charge rearrangements arising from more accurate description of exchange correlation.

The necessity of accurate quantum mechanical models can also be justified because DFT calculations are used to develop machine learning approaches to handle large and complex systems. Such simulations will only be as good as the DFT training used in such machine learning approaches.

Beyond the present case, our findings may constitute relevant groundwork towards a better understanding of novel 2-D systems.

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P11 Dall'Osto, Giulia

Time-dependent open-quantum approach to two-dimensional electronic spectroscopy within a GW/BSE active space

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Ultrafast spectroscopies allow to probe femtosecond dynamics in molecular and complex systems. These advanced techniques provide a time-resolved perspective on how systems evolve following excitation.1 Within the family of nonlinear techniques, we have recently proposed a theoretical approach to simulate two-dimensional electronic spectroscopy (2DES).2 This technique is based on the interaction of the sample with three ultrafast pulses, where the delay times between the pulses, as well as their wave vectors, are controlled to ensure that the nonlinear signal is collected along a specific direction satisfying the phase-matching conditions. One effective way to simulate ultrafast spectroscopies is through time-dependent methods based on wavefunction dynamics. These approaches explicitly account for the light–matter interaction, thereby closely reflecting the experimental setup.3 The system wavefunction can be propagated using the time-dependent Schr\"odinger equation (TDSE) or, when moving beyond closed-system dynamics to include dissipative processes, the stochastic Schrödinger equation (SSE).4 This framework naturally allows control over the delay times between the pulses; however, spatial degrees of freedom are not explicitly included. Therefore, to simulate the nonlinear response, real-time dynamics are combined with a phase-cycling scheme.5 This method enables extraction of the polarization along a specific direction as a linear combination of polarizations computed with different combinations of pulse phases. Finally, the 2D spectrum is obtained via a two-dimensional Fourier transform. The system wavefunction can be constructed using various quantum chemistry methods and software packages. In the present study, ab initio calculations have been performed within the GW/BSE framework, a many-body perturbation theory approach that goes beyond density functional theory, particularly in the description of excited states.6 This approach has been applied to several systems (benzene, benzene–phenol dimer, and porphyrin core of chlorophyll B) to investigate the effect of varying key parameters, as well as the role of pure dephasing, modeled through suitable operators within the SSE.

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P12 Das, Arathi

Modelling the Chiro-Optic Response and Ligand Effects in [Au25(AcCys)18]- Monolayer – Protected Nanocluster

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Monolayer-protected nanoclusters (MPCs) are atomically precise nanoparticles composed of a metallic core wrapped in a stabilizing organic ligand shell. MPCs possess discrete, molecule-like electronic structure that give rise to unique chiro-optical properties. The presence of chiral ligands or an asymmetric core results in these clusters exhibiting distinct circular dichroism (CD) responses through the differential absorption of circularly polarized light. Understanding the effect of structural features, ligand conformations, and environmental effects on the chiro-optic behavior is essential for the rational design of these materials. In this work, Time – Dependent Density Functional Theory (TDDFT) is used to investigate the chiro-optic properties of the [Au25(AcCys)18]- (AcCys = N-acetyl-cysteine) nanocluster. Multiple conformations derived from a molecular dynamics simulations were analyzed, and the resulting spectra were Boltzmann averaged. The results reveal a strong dependence of the CD response on the ligand conformations and solvent effects. These findings highlight the critical importance of accurately incorporating ligand flexibility and solvent effects in computational models aimed at predicting the optical and chiro-optical properties of monolayer-protected nanoclusters.

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P13 De Troia, Rosa

FIRST-PRINCIPLES INVESTIGATION OF NON-FULLERENE MOLECULAR SPECIES AS ELECTRON TRANSPORT MATERIALS FOR PEROVSKITE SOLAR CELLS

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Inverted p–i–n perovskite solar cells (PSCs) are among the most promising architectures for scalable photovoltaic technology, owing to their low hysteresis and low-temperature processing compatibility. A key component of these devices is the electron transport layer (ETL), which must combine efficient charge extraction, hole blocking, and energy-level alignment with the perovskite absorber. Fullerene derivatives — most notably PCBM — have long served as the ETL benchmark, but suffer from limited tunability of electronic energy levels, poor morphological stability, and high synthesis costs. Non-fullerene organic semiconductors based on diketopyrrolopyrrole (DPP) and isoindigo (iI) cores represent attractive alternatives owing to their strong electron-accepting character and readily tunable frontier orbital levels, yet their employment as ETLs in PSCs remains largely unexplored. Building on previous synthetic work on these molecular families [1, 2], we report a computational screening of twelve donor–acceptor–donor small molecules based on DPP and iI cores, each flanked by thiophene spacers and functionalized with six electron-withdrawing terminal groups (DCV, CNBu, CNOx, ID, IDM, TB). Gas-phase DFT and TD-DFT calculations at the B3LYP/6-311G(d,p) level with D3(BJ) dispersion correction were employed to evaluate four intrinsic molecular descriptors relevant to ETL performance: energy-level alignment with a triple-cation perovskite reference, adiabatic electron affinity, reorganization energy, and charge-density variation upon electron addition. Among all candidates, DCV- and IDM-functionalized molecules emerge as the most promising across both cores: DCV uniquely satisfies all four descriptors simultaneously, while IDM ranks second in both series. Computational predictions are validated against experimental data from available synthesized DPP derivatives (DCV, ID, IDM, TB; Carella et al., unpublished results). Cyclic voltammetry shows good agreement between computed and experimental HOMO levels. On the reduction side, electrochemical reduction potentials are more consistently captured by the adiabatic electron affinity than by the TD-DFT-derived acceptor level — and notably, the former correctly identifies IDM as the strongest acceptor of the series, in agreement with experiment. Moreover, solution UV-Vis absorption spectra ($CHCl_3$) show that the experimental optical gap sequence DCV < ID < TB < IDM is correctly reproduced by TD-DFT. Ongoing work is extending the screening to a thienoisoindigo (TI) core and includes PCBM as an explicit computational reference to both validate the descriptor methodology and position the non-fullerene candidates relative to the current standard.

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P14 Di Giovanni, Rossella

Characterization of methyl acetate through the interplay of vibrational spectroscopy and quantum chemical calculations

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Methyl acetate (CH_3COOCH_3), the simplest saturated ester, was first detected in the molecular cloud Orion KL in 2013 [1], and very recently confirmed toward the Galactic Center molecular cloud G+0.693 [2]. Being the second most stable species within the C3H6O2 isomeric family [2], methyl acetate is a complex organic molecule (COM) of particular interest in astrochemistry due to its potential involvement in the reaction mechanisms that lead to the formation of ester-bearing molecules and prebiotic species, both in icy mantles and warm gas of the interstellar medium (ISM). Given this importance, its spectroscopic characterization is therefore crucial to contribute to the spectroscopic databases that might help observation in the interstellar gas and ices. In the present work, the vibrational and ro-vibrational properties of methyl acetate are studied by state-of-the-art quantum chemical calculations. Equilibrium geometries and harmonic frequencies are computed by CCSD(T) based composite schemes [3], which are then augmented through anharmonic contributions evaluated in the frame of density functional theory [3]. From this hybrid force field, excited state rotational constants and vibrational transition frequencies and absorption intensities are worked out by resorting to vibrational perturbation theory to second order. Simulated spectra were used to assist the analysis of the gas-phase infrared (IR) spectrum, recorded in the 150–6500 cm−1 region at a resolution of 0.5 cm-1 by using a Bruker Vertex 80v equipped with a 199 mm cell with polyethene and KBr windows for the far- and medium-IR region, respectively. Finally, the full characterization of the IR features was completed with the experimental determination of absorption cross sections over the same region, by using spectra acquired at sample pressures in the 9 – 100 hPa range.

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P15 Dongmo Foumthuim, Cedrix Jurgal

Decoding Spectroscopic Properties of Biomolecules

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Spectroscopic techniques including infrared (IR) spectroscopy are widely used methods particularly useful in probing the structural organization of (bio)molecular systems, including proteins and nucleic acids. In fact, several IR bands are highly sensitive to the changes in the structural organization of biomolecular assemblies. One of the most used signals is that arising from C=O stretching vibrations as it proved to display relevant changes depending on e.g. the secondary structure in peptides and proteins or distinct structural motifs in nucleic acids. Nevertheless, the direct mapping between IR spectral bands and specific structural features is not straightforward, in particular for systems with a rugged conformational landscape. Here, we use a tandem quantum/classical computational approach based on the perturbed matrix method (PMM-MD) formalism [1] for the calculation of IR spectra. This approach has been already successfully applied to the calculation of IR spectra in polypeptides, both in the amide I region [2] and for specific side chains bands [3,4]. Recently, it has been extended to compute IR bands in DNA nucleobases [5,6]. More specifically, we compute the IR spectrum arising from C=O stretching modes of all carboxyl containing bases, i.e. thymine, guanine and cytosine, in both water and deuterated water. We use as a first benchmark the isolated bases in solution, both with and without the ribose and phosphate moieties. Then, we move to more extended systems and compute the spectra of single-stranded deca-homonucleotides. At last, we consider an oligomer whose sequence embodies the combination of all nucleic acid building blocks, thus enabling the calculation of C=O stretching in any DNA system. For completeness, more realistic biomolecular systems were studied including the leucine zipper of the yeast transcriptional activator GCN4 protein in complex with the double stranded DNA oligomer ARG1. The comparison of the calculated spectra with the corresponding experimental ones shows an overall good agreement. Most importantly, our approach shows to be able to reproduce the experimentally observed variations including frequency shifts and intensity changes due to conformational diversity, including stacking and hydrogen bonding interactions among the bases.

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P16 FARINA, MATTEO

Computational Investigation of Carbazole-Based Dyes solvated in Deep Eutectic Solvents for Green Hydrogen Production

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Nowadays, hydrogen represents a promising sustainable energy vector, but its industrial production still relies on processes with a significant environmental impact, such as steam-reforming. Consequently, there is an increasing interest in promising photocatalytic and photoelectrochemical systems that could allow truly green hydrogen production. In these devices, a semiconductor surface (TiO2) is sensitized with an adsorbed organic dye that allows visible-light harvesting [1]. As underlined in recent works [2,3], both the dye functionalization and the interactions at the dye/solvent interface strongly influence the performance of the corresponding devices. For this reason, novel organic dyes have been designed. In particular, most promising organic molecules are based on a D-π-A architecture, where an electron-rich donor group (D) is connected via a conjugated linker (π) to an electron-acceptor group (A), which is directly anchored to the semiconductor surface [4].

Recently, carbazole-based dyes (CBZ) functionalized with ethylene glycol and glycerol chains (respectively denoted as CBZ-EG and CBZ-Gly) were reported in dye-sensitized solar cells (DSSCs) together with the corresponding deep eutectic solvents (DESs) as electrolytes (ChCl: EG 1:2 and ChCl:Gly 1:2) and were used for the first time to realize dye-sensitised photocatalytic H2 evolution in DES [2,3]. These experimental studies underlined that the interactions between the functional chain of the dye and the surrounding media could significantly influence the electronic properties of the dye, possibly enhancing the efficiency of the corresponding device.

Taking inspiration from these works, we have developed and applied a hybrid computational protocol based on the combination of molecular dynamics (MD) simulations and ab initio calculations to investigate the key interactions at the dye/DES interface. Firstly, we demonstrated that our computational protocol has strong predictive value, being able to accurately reproduce the electronic and spectroscopic properties of these dyes with excellent agreement with experimental data. Concurrently, thanks to the integration of molecular dynamics and Gaussian Plane-Wave (GPW) calculations, we conducted an accurate analysis of the interactions at the interface between the DES solvent and the absorbed dye, unveiling the presence of hydrogen-bond networks and solvation effects and thus explaining how the solvent could influence the electronic properties of the investigated systems.

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P17 Frustaci, Alice

Isomer-selective reactivity of $H_2CO^{+\cdot}$/$HCOH^{+\cdot}$ with acetylene: a combined experimental and theoretical study.

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Gas-phase ion-molecule reactions are of particular interest in astrochemistry due to their large reaction cross sections at low temperature. The formaldehyde radical cation ($H_2CO^{+\cdot}$) and the hydroxymethylene radical cation ($HCOH^{+\cdot}$) can exist as two distinct species in the interstellar medium (ISM), since their interconversion barrier (1.97 eV) is inaccessible under such conditions, as shown in recent theoretical studies [1].

In this work, we investigate the reactions of both $H_2CO^{+\cdot}$ and $HCOH^{+\cdot}$ with acetylene (C_2H_2/ C_2D_2) through a combined experimental and theoretical approach.

Experiments were conducted using a guided ion beam mass spectrometer, the CERISES apparatus [2,3], associated with the DESIRS VUV beamline of the SOLEIL Synchrotron Radiation Facility (France). To ensure selective formation of this isomer, the $DCOH^{+\cdot}$ isotopologue of $HCOH^{+\cdot}$ was generated from trideuterated methanol (CD_3OH), with an isomeric purity of 99% [4]. Absolute reaction cross sections and branching ratios for both isomers were measured as a function of both photon energy, that acts as a proxy for the internal energy of the cation, and collision energy of the reactants.

To interpret the experimental findings, a theoretical characterization of the relevant potential energy surfaces is currently in progress. Exploration of possible reaction products and intermediates will be followed by an optimization of the relevant stationary points, including minima and transition states, in order to obtain a comprehensive mapping of the PES. Branching ratios, and rate constants will also be computed, enabling direct comparisons with the experimental observables.

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P18 GIL PEREZ, GABRIEL JOSE

A fully frequency-dependent formulation of the Open Quantum System Polarizable

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Molecular photophysics in solution is governed by the coupling between a quantum solute and its polarizable environment, which modifies electronic structure, spectral features, and ultrafast dynamics. Continuum embedding strategies, such as the Polarizable Continuum Model, provide an efficient route to describe these effects, but conventional implementations rely on simplified time-scale separations of solute and environment electronic degrees of freedom and treat weak solute–solvent interactions beyond electrostatics only approximately [1,2]. Here, we introduce OQS-PCM(ω) [3], a fully frequency-dependent formulation of the Open Quantum System Polarizable Continuum Model [2]. The method is derived from the non-Markovian stochastic Schrödinger equation formalism in the averaged-fluctuation limit [4]. Within OQS-PCM(ω), the solvent response naturally gives rise to state-specific polarization, dispersion, and energy dissipation phenomena, providing a unified and physically transparent description of environmentally induced effects in electronically excited states. The proposed approach spans the full range of solute–solvent electronic timescales, interpolating between the self-consistent and Born–Oppenheimer solvation limits. Therefore, OQS-PCM(ω) extends beyond nonequilibrium polarization methods [5,6] and ad hoc dispersion models [7] within the general PCM framework [1]. Simulations of absorption spectra in water and benzene for a dataset of test molecules illustrate how solvent electronic timescales influence solvatochromic shifts and energy redistribution processes. These results highlight the potential of OQS-PCM(ω) for predictive simulations of optoelectronic properties, photophysics, and non-equilibrium excited-state phenomena in complex molecular environments.

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P19 Iuzzolino, Gabriele

Realistic Models of Soot for Innovative Graphite Production

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Graphite is one of the critical materials for the energy transition, thanks to its electrical conductivity, chemical stability and the ability to reversibly intercalate lithium ions. However, both mining graphite and its traditional synthesis from coke have a high environmental impact and are dominated by China, leaving Europe with a competitive disadvantage.

In this context, X-Nano has developed a new electrical reactor to produce graphite and hydrogen via direct methane pyrolysis, followed by gradual thermal graphitization. The reactor is powered by a fraction of the hydrogen output, while methane can be locally and renewably sourced from biogas.

To the aim of optimizing the yield and quality of the graphite output, the G2G project is characterizing the composition and morphology of the intermediates and byproducts (soot) of the graphitization: in this study, specifically, we built a realistic molecular model of the soot, able to interpret the inputs from the different experimental channels.

Both the XRD, IR and Raman spectra show the markers of a partially graphitized structure: we thus conceived a model formed by sheets of aromatic carbon, but with several defects blocking them from assembling into a stacked structure with long-rang order. The challenge was to model, on one hand, the random defects of the aromatic sheet, on the other, the disordered assemblement of sheets. The former problem was solved by an ad hoc program inserting defects at random points of a nanographene sheet; to assemble the sheets, we adapted the methodology by Wood (2024) for biochar - based on simulated annealing.

By varying the frequency and type of defects, our automatized procedure is able to efficiently create a wide variety of defective aromatic and curved carbon sheets, among which we selected the ones best fitting the experimental data. We believe that the methodology we developed will be useful to model also other kinds of carbon-based partially disordered materials.

P20 Lazzari, Federico

The Quest for Geometrical Accuracy: From Chemical Models to Spectroscopic Observables

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The determination of accurate molecular structures remains one of the central challenges of modern computational chemistry. Although the term “accuracy” is routinely employed in the literature, its practical meaning is often ambiguous. Geometry optimization algorithms can routinely converge structures with numerical precisions of the order of 10^-5 Å, but such precision does not necessarily translate into physical accuracy. The latter is ultimately governed by the quality of the underlying potential energy surface (PES), which depends on the adopted electronic structure method and basis set. Recently, machine-learning methodologies have often been proposed as a way to bypass, or at least mitigate, some of these limitations. However, ML strategies are sometimes implicitly regarded as unbiased routes to the characterization of chemical phenomena, including PESs. The problem with this approach is that it does not remove the intrinsic ambiguity; rather, it often displaces it into the choice of descriptors (e.g. which charge model or geometric descriptor is employed to describe the chemical system) and reference target data (with its own intrinsic bottleneck of accuracy). Thus, in order to train better ML models, a conversation about the nature of descriptors and the final target accuracy must still be performed. It is not just about the quantity of data, but also about their quality.

A direct assessment of structural accuracy therefore requires comparison with experimental observables. Among available techniques, high-resolution rotational spectroscopy represents one of the most stringent benchmarks for isolated molecules, providing access to molecular geometries through rotational constants. However, even this comparison between theory and experiment is not straightforward. Experimental rotational constants correspond to vibrationally averaged structures, whereas quantum-chemical optimizations provide equilibrium geometries located at the minimum of the PES. Consequently, vibrational effects, including anharmonic contributions, must be taken into account in order to establish a meaningful correspondence between theoretical and experimental results. A further source of ambiguity originates from the geometrical models themselves. Many geometry-oriented composite schemes rely on the refinement of structural parameters through Z-matrix representations. However, the mapping between a molecular geometry and a given set of internal coordinates is not unique. Consequently, the application of geometrical corrections within a Z-matrix framework may depend on the chosen parametrization, introducing an additional source of ambiguity and potentially affecting the final optimized structure.

In this contribution, we discuss the concept of structural accuracy for semi-rigid systems in which the reference energy minimum is well-defined. By analyzing the relative impact of electronic structure approximations, basis-set effects, vibrational corrections, and experimental uncertainties, we show that achieving sub-percent agreement on rotational constants requires a balanced treatment of all contributions. We illustrate these concepts through recent applications of parameter-free composite schemes (PCS2, PCS3, and related methodologies), discussing the extent to which improvements in electronic energies translate into measurable improvements in experimentally observable structural parameters. Particular attention is devoted to the practical definition of an accuracy threshold, highlighting that errors below approximately 0.1% in rotational constants become increasingly difficult to interpret due to the interplay between residual electronic-structure errors and uncertainties associated with vibrational corrections.

These considerations provide a pragmatic framework for assessing molecular structures and for defining meaningful accuracy targets in modern computational spectroscopy.

P21 Manenti, Alessandro Dante

GRIPkit: A Comprehensive Computational Suite for the Characterization and Quantification of Non-Covalent Interactions in Protein–Ligand Complexes

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Non-covalent interactions (NCIs) govern molecular recognition and binding affinity, yet they are often reduced to coarse, empirical terms in computational drug-discovery workflows. We present GRIPkit, a comprehensive computational suite for the characterization and quantification of NCIs in protein–ligand complexes, built on two integrated modules: GRIProfiler (heuristic geometric profiling) and GRIPqm (physics-based characterization).

GRIProfiler is a consensus profiling framework integrating complementary state-of-the-art tools (e.g., PLIP [1], ProLIF [2], BINANA [3]) that detects, classifies, and merges NCIs from 3D binding site structures into a unified, deeply annotated dataset, with efficient, parallelized scaling to large structure datasets.

GRIPqm is an automated quantum-mechanics workflow for the physics-based characterization of NCIs, built on both GPU- and CPU-based engines (GPU4PySCF [4], ORCA [5]). It comprises DFT calculation of the electron density of the ligand–binding-site clusters, an ensemble of methods for electron-density analysis (e.g., Multiwfn [6]), and the DFT-based quantification of local fragment–fragment interaction energies.

GRIPkit adopts a dual architecture: a core Python library optimized for parallelized, high-throughput screening and workflow integration, and a standalone Graphical User Interface (GUI) for non-programming users that exposes all GRIPkit modules and provides interactive 2D/3D visualization of single- and multi-complex analysis results. GRIPkit serves multiple purposes in computational drug discovery: as a physics-informed component to guide generative artificial intelligence models; as an efficient filtering and ranking tool to prioritize large candidate sets of molecular docking/co-folding poses; and as a stand-alone, intuitive GUI profiler for structural interaction analysis.

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P22 Mangiacapre, Emanuela

Decoding Molecular Structure in Sustainable Electrolytes for Ni-Rich Lithium-Ion Batteries

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Ni-rich layered oxide cathodes such as $LiNi_{0.92}Mn_{0.04}Co_{0.04}O_2$ (NMC92) are promising candidates for next-generation lithium-ion batteries due to their high operating voltage and enhanced energy density. However, their practical utilization requires advanced electrolytes capable of sustaining high-voltage conditions while ensuring safety, low flammability, sustainability, and stable electrode–electrolyte interfaces [1]. Conventional carbonate-based electrolytes often fail to meet these combined requirements, motivating the search for innovative solvent formulations.

In this context, a recently optimized electrolyte formulation based on lithium bis(fluorosulfonyl)imide (LiFSI), lithium difluoro(oxalato)borate (LiDFOB), diethylene glycol butyl ethyl ether (DEGBEE), and bio-derived γ-valerolactone (GVL) outperformed its analogous propylene carbonate (PC)-based counterpart, exhibiting lower viscosity, higher ionic conductivity, enhanced Li^+ transport, and superior long-term cycling stability in NMC92 half-cells [2].

Despite these substantial macroscopic differences, the two key formulations differ only in the substitution of GVL for PC, solvents whose molecular structures vary by only a single oxygen atom.

To elucidate the molecular origins of these differences, molecular dynamics (MD) simulations were performed using the previously developed and validated AMOEBA polarizable force field [3,4]. MD results were compared with pulsed-field gradient NMR self-diffusion coefficients of all electrolyte species, as well as with Li^+ transport numbers, showing excellent agreement.

Detailed structural analysis revealed that GVL contributes more effectively than PC to the first Li^+ solvation shell, enhancing Li^+ shielding and reducing Li^+–FSI^- association. This promotes greater ionic dissociation and reduced ionic aggregation, consistent with the experimentally observed increase in Li^+ transport number and ionicity index for the GVL-based formulation.

Overall, this integrated computational–experimental approach effectively resolves subtle yet critical molecular-scale differences governing electrolyte performance, establishing a powerful framework for both mechanistic understanding and the rational design of next-generation safe, sustainable, and high-performance electrolytes for advanced lithium-ion batteries.

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P23 Morittu, Alessandro

Revealing the First Step of MTO process: Machine learning-Enhanced Sampling of Methanol Dehydration in Zeolites.

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The methanol-to-olefins (MTO) process, which uses acidic zeolites to convert methanol into light olefins, is a key route for producing Sustainable Aviation Fuels (SAFs)1. This process involves a complex network of reactions, with multiple competing pathways and mechanisms2. The initial and critical step is the dehydration of methanol to form dimethyl ether (DME). Experimental and computational studies have revealed two main reaction pathways for this step3: an associative pathway in which two methanol molecules convert directly to DME and water, and a dissociative pathway that proceeds via a surface methoxy species (SMS) intermediate. The relative predominance of these pathways depends strongly on temperature and on the zeolite environment 4–6. Given the central role of this step in shaping the subsequent formation of the so-called hydrocarbon pool (HP)7, it is essential to achieve a clear and detailed molecular-level description. However, current modelling approaches relies on static DFT3,8,5, failing on capturing the thermodynamic and kinetic complexity of the process under operando conditions9.

Here we overcame those limitations by combining enhanced sampling techniques such as metadynamics10 (MetaD) with machine learning interatomic potentials11 (MLIP) trained on accurate ab initio data. We performed free-energy MetaD simulations of methanol dehydration at 600, 800, and 1000 K in five zeolite frameworks (chabazite, ZSM-5, mordenite, beta, and ferrierite). This approach yields atomistic reaction mechanisms and converged free-energy profiles for both associative and dissociative routes. From the computed free-energy surfaces we determined reaction free energies, and we quantified how temperature and zeolite topology affect the relative stability of reactant, intermediate, and product states. We also determined barrier free energies through which we identified the associative pathway as the kinetically favoured one at the temperatures and frameworks studied, indicating it is the dominant route to DME formation under the simulated operando conditions. Our work established a transferable, high-accuracy framework for mechanistic studies of catalytic reactions in complex environments and provided new molecular-level insight into the early stages of the MTO process that controls heavier olefins formation in HP mechanism. These results paved the way for targeted investigations of subsequent olefin formation (e.g., ethene and propene) and for rational zeolite design to optimize SAF precursors.

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P24 Negri, Fabrizia

Dark States, Bright Emission: Computational Insights into the Luminescence of Halogenated Thiele Diradicaloids

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Open-shell singlet diradicaloids based on para-quinodimethane (pQDM) frameworks are emerging as an intriguing class of luminescent materials, where subtle electronic and structural perturbations strongly affect excited-state dynamics and emission properties. In this contribution, we present a combined experimental and computational investigation of halogenated Thiele hydrocarbons aimed at elucidating the microscopic origin of their remarkable photophysical behavior.

These systems exhibit highly unusual luminescence properties for open-shell π-conjugated molecules, including intense deep-red/near-infrared emission, exceptionally large Stokes shifts, pronounced solvatochromism, and high photoluminescence quantum yields. In mixed-halide Thiele hydrocarbons, subtle modifications of the halogenation pattern produce dramatic changes in the optical response, enabling modulation of emission color, fluorescence efficiency, excited-state lifetime, and solvent sensitivity. Notably, one folded derivative displays pronounced mechanofluorochromism, switching from a non-emissive to an emissive state upon mechanical grinding, highlighting the strong coupling between molecular conformation and photophysical behavior.

Quantum-chemical calculations, including multireference approaches (CASSCF/NEVPT2, DFT-MRCI), reveal that the low-energy photophysics of these systems is governed by the interplay between a bright singly excited (SE) state and a formally dark doubly excited (DE) state. The calculations demonstrate that photoexcitation induces substantial elongation of the exocyclic C═C bonds, reducing the SE/DE energy gap and enabling efficient state mixing through torsional relaxation. This process generates zwitterionic excited states with pronounced charge-transfer character, rationalizing the experimentally observed giant Stokes shifts, solvatochromism, and near-infrared emission [1-3].

Overall, these results establish a general framework for understanding luminescence in these open-shell singlet diradicaloids and demonstrate how electronic correlation, excited-state structural relaxation, and conformational control can be exploited to design highly tunable fluorophores and multi-responsive molecular materials with tailored optical and electronic properties.

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P25 Palumbo, Valeria

A new approach for an accurate evaluation of the accessible surface area of atomistic models and real porous materials

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Specific accessible surface area (ASA) is a key property of porous materials and represents one of the main parameters used to compare different materials and their adsorption capacities. Consequently, accurate and reliable methods for its estimation are of primary importance. ASA can be determined for atomistic models using different computational approaches or for experimental samples through the adsorption isotherms, commonly analyzed using the BET (Brunauer–Emmett–Teller) model. Despite its widespread use, BET theory has known limitations, including the assumption of a homogeneous surface. Furthermore, several critical issues arise in its application to highly microporous materials, for which the choice of relative pressure range and the nature of the adsorbate can significantly influence the value of the surface area.

A valid alternative is provided by PoLA (Porosity Local Analysis), a new computational approach (presented in another communication at this conference) based on a point-by-point analysis of the inner void volume, leading to the characterization of the porous volume (V) as a function of the “minimum distance from opposite walls“ (MinD).

PoLA effectively computes the volume of the “surface monolayer” in contact with the material walls leading to a robust and reliable definition of ASA. An important strength of PoLA is its applicability to atomistic models and experimental materials as well.

We’ll show that PoLA ASA is in perfect agreement with the specific surface computed with Monte Carlo simulations in atomistic models, suggesting that it’s more reliable than BET for real adsorbent materials, too.

P26 Pandey, Prachi

From Vibronic Photoelectron Spectroscopy to Time-Resolved Nonadiabatic Dynamics: A Combined Computational Study of Adenine Photophysics in Solution

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We present two complementary computational studies on the spectroscopy of adenine and its 9-methylated derivative, presented here as two separate branches rooted in the same electronic structure calculations. The central motivation is to investigate how vibronic couplings within the same coupled excited state manifold manifest themselves depending on the flavour of spectroscopic method chosen— a parallel that makes these two strands of work mutually insightful. In the first leg of work, we present vibronic photoelectron spectra in both steady-state and time-resolved domain, addressing the challenge of correctly assigning ionisation transitions originating from a coupled manifold of dark and bright excited states to cationic states of distinct character[1]. The computational workflow proceeds from TD-DFT//ωB97X-D/6-311+G(d,p) electronic structure calculations, including non-equilibrium solvation effects at PCM level[2], through Franck-Condon vibronic profiles computed with FCclasses[3], and the computation of photoelectron cross-sections with Tiresia code[4]. Cationic states are described at the TDA level. The second leg of work concerns the simulation of transient absorption spectrum in aqueous solution, capturing the nonadiabatic wavepacket dynamics in the regime of coupled excited states. Building on the same scaffold of electronic structure calculations as done for the photoelectron spectroscopy, a linear vibronic coupling (LVC) Hamiltonian was parametrised with Overdia code[5] and the wavepacket dynamics was achieved through multilayer multiconfiguration time-dependent Hartree (ML-MCTDH) approach implemented in Quantics software[6]. Next, the pump-probe spectra were computed from quantum dynamics further elaborating from the short-time approximation presented in References[7-8].

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P27 Patta, Alice

PFAS adsorption on nanoplastics: a computational investigation

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Perfluoroalkyl substances (PFAS) represent a large group of man-made chemicals characterized by a fluorinated alkyl chain and a polar head [1]. PFAS exhibit high thermal and chemical stability and great resistance to degradation. These characteristics make them extremely valuable from an industrial point of view, in fact they are widely used in many industries and consumer products [2]. However, PFAS widespread use started raising serious concerns due to their persistence and harmful impact on both ecosystems and human health: many PFAS can remain in the environment for decades and accumulate in the human body with elimination half-lives that span several years. Their presence has been linked to cancer, disruption of the endocrine system and many chronic health conditions. For these reasons PFAS contamination is now recognized as a global emergency [3]. The most widespread and concerning form of PFAS contamination affects water basins, which are polluted not only by these persistent chemicals but also by nanoplastics (NPs). NPs represent another environmental emergency due to their abundance, strong interaction with microorganisms and ability to penetrate biological tissues. Moreover they are able to work as adsorbers/vectors of other contaminants, such as PFAS, causing an enhancement of their mobility which leads to their presence in remote areas [4]. Due to their simultaneous presence in the aquatic ecosystems, it is crucial to understand how NPs and PFAS interact with each other, in particular how they can give rise to co-transport phenomena. To this end, we have carried out a computational investigation on the adsorption mechanism of PFAS on NPs through an ad-hoc computational procedure. This procedure was successfully used in a previous study where the adsorption of several PFAS on a polypropylene NP was investigated [5]. Using this approach, the role of the adsorbent in the adsorption mechanism was clarified by comparing the adsorbing properties of three different NPs among the most abundant in aqueous ecosystems: polyethylene, polyethylene terephthalate and polyvinyl chloride.

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P28 Pistillo, Simone

Mechanistic Study of the Hydrogen Evolution Reaction on CTF-1 through Constant-Potential Calculations

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Grand canonical density functional theory (GC-DFT), as implemented in VASPsol++ [1], was applied to investigate the reaction mechanism underlying the hydrogen evolution reaction (HER) on covalent triazine frameworks (CTFs), using CTF-1 as a model system. CTFs are a class of organic polymers characterized by high porosity, nitrogen-rich structures, and tunable electronic properties [2,3]. These features, together with their ability to absorb visible light, make them promising materials for photoelectrochemical applications.

Computational studies of HER activity are commonly performed using the computational hydrogen electrode (CHE) approach [4], which has been successfully applied to several electrochemical reactions. In the CHE model, the effect of the applied potential is introduced through a thermodynamic correction for proton-electron transfer steps. However, this approach does not explicitly account for potential-induced changes in the electronic structure of reactants, products, and transition states. To overcome this limitation, GC-DFT calculations were performed to explicitly include the effect of the electrode potential on the HER mechanism.

The calculated reaction pathway shows that the Volmer step proceeds without an energy barrier at nitrogen sites, identifying these atoms as the most favorable centers for the initial hydrogen adsorption. At potentials of about −0.3 V, nitrogen sites can further adsorb a second hydrogen atom, leading to the formation of $*NH_2$ species. However, the subsequent Tafel step involving $*NH_2$ is associated with a relatively high energy barrier, whereas the Heyrovsky step can proceed through a lower-energy pathway. This result is consistent with the experimentally reported Tafel slope of 120 mV dec^{-1} for CTF-1 under high-coverage conditions [5-6], suggesting that HER proceeds predominantly through a Volmer–Heyrovsky mechanism.

To model the reaction a hybrid implicit/explicit solvation model was employed [7], in which hydronium ions are solvated by a cluster of water molecules and embedded in a nonlocal and nonlinear implicit electrolyte. The effect of the size of the explicit solvation shell on the calculated energy barriers was also evaluated, highlighting the importance of an accurate description of the electrochemical interface in constant-potential simulations.

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P29 Plakaj, Rilinda

Structural Design for Electronic Circular Dichroism Enhancement in CO-Functionalized Plasmonic Au Nanowires

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In this work we present a TDDFT investigation of the optical and chiroptical properties of CO-functionalized Au nanowires (NWs). The systems consist of Au152 in two morphologies (5-ring and 7-ring). Two atomic chains are functionalized with CO in either full (1:1 Au-CO) or half (2:1) coverage. Using the polTDDFT formalism[1], supported by Individual Component Map analyses (ICM-OS/RS) and induced electron density mapping, we demonstrate how ligand coverage, spatial arrangement, and NW morphology affects plasmonic and chiral responses[2]. Full CO coverage quenches longitudinal plasmon modes and produces weak ECD signals due to destructive interference and strong ligand induced perturbations[3]. In contrast, half-CO NWs retain collective excitations, enabling efficient plasmon-ligand coupling and pronounced ECD enhancements, particularly in elongated 5-ring structures that favor charge separation along the NW axis. Tip functionalization suppresses field coupling and weakens chiroptical activity, whereas tip-free configurations maximize plasmonic response. Comparison with bare NWs further underscores the key role of geometry in controlling plasmon strength and its ability to drive chiral signatures[4]. These results provide design rules for engineering plasmon-driven chirality in ligand-functionalized Au nanostructures.

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P30 Ranaudo, Anna

A Molecular Dynamics investigation of a polyhydroxyurethane-based formulation

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Understanding the molecular factors that govern the miscibility of complex polymer-based formulations can provide insights for their rational optimization.

In this work, molecular dynamics (MD) simulations are employed to investigate a formulation composed of polyhydroxyurethane (PHU), dicaprylyl ether, and ethanol. Experimental observations indicate that ethanol plays a crucial role in achieving a homogeneous formulation, whereas binary combinations of the individual components exhibit limited mutual solubility. The aim of this study is to elucidate the molecular mechanisms by which ethanol promotes miscibility within the multicomponent system.

As a preliminary step, MD simulations of the pure liquid components were performed with the OPLS-AA force field and GROMACS. The calculated densities of ethanol, dicaprylyl ether, and dimethylformamide (DMF, in which the polymer is partially soluble) were compared with available experimental data, showing good agreement and providing initial validation of the adopted simulation protocol. To enable the investigation of the polymer-containing systems, topologies of both the monomer and the polymer were then generated. A polymer chain consisting of 20 repeating units was constructed using the Polymer Builder tool available in the Schrödinger Suite. Molecular dynamics simulations of the polymer in DMF are currently being performed to sample representative conformations and identify suitable starting structures for subsequent formulation studies.

The next stage of the project will focus on the construction and simulation of ternary systems containing PHU, dicaprylyl ether, and ethanol at experimentally relevant compositions. Initial configurations for the MD will be generated using the Disordered System Builder module of the Schrödinger Suite. The resulting trajectories will be analysed to characterize intermolecular interactions, local organization, hydrogen-bonding networks, and preferential solvation phenomena. These analyses will provide an atomistic interpretation of the experimentally observed role of ethanol in promoting formulation miscibility.

P31 Ritacco, Ida

Selective C–O cleavage and C=O deoxygenation of carbamates and polyurethane catalyzed by organoactinide complexes

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The remarkable ability of actinide complexes to activate carbamates is presented in this study, exemplified by the carbamate hydroboration using various Th and U complexes. The activation mode involves the selective catalytic cleavage of the C–O bond and the deoxygenation of the double C[double bond, length as m-dash]O bond, utilizing pinacolborane (HBpin) as a hydride source. The broad scope of the organoactinides allows us to perform the activation reaction with diverse structural and functional carbamates, offering a flexible strategy for the synthesis of complex amines and amino alcohols. For example, the synthesis of (−) ephedrine and other bioactive analog molecules was achieved in a one-pot, two-step reaction utilizing commercially available carbamate derivatives, including multigram-scale reactions. Additionally, the capability of actinide catalysts to facilitate late-stage modifications of drugs has been extensively studied, and various pharmaceutical compounds have been examined. Notably, we also present the homogeneous catalytic depolymerization of a polyurethane polymer, recycling it to its valuable diamine [Me–N(H)–R–N(H)–Me] through hydroboration followed by hydrolysis. The use of an organic-f-lanthanide compound is also presented as a comparison to the actinides to show their industrial applicability. To understand the reactivity of the actinide complexes, stoichiometric reactions, together with kinetic experiments, thermodynamic measurements, and deuterium labeling studies, were performed, allowing us to propose a mechanistic pathway. Computational DFT calculations further substantiate the proposed mechanism.

P32 Russo, Stefano

Generalized Non-Periodic Boundary Conditions Models for Molecular Simulations

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Hybrid explicit/implicit approaches have attracted increasing interest for their balance between computational efficiency and accuracy in the description of solute–solvent interactions.[1] In this work, we investigate a simple yet effective framework[2] that combines discrete and continuum representations of the solvent. The proposed non-periodic boundary conditions (NonPBC) model reduces the number of explicitly treated solvent molecules while retaining the key advantages of a continuum description for the surrounding environment.

The original formulation was developed for small molecular solvents represented through spherical cavities. Here, we present recent methodological developments that extend the NonPBC framework to cavities of arbitrary shape and to solvent environments that cannot be accurately represented by a simple spherical geometry. These extensions significantly broaden the applicability of the model to more realistic molecular systems and heterogeneous solvation environments.

Applications will be presented to illustrate the calculation of structural, thermodynamic, and spectroscopic properties in solution, as well as the investigation of solvent effects on chemical reactivity. Attention will be devoted to assessing the impact of cavity shape and solvent representation on the accuracy of the computed observables, highlighting the potential of the generalized NonPBC approach for the simulation of complex solvated systems.

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P33 Sarkar, Ranjini

Adsorption and Interfacial Reactivity of Na+ Salts, Room-Temperature Ionic Liquids, and Poly(ethylene oxide) on Sodium Metal Surfaces: A DFT and AIMD Investigation

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Sodium metal batteries are promising next-generation energy storage systems owing to their high theoretical capacity and the natural abundance of sodium. However, their practical implementation is limited by dendrite growth and the formation of unstable solid-lectrolyte interphases (SEIs) in conventional organic electrolytes. The development of stable electrolytes is therefore essential for improving sodium metal anode performance. Room-temperature ionic liquids (RTILs) offer high thermal and electrochemical stability, while poly(ethylene oxide) (PEO)-based solid and gel polymer electrolytes can enhance interfacial stability and suppress dendrite formation.

In this work, we employ density functional theory (DFT) and ab initio molecular dynamics (AIMD) simulations to investigate the initial stages of SEI formation at the Na(110)/electrolyte interface. To obtain atomistic insights into intrinsic interfacial reactivity, we explicitly examine single ion pairs of RTILs and sodium salts, as well as isolated PEO oligomer chains adsorbed on Na(110) surface. The systems studied include RTILs composed of the N-methyl-N-propylpyrrolidinium (PYR13+) cation paired with bis(fluorosulfonyl)imide (FSI-) or bis(trifluoromethanesulfonyl)imide (TFSI-) anions (PYR13FSI and PYR13TFSI), their corresponding sodium salts (NaFSI and NaTFSI), and PEO dimer, tetramer, and hexamer oligomers.

The PYR13+ cation interacts weakly with Na(110) and remains intact in all RTIL systems. In contrast, interfacial reactivity is governed by the anion. FSI- strongly adsorbs on Na(110) and undergoes spontaneous dissociation at 0 K in both RTIL and salt environments. AIMD simulations at 298 K reveal distinct decomposition pathways, accompanied by migration of F atoms into subsurface Na layers. TFSI- exhibits greater stability, showing no spontaneous dissociation at 0 K and delayed decomposition at room temperature. In both cases, sodium salts are more reactive than their RTIL counterparts, with NaF emerging as the dominant inorganic SEI product.

PEO also plays an active role in interphase formation. Tetrameric PEO undergoes spontaneous decomposition on Na(110) at 0 K, forming Na2O-rich interphase species, while the hexamer exhibits an ultralow dissociation barrier (~0.01 eV) at 0 K, indicative of nearly spontaneous dissociative adsorption at room temperature. In contrast, the dimer shows a substantially higher barrier (~1 eV), highlighting a pronounced chain-length dependence of PEO reactivity. Overall, these results demonstrate that both electrolyte anion chemistry and PEO decomposition pathways critically influence the composition and evolution of the initial stages of SEI on sodium metal.

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P34 Sarnataro, Sofia Chiara

Computational Design of β-Cyclodextrin-Citric Acid Nanosponges via Automated Molecular Assembly

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Cyclodextrins (CDs) are cyclic oligosaccharides composed of α-D-glucopyranose units linked by α-(1,4) glycosidic bonds, forming a truncated cone-shaped cavity able to host a wide variety of guest molecules. Thanks to their inclusion properties, CDs are widely employed in Drug Delivery Systems (DDS), where native cyclodextrins are used to improve the solubility, stability, and bioavailability of pharmaceutical compounds. In addition, derivatized systems such as randomly methylated cyclodextrins and hydroxypropyl-cyclodextrins are extensively exploited to modulate physicochemical properties including solubility, cavity accessibility, and host-guest affinity.

To further enhance drug encapsulation capability and intermolecular interactions, cyclodextrins are frequently assembled into crosslinked polymeric nanosponges (NSs). Among the different synthetic strategies, citric-acid-based nanosponges have attracted particular attention due to the use of biocompatible and environmentally friendly cross-linking agents. These polymeric networks contain multiple interconnected cyclodextrin cavities, improving loading capacity and transport properties compared to monomeric CDs.

However, the structural heterogeneity of cyclodextrin nanosponges makes their computational modelling particularly challenging. In most cases, nanosponge models are manually constructed, introducing operator bias and limiting the exploration of possible crosslinking arrangements, by arbitrarily choosing the regiochemistry of the system. To address this issue, we developed an automated combinatorial workflow for the generation of β-cyclodextrin/citric acid nanosponges models using the stk, a Python module, capable of constructing complex structures through stochastic assembly. This approach enables the statistical construction of intermolecular connections between building blocks, allowing the generation of structurally diverse polymeric fragments without manual intervention.

This workflow generates a large number of possible nanosponge topologies, so to evaluate their relative stability, they were optimised using xTB methods, followed by higher-level methods such as those based on density functional theory (DFT), in order to obtain reliable structural descriptions and relative energetic ranking. This automated strategy enables efficient sampling of the conformational and topological complexity of cyclodextrin nanosponges, providing representative computational models suitable for studying their structural and properties.

The resulting models can also be employed in molecular dynamics simulations under equilibrium and non-equilibrium conditions to investigate diffusion and transport processes in cyclodextrin-based systems, including the effects of chemical concentration gradients.

P35 Silveri, Fabrizio

Ab initio multiscale modeling of ionic liquids: towards the description of molecular electronic properties in complex electrolyte solutions using subsystem density embedding.

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In the effort to extend quantum mechanical investigations to large nanoscale systems, embedding approaches have emerged as powerful and flexible techniques that focus most of the available computational resources towards the core physical problem. Among these approaches, subsystem density embedding is particularly suitable for the description of molecular liquid phases, as these provide natural boundaries to partition the electron density.

The Pavanello Research Group, responsible for the eQE[1] and eDFTpy[2] density embedding codes, has been working on the application of subsystem Density Functional Theory (sDFT) to the description of the electronic and electrochemical properties of room-temperature ionic liquids (RTILs); the eDFTpy subsystem approach supports the description of each molecule as a separate DFT subsystem, which interacts with its environment via an embedding potential dependent on the Hartree, exchange-correlation, and kinetic potentials of the full periodic system. This approximation, exact in the limit of separable subsystem densities, leads to a computational scaling that is linear with the number of subsystems, supporting the simulation of liquid-phase models of up to tens of thousands of atoms.[3]

Here we present our prediction of the liquid-phase electronic structure and electrochemical reactivity of Pyr13TFSI calculated at the hybrid-GGA, metaGGA, MP2, and CCSD levels, achieved by combining classical and ab initio molecular dynamics simulations with an impurity model for the description of the sDFT embedding potential[4] and with embedded quantum chemistry simulations. The computational results can be correlated with high-accuracy experimental electronic structure data, as well as with electrochemical stability measurements.

The new methodology opens a path for the description of accurate molecular electronic properties in extended liquid phases of any composition, overcoming previous limitations correlated with periodicity, long-range ordering, and molecular charge.

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P36 Trinari, Marco

MCTDH Quantum Dynamics of Gas-Phase and Microsolvated Glycine: From Nuclear Wavepacket Evolution to Vibronic Spectra

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Quantum dynamics simulations are essential to describe molecular processes where electronic excitation is strongly coupled to nuclear motion. In this work, the Multi-Configurational Time-Dependent Hartree (MCTDH) method is used to study glycine in the gas phase and in a microsolvated environment.

Potential energy surfaces are computed for five electronic states at the state-averaged (SA) CASPT2 level of theory. The dynamical model includes the main normal modes of glycine, focusing on those involving the carboxylic group, the most chemically active region of the molecule. The nuclear wavepacket propagated on these coupled electronic states is used to compute the absorption spectrum from the autocorrelation function and to resolve its vibrational substructure.

The spectral analysis is supported by the characterization of the underlying dynamics through electronic populations, electronic coherences, time-dependent expectation values $\langle q \rangle(t)$, and mode-resolved variations $\langle dq \rangle(t)$. This allows the vibrational modes with the largest displacements and strongest couplings to be identified and related to the main vibronic features of the spectrum.

By comparing gas-phase and microsolvated glycine, this work investigates how a local aqueous environment modifies the wavepacket evolution, the vibronic coupling pattern, and the resulting vibrationally resolved absorption spectrum.

P37 Uribe Grajales, Lina Marcela

Integrated theoretical and experimental investigation of HNCO···H2O2 complexes

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This study presents the first integrated theoretical and experimental analysis of HNCO· · · H2O2 complexes by quantum–chemical calculations and matrix isolation infrared spectroscopy (MI–IR).

The potential energy surfaces of the HNCO · · · H2O2 , (HNCO)2 · · · H2O2 , and HNCO · · · (H2O2)2 complexes are sampled using the CREST program[1] . The resulting clusters are first optimized at the B3LYP[2] level of theory in conjunction with the 6-31+G*[3] basis set and DFT–D3[4] empirical dispersion (hereafter referred to as B3). The structures are subsequently refined using the double–hybrid rev-DSD-PBEP86–D3[5] functional with the 3F12− basis set[6] (all together denoted as rDSD). Thermochemical parameters are then obtained by performing anharmonic frequency calculations using the Hybrid Degeneracy-Corrected Vibrational Second-Order Perturbation Theory (HDCPT2)[7] methodology at the B3 level. Relative populations are subsequently derived from Boltzmann distributions. Finally, anharmonic spectra are computed at the rDSD level using the Reduced–Dimensionality Generalized Vibrational Second-Order Perturbation Theory (RD–GVPT2) model[8] . Simulated spectra are used to assit the interpretation of MI–IR spectra acquired experimentally by co–deposition of HNCO and H2O2 within an inert matrix of eiter Ar or N2 at 15 K. Under this conditions, complexation induces measurable shifts in vibrational frequencies, such as the redshifts observed in stretching modes involved in hydrogen bonding, thereby offering direct insight into intermolecular interactions[9,10]. The comparison between theoretical and experimental spectra allowed the identification of the complexes formed in the experiments.

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P38 Amante, Giuseppe

Path Integral Molecular Dynamics under Non-Periodic Boundary Conditions for Proton Transfer in Aqueous Solution

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The molecular system investigated in this study consists of an ammonia/ammonium pair embedded in a cluster of explicit water molecules confined within a spherical NonPBC cavity. The free energy profile for proton transfer is obtained through thermodynamic integration along a reaction coordinate describing the proton motion between the two nitrogen centers. Constraint algorithms such as SHAKE and RATTLE are employed to ensure efficient sampling along the reaction path. Particular attention will be devoted to understanding how the description of the solvent environment affects the thermodynamics of the proton transfer process. By exploiting the flexibility of the NonPBC framework, the influence of confinement and cavity size on the free energy barrier will be investigated and compared with more conventional solvent representations. Furthermore, the study aims to assess the role of nuclear quantum effects, including zero-point energy and proton delocalization, in modulating the reaction energetics. The combined analysis of solvent confinement, environmental modeling, and quantum contributions is expected to provide insight into the factors governing proton transfer in heterogeneous and locally structured aqueous environments.