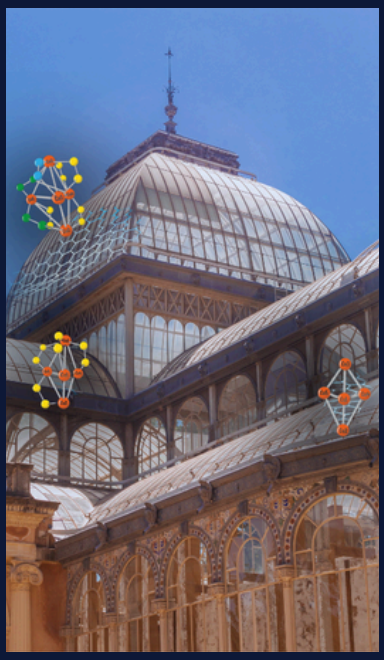
# CATCOSY 2024


# BOOK OF ABSTRACTS

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COSY COST ACTION
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MINISTERIO DE CIENCIA, INNOVACIÓN Y UNIVERSIDADES
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# Preface

August 29, 2024

Dear Participants,

We are delighted to introduce the event:

"CATCOSY 2024. A Meeting Facing Challenges on Subnanometric Metal and Metal-Oxide Catalysts and Photocatalysts"

CATCOSY is a meeting framed within the COST (European Cooperation in Science and Technology) Action CA21101: Confined Molecular Systems: From a New Generation of Materials to the Stars ("COSY"). It is directed at established researchers, post-doctoral researchers, and PhD and Master students, who are interested in subnanometric science, especially in the synthesis, characterization and molecular-level understanding of transition-metal and metal-oxide (photo)catalysts on the (sub)nanoscale. The meeting leverages the strategic position of the "COSY" network in the synthesis of atomically precise metal clusters of nano- and sub-nanometer sizes in various environments (gas-phase, solution, within helium nanodroplets, and in biologically relevant media) and their characterization via experimental methods (e.g., infrared and X-ray absorption spectroscopy and scanning transmission electron microscopy) as well as state-of-the-art computational methods (ab initio, density functional theory - DFT - and molecular dynamics).

This meeting has been conceived as an opportunity for active networking between action members as well as external experts with complementary and highly diverse expertise. It emphasizes the need to combine advanced computational tools with experimental synthesis and characterization techniques, focusing on building fundamentals in connecting model metal and metal oxide (photo)catalysts with the 'real world' of nanotechnology, based on the perspective that only processes that are fundamentally well understood can be controlled (see Memorandum of Understanding of the "COSY" COST Action). In this way, the meeting addresses challenging aspects such as:

1. The use of helium nanodroplets as an ultra-cold, chemically inert confining environment, to synthesize and study metal and metal oxide clusters, including charged helium droplets and the interaction of these clusters with small molecules and polycyclic aromatic hydrocarbons (PAHs) of catalytic relevance.

2. Bare atomically precise metal clusters of up to 10 atoms can now be synthesized in solution through electrochemical methods with kinetic control. The special chemical and physical properties of the smallest metal clusters are yet to be unveiled and understood.

3. The development of frameworks that combine different experimental, computational, and theoretical methods for characterizing surface-supported atomically precise metal clusters of subnanometer size is needed. This includes infrared and X-ray absorption spectroscopic techniques as well as the most advanced scanning transmission electron microscopy tools.

4. The characterization of the stability and catalytic properties of surface-supported atomically precise metal clusters as a function of their composition, size, structural fluxionality, and surface modifications in different thermodynamical conditions (temperature and pressure), including unsupported and surface-supported naked clusters in the gas phase and ligand-protected, atomically precise metal clusters in solvent environments.

5. Combining static and dynamic computational approaches to understand and characterize the chemical reactions of metal and metal oxide clusters in solvents, aiming to extend these insights into the complex environments of soft matter and bio-macromolecular systems.

6. Understanding the mechanisms of chemical processes involved in the oxidation of metal sulfide crystalline surfaces, and characterizing properties of the subnanometric metal-oxide clusters formed as products of these reactions through both experimental and theoretical approaches.

7. Understanding the nature of cluster–support (cluster–cluster) interactions at the molecular-level is essential for optimizing (photo)catalyst performance and designing novel catalysts with improved properties. Ab initio methods that can be applied to open-shell metal cluster–support (cluster–cluster) interactions are necessary. Besides complementing state-of-the-art dispersion corrected DFT approaches, they serve to develop inter-atomic potential models that can be applied to study the molecular dynamics of supported metal clusters (e.g., diffusion and aggregation processes) on the nanosecond scale.

8. Ab initio molecular dynamics (AIMD) is vital for studying subnanometric metal and metal-oxide clusters, providing insights into their dynamic behavior and reactivity at the atomic level. These simulations are crucial for understanding catalytic processes and time-dependent properties. However, AIMD demands significant computational resources, limiting the scope of simulations. To mitigate these challenges, GPU and machine-learning (ML) accelerators have been developed, enhancing computational speed and reducing costs. Despite these advancements, further optimization of MD simulation codes for GPU usage and improvements in ML model transferability are still needed.

9. Conical intersections play an important role on the (photo)stability, (photo)reactivity, and structural fluxionality of supported metal clusters on the sub-nanoscale. Describing these conical intersections represents a significant challenge for the current state-of-the-art in theoretical-computational modeling. Work is necessary to make it possible using multistate ab initio theory followed by multistate quantum or semi-classical non-adiabatic descriptions of the underlying dynamics.

10. Recent research has unveiled the formation of polaronic states on transition metal oxide surfaces upon decoration with atomically precise metal clusters. The characterization of the catalytic properties of these metal clusters-induced surface polarons remains a largely unexplored area.

11. For the functionalization of subnanometric metal clusters as photocatalysts, three challenging topics bearing significant social-economic impact are 1) the design of photocatalysts for applications such as water purification (i.e., degradation of organic pollutants), with an emphasis on their viable production, 2) the sunlight-induced decomposition of greenhouse gases (e.g., $CO_2$), and 3) the hydrogen photoproduction from water. There is a need to combine advanced computational tools with experimental synthesis and characterization techniques to effectively address these challenges while achieving a better understanding of the underlying mechanisms.

The scientific program comprises 7 sessions, with 14 lectures, 10 hot topic presentations, and 14 poster presentations. An “Open Discussion” (Round Table) session is scheduled at the end of the meeting.

We are thankful to the COST Association and our sponsor, the journal “Physical Chemistry Chemical Physics” from the Royal Society of Chemistry, for having supported us in organizing this event. In particular, we extend our heartfelt thank to our COST Action CA21101 ”COSY” for having provided the funding and to our Grant Holder Institution (The Universidad de Cádiz), specially our Scientific Grant Holder Representative, Juan Carlos Hernández-Garrido, for their administration. We are also thankful to our host institution (CSIC) and in particular the Protocol Department at Central CSIC, the “Centro de Física Miguel Antonio Catalán”, and the “Institute of Fundamental Physics” (IFF) at Madrid, for their human and logistic resources. The Fundación Española para la Ciencia y la Tecnología (FECYT), the Ministerio de Ciencia, Innovación y Universidades, and the COST National Coordinator, Noelia Romero López, are thankful for all the support provided to our “COSY” COST Action. And last but not least, we would like to express our gratitude to all of you, the participants of this meeting, for your invaluable contributions.

We welcome all of you to Madrid and wish a very pleasant stay and plenty of interesting scientific discussions.

The Organizers (AbinitSim Unit, IFF-CSIC),

María Pilar de Lara-Castells, Chair of the COST Action CA21101 “COSY”
Lenard L. Carroll
Katarzyna M. Krupka

## Madrid (CSIC), 26-27 September 2024

Organizing Committee: María Pilar de Lara-Castells – Chair of the COST Action CA21101, Lenard L. Carroll, Katarzyna M. Krupka

Invited speakers presenting invited lectures have a total of 30 minutes for their presentation. Invited speakers presenting hot topic presentations have a total of 15 minutes. Speakers presenting flash poster presentations have a total of 2 minutes (2 slides). A poster session is taking place on Thursday afternoon (26 September). Material to fix your poster such as adhesive tapes or pins will be provided. All participants are encouraged to prepare 1-2 slides to be presented during the round table discussion on Friday afternoon (27 September), showcasing their ideas for potential collaborative projects.

**Meeting Venue:**
"Salón de Actos" Serrano 117 (Lectures – 26 September), Center of Physics "Miguel Antonio Catalán": "Claustro" Serrano 123 (Coffee Breaks and Poster Session) and "Sala de Prensa" Serrano 113 (Lectures – 27 September), "Residencia de Estudiantes" Pinar 21-23 (Accommodation and Lunches for participants staying at the "Residencia de Estudiantes"), "Cafetería Comedor" Serrano 117 (Lunches), Consejo Superior de Investigaciones Científicas

**PROGRAM**

**Thursday 26th September**

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8.30 – 9.00 **Registration**

9.00 – 9.15 **Welcome and Introduction** by María Pilar de Lara-Castells (AbinitSim Unit, Institute of Fundamental Physics, CSIC, Chair of the COST Action CA21101) and Wolfgang E. Ernst (Institute of Experimental Physics, Graz University of Technology, Associate Editor of RSC PCCP)

Session 1 – "Synthesis and applications"

Chair: María Pilar de Lara-Castells (AbinitSim Unit, Institute of Fundamental Physics, CSIC, Chair of the COST Action CA21101)

9.15 – 9.45 **Wolfgang E. Ernst** (Institute of Experimental Physics, Graz University of Technology) – Invited Lecture
*Metal and Metal Oxide Clusters Created in the Confinement of Helium Droplets*

9.45 – 10.15 **M. Arturo López-Quintela** (iMATUS, University of Santiago de Compostela) – Invited Lecture
*Exceptional catalytic properties of Ag and Cu pentamers*

10.15 – 10.45 **Paul Scheier** (Institut für Ionenphysik und Angewandte Physik, Universität Innsbrück) – Invited Lecture
*Properties and Applications of Charged Helium Droplets*

10.45 – 11.15 **Coffee Break**

Session 2 – "Characterization"

Chair: Lyudmila V. Moskaleva (Department of Chemistry, University of the Free State)

11.15 – 11.45 **María J. López** (Departamento de Física Teórica, Átomica y Óptica, University of Valladolid) – Invited Lecture
*Infrared spectra, structures and deuterium adsorption on $C_{60}Rh_n^+$ complexes*

11.45 – 12.15 **Félix G. Requejo** (Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CONICET – FCE – UNLP) – Invited Lecture
*In situ characterization of small atomic clusters using X-ray absorption spectroscopy*

12.15 – 12.45 **Juan Carlos Hernández-Garrido** (Instituto de Microscopía Electrónica y Materiales (IMEYMAT), Universidad de Cádiz) – Invited Lecture
*Advanced STEM methods, including single atom imaging, high precision analysis, and in-situ electron microscopic methods for the characterization of catalytic nanomaterials*

Session 3 – "Catalysis"

Chair: Alessandro Fortunelli (CNR-ICCOM&IPCF, Italian National Research Council)

12.45 – 13.15 **Stefan Vajda** (J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences) – Invited Lecture
*Copper-Palladium Tetramers and Pentamers in Oxidative Dehydrogenation Reactions: Altering Catalyst Performance by Changing Cluster Size & Composition Atom a Time*

13.15 – 13.45 **Lyudmila V. Moskaleva** (Department of Chemistry, University of the Free State) – Invited Lecture
*Exploring the Surface Properties and Catalytic Behavior of Nanoporous Gold: A Computational Study*

13.45 – 14.15 **Noelia Barrabés** (Institute of Materials Chemistry, TU-Wien) – Invited Lecture
*Tuning catalytic activity by controlling and understanding the cluster-ligand-support interface*

14.15 – 14.30 **Johannes Reichegger** (Institut für Ionenphysik und Angewandte Physik, Universität Innsbrück) – Invited Hot Topic Presentation
*Investigation of the reactivity of gold clusters via He tagging spectroscopy*

14.30 – 15.45 **Lunch**

Session 4 – "Dynamics and excited states"

Chair: Berta Fernández-Rodríguez (Department of Physical Chemistry, University of Santiago de Compostela)

15.45 – 16.15 **Leticia González** (Institute of Theoretical Chemistry, Faculty of Chemistry, University of Vienna) – Invited Lecture
*Characterization of a Manganese-Vanadium Water Oxidation Catalyst: from Solution to a Soft-Matter Environment*

16.15 – 16.30 **Alexandre Zanchet** (Institute of Fundamental Physics, CSIC) – Invited Hot Topic Presentation
*Electronic structure of the smallest iron carbide: FeC*

16.30 – 16.45 **Yeha Lee** (Laboratory of Theoretical Physical Chemistry, Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL)) – Invited Hot Topic Presentation
*Nonadiabatic dynamics in the reversible oxidation of $Cu_5$ clusters*

16.45 – 17.20 **Flash Poster Presentations** (in alphabetical order):

Chair: Katarzyna M. Krupka (AbinitSim Unit, Institute of Fundamental Physics, CSIC)

**Alvaro Gallego de Roa** (Departamento de Física de la Materia Condensada, Instituto "Nicolás Cabrera" and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid)
*Theoretical Investigation of Imidazole Derivatives Adsorption on an Ag(100) Surface to Evaluate Their Potential as Radiosensitizers*

**Estefanía Germán** (Departamento de Física Teórica, Átomica y Óptica, University of Valladolid)
*Computational prediction of a new two-dimensional material obtained by functionalization of boron graphdiyne layers with transition metal atoms*

**Yako Irusta Salles** (Departamento de Química, Facultad de Ciencias, Universidad Autónoma de Madrid)
*Theoretical study of the electronic properties of surfaces for catalysis*

**Sahar Mahnaee** (Departamento de Física Teórica, Átomica y Óptica, University of Valladolid)
*Separation of $CO_2/CH_4$ gas mixtures using nanoporous graphdiyne and boron-graphdiyne membranes: influence of the pore size*

**Edgard Alejandro Miranda Sáenz** (Department of Electrochemistry, Universidad Autónoma de Madrid)
*Theoretical Study of Electroreduction of $CO_2$ Using Metal-Doped Graphene Sheets with Metals*

**Luis M. Molina** (Departamento de Física Teórica, Átomica y Óptica, University of Valladolid)
*Structure and chemical reactivity of Pt-Zr binary nanoclusters*

**Sebastián Negrete Aragón** (Nanophysics Lab, Centro de Física de Materiales CSIC/UPV-EHU)
*Merging reactive molecular beams and XPS to simulate high pressure surface reactions*

**Emma-Rose Newmeyer** (Department of Chemistry, Northwestern University)
*Investigating Dilute Plasmonic Alloys for Photocatalytic Propane to Propylene Dehydrogenation*

**Junjie Shi** (Institute of Materials Chemistry, TU Wien)
*Rational design of Ceria mixed oxides supported Pt catalyst for Water Gas Shift Reaction: Engineering the O vacancy chemical environment*

**Saeed Sovizi** (Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw)
*Synthesis and characterization of sub-nm clusters of $MoO_3$ onto $MoS_2$ basal planes*

**Mauro Stener** (Dipartimento di Scienze Chimiche e Farmaceutiche, University of Trieste)
*Peeking into the Femtosecond Hot-Carrier Dynamics Reveals Unexpected Mechanisms in Plasmonic Photocatalysis*

**Martin Šulka** (Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava)
*Adsorption and catalytic properties of doped aluminum clusters*

**Katarína Šulková** (Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava)
*Analyzing the nature of electron correlation in small metal clusters*

**Thantip Roongcharoen** (CNR-ICCOM, and CNR-IPCF Consiglio Nazionale delle Ricerche)
*Machine-Learning-Accelerated DFT Conformal Sampling of Catalytic Processes*

17.20 – 19.00 **Poster Session with Coffee and Cakes**

**Friday 27th September**

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Session 5 – "Reactivity"

Chair: María J. López (Departamento de Física Teórica, Átomica y Óptica, University of Valladolid)

9.00 – 9.30 **Alessandro Fortunelli** (CNR-ICCOM&IPCF, Italian National Research Council)) – Invited Lecture
*Nanocluster Structures for the Oxygen Reduction Reaction*

9.30 – 9.45 **Robert Szoszkiewicz** (Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw) – Invited Hot Topic Presentation
*Oxidation, etching and $MoO_x$ phases/clusters onto $MoS_2$ crystals*

9.45 – 10.00 **Michele Reticcioli** (Faculty of Physics and Center for Computational Materials Science, University of Vienna) – Invited Hot Topic Presentation
*Characterization and Effects of Polarons on Oxide Surfaces via Machine Learning*

10.00 – 10.15 **Johanna Y. Sandoval** (Departamento de Física Teórica, Átomica y Óptica, University of Valladolid) – Invited Hot Topic Presentation
*Single atom and single cluster transition metal catalysts supported on GDY and BGDY layers*

10.15 – 10.30 **Daniel Farías** (Departamento de Física de la Materia Condensada, Instituto "Nicolás Cabrera" and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid) – Invited Hot Topic Presentation
*Simulating high-pressure surface reactions with molecular beams*

10.30 – 11.30 **Coffee Break and Group Photo**

Session 6 – "Method Development"

Chair: José María Campos Martínez (Institute of Fundamental Physics, CSIC)

11.30 – 12.00 **Berta Fernández-Rodríguez** (Department of Physical Chemistry, University of Santiago de Compostela) – Invited Lecture
*Towards the accurate description of interactions in metal clusters*

12.00 – 12.30 **Kaido Sillar** (Institute of Chemistry, University of Tartu) – Invited Lecture
*Ab Initio Calculations of Chemically Accurate Molecule–Surface Interaction Energies*

12.30 – 12.45 **Agnieszka Krzemińska** (*Institute of Physics, Lodz University of Technology*) – Invited Hot Topic Presentation
*Exploring Molecular Interactions in $\pi \rightarrow \pi^*$ Excited States of Anisole Complexes Using Multiconfigurational SAPT*

Session 7 – "Overview"

Chair: Stefan Vajda (J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences)

12.45 – 13.00 **Lenard Leslie Carroll** (AbinitSim Unit, Institute of Fundamental Physics, CSIC) – Invited Hot Topic Presentation
*Subnanometric Metal Clusters: Catalytic Properties, Zeolite Encapsulation and Infrared Spectra, a DFT and AIMD Study*

13.00 – 13.15 **Katarzyna M. Krupka** (AbinitSim Unit, Institute of Fundamental Physics, CSIC) – Invited Hot Topic Presentation
*A practical ab initio approach to open-shell metal cluster-support interactions*

13.15 – 14.30 **Lunch**

14:30 – 16:00 **Round Table – "Open Discussion"**

*A journey towards the molecular level understanding of metal and metal-oxide clusters down to the subnanometer scale*
Moderator: María Pilar de Lara-Castells (AbinitSim Unit, Institute of Fundamental Physics, CSIC, Chair of the COST Action CA21101)

16:00 – 16:30 **Coffee Break**

16.30 – 17.00 **RSC Poster Prizes –** Wolfgang E. Ernst (Associate Editor of RSC PCCP, Institute of Experimental Physics, Graz University of Technology) **and Closing**

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# LECTURES

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# Metal and Metal Oxide Clusters Created in the Confinement of Helium Droplets

Wolfgang E. Ernst[1]

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Nanoparticles of a few nanometer diameter consisting of different materials in layered core@shell structures are synthesized by sequential doping of cold helium droplets in a molecular beam apparatus and deposited on solid carbon, h-BN, SiN, or ITO substrates[1]. After surface deposition, the samples are removed and various measurement techniques are applied to characterize the created particles: scanning transmission electron microscopy at atomic resolution, electron tomography, temperature dependent STEM and TEM up to 1000 degree C, energy-dispersive x-ray spectroscopy (EDXS), electron energy loss spectroscopy (EELS), optical absorption, and photoelectron spectroscopy[1,2]. Our investigations have included alloy formation at high temperature as well as the chemical reactivity and stability of Ni, Fe, and Co cores of 2 to 3 nm diameter passivated by a few layers of gold[3]. Combinations of a plasmonic core and a metal oxide shell exhibit enhanced photoelectron yields with impact on the catalytic properties of the nanoparticles[2]. On the way towards cluster catalytic experiments, we have shown that $V_2O_5$ nanoparticles can be generated by sublimation from the bulk[4] and deposited while keeping the original stoichiometry[5]. Our attempts to create Au-$V_2O_5$ coreshell particles in the way described above, did not yield the expected encapsulated structure but after deposition, Janus particles of Au and $V_2O_5$ with radii of about 20 nm were identified[6].

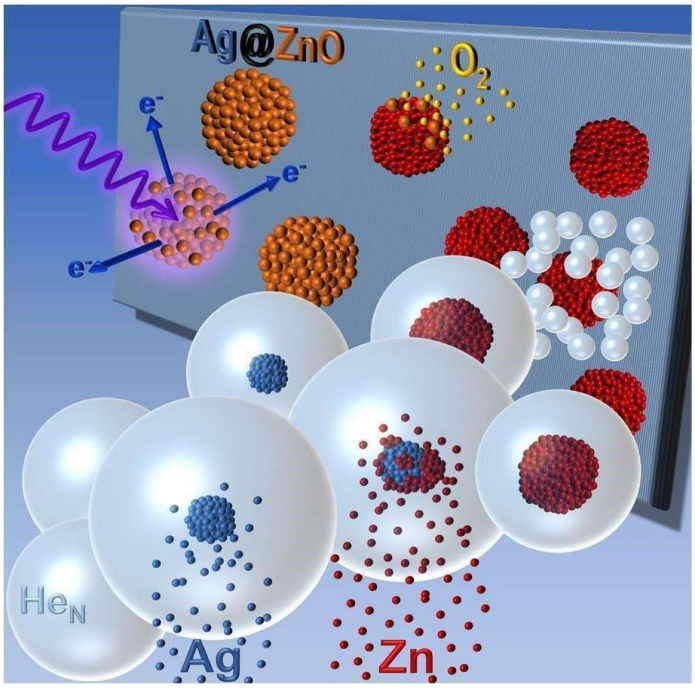


*Figure 1. Formation of a silver cluster core coated with a zinc shell inside a helium droplet, followed by deposition on an ITO substrate, controlled oxidation, and energy resolved photoemission microscopy.*

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# Exceptional catalytic properties of Ag and Cu pentamers

M. Arturo López-Quintela

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Metal nanoclusters show very different properties than both, nanoparticles, and bulk, due to the quantum confinement of the free electrons.[1] Such nanoclusters can be seen as super-atoms (or molecules) in which atoms are linked by strong covalent bonds.[2] In the past decade, we have developed wet-synthetic methods, based on kinetic control without binding ligands, to produce monodisperse nanoclusters (mainly of Au, Ag and Cu) of small atomicity.[3,4,5] We will show in this presentation the catalytic properties of Ag and Cu clusters, containing 5 atoms, for different type of reactions -both in solution and supported onto different substrates- we studied in the last years.

In solution, such pentamers catalyze the partial and total oxidation of sulfur groups, depending on the cluster/sulfur ratio.[4,5] Also, they catalyze a new chemical route for the dual activation of the strong C-O $\sigma$—bond in ethers containing epoxides and doble bonds to achieve the coupling reaction between these groups. This induces the formation of thermostable polymers preserving the epoxide groups.[6] When the pentamers are supported on (almost) non-interacting substrates (e.g. metals and carbon-based materials) they can catalyze 2D-polymerization reactions at low temperatures and the anisotropic growth of metal nanoparticles.[7,8]

When supported on strong interacting metal oxides, they activate different reactions depending on the support. The most interesting observed catalysis of the pentamers is related to the energy decrease for the formation of oxygen vacancies (VO).[9] Due to the very important role of VO in many fields (electro-, photo- and thermal-catalysis), we just began to explore the use of pentamers supported on $TiO_2$, $CeO_2$ and perovskites for hydrogen production through a photothermal chemical looping, as well as the production of syngas. In those cases it is found that the catalytic activities of clusters are higher and/or with lower activation energies than the current benchmark catalysts, showing the versatility of such small clusters for catalytic applications.

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# Properties and Applications of Charged Helium Droplets

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Helium droplets have been demonstrated to pick up dopants from the gas phase, and evaporative cooling enables experiments at temperatures below 1 K[1]. Massive doping of neutral droplets leads to the formation of nanoparticles and quantum wires which were studied after deposition with high resolution microscopy[2] and in situ via coherent X-ray diffraction[3]. Recently, we discovered that large helium droplets can become highly-charged[4]. The charge centers self-organize as two-dimensional Wigner crystals at the surface of the droplets and act as seeds for the growth of dopant clusters[5]. Cluster ions and charged nanoparticles of a specific size and composition can be formed by this technique with unprecedented efficiency. Dopant cluster ions can be extracted by collision induced evaporation of the host droplet[6] or by splashing of the droplet upon surface impact[7]. Both methods are suitable to form high yields of He tagged ions of both polarities which enables messenger type spectroscopy of all kinds of cold ions[8]. The location of charge centers in multiply charged He droplets close to the surface makes them accessible for subsequent interactions with metastable He atoms which leads to Penning ionization and the formation of cold multiply-charged dopant ions. In the case of dopant clusters, we obtain critical sizes of di- and trications that are well below the values obtained by conventional measurements[9].

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# Infrared spectra, structures and deuterium adsorption on $C_{60}Rh_n^+$ complexes

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Transition metal-fullerene complexes have potential application in catalysis and hydrogen storage among other fields. In addition, these complexes are ideal test benches to investigate in a well-controlled environment the interactions and the structural and electronic characteristics of transition metals on carbon substrates, which largely determine their catalytic activity and selectivity. We have focused on rhodium, which is a widely used catalyst. Infrared (IR) spectroscopy is a powerful tool to determine structural characteristics of clusters and nanoparticles. The infrared spectra of $C_{60}Rh_n^+$ complexes have been determined using Infrared Multiphoton dissociation spectroscopy of $D_2$-tagged complexes.[1] Since this methodology provides only an indirect measurement of the IR spectra, the comparison with theoretical calculations is mandatory for a fair interpretation of the spectra and to gain insight on the properties of the complexes. We have calculated the electronic and structural properties and the IR spectra of $C_{60}Rh_n^+$ (n=1-6) complexes with and without adsorbed deuterium using the Density Functional formalism. We found that clustering of Rh on the surface of the fullerene is preferred over surface wetting. For $Rh_4^+$ and $Rh_6^+$, the structures of the adsorbed clusters are different from those of the free clusters. IR spectra were measured in the 300–850 $cm^{-1}$ range. Agreement is obtained, in general, between the experimental IR spectra of D2-tagged $C_{60}Rh_n^+$ and the calculated spectra for untagged $C_{60}Rh_n^+$, except in the 600–750 $cm^{-1}$ region, where features mainly arise from the presence of $D_2$-messenger molecules adsorbed on the $Rh_n$ clusters.

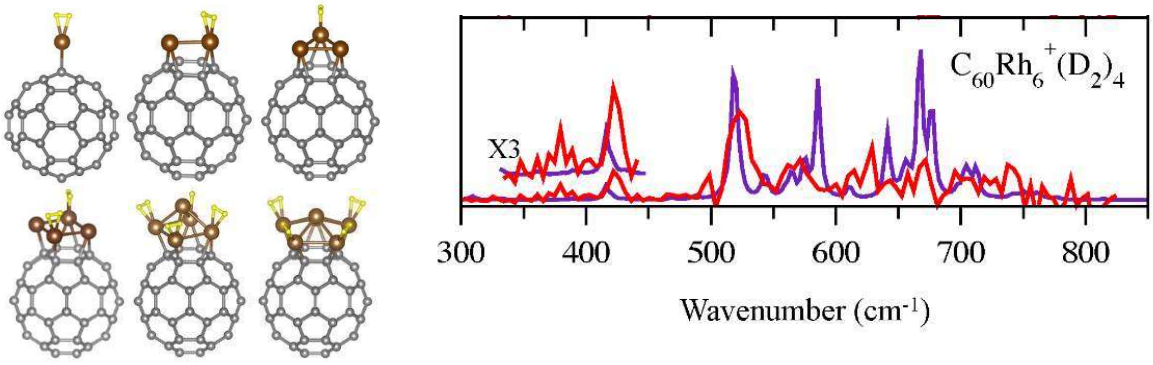


*Figure 1. Calculated lowest energy structures of $C_{60}Rh_1^+D_2$, $C_{60}Rh_2^+D_2$, $C_{60}Rh_3^+D_2$, $C_{60}Rh_4^+(D_2)_2$, $C_{60}Rh_5^+(D_2)^4$, and $C_{60}Rh_6^+(D_2)_4$ (left) and comparison between the experimental (red) and calculated (purple) IR spectrum of $C_{60}Rh_6^+(D_2)_4$ (right).*

Work supported by Ministerio de Ciencia e Innovación of Spain MCIN/AEI/ 10.13039/501100011033 and FSE+ (Grant PID2022-138340OB-I00); computer resources provided in part by Barcelona Supercomputing Center (FI-2019-3-0029; FI-2020-1-0032).

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# In situ characterization of small atomic clusters using X-ray absorption spectroscopy

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X-ray absorption techniques (XAS) offer high accuracy for the study of nanomaterials, particularly for atomic quantum clusters (AQCs) with few atoms, which mainly relies on their high sensitivity to local order and their chemical selectivity for exciting the elements present in the sample[1]. Furthermore, synchrotron radiation sources allow working with highly diluted samples and incorporating additional instrumentation for in situ or operando studies that are essential for obtaining a direct insight into the stability and physicochemical properties of AQCs in a representative environment relevant to their potential applications.

We will present a study on the thermal stability of atomic quantum clusters of five Cu atoms (Cu5-AQC) as a function of their concentration in an aqueous solution and the support employed, using near-edge X-ray absorption spectroscopy at the Cu K-edge (Cu K-XANES) and photoelectron spectroscopy near the ambient pressure conditions (NAP-XPS). These experiments directly indicate different limits to AQC stability based on mentioned parameters (concentration, temperature, and interaction with support), allowing us to distinguish intrinsic properties of clusters and how they are affected by their surroundings. Additionally, in situ results on catalytic reactivity are provided for sulfur oxidation reactions which typically require high temperatures but show evidence here of complete sulfur oxidations at ambient temperature due to high cluster reactivity.

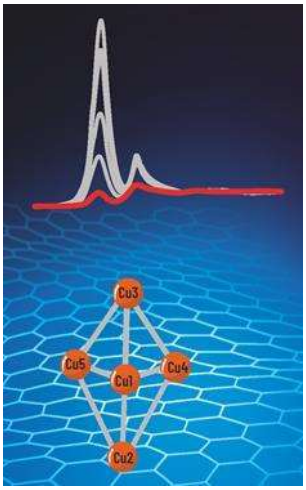


*Figure 1. Cu-K XANES spectrum is directly correlated with Cu atomic quantum cluster configuration (structure) and Cu average oxidation state (chemistry).*

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# Advanced STEM methods, including single atom imaging, high precision analysis, and in-situ electron microscopic methods for the characterization of catalytic nanomaterials

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# Copper-Palladium Tetramers and Pentamers in Oxidative Dehydrogenation Reactions: Altering Catalyst Performance by Changing Cluster Size &Composition Atom a Time

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The presentation will address the tuning knobs available at the subnanometer scale to control the catalytic performance of the catalytic sites made of subnanometer four- and five-atom Cu, Pd and CuPd clusters, supported on oxide- and carbon-based supports.

As prime example for tuning catalytic activity and selectivity, the oxidative dehydrogenation of cyclohexene will be used, under realistic conditions of pressure and temperature.

In addition to leveraging the atomic precision control of the size and composition of the mono- and bimetallic clusters for controlling their catalytic propensities, also support effects, including the thickness of e.g. zirconia support and the morphology or doping of nanocrystalline diamond supports were also explored as additional variables for the design of catalysts with optimized performance. The obtained results show that in these systems the catalytic activity could be increased by up to two orders of a magnitude and selectivity switched between the products made. Notably, the combustion channel was suppressed, which further underlines the potential of these catalysts for oxidative dehydrogenation reactions.

# Exploring the Surface Properties and Catalytic Behavior of Nanoporous Gold: A Computational Study

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Nanoporous gold (np-Au) has recently emerged as a highly selective catalyst, potentially suitable for green and low-temperature applications.[1] In contrast to the more extensively studied gold nanoparticle catalysts, the mechanistic understanding of catalytic processes on pristine and oxide-coated np-Au is far less developed. In this work the activation of $O_2$ and the formation of quasi-ordered oxygen chain structures on nanoporous gold have been studied by DFT calculations, microkinetic modeling, and ab initio molecular dynamics (AIMD) simulations.[2-5]

Modern surface science has revealed that a catalyst is not a rigid body, but undergoes rapid (sometimes irreversible) dynamic changes during chemical processes occurring on its surface. Many theoretical studies still use an oversimplified model of a metal catalyst as a rigid, clean, and perfect surface. In addition to applying traditional "static" DFT calculations, this work theoretically investigates the dynamic processes occurring on the surface of np-Au in response to changes in the chemical environment using ab initio molecular dynamics (AIMD) simulations. We will present new insights into the mechanisms of oxidation catalysis, in particular the $O_2$ activation step, on pristine and ceria-coated np-Au (Figure 1) as revealed by first-principles based modeling studies.

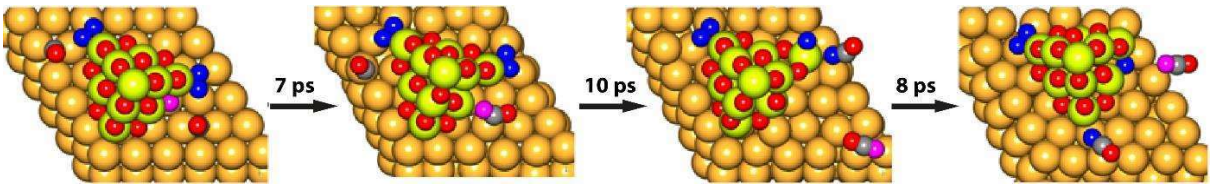


*Figure 1. The AIMD simulation of CO oxidation reaction on Au-supported $Ce_{10}O_{19}$. Colour coding of elements: orange, Au; lime, Ce; red and magenta, O; blue, adsorbed $O_2$; grey, C. Modified from.[3]*

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# Tuning catalytic activity by controlling and understanding the cluster-ligand-support interface

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Our work focuses on supported nanocluster catalysts, aiming to bridge the gap between model and real catalysts by establishing design principles rooted in structure-performance correlations. Key challenges include precise control of cluster parameters (size, composition, surface modification) and maintaining structural integrity upon deposition and activation. Through spectroscopic studies, we investigate cluster-support interactions and link cluster structure to reactivity using in situ techniques.

Our findings demonstrate the significant influence of cluster structure, ligand shell, and support material on stability and reactivity in various reactions. We have explored the structural changes of different atomic sizes of gold nanoclusters (Aux, where x=25, 38, and 144) on various metal oxides ($CeO_2$, $Al_2O_3$, and $SiO_2$) under thermal oxidation treatments and reaction conditions such as CO oxidation, cyclohexane oxidation and WGS. We also investigated the impact of surface ligands on the catalysis of metal nanoclusters. Our pioneering XAFS measurements on $Au_x/CeO_2$ revealed the fate of ligands during cluster deposition and activation. We demonstrated that ligands migrate onto the support, which has consequences for the support surface properties. Furthermore, we have observed the dynamics of dopant metal atoms within the cluster structure during pretreatment and reaction. In summary, our use of advanced spectroscopic techniques has provided deep insights into the interaction and stability of nanoclusters on oxide materials under novel reaction conditions. These insights are crucial for the development of optimal nanocatalysts.

Moreover, we have made significant strides in the realm of chirality at the atomic level, successfully developing chiral nanoclusters and enhancing their stability against racemization. Our findings underscore the preferential formation of intrinsically chiral clusters and the beneficial effect of hierarchical chirality, paving the way for applications in asymmetric catalysis. Addressing the challenge of preserving chirality upon cluster immobilization, we propose ligand-exchange reactions as a viable strategy, with promising results in functionalizing immobilized clusters while retaining their chiral properties. These findings lay the groundwork for exploring the catalytic activity of chiral clusters in asymmetric reactions, both in solution and on surfaces, marking a significant advancement in heterogeneous asymmetric catalysis.

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# Characterization of a Manganese-Vanadium Water Oxidation Catalyst: from Solution to a Soft-Matter Environment

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Light-responsive molecular components, such as photocatalysts and photosensitizers, embedded within hierarchically structured soft matter offer many perspectives for large-scale industrial applications. Here I will present a manganese-vanadium cubane water oxidation catalyst, $[Mn_4V_4O_{17}(OAc)_3]^{3-}$, which we have characterized in detail in various aspects, first in solution[1] and recently in a block copolymer membrane based on poly[2(dimethylamino)ethyl methacrylate] (pDMAEMA). For such purposes, a large tool of computations is needed, leveraging molecular dynamics simulations, density functional theory, and quantum mechanics/molecular mechanics calculations. Furthermore, a custom-developed force field[2] was employed to determine the redox potentials for the $[Mn^{III}Mn_3{}^{IV}] \rightarrow [Mn_4{}^{IV}]$ + e— and $[Mn_2{}^{III}Mn_2{}^{IV}] \rightarrow [Mn^{III}Mn_3{}^{IV}]$ + e- half-reactions in various water/acetonitrile mixtures, mimicking experimental conditions.[1] The different challenges involved in the description of catalytic processes in such polyoxometalate complexes will be highlighted.

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# Nanocluster Structures for the Oxygen Reduction Reaction

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The widespread adoption of proton-exchange membrane fuel cell (PEMFC) devices for electrochemical energy conversion is currently limited by the lack of appropriate catalysts. Highly active and durable (under acidic condition) platinum-based catalysts would in fact be indispensable to accelerate the sluggish oxygen reduction reaction (ORR), but their development face serious issues.[1,2] In the present talk, I will present recent results of experimental/theoretical studies to single out the factors affecting activity and stability of Pt based systems under ORR conditions,[3] and to propose novel systems exhibiting state-of-the-art catalytic activity and robustness.[4] Descriptor quantities, describing strain and stoichiometry phenomena, defined on experimental and theoretical observables, and correlating with oxygen binding energy and the experimentally determined ORR activity, will be used to discuss and rationalize the results of extensive ML-accelerated Global Optimization stochastic first-principles searches. The proposed systems surpass DoE 2025 target in terms of catalytic activity and durability, and set the stage for future further developments.[4]

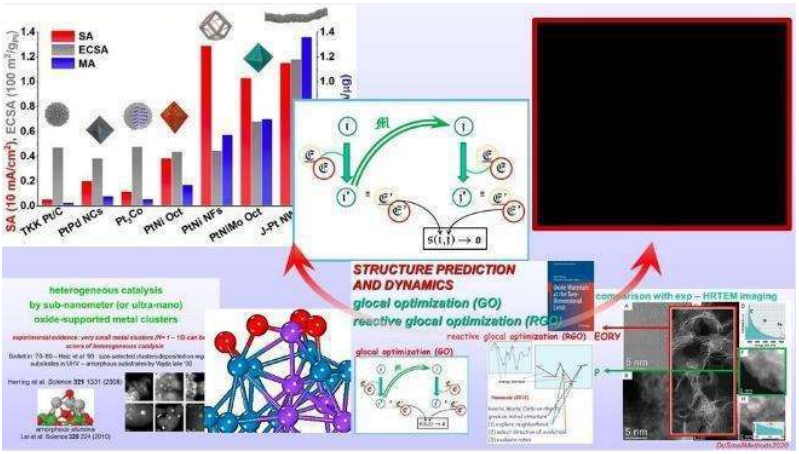


*Figure 1. Theoretical Approaches to Pt-based ORR Catalysts.*

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# Towards the accurate description of interactions in metal clusters

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I will present the results of two investigations we recently carried out on Cu and Ag+ metal clusters. In the first one,[1] we applied multireference ab initio theory to show the formation of coupled atomic metal cluster (AMC) –AMC clusters in which the AMC partners maintain their 'identity' to a large extent in terms of their initial structures and atomic Mulliken charges, and their further oligomerization (Figure 1 left). The second work studies the superfluid helium droplet-mediated surface-deposition of neutral and charged silver atomic species through combination of high-level ab initio intermolecular interaction theory with a full quantum description of the superfluid helium nanodroplet motion.[2] Evidence is presented that the fundamental mechanism of soft-deposition is preserved in spite of the much stronger interaction of charged species with surfaces, with high-density fluctuations in the helium droplet playing an essential role in braking them. Corroboration is also presented that the softlanding becomes favored as the helium nanodroplet size increases (Figure 1 right).

In both cases good agreement with the experimental available data was obtained.

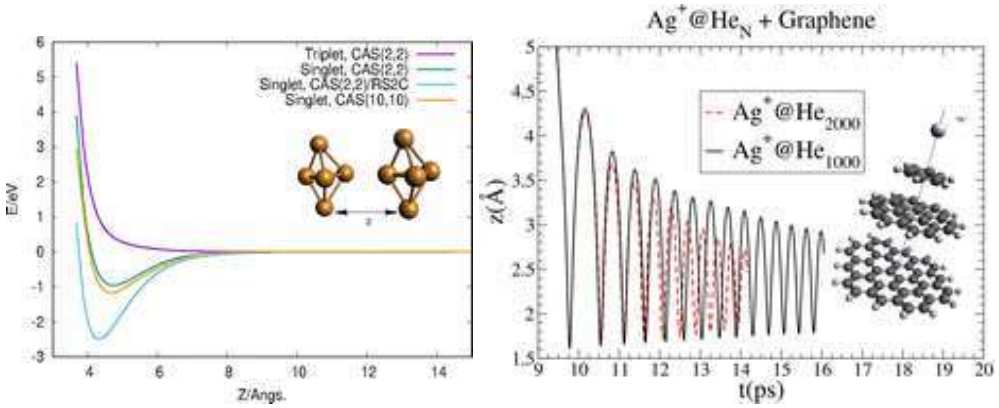


*Figure 1. Energy curves showing the interaction of two $Cu_5$ clusters (left) and oscillations in the $Ag^+$ motion as a function of time for droplets of He atoms together with the other investigated $Ag^+$ complexes (right).*

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# Ab Initio Calculations of Chemically Accurate Molecule–Surface Interaction Energies

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Designing new catalytic processes and materials requires an atomistic understanding of both adsorption and reaction steps. Accurate predictions for these key steps need to be within a chemical accuracy of ±4 kJ/mol. However, this level of accuracy is rarely achieved with the standard computational model, which uses density functional theory (DFT) with dispersion (DFT-D) and the harmonic approximation for sampling the potential energy surface (PES). We have shown that chemical accuracy can be reached with the local approach[1,2] for adsorption if improvements are made to both the Taylor expansion and the quality of the PES.[3-5]

Our anharmonic QM:QM approach (i) includes higher-order terms in the Taylor expansion and calculates anharmonic vibrational energies, and (ii) uses a hybrid QM:QM methodology to improve the energy of stationary points beyond DFT-D to the level of second-order Møller–Plesset perturbation theory (MP2) or coupled cluster expansion with single and double substitutions and perturbative treatment of triple substitutions (CCSD(T)).

As a representative system, we present the results for $CO_2$ and $H_2O$ adsorption in the metal–organic framework (MOF) Mg-MOF-74, also known as CPO-27-Mg. From a fundamental surface science perspective, the main adsorption sites at $Mg^{2+}$ ions in this MOF share the five-fold oxygen coordination with the terrace sites on the MgO(001) surface. We show that quantum effects on nuclear motion must be taken into account when calculating adsorption thermodynamics. Additionally, at higher surface coverages, lateral interactions between adsorbed molecules become significant.

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CATCOSY 2024

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

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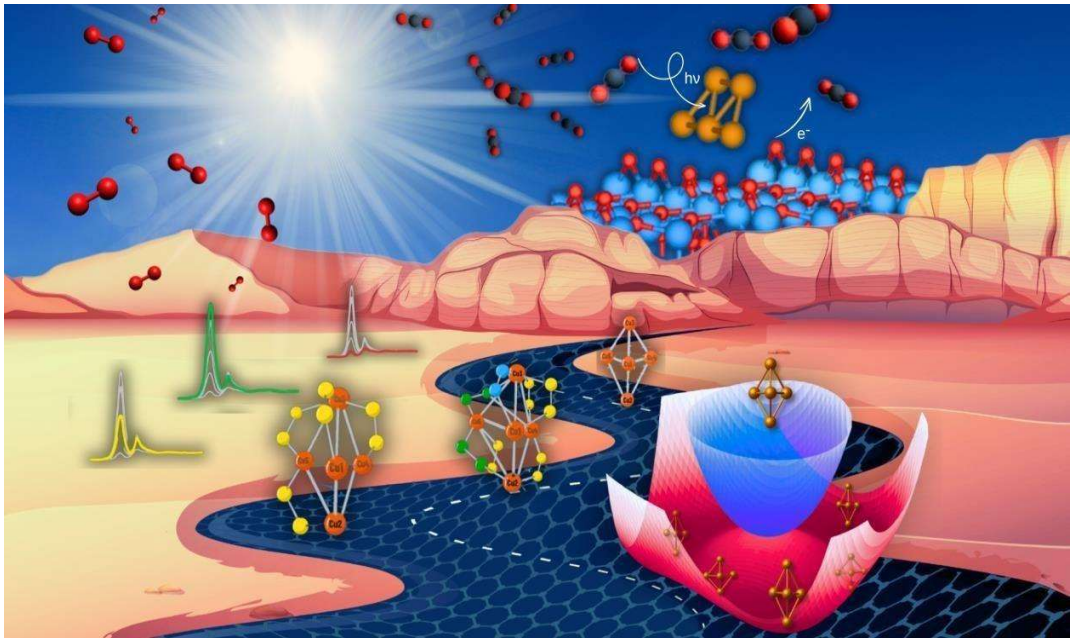
Current advances in synthesizing and characterizing atomically precise monodisperse metal clusters (AMCs) at the subnanometer (Angstrom) scale have opened fascinating possibilities in new quantum materials research. Their quantized 'molecule-like' electronic structure showcases unique stability and physical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



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CATCOSY 2024

# HOT TOPIC PRESENTATIONS

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# Investigation of the reactivity of gold clusters via He tagging spectroscopy

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Modern chemistry lays special emphasis on the understanding and advancement of catalytic performance by unveiling the basic steps of catalytic reactions. Gas-phase metal clusters offer a promising potential for gaining an in-depth view of the energetics and kinetics of bond-making and bond-breaking process in catalytic reactions at the molecular level.[1] Additionally, the high surface-to-volume ratio and the high number of uncoordinated sites of clusters can enhance the catalytic potential of metals compared to their bulk configurations. A vivid example of such behaviour is gold. A noble metal in bulk, prized for its inertness, can become a potent catalyst when reduced to small enough particles, as demonstrated by examples involving CO and various hydrocarbons.[2] When particles consist of only a few atoms (clusters), each atom becomes significant, and clusters exhibit size-dependent properties.

This work focuses on investigating the structure and size-dependent reactivity of small cationic gold clusters $Au_n^+$ (n = 1–5), which are formed within multiply-charged superfluid helium nanodroplets and furthermore reacted with carbon dioxide $(CO_2)_x$ (x = 1–4) or acetylene $(C_2H_2)_y$ (y = 1–4). These complexes are solvated with helium, unclosing the possibility to employ IR photodetachment spectroscopy of the He-tagged cluster ions.[3] The experimentally obtained IR spectra are complemented by in-house computational analysis. This synergy not only enables a deeper understanding of the cluster-molecule interaction, including structural arrangement and bonding characteristics, but also serves as a benchmark for existing computational methods.

The gathered information on these cluster-molecule complexes will further broaden the understanding of catalysis at the nanoscale, laying the foundation for future designs of efficient and selective catalysts for chemical reactions.

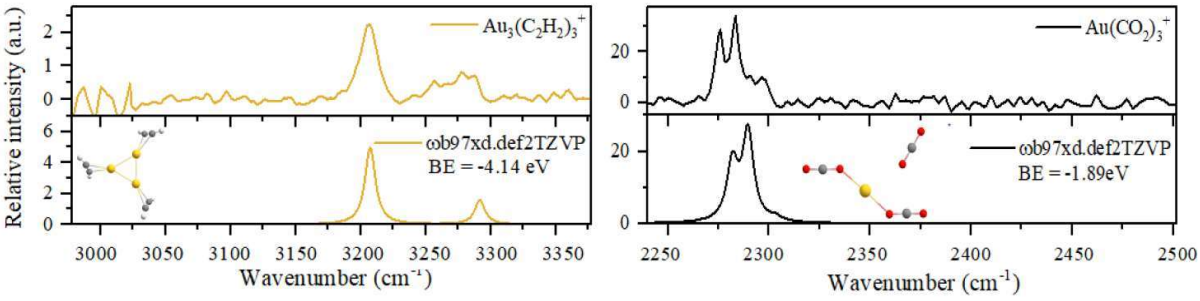


*Figure 1. IR spectrum of $Au_3(C_2H_2)^{3+}$ (dark yellow) and $Au_3(CO_2)^{3+}$ (black) showing the asymmetric stretch vibration of $C_2H_2$ and $CO_2$, respectively. The experiment is supported by quantum chemical calculations at ωb97xd.def2TZVP level of theory, providing insight into the structure and the binding energy (BE) of both complexes.*

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# Electronic structure of the smallest iron carbide FeC

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Iron and carbon are two elements with strong affinity which are known to combine in any proportion since several centuries giving rise to a rich variety of refractory alloys known as steel. Due to their refractory nature, their facility to condense and their high reactivity, subnamoteric iron carbide clusters are thought to be the first seeds that may trigger the nucleation process giving rise to the formation and growth of dust grains in circumstellar envelopes. Those iron-containing refractory grains are widely present in meteorites of our solar system and are considered as the principal components to the formation of rocky planets.

It is known that nucleation becomes spontaneous once the particle grow above a critcal size[1]. Nevertheless, the first steps of formation and growth of iron carbide seeds are still not understood. Interestingly, the recent detection of FeC diatomic radical in the circumstellar envelope of the carbon-rich asymptotic giant branch star IRC+10216[2] give us a hint on one possible canditate able to trigger nucleation of interstellar dust. To understand better this specie, extensive calculations on the electronic structure of this radical in several electronic states have been performed to determine its spectroscopy and shed light on the complexity of iron-carbon bonding.

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# Nonadiabatic dynamics in the reversible oxidation of $Cu_5$ clusters

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

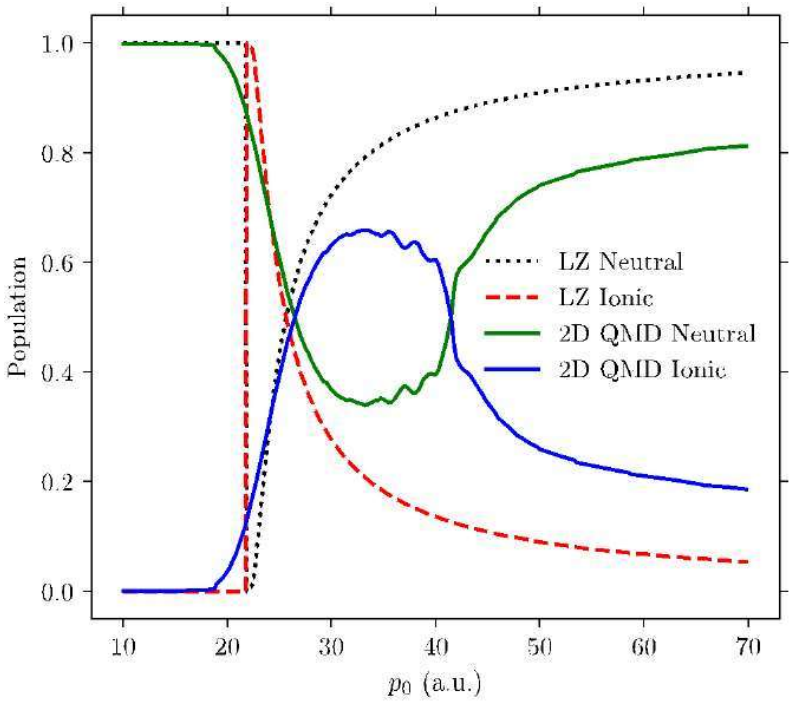


*Figure 1. Electronic transition probability as function of the magnitude of the momentum in the dimension of distance between $Cu_5(O_2)_2$ and $O_2$.*

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# Oxidation, etching and $MoO_x$ phases/clusters onto $MoS_2$ crystals

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Thin $MoS_2$ crystals became indeed a nodal point in flexible nanoelectronics, but their usage extends as well into novel generation of chemical sensors and catalysts for important reactions, such as hydrogen evolution reaction. All these phenomena depend critically onto chemical stability of thin $MoS_2$ crystals. In this talk I will present our selected recent research efforts into understanding of local mechanisms for oxidation and etching of the $MoS_2$ crystalline surfaces as well as formation and structural resolution of originating $MoO_x$ nanometric and sub-nanometric clusters together with their interesting electrical properties.

# Characterization and Effects of Polarons on Oxide Surfaces via Machine Learning

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The physics of oxides is shaped by the presence of atomic impurities, often leading to formation of strongly localized charge carriers known as polarons. The characterization of these electronic states poses challenges for first-principles simulations and experiments. We propose a machine-learning-accelerated density functional theory approach to analyze defects and polarons on oxide surfaces.[1] On rutile $TiO_2$(110), scanning microscopy measurements show high concentration of oxygen vacancies (~20%); our methodology reveals the role of polarons in mediating repulsive interactions between the defects, leading to the formation of such dense areas.[2] By introducing Nb doping, the optimal distributions are altered.[3]

This computational scheme efficiently predicts stable defect-polaron arrangements on oxide surfaces and suggests mechanisms to favor formation of functional complexes: e.g., tensile strain stabilizes surface polarons trapped between [011]-aligned oxygen vacancies that enhance the catalytic properties of the surface. Our machine learning approach overcomes practical limitations of first-principles calculations, moving the modeling of polaronic oxides to unprecedented length scales, possibly opening the path for studies on nanoclusters.

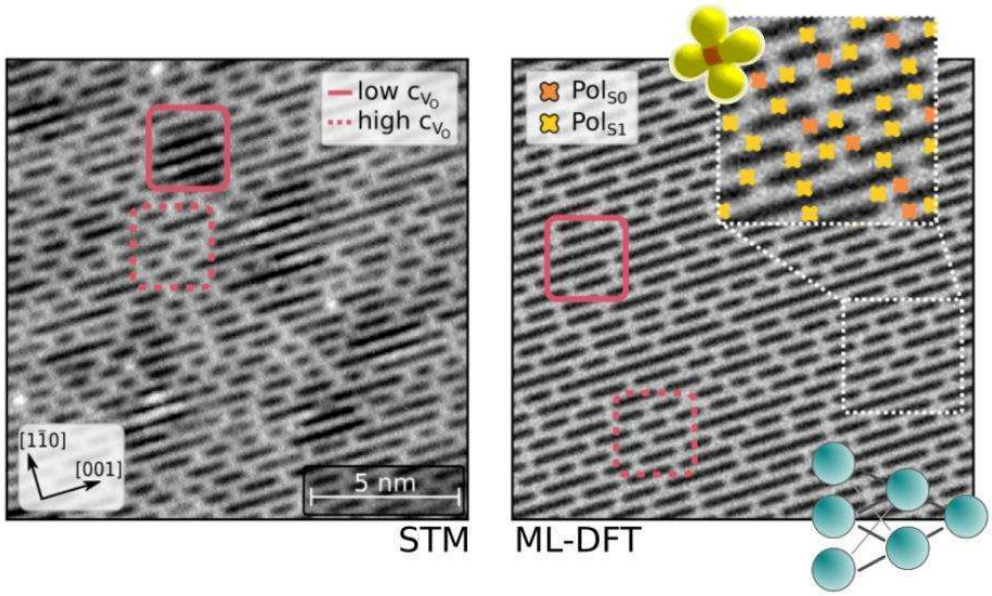


*Figure 1. $TiO_2$(110) surface at the nanoscale: experiment (left) and simulations (right). Oxygen vacancies are visible as bright spots, between Ti [001] rows (polarons shown in the inset).*

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# Single atom and single cluster transition metal catalysts supported on GDY and BGDY layers

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Transition metals (TM) are often used as excellent catalysts in many reactions because of their different oxidation states, activity, selectivity, and unfilled d-orbitals. Supported TM catalysts have been strongly investigated in the last decades, and one of the reasons for using supports is to reduce the amount of catalyst needed while retaining the same catalytic effect, this is attributed to the fact that support helps to keep the metal catalyst in a dispersed state.[1] Carbon-based materials are proposed as efficient support platforms for catalysis due to their excellent electronic and mechanical properties, high superficial area, and low cost. Along with the metal-support interactions, the performance of the catalysts can be adjusted by varying the size of the supported metal nanoparticles.[2] Structural deformations of the supports can be triggered depending on the selected metal and support and on the nanoparticle coverage. We have performed DFT calculations to study the structural and electronic properties of single atom and single cluster catalyst of cobalt, palladium, and vanadium adsorbed on Graphdiyne (GDY) and Boron-Graphdiyne (BGDY) layers. The main goal is to investigate the effect of coverage. Our results suggest a strong dependence on the specific metal and the support.

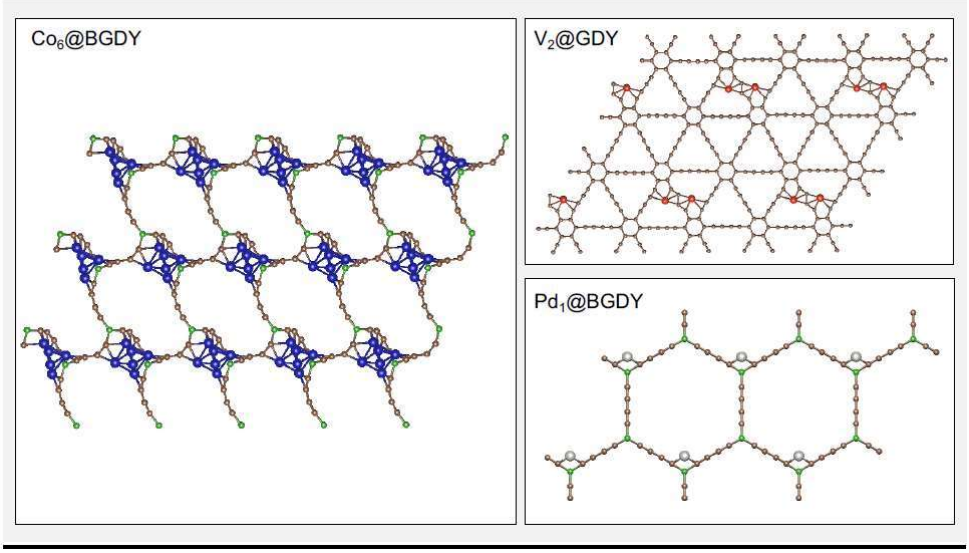


*Figure 1. TM catalysts supported on BGDY and GDY layers.*

Work supported by Ministerio de Ciencia e Innovación of Spain MCIN/AEI/10.13039/501100011033 and FSE+(Grant PID2022-138340OB-I00). J.S. acknowledge the doctoral grant from The Schlumberger Foundation, Faculty for the Future.

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# Simulating high-pressure surface reactions with molecular beams

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Using a reactive molecular beam with high kinetic energy ($E_{kin}$) it is possible to speed gas-surface reactions involving high activation barriers ($E_{act}$), which would require elevated pressures ($P_0$) if a random, Maxwell-Boltzmann gas is used (Fig. 1a). By simply computing the number of molecules that overcome the activation barrier in a random gas at $P_0$ and in a molecular beam at $E_{kin}$=$E_{act}$ (Fig. 1a), we establish a $P_0(E_{kin})$ equivalence curve (Fig. 1b). Based on this curve, we postulate that molecular beams are ideal tools to investigate gas/surface reactions that involve high $E_{act}$, such as the activation of greenhouse gases ($CH_4$ and $CO_2$) on metal catalysts.[1] In particular, we foresee the use of molecular beams to simulate the industrial-range in such reactions (>10 bar) while making use of X-ray photoemission spectroscopy (XPS). To test this idea, we revisit the oxidation of Cu(111) combining $O_2$ molecular beams and XPS.[2] By tuning the kinetic energy of the $O_2$ beam in the range 0.24-1 eV we achieve the same sequence of surface oxides obtained in Ambient Pressure Photoemission (AP-XPS) experiments,[3] in which the Cu(111) surface was exposed to a random $O_2$ gas up to 1 mbar. Moreover, we observe the same surface oxidation kinetics as in the random gas, but with a much lower dose, close to the expected value derived from the equivalence curve in Fig. 1b.

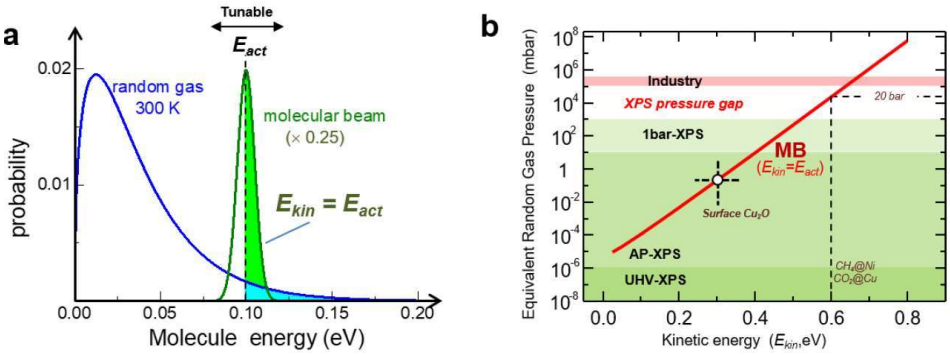


*Figure 1. (a) Probability distribution curves for molecules in a random, Maxwell-Boltzmann gas at 300 K (blue), and within a molecular beam tuned to* $E_{kin}$ = $E_{act}$ = *0.1 eV (green). The area under the curve is normalized to 1 in both cases. The shaded areas mark the number of molecules* $n$ *that are active in each case, being* $n_{molecular-beam} = 20 \times n_{random-gas}$. *(b) Molecular-beam/random-gas equivalence curve (red) for molecular reactions of activation energy* $E_{act} = E_{kin}$, *assuming a molecular beam of standard flux (*$10^{15}$ *mol/cm²·s). The equivalence line has been satisfactorily proved in the oxidation of the Cu(111) surface.*[1]

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# Exploring Molecular Interactions in π → π* Excited States of Anisole Complexes Using Multiconfigurational SAPT

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The nature and strength of intermolecular forces determine the physicochemical properties of matter. While interest in accurately describing noncovalent interactions has grown, most research has focused on ground-state properties. However, predicting the spectroscopic and photodynamical characteristics of molecules requires examining excited states. To study weak non-covalent interactions in both ground and excited states, aromatic chromophores and their prototypes, such as the anisole molecule in various solvents, are commonly used as model systems detectable spectroscopically.

We have developed a variant of symmetry-adapted perturbation theory (SAPT) to describe noncovalent interactions in dimers with multireference character, applicable to both ground and excited states. The SAPT(MC) method is implemented in the GAMMCOR code. The SAPT(MC) method was used to investigate anisole-water and anisole-ammonia complexes, known to exhibit blue or red shifts upon excitation from S0 to S1 states. A detailed analysis of the SAPT interaction energy components allowed us to elucidate the changes in interactions induced by vertical and adiabatic excitation. This numerical study was further enriched by visualizing shifts in local dispersion energy descriptors.

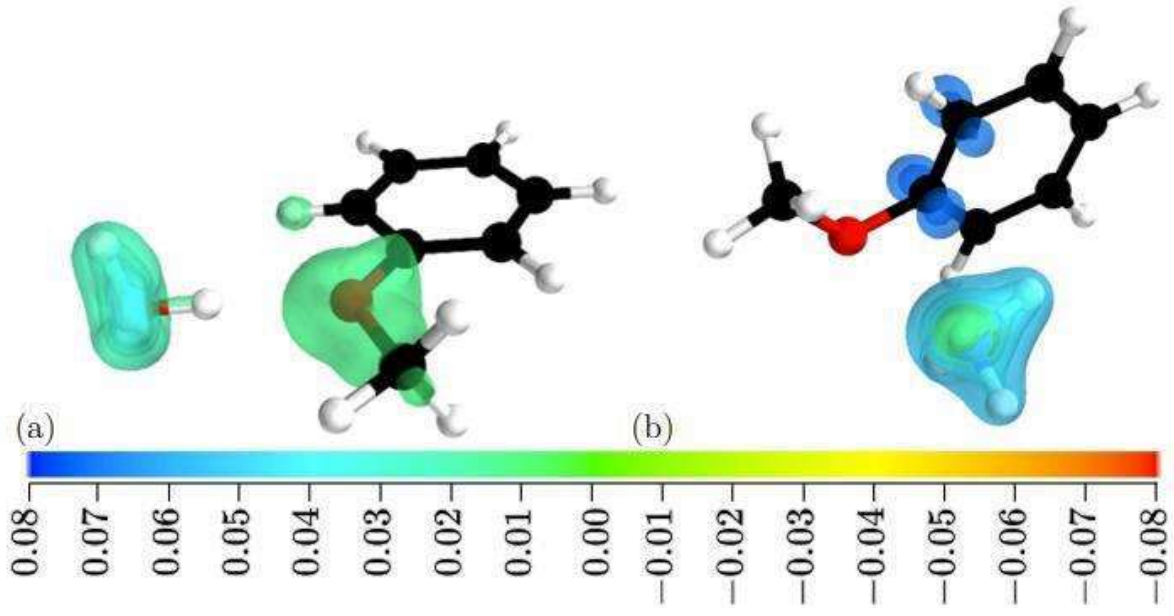


*Figure 1. Differences in dispersion energy interaction density between the ground state and π → π* excited state for (a) anisole-$H_2O$ and (b) anisole-$NH_3$ complexes. Values are reported in milliHartree.*

# Subnanometric Metal Clusters: Catalytic Properties, Zeolite Encapsulation and Infrared Spectra, a DFT and AIMD Study

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Subnanometric metal clusters, composed of one to tens of metal atoms, have garnered significant interest in various fields due to their unique properties and potential applications in catalysis,[1] therapeutics,[2] bioimaging,[3,4] sensing,[5] and photocatalysis.[6,7] In this work, three uses of subnanometric metal clusters are considered: a comparison of catalytic properties for $Cu_1$ and $Cu_5$ supported on $TiO_2$, how $Cu_5$ can be stabilized as a $Cu_5/TiO_2$ cluster encapsulated in zeolite, and analyzing the infrared (IR) spectra of $Ag_1$ and $Ag_3$ on coronene and graphene surfaces, using *ab initio* molecular dynamics simulations (AIMD).

Encapsulating subnanometric metal clusters within zeolite frameworks has emerged as a promising strategy to enhance catalytic performance and stability. This approach leverages the unique properties of metal clusters, while benefiting from the structural advantages of zeolites. Zeolites, with their well-defined pore structures and high thermal stability, provide an ideal environment for stabilizing these clusters, preventing their migration and aggregation during high-temperature processes.[8,9] Despite the experimental success in using such encapsulated systems in various catalytic reactions, including hydrogen evolution and formic acid decomposition,[10,11] the theoretical understanding of these systems remains underdeveloped. This gap is addressed by applying advanced density functional theory (DFT) methods to investigate the encapsulation of $Cu_5$ clusters supported on $TiO_2$ within a zeolite framework. Our work builds on AbinitSim Unit's previous findings, which demonstrated the enhanced catalytic and photoactive properties of $Cu_5/TiO_2$, including the reduction of the C–O bond-breaking barrier in $CO_2$,[7,12] and the promotion of visible-light photoactivity.[13] A recent study[6] highlighted the successful use of $TiO_2$ nanoparticles within MOF mesopores for $CO_2$ photoreduction under UV light.[14] By modeling the same process with $Cu_5$-modified $TiO_2$ nanoparticles instead, the photoreduction could potentially be extended into the visible light spectrum, enhancing its applicability and efficiency.[14]

Building on our previous findings, we chose to replace the $Cu_5$ cluster with a single $Cu_1$ atom in the $Cu_5/TiO_2$ system. This adjustment enables us to gain a deeper understanding of how the structural fluxionality of $Cu_5$ clusters may influence the bond-breaking process of $CO_2$. This work has been carried out using advanced DFT methods, such as including Hubbard U parameters[15] and incorporating the HSE06 functional.[16]

A key factor in studying the fluxionality and geometric changes of subnanometric metal clusters on carbon-based surfaces, is by considering the IR spectra as affected by temperature. Standard DFT approaches only allow for considering the IR spectra at 0 K, but using AIMD simulations, the IR spectra can be calculated at various temperatures, while throughout these AIMD simulations we can visually see the changes in cluster geometries as well as the cluster-to-surface distances. In this work we first consider the adsorption of $Ag_1$ and $Ag_3$ on the surfaces: coronene and graphene, while performing AIMD simulations of these systems at 400 K. Our goal is to test these systems out to eventually progress to $Ag_5$ on coronene and graphene, to consider fluxionality and geometrical changes.

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# A practical *ab initio* approach to open-shell metal cluster-support interactions

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Recent advancements in synthesizing metal atomic quantum clusters (AQCs) have paved the way for innovative (photo)catalysts.[1,2] To optimize these catalysts, a detailed understanding of AQC–support interactions at the molecular level is essential.[1,2] Although MP2 is a cost-effective method for studying these interactions, it tends to overestimate them. The MP2C scheme, which refines Hartree-Fock dispersion energy with a coupled dispersion contribution, has shown accuracy for closed-shell AQCs on carbon-based supports.[3] This presentation introduces a modified UMP2C scheme tailored for open-shell AQC–support interactions, using $Cu_3$–benzene and $Cu_3$–coronene as models.[4] The UMP2C approach has been validated against CCSD(T), CCSD(T)-F12, UMP2, and DFT-D3 methods, effectively capturing energy differences between uncoupled and coupled dispersion contributions. The derived dispersionless and dispersion energy components are then fitted to an additive pairwise potential model (PPM).[4-6]

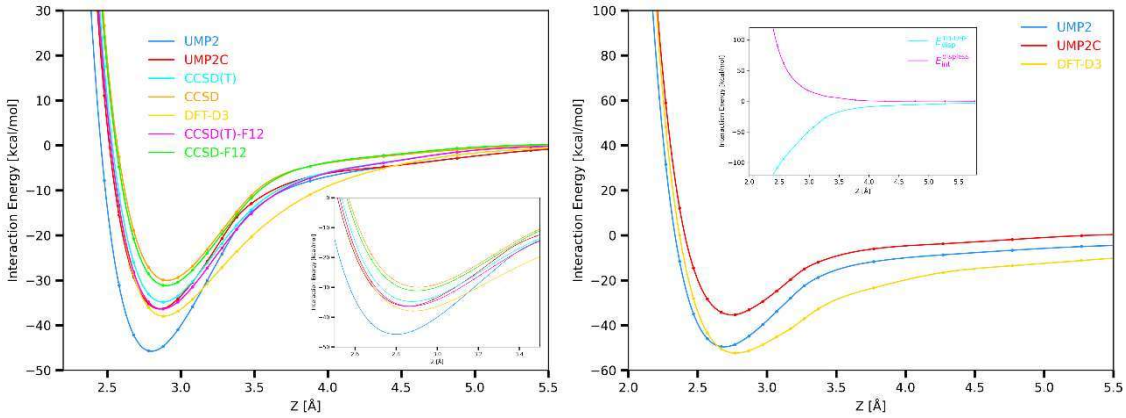


*Figure 1. Interaction potentials for $Cu_3$–benzene (left-hand panel) and $Cu_3$–coronene (right-hand panel). The right inset shows the dispersion and dispersionless contributions to the interaction energies.*

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# Theoretical Investigation of Imidazole Derivatives Adsorption on an Ag(100) Surface to Evaluate Their Potential as Radiosensitizers

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Cancer is one of the diseases that most concern doctors around the world, as more and more cases are diagnosed every year in all countries. In 2022, around 295,000 cases were registered in Spain, according to the Spanish Association Against Cancer (AECC). Another major problem associated with this disease is its treatments, because, although they are highly effective, they are painful and involve risks to patients' lives. That is why many scientists, especially experimental and theoretical chemists, have set themselves the challenge of proposing viable alternatives to deal with this disease. Recently, a novel treatment has emerged: radiosensitizers. These are chemical species that, combined with radiation, stimulate the elimination of cancerous tumors.[1] In this work, we present a DFT theoretical study on the adsorption of imidazole derivatives to a silver metal surface, Ag(100), since it has been theorized that these molecules are suitable to serve as radiosensitizers.[2] The silver surface aims to reproduce a silver nanoparticle, since nanoparticles have also been studied as possible radiosensitizers, since they are able to enhance the radiosensitivity of imidazole derivatives.[2] Along with the adsorption positions of the molecules, we also analyze some interesting properties of the systems, such as charge transfer, which lead to a better understanding of the interaction between the molecules and the surface. This aids in predicting potential future applications of systems that integrate nanoparticles and small molecules as radiosensitizers.

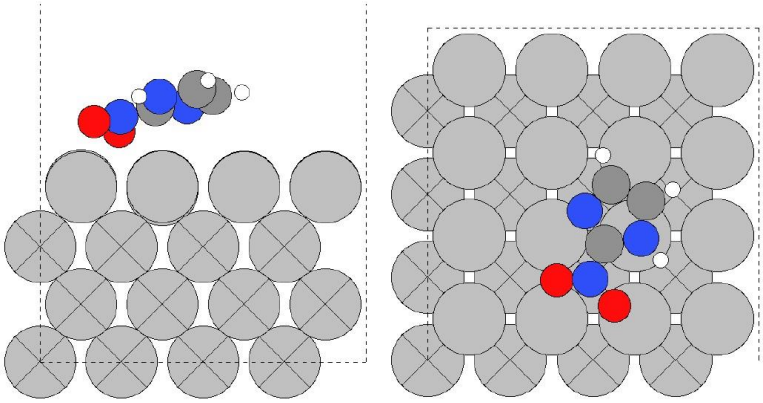

*Figure 1. Side (left) and upper (right) view of 2-nitroimidazole adsorbed on Ag(100).*

**References:**

[1]Gong, L., Zhang, Y., Liu, C., Zhang, M., & Han, S. (2021). Application of Radiosensitizers in Cancer Radiotherapy. International Journal of Nanomedicine, Volume 16, 1083–1102. https://doi.org/10.2147/ijn.s290438

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# Computational prediction of a new two-dimensional material obtained by functionalization of boron graphdiyne layers with transition metal atoms

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Decoration of hexagonal boron graphdiyne (BGDY) layers by adsorption of transition metal atoms of Nickel has been investigated by density functional calculations. For one, two and three metal atoms per hexagon, the BGDY structure is maintained. Decoration with six metal atoms leads to the formation of a novel two-dimensional material (BGDY-Ni) in which the hexagonal structure is heavily distorted. Atomic decoration of BGDY with six metal atoms is more stable than adsorption of six-atom clusters on the original BGDY layers. BGDY-N is a semiconductor with a small band gap that can be useful for infrared detectors. The electronic bands of BGDY-Ni near the Fermi level show some cone-like features like those in graphene, with large band curvatures, and quite low effective masses of electrons and holes, making the material promising for semiconductor technologies. The work shows that computer simulation helps to discover new materials by functionalization of layered carbon materials with metal atoms.

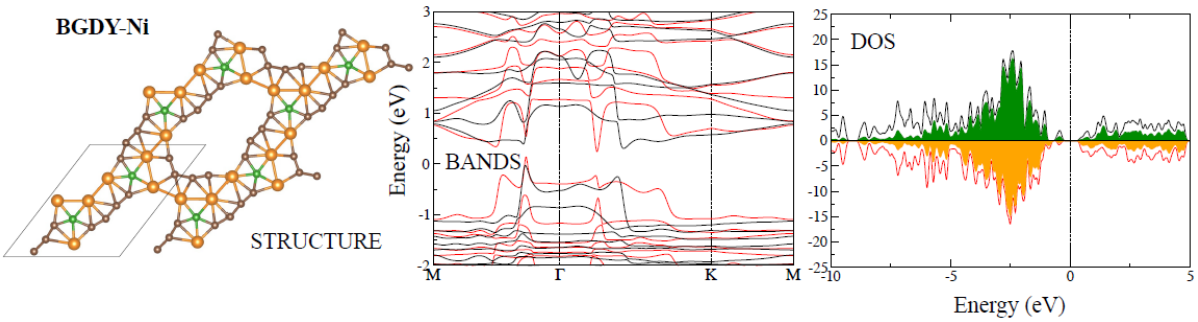


*Figure 1. New phase of BGDY-Ni, promising material for semiconductor technologies. From left to right, structure, brown, green and orange spheres represent C, B, ad Ni atoms, respectively, spin up (red) and spin down (black) electronic bands, and Density of States (green and orange filled areas are DOS projected over the Ni atoms).*

Work supported by Ministerio de Ciencia e Innovación of Spain MCIN/AEI/10.13039/501100011033 and FSE+(Grant PID2022-138340OB-I00).

# Theoretical study of the electronic properties of surfaces for catalysis

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Due to the large increase in energy consumption, alternative methods are being researched to find new ways of clean and efficient energy storage. Hydrogen fuel cells are one of the most promising candidates for clean energy due to its abundance. One of the main problems with hydrogen energy comes from its high-cost production. It is important to find new catalysts which can produce large quantities of hydrogen reducing the production cost. For this reason, we will study the electronic properties of different surfaces for catalytic applications. We will make calculations based of density functional theory to comprehend the adsorption mechanisms on different surfaces. We will also study the electronic properties and the charge density for the different configurations. Finally, theoretical calculations of the surface energies and Wulff construction will be made to determine the shape and sizes of the nanoparticles.

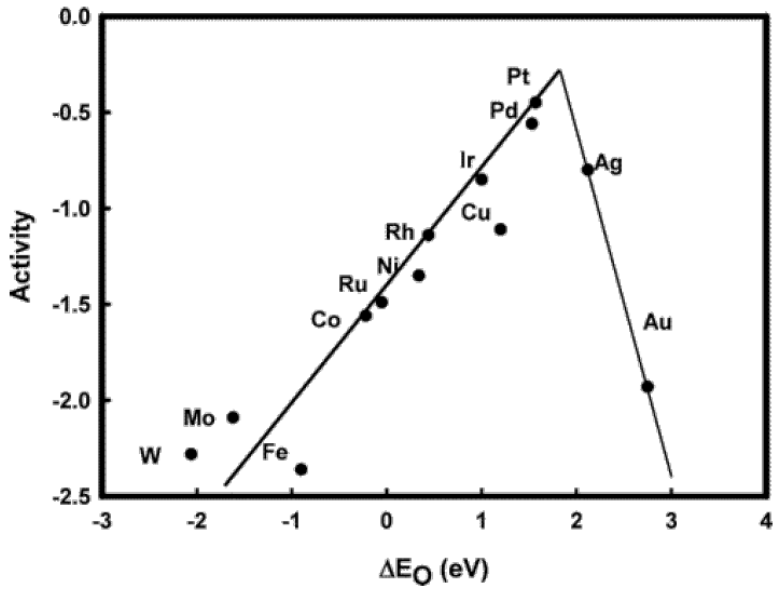


*Figure 1. Trends in oxygen reduction activity plotted as a function of the oxygen binding energy.*[1]

The results shown are from different surfaces where adsorption energies have been studied and surface reconstructions have been optimized to determine wulff shape of the nanoparticles.

Conclusions of this work will be made for the surfaces studied and potential catalytic applications.

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# Separation of $CO_2/CH_4$ gas mixtures using nanoporous graphdiyne and boron-graphdiyne membranes: influence of the pore size

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Nanoporous carbon-based membranes have garnered significant interest in gas separation processes owing to their distinct structure and properties. We have investigated the permeation and separation of the mixture of $CO_2$ and $CH_4$ gases through membranes formed by thin layers of porous graphdiyne (GDY) and boron graphdiyne (BGDY) using Density Functional Theory. The main goal is to investigate the effect of the pore size. The interaction of $CO_2$ and $CH_4$ with GDY and BGDY is weak, and this guarantees that those molecules will not be chemically trapped on the surface of the porous membranes. The permeation and separation of $CO_2$ and $CH_4$ through the membranes are significantly influenced by the size of the pores in the layers. The size of the hexagonal pores in BGDY is large in comparison to the size of the two molecules, and the passing of these molecules through the pores is easy because there is no barrier. Then, BGDY is not able to separate $CO_2$ and $CH_4$. In sharp contrast, the size of the triangular pores in GDY is smaller, comparable to the diameter of the two molecules, and this raises an activation barrier for the crossing of the molecules. The height of the barrier for $CO_2$ is one half of that for $CH_4$, the reason being that $CO_2$ is a linear molecule which adopts an orientation perpendicular to the GDY layer to cross the pores, while $CH_4$ has a spherical-like shape, and cannot profit from a favorable orientation. The calculated permeances favor the passing of $CO_2$ through the GDY membrane, and the calculated selectivity for $CO_2/CH_4$ mixtures is large. This makes GDY a very promising membrane material for the purification of commercial gases and for the capture of the $CO_2$ component in those gases.

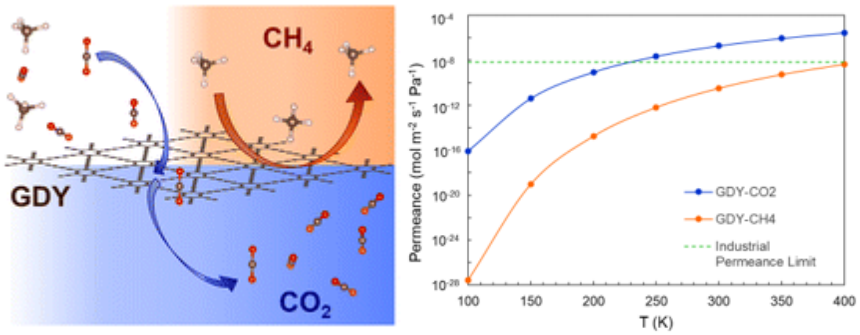


*Figure 1. Permeance of $CO_2$ and $CH_4$ through GDY*

To perform the calculations, we have employed the Kohn-Sham DFT method as implemented in the Quantum Espresso computational package.[1] The Perdew-Burke-Ernzerhof (PBE) generalized gradient (GGA) functional was used for electronic exchange-correlation effects. The interaction between valence and core electrons was described by Projector-Augmented Wave (PAW) pseudopotentials, and dispersion interactions effects were included using Grimme's DFT-D3 method.

Work supported by Ministerio de Ciencia e Innovación of Spain MCIN/AEI/ 10.13039/501100011033 and FSE+(Grant PID2022-138340OB-I00). S.M. acknowledges doctoral grant from Valladolid University.

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[1] https://www.quantumespresso.org (accessed 19 February 2024).

# Theoretical Study of Electroreduction of $CO_2$ Using Metal-Doped Graphene Sheets with Metals

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This study addresses high $CO_2$ emissions from fossil fuels and their ecological impact. We explore $CO_2$ capture and electroreduction, focusing on theoretical pathways to produce high value products like CO using a copper- and tin-doped graphene catalyst. Conformational studies, comparative analyses, and thermodynamic calculations at the B3LYP/LANL2DZ level in gas and aqueous phases indicate a high predisposition for CO formation. Different routes, leading to different products, have been considered. The 'c' route produces CO through a less favorable radical cation pathway, while the 9.a route transforms the $CO_2$ radical anion into COOH before reducing to CO.

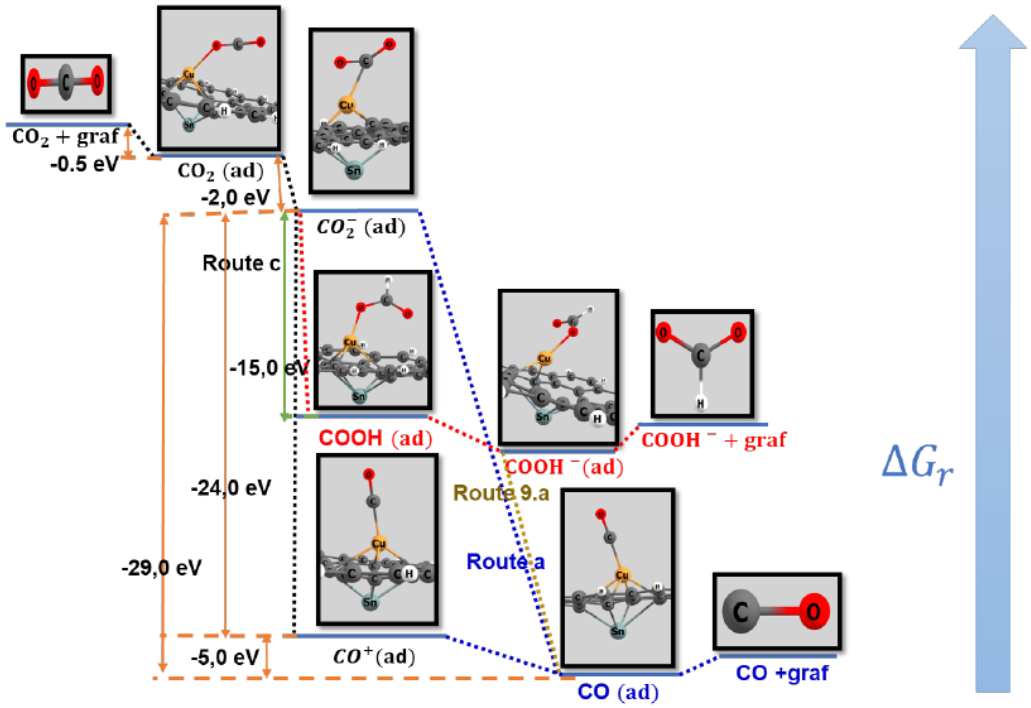


*Figure 1. $CO_2$ electroreduction pathways with Cu-Sn graphene for the production of CO in three stages in gas phase: Route c, Route 9.a, and Route a. The most stable route is the 'a'.*

Although other products like $CH_4$, $CH_3OH$, and $HCOO^-$ are considered,[1] CO is prioritized due to higher concentrations observed by the UAM Electrochemistry Group.

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# Structure and chemical reactivity of Pt-Zr binary nanoclusters

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The high binding energy of CO at platinum nanoclusters can result in poisoning effects, a major problem during a variety of oxidation reactions. One interesting way to solve this problem is doping these clusters with small quantities of other metals, to induce a weakening of the CO-Pt bonds. In this contribution, using DFT we have studied both the structure and chemical reactivity of platinum clusters doped with approximately 25% of Zr atoms ($Pt_3Zr$). At this concentration, a very stable alloy is formed. After performing an extensive study for the structure of clusters with varying sizes, we have chosen the $Pt_9Zr_3$ cluster to simulate the adsorption of oxygen and carbon monoxide, and their reaction to form $CO_2$. The results show that the presence of Zr greatly enhances tendency towards a complete oxidation of the cluster. Also, it causes sizable changes to the CO binding energies at the Pt sites. Finally, the interaction between CO and adsorbed oxygen takes place with moderate barriers, indicating that these clusters will be active for the CO oxidation reaction.

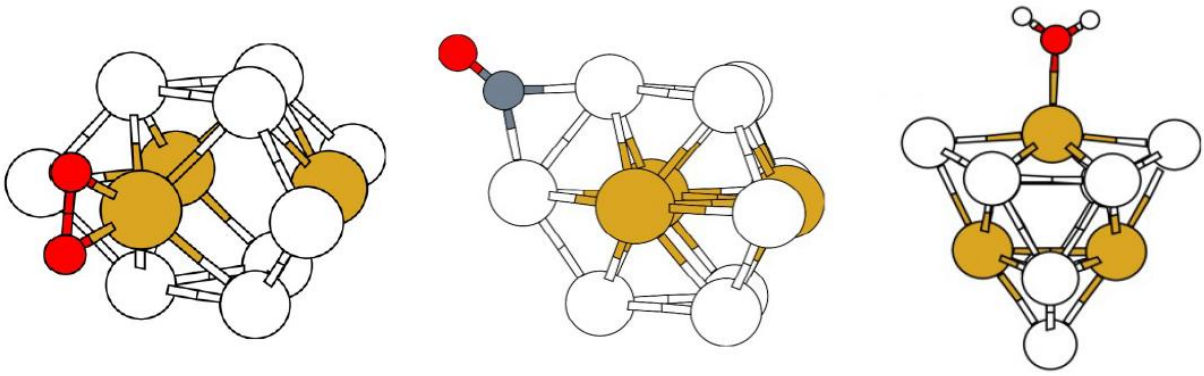

*Figure 1. Relaxed structures for adsorption of $O_2$, CO and $H_2O$ at $Pt_9Zr_3$ cluster.*

# Merging reactive molecular beams and XPS to simulate highpressure surface reactions

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Relevant catalytic reactions are studied by exposing the surface of interest to high-pressure gas environments. These include the reduction of greenhouse gases, such as $CO_2$ and $CH_4$ on metal surfaces. The ultimate reason for the high-pressure needed in such reactions is the reduced number of molecules within the random gas that possess enough energy to overcome the activation barrier of the elementary chemisorption/dissociation step (Fig. 1. (a)). However, the high pressure represents a challenge to carry out research in realistic operando conditions since the most powerful surface sensitive techniques, such as X-ray photoemission spectroscopy (XPS) have the optimum performance in ultra-high vacuum (UHV) conditions.

An alternative to investigate high activation barrier reactions with XPS in UHV consists of using a molecular beam (MB), which is a collimated stream of gas formed by the supersonic expansion from a high-pressure gas source. The resulting beam of molecules has a well-defined translational energy that can be tuned readily, and as well as a narrow energy spread (10%) (Fig. 1. (b)). These properties translate into a scenario in which using a standard MB tuned to match the activation energy of, e.g., 0.6 eV ($CO_2$ on Cu), would be sufficient to achieve reaction rates that would otherwise require pressures over 20 bar. [1]

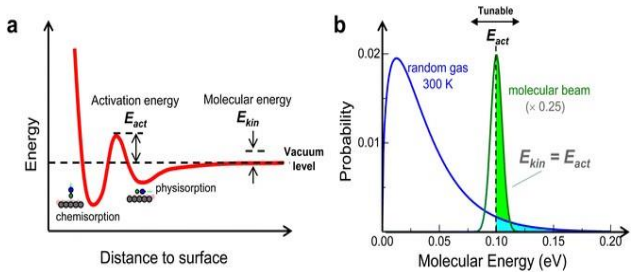


*Figure 1. (a) Molecule–surface interaction potential for an activated chemisorption process with $E_{act}$ barrier height and $E_{kin}$ molecular energy. (b) Normalized probability distribution of molecular energies for a random, Maxwell–Boltzmann gas at 300 K, versus a monochromatic, supersonic molecular beam. [1]*

We have implemented an UHV system that enables the simultaneous use of MB and XPS, so that in gas/surface reactions the gas phase is tuned and monitored through time-of-flight techniques with molecular beams (TOF-MB), while the evolution of the surface chemical species is studied with XPS. Our comparative analysis of the Cu (111) oxidation by exposing to a random $O_2$ gas and to an energy-tunable $O_2$ beam demonstrates the validity and potential of the MB/XPS approach to assess gas/surface reactions with high activation barriers.[1] First results from a similar analysis of the Ru (0001) oxidation will also be presented.

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**References:**

[1]Al Taleb, Amjad, et al. "Simulating high-pressure surface reactions with molecular beams." *Physical Chemistry Chemical Physics* 26.3 (2024): 1770-1776.

# Investigating Dilute Plasmonic Alloys for Photocatalytic Propane to Propylene Dehydrogenation

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For over a century, society has relied on catalysts to facilitate chemical transformations to generate fuel, food, and essential products. With the growing need for a more circular carbon economy, radiant electromagnetic energy, a ubiquitous energy resource, will become indispensable. Engineering catalysts to convert light into chemical energy rather than relying on traditional phononic heating provided by fossil fuels has implications both in sustainability and in reaction selectivity. Combining the optical properties of plasmonic nanoparticles, materials that exhibit collective oscillations of their free electrons after interaction with light, with small concentrations of catalytically active late transition metals, allows for the design of optically tunable photocatalysts with engineered active sites down to the single atom limit. This emerging class of photoactive materials are known as dilute plasmonic alloys. Upon plasmon decay, hot carriers are generated from the optically active solvent and become available to transition metal active sites where molecules of interest are adsorbed, leading to enhanced rates and reaction selectivity by scattering into adsorbate antibonding orbitals. When trying to influence reactivity and selectivity enhancements in bimetallic plasmonic systems, it is invaluable to understand the role dilute transition metal sites play in converting radiative energy to chemical energy. Specifically, this work aims to understand these processes in situ and in operating conditions to ensure structure/reactivity relationships and mechanistic inferences are correctly attributed. I target propane to propylene dehydrogenation due to its market size worth as a small molecule feedstock in the chemical manufacturing industry and its high thermocatalytic energy demand. I use supported CuPt nanoparticles as catalysts due to platinum's prevalence in the thermocatalytic industrial reaction and copper for its plasmonic properties. This work informs on the behavior of single atom, clusters, and nanoparticle platinum sites in CuPt dilute plasmonic alloys and investigates their contribution to hot carrier transfer into propane. While gas chromatography and mass spectrometry studies confirm the light enhancement observed in this system, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is used to inform on the nature of the Pt dilute sites in the Cu host. X Ray Absorption Spectroscopy studies complement these experiments by deciphering the coordination sphere of Pt sites in reaction conditions and in situ Scanning Transmission Electron Microscopy (STEM) experiments inform on the changing morphology of the catalyst surface. The results of these studies are anticipated to teach more about structure-function relationships of this new class of photocatalytic nano materials and advance methods for atomic scale characterization.

# Rational design of Ceria mixed oxides supported Pt catalyst for Water Gas Shift Reaction: Engineering the O vacancy chemical environment

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The oxygen vacancy in metal oxides are usually considered as the active site and play a key role in catalytic reactions. However, how to precisely modulating the oxygen vacancy is still challenging. One effective way is by doping metal cations which will lead to the distorted lattice distance, changed bond length and electron density inside the oxide crystal, thereby changing the chemical coordination environment, formation energy and chemical reactivity of oxygen vacancy. Both theoretical and experimental studies point that O vacancy is directly involved in the H2O dissociation, a limiting step for the water-gas shift reaction (WGSR). However, the current understanding of the relationship between the coordination structure of oxygen vacancy and the catalytic performance is still not clear. Cerium oxide as a reducible oxide its O vacancy can be studied by many characterization methods like XPS, Raman , EPR, therefore, its mixed oxide-supported metal catalyst can be used as an ideal system to study the oxygen vacancy chemical environment's effect for the water-gas shift reaction. In this study, we synthesized a series of cerium-mixed oxides supported Pt catalysts. A hydrothermal method was used to synthesis the mixed oxide support, by controlling the type and amount of doped metal cations ($La^{3+}$, $Pr^{3+}$, $Zr^{4+}$) the oxygen vacancy coordination environment can be precisely modulated. In-situ characterization methods were used to identify and track the change of the active sites and intermediates under working conditions, and the reaction mechanism was analyzed. This work provides a model for rational designing of new catalyst systems and the precise modulation of active sites.

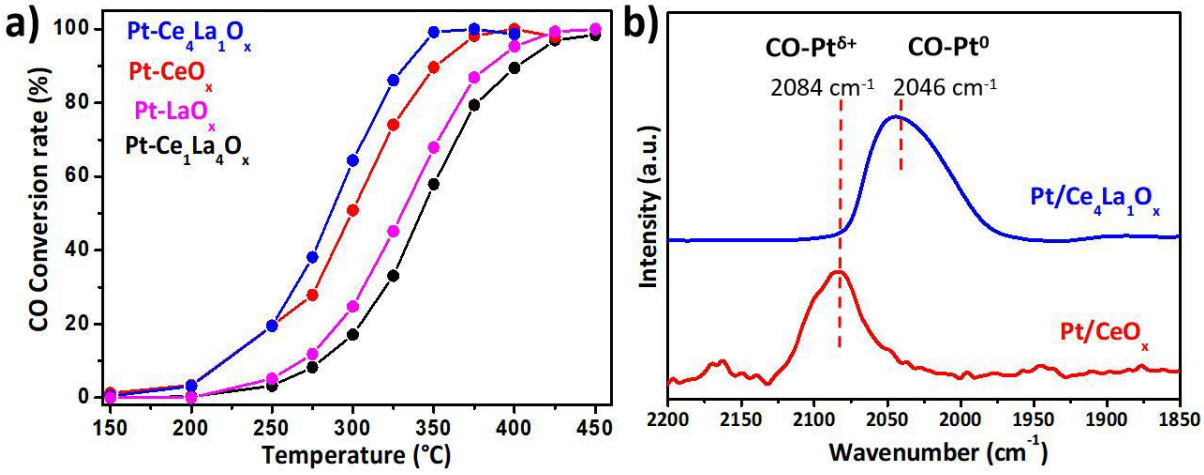


*Figure 1. a) Steady-state temperature profiles of $Pt/Ce_aLa_bO_x$, $Pt/CeO_x$ and $Pt/LaO_x$ catalysts for the WGS reaction (conditions: 2 vol% CO/10 vol% $H_2O$/Ar, 50 mL/min, mcatal = 50 mg, space velocity 54000 mL $h^{-1}$ gcat-1 ); b) CO FT-IR at room temperature on $Pt/Ce_4La_1O_x$ and $Pt/CeO_x$.)*

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# Synthesis and characterization of sub-nm clusters of $MoO_3$ onto $MoS_2$ basal planes

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$MoS_2$, $MoO_3$ and their heterostructures as well as nanocomposites are interesting candidates for catalysis.[1,2] In this study, sub-nm Mo oxide clusters were synthesized by heating $MoS_2$ flakes in the etching regime (370 °C) in air. Comparison between height profiles of formed clusters obtained by atomic force microscopy (AFM) imaging and density functional theory simulations on the sub-nm $Mo_xO_y$ fragments onto a $MoS_2$ monolayer suggested that such clusters are mainly $MoO_3$ monomers and dimers at sulfur vacancies (Figure 1). Several surface characterization methods such as energy and wavelength dispersive X-ray spectroscopies, Raman measurements, as well as Kelvin probe force microscopy showed that $MoS_2$ surface is covered sparsely with $MoO_3/MoO_x$ species. X-ray absorption near edge structure data verified the $MoO_3$ nature of synthesized clusters. These results show that removal of Mo atoms at the atomic level during oxidative etching follow predominantly by formation of single $MoO_3$ molecules. Such observations confirm the previously proposed oxidative etching stoichiometry at the nanoscale.[3]

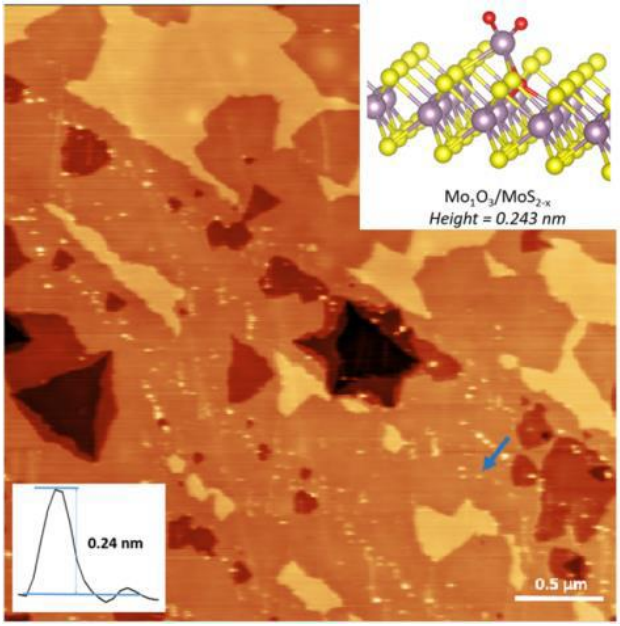


*Figure 1. High-resolution AFM topography image of an etched $MoS_2$ flake in air. The upper inset shows a simulated structure and calculated height of a $MoO_3$ monomer at sulfur vacancy in $MoS_2$ monolayer. The lower inset shows the height of a sub-nm cluster depicted by blue arrow.*[3]

The work of SS and RS has been supported by the National Science Center, Poland, grant no. 2017/27/B/ST4/00697.

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[3]Sovizi, S.; Tosoni, S.; Szoszkiewicz, R. $MoS_2$ oxidative etching caught in the act: formation of single $(MoO_3)_n$ molecules. Nanoscale Adv. 2022, 4, 4517-4525.

# Peeking into the Femtosecond Hot-Carrier Dynamics Reveals Unexpected Mechanisms in Plasmonic Photocatalysis

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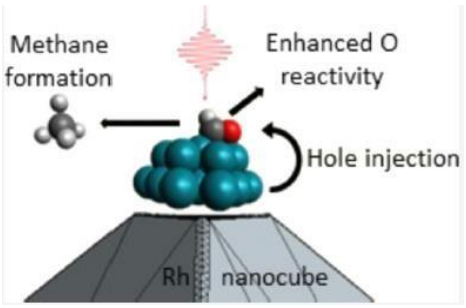
Plasmonic-driven photocatalysis may lead to reaction selectivity that cannot be otherwise achieved. A fundamental role is played by hot carriers, i.e., electrons and holes generated upon plasmonic decay within the metal nanostructure interacting with molecular species. Understanding the elusive microscopic mechanism behind such selectivity is a key step in the rational design of hot-carrier reactions. To accomplish that, we present state-of-the-art multiscale simulations, going beyond density functional theory, of hot-carrier injections for the rate-determining step of a photocatalytic reaction[1]. We focus on carbon dioxide reduction, for which it was experimentally shown that the presence of a rhodium nanocube under illumination leads to the selective production of methane against carbon monoxide. We show that selectivity is due to a (predominantly) direct hole injection from rhodium to the reaction intermediate CHO. Unexpectedly, such an injection does not promote the selective reaction path by favoring proper bond breaking but rather by promoting bonding of the proper molecular fragment to the surface.

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**References:**

[1]Giulia Dall'Osto, Margherita Marsili, Mirko Vanzan, Daniele Toffoli, Mauro Stener, Stefano Corni, Emanuele Coccia, J. Am. Chem. Soc. 2024, 146, 2208−2218.

# Analyzing the nature of electron correlation in small metal clusters

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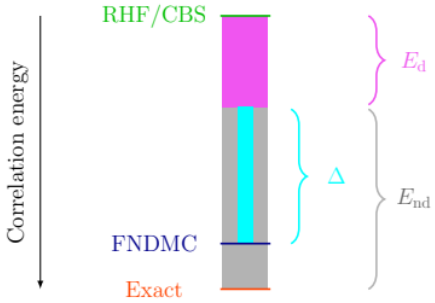
Atomically precise nanoclusters (NCs) are a class of nanoparticles with fascinating chemical and physical properties, which stem from their underlying electronic and geometric structure. Such precisely described structures give us the power to tune e.g. catalytic properties by hetero-atom doping. Ab initio modeling of transition metal-doped clusters usually rely on Density Functional Theory (DFT) calculations assuming a single-reference nature of the studied systems. We have recently developed a method[1,2] for partitioning an exact electron correlation energy into the dynamic and non-dynamic components, which is based on the Fixed-node diffusion Monte Carlo (FNDMC) method utilizing the nodes derived from restricted Hartree-Fock Slater determinant. The proposed method allows for unambiguous separation of electron correlation energies and will be applied to analysis of the nature of electron correlation in small metal clusters.




$$E_\mathrm{d} = E^\mathrm{FN}(\Gamma_\mathrm{RHF}) - E_\mathrm{RHF/CBS} - \Delta$$

$$E_\mathrm{nd} = E_\mathrm{exact} - E^\mathrm{FN}(\Gamma_\mathrm{RHF}) + \Delta$$

$$\Delta = E_\mathrm{UHF/CBS} - E_\mathrm{RHF/CBS}$$

*Figure 1. Schematic representation of electron correlation energy $E_{cor}$ decomposition into dynamic and non-dynamic components $E_d$ and $E_{nd}$, based on HF nodes and FNDMC method.*

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**References:**

[1]Šulka, M,; Šulková, K.; Jurečka, P; Dubecký, M.; Dynamic and Nondynamic Electron Correlation Energy Decomposition Based on the Node of the Hartree–Fock Slater Determinant. Journal of Chemical Theory and Computation 2023 19 (22), 8147-8155. https://doi.org/10.1021/acs.jctc.3c00828
[2]Šulka, M,; Šulková, K.; Dubecký, M.; Unveiling Hidden Dynamic Correlations in CASSCF Correlation Energies by Hartree-Fock Nodes. Journal of Chemical Physics 2024. *In press.*

# Adsorption and catalytic properties of doped aluminum clusters

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This study employs density functional theory to explore how doping within clusters impacts their structure and reactivity. We focus on aluminum cluster anions ($Al_{12}X^-$) where X represents various dopant elements. Our findings reveal that the dopant's position (central or surface) significantly affects the cluster's electronic structure and its interaction with water molecules. The study highlights the importance of electron affinity for centrally doped clusters and how doping modifies the reactivity through the creation of complementary active sites. On the other hand, surface doping influences the cluster's behavior due to uneven charge distribution, making the adsorption and reactivity of surfacedoped clusters being dominated by electrostatic effects. This work demonstrates the crucial role of dopant placement for cluster properties and paves the way for a deeper understanding of doping effects on cluster reactivity.

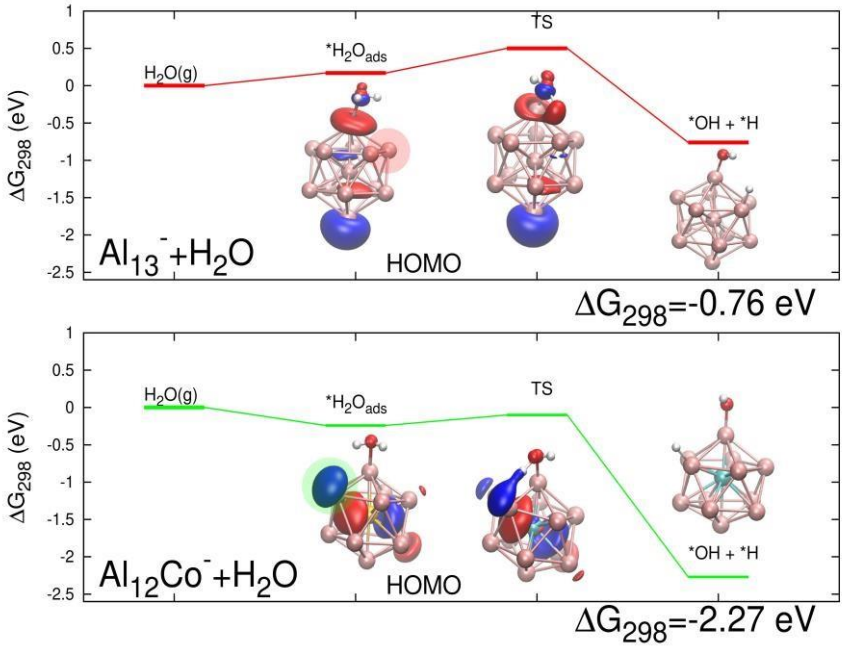


*Figure 1. Complementary active site formation causes an increased reactivity of central doped $Al_{12}Co^-$ cluster with water.*

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**References:**

[1]Šulka, M,; Šulková, K.; Antušek A.; Exploring water adsorption and reactivity in a series of doped aluminum cluster anions. Phys. Chem. Chem. Phys., 2021, 23, 23896–23908. https://doi.org/10.1039/D1CP03104J

# Machine-Learning-Accelerated DFT Conformal Sampling of Catalytic Processes

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Developing new catalytic materials and processes that address and solve the present energy and environmental problems is one major challenge of today's chemistry. To meet this challenge, theory and simulations can play a critical role, by predicting performance and screening materials for catalytic reactions, and providing operative directions for experimental verification and realization. In this work, we develop and validate a novel approach, the Conformal Sampling of Catalytic Processes (CSCP)[a], that aims at drastically accelerating the exploration of unknown catalytic systems by transferring knowledge from a previously investigated, worked-out case. We demonstrate the CSCP approach on methanol decomposition and $CO_2$ hydrogenation reactions over two paradigmatic metal facets: fcc(111) and fcc(100), modeled as periodic slabs. We apply MACE Machine Learning Interaction Potential to interpolate the reactive PES of the new systems, and we combine it with a basic assumption of catalytic mechanism conformality to construct physically grounded minimal fitting databases. We show that, using CSCP after a few active learning steps (high-throughput) and with reasonably sized DFT databases (efficiency), it is possible to construct a single, physically grounded MLIP that is able to describe the whole PES and attain a level of precision reaching chemical accuracy in the energetics of both local minima and reaction energy barriers for the whole RED along the reaction pathways.

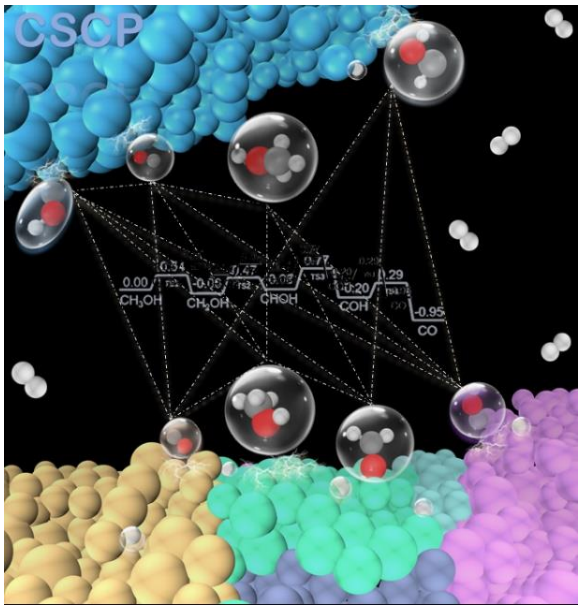


*Figure 1. Conformal Sampling of Catalytic Processes (CSCP) demonstrated on $CH_3OH$ decomposition*

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**References:**

[a] Roongcharoen, T; Conter, G; Sementa, L; Melani1, G; Fortunelli, A. Machine-Learning-Accelerated DFT Conformal Sampling of Catalytic Processes. Journal of Chemical Theory and Computation, *accepted*, https://doi.org/10.1021/acs.jctc.4c00643.

# VENUE

The meeting will be held at the Central Campus of the Consejo Superior de Investigaciones Científicas (CSIC). The event will be distributed across several locations within the campus:

- Central Building of the CSIC at Serrano 117:

Salón de Actos: Lectures on 26 September.
Cafetería Comedor: Lunches.

- Center of Physics "Miguel Antonio Catalán":

Claustro: Coffee Breaks and Poster Session, located at Serrano 123.
Sala de Prensa: Lectures on 27 September, located at Serrano 113.

- Residencia de Estudiantes, Pinar 21-23:

Accommodation and lunches for participants staying at the "Residencia de Estudiantes".