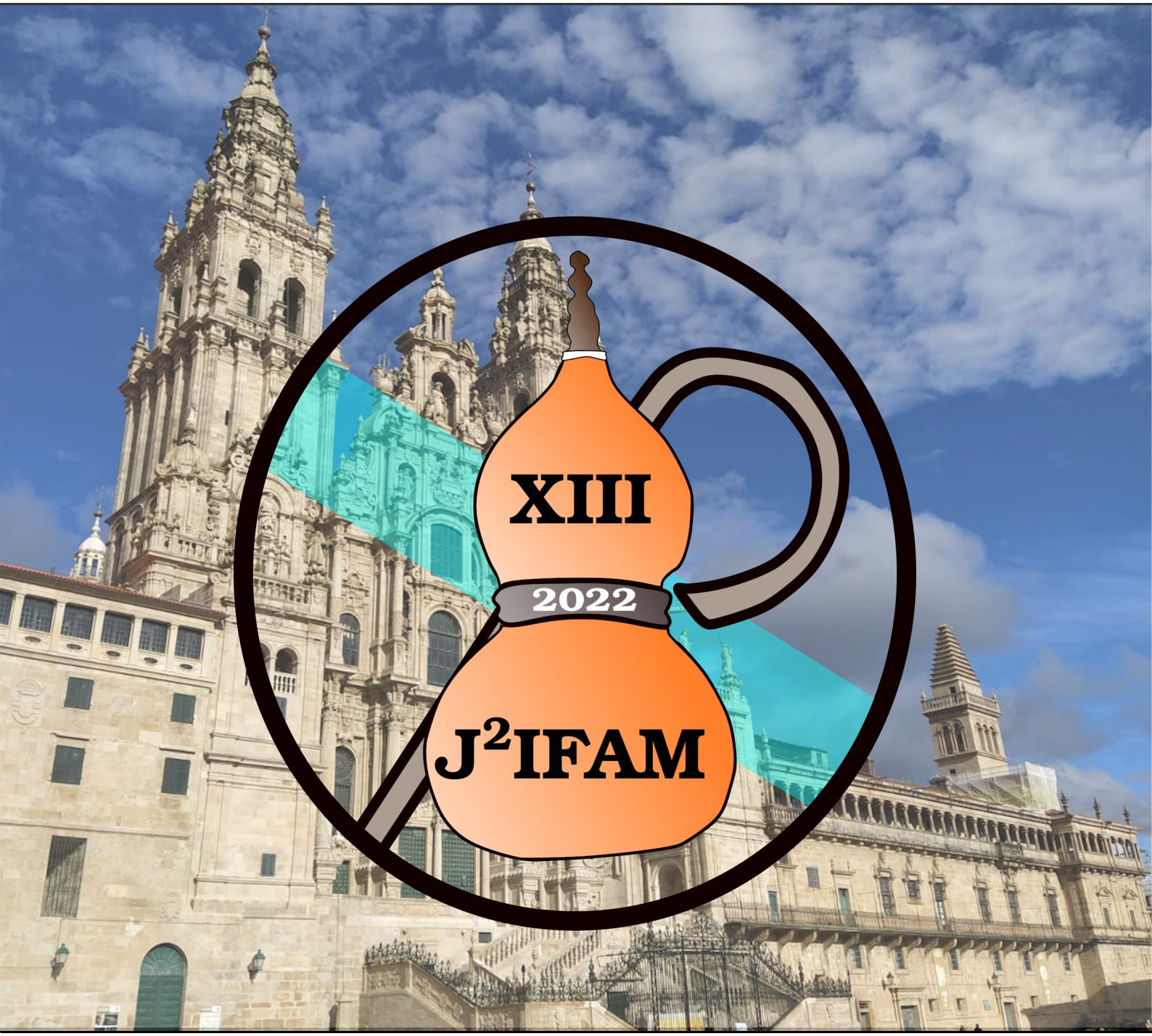
March 15th-17th 2022

Santiago de Compostela (Spain)

XIII Jornadas de Jóvenes Investigadores en Física Atómica y Molecular



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Sara Illodo

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March 15th

Start	End	Event
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11:30	11:50	OC 1 (Pg. 14) - Maider Parra Santamaría
11:50	12:10	OC 2 (Pg. 15) - María Judit Montes de Oca Estévez
12:10	12:30	OC 3 (Pg. 16) - Francisco García González
12:30	12:50	OC 4 (Pg. 17) - Otger Crehuet Viladelbosch
13:00	15:00	*Lunch Break*
15:00	15:30	IT 2 (Pg. 11) - David Mellado Alcedo
15:30	15:50	OC 5 (Pg. 18) - Álvaro Pérez Barcia
15:50	16:10	OC 6 (Pg. 19) - Anzhela Veselinova Marinova
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12:00	12:20	OC 13 (Pg. 26) - Fernando Aguilar Galindo
12:20	12:40	OC 14 (Pg. 27) - Gustavo Cárdenas
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15:00	15:20	OC 16 (Pg. 29) - Patricia González Berdullas
15:20	15:40	OC 17 (Pg. 30) - Pedro Recio Ibáñez
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17:10	17:30	OC 21 (Pg. 34) - Sara Espinosa Gómez
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Start	End	Event
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12:10	12:30	OC 27 (Pg. 40) - Jesús Lucia Tamudo
12:30	12:50	OC 28 (Pg. 41) - Carmen Domínguez Castillo
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15:40	16:00	OC 31 (Pg. 44) - Tomás Sánchez Pastor
16:00	16:30	Closing Ceremony
21:00	-	Congress Dinner

Modeling Biological Systems: Electronic Structure, Sampling and Environment

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Abstract

The simulation of biological processes is a complex task which requires the combination of different quantum and classical mechanical techniques. Moreover, these hybrid calculations are often performed within a dynamic framework in order to account for vibrational and conformational sampling. In the case where the process under investigation takes place in a long-time scale, the application of enhanced sampling approaches may also be needed. In this contribution, the modeling of several physical processes occurring in different biological media will be discussed, including the permeation of drugs across lipid membranes [1], the conduction of ions through voltage-gated ion channels [2], electron-transfer events on solvated nucleobases in terms of reduction potentials [3], the binding of drugs to proteins [4], and the interaction between small molecules and their environments [5]. In addition, the automatization of the calculation of many of these properties for ensembles of geometries by means of the MoBioTools software [6] developed in our group will be illustrated.

Acknowledgements

The MoBioChem research group (mobiochem.com) thanks the following funding agencies: the Comunidad de Madrid through the Attraction of Talent Program (Grant Ref. 2018-T1/BMD-10261), the Spanish Ministry of Science and Innovation (Project PID2020-117806GA-I00) and the European Social Fund through the Programa Operativo de Empleo Juvenil y la Iniciativa de Empleo Juvenil. Moreover, the Centro de Computación Científica of the Universidad Autónoma de Madrid is thanked for computational resources.

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[6] https://github.com/mobiochem/MoBioTools

Photodissociation and photoionization study of free radicals by ion and photoelectron imaging

David Chicharro Vacas

Abstract

Free radicals are present in a large number of processes as intermediates in reactions in atmospheric and interstellar chemistry and even hydrocarbon combustion [1, 2]. The simplest alkyl radicals, such as methyl and ethyl radicals, are considered as prototypes for theoretical and experimental studies. Moreover, halogenated free radicals are of great importance as a source of halogens for the atmosphere [3], becoming precursors for the formation of aerosols or particles and even other compounds of great interest, such us Criegee [4] intermediates, which improve the oxidizing capacity of the atmosphere thus favoring the formation of secondary organic aerosols. Hence, it is of great interest to know the dynamics of photodissociation and photoionization of these radicals.

Here I report the most relevant results that I obtained during my thesis. Ranging from the methyl radical, where the photodissociation dynamics from the $3p_z$ Rydberg state have been studied, to the ethyl radical, where a novel site-specific H-atom elimination have been observered for the first time (see Figure 1). In addition, I will present the results regarding the photoionziation dynamics of the simplest Criegee intermidiate.

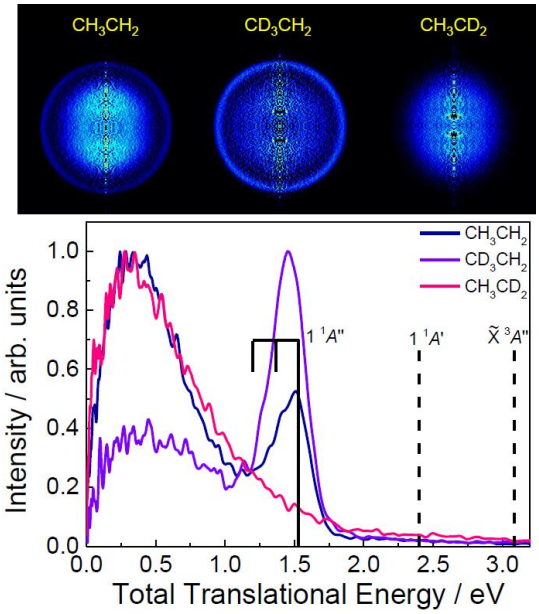

Figure 1: H-atom abel inverted images for the ethyl radical photodissociation dynamics through the 3p Rydberg state.

Acknowledgements

I acknowledge financial support from Spanish MINECO under the FPI predoctoral program and my supervisors Prof. Luis Bañares Morcillo and Sonia Marggi Poullain for their support.

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Linear polar molecule in a two-color cw laser field: A symmetry analysis

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Abstract

The spherical symmetry of a thermal sample of molecules is broken by inducing orientation and alignment with experimental techniques such as combined electrostatic and non-resonant laser fields or the phase-locked two-color laser field. An aligned molecule is characterized by the confinement of the molecular fixed axes along the laboratory fixed frame. For an oriented molecule, the dipole moment is pointing towards one hemisphere rather than the opposite. The control of the rotational motion allows for interesting applications such as photoelectron angular distributions or control of chemical reaction dynamics.

In this work, we perform the first systematic analysis of the implications that the Hamiltonian symmetries have on the rotational dynamics of a linear polar molecule in a two-color continuous-wave non-resonant laser field [1]. The system is described under the Born-Oppenheimer and rigid-rotor approximations, and in a regime where the time-average approximation is not correct. By systematically considering the interactions of the field with the electric dipole moment, polarizability and hyperpolarizability of the molecule, the rotational dynamics has been analyzed as a function of the laser parameters. We show that the alignment and orientation satisfy a series of identities as functions of the phases and electric field strengths of the laser, and that they can be expressed as analytic functions in terms of these parameters. The identities are fulfilled independently of the initial state, the rotational temperature or the interactions included in the Hamiltonian. In addition, we find that the molecule cannot be oriented by a one-color cw laser field, being necessary a two-color one having odd and even multiple harmonics of the laser frequency.

Acknowledgements

D. M.-A thanks Grupo Especializado de Física Atómica y Molecular (GEFAM) for awarding this work as the best paper published by a member in 2020 and for the invitation to present it in XIII Jornadas de Jóvenes Investigadores en Física Atómica y Molecular. Financial support by the Spanish Project No. PID2020-113390GB-I00, and by the Andalusian research group FQM-207 is gratefully acknowledged.

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Development of 2D metallic nanomaterials for nanofluids with application in concentrating solar power

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Abstract

We will harness this space to revisit ideas and findings from the PhD thesis entitled 'Development of 2D metallic nanomaterials for nanofluids with application in concentrating solar power'.

This thesis was born in the context a global climate crisis and a growing demand for reliable, affordable and clean power supply. Reliability is a challenging issue for those renewable technologies whose sources are inherently intermittent. The integration of concentrating solar power plants in our energy market can mitigate the consequences of this intermittency by taking advantage of thermal energy storage to maintain production and compensate the supply. A limitation for this solution is the low solar-to-thermal energy conversion in concentrating solar power plants, due to the poor thermal properties of the heat transfer fluid in solar collectors. The use of nanofluids (colloidal suspensions of nanomaterials) as heat transfer fluids has been proposed to overcome this barrier. Here we provide deep understanding, from a Physical Chemistry perspective, on the relation between the microscopic structure and dynamics of solid-liquid interfaces and the macroscopic properties of nanofluids, particularly those defining their stability [1] and heat storage and transfer capabilities [2-4], on the basis of experiments and simulations at the density functional theory and molecular dynamics levels-of-theory.

Acknowledgements

I.C.-B. acknowledges *Ministerio de Universidades del Gobierno de España* for endorsing this thesis with financial support in the form of a FPU16/02425 fellowship. J.N. acknowledges *Ministerio de Ciencia e Innovación del Gobierno de España* for funding under grants RTI2018-096393-B-I00 and UNCA15-CE-2945, and *Junta de Andalucía* for funding under grant FEDER-UCA18-107510. This work made use of ARCHER, the UK's national HPC service, via Ricardo Grau-Crespo's membership in the HPC Materials Chemistry Consortium, which is funded from EP/R029431 by the Engineering and Physical Sciences Research Council, and also of CAI3, the HPC service at Universidad de Cádiz.

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The Reactivity of ^3C Interacting with H_2O Ices: Water Catalysed Formation of H_2CO

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Abstract

Despite the cold conditions found in interstellar molecular clouds, where temperatures are as low as 10-20 K, a rich chemistry allows for the build-up of organics that eventually will be inherited in subsequent star and planet formation processes. In the earliest stages of a molecular cloud, carbon is predominantly present in its atomic form C($^3P_0$) [1]. Furthermore, at the shallow temperatures of the interstellar medium (ISM) simple molecules such as water or carbon monoxide accrete or form atop surfaces, creating an ice mantle. These ice mantles serve as templates for interstellar surface chemistry. In this work, I will focus on surface reactions of carbon atoms with amorphous solid water (ASW) ices. The interaction of carbon atoms with said surface has been recently studied experimentally in the presence of additional agents, e.g., H_2 molecules and H atoms [2]. Among the products that are observed experimentally are methane (CH_4) and formaldehyde (H_2CO). The formation of H_2CO in the gas-phase requires surmounting a significant kinetic barrier [3] and therefore it is not an expected product of the interaction of ^3C with water. In our work [4], using theoretical calculations in combination with tailored experiments, we demonstrated that the reason behind the apparent formation of H_2CO lies in the catalytic behavior of the ice, that promotes proton transfer reactions in the ice, decreasing the activation barrier for the formation of H_2CO by 60-130 kJ/mol for the different steps of the reaction. This finding has important implications in many aspects for the physical chemistry of the ISM, namely:

- The formation of H_2CO in young molecular clouds points to a formation of organics earlier than previously anticipated, hinting to more complex chemistry than previously anticipated.
- Water ice is not only a template for interstellar molecules, radicals and ions but also an active player in the ISM chemistry.
- The non-impeded route to H_2CO is also coherent with the formation of deuterated species, that are commonly attributed to later stages of a molecular cloud life [5|.

During the talk I will deepen in the theoretical and experimental results leading to the conclusions mentioned above.

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Challenging the limits of rotational spectroscopy: gas phase structural elucidation of multiconformational macrolactones.

Maider Parra-Santamaria[a,b], Imanol Usabiaga[a,b], Aran Insausti[a,b], Elena R. Alonso[a,b,c], Francisco Basterretxea[a], Camilla Calabrese*,[a,b,d] and Emilio J. Cocinero*,[a,b]

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Abstract

The structural determination of molecular systems is an aspect of science that has been widely explored. Among all the techniques capable of carrying out this task, high-resolution gas phase microwave spectroscopy is one of the most accurate ones for the conformational analysis of molecules or complexes. This technique is able to detect with unrivalled precision a large number of conformations in their bare state in an isolated environment, in absence of solvent or crystal packing effects allowing for the unambiguous identification of conformers,[1] tautomers,[2] isotopologues[3] and enantionmers[4]. The development in the last years of the chirp-pulsed (CP) technology, has given rise to a break-through in molecular coherence spectroscopy, increasing bandwidth, sensitivity and timing of the experiments. This has meant that molecular targets previously out of reach in terms of size and conformational complexity are now affordable.[5] In this work, we have pushed the limits of the technique, exploring for the first time the conformational landscapes of two macrolactones of increasing size, oxacyclotridecan-2-one and 16-hexadecanolide, using the chirped-pulse technique (CP) and quantum chemistry calculations. These compounds are considered “privileged scaffolds” within the medicinal chemistry community because their study led to the discovery of bioactive compounds. The study has concluded with the observation of 22 conformers for oxacyclotridecan-2-one and 20 different structures for 16-hexadecanolide, a record in conformational detection.

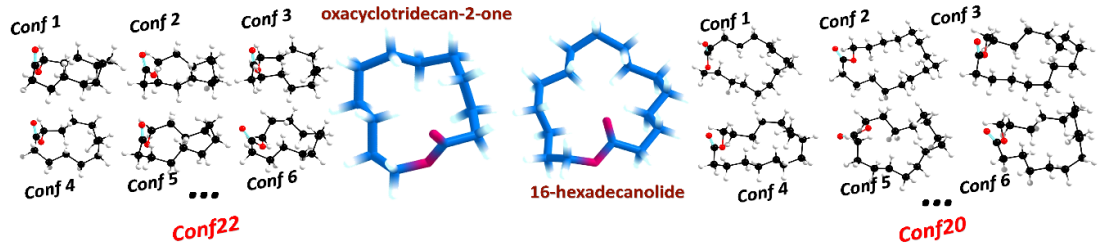

Figure 1. 22 and 20 different structures were detected for each of the macromolecules; the most stable conformers are shown in the figure.

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Quantum computations for spectroscopic characterization of $[Ar_2H]^+$ dimer

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Abstract

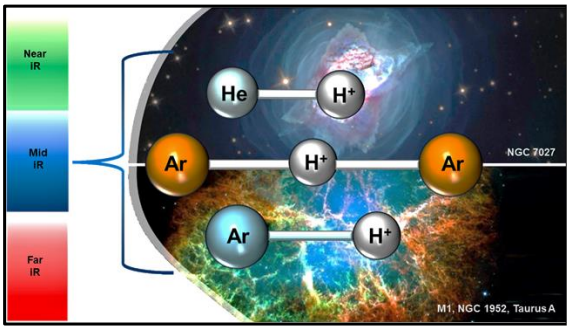

Figure 1. *Visual description for HeH^+ and ArH^+ discovery.*

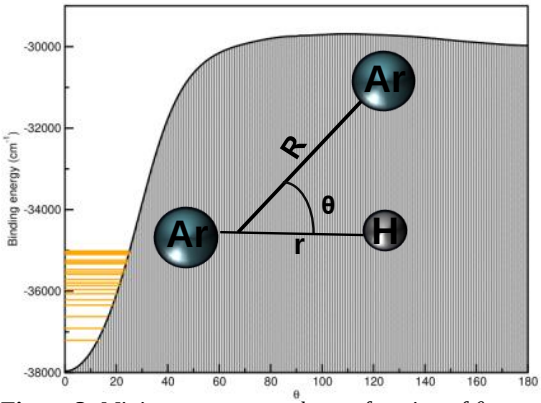

Figure 2. *Minimum energy path as a function of θ and vibrational bound states of $^{36}Ar_2H^+$.*

The recent discovery in the interstellar medium of ArH^+ and HeH^+ molecules [1,2], has changed the concept of noble gas compounds, improving our knowledge of these species and opening a new range of possibilities around the same (see Figure 1). One of the most revolutionary aspects that these recorded presences have provoked is comprehension that in extreme conditions such as low-temperatures and high-pressure, as well as the interaction with the proper ligands, noble-gas can form strong covalent bonds [3].The purpose of the present study is contribute to understanding the chemical bonding and electron sharing of the simplest argon-hydride cation cluster ($[Ar_2H]^+$), and further to provide spectroscopic data through quantum chemical tools [4,5]. Such accurate predictions on energetics and spectroscopic properties could facilitate the astrochemical detection of such noble gas compounds in new ISM regions. The ground electronic potential energy surface was obtained from benchmark *ab initio* electronic structure calculations, CCSD(T)/CBS [56] (see figure 2). As the accuracy issues have profound implications in developing cheminformatics models, such reference datasets can serve to guide and cross-check computational approaches for building up predictive data-driven models for larger cationic noble gas

Acknowledgements

The authors thank to the Centro de Calculo del IFF/SGAI-CSIC and CESGA-Supercomputing centre for allocation of computer time. We acknowledge financial support by the Comunidad de Madrid grant Ref: IND2018/TIC-9467, MINECO grant No. PID2020-11654GB-100, and COST Action CA18212(MD-GAS).

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The influence of electrode potential on SERS through the electronic structure of nanostructured metal-cyanide interfaces

Francisco García-González[1], Daniel Aranda[1], Juan C. Otero[1*] and Francisco J. Ávila Ferrer[1]

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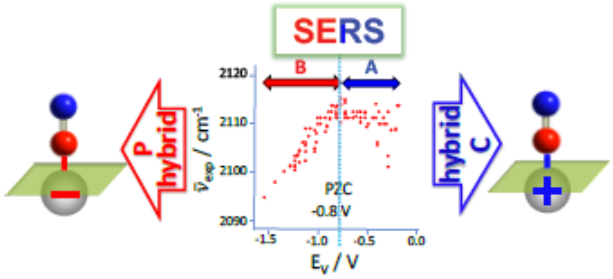
Abstract

Experimental and theoretical calculations confirm the existence of two different electronic structures of a surface complex formed by a particular molecule bonded to charged metal electrodes, clusters, or nanoparticles. Each electronic structure of the metal-molecule hybrid system is selected by sign of the surface excess of charge of the metal at potentials more negative or positive than its potential of zero charge (PZC).

Surface-enhanced Raman scattering (SERS) of cyanine adsorbed on a silver electrode shows two regions, which are selected by the voltage and characterized by the differentiated response of the vibrational wavenumbers of the ν(CN) stretching band. The combination between the experimental SERS and theoretical DFT calculations has allowed for relating the two regions to chemisorbed (C-hybrid, region A) and physisorbed (P-hybrid, region B) surface complexes, where cyanide is bonded through the carbon on top of a single silver atom of the surface. The electrode potential selects one or another type of electronic structure of the system, which are of different nature having a differentiated response to the applied voltage. Electric potentials tune smoothly the wavenumbers, bond energies, and injected charges of the P-hybrid at more negative potentials than PZC, but the very strong C-hybrid prevents significant changes of these properties at positive excesses of charge. The existence of the dual electronic structure of metal-molecule interfaces might require reinterpreting experiments that are usually discussed by resorting to, for instance, the reorientation of the adsorbate, the formation of complexes with different stoichiometries, the existence of nonequivalent local sites on the surface, or to instrumental artifacts. Moreover, this dual behaviour also determines the properties and responses of technological devices where metal-molecule interfaces are involved.



Key Words: Electrochemical SERS, Electronic structure, DFT calculations.

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Astrochemistry, search in the interstellar medium and laboratory detection of biologically relevant molecules

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In the later years, astrochemistry has aroused a lot of interest along the scientific community. Due to the technical advances in modern radio telescopes, we are now capable of detect radiation coming from the interstellar medium (ISM) with enough resolution to distinguish the spectra of the molecules present in it. The identification of this molecules is done by comparing these records with the spectra of a molecule of interest previously obtained using spectroscopic techniques. At this point is where rotational spectroscopy plays a key role. Microwave spectroscopy is a high-resolution gas phase technique, this allows to study a system isolated of any interaction to unveil its structure and dynamic effects.

Lately a growing number of organic molecules has been detected [1][2], the interest of finding organic molecules in the ISM than could be precursors of DNA or RNA [3] may solve the question of where life comes from, an old and yet not answered question.

In this work a rotational study of 4-oxo-butanenitrile, an amino acid precursor, has been carried out. The spectrum from 2 to 18 GHz has been recorded using a chirp-pulsed Fourier transform microwave spectrometer [4]. Three conformations had been detected in the rotational spectrum and this data will be used to search for them in different regions of the ISM.

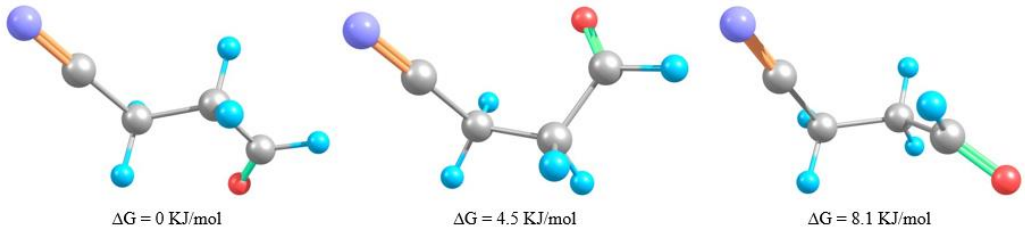

Image 1: Detected conformations of 4-oxobutanenitrile

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Solute-solvent interactions in water: a QM/MM Energy Decomposition Analysis approach

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Abstract

QM/MM techniques have enabled the extension of quantum chemical tools to the study of more complex systems, resulting in a qualitative leap in their application. In the framework of intermolecular interactions, the Energy Decomposition Analysis (EDA) [1,2], an analytical tool partitioning the interaction energy into its electrostatic, polarisation and exchange-repulsion components, has seen application in the description of biochemical processes hand in hand with QM/MM methods [3].

In this framework, the EDA is extended in the context of a QM/MM calculation where the solute-solvent interaction energy is decomposed for three solutes of varying polarity in water: the ammonium cation, zwitterionic glycine and the formate anion. A convergence study of each interaction energy component with increasing size of the QM region, with the inclusion of up to 240 water molecules, is performed to determine the optimal partitioning of the studied systems.
The convergence rate of each solute is found to be dependent on its polarity with long-range interactions governing the process. The presence of the external potential generated by the fixed MM charges is related to an improvement in the convergence rate when compared to a pure QM approach. Aiming at improving the obtained results, it is found that the use of a larger basis set for the QM region does not result in a faster convergence despite the overall improvement in the computed values. Finally, the use of a polarisable fore field may be necessary for an adequate study of the polarisation components, particularly induction.

The results derived from this study might be of interest for the set-up of a QM/MM EDA calculation as the magnitudes computed for the investigated test models reveal a clear dependency on both QM size and external MM potential, where the presence of the latter is required even for large QM regions.

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Global Potential Energy Surfaces for the O(^{3}P)+C$_2$($^1\Sigma$, $^3\Pi$) reaction

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Abstract

The reaction between O(^{3}P) and C_2 reaction plays an important role in combustion processes, soot formation, and is relevant to describe the chemistry of molecular clouds and dying carbon stars.*[1][2]* It is also important in the formation of polycyclic aromatic hydrocarbons (PAH) and carbon nanostructures.*[3]* In spite of this, the dynamics of the O(^{3}P) + C_2($^1\Sigma_g^+$,$^3\Pi_u$) → CO + C reaction has been barely studied.

From a computational point of view, the study of the O(^{3}P) + C_2 reaction is particularly cumbersome. On the one hand, in the reactants asymptote we deal with two open-shell fragments. On the other hand, the energy difference between the ground and the first excited state of C_2 ($^1\Sigma_g^+$ and $^3\Pi_u$) is only 0.09 eV, so both are populated at thermal energies. Accordingly, many configurations and electronic states have to be considered. Here, we present global potential energy surfaces (PESs) of the O(^{3}P) + C_2($^1\Sigma_g^+$,$^3\Pi_u$) reaction. The ab-initio energies have been calculated at the MRCI(+Q)/aVTZ level using Molpro 2020 *[4]*, and the PESs are fitted using the many-body expansion procedure. *[5]*

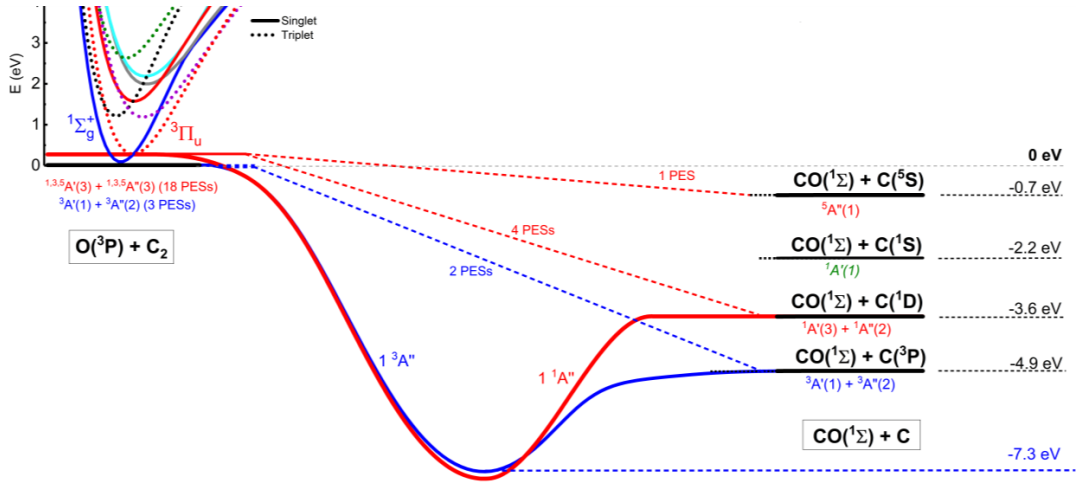

Figure 1. Correlation diagram for the O+C_2 reaction. In the left side, the entrance valley, and the lowest electronic states of the C_2 molecule. In the right side, CO($^1\Sigma$)+C electronic asymptotes. The minimum energy path connecting the reactants and products on the 1^{1}A"and 1 ^{3}A" PESs is also shown.

Acknowledgements

The authors acknowledge grant PID2020-113147GA-I00 funded by MCIN/AEI/10.13039. A. V. acknowledges Grant. No. EDU/1508/2020 (Junta de Castilla y León and European Social Fond).

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Photoswitchable Psychedelics – To the Discovery of Consciousness

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Abstract

The majority of drugs used in psychiatry were developed during an era where we understood very little about neuropsychiatric disorders [1]. Unfortunately, since the end of the 60', the "War on Drugs" and the lack of interest of the pharmaceutical industry in funding clinical trials reduced substantially the research on psychedelic drugs for therapeutic purposes [2]. After six decades, the use of psychedelics became one of the most exciting developments in neuropsychiatry since these drugs appear to produce rapid and substantial therapeutic effects in curing depression, post-traumatic stress disorders and drug addiction [3]. Also, they promote neural plasticity and produce such profound effects on perception and dream-like experiences that they will be a powerful tool to elucidate the chemical basis of consciousness [4]. Despite their complex polypharmacology, the 5-HT_{2A} receptor has emerged as the main molecular target for hallucinogenic actions of psychedelics in humans [5]. The crystal structure of this protein receptor bound to LSD, 25CN-NBOH and methiothepin was resolved via cryo-electron microscopy only last year [6]. While no structure of 5-HT_{2A} bound to its endogenous ligand serotonin (5-HT) exists, the bound structure of LSD may provide a potential indication of the binding mode of 5-HT. Moreover, photopharmacology recently became a fundamental tool to gain more spatio-temporal precision on the administration of drugs, and the synthesis of a light sensible psychedelic could give higher precision in differentiating molecular signalling of 5-HT in comparison to its hallucinogenic analogues [7]. In the present research, the binding modes of 5-HT and one of the strongest psychedelics, N,N dimethyltryptamine (DMT), are compared to gain molecular insights on the different residues involved in the binding of those two extremely similar molecules, which have very different physiological effects. A combination of molecular docking, molecular dynamics, 1A-MMGBSA and pairwise residue ligand energy decomposition analysis are employed to identify the different binding modes of those two drugs. In addition, the binding modes of their photoswitchable analogues azo-5HT and azo-DMT are studied to identify similar binding modes to their natural counterparts.

Acknowledgments
We thank the CCC-UAM for the computational resources and the Comunidad de Madrid for funding through the Attraction of Talent Program (Grant Ref. 2018-T1/BMD-10261).

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Exploring 2-Phenylethanethiol interactions by laser spectroscopy

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Abstract

Molecular interactions play an important role in the emergence and evolution of life, The study of these non-covalent interactions, enables determining the molecular behavior and it is necessary for the understanding of several biological process. One of the most important intermolecular interactions is the hydrogen bond, because it is the main responsible of the structures of proteins and DNA [1]. Thus, the need of analyze hydrogen bonds involving heteroatoms such as oxygen, nitrogen and sulphur is clear. Among the techniques used to study this interaction, the mass-resolved laser spectroscopy in combination with computational methods, have successfully been applied to obtain information regarding the molecular conformation, intra- and intermolecular interactions, and relative energies.[2]

We explore in this work the conformational landscape of 2-Phenylethanethiol [3] and its clusters (Figure 1), using mass-resolved excitation spectroscopy and quantum chemical calculations. Experimental setup consists of a pulse valve that injects the sample into a high-vacuum chamber, forming a supersonic expansion. Molecular aggregates present in the generated beam, are excited and ionized using resonance enhanced multiphoton ionization (REMPI) and sent to a time-of-flight (TOF) mass spectrometer. REMPI technique can be combined with IR and other UV laser (double resonance techniques), to obtain more detailed structural information. Our goal is to characterize thiol aggregates and their non-covalent interactions.

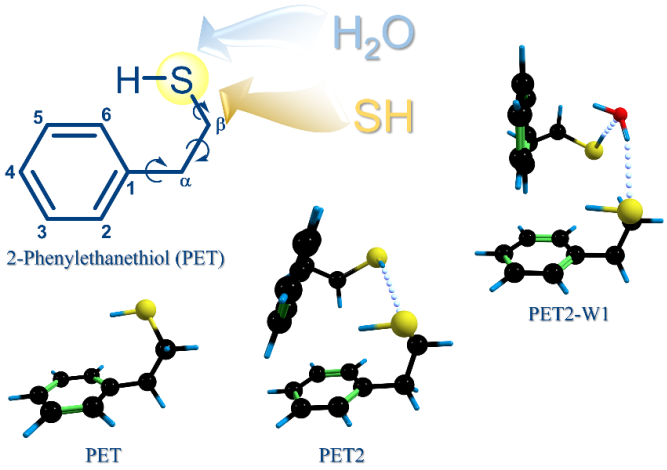

Figure 1. 2-Phenylethanethiol and its clusters.

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Experiments on the photodissociation of CH_2BrI on the first absorption band

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Abstract

The photodissociation of polyatomic molecules, which is understood as the breaking of atom bonds through the absorption of one or several photons, is an important chemical process that occurs in nature itself. The presence of halocarbon molecules, such as CH_2BrI, in nature mainly results from the synthetic organic compounds, like plastic polymers. However, their existence in nature was recently found in chemical interactions regarding microbial action [1, 2] as well. So, the fundamental understanding of the photodissociation of these molecules, as well as, the determination of the electronic structure, could help to predict their behavior, and their presence in extreme environments.

There are several experimental techniques that are helpful to study of photodissociation of these molecules. For the experiments, we used an excimer nanosecond laser for exciting the molecule at 193 nm. Then the generated photofragments were detected by a MOPO nanosecond laser using the REMPI (Resonant Enchanted Multiphoton Ionization) technique couple with the Direct Current Slice Imaging (DC Slicing) method. This method selects a slice from the central part of the Newton sphere which produces a better resolution. The Br, I, Br* and I* detected fragments presented in this work, will be discussed in terms of both experimental and theoretical calculation. In addition, a comparison with a previous experiment performed by our group [3] exciting the CH_2BrI at 266 nm, will be made.

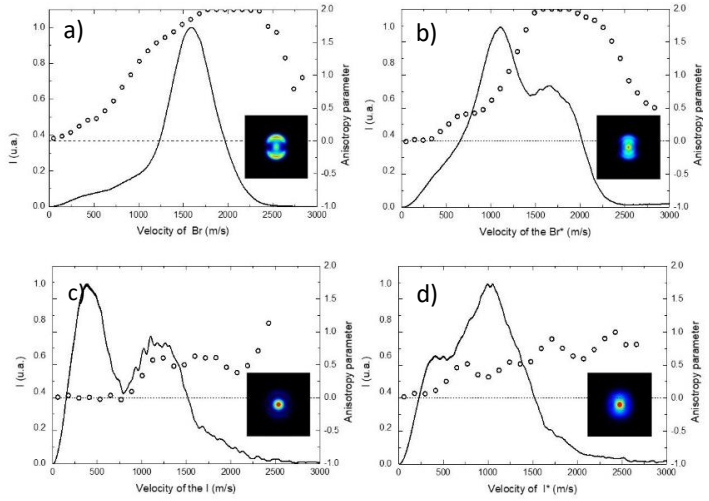

Figure 1. *a)* Br, *b)* Br^*, *c)* I and *d)* I^*fragment from CH_2BrI molecule.

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Rotational and vibrational relaxation of CO2 in supersonic jets: A fluid dynamic, kinetic and thermodynamic study by Raman spectroscopy

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Abstract

CO2 is a linear molecule which plays an important role in the energy budget of the Earth's atmosphere and its global warming. In spite of its importance and the extensive literature, there exist several processes concerning CO2 internal relaxation, both rotational and vibrational that are not well understood, especially the latter. [1]

Supersonic gas jets are a well suited environment to study elementary processes between molecules in the laboratory under non-local equilibrium (n-LTE) conditions. Since the molecules move at supersonic speed, they become isolated of any external perturbation. One of such elementary processes are elastic and inelastic collisions which are the principal mechanisms involved in the relaxation of the internal degrees of freedom of these molecules.[2]

We probe the supersonic jet by Raman spectroscopy with high-spatial resolution. The direct relation between the intensity of the Raman signal and the population of the internal degrees of freedom allows us to measure both the individual populations of the rotational and vibrational energy levels of the molecules and the number density of molecules in the volume under study.

We present an original approach to the CO2 relaxation problem. Both rotational and vibrational temperatures have been measured in n-LTE conditions, as well as the breakdown of equilibrium between the rotational and translational degrees of freedom. Several thermodynamic magnitudes under non-equilibrium conditions have been obtained, such as entropy and heat capacity, for which, we have developed an empirical model. We will present a set of rate coefficients for both rotational and vibrational inelastic collisions.

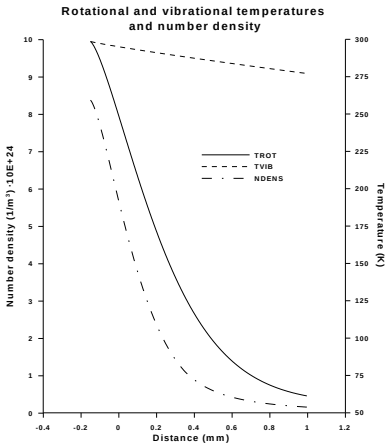

Figure 1: CO2 supersonic jet at room temperature: T0=298 K; P0= 384 mbar; Q[CO2]=0,34 l/min Nozzle diameter: 0,4 mm

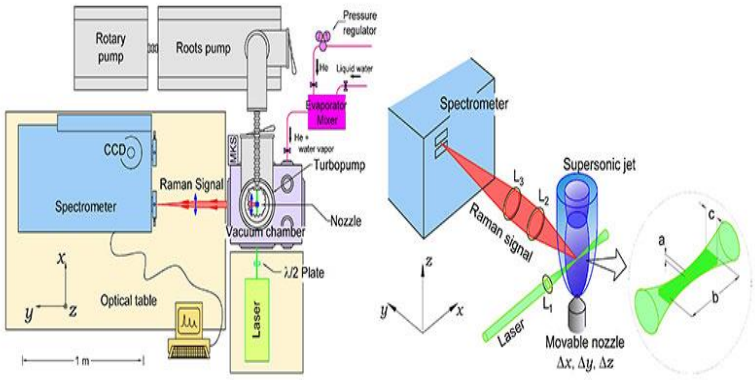

Figure 2: Laboratory equipment and experiment set up.

Acknowledgements

This research is funded by a scholarship of the Ministerio de Ciencia, Innovación y Universidades.

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Repurposing artificial sweeteners as novel antitumoral drugs

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Abstract

Tumor growth and cancer development have been associated with the presence of high levels of leukotrienes and lipoxins in human cells. These compounds are naturally produced by the lipoxygenase (LOX) enzyme, which, according to significant evidence, is overexpressed in different types of cancer. Under the umbrella of repurposing existing compounds for their potency to serve as significant drugs, in this study, we decided to evaluate all the commercially available artificial sweeteners as possible antitumoral drugs. Molecular docking studies have been performed for all the artificial sweeteners in order to unveil the details of their binding to LOX enzyme. Aspartame has indicated the strongest binding to LOX's cavity and the stability of the "enzyme-aspartame" complex has been further investigated with Molecular Dynamics, Molecular Mechanics/Generalized Born Surface Area and Quantum Mechanical calculations, as well as with Saturation Transfer Difference NMR and *in vitro* biological assays. Furthermore, aspartame has been evaluated as an allosteric binder to the enzyme and the possibility to inhibit other LOX isoforms has been extensively studied. Finally, aspartame's analogues have been designed and investigated through *in silico* methods for their interactions with LOX's cavity.

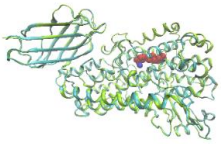

Figure 1. Aspartame in the catalytic site of LOX

Acknowledgements

The work has been performed under the Project HPC-EUROPA3 (INFRAIA-2016-1-730897), with the support of the EC Research Innovation Action under the H2020 Programme; in particular, the author gratefully acknowledges the support of Dr. Juan Jose Nogueira Perez in Autonomous University of Madrid, and the computer resources and technical support provided by Barcelona HPC centre.

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Hydrogen Isotopes Quantum Sieving through a Graphdyine Membrane

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Abstract

Molecular deuterium is a relevant gas for many different purposes in industry and scientific research. Thus, it is crucial to separate it from other substances in a gas mixture, specially its isotopes. Standard methods have proved not to be very efficient for this separation as deuterium and hydrogen have similar chemical properties. In this work [1] we have exploited a theoretical approach based on quantum sieving [2], which takes advantage of the enhancement of mass-dependent quantum effects in confined spaces. Subnanometric pores of graphdyine (GDY), a porous derivative of graphene, provide such a confined environment. In the simulations H_2/D_2 molecules have been treated as pseudoatoms and their interaction with the porous membrane has been modelled by a sum of atom-atom improved Lennard-Jones contributions, which have been obtained by exploiting the comparison with accurate ab initio estimations [3]. With the latter, we have performed three-dimensional time-dependent wavepacket propagations, which yield the transmission probabilities of the gas molecules through GDY [4]. These probabilities are used to compute the permeances (thermal flux divided by gas pressure) at different temperatures. The selectivity of deuterium over hydrogen, shown in Figure 1, is obtained as a quotient of their permeances. We can see how the selectivity increases as the temperature decreases reaching its highest value around 50 K. This is due to the quantization of the energy levels of the transition state at the centre of the pore. Preliminary results indicate that at lower temperatures the selectivity will eventually decrease because of the tunnelling effect favouring hydrogen over deuterium.

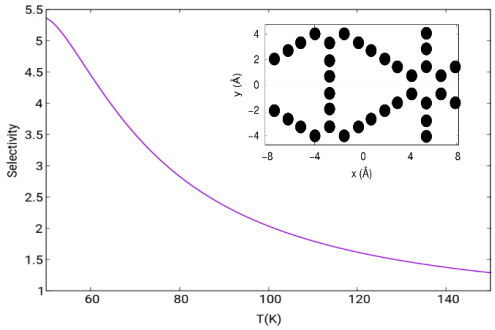

Figure 1. D_2/H_2 selectivity vs temperature. Upper panel shows the GDY unit cell with its triangular pores.

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Ultrafast electron dynamics in molecules and nanostructures: a Wave Packet Propagation Approach

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Abstract

Quantum chemical calculations are typically carried out in the framework of the Born-Oppenheimer approximation, where the electron density adapts instantaneously to the coordinates of the nuclei. Thus, electron dynamics are not considered in standard calculations. However, for some properties they can play an important role and more sophisticated methods must be used.

Here, I present a methodology based in Wave Packet Propagation (WPP) to study electron dynamics with the possibility of an explicit consideration of the atomic structure of the system [1].

Some examples of possible applications of WPP will be also presented. Specifically, I will show the importance of the electron dynamics in the lifetime of excited states of molecules adsorbed on surfaces, a reason behind the quenching of the signal in the STM-induced fluorescence [2]. Thanks to WPP calculations, it has been possible to provide a detailed explanation of these experimental observations [3].

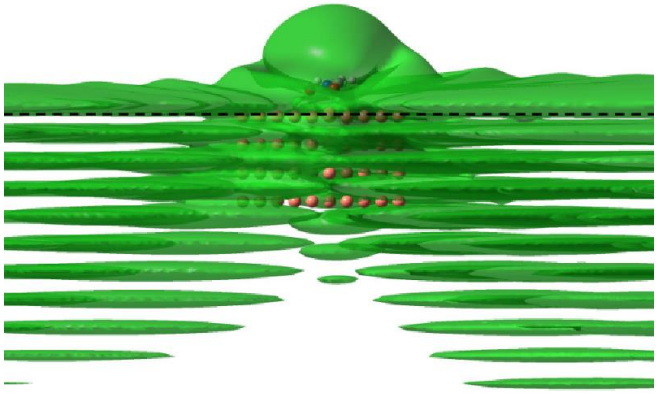

Figure 1. Decay path of a molecular electronic state coupled with a metal surface.

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QM/MM Energy Decomposition Analysis: Interactions of Cisplatin with a Lipid Membrane as Showcase

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Abstract

One of the most widely used drugs in chemotherapy for the treatment of different types of human cancer is cis-diamminedichloroplatinum (II) (cisplatin), for which it has been evidenced that the cell uptake can occur via passive diffusion through the lipid membrane.[1] In this regard, the energetics of the permeation mechanism of cisplatin into a lipid bilayer have been studied in great detail by means of computational simulation, specifically via classical molecular dynamics in conjunction with enhanced sampling techniques, such as umbrella sampling.[2,3] However, to our knowledge, the nature of the interactions between cisplatin and the membrane molecules have only been characterized in terms of classical force field contributions,[3] which provide a qualitative insight into the interactions that favor the uptake process, but neglects (or oversimplifies) contributions that are inherently quantum mechanical and thus require a higher degree of sophistication to be studied. For this reason, in this contribution we compute the interaction energies between cisplatin and the lipid membrane molecules within a hybrid electrostatic embedding quantum mechanics/molecular mechanics (QM/MM) framework, and extend an energy decomposition analysis scheme of the interaction energy based on deformation densities[4] to the QM/MM paradigm.[5] In this context, the decomposition of the interaction energy is performed for ensembles of geometries, so that conformational sampling is accounted for. It is evidenced that, unlike in the classical force field case,[3] the electrostatic and repulsive components are predominant both in the polar and in the non-polar regions of the lipid bilayer.

Acknowledgements

This work was funded by the Comunidad de Madrid through the Attraction of Talent Program (Grant Ref. 2018-T1/BMD-10261) and Xunta de Galicia through the project GRC2019/24. The Centro de Computación Científica of Universidad Autónoma de Madrid is thanked for computational resources.

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He Inclusion in Clathrate-like Frameworks: a Computational Study

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Clathrate hydrates are complex crystalline structures in which a firm host skeleton of H-bonded water molecules forms cage-like structures that encapsulate guest molecules under specific thermodynamic conditions. In this context, noble gas hydrates are of particular interest, due to the simple electronic structure of these inert atoms and their unique stability and properties. This fact, together with the scarcity of information on such complexes, makes its computational study an interesting and challenging task.

Focusing our attention in the He@hydrates, motivated by the recent experimental synthesis of He@sII [1] and in relation with the current emerging research on new low-density ice polymorphs [2,3], we have carried out a quantum chemistry study from the most basic finite-size clathrate-like structures [4,5] to the periodic crystalline frameworks [6]. In this way, we have first performed a benchmark study on the fundamental units and building blocks present in the most common clathrate hydrates in order to evaluate the performance and accuracy of different DFT-D functionals. Thus, we have found the most suitable approach available for more demanding computational calculations in larger structures. In turn, we have analysed the stability of the cages forming the He@sII clathrate, through thermochemical calculations (enthalpy, Gibbs free energy), at a range of temperature and pressure values comparable to the experimental conditions [1]. Finally, we have explored the effects on the encapsulation of the light He atom in the sI/sII crystals by computing (with the same DFT-D approach) structural and energetical properties contrastable with other theoretical/experimental results in both empty and He-filled systems. All these insights are useful to better understand the role of the entire interactions (guest-guest, guest-host, host-host) in the stabilization of clathrate hydrates and can benefit research into the development of new data-driven models.

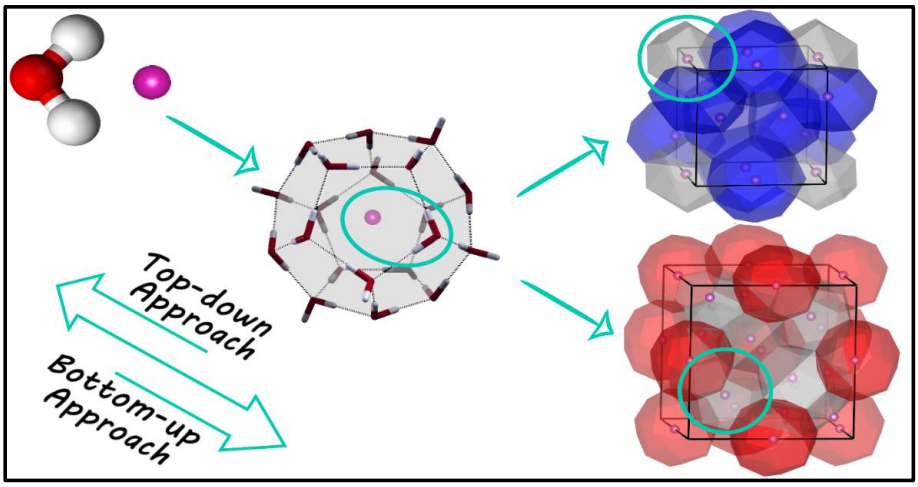

Figure 1. The simplest system, followed by a building block common to sI and sII, up to the crystal lattices.

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Tuning the chemiexcitation process of self-activated photosensitizers through the heavy-atom effect

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Abstract

Photodynamic Therapy (PDT) is a non-invasive, cheap, and precise cancer treatment. In traditional PDT, a photosensitizer (PS) is administered to the patient and then locally activated upon irradiation with light of a certain wavelength in the presence of molecular oxygen. However, light has a low penetration rate in biological tissues, which is one of the main limitations of PDT. [1] Our research group has developed a library of single-molecule sensitizers based on the scaffold of marine coelenterazine (Figure 1, left), which self-activate in the presence of a general tumor marker (superoxide anion) instead of in the presence of light, eliminating the need of an external source in PDT. They show relevant cytotoxicity toward different tumor cell lines *in vitro*, while being safe for healthy cell lines. [2,3,4] We have studied the heavy-atom effect to assess whether it favors the formation of readily available triplet states when in the presence of superoxide anion and for this, we have designed and synthesized bromo-, chloro-, and hydroxy-substituted analogs. We have studied their chemiluminescent processes and *in vitro* antitumoral effects and have found that their antiproliferative activity is dependent on this chemical modification, following the sequence hydroxyl < chlorine < bromine. [4]

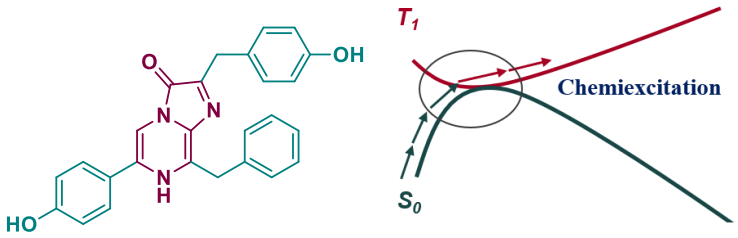

Figure 1 *Left*: Natural Coelenterazine. The imidazopyrazinone core is highlighted in magenta. *Right*: Schematic representation of the potential energy curves for the T_1 and the S_0 states during thermolysis.

Acknowledgements

Work made in the framework of the project PTDC/QUI-QFI/2870/2020, funded by the Portuguese Foundation for Science and Technology (FCT, Lisbon). L. Pinto da Silva (CEECIND/01425/2017), P. González-Berdullas (PTDC/QUI-QFI/2870/2020), and C. M. Magalhães (SFRH/BD/143211/2019) acknowledge FCT for their post- and predoctoral positions respectively.

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Dynamics of the photodissociation of methylamine: H and CH_3 displacement channels

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Abstract

Due to its similarity with ammonia (NH_3) and because it has been observed in the interstellar medium [1], methylamine (CH_3NH_2) has received considerable attention in the last decades. It is also relevant in astrochemistry and astrobiology areas since methylamine is a precursor of amino acids and a variety of heterocyclic molecules. The UV (ultra-violet) molecular photodissociation of methylamine was studied using the pump-probe method with nanosecond laser pulses. The molecule was ionized in the 198 - 203 nm range, and the generated photofragments were detected with the velocity map imaging (VMI) technique.

The two channels have been studied and analyzed separate. On one hand, the H displacement channel presented three different dissociation pathways. Those at higher energies have been attributed to the formation of CH_3NH in the ground state via a conical intersection and the slower pathway to CH_3NH in the excited state. The former pathways have already been reported [2,3], while the slower pathway has been observed for the first time. On the other hand, the energy distributions of the NH_2 + CH_3 channel, were fit to the rovibrational modes of the NH_2 from the ground state and the excited state [4]. It has been observed that the excited state starts to populate at high excitation energies, which indicates the formation of the $NH_2(\tilde{A})$ + CH_3 channel. All the results and possible mechanisms are discussed based on theoretical calculations performed for both dissociation channels.

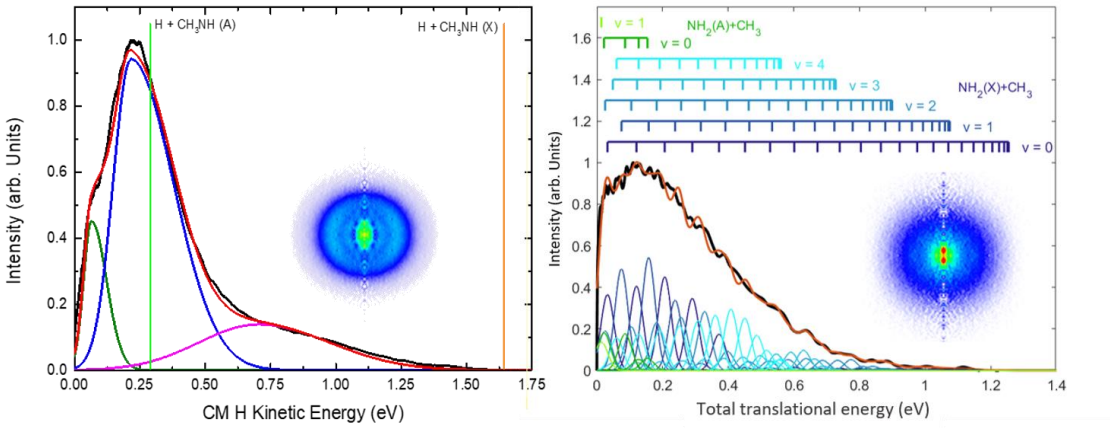

Figure 1. Energy distributions and their corresponding VMI image for the excitation of methylamine at 198 nm. Detecting the CH_3NH + H channel (right panel) at 364.8 nm and CH_3 + NH_2 channel (left panel) at 333.45 nm.

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π-STACKING INTERACTIONS IN THE 2-NAPHTHALENETHIOL HOMODIMER USING SUPERSONIC JET ROTATIONAL SPECTROSCOPY

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Following previous studies of gas-phase dimerization of sulfur-bearing aromatic thiols, like thiophenol[1], benzyl mercaptan[2] and 2-phenylethyl mercaptan[3], we conducted a structural investigation of 2-naphthalenethiol and its homodimers using chirped-pulse Fourier transform microwave spectroscopy in a jet-cooled expansion. Two conformers of the monomer have been observed in the frequency region 2-8 GHz. All monosubstituted (^{34}S and ^{13}C) isotopologues could also be observed. Finally, two homodimers of 2-naphthalenethiol were identified. The homodimers are stabilized by π-stacking interactions, with no hydrogen bond interaction between the two thiol groups. Supporting ab initio and DFT calculations will be presented.

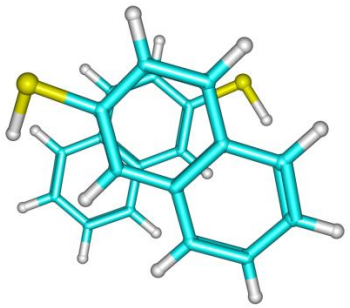

Figure 1.*Structure of C_2-symmetric 2-naphthalenethiol dimer*

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Investigation of Non-Covalent Interactions Involving Selenium Compounds: A Comparison of the Dimers of Selenophenol-H_2O and Selenophenol-H_2S by Supersonic Jet Rotational Spectroscopy and Computational Calculations

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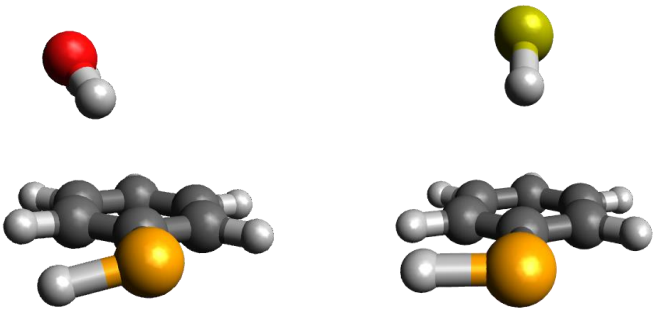
Abstract

The element selenium (Se) plays a vital role in biochemistry and many physiological processes. However, the noncovalent interactions in intermolecular clusters involving selenium compounds are scarce. In this work we studied the noncovalent interactions originated by selenophenol on aggregation with water and hydrogen sulfide. Since selenophenol is structurally analogue to thiophenol and phenol, this work will permit to compare the aggregation properties of the selenol group (—SeH) with those of the thiol (—SH) and alcohol (—OH) groups. The experimental investigation used broadband Chirped-Pulsed Fourier Transform Microwave (CP-FTMW) Spectroscopy combined with ab initio and density functional calculations. The selenophenol-H_2O and selenophenol-H_2S complexes were generated in a jet-cooled expansion and probed by the rotational spectrum in the 2-8 GHz region. The selenol group can act in the dimers as proton donor or acceptor. For selenophenol-H_2O we found two isomers (one with OH···Se and OH···π hydrogen bonds, another one with SeH···O and OH···π hydrogen bonds), while one isomer was observed for selenophenol-H_2S (stabilized with OH···Se and OH···π hydrogen bonds). Rotational parameters and supporting electronic calculations will be reported for the two clusters.



Computational studies of metal–organic framework catalysts for biomass conversion

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Abstract

The use of oil and natural gas as main feedstocks is no longer feasible and we must seek renewable resources to fulfill the increasing needs of society. Biomass feedstocks, such as lignin and (hemi)cellulose, are readily available and it can lead the way toward a sustainable economy. However, first we must design proper catalysts to upgrade them in an efficient manner.

In this contribution, we employ quantum mechanical simulations to study metal–organic frameworks (MOFs). These materials present well-defined sites and tunable node-linker combinations, which become beneficial for selective biomass catalytic processes. We will use periodic density functional theory (DFT) to elucidate the reaction mechanisms and understand how these reactions proceed at atomic level of detail. Such insight would further guide the experimental screening of new and improved catalysts. Herein, we focus on the conversion of methyl levulinates (easily obtained from sugars) to gamma-valerolactone (a platform molecule used as feedstock, solvent, and fuel) by means of UiO-66,[1] a the thermally stable MOF with Zr-based nodes (Figure 1).

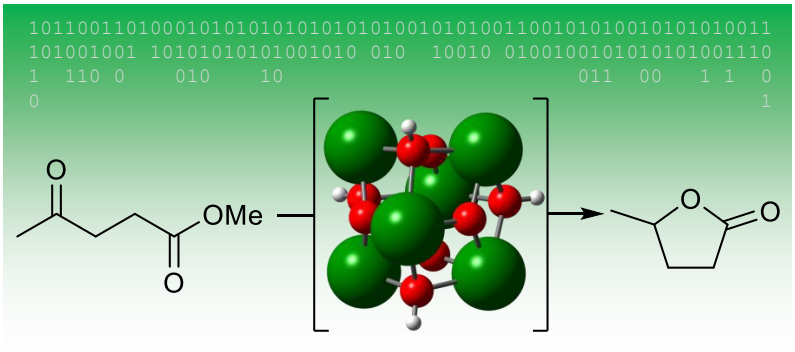

Figure 1. Conversion of methyl levulinate to gamma-valerolactone with UiO-66.

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Are $CF_3CH_2OCH_3$, $CHF_2CF_2CH_2OCH_3$, and $CF_3CF_2CH_2OCH_3$ suitable replacements for greenhouse gases?

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Abstract

Hydrofluoroethers (HFEs) are a kind of compounds which have been proposed in the last decades as the best families to replace potent greenhouse gases as chlorofluorocarbons and halons in several industrial applications (*i.e.* refrigerants) because they have no ozone depletion and relatively low global warming potential (GWP). To assess the ability to HFEs as environmentally friendly candidates for replacing high GWP species is indispensable to evaluate their atmospheric impacts prior to widespread use. Fot that purpose, the present work presents the first kinetic study of the tropospheric reaction of OH radicals with $CF_3CH_2OCH_3$ (HFE-36 263fb2), $CHF_2CF_2CH_2OCH_3$ (HFE-374pcf) and $CF_3CF_2CH_2OCH_3$ (HFE-365mcf3) as a function of temperature (263-353 K) and pressure (50-500 Torr) using the pulsed laser photolysis/laser induced fluorescence technique.[1] No pressure dependence of the rate coefficient for these OH-reactions, $k_{OH}(T,P)$, was observed in the studied range. In contrast, a slightly positive temperature dependence was observed in all cases and it is well-described by the following Arrhenius expressions:

HFE-263fb2: $k_{OH}(T) = (3.88\pm0.89)\times10^{-12} \exp[-(508\pm69)/T]$ $cm^3molecule^{-1}s^{-1}$

HFE-374pcf: $k_{OH}(T) = (2.81\pm0.33)\times10^{-12} \exp[-(312\pm35)/T]$ $cm^3molecule^{-1}s^{-1}$

HFE-365mcf3: $k_{OH}(T) = (2.60\pm0.31)\times10^{-12} \exp[-(319\pm35)/T]$ $cm^3molecule^{-1}s^{-1}$

The activation energy of these processes are found to be (4.2±0.6) kJ mol^{-1} for HFE-263fb2, (2.6±0.3) kJ mol^{-1} for 254 HFE-374pcf and (2.7±0.3) kJ mol^{-1} for HFE-365mcf3. Based on the kinetic measurements, atmospheric lifetimes due to OH-reaction were calculated to be 12 days for of HFE-263fb2, 17 days for HFE-374pcf and 13 days for HFE-374pcf. To evaluate the impact of 1 kg of the investigated HFEs emitted into the troposphere, we also determined in this work the infrared (IR) absorption cross sections in the range of 500-3100 cm^{-1}, the radiative efficiencies (REs) corrected with the lifetime, and the GWP at time horizon of 100 years relative to CO_2.[2] REs were determined to be 0.03 W m^{-2} $ppbv^{-1}$ for HFE-263fb2 and HFE-374pcf, and 0.04 W m^{-2} $ppbv^{-1}$ for HFE-365mcf3. Considering the short atmospheric lifetime of these HFEs, the resulting GWPs at time horizon of 100 years were 0.76 for HFE-374pcf, 0.40 for HFE-263fb2 and 0.51 for HFE-365mcf3. When comparing these GWPs with those of the greenhouse gas to be replaced, a drastic reduction is observed. Therefore, from the atmospheric point of view these HFEs minimize the effect on the global warming of the planet.

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Nanofabrication of metallic Pd deposits by focused Ga^+ beam irradiations on $Pd_3(OAc)_6$ spin-coated films for a wide variety of applications.

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Abstract

Nowadays, the fabrication of metallic nanopatterns is of great interest in applications that exploit the electrical conduction at the nanoscale, such as in interconnects, electrical nanocontacts and small gaps between metallic pads. Mature techniques such as optical lithography, electron beam lithography, or nanoimprint lithography are commonly used for metal patterning with high resolution and throughput but with the main disadvantage of being multi-step resist-based techniques. Furthermore, direct-write techniques such as focused ion beam or scanning probe lithography show high-resolution capabilities, but at the expense of low throughput.

In this work, we present the efficient decomposition of $Pd_3(OAc)_6$ spin-coated films by means of Ga^+ irradiations which leads to metallic Pd deposits without the use of any post-treatment step, as described in previous works [1,2]. After optimizing the growth parameters, we found that using a low dose of 30 $\mu C/cm^2$ is sufficient to create deposits with a high palladium content (>50%) and with a low resistivity (70 $\mu\Omega \cdot cm$). The low processing time together with the good electrical conductivity make these Pd deposits very interesting for a wide variety of applications. As a proof of concept, three different applications are demonstrated in the present work. Firstly, these deposits are used as metallic contacts to measure Pt nanowires. Secondly, two large structures are fabricated faced one each other separated by only 40 nm for possible application in molecular electronics. Finally, the construction of large-area meshes with additional physical properties such as optical transparency is also demonstrated.

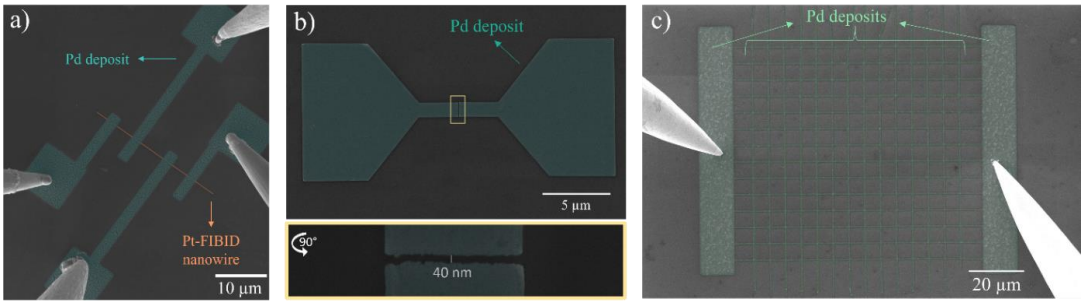

Figure 1. Different applications using Pd deposits created by means of Ga irradiations on $Pd_3(OAc)_6$ spin-coated films. a) Four electrical contacts to measure a Pt nanowire grown by FIBID technique. b) Two structures face one each other horizontally with a gap of 40 nm. c) Device composed by a large-area mesh together with two electrical contacts.

Acknowledgements

Authors acknowledge grants PID2019-105881RB-I00 and PID2020-112914RB-I00 funded by MCIN/AEI/ 10.13039/501100011033 and PIE 202060E187 funded by CSIC.

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Building Large-Scale UniMolecular Scaffolding for Electronic Devices

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Abstract

The properties of advanced materials are closely related to the internal organization of their structures. In this context,[1] the development of the forthcoming generation of molecular electronic devices will require accurate control over the orientation and spatial distribution of functional molecules.[2] Although unimolecular electronics is already a reality, not all results are consistent with each other, and the difficulty of precisely controlling the geometry in the molecule-metal junctions[3] remains a problem. For these reasons, manufacturing multiple unimolecular devices in parallel in the same system is one of the long-standing challenges of this field.[4]

In this work, we have developed a versatile, simple, and easy-to-implement strategy to fabricate molecular scaffoldings composed of millions of unimolecular devices in parallel, following a "layer-by-layer" methodology. The procedure combines alternately self-assembled layers of a metalized porphyrin derivative and layers of functional molecules that act as molecular wires. These perpendicularly bind to the metal center of the porphyrin, maintaining a stoichiometric ratio of 1:1 between layers through electrical contact and spaced from each other (Figure 1). This novel strategy allows modulation of the final structure of the scaffold by varying the functional molecule according to the desired application. This methodology makes it possible to extend to a wide variety of compounds and, thereby, towards the fabrication of more complex devices with other potential nanotechnological applications.

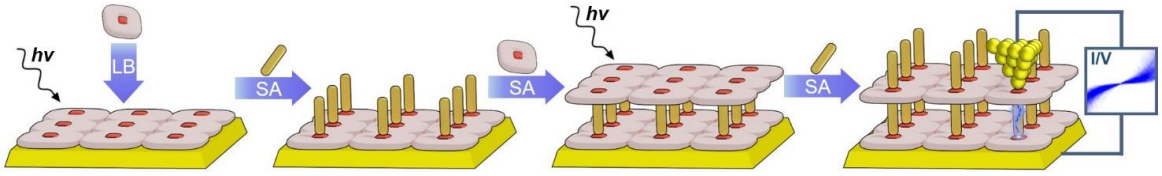

Figure 1. Scheme of the layer-by-layer procedure to build the supramolecular scaffolding device.

Acknowledgements

Authors are grateful for financial assistance in the framework of the projects PID2019-105881RB-I00 funded by MCIN/AEI/10.13039/501100011033 and PGC-2018-097583-I00 and Gobierno de Aragón through the grants E31_20R and E47_20R with European Social Fund (Construyendo Europa desde Aragón).

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Metal-Organic Frameworks for local magnetic refrigeration

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Abstract

Dense metal-organic frameworks (MOFs) of Gadolinium (III) are an excellent option for being applied in magnetic refrigeration at low temperatures (from 0.3 K to 30 K), due to their regular organization of paramagnetic ions with low anisotropy and high spin [1][2]. Our main objective is to synthesize nanoparticles of Gd-MOFs with large magnetocaloric effect (MCE) and good size homogeneity and colloidal stability, to arrange them in monolayers or multilayers by using the Langmuir-Blodgett technique, thereby providing the means for efficient on-chip local cooling [3].

Along this work, different Gd(III) MOFs nanoparticles have been synthesized. The materials under study are $Gd(OH)(CO_3)\cdot 0.8H_2O$ (**1**) and $Gd(HCOO)_3$ (**2**), both based on light organic ligands, to maximize the MCE. Figure 1a and b show the homogenous size of the obtained particles. Their bulk magneto-thermal properties (magnetisation and heat capacity) have been studied at different magnetic fields and temperatures, allowing to determine their MCE. Figure 1c shows a large value of $-\Delta S_m \approx 53$ $Jkg^{-1}K^{-1}$ at 3 K, $\Delta B = 7$ T for **1**, that can compete against the best magnetic refrigerants. Langmuir films formed by the nanoparticles at the air-water interface are homogeneous, dense and structured, as derived through in-situ Grazing Incidence Small-Angle X-ray Scattering. Characterization of the cooling power of the deposits, obtained by transferring these films, as well as use of other methods than Langmuir-Blodgett are in progress.

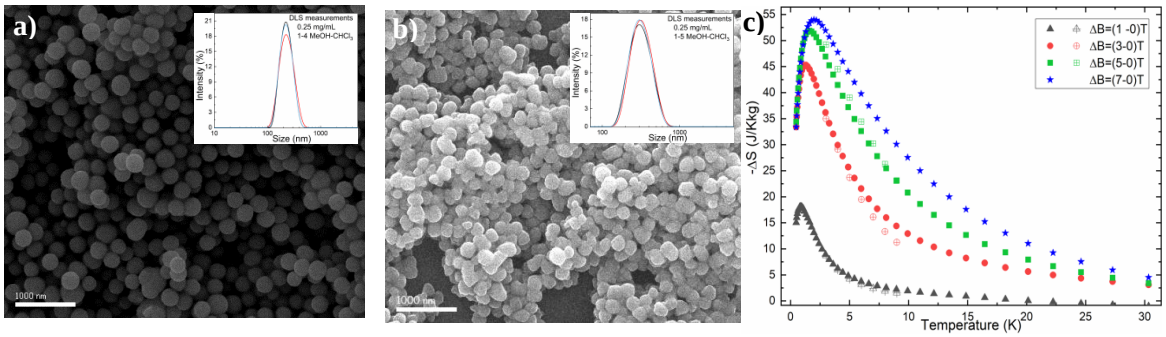

Figure 1. a) and b) SEM images show a homogenous size synthesis of 1 (276.7 ± 27.8 nm) and 2 (243.8 ± 32.3 nm), respectively; Inset: Particle size distribution based on DLS measurements of 0.25 mg/mL dispersions in a mixture methanol-chloroform 1:4 (1) and 1:5 (2); c) Temperature dependence of the magnetic entropy change for various applied fields for **1**.

Acknowledgements

Authors would like to acknowledge founding from Aragon Government (DGA) and FEDER (research group E31_20R) and from MCIN / AEI and FEDER (proyect PID2020-118329RB-100).

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The Permeation Mechanism of Cisplatin Through a Dioleoylphosphocholine Bilayer

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Abstract

Lipid membranes are involved in many relevant functions as the permeation of drugs. Therefore, the investigation of the intermolecular interactions between platinum-based drugs and lipid bilayers is of special relevance to get insight into the mechanism involved in the different steps of the anticancer mode of action of these platinum drugs. Furthermore, the nature of these interactions regulates the uptake efficiency of the drugs and are involved in resistant mechanisms and programmed cell death or apoptosis. In this talk, I will discuss about the simulation of the passive transport of the anticancer drug cisplatin through a model lipid membrane DOPC by means of umbrella sampling classical molecular dynamics, and the subsequent energy decomposition analysis at classical mechanics level along the permeation pathway.[1]

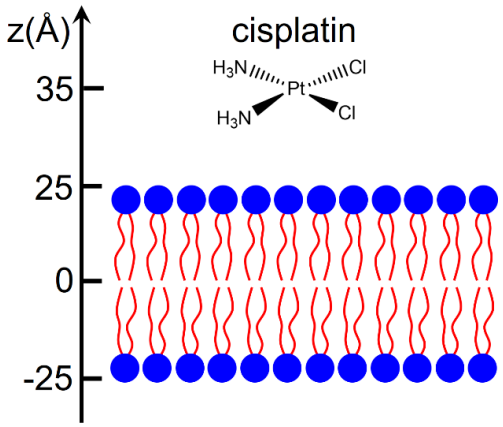

Figure 1. Schematic representation of cisplatin and the DOPC membrane.

Acknowledgements

We thank the Comunidad de Madrid for funding through the Attraction of Talent Program (Grant Ref. 2018-T1/BMD-10261). The Centro de Computación Científica (CCC) of Universidad Autónoma de Madrid is thanked for generous computational resources.

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Molecular dynamics simulations of the calmodulin-induced α-helix in the SK2 calcium-gated potassium ion channel

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Abstract

Small-conductance (SK) calcium-gated potassium ion channels are found in the membranes of neurons and cardiac cells. The SK2 subtype regulates the firing of neurons, and its dysfunction has been associated to several movement, neurodegenerative, and psychiatric disorders [1].

These channels are open and closed depending on the intracellular Ca^{2+} concentration. The sensitivity to this ion is provided by the binding of the calcium-sensing protein calmodulin (CaM). SK2 channels have the unique property of displaying a small prefolded α-helical region in aqueous solution, in the absence of CaM. This region is essential for CaM binding and for the subsequent formation of a full α-helix along the whole CaM binding domain, required for the channels to be functional [2]. The molecular details of this physiologically relevant process are, however, not fully understood.

In this work, we conduct atomistic Hamiltonian replica exchange molecular dynamics simulations to identify the amino acid residues involved in the formation of this full α-helix and to understand the significance of the prefolded core of SK2 channels in this process.

Our results show that this prefolded core is indeed necessary for the induction of the full α-helix. However, it is not sufficient, since the proper orientation of three specific amino acid residues in SK2 (Val32, Leu33 and Trp37) is also necessary for the process to proceed. The interactions of Val32 and Leu33 with a hydrophobic pocket in CaM including Phe92, Met109 and Phe145 drives the formation of the full α-helix, and Trp37 needs to face the solvent so as not to compete for this hydrophobic pocket. The prefolded core favours this Trp37 orientation.

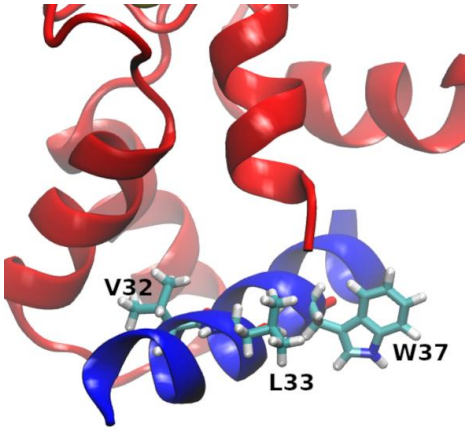

Figure 1. Orientations of Val32, Leu33, and Trp37 for the proper induction of the full α-helix.

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Computation of Oxidation Potentials of Solvated Nucleobases by Static and Dynamic Multilayer Approaches

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Abstract

The modeling of DNA-based biosensors require the determination of the redox properties of nucleobases to get insight into the charge-transfer processes that play an important role in the detection task.[1,2] Although a large amount of theoretical and experimental studies has been carried out, the value of the one-electron oxidation potentials of nucleobases is not well defined and the most appropriate theoretical protocol to model this redox property is not well established. In this work, different static and dynamic approaches to compute the one-electron oxidation potentials of solvated nucleobases have been implemented and evaluated, using a combination of density functional theory, within QM/continuum and QM/MM frameworks, and classical molecular dynamics. Within the static scheme, two versions of a thermodynamic cycle have been tested to assess their accuracy against the direct determination of the oxidation potentials from the adiabatic ionization energies. Then, the introduction of vibrational sampling, the effect of implicit and explicit solvation models, and the application of the Marcus theory have been analyzed through the dynamic methods. Finally, the effect of tautomerism was also evaluated.

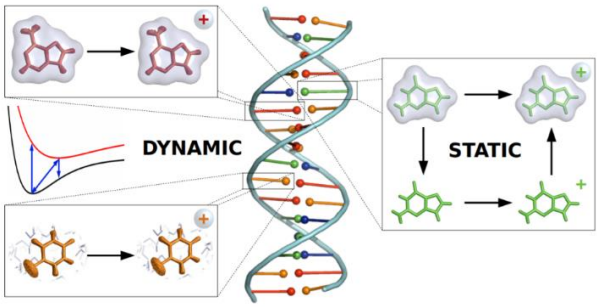

Figure 1. Schematic representation of the different theoretical protocols employed.

Acknowledgements

We thank the Centro de Computación Científica at the Universidad Autónoma de Madrid (CCC-UAM) for generous computational time. J.J.N. and G.C. acknowledge the Comunidad de Madrid for funding through the Attraction of Talent Program (Grant ref 2018-T1/BMD-10261). N.A.O. acknowledges the Comunidad de Madrid and European Social Fund for funding through the Programa Operativo de Empleo Juvenil y la Iniciativa de Empleo Juvenil. J.L.T. acknowledges the FPU19/02292 grant from the Spanish Ministry of Education and Vocational Training.

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High-resolution mass spectrometry of ancient biological samples

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Abstract

Mass spectrometry is consolidating as a central tool for the characterization of ancient organic materials thanks to its great sensitivity and resolution. Our research focuses on the application of high-resolution mass spectrometry to the biomolecular analysis of archaeological samples.

In a first application, based on a metabolomic biomolecular approach, we have characterized an american cochineal (*Dactylopius coccus*) found in a sunken wreck from the 16th century in Cadiz. This cochineal was a highly valuable dye material in the XV-XVI centuries, owed to the quality and high content of colouring polyphenolic glycoside compounds, mainly carminic acid (94-98%) and kermesic and flavokermesic acids as minor compounds (2-6%). For our study, we have set up a chromatography/mass spectrometry UHPLC/ESI-MS/MS method in negative ion mode to detect the profile of polyphenolic glycosides as a signature of the cochineal species [1].

In a second application, which currently constitutes our central line of work, we have performed proteomic analysis of archaeology bone samples. This approach is converging to an emerging field of research for which the acronym ZooMS (Zooarchaeology by Mass Spectrometry) has been coined. The application of mass spectrometry to fossil remains has become an attractive alternative source for ancient molecular sequences for evolutionary studies, particularly in specimens older than the proposed limit of amplifiable DNA detection. Bones can be abundant reservoirs of ancient biomolecules. Collagen, the dominant protein in bone, has been shown to survive longer than other genetically informative biomolecules [2]. Moreover, other non-collagenous proteins, such as biglycan or alpha-2-HS-glycoprotein, provide a further resource for phylogenetic information [3]. We have applied high-sensitivity, high-resolution tandem mass spectrometry to shotgun sequence ancient protein remains extracted from bones of different species and will present preliminary results obtained in our laboratory for horse (*Equus caballus*) and donkey (*Equus asinus*) bones from the Neolithic to the Modern Age.

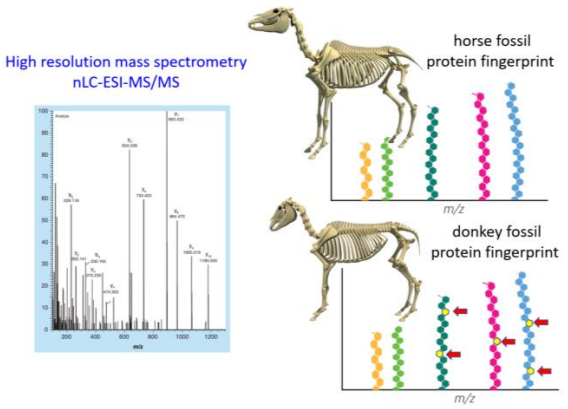

Figure 1: ZooMS identify species from high-resolution mass spectrometry of the protein fingerprint of fossil bones

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The viscoelasticity of adherent cells follows a single power-law with distinct local variations within a single cell and across cell lines

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Abstract

AFM-based force–distance curves are commonly used to characterize the nanomechanical properties of live cells[1]. The transformation of these curves into nanomechanical properties requires the development of contact mechanics models[2]. Spatially-resolved force–distance curves involving 1 to 2 μm deformations were obtained on HeLa and NIH 3T3 (fibroblast) cells. An elastic and two viscoelastic models were used to describe the experimental force–distance curves (FDCs). The best agreement was obtained by applying a contact mechanics model that accounts for the geometry of the contact and the finite-thickness of the cell and assumes a single power-law dependence with time. Our findings show the shortcomings of elastic and semi-infinite viscoelastic models to characterize the mechanical response of a mammalian cell under micrometer-scale deformations. The parameters of the 3D power-law viscoelastic model, compressive modulus and fluidity exponent showed local variations within a single cell and across the two cell lines. The corresponding nanomechanical maps revealed structures that were not visible in the AFM topographic maps[3][4].

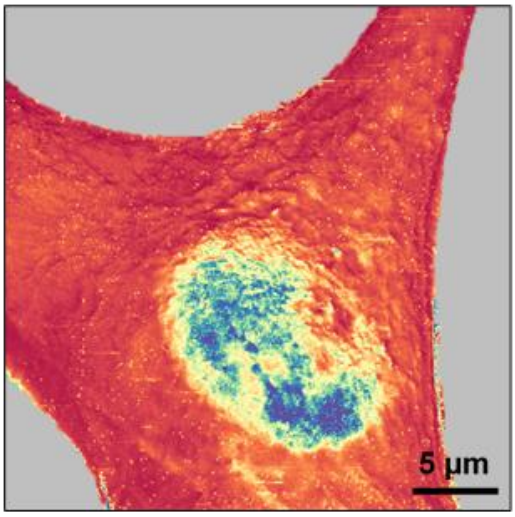

Figure 1. Compressive modulus map of a fixed NIH 3T3 cells, clearly differentiating between the cytoplasm and the nuclear regions. FDCs taken at $F_{peak} = 3\ nN, v = 150\ \mu m/s$, map of 512 x 512 pixels.

Acknowledgements

This project was supported by the Ministerio de Ciencia e Innovación (PID2019-106801GB-I00) and the Comunidad de Madrid S2018/NMT-4443 (Tec4Bio-CM).

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Electric Dipole Forces on a Binary System of Atoms

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Abstract

Dispersion forces between neutral atoms are the result of the coupling of the quantum fluctuations of the electromagnetic field in its vacuum state with the fluctuations of the atomic charges in (meta)stable states. In the electric dipole approximation, these forces are known as van der Waals (vdW) forces [1]. In recent decades renewed interest has been drawn to the interaction between excited atoms. From a practical perspective, this is the kind of interaction between Rydberg atoms which makes possible the coherent manipulation of their quantum states, facilitating the entanglement between separated quantum systems as well as the storage of quantum information [2]. On the other hand, from a fundamental perspective, the attention has focused on different aspects of the interaction, namely, its scaling behaviour with the distance, the role of dissipation, its inherent time dependence, and the net forces induced by parity and time-reversal violation on a binary system [3,4]. Here we address this problem on a system made of two two-level identical atoms. Following a fully Hamiltonian and time-dependent approach we show that, once the system is released with one of the atoms initially excited, two kinds of forces are involved in the interatomic interaction. On the one hand, conservative forces act along the interatomic axis. These forces are different on each atom, resulting in a net force upon the whole system. This apparent violation of the action-reaction principle is explained by the excess of linear momentum carried by the virtual photons which mediate the interaction. On the other hand, there exist nonconservative forces as a consequence of the time variation of the so-called Röntgen momentum which possess components orthogonal to the interatomic axis. Both kinds of forces might be accessible experimentally [5,6].

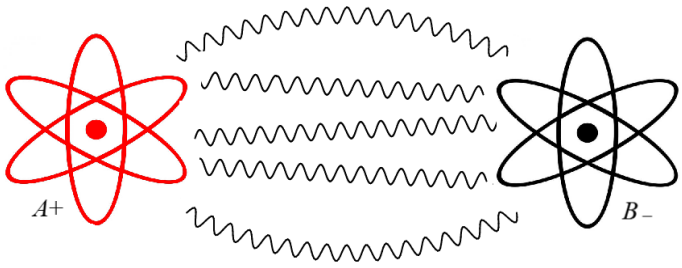

Figure 1. Interatomic Interaction

Acknowledgements

Financial support is acknowledged from grants PID2020-113406GB-I00 and QCAYLE project (NextGenerationEU funds).

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Do the dimension matters in systems of ultracold atoms in optical traps?

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Abstract

The Inelastic Confinement-Induced Resonances (ICIR's) were first observed in [1] in systems of ultracold quantum gases in quasi-1D optical traps and also in 3D confinements. ICIR's have its origin in the coupling between the center-of-mass and relative-motion coordinates due to the anharmonicities of the trapping potential [3, 4]. Here, we are interested in study the effect of the dimensionality on the resonances. For this purpose, we examine the ICIR's in mixed-dimensional optical traps with full CI *ab initio* simulations solving the corresponding Sch. Eq. for a system of two ^{7}Li atoms confined in several settings of the traps, as seen in Fig. 1. This approach will be used in the near future for reproducing the experimental observations of quasi2-D—3D traps of [6] with heterogeneous species.

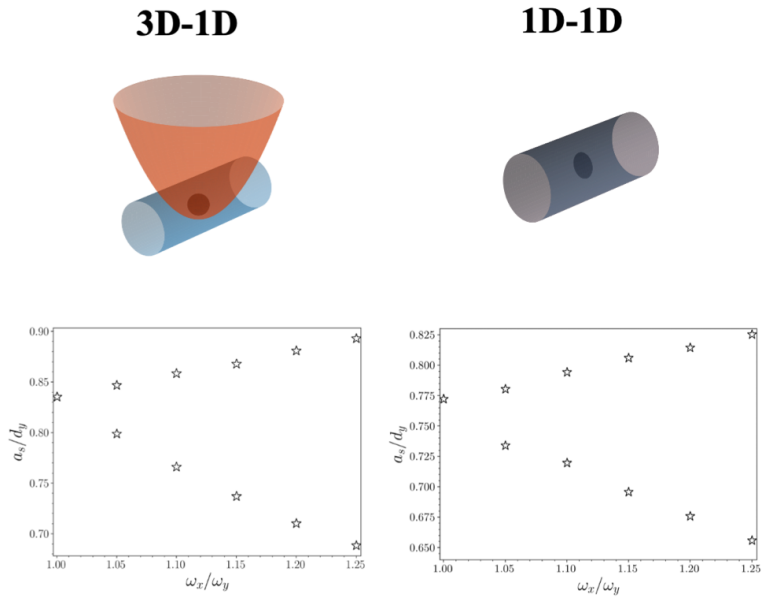

Figure 1. Inelastic Confinement-Induced Resonances produced by two atoms of ^{7}Li in quasi-1D optical traps (right) and in mixed 3D–quasi-1D confinement (left) as a function of the anisotropy between the longitudinal (X) and transverse directions (Y, Z). Upper branch corresponds to the atomic level (nx,ny,nz) = (0,2,0) and the lower one to (nx,ny,nz) = (2,0,0).

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Towards the fabrication of molecular assemblies with optoelectronic properties

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Abstract

Although technical improvements of electronic devices in the last decades have been remarkable, the empirical law that predicts this trend (Moore's law) is beginning to fail. One of the alternatives to conventional silicon electronics attempting to meet society's demands is **molecular electronics**, which studies the use of single molecules, or molecular assemblies as components in electronic circuits.[1] In this approach, custom-made molecules with different structures are synthesized to perform as diodes, transistors, wires, switches... Working with molecules allows continuing downsizing devices and also exploring and applying the new phenomena that appear at the nanoscale.

In this work, we describe the study of a compound containing a diketopyrrolopyrrole (DPP) moiety (**Figure 1.A**), an electron acceptor, which bonded to donor groups forms π-conjugated donor-acceptor systems. Depending on the donor groups used, the resulting complex will have a specific band gap, and consequently, tunable optical properties.[2] Moreover, these compounds exhibit a large tendency to form bidimensional aggregates, which results in highly ordered films. Once the compound was characterized in solution and at the air-water interphase, Langmuir-Blodgett (LB) and self-assembled (SA) films were prepared to study the structure of the transferred monolayers onto solid substrates. Formation of J-aggregates in the LB films has been observed, with a distinctive red shift of the DPP UV-vis peak (**Figure 1.B**).[3] On the other hand, molecules in SA films interacted differently, without forming J-aggregates These results pave the way for the application of the obtained LB molecular assemblies, with tunable optical properties, in optoelectronic devices.

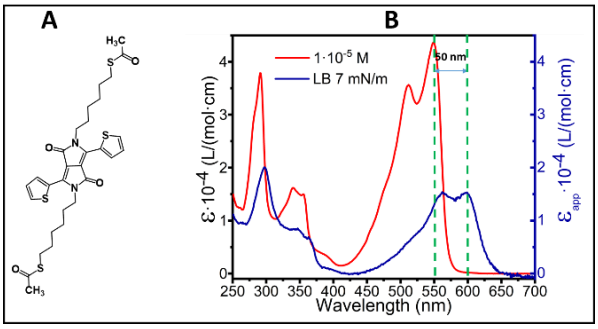

Figure 1. **A**: Structure of the compound here studied. **B**: UV-vis spectrum in solution (red) and spectrum of a LB film (blue).

Acknowledgements

Authors acknowledge grant PID2019-105881RB-I00 funded by MCIN/AEI/10.13039/501100011033. J.M. B acknowledges Grant PRE2020-093409 funded by MCIN/AEI/10.13039/501100011033.

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Experimental study of the reaction of 2-methylpentanal with Cl atoms in an atmospheric simulation chamber: Kinetics and degradation products detected by spectroscopic methods

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Abstract

Aldehydes are emitted into the lower atmosphere from diverse sources, but they are primarily of biogenic origin. For example, 2-methylpentanal (2MP) is emitted into the troposphere from vegetation[1]. These carbonyl compounds can be removed by tropospheric oxidation initiated by NO_3 radicals during the night-time or by OH radicals and Cl atoms during the day-time, being important contributors to the formation of peroxyacylnitrates (PAN), ozone, and secondary organic aerosols[2]. The gas-phase kinetics of OH and NO_3 radicals with 2MP have been reported[3]. However, no kinetic measurements of the reaction with Cl atoms were found in the literature.

For this reason, in this work the gas-phase kinetics of the reaction of 2MP with Cl (k_{Cl}) has been investigated at ground level conditions of T and P (298±2K and 760±5 Torr of air) to evaluate the contribution of this homogeneous degradation route to the total loss of 2MP in the atmosphere. For that purpose, an atmospheric simulation chamber coupled to a Fourier Transform Infrared (FTIR) spectrometer was used to determine k_{Cl} by a relative kinetic method [4]. Cl atoms were generated by photodissociation of Cl_2 by using actinic UV lamps (λ=340-400 nm). Moreover, in separate experiments the gaseous products generated in the titled reaction were identified using complementary detection techniques, such as FTIR spectroscopy and proton transfer time-of-flight mass spectrometry[5]. It is important to note that all experiments were carried out under free-NOx conditions, simulating a clean atmosphere.

Finally, the atmospheric implications of 2MP reactivity will be discussed in terms of its lifetime due to homogeneous reaction with Cl and the observed reaction products.

Acknowledgements

All authors wish to thank the regional government Junta de Comunidades de Castilla-La Mancha (project “CINEMOL” SBPLY/19/180501/000052) for supporting this research.

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Mechanisms of Ion Conduction through Eukaryotic Ion Channels by Molecular Dynamics Simulations.

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Abstract

Ion channels are key transmembrane proteins which are involved in the transport of inorganic ions, such as Na^+, K^+, Ca^{2+}, or Cl^- across cell membranes.[1] These ion channels are in a "gated" conformation, i.e., they open in response to a specific stimulus, for example, the binding of a neurotransmitter or a change in the membrane potential. In the latter case, they are known as voltage-gated ion channels and they allow the permeation of ions in a selective way. The membrane potential is produced in the internal and external environments of the cell as a result of the electrical potential difference caused by the flow of ions.[2] This potential plays an essential role in various physiological processes in our body, such as muscle contraction, signal transduction and hormone secretion, among others.[1,3,4] Hence, it is fundamental to study the mechanism of permeability and selectivity of ion channels for understanding the function of cells and for the discovery of new drugs. In this project the mechanism of ion conduction and selectivity is being investigated by means of conventional and electric-field biased classical molecular dynamics simulations, with the aim of accelerating ion permeation. Our goal is to elucidate the key factors that are involved in ion conduction, such as the interactions between the ions and the selectivity filter or the desolvation of the ions when entering the pore, and to test whether the commonly employed force fields are able to describe ion selectivity.[4]

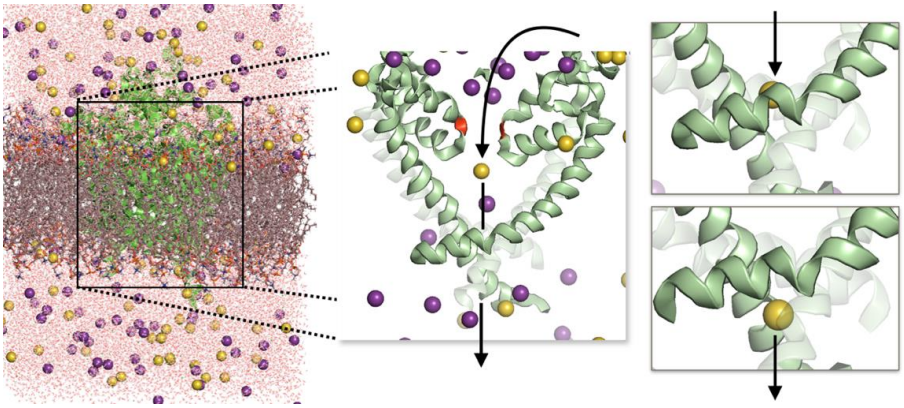

Figure 1. Schematic representation of ion conduction through a eukaryotic sodium-selective channel.

Acknowledgements

J.J.N. acknowledge the Comunidad de Madrid for funding through the Attraction of Talent Program (Grant ref 2018-T1/BMD-10261). N.A.O. acknowledges the Comunidad de Madrid and European Social Fund for funding through the Programa Operativo de Empleo Juvenil y la Iniciativa de Empleo Juvenil. We also thank the Centro de Computación Científica at the Universidad Autónoma de Madrid (CCC-UAM).

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Growth and electronic structure of 2D transition metal dichalcogenide in-plane heterostructures

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2D materials such as transition metal dichalcogenides (TMDs) exhibit emergent properties different from those of the bulk when thinned down to the monolayer[1]. Incorporating heterostructures is one way to tune such properties. Most works involve the fabrication of vertical heterostructures combining TMDs with other layered materials[2] but the in-situ fabrication of high-quality in-plane lateral heterostructures remains a challenge. This work explores the growth of novel TMD lateral heterostructures by molecular beam epitaxy and study their atomic and electronic structures by means of Scanning Tunneling Microscopy and Spectroscopy (STM and STS). We found hexagonal islands composed of two $NbSe_2$ phases with different atomic structures (H- and T-phase) surrounded by $TiSe_2$ with very clear boundaries. Charge density waves present in each phase were observed and agree with previously reported modulations[3]. Low-temperature STS measurements allowed to resolve the $NbSe_2$ superconducting gap which disappears abruptly in the $TiSe_2$ domain suggesting that no proximity effects transmit superconductivity to $TiSe_2$.

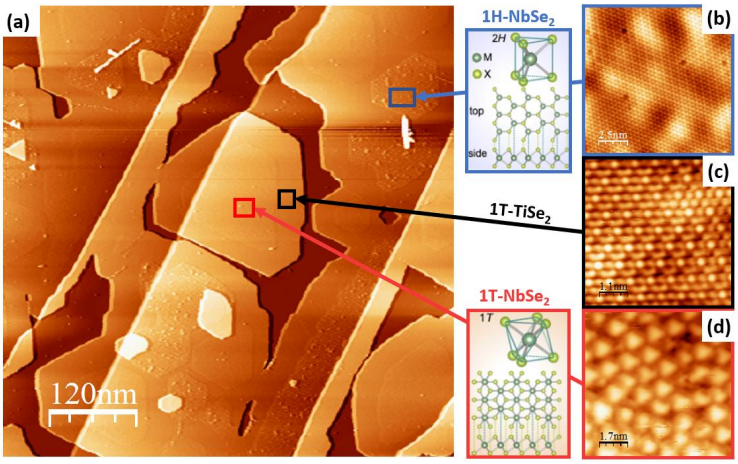

Figure 1. (a) STM topography image of $NbSe_2$-$TiSe_2$ heterostructures (V_s = 1 V, I_t = 50 pA, T = 4.2 K). Colored squares indicate the different domains. High resolution STM images of (b) H-$NbSe_2$ phase (V_s = 0.4 V, I_t = 1 nA, T = 4.2 K), (c) T-$TiSe_2$ phase (V_s = 0.6 V, I_t = 125 pA, T = 4.2 K) and (d) T-$NbSe_2$ phase (V_s = -1.3 V, I_t = 835 pA, T = 4.2 K). Insets adapted from ref 4.

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Kinetics of the OH+CH_3NH_2 Reaction: Experiments and Theory

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Abstract

The interstellar medium (ISM) is an immense chemical reactor with different physical conditions, capable of producing more than 250 molecules, known so far [1]. These conditions are present in the interstellar clouds, which provide the raw material for star and planet formation. Nowadays, understanding how all these molecules could have formed and can be destroyed in these surroundings is a big challenge. For this purpose, the determination of chemical-physical parameters, such as the rate coefficients (k) of the bimolecular reactions, in the extreme conditions of temperature present in these clouds (10-100 K) is crucial to better understand the chemical processes occurring there.

Therefore, in this work, we have used the most powerful pulsed CRESU reactor [2] to reproduce a large range of ultra-low temperatures (11.7-177.5 K) in order to obtain the experimental rate coefficients of the OH+CH_3NH_2 reaction, both species detected towards several sources of the ISM. In addition, the electronic structure calculations were performed at the M08HX/MG3S level, and the rate coefficients were evaluated from 10 to 500 K (in the low and high-pressure limits) using the competitive canonical unified statistical (CCUS) theory [3]. Branching ratios to form the main products, CH_2NH_2 or CH_3NH were also computed as a function of temperature. All kinetic simulations were performed with the Pilgrim program [4]. The results show that this reaction is faster when decreasing temperature and this will be discussed in terms of the relative stability of the stationary points.

Acknowledgements

All authors wish to thank the Spanish Ministry of Science and Innovation (MICINN) (project "CHEMLIFE" PID2020-113936GB-I00), and University of Castilla-La Mancha (UCLM) (Ayudas para la financiación de actividades de investigación dirigidas a grupos: 2020-GRIN-29016 and 2021-GRIN-31279) for supporting this research. Daniel González and Sara Espinosa also acknowledge UCLM (Plan Propio de Investigación) and CHEMLIFE project, respectively, for funding their contracts during the performance of this investigation.

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New Tools for Computational Chemical Kinetics

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Abstract

In our research group we are contributing to the development of an integrated computational code able to simulate multiple aspects of chemical reactions dynamics. Specifically, we have developed three programs (part of what we call *The Cathedral package*), available at the Github webpage [1]:

- *Pilgrim* [2], designed to use direct-dynamics to calculate thermal rate constants of chemical reactions and to simulate chemical kinetics mechanisms;
- *Torsiflex* [3,4], which searches for and locates all the conformational isomers of flexible acyclic molecules;
- *Q2DTor* [5], a program to treat torsional anharmonicity in flexible molecules with two torsions by means of the extended two-dimensional torsional (E2DT) method [6].

The codes can be used in different fields, as: organometallic catalysis, gas-phase mass spectrometry, the simulation of microwave spectra, the calculation of thermodynamic properties and the study of many chemical reactions occurring in the gas phase.

Acknowledgements

D. F.-C. thanks Xunta de Galicia for the financial support through a postdoctoral grant (modalidade A 2017), which made possible the development of the aforementioned programs.

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