BOOK OF ABSTRACTS

COST Training School

COST action CA21101 COSY

Multiscale modeling of the properties of compounds: From isolated molecules to 3D materials relevant for industrial and astrophysical applications

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EUROPEAN COOPERATION
IN SCIENCE AND TECHNOLOGY

COSY
COST ACTION

Belgrade, 19th – 22nd September, 2023

The Training School of COST action CA21101 COSY

Multiscale modeling of the properties of compounds: From isolated molecules to 3D materials relevant for industrial and astrophysical applications

$19^{th} – 22^{nd}$ September 2023, Belgrade, Serbia

BOOK OF ABSTRACTS

Design, layout, copy-editing, and typesetting (*August-September 2023*)
by Ivana S. Đorđević & Dragan M. Popović

Welcome Message

We are pleased to welcome you all to the first Training School of the COST Action CA21101 - CONFINED MOLECULAR SYSTEMS: FROM A NEW GENERATION OF MATERIALS TO THE STARS (COSY).

The Training School "Multiscale modeling of the properties of compounds: From isolated molecules to 3D materials relevant for industrial and astrophysical applications" will cover the expertise in a broad field of multiscale modeling. The topics will include physical and chemical aspects of multiscale modeling of solids, gases, liquid mixtures, fluid-structure interaction and biopolymers (proteins and nucleic acids), focusing on a better understanding and recognition of issues relevant to the application of the novel computational approaches for modeling molecular systems either isolated or in confined environments, which may consist of enclosing molecular cages, surfaces, interfaces as well as of strong electromagnetic static or optical fields. Accurate characterization of phenomena of astrochemical relevance, using the most advanced spectroscopic techniques and the highest-level ab initio theories will also be included. The Training School will address modern problems where the system complexity involves multiple time scales. As a result, the scientific program is very broad. To achieve aims of the Training School we have a great team of eminent teachers from Spain, France, Switzerland, Italy, Sweden, Romania, Czech Republic and Serbia.

The scientific program consists of four days of lectures, complemented by exercises aimed to provide a practical insight into the selected problems from the different covered fields. We have also scheduled a poster session, where the trainees will have the opportunity to present their work, promote themselves and create new synergies with other attendees.

We are grateful to the sponsors, colleagues and friends for helping with the organization of this Training School. In particular, we are thankful to the COST Action CA21101 "COSY" for having provided the financial support, and especially to the COST Action Chair (Prof Maria Pilar de Lara-Castells) and Grant Holder (Prof Juan Carlos Hernandez-Garrido); the host institution (Institute for Chemistry, Technology and Metallurgy) in Belgrade, Serbia, for all the human, logistic, and complementary funding resources provided.

We would also like to express our gratitude to all of our teachers and all trainees for coming to this meeting and hope that you will have a very pleasant stay in Belgrade and plenty of interesting scientific discussions.

The Chairs of the 1st COSY Training School: Sonja Grubišić and Jiří Vaníček

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Timetable of the COST Training School 2023

"Multiscale modeling of the properties of compounds: From isolated molecules to 3D materials relevant for industrial and astrophysical applications"

19th – 22nd September 2023, Belgrade, Serbia

TUE, Sep 19	
9:30-10:15	**Registration**
10:15-10:30	**Opening and school presentation (Sonja Grubišić and Jiří Vaníček)**
10:30-11:30	**María Pilar de Lara-Castells (Spain)** "*On the computational modelling of atomic metal clusters: soft-deposition, stabilization, aggregation, oxidation, and photo-absorption* "
11:30-12:00	Coffee break
12:00-13:30	**Majdi Hochlaf (France)** "*Capture of carbon dioxide on functionalized gold clusters and surfaces*"
13:30-15:00	Lunch
15:00-16:30	**Cristina Puzzarini (Italy)** "*Quantum-chemical composite schemes in gas phase: Accurate molecular structures, spectroscopic properties and energetics*"
16:30-17:00	Coffee break
17:00-18:00	**Vladimir Srećković (Serbia)** "*Molecular data for confined molecular systems and astrochemical modelling*"
18:00-18:30	Practice (program installation)

WED, Sep 20	
9:30-10:30	**Cristina Puzzarini (contd.)** "*Quantum-chemical composite scheme in gas phase: Application to astrochemistry* "
10:30-11:30	**Aatto Laaksonen (Sweden)** *"Introduction to modern molecular modelling and simulations"*
11:30-12:00	Coffee break

12:00-12:30	**Aatto Laaksonen (contd.)** *"Introduction to modern molecular modelling and simulations "*
12:30-14:00	**Francesca Mocci (Italy)** "*Molecular dynamics and coarse-grained models for Bio & Soft Matters* "
14:00-15:30	Lunch
15:30-16:30	**Sonja Grubišić (Serbia)** "*Grand canonical Monte Carlo simulations of gas adsorption in metal-organic frameworks*"
16:30-17:00	Coffee break
17:00-18:30	Practice (Francesca Mocci)

THU, Sep 21	
9:30-11:00	**Martin Quack (Switzerland)** "*Molecules in motion: symmetries and primary processes between less than yoctoseconds and more than days*"
11:00-11:30	Coffee break
11:30-13:00	**Andrei Neamtu (Romania)** "*Sampling strategies for complex systems: enhanced-sampling simulations for the study of biomolecules"*
13:30-15:00	Lunch
15:00-16:30	Practice (Andrei Neamtu)
16:30-17:00	Coffee break
17:00-18:30	**Miljan Dašić (Czech Republic)** "*Computer-aided drug design*"

FRI, Sep 22	
9:30-11:00	**Jiří Vaníček (Switzerland)** "*Semiclassical dynamics and electronic spectroscopy*"
11:00-11:30	Coffee break
11:30-13:00	Practice (Miljan Dašić)
13:30-15:00	Lunch
15:00-17:00	*Poster session and coctail
17:00	**Closing addresses**
17:00-20:00	Free afternoon
20:00-	Social dinner

All lectures will take place in the Lecture Hall "Belgrade panorama" of Palace Hotel (6th floor).

*Poster session will be held in the Banquet Hall, 1st floor (Hotel Palace)

LECTURES

On the computational modelling of atomic metal clusters: soft-deposition, stabilization, aggregation, oxidation, and photo-absorption

María Pilar de Lara-Castells

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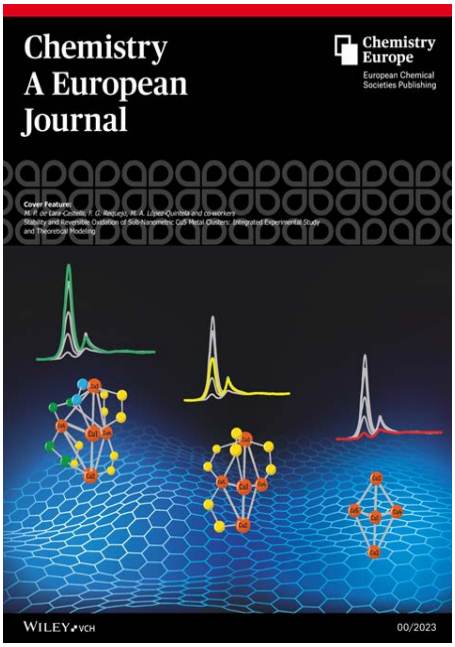
Novel highly selective synthesis techniques have enable the production of atomically precise mono-disperse metal clusters (AMCs) of subnanometer size,[1,2] which exhibit "molecule-like" structures that have physical and chemical properties significantly different from those of nanoparticles and bulk material.[1,2] I will present our latest advances in the computational characterization of model ACMs by utilizing both density functional-theory (DFT)-based approaches and high level ab initio methods capable of describing the multi-reference character of the wave-function at the crossing between different electronic states. First, I will present the theoretical background in full quantum dynamics simulations in order to illustrate how superfluid helium droplets can be used for the soft-deposition of metal species on surfaces such as graphene.[3] Second, I will explain why trigonal bypiramidal Cu_5 clusters are distorted Jahn-Teller (JT) molecules, discussing how JT effects are intimately connected to the fluxionality of AMCs, which give them a "floppy" character that facilitates their interaction with environmental molecules and thus enhances their functioning as catalysts.[4] This will be followed up with an analsyis of the aggregation of either unsupported or graphene-supported Cu_5 clusters from first principles.[5,6,7] Next, we will see how experimental measurements on the reversible oxidation of graphite-supported Cu_5 clusters have been explained using first-principles modelling (see figure on a recent cover feature from Ref. 8). Finally, I will explain how the photo-absorption spectra of AMC-modified semiconductor surfaces can be calculated.[2]



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Semiclassical Dynamics and Electronic Spectroscopy

Jiří Vaníček

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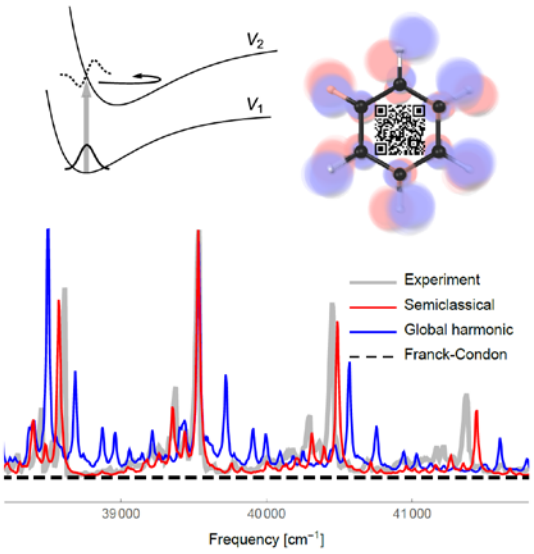
Vibrationally resolved electronic spectra pose a challenge to the theory of chemical dynamics because an accurate description of such spectra depends both on the quality of the electronic potential energy surfaces and on the inclusion of nuclear quantum effects. Semiclassical dynamics[1,2] captures these quantum effects at least approximately and, at the same time, avoids the exponential scaling of the exact solution of the molecular time-dependent Schrödinger equation. After briefly reviewing the Lagrangian and Hamiltonian mechanics, I will present several basic semiclassical dynamics methods, including the time-dependent WKB approximation and various forms of Gaussian wavepacket dynamics.[1,2,3] After introducing the time-dependent approach to spectroscopy,[1,3] I will present an ab initio implementation,[4,5] of the semiclassical thawed Gaussian approximation,[6] which permits evaluating the electronic structure "on the fly". Despite its simplicity, this method goes far beyond the standard approaches by including vibrational mode distortion, Duschinsky rotation, and anharmonicity. I will also discuss several extensions:

1) the extended thawed Gaussian approximation,[7] which describes electronic spectra beyond the Condon approximation; the electronically forbidden transition in benzene provides a beautiful extreme example because the Condon approximation yields a "zero" spectrum (see figure);

2) the single-Hessian approximation,[8] which not only speeds up calculations but also conserves the effective energy, and

3) the Gaussian thermo-field dynamics,[9] which includes finite-temperature effects on the spectra.

To demonstrate the theory, I will show examples of absorption, emission, and photoelectron spectra of both floppy and large molecules.



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Quantum-chemical composite schemes in gas phase: Accurate molecular structures, spectroscopic properties and energetics

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The focus is on isolated systems: molecules or non-covalent complexes. The accuracy that can be reached in electronic structure calculations depends on the proper account of electron correlation and basis-set convergence. To recover the errors introduced by the truncation of the basis set and wave function models, quantum-chemical composite schemes have been introduced. They rely on the additivity approximation, thus splitting a huge and unsolvable problem in the sum of smaller tasks that can be tackled. The various parts of the problem are computed at the best possible level and then combined together.

Contents:

- Errors and accuracy in quantum-chemical calculations.
- Composite scheme in equilibrium geometry determinations: additivity applied at the energy gradient level.
- Composite schemes in equilibrium structure determinations: from small to large systems.
- Composite schemes in electronic energy calculations: thermochemistry and non-covalent interaction energies.
- Composite schemes in molecular spectroscopy in the gas phase: the rotational and vibrational motion.

Quantum-chemical composite scheme in gas phase: Application to astrochemistry

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The focus is on the gas phase part of the interstellar medium (ISM). Highly accurate quantum-chemical predictions of the spectroscopic properties are required to guide the experimental characterizations that lead to the astronomical catalogues used in radioastronomical observations. Because of the difficulties in mimicking the harsh conditions of the ISM (very low temperature and density) in the laboratory, theoretical studies of the chemical reactivity play a crucial role in understanding in astrochemistry.

Contents:

- From the laboratory to the interstellar medium: the role of quantum-chemical composite schemes in the detection of new molecules.
- Gas-phase formation pathways of interstellar molecules: the importance of highly accurate energetics.

Capture of carbon dioxide on functionalized gold clusters and surfaces

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Using first-principles approaches, we characterized the bimolecular interactions between CO_2 and medium-sized molecules (imidazole, triazole, …). The medium-sized molecule is either isolated, attached to a metallic cluster, a metallic surface, or to a liquid-solid interface modeled by ionic liquids attached to the gold surface. For these purposes, the minimum energy geometries corresponding to these systems have been searched and optimized using various ab initio and DFT methods. Computations show that the bimolecular complex formation process can follow energetically favored multi-channel, where long-range interactions between these medium-sized molecules and CO_2 are in action. In addition, we show that charge transfer processes are occurring through weakly bonds, which are on the origin of the activation of CO_2 and its possible efficient conversion into value-added products. For illustration, diverse examples will be presented.[1–12]

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Grand canonical Monte Carlo simulations of gas adsorption in metal organic frameworks

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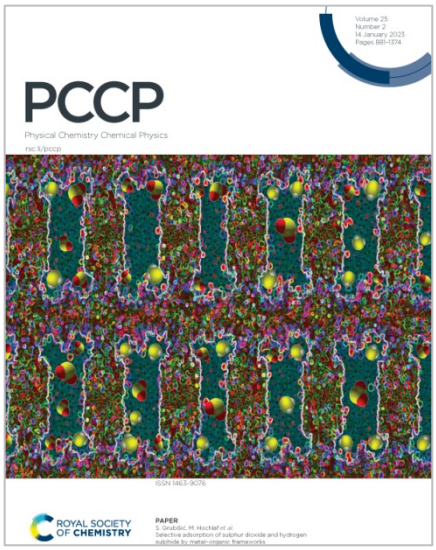
In recent years, the design, synthesis, and development of new metal-organic frameworks (MOFs) have attracted a great deal of attention in the literature. Their flexible construction – based on a combination of one or more types of metal node coordinated with one or more types of organic ligands allows for a wide range of topologies, pore sizes, surface areas and chemical environments. MOFs are used in variety of applications, including catalysis, drug delivery, gas storage and separations. The topic of the lecture will cover current research and methodologies related to the computational studies and prediction of gas adsorption in metal-organic frameworks (MOFs). Molecular simulation of adsorption allows us to shed light on the microscopic behaviors observed experimentally. The standard molecular simulation technique which can be used to study the adsorption of gases/fluids in nanoporous materials is Grand Canonical Monte Carlo (GCMC), which has been extensively used and validated in a large variety of nanoporous materials, including zeolites, nanoporous carbons, mesoporous materials, etc. GCMC simulations can be performed with the Monte Carlo suite of the RASPA code.[1]



In the grand canonical ensemble, the chemical potential μ, the volume V and the temperature T are fixed. The pressure p in the reservoir is related to the chemical potential μ. The output of GCMC includes the absolute adsorption uptake (N), i.e., the average number of adsorbed molecules in the porous system, which is used in plotting adsorption isotherms. Each point of an adsorption isotherm in GCMC is the result of a simulation at fixed μVT, and the full isotherm Nads (μ) can be obtained by running simulations at different values of μ. This is close to experimental isotherms, which are typically measured as Nads (P), where P is the pressure of the external fluid. Differences between simulated and experimental adsorption isotherms need to be taken into account for quantitative comparison.

The choice of force fields (FFs) is one between accuracy and transferability.[2] The most used FFs for MOFs are UFF (Universal Force Field) and DREIDING. Both force fields are generic enough to provide potential parameters for elements throughout the periodic table, covering both the organic linkers and metal atoms of MOFs.

In addition to confirming the power of slightly modified generic force fields to quickly and accurately predict gas adsorption isotherms in triazolate based MOFs,[3] with and without the presence of water, I shall demonstrate that these force fields are capable of providing adsorption information which are in good agreement with available experimental data.[4,5]

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Introduction to Modern Molecular Modelling and Simulations

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This lecture explores the evolution, current states and emerging applications of Molecular Modelling and Simulations, an area we know as Computational Chemistry, that began in the 1950s. Over six decades, Computational Chemistry has vastly expanded. Using Molecular Dynamics (MD) we now simulate millions of particles over longer timescales, thanks to both computing advances and method improvements. The field has grown rapidly in complexity, with more accurate interaction models and lately with the integration of machine learning. These advancements enable simulations on a scale comparable to real-world experiments, paving the way for designing advanced materials and even simulating genomic materials. Molecular Modelling has educational benefits too, offering a way to visualize molecular behavior and contributing to our understanding of chemistry. The method has been enhanced by software developments, some of which are inspired by the gaming industry. We'll focus on key developments, acknowledging its historical roots and discussing its future potential.

Molecular dynamics and Coarse-grained models for Bio & Soft Matter

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Molecular dynamics has emerged as an indispensable tool within the realms of chemistry laboratories, enabling the profound exploration of diverse materials' structures, dynamics, interactions, and inherent properties. This pivotal technique underpins the rational design of novel molecules and materials, spanning a broad spectrum of applications encompassing fields as diverse as medicine and energy.

In this lecture, the focus will be directed towards comprehending the intricacies of both atomistic and coarse-grained particle classical molecular dynamics (MD). The initial segment of the lecture is dedicated to the foundational aspects of molecular dynamics, elucidating key concepts such as force fields (FF), atomic types, FF parameters and parameterization, fundamental approximations, and algorithms. By delving into the calculation of discernible properties, a clearer understanding of the technique's potency will emerge. Furthermore, a comprehensive examination of distinct force fields tailored to diverse chemical systems will be presented, underscoring the remarkable versatility of MD methodologies.[1]

The subsequent section of the lecture is dedicated to coarse-grained models, covering top-down and bottom-up approaches, and their hybrids. The synergistic interplay between higher-level approximations and computational feasibility will be underscored, exemplifying how coarse-grained modelling effectively bridges the gap between molecular detail and system size.

The final part of the lecture will be dedicated to illustrating the significance of molecular dynamics through carefully chosen applications. A particular emphasis will be placed on biological systems, with a keen focus on nucleic acids, and highly ionic systems.[2,3]

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Sampling strategies for complex systems: enhanced-sampling simulations for the study of biomolecules

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Enhanced-sampling techniques have emerged as indispensable tools for unraveling the intricacies of complex biomolecular systems. This presentation navigates through two prominent classes of these techniques: replica exchange methods encompassing temperature replica exchange and solute tempering (REST2), followed by umbrella sampling. The introduction underscores the significance of enhanced sampling in biomolecular research. Traditional simulations often falter in navigating complex energy landscapes, prompting the need for innovative methodologies that surmount energy barriers and enable the exploration of rare events. The discussion then moves to the core principles of replica exchange methods and umbrella sampling. Temperature replica exchange involves the exchange of configurations between replicas at varying temperatures, expanding exploration across energy basins. Concurrently, solute tempering (REST2) tailors sampling by modifying solute-solute and solute-solvent interactions for more efficient exploration in terms of computing resources. Further, the presentation details the workflows of replica exchange methods and umbrella sampling, highlighting technical aspects for enhancing conformational sampling. Examples are provided to showcase the utility of these techniques in uncovering biomolecular insights, revealing reaction pathways and thermodynamic characteristics. The comparative strengths of replica exchange methods and umbrella sampling are explored, showcasing their distinct advantages and limitations. Replica exchange methods harness the power of temperature diversity to explore conformational space, while umbrella sampling homes in on specific reaction coordinates. This comparative analysis assists researchers in selecting the appropriate technique for their inquiries. The presentation concludes by underlining the broader impact of these techniques across scientific fields. From drug discovery to materials science, their contributions span a spectrum of disciplines, enriching our comprehension of intricate phenomena. Case studies illustrating the applications of replica exchange methods and umbrella sampling for biomolecular systems are provided. These instances underscore the pivotal role these techniques play in deciphering the complex behavior of macromolecular biological systems.

Computer-Aided Drug Design

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Advances in computational methods, in both hardware and software aspects, have revolutionized the field of drug discovery, making it possible to predict and optimize the interactions between small molecules (order of size: 10 - 100 atoms) and their target proteins (order of size: 1000 - 10000 atoms). This lecture aims to provide a comprehensive introduction into the multidisciplinary scientific discipline named **Computer Aided-Drug Design** (**CADD**) for an audience with diverse scientific backgrounds. In the ever-evolving efforts of pharmaceutical research, *CADD* has emerged as a fundamental discipline which combines the knowledge and insights of physics, chemistry, biology, and computer science. The key impact of *CADD* comes from speeding-up the drug discovery processes and reducing their experimental costs. Utilization of *CADD* belongs to the so called *in situ drug design*, which represents the first step of a long process - from designing potential drugs on a computer, over their clinical testing, and finally their approval and arrival to pharmacies, where patients can obtain them.

This lecture will consider the essential concepts, without overwhelming the audience with peculiar details. Throughout the 1.5 hour presentation, we will explain the key stages of the drug discovery process, from both experimental and computational point of view, emphasizing the *CADD*. Starting from an overview of molecular interactions and the role of proteins in disease pathways, we will explore the challenges of identifying suitable drug targets. The lecture starts by unraveling the foundational principles of molecular interactions, shedding light on the key role of proteins in diseases. Considering the target identification, students will gain insights into the crucial task of pin-pointing proteins that serve as potential drug targets. As the lecture unfolds, the focus moves toward molecular docking, which is a cornerstone of *CADD*. We will highlight the significance of molecular docking, in which computer simulations predict how do potential drugs interact with their target proteins. After providing a general theoretical background, we will move forward by presenting selected research studies done in the Department of Noncovalent Interactions of the *IOCB* in *Prague*, *Czech Republic*. Through different illustrative examples, students will get to know how computer simulations predict the binding affinities between drug candidates and target proteins. The procedure called *scoring* is essential for ranking the studied drug candidates, and hence selecting the most promising ones. We will provide a brief introduction into the physics-informed scoring methods developed and employed in the research studies done at the *IOCB* in *Prague*. Within the field of *CADD*, there are two principally different approaches: *Ligand-Based Drug Design* (*LBDD*) and *Structure-Based Drug Design* (*SBDD*). Since the lecturer's research group at the *IOCB* in Prague works mainly within the framework of *SBDD*, the key processes of *SBDD* will be presented, including:

1. *Protein Structure Determination* - The process starts by determining the 3D structure of the target protein using experimental techniques like X-ray Crystallography or Nuclear Magnetic Resonance (*NMR*). By using those experimental techniques, it is possible to

obtain a detailed information about the protein's active site, where drug binding occurs. Visualization on a computer (e.g., using the software named PyMOL) can help in designing the drug candidates.

2. *Ligand Screening* - Potential drug molecules, usually referred to as ligands, are virtually screened or experimentally tested to identify those that could potentially interact with the target protein's active site.
3. *Molecular Docking and Scoring* - Computational tools simulate how do ligands bind to protein's active site, predicting their binding orientations, non-covalent interactions and affinities. This helps in selecting the most promising drug candidates.
4. *Lead Optimization* - Based on the docking results, chemists modify the structure of selected ligands in order to enhance their binding affinities with the target protein. Furthermore, iterative cycles of design, synthesis, and testing, refine the compounds' physico-chemical properties (e.g., solubility).
5. *Validation* - Promising compounds are synthesized and experimentally tested to confirm their predicted target binding and biological activity. This process helps in bridging the gap between the computational predictions and the real-world biochemical behavior of the drug candidates.
6. *Clinical Development* - Compounds that demonstrate strong binding affinity, desirable pharmacological properties, as well as safety characteristics, move into the clinical trials, which represent a critical step in bringing potential drugs to the pharmacies.

The power of *SBDD* lies in its ability to rationally design drug candidates that align with the complex molecular landscape of diseases. By visualizing and understanding their physico-chemical interactions, researchers can develop molecules that selectively modulate target proteins, at the same time reducing unwanted side effects and increasing the therapeutic efficiency. Structure-Based Drug Design relies on the synergy of physics, chemistry, biology, and computer science. In a nutshell, *SBDD* is an approach that transforms static protein structures into dynamic tools for guiding the discovery of next-generation medicines. Through a symbiosis of cutting-edge technology and scientific insights, *SBDD* accelerates the drug discovery process, directing us closer to the realization of precision therapies for a range of medical challenges. Speaking about the cutting-edge technology, we refer to the advanced hardware (i.e., High Performance Computing (*HPC*) resources) and to the advanced software (development of *CADD* software in high-level object oriented programming languages, mainly in Python).

In conclusion, this introductory lecture on *Computer Aided-Drug Design* aims to explain the complexities of the field, thus offering a good starting point for master and doctoral students coming from diverse scientific backgrounds. As we point out the strong synergy between physics, chemistry, biology, and computer science, participants coming from any of those scientific disciplines will understand what could be their role, in case they choose to orient their scientific path in the direction of *CADD*. Expectedly, the field of *CADD* incorporates a strong interplay between academic research and industrial research and development (*R&D*) sector, mainly of the pharmaceutical and medical industries.

Molecular data for confined molecular systems and astrochemical modelling

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Molecular clouds play a crucial but poorly understood role as confined systems despite their huge size. Almost 300 molecular species, including neutrals, cations, and anions ranging in size from diatomic to enormous, are currently known to exist in interstellar space. Deep inside molecular clouds, interstellar radiation is scattered and absorbed, preventing photodissociation and/or photoionization of molecules. Consequently, it is critical to investigate this. The goal of this contribution is to explore hydrogen, helium, and silicon molecules and their cations, primarily small ones, as well as the described processes, and to offer data relevant to interstellar chemistry characterisation.

Molecules in Motion: Symmetries and Primary Processes between less than Yoctoseconds and More than Days

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Molecular quantum dynamics, the primary processes of molecules in motion, provide the foundation of all chemical processes, covering combustion as an early and still today important use of chemistry by mankind, the chemistry of planetary atmospheres and of interstellar space, of large scale industrial syntheses, catalysis, and also of the microscopic biomolecular processes in the chemistry of life, its persistence and evolution.[1–30] Spectroscopy with either high frequency or with high time resolution, possibly also with an uncertainty principle limited combination of both, provides the most powerful experimental techniques to study such processes.[13–18] Symmetry and asymmetry are concepts, which are used in a wide range of contexts, from the fundamental sciences, mathematics, physics, chemistry and biology to the arts, music and architecture.[1] We shall start with an introductory outline of how symmetries can be applied to the understanding of the time scales in fundamental kinetic primary processes. We then briefly discuss our approach to derive molecular quantum dynamics from high resolution spectroscopy. We shall present some selected examples from our recent research including hydrogen fluoride clusters as prototypes for potentials and dynamics of hydrogen bonds,[11,19–22] as well as other systems with parity and nuclear spin symmetry conservation and violation, molecular tunneling and tunneling switching phenomena notably also in chiral molecules[23–28] and isotopically chiral molecules important for astrophysical observation[30] and the chemistry of the homochirality of life.[1,30] We shall also include examples such as mode selective intramolecular vibrational energy flow[16–18] and laser chemistry, hydrogen bond dissociation dynamics and rearrangement tunnelling,[19–22] as well as stereomutation tunnelling reactions, including quasiadiabatic channel above barrier tunnelling.[15,25] We shall include a brief report on current progress towards the observation of the theoretically predicted, new process of parity change with time due to parity violation in isolated chiral molecules and a proposal towards testing CPT symmetry in hydrogenic clusters. For background reading and some recent results see,[1–30] notably reviews and books.[2,3,13–16, 25, 27]

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ABSTRACTS OF POSTER PRESENTATIONS

Modelling Glibenclamide in Aqueous Mixtures of Bioactive Ionic Liquids

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Glibenclamide, also known as glyburide, is a sulphonylurea drug used to treat type 2 diabetes. New ways to use this compound for inhibiting headaches or various inflammations are also being found [1]. Unfortunately, glibenclamide is poorly soluble in water (15-24 μg/mL) [2], which makes it harder to find new pharmaceutical applications. To improve the solubility of glibenclamide, a biological choline-tryptophanate ionic liquid [Cho][Trp] was added to water, increasing glibenclamide's solubility to 27 mg/mL – by 130-600 times compared to the solubility in pure water [3].

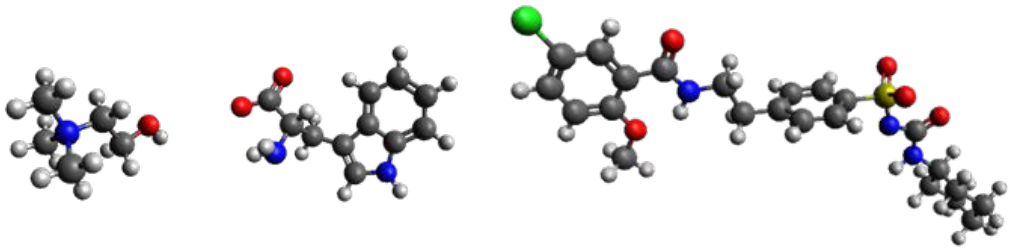

Fig 1. Optimized structures of choline, tryptophanate and glibenclamide ions.

The main goal of this study was to find out what intermolecular interactions result in the increase of glibenclamide's solubility in aqueous mixtures with ionic liquid by using molecular dynamics (MD) simulations and quantum mechanics/molecular mechanics (QM/MM) methods. One of the main tools for studying intermolecular interactions is nuclear magnetic resonance (NMR) spectroscopy as 1H NMR chemical shifts depend on the surroundings of the molecule. The NMR parameters of two systems: glibenclamide in an aqueous solution (Glb_{aq}) and in an ionic liquid mixture with water ($Glb_{IL/aq}$), as well as additional structural parameters, were computed and investigated. NMR experiments for these systems were also done.

By analysing the dihedral angles between glibenclamide atoms it was found that the conformational equilibrium of glibenclamide is somewhat different in an aqueous solution as compared to the one in the aqueous mixture of [Cho][Trp]. There were no significant specific interactions formed between glibenclamide and ions of the ionic liquid. However, quite a few ions were found in the vicinity of the glibenclamide thus screening this hydrophobic drug from water molecules and possibly improving its solubility. The MD/QM/MM scheme reproduced the experimentally recorded changes in the ^{1}H NMR spectrum of glibenclamide going from aqueous solution to the [Cho][Trp]/water mixture in qualitative terms rather well.

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Modelling intermolecular structure and NMR parameters of the $[C_4mim][NO_3]$ ionic liquid and of its mixtures with water

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1-alkyl-3-methylimidazolium-based ionic liquids (ILs) are widely investigated materials that are characterized by a unique set of properties such as negligible volatility, amphiphilic character of cation, high structural tunability, etc. Both experimental and theoretical studies are conducted to explain the properties of such ILs.

The focus of this study is on 1-butyl-3-methylimidazolium nitrate $[C_4mim][NO_3]$ and its mixtures with water. These systems are noteworthy for their nano-heterogeneous structure. $[C_4mim][NO_3]/H_2O$ mixtures are claimed to contain several nanometer-sized water nanopockets [1]. Both spectroscopic and molecular modelling (MD) studies bring conflicting results about the existence of water nanopockets. This study aims to achieve conclusive results about the intermolecular structure of $[C_4mim][NO_3]/H_2O$ mixtures using classical MD simulations and a modern QM/MM (quantum mechanics / molecular mechanics) approach.

Four different compositions $[C_4mim][NO_3]/H_2O$ (water molar fractions: 0 %, 20 %, 50 %, 80 %) ensembles were constructed and MD simulations were performed (canonical ensemble at 343 K, 20 ns equilibration and 20 ns production run). Then radial and combined (radial and angular) distribution functions and coordination numbers of nitrate ions and water molecules around the $[C_4mim]^+$ cations were calculated, using MD trajectories. Furthermore, a water clusterization analysis was conducted. Major structural motifs of the mixtures were described.

QM/MM calculations of $[C_4mim]^+$ cations and H_2O molecules were performed on 100-200 configurations taken from MD trajectories. ^1H NMR chemical shifts were obtained by averaging the QM/MM results of all configurations. Chemical shifts were predicted for some protons both quantitatively and qualitatively accurately, although several mismatches occurred. A further study on improving QM/MM methodology for NMR parameters of ionic liquids is required.

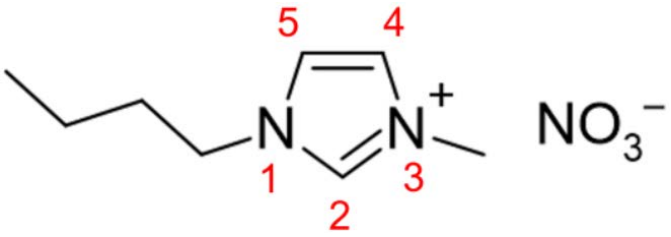

Fig 1. $[C_4mim][NO_3]$ chemical structure with added numbering of imidazole ring atoms.

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7-Hydroxyquinoline Tautomerism: Investigating the Effects and Influence of the External Electric Field

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Tautomerism, the reversible isomerization process in organic compounds, plays a crucial role in various chemical and biochemical reactions. In this study, we investigate the effects of the external electric field on tautomerism in 7-hydroxyquinoline (7OHQ), which represents an interesting example for a long-range proton transfer. It should be noted that, particularly in 7OHQ, this proton transfer is solvent and concentration-assisted [1].

Based on analysis of the absorption and emission spectra, an equilibrium between the enol and keto tautomers in 7OHQ in some solvents has been detected. Notably, the enol form exhibits greater stability in the ground state, while the keto form displays enhanced polarity. Exploiting this unique property, we introduce an innovative approach to mimic the solvent effect using an oriented external electric field (OEEF) [2]. For this purpose, a specific experimental setup to simultaneously analyze the absorption and fluorescence spectra in solution under the influence of an OEEF has been designed and implemented.

Acetonitrile, which is an aprotic solvent, unable to affect the equilibrium through specific solute-solvent interactions, was used as a solvent. An electric field in the range of 10-15 kV, was used, in order to avoid an electric breach.

Our study aims to shed light on the selective stabilization of a specific tautomer by utilizing the OEEF technique. By better understanding the behavior of tautomers under the influence of an external electric field, we can develop innovative strategies to control and manipulate chemical equilibria effectively. The insights gained from this study have the potential for far-reaching applications in various equilibrium processes in solution.

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DFT/Solvation Continuum Electrostatic Calculations of Proton Pumping in Mammalian Cytochrome *c* Oxidase

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The intricate process of proton pumping in cytochrome c oxidase (CcO) is vital to cell respiration. By harnessing the power of oxygen reduction, CcO produces energy and pumps protons across the mitochondrial membrane, creating an electrochemical gradient. The coupling of protonation and redox reactions, as well as the electrostatic interactions between protonatable and redox-active groups, are pivotal in this process. Knowledge of the identity of proton-binding groups is paramount to interpreting the reaction mechanism in CcO, and protonation states of essential residues have been studied extensively by experimental and computational methods. Recent computational analyses have shed light on His291, a ligand of the Cu_B center, as a potential proton-loading site. With computer simulations that assess pK_as of critical residues, explore electron and proton pathways, and evaluate the energetics of PT and ET processes, we can provide a more in-depth understanding of the molecular mechanism and catalytic cycle of CcO. Combining the DFT electronic structure and energy calculations with reaction and protein field contributions allows self-consistent solvation energy calculations to be iteratively performed. Moreover, valuable insights into mechanistic details and energetics of proton pumping and coupled ET/PT reactions are gained at the atomic level [1–6]. With this knowledge in hand, we have the potential to discover innovative approaches for energy generation and propel the field of molecular pumps forward.

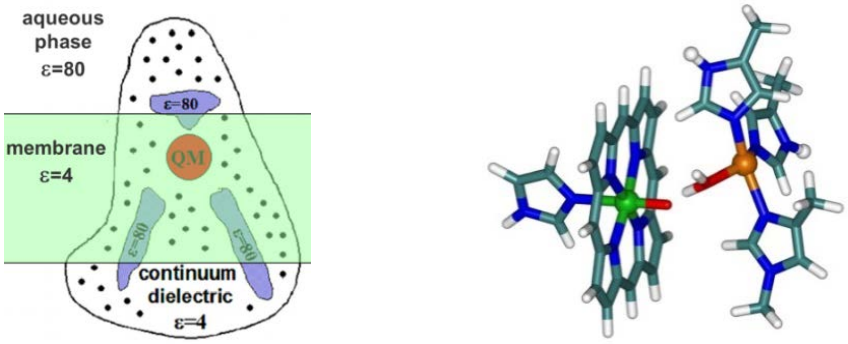

Fig 1. The DFT/SCE model of CcO with its quantum-mechanical part.

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Bottom-up design of functional bio-inspired polymeric materials: from in silico chemistry to their green production

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The antibody market is expected to reach EUR 218 billion at the end of this year, growing at an annual rate of ~12 % [1]. However, antibody production/purification has several limitations, such as the use of low-efficient isolation methods and low cost-effectiveness [1]. Moreover, the development of more sustainable functional materials and processes is needed to address environmental challenges, efficiency, scale-up, and low cost. Molecular Imprinted Polymers (MIPs) are synthetic materials within specific affinity sites complementary in size, conformation, and functionality to the target molecule. MIPs are significantly advantaged when compared to natural antibodies, since they use low-cost starting materials, are robust, stable under harsh conditions, have a long lifetime, and are easily stored [2]. Herein, L-leucine (LEU)-MIPs are being developed as sustainable bio-inspired polymers from a bottom-up perspective. Firstly, rational design using quantum mechanics calculations and molecular modeling was performed to select the most appropriate functional monomers and understand their interactions with the template (LEU). LEU-MIPs were synthesized by two different green technologies supercritical carbon dioxide ($scCO_2$) technology and mechanochemistry (ball milling). $ScCO_2$ technology is non-toxic, non-flammable, scalable, has a very accessible critical point, and is easily tuned by simply adjusting pressure and temperature. On the other hand, a ball mill is an expanding technology that is also easily scalable, requires low-cost equipment, and operates under solventless conditions. Both green technologies were effectively applied in the syntheses of LEU-MIPs, which were obtained as dry, free-flowing powders [3]. The performance of the materials produced was assessed by static binding tests using several concentrations of LEU (0.5 and 1.5 mg/mL) that revealed very promising results, with a maximum imprinting factor (*IF*) of 12 for the LEU-MIP synthesized in $scCO_2$, and an *IF* of 1.4 for the ball milled LEU-MIP. Both green technologies have been showing high potential in obtaining ready-to-use, stable, and low-cost bio-inspired polymers with biorecognition ability for target biomolecules, envisaging a great potential for bio-applications including bio-purification processes.

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Structure, spectra and photochemistry of 2-amino-4-methylthiazole: FTIR matrix isolation and theoretical studies

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The structure, tautomerization pathways, vibrational spectra, and photochemistry of the 2-amino-4-methylthiazole (AMT) molecule were studied by matrix isolation FTIR spectroscopy and DFT calculations undertaken at the B3LYP/6-311++G(3df,3pd) level of theory [1]. The most stable tautomer with the five-membered ring stabilized by two double C=C and C=N bonds, was detected in argon matrices after deposition. When the AMT/Ar matrices were exposed to 265 nm selective irradiation, three main photoproducts, N-(1-sulfanylprop-1-en-2-yl)carbodiimide, N-(1-thioxopropan-2-yl)carbodiimide and N-(2-methylthiiran-2-yl)carbodiimide, were photoproduced by cleavage of the CS–CN bond together with hydrogen atom migration. The minor photoreaction caused by the cleavage of the CS–CC bond and followed by hydrogen migration formed 2-methyl-1H-azirene-1-carbimidothioic acid. Moreover, cleavage of the CS–CN bond followed by disruption of the N–C bond produced cyanamide, and the $^{\cdot}C(CH_3)=CH\text{-}S^{\cdot}$ biradical that transformed into 2-methylthiirene and further photoreactions produced 1-propyne-1-thiole or methylthioketene. Cleavage of the CS–CC bond followed by disruption of the N–C bond produced propyne and the $^{\cdot}S\text{–}C(NH_2)=N^{\cdot}$ biradical that transformed into 3-aminethiazirene; further photoreactions produced N-sulfanyl carbodiimide. As a result of these transformations, several molecular complexes were identified as photoproducts besides new molecules in the AMT photolysis process [2,3].

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Modeling collective vibrations of DNA hydration shell

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The ion-hydration shell surrounding DNA, consisting of water molecules and metal counterions, plays a crucial role in stabilizing its structure and facilitating its biological functions. To understand the role of the ion-hydration shell in DNA function, a detailed study of its structure and dynamics should be conducted. For this purpose, we used the classical all-atom molecular dynamics (MD) method to study the collective vibrations of water molecules surrounding DNA. Specifically, we focused on the low-frequency spectra (< 300 cm^{-1}), where intramolecular vibrations are observed. Water molecules located in different regions of the double helix (phosphate groups, minor and major grooves) were analyzed.

The low-frequency spectra of bulk water consist of several modes, appearing due to hydrogen bond (H-bond) bending and stretching (symmetric and asymmetric), including a specific mode associated with bond bifurcation. To study water intermolecular vibrations in different regions of DNA, a theoretical approach and MD simulations were used. To obtain the frequency of translational vibrations related to H-bonds stretching of water in the DNA minor groove, a theoretical model was developed [1]. Based on our approach, the frequencies of these vibrations were obtained within the range of 185 ± 20 cm^{-1}, revealing a strong dependence on the nucleotide type. Subsequent MD simulations [2] uncovered significant differences in the vibrational behavior of water molecules near the DNA surface compared to bulk. Analyzing the velocity density of states for the atoms of water molecules around the DNA, we distinguished six vibrational modes. All modes of the DNA hydration shell exhibited a notable shift of approximately 15–20 cm^{-1} towards higher frequencies, being more pronounced in the minor groove. Furthermore, interactions between water molecules and DNA atoms led to a decrease in the intensity of the H-bond symmetrical stretching mode (approximately 150 cm^{-1}), resulting in its absence in the calculated spectra.

Our findings emphasize the distinct organization and dynamics of water around DNA, especially in the minor groove. This could help in understanding DNA experimental low-frequency spectra, how water molecules influence DNA dynamics, and how they affect biological processes. In perspective, it is important to analyze the common vibrational dynamics of water molecules and metal counterions.

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Synthesis of a New Family of Zn(II) Hydrazone Complexes: Characterisation, Catalytic Activity, and DFT Calculations

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The ligand (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide (**HL^1**) was obtained from the condensation of 2-acetylthiazole and thiosemicarbazide. Upon reacting **HL^1** with $Zn(BF_4)_2{\cdot}6H_2O$ and NaN_3 in a solvent mixture of water/methanol, mononuclear Zn(II) complex **1** with the composition [Zn**L^1**$(N_3)_2$] was obtained. In complex **1**, Zn(II) is pentacoordinated with the thiazole nitrogen, the azomethine nitrogen, and thiolate sulfur atoms from the deprotonated hydrazone ligand, as well as with two azido ligands. Complex **1** crystallises in the monoclinic crystal system with space group No.14 ($P2_1/c$ cell setting). The unit cell of **1** contains four [Zn**L^1**(N_3)] asymmetric units. In complex **1**, the Zn(II) site shows a distorted geometry, almost midway between the square pyramid and trigonal bipyramid, established on the basis of a calculated τ_5 parameter of 0.46.

The hydrazone ligand (*E*)-1-(2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethyl)-pyridine-1-ium chloride (**HL^2**Cl) was obtained from the condensation reaction of 2-acetylpyridine and Girard's P reagent. Reaction of **HL^2**Cl with $Zn(BF_4)_2{\cdot}6H_2O$ and NaN_3, in a mixture of acetonitrile/water/methanol, gives mononuclear Zn(II) complex **2** with the composition [Zn**L^2**$(N_3)_2$]. Reaction of **HL^2**Cl with $Zn(BF_4)_2{\cdot}6H_2O$ and NaN_3, in a mixture of acetonitrile/water/methanol, gives mononuclear Zn(II) complex 2 with the composition [Zn**L^2**$(N_3)_2$]. In complex **2**, the Zn(II) ion has fivefold coordination with NNO-set of donor atoms of L2 and two nitrogen atoms from the azido ligands. The calculated τ_5 value of 0.08 for [Zn**L^2**$(N_3)_2$] indicates that the five-coordination geometry of the Zn(II) ion is slightly distorted square pyramidal.

Evaluation of the catalytic properties of the Zn(II) complexes in the KA2 reaction shows that the most active compound, when used as a catalyst, is complex **1**. It leads to a 92 % isolated yield of the desired propargylamine product. The catalytic activity results are in full agreement with the findings of the DFT calculations. Complex **1** shows the highest value of molecular softness and the lowest value of molecular hardness. This correlation, between experimental and theoretical results, is excellently visualised in the linear relationship between the isolated yield of the desired propargylamine product and the calculated molecular softness, *S*.

Interaction of Acetylcholine-Binding Protein from *Aplysia californica* with Imidacloprid: a Computational Investigation

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Pesticides have been designed for effectively managing pests or regulating plant growth, nevertheless, their extensive utilization has resulted in significant environmental issues, particularly water contamination. To address this matter, several methodologies have been employed for water treatment. In such a manner, insightful knowledge of the physicochemical properties of pesticides and the elucidation of their interaction with live-organisms target proteins may be relevant for the design of new materials for their remediation from water [1]. Imidacloprid is a neonicotinoid insecticide, which is among the most used pesticides, consequently, they are currently found in high concentrations in water ecosystems. Previous works have already reported the imidacloprid mode of action as an insecticide, which is based on the interaction of the nicotinoid with the nicotinic acetylcholine receptor (nAChRs) of several insects, interfering with the transmission of stimuli in the insect nervous system [2]. Acetylcholine-Binding Protein from *Aplysia californica* (Ac-AChBP) is frequently used as a model of the ligand-binding domain of the nAChRs since it has similar pharmacological properties, residues, and it can bind to the known nAChRs agonists, competing with antagonists such as acetylcholine and nicotine [3]. In this work, we employed electronic structure calculations, docking, and molecular dynamics simulations to explore the interaction between imidacloprid and the Acetylcholine-Binding Protein from *Aplysia californica* in water. To characterize de protein-imidacloprid interactions, several properties were calculated: root-mean-square deviation; root-mean-square-fluctuation of each protein residue; protein-ligand distances; number of hydrogen bonds; intermolecular interaction fingerprints; visual inspection. The results allowed the identification of several interaction sites and the amino acids directly involved. This knowledge may be relevant to the future design of new materials for pesticide remediation from water.

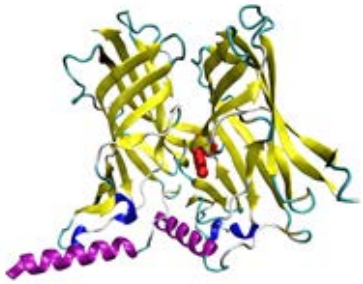

Fig 1. Interaction of Acetylcholine-Binding Protein from *Aplysia californica* with Imidacloprid.

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Reactive collisions between electrons and molecular cations at extreme energy. Applications in astrophysics

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The Multichannel Quantum Defect Theory (MQDT) has been employed in computing cross-sections and Maxwell rate coefficients for electron-driven reactions involving molecular cations. The results of the present work are an extension of our previous studies on the reactive collision of HD^+ ion [1] and H_2^+ ion [2] with electrons to a wider range of incident collision energy and to mixed rotational and vibrational.

The provided collisional data are useful in the kinetics modeling in astrochemistry – early Universe, interstellar molecular space - and cold plasma physics.

In order to model and diagnose the low-temperature edge plasmas, a complete database for electron-impact collision processes is required for molecular species containing beryllium and hydrogen. The previous study of dissociative recombination, vibrational excitation, and vibrational de-excitation of the BeH^+ ion [3] is extended to collision energies above the dissociation threshold, taking into account the dissociative excitation of the BeH^+ ion.

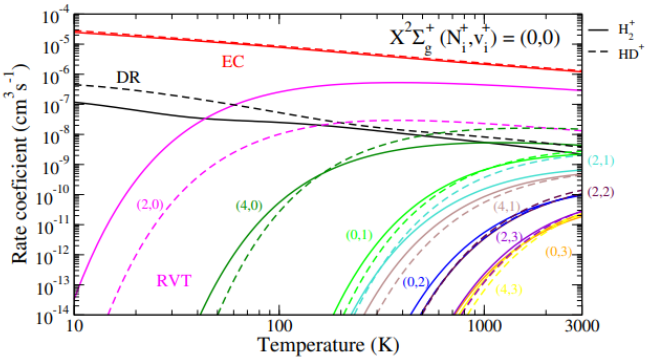

Fig 1. Electron-impact dissociative recombination and rovibrational transitions of HD^+ and H_2^+ ions.

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Unravelling the role of quantum effects in the peroxidation of organic substrates

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Reactions between molecular oxygen and closed-shell organic molecules, leading to the formation of stable (closed-shell) adducts, are expected to proceed through an intersystem crossing, which should be slow at room temperatures. However, certain enzymes possess the remarkable ability to catalyze these reactions without relying on cofactors. In this context, we focus on the specific enzymatic peroxidation of the DPA-CoA, which occurs within the active site of the DpgC enzyme without cofactors [1,2].
Previous studies [3] showed that this process involves two electron transfer steps, the first of which is concomitant with the intersystem crossing. To understand this process, the spin-orbit coupling emerges as a crucial property in facilitating intersystem crossing. We report quantum scattering calculations on seven MRCI 2D PESs (six singlets and the triplet state), including the spin-orbit coupling between them.

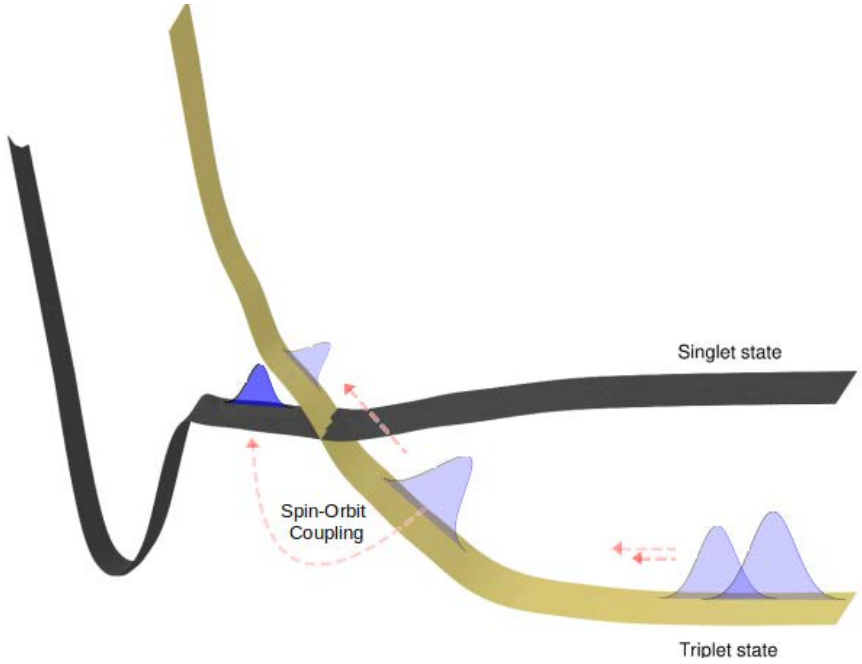

Fig 1. Schematic representation of the wave packet propagation along the intersystem crossing between a singlet state (black) and a triplet state (golden) potential energy surfaces.

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Attaching symmetric porphyrins to c-MYC promoter Pu24I G-quadruplex: toward more specific ligand recognition by flanking bases

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Overexpression of the oncogenes in cancer cells can be decreased by stabilization of G-quadruplexes formed in the promoter region by binding small drug molecules. Many G-quadruplex stabilizers interact with a terminal G-quartet by π–π stacking and electrostatic interactions, but additional interactions with flanking nucleotides are needed to ensure selectivity towards a specific G-quadruplex sequence [1]. In this work, binding affinities of various TMPyP4 analogues (Fig. 1) to a c-MYC promoter Pu24I G-quadruplex were investigated using density functional theory and force field molecular dynamics [2]. Van der Waals interactions in the binding pocket were mainly responsible for the order of binding energies in the end-stacking pose, TMABP4 > TMPyP4 ≈ TPyAP4 > TPyP4 ≈ TBP. A new binding pose was found for TPyP4 ligand where the ligand intercalates between A3 and G2 bases and stacks on the two guanines on the top G-quartet. This intercalating binding pose showed stronger binding energy and could be more selective, contrary to the believes that this cannot be achieved with a symmetric porphyrin derivative [3].

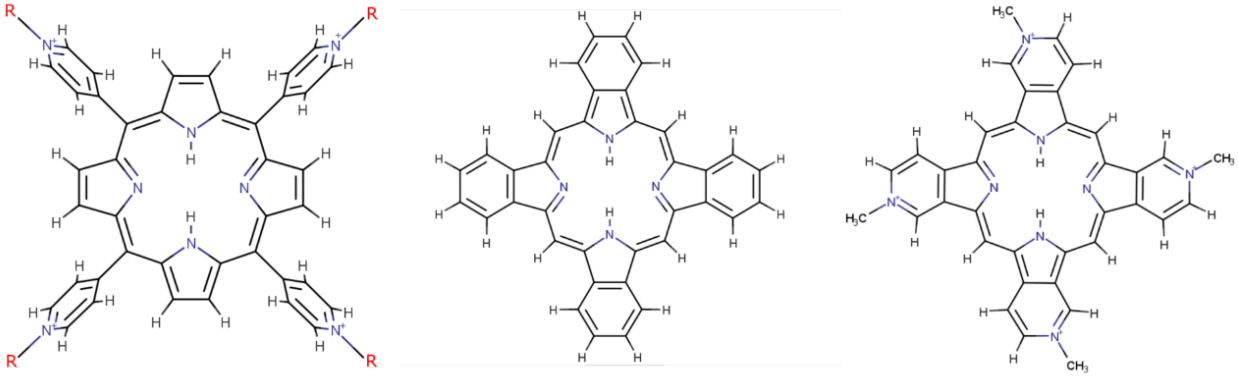

Fig 1. Structures of TMPyP4 (R = CH_3), TPyP4 (R = H), TPyAP4 (R = CHO) (left), TBP (centre), TMABP4 (right).

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Computer simulations of efficient CH_4/CO_2 Gas Mixture Separation through Nanoporous Carbon-based Membranes Designs

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Nanoporous carbon-based membranes have garnered significant interest in gas separation processes owing to their distinct structure and properties. However, the intricate nature of comprehending these membrane designs has limited their extensive application in gas separation [1]. In this current investigation, our objective is to introduce viable designs aimed at addressing this technical hurdle. In this regard, we investigated the permeation and separation of the mixture of adsorptive gases CO_2 and CH_4 through membranes formed by thin layers of porous graphdiyne and boron graphdiyne using Density Functional Theory [2]. We perform calculations with the Quantum Espresso code [3]. The relaxation of the atomic structure of the membranes during the processes of gas permeation was carefully considered. The main goal is to investigate and compare the effect of the two different membranes, graphdiyne, GDY, and boron-graphdiyne, BGDY. The permeation and separation of the CO_2 and CH_4 molecules while crossing through the membrane are significantly influenced by the size of the pores of the layers. The interaction energies between the CO_2 and CH_4 molecules and the porous layers were calculated as a function of the vertical separation between molecules and layer. The calculations allow us to obtain the molecule-layer interaction potential, which is negligible at a sizeable molecule-membrane distance, goes through an energy minimum at distances of 2-3 Å, and shows a barrier at the layer plane. Those barriers, which control the permeation and the selectivity, depend on the size of the pores and on the nature of the molecules. The larger pores in BGDY yield to the passage of both molecules, CO_2 and CH_4, through the layers of BGDY with almost no activation barriers. In contrast, the smaller pores of GDY lead to moderate activation barriers, substantially larger for CH_4 than for CO_2. Our findings provide a suitable design for efficient separation of CH_4/CO_2 gas mixtures by testing new nanoporous Graphene-related materials.

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A Multiscale Approach to Simulate Sonochemical Reactions

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Chemical reactions which are enabled via the use of an ultrasonic wave generator can be summarized as sonochemical reactions. The highly reactive conditions of sonochemistry result from the formation of microscopic cavities and their subsequent implosion, which can generate temperatures of approximately 5000 °C and pressures of roughly 500 atm [1]. Advances in many research fields have been made by the utilization of sonochemically enforced chemical reactions. These include, for example, the medical sector, where sonochemical conditions offer promising potential for the release of small cargo molecules via sonication of disulfide-containing polymers [2]. Recent developments in the computational simulation of sonochemical reactions have been made using molecular dynamics (MD), which allowed the simulation of a shock-induced cavitation bubble collapse and the investigation of the resulting reaction parameters [3]. These parameters are essential for a quantum mechanical (QM) investigation of sonochemical reactions. However, there is no model yet available allowing the calculation and the corresponding prediction of sonochemical reactions. Therefore, the development of MD methods that allow the examination of polymer reactions, including bond scission and radical-induced reactions, is essential. For this purpose, MD simulations of polymer chains with and without mechanophores using reactive force fields are needed, allowing the investigation of strain and determination of bond scission within the polymer chain. In addition, the development of QM models that allow a more thorough investigation of the radical-generating reactions that happen inside an imploding cavitation bubble is needed. For this purpose, spin-flip time-dependent density functional theory (SF-TDDFT) is to be used.

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Energetics and Kinetics of Steps in Proton Pumping Mechanism of Mammalian Cytochrome *c* Oxidase

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Cytochrome *c* oxidase (CcO), the terminal enzyme of cell respiration, is responsible for processing most of the biological oxygen and generating electrochemical proton gradient in aerobic cells. The energy released from the reduction of molecular O_2 to H_2O is used to pump protons across the inner-mitochondrial membrane [1, 2]. Recent time-resolved optical and electrometric experiments on the O→E transition have anticipated a sequence of reaction steps for the proton translocation mechanism in CcO. Besides kinetic gating, the CcO pump function encompasses a mechanistic principle of conformational gating control that can help to prevent protons from backward outflow during the process. It was also found that Glu242, an essential residue in transferring pump protons to the proton-loading site (PLS) and chemical protons to the site of oxygen reduction, accomplishes the function of the gating site by avoiding simultaneous contact with the pump site, oxygen ligands in the BNC, and the proton-conducting D-channel. Moreover, the microscopic reversibility of the individual steps and the importance of kinetic barriers in maintaining the unidirectionality of the overall process in CcO is noteworthy [2, 3].

Here we have included the conformational gating by Glu242 into a framework of the proposed His291 pumping model [4]. DFT/electrostatic calculations are employed to obtain energetics of the proton and electron transfer reaction steps during the O→E transition [2, 3, 5–7]. In addition, transition state theory estimates activation energies and kinetic barriers from the rate constant of transitions. The energy profile of the reaction mechanism is studied by exploring how the redox state of the metal centers, dielectric solvation effects, and membrane potential gradient affect the energy levels and possible leakage of the protein pump through the Glu242 gating site. Particular emphasis is made on side reactions that may short-circuit the pump, resulting in a loss of proton pumping, and how this may be avoided in natural biological systems [2, 3]. CcO employs several control mechanisms and gating situations to ensure the proton translocation unidirectionality and prevent proton leak in the opposite direction.

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Modeling self-diffusion coefficient and viscosity of chain-like fluids based on electrolyte perturbed-chain statistical associating fluid theory (ePC-SAFT)

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Transport properties (i.e., viscosity η and self-diffusion coefficient D) of chemicals are important for their process and product design in industrial technology. Considering that the measurement is time-consuming and expensive, developing models to represent transport properties is important. Numerous theoretical models have been developed to describe the transport properties of different fluids [1]. These models commonly require thermodynamic properties, such as density, obtained from experiments or models as input to determine transport properties. However, the model parameters for transport and thermodynamic properties typically differ. Developing models with one set of molecular parameters to simultaneously represent both transport and thermodynamic properties will be feasible and important. Several models have been developed to achieve this goal, such as Eyring's model and entropy-scaling models, but they mainly focus on simple molecules and have not been extended to advanced and complex fluids, such as ionic liquids (ILs) with charges.

In this work, a new diffusion equation was developed based on the diffusion coefficient of Lennard-Jones spherical fluids [2] by incorporating a correction function to describe the characteristics of chain-like molecules. Subsequently, the Stokes-Einstein equation was used to calculate the viscosity. Based on the molecular parameters in ePC-SAFT [3], a set of universal parameters was determined from experiment data of η and D of 19 n-alkanes. Furthermore, the results of η and D for the other 17 compounds, including branched alkanes and cyclic compounds, were predicted. Finally, the proposed model was extended to ionic liquids.

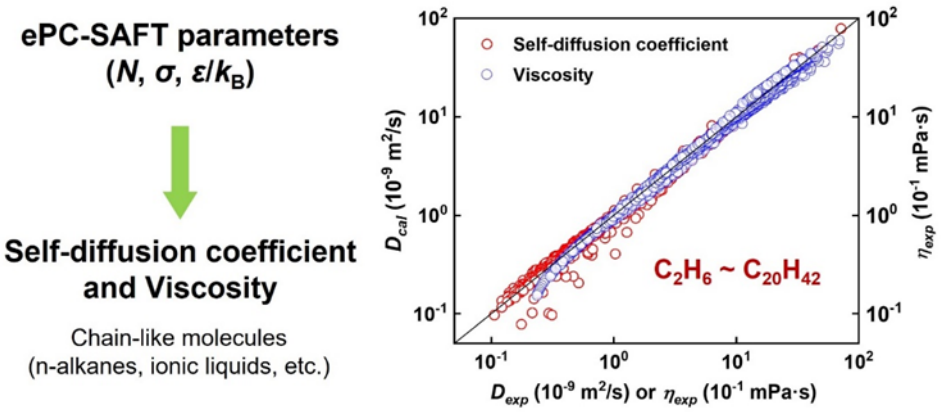

Fig 1. Comparison of calculated and experimental self-diffusion coefficients and viscosities for the studied n-alkanes (C_2H_6 ~ $C_{20}H_{42}$).

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Computational study of a human G-Quadruplex and its interactions with a porphyrin ligand

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The DNA in the cell nucleus is primarily present in a double-helix conformation. However, there are other secondary structures such as quadruplexes (G4s) that are biologically significant, as they are involved in genetic activity regulation and DNA replication. Due to these biological roles, G4s stabilization or destabilization can be important for medical purposes to control processes involved in cancer and other diseases. One method to stabilize G-quadruplex formation is to introduce ligands capable of forming complexes with G4 and stabilizing this type of structure.

We studied the structure of the human telomeric G4 (PDBID:1KF1 with parallel topology), aiming to assess, through the computational method of molecular dynamics (MD), the effect of a porphyrin-based ligand (p11b) on the stability of G4. For the G4, the OL15 force field was employed, along with the GAFF force field for the ligand, the SPCE water model, and a salt concentration of 150 mM KCl. Appropriate parameters for the solvent model were used for ions. MD simulations were conducted at both room temperature (300 K) and high temperatures (500 K, 550 K, and 525 K) both with and without the ligand. In the simulations at high temperatures, the volume and temperature are kept constant. Simulations at room temperature were performed at constant pressure and temperature. The simulations at the high temperature are aimed to verify the stabilizing or destabilizing effects of the ligand: if the temperature at which the complex denature is higher than that of the G4 alone, the ligand is considered to stabilize the G4, while if it is lower, a destabilizing effect is implied [1,2].

To monitor structural changes of the quadruplex during simulations, Root-Mean-Square Deviation (RMSD) analyses were carried out over time for different portions of the molecule. Through the study of RMSD, it was possible to observe system denaturation at certain temperatures. Results obtained from the simulations indicated that the ligand-free quadruplex exhibits a higher propensity for denaturation, and thus a stabilizing effect of the p11b ligand.

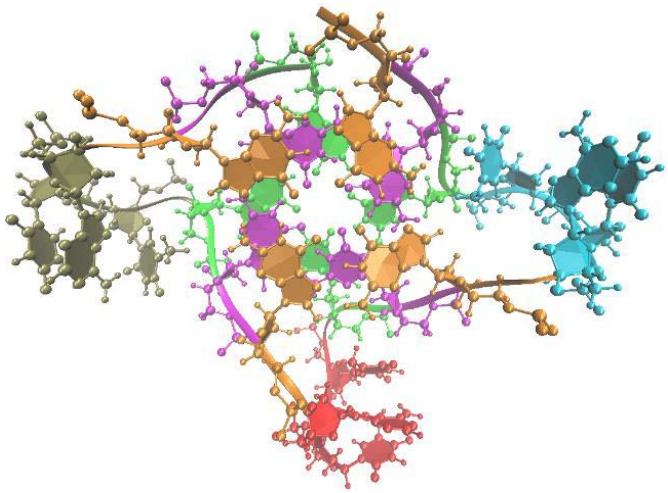

Fig 1. Graphical representation of 1KF1 using a different color for each loop and tetrad.

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Cobalt functionalization of Carbon-based materials for Hydrogen storage

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Nowadays, the study of materials that allow Hydrogen storage in safe and efficient conditions has become very important. Carbon-based materials are outlined as candidates for this application and functionalization of these materials with transition metals improves their hydrogen storage capacity. Hydrogen storage on graphdiyne (GDY) and boron-graphdiyne(BGDY) layers doped with clusters of six cobalt atoms has been investigated by performing density functional (DFT) calculations.

Graphdiyne and Boron-graphdiyne are novel carbon-based materials with sp and sp^2 hybridization. In our work, GDY was modelled as a periodic supercell with 72 carbon atoms. In the case of BGDY, the periodic supercell contains 14 atoms (12 Carbon atoms and 2 Boron atoms). The GDY and BGDY layers were functionalized with the Co_6 cluster. In the GDY layer, the Co_6 cluster fits well on the triangular holes and is adsorbed with an energy of 6.41 eV, while in the BGDY layer, the preferred position of Co_6 is above the Boron atom, with an energy of 4.12 eV. The doping of Carbon fullerenes with Co_6 has been studied previously; in this case, the Co_6 cluster is adsorbed with a lower energy of 2.04 eV [1].

We find that for low coverage (1 cluster per cell) Co_6GDY adsorbs 9 H_2 molecules, and Co_6BGDY adsorbs 12 H_2 molecule. The difference between the two materials is that Co_6 is less constrained and more available to interact with the H_2 molecules in the BGDY layer. Furthermore, it becomes interesting to make a comparison with results for H_2 adsorption on Co_6C_{60} [1] and with the isolated Co_6 cluster [2]. Co_6C_{60} adsorbs up to 13 H_2 units, and 16 H_2 molecules were adsorbed on the isolated Co_6 cluster. In conclusion, materials composed of Co clusters and carbon nanostructures adsorb a large amount of Hydrogen and we can view the Co_6 clusters saturated with hydrogen as nanohydrides.

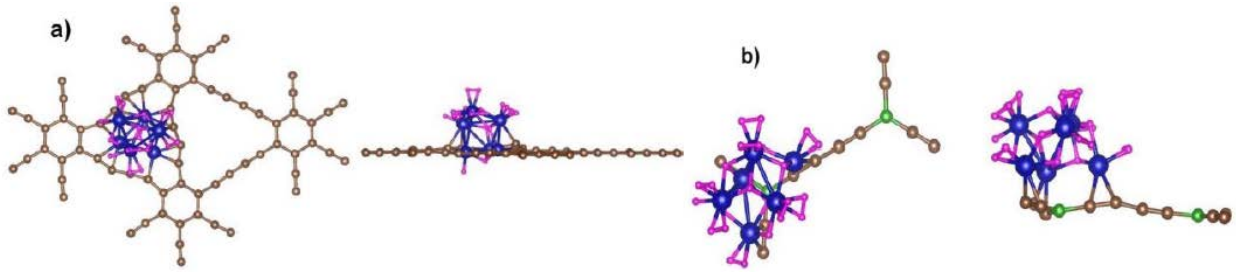

Fig 1. Top and side view of a) hydrogenated Co_6GDY and b) hydrogenated Co_6BGDY.

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Self-discriminating assembly and biorecognition of a spirohydantoin derived from α-tetralone

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The hierarchical development of the crystal structure of racemic 3-(4-methoxybenzyl)-6,7-benzo-1,3-diazaspiro[4.5]decane-2,4-dione was analyzed through cooperativity of various homo and heterochiral dimeric motifs associated with the presence of different intermolecular interactions, namely strong N–H···O and weaker C–H···O, C–H···π and PILOs.[1] Although a bigger number of the contacts in the environment of the tetralin unit results from its larger contact surface, the 4-methoxybenzyl unit provides a greater contribution to the overall stabilization. In addition, the investigated compound is identified as a potential inhibitor of kinase enzymes and AG protein-coupled receptors, with a slightly higher affinity for the later enzyme. An analysis of the nature of the amino acid residues around the tetralin and 4-methoxy benzyl units revealed that interactions with nonpolar groups are the most prevalent and even more numerous than interactions with other amino acid residues (polar, positive and negative).

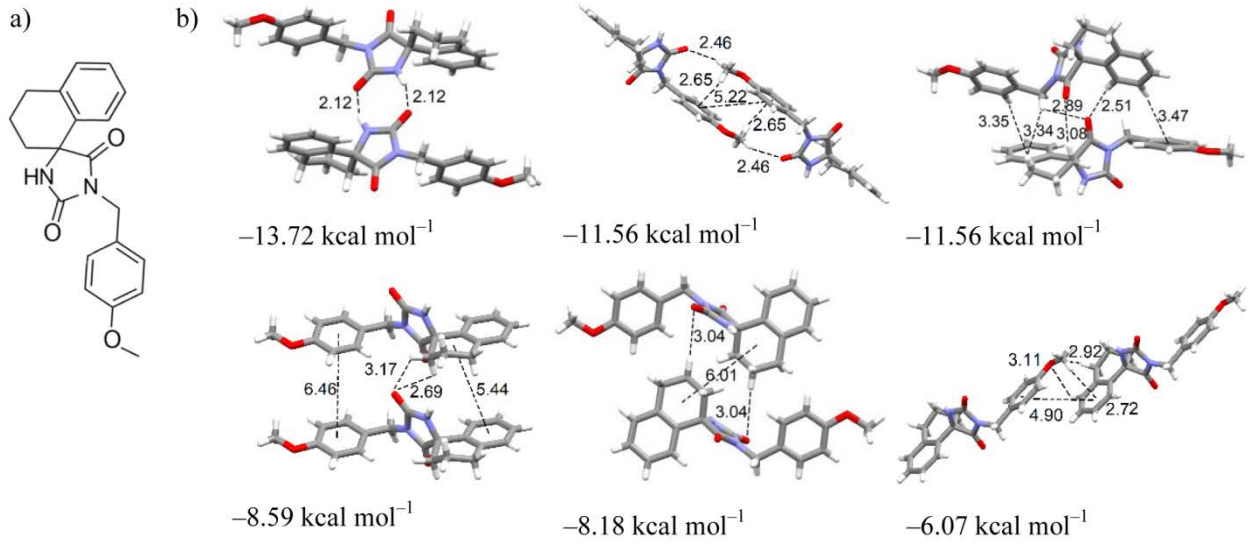

Fig 1. a) Chemical structure of 3-(4-methoxybenzyl)-6,7-benzo-1,3-diazaspiro[4.5]decan-2,4-dione and b) Dimer motifs observed in the crystal structure with their interaction energies.

References:

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Fragmentation of tyrosine by high-energy electron impact

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The experimental mass spectra of the amino acid tyrosine molecule were measured at different microtron accelerator-induced high-energy electron irradiation doses, i.e., 0, 5, and 20 kGy, and have been identified and analysed [1]. Along with the experimental investigation, we have conducted numerical calculations based on Becke's three-parameter hybrid density functional approach with non-local correlation by Lee, Yang, and Parr (B3LYP) [2]. Our calculations were performed utilizing the cc-pVTZ basis set and a modified cc-pVTZ basis set, in which we introduced correction coefficients into the wave functions of the s- and p-orbitals. The correction coefficients were implemented via the Anisotropic Gaussian-type orbital method to reflect the elongation of electron orbitals and densities caused by the magnetic field of radiation, similar to our previous work [3].

The results of our investigation show that the geometrical structure of the molecule could be changed due to the presence of the electric field, and the molecule could decompose in an electric field with a strength higher than 0.31 a.u. We also found that the electromagnetic radiation field is capable of facilitating the intramolecular hydrogen migration, quenching at the same time some fragmentation processes in the tyrosine molecule. The inclusion of the influence of the magnetic radiation field in our numerical studies showed the possibility for further decomposition of the fragments, thus indicating that magnetic field effects are crucial for the intramolecular hydrogen migration and/or electron transfer processes.

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Unlocking the Kinetic and Thermochemistry of Hydrocarbon Combustion Reactions Involving Hydroperoxyalkyl Radicals

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Hydroperoxyalkyl (QOOH) radicals play an important role as intermediates in low-temperature (< 1200 K) hydrocarbons combustion. However, our understanding of their reaction thermochemistry and kinetic properties still has significant uncertainties. To provide a thorough understanding of the gas-phase chemistry of hydrocarbon fuels, it is necessary to employ a valid chemical kinetics model, which requires a reliable thermochemistry data. In this study, we performed detailed quantum mechanical calculations in order to improve model accuracy leading to better estimation of reactions thermochemistry and kinetics. We studied non-cyclic and cyclic alkyl hydrocarbon radicals (R) and triplet molecular oxygen ($^3O_2$) systems through bimolecular O_2 addition and unimolecular hydroperoxyl (RO_2) and QOOH reaction mechanisms shown in Fig1. The W1U composite method, which was used to obtain the potential energy surfaces, was also utilised to benchmark the selected composite post-Hartree Fock methods and density functional theory (DFT). Zero-point vibrational energies and scaled harmonic vibrational frequencies were obtained at B3LYP/cc-pvtz+d. Standard enthalpies of formation of the reaction species were determined by various methods based on reference reactions. Variational transition state theory (VTST), transition state theory (TST) and Rice Ramsperger Kassel Marcus theory (RRKM) were used to determine temperature-pressure dependent rate constants. The RRKM rate constants were calculated for 1atm - 100 atm pressure and 300 K - 1200 K temperature ranges. The analysis of the results indicates that the investigated elementary reactions have barriers except the O_2 addition step. The concerted $^{\bullet}$OOH elimination and hydrogen atom transfer steps have barrier heights with values between 30 kcal/mol to 38 kcal/mol, whereas the $^{\bullet}$OOH elimination and $^{\bullet}$OH elimination steps have barrier heights with values between 9 kcal/mol to 22 kcal/mol. The benchmarking relative energy results indicate that the best performing methods are G4, CBS-QB3, G4MP2 and DFT (M06-2X>DSDPBEP86>M05-2X). Additionally, the RRKM data shows an increase of the rate constants as temperature and pressure rise, reaching a falloff phase between 500 K and 900 K. The findings of this investigation agree with the observation found in literature [1].

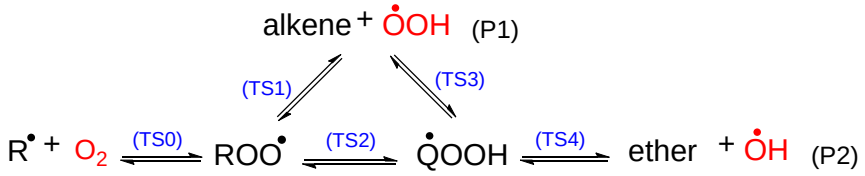

Fig 1. Selected elementary steps for the reactions of hydrocarbon radicals with molecular oxygen.

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FTIR spectroscopic studies of matrix-isolated 3-thio-1,2,4-triazole complexes with dinitrogen. First experimental evidence for the UV-induced formation of thiol···N_2 complexes

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Weakly bound molecular complexes are involved in many biological and chemical processes, including those occurring in the Earth's atmosphere. Dinitrogen, being its most abundant component, was found to interact strongly with various molecules, considerably changing their spectroscopic properties [1, 2]. Heterocyclic compounds are often characterized by the presence of a rigid structure containing acidic A-H moieties as well as electron pair donors. They are widely used e.g. as building blocks for the formation of various metal–organic frameworks (MOFs) designed for many purposes, including gas storage and separation [3].

In this work, complexes of 3-thio-1,2,4-triazole (ST) with N_2 were studied theoretically by the DFT/B3LYP-D3 method and experimentally by FTIR spectroscopy combined with the matrix isolation technique and UV laser irradiation. The computational results show that ST interacts specifically with dinitrogen in several different ways. For the 1:1 complexes of the most abundant ST thione tautomer, three stable minima were located on the potential energy surface. The two most stable structures, containing both N-H···N hydrogen bond and S···N van der Waals contact, were detected experimentally in the argon matrix after deposition. Interestingly, it was found that laser irradiation at $\lambda = 270$ nm, besides generating the thiol tautomer of ST, also leads to the formation of its corresponding complexes, characterized by N-H···N hydrogen bonds. What is more, it appeared that the efficiency of hydrogen atom transfer in ST complexed with N_2 is lower than in the monomeric form. Based on the kinetic profiles, it could be also concluded that even a small admixture of N_2 (0.1 %) in the matrix environment noticeably slows down the process.

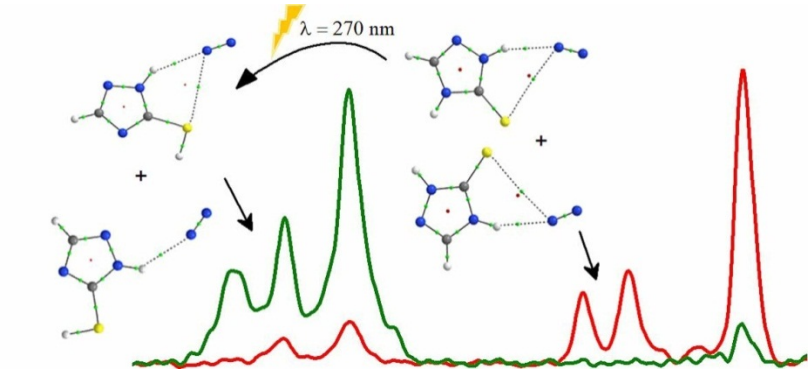

Fig 1. Summary of the thione-thiol tautomerization process for 1,2,4-triazole-3-thiol complexes in a nitrogen-doped argon matrix.

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Synthesis and characterization of Mn(II) and Fe(III) complexes with the condensation product of thiosemicarbazide and 2-acetylthiazole

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The HL ligand, (E)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide, was obtained from the condensation reaction of thiosemicarbazide and 2-acetylthiazole in water. The reaction of the HL ligand with the metal salt $MnCl_2 \cdot 4H_2O$ in a molar ratio 1:1 in methanol/water mixture results in the formation of bis Mn(II) complex with composition $[MnL_2]$. Complex 1 crystallizes in the triclinic crystal system with space group $P\bar{1}$. The Mn(II) ion is hexacoordinated with two tridentate ligands L through NNS sets of donor atoms. The geometry around the Mn is described as a distorted trigonal prism (Fig. 1).

The reaction of the ligand HL with $Fe(BF_4)_2 \cdot 6H_2O$ in a molar ratio 1:1 in methanol results in the formation of bis Fe(III) complex with composition $[Fe(L)_2]BF_4 \cdot H_2O$. The Fe(III) ion with L form six-coordinate complex in which two deprotonated ligand molecules coordinate in a mer arrangement, forming a distorted octahedral complex by chelation through NNS sets of donor atoms (Fig. 1). Complex 2 crystallizes in the orthorhombic crystal system with space group *Pbca*.

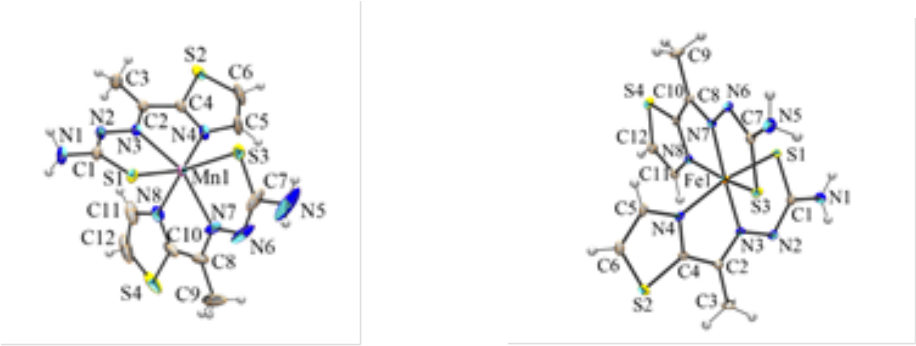

Fig 1. Molecular structure of complex 1 $[MnL_2]$ (left) and complex cation 2 $[Fe(L)_2]^+$ (right).

On the presence of metallofullerenes in fullerene-rich circumstellar envelopes

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The presence of neutral C_{60} fullerenes in circumstellar environments has been firmly established by astronomical observations, as well as laboratory experiments and quantum-chemistry calculations. However, the large variations observed in the C60 17.4 μm/18.9 μm band ratios indicate that either additional emitters should contribute to the astronomical infrared (IR) spectra or unknown physical processes exist besides thermal and UV excitation. Metallofullerenes can arise as a possible explanation for the 17.4 μm/18.9 μm band ratios trend since small metal-containing molecules have been detected in circumstellar envelopes. Therefore, the conditions in these circumstellar environments are appropriate for the possible formation of metallofullerenes. In this work is reported a model based on quantum-chemistry calculations and IR spectra simulation of neutral and charged endo(exo)hedral metallofullerenes, showing that they have a significant contribution to the four strongest IR bands commonly attributed to neutral C_{60}. These simulations may explain the large range of 17.4 μm/18.9 μm band ratios observed in very different fullerene-rich circumstellar environments like those around planetary nebulae and chemically peculiar R Coronae Borealis stars. The proposed model also reveals that the 17.4 μm / 18.9 μm band ratio in the metallofullerenes simulated IR spectra mainly depends on the metal abundances, ionization level, and endo/exo concentration in the circumstellar envelopes.

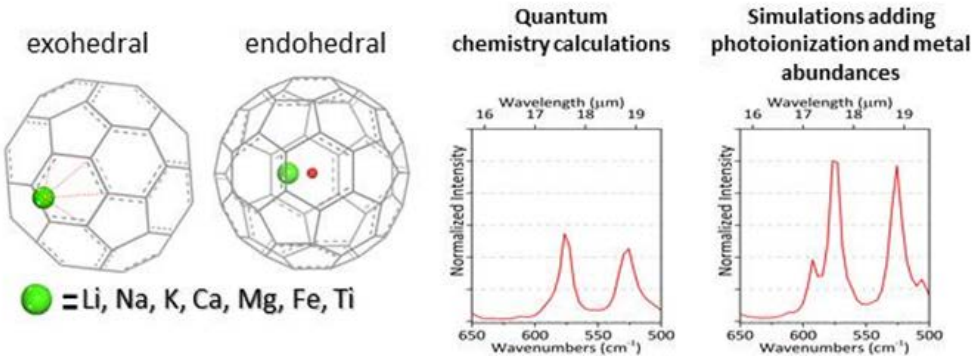

Fig 1. Schematic of the endo(exo) metallofullerenes representing the metal position. Total infrared spectra from a pure quantum chemistry approach and in the case of typical conditions of photoionization and metal abundances for circumstellar envelopes.

References:
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Production of abiotic O_2 cation from formic acid following multiple ionization processes

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The Great Oxidation Event enabled the emergence of aerobic life forms on Earth thanks to the production and accumulation of atmospheric O_2. The biotic origin of O_2 via biogenic processes is relatively well understood but very little is known about its abiotic origin. Early earth's atmosphere presents multiple types of compounds, such as CO_2 and SO_2, which can absorb sun radiations to induce fragmentation reactions either on neutral species or on the corresponding ionized molecules. For instance, it has already been shown experimentally and theoretically that the photodissociation of neutral SO_2 at 193 nm produces O_2 with a 2% yield [1]. Prior to that, a combined theoretical and experimental work showed that the ionic fragmentation pathways of SO_2^{2+} lead to a 12% yield of O_2^+ under a 40.8 eV light [2]. Therefore, the ionic pathway seems to be more efficient and our goal is to extend these studies to investigate atmospheric molecules, in particular volatile organic compounds (VOCs) such as formic acid.
Formic acid is the simplest and the most abundant atmospheric organic acid in the atmosphere. It is produced by photochemical oxidation of hydrocarbons. This acid could have played a role during the oxidation of the atmosphere. In this work, we present a preliminary study of the fragmentation of formic acid dication and the He (II) photoelectron spectra of formic acid using experimental and theoretical methodologies.

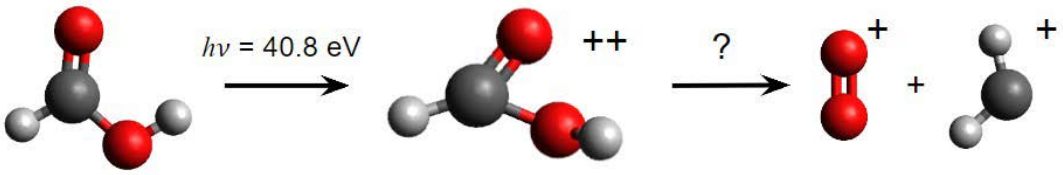

Fig 1. Diagram of fragmentation of formic acid leading to O_2^+ after single-photon double ionization processes.

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Computational study of a viral G-Quadruplex and its interactions with potential ligands

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In the cell nucleus, DNA is mainly present as a double helix, but other secondary structures are also present in vivo and may have important biological functions. In particular, the quadruple helix structure can be adopted especially by guanine-rich sequences. These structures, called G-quadruplexes (G4s), are involved in the regulation of key cellular processes, such as transcription and replication [1]. Comprehensive bioinformatics analyses have traced the presence of G4s forming sequences (PQS) in the genome of almost all human viruses. Therefore, the possibility of modulating their stability with ligands makes G4s an important therapeutic target in the fight against viruses. In the search for drug-like molecules capable of selectively binding to G4s, computational methods can be considered advantageous methods to verify the typology of interaction with different G4s and to propose ligands that act selectively on particular quadruplexes. In this investigation, the focus is on the only known G4 structure of HPV [2], HPV52, and the aim is to verify the ability of the force field mostly used for the G4s to reproduce the structure and dynamics of this quadruplex, that has never been simulated by MD before. Additionally, it was verified whether the G4-HPV52 interactions with a porphyrin ligand (P11B) predicted by a molecular docking procedure in the absence of solvent are confirmed in aqueous solution and the effect of these interactions on the G4 structure and its stability was investigated.

Ideally, it would be useful to test whether stabilizing compounds can actually keep the G4-HPV52 structure stable at the denaturation temperature of quadruplex alone. However, the time required for denaturation of real samples is too long to be simulated "in silico" at the denaturation temperature. One approach used in computer simulations to follow denaturation in a reasonable simulation time takes advantage of the ability to induce and accelerate the process by increasing the temperature, and this approach has been already successfully employed on G4 [3]. The combination of the force field and solvent model during the 300 K simulations of the G4-HPV52 resulted in the maintenance of the quadruplex structure similar to the experimental one, proving suitable for modeling this system. The simulations with the ligand suggest that it is able to stabilize the central core of the quadruplex formed by the tetrads, even at high temperatures in NVT conditions, up to 600 K, contrary to other previously studied G4s [3]. At the temperature of 650 K, the denaturation occurs within a few ps in the absence of the ligand while it requires over 50 ns in the presence of the ligand, further indicating a stabilizing effect.

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Synthesis of novel agents based graphene oxide modified with benzo[b]thiophene derivatives

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C–H activation offers a direct way to convert C–H bonds into more reactive intermediates, which can then undergo various transformations. C–H activation reactions can be tailored to perform various transformations, such as C–C, C–N, C–O, and C–X bond formations. Applying C–H activation to medicinal chemistry enables the rapid generation of diverse compound libraries, which can be screened for biological activity. Taking all this into account, the synthesis of new compounds based on benzo b thiophene is carried out using a C–H activation reaction. The purpose of choosing the benzo[b]thiophene molecule is that benzo[b]thiophene derivatives are of interest in medicinal chemistry due to their potential pharmacological activities. At this time, a cross-coupling reaction between benzo b thiophene boric acid and organic halides was carried out using a palladium catalyst. The main purpose in choosing this method is to carry out the reaction in one step and at a high speed, the reaction conditions are mild, water can be used as a solvent, and the yield is high. The mentioned ones facilitate the application in the industry and are economically versatile.

On the other hand, 2D materials have interesting properties in the field of medicine. Graphene oxide (GO), a 2D material model, and its composites are a new generation for drug delivery and offer exciting opportunities for the development of a wide range of applications, including biosensors and nanocarriers, and are emerging as novel biomaterials in the field of nanomedicine. Preparation and testing of biological activities of novel biologically active agents based on a heterocyclic core that will combine the properties of graphene oxide nanolayers and heterocyclic compounds.

a) b)

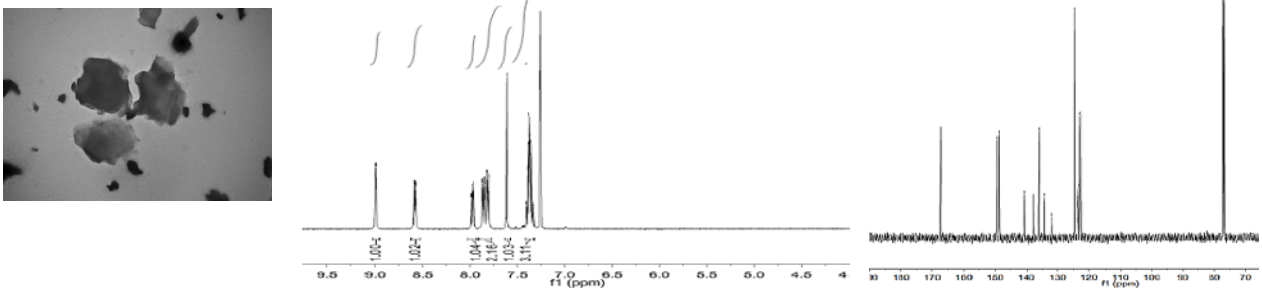

Fig 1. a) TEM images of graphene oxide, b) ^{1}H and ^{13}C NMR spectra of 5-(benzo[b]tiophen-2) nicotinic acid.

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Roles of substance phylothion

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The substance known as phylothion, literally translated from Greek as sulfur-loving, was first isolated in 1888 by De-Rey-Pailhade. The substance is a tripeptide, γ-Glu-Cys-Gly, nowadays known as glutathione (GSH). Glutathione occurs in two free forms: the reduced (GSH) thiol and the oxidized (GSSG) disulfide forms. GSH plays a vital role in a variety of cellular functions including maintaining an intracellular redox balance, reducing hydrogen peroxide or oxygen radicals, detoxification of electrophiles, storing cysteine, and regulating multiple other cellular processes. Intracellular levels of GSH are maintained by direct uptake of exogenous GSH, de novo GSH synthesis, and GSH redox cycling. Multiple cellular functions exist due mainly to the reactivity of the cysteine –SH group. The wide array of posttranslational modifications of the –SH group are responsible for glutathione's broad distribution in organisms. Under conditions of oxidative stress de novo biosynthesis or a catabolic supply of cysteine is not sufficient to meet the high demand for antioxidant synthesis. Most cells rely on nutrient transporters that can import extracellular cystine (the oxidized dimer form of cysteine). Solute Carrier Family 7 Member 11 (SLC7A11) or xCT is the functional light chain subunit of system x–c, which is a sodium-independent, chloride-dependent, anionic L-cystine/L-glutamate antiporter on the cell surface. Cystine is reduced to cysteine, which is a rate-limiting precursor in glutathione synthesis. A process that protects cells from oxidative stress and is, therefore, critical to cell growth, proliferation, and metabolism. Disulphides are toxic in high amounts and the lack of homocistine transporter is mainly responsible for observed homocysteine toxicity.

Crystal structure determination via machine-learning assisted DFT-PDF fitting

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Crystal structure determination is a fundamental need for material science. Respective X-ray and neutron diffraction and scattering techniques provide direct insights into the atomic arrangement within solids. Capitalizing on 3D single-crystal diffraction data, these techniques routinely uncover the atomic structure of unknown compounds. Yet, when addressing powdered samples, challenges arise as the structural information condenses into a 1D diffractogram, leading to significant peak overlap and the loss of directional information. Furthermore, when measuring nano- and quantum-crystalline phases, phenomena such as peak broadening and heightened peak overlap dominate the diffraction pattern. The pair distribution function (PDF) analysis is a valuable tool to study such materials [1]. However, many carried out PDF analyses rely on a priori structural information and serve as real-space analogues to Rietveld refinements (called PDF-Rietveld). Additionally, large-box global optimization, specifically reverse Monte-Carlo (RMC), is widely used to study atomic arrangements in amorphous materials, where a unique structural solution may be elusive [2]. However, the iterative and unguided random-guessing approach often leads to inefficiencies and susceptibility to local minima.

To address these challenges, we present a machine learning (ML) algorithm, for solving atomic arrangements and crystal structures from experimental PDFs in combination with density functional theory (DFT) calculations [3]. This method conducts a global optimization on an R-factor landscape, employing an on-the-fly, ML-trained surrogate model. Through a fusion of DFT calculations and PDF modelling, the ML algorithm, trained within a combined artificial R factor/DFT landscape, can proficiently determine the structure of even metastable phases correctly. Furthermore, the method can identify multiple phases such as stacking motifs by applying a consecutive multi-phase refinement.

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High-order geometric integrators for light-induced nonadiabatic molecular quantum dynamics in the adiabatic representation

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Grid-based exact methods for nonadiabatic molecular quantum dynamics allow highly accurate calculations for small molecules. Interaction potential with the time-dependent electromagnetic field is added to the Hamiltonian in the adiabatic representation to compute light-induced nonadiabatic dynamics. The trapezoidal rule and implicit midpoint methods are symmetric second-order integrators that can be used in the adiabatic representation, in which the Hamiltonian is nonseparable. The composition of symmetric second-order integrators is extended to the time-dependent Hamiltonians to obtain higher-order geometric integrators. The order of convergence in the error with respect to the time step was verified on a vertical harmonic model with the trapezoidal rule and implicit midpoint integrators and their compositions. We also showed that the time-dependence in the Hamiltonian breaks the unitarity and therefore norm conservation of the trapezoidal rule, while the implicit midpoint preserves them. The efficient high-order integrators for Hamiltonians in adiabatic representation will aid grid-based exact calculations of light-induced nonadiabatic dynamics of small molecules to high accuracy, especially when the system is not strictly diabatisable.

MCrafting Soft-Matter Confining Environments: In Silico Studies of pDMAEMA Membranes

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Embedding light-driven molecular components such as photocatalysts and –sensitizers in hierarchically ordered soft-matter structures holds great promise for future large-scale industrial applications [1]. In this work, we present a protocol for the construction of a simulation model for a pDMAEMA-based block copolymer membrane (Figure 1). Molecular dynamics simulations have been carried out to provide insights into the membrane's behaviour in solution. Different packing densities and membrane geometries have been investigated. The radius of gyration and radial distribution functions have been calculated and compared to a single pDMAEMA strand. Our simulations unveil the distinctive behaviour between the properties of a single solvated pDMAEMA thread and pDMAEMA in a densely packed environment.

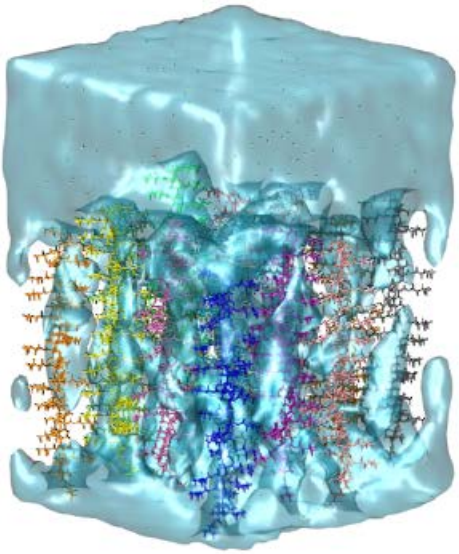

Fig 1. Computational model of a pDMAEMA block copolymer membrane solvated in water.

The effect of thermal annealing and concentration of GO in GO/PVA nanocomposites on their structural, electrical, and optical properties

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Due to its outstanding electrical characteristics, the combination of PVA and GO can function as an alternate electrode in supercapacitors and lithium-ion batteries. It is important to study the temperature and concentration dependence of the properties of devices and elements based on GO/PVA. The results of this research will allow for optimizing the parameters of devices and elements to be created based on these composites. At the same time, determining temperature-resistant materials by testing sample thermal stability and their use in relevant fields are critical challenges.

The GO was synthesized by the modified Hummers method. GO/PVA nanomaterials have been prepared in different amounts of GO (1, 2, 3, 5, and 20 %). To investigate the effect of temperature on the physical properties of GO/PVA composites prepared at different percentages, they were thermally annealed at different temperatures (40 °C, 70 °C, and 110 °C). The crystallite size of the 2 % GO/PVA composite was determined depending on the temperature and the percentage of GO in the PVA matrix. In order to determine the effect of thermal annealing temperature on the optical properties of GO/PVA composite, band gap values were calculated on the example of 2 % GO/PVA composite. The variation of the band gap value for GO/PVA composites with 2 % concentration depending on the thermal annealing is shown in Table 1.

Table 1. Dependence of the band gap on thermal annealing for 2% concentrated GO/ PVA composite.

Composite	**25 °C**	**40 °C**	**70 °C**	**110 °C**
2 % GO / PVA	2.40 eV	2.35 eV	2.30 eV	2.20 eV

As seen in Table 1, the band gap value decreases with the increase in the thermal annealing temperature. The reason for this is that the mobility of the polymer increases with the increase in the temperature of the thermal annealing, and their aggregation processes become easier. As a result, the size of the particles increases. This leads to a decrease in the band gap value.

Dependence of the specific resistance of a) 1 %, b) 2 %, c) 3 %, d) 5 %, and e) 20 % concentrated GO/PVA composite on the logarithmic value of electric field frequency at different temperatures.

Based on the results obtained from the study of the electrical properties of the samples, it can be summarised that annealing at elevated temperatures can facilitate the reduction of functional groups of GO, resulting in increased electrical conductivity and a decrease in specific resistance. At the same time, the influence of the temperature as a result of the structural reorganization within the GO/PVA composite can lead to better alignment and connectivity of the GO sheets, which improves charge transport pathways and reduces resistance. As a result of the reduction of defects enhances charge carrier mobility and conductivity, resulting in a decrease in specific resistance.