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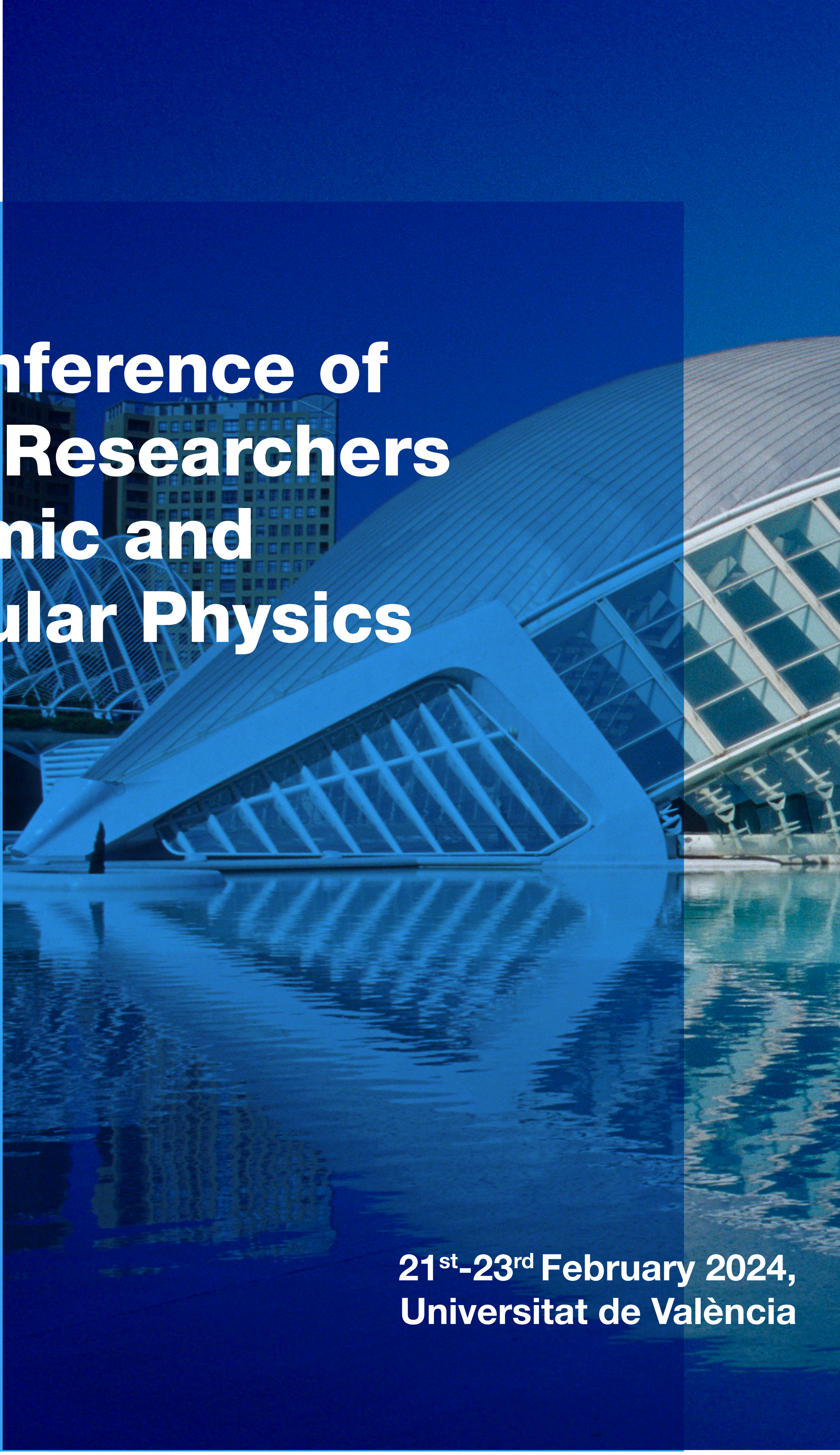

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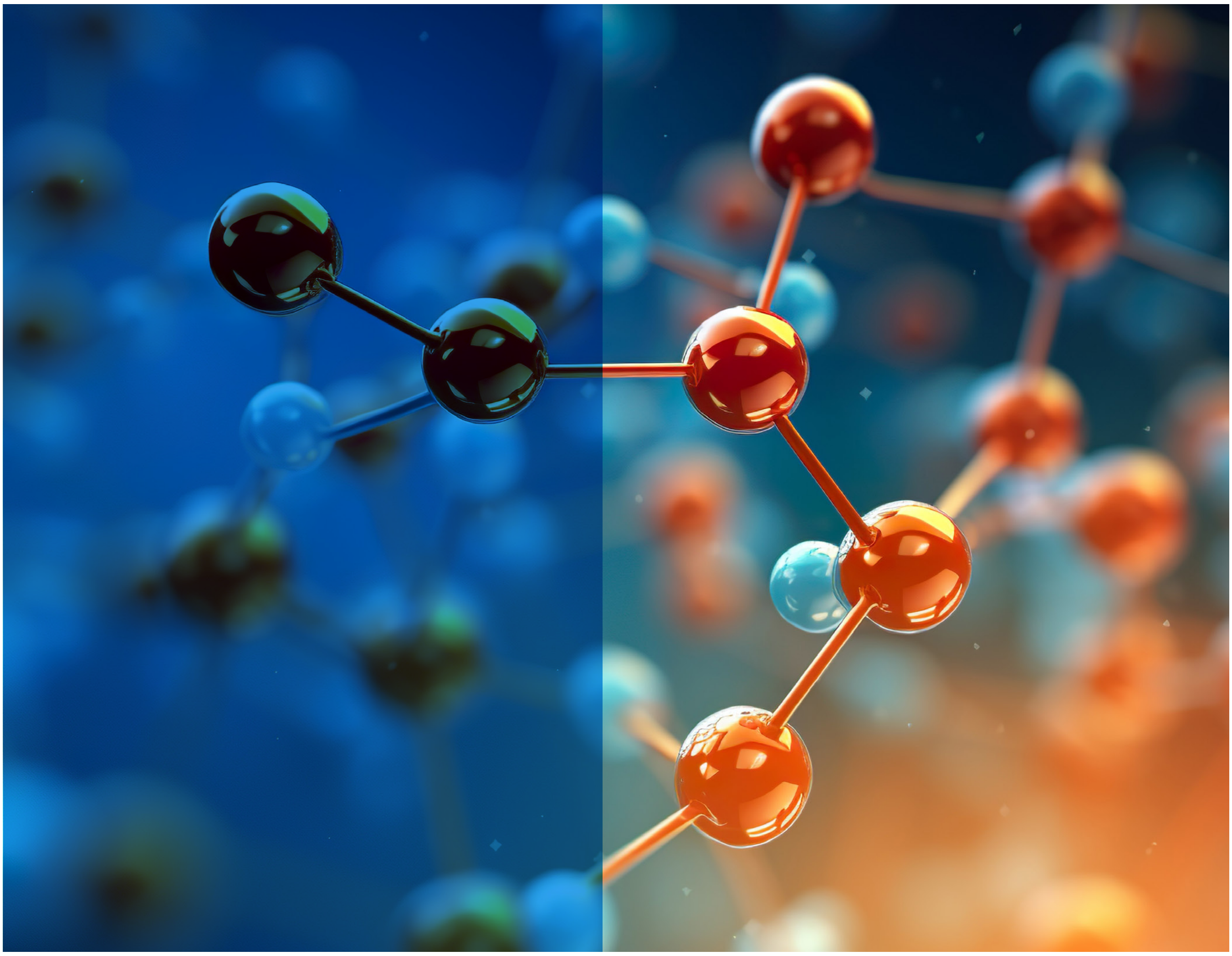

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PROGRAMME

	21/02/2024	22/02/2024	23/02/2024
8:30h – 8:35h		Plenary: Alexandre Blanco-González	Farha Sajeev Hussain
8:35h – 8:40h			Noura Aflak
8:40h – 8:45h			Axel Melchor Gaona Carranza
8:45h – 9:00h			Edward Binns
9:00h – 9:15h		Javier Hernández Rodríguez	Alberto Martín Santa Daría
9:15h – 9:30h		Julia Arnanz Sebastián	Marta Castiñeira Reis
9:30h – 9:45h		Jorge Alonso de la Fuente	Álex Pérez-Sánchez
9:45h – 10:00h		Javier Domínguez-Calvo	Gema Raposo Hernández
10:00h – 10:15h		Jesús Cerdá Calatayud	Pablo Botella Vives
10:15h – 10:45h		Coffee break	Coffee break
10:45h – 11:00h		Lucía López-Pacios	Pablo García-Aznar
11:00h – 11:15h	Social activity: Tourism around Valencia	Domingo Heras Elvira	Alberto Fernández Alarcón
11:15h – 11:30h		Gerliz Mercedes Gutiérrez Finol	Víctor Camús Hernández
11:30h – 11:45h		Andrea Lázaro Gómez	Carlos Montero Galán
11:45h – 12:00h		Marta Ibáñez-Deluis	Sergio Mato Domínguez
12:00h – 12:15h		Jesús Lucía Tamudo	Nadia El Alouani Dahmouni
12:15h – 12:30h		Anzhela Veselinova Marinova	Parmenio Boronat Sevilla
12:30h – 12:45h		Andrea Vázquez Abascal	José Ricardo Morán Cabezas
12:45h – 13:00h		Alejandro Cortés Villena	Gonzalo Rivero Carracedo
13:00h – 13:15h	Registration	Juan Manuel García Garrido	Alberto M. Ruiz
13:15h – 13:30h		Joshua Vogwell	Nayara Carral Sainz
13:30h – 13:35h		Jesús Fernández Sancho	Daniel Barrena
13:35h – 13:40h		Nicolas Cartier	Carmen Rosales Martínez
13:40h – 13:45h		Diogo José Lopes Rodrigues	Ashok Ugale
13:45h – 15:00h		Lunch	Lunch
15:00h – 15:20h	Opening and welcome		
15:20h – 15:50h		Plenary: Iker Lamas Frejo	Plenary: Darío Barreiro-Lage
15:50h – 15:55h		Valentin Gradisteanu	Ignacio Martínez Casasús
15:55h – 16:00h		María Amparo Lopo March	Swaroop Venkata Sai Kunapuli

	21/02/2024	22/02/2024	23/02/2024
16:00h – 16:05h	Plenary: Fernando Martín	Lucía Velasco	Cristina López Cava
16:05h – 16:20h		Lorena Ruano de Domingo	Carlos García Arcos
16:20h – 16:35h		Miguel Gallegos	Henar Mateo de la Fuente
16:35h – 16:50h		Shivam Gupta	Fabian Kellerer
16:50h – 17:05h		Anargyros Drolapas	Daniel Félix González
17:05h – 17:35h	Coffee break - Horchata	Coffee break	Closing ceremony
17:35h – 17:50h		Toraya Fernández Ruiz	
17:50h – 18:05h	Benedito Donizeti Botan Neto	Juan Antonio Soler	
18:05h – 18:20h	Maxime Sauvan	Francisco Javier Ortín Fernández	
18:20h – 18:35h	Markel Ylla	Inés Sánchez-Movellán	
18:35h – 18:40h	Milorad Anđelković		
18:40h – 18:45h	Tanvi Batta		
18:45h – 18:50h	Costanza Borghesi		
21:00h		Closing dinner	

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Scientific Programme

Wednesday, 21st February

13:00h – 15:00h	**Registration**
15:00h – 16:00h	**Opening and Welcome**
16:00h – 17:05h	**Plenary Lecture (p. 12)** Attosecond Chemistry Fernando Martín, *Universidad Autónoma de Madrid*
17:05h – 17:50h	**Coffee break – Horchata**
17:50h – 18:05h	**Oral Communication (p. 13)** Exploring the structural stabilitiy of hydrated potassium carbonate at high pressure and high-temperature conditions Benedito Donizeti Botan Neto, *Institute of Material Science – Universitat de València*
18:05h – 18:20h	**Oral Communication (p. 14)** Characterization of Monomeric, Dimeric and Trimeric Zn (II) Phenanthroline Photosensitizers by X-ray Absorption Spectroscopy and Time-Resolved XAS Maxime Sauvan, *Instituto de Ciencia de Materiales de Madrid – CSIC*
18:20h – 18:35h	**Oral Communication (p. 15)** Development of correlation indicators Markel Ylla, *Euskal Herriko Unibersitatea*
18:35h – 18:40h	**Flash Communication (p. 16)** A Comparative Study of the Reaction Mechanism in hASNase3 and gpASNase1 using Multiscale Simulations Milorad Andlekovic, *Universitat de València*
18:40h – 18:45h	**Flash Communication (p. 17)** Ab initio investigations on hydrogen bond interactions of 1:1 theobromine-water complexes Tanvi Batta, *Panjab University*
18:45h – 18:50h	**Flash Communication (p. 18)** Tailoring High Entropy Oxides (HEOs) as Emerging Radiative Materials for Green Energy Saving Buildings Costanza Borghesi, *Università degli Studi di Perugia*

Scientific Programme

Thursday, 22nd February

08:30h – 09:00h	**Plenary Lecture (p. 19)** Looking for the Good Vibrations: Tuning Focused Ultrasounds for Lipid Membrane Therapy Alexandre Blanco-González, *Universidad de Santiago de Compostela*
09:00h – 09:15h	**Oral Communication (p. 20)** A step towards quantum dynamics in tetraphenylpyrazine molecular crystals Javier Hernández Rodríguez, *Universidad de Salamanca*
09:15h – 09:30h	**Oral Communication (p. 21)** Sunbathing with the enemy: theoretical assessment of the photostability of p-aminobenzoic acid Julia Arnanz Sebastián, *Universidad Autónoma de Madrid*
09:30h – 09:45h	**Oral Communication (p. 22)** Theoretical Spectroscopic study of PH^{+} Jorge Alonso de la Fuente, *Instituto de Física Fundamental – CSIC, Madrid*
09:45h – 10:00h	**Oral Communication (p. 23)** An unexpected problem of astrochemical significance and a healing strategy Javier Domínguez Calvo, *Donostia Internatinal Physics Center*
10:00h – 10:15h	**Oral Communication (p. 24)** The interplay of charge-transfer states in enhancing exciton diffusion Jesús Cerdá Calatayud, *University of Mons*
10:15h – 10:45h	**Coffee break**
10:45h – 11:00h	**Oral Communication (p. 25)** Binding and photoisomerization of trans and cis DAD in the NaV1.5 channel Lucía López Pacios, *Universidad Autónoma de Madrid*
11:00h – 11:15h	**Oral Communication (p. 26)** Molecular insights into zileuton: An asthma treatment drug revisited by rotational spectroscopy Domingo Heras Elvira, *Universidad de Valladolid*
11:15h – 11:30h	**Oral Communication (p. 27)** STOSS: A stochastical spin simulator for molecular nanomagnets Gerliz Mercedes Gutiérrez Finol, *Instituto de Ciencia Molecular – Universitat de València*
11:30h – 11:45h	**Oral Communication (p. 28)** Exploration of New Tri-biphenylamine-Based Systems for Sensing G-quadruplex DNA: A Biophysical and Computational Study Andrea Lázaro Gómez, *Instituto de Ciencia Molecular – Universitat de València*
11:45h – 12:00h	**Oral Communication (p. 29)** Photophysical exploration of monomeric and dimeric canonical nucleobase derivatives Marta Ibáñez Deluis, *Universidad Autónoma de Madrid*
12:00h – 12:15h	**Oral Communication (p. 30)** Electronic excitation and ultrafast charge transfer in nitrothiophenol molecules adsorbed on a gold surface Jesús Lucía Tamudo, *Universidad Autónoma de Madrid*
12:15h – 12:30h	**Oral Communication (p. 31)** Change in the Λ-doublet population due to dynamical effects: the O(3P) + D2 → OD(2Π) + H reaction Anzhela Veselinova Marinova, *Universidad de Salamanca*
12:30h – 12:45h	**Oral Communication (p. 32)** Exploring the microsolvation and conformational dynamics of pyruvic acid in the gas phase Andrea Vázquez Abascal, *Euskal Herriko Unibersitatea*
12:45h – 13:00h	**Oral Communication (p. 33)** Tuning the emissive properties of push-pull systems via the restricted torsion of N,N-disubstituted amino moieties Alejandro Cortés Villena, *Instituto de Ciencia Molecular – Universitat de València*
13:00h – 13:15h	**Oral Communication (p. 34)** Rovibrational dynamics of Rb2 in a high intensity optical centrifuge Juan Manuel García Garrido, *Universidad de Granada*
13:15h – 13:30h	**Oral Communication (p. 35)** Ultrafast, all-optical, and highly efficient imaging of molecular chirality via low-order nonlinear interactions Joshua Vogwell, *Imperial College London*

Scientific Programme

Thursday, 22nd February

13:30h – 13:35h	**Flash Communication (p. 36)** Probing tautomerism imine-enamine of nitrogen bases by the rotational study of 2-aminopyrimidine Jesús Fernández Sancho, *Universidad de Valladolid*
13:35h – 13:40h	**Flash Communication (p. 37)** Towards an Efficient SCF Algorithm for RDMFT Nicolas Cartier, *Vrije Universiteit Amsterdam*
13:40h – 13:45h	**Flash Communication (p. 38)** Domain-average Local Spin Densities Diogo José Lopes Rodrigues, *Universidad de Oviedo*
13:45h – 15:20h	**Lunch**
15:20h – 15:50h	**Plenary Lecture (p. 39)** Ultrafast Dynamics in Isolated Molecules, Molecular Clusters and Solutions Iker Lamas Frejo, *Euskal Herriko Unibersitatea*
15:50h – 15:55h	**Flash Communication (p. 40)** Development of embedded machine learning potentials for simulations of enzymatic catalysis Valentin Gradisteanu, *Universitat de València*
15:55h – 16:00h	**Flash Communication (p. 41)** Development of multifunctional architectures to target G4s and deliver anticancer drugs Maria Amparo Lopo March, *Instituto de Ciencia Molecular – Universitat de València*
16:00h – 16:05h	**Flash Communication (p. 42)** Time-resolved X-ray spectroscopy as a tool to unravel elusive intermediates of catalysts and photosensitizers used in H2 reduction processes Lucía Velasco, *Instituto de Ciencia de Materiales de Madrid – CSIC*
16:05h – 16:20h	**Oral Communication (p. 43)** Computational Characterization of the Toxicity Mechanism of Dioxins: Membrane Permeation and Binding to the AhR Protein Lorena Ruano de Domingo, *Universidad Autónoma de Madrid*
16:20h – 16:35h	**Oral Communication (p. 44)** A Gaussian Mixture Model Approach for the Automated Construction of Chemical Features Miguel Gallegos, *Universidad de Oviedo*
16:35h – 16:50h	**Oral Communication (p. 45)** Fusion Plasma Diagnostic Driven EUV Spectral Analysis of Ionized Kr Gas Atom Shivam Gupta, *National Institute for Fusion Science, Japan*
16:50h – 17:05h	**Oral Communication (p. 46)** DNA-grafted Metal-organic Frameworks: The key parameters for robust synthesis of stable nano-formulations Anargyros Drolapas, *Instituto de Ciencia Molecular – Universitat de València*
17:05h – 17:35h	**Coffee break**
17:35h – 17:50h	**Oral Communication (p. 47)** Many-body modelling of vibronic coupling problem in crystals displaying degenerate electronic states Toraya Fernández Ruiz, *Universidad de Cantabria*
17:50h – 18:05h	**Oral Communication (p. 48)** In vitro study of the phototoxic potential and photosensitizing properties of a topical retinoid Juan Antonio Soler, *Instituto Universitario Mixto de Tecnología Química – UPV-CSIC*
18:05h – 18:20h	**Oral Communication (p. 49)** DNA distortion mechanisms of novel cisplatin-ferrocene derivatives: predicting cancer drugs cytotoxicity through molecular dynamics simulations Francisco Javier Ortín Fernández, *Universidad Autónoma de Madrid*
18:20h – 18:35h	**Oral Communication (p. 50)** Spin crossover in K_2CuF_4 and Cs_2AgF_4 layered perovkites Inés Sanchez-Movellán, *Universidad de Cantabria*

Scientific Programme

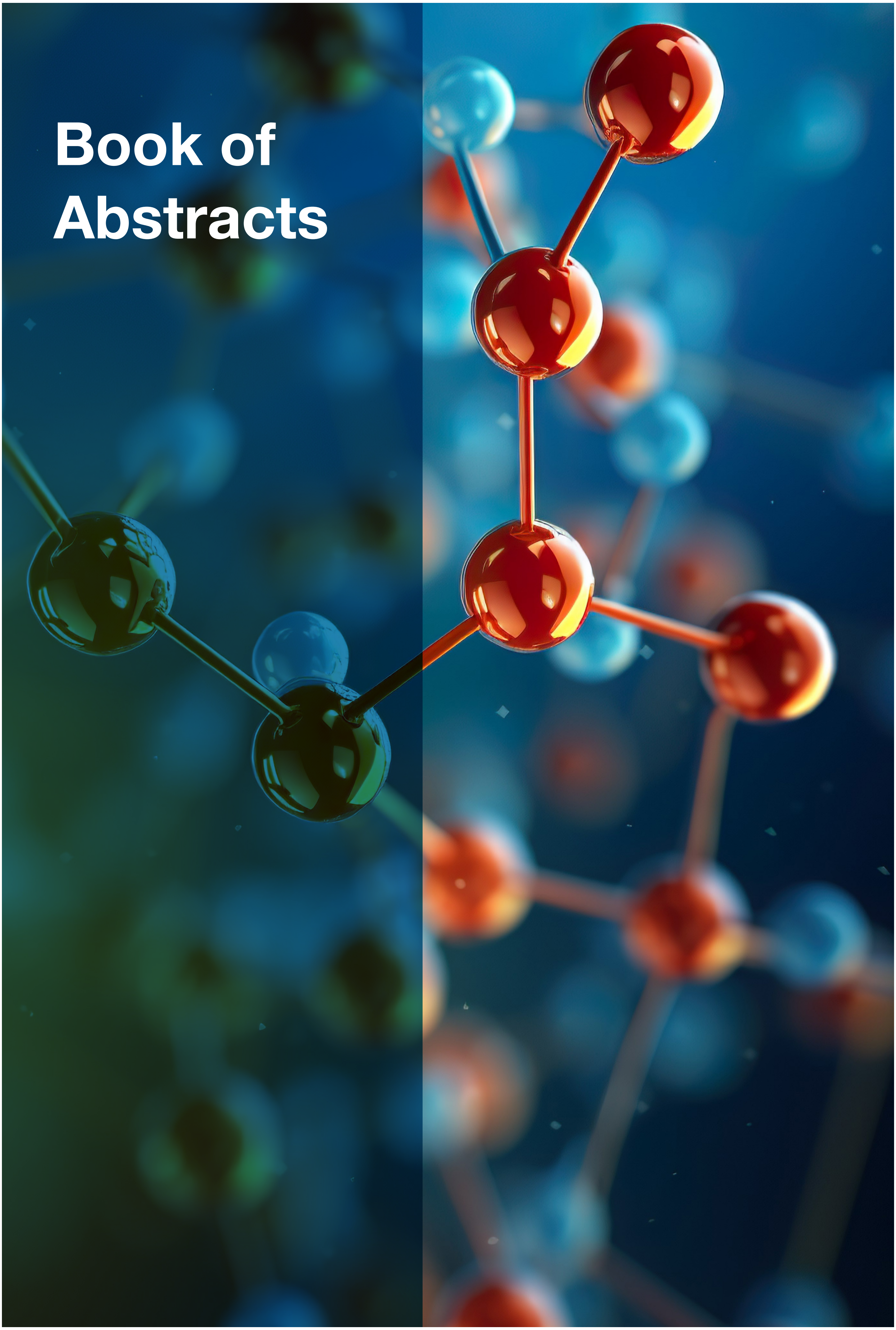
Friday, 23rd February

08:30h – 08:35h	**Flash Communication (p. 51)** Structural determination of Dibenzothiophene with Broadband Rotational Spectroscopy Farha Sajeev Hussian, *Universidad de Valladolid*
08:35h – 08:40h	**Flash Communication (p. 52)** Revealing the Influence of Substituents on the Selectivity of [3+2] Cycloaddition between Azides and Nitriles from the Molecular Electron Density Theory (MEDT) Perspective Noura Aflak, *Université Cadi Ayyad*
08:40h – 08:45h	**Flash Communication (p. 53)** Study of two-dimensional elemental tellurium through density functional theory for spintronic applications Axel Melchor Gaona Carranza, *Instituto de Ciencia Molecular – Universitat de València*
08:45h – 09:00h	**Oral Communication (p. 54)** Driving and Imaging Achiral-to-Chiral Transitions in an All-Optical Setup Edward Binns, *Imperial College London*
09:00h – 09:15h	**Oral Communication (p. 55)** Simulating the photofragmentation of cyclobutanone using non-adiabatic dynamics methods Alberto Martín Santa Daría, *Universidad de Salamanca*
09:15h – 09:30h	**Oral Communication (p. 56)** Understanding the formation of poliaromatic compounds in the interstellar space (ISM) Marta Castiñeira Reis, *Center for Research in Biological Chemistry and Molecular Materials – Universidad de Santiago de Compostela*
09:30h – 09:45h	**Oral Communication (p. 57)** Understanding COX-2 for the Design of New Cancer Drugs: Computational Study with Specific Photochromic Compounds Álex Pérez-Sánchez, *Universitat Autònoma de Barcelona*
09:45h – 10:00h	**Oral Communication (p. 58)** The Electronic Absorption Spectra of Ce(III) aqueous solution: A theoretical study including average statistical ingredients Gema Raposo-Hernández, *Universidad de Sevilla*
10:00h – 10:15h	**Oral Communication (p. 59)** A high-pressure study on the effects of pressure-transmitting media on $Bi_{14}MoO_{24}$ and $Bi_{14}CrO_{24}$ compounds Pablo Botella Vives, *Instituto de Ciencia de Materiales – Universitat de València*
10:15h – 10:45h	**Coffee break**
10:45h – 11:00h	**Oral Communication (p. 60)** MXenes as heterogeneous catalysts. Computational insight into the regioselective anti-Markonikov hydroamination of terminal alkynes Pablo García-Aznar, *Instituto Universitario Mixto de Tecnología Química (UPV-CSIC)*
11:00h – 11:15h	**Oral Communication (p. 61)** A real space study of the hydrogen bond Alberto Fernández Alarcón, *Instituto de Ciencia Molecular – Universitat de València*
11:15h – 11:30h	**Oral Communication (p. 62)** Graphene oxide reduction through the change on its nanoscale properties Víctor Camús Hernández, *Instituto de Ciencia de Materiales – Universitat de València*
11:30h – 11:45h	**Oral Communication (p. 63)** Cytosine derived etheno adducts: study of their photoreactivity and photochemistry Carlos Montero Galán, *Instituto Universitario Mixto de Tecnología Química (UPV-CSIC)*
11:45h – 12:00h	**Oral Communication (p. 64)** Extending the Laboratory Measurements of 2-Aminooxazole by means of Millimeter Wave Spectroscopy Sergio Mato Domínguez, *Universidad de Valladolid*
12:00h – 12:15h	**Oral Communication (p. 65)** Solvatotuning of the slow magnetic relaxation through a single-crystal-to-single-crystal transformation in pentanuclear gadolinium(III)-nickel(II) molecular nanomagnets Nadia El Alouani-Dahmouni, *Instituto de Ciencia Molecular – Universitat de València*

Scientific Programme

Friday, 23rd February

12:15h – 12:30h	**Oral Communication (p. 66)** Dynamic evolution of surface states under illumination in single crystal perovskites Parmenio Boronat Sevilla, *Instituto de Ciencia de Materiales – Universitat de València*
12:30h – 12:45h	**Oral Communication (p. 67)** Oxidation product analysis of an α-pinene discharge by microwave spectroscopy José Ricardo Morán Cabezas, *Universidad de Valladolid*
12:45h – 13:00h	**Oral Communication (p. 68)** Molecular/2D hybrid heterostructures for magnonic applications Gonzalo Rivero Carracedo, *Instituto de Ciencia Molecular – Universitat de València*
13:00h – 13:15h	**Oral Communication (p. 69)** Tailoring magnetism in low-dimensional materials Alberto M. Ruiz, *Instituto de Ciencia Molecular – Universitat de València*
13:15h – 13:30h	**Oral Communication (p. 70)** Building tight-binding models for second-principles simulations employing finite differences in real-space Nayara Carral Sainz, *Universidad de Cantabria*
13:30h – 13:35h	**Flash Communication (p. 71)** Mapping electron presence: a study of QTAIM∩ELF intersections Daniel Barrena, *Universidad de Oviedo*
13:35h – 13:40h	**Flash Communication (p. 72)** Understanding the growth of Zr Multivariate Metal-Organic Frameworks Carmen Rosales Martínez, *Instituto de Ciencia Molecular – Universitat de València*
13:40h – 13:45h	**Flash Communication (p. 73)** Noble-Metal-Free Photosensitizer and Catalysts for CO_2 Photoreduction Ashok Ugale, *Instituto de Ciencia de Materiales de Madrid – CSIC*
13:45h – 15:20h	**Lunch**
15:20h – 15:50h	**Plenary Lecture (p. 74)** Design of computational strategies for the study of photo-induced reactivity in molecular clusters Darío Barreiro-Lage, *Aix-Marseille University*
15:50h – 15:55h	**Flash Communication (p. 75)** Rediscovering Strong-Field Effects in Ammonia Ignacio Martínez Casasús, *Universidad Complutense de Madrid*
15:55h – 16:00h	**Flash Communication (p. 76)** Modeling fragmentation of non-covalent molecular clusters in soft-ionisation mass spectrometry of deep eutectic solvents Swaroop Venkata Sai Kunapuli, *Université de Strasbourg*
16:00h – 16:05h	**Flash Communication (p. 77)** Unraveling ClOOCl: UV/Vis Absorption Spectrum, Cross Sections, and Photodissociation Channels for Enhanced Understanding of Ozone Depletion Mechanisms Cristina López Cava, *Instituto de Ciencia Molecular – Universitat de València*
16:05h – 16:20h	**Oral Communication (p. 78)** Geometrical optimization in fast photodissociation dynamics: the role of momentum Carlos García Arcos, *Universidad Nacional de Educación a Distancia*
16:20h – 16:35h	**Oral Communication (p. 79)** Oxyluciferin Emitters Force Field Parameterization for Ground and Excited-State Dynamics Henar Mateo de la Fuente, *Universidad Autónoma de Madrid*
16:35h – 16:50h	**Oral Communication (p. 80)** NEXT: A Search for the Neutrinoless Double Beta Decay Fabian Kellerer, *Instituto de Física Corpuscular – Universitat de València*
16:50h – 17:05h	**Oral Communication (p. 81)** Time Independent Close-Coupling Approach to Non-Reactive H_3^+ + H Collisions Daniel Félix González, *Unidad Asociada UAM-CSIC*
17:05h	**Closing Ceremony**



Book of Abstracts

Attosecond chemistry

Fernando Martín[1,2]

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From water to DNA, all chemical reactions involve breaking and forming bonds, in which atomic nuclei are forced to live close to each other or to separate forever. But this is the consequence of the way electrons move. Thus, chemical reactivity results from the combined action of the "fast" electronic motion and the "slow" motion of atomic nuclei. Following the motion of the latter was possible by the end of the twentieth century with the help of femtosecond laser pulses. With the advent of attosecond light pulses at the dawn of the twenty first century, access to the time scale of electronic motion, i.e., the ultimate time scale responsible for chemical transformations, was finally at our reach. This was accomplished in 2010[1] for the simplest molecule in nature, hydrogen, and, in 2014[2], for phenylalanine amino acid. Since then, the field has grown exponentially, leading to a discipline called attochemistry[3]. In this talk, I will review some of the most recent experimental and theoretical achievements in attosecond chemistry. All these guided by theoretical modelling[4], which has been an essential ingredient since the very beginning of this discipline. Attochemistry is still at its infancy, but its long-term goal, achieving control of chemical processes by acting on electronic motion at its natural time scale does not seem to be a remote possibility anymore[5].

References

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[2] F. Calegari, D. Ayuso, A. Trabattoni, L. Belshaw, S. De Camillis, S. Anumula, F. Frassetto, L. Poletto, A. Palacios, P. Decleva, J. B. Greenwood, F. Martín, and M. Nisoli, *Science,* **2014,** *346*, 336.
[3] M. Nisoli, P. Decleva, F. Callegari, A. Palacios, and F. Martín, *Chem. Rev.* 2017, *117*, 10760.
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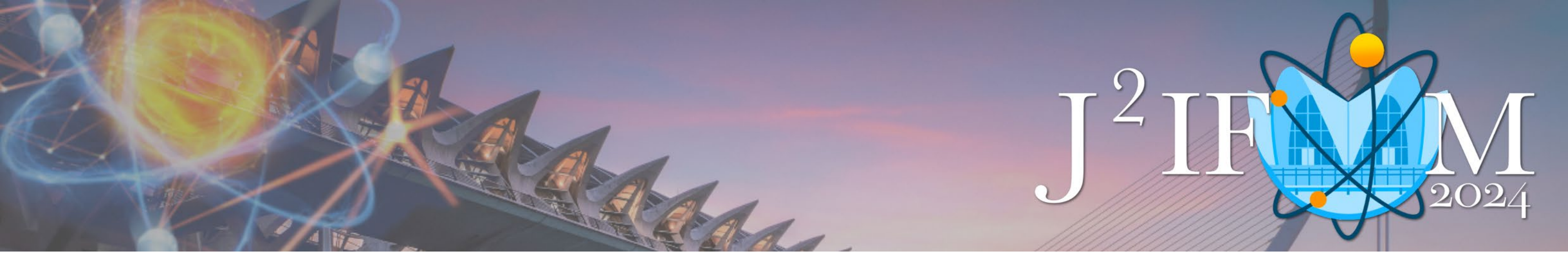
[5] F. Calegari and F. Martín, *Commun. Chem.* **2023**, *6*, 184.



Exploring the Structural Stability of Hydrated Potassium Carbonate at High Pressure and High-Temperature Conditions

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Knowledge of the phase stability of carbonates under extreme pressure and temperature conditions is crucial to understanding Earth's carbon cycle and the fate of carbon-based compounds in the Earth’s interior[1]. Moreover, natural processes suggest that carbon dioxide can be stably sequestered by mineral carbonation, making this methodology a potential route to control carbon pollution[2]. Our study aims to give insight into the ternary K_2O-CO_2-H_2O system, characterizing the structural behavior of the anhydrous K_2CO_3 and hydrous $K_2CO_3.1.5H_2O$ phases at different thermodynamic conditions[3,4]. We report the results of a joint experimental and computational study of the phase stability of these materials using in situ synchrotron powder X-ray diffraction measurements in resistive-heated diamond anvil cells plus density-functional theory calculations. Under cold compression, the sesquihydrate carbonate exhibits highly anisotropic compressibility (κ_a, κ_b, and κ_c being $7.62 \cdot 10^{-3}$, $4.97 \cdot 10^{-3}$, and $5.98 \cdot 10^{-3}$ GPa^{-1}, respectively) while maintaining its initial structure up to 14 GPa (2.72 $g \cdot cm^{-3}$). $K_2CO_3 \cdot 1.5H_2O$ is initially highly compressible with an experimental bulk modulus $B_0 = 20(3)$ GPa due to the existence of hydrogen bonds, but the bulk modulus rapidly increases upon compression ($B_0' = 13(2)$). This hydrated carbonate undergoes two reversible phase transitions after thermal activation (around 180 °C). In addition, we examined the structural behavior of anhydrous K_2CO_3 carbonate and identified a distinctive phase transition occurring above 6 GPa. These findings collectively advance our understanding of water's role in carbonate in extreme conditions.

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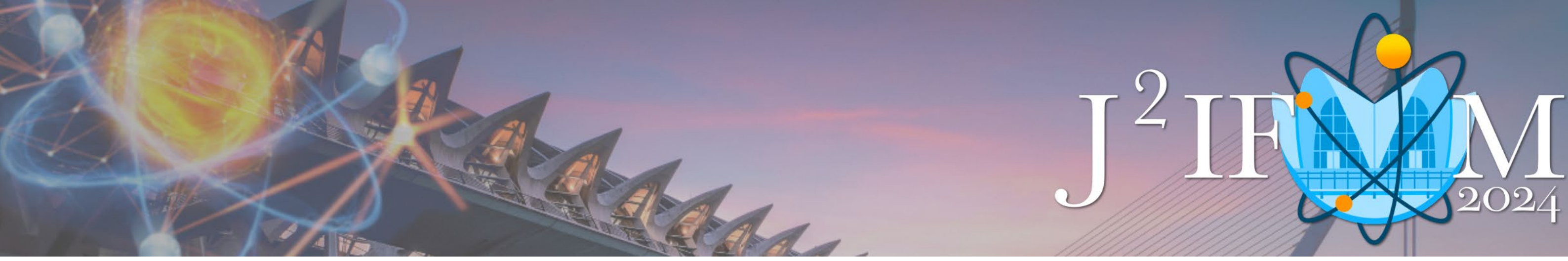

Characterization of Monomeric, Dimeric and Trimeric Zn (II) Phenanthroline Photosensitizers by X-ray Absorption Spectroscopy and Time-Resolved XAS

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In the aim of fighting against global warming, improving green energy technology is a main topic. Photochemical cells are such devices that doesn't involve any fossil energy consisting in an assembly of a photosensitizer to harvest sunlight and a catalyst to help the water splitting reaction into H_2 and O_2.[1] Lately, Zn (II) multinuclear complexes have been studied as it is a part of the $3d^{10}$ electronic layer transitions metals that implies an inter-ligand π- π* interactions and therefore the photochemical properties are controlled by the ligands leading to weak excited states energies. Phenanthroline used as bridging ligand for Monomer, Dimer and Trimer Zn complexes improve their molecular stability.[2] Within this work, the lifetimes of these three Zn complexes excited state in acetonitrile solution and in solid state have been probed by transient absorption spectroscopy with the time-Dependent Density functional Theory (TD-DFT) calculations to ascertain the correlation between experimental data and theoretical data. Also, X-ray absorption spectroscopy (XAS) has been carried out to scrutinize the electronic and geometrical structures of these complexes in direct comparison with DFT calculations.

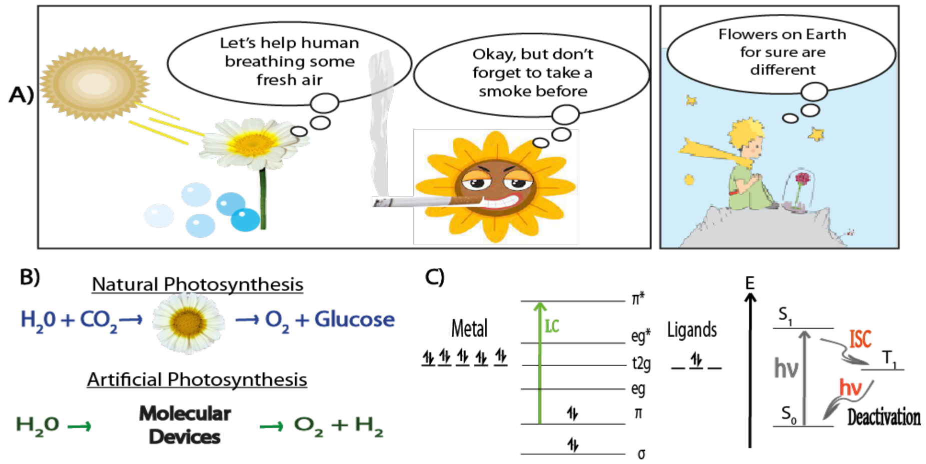

Figure. **A)** Natural Photosynthesis Picture, **B)** Artificial Photosynthesis scheme, **C)** Molecular Orbital (Left) and Jablonski diagram (right) of the Zn (II)-Phenanthroline molecule.

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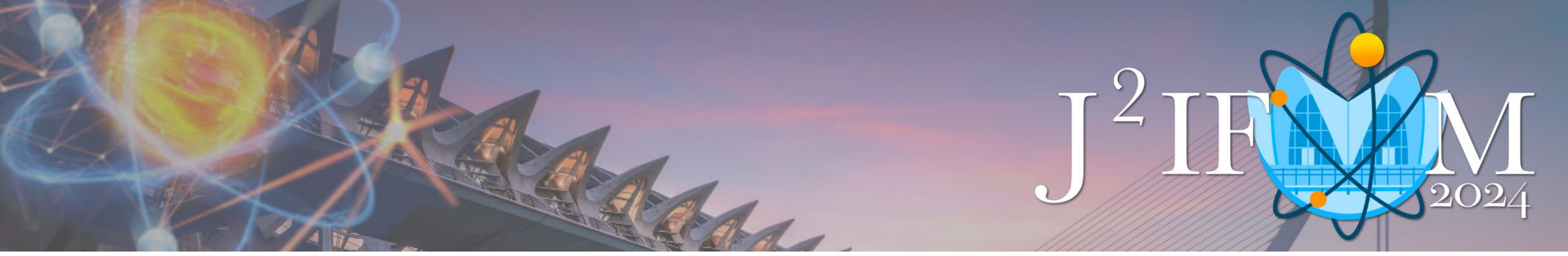

Development of correlation indicators

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Understanding molecules behavior relies on electronic structure methods, which are grouped by their ability to account for dynamic or nondynamic electron correlation effects. Accurately portraying molecular systems depends on wisely choosing a suitable electronic structure method. Specifically, when dealing with systems with predominant nondynamic correlation (known as multireference or MR), using single-reference methods can lead to major errors in describing the molecule's properties and energies. In an era dominated by the generation of extensive molecular datasets requiring computational treatment, there's a growing demand for affordable methods to identify multireference characteristics. Unfortunately, as far as we know, there are no cost-effective tools available for a quick assessment of a molecule's multireference nature.

Recently, we have conducted a thorough analysis of wavefunction theory based MR diagnostics using extensive datasets [1], identifying a single well-behaved representative metric of electron correlation that could be employed in single-reference wavefunctions. In this work, we present the extension of the multireference diagnostic to be applied in density functional theory. We used machine learning to establish a map between Kohn-Sham orbital energies and the MR character of the molecule, achieving an excellent agreement with the predictions furnished by MP2 and CCSD calculations.

This work thus offers an economical approach requiring a single DFT calculation to assert the MR character of a molecular system, showcasing its potential as a cost-effective, high-accuracy solution for the detection of strong correlation.

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A Comparative Study of the Reaction Mechanism in hASNase3 and gpASNase1 using Multiscale Simulations

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L-asparaginases (ASNases) are a group of enzymes catalyzing asparagine (Asn) hydrolysis reaction to aspartate (Asp). They play a significant role as a powerful treatment for acute lymphoblastic leukemia (ALL) due to the fact that ALL cells are unable to produce their own Asn and therefore the hydrolysis of Asn in blood can lead to their death.[1] Due to the immunogenic response and various side effects of enzymes of bacterial origin, many experimental attempts have been made to replace enzymes of bacterial origin with mammalian enzymes such as human asparaginase (hASNase) and guinea pig asparaginase (gpASNase) of types 1 and 3.[2]

This study investigated the mechanistic proposals of hASNase3 and gpASNase1 through molecular dynamics simulations, QM/MM, and the Adaptive String Method.[3] Molecular dynamic simulations revealed that the dimeric form of the hASNase3 plays a vital role in stabilizing the substrate in the active site, despite the active site residues stabilizing the substrate originated from a single protomer. Similarly, our results indicated tetramer as the active form of the gpASNase1, given that our simulations did not show any instabilities while the simulations on the dimeric gpASNase1 performed by others[4] reveled the substrate leaving the active site after a few nanoseconds.

Our QM/MM simulations, performed at the GFN2-xTB/MM level of theory, indicated that the enzymatic cycle of both enzymes, share several common features and that similar residues are being involved in the catalysis. Enzymatic cycles of both enzymes be divided into two parts: (i) formation of the acyl-enzyme (covalent bond within the catalytic threonines) and (ii) hydrolysis of the acyl-enzyme by a water(s) molecule(s). The rate-determining steps were found to be in the good agreement with the experimentally obtained free energy values in both enzymes. Furthermore, great consistency between the theoretically obtained tetrahedral acyl-enzymes structures in both enzymes with the X-ray structure provided further verification of the proposed mechanisms.

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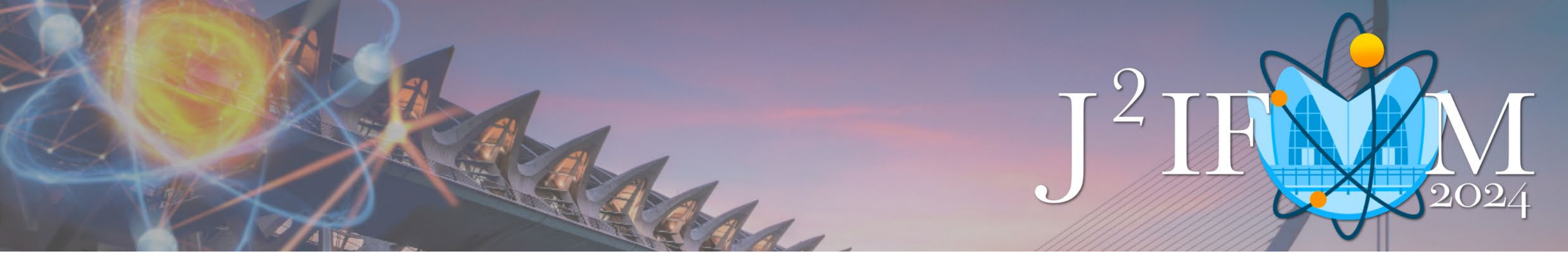

AB INITIO INVESTIGATIONS ON HYDROGEN BOND INTERACTIONS OF 1:1 THEOBROMINE-WATER COMPLEXES

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Theobromine, a derivative of caffeine commonly present in chocolates, tea plant leaves, cola nuts, cocoa, guarana berries, etc., has garnered significant scientific interest for its diverse biological and pharmacological properties.[1,2] As a heterocyclic molecule, Theobromine exhibits multiple potential sites that can function as either hydrogen bond (H-bond) donors or acceptors when interacting with other biological molecules.[3] To develop the fundamental understanding about the nature of interaction of these active sites, we have studied here the 1:1 interaction of Theobromine molecule with water molecule. The electrostatic potential energy surface of 1:1 interaction between Theobromine and water molecule has been explored using MP2 and wB97XD level of calculations with 6-311++ G(d,p) basis set. Through a comprehensive search, seven distinct structures of the 1:1 complex involving various H-bond interactions (O-H---O, N-H---O, O-H---N, and C-H---O) have been identified. Dual H-bond interactions play a crucial role in stabilizing all the structures, with the configuration featuring O-H---O and N-H---O interactions representing the global minimum in stability. Conversely, the structure involving C-H---O interactions is found to be the least stable. Also, NBO analysis has also been performed to reveal the role of hyperconjugation interaction in the stability of the complexes. Charge density topology for each complex has been analyzed using AIM calculations. Tautomerization barriers have also been calculated for Theobromine monomer and its wáter complexes, revealing a substanial reduction in the barrier height in the presence of wáter molecules as opposed to the monomer.

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Tailoring High Entropy Oxides (HEOs) as Emerging Radiative Materials for Green Energy Saving Buildings

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Passive radiative cooling is a natural nocturnal phenomenon that can cool surfaces without energy consumption. Mimicking this natural process, daytime passive radiative cooling (DPRC) has been proposed as a very appealing mechanism for abating urban overheating and reducing the consequent thermal comfort deterioration in the built environment. This is possible because only a fraction of the thermal radiation ($8 - 13\ \mu m$, atmospheric window band) can penetrate the atmosphere to outer space. For that reason, in order for the heat to be released into the universe through the sky window, the IR radiation of the cooled object through this spectral range needs to be maximised. Adequate passive coolers should then reflect most of the incoming UV/ Vis/NIR radiation while dissipating excess heat selectively in the specific waveband range of the atmospheric window in order to achieve an efficient cooling performance. In the present work, we propose first-principles DFT calculations as an effective tool for advanced material design and development in the field of radiative cooling[2]. We therefore expanded the possible technological applications of HEOs, an emerging class of materials, investigating their potential for daytime passive radiative cooling applications, exploring the possible benefits of this relevant technology that could effectively mitigate the detrimental urban overheating effects and reduce anthropogenic CO_2 production as well as electricity consumption.

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Looking for the Good Vibrations: Tuning Focused Ultrasounds for Lipid Membrane Therapy.

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Lipid membranes are ubiquitous in nature since they constitute the envelope of every cell, the elementary form of life, and play crucial roles in processes like protein anchoring and folding[1], signal modulation[2], matter transport[3] and cell motility[4], among others. Moreover, the lipidic composition of membranes displays great variability depending on factors such as cell type or disease.

These differences open up a window for the targeting of specific cells using techniques such as mechanotherapy, of which Focused Ultrasounds (FUS) are a promising alternative to conventional procedures. Following a previous work[5], we have studied the influence of the amplitude and frequency of FUS on lipid membranes at the molecular level using Non-Equilibrium Molecular Dynamics. Our results shed light on how choosing the correct FUS parameters can have a great impact on the response of cellular membranes, as well as the nuances introduced by the specific lipid composition.

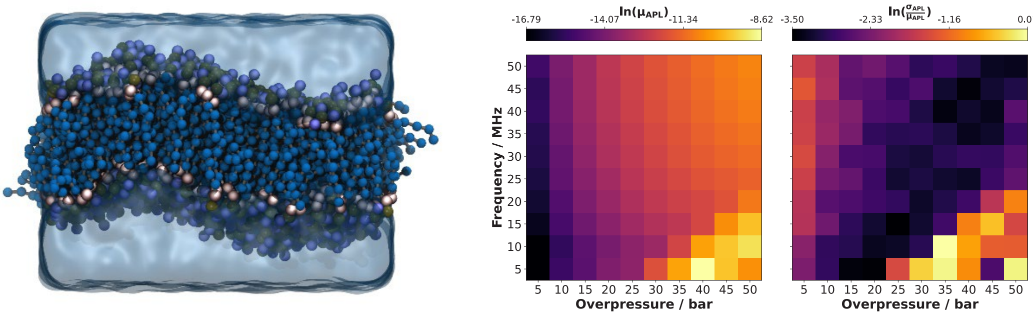

Figure 1. Molecular representation of a lipid membrane at an instant of low pressure (left), and response surface of the membrane's Area per Lipid as a function of overpressure and frequency (right).

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A step towards quantum dynamics in tetraphenylpyrazine molecular crystals

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Photodynamic therapy (PDT) for cancer treatment is based on the interaction between photosensitizers, light, and molecular oxygen. Traditional photosensitizers face limitations in their aggregation state, lowering emission efficiency. To overcome this, Aggregation-induced emission luminogens (AIEgens), like tetraphenylpyrazine (TPP), have been introduced.[1] AIEgens increase their quantum yield when aggregated, improving PDT efficiency.

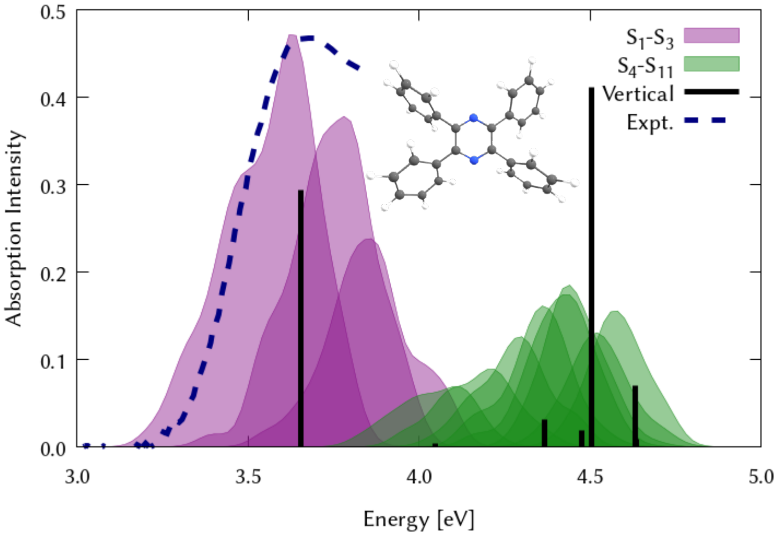

Figure 1. Vertical absorption spectrum of TPP calculated with TD-DFT.

This study delves into the excited state quantum dynamics of the TPP molecule in gas phase. For this purpose, a Linear Vibronic Coupling (LVC) method was used to approximate the potential energy surfaces (PESs) and the nuclear dynamics was carried out using the ML-MCTDH method as provided by the QUANTICS package.[2] This approach allowed to calculate the non-adiabatic dynamics for TPP across 144 vibrational normal modes. Future research aims to expand the system size to further elucidate mechanisms of aggregation-induced emission in AIEgens.

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Sunbathing with the enemy:
theoretical assessment of the photostability of *p*-aminobenzoic acid

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Para-aminobenzoic acid is a formerly used UVB filter that was found to react with the DNA when exposed to sunlight.[1] Molecular Dynamics (MD) simulations show that the neutral species of PABA binds favourably DNA by intercalation between two nucleobase pairs. Simulation of the joint PABA-DNA absorption spectrum by Quantum Mechanics/Molecular Mechanics (QM/MM) calculations on top of a MD ensemble of geometries, followed by transition density matrix analysis, suggests that charge transfer states could play a role in the deactivation of the system and lead to the formation of radical species that might trigger DNA lesions.[2] Moreover, the identification of relevant deactivation routes of excited PABA in vacuum revealed the favourable population of a long-lived triplet state, which can participate in photosensitising mechanisms, such as energy transfer processes to thymine or to molecular oxygen,[3] thus potentially explaining the reported phototoxicity of PABA in the DNA environment.

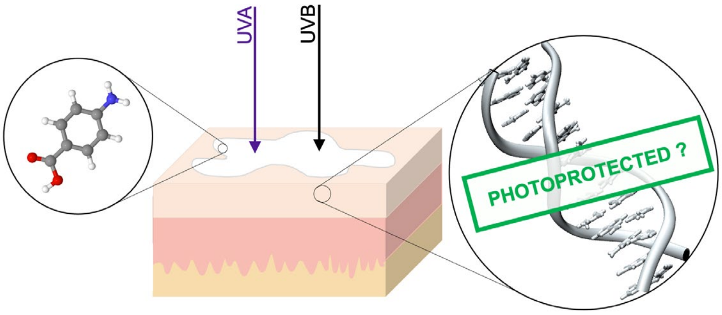

Figure 1. Graphical representation of the unclear photoprotective effects of a PABA-based sunscreen applied on skin.

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Theoretical Spectroscopic study of PH^+.

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The astrochemical studies of the P-bearing molecules have attracted great interest in the latest years, since the increase of observations of these kind of molecules in several astrophysical objects. However, the chemistry of the P atom is neither very well-known nor well understood, making it difficult to develop chemical models to understand the origin of these molecules.[1] One of the possible triggers for the chemistry of the P atom are the phosphorous hydride molecules, supported by the great abundance of the H_2 of H_3^+ molecules.[2] To test the hypotesis and gather data on P chemistry, the main goal of this project is to study the formation and destruction processes of the different phosphorous hydrides and their cations. To start this project, we choose to focus first on the PH^+ diatomic molecule, with the objective of studying its photoionization from the PH radical. Hence, we have calculated the PECs of the first 9 low-lying electronic states with the Multireference Configuration Interaction (MRCI) method using the aug-cc-pV5Z basis set. We have also included the Spin-Orbit Coupling (SOC) to describe its effect in the curves. The PECs also allowed us to calculate the rotational and rovibrational spectra in the $X\ ^2\Pi$ state and the rovibronic spectra (which are unknown) with the $A\ ^2\Delta$ state, with and without including the SOC.

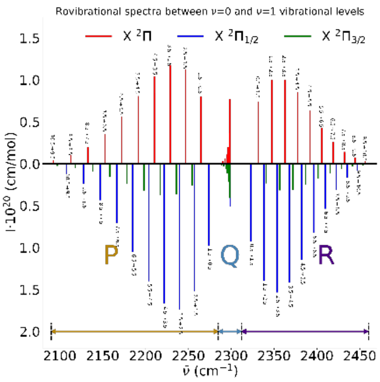

Figure 1. Rovibrational spectra of the $X^2\prod$ with and without including the SOC.

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An unexpected problem of astrochemical significance and a healing strategy

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Spectroscopy is one of the main tools astrochemistry uses day-to-day. The analysis of radiation coming from space can aid in a better understanding of our surrounding chemistry or even shed light on one of the most intriguing questions for humanity: the origin of life on Earth. In this regard, the computation of precise vibrational frequencies is essential to identifying interstellar species by modeling IR spectra. It could also help anticipate new ones not found thus far in the space. Nevertheless, several Ab Initio wave function methods fail to describe C=C multiply bonded systems accurately[1, 2], many of which are particularly relevant in studying the universe's chemistry. The problem manifests in wrong-optimized geometries or through the appearance of spurious vibrational frequencies. Moreover, the underlying cause of this issue is still unknown.

Among the methods presenting problems, we encounter some of the most accurate ones, such as the MPn or CC families. We have found that the cause behind the errors in such methods comes from the computation of some components of the energy second derivative, which is ultimately necessary to calculate the frequencies. We have also found that such a problem appears only in a subset of basis sets and that no noticeable trends exist among them. Our study evaluates and compares the different components of the energy derivatives in every frequency calculation to trace the origin of the problem.

Our other concern is to get rid of this spurious situation in a most general and easy manner. We demonstrate that floating functions (FF)[3] can reduce or eliminate such spurious behaviour. In some cases, only a few FF are necessary, making our method a cheap way to correct the initial problem since it demands minimal extra computational resources and can be generalized and easily implemented in standard code.

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The interplay of charge-transfer States in enhancing exciton diffusion

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Energy transport, specifically exciton diffusion, delineates the transfer of excess energy from an excited state between molecular sites. Within organic solar cells, exciton diffusion stands as a crucial process, yet it is one of the main bottlenecks for OPVs efficiency. Evaluating this process relies on the exciton diffusion length—a metric quantifying the distance an exciton travels during its lifetime. Recent decades have witnessed the emergence of highly ordered molecular systems, including tubular aggregates of cyanine dyes,[1] structured poly(di-n-hexylfluorene) and poly(three-hexylthiophene) (P3HT) nanofibers,[2] and N-heterotriangulene-based supramolecular fibers,[3] exhibiting exciton diffusion lengths surpassing 100 nm.

These advancements necessitate a novel theoretical framework because energy diffusion within these nanostructures challenges the conventional Förster hopping formalism. Hence, alternative mechanisms are required. Specifically, exploring the potential of charge transfer (CT)-mediated mechanisms, which have already proven pivotal in similar fields such as optical properties of aggregates or the singlet-fission process, becomes crucial. In this contribution, we delve into the impact of CT states on exciton diffusion, estimating how they contribute to the large exciton diffusion lengths observed in N-heterotriangulene supramolecular fibers.

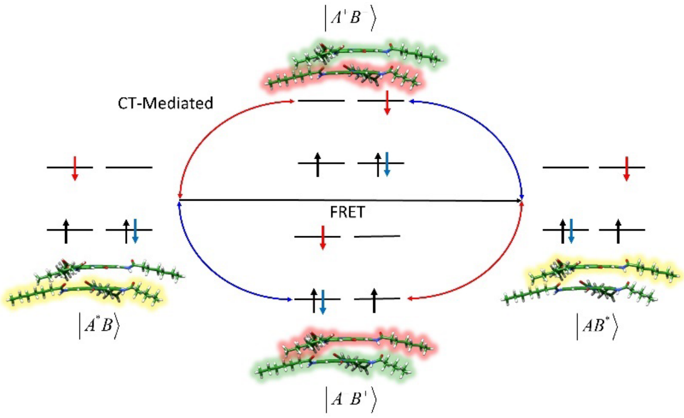

Figure 1. Scheme of direct Förster resonance energy transfer mechanism and alternative CT mediated mechanism.

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Binding and photoisomerization of *trans* and *cis* DAD in the Nav1.5 channel.

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Azobenzene derivatives are becoming increasingly popular in pharmacology due to their improved selectivity based on *trans-cis* isomerization upon light irradiation. In the context of ion channels, one of the conformations may block ion conduction, while the other allows it. We have studied an azobenzene derivative, DAD[1] (diethylamino-azo-diethylamino), designed with the aim of avoiding excitation wavelengths in the UV region. The binding pockets of *cis* and *trans* DAD in the cardiac sodium channel ($Na_V1.5$)[2] were obtained by means of Gaussian Accelerated Molecular Dynamics combined with free-energy calculations, showing different binding affinities between the two conformations. Comparison of the absorption spectra computed by QM/MM calculations on an ensemble of geometries reveals similar results in water and in the binding pockets. The photoisomerization calculated by TD-DFT shows an energetically more favourable process in the case of DAD. Aside from that, the mechanism is analogous to azobenzene: it begins with the population of the second excited state (S_2), fast internal conversion to S_1 and relaxation along the rotation of the azo dihedral to a S_1/S_0 conical intersection that connects the *trans* and *cis* geometries on the ground state.

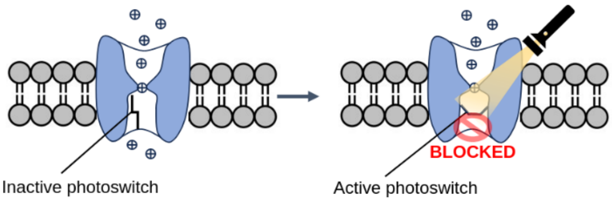

Figure 1. Graphical representation of the ion channel blocking induced by the photoisomerization of a photoswitch.

Acknowledgments: This work has been performed with the support of the TCCM consortium and FPI-UAM scholarships funded by Universidad Autónoma de Madrid. The computational resources from CCC-UAM are also acknowledged. Finally, we acknowledge the Spanish Ministry of Science and Innovation (PID2020-117806GA-I00) and Comunidad de Madrid (2022-5A/BMD-24244) for funding support.

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Molecular insights into zileuton: An asthma treatment drug revisited by rotational spectroscopy

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Zileuton is a benzothiophene-derived hidroxiurea which has been extensively studied for its implication as inhibitor of leukotriene production by targeting the 5-lipoxygenase enzime.[1] Hence, since leukotrienes are crucial part of some human diseases, zileuton has been proposed as a strong drug candidate, in particular for asthma treatments, for which it has been approved by the Federal Drug Administration since 1996.[2]

Here we have addressed the zileuton structure using computational methods and microwave spectroscopy. Theoretical calculations have included density functional predictions (B3LYP-D3 and B2PLYP-D3) and a triple-ζ Ahlrichs basis set (def2-TZVP). The rotational spectrum was recorded with a broadband chirped-pulse Fourier transform microwave spectrometer in a supersonic jet expansion, operating in the 2-8 GHz region.

Accurate spectroscopic parameters have been determined which allowed a univocal assignment of the preferential conformation of the zileuton molecule. More experimental details will be given in the conference which might help in the grasp of its biochemical properties.

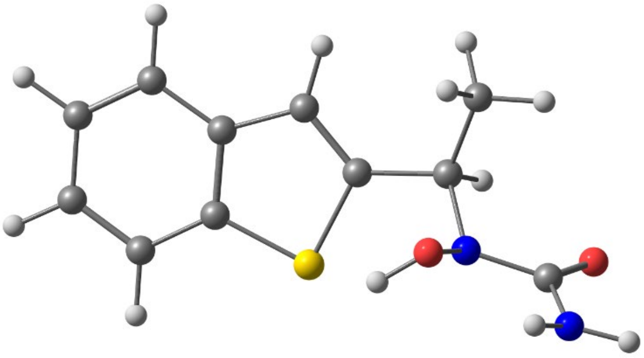

Figure 1. Zileuton preferential conformation according to quantum chemical calculations.

Acknowledgments: Funding from the Spanish MICIN-FEDER (PID202-125015NB-I00) is gratefully acknowledged

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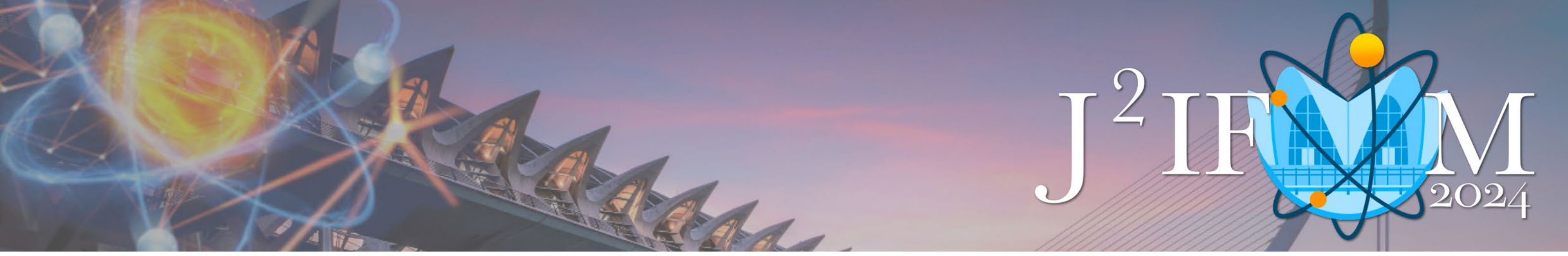

STOSS: A stochastical spin simulator for molecular nanomagnets

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Initial studies on molecular nanomagnets assumed that a simple Orbach process was the main relaxation mechanism at high temperatures, thus the focus was set on modelling the effective barrier (Ueff), (1) with a Quantum Tunneling of the Magnetisation (QTM) model being responsible for spin relaxation at low temperatures (2) including Raman with a key role of other relaxation mechanisms. Combining the previous idea and the correspondence between Binary Stochastic Neurons (3) and p-bits, we present STOSS (STOchastic Spin Sumulator), a microscopic simulator code for spin p-bits based on molecular nanomagnets. STOSS (4) is able to reproduce the most characteristic macroscopic magnetic dynamics of molecular nanomagnets, namely magnetization relaxation, and in-phase, out-of-phase susceptometry, by simulating the individual states in a collective of spin p-bits. Furthermore, we employed the code to simulate the thermal- and field- dependence of hysteresis in a novel endohedral metallofullerene.

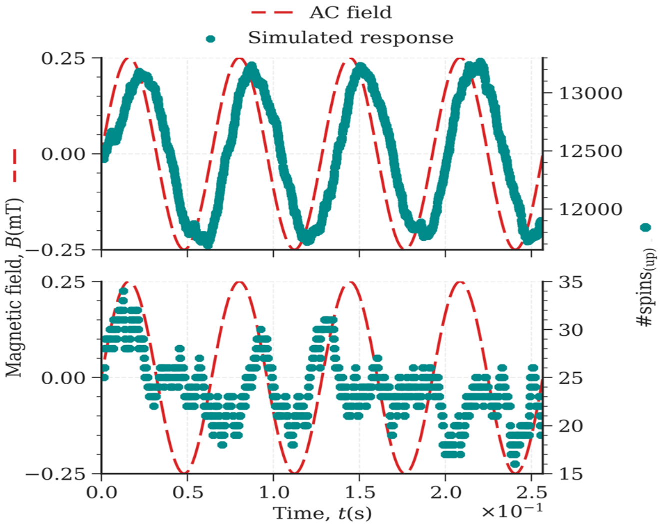

Figure 1. Periodically driven p-bits, when simulated by our Markov Chain Monte Carlo calculations, behave qualitatively as spins in an ac susceptometry experiment.

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Exploration of New Tri-biphenylamine-Based Systems for Sensing G-quadruplex DNA: A Biophysical and Computational Study

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Over the past two decades, G-Quadruplex (G4) DNA/RNA structures have gained significant attention among various alternative DNA conformations. These non-canonical secondary DNA structures form naturally under physiological conditions through the self-assembly of guanine-rich nucleic acid sequences. They are predominantly found in biologically critical regions, such as gene promoters and telomeres, which play vital roles in DNA replication, gene transcription, and genome maintenance. However, their precise biological roles remain poorly understood. Emerging evidence suggests their significance in neurological diseases, the aging process, and cancer[1]. Consequently, G4 structures have been proposed as potential targets for therapeutic intervention. Several strategies have emerged to tackle their formation in cells, including the use of antibodies and small molecular probes[2-3].

Our research team embarked on a project involving G4 probes based on the triphenylamine scaffold, resulting in the identification of two ligands exhibiting strong interaction and selectivity for G4 structures[4-5]. In this context, we present our synthetic endeavors to create a second generation of extended triphenylamine-based molecules with an expanded aromatic core. This expansion aims to enhance their photophysical properties for bioimaging. In addition to the previously reported NBTE[6], a molecule featuring a triphenylamine core with three ethylenic chains in the para position, we have developed its methylated versions with the amine in the para (TPPA-4pyrM) and meta (TPPA-3pyrM) positions.

To investigate their potential application as probes, we employed a range of biophysical assays, including FRET melting, fluorescence spectroscopy, and molecular modelling. Overall, our findings underscore the significance of the organic core, the expanded aromatic framework, and the aliphatic conjugation in obtaining selective G4 DNA ligands with optimal fluorescent emission properties.

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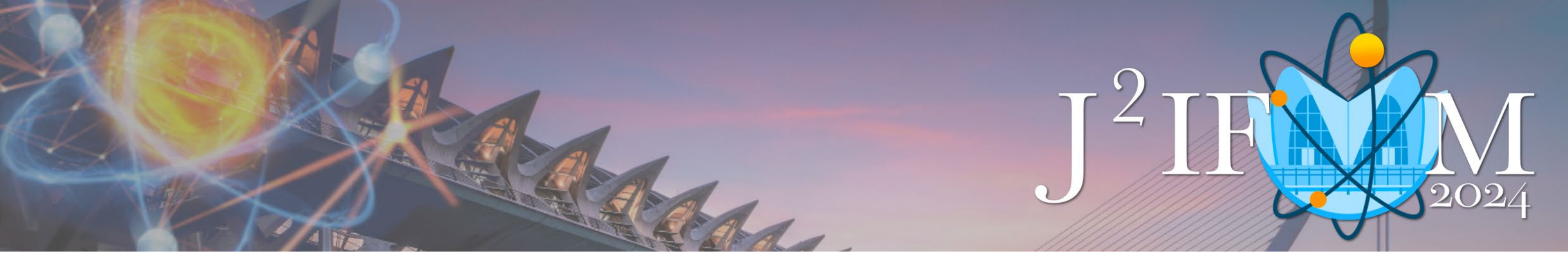

Photophysical exploration of monomeric and dimeric canonical nucleobase derivatives

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DNA, a fundamental biomolecule for life, comprises nucleobases, organic compounds susceptible to electronic excitations upon exposure to UV light. Such transitions can induce hazardous processes, which can potentially lead to genetic information loss due to DNA damage.[1,2] This communication focuses on the scrutiny of the photophysics of 2,6-diaminopurine, an adenine analogue, in order to stablish its differences with canonical nucleobases and understand the electronic foundations behind their photophysics.

Not only the 2,6-diamunopurine monomer has been studied, but also different dimer structures formed with thymine, the natural counterpart of adenine in canonical DNA, were considered. The photophysics of the monomer, four different stacked dimers considering the backbone and a Watson-Crick dimer were studied resorting to either MCSCF or TD-DFT methods. The aim of this work is to study the differences between the isolated nucleobase and the multiple-base species when exposed to UV light, since it is known that isolated canonical nucleobases deactivate in an ultrafast manner[3] whereas dimers may present longer-lived excited states due to the existence of charge-separated states.[4]

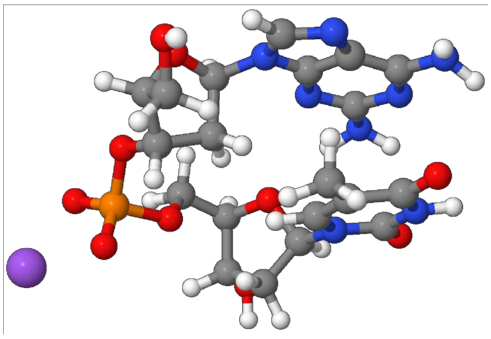

Figure 1. 2,6-diaminopurine-thymine dimer with the backbone structure.

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Electronic excitation and ultrafast charge transfer in nitrothiophenol molecules adsorbed on a gold surface

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Light induced chemistry on reactants adsorbed on metal surfaces or nanoparticles supposes a new approach to heterogeneous photocatalysis. One recent example is the dimerization of p-nitrothiophenol (4NTP) adsorbed on gold nanoparticles[1]. Activation of the metal plasmon, heating and electron transfer from the metal to the molecules are processes that might play a role in the reaction, but the mechanism is not clear. In this work, we analyze the differences in the geometry and in the electronic structure when one or two 4NTP molecules are adsorbed onto a gold surface. We also study the properties of electronic excited states localized on both organic interfaces, characterizing their energy, lifetime, and resonant wave functions. Moreover, investigate the ultrafast molecule-to-surface electron transfer explicitly by means of electron dynamics. The calculations were performed using the density functional theory calculations to compute the static electronic structure and a wavepacket propagation technique[2] to study the electron dynamics.[3] By calculating the properties of electronic excited states located in the molecules it is possible to shed light on the first stages of the reaction and to infer the role played by such states in activating the dimerization process.

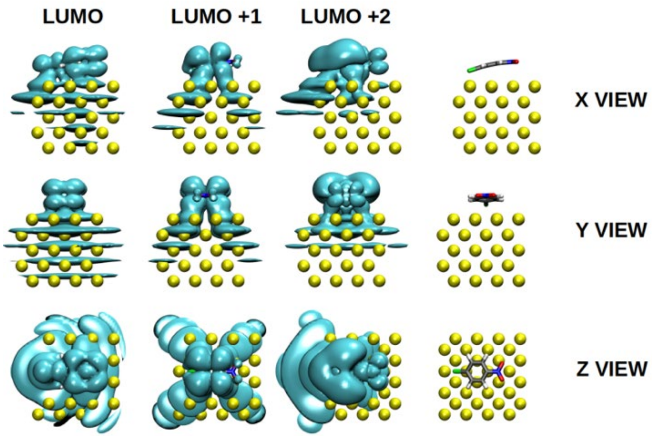

Figure 1. Representative excited molecular orbitals of 4NTP adsorbed on Au(100).

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Change in the Λ-doublet population due to dynamical effects: the O(^{3}P) + D$_2$ → OD(^{2}Π) + H reaction

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The O(^{3}P) + D$_2$ → OD(^{2}Π) + H reaction takes place on two concurrent Potential Energy Surfaces (PESs) of symmetries ^{3}A' and ^{3}A''. These states are degenerate for collinear configurations and this degeneracy is broken for non-collinear approaches. Given the shape of these PESs, we could predict that the ^{3}A' surface should be less reactive than the ^{3}A'' one. Recently, we have presented a method[1-2] to calculate the Λ-doublet ratio when concurrent PESs participate in the reaction. This method could reproduce the experimental Λ-doublet populations via explicit consideration of the stereodynamics of the process. Our results showed that the different mechanism on the two concurrent PESs causes the propensity of the Π(A') Λ-doublet states.

Here we present a computational study of the O(^{3}P) + D$_2$ reaction from the deep-tunnelling regime to hyper-thermal energies by using Quantum Scattering calculations.[3] For this, we have obtained the quantum differential cross sections (QM-DCS) and the quantum generalized deflection functions on both PESs. Our calculations characterize the reorienting mechanism and demonstrate that at high energies the preference for the Π(A') states is caused by an increase of the reactive flux at sideways angles and high partial waves on the A'' PES.

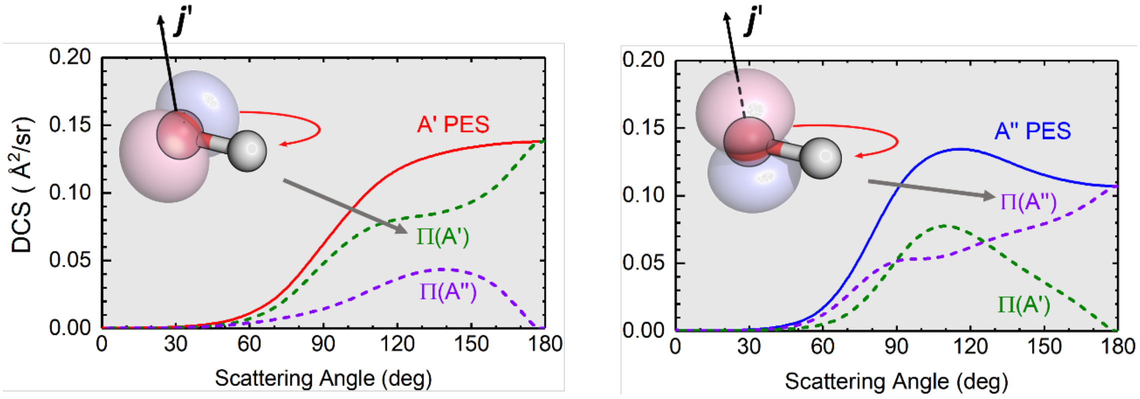

Figure 1. QM-DCS resolved on the two Λ-doublet manifolds for the O(^{3}P) + D$_2$ (v=0, j=0) reaction at E$_{coll}$ = 1.0 eV.

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Exploring the microsolvation and conformational dynamics of pyruvic acid in the gas phase

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The conformational landscape of small organic acids and their complexes provides valuable insights into their behavior in various environments. One of the most important carboxylic acids is pyruvic acid, a simple alpha-keto acid, which plays a significant role in atmospheric chemistry, influencing aerosol formation, cloud properties, and ultimately, climate.[1] Using chirped-pulse Fourier transform microwave (CP-FTMW) spectroscopy,[2] we have studied the structural behavior of pyruvic acid after the addition of individual solvent molecules (water and 2,2,2-trifluoroethanol). This technique allows for the detection of a large number of conformations in an isolated environment, facilitating the unambiguous identification of conformers, tautomers, isotopologues, and enantiomers. Based on the previous rotational study of the structures of the pyruvic acid-water complexes,[3] our investigation has been instrumental in elucidating the intermolecular interactions involved, revealing a greater tendency for water molecules to bind to a single hydration site, specifically the hydroxyl and carbonyl groups of the ketone. The cluster with 2,2,2-trifluoroethanol is estabilized by interactions with the carbonyl and methyl groups. This study underscores the importance of microwave spectroscopy as a tool for the experimental structural elucidation of microsolvated complexes in the gas phase.

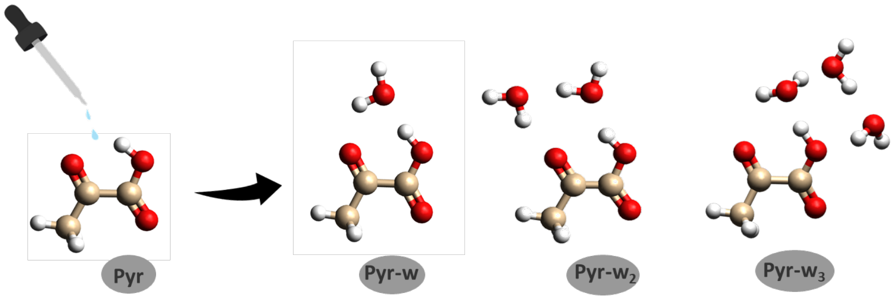

Figure 1. The addition of water molecules to pyruvic acid.

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Tuning the emissive properties of push-pull systems via the restricted torsion of *N*,*N*-disubstituted amino moieties

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The control of the optical and optoelectronic features of push-pull systems by modulation on the donor and acceptor moieties is an interesting way to achieve tailored properties that can be used in application for advanced functional materials.[1] We demonstrate here, a comprehensive investigation of the impact of the torsion angle of the *N*,*N*-disubstituted amino moieties on the emissive efficiency of two pull-push systems: **D1** and **D2**.[2] A strong deactivation on the steady-state and time-resolved fluorescence properties of **D1** is observed as the polarity of the solvent increases whereas **D2** maintains its emission. Theoretical calculations agree with these findings and support the presence of a non-emissive twisted geometry for the lowest energy in polar solvents for **D1** while it is absent in **D2**. This research contributes to understanding the relationship between molecular structure and fluorescence properties of push-pull systems.

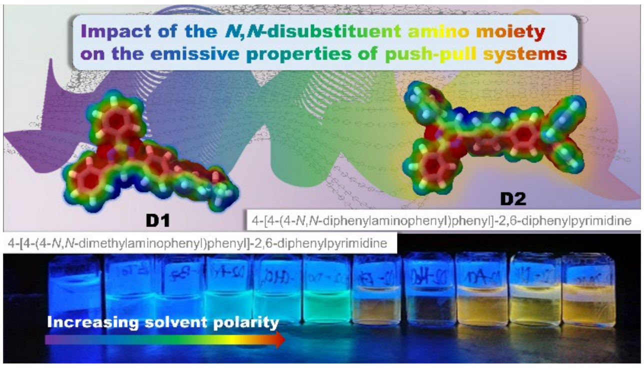

Figure 1. Impact of **D1** and **D2** on the emissive properties of push-pull systems.

Acknowledgments: We thank the MCIN/AEI of Spain (PID 2021-128569NB-I00, and CEX 2019-000919-M (predoctoral fellow: PRE2018-084294) and the Generalitat Valenciana (IDIFEDER/2018/064, IDIFEDER/2021/064, CIPROM/2022/57, PROMETEO/2020/077, MFA/2022/017, and MFA/2022/051).

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Rovibrational dynamics of Rb_2 in a high intensity optical centrifuge

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An optical centrifuge laser pulse consists on a linearly polarised pulse whose polarization axis describes an accelerated circular motion around its propagation axis. It has been shown that this kind of pulses favourishes rotational excitation due to the molecules rotating along them[1]. Taking Rb_2 as a prototype, we investigated rovibrational dynamics within the electronic state $^3\Sigma$ in a electric field produced by an optical centrifuge. Schrödinger equation was solved by including a time profile similar to the experimental laser pulse used by the group of V. Milner[2], considering peak intensities of the order of 10^{11} W/cm^2.

Peak intensity thresholds for vibrational transitions turned out to be lower for centrifuge pulses compared with non-modulated ones. Changing peak intensity in the latter so that they had the same energy as the former, vibrational spectrum was shown to be wider after centrifuge pulses, without significant change in rotational spectrum.

Regarding time evolution of bound states, for several initial rotational states (J_0=2, 4, 6, 14), transition rates to $J_0 \pm 2k$ states, with $k \in \mathbb{N}$, were very similar, and the difference between them reduced when J_0 increased. Besides, for ν_0=25 and J_0=0, population transitions to other vibrational bands was delayed when peak intensity was decreased.

Furthermore, considering a thermalised molecular set following a Maxwell-Boltzmann distribution, adiabatic behaviour appeared when we began in the ground state, but not for initial vibrational states far from it ($\nu_0 \lesssim 5$).

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Ultrafast, all-optical, and highly efficient imaging of molecular chirality via low-order nonlinear interactions

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Like a chiral glove either fits only our left *or* right hand, two enantiomers of a chiral molecule interact very differently with other chiral objects. Since most biological molecules are chiral, methods for observing and manipulating molecular chirality are of great importance, especially in biochemical and pharmaceutical contexts.[5]
Traditional chiral spectroscopy relies on the helix of circularly polarized light. However, the pitch of this helix is much larger than the molecules, leading to tiny enantiosensitivity (<0.1%). To overcome this, one can shape light's local polarization to drive chiral effects via electric-dipole interactions[2-4] with 100% enantiosensitivity. We bring this to the perturbative regime by combining sum-frequency generation (SFG) and third-harmonic generation (THG).
Here[1] we show how we can achieve full control over the intensity of SFG in randomly oriented chiral molecules by using interference between SFG and THG. By controlling the two-color phase delay in our setup (Fig. 1a), we control the field's local chirality, and thus the interference. Hereby, we can maximize emission at 266nm in one molecular enantiomer while fully quenching it in its twin (Fig. 1c).
Our approach enables ultrafast imaging of molecular chirality via low-order nonlinear processes, requiring gentler laser intensities, creating exciting opportunities for efficient chiral recognition in the liquid phase, the natural medium of biological molecules.

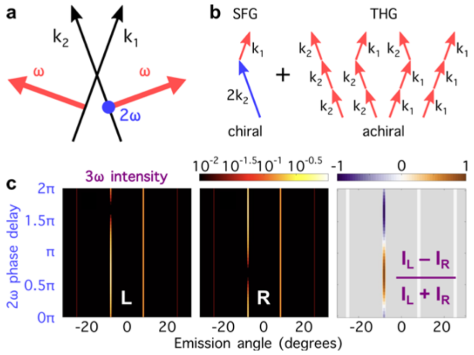

Fig. 1. **a**, Non-collinear setup combining linearly polarised ω and 2ω colors. **b**, Multiphoton diagrams of momentum conservation in chiral SFG (left) and achiral THG (right). **c**, Intensity emitted from left/right propylene oxide at frequency 3ω (266nm). TDDFT results; laser parameters: ω=0.057au. (800nm), opening angle 25º, $I_\omega=3\cdot10^{12}$Wcm^{-2}, $I_{2\omega}=7\cdot10^{11}$Wcm^{-2}, T=7fs.

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Probing tautomerism imine-enamine of nitrogen bases by the rotational study of 2-aminopyrimidine

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Intermolecular interactions among nitrogen bases are crucial for life, as they dictate the structure of nucleic acids such as DNA and RNA. The configuration of nitrogen bases and the tautomeric equilibria of nitrogen bases significantly impact the intermolecular interactions they can exhibit. This study focuses on the tautomeric equilibria imine-enamine: $R_1\text{-N=C}(R_2)\text{-NH}_2 \leftrightarrow R_1\text{-NH-C}(R_2)\text{=NH}$, which can be present in guanine and cytosine nitrogen bases. In 2-aminopyrimidine (Figure 1), we observe a similar type of tautomerism between the two nitrogens of the ring and the one outside the ring.

This research explores the influence of the presence of a second nitrogen in the tautomeric equilibria of nitrogen bases. The conformational/tautomeric behavior of 2-aminopyrimidine is unveiled through the analysis of its rotational spectra up to 110 GHz combined with quantum chemical calculations. This work expands upon a previous study[1] that was confined to the 25-40 GHz range, where the hyperfine structure was not resolved.

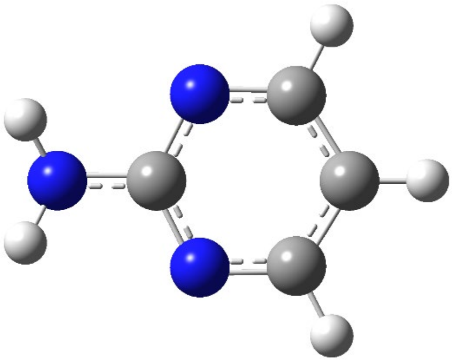

Figure 1. Most stable structure found for 2-aminopyrimidine evaluated at MP2/ 6-311++G(d,p).

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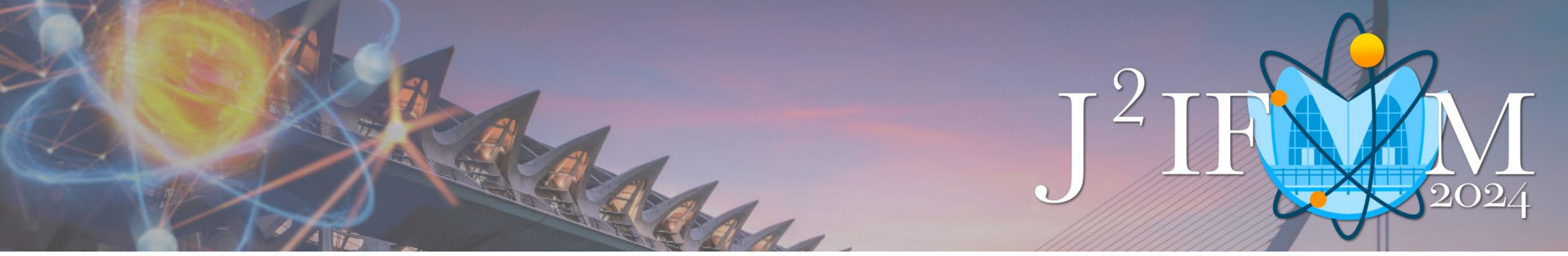

Towards an Efficient SCF Algorithm for RDMFT

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One-body reduced density matrix functional theory (RDMFT) provides an alternative to Density Functional Theory, able to treat static correlation[1] while keeping a relatively low computation scaling. However, this method is still not widely applied by the community because of its disadvantageous cost, which comes mainly from a slow convergence of the self-consistent energy optimization.[2] To improve on that problem, we propose to use the Hessian of the energy, including the coupling term between natural orbitals and natural occupations. In the same vein, we derive the expression of the exact Hessian, extract an affordable part from it, and test different approximations of the remaining expensive part.

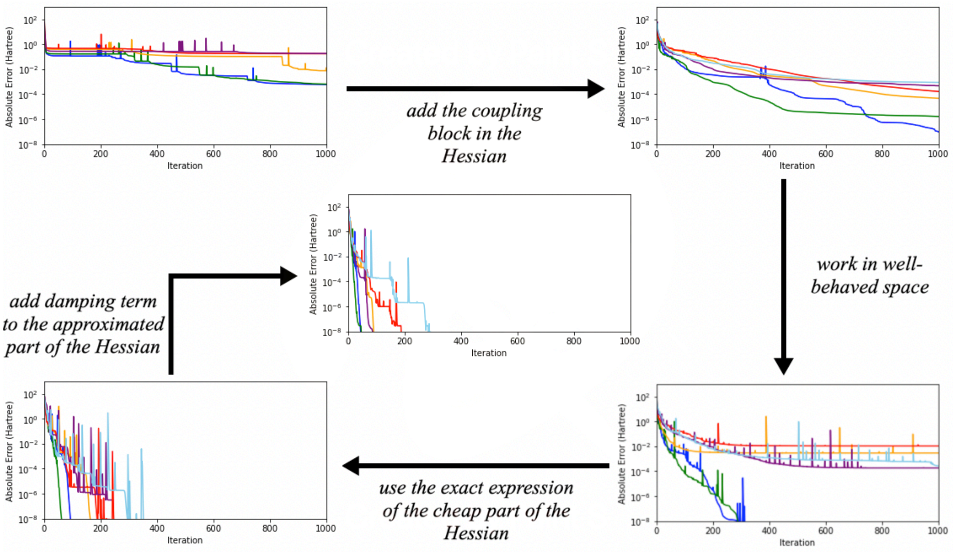

Figure 1. Energy convergence (absolute error with respect to the iterations) for increasingly efficient SCF algorithms in RDMFT, starting from a 'naive' algorithm. The different colors correspond to the convergence of different molecules (dark blue for H_2O, green for CH_4, yellow for CH_3OH, red for C_2H_6, purple for HF and light blue for N_2).

Acknowledgments: We thank the Dutch Research Council, NWO, for its support (Grant No. OCENW.KLEIN.434).

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Domain-averaged Local Spin Densities

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The partition of the expectation value of the squared electronic spin operator of a system into real space fragment contributions (local spins) is a topic that has been extensively investigated in recent years[1,2]. Local spins are particularly important in singlet di- or polyradicals, where the spin density vanishes identically thus precluding an easy access to the spatial distribution of up and down contributions. Projecting $<S^2>$ into real space domains provides a picture of the spatial distribution of this expectation value in a domain-averaged fashion that is independent of whether the spin density vanishes or not[1]. The partition of space for these local spins can be arbitrarily chosen, but it is especially interesting to use atomic domains or molecular fragments, which can be obtained with real space partition methods like QTAIM (Quantum Theory of Atoms In Molecules)[3].

In this work we built and implemented domain-averaged local spin densities, making use of the QTAIM partition of real space into atomic basins to: (i) draw conclusions from practical chemical examples, at different levels of theory; (ii) obtain insights into the properties of the local spin concept. The construction of local spin densities based on the theory of open quantum systems[1] is also planned.

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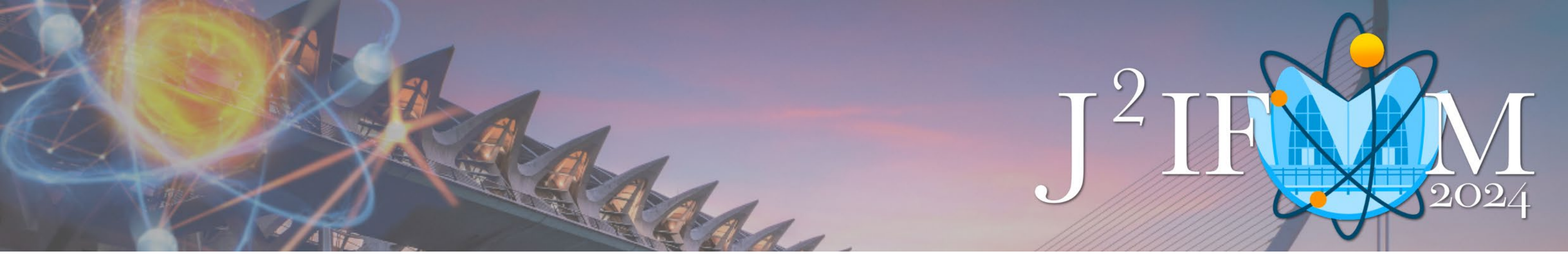

Ultrafast Dynamics in Isolated Molecules, Molecular Clusters and Solutions

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Photoinduced phenomena in molecular systems are, in general, governed by nonadiabatic processes, which result from a strong coupling between nuclei and electrons. Conical intersections are a particular case of these phenomena as they enable the ultrafast nonradiative population transfer through the coupling of electronic states with different character in sub-ps timescale. This is especially relevant in the photodynamics of aromatic biomolecules because these molecular systems present aromatic chromophores with bright ππ* states that can be efficiently photoexcited. Then, depending on the topology of the potential energy surfaces, the access to different conical intersections can be favored or inhibited, determining the ultimate behavior of the molecule after photoexcitation.[1,2] In this sense, time-resolved spectroscopic techniques make possible to monitor the photophysical and photochemical behavior of the system. However, attending to the system under study or to the observable detected as pump-probe signal, different time-resolved methods could be employed.[3]

In this talk, I will present examples of ultrafast processes in different molecular systems, in either vacuum or solution, using isolated-phase time-resolved ion yield spectroscopy along with condensed-phase transient absorption, fluorescence up-conversion or two-dimensional electronic spectroscopy.

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Development of embedded machine learning potentials for simulations of enzymatic catalysis

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Enzymatic catalysis has been a central focus both in describing biological systems and in advancing methods for quantum chemistry. This work aims to develop a machine learning (ML) potential for application within a ML/MM hybrid model focused on the well-studied chorismate mutase enzyme.[1] The calculations achieve accuracy comparable to DFT/MM level simulations while maintaining the computational cost of a semi-empirical/MM simulation. The ML model is designed to train on the *in-vacuo* ligand in two distinct environments: within the enzyme and in water, utilizing an active learning methodology. Notably, the ML potential not only distinguishes between reactants and products but is also trained from a broader potential energy surface (PES), enabling the exploration of stationary points for chorismate mutase catalyzed reaction. A significant limitation, however, lies in coupling ML potentials trained solely on the ligand and its interaction with the rest of the enzyme. This work represents the first application of the recently developed EMLE embedding scheme and its corresponding software implementation.[2,3] The potential for this work lies in its promise to train using more precise electronic structure methods, thereby significantly cutting down computational expenses. This advancement could lead hybrid QM/MM simulations to reach the microsecond scale while retaining accuracies akin to first-principle methods.

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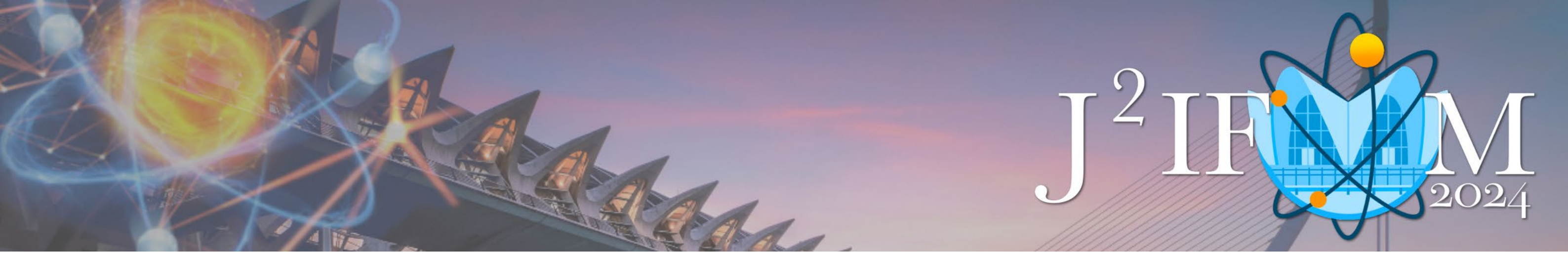

Development of multifunctional architectures to target G4s and deliver anticancer drugs.

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Supramolecular structures such as capsules, cryptands or macrocycles are interesting systems for the selective recognition of small molecules and capable to transport cargoes through synthetic and natural barriers.[1] These systems could be applied in drug delivery, pollution remediation, catalysis and in many other areas. Of outmost importance, the supramolecular systems could target biomolecules such as nucleic acids or proteins and exert a synergetic effect of the encapsulated molecule and the capsule itself.

Among the novel drug targets in drug discovery, epigenetic alterations, including histone modification, nucleosome remodeling and other non-coding mediated structures have attracted the attention in the last decades because of the development of drug resistance.[2] One of the most attractive non-coding structures in anticancer drug development are G-quadruplex (G4) DNA and RNA. G4s are non-canonical nucleic acid structures formed in guanine-rich sequences.[3] Strikingly, a large number of putative G-quadruplex forming sequences have been identified in the genomes of human, microorganisms and viruses, and evidences suggest their pivotal role in key biological processes. Telomeres are regions enriched with putative G4-forming DNA sequences and have been associated to ageing and cancer. Telomere sequences comprise hundreds of TTAGGG repeats which form a superstructure constituted by multiple G4s, termed as multimeric G4s (multG4s). Therefore, multG4 structures are currently tested as a therapeutic target to block telomere elongation in cancer cells.

Herein, we present our synthetic efforts to develop new organic capsules with multifunctional activity aimed to interact with multG4s and deliver drugs. We have prepared a family of macrocyclic and cryptand ligands containing triphenylamine moieties[4] and evaluated the encapsulation ability of our ligands for PARP-1 inhibitor. This supramolecular approach could be applied to target the telomeric regions and other important pathway involved in cancer biology.

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Time-resolved X-ray spectroscopy as a tool to unravel elusive intermediates of catalysts and photosensitizers used in H_2 reduction processes

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X-ray spectroscopy is a powerful tool that can help unravel elusive and key structures involved in an endless number of reactions, such as water splitting and hydrogen evolution processes. Capturing and disentangling the intermediates present in the photocatalytic production of H_2 is critical for the design of light-driven devices capable of reducing the crescent need for scarce and pollutant fossil fuels. Formed by a metal-based catalyst and photosensitizer, these structures are able to mimic natural photosynthetic reactions, bringing the idea of a H_2 fuel technology closer to reality. Hence, finding inexpensive, earth-abundant metal complexes made of Cobalt, Zinc, Copper, Iron or Nickel that can act as a catalyst or as a photosensitizer is essential. In our group we use ultrafast time-resolved X-ray absorption (XAS) and emission spectroscopy (XES) in the pico-nanosecond timescale to characterize the intermediates present in water splitting reactions. Resolving the oxidation state of the metal center, their coordination and lifetimes is indispensable towards understanding their robustness, activities and therefore, their feasibilities as catalysts or photosensitizers. By coupling this technique with steady-state XAS/XES, transient absorption measurements, Raman, UV-Visible spectroscopy, electron paramagnetic resonance and Density Functional Theory (DFT) calculations, we have been able to disentangle the electronic, spins, vibrational states and structural conformations of a wide number of complexes. Through these techniques we have further established the coordination behavior and the excited-state dynamics of a group of Cu^I multidentate photosensitizers and the light-induced kinetics and ultrafast electronic and structural states of a series of Co-based photocatalysts[1,2]. Currently we are working on improving the structural features of promising Ir-Co dyads in order to maximize their performance in H_2 photo-evolution processes.

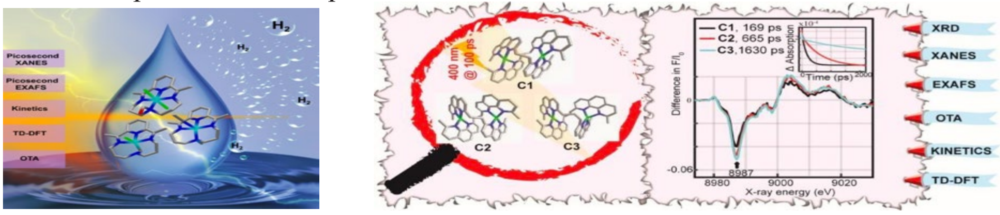

Figure 1. ChemSusChem (left) and PCCP (right) papers published by our group

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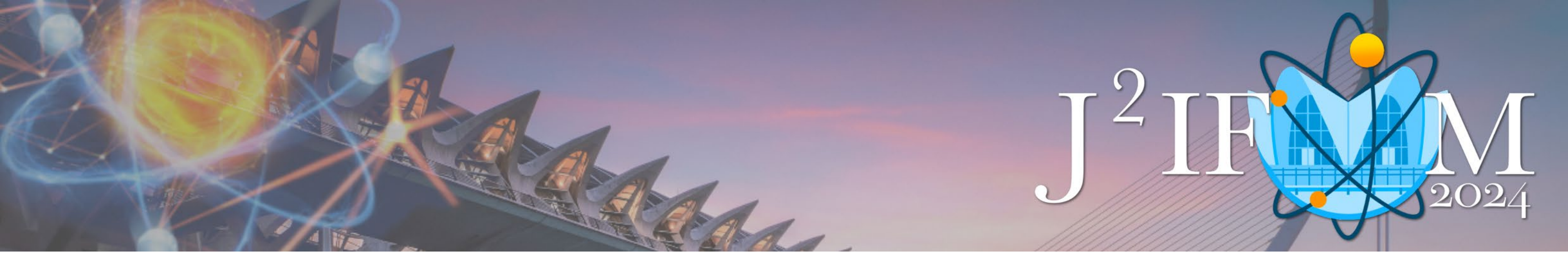

Computational Characterization of the Toxicity Mechanism of Dioxins: Membrane Permeation and Binding to the AhR Protein

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Polychlorinated dibenzo-p-dioxins (PCDDs) are persistent environmental pollutants which bioaccumulate in cell membranes and bind to the aryl hydrocarbon receptor (AhR) producing many toxic effects, such as carcinogenesis, among others.[1,2] Therefore, the study of the binding mechanism of these contaminants to the AhR and their permeation through lipid membranes is important to get insight into the relevant factors that control their mode of action.

In this computational research, the binding pockets of seven PCDD compounds in the AhR have been found by means of molecular docking. In a second step, the interaction energies between the pollutants and the protein have been characterized classical and quantum mechanically by means of the MM/GBSA approach and a QM/MM electron density-based EDA method, respectively. Finally, umbrella sampling simulations have been carried out to investigate the permeation mechanism through a model bilayer. The goal is to unveil possible structure/energetics relations which could contribute to predict and understand the toxicity of these organic compounds.

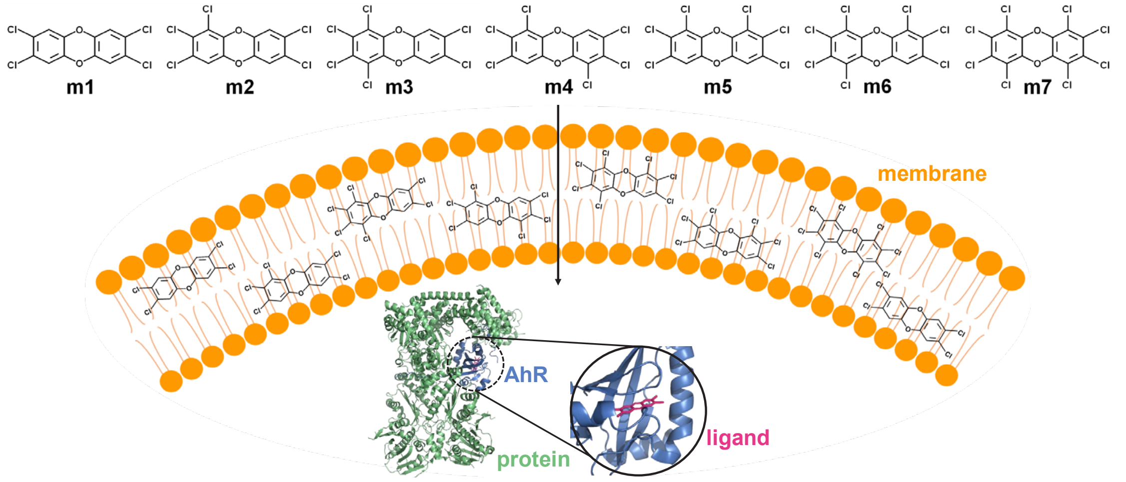

Figure 1. Schematic representation of the two steps investigated: Membrane permeation and interaction with the AhR protein.

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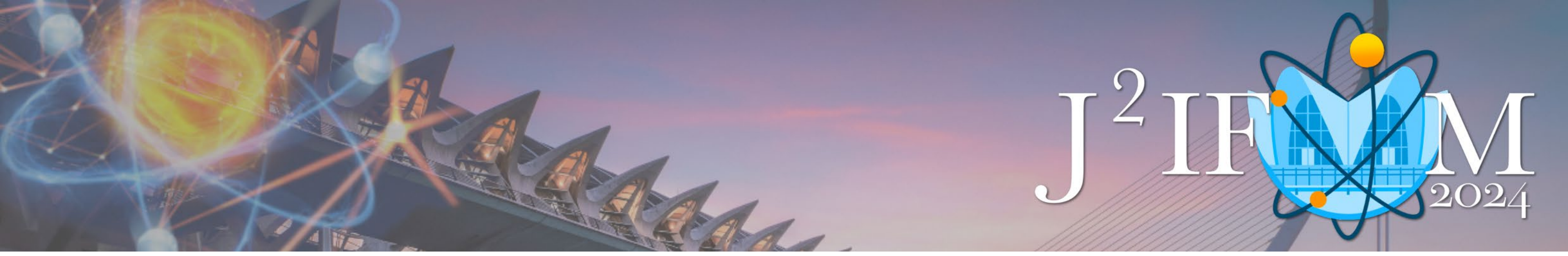

A Gaussian Mixture Model Approach for the Automated Construction of Chemical Features

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A critical bottleneck in the application of Artificial Intelligence (AI) to chemistry lies in the complexity of transforming the many physical variables defining a system into a fixed-size array. Existing methods, such as Symmetry Functions (SF), demand meticulous parameter tuning, which, if done incorrectly, can lead to sub-optimal model performance. In this study, we introduce an unsupervised Machine Learning strategy, summarized in Fig. 1, that leverages a Gaussian Mixture Model (GMM) for the automatic selection of descriptor parameters. GMMs partition the chemical space into well-defined clusters, SF are then crafted to optimize the description of intrinsic chemical patterns, such as functional groups. To validate our approach, we apply it to the estimation of local quantum chemical properties for a prototypical capped amino acid. Our results demonstrate that the self-optimized SFs yield high-quality descriptors. Notably, breaking the symmetry of the features proves to be crucial for accurately describing these patterns. Our approach not only facilitates the construction of chemical descriptors but also provides valuable insights into the mapping of radial and angular spaces. Furthermore, it lays the groundwork for encoding many-body information beyond angular terms into forthcoming Machine Learning features. This work represents a significant stride toward enhancing the efficiency of chemical AI, offering a methodological framework for robust descriptor construction, and shedding light on the nuanced interplay of radial and angular spaces in molecular representation.

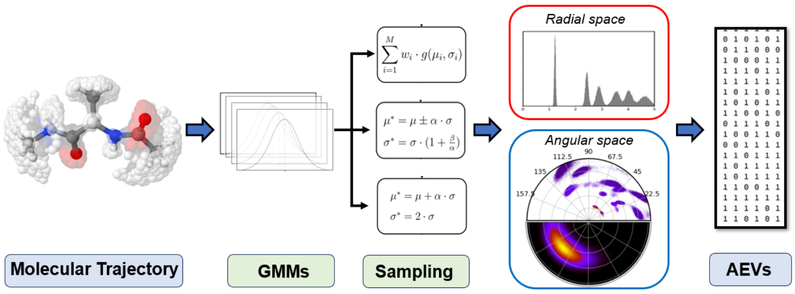
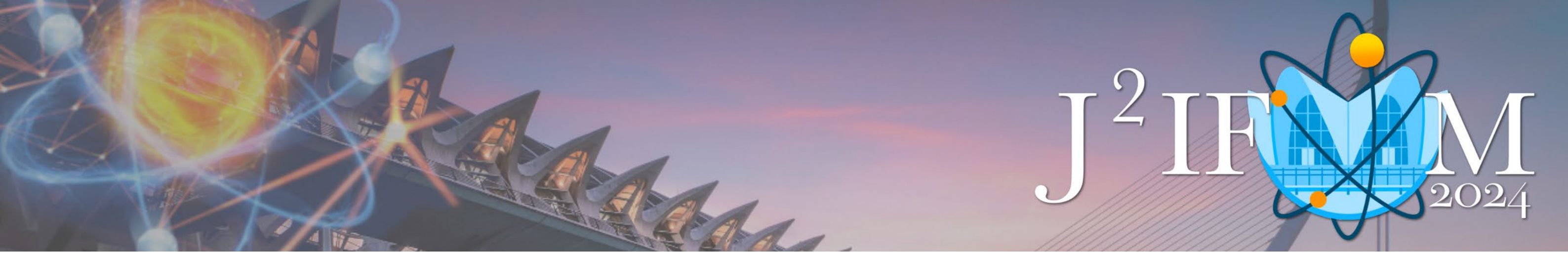


Figure 1. Schematics of the GMM clustering of the chemical space, and the subsequent construction of Atomic Environment Vectors (AEVs).



Fusion Plasma Diagnostic Driven EUV Spectral Analysis of Ionized Kr Gas Atom

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Spectroscopy of high-temperature fusion plasma is essential to investigate different plasma diagnostics associated with magnetic confinement fusion devices. In large tokamak and stellarator devices, inert gases are injected as the coolant gases to study the divertor detachment and fusion plasma diagnostics in such devices.[1] In view of this, a Krypton (Kr) gas impurity seeding experiment was conducted in a Large Helical Device (LHD) and Kr spectra were measured in an Extreme Ultraviolet (EUV) wavelength region. The detailed spectral analysis of measured Kr-ions was performed to validate the theoretical collisional data and Collisional-Radiative (CR) model calculations. To generate the theoretical synthetic spectra, extensive calculations concerning the excitation of Kr ions through electron impact were performed for the development of a plasma model. Theoretical spectra and linked atomic ion and collision calculations facilitate the analysis of EUV spectra for fusion plasma diagnostics linked with the LHD and other tokamak devices.

Theoretical Relativistic Multiconfiguration Dirac-Hartree-Fock method, along with its extension to the Relativistic Configuration Interaction (RCI) method, were employed for the wave functions and energy levels computations using the General Relativistic Atomic Structure Package 2018.[2] In another set of calculations, the Relativistic Many-Body Perturbation Theory and RCI methods integrated within the Flexible Atomic Code were utilized.[3] Further, detailed electron impact excitation cross-sections and their respective rate coefficients were obtained using the fully relativistic distorted wave method and incorporated into the CR plasma model to generate the synthetic spectra. The emission lines of Kr ions measured in the LHD plasma experiment were compared with the emission spectra generated from the present theoretical CR model.[4] Detailed experimental and theoretical results will be discussed at the conference.

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DNA-grafted Metal-organic Frameworks: The key parameters for robust synthesis of stable nano-formulations.

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Metal-organic frameworks (MOFs) constitute outstanding candidates among nanocarriers in medical imaging, due to their unique properties, including ultra-high surface area, permanent porosity, multifunctionality and facility in chemical modification.[1] Post-synthetic functionalisation of MOFs' surface with ligands, such as DNA oligonucleotides, is a promising option for building nano-scaffolds that are not only stable, but also equipped with advanced biological properties, including active targeting.[2] In the present work, UiO-66 was selected as an archetypal MOF to investigate the effect of DNA grafting on nanoparticle stability. UiO-66 NPs with different morphologies were synthesised via the solvothermal method, by adjusting key parameters (e.g., modulator type, metal precursor). Each MOFs' structure, size and shape were confirmed by Powder X-ray Diffraction, TEM and SEM. DNA was grafted via non-covalent interactions, by applying different bottom-up methodologies. To investigate the effect of DNA sequence on the grafting procedure, four single-stranded oligonucleotides were used (A-, T-, C- and G-rich sequences). The amount of anchored DNA was quantified by fluorescence spectroscopy. To evaluate colloidal stability, hydrodynamic size of all materials was monitored over the time in biological buffers using Dynamic Light Scattering. Bare UiO-66 NPs aggregated rapidly in the presence of phosphate ions and sedimented from the dispersant, while DNA motifs successfully reduced the aggregation rate in every case. Currently, we are fully characterising the novel systems by complementary techniques such as internalization assays in cancer cell lines.

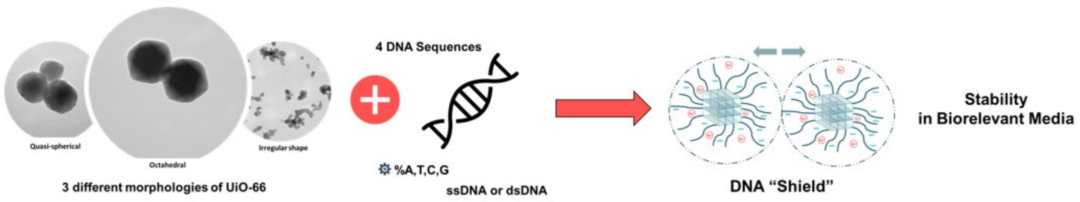

Figure 1. DNA grafting as a novel method for obtaining stable MOFs in biological media.

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Many-body modelling of vibronic coupling problem in crystals displaying degenerate electronic states

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The coupling between the electronic and vibrational degrees of freedom is a crucial physical phenomenon to understand the origin of the low symmetry geometry of multiple compounds as well as playing an important role in many phenomena such as spectroscopy[1], colossal magnetoresistance[2] and having been the inspiration for the discovery of high-Tc superconductivity[3].

In this work a many-body model of vibronic coupling in periodic crystalline structures is proposed with the aim of understanding the cooperative distortion and orbital ordering in systems containing unpaired electrons in locally degenerate e-shells. Usual approaches are often based on Heissenberg-type expressions[4] that does not include a formal treatment of the band structure of the solid and allow the orbitals to rotate independently in each of the centers of the solid.[5] We show this approach leads to a lack of consistency with Bloch's theorem. In our model, based on a different perspective, the crystal problem is expressed as a $[E_g(\Gamma)+E_g(R)]\otimes[e_g^{st}(\Gamma)+e_g^{ph}(R)]$[6,7] combined Jahn-Teller and pseudo Jahn-Teller problem where $E_g(\Gamma)$ and $E_g(R)$ are many-body electronic states transforming according Γ and R points in reciprocal space while the involved distortion modes $e_g^{st}(\Gamma)$ and $e_g^{ph}(R)$ are, respectively, a ferrodistortive strain mode and an antiferrodistortive phonon mode that are strongly coupled among themselves. This model is fully consistent with both experimental results and first principles simulations.

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In vitro study of the phototoxic potential and photosensitizing properties of a topical retinoid

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Adapalene, a third-generation topical retinoid, is used as a treatment for acne vulgaris. It is currently one of the three topical retinoids approved so far by the Food and Drug Administration (FDA), along with tazarotene and tretinoin.[1] However, a combination of adapalene and sun exposure might result in the appearance of adverse effects. They have been associated with different causes such as skin irritation that can upset the natural skin photoprotection and increase ultraviolet rays hurt, or a decrease in the thickness of the stratum corneum reducing the natural photobarrier.[2]

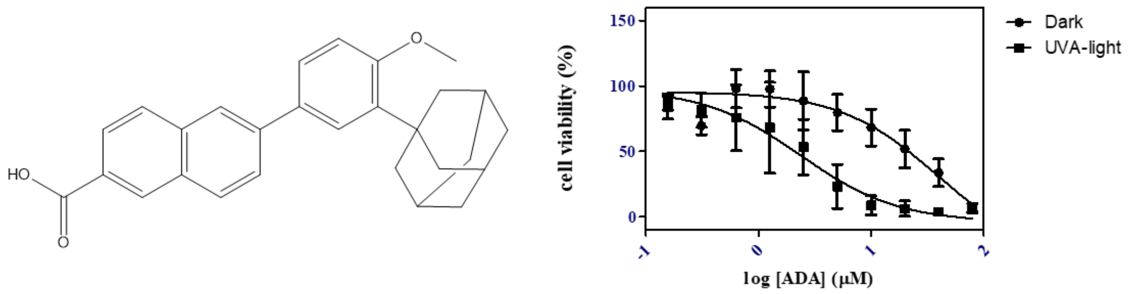

Figure 1. Left, the structure of the adapalene molecule. Right, cell viability at different concentrations of adapalene in the absence of light (circles) and under irradiation (squares).

The aim of this study is, firstly, to determine the photophysical properties of adapalene to investigate its photoactive potential toward biomolecules. For this, experiments were carried out combining UV-vis spectroscopy, fluorescence and phosphorescence (steady state and temporal resolution), and laser flash photolysis. Second, an in vitro study was carried out to determine its phototoxic potential activated by exposure to light. Obtaining a photo irritation factor (PIF) of 16.6, considering a value greater than 5 as phototoxic.3

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DNA distortion mechanisms of novel cisplatin-ferrocene derivatives: predicting cancer drugs cytotoxicity through molecular dynamics simulations.

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Cisplatin has been used for decades for the treatment of sixteen different types of cancer[1]. However, severe limitations related to its elevated cytotoxicity on non-cancerous cells and its efficiency loss due to cellular resistance to the treatment[1] have contributed to the search of alternative drugs with improved performance, such as oxaliplatin or nedaplatin. With the same purpose, the group of A.M. González-Vadillo (Universidad Autónoma de Madrid) has recently designed and synthetized a new family of cisplatin derivatives aiming at producing synergistic cytotoxic effects combining the distortion of the DNA strand and the generation of reactive oxygen species resulting from redox reaction propelled by a ferrocene moiety[2]. In this contribution, the distortion mechanism of cisplatin and three of these novel cisplatin derivatives has been explored through molecular dynamics simulations. A comprehensive analysis of the dynamics of a platinated DNA double strand model followed by the monitoring in time of non-covalent interactions established between the drugs and the biomolecule has contributed to the rationalization of the improved cytotoxicity of the new drugs compared to cisplatin.

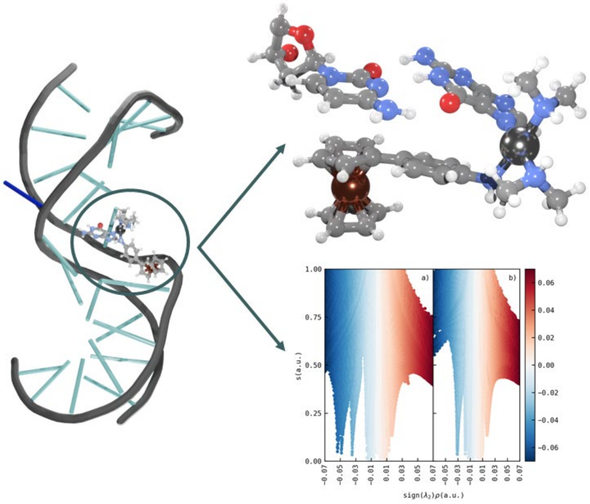

Figure 1. Platinated DNA double strand (left), one of the proposed cisplatin derivatives (right, top) and a non-covalent interaction analysis of the same derivative with DNA (right, bottom).

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Spin crossover in K_2CuF_4 and Cs_2AgF_4 layered perovkites

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The current interest in layered materials containing transition-metal (TM) ions is driven by the wide range of properties and effects exhibited in these systems, including superconducting states, 2D magnetism and their potential applications in spintronics [1]. Specifically, unraveling the mechanisms for high-T_C superconductivity stands as one of the most formidable challenges in solid state physics [2]. Since the discovery of superconductive antiferromagnetic (AFM) oxocuprates in the late 1980s [3], intense efforts have been invested in the search of novel TM-based high-T_C superconductors.

Copper oxide superconductors exhibit strong AFM coupling within the CuO layer, while similar compounds like K_2CuF_4 and Cs_2AgF_4, belonging to the orthorhombic Cmca space group, display weak in-plane ferromagnetism (FM). This change in the magnetism has been linked to an orthorhombic distortion [4], absent in the cuprates. Our first principles calculations [5, 6] reveal that the ground state in the high-symmetry phase (tetragonal I4/mmm) of the fluorides is AFM. In this phase, the MF_6 ($M = Cu^{2+}$, Ag^{2+}) complexes are axially compressed, with four equivalent in-plane ligands. The orthorhombic distortion breaks this equivalency, resulting in negligible covalency in the longest bond, thereby favoring the FM order. Our qualitative valence-bond model and second-principles simulations illustrate that the factor in superexchange favoring the AFM order decreases as the ligand shifts from the symmetric position in the metal-ligand-metal dimer. Notably, the distortion is found to be sensitive to epitaxial strain, providing control over the magnetism. Indeed, for strains larger than 5.1%, this magneto-elastic coupling makes K_2CuF_4 and Cs_2AgF_4 AFM, establishing them as chemical analogs to copper oxide superconductors.

Acknowledgments: We acknowledge financial support from Grant No. PID2022-139776NB-C63 funded by MCIN/AEI/10.13039/501100011033. I. S.-M. (grant BDNS:589170) acknowledges financial support from Universidad de Cantabria and Gobierno de Cantabria.

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Structural determination of Dibenzothiophene with Broadband Rotational Spectroscopy

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Rotational spectroscopy can provide insights of unparalleled precision with respect to the structure and dynamics of molecular systems that have relevance in fields as diverse as astronomy and biology[1]. The broad frequency and large dynamic range of this technique make possible the structural determination in molecular systems of increasingly larger size from measurements of heavy atoms (^{13}C, ^{15}N, ^{18}O) isotopes recorded in natural abundance in the same spectrum as that of the parent isotopic species[2]. In this work the structure of Dibenzothiophene (DBT) obtained via Broadband rotational spectroscopy (2-8 GHz) will be presented. DBT, is a tricyclic aromatic sulfur heterocycle with a 14π electron ring system formed by the fusion of two benzene rings with a thiophene ring. Dibenzothiophene is a thermally stable compound and resistant to mild oxidizing agents. It is potentially useful as electrophilic trifluoromethylating agents. It has been used as a drug to expose the mycelia of infecting fungi or to treat corns, warts, and certain other skin diseases. Computational methods such as B3LYP and B2PLYP with several basis sets were performed to obtain the structural parameters. The accuracy of such calculations will be discussed.

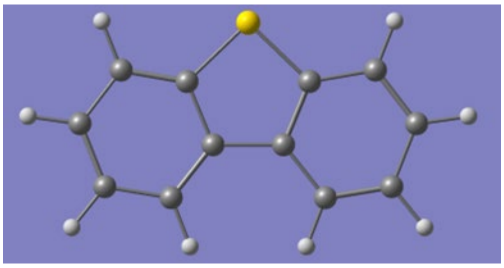

Figure 1. The structure of Dibenzothiophene according to quantum chemical calculation

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Revealing the Influence of Substituents on the Selectivity of [3+2] Cycloaddition between Azides and Nitriles from the Molecular Electron Density Theory (MEDT) Perspective

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The substituent effects in the catalyst-free [3+2] cycloaddition (32CA) reaction between azides and nitriles has been studied using molecular electron density theory at the M06-2X/6-311+G(d,p) computational level. In this study, the theoretical scale of reactivity was explained by the electrophilic activation/deactivation effects that promoted by electron-withdrawing and electron-releasing substituents in both azide and nitrile components. The most electron-withdrawing and electron-releasing substituents in components were selected to study the regioselectivity of the expected correspondent tetrazole products by the global electron density transfer (GEDT) analysis at the transition state structure (TS) (Figure 1).

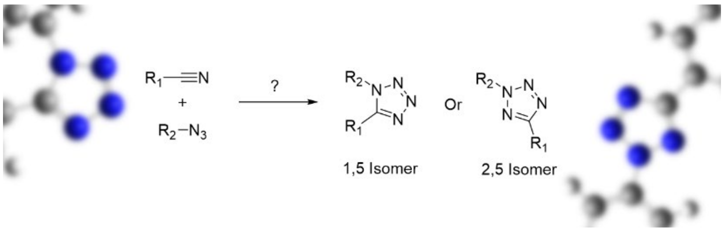

Figure 1. The [3+2] cycloaddition (32CA) reaction between azide and nitrile.

Study of two-dimensional elemental tellurium through density functional theory for spintronic applications

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Previous studies based on density functional theory (DFT) predict the existence of the β, α and α∗ two-dimensional phases of elemental tellurium,[1,2] the former belonging to the P21/m, and the last two to the P21 space group. The β phase have a direct band gap at the Γ point. On the other hand, in the α and α∗ cases, spin textures and band structure calculations reveal that the valence band maximum lie out of the range from the high symmetry point paths of the first Brillouin zone, near the Γ − M path. These two phases present spin expectation values of the Sx component and phonon modes that are symmetry-protected states in the momentum space along the X − M direction. Furthermore, spin-resolved band structures show that, for all three phases, the electron spin-momentum is locked in reciprocal space due to the symmetry of the two-dimensional crystals.

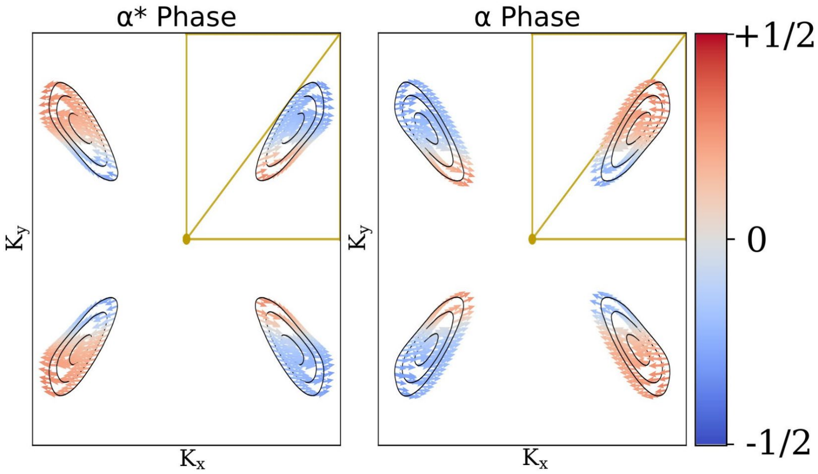

Figure 1. Spin textures for α∗-phase and α-phase at 10, 50, and 90 meV below VBM. Golden lines represent the high-symmetry lines in the Brillouin zone. Color map indicates the Sz component. Sx and Sy components are represented in-plane.

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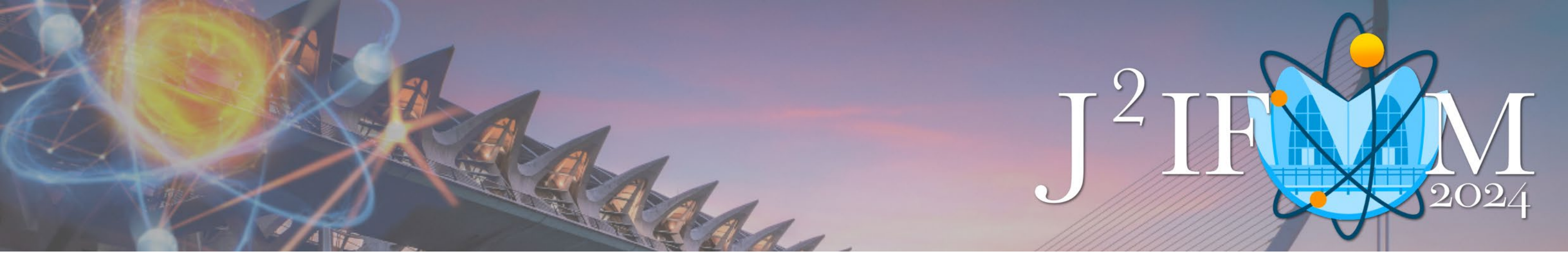

Driving and Imaging Achiral-to-Chiral Transitions in an All-Optical Setup

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Synthetic chiral light[1] enables ultrafast and highly efficient imaging of molecular chirality. Such light is locally chiral: the tip of the electric-field vector draws a chiral (3D) Lissajous figure in time, at each point in space. Such tailored light can also be used to create chiral electronic states in atoms[2,3], which emit chiral photoelectron currents and exhibit photoelectron circular dichroism[2]. Here we show how to apply synthetic chiral light[1] to drive ultrafast chiral electron motion in systems which are initially achiral, driving ultrafast achiral-to-chiral phase transitions. We solved the time-dependent Schrödinger equation for the hydrogen atom exposed to an ultrashort, intense, locally chiral field. The laser drives ultrafast chiral electron motion at its fundamental frequencies. This motion includes high-frequency components which create a chiral structure in time giving rise to chiral high harmonic generation (HHG).

Chiral HHG is suppressed after the pulse is gone and the atom remains in a chiral coherent superposition of stationary states. Thus, the electron continues to undergo ultrafast chiral dynamics. This chiral electron motion results from having populated excited states of the atom with different energy and angular momentum. The ultrafast chiral current gives rise to chiral free-induction decay radiation with elliptical polarization. The imprinted handedness is recorded in the polarization of the emitted light.

We believe that this work creates exciting opportunities for driving and monitoring achiral-to-chiral phase transitions in all-optical setups, also in complex systems, as well as for driving chiral photo-chemical reactions using achiral reagents.

Figure 1. Ultrafast polarization induced in the hydrogen atom by our locally chiral field[1] **a**, total polarization the presence of the field. **b**, high-order components, resulting from filtering out the linear response in a. **c**, induced polarization after the pulse is gone.

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Simulating the photofragmentation of cyclobutanone using non-adiabatic dynamics methods

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The modeling of photochemical molecular dynamics using theoretical chemistry has been a longstanding challenge due to the consideration of quantum effects on both nuclei and electrons. The objective of this study is twofold: First we further our understanding of cyclobutanone photochemistry through a detailed simulation of its excited states molecular dynamics[1], and second the capabilities of our excited state dynamics as predictive models for the outcome of photoinduced processes will be tested thanks to new ultrafast electron diffraction experiments[2]. The Tully surface hopping (TSH)[3] mixed quantum-classical non-adiabatic dynamics method was our choice to propagate the nuclei, where the electronic energy is evaluated on-the-fly using TDDFT and CASSCF.

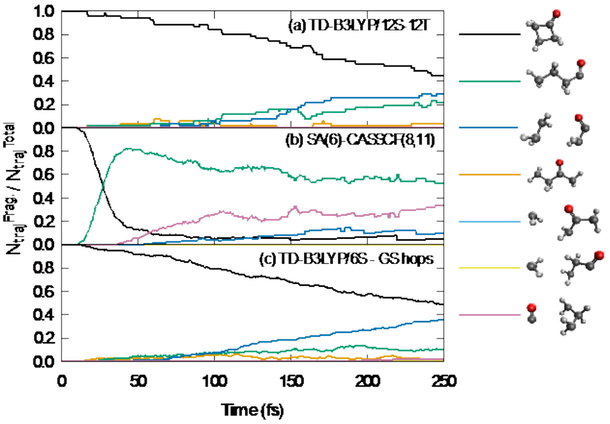

Figure 1. Photodissociation products after excitation of cyclobutanone to its n-3s (S_2) band, along the Surface Hopping trajectories using TD-B3LYP and SA(6)-CASSCF(8,11).

A strong difference between both methods has been found for the deactivation pathways followed by the excitation to the n-3s excited state. Moreover, gas-phase ultrafast electron diffraction signals have been computed for both electronic structure methods to reveal the reliability of each method for predicting photoinduced processes in organic molecules.

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Understanding the formation of poliaromatic compounds in the interstellar space (*ISM*)

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Understanding the formation of PoliAromatic Hydrocarbons (PAHs) can shed light on the origin of the prebiotic Earth and even on the origin of life.[1] Unfortunately, to date, the formation of organic compounds in space is a scarcely understood area.

In this arena, automated protocols for the identification of reaction mechanisms show great potential to aid in the learning of how PAHs are formed in space. Taking advantage of the AutoMeKin[2,3] program, we have found thousands of potential paths that account for the formation of the simplest (poli)aromatic compounds present in space, such as benzyne or bencene but also naphthalene and its derivatives. We have not only uncovered several direct paths, for which reactants have been detected in space, but also some more indirect paths in which well-known intermediates such as the phenyl radical or even the ethynyl radical play a crucial role.

Acknowledgements

M.C.R. thanks the Centro de Supercomputación de Galicia (CESGA) for the free allocation of computational resources and the Xunta de Galicia (Galicia, Spain) for financial support through the ED481B-Axudas de apoio á etapa de formación posdoutoral (modalidade A) fellowship.

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Understanding COX-2 for the Design of New Cancer Drugs: Computational Study with Specific Photochromic Compounds

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Cyclooxygenases are a family of enzymes essential in the regulation of inflammation and other processes in the human body. There are two main isoforms, COX-1 and COX-2, with different roles and patterns of expression in tissues. COX-1 is widely expressed and maintains homeostasis, while COX-2 is restricted to specific regions and it is inducible, especially in at inflamed tissues and cancer cells. COX-2 overexpression is associated with the development of cancer in several types of tumors. To investigate this phenomenon, fluorescent compounds derived from anti-inflammatory drugs are usually experimentally used for the detection of COX-2 in cancer cells[1]. Using different computational techniques (Molecular Docking, Molecular Dynamics Simulations, QM/MM and TD-DFT Calculations) we have calculated and analyzed the fluorescence spectra of a photochromic compound bound to the monomer and dimer of human COX-2. The differences between the monomeric and dimeric spectra reveals molecular insights of the protein's behavior in cells with COX-2 overexpressed. This research provides valuable information for the possible future design of specific drugs for cancer treatments.

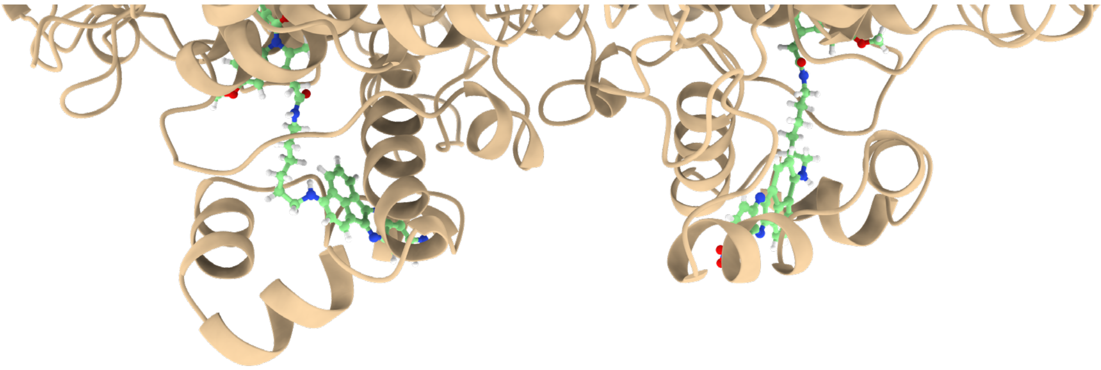

Figure 1. Dimer of human COX-2 enzyme accommodating the fluorogenic designed drugs inside its two monomers.

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The Electronic Absorption Spectra of Ce(III) aqueous solution: A theoretical study including average statistical ingredients

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This study presents the electronic absorption spectrum of Ce^{3+} in aqueous solution computed by means of highly-correlated quantum mechanical wavefunctions, as described in a previous study [1], applied on a set of structures obtained from Molecular Dynamics simulations. We show that the convolution of individual vertical transitions yields accurate shapes and widths of spectrum bands. The study incorporates a recently proposed statistical machine learning algorithm, Gaussian Mixture Models-Nuclear Ensemble Approach (GMM-NEA) [2], to convolute individual spectra, achieving excellent agreement with experimental results. We explore alternative methods for obtaining statistically representative structures, such as Wigner-sampling. The combination of Wigner-sampling and GMM-NEA broadening holds promise for broad applications in spectroscopic analysis and predictions, offering a computationally efficient alternative to traditional methods.

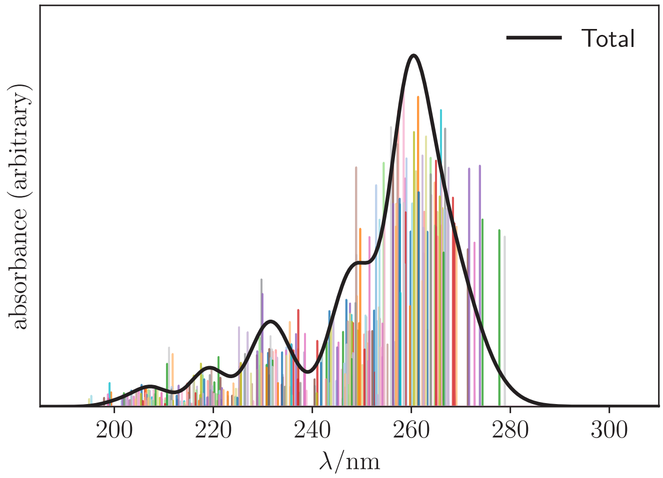

Figure 1. *Representation of the individual spectra and the reconstructed spectrum shape.*

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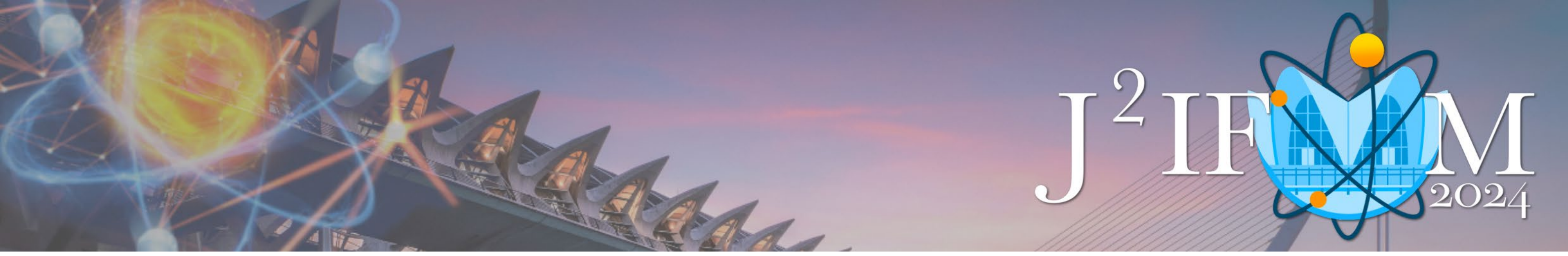

A high-pressure study on the effects of pressure-transmitting media on $Bi_{14}MoO_{24}$ and $Bi_{14}CrO_{24}$ compounds

Pablo Botella[1],*, Josu Sánchez-Martín[1], Oscar Gomis[2], Robert Oliva[3], Samuel Gallego-Parra[4], Julio Pellicer-Porres[1], Gastón Garbarino[4], Frederico G. Alabarse[5], Daniel Errandonea[1]

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The study under pressure of the isostructural compounds $Bi_{14}MO_{24}$ where (M = Cr or Mo) have been extended up to 30 and 40 GPa, respectively. The changes in the crystal structure due to the pressure and different pressure-transmitting media (PTM) have been monitored by synchrotron X-ray diffraction. The results obtained in this study are compared and discussed alongside our previous work[1,2]. Similar phase transitions have been observed in the case of no PTM but having an earlier pressure onset phase transition. On the other hand, using He gas several isostructural phase transitions were observed for the first time. In the case of $Bi_{14}MoO_{24}$, apart from the tetragonal to monoclinic transition previously reported, other two isostructural (monoclinic) phase transitions have been reported (see Figure 1). For $Bi_{14}CrO_{24}$, two new isostructural (tetragonal) transitions are observed before the monoclinic transformation using He gas as PTM.

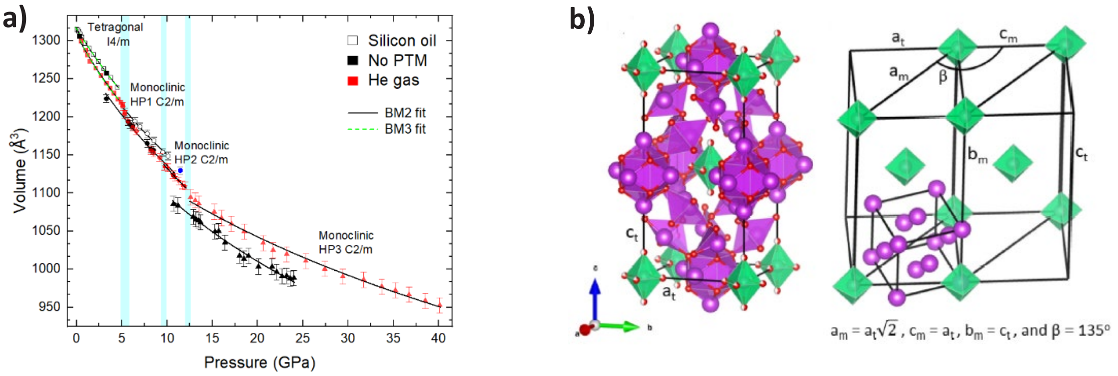

Figure 1. a) Unit-cell volume evolution under pressure of $Bi_{14}MoO_{24}$. B) Schematic representation of the tetragonal (*I*4/*m*) structure and transformation from the body-centered tetragonal to the C-centered monoclinic structure

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MXenes as heterogeneous catalysts. Computational insight into the regioselective anti-Markonikov hydroamination of terminal alkynes.

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Two-dimensional metal carbides (MXenes) are a group of recently discovered materials, which have attracted growing interest over the last years due to their 2D morphology and the large possibilities in chemical composition, which might allow a vast applicability in heterogeneous catalysis, among other fields. We report that Ti_3C_2 Mxenes exhibit catalytic activity for hydroamination of terminal alkynes, being very selective to the anti-Markonikov product, both in the case of aliphatic amines as well as in the less reactive aromatic amines. According to XPS analysis, the Ti_3C_2 surface is functionalized by oxygen and fluorine groups, accompanied by both vacancies and defects that confer this material unique Lewis-acid catalytic properties for this reaction. These unique structural properties have been modelled computationally, by means of quantum chemical DFT calculations at the B3LYP/Def2SVPD level of theory. After modelling a 35-atom cluster of the described Mxene, a full reaction coordinate analysis has been carried out in order to determine the underlying reaction mechanism, and to explain the specific regioselectivity that has been described experimentally. Three transition states have been characterized for this mechanism: a) Cycloaddition of the alkyne on the catalyst. b) 1st proton transfer on the product. c) 2nd proton transfer on the product.

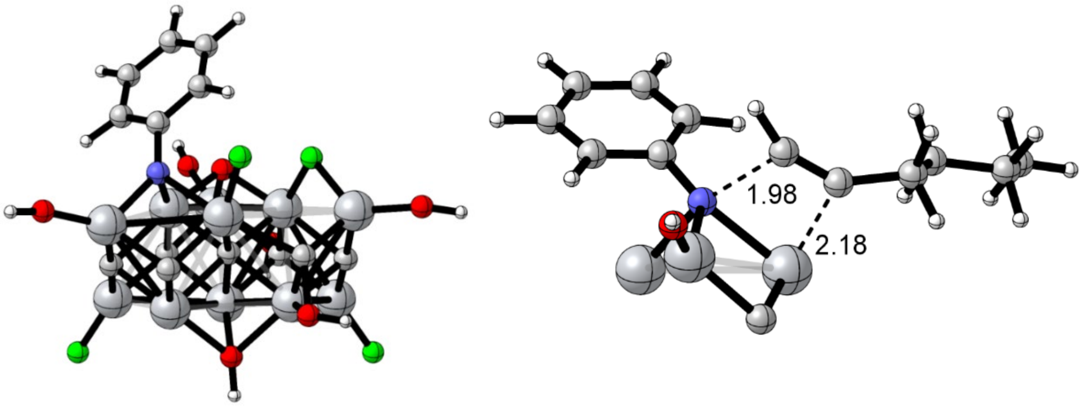

Figure 1: Representation of the cluster of the proposed catalyst (left) and the first transition state (right) of the anti-Markonikov hydroamination reaction.

Acknowledgments: We thank ASIC-UPV and SGAI-CSIC for the use of computational facilities. We also thank MICIN for Severo Ochoa excellence research grant, and BASF for PhD scholarship.

A real space study of the hydrogen bond

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Noncovalent interactions (NCI) are important are central in physical chemistry[1]. The mere existence of the condense phase is a compelling reason to accept the presence of this kind of interactions[2]. The strong relationships between some energetics, such like boiling temperatures and enthalpies, with the NCI allow to estimate them, not just theoretically but experimentally. Stone wrote in his seminal monograph on this matter "*At the time of the first edition [1995], the balance was already shifting from experiment to computation as the prime source of information about intermolecular forces, and this shift has continued. Experiment will continue to have an essential role, but its task now is more to check the validity of calculations and to refine calculated potentials, rather than to provide the principal source of data for them*"[2]. Nevertheless, there is still a need to get a further understanding on the origin of NCIs. In this regard, the quantum theory of atoms in molecules (QTAIM)[3] and the interacting quantum atoms (IQA)[4,5] energy partitions are methods of wave-function analyses that have been successfully exploited in the study of covalent bonding and they can be utilized for the examination of NCIs without any loss of generality. Herein, we will focus on the application of IQA and QTAIM on the investigation of arguably the most important noncovalent interaction, the hydrogen bond (HB).

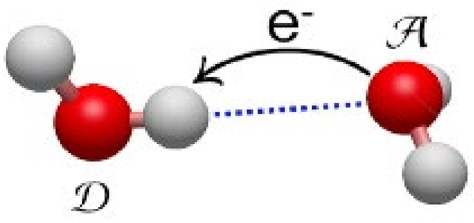

Figure 1. Electronic transfer in $(H_2O)_2$ which strengthens the H-bond donor capacity of molecule A and the H-bond acceptor character of molecule D

Acknowledgments: T.R.-R. is thankful to DGTIC/UNAM for computer time (project LANCAD-UNAM-DGTIC 250).

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Graphene oxide reduction through the change on its nanoscale properties

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Graphene oxide (GO) is a graphene-derived 2D material made of a defective carbon basal plane randomly scattered with several oxygen-containing functional groups. Such defects change the properties remarkably, making GO hydrophilic and insulating. Removing these functional groups produces its reduced form (rGO), which is both hydrophobic and a good electrical conductor. The reduction process is a gradual transformation that gives rise to a whole family of materials according to the method of reduction and its degree of completion[1]. They are usually characterized by their macroscopic properties, such as C/O atomic or sp2/sp3 hybridization bond ratios, but a reliable metric on the nanoscale is yet to be found.

In this work we have correlated the local reduction degree of different rGO and mixed GO/rGO samples, both chemically and thermally reduced, with their nanoscale electronic properties, chemical composition, and structural defects; measured with both Kelvin probe force microscopy and co-localized Raman spectroscopy.

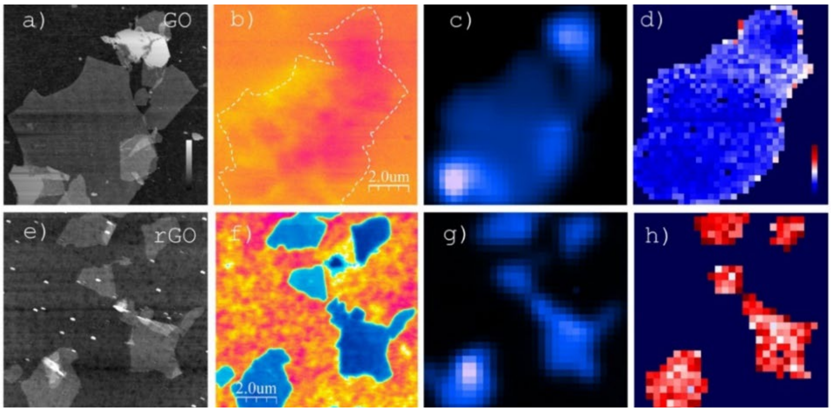

Figure 1. Co-localized KPFM-Raman scattering maps corresponding to GO (top row) and rGO (bottom row) flakes. a) and e) topography (z scale: 10 nm); b) and f) surface potential (200 mV); c) and g) integrated Raman intensity (12000 a.u.); d) and h) Raman peak intensity ratio ID*/IG (0.2). [2]

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Cytosine derived etheno adducts: study of their photoreactivity and photochemistry

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Lipid peroxidation is a biochemical process that involves the oxidation of polyunsaturated fatty acids, the components of cell membranes. In this process, highly reactive species, such as α,β-unsaturated aldehydes, are generated and react with DNA bases, forming the so-called **etheno adducts**. These DNA lesions exhibit **mutagenic properties**[1]. Indeed, the increase of lipid peroxidation in inflammatory processes[2] has been related to the high levels of etheno adducts in diseases that can lead to cancer, such as Chron's disease or ulcerative colitis[1]. Consequently, they are excellent **bio-markers** for different types of cancer (lung, colon or prostate cancer). Although their mutagenic properties have been clearly established, their photoreactivity has not been studied yet.

Here, the attention is centered on the cytosine etheno derivative (eC). Recently, the increase of its singlet excited state lifetime compared to that of cytosine was reported,[3] which points toward a **potentially increased reactivity**. A model compound containing two eC covalently linked by a trimethylene bridge was synthesized and irradiated to evaluate its photoreactivity under **direct irradiation** or through a **photosensitization** process. Especially, cyclobutane pyrimidine dimer formation, the most common lesion caused by UV light in DNA, was considered taking into account the possibility of a **[2+2] photocycloaddition** involving the double bond at 5,6 of the cytosine moiety or that of the etheno ring.

Formation of edC already means a damage by itself, but its harmfulness could be increased if it can form a CPD-type photoproduct. Thus, the aim of this study is to evaluate the photoreactivity of these etheno adducts, considering especially the formation of new CPD-like lesions.

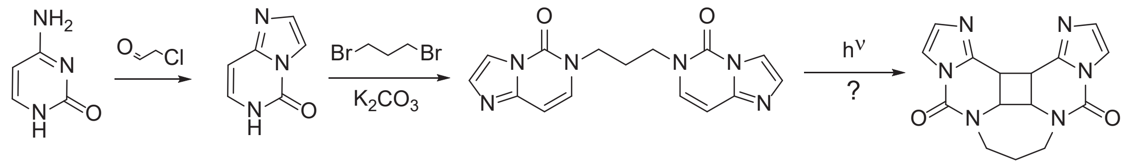

Figure 1. Synthesis and potential photoreactivity of the eC model

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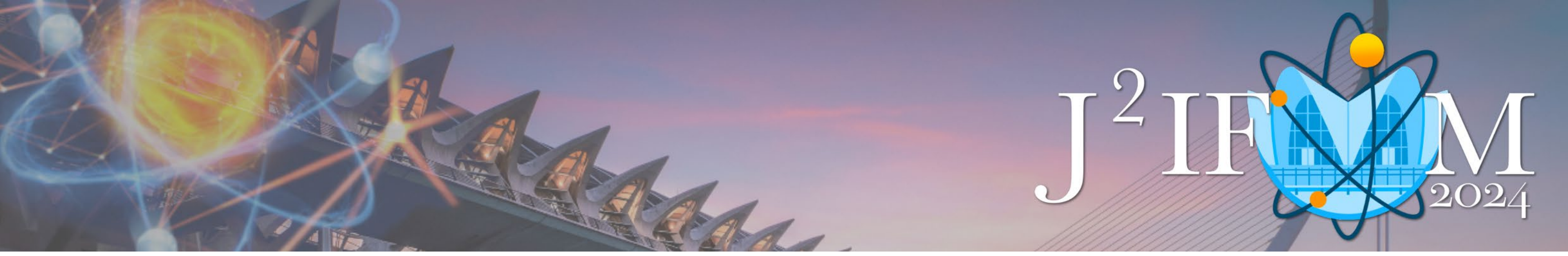

Extending the Laboratory Measurements of 2-Aminooxazole by means of Millimeter Wave Spectroscopy.

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The question of the origin of life remains unresolved despite various hypotheses have been proposed to shed light on this mystery. One prominent hypothesis focuses on RNA-world, suggesting that RNA is responsible for storing genetic information and triggering chemical reactions for early forms of life. 2-aminooxazole (N-heterocyclic molecule) has been proposed as a prebiotic species that could be involved in the astrochemical formation of pyrimidine ribonucleotides.[1] The recent interstellar detection of its possible direct precursors, glycolaldehyde and cyanamide, makes it as a potential candidate to be present in the interstellar medium (ISM). Although a previous work by Møllendal and Konovalov[2] provided experimental rotational constants for this molecule between 26.6 and 80.0 GHz, it is necessary to extend the measurements to higher frequencies to enable its search in other surveys of ISM regions within the millimetre wave frequency range. Here we present the experimental study of this molecule in the 75-110 GHz region and at room temperature, carried out with the millimeter-wave spectrometer[3] built at GEM (Universidad de Valladolid). Due to the inversion of the amino group, accurate experimental rotational constants were derived for 0^+, 0^-, 1^-, 1^+ vibrational states. This data will be useful to extend its radioastronomical search in other regions of the ISM.

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Solvatotuning of the slow magnetic relaxation through a single-crystal-to-single-crystal transformation in pentanuclear gadolinium(III)-nickel(II) molecular nanomagnets

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Mixed 4f/nd (n = 3–5) metal-organic clusters (MOCs) offer unique examples of stimuli-responsive multiproperty single-molecule magnets (SMMs) for molecular spintronics (MS) and quantum information processing (QIP).[1] Because of the intriguing spin relaxation dynamics of lanthanide ions combined with the intrinsic magnetic, optical, or redox activities of transition metal ions and their organic ligand counterparts, 4f/nd- MOCs are promising candidates for optically-addressable and chemo- or electroswitchable SMMs for nanotechnological applications as spin quantum sensors and switches in MS and QIP.[2–4]

In this contribution, we report our first results along this line covering the synthesis, the physicochemical and structural characterizations, as well as the direct (dc) and alternating current (ac) magnetic properties of the heterometallic gadolinium(III)-nickel(II) dithiooxalate (dto) hydrates of general formula $[Gd_2Ni_3(dto)_6(H_2O)_{10}]\cdot nH_2O$ [n = 12 (1) and 2 (2)].

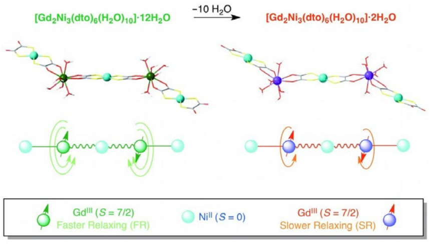

Figure 1. This unique solvatomorphic pair of neutral dithiooxalato-bridged 4f/3d-mixed pentanuclear complexes containing magnetically isotropic $4f^7$ Gd^{III} and diamagnetic low-spin $3d^8$ Ni^{II} ions exhibits an impressive solvatoswitching of the slow magnetic relaxation, being then proposed as a new class of solvatoswitchable SMMs.

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Dynamic evolution of surface states under illumination in single crystal perovskites

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Metal halide perovskites have arisen as one of the most promising semiconductor materials for optoelectronic devices on account of their low-cost production and tunable properties. Consequently, huge scientific efforts are being carried out to achieve a proper and lasting behavior. Recently, there have been developments on feasible single crystal (SC) synthesis methods to avoid any bulk defects, and interface/surface treatments[1], which are the most sensitive elements in perovskite devices as they are prone to degradation due to air exposure or contact with other materials[2]. Degradation is not always irreversible, and the original properties can be almost recovered using treatments like light soaking or passivation[1] that ensure longer lifetimes. In order to study the surface degradation mechanisms, surface sensitive techniques are required. Surface photovoltage (SPV), for example, provides information about surface electronic states and is affected by charge carrier dynamics that are stimulated by light, so a change in SPV can be correlated with degradation processes.

In this work, we study the surface potential of bulk SC MAPbBr3 perovskites in different degradation stages. Light-assisted Kelvin probe force microscopy (KPFM) has been used to measure the different SPV response of degraded, cleaved and UV passivated perovskites at the nanoscale. Furthermore, the SPV transients have been fitted into a single state model[3] in both light and dark evolution. This method grants a quantified viewpoint to our results, as trapping and time relaxation have been estimated under all prepared conditions and surfaces can be classified and distinguished according to these values.

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Oxidation product analysis of an α-pinene discharge by microwave spectroscopy

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Monoterpenes ($C_{10}H_{16}$) are biogenic organic volatile compounds (BVOCs) emitted into the atmosphere from vegetation. Amongst them, α-pinene is ubiquitous and is often observed to have the highest emission rates in the troposphere. Its photo-oxidation leads to a variety of monoterpenoids with lower vapor pressures that may participate in the formation of secondary organic aerosols (SOA). The formation of SOA using α-pinene as precursor has been the subject of numerous studies. However, the mechanisms of oxidation in the atmosphere are complex and far from being completely understood. Here, using chirped-pulse Fourier transform microwave spectroscopy, new assignment tools, and databases of computed structures, the discharge products of α-pinene in combination with molecular oxygen have been characterized in the 2 to 8 GHz frequency range. Among the oxygenated species observed, α-pinene oxide[1] has been identified in our experiment, thus continuing to highlight the use of electrical discharge sources as a valuable tool to generate oxidation products of atmospheric relevance.

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Molecular/2D hybrid heterostructures for magnonic applications

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Magnonics is an emerging research field that is recognized as a paradigm shift for information technologies, which is based on the use of spin waves. However, the low flexibility and variety of the existing systems is still far away from actual applications. In this computational work, we propose an unprecedented chemical approach to magnonics based on the creation of hybrid molecular/2D heterostructures. We analyze the interfacial interactions between selected organic molecules and a 2D magnetic material, where the magnetic properties are affected after molecular deposition. Our results predict a modulation of magnetic exchange interactions, a shift in the magnon frequencies and an enhancement of their group velocities up to ~7%. We strongly believe that this will open new avenues for the design of a new class of smart molecular/2D materials in which the magnonic properties can be selectively tailored by a chemical approach.

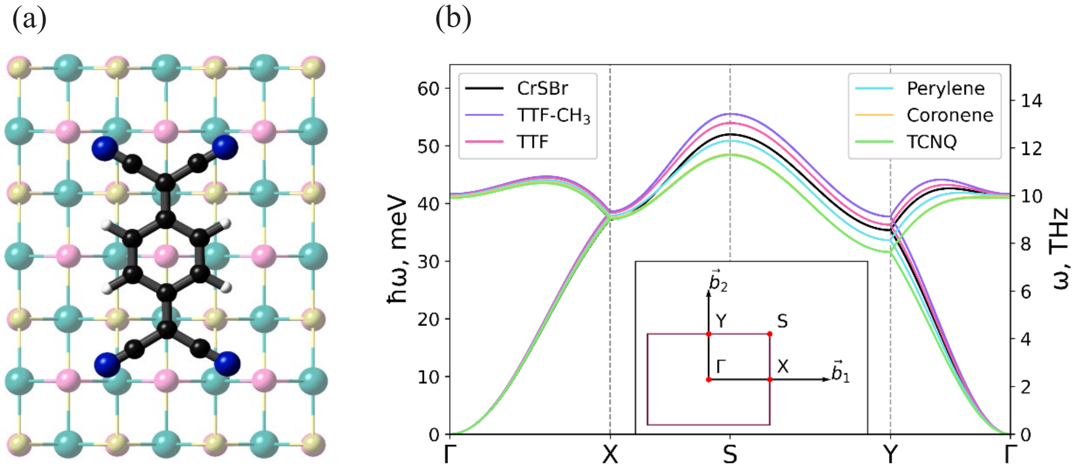

Figure 1. (a) Top view of a TCNQ/CrSBr hybrid heterostructure. (b) Magnon dispersion of pristine CrSBr and the different molecular/2D heterostructures.

Tailoring magnetism in low-dimensional materials

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The recent discovery of two-dimensional (2D) magnets has provided an unexplored and ideal platform to manipulate and control 2D magnetism and thus having applications in spintronics, or magnonics. CrSBr is a Van der Waals magnetic material, recently isolated to the monolayer limit.[1] It presents a ferromagnetic character with spins pointing in plane, showing a curie temperature (T_c) of 145 K and excellent magnetotransport properties[2] and whose magnetic properties have been selectively modified by strain engineering or atomic layer substitution, among others.[3] Herein, we propose a new route to modify its magnetic interactions by means of the creation of hybrid molecular/2D heterostructures. In this talk, we analyse the stability and modulation of the magnetic properties of a single layer of CrSBr after the deposition of sublimable organic molecules via first-principles calculations. Our results predict a prominent modulation of magnetic exchange, where we show that charge transfer is the main source of interaction between the molecules and the 2D material, allowing us to selectively correlate both properties.

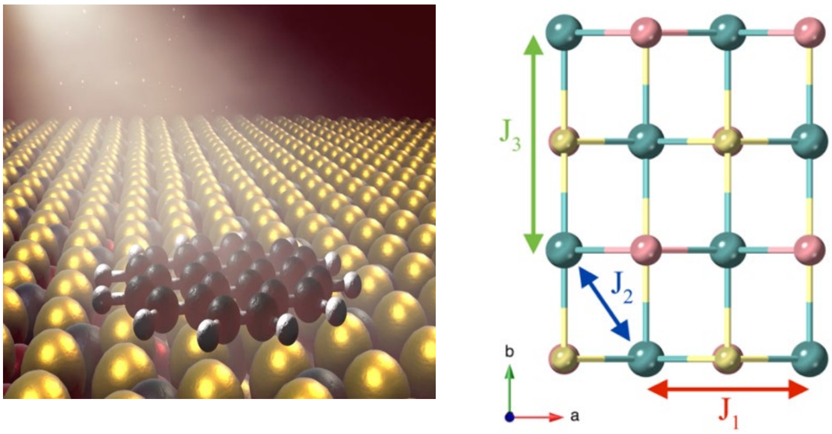

Figure 1. Graphical representation of a molecule deposited on a 2D material (left). Top view of CrSBr monolayer where J_1, J_2 and J_3 represent the magnetic exchange parameters between first, second and third neighbours, respectively (right).

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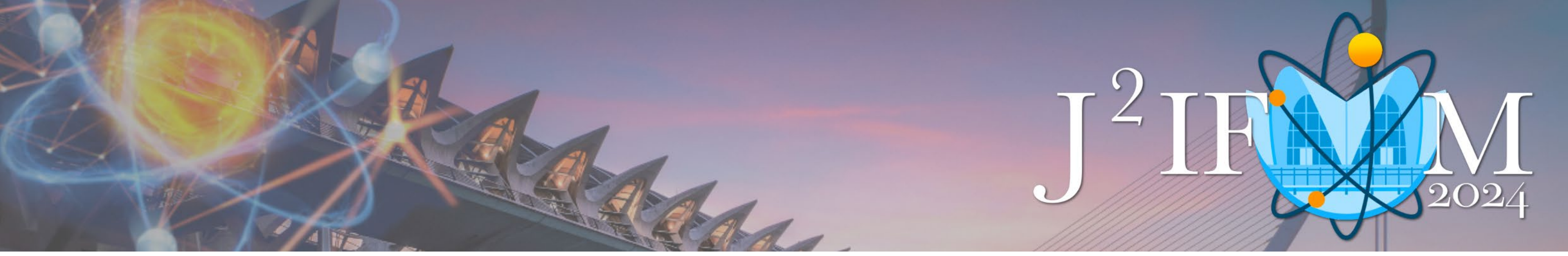

Building tight-binding models for second-principles simulations employing finite differences in real-space

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First-principles calculations allow to compute the energy and properties of a compound from essential information about its structure and composition. In principle, even the finite temperature behavior of materials is accessible from first-principles simulations since the early stage of density functional theory (DFT). Nowadays, however, such simulations remain practically limited by computational resources to very small length scales (a few hundreds of atoms per cell) and timescales (a few picoseconds). Nevertheless, many important fundamental and applied problems require to explore these large time and length scales at operating conditions (finite temperature, electric fields, etc). A practical way to overcome these limitations is to work with effective atomistic models, integrating out the electronic degrees of freedom and providing a simple parametric description of the Born–Oppenheimer energy surface in terms of structural degrees of freedom. This might be a constriction in some cases, specially, in those problems where the relevant physics is dominated by the electronic degrees of freedom. Recently, a method has also been proposed to reintroduce explicitly the treatment of the meaningful electronic degrees of freedom in the form of a tight-binding model, while avoiding double-counting with the effective atomic potentials[1].

This tight binding approach is based on the Taylor expansion of the DFT energy around a reference electronic density. The deformation density with respect this reference, as well as the hamiltonian matrix elements, is expressed in a basis of Wannier functions which are obtained from the band manifolds of interest in the problem. Only the relevant electrons to the problem can be retained in the description, reducing by orders of magnitude the computational cost. This gain in efficiency would come at the cost of finding the right parameters in the tight binding hamiltonian matrix elements, that would reproduce as close as possible the first-principle hamiltonian matrix elements.

Here we propose a method implemented in python, the MODELMAKER code, for the automatic parametrization of such tight binding hamiltonian. The starting point is made of first-principles calculations (from the SIESTA code[2]) in training sets with a small number of atoms in the unit cell. Since there is not input coming from the experiment, our method retains full predictive power, and that is why it is coined as second-principles simulations. Both electron-lattice coupling and electron-electron interactions are included in the parametrization of the electronic model. Electron-lattice coupling is caught by first and second order parameters computed through finite differences in real-space fed with calculations characterized by specific geometry distortions. Electron-electron interactions are studied by simulations exploring electronic states beyond the Born-Oppenheimer surface. The obtained parameters are validated comparing the band structures computed from first and second-principles in configurations that are not included in the training set. This methodology has been applied to the hydrogen chain, the prototypical ionic system LiF (linear chain), as well as to the paradigmatic functional oxide $SrTiO_3$.

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Mapping electron presence: a study of QTAIM∩ELF intersections

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Electron distribution functions (EDFs) offer a valuable means to elucidate fundamental aspects of chemical bonding theory, including electron pairs, polarity, charge transfer, and multiple bonding, by examining the statistical properties of multivariate electron number distribution functions[1]. Following the instructions of Quantum Chemical Topology (QCT), they have generally been applied to the Quantum Theory of Atoms in Molecules (QTAIM) partition, which allow to divide the real space into basins associated to individual atoms, or to the Electron Localization Function (ELF), whose partition of the real space is associated to Lewies entities, such as lone pairs, chemical bonds and atomic cores, albeit to a somewhat lesser extent.

While this established approach provides a valuable tool for characterizing chemical bonding while retaining essential concepts like atomic contributions and electron pair sharing commonly employed in chemical jargon, it would be desirable to leap forward and be able to divide even more the space into contributions coming from the portion of electron pairs associated to atomic regions. In this vein, our study employs EDF analysis at the intersection of ELF and QTAIM basins (Figure 1) to discern the electron pair contributions of each atom within the molecular bonding regime[2]. To achieve this, we focused on the hydrides of the first four-row elements, AH_n, and conducted an analysis of the ELF∩QTAIM EDFs at both DFT and multireference CAS levels.

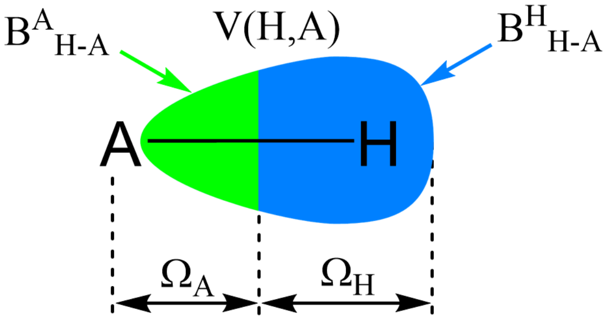

Figure 1. QEI partition scheme of a generic hydrogen V(H,A) ELF basin divided into $B^{A}_{H\text{-}A}$ and $B^{H}_{H\text{-}A}$ sub-regions, belonging to the Ω_A and Ω_H atomic basins, respectively.

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Understanding the growth of Zr Multivariate Metal-Organic Frameworks

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Multivariate Metal–Organic Frameworks (MTV MOFs) [1] are hybrid materials with multiple linkers or metals in a single structure. These porous crystalline materials have awaked a tremendous interest due to the fact their properties are not the result of the lineal combination of their single-component counterparts, and thus have potential applications in different fields, including photocatalysis, drug delivery or gas separation among others. However, there is still a lack of understanding of the effect of the synthetic parameters that govern their resultant properties at a molecular level, hindering their controlled design and applications.

Herein, we present a comprehensive understanding of the synthesis of a new multivariate Zr-based MOF family composed of two linkers. We prove that different the synthetic parameters can be tuned to selectively obtain fcu and hcp phases [2] with controlled incorporation ratios of the different linkers. We have applied Small-Angle X-Ray Scattering and Wide-Angle X-Ray Scattering using synchrotron sources to study their selective formation *in situ*, [3] providing information of the effect of synthetic parameters in the nucleation and crystallization kinetics of the different crystalline phases, which can be directly correlated to the controlled composition and particle size of the MOFs among other properties, such as their bandgap, defects or porosity, which are beneficial for photocatalytic applications.

Acknowledgments:

The authors acknowledge 'la Caixa Junior Leader' program (LCF/BQ/PR23/11980041) and ALBA Synchrotron (**BL11 – NCD-SWEET, 2023027311)** for funding.

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Noble-Metal-Free Photosensitizer and Catalysts for CO_2 Photoreduction

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Overcoming the hurdle of developing efficient photocatalytic CO_2 reduction systems that do not employ noble metals requires innovative approaches. The complexity of CO_2 reduction, including multiple proton-coupled electron-transfer processes and a diverse product distribution, presents a significant obstacle.[1] Hence, the electronic and structural conformations of photocatalytic system is important. We report a highly active Al photosensitizers (Al_3/Al_4), Fe-Quaterpyridine catalyst, TEOA (Triethanolamine) and BIH (1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[*d*]imidazole) as sacrificial electron donor for photoreduction of CO_2 reduction to CO in a noble-metal-free system. The application of time-resolved X-ray and optical spectroscopy in combination with time-dependent density functional theoretical (TD-DFT) calculations were used to monitor the electronic and structural dynamics of the elusive Fe^I species in two sets of Al/Fe^{II} CO_2 reduction systems. Upon excitation of the Al photosensitizer, the Fe^{II} catalyst is reduced to a distorted tetrahedral Fe^I complex. The formation and decay time kinetics for the photoreduced Fe^I species was further observed to~1.02-1.72 µs and ~23.2-28.9 µs respectively. These findings are crucial towards increasing our understanding of charge separation dynamics in Al-Fe photocatalytic systems and is an important step in the rationalization and design of sustainable artificial molecular photosensitizer /catalytic assemblies.

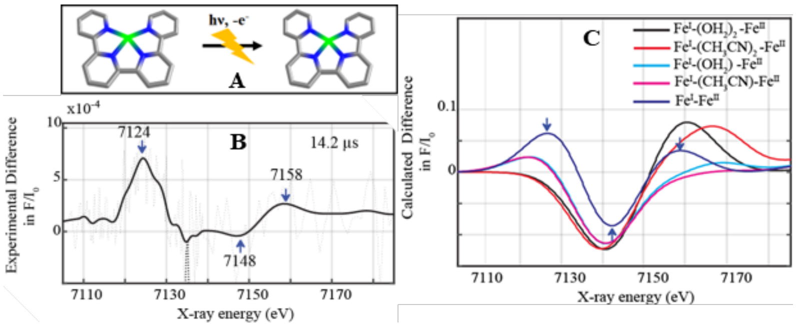

Figure 1. **A.** Stick diagrams illustrating the formation of a distorted tetrahedral photoreduced Fe^I species. **B**. Experimental difference spectra corresponding to the formation of Fe(I) photo-reduced transient signal at 14.2 µs. **C.** Theoretical XANES simulations.

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Design of computational strategies for the study of photo-induced reactivity in molecular clusters

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Motivated by the need for a better understanding of the reactivity of molecular systems of both astronomical and astrophysical interest under ionization or excitation by various light sources, my thesis centered on devising diverse theoretical strategies. These strategies aimed at aiding in the interpretation of experimental findings and advancing our understanding by offering profound theoretical insights. In this talk, we will look closer to the nature of the ionization, as we design a theoretical strategy that targets: Local Auger decay or Intermolecular Coulombic Decay (ICD), for the prediction of the formation of O_2^+ from CO_2 molecular clusters, and photon induced fragmentation for the prediction of the formation of new possible 'seeds of life' from ionized diketopiperazines.

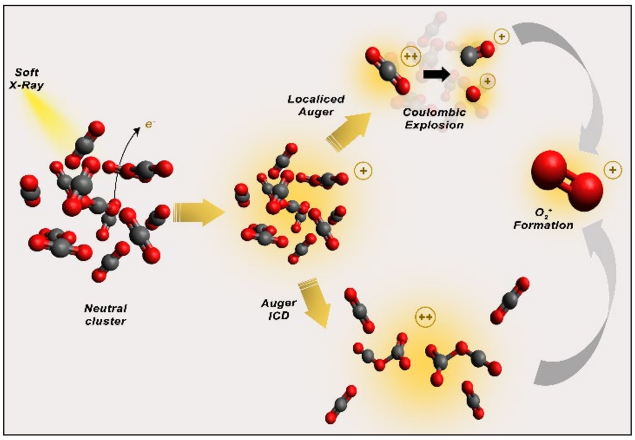

Figure 1: Simplified representation of a theoretical strategy used for the prediction of the formation of O_2^+ from CO_2 clusters when interacting with soft X-Ray photons.

Acknowledgments: This talk is based on my PhD thesis which was performed in the Universidad Autónoma de Madrid under the direction of Dr. Sergio Díaz-Tendero and the tutorship of Prof. Manuel Alcamí. The work was partially supported by MICINN (Spanish Ministry of Science and Innovation) project PID2019-110091GB-I00 and the COST action CA18212 - Molecular Dynamics in the GAS phase (MD-GAS). I would also like to acknowledge the generous allocation of computer time at the Centro de Computación Científica at the Universidad Autónoma de Madrid (CCC-UAM)

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Rediscovering Strong-Field Effects in Ammonia

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Ammonia (NH_3) has been investigated with femtosecond laser pulses centered at 800 nm with photoelectron (PE) imaging detection in a velocity map imaging setup. By gradually modifying the external field-intensity, a variety of strong-field phenomena has been induced. By scanning the 6-45 TW·cm^{-2} intensity range, non-resonant and resonance-enhanced multiphoton ionization processes (nrMPI and REMPI), Stark-induced Freeman resonances, above-threshold ionization (ATI) and strong-field ionization (SFI) regimes could be observed. Excitation or ionization from an electron of the nitrogen lone pair, responsible for the pyramidal geometry, generates Rydberg and ionic states with planar geometry. Due to this geometry change, they display long vibrational progressions in the umbrella mode (ν_2), which simplifies the vibrational analysis. We find that non-resonant contributions favour the generation of a cation that is vibrationally excited 2_0^6. We observe four (7+1) REMPI signals in the unperturbed regime. Two of them do not involve vibrational change from the Rydberg to the cation, while the other two do. The relative intensities of the resonances are modulated by vibrational selection while external field-strength is increased, favoring the one that does not involve any vibrational quanta variation. Finally, a weak Stark-induced Freeman resonance is generated, which displays ATI replicas that dominate the PE spectra. Through an 8-photon absorption process, a Stark-shifted high-lying Rydberg state is reached, from which a slow autoionization process occurs. The system is frozen while autoionization proceeds, providing more time to the system to absorb the extra necessary photons to produce the ATI replicas, thus removing population from the direct autoionization. At the highest-intensities, SFI produces structure-less ionization, closing the window of appearance of the previous resonances.

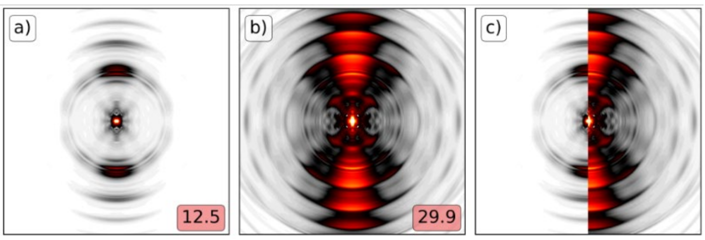

Figure 1. (a,b) Selected Abel-inverted photoelectron images obtained by photoionization of NH_3 with femtosecond pulses centred at 800 nm. Approximate laser intensities at the interaction region with the molecular beam are indicated in the bottom-right corner of each image, corresponding to (a) 12.5 and (b) 29.9 TW·cm^{-2}. (c) Side-by-side comparison of the previous images.

Modeling fragmentation of non-covalent molecular clusters in soft-ionisation mass spectrometry of deep eutectic solvents

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Computational modeling of mass spectrometry (MS) experiments gives us insight into the information unavailable from the experiments such as the structure of initial precursor ion after desolvation and the fragmentation energy of the parent and daughter ions. The contemporary universe of computational models for MS can be categorized into two modes based on their treatment of the experimental data: Top-down approach of training dissociation metrics on the available library of metabolomic and proteomic data to annotate and predict the MS processes; Bottom-up approach of statistical fragmentation of molecular entities using the quantum chemical thermochemistry and molecular dynamics simulations.

The analysis of non-covalent molecular clusters observed in soft-ionisation MS (SI-MS) techniques cannot utilize either of the above approaches as the systems are too large to be simulated quantum chemically, and a reference library of MS data and breaking curves for non-covalent clusters similar to the data libraries of protein MS does not yet exist.

In this work, we are proposing an approach to bridge the gap between the two above computational models. Our integrated approach preserves the first-principles nature of a statistical simulation of fragmentation with the potential scale-up to the chemical systems of sizes of dozens of non-covalently held molecules (supra molecules). Our model integrates the CREST software suite[1] for conformer sampling and thermochemistry calculations, with the M_3C fragmentation simulation algorithm[2]. A similarity metric is used to compare the simulated and experimental breaking curves, and combinatorial sampling of precursor ions produce the best candidates for the structure of the original chemical system of interest (figure 1).

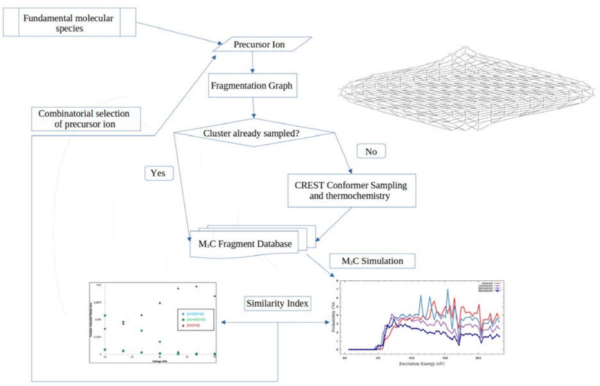

Figure 1. Work flow of the integrated suite for simulation of fragmentation process of molecular clusters in soft-ionisation mass spectrometry.

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Unraveling ClOOCl: UV/Vis Absorption Spectrum, Cross Sections, and Photodissociation Channels for Enhanced Understanding of Ozone Depletion Mechanisms

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In 1985, a significant thinning of the Antarctic ozone layer prompted research into the chemical mechanism responsible. ClOOCl emerged as a key contributor, absorbing sunlight to generate Cl atoms, which react efficiently with O_3. This study addresses NASA's recommendations[1]: "Additional determinations of photolysis quantum yields and product branching ratios at wavelengths longer than 300 nm would be desirable". Presenting data on ClOOCl's UV/vis absorption spectrum, cross sections, and photolysis rates.

Various CASPT2 methods and AINAMD were employed, revealing larger absorption cross sections than experimental spectra[2]. Photodissociation channels[3] were quantified, providing insights into ClOOCl's dynamics. Highlighting the increased importance of the 2Cl + O2 channel in ozone depletion, major photoproducts involve ClOOCl cleavage, exceeding NASA's expected percentages. This underscores the significance while also providing missing data on the UV/vis absorption spectrum and cross sections of ClOOCl. The results expanded our understanding of the reaction pathways and branching ratios of ClOOCl, contributing to the refinement of atmospheric models and enhancing our knowledge of its atmospheric behavior and ozone depletion mechanisms.

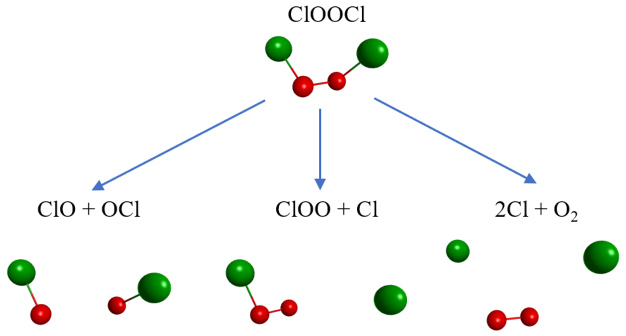

Figure 1. Illustration of the three photodissociation channels investigated in ClOOCl.

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Geometrical optimization in fast photodissociation dynamics: the role of momentum

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By coherent control, the yield of photodissociation reactions can be maximized starting in a suitable superposition of vibrational states [1]. In ultrafast processes, the interfering pathways are borne out of the early coherences in the ground electronic potential [2]. We interpret their effect from a purely classical picture, where the correlation between the initial position and momentum helps to synchronize the vibrational dynamics at the Franck-Condon window when the pulse is at its peak. In the quantum domain, we show that this localization in time and space is mediated by dynamical squeezing of the wave packet.

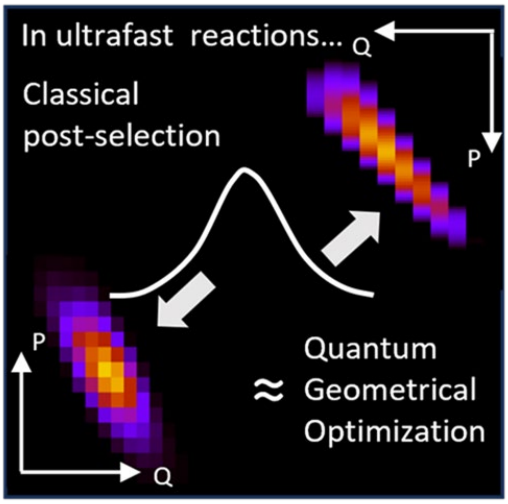

Figure 1. Illustrative diagram of the correspondence between the distributions of the conjugate variables of position and momentum for the semiclassical domine after a post-selection process (left) and those obtained in the quantum domine (right).

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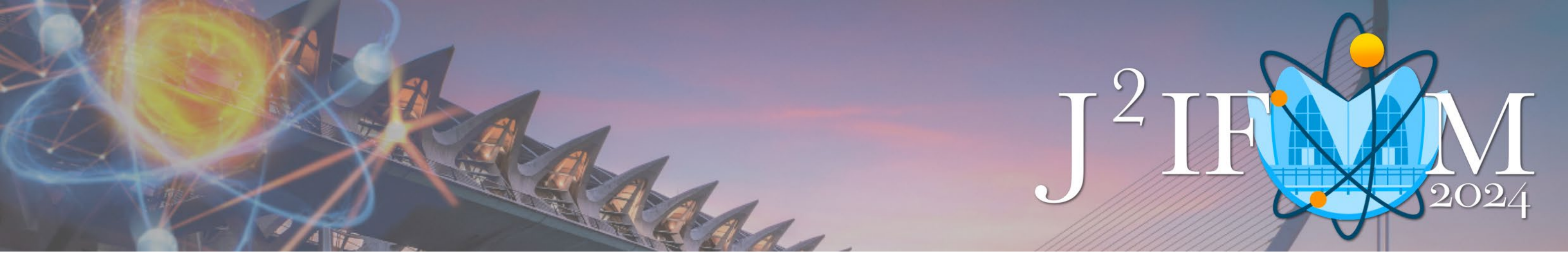

Oxyluciferin Emitters Force Field Parameterization for Ground and Excited-State Dynamics

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Nature presents a wide variety of bioluminescent systems. All of them are characterized by their ability to emit light in the visible region after an enzymatic reaction occurs, which leads to a chromophore in an electronically excited state.[1] Such a photochemical process can be employed in many technological and medical applications. Specifically, the bioluminescent system of fireflies has been extensively used in bioimaging[2,3] and biosensing[4,5] to detect carcinogenic cells and contamination of sterilized environments, respectively. However, the luciferin/luciferase complex can be tuned in order to improve its photophysical properties. This tunning process can be guided by theoretical studies, leading to a deep understanding of the key factors that influence the photophysics of the system.

Due to the extremely large size of the chromophore/enzyme complex, it is not possible to use quantum-mechanical methods to describe the entire system and some approximations are required. In the biological context, it is very common to use classical molecular dynamic to describe the movement of the atoms and thus, sample the conformational space. This methodology requires the use of analytical functions, named force fields, which have been parameterized to reproduce experimental or high-level calculations. However, while it is true that there exist accurate parameters to describe biomolecules, this is not the case for specific small organic molecules, especially in electronically excited states as we proved in a previous work. [6]

In this work, we present the parametrization process of the possible emitters of the oxyluciferin chromophore in both ground and first excited state based on quantum mechanical calculations. The new force field improves the current description of this bioluminescent system and could help unravel the unknown reasons of the emitted color modulation, since the structure of the enzyme modulates the emitted color in nature.

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NEXT: A Search for the Neutrinoless Double Beta Decay

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The NEXT (Neutrino Experiment with a Xenon TPC) collaboration aims to search for the hypothesised rare neutrino less double beta decay (0νββ) of ^{136}Xe. A detection of this process would confirm the Majorana nature of neutrinos and be a major milestone in particle physics.[1]

In the final phase of the experiment, a radiopure, high-pressure time projection chamber will be used. It will be filled with up to a ton of gaseous Xenon, enriched with ^{136}Xe. This approach allows for topological reconstruction of the events for background rejection, excellent energy resolution better than 1% FWHM in the energy region of interest,[2] as well as potential for detecting the daughter barium ion.[3]

The NEXT technology has been tested and validated in stages, recently successfully measuring the two-neutrino decay mode of ^{136}Xe.[4] The upcoming stage, NEXT-100, aims to set a first competitive limit on the 0νββ decay and is set to reach a sensitivity to the half-life of 4.1×10^{25} y after 3 years of data taking. In this talk I will give an overview over the current status of the experiment as well as ongoing research and development towards the final stage.

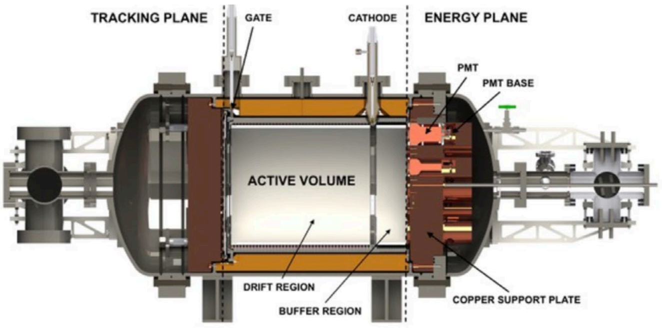

Figure 1. Schematic view of the NEXT-White TPC. This device, operated at the Laboratorio Subterraneo de Canfranc (LSC), represents the latest successful iteration of NEXT that was able to detect the two-neutrino decay mode of ^{136}Xe.[4]

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Time Independent Close-Coupling Approach to Non-Reactive H_3^+ + H Collisions

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Among all the species present in the Interstellar Medium (ISM), hydrogen-based compounds are the most abundant and play a fundamental role in the chemistry in space[1]. The complex chemical networks occurring in cold clouds begin with proton transfer reactions involving the extensively studied[1,2] *universal protonator* H_3^+. In a previous study[1] of the present research group, the formation reaction of this species ($H_2 + H_2^+ \rightarrow H_3^+ + H$) was analyzed for a wide energy range using a *quasi-classical trajectory method* (QCT), starting with the development of an accurate *Neural Network Potential Energy Surface* (NN-PES) and further application to plasma modelling. In this occasion, the non-reactive H_3^+ + H collisions with rovibrational excitations are studied in the ground electronic state of the already mentioned NN-PES. The *rovibrational levels*[2] of the triatomic fragment H_3^+ are initially calculated using the proposed *hyperspherical coordinates* of Pack & Parker[2] (APJH), with an explicit and careful treatment of the existing fragment symmetries – and estimating the dominant values of the *body-fixed projections* ω of the fragment angular momentum j. Then, for the modelling of rigid rotor-atom collisions, the authors have developed the program "DTICC", which computes the *space-fixed state-to-state reaction cross sections* $\sigma_{\alpha\alpha'}$ following a *Diabatic Time-Independent Close-Coupling* equation formalism[3].

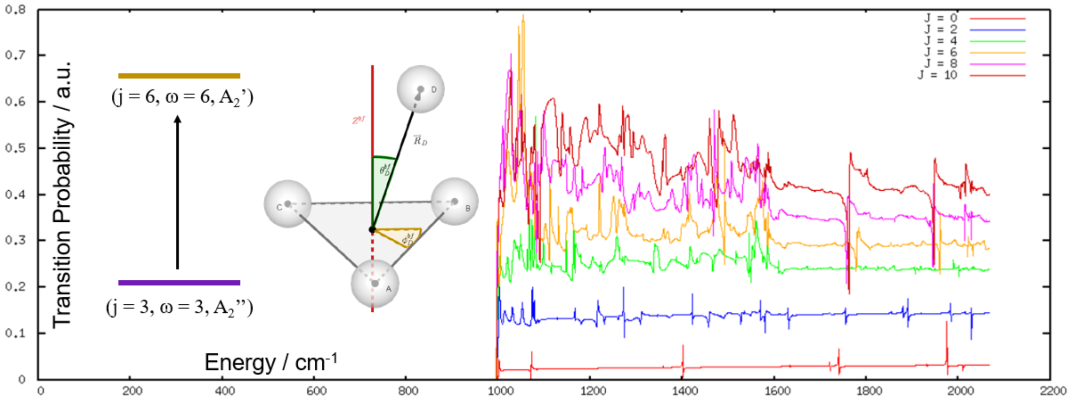

Figure 1. Calculated collisional transition probabilities for the transition from (j = 3, ω = 3, A_2'') to (j = 6, ω = 6, A_2') for total parity = +1 and J ≤10, in the ground vibrational state ($0,0^0$).

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