Book of Abstracts

UCZELNIA BADAWCZA
INICJATYWA DOSKONAŁOŚCI
Uniwersytet Wrocławski

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COSY 2ndGM Wroclaw 1-3 Jul 2024
WhatsApp group

Welcome!

We cordially welcome members of the COST Action CA21101 ("COSY"), as well as all interested parties, at Wroclaw, for the Second General Meeting of our COST Action organized by University of Wrocław.

The meeting is focused on the experimental and theoretical characterization of confined molecular systems, from those relevant in new materials research, to those playing a key role in astrochemistry. It is an opportunity for active networking between Action members with complementary and highly diverse expertise in confined molecular systems.

The 2nd COSY General Meeting is expected to strengthen existing ones and establish new collaborations between the Action members, it will be also an invaluable vehicle to connect all WGs together, as necessary to achieve the Grant Period Goals.

The meeting will host **6 invited overview talks**, as well as **29 invited talks** reporting already active joint projects between Action members, including the ones related to STSM as well as proposing new possibilities for the collaboration. Additionally, there will be **8 invited short talks** and **12 posters** accompanied by "Flash" poster presentations.

On behalf of Scientific Committee

María Pilar de Lara-Castells

Juan Carlos Hernández-Garrido

On behalf of Local Organizing Committee

Justyna Krupa and Małgorzata Biczysko

UCZELNIA BADAWCZA
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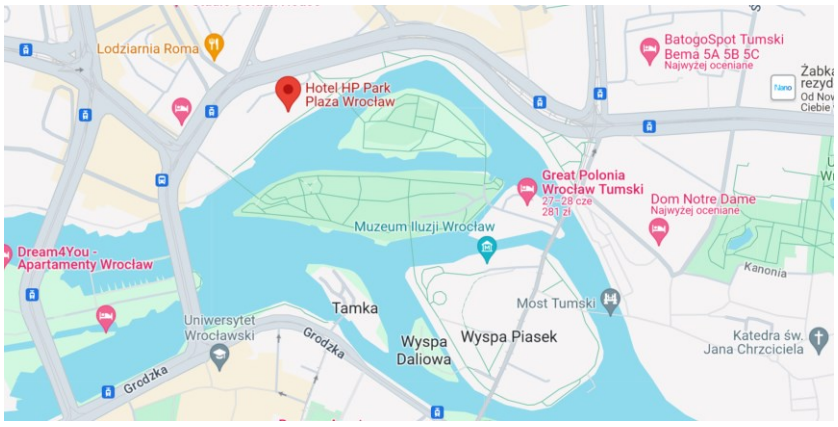
Conference Venue

Conference will take place in the **Rotunda** , round tower on the right hand side of the hotel. The entrance from the outside is in the corner marked on the map. The lecture room is on the second floor (counting ground floor as the first) with the access by the stairs and the elevator.

For participants staying in the Hotel HP Park there is a direct access from the hotel, either through first (ground) floor as well as on the second floor.

Hotel address + QR code to google map:
Bolesława Drobnera 11-13
50-257 Wrocław, Polska
Tel: +48 71 320 84 00



	01-Jul	
	Monday	
	Chair: Małgorzata Biczysko	
9:00-9:20	**Welcome**	
9:20-10.00	**María Pilar de Lara-Castells**	An *ab initio* journey towards the molecular-level understanding of subnanometric metal clusters
10:00-10:20	**Sonja Grubišić**	Design, parametrization and application of atomic force field for adsorption in nanoporous materials and dynamics of biomolecules
10:20-10:40	**Alessandro Fortunelli**	Polyfunctional Confined Carbonaceous Phases: Electrocatalytic Supports, Ductile Aerogels, Sensors, Masking Agents
10:40-11:00	**Miroslav Medveď**	Computational Design of Carbon Dots for Photocatalytic Applications
11:00-11:30	**Coffee Break**	
	Chair: Piotr Żuchowski	
11:30-11:50 11:50-12:10	**Michał Hapka**	Noncovalent interactions through the lens of symmetry-adapted perturbation theory
12:10-12:30	**Berta Fernández Rodríguez**	The Functional Group Corrections approach versus machine learning
12:30-12:50	**Francesca Mocci**	Effect of the aggregation on the chemical-physical properties of bio-organic molecules under variable confinement
12:50-13:02	**Bartosz Tyrcha**	Obtaining interaction-induced properties directly in the framework of symmetry-adapted perturbation theory
13:02-13:14	**Iulia Emilia Brumboiu**	Computational X-ray spectroscopy for organic molecules used in photovoltaics
13:14-14:30	**Lunch Break**	

	01-Jul	
	Monday	
	Chair: Aneta Jezierska	
14:30-15:10	**Sergiy Perepelytsya**	Effects of DNA-Induced Confinement on Interaction with Metallic or Molecular Flexible Counterions
15:10-15:30	**Halima Mouhib**	Towards Artificial Olfaction
15:30-15:50	**Kęstutis Aidas**	Bioactivity of Ionic Liquids: Insights from Integrated MD-QM/MM Modelling
15:50-16:02	**Urszula K. Komarnicka**	Three Musketeers Fight against Cancer: Synthesis, Physicochemical, and Biological Properties of Phosphino Cu^{I}, Ru^{II}, Ir^{III} Complexes
16:02-16:14	**Petra Čechová**	Mechanistic Insights into Interactions Between Ionizable Lipid Nanodroplets and Biomembranes
16:14-16:45	**Coffee Break**	
	Chair: Kaido Sillar	
16:45-17:05	**Markéta Paloncýová**	Interaction of Carbon Nanomaterials with Biomaterials
17:05-17:25	**Qin Yang**	Combination of Resonance and Non-Resonance Chiral Raman Scattering in Organometallic Compounds
17:25-17:45	**Maciej Witwicki**	Metal Cation Radical Complexes: From Environmental Pollutants to Functional Materials
17:45-18:05	**Marcel Mudrich**	Ultrafast relaxation processes in photoexcited helium nanodroplets
18:05-18:45	**Flash presentations**	D. Bumažnik, L. Donà, Ž. Einorytė, A. Kowaliński, K. M. Krupka, Y. Lee, K. Matuszak, K. Mucha, C. Olla, S. Pantaleone, R. Szabla, B. Szyja
19:30-21:30	**Welcome Grill**	

	02-Jul	
	Tuesday	
	Chair: Heribert Reis	
9:00-9:40	Jiri Vanicek	Molecular quantum dynamics
9:40-10:00	Alberto García-Vela	Absolute Control of the Lifetime of Resonance-Mediated Molecular Photodissociation Processes using Strong Fields
10:00-10:20	Dariusz Kędziera	Generating the Potential Energy Surfaces for complexes relevant to astrochemistry
10:20-10:40	Jorge M. C. Marques	Microsolvation of Alkali-Metal Ions with Rare-Gas Atoms: Structure and Thermodynamics
10:40-11:00	Patryk Jasik	High-accuracy photoinduced quantum dynamics of the multi-coupled electronic states in the diatomic molecules
11:00-11:30	Coffee Break	
	Chair: Rafał Podeszwa	
11:30-12:10	Nevin Uras-Aytemiz	Clathrate Hydrates from All-Vapor Method: Experiment and Theory
12:10-12:30	Majdi Hochlaf	First principles studies of proton transfers at the surface of clusters and at surfaces and applications
12:30-12:50	Unal Sen	Defect-Engineered Metal-Organic Frameworks for Enhanced Gas Storage and Separation
12:50-13:02	Uğur Bozkaya	Multilayer Ab Initio Molecular Dynamic Simulations with Perturbation Theory and Coupled-Cluster Methods for Molecular Clusters
13:02-13:14	Javier Hernández-Rodríguez	N-doped PAH non-adiabatic dynamics with the ML-MCTDH method
13:14-14:30	Lunch Break	

	02-Jul	
	Tuesday	
	Chair: Lauri Halonen	
14:30-15:10	**Cristina Puzzarini**	Astrochemistry: challenges and perspectives
15:10-15:30	**Marco Mendolicchio**	Computational Vibrational Spectroscopy and Astrochemistry: Current Challenges and Future Perspectives
15:30-15:50	**Vladimir A. Srećković**	Data for confined molecular systems and astrochemistry
15:50-16:02	**Francesca Tonolo**	Collisional Excitation of PO+ by *para*-H_2: towards the Accurate Modeling of Phosphorus Abundance in the Interstellar Medium
16:02-16:14	**Milan S. Dimitrijević**	Databases for Molecular Data - VAMDC - Virtual Atomic and Molecular Data Center
16:14-16:45	**Coffee Break**	
	Chair: Maria Wierzejewska	
16:45-17:05	**Martin Quack**	Molecular Quantum Dynamics, Confinement, Tunneling, Chirality and the Parity Violating Electroweak Force: Concepts and Some Recent Results from High Resolution Spectroscopy and Theory
17:05-17:25	**Pop Nicolina**	Reactive collisions between electrons and cations with applications in astrophysics and fusion plasma
17:25-17:45	**Aggelos Avramopoulos**	Design of Efficient Molecular Photoswitches
17:45-18:05	**Janez Cerar**	Water in strong electric fields of ions – experiments and theory
18:05-18:25	**Stefan Vajda**	Dehydrogenation of Cyclohexene by Subnanometer Clusters: Tuning Catalytic Performance by Size, Composition and Support
18:25-18:45	**Meenu Upadhyay**	Surface Diffusion and Molecule Formation on Amorphous Solid Water at Low Temperatures
19:30-21:30	**Buffet Dinner**	

	03-Jul	
	Wednesday	
9:00-11:00	MC meeting	
11:00-11:30	Coffee Break	
11:30-14:00	MC meeting	
14:00-15:00	Lunch Break	
	Chair: Magdalena Sałdyka	
15:00-15:20	Magdalena Malik	Spectroscopic Investigations in Forensic Science and Related Fields
15:20-15:40	İdris Yazgan	Understanding the Carbohydrate Derivative and Fluorescein
15:40-16:00	Teodora Kirova	Discrimination of leucine and isoleucine via fragmentation by electromagnetic field
16:00-16:20	F. Mine Balcı	Vacancy Defects in s-I Clathrate Hydrates
16:20-16:50	Coffee Break	
	Chair: Juan Carlos Hernandez Garrido	
16:50-17:10	Ljiljana T. Suručić	Investigation of Hexavalent Chromium Sorption Mechanisms Using Functionalized Magnetic Polymer Nanocomposites
17:10-17:30	Alia Tadjer	Sodium Clusters Confined in Hard Carbon Fragments
17:30-17:50	Abdulkadir Sezai Sarac	Advanced Characterizations of Magnetic Metal Nanoparticles Containing Biocompatible Polyacrylonitrile Nanofibers
17:50-18:10	Carlo Maria Carbonaro	Confining molecules on Carbon Dots structure: experimental and theoretical approach
18:10-18:25	Closing	
19:30-21:30	Buffet Dinner	

Overview Talks

An *ab initio* journey towards the molecular-level understanding of subnanometric metal clusters

María Pilar de Lara-Castells[1]*
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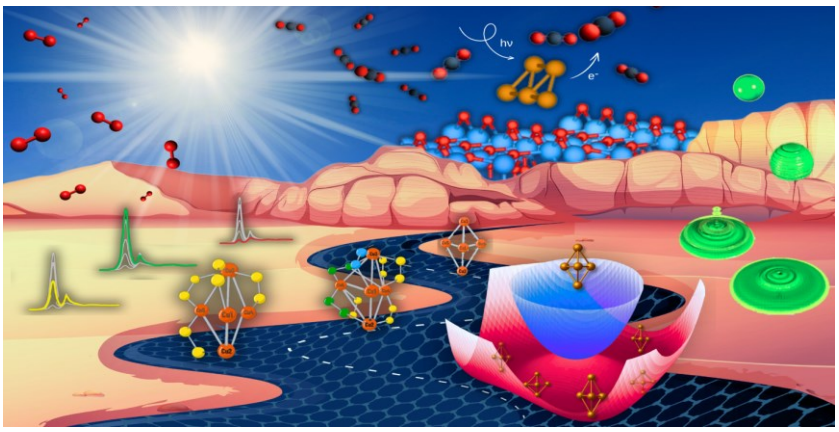
Current advances in synthesizing and characterizing atomically precise monodisperse metal clusters (AMCs) at the subnanometer (Angstrom) scale have opened fascinating possibilities in new quantum materials research. Their quantized 'molecule-like' electronic structure showcases unique stability and physical and chemical properties different from those of nanoparticles and bulk materials. The COST Action CA21101 "COSY" leverage a strategic position in the synthesis of atomically precise metal clusters in various environments (gas-phase, solution, within helium nanodroplets, and in biologically relevant media), their characterization via. e.g., transmission electron microscopy and state-of-the-art computational methods (*ab initio*, DFT and molecular dynamics). When integrated into materials that interact with environmental molecules and sunlight, AMCs may exhibit enhanced (photo)catalytic activity, electronic properties, and even optical behavior. Their tiny size (below 1 nm) makes free AMCs amenable to atomic-scale modelling using at a high level of *ab initio* theory, even including nonadiabatic (e.g., Jahn-Teller) effects. Surfaces supported AMCs can routinely be modelled, enabling real-time molecular dynamics simulations on the picoseconds scale and the study of their optical properties. All these experimental and computational-theoretical efforts aim to achieve a molecular-level understanding of the stability and properties of AMCs as function of their chemical composition, size, and structural fluxionality in different thermodynamical conditions (temperature and pressure). In this talk, covering the topics of COST Action "COSY" Groups, the potential of state-of-the-art *ab initio* modelling will be emphasized through an illustrative overview of recent studies of free and surface-supported AMCs, starting with the helium nanodroplet-mediated surface deposition of single metal atoms, going through the enhancement of the optical properties of titanium dioxide surfaces, and ending with a polarization phenomena in supported silver cluster-induced surface polarons.



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3. A. O. Mitrushchenkov, M. P. de Lara-Castells,* *ChemPhysChem* (2023), **24**, e202300317.

Noncovalent interactions through the lens of symmetry-adapted perturbation theory

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We present the key SAPT insights into various kinds of noncovalent interactions such as hydrogen bonding, σ-hole interaction, or π-π* stacking. SAPT provides classification of noncovalent complexes that is both chemically intuitive and more quantitative, in terms of the relative importance of different binding forces. Taking advantage of SAPT interaction energy decomposition, we compare it with a qualitative picture of simpler models. From the water dimer, through metal-containing systems, to solvation effects, we highlight several theoretical developments, including SAPT extensions to open-shell systems [1] and excited states [2].

References

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Effects of DNA-Induced Confinement on Interaction with Metallic or Molecular Flexible Counterions

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DNA is a polyelectrolyte macromolecule with a double helical form, stabilized by water molecules and positively charged metal and molecular ions (counterions). The counterions neutralize the negative charge of DNA, forming an ion-hydration shell around the double helix. The structure of the DNA double helix causes the confinement of the ions localized in the outer and inner regions of the macromolecule. Despite the extensive number of studies on the DNA-ions system,[1] the effects of DNA-induced confinement on the structural and dynamical features of counterions around the double helix are not completely understood. In the presentation, the problem of DNA-counterion interaction will be reviewed, beginning with the earliest research papers related to the modeling of the system at the atomistic level[2] up to the most recent results[3-8]. The prominent effects due to the increased confinement induced by the DNA structure will be emphasized. Specifically, the effects of hydration of metal ions (Li^+, Na^+, K^+, Rb^+, Cs^+, Mg^{2+}) localized in different regions of the DNA macromolecule will be discussed,[4,5] as well as the conformational effects for molecular ions (putrescine^{2+}, spermidine^{3+}, and spermine^{4+}).[6,7,8] The presented results are of interest in understanding the physical mechanisms of DNA's biological functioning and the development of DNA-based materials for nanotechnological applications.

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Molecular quantum dynamics

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Clathrate Hydrates From All-Vapor Method: Experiment and Theory

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Clathrate hydrates (CHs) are cage-like structures of water molecules that host guest gas molecules. The particular hydrate structure formed depends on the size and chemical interactions of the guests that react with water/ice to form the hydrate. Structure I (s-I) and structure II (s-II) are the two most common ones studied here. Generally, two methods are employed in laboratories for the formation and growth of clathrate hydrates (CHs). The first method predominantly relies on transforming ice/water into gas CHs. This process typically involves exposing these substances to guest molecules under several mega-Pascals of pressure and near ambient temperatures. Despite the use of high pressures and moderate temperatures, this method often requires multiple hours for a significant conversion percentage. The second method uses some certain molecules, such as small ethers (ethylene oxide, tetrahydrofuran, dimethyl ether, etc.), that enable H-bonding with the water of the host cages. With a technique, called as “all-vapor method” developed under this category, it has been shown that the incorporation of these special molecules into the vapor mixture of clathrate hydrate in a certain ratio produces a clathrate hydrate within a sub-second time scale monitored using standard FTIR spectrometer.[1-4] A defect-based catalytic action of these molecules within the hydrate network during the formation of aerosols of the clathrate hydrates from the all-vapor approach is responsible such an observed reaction rate. In this overview talk, I will present the research behind the “all-vapor approach”.

References

1. J. P. Devlin and I. A. Monreal, Chem. Phys. Lett., 2010, **492**, 1–8.
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Astrochemistry: challenges and perspectives

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The development of a comprehensive understanding of the chemistry that led to the formation of hundreds (likely thousands) of molecules in space is a challenging but fundamental goal of astrochemistry.[1,2] In the last couple of years, we have witnessed spectacular achievements in the discovery of molecular species in terms of number and chemical complexity. This contribution focuses on the challenges and perspectives of the chemistry in the interstellar medium (ISM), the matter (gas and dust) in the galaxy between star systems. The ISM is a hostile environment, characterized by extremely low density and temperature, which is however characterized by a rich chemistry. It is abundantly clear that the ISM is characterized by a rich chemistry, but several are the open questions: Can we explain how the detected molecules were formed? How far does chemical complexity go? What is their role (if any) in the origin of life on Earth? How many molecules are still escaping detection?

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Talks

Design, parametrization and application of atomic force field for adsorption in nanoporous materials and dynamics of biomolecules

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The crystalline hybrid porous materials such as Metal-Organic Frameworks (MOFs) have potential to help address health challenges and environmental challenges like, water and sustainable energy due to their high degree of porosity, functional tunability, chemical and structural versatility. However, translating metal organic framework basic research from laboratory to industrial applications is still hampered by the lack of precise control over their structure, properties and performance from the molecular-level framework to three dimensional porous materials. The Calgary Framework-20 (CALF-20) is a MOF that has recently received great attention and interest from both, the scientific and industrial communities. CALF-20 is composed of layers of 1,2,4-triazolate-bridged zinc (II) ions, pillared by oxalate ions to form a 3D lattice and pore structure. To better understand, characterize, and gather more information about CALF-20 adsorption properties, we have conducted a detailed computational study (combining force field based grand canonical Monte Carlo (GCMC) simulations and density functional theory (DFT) calculations) of both polymorphic forms (α and β) of CALF-20.[1] Similar to our previous work,[2-4] chosen LJ force-field parameters and derived atomic partial charges for the CALF-20 have been validated by an excellent agreement between the CO_2 and N_2 adsorption isotherm simulated for α - CALF-20 with the corresponding available experimental data in the pressure domain of 0–1 bar. More details can be found in Ref. 2-4. The GCMC simulations were performed using RASPA code on PARADOX IV supercomputing facilities.[5] The second part of talk is devoted to the development of more sophisticated, non-polarizable potentials typically used for simulations involving biological molecules, such as proteins with non-standard amino acids.[6,7]

References:

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Polyfunctional Confined Carbonaceous Phases: Electrocatalytic Supports, Ductile Aerogels, Sensors, Masking Agents

Alessandro Fortunelli,[1,2]* Giorgio Conter,[1,3] Luca Sementa[1], Charles Musgrave[2], William A. Goddard[2]
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We present results from studies aimed at exploring the novel, poly-functional properties of confined carbonaceous phases. In terms of mechanical plastic response, we focus on low-density carbon aerogels,[1a] and by exploiting DynReaxMas atomistic configurations,[1b] coupled with an inherent-structure analysis approach,[1c] we demonstrate how these materials possess shear plastic relaxation modes with extremely low values of yield stress, taking the form of nanoscopic shear bands within the clumps, thus rationalizing experimental observations of very low-stress plastic deformation modes in carbon aerogels. In terms of the effect of confined carbonaceous phases as catalyst support, we first briefly recall how the masking activity of carbonaceous supports can be exploited to orient selectivity in cyclohexane oxidative dehydrogenation.[2] We then focus on two electrochemical systems: platinum clusters (of interest for the Oxygen Reduction Reaction, ORR) and a cobalt-II complex (of interest for the Oxygen Reduction Reaction, OER). In the former case,[3] we show how the presence of pyrrolic N-doping sites strongly increases the binding energy of paradigmatic Pt_{13} clusters to the support, modeled as a graphene-like sheet with or without substitutional nitrogen atoms, as a function of applied potential, thus rationalizing the increased cluster stability against detachment derived from experimental evidence. In the latter case,[4] we instead focus on the OER activity of the 6-FP-Co-OMC-1 complex, a Co-III complex containing "capping arene" bidentate ligands with nitrogen atom donors, and we investigate whether and how the energetics of local minima and saddle points at the rate-determining step is affected by various forms of binding of the complex to a graphene-like support.

References

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Computational Design of Carbon Dots for Photocatalytic Applications

Miroslav Medveď,[1,2*] Tomáš Hrivnák,[3] Lukáš Zdražil,[2,4] Markéta Paloncýová,[2] Michal Otyepka[2,3*]
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For a long time, the most exploited feature of carbon dots (CDs) has been their intense photoluminescence (PL), while competitive non-radiative de-excitation pathways have been considered undesirable. Consequently, the optimization of CDs properties has so far been primarily focused on their PL characteristics.[1] Recently, the formation of long-living charge-separated states in photo-excited CDs has been found an attractive strategy to produce cheap and environmentally friendly photocatalysts.[2] To design efficient photocatalysts, the electronic structure of CDs needs to be optimized to produce charge separated trap states with long lifetimes featuring appropriate redox strength for specific catalytic reactions. The rational design of such photocatalysts requires deep understanding of the relationships between their structure and photophysical properties. However, the elucidation of such links is hampered not only by the limited knowledge about the structure and the multi-chromophoric character of CDs, but also by the complexity of processes taking place in the photocatalytic cycle. In our group, we computational tools to investigate the nature of excited states and processes leading to the formation of long-living charge transfer states in CD model systems.

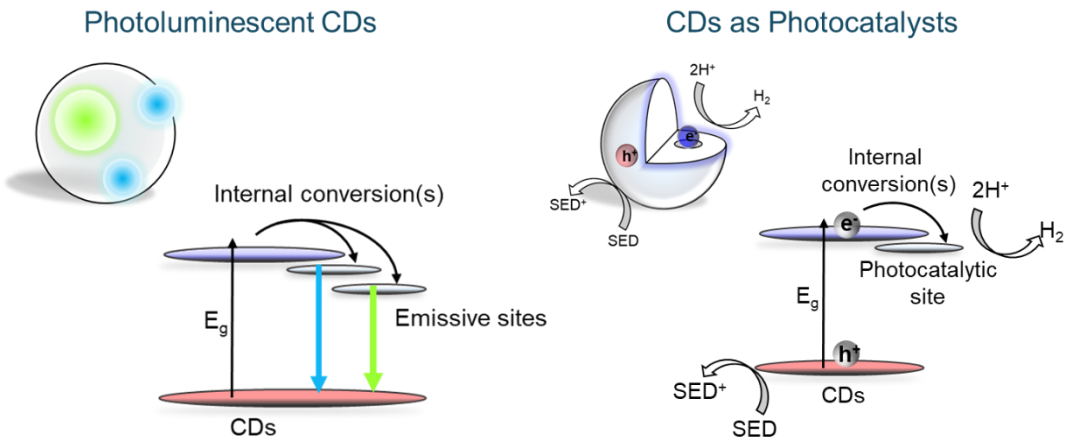

Figure 1. Carbon dots as photoluminescent species (left) and photocatalysts (right).

References

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The Functional Group Corrections approach versus machine learning

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I will present the results of recent work[1] where analytical corrections were developed to improve the accuracy of the PM6 and GFN2-xTB semiempirical quantum mechanical methods for the evaluation of noncovalent interaction energies in alkanes and alkenes. We followed the approach of functional group corrections (FGC),[2] wherein the atom–atom pair corrections depend on the nature of the interacting functional groups. The training set includes 21 alkane and 13 alkene complexes taken from the Donchev et al.'s database [Sci. Data 8, 55 (2021)], with interaction energies calculated at the CCSD(T)/CBS level, and our own data obtained for medium-size complexes (of 100 and 112 atoms). In general, for the systems included in the training and validation sets, the errors obtained with the PM6-FGC and xTB-FGC methods are within the chemical accuracy. The FGC results will be compared to those obtained using recently developed Machine Learning (ML) approaches.

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Effect of the aggregation on the chemical-physical properties of bio-organic molecules under variable confinement

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L-lysine, an essential amino acid, demonstrates intriguing optical properties in aqueous solutions that are not yet fully understood. Although L-lysine in its crystalline form does not emit light, in aqueous solutions, it emits a blue light as its concentration increases. These optical properties cannot be explained by structural features such as aromatic species or conjugated bonds. This talk will focus on understanding the role of aggregation in the optical phenomena of lysine and its aggregate. Although the zwitterionic nature of amino acids at their natural isoelectric point suggests that the aggregates responsible for these optical properties might form through ionic interactions and hydrogen bonds, TD-DFT calculations of UV absorption do not support this hypothesis.[1] Given the flexible nature of L-lysine, sampling the aggregates formed in aqueous solution at various concentrations is a complex task and a detailed analysis of the molecular dynamics simulations[2] is necessary to gain insight into the organization of the aggregates responsible for the observed optical absorbance (Figure 1).

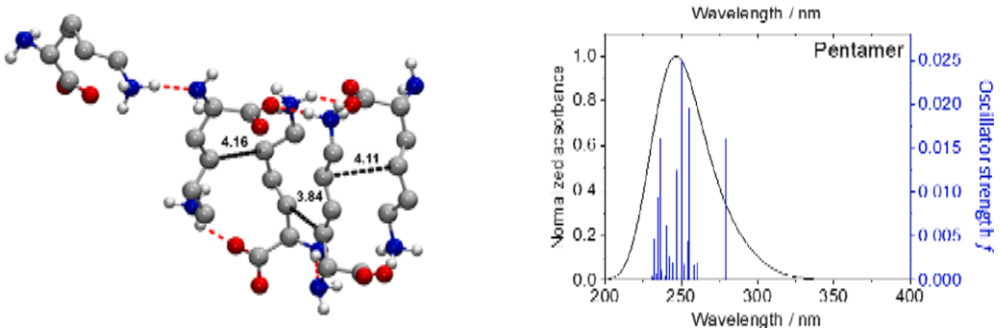

Figure 1. Examples of hydrophobic associations in a lysine pentamer observed in MD simulations of lysine's aqueous solution.

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Towards Artificial Olfaction

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Despite numerous efforts to design novel gas sensors for odorants and other volatile organic compounds, the current state-of-the-art is still far from providing efficient devices that can act as electronic artificial noses. One problem that is currently holding back the advancement in the field is our fragmentary understanding of the olfactory sense and its underlying detection mechanisms. To address one of these issues, our group adapted a multi-scale approach using mixed computational techniques and high-resolution microwave spectroscopy experiments.

Our objective is to unravel how different odorants vary in their conformational flexibility in the gas and the solvated phase, to quantify their uptake mechanisms through binding proteins. In future, we aim to move towards the rational design of new protein candidates of increased selectivity and sensitivity to detect odorants in applications such as medical care or industrial production chains.

Bioactivity of Ionic Liquids: Insights from Integrated MD-QM/MM Modelling

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To rationalize the bioactivity of ionic liquids (IL), it is important to understand the structure of aqueous IL mixtures or solutions on the molecular level. In our recent study, we have scrutinized the molecular mechanism behind the observed non-monotonic dependence of the ^{1}H NMR chemical shift of water on the composition of the aqueous mixtures of the 1-butyl-3-methylimidazolium chloride, [C4mim][Cl], IL.[1] Extensive classical MD simulations of these mixtures were carried out, and linear response QM/MM approaches were applied to predict the NMR chemical shifts. The proliferation of strongly hydrogen-bonded complexes between chloride anions and water molecules is found to be the reason behind the increasing chemical shift of water when its molar fraction in the mixture is low and decreasing. The model shows that the chemical shift of water molecules that are trapped in the IL matrix without direct hydrogen bonding to the anions is considerably smaller than the chemical shift predicted for the neat water. The ^{1}H NMR spectrum of neat [C4mim][Cl] was predicted and found to be in very reasonable agreement with the experimental data.

In our very recent study, we have used the integrated MD-QM/MM scheme to scrutinize the molecular mechanism behind the increased solubility of antidiabetic drug molecule glibenclamide in aqueous solution of choline tryptophanate, [Cho][Trp], IL. Classical MD simulations indicate prolific interactions between the constituent ions of the IL and glibenclamide, and thus these ions are screening the hydrophobic drug molecule from the polar water molecules. However, essentially no hydrogen bonding interactions between glibenclamide and choline or tryptophanate ions were seen to be formed. QM/MM results for the ^{1}H NMR chemical shifts of glibenclamide in aqueous solution and in aqueous [Cho][Trp] mixture generally agree well with corresponding experimental data, thus validating the structural results obtained using MD simulations.

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Interaction of Carbon Nanomaterials with Biomaterials

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Carbon nanomaterials have revolutionized the field of biomedicine, offering opportunities for their diverse applications. Their unique tunable physicochemical, optical, mechanical and electronic properties make them ideal candidates for a wide range of biomedical applications such as drug delivery, biosensing, and imaging. However, to harness their full potential and ensure their safe and efficient use, it is crucial to gain a comprehensive understanding of their interactions with biomaterials at the molecular level. For this, experimental techniques yet lack the required atomistic resolution and therefore we can rely on molecular dynamics simulations, which can provide valuable insights into the underlying mechanisms governing the biocompatibility of carbon nanomaterials.

Here we focus on the modeling of carbon dots (CDs) and their interactions with biomolecules. Using our dedicated builder (cd-builder.upol.cz), we generated structures and topologies of CDs for simulations. We specifically investigated the interaction of CDs with biomolecules, particularly nucleic acids. Through simulations, we identified preferential modes of interaction between CDs and various nucleic acid shapes. Such simulations require a careful choice of simulation set-up compatible with each system part.

Further, we focused on understanding of the behaviour of graphene derivatives and their interactions with complex lipid membranes in multiscale resolution. Through these simulations, we elucidated the nature of interactions between graphene derivatives and lipid membranes, providing insights into graphene-membrane interactions and the effect of graphene on membrane organization.

We present a complex approach to simulations of the bio-nano interface in multiscale resolution, necessary for capturing the required level on details. These simulations can be a start of in-silico studies on nanotoxicity of the nanomaterials or used for targeted design increasing their biocompatibility.

Combination of Resonance and Non-Resonance Chiral Raman Scattering in Organometallic Compounds

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Organometallic compounds play a significant role in organic synthesis as well as biological metabolism. Resonance Raman optical activity (RROA) is an emerging and promising tool to characterize them with high sensitivity. It can reveal the details on molecular structure, chirality, and excited electronic properties. Thanks to the second-generation ROA spectrometer developed in Olomouc, we managed to gain RROA signals with an exceptional high quality from a family of organometallic complexes. Coupled with density functional and vibronic theories, the molecular resonance behavior can be studied in unprecedented details. For a cobalt complex we observed a huge enhancement of the chiral scattering, contribution of the antisymmetric polarizabilities to the signal, and the Herzberg‐Teller effect resulting in bisignate RROA spectra. The chiral component is about one order of magnitude bigger than for the analogous complexes without resonances. We studied in detail Al and Co ethylenediaminedisuccinic acids (EDDS) complexes, the investigations will be extended to other metallic EDDS complexes.

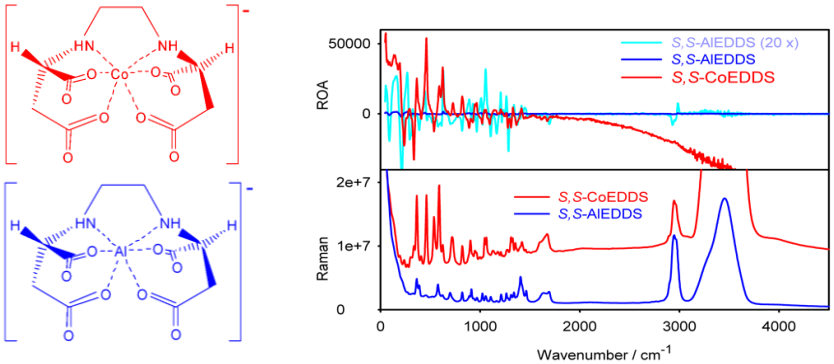

Figure 1. The structure of CoEDDS and AlEDDS and their measured RROA and resonance Raman.

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Metal Cation Radical Complexes: From Environmental Pollutants to Functional Materials

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Radicals are typically unstable, however their stability can be enhanced through steric protection, spin density delocalization or coordination with metal cations. Environmentally persistent free radicals (EPFRs) are pollutants that may contribute to health problems. Most studies focus on EPFRs from combustion, but we demonstrated, using multifrequency EPR spectroscopy, that EPFRs can also form from natural polyphenols exposed to heavy metal ions like Pb(II) and Hg(II). Our relativistic DFT computations revealed these radical species are semiquinonato complexes of heavy metal ions.

Radical species have applications in material science. We isolated a stable semiquinonato complex of aluminum from 1,2-dihydroxybenzene and characterized it using multifrequency cw-EPR spectroscopy and computational techniques (DFT and DLPNO-CCSD). Recently, we synthesized complexes of Al^{3+}, Co^{2+}, Gd^{3+}, and Dy^{3+} with a redox-active pincer O,N,O ligand (Figure 1) for single-molecule magnet (SMM) applications and analyzed them using X-ray crystallography, multifrequency EPR, SQUID measurements and detailed theoretical calculations (fractional occupation number weighted electron density and CASSCF/NEVPT2).

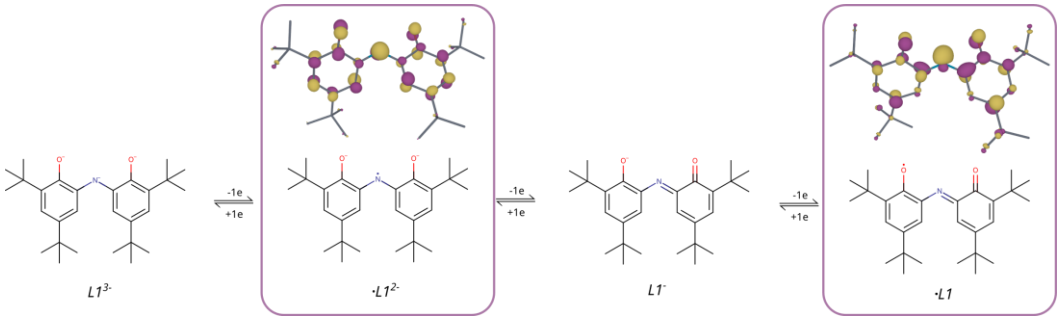

Figure 1. Oxidation states of the pincer O,N,O ligand. For the radical forms SOMOs are shown.

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Ultrafast relaxation processes in photoexcited helium nanodroplets

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Helium nanodroplets are quantum fluid clusters that feature extraordinary properties such as ultralow temperature and superfluidity. They have mostly been used as inert nanometer-sized cryo-matrices for isolating molecules and for aggregating molecular complexes and nanostructures that are hard or impossible to form by other means.

In this contribution I'll present experiments probing the ultrafast dynamics of pure and doped helium nanodroplets initiated by resonant photoexcitation and ionization of the helium droplets. Using synchrotron radiation, free-electron lasers and high-harmonic generation, we track ultrafast relaxation processes such as internal conversion, bubble formation, energy- and charge-transfer ionization between (super-)excited helium atoms and attached dopant atoms and molecules.[1-6] Surprisingly, we find interatomic Coulombic decay processes to prevail nearly in the entire extreme-ultraviolet range of the spectrum.[7,8] By forming tailored complexes in helium nanodroplets, their ionization and fragmentation dynamics can be studied under controlled conditions.[9,10]

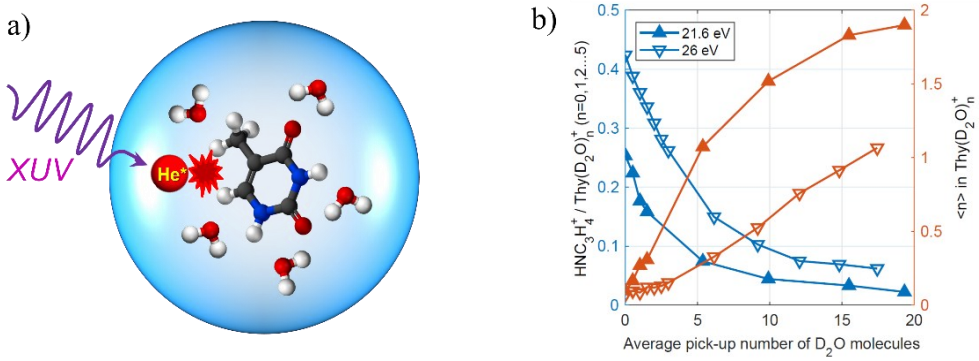

Figure 1: Helium nanodroplets serve as test tubes for studying the ionization and fragmentation dynamics of molecular complexes such as microhydrated biomolecules. a) Thymine-water clusters are formed in helium nanodroplets and ionized by Penning- or charge-transfer ionization [9]. b) The rate of thymine fragmentation in thymine-(D2O)n clusters steeply drops with n (blue triangles) indicating a reduction in radiation damage.

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Absolute Control of the Lifetime of Resonance-Mediated Molecular Photodissociation Processes using Strong Fields

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A variety of molecular reaction processes are governed or mediated by resonance states. Some examples are the photodissociation of intermediate molecular species in atmospheric cycles, and the resonance-mediated reactive collisions of such intermediate species with other atmospheric reagents. When these resonance-mediated processes compete, control over the resonance behavior (essentially the resonance lifetime and the product fragment distributions) can be crucial in order to steer the molecular reaction process in a desired direction. In previous works, control schemes using weak laser fields were applied to induce quantum interference in order to modify the lifetime[1,2] and the product fragment distributions[3,4] of resonance-mediated molecular photodissociation. In the work presented here, moderately intense (of the order of 10^{10}-10^{12} W/cm^2) laser fields are applied to change the resonance lifetime of a photodissociation process.[5] A control scheme is suggested to reduce the lifetime of a long-lived resonance to make it as short-lived as desired. Also a control scheme able to increase the lifetime of a short-lived resonance will be presented. The conditions required to apply the different schemes proposed will be discussed. The schemes appear to be of universal application to resonance-mediated molecular photodissociation.

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Generating the Potential Energy Surfaces for complexes relevant to astrochemistry

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Generating Potential Energy Surfaces (PES) for complexes relevant to astrochemistry is a challenging endeavor. Obtaining accurate PES for noncovalently bound molecular dimers presents two primary challenges. Firstly, there is the computational cost associated with accurately calculating interaction energies. Secondly, the number of grid points required increases exponentially with the dimensionality of the problem. One potential solution to the computational cost issue is to transition from established methods like CCSD(T) or CCSD(T)-F12 to SAPT or even more cost-effective SAPT(DFT). Both SAPT and SAPT(DFT) have demonstrated reliability in describing noncovalent interactions. Addressing the challenge of the exploding number of grid points can be achieved by seamlessly integrating short-range interactions (calculated within a given approximation) with long-range interactions (using multipole expansion). Additionally, rather than using evenly spaced grid points, selecting grid points based on physical information obtained from earlier versions of potentials for a given system can lead to significant savings in computational resources. These solutions have been implemented in the autoPES code developed in Szalewicz's group.

This presentation will cover some technical aspects of the autoPES code, as well as successful applications such as the recently published studies on the bensonitrile-He and HCN-H2O systems.[1,2] As well as calculations of the potential energy surface for the H_2Cl^+ –H_2 performed during STMS financed by Cosy COST Action.

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Microsolvation of Alkali-Metal Ions with Rare-Gas Atoms: Structure and Thermodynamics

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Microsolvation consists of a step wise addition of atoms or molecules of solvent to the solute species, which then allows for the study of the clusters that arise in such a building-up process. In this presentation, we will describe the microsolvation of alkali-metal ions by argon and krypton. Particular emphasis will be given to the study of the structures and thermodynamics of clusters resulting from the microsolvation of Li^+, which resorts to the application of state-of-the-art global optimization algorithms[1] and the parallel tempering Monte Carlo (PTMC) method,[2] respectively. These studies follow a workflow that consists of three main tasks: (i) modeling the analytical potential energy surface (PES) of the clusters; (ii) searching for the low-energy structures of the clusters; (iii) the structures so obtained may be refined at a higher level of theory (by using ab initio or DFT methods), and employed as starting geometries for performing PTMC calculations.

The results for Li^+Ar_n, Na^+Ar_n, and K^+Ar_n clusters show that strong "magic numbers" are associated with the closure of the first solvation shell, which occurs at n=6, 8, and 12, respectively. It is also worth noting that Li^+ tends to occupy a more central position in the microsolvation cluster than Na^+ or K^+. Regarding the microsolvation of Li^+, we will discuss the effect of the solvent as well as the importance of including three-body terms in the PES. It has been observed that the octahedral structure of the first solvation shell is maintained as the microsolvation cluster grows up and, by contrast, a great diversity of energetically similar low-lying minima appear due to modifications in the second solvation shell.[3] Accordingly, PTMC calculations for Li^+Ar_n have shown that the first solvation shell melts at high temperatures, while the fluxional character of the external argon atoms leads to a prominent maximum of the heat capacity at low temperatures and, in some cases, also to premelting structural transitions.[2,3]

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High-accuracy photoinduced quantum dynamics of the multi-coupled electronic states in the diatomic molecules

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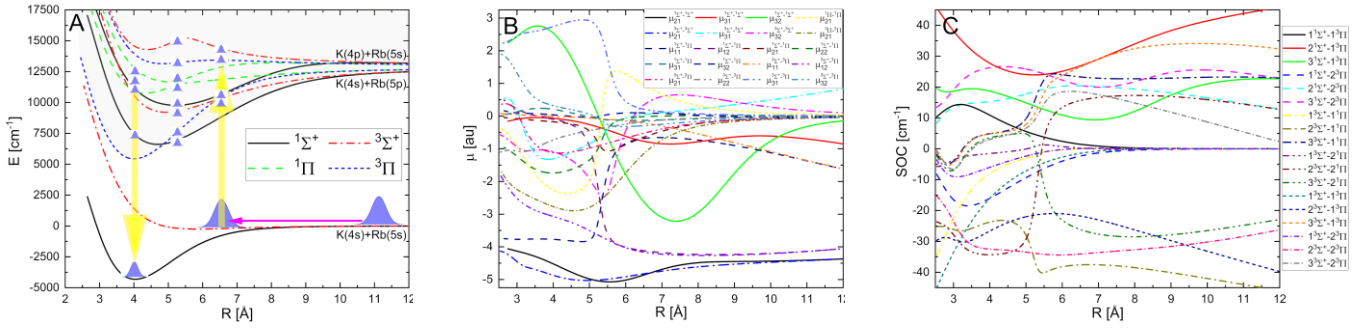
Quantum dynamics is a growing discipline at the interface of chemistry, physics, and materials science[1]. It allows us to study the behavior of objects in a way that emphasizes the quantum nature of their evolution in various time scales (from seconds to attoseconds). Quantum dynamics simulations are indispensable for investigating chemical reactions, field-atom and field-molecule interactions, cold physics, and cold chemistry, including cold collisions or even quantum computing areas. The particular emphasis is focused on exploring the photoinduced dynamics of breaking (dissociation) and creating (association) of the chemical bonds in the molecular systems. In the present work, we focus on the theoretical time-dependent descriptions of the photoinduced processes in the system of 10 multi-coupled electronic states of the KRb molecule (Fig. A). We investigate these processes based on the high-accuracy rovibrational and electronic structure of the KRb molecule[2], appropriate permanent and transition dipole moments[2] (Fig. B), and various types of coupling matrix elements, like spin-orbit couplings[3] (Fig. C). In the quantum simulations, we use our newly developed quantum dynamics code[4] to study the nano- to femtoseconds time-scale dynamics of multiple coupled electronic states of KRb under the influence of an arbitrary time-dependent external field to investigate laser-driven processes like association and dissociation.



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First principles studies of proton transfers at the surface of clusters and at surfaces and applications

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Using first-principles computational methodologies, we investigate the microsolvation of proton at organic/inorganic and water clusters. For instance, we considered protonated water clusters interacting with aromatic compounds, [1] and protonated aromatics [2] or protonated polyhedral oligomeric silsesquioxane [3] complexed to water clusters. For these species, we identified the most stable forms, where the solvation of the protonated organics due to a network of water clusters, whereas the excess proton undergoes a complex dynamic at the water-organic/inorganic interface, resulting in the formation of Eigen and Zundel features. These identifications are based on diverse analyses of the bonding and of weak interactions occurring at these interfaces. Besides, we discuss the extension of our finding to 2D and 3D materials. Our work should be useful for understanding, at the microscopic level, of the effects of water interacting with organic/inorganic compounds relevant for organic chemistry, inorganic chemistry astrochemistry, atmospheric chemistry, combustion and materials science.

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Defect-Engineered Metal-Organic Frameworks for Enhanced Gas Storage and Separation

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Metal–organic frameworks (MOFs) have garnered significant interest owing to their diverse structural topologies and chemical functionalities, making them promising materials for various applications, including gas storage, separation, catalysis, and environmental remediation. This study explores the transformative impact of defect engineering on MOFs, focusing on zirconium-based MOFs (Zr-MOFs), cerium-based MOFs (Ce-MOFs), and zeolitic imidazolate frameworks (ZIFs). By intentionally introducing structural imperfections such as linker fragmentation, ligand exchange, and post-synthetic modification, we observed significant improvements in gas storage and separation capabilities. For example, in Zr-MOFs, the incorporation of boronic acid moieties via linker fragmentation creates additional active sites, leading to increased hydrogen uptake and CO_2 selectivity.[1] Similarly, replacing 2-methylimidazole with 1,2,3-triazole in ZIFs transforms the framework topology and enhances the gas adsorption properties. The ability to control and manipulate defects within MOFs is crucial for optimizing their performance and tailoring their properties to meet specific needs.[2] Defective Zr-MOFs show promise in various applications, including environmental remediation, detoxification of chemical warfare agents, and energy conversion processes. The presence of defects facilitates effective adsorption and remediation of pollutants and contributes to the catalytic activity of MOFs. This study highlights the promising prospects of defect-engineered MOFs for addressing energy and environmental challenges, positioning them as versatile tools for sustainable solutions, and paving the way for advancements in various industrial sectors.

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Computational Vibrational Spectroscopy and Astrochemistry: Current Challenges and Future Perspectives

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A fascinating challenge of modern chemistry is the investigation of extraterrestrial chemistry, be it in the interstellar medium (ISM)[1] or planetary atmospheres. There, microwave and infrared spectroscopies play a crucial role in driving the interpretation of observational spectra. However, the latter are the result of an unknown mixture of species, in conditions which may be difficult to reproduce in the laboratory. Therefore, the availability of reliable computational models[2] able to provide accurate predictions of the transition energies and intensities is mandatory to drive experiments and assist the interpretation of the spectrum. Among the various methods for the inclusion of anharmonic effects, the vibrational second-order perturbation theory (VPT2),[3] allows the effective study of medium-to-large size molecular systems. While VPT2 can be successfully applied in many cases, it is also characterized by some intrinsic drawbacks that prevent its use in some situations, especially when large amplitude motions (LAMs) are present. As shown in previous studies,[4-7] the definition of a suitable set of internal coordinates able to decouple the different classes of vibration allows to treat each normal mode through the most appropriate method. Based on this premise, a general and effective VPT2 framework in terms of curvilinear coordinates has been developed, starting from the calculation of vibrational transition energies, and proceeding up to thermochemistry and vibro-rotational interaction parameters. The performance of the new engine will be illustrated by its application to systems of biological and astrochemical interest.

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Data for confined molecular systems and astrochemistry

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Computational chemistry techniques have grown in significance over the past few decades for studying the dynamics and interactions of small molecules encased in larger structures. Despite their huge size, molecular clouds perform an important but little understood role in confined systems. Currently, there are a few hundred known molecular species in interstellar space, which include neutrals, cations, and anions ranging in size from diatomic to enormous ones. Because of the scattering and absorption of interstellar radiation, molecules deep within molecular clouds can prevent photodissociation and/or photoionization [1]. As a result, it is critical to analyze both radiative and concurrent collisional processes [2]. The purpose of this contribution is to examine such processes of small molecules, such as hydrogen, helium, and silicon molecular ions, and to offer data relevant for characterizing interstellar chemistry.

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Molecular Quantum Dynamics, Confinement, Tunneling, Chirality and the Parity Violating Electroweak Force: Concepts and Some Recent Results from High Resolution Spectroscopy and Theory

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Potential wells for tunneling and the parity violating electroweak force provide fundamental examples for confinement potentials. We shall briefly outline the concepts for their interplay in chiral molecules and illustrate this with some recent examples. Notably for isotopic chirality the electroweak force leads to a fundamentally new isotope effect arising from the different electroweak charge of isotopic nuclei with different numbers of neutrons: This changes potentials for tunneling in chiral molecules from strictly symmetric under inversion to dominantly asymmetric in spite of the small size (aeV to feV ranges) of the antisymmetric contribution to the potentials[1-3] . Indeed, our new theoretical approaches to electroweak quantum chemidstry led to an increase of the parity violating potentials by one to two orders of magnitude, typically.[2] This order of magnitude increase has in the meantime been confirmed by many theory groups (see reviews in refs.2,3). One important conclusion from current theory is that for ordinary stable chiral molecules parity violation dominates the quantum dynamics and leads to localized quantum ground states of the enantiomers of chiral molecules separated by a parity violating energy difference D_{pv} , which can, in principle, be measured by special experiments although no successful experiment has been reported so far. We shall illustrate in the lecture current progress in spectroscopic experiments towards this goal for selected examples for which theoretical predictions of D_{pv} exist such as CHFClBr (D_{pv} = 235aeV), 1,2 Dithiine ($C_4H_4S_2$, D_{pv} =1.36 feV) or isotopically chiral $PF^{35}Cl^{37}Cl$ (D_{pv} =3.5aeV) and others (see refs. 1-4, and references cited therein).

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Reactive collisions between electrons and cations with applications in astrophysics and fusion plasma

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Dissociative recombination (DR) of molecular cations with electrons is a major elementary process in the kinetics and in the energy balance of astrophysical ionized media (supernovae, interstellar molecular clouds, planetary ionospheres), fusion plasmas in the divertor region, hypersonic entry plasmas and in many other cold media of technological interest. Using Multichannel Quantum Defect Theory (MQDT), cross sections and Maxwell rate coefficients have been obtained for DR and ro-vibrational transition (RVT) of H_2^+ and HD^+ for numerous ro-vibrational states of the ion. The computational results obtained are in reasonable agreement with experimental data[1,2].

A complete set of vibrationally resolved rate coefficients for BeH^+ cation and its isotopomers: BeD^+, BeT^+ reactive collisions with electrons below the ion dissociation threshold has been provided[3,4,5]. The resulting data are useful for the modeling of the kinetics of the Early Universe and of the magnetic-confinement-fusion-edge plasma. Our previous studies of DR, vibrational excitation/de-excitation and dissociative excitation of the BeH^+ ion, based on the MQDT, are extended to collision energies above the dissociation threshold (up to 12 eV) by increasing the number of dissociative states for all molecular symmetries[6].

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Design of Efficient Molecular Photoswitches

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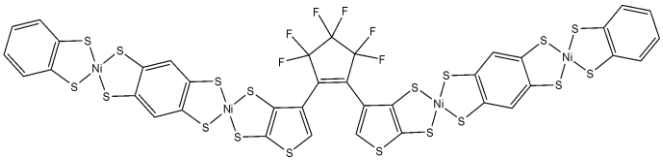
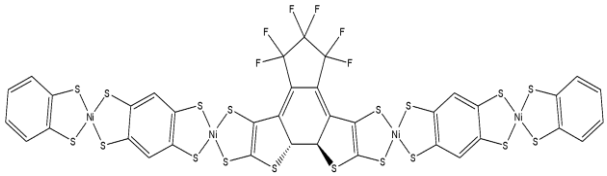
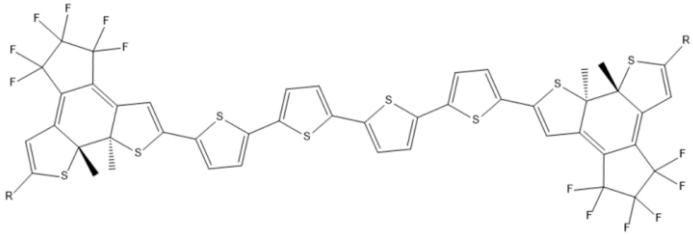
Design at the molecular level is an important issue for material science. One specific challenge is the understanding of factors that govern light-matter interactions and how one can tune them in an efficient way. Photochromic materials, having two or more states with very different properties, have a large number of applications (e.g. molecular electronics). A particular case of promising photochromic materials are the 1,2-diarylethenes (DAEs With the aid of computational techniques we have recently demonstrated a mechanism for the design of derivatives involving DAE, bis(dithiolene) [NiBDT] and benzene , acting as molecular photoswitches (Fig. 1) These could be the building blocks for the design of promising molecular materials with exceptional and tunable NLO properties.



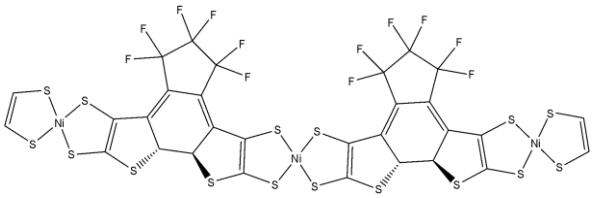
α=2024, **β=5246, γ(x10^3) = 49870**



α=2923, **β=63000, γ(x10^3) = 652100**



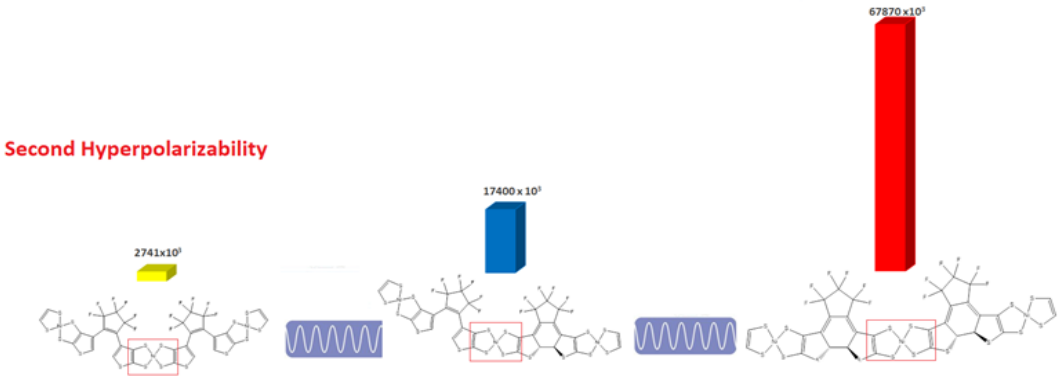
R=Ph, α=1239, **β=-310, γ(x10^3) = 23611**



α=1577, **β=-13000, γ(x10^3) = 68890**

Figure 1. The electronic polarizability (α/a.u.), the first (β/a.u.) and second hyperpolarizability (γ/a.u.) of some selected molecular DAE-based molecular materials (method:CAM-B3LYP)

Results1,2 have shown that:, I) large NLO contrast between the "open" and "closed" isomers is obtained by substituents, bonded to both sides of the DAE switch. II) the sensitivity of the 1(hyper)polarizabilities could be used as a probe for the identification of the photoswitching process and the existence of the possible isomers.



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Water in strong electric fields of ions – experiments and theory

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Many experimentally measured physico-chemical properties of aqueous solutions of electrolytes and polyelectrolytes today cannot be satisfactorily predicted by theory, including MD simulations.[1] This is especially true for heat effects, but even if the system contains ions exerting a strong electric field, MD simulations can be completely wrong. One of the main reasons for the poor performance of MD simulations in these cases is the neglect of the polarization force of ions on water.[2]

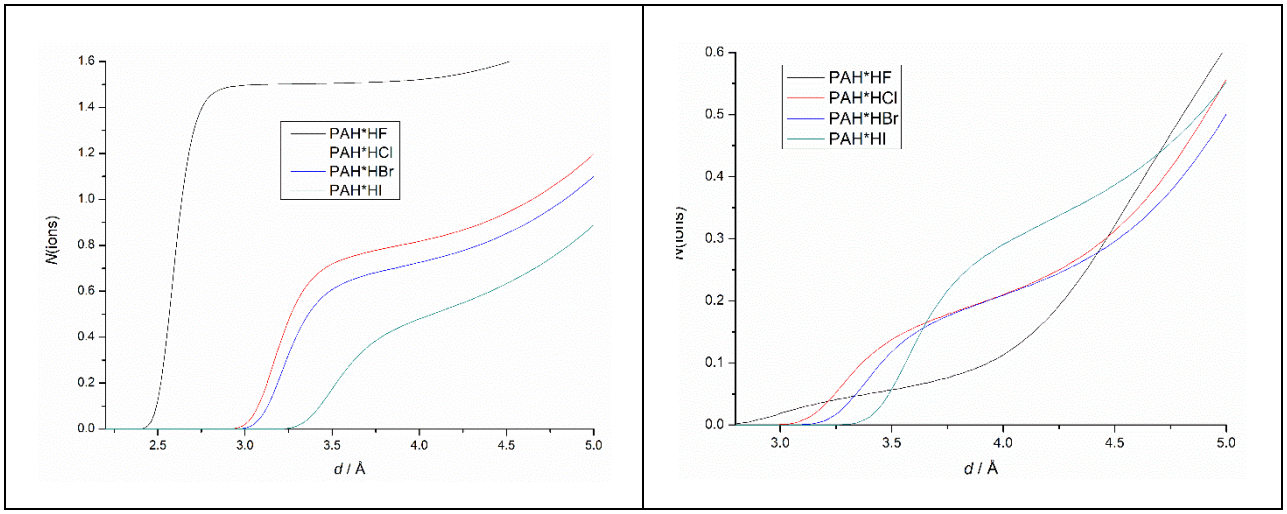

Figure 1. Comparison of the cumulative RDF of halide ions (distance from the PAH chain) as obtained by OPLS-AA (left) and by Drude polarizable force field (right) MD simulations at T = 25 °C. Only MD simulations using polarizable force fields can deliver theoretical results that can be at least qualitatively comparable to the experimental findings.

We will present some of our studies where a strong electric field of (poly)ions (e.g. PAH polyion) strongly influences water and confines counterions, while existing theoretical calculations often fail in reproducing experimental data.

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Dehydrogenation of Cyclohexene by Subnanometer Clusters: Tuning Catalytic Performance by Size, Composition and Support

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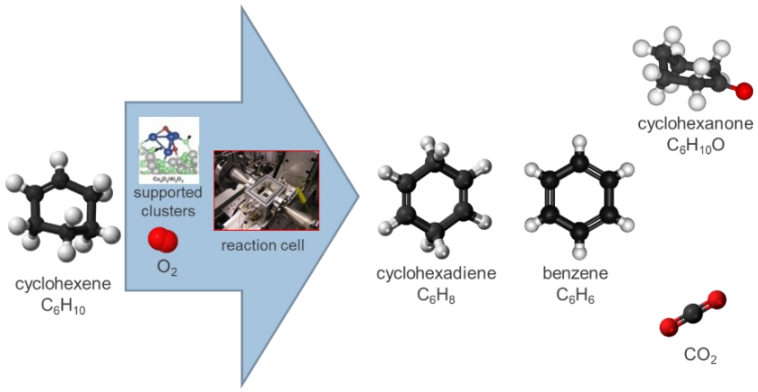
Catalysis by supported mono-disperse subnanometer Cu, Pd and CuPd clusters, supported on technologically relevant oxide- and model carbon-based supports, will be presented in the oxidative dehydrogenation of cyclohexene. [1-3]



The performance of the clusters will be discussed, demonstrating that the atomic precision design of mono- and bimetallic clusters allows for the fine-tuning of their activity and selectivity by the combination of varying the composition of the clusters in an atom-by-atom fashion and support effects.

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Surface Diffusion and Molecule Formation on Amorphous Solid Water at Low Temperatures

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Atomistic simulations, with their increasing accuracy and predictive power, have emerged as essential tools for characterizing the energetics and dynamics at the atomic level. In this presentation, I will present results from molecular dynamics simulations on the formation of O_2, CO_2 and NO_2 resulting from atom+atom and atom+diatom collisions on amorphous solid water (ASW) under conditions typical in cold molecular clouds. Accurate machine learning-based energy functions combined with fluctuating charge models are used to investigate the diffusion, interactions and recombination dynamics of O+O, O+CO and O+NO on ASW. Reactive molecular dynamics simulations show that the surface diffusion of reactants leads to recombination on the nanosecond timescale for initial separations up to 20 Å. The dynamics and energy relaxation were analyzed, revealing that molecules stabilize through energy transfer to water internal and surface phonon modes on the picosecond time scale. The surface diffusion and desorption energetics are further explored through extended and nonequilibrium molecular dynamics simulations and are compared with experimental data wherever possible.

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Short Talks

Obtaining interaction-induced properties directly in the framework of symmetry-adapted perturbation theory

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Interaction-induced properties are understood as the difference of a given property calculated for the weakly bound complex with respect to the sum of the same property calculated for non-interacting subsystems. Among many quantum chemical methods, symmetry-adapted perturbation theory (SAPT) has been developed for the treatment of such systems. Here, we extend the approach proposed by K. Piszczatowski et. al.[1] by performing a perturbative expansion of the dimer wavefunction in a form known from SAPT to obtain direct expressions for the induced dipole moment valid up to the second-order in the intermolecular interaction. The proposed scheme requires the usage of neither numerical derivatives (in contrast to a different SAPT-based approach proposed by T. G. Heijmen, R. Moszyński and co-workers[2,3] where the finite filed procedure is utilized) nor the subtraction of independently computed values to obtain a relatively small difference as in supermolecular calculations.

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Computational X-ray spectroscopy for organic molecules used in photovoltaics

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An overview of different methods used in the computation of X-ray absorption and photoelectron spectroscopy will be given, with focus on the accuracy and precision of linear response time-dependent density functional theory (TD-DFT) and ΔDFT approaches.[1] The importance of including orbital relaxation in X-ray spectroscopy calculations will be briefly discussed, in connection to the use of localized or delocalized core-holes for its description.[2] Finally, an example of how joint computational and experimental spectroscopy approaches can be used to elucidate the final products of photodegradation will be illustrated for the fullerene derivative $PC_{60}BM$, an electron acceptor material used in organic photovoltaics.[3]

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Three Musketeers Fight against Cancer: Synthesis, Physicochemical, and Biological Properties of Phosphino Cu^{I}, Ru^{II}, Ir^{III} Complexes

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Novel phosphine ligands, and group of new phosphine mononuclear (Cu(I), Ir(III), Ru(II)) and binuclear complexes were synthesized and characterized using many various techniques. Some of the studied complexes exhibited promising cytotoxicity towards various cancer cell lines *in vitro* with IC_{50} values significantly lower than that of the reference drug—cisplatin. Confocal microscopy analysis showed that Ru(II) and Ir(III) complexes effectively accumulate inside A549 cells with localization in cytoplasm and nuclei in opposite to Cu(I) complexes that accumulate inside mitochondria. A precise cytometric analysis provided clear evidence for the predominance of apoptosis in induced cell death. Furthermore, the complexes presumably induce the changes in the cell cycle leading to G2/M phase arrest in a dose-dependent manner. Additionally, metal complexes were able to generate reactive oxygen species because of redox processes, proved by gel electrophoresis and cyclic voltammetry. *In vitro* cytotoxicity assays were also carried out within multicellular tumor spheroids and efficient anticancer action on these 3D assemblies was demonstrated.[1-5]

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Mechanistic Insights into Interactions Between Ionizable Lipid Nanodroplets and Biomembranes

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Lipid-based drug delivery systems, such as lipid nanoparticles (LNPs), are a promising branch of current medical research. The most notable recent example of such LNP-based molecular delivery are the novel COVID-19 vaccines, where the carrier of an mRNA molecule is a LNP containing ionizable lipids.[1]

To deliver its cargo into the cell's cytoplasm, the LNP must first cross the outer cellular membrane. There are several proposed mechanisms of this process, however, the exact nature of the LNP-membrane dynamics has so far gained only limited attention as it is challenging to study experimentally. In contrast, molecular dynamics simulations can provide an insight into complex structures with atomic and femtosecond resolution. In this project, biased and unbiased molecular dynamics is used to visualize and describe the interactions of the ionizable and membrane lipids, to help understand the fine details of a LNP entering the cell on a molecular level.[2]

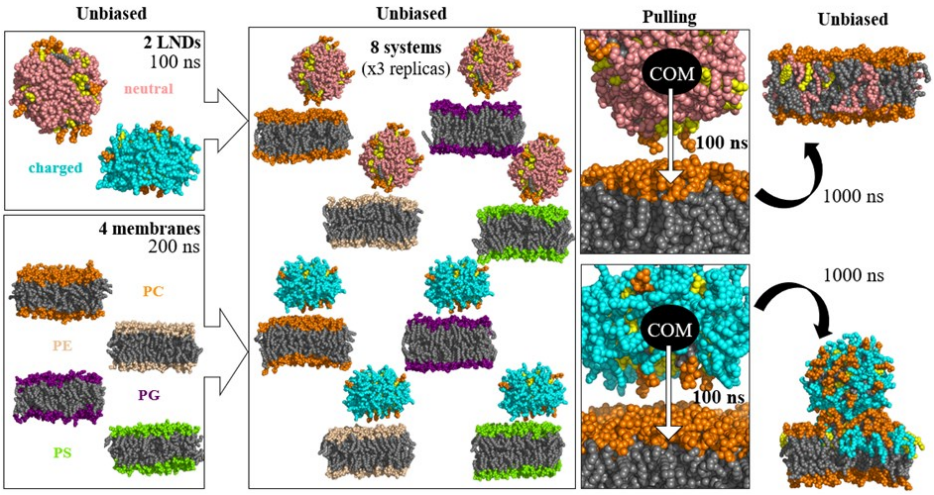

Figure 1: Scheme of the simulation protocol.

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Multilayer Ab Initio Molecular Dynamic Simulations with Perturbation Theory and Coupled-Cluster Methods for Molecular Clusters

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Molecular dynamic (MD) simulation is a computational simulation method in which the motions of atoms and molecules are investigated in time. For large molecules, due to its low cost, the molecular-mechanic (MM) force field is generally used to calculate the huge number of forces. Ab initio gradient (force) computations are needed to overcome the low accuracy problem of classical MD methods (AIMD). High-level methods, such as coupled-cluster (CC), should be considered to obtain high-accuracy results that are close to experimental outcomes. However, the computation of the gradient for conventional ab initio methods, especially for CC methods, is very expensive. For this reason, AIMD computations in the literature are restricted to small-size molecules, small basis sets, and density functional theory (DFT).

To overcome this bottleneck, efficient implementations of analytic gradients for the density-fitted Moller-Plesset (MP) and CC methods have been performed.[1-3] To further, enhance the applicability of our AIMD method, we also consider a multi-layer algorithm where two or more methods are simultaneously used for large molecular systems. Additionally, we developed the linear-scaling coupled-cluster methods, which take advantage of the molecular fragmentation approaches, such as systematic molecular fragmentation (SMF) are reported.[4] We demonstrate that the fragment-based CC methods are promising for the study of large-scale chemical systems where the conventional methods are computationally prohibitive. Our AIMD methods are applied to the simulation of molecular clusters.

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N-doped PAH non-adiabatic dynamics with the ML-MCTDH method

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The efforts of our research group have recently been directed towards understanding the after photoexcitation behavior of molecular crystals with potential photosensitizing applications, i.e. with the ability to absorb light to create reactive oxygen species to combat diseased tissues. This work focuses specifically on tetraphenylpyrazine (TPP), known for its fluorescence enhancement due to aggregation in the form of molecular crystals.[1]

We performed an initial gas-phase study, employing non-adiabatic dynamical methods such as surface hopping of trajectories and multilayer MCTDH to probe the photodeactivation of TPP. Surface hopping was used to validate the precalculated potentials, evaluate the role of the electronic ground state, and determine the intersystem crossing rate. Long-term dynamic simulations were performed with the ML-MCTDH method to obtain timescales and electronic state yields.

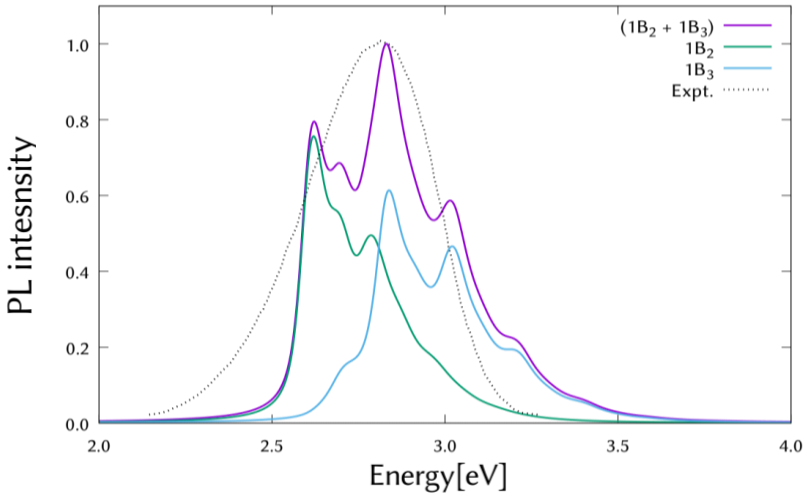

Figure 1. Emission spectra

The excited state dynamics of TPP was compared with two parent compounds, tetraphenylethylene and pyrazine, revealing both differences and similarities in their photophysical properties. Through elucidating these deactivation mechanisms, we aim to improve the understanding of the capabilities of TPP and pave the way for the design of more efficient photosensitizers.

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Collisional Excitation of PO^+ by *para*-H_2: towards the Accurate Modeling of Phosphorus Abundance in the Interstellar Medium

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When looking to the astrophysical networks that could be linked to abiogenesis (i.e., the formation of prebi- otic species from abiotic systems), phosphorus chemistry deserves a special attention.[1]

The recent discovery of PO^+ in the G+0.693-0.027 molecular cloud has prompted a collisional investigation of this ion to support the modeling of current and future observations in the interstellar medium (ISM).[2] Hence, the molecular cloud under study possesses a relatively low density of H_2 gas, making local thermodynamic equilibrium (LTE) conditions unrealistic. To meet the astrophysical requirements, the collision between PO^+ and *para*-H_2 was thus examined.[3] The interaction potential energy surface (PES) was accurately characterized by computing a grid of energy points in the in the four Jacobi coordinates using the CCSD(T)-F12/aug-cc-pV(Q+d)Z level of theory, and the potential was then fitted as an expansion over angular functions. A comparison between *para*-H_2 and *ortho*-H_2 indicated a good agreement, suggesting that the results obtained with *para*-H_2 adequately describe the collisional behavior of PO^+. State-to-state collisional coefficients were then derived for the twenty lowest rotational levels of PO^+ at temperatures ranging from 5 to 200 K. These newly obtained collisional data allowed for testing the validity of the LTE approximation and helped to refine the H_2 density and column density estimation of PO^+ based on the observations of the G+0.693-0.027 molecular cloud. Additionally, radiative transfer calculations indicated a strong maser behavior for the first rotational transitions of PO^+ at various kinetic temperatures and densities typically found in interstellar sources. This emphasizes the importance of accurate collisional coefficients for precise modeling of the abundance of PO^+ in the ISM.

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Databases for Molecular Data - VAMDC - Virtual Atomic and Molecular Data Center

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For investigation and understanding of confined molecular systems and accurate characterization of phenomena of astrochemical and astrophysical relevance, reliable molecular data may be of great interest. However, the main problems which are an obstacle for efficacious search and use of atomic and molecular data are among others: a) Lack of standards; b) Interoperability; c) Data exchange; d) Critical evaluation. In order to solve these problems on July 1 2009 Virtual Atiomic and Molecular Data Center (VAMDC) started, first as a FP7 project: Now it is is a Consortium of Databases & Services Providers that has built a unified, secure, documented, flexible and interoperable e-science environment-based interface e-Infrastructure for the exchange of atomic and molecular data. It connects 41 database which can be searched simultaneously and its partners are from Australia, Austria, France, Germany, India, Italy, Japan, Korea, Russia, Serbia, South Africa, Sweden, UK, USA and Venezuela. The databases contain many different molecular data of interest as for example a collection of theoretical spectroscopic data about Polycyclic Aromatic Hydrocarbons and carbon clusters, kinetic data interesting for astrochemical (interstellar medium and planetary atmospheres) studies, photodissociation cross-sections of molecular ions from individual ro-vibrational states and cross-sections and rate coefficients for radiative ion-atom collisional processes, collisional ro-vibrational excitation of molecules by colliders such as atom, ion, molecule or electron, catalog of radio frequency and microwave to far-infrared spectral lines of atomic and molecular species that (may) occur in the interstellar or circumstellar medium or in planetary atmospheres, bibliographic database of literature on fundamental atomic and molecular processes etc. In this contribution we will present Virtual Atomic and Molecular Data Center and molecular databases which it comnnects and discuss their content of interest for confined molecular systems and for different astrochemical and astrophysical problems relevant for molecules and molecular system in space.

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Spectroscopic Investigations in Forensic Science and Related Fields

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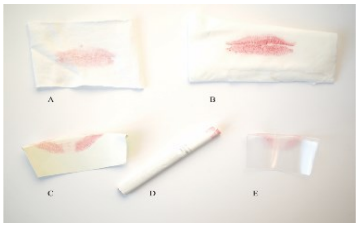
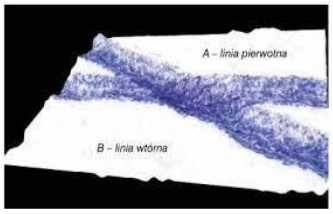
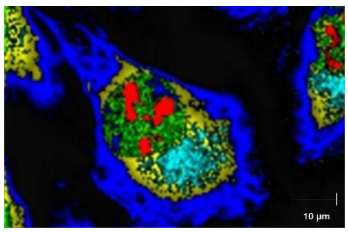
Vibrational spectroscopy, a field of science that studies the interaction of electromagnetic radiation with matter through absorption (IR spectroscopy) or scattering (Raman spectroscopy), is currently widely used in the structural analysis of coordination compounds. Beyond standard characterization of molecular systems, confirming coordination modes, and defining the symmetry of coordination compounds, it is also possible to determine the stability of complex compounds in solution.[1,2] Vibrational spectroscopy is also applied in related fields such as forensic sciences. It enables the detection of addictive substances, the examination of traces like lipstick marks (cheiloscopy), toxic substances, and secretions. Additionally, it is popular for determining the sequence of intersecting lines on records or prints. Qualitative analysis using vibrational spectroscopy techniques finds applications in gemmology. The use of Raman spectroscopy is significant in the imaging of cells and tissues *in vitro* and *in vivo*.



Cheiloscopy combined with analysis of Raman spectra of lipstick placed on different materials.



The sequence of intersecting lines.



Raman imaging of the bone cells[3].

Figure 1. The practical application of vibrational spectroscopy.

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Understanding the Carbohydrate Derivative and Fluorescein

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Fluorescein dyes in the optical biosensors relying on carbohydrate-lectin interactions is among the common tag owing to its stability, inexpensiveness, ease of use and decent Δλ between excitation and emission wavelengths [1,2]. Carbohydrates are naturally occurring biomolecules and their regulations are under strict biochemical control. Besides their critical roles in energy metabolism and cellular structures, their specific interactions with lectins make them appealing in biological and biomedical applications [3]. Lectins are carbohydrate binding proteins that play roles in cell-cell communication, immune response, cell-surface adhesion, and some of them take place in regulation of cellular metabolism [4]. In this study, we utilized 10 different carbohydrate derivatives that interacted with Fluorescein. While some of them enhanced the PL intensity of fluorescein, some of the sugar ligands eliminated the PL intensity resulting from fluorescein excitation. Molecular and in silico studies were performed to understand how the sugar ligand chemistry played roles in enhancement and elimination of the PL intensity.

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Discrimination of leucine and isoleucine via fragmentation by electromagnetic field

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Determination of complete amino acid sequence of proteins remains a challenge, especially for proteins whose residues are the isomers leucine (*Leu*) and isoleucine (*Ile*), specifically via the mass spectrometry-based methods.[1] We investigated numerically the interaction of *Leu* and *Ile* with dipole electric (DE) and electromagnetic (EM) radiation fields, conducting a comparative study between the two isomers.[2] Geometry optimization of the molecular structures under the action of DE field was performed, employing the original cc-pVTZ basis with the computational GAUSSIAN09 package.[3]

In the case of EM field, we used a modified cc-pVTZ basis set, introducing correction coefficients to the molecular wave functions, in order to reflect the effects of the magnetic field (similarly to our recent work).[4] In the DE and EM fields, *Leu* was partially deformed, while for *Ile1* and *Ile2* (the two *Ile* conformers) we observed a H transfer, or O-H and N-H bond rotations, respectively. The fragmentation products in the DE or EM fields also exhibit different behaviour for *Leu* vs *Ile* (as well as *Ile1* vs *Ile2*). For example, in the case of *Leu* for field strength 0.5 a.u. the fragmentation is field-independent, giving CO_2, C_2H_5N, C_3H_6, and 2H, while *Ile* decomposes into CH_3, C_3H_6, $C_2H_4NO_2$ in the DE, and into CO_2, C_3H_8N, C_2H_4, H in the EM field. The latter suggests the relevance of our numerical calculations, which account for corrections to the molecular orbitals due to the magnetic field, and they could be proposed as a possible tool for isomer/conformer discrimination.

This abstract is based upon work from COST Action CA18212-Molecular Dynamics in the GAS phase (MD-GAS), supported by COST (European Cooperation in Science and Technology). Numerical calculations with GAUSSIAN09 package were performed at the High Performance Computing Center of Vilnius University "HPC Sauletekis".

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Vacancy Defects in s-I Clathrate Hydrates

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Clathrate hydrates are known as structures that form cage-like arrangements of water molecules, hosting guest gas molecules. The specific structure of the resulting hydrate depends on the size and chemical interactions of the guest molecules reacting with water/ice to form the hydrate[1]. One of the most common structures studied in this research is structure I (s-I). The energy and structure of vacancy defects in s-I gas hydrates have been investigated using first-principle calculations for finite-size clusters and periodic 3D lattice systems. The formation energies of these defects have been calculated for the first time under conditions where the cages of s-I are completely empty and the large cage is filled with an EO (ethylene oxide) molecule. Additionally, the interaction energy between the EO molecule and the vacancy defect and vibrational frequencies have been calculated for the first time using ab initio calculations. It is believed that these defect-containing structures are important for the transport of guest gas molecules through the cages of the host water[2,3].

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Investigation of Hexavalent Chromium Sorption Mechanisms Using Functionalized Magnetic Polymer Nanocomposites

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In previous extensive studies, polymers composed of glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA) have demonstrated high efficiency in adsorbing heavy metal ions from aqueous solutions[1,2,3,4,5,6]. This study aims to synthesize an amino-functionalized magnetic polymer nanocomposite based on GMA and EGDMA, named Fe_3O_4-APTMS/PGME-deta, as an effective sorbent for removing toxic hexavalent chromium (Cr(VI)) from water. Characterization of the synthesized Fe_3O_4-APTMS/PGME-deta included analysis of its chemical and morphological structure using techniques such as SEM, TEM, ATR-FTIR, XRD, and SQUID, revealing smooth spherical particles with a macroporous morphology and encapsulation of magnetic nanoparticles within the polymer matrix. Sorption experiments demonstrated the efficient removal of Cr(VI) from aqueous solutions. Isothermal analysis suggested the Freundlich model as the most suitable. Thermodynamic investigations indicated the spontaneous nature but endothermic process of sorption. FTIR and XPS analyses elucidated the interaction mechanisms between Cr(VI) oxyanions and the Fe_3O_4-APTMS/PGME-deta nanocomposite, including Cr(VI) reduction and Cr(III) coordination on the sorbent surface. Quantum chemical modeling further confirmed the high binding affinity between Cr(VI) oxyanions and the sorbent's active sites[7].

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Sodium Clusters Confined in Hard Carbon Fragments

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Lithium-ion batteries (LIBs) are the acknowledged market favorite at the moment, but along with undeniable advantages, they also have a number of disadvantages. A promising alternative are sodium-ion batteries (SIBs), as they are cheaper and safer. In order to limit, as much as possible, the changes in the established production technologies, it is natural to look for anode materials with characteristics closest to graphite, but still suitable for SIB. One such material is the non-graphitized (hard) carbon, which is most commonly obtained from biomass and has a porous structure that allows sodium ions to migrate. The material in question has an incompletely defined structure that depends on the raw material from which it is obtained. In order to evade graphitization, while maintaining satisfactory conductivity, it certainly contains non-planar conjugated fragments and a variety of nanometer-sized cavities of different shapes and sizes.

Sodium is renowned for its proclivity to form clusters, especially when the latter are positively charged.[1] The pores of hard carbon are particularly suitable for the formation and growth of these clusters, and they become sodium depots.[2] It is not yet fully understood whether the formation of these deposits leads to increased reversible or irreversible capacity.[3] The aim of our research is to trace the mechanism and energetics of formation, growth and decomposition of sodium clusters on non-planar conjugated carbon sites and in pores of different shapes using molecular modeling (DFT). The electrode potential at which the clusters form was calculated and the charge transfer as a function of their size and shape was estimated.

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Advanced Characterizations of Magnetic Metal Nanoparticles Containing Biocompatible Polyacrylonitrile Nanofibers

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Electrospinning is an important processing method for deriving micro- and nanofibers from polymer solutions in the presence of electrical forces,to produce diverse forms of polymeric fibrous assemblies[1-3]. In this study, production and advanced experimental characterizations and interfacial interaction of confined and homogenously dispersed magnetic nanoparticles of iron oxide(Fe_2O_3) and manganese zinc ferrite(MnZnFerrite) in polyacrylonitrile (PAN) matrix as in the nanofiber form are studied in detail.Electrospinning was successfully used to fabricate polyacrylonitrile nanofibers blended with iron oxide and MnZn Ferrite nanoparticles, which were thermomechanically, morphologically, and spectroscopically characterized in detail. With the application of an external magnetic field in the course of dynamic mechanical measurements under tension, the storage modulus of the glass transition T_g of PAN/Fe_2O_3 rises at the expense of the loss modulus, and a new peak emerges at ~350 K. For the PAN/MnZn Ferrite nanofibers a relatively larger shift in T_g (from ~367 K to ~377 K) is observed, emphasizing that in comparison to Fe_2O_3, MnZn Ferrite nanoparticles exhibit a larger antiferromagnetic coupling between Mn and Zn leading to a larger magnetic moment.

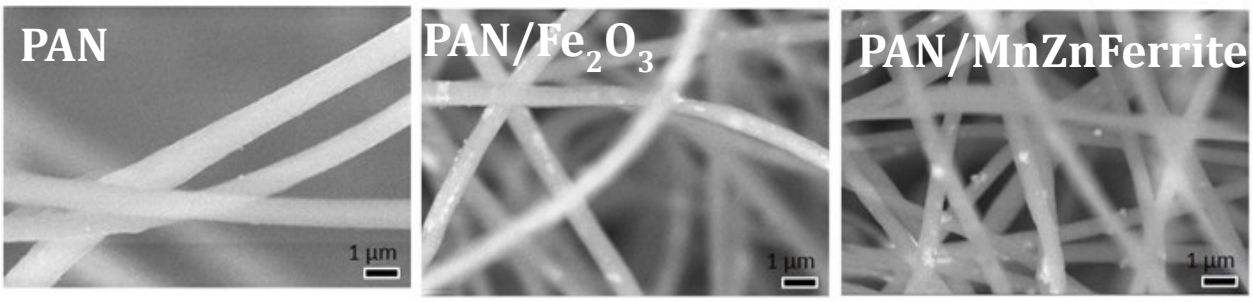

Figure 1. HRSEM imaging for three nanofiber types

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Confining molecules on Carbon Dots structure: experimental and theoretical approach

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Carbon Dots (CDs), and in particular N-doped CDs, are C-based rounded nanoparticles (diameter < 10 nm) with high emission quantum yield and large emission tunability across the visible range, depending on composition and structure. These optical properties, along with high chemical inertness, resistance to photobleaching, and biocompatibility, make CDs highly desirable for many technological purposes. The emission properties are not exclusively ascribed to a single mechanism: quantum confinement, due to hypothesized nanosized sp^2 carbon core, and molecular states or surface states, due to fluorophores formation and surface traps, respectively, are both considered. In addition, the optical emission is in general excitation-dependent, suggesting the presence and possibly the interplay of more than one mechanism. In this work we consider CDs prepared by solid-state synthesis of citric acid and urea in different molar ratio at 180 °C at various synthesis time. Optical spectroscopy, NMR spectroscopy, XPS spectroscopy, structural and morphological analysis were considered to characterize the structure and properties of CDs. Quantum chemistry calculations were applied to model the emitting centers and their formation during the synthesis. By changing the molar ratio of the precursors, CDs with main emission in the blue and green range can be prepared. The structural features indicate the presence of a carbon network with a large degree of disorder increased by the presence of N doping. The emission properties are related to both surface groups and molecular centers, whose formation starts from the very first minutes of the synthesis. The calculations allow ascribing the optical properties to some specific centers and to follow their genesis during the synthesis aiming at understanding their confinement within the CDs' structure or at their surface.

Posters

Photochemistry of thiazole derivatives isolated in Noble Gas Cryomatrices

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The structure, spectroscopic properties and photo-induced structural changes of two thiazole derivatives, 2-amino-4-methylthiazole (AMT) and 2-aminothiazole-4-carboxy-lic acid (ACA), isolated in argon and nitrogen matrices were studied using matrix-isolation FTIR spectroscopy and DFT calculations undertaken at the B3LYPD3/6-311++G(3df,3pd) level of theory.[1,2] The most stable structures, one for AMT and three for ACA, were identified in matrices after deposition. In the most stable AMT and ACA tautomers the five-membered ring was stabilized by two C=C and C=N double bonds, additionally ACA tautomers were characterized by different arrangement of the carboxyl group. For both compounds, the phototransformations upon irradiation provided by an Optical Parametric Oscillator (OPO) tunable laser system were studied. Following irradiation at 285 or 1456 nm, a rotation of the OH group around the C–O bond in ACA1 leading to increase of ACA2 was detected. The corresponding reverse photo-rotamerization was detected at 296 or 1434 nm, resulting in the recovery of the initial isomer ACA1. Selective UV irradiation of matrices with shorter wavelengths led to photolytic decomposition of AMT and ACA compounds. Main photoproducts, the carbodiimide derivatives, were produced by a cleavage of the CS-CN bond together with hydrogen atom migration. We also observed minor products of photoreactions: cleavage of the CS–CC bond followed by hydrogen migration (e.g. 2-methyl-1H-azirene-1-carbimido-thioic acid) and cleavage of the CS–CN or CS–CC bonds followed by disruption of the N–C bond (e.g. cyanamide, methylthioketene or propyne). Also several molecular complexes were identified as photoproducts besides new molecules.

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Hybrid HF/DFT composite methods for molecular confinement in Metal-Organic Frameworks

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Due to their chemical versatility and their modular nature, thousands of Metal-Organic Frameworks (MOFs)[1] of different size and topology have been either synthesized or built by design. In addition, framework modifications, host-guest interactions, defects and lattice interpenetration can occur thus further complicating the structure. Despite this, all these features make them unique materials for several important applications.[2] Apparently, the structural and chemical complexity of MOFs can pose a limit to the applicability of quantum mechanical methodologies. To cope with this, low cost, yet accurate ab initio methods are needed. Recently, a new class of cost-effective ab initio methods for solid-state calculations have been developed and implemented by us in the CRYSTAL code[3] with the main target to predict accurate structural, electronical, vibrational and energetic properties. These composite methods[4] rely on a HF/DFT hybrid functionals (e.g., PBEsol0, HSEsol and r^{2}SCAN0) evaluated in a double-zeta or triple-zeta quality basis set tuned for solids and augmented with two semi-classical corrections to take into account dispersive interactions (D3)[5] and the basis set incompleteness error (gCP).[6] Here, we show how these methods can be effectively applied to predict adsorption of gas and drugs confinement in MOFs. Calculations on very large and complex MOFs containing up to 3700 atoms in the unit cell such as MIL-100 and MIL-101 are feasible with small-scale computing resources (e.g. 128 cores).

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Study of Enhanced Solubility of Glibenclamide in Aqueous Ionic Liquid Solutions

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Glibenclamide is a sulphonyl urea drug used to treat type 2 diabetes. Recently, scientists have discovered its novelty properties for inhibiting headaches and various inflammations.[1] What makes it harder to find new pharmaceutical applications of glibenclamide is its poor solubility in water (15-24 μg/mL)[2], which was shown to be improved by 130-600 times compared to pure water by dissolving glibenclamide in a mixture of water and choline-tryptophanate ionic liquid [Cho][Trp].[3]

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. The nuclear magnetic resonance (NMR) ^{1}H chemical shifts well known for being dependent on the surroundings of the molecule were used as probes in aqueous solution and in ionic liquid mixture with water. Experimental NMR measurements for glibenclamide in these systems were also done.

It was discovered that the conformational equilibrium of glibenclamide differs between the two examined systems. While there were no significant specific interactions between glibenclamide and ionic liquid ions, the ions were found in the vicinity of glibenclamide screening it 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, approving the aforementioned statement.

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Synthesis and structural studies of sandglass-like nonanuclear rare-earth molecular cluster aggregates

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Over the past few decades, lanthanide molecular cluster aggregates (MCAs) composed of multinuclear metal core encapsulated by organic ligands have garnered much attention because of their interesting solid-state structures and versatile application in the field of single molecular magnetism[1], magnetic refrigeration systems[2], luminescent sensors/probes[3], and catalysis[4]. Recently, MCAs are being considered as the new generation of highly efficient optical materials that can unify the properties of lanthanide nanoparticles and molecular complexes. During our research, the family of rare earth molecular cluster aggregates $[RE_9(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_8(sal\text{-}R)_{16}]X$ (RE = Y, Eu, Dy, Tm, Yb, Lu); $X^- = Cl^-$ or $DyCl_4^-$; sal-R = methyl or ethyl salicylate) was prepared by direct reaction of $RECl_3$ (where RE = Y, Eu, Dy, Tm, Yb, Lu) with generated in situ lithium or zinc methyl salicylate salts in a ROH/THF solution (ROH = Me, Et) under the controlled moisture conditions.

Figure 1. The molecular structure of $[Y_9(\mu_4\text{-}OH)_2(\mu_3\text{-}OH)_8(sal\text{-}R)_{16}]Cl$ (for R = Me (0.38), Et (0.62)).

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An *ab initio* approach to open-shell metal cluster-support interactions.

Case study of Cu_3 adsorption on benzene and coronene.

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Recent advances in synthesizing metal atomic quantum clusters (AQCs) have enabled novel (photo)catalysts.[1] Optimizing these catalysts requires a molecular-level understanding of AQC–support interactions.[1] While MP2 is cost-effective for studying these interactions, it often overestimates them. The MP2C scheme, which corrects Hartree-Fock dispersion energy with a coupled dispersion contribution, has proven accurate for closed-shell AQCs with carbon supports.[2] In this poster, a modified MP2C scheme for open-shell AQC-support interactions is presented, using Cu3–benzene and Cu3–coronene as models. The accuracy of the MP2C approach has been demonstrated against the CCSD(T), CCSD(T)-F12, UMP2, and DFT-D3 methods, capturing the energy differences between uncoupled and coupled dispersion energy contributions. The resulting dispersionless and dispersion energy contributions can be fitted to an additive pairwise potential model (PPM).[3,4]

Figure 1. Interaction potentials for Cu3–benzene (left-hand panel) and Cu3–coronene (right-hand panel). The insets show the dispersion and dispersionless contributions to the interaction energies.

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Nonadiabatic dynamics in the oxidation of Cu_5 clusters

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Nonadiabatic effects can be significant in the subnanometric particle regime. We study the nonadiabatic quantum dynamics of the oxidation of the trigonal bipyramidal $Cu_5(O_2)_2$ and the incoming O_2. The two-dimensional diabatic potential energy surfaces were obtained directly from electronic structure calculations.[1] We perform split-operator wavepacket dynamics[2] to obtain the probability of electron transfer from the copper cluster to the incoming molecular oxygen upon the first collision. Boltzmann averaging gives the estimate of the temperature-dependent electron transfer probability.[1,3] We find that the balance between the conflicting effects of adiabatic barrier and nonadiabatic coupling leads to resistance to changing electronic character. The semiclassical Landau-Zener theory offers qualitative prediction from the local description of the crossing point along the reaction coordinate. We demonstrate the importance of nonadiabatic effect in understanding the behaviour of subnanometric metallic clusters.

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Synthesis of alkyl esters of ω-hydroxy fatty acids by alcoholysis of macrocyclic lactones catalyzed by zinc aryloxides

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The aim of the work was to develop an effective method for the synthesis of zinc complexes having different nuclearity, central core topology, and containing ligands of different basicity and coordination abilities. As a result, a series of zinc aryloxides, namely $[Zn_4(sal\text{-}Me)_8]\cdot 2.5(C_7H_8)$ (**1**), $[Zn_4(sal\text{-}Me)_8]\cdot CH_2Cl_2$ (**2**), $[Zn_4(\mu_3\text{-}OR)_2(sal\text{-}R)_6]$ (**3**) (for R = Me (0.51), Et (0.49)), $[Zn_4(\mu_3\text{-}OMe)_4(sal\text{-}Me)_4(HOMe)_4]$ (**4**), $[Zn(sal\text{-}Me)_2(py)_2]$ (**5**), $[Zn(sal\text{-}Me)_2(tmbpy)]_n$ (**6**), $[Zn_2(sal\text{-}Me)_2(THF)_2Cl_2]$ (**7**), and $[Zn_4(\mu_3\text{-}OMe)_2(sal\text{-}Me)_4Cl_2]$ (**8**), and [Zn(Hsal-Me)Cl2] (**9**), (where sal-Me = methyl salicylate ligand, py = pyridine, tmbpy = 4,4'-trimethylenedipyridine) were obtained.[1,2] The catalytic activity of **1-9** was tested in the synthesis of methyl esters of ω-hydroxy fatty acids (MHHD = methyl 16-hydroxyhexadecanoate; MHPD = methyl 15-hydroxypentadecanoate) via alcoholysis of pentadecanolide (PDL) and hexadecanolide (HDL) as shown in Figure 1a.[2] Compound **7** (Figure 1b) exhibited the highest catalytic activity in both investigated reactions. Based on the crystal structure of **7**, the addition of $ZnCl_2$ to zinc aryloxides **1-6** and **8** was used as a novel approach to form molecular adducts with enhanced activity in macrolactone alcoholysis.

a) b)

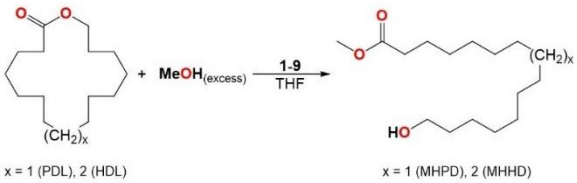

Figure 1. *a) Synthesis of MHPD or MHHD by alcoholysis of cyclic macrolactones using* ***1-9*** *as catalysts; b) The molecular structure of* $Zn_2(sal\text{-}Me)_2(THF)_2Cl_2]$ *(**7**).*

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Molecular complexes between 3-mercapto-1,2,4-triazole and atmospheric gases (CO_2, N_2). FT-IR spectroscopic and photochemical studies based on simple DFT calculations

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Weakly bound molecular complexes are involved in many biological and chemical processes, including those occurring in the Earth's atmosphere. 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 [1]. A common method for studying molecular complexes is matrix isolation, which allows detection of even very weak interactions [2].

In this work, complexes of 3-thio-1,2,4-triazole (ST) with CO_2 and N_2 were studied theoretically by the DFT/B3LYP-D3 method and experimentally by FTIR spectroscopy combined with the matrix isolation technique. The computational results show that ST interacts specifically with both gases in several different ways. As for 1:1 complexes of the most abundant ST thione tautomer, four and five stable minima were located on the potential energy surface for ST···CO_2 and ST···N_2, respectively. Two the most stable structures of CO_2 complexes contain a N-H···O hydrogen bond and an additional S···N van der Waals contact. They were detected experimentally in the argon matrix directly after deposition, whereas irradiation of the matrix at $\lambda = 270$ nm resulted in the simultaneous formation of the less abundant thiol tautomer as well as its three corresponding complexes, also bound by weak interactions. In turn, two ST···N_2 structures present in the matrix are transformed into analogous geometries bound by mainly N-H···N hydrogen bonds Simple calculations carried out at B3LYP-D3/6-311++G(3df,3pd) level were enough to obtain very good agreement with the experiment in terms of harmonic frequencies and IR intensities of weakly bound molecular complexes. [3]

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Chemical and Physical confinement of Carbon Dots in silica matrices for optical spectroscopy and size tuning

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In recent years, significant efforts have been directed toward replacing rare-earth-based materials in optoelectronics and photonics with green and cost-effective alternatives. Carbon Dots (CDs) have emerged as a promising candidate due to their efficient and tunable emission properties, facile chemical functionalization, and biocompatibility. This study[1] uses a static open-air oven synthesis method to investigate CDs synthesized within solid-state matrices of commercially available mesoporous silica. The photophysical properties of these solid-state hybrids were compared with those of reference CDs prepared without silica matrices and dispersed in water. We performed a bottom-up synthesis starting with citric acid and urea, which assembled inside two different silica matrices (commercial MCM-48 and SBA-15), forming two carbon dots-silica hybrid systems. Their structural and optical properties were characterized using TEM, ATR, XPS, UV-Vis, SS and TR-PL. In silica, we observed a variation in the optical properties of the CDs compared to the nanoparticles dispersed in water, with an increase in the green emissive band relative to the blue band. The interaction with the matrix was confirmed by studying the irradiation effect on the hybrids over time, which resulted in an overall increase in the green luminescence intensity in the hybrid. XPS measurements showed a higher degree of doping at the expense of pure aromatic systems and different types of nitrogen dopants. TEM images, obtained after extracting carbon dots from the host matrix, demonstrated that silica could serve as a suitable nanoreactor to control the size and distribution of these particles. The synthesis of CDs in a silica environment favored greater control over nanoparticle size and the production of more green-emitting centers. In contrast, synthesis outside of silica resulted in less size control and higher production of blue-emitting channels.

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Towards microporous photocatalysts - the active sites and properties of a modified TS-1

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Semiconductors are providing the necessary properties photocatalysis, and the unique structure of microporous semiconductors can help in better separation of photogenerated electron-hole pairs, reducing the chances of recombination and thus increasing the efficiency of the water splitting process. Moreover, microporous structures can facilitate the incorporation and distribution of co-catalysts, which can further improve the catalytic efficiency.[1]

In this work, we explore the Silicalite-1 modified by means of Si→Ti,V substitution in 12 different T-sites. These sites are then considered as the active sites for catalytic water splitting with the aim of determing the most stable system providing the least overpotential of the oxygen evolution reaction.

Calculations have been carried out within the DFT framework, and allowed us to determine the T4 as the most stable susbtitution site. Moreover, in all investigated cases, Si→V substitution is prefered, however the energy difference is often negligible. Unfortunately, the system are characterized by a relatively high overpotential.

a) (b)

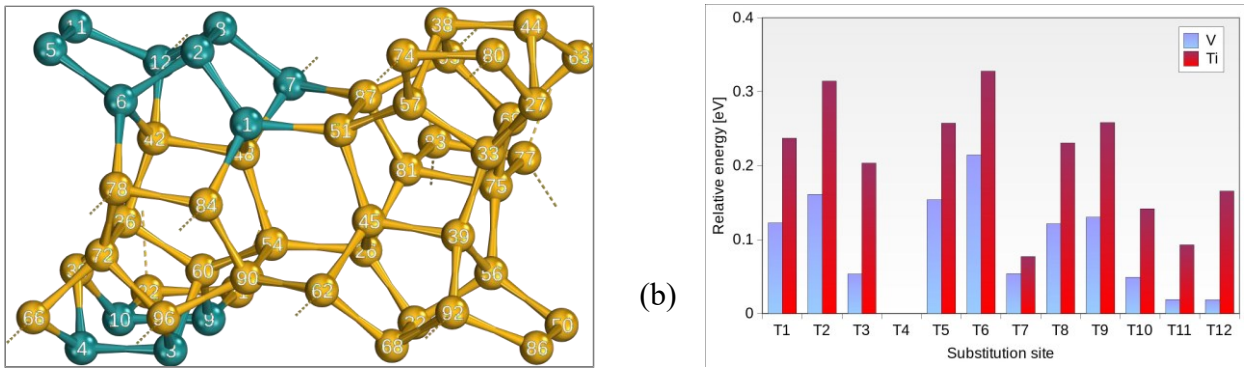

Figure 1. Structure of Silicalite-1 and substitution sites (a); Relative stability of the Si→Ti,V susbtitutions.

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