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Book Of Abstract

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Summary

MULTIREFERENCE SYSTEMS IN OPTICAL CAVITIES

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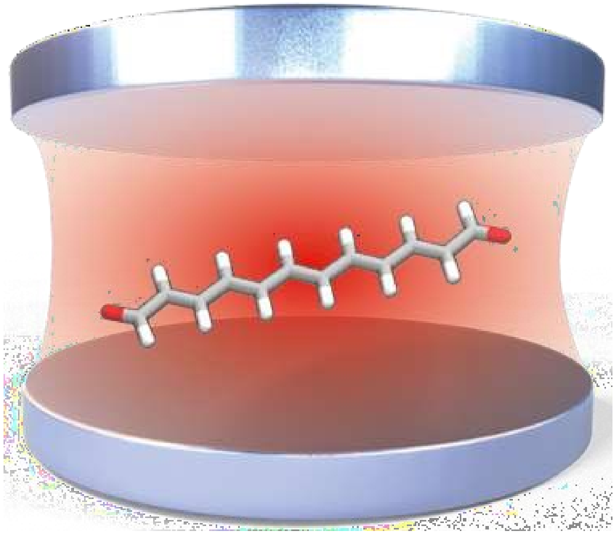
Polaritonic chemistry recently emerged as a new way to control and manipulate non-invasively the properties of molecules and materials exploiting the strong coupling between light and matter[1]. This can be achieved by placing molecules in optical devices as Fabry-Pérot cavities, generating mixed states with partial light and matter character known as "polaritons"[2].

In recent experiments it has been demonstrated that optical cavities could be used as an effective tool to control chemical reactivity[3]. However, the physics behind many of these processes remains unclear.

In recent years various ab initio methods have been extended to treat electron-photon correlation at different level of accuracy[4-6], but these methods are not suited for multireference systems.

The inclusion of multireference effects when dealing with electron-photon interaction is crucial not only to analyze the properties of multiconfigurational systems in strong coupling conditions but also because the coupling to the field can induce unexpected multireference behaviors.

In this talk I will present the first extension of the Complete Active Space Self-Consistent Field (CASSCF) method for the description of multireference systems in optical cavities. In the last part of the talk I will also address the inclusion of dynamical correlation by Second-order N-Electron Valence Perturbation Theory (NEVPT2) methods.



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HIGH-ENTROPY PEROVSKITE OXIDES: STRUCTURAL STABILITY, SOLUBILITY LIMITS AND CATALYTIC POTENTIAL

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High-entropy perovskite oxides have emerged as a versatile class of materials, with well-documented stability and a growing range of potential applications since their discovery. These materials, characterized by the general formula ABO_3, offer a remarkable degree of tunability in their structural and functional properties through compositional adjustments. Despite extensive research into applications, a systematic investigation into their stability, solubility limits, and compositional domains remains comparatively underexplored. This gap persists even with the availability of large datasets and computational tools that provide theoretical insights. [1,3,4]

In this work, we adopt a chemometric approach to examine the structural features and solubility boundaries of two specific families of perovskite oxides. The focus lies on compositions where the A-site is occupied by lanthanum, chosen for its inherent stability, and the B-site hosts a diverse array of cations, including Cr, Mn, Fe, Co, Ni, and Zn. Our goal is to establish experimental domains based on a comprehensive dataset that includes crystal structure, oxygen vacancy concentrations, temperature dependence, and chemical composition. [2]

The synthesized samples underwent x-ray diffraction (XRD) analysis, followed by Rietveld refinement, to extract precise crystallographic parameters. Employing multivariate analysis, we correlated elemental concentrations with phase stability and lattice parameters, enabling a deeper understanding of structure-property relationships. Furthermore, thermogravimetric analysis was employed to investigate non-stoichiometry, phase transitions, and redox behavior, integrating these findings into the broader experimental dataset.

Our systematic approach aims to identify correlations between crystal symmetry and catalytic performance, providing insights into the design of advanced materials. The resulting dataset will aid in optimizing compositions for targeted applications such as heterogeneous catalysis, solid-oxide fuel cells, thermochemical conversion, and oxygen transport membranes. By bridging experimental results with computational insights, this study advances the understanding of high-entropy perovskite oxides and their potential as multifunctional materials.

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NOVEL COMPUTATIONAL STRATEGIES FOR THE STUDY OF CHEMICAL SELECTIVITY: COMBINING HIGH ACCURACY AND CHEMICAL INSIGHT

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In this contribution, local correlation methods,[1] advanced conformational sampling strategies,[2-3] innovative electronic structure analysis tools[4-5] and machine learning models are combined to establish accurate computational protocols for the study of chemical selectivity in complex transformations. These protocols are employed to elucidate the mechanisms that govern the selectivity of challenging processes, encompassing for example asymmetric catalytic reactions for the synthesis of important pharmaceuticals and natural products.[6] The knowledge gained is then used to identify simple rule of thumbs for the design novel catalysts with tailored selectivity, and to provide insights into their potential validity across diverse chemical scenarios.[7]

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EFFECT OF A-SITE CATION ON THE OPTOELECTRONIC PROPERTIES OF TIN IODIDE PEROVSKITES

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Tin Halide Perovskites are promising materials for photovoltaic applications. However, they have received less attention compared to Lead-based Perovskite. In this work we have studied the role of the prototypical A-Site cations (such as FA^+, MA^+ and Cs^+) on the optoelectronic properties of Tin Perovskites. Firstly, we have operated several fabrications, changing some parameters the antisolvent or the temperature of annealing. Then we obtained three films with similar morphology (***Figure 1***), so we could study the electrical and optoelectronic properties excluding the effect of the morphology. After that, we considered the effect of different cations on the p-doping of the thin film via self-doping process. Where the low energy formation of tin vacancy defects is the main responsible of the intrinsic doping of tin perovskites. Our preliminary spectroscopic investigation exhibit small differences between the optoelectronic properties of the three perovskites. Consistently, DFT calculations show a minimal modulation of electronic and defect properties with different A-site cations (***Figure 2***).

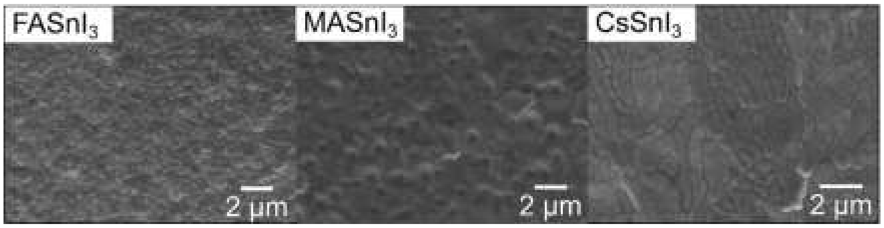

Figure 1: Top view SEM images of optimized $FASnI_3$, $MASnI_3$ and $CsSnI_3$ thin films.

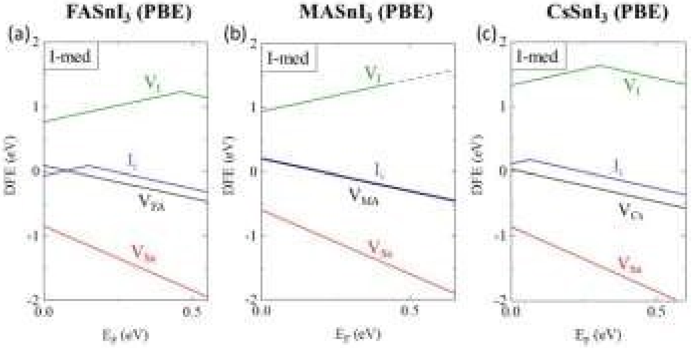

Figure 2*: Defect Formations Energies (DFEs) of main defects in FASnI3 calculated by using PBE functional for (a) I-rich, (b) I-medium and (c) I-poor chemical conditions.*

INTRODUCING ML METHODS IN THE DEAR OLD DFT

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Density functional theory (DFT) is one of the most effective methods to obtain optoelectronic properties of materials and molecules. While DFT offers a good compromise between accuracy and computational cost compared to other methods (Coupled Cluster, GW, ...), its use is restricted by computational power to systems of at most a few hundred atoms. Models of this size are large enough to study pristine materials or simple defective models but are far from reaching the description of realistic or in-operando conditions. However, to overcome these limits, machine-learning techniques have been developed to pair *ab-initio* DFT molecular dynamics simulations with the training of force fields. This allows for obtaining force fields to describe models with thousands of atoms restraining the DFT accuracy. In this talk, we present some preliminary results about the vibrational properties of the well-studied $CH_3NH_3PbI_3$ metal halide perovskite obtained using such force fields.

POLARITONIC BLOCH THEOREM BEYOND LONG-WAVE LENGTH APPROXIMATION

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Crystalline materials are undoubtedly the pillars of our modern high-tech society. In fact, their peculiar properties make them suitable for a plethora of engineering purposes, from the most common applications in electronics to the most recent and exotic ones in the field of quantum materials, whose phenomenology is strictly related to the formation of various quasiparticles. In this sense, the emerging field of polaritonic material science provides promising tools to control materials properties through the strong coupling to electromagnetic fields in optical devices. Despite its noteworthy potential, this field is still in its infancy and several experimental and theoretical efforts need to be made to unveil and exploit the physics of polaritonic systems. From a theoretical perspective, the development of effective first principles methodologies to describe crystals strongly coupled to photons still remain a major challenge[1]. In fact, in contrast to molecules, crystals match the cavity's dimensions, basically preventing the employment of the exceptionally convenient long-wave length (LWL) approximation[2,3]. In this talk, a proof of the extension of Bloch Theorem to polaritonic systems beyond the LWL approximation in the framework of minimal-coupling rule will be presented for the first time. Besides, a systematic strategy to simulate the effect of quantized electromagnetic fields on Bloch states will be proposed. By means of a general mathematical approach, this work represents a new step towards a more consistent theory of periodic materials embedded in optical cavities as well as a more realistic model of these devices.

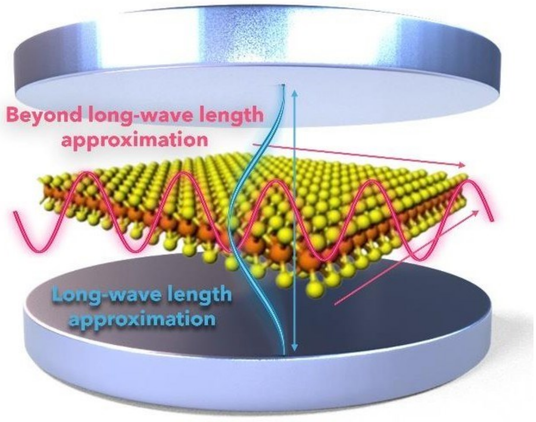

Figure 1: *Representation of a crystal embedded in a Fabry-Pérot cavity. The LWL (see text) approximation is only valid along the cavity axis (light blue sinusoid) while it fails along the axis orthogonal to the latter (pink sinusoids).*

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ULTRAFLAT EXCITONIC DISPERSION, HALF METALLICITY AND BAND FERROMAGNETISM IN SINGLE LAYER g-C_3N_4

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Graphitic carbon nitride (g-C_3N_4) is widely regarded as one of the most promising two-dimensional photocatalysts for hydrogen generation via water splitting. Single layer g-C_3N_4 hosts lone pairs arising from broken carbon-nitrogen bonds. These strongly localized and weakly hybridized lone pairs form ultraflat bands leading to peculiar optical properties and potentially leading to strongly correlated states when doped.

In this work[1], we employ many-body perturbation theory and the Bethe–Salpeter equation to provide a comprehensive description of the optical absorption and finite-momentum energy loss function for both s-triazine and tri-s-triazine structures. Our findings reveal the presence of ultraflat exciton bands with velocities that are two orders of magnitudes smaller than the typical ones in two-dimensional materials and of the same order or smaller than the optical phonon frequencies in single layer g-C3N4. As the time-scale for inter-site exciton hopping is longer or similar to a phonon period, our results point to a highly non-conventional exciton propagation.

Moreover, we consider the possible emergence of correlated states upon field effect doping. We show that the lone-pair depletion generates a very rich phase diagram. At low hole concentrations, a half-metallic state emerges with tunable magnetization, increasing linearly with carrier density and reaching up to $\approx \frac{1}{3}\mu_B$ per f.u.. At an integer filling of one hole per cell, a band-insulating ferromagnetic state is stabilized, followed by an interplay of metallic and half-magnetic phases with further doping, ultimately leading to a second ferromagnetic insulating state[2].

Our work highlights nitrogen-based lone-pair systems as a novel platform for strongly correlated states, with implications for magnetism even at small carrier concentrations

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COUPLED CLUSTER ANALYSIS OF INTERMOLECULAR AND INTRAMOLECULAR INTERACTIONS IN COMPLEX SYSTEMS: FROM WEAK INTERACTIONS TO COVALENT BONDS

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Non-covalent interactions play a pivotal role in various areas of chemical research, including catalysis, materials science, and biochemistry. Nevertheless, their weak nature makes their experimental quantification challenging. In this context, theoretical chemistry offers highly accurate methods for their quantification and interpretation. Among these, the DLPNO-CCSD(T)[1,2] method, a local variant of the CCSD(T) method, together with the LED[2] scheme, has been widely applied to complex systems containing hundreds of atoms[3]. This approach allows to quantify and analyse interaction energies between an arbitrary number of fragments (molecules or functional groups) in a system from a single supramolecular calculation. It has found applications in catalysis, materials science and in the study of protein-ligand interactions.[4] (**Figure 1**).

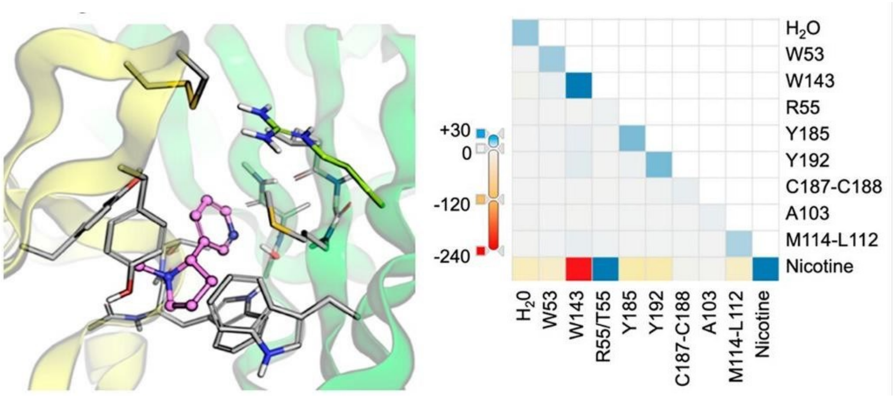

***Figure 1**: Nicotine binding to nAChR protein, highlighting key protein-ligand interactions using the LED map.[4] The visualization provides insights into the strength and nature of interactions with surrounding amino acid residues.*

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In this work, we discuss our recent efforts to extend the LED scheme to covalent bonds, aiming to develop a more general decomposition framework applicable to both covalent and non-covalent interactions. This advancement addresses a key limitation of the current methodology and opens new avenues for analyzing chemical bonding in complex systems.

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ELUCIDATING STRUCTURE-OPTICAL PROPERTY RELATIONSHIPS OF LOW-DIMENSIONAL PEROVSKITES VIA ssNMR SPECTROSCOPY

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Low-dimensional metal halide perovskites are attracting great interest for photovoltaics and photonics. In particular, 2D tin perovskites have been shown to have good optical gain properties which make them promising for applications as coherent light sources. [1] On the other hand, the ability of lead-based 2D perovskites to sustain lasing remain highly controversial. [2] Here we show that both Sn and Pb-based 2D perovskites thin films can achieve amplified stimulated emission, and compare their properties as function of the optical pumping conditions as well as of the materials' structural characteristics. By employing 1H, 13C, 15N, 119Sn and 207Pb solid state NMR spectroscopy, we were able to discern the local structural environments of the 2D perovskite of interest through their characteristic spectral fingerprints. Spin relaxation dynamics measurements reveal that the local supramolecular spatial arrangements, the molecular motions and structural rigidity are key factors shaping the energetic landscape of the material and its luminescence properties. Our work provides a deeper understanding of the structure-properties relationship of these soft semiconductors to assist the rational engineering of materials with improved optical properties for lasing applications.

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EXPLOITING FLEXIBILE MOFs PROPERTIES IN CO_2 ADSORPTION AND SELECTIVITY

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Metal-organic Frameworks for CO_2 capture from flue gas emission points, for biogas upgrade and for direct air capture are exploited for their industrial and large-scale applications. In recent years, promising materials have been employed as solid efficient sorbents for CO_2 absorption in real conditions, such as CALF-20 MOF, a zinc-triazolate-oxalate MOF able to selectively capture CO_2 up to 3.5 mmol/g at 343K in the presence of water vapour.[1] Crucial factors that enhance CO_2 capacity are related to the energy needed to regenerate the sorbent and the competition with other gases frequently present in the gas mixture, such as water vapour. For the absolute CO_2 uptake, the relevant parameter is the working capacity under the operational cycling conditions to regenerate the solid sorbent. Phase-change MOFs are flexible materials able to change their structure, by means of pore opening or ligands rotation, upon gas uptake with a drastic increase in the working capacity and in the selectivity towards CO_2. In this contribution, we report on the application of a multi-technique approach, based on in situ infrared spectroscopy, in situ laboratory and synchrotron powder X-ray diffraction, gas adsorption and microcalorimetry, periodic density functional theory simulations, solid state NMR and XAS spectroscopies, for disclosing the structural dynamics, phase transition and gas absorption mechanisms of several perfluorinated MOFs, a class of fluorine-containing porous materials with polar channels and, generally, with enhanced hydrophobicity with respect to the non-fluorinated counterparts. The presented MOFs are based on Al(III) and Ce(IV) as metal ions and simple dicarboxylic acids, such as terephthalic or succinic acid with different degree of fluorination.[2,3] The impact of fluorination degree on structural changes, on the breathing behavior and on CO_2 absorption dynamics is also discussed.

Acknowledgements**:** *Authors thank MIUR through the project PRIN2020 "doMino" (2020P9KBKZ).*

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ADDITIVES IN METAL-HALIDE PEROVSKITE SOLAR CELLS: A COMPUTATIONAL STUDY

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Perovskite solar cells (PSC) have gained attention in the last years because of their low-cost materials constituents, simple solution fabrication process[1], high absorption coefficient in a wide wavelength range[2] and increasing power conversion efficiency (PCE), which has recently reached the value of 26.7 %[3]. However, long-term stability is still one of the key issues that impedes rapid commercialization[4]. To overcome this problem, different strategies for stabilizing the active layer have been explored, including compositional engineering, controlled morphology, grain size control, perovskite deposition techniques, interfacial engineering, and many others[5]. An easy-to-implement approach is the use of additives, which in small quantities fine-tune the materials properties and increase the stability of the devices[5]. In this work, I present the results of DFT calculations that have been conducted in this field, placing some additives on a PbI_2 terminated surface of a $MAPbI_3$ perovskite. The results include optimized geometries, adsorption energies, contact energies, molecular distortion energies and perovskite distortion energies. These results are important to evaluate the influence of the functional groups on the interactions with the surface. In particular, the final geometries show how the additives connect with the perovskite: for example, the camphorsulfonic anion of the chitosan canphorsulfonate interacts with the perovskite bridging two undercoordinated surface Pb^{2+} ions[6]. The values will be used to predict target properties of the perovskites, training a machine learning algorithm. For this reason, a general overview on machine learning techniques will be also given.

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METAL-MODIFIED ZIRCONIUM PHOSPHONATE AS ELECTROCATALYSTS FOR THE OXYGEN EVOLUTION REACTION

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The electrochemical oxygen evolution reaction (OER) is the oxidative half reaction of water electrolysis, useful for many clean-energy production. In particular, the OER involves the reaction of two water molecules to give molecular oxygen, four electrons and four protons and it is undoubtedly the one with more complex kinetics and with higher activation energy barrier.

OER suffers from considerable overpotential losses due to its sluggish kinetics, hindering the large-scale implementation of sustainable energy production. As a consequence water oxidation half reaction is the rate determining step of the overall reaction.

Therefore, electrocatalysts have a significant role because they are able to reduce the kinetic barrier and they are used to enhance the efficiency of water electrolysis process. A good OER electrocatalyst should posses mechanically and chemically stability, corrosion resistance under normal operating conditions, stability for a wide pH range, low cost and simple preparation and fabrication methods. The most common OER electrocatalysts are based on noble metal oxides, (Ru and Ir) that offer the best catalytic performance for OER, but the high cost, low availability and poor chemical stability in alkaline electrolyte preclude their use on large scale. Thus, further research is needed to find more efficient, robust, stable, noble metal free and low cost OER electrocatalysts to promote large scale water electrolysis. [1]

Zirconium phosphonate based on glyphosine is an inorganic layered material characterized by high insolubility, good ion exchange and intercalation properties.[2] For these reasons, this material is a promising candidate as a catalyst support for transition metal-based electrocatalysts for the OER. Metal-modified electrocatalysts have been synthesised after exfoliation of zirconium phosphonate with intercalation of Fe(III), Co(II) and Fe(III), Ni(II), respectively. Then they were investigated for OER in alkaline media with various electrochemical measurements using a one-compartment three-electrode cell. Additionally, several strategies are used to improve the electrochemical performance, such as varying the relative amount of each metal within materials.

***Acknowledgements*:**

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FROM SOLUTION TO VACUUM DEPOSITION OF HALIDE PEROVSKITE THIN FILMS FOR SOLAR CELL APPLICATIONS

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Perovskite solar cells (PSCs) are an innovative photovoltaic technology offering high efficiencies and cost-effective production, primarily using solution processes. PSCs have versatile applications, including flexible solar cells, building integration, large-scale energy harvesting, and tandem devices. However, solution processes face challenges for industrial large-area production, such as solvent handling and material purity. To address this, vacuum deposition techniques were developed.
A hybrid vacuum/solution process was designed for fabricating perovskite on textured silicon solar cells, optimizing morphology through specific growth approaches and surface treatments. This method demonstrated efficient monolithic perovskite/silicon tandem cells surpassing silicon-only efficiencies. Further advances include co-evaporation, a solvent-free technique producing uniform, pinhole-free thin films. The major difficulty in co-evaporation resides in the control of the organic component in respect to the inorganic one together with an accurate knowledge of the interfaces structure. The deposition mechanism by double sources co-evaporation of organic formamidinium iodide (FAI) and inorganic lead iodide (PbI2) to deposit perovskite $FAPbI_3$ (FAPI) films is investigated as function of substrate temperature and deposition time. Studies on substrate temperature and deposition time improved perovskite film quality. Fully inorganic CsPbI2Br films fabricated by dual-source evaporation at high substrate temperatures achieved 13.2% efficiency in p-i-n cells, with optimized film morphology and bandgap. We will also discuss other approaches to deposit perovskite films by physical deposition, in particular Chemical Vapor Deposition[1] and Pulsed Laser Deposition[2]. Lastly, molecular beam epitaxy (MBE) was employed to grow $CsPbBr_3$ perovskite films with orthorhombic structures and exceptional crystallinity.[3] Films exhibited narrow diffraction peaks and high-quality morphology, making them promising for electronic and photovoltaic applications. These innovations enhance PSC fabrication and expand their potential in next-generation solar technologies.

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MODELLING DISORDER EFFECTS IN ORGANIC SOFT MATERIALS

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π-conjugated soft materials enable disruptive technologies such as organic photovoltaics, transistors, thermoelectrics, bioelectronics and batteries.[1] Tremendous progress in the synthesis, processing and characterization of organic electronic semiconductors has been achieved over the past decades, however fundamental *structure-properties functions* remain elusive yet.[2] Amongst those, are solid state *charge* and *ion transport*, representing complex multiscale phenomena developing in *space* (from the molecular- up to the mesoscopic-scale) and *time* (from ultrafast to continuous state) domains.[3] In this contribution, I will report case-studies of organic conjugated soft materials where the interplay between molecular structure, supramolecular organization, inter-molecular interactions and thermal effects governs the solid-state phase transitions, the electronic and the ionic transport properties.[4,5,6] Density functional theory and force-field based molecular dynamics of both crystalline and amorphous materials will be critically discussed, by emphasising the impact of static and dynamic disorder effects on tuning the properties of functional materials.

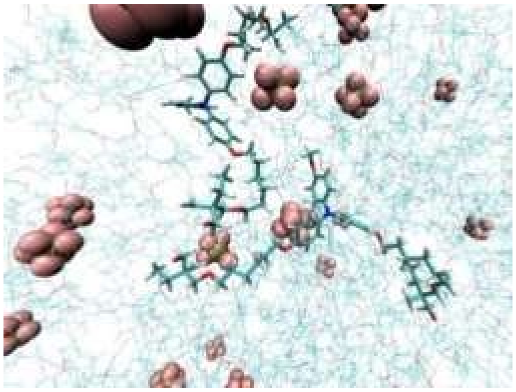

Figure. *Atomistic simulations of an organic cathode based on cross-linked polymer interacting with PF_6^- ions.*

Acknowledgements**:** *Global Faculty Program of the University of Cologne, DFG Research Training Group 2591 ''Template-designed Organic Electronics (TIDE)'', the National Recovery and Resilience Plan (NRRP), Mission 04 Component 2 Investment 1.5 – NextGenerationEU, Call for tender no. 3277 dated 30/12/2021, Award Number: 0001052 dated 23/06/2022, and the National Project funded by the European Union – Next Generation EU, Project title ''Modelling and design of organic conjugated redox materials for energy-saving applications: a bottom-up strategy'', code MUR 2022WKTH9E – CUP J53D23008810006.*

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THz SPECTROSOPY OF TIN PEROVSKITES: UNDERSTANDING DOPING AND POLARONIC COUPLING

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Tin-based halide perovskites (THPs) have emerged as promising candidates for both photovoltaics and near - IR light emitting applications thanks to their high carrier mobilities, low band gap, ideal for pairing with silicon in tandem solar cells[1,2]. THPs present highly stable acceptor defects such as Sn vacancies and I interstitials, which result in a permanent population of holes: the material than behaves as a p-doped semiconductor, with self-doping densities as high as 10^{22} cm^{-3} that can negatively impact device performances. As such, it is of critical importance to devise strategies to both quantify and control the dopant hole densities in THPs by compensating the oxidation state of Sn during material fabrication using additives such as SnF_2. In this context, terahertz (THz) spectroscopy represents a powerful tool to characterize the carrier populations and dynamics in THPs. THz radiation is sensitive to mobile charged carriers[3], as well as their coupling with lattice phonons[4]: it can then be used to shed light on charge transport properties in THPs, as low frequency phonons in the THz range have been shown to limit their thermal and electrical conductivity. Moreover, as the doping density affects both transparency to THz radiation and carrier phonon coupling, THz absorption can be used as a sensitive, contactless probe to characterize the self – doping density even in samples where it has been brought down to levels comparable to background carrier densities suitable for device applications (e.g. 10^{15} cm^{-3}), and that could be challenging to characterize by traditional Hall effect measurements. Furthermore, time resolved THz spectroscopy after optical excitation of the material allows to follow the dynamics of photogenerated carriers with ps temporal resolution. Here we develop a robust technique to study the doping hole density in $FACsSnI_3$ thin films by analyzing the static THz conductivity response, and characterize ultrafast carrier dynamics using time resolved THz spectroscopy. By supporting our results with DFT calculations, we also investigate the effect of doping concentration and defect states on optical phonon frequencies and their coupling to charge carriers. Finally, the possibility of studying the material polaronic response by combining THz and XUV absorption spectroscopy will be discussed.

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WATER REPELLENT LOW-DIMENSIONAL PEROVSKITES FOR PHOTOVOLTAIC APPLICATIONS

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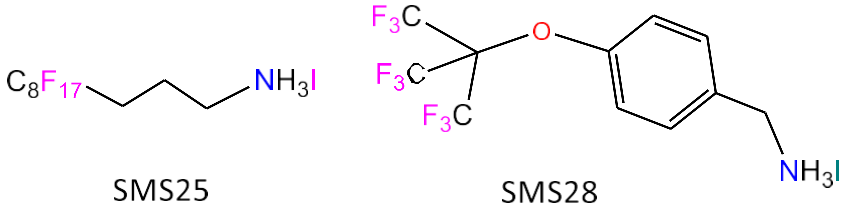
Low-dimensional perovskites (2D-PVK) represent a promising class of layered materials for applications in perovskite solar cells (PSCs).[1] The integration of these materials with typical 3D perovskites can combine the excellent optoelectronic properties of the last ones with a greater environmental and chemical stability of the formers due to the presence of larger organic linkers between the inorganic layers.[2] Furthermore, the introduction of fluorinated organic cations improves not only the structural rigidity but also the moisture stability of the resulting 2D-PVK.[3-5] In this work, we have designed 2D-PVKs based on aliphatic (SMS25) and aromatic (SMS28) fluorinated ammonium cations in order to evaluate their potential applicability in PSCs as moisture-resistant capping layers on the top of the absorbent material, as previously reported in literature for similar systems.[6] 2D-PVKs synthesis was carried out with a slow solvent evaporation procedure and the corresponding thin films were fabricated with a spin-coating protocol. The 2D-PVKs powders were characterized through X-Rays Powders Diffraction (XRPD) and their thermal robustness was established using Thermogravimetric (TGA) and Differential Thermal Analysis (DTA). To investigate the thin films optical properties, we have performed UV−vis absorption analysis and estimated the band gap values through a Tauc Plot extrapolation method. Finally, the moisture resistance of the 2D-PVK films was monitored in controlled relative humidity chambers to evaluate their potential use as humidity-protective layers in photovoltaic devices.



SMS25 SMS28

***Figure 1**: Aliphatic (**SMS25**) and aromatic (**SMS28**) ammonium cations employed in this project for the synthesis of fluorinated 2D-PVKs.*

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ADVANCING STABILITY AND EFFICIENCY IN METAL HALIDE PEROVSKITES FOR SOLAR ENERGY APPLICATIONS

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The remarkable optoelectronic characteristics of metal halide perovskites (MHPs), such as their variable band gaps, high absorption coefficients, and defect tolerance, have made them a groundbreaking class of materials in photovoltaic research. Even though solar cells have achieved impressive power conversion efficiency, issues including lead toxicity, unstable environments, and inconsistent manufacturing prevent their widespread use.

The optoelectronic behaviour and defect chemistry of MHPs are examined in this study using sophisticated computational techniques, including Density Functional Theory (DFT). The impact of internal and extrinsic flaws on stability and performance is thoroughly examined, with a focus on the functions of chemical passivation techniques, dimensional engineering, and halide alloying. Novel strategies, including as hybrid compositional designs and surface treatments, show improved device resilience to environmental stresses. These findings open up the possibility to scalable, environmentally friendly perovskite-based solar technology applications and improved production procedures. This work paves the door for next-generation energy solutions by offering insightful information on how to overcome the material and environmental issues facing MHPs.

NOVEL MACHINE LEARNING STRATEGIES FOR THE CALCULATION OF RELATIVE ELECTRONIC ENERGIES

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Reducing the computational cost of electronic structure calculations has long been a central challenge in Computational Chemistry. This talk presents a strategy to address this challenge by integrating Machine Learning (ML) models with low-level electronic structure calculations, following a ΔML approach.[1][2]

Specifically, linear ML models are developed to approximate relative electronic energies at the Coupled-Cluster (CC) level of theory, using descriptors derived from Density Functional Theory (DFT). By training these models on the extensive GMTKN55 benchmark set,[3] a significant reduction in DFT errors relative to the gold standard CCSD(T) level of theory was achieved for various functionals (PBE, PBE0, and M06-2X), as illustrated in Figure 1.

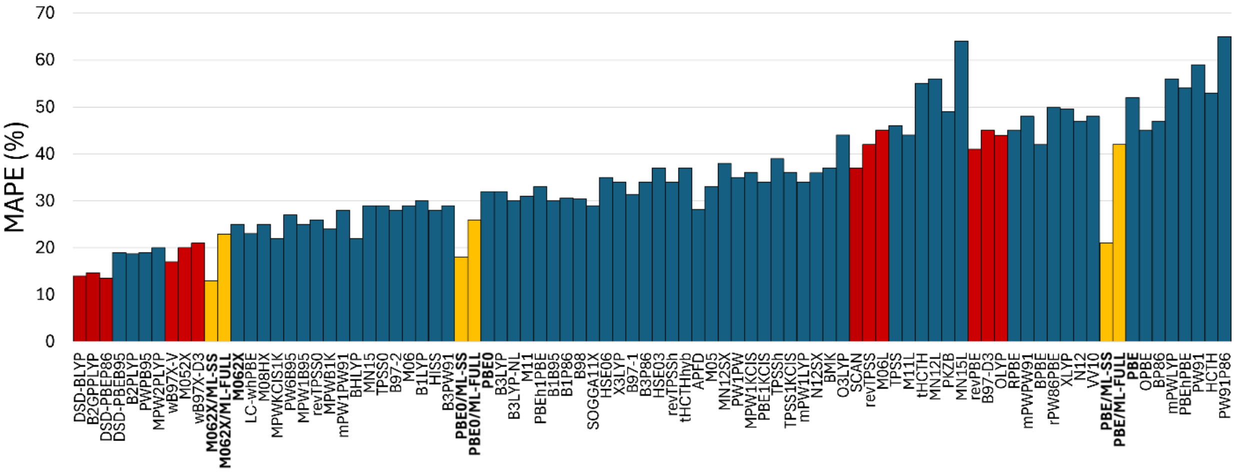

***Figure 1**: Jacob's Ladder for the Mean Absolute Percentage Error of the functionals of the GMTKN55 benchmark set with ML-Corrections*

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ML-RAMAN CALCULATIONS FOR CHARACTERIZING MOBILE IONS IN SOLID-STATE ION CONDUCTORS

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Raman spectroscopy is a non-invasive and widely accessible technique for probing atomic vibrations in solid-state materials. However, its interpreting often relies on comparisons with preselected reference materials. While first-principles calculations offer a robust alternative for interpretating experimental Raman measurements, they become computationally prohibitive for systems with large unit cells, defects, or mobile ions. To overcome these limitations, we developed rapid computational frameworks that leverage machine-learning force fields (MLFFs)[1] and machine-learned polarizability tensors to predict Raman signatures of mobile ions and point defects in solid-state ion conductors.

Using this ML-Raman framework, we identify low-energy Raman modes in superionic conductors and broadened Raman peaks in disordered systems, offering insights into the conductivity mechanism of mobile cations[2]. Additionally, we present a novel method for predicting Raman modes of ionic point defects by combining MLFFs and atomic Raman tensors[3]. This approach was successfully applied to characterize temperature-dependent changes in experimentally measured Raman spectra of Ni-doped $SrTiO_3$, which were attribute to local variations in the dominant ionic point defects. Our framework opens synergies between theory and experiments, advancing the understanding of the dynamical properties of energy materials.

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FIRST PRINCIPLES VIBRATIONAL PROPERTIES OF DEFECTED AND DISORDERED SYSTEMS

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The recent advances in scanning tunneling electron microscopy (STEM) instrumentation, bringing the energy resolution of electron energy loss spectroscopy down to the sub-10 meV regime while maintaining atomic resolution, has opened a new field of research focused on the local investigation of atomic vibrations in systems, ranging from interfaces [1] to point [2] or extended defects [3]. Given the intrinsically long-range nature of vibrational modes, the proper modelisation of these newly available experimental results involves structures with a very large number of atoms, making the direct use of the available first-principles approaches rather impractical. Indeed, first-principles description of phonon scattering from defects, even of the most elementary kind (point defects such as vacancies or substitutional defects) is sporadic, if not entirely lacking. This situation can be overcome starting from the observation that the change of the interatomic force constants (IFCs) induced by a structural or chemical defect is, in most of the cases, very well localised. This idea is at the core of the approach that we implemented in [2]: first, the IFCs of a relatively small system (hundreds of atoms) are calculated from first-principles (density functional theory, DFT); then, these IFCs are assembled with those of the "undefected" crystal to build the dynamical matrix of a more realistic system (several thousands of atoms). This strategy preserves the accuracy of DFT techniques providing a direct access to the delocalised nature of the vibrational modes. In [2], this approach allowed us to determine the quasi-localised nature of the vibrations of a Si substitutional defect in graphene and explain STEM observations.

The same approach can be used to study even more complex systems, such as the interface between an hexagonal SiC substrate and a few-layer-thick epitaxially-grown graphene (a system considered nowadays of technological interest [4]). In particular, I will present a detailed study of the vibrations occurring in the first graphitic layer (buffer layer) which is directly interacting with the silicon-terminated surface of the substrate, showing that, with about a quarter of carbon atoms covalently bound to the substrate, the buffer layer can be considered as a prototypical model for local chemical and structural disorder in graphene. Calculations will be used to interprete very recent atomic-resolution EELS obtained at the SuperSTEM Daresbury (group of Q.Ramasse). The evocation of disorder will then be an opportunity to discuss the results we have recently obtained on acoustic phonon branches of ice VII [5]. This high-pressure phase of ice indeed displays a complete proton disorder while retaining a quasi-bcc oxygen sublattice. Due to its specific atomic structure, ice VII provides a very pedagogical example where the X-ray (or, equivalently, the energy loss) scattering cross-section naturally unfolds the phonon dispersion of this disordered system.

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TOOLS FOR THE RATIONAL DESIGN OF MATERIALS: CHEMICAL INSIGHT FROM ACCURATE AND EFFICIENT CALCULATIONS

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Like many fields, material development can greatly benefit from rational design strategies informed by quantum chemical calculations. This contribution will detail recent developments in tools to this end, focusing on fragment-pairwise Local Energy Decomposition (fp-LED) analysis.[1] Unlike other methods for the analysis of chemical calculations, which suffer from the inaccuracies of Density Functional Theory that underlies them, fp-LED relies on Coupled Cluster with Single, Double, and perturbative Triple excitations (CCSD(T)) – widely considered the "gold standard" of accuracy – in its efficient (linear scaling) form, utilizing the Domain-based Local Pair Natural Orbital (DLPNO) approximations.

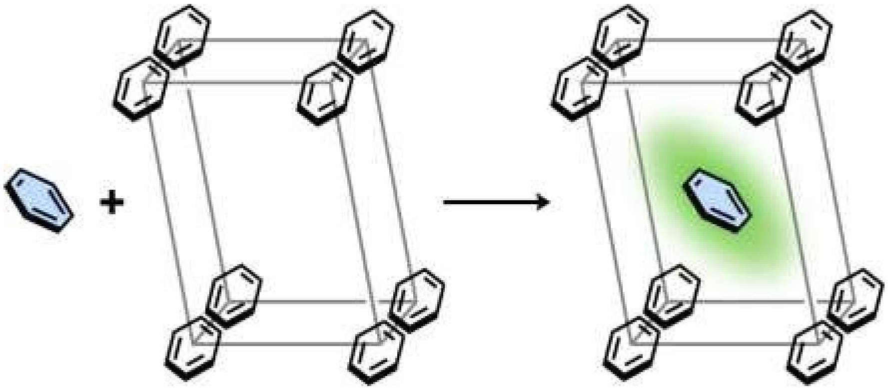

Figure 1*: Schematic representation of the non-covalent interactions in the lattice formation of the benzene crystal.*

fp-LED exactly decomposes the DLPNO-CCSD(T) energy into contributions from user-defined fragments, providing chemical insight at the functional-group or atomic scale. For example, a section of a lattice can be modelled (Figure 1), and the lattice energy is decomposed into chemically meaningful contributions such as electrostatics, Slater exchange, and London dispersion energy. Repeating the process with additional functional groups could identify potential synthetic targets. Other examples covered will include organic polymeric materials with potential applications in energy storage. fp-LED is currently implemented in a developmental version of the ORCA code,[2] and will be made freely available upon its next release.

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SHEDDING LIGHT ON PHOTOCATALYSIS BY COBALT COMPLEXES: A COMPUTATIONAL STUDY

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Recently a cobalt-catalyzed, light-induced synthesis of amides was experimentally reported [1], achieving 100% atom economy by coupling amines and alkenes under 390 nm LED illumination. Despite its practical advantages, the underlying mechanism remains poorly understood. Herein we reveal the role of vibrational modes in enabling efficient photoabsorption at 390 nm. Furthermore, we present a detailed exploration of the potential energy surface of the catalytic reaction, which identifies an amine-facilitated nucleophilic substitution pathway as the most favorable route to amide formation.

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TUNING STRATEGIES TO ENGINEER CHIRAL METAL HALIDES

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Chiral hybrid organic–inorganic metal halides, including low-dimensional perovskites, showing peculiar nonlinear optical and spin-dependent properties, are triggering a huge interest for their potential use in different applicative areas such as chiroptoelectronics and spintronics. In addition, their intrinsic noncentrosymmetric structure may be exploited in ferroelectric and piezoelectric devices. To date, the number of chiral systems is growing very quickly, and among the different structures reported, 2D chiral perovskites represent the vast majority. However, the structural family of chiral metal halides extends well beyond 2D perovskites and includes several 0D and 1D systems as well as 3D and quasi-2D motifs, which have been prepared using the commercially available chiral amines. As for other metal halide perovskites and low-dimensional systems, a wide range of tuning strategies can be put in place to modulate the (chiro)optical properties also going beyond Pb-based materials. In this presentation, we will show the recent progress of our group in the design of novel chiral metal halides making use of: i) chiral cation modulation (also considering ad-hoc synthesized cations); ii) modulation of B-site metal (i.e., Sn. Ge, Bi, Sb, Cu, Ni, Mn); and iii) halide substitution. The range of structural motifs arising by playing with "chemical degrees of freedom" is huge, providing also novel crystal structures not yet observed in current chiral (and achiral) metal halides. This work on the chemical modulation allows to understand which are the parameters mostly affecting the chiroptical properties of chiral metal halides thus paving the way for a rational design of novel materials.

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C-N CROSS COUPLING WITH NICKEL BIPYRIDINE COMPLEXES: MECHANISTIC INSIGHTS FROM THEORY

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Carbon-nitrogen cross-couplings are a crucial class of reactions as they enable the formation of C-N bonds, which are found in a wide range of valuable compounds for pharmaceutical, polymeric, and agrochemical industries.[1–3] One of the most widely used protocols for C-N cross-coupling employs palladium as the catalyst.[4] However, the high cost of palladium and the associated ligands remains a significant drawback for large-scale applications. In this regard, nickel has emerged as a prominent alternative as a catalyst capable of promoting C-N cross-coupling.[5–7] Despite its potential, many aspects of the reaction mechanism remain unclear. This work investigates the cross-coupling reactions of aryl halides and amides using nickel and iridium as catalysts, focusing on experimental works by the Bahamonde group.[5,6] Our objectives include investigating whether a dark or photocatalyzed cycle is operative, identifying the rate determining states, understanding the differences in reactivity between the reactants, and exploring the role of potassium phosphate as a substitute for commonly used redox-active bases *e.g.* DABCO and quinuclidine.

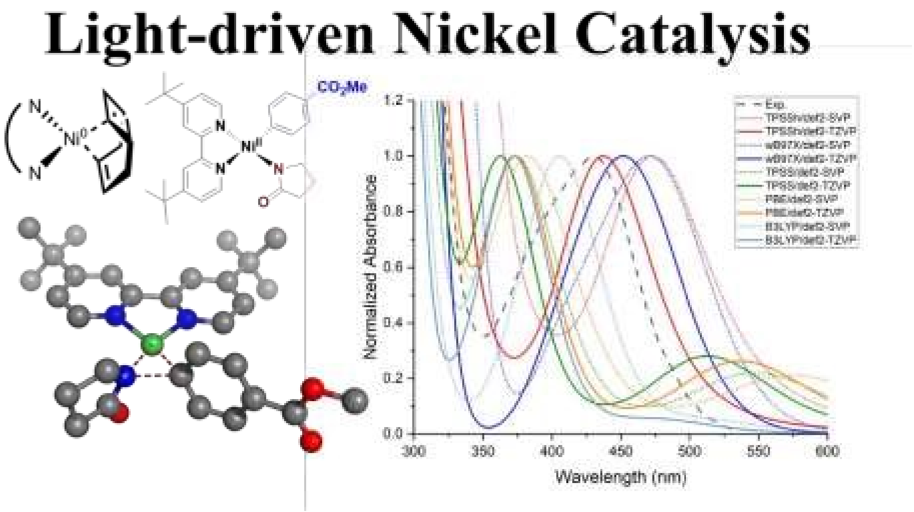

Figure 1. *Catalytic cycle intermediates and TD-DFT spectrum computed with multiple theory levels in order to evaluate the most efficient one.*

Acknowledgements**:** *This work was supported by CAPES (Fundação Coordenação de Aperfeiçoamento de Pessoal de Nível Superior) agency and the Università degli studi di Perugia.*

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ECONOMICAL PROCESSES TO SEPARATE D_2 FROM H_2: OXIDES OR DECORATED POLYCYCLIC AROMATIC HYDROCARBONS?

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Whether for a usage as marker in interesting molecules, or as potential nuclear fusion fuel, the separation of deuterium from its lighter protium counterpart has been attracting attention for quite some time, the main thrust being the necessity of reducing operational costs. In this contribution, we report on the computational exploration of two different classes of materials investigated as possible chromatographic stationary phases for D_2/H_2 separation, namely amphoteric oxides[1] and decorated polycyclic aromatic hydrocarbons (PAH)[2,3].

Among the possible members of the first class, we have considered group III oxides (i.e. Al_2O_3, Ga_2O_3, In_2O_3) and ZnO, all of which present markedly negative zero-point corrected adsorption energies spanning the range 5500-22800 K, as estimated on previously validated cluster models representing surface defects. The latter values are a clear indication of chemisorption processes leading to the heterolytic dissociation of hydrogen diatoms. Adsorption selectivity toward D_2 can be easily estimated employing the harmonic approximation to describe the vibrational spectrum of the chemisorbed species, and appear to remain well above 10 even at 300 K. Isotopic scrambling due to the collision between chemi-sorbates and gas phase species is predicted to be far slower than the desorption process, leaving the isotopic composition of the former unchanged.

As for PAH, sodium atom-decorated coronene[2] and circumcircumcoronene (CCCor)[3], while uncapable of dissociating diatoms, can easily adsorb 5-6 molecules around the Na atoms releasing 800-1400 K of energy per molecule, depending on the specific composition. The latter is partially ionized as it delocalizes its valence electron in the PAH conduction band. Due to the smaller adsorption energies, lower operational temperatures would be required. Despite this, selectivity above 50 are easily obtainable in the range 20-40 K independently of the gas phase composition. A comparative discussion on main advantages/shortcomings for the two classes of materials will be provided to shed light on their possible industrial application.

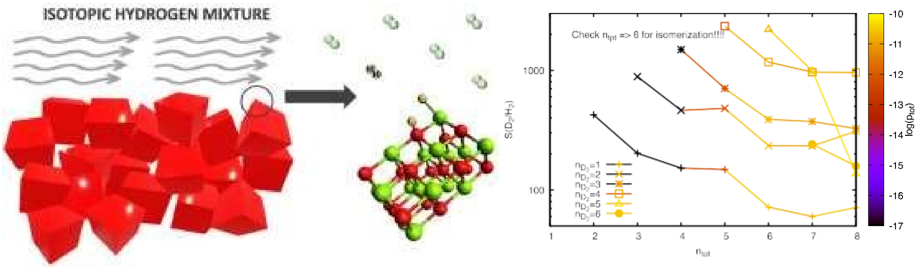

***Figure 1**: (left) schematics of chromatographic processes; (right) selectivity on Na-decorated CCCor.*

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THE OUT-OF-PLANE OPTICAL CONSTANT OF A TWO-DIMENSIONAL CRYSTAL: EXPERIMENTAL OBSERVATION OF AN ELUSIVE QUANTITY

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Two-dimensional (2D) materials have shown a lot of promise for optical applications. Recent proposals include flat optical devices with the same performances of traditional bulky optical structures[1], and wafer-scale monolayer film integration for stable, efficient perovskite solar cells[2]. Despite this, much remains to be done in terms of fundamental research.

One example comes from the experimental observation and the theoretical description of the out-of-plane optical constants of these materials, that have proven to be experimentally elusive. Owing to the reduced dimensionality of 2D crystals, optical measurements have limited sensitivity to these properties which are hidden by the optical response of the substrate. Therefore, there remains an absence of scientific consensus on how to correctly model these crystals.

Here we present an experiment on the optical response of a 2D crystal that addresses these problems. We successfully remove the substrate contribution to its optical response by a step deposition of a monolayer crystal inside a thick polydimethylsiloxane prism. This allows for a reliable determination of both the in-plane and the out-of-plane components of its surface susceptibility tensor. Our results prescribe one clear theoretical model for these crystals[3-6].

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THIN-FILM MATERIALS FOR PHOTOVOLTAICS TOWARD HIGH EFFICIENCY AND INTEGRATED SOLUTIONS

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Photovoltaics (PV) stands out as a key player for the transition to a sustainable energy future. The numbers give evidence of a fast-growing market. The global cumulative installed capacity reached over 1.6 TW in 2023, and among the new installations PV represented more than 75% of all new renewable electricity technologies. All is set to meet the net-zero emission ambitions, but big challenges must be faced: high PV growth rates must continue and ubiquitous PV deployment is needed. Research is active on many fronts to find more efficient and cost-effective solutions at solar cell level. Strong effort is also placed into solutions that integrate PV with competing applications, as in agrivoltaics for optimal shared land use with agriculture, thus tackling the issue of the considerable land resources.

This talk will start with a review of this scenario and then present the pathways followed at ENEA - Portici Research Center, in the Innovative Device Lab (Energy Technologies and Renewable Sources Department, Solar Photovoltaics Division). A wide range of PV technologies is under investigation toward high efficiency solar cells and toward novel integrated solutions for agrivoltaics, with the common thread being research and development of thin films and interfaces. Among the wafer-based PV technologies, building on the former experience on amorphous and nanocrystalline thin-film silicon, our activities are focused on the silicon heterojunction (SHJ) architecture with novel carrier-selective passivating contacts, also dopant-free. Alongside, we are developing hybrid and inorganic metal-halide perovskite solar cells, via solution- and vacuum-based fabrication methods, testing different transport layers and both opaque and semi-transparent designs, with the latter requiring adjustment of transparent electrodes and/or introduction of buffer layers. Semi-transparent perovskite solar cells are then being tested as top component into monolithic perovskite/SHJ tandem devices accommodating both p-i-n and n-i-p designs, toward high efficiency applications. About agrivoltaics, we are pursuing two possible implementations of semitransparent spectrally-selective thin film PV. This approach aims at an integrated complementary use of solar light for PV and photosynthesis by tuning the transmission of the PV modules on the absorption spectrum of the plants. We are developing spectrally-selective organic solar cells, leveraging the tunable absorption characteristics of the active materials and, meanwhile, exploring a configuration based on amorphous silicon solar cells, where the required selectivity is obtained with engineered multilayer designs. The latter configuration can serve as a testbed for the concept. The higher maturity of this technology makes for a faster route toward large area implementations and first experiments could be initiated about effects of the filtered light on plant growth and physiology. The latest progress in all these pathways will be shown and discussed.

***Acknowledgements**: We acknowledge support from the Italian Ministry of Environment and Energy Security through the Operating Agreement with ENEA for Research on the Electric System, through the Project GoPV (CSEAA_00011) for Research on the Electric System, and from the European Union through the "Network 4 Energy Sustainable Transition – NEST" project, Spoke 1, funded under the National Recovery and Resilience Plan.*

2D OR NOT 2D, THAT IS THE QUESTION

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Surface passivation with ammonium salts, such as phenylethyl ammonium iodide (PEAI), is a well-established strategy to enhance the stability and optoelectronic properties of 3D metal-halide perovskites (MHPs)[1]. PEAI efficiently passivates surface defects and shields perovskite films from environmental stress, while also facilitating the formation of quasi-2D perovskite layers[2]. Over time, the higher thermodynamic stability of 2D perovskites can lead to the abstraction of PbI_2 layers from the underlying 3D perovskite, resulting in mixed-dimensional structures. To investigate this dynamic, we performed first-principles Density Functional Theory (DFT) calculations, assessing the thermodynamic competition between PEAI surface passivation and the formation of 2D perovskite layers. Our findings demonstrate that hybrid 2D/3D structures are more stable than 3D perovskites passivated solely by PEAI. These results provide valuable insights into the development of MHPs with enhanced stability and optoelectronic performance, highlighting the critical role of processing conditions in optimizing dimensionality.

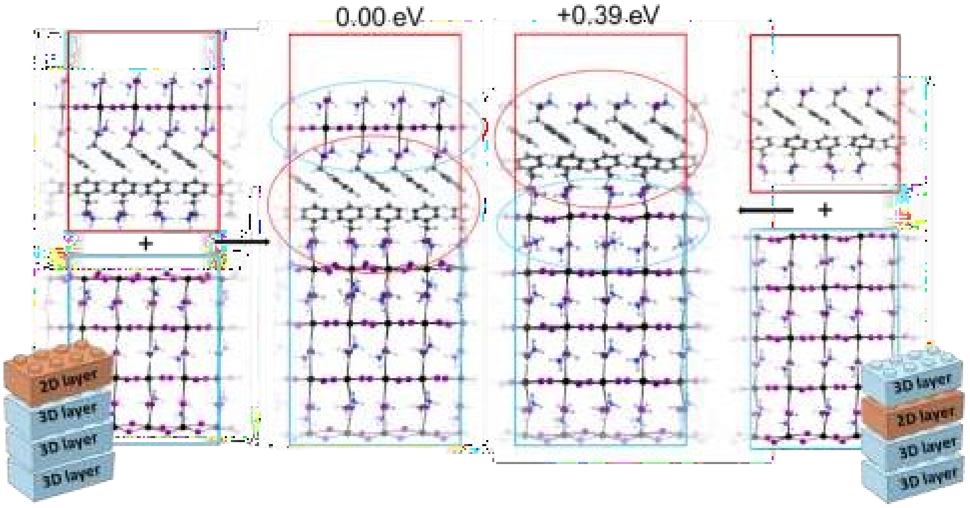

Figure 1: *Representation of the assembly of the two modelled structures*

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***Acknowledgements*:** *(Optional)*

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COMPUTATIONAL MODELING OF PHOTOACTIVE MATERIALS AND INTERFACES FOR SOLAR ENERGY CONVERSION

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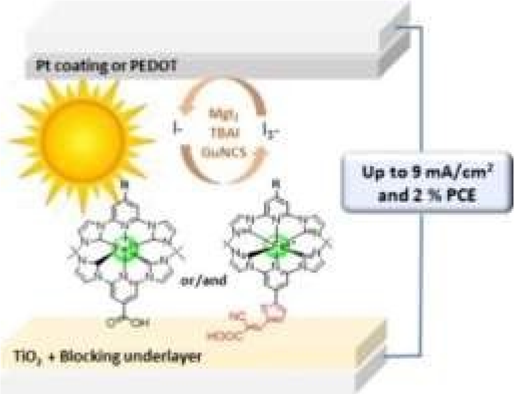
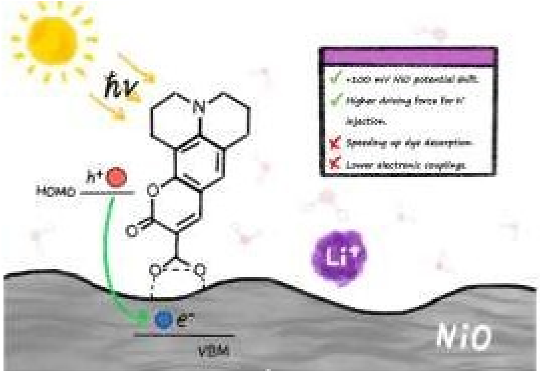
In the context of solar energy exploitation, dye-sensitized solar cells (DSCs) and dye-sensitized photoelectrosynthetic cells (DSPECs) offer the promise of cost-effective sunlight conversion and storage, respectively. Dye-functionalization of bot n- and p-type semiconductors (like TiO_2 and NiO) can be either exploited to build active DS photoelectrodes or tandem DSC and DSPECs devices. Computational modelling has played a prominent role in the development of the DSC technology, affording accurate prediction of both isolate components (dye's optical properties, catalysts, and redox mediators, etc…) and semiconductor sensitization (structure, electronic structure, optical properties, charge transfer kinetics).

Here I will discuss the recent advances concerning first principles modeling of materials, interfaces, and processes of n- and p-type photoelectrodes. In the first part of the talk, I will present recent progresses in the developments of iron-based DSCs and photoactive Fe-carbene sensitizers.[1] Then, moving to p-type semiconductor interfaces, I will mainly discuss the modeling of electronic and structural properties of the complex NiO/solvent/dye/electrolyte interface [2,3] I will address the problem of accurately predicting the energy level alignment across the dye/semiconductor interface by state of the art DFT and large scale GW calculations and the challenging definition of a proper structural model needed to reliably capture the interface complexity.





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DEFECTS ACTIVITY IN METAL HALIDE PEROVSKITES

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Metal halide perovskites (chemical formula ABX3, A = formamidinium (FA+), methylammonium (MA^+), or Cs^+ , B = $Pb2^+$, Sn^{2+}, X = I^-, Br^-, or Cl^-) have demonstrated their potential as a material platform for a new generation of optoelectronic technology. One superior feature of metal halide perovskites is their continuously tunable bandgap from near infrared to ultraviolet by designing the chemical composition of the semiconductor crystalline unit. This enables them to provide top absorbers with matched bandgaps for tandem solar cells.

Here I will assess the most recent advances in elucidating the (photo)chemistry of defects related to the chemical composition of the perovskite crystalline unit. I will show how they define the charge carrier dynamics in the semiconductor and they affect the figures of merit and stability of perovskites based solar cells.

Acknowledgements: *(Optional)*

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[1] A.B. Author, *Journal Title***Year**, *Vol*, pages (Times New Roman, 10 pts, justified).
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COMBINING MACHINE-LEARNING-INTERATOMIC-POTENTIALS MD AND MICROKINETIC MODELING TO UNRAVEL THE MECHANISM OF PHOTOELECTROCHEMICAL WATER OXIDATION ON HEMATITE

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The oxygen evolution reaction (OER) plays a crucial role in (photo)electrochemical devices that use renewable energy to produce synthetic fuels. While the mechanism of this reaction is still debated, recent measurements on semiconducting oxides[1,2] have shown that the dependence of the rate of OER on the surface hole density is a power law, suggesting a multihole mechanism via surface hole accumulation. This is reminiscent of the mechanism for OER promoted by the oxygen evolving complex in Photosystem II and in stark contrast with metallic oxides like IrO_2[3], where the dependence is exponential. Modeling this reaction requires all-atom simulations to capture the effects of the H-bond network of the solvent on the reactants, long molecular dynamics simulations to sample accurately the solvent degrees of freedom and enhanced sampling to model activated process like O-O bond formation. We have used machine learning interatomic potentials (MLIP) trained on DFT energy and forces to achieve this goal. In contrast to what was previously assumed, we find that the reaction proceeds via a lattice oxygen mechanism, triggered by the oxidation of terminal oxygen sites. This process is considerably faster than competing mechanisms like the nucleophilic attack of a water molecule of hydroxide ion. We tested the accuracy of these MLIP predictions, validating the kinetics of this process with DFT calculations. Microkinetic modeling was then used to predict the overall rate of the catalytic process and to relate the photocurrent so the surface charge accumulation. We find a power-law with a third order dependence, in agreement with experiments, and we assign its origin to the facile formation of the superoxo intermediate, a step whose activation energy is weakly dependent on the surface hole coverage.

Acknowledgements**:** *We acknowledge partial financial support from the Italian Ministero dell'Università e della Ricerca (MUR) through the program NEST - Network 4 Energy Sustainable Transition, Spoke 4:Clean hydrogen and final uses, and from ICSC - High-Performance Computing, Big Data e Quantum Computing Research Centre, Spoke 7: Materials & Molecular Sciences, both by funded by the European Union – NextGenerationEU.*

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AN AI-AIDED APPROACH TO MATERIALS PREPARATION AND OPTIMIZATION

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Artificial Intelligence (AI) has already become a pervasive tool in several aspects of daily life and science is not excluded from this revolution, with plenty of applications of AI-related technologies ranging from the biomedical field and drug discovery to materials optimization. In this sense, AI has the potential to guide towards solutions even to real-life industrial problems, thus saving time and money and lowering the environmental impact of industrial processes. As a study case, here a specific problem - the reutilization of marble cutting sludges - is discussed from an AI-guided point of view. The production of marble sludges from marble cutting is in fact an economical and environmental issue, with tons of produced wastes that needs to be correctly treated. Instead of discarding them, these byproducts can be repurposed by mixing with other ingredients to prepare new materials (also known as mix-designs) that can be used for buildings and constructions. Determining the optimal mix design is challenging due to the variability in sludge composition and the costly, time-consuming nature of experimental data collection, and is mostly performed in an empirical way. The utilization of machine learning models can estimate the correct quantity of stone-cutting sludge to be used in aggregates to obtain a mix design with tailored mechanical properties, thus promoting sustainability and efficiency in the stonecutting sector.

DECIPHERING RESONANCE, CHARGE, AND SPIN EFFECTS ON LONDON DISPERSION ENERGY IN MOLECULAR SYSTEMS WITH ATOMIC RESOLUTION

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We present a computational method for the accurate quantification of the atomic contributions to the London dispersion energy in molecular systems and provide new fundamental insights into the key features of this fundamental physical component of all intermolecular interactions. Our approach, termed Atomic Decomposition of London Dispersion energy (ADLD), employs the "gold-standard" CCSD(T) level of theory within the Local Energy Decomposition[1,2] framework to isolate London dispersion from other electron correlation effects. Using ADLD, we show unambiguously that London dispersion is significantly influenced by a variety of electronic structure effects, including the spin state, charge, and resonance characteristics of molecular systems. Furthermore, we explain the origin of the recently proposed *gravitational-like* relationship[3] describing the distance dependence of London dispersion energy in molecular systems.

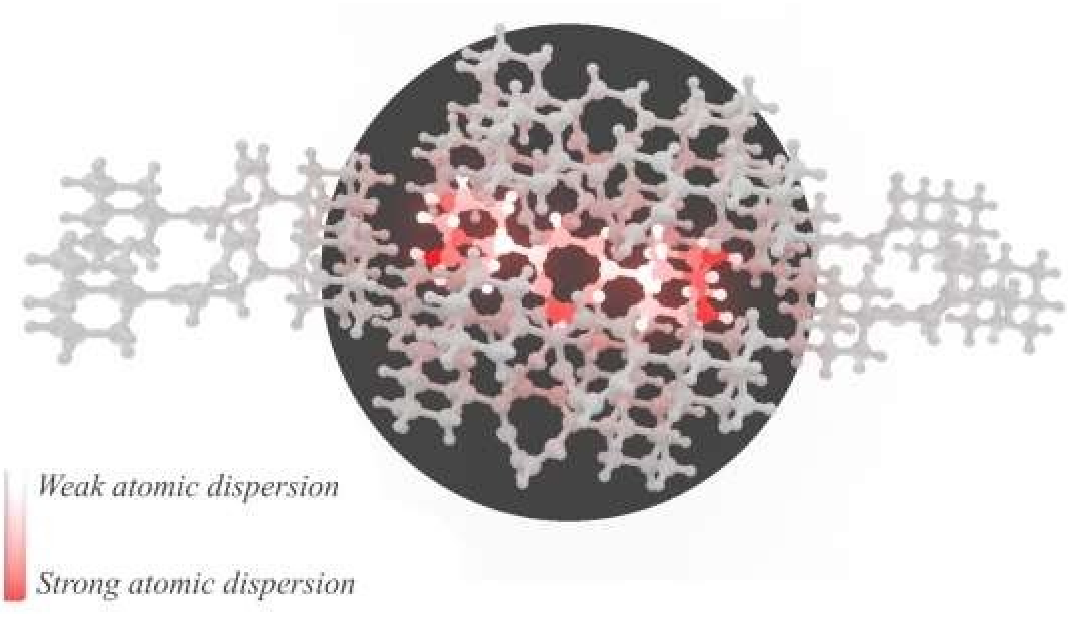

***Figure 1**: Dispersion density of a 1,4-di-adamantyl-cyclooctatetraene crystal. Red (white) indicates strong (weak) atomic dispersion interaction between the central and the surrounding monomers.*

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MODELING OF GOLD NANOBIPYRAMIDS: FROM ANISOTROPIC GROWTH TO CHIRAL PROPERTIES

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The great and tunable plasmonic properties of gold nanobipyramids (AuBPs), superior for instance to those of gold nanorods, make them highly effective for many applications, including sensing and catalysis. In this presentation, I will illustrate our latest advancements in computational modeling of AuBPs.[1–3] Our results provide insights into the critical role of surfactants in the anisotropic growth of AuBPs, enabling the formation of monodisperse structures with exceptional optical characteristics. We simulated the plasmonic response of various AuBPs and compared different methodologies (discrete dipole approximation, boundary element methods and quasi-static approximation) aiming for a reliable approach to simulate the electronic coupling with molecular chromophores in nano-hybrid systems. Additionally, we examined how AuBPs can serve as versatile templates for creating multi-metallic composites with tunable shape and peculiar optical properties. In particular, we investigated Au@Ag and Au@Au nanoparticles designed to achieve intense plasmonic circular dichroism. Combined experimental and computational results highlighted the key role played by the nanoparticles' surface on the chiral properties. Finally, recent results revealing the role of molecular chiral encoders on the formation of the chiral surfaces and the presence of chiral-induced aggregation in AuBPs aggregates are presented.

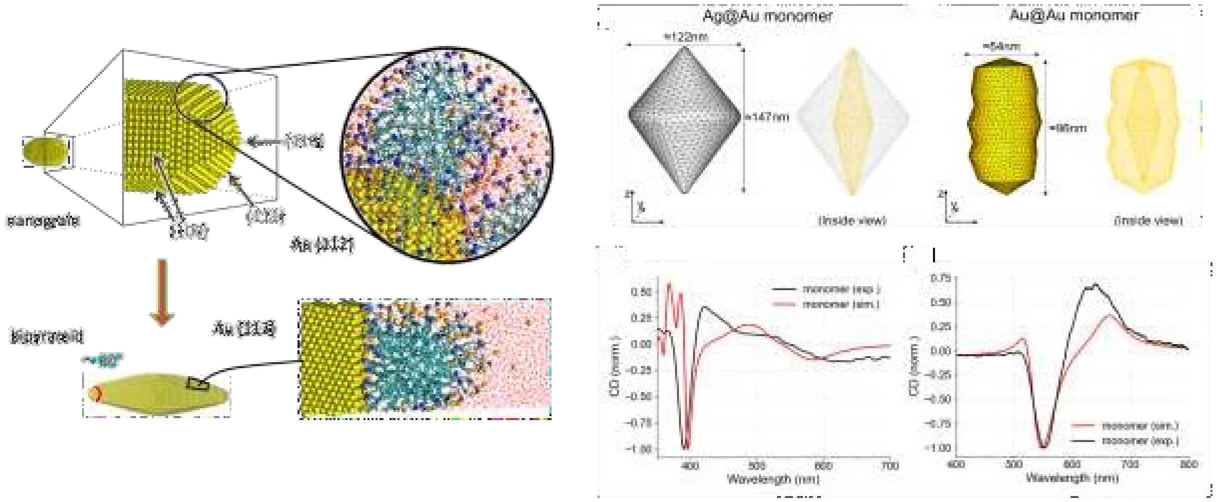

Figure 1: *Modeling of gold nanobipyramids structures and photophysical properties*

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POLARITONIC CHEMISTRY: A FIELD AS PROMISING AS OBSCURE

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It is now almost ten years that polaritonic chemistry is proposing itself as a new non-intrusive alternative to manipulate properties of molecules and materials using strong coupling to photons.[1,2] Despite several experimental studies demonstrated that strong-light matter interaction can be used to modify photochemistry and chemical reactivity[1] the fundamental physical origin of these effects is still very debated.

In this talk, I will provide a critical analysis of the ab-initio theoretical results my group and our collaborators obtained in the past years to highlight the still unresolved fundamental aspects in polaritonic chemistry.[3-7] In the last part of the talk I will analyze new directions that our group and the rest of the scientific community are following to provide, hopefully in a near future, a definitive answer to this very interesting physical phenomenon.[8,9]

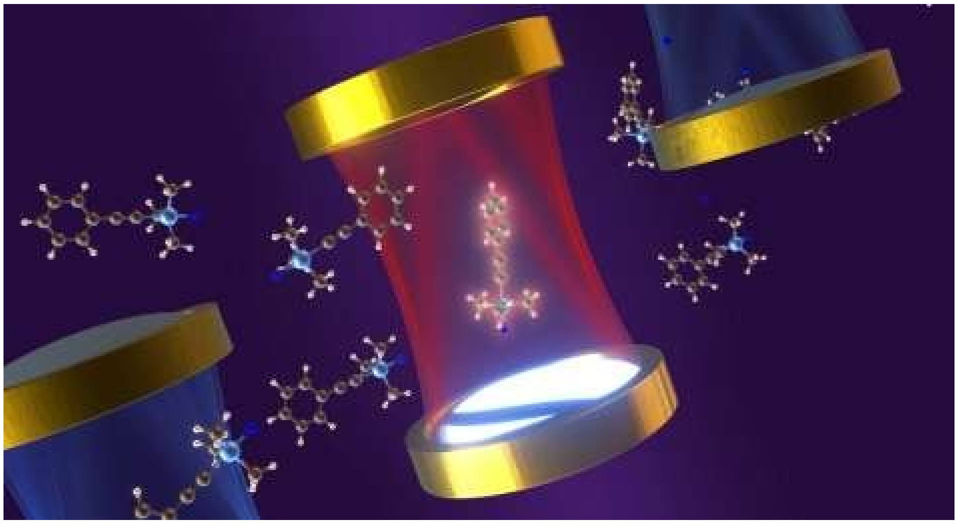

***Figure 1**: Chemical reactivity in an optical cavity*

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INVESTIGATING THE INFLUENCE OF RELATIVISTIC RETARDATION EFFECTS IN SPIN POLARITONICS

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Spin polaritonics is becoming a very good candidate to implement devices interesting for quantum computation applicationss. This is usually obtained coupling magnetic molecules with quantum fields in superconducting optical cavities.[1,2] The molecules used in this context, need to have long lasting magnetizabilities that can be manipulated by properly engineering the quantum field of the cavity. Such systems contain heavy metallic atoms (lanthanides, etc.) that have usually a strong relativistic character. Having a full control on these devices requires a deep knowledge of the fundamental physics lying at the foundation of the coupling between the light and the spins of matter. However, theoretical models capable to provide this kind of information are still unavailable.
In this talk I will present a fully relativistic theory for molecules strongly interacting with quantum fields.[3] Particular attention has been dedicated to the study of retardation effects, usually neglected in standard relativistic quantum chemistry calculations. In the last part of the talk, I will discuss how this theory can be used to investigate the physical origin of the electromagnetic field confined in the optical cavity.

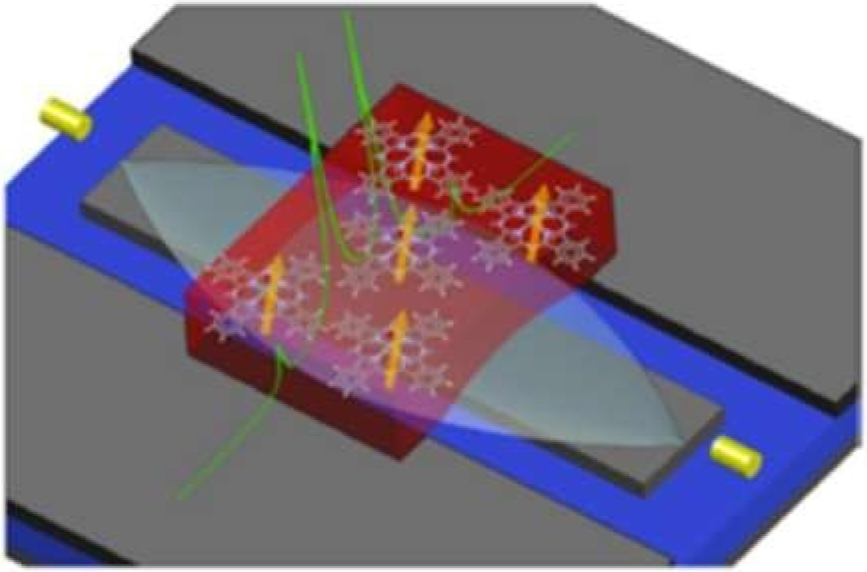

Figure 1*: Molecules in a superconducting cavity.*[2]

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MODELLING THE DEGRADATION OF COLORS IN PAINTINGS: EXPLORING POTENTIAL LINKS TO ENERGY APPLICATIONS

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Several historical colored pigments from paintings of the late 1800s and early 1900s are undergoing irreversible degradation processes, the causes of which remain unclear. This study focuses on three key pigments – cadmium yellow, cadmium red, and Prussian Blue – widely recognized in the field of Cultural Heritage and explores their potential relevance in advanced materials for energy applications.

For cadmium yellow, which derives its color from cadmium sulfide (CdS), a II-VI wide-gap semiconducting compound, our findings emphasize the role of structural defects with the aim to link the history of the material to the reactivity of the pigment surface. In contrast, investigations into cadmium red and Prussian Blue are still at a preliminary stage. Nevertheless, early results indicate promising parallels with their potential applications in nanotechnology and photocatalysis. The study is carried out by means of a fully theoretical approach based on the density functional theory.

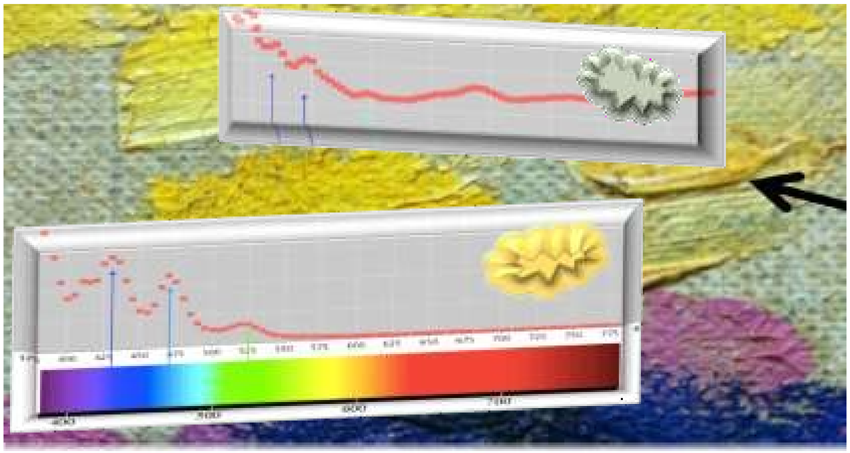

***Figure 1**: Absorption spectrum of clean and defective {10.0} surface of CdS*

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[1] A. Satta and S. Fantacci, *Modeling Luminescence in Cultural Heritage: Theoretical Insight into the Luminescence of Dyes and Pigments. In: Springer Series on Fluorescence,* ***2023****, Springer, Cham.*

ORGANIC CATIONS AND CRYSTAL DEFECTS IN HYBRID PEROVSKITES

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The photoconversion efficiency record of silicon-perovskite solar cells exceeds 30% owing to hybrid perovskites ΆPbX3 with organic cations Ά that stabilize the perovskite sublattice not only by ionic bonding but also by non-covalent bonding (that is absent in all-inorganic perovskites). As the lowest-energy electronic transitions mainly involve orbitals of the inorganic skeleton, the optoelectronic properties are determined by the halogen composition X, PbX6 tiltings and rotations, and bulk and surface defects. The main drawbacks of hybrid perovskites are their intrinsic instability towards photoinactive δ-phases and degradation by light, heat, oxygen, and moisture, for example. We address the stability issue from the perspectives of the bulk crystal phases, point defects, and surfaces and interfaces. It is shown that the softness of the lattice allows various organic cations to fit into and bond stronger with the inorganic skeleton than methylammonium and formamidinium, enabling mixed-cation compositions of higher stability. It is also shown that the inorganic Ba, Hg, and Tl cations provide stabilization, with Ba and Tl additionally suppressing halogen migration. I-defects creating I···I2···I motives are beneficial by inducing localized states below the conduction band edge, while defects creating Pb-Pb or I-O bonds as well as O2 interstitials turn out to be detrimental for the optoelectronic properties. Heteroaromatic functionalization of the methylammonium and formamidinium cations as well as I2 treatment creating surface I···I2···I motives stabilize surfaces and interfaces, enhancing the charge transfer to C60-based charge transport layers.

Creating a digital twin of a perovskite solar cell

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Digital twins are virtual copies of objects, structures and environments that can be used to simulate scenarios that could then be applied to the real world. This talk will cover our recent work combining machine learning and simulation methodologies to produce a digital twin that can characterise a perovskite solar cell in real time, i.e. on the same timescale as the cell degrades under illumination. Our virtual model is a combination of the device transport model IonMonger and machine learning [1]. It can be used to test hypotheses about the physical processes responsible for degradation. These processes include the role of mobile iodide vacancies that through charge accumulation/depletion at interfaces influence charge transport across the interface and trap assisted recombination at these interfaces along with the contributions of other impurities. Our work aids the identification of more stable perovskite compositions and will establish potential mitigation routes to prevent degradation.

1. McCallum, S. G.; Nicholls, O.; Jensen, K. O.; Cowley, M. V.; Lerpinière, J. E.; Walker A. B. Bayesian parameter estimation for characterising mobile ion vacancies in perovskite solar cells J Physics: Energy 2024, 6, 015005