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- **Nadia Rega**, Università degli Studi di Napoli "Federico II"

Scientific Program

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17.30 – 17.50	TEO-PZ02: Alfonso Pedone *From First-Principle Chemical Shift and EFG Tensors Calculations to Solid-State 1D and 2D NMR Spectra Simulations of Complex Systems*
17.50 – 18.10	TEO-PZ03: Franco Egidi *Development of Theoretical and Computational Models for the Calculation of Spectroscopic Properties of Molecules in the Gas Phase and in Solution*
18.10 – 18.20	TEO-PZ04: Greta Donati, Alessio Petrone, Nadia Rega *Wavelet Analysis for Non-Equilibrium Processes in Chemistry*
18.20 – 18.25	TEO-PZ05: Marco Mendolicchio, Nicola Tasinato, Vincenzo Barone *New Models and Computational Strategies for Molecular Structure Prediction*
18.25 – 18.30	TEO-PZ06: Sergio Rampino, Marco Fusè, Andrea Salvadori, Giordano Mancini, Vincenzo Barone *Chemical bonding and spectroscopic observables in coordination complexes: analysis techniques and applications*
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9.40 – 10.00	TEO/INO-OR01: Ana B. Muñoz-García, Michele Pavone *Computational Design of* $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\Delta}$ *(SFMO)-based Bifunctional Electrodes for Proton-Conducting Solid Oxide Electrochemical Cells*
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17.15 – 17.30	TEO/FIS-OR05: Francesco Di Maiolo, Carlotta Pieroni, Anna Painelli *Intermolecular Energy Transfer in Real Time*
17.30 – 17.50	TEO/FIS-OR06: Enrico Bodo, Andrea Le Donne *Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations*
17.50 – 18.10	TEO/FIS-OR07: Nicola Tasinato, Lorenzo Spada, Cristina Puzzarini,Vincenzo Barone *Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer*
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18.25 – 18.40	TEO/FIS-OR09: Olga Russina, Ruggero Caminiti

	Fluorous Mesoscopic Domains in Room Temperature Ionic Liquids
18.40 – 18.55	TEO/FIS-OR10: Ettore Fois, Rossella Arletti, Lara Gigli, Giovanna Vezzalini, Simona Quartieri, Gloria Tabacchi *Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure*

Premi alla ricerca

Premio Roetti

Dott. **Julien Bloino**, *Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici*

Premio Roetti

Prof. **Alfonso Pedone**, *Università degli Studi di Modena e Reggio Emilia*

Premio Scrocco

Dott. **Franco Egidi**, *Scuola Normale Superiore di Pisa*

Premio del Re

Dott. **Greta Donati**, *Università degli Studi di Napoli* "Federico II"

Premio Nordio

Dott. **Marco Mendolicchio**, *Scuola Normale Superiore di Pisa*

Finalista Premio Levi

Dott. **Sergio Rampino**, *Scuola Normale Superiore di Pisa*

Premio Roetti
Accurate Spectra of Medium-Large Molecules: Recent Developments and New Challenges

Julien Bloino[a]

[a]*Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa,*
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Computational spectroscopy is nowadays routinely used as a predictive and interpretative tool to complement and support experimental results, providing insights of the underlying elementary phenomena responsible for the overall band-shape. However, its reliability is strongly correlated to the underlying models, which affect the level of accuracy of the calculated results. This aspect can be especially critical in some fields of applications like chiropticalanalysis or astrochemistry for instance. Such considerations emphasize the need of carefully setting up computational protocols, in particular by selecting the most appropriate level of theory available. For medium-to-large molecular systems with possible environmental effects, a trade-off is indeed necessary between accuracy and feasibility, and several strategies can be devised, with suitability varying depending on the cases.

To facilitate the setup of the most efficient and reliable route for the simulation of accurate spectra, we have been developing a versatile and modular platform, called virtual spectrometer.(1) A primary objective in its design has been its simplicity of use and its computational efficiency. The spectrometer has currently two major modules. The first one (2,3) aims at simulating vibrational spectra beyond the harmonic approximation, using second-order perturbation level of theory (VPT2) to compute both transition energies and intensities. The second module (4,5) adds vibrational contributions to electronic spectra.

In this presentation, I will describe some key features of the virtual spectrometer and discuss the theoretical frameworks used for the simulation of anharmonic vibrational and vibronic spectra. The simplicity of use of the tool is strongly conditioned by its capability to identify and possibly overcome the shortcomings in the approximations adopted by the basic models on which it relies. The potential impact of such issues, like resonances in VPT2 calculations or molecular deformations and mode mixing upon electronic transition, and strategies to ensure the reliability and accuracy of the results will be discussed. Those aspects, as well as current projects, will be illustrated with different case studies.

References: 1. J. Bloino et al., Int. J. Quantum Chem. 116, 1543 (2016). 2. J. Bloino et al., J. Chem. Phys. 136, 124108 (2012). 3. J. Bloino et al., J. Phys. Chem. A 119, 11862 (2015). 4. J. Bloino et al., J. Chem. Theory Comput. 6, 1256 (2010). 5A. Baiardi et al., J. Chem. TheoryComput. 9, 4097 (2013).

Premio Roetti
From First-Principle Chemical Shift and EFG Tensors Calculations to Solid-State 1D and 2D NMR Spectra Simulations of Complex Systems.

Alfonso Pedone[a]

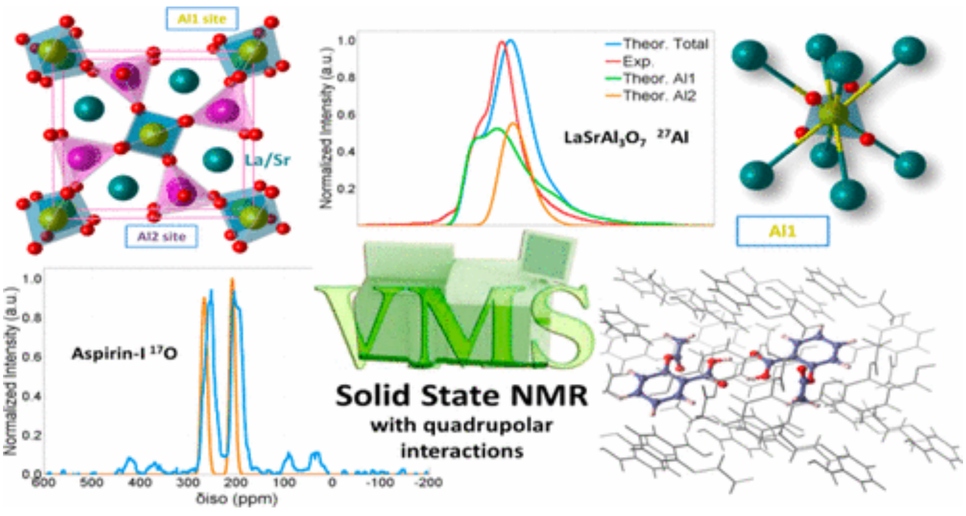
[a]*Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, via G. Campi 103, 41058, Modena*

In the last decades, NMR spectroscopy has arisen as one of the most powerful techniques to probe the atomic level structure of polycrystalline or disordered systems for which XRD techniques can provide only an average vision of the structure.

Although, several high-resolution 1D and 2D NMR experiments have been devised for the solid state such as Magic Angle Spinning (MAS), Variable Angle Spinning (VAS), Dynamic Angle Spinning (DAS) and Multi-Quantum MAS (MQMAS), their interpretation remains difficult in most cases. This is often because in disordered systems the continuous distribution of structural parameters and topological environments leads to a continuous distribution of NMR parameters and thus broad spectra with peaks in most cases strongly overlapped are observed. It is thus necessary to have a deep knowledge of the correlation between the NMR parameters and the local structure. In the past this was pursued empirically by referencing to known crystalline structures but the development of cost-effective quantum mechanical methods like DFT and the implementation of methods and algorithms to compute NMR parameters for periodic systems has allowed gain more reliable insights on the atomic structure theoretically.(1)

In this communication, I will show the recent advances achieved in the computation of ab initio NMR parameters of spin active nuclei in several complex systems and present a new software tool (SoSNMR) developed in our group to simulate several 1D and 2D solid state NMR spectra of half-integer and quadrupolar nuclei.(2)

The SoSNMR module, also implemented in the graphical user interface of VMS (VMS-Draw),(3)can work under both periodic and non-periodic conditions. Therefore, it can simulate spectra resulting from NMR calculations by some popular quantum chemistry codes, namely Gaussian09/16, Castep, and Quantum Espresso.



References: 1. Charpentier, T.; Menziani, M.C.; Pedone, A. RSC Advances, 2013, 3 (27), 10550-10578.
2. Presti, D.; Pedone, A.; Licari, D.; Barone, V. J. Chem. Theor. Comp. 2017, 13(5), 2215-2229.
3. Licari et al., J. Comput. Chem. 2015, 36, 321-334

Premio Scrocco
Development of Theoretical and Computational Models for the Calculation of Spectroscopic Properties of Molecules in the Gas Phase and in Solution

Franco Egidi[a,b,c]

[a]*Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa, Italy;* [b]*Gaussian Inc., 340 Quinnipiac St, Bldg 40, Wallingford, Connecticut 06492, USA;* [c]*Department of Chemistry, University of Washington, Seattle, WA 98195, USA; franco.egidi@sns.it*

The accurate simulation of spectroscopic properties requires the inclusion of multiple effects into the theoretical model. Both the electronic and vibrational degrees of freedom need to be treated with sufficient accuracy to be able to reproduce experimental findings. This means choosing an appropriate electronic structure model, whether wave function theoryor DFT based, and going beyond the harmonic approximation for the vibrational component. In addition, since most experiments are carried out on solvated samples, an accurate treatment of the effect of solvation on a molecule's spectroscopic properties is crucial (1). We show that by carefully combining vibrational effects with either continuous and discrete solvation models, it is possible to simulate a wide variety of spectra that can be directly compared with experimental measurements, provided the solvation model also takes into accounts effects due to solvation dynamics and the screening of the electromagnetic radiation caused by the solvent (2-8). All such effects can be effectively combined with a description of the molecular vibrations that goes beyond the harmonic approximation (3-7).This framework can be applied to all kinds of properties, whether purely vibrational, vibronic, and involving both electric and magnetic perturbations (2-7). The developed methods are both accurate and easy to use, allowing these methods to be used by non-specialists as well as expert theoreticians, thus bridging the gap between theory and experiment in a synergistic way. The research leading to some of these results has been performed in the framework of the ERC Advanced Grant Project DREAMS "Development of a Research Environment for Advanced Modelling of Soft Matter", GA No. 320951.

References:1. F. Egidi, C. Cappelli,*Reference Module in Chemistry, Molecular Sciences and Chemical Engineering* (2015) Elsevier 2. F. Lipparini et al, *J. Chem. Theory Comput.*9 (2013) 234303.3. F. Egidi et al, *Chirality* 25 (2013) 701. 4. F. Egidi et al, *J. Chem. Theory Comput.*8 (2012) 585. 5. F. Egidi et al, *Mol. Phys.* 111 (2013) 1345. 6. F. Egidi et al, *J. Chem. Theory Comput.*10 (2014) 2456. 7. F. Egidi et al, *J. Phys. Chem. A* 119 (2015) 5396. 8. F. Egidi et al, *J. Chem. Theory Comput.* 10 (2014) 346

Premio del Re
Wavelet Analysis for Non-Equilibrium Processes in Chemistry

Greta Donati[a], *AlessioPetrone*[a], *Nadia Rega*[a,b]

[a] Department of Chemical Sciences, University of Napoli Federico II, Napoli, 80126, Italy;
[b] Italian Institute of Technology, IIT@CRIB Center for Advanced Biomaterials for Healthcare, Napoli, 80126, Italy; ¶ Current address: Department of Chemistry, University of Washington, Seattle, WA, 98195;
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New and sophisticated computational tools represent the *conditio sine qua non* information provided by simulation techniques in the field of theoretical modeling of molecules, such as molecular dynamics, can be extracted in the most efficient way.

Nowadays, excited state ab-initio molecular dynamics (AIMD) in Born-Oppenheimer approximation(1) can be also employed for the simulation of molecular systems with huge number of degrees of freedom (such as biomolecules) in non-equilibrium conditions (i.e. after interaction with light). But nevertheless, this method still represents a non-conventional approach because of the huge computational cost.

This work represents a challenge not only because excited state AIMD simulations were employed for studying the photo-induced proton transfer of the Green Fluorescent Protein(2), but also because we employed for the first time a multiresolution and time-resolved vibrational analysis, the continuous Wavelet transform (3,4), to investigate the protein conformational rearrangements favouring the reaction event and the reaction mechanism itself. The Wavelet analysis allowed to perform a reciprocal-space domain based analysis of structural properties extracted from the excited state AIMD simulations. The extracted time-evolving vibrational bands revealed that the protein active site undergoes an important rearrangement to reach the best conformation to start the reaction. We found that the main molecular motions involved in this step were collective low frequency in nature, involving not only the chromophore but also other residues sometimes not *directly* involved in the active site.

The Wavelet based approach gave access to thereal time evolution of the molecule rearrangements immediately after the excitation and so to obtain a clear and complete picture of the non-equilibrium events.Moreover, the capability to disentangle in a more accurate way the different frequency range contributions (because of the multiresolution nature of the transform) allowed for a more accurate description of the vibrational bands. Last but not least, we found excellent agreement with time-resolved spectroscopic experiments.

On the basis of this work an innovative, not molecule dependent and efficient protocol is established for the investigation of photo-induced chemical processes.

References: 1. T.Helgaker, E.Uggerud, H.J A.Jensen, Chem.Phys.Lett. 173, 145 (1990).2.P.J.Tonge, S.R.MeechJ.Photoch.Photobio.A 205, 1 (2009).3.R.Carmona, W.L.Hwang, B.Torresani, *Practical time-frequency analysis* (Academic Press, San Diego. 1998).4.A.Petrone, G.Donati, P.Caruso, N.Rega JACS 136, 14866 (2014).

Premio Nordio
New Models and Computational Strategies for Molecular Structure Prediction

Marco Mendolicchio[a], *Nicola Tasinato*[a], *Vincenzo Barone*[a]

[a] *Scuola Normale Superiore, Pisa, I-56126, Italy; marco.mendolicchio@sns.it*

The knowledge of the equilibrium structures of isolated molecular systems of chemical and biological interest is of fundamental relevance to gain detailed information on many chemical-physical processes, in the framework of the so-called structure-property relationships. Moreover, accurate equilibrium geometries serve as benchmarks in the development of new computational strategies. Molecular structures obtained through isotopic substitution are subject to vibrational average, nevertheless vibrational effects are often not explicitly considered during the inversion of the spectroscopic data. Hence, the resulting structures strongly depend on the isotopic species under investigation. From this point of view, the determination of the equilibrium structure, i.e. the geometry associated with the Born-Oppenheimer (B-O) potential energy surface minimum, is the most appealing alternative (1). While this type of structure is more challenging to be inferred at the experimental level, its determination allows the inclusion of vibrational effects and, within the B-O approximation, it is isotopic substitution independent. Furthermore, such structures are directly comparable with theoretical results. In this contribution we present the new program MSR (Molecular Structure Refinement) (2), specifically devised for computing equilibrium structures by means of the semi-experimental approach (3,4). The program includes a large panel of optimization algorithms and an extended error analysis (5). Particular attention has been devoted to the definition of the internal coordinates to be employed in the refinement. The most widespread set of internal coordinates used in this context, defined in terms of the so called Z-matrix, has proven to be often problematic when complex molecular topologies are faced, not to speak about their intrinsic user-dependency. In order to overcome these issues, a different procedure is proposed, based on the identification of all the A_1 coordinates belonging to a set of non-redundant internal symmetry coordinates, which can be, in turn, derived from the redundant set formed by all the bond lengths, valence, and dihedral angles. This approach, which is particularly advantageous when symmetric molecules are studied, is implemented as a completely automatic black-box procedure. The MSR program is also equipped with the possibility of including predicate observations in the fit (6). By means of this method, the set of input data (i.e. the rotational constants of different isotopologues) can be augmented by estimates of structural parameters obtained, for example, through quantum-chemical calculations. In this contribution, the underlying theory and the organization of our implementation are presented in some detail. The reliability of the new code is proven by applications of A_1 coordinates and predicate observations to the determination of the equilibrium structure of medium-size organic and biological molecules.

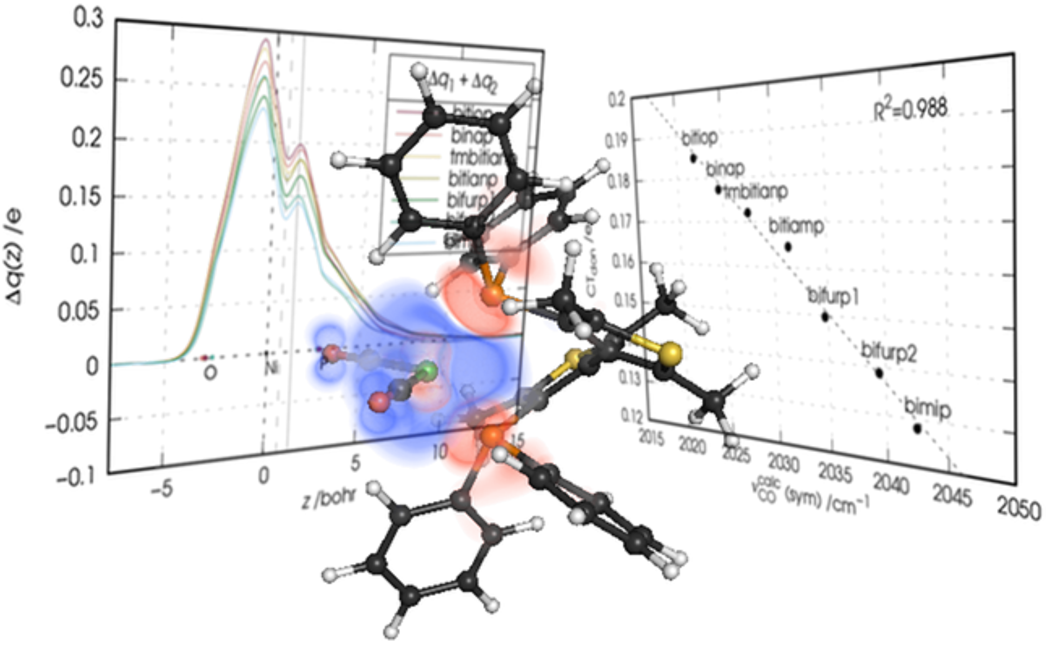
References: 1. J. Demaison, J. Boggs, J. Császár, *Equilibrium Molecular Structures: From Spectroscopy to Quantum Chemistry*, edited by J. Demaison (CRC Press, 2011). 2. M. Mendolicchio, E. Penocchio, D. Licari, N. Tasinato, V. Barone, *J. Chem. Theory Comp.* (2017) DOI: 10.1021/acs.jctc.7b00279. 3. P. Pulay, W. Meyer and J. Boggs, J. Chem. Phys. 68. (1978). 5077. 4. J. Demaison, Mol. Phys. 105. (2007). 3109. 5. E. Penocchio, M. Mendolicchio, N. Tasinato, V. Barone, Can. J. Chem. 94. (2016). 12. 6. L. Bartell, D. Romenesko, T. Wong, G. Sims, L. Sutton, *Chemical Society Specialist Periodical Report No. 20: Molecular Structure by Diffraction Methods*. 3. (1975). 72.

Finalista Premio Levi
Chemical Bonding and Spectroscopic Observables in Coordination Complexes: Analysis Techniques and Applications

Sergio Rampino[a], *Marco Fusè*[a], *Andrea Salvadori*[a], *Giordano Mancini*[a], *Vincenzo Barone*[a]

[a] *Scuola Normale Superiore, Piazza dei Cavalieri 7, 56126 Pisa; sergio.rampino@sns.it*

The relation between spectroscopic observables and the detailed metal–ligand bonding features in coordination complexes is addressed. A theoretical scheme based on a double analysis in orbital space and real space is shown to provide a detailed, quantitative description of the several charge fluxes following the metal–ligand bond formation, whence clear-cut estimates of donation and back-donation charge transfers can be extracted (1). Through two case studies on metal-carbonyl complexes (2,3), we elucidate the role of the metal–ligand bond components in altering the distance and stretching frequency of the carobnyl group and provide the framework in which spectroscopic data on coordinated CO can be used to extract quantitative information on the donor/acceptor porperties of the metal–ligand moieties. The porting of the discussed bond-analysis tools in a virtual laboratory exploiting immersive virtual reality (IVR) through the Caffeine project (4) and combining the immediacy of an IVR experience with quantitative numerical analysis will also be discussed.



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Keynote

- TEO KN01: Massimiliano Aschi, Università degli Studi dell’Aquila
- TEO KN02: Giuseppe B. Suffritti, Università degli Studi di Sassari
- TEO/INO KN01: Bartolomeo Civalleri, Università degli Studi di Torino
- TEO/INO KN02: Nazzareno Re, Università degli Studi di Chieti-Pescara "G. d'Annunzio"
- TEO/FIS KN01: Chiara Cappelli, Scuola Normale Superiore di Pisa

Toward a Computational Modelling of Charge-Transfer Reactions in Condensed Phase: from Ultrafast Photo-Induced to Slow Thermal Processes.

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During the last five years we have been focusing much of our efforts for developing and testing a theoretical-computational approach, based on Molecular Dynamics simulations and basic Statistical Mechanics, for modelling the kinetics of charge-transfer and spin-transfer reactions in condensed phase. The method, based on arguments extremely different (and somewhat complementary to) the Marcus model, has been tested on a number of processes ranging from the ultrafast photo-induced charge-transfer reactions to slow bimolecular thermal processes. In this talk I will present the basic underlying theory, the results from a number of selected examples and the limitations still present in our model.

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Reverse Mössbauer Effect as a Source of “Hot” Protons in Hydrogen Absorbing Metals

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As an attempt to explain some of the many anomalies and unresolved problems, which have been reported about the dynamic behavior of particles and molecules absorbed in crystalline solids, in a recent paper (1) we derived an extension of the Bragg – von Laue scattering law to high-energy colliding particles, which is related also to the Mössbauer effect (2),and was referred to as “reverse Mössbauer effect” (RME). In particular, we proposed an explanation of a specific and well characterized anomalous behavior found in neutron inelastic-scattering spectra (recoiled bands) of methane adsorbed in a zeolite (3).

According to RME, a particle in non-equilibrium state with respect to a crystal (colliding with the crystal or adsorbed/absorbed in it, and, set *out of thermal equilibrium* with the crystal by some external cause), can be scattered by the whole crystal with momentum proportional to a vector representing a reciprocal lattice point. The scattering is expected to occur with a well-defined probability and the momentum transferable to the particle is expected to follow a predictable distribution.

As hydrogen is lighter than methane and is adsorbed not only in nanoporous materials, but also is absorbed in a number of metals, we wondered if RME could be present also in H-metal systems and could be detected through some anomalous behavior. RME is essentially a non-equilibrium phenomenon occurring in crystals. Therefore, it could be detected, in principle, by looking for behaviors, which for similar systems differ whether the systems are or not in equilibrium, as well as whether they are crystalline or amorphous.

Enhanced diffusion of H under irradiation by ions and electrons (4,5)was observed. Enhanced diffusion was even reported for hydrogen atoms absorbed in bulk Pd in low-temperature scanning tunneling microscopy(6). In a recent paper (7), the interpretation of the anisotropic diffusion of hydrogen in Nickel required unexpectedly high fitting parameters, at least one order of magnitude larger than the values derived from experimental and *ab initio* studies.

The consideration of all these phenomena encouraged us to study the features of the RME for H absorbed in metals, and, as some examples, we evaluated its general features for H absorbed in Ni, Nb, Pd and Ti, because they are among the most frequently studied systems.

It was then applied to explain, at least in part, the above reported anomalies.

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Ab Initio Modeling of Metal-Organic Frameworks: from Gas Adsorption to Stimuli Responsive Properties

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Metal-organic frameworks (MOFs) are amongst the most extensively studied hybrid framework materials and they have garnered major developments in the last decade mainly because of their nanoporous architectures and tunable physical and chemical properties (1). They are comprised of an inorganic part, usually formed by either metal ions or small clusters (e.g. metal-oxide) that acts as a node in a network, and an organic ligand that operates as a linker, or a spacer, among the nodes to form the framework through metal-ligand coordination bonds. In addition, they have a porous (and in most cases crystalline) structure that is architecturally stable with a high and ultra-high porosity. Traditionally, this has lead to applications such as gas storage and separation, catalysis and drug delivery (2).Nevertheless, the incredibly rich structural diversity and chemical versatility of such materials can lead to the emergence of many unique and novel properties that opens access to a wide spectrum of multifunctionalities not present in traditional materials (3). The exploration of structure-function relationships has then attracted considerable interests in broadening the combination of chemically bound organic and inorganic building blocks. Therefore, other promising technological applications have emerged, in particular, for electronics and opto-electronics, sensors and nonlinear optics (4).

Here, we give an overview of our recent results on a throughout theoretical characterization and prediction of adsorption properties of different MOFs from small to giant frameworks (5), structural flexibility and framework dynamics (6), as well as tunable electronic and dielectric properties in response to diverse physical and chemical stimuli (7).

The combined use of ab initio modeling in conjunction with experimental techniques (e.g. neutron and synchrotron spectroscopy or infrared and Raman spectroscopy) will be also highlighted.

All results have been obtained through a fully periodic ab-initio approach with the CRYSTAL program (8).

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Insight into the Electrochemical Reduction Mechanism of Pt(IV) Anticancer Complexes

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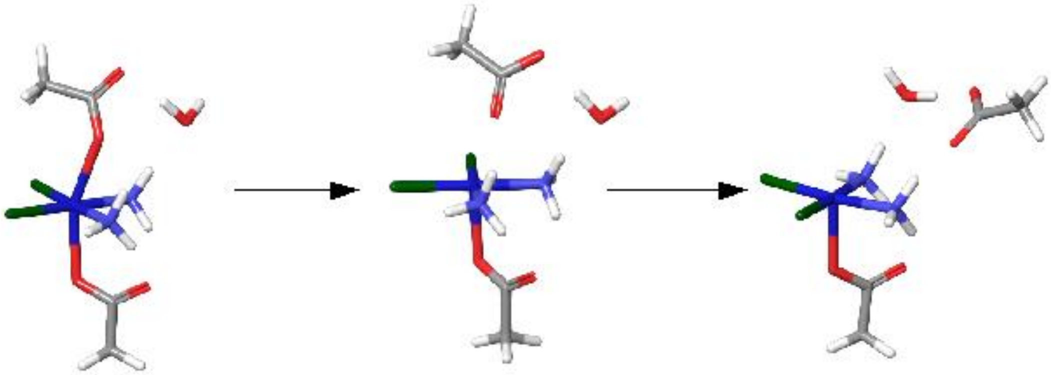
A theoretical study was carried out on the mechanism of electrochemical reduction of the prototypical platinum(IV) anticancer complex [Pt(NH_3)$_2$(CH_3COO)$_2$$Cl_2$] to the corresponding platinum(II) [Pt(NH_3)$_2$(CH_3COO)$_2$] derivative.

Energies and geometric structures of the original Pt(IV) complex and all possible Pt(III) and Pt(II) intermediates and transition states during the reduction process have been calculated using several levels of theory, and allowed to formulate a detailed mechanism for the two-electron reduction of the [Pt(NH_3)$_2$(CH_3COO)$_2$$Cl_2$] complex. Solvation was accounted for both by a continuum solvent model and through the inclusion of an increasing number of explicit water molecules.



The results show that, in agreement with the experimental evidence from cyclic voltammetry, the initial one electron reduction of the [Pt^{IV}(NH_3)$_2$(CH_3COO)$_2$$Cl_2$] complex occurs through a stepwise mechanism via a metastable hexacoordinated platinum(III) [Pt^{III}(NH_3)$_2$(CH_3COO)$_2$$Cl_2$]$^-$ intermediate and a subsequent acetate ligand detachment with a low but significant activation free energy. On the other hand, the second electron reduction of the resulting pentacoordinated [Pt^{III}(NH_3)$_2$(CH_3COO)Cl_2] species occurs through a barrierless concerted process to the final [Pt^{II}(NH_3)$_2$(CH_3COO)$_2$] derivative. Accurate values for the redox potential were obtained in good agreement with the experimental data.

A deeper insight into the dependence of the mechanism of reduction of Pt(IV) complexes would be very important to understand its mechanism of action *in vivo* and may be useful to design new and more potent platinum(IV) anticancer drugs.

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A Fully Polarizable Embedding Model for Molecular Spectroscopy of Aqueous Solutions

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The computational modeling of molecular spectra of aqueous solutions is particulary challenging. In fact, it requires at the same time an accurate modeling of the response of the solute to the external radiation field and a reliable account of the effects of the surrounding environment, which can hugely modify the solute's spectral features as a result of specific/directional interactions (1).

A recently developed Quantum-Mechanical (QM)/polarizable molecular mechanics (MM)/polarizable continuum model (PCM) (2) embedding approach has shown extraordinary capabilities, yielding calculated spectra in excellent agreement with experiments.

An overview of the the theoretical fundamentals of this methods, which combines a fluctuating charge (FQ) approach to the MM polarization with the PCM is given, and specific issues related to the calculation of spectral responses (3) are discussed in the context of selected applications (4).

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Contributi Orali

Astrochemistry: a Computational Spectroscopy's View

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For many years, the interstellar medium (ISM) was considered too hostile an environment for organic molecules. This paradigm of thought began to deteriorate roughly forty years ago with the discovery of molecules containing carbon chains and rings. As time has gone on, the pace of molecular discovery has accelerated, and the detection in the last decade of molecules showing some significant complexity (for example, glycolaldehyde, acetamide and methyl acetate), has served to completely erase the original point of view. Indeed, the detection of almost two hundred molecules in space suggests that the ISM is characterized by a rich chemistry. Among the "complex" organic molecules detected, "prebiotic" molecules – those similar to, or the same as, molecules involved in the biochemistry of Earth – have attracted particular interest. Debate on the origin of the biomolecular building blocks has been further stimulated by the discovery of nucleobases and amino acids in meteorites and other space environments.Understanding the chemical evolution of the universe is one of the main aims of astrochemistry. The starting point for the development of astrochemical models is the knowledge of whether a particular molecule is present in the astronomical environment and, if so, its abundance. In this scenario, molecular spectroscopy plays a critical role since it provides the information needed to make definitive astronomical searches. Increasingly, these astrochemical-spectroscopic investigations areassisted by quantum-chemical calculations of structures as well as spectroscopic and thermodynamic properties, such astransition frequencies and reaction enthalpies, to guide and support observations, line assignments, and data analysis in these newand chemically complicated situations (1).In this contribution, the state-of-the-art computational approaches purposely set up in our research groups are presented through the discussion of selected and exemplificative examples. Starting from the accurate spectroscopic characterization of oxirane - a potential prebiotic species in Titan's atmosphere - as a test case (2), the small prebiotic molecules under investigation in the frame of the "STARS in the CAOS (Simulation Tools for Astrochemical Reactivity and Spectroscopy in the Cyberinfrastructure for Astrochemical Organic Species)" PRIN 2015 project and the challenge of the spectroscopy of building blocks of polycyclic aromatic hydrocarbons (PAHs), like the phenalenyl radical, are addressed.Emphasis will be also given to the powerful support provided by the Virtual Multi-frequency Spectrometer, VMS (3), and in particular by the newborn rotational module VMS-ROT (4) – those that are interested are referred to the dedicated contribution. VMS is intimately related to theoretical calculations, to be used as a starting point for guiding experiments and spectral interpretations, and also features VMS-Draw, a multiplatform graphical user interface (GUI).

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Modeling Charge Transport in Organic Materials

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Understanding charge transport in molecular systems is of paramount importance, both for designing new molecular materials for modern optoelectronic devices (1),such as organic light emitting diodes, bulk heterojunction solar cells, and field effect transistors,and for understanding important biochemical processes (2), such as photosynthesis, respiration, and DNA oxidative damage.

Herein, we discuss different theoretical approaches for treating charge transport between molecular blocks at full quantum mechanical level: Fermi's Golden Rule, second order cumulant approximation of Liouville equation (3), and the numerical solution of the time dependent Schrödinger equation (4), focusing attention on charge transport in DNA oligomers and charge transport in organic semiconductor.

As concerns hole transfer in DNA, we analyze the rates of hole transfer between guanines separated by up to five adenines or thymines, exploring both the coherent single step superexchange mechanism and the incoherent multi step hopping. Theoretical simulations show that in short oligomers, consisting of two guanines separated by a high energy bridge of up to threethymine bases, hole tunnelling between guanines can occur on picosecond timescales, about three order of magnitude faster than hole hopping. However, tunnelling becomes extremely slow in longer oligomers, containing more trap sites, where charge can bounce among them. Our results are able to reconcile conflicting experimental results (5,6), showing the great complexity of charge transport in molecular systems.

As concerns charge transport in organic semiconductors, we will show that Fermi's golden rule can be inadequate for systems exhibiting ultrafast hole hopping rates, while cumulant second order approximation is extremely more accurate in those cases.

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Ab Initio Molecular Dynamics to Simulate Excited State Proton Transfer to Solvent: the Strange Case of a Super Photoacid in Water and Methanol Solutions

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Light irradiation adds new dimensions to the conventional ground state chemistry.Basically, the strongly perturbed electronic structure, reached when molecules get excited, leads to a reactive behavior that ground state chemistry cannot achieve. In this way weak acids in the ground state can turn theirself in very strong photoacids upon the electronical excitation.(1) Unveiling at molecular level the complex aspects of Excited State Proton Transfer (ESPT) reactions, with solvent molecules acting as proton acceptor, is extremely difficult.Indeed, a wide range of time scales affects the ESPT kinetics, going from the femtosecond (electron density redistribution of the chromophore) to the nanosecond (diffusion process after the reaction) scale.(1) Furthermore the reaction phase space is very complex, involving both the photoacid and solvent degrees of freedom.(1,2)The exploration of different time scales in a very complex reaction space represents the main challenge for the theoretical simulation of ESPT processes. What is more, theoretical approaches are called to handle at the same time both the electronic redistribution of the chromophore and the solvent relaxation around the proton transferring complex, finely modulating the kinetics and thermodynamics of the reaction.(3)In this contribution we took up this challenge, investigating the mechanism and driving forces of ESPT reactions by means of Time-Dependent Density Functional Theory based ab-initio molecular dynamics simulations. An effective hybrid implicit/explicit model of solvation, was adopted to consider in an explicit way the solvent coordinate in the ESPT process.(4) The solvation and photoreactivity of a super photoacid, named QCy9, was investigated in water and methanol solution, both in the ground and the excited state. More closely, QCy9 is a super photoacid, which exhibits a very large ESPT rate constant, $k_{PT} = 1 \times 10^{13}\ s^{-1}$, the largest value reported in the literature so far. This constant is the same independently on the nature of the solvent (water or methanol).(1)The solvent configuration space at the ground electronic state was deeply investigated analyzing the hydrogen bond network around the acid group and the proton acceptor solvent molecule.Several configurations in the Franck-Condon region, describing an average solvation, were then chosen as starting points for the excited state dynamics. In any case the excited state evolution spontaneously leads to the proton transfer event, whose rate is strongly dependent from the hydrogen bond network around the proton acceptor solvent molecule. This is true both in water and methanol solution. Our calculations revealed that the explicit and polarizable representation at least of three solvation shells around the proton acceptor molecule is necessary to stabilize the solvated proton and allow its diffusion across the solution. Moreover the analysis of the solvent molecules motions in proximity of the reaction site confirmed that the ESPT event between the donor and the acceptor molecules is actually assisted by the oscillations of solvent molecules belonging to the first and second solvation shell of the accepting molecule.

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Real-Time Coupling between Molecules and a Continuum Environment

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We have recently developed a real-time approach for including the non-equilibrium response of a continuum environment in the propagation of the wavefunction (1,2) or the electronic density (3) of a molecule, respectively described with the Real-Time TDCI and TDDFT.
The molecule-environment interaction is treated with the Boundary Element Method (BEM), that we reformulated using a diagonal representation for the frequency-dependent response matrices. Our *diagonal BEM* formulation is equivalent (i) to the Polarizable Continuum Model (PCM) (4) when the space is occupied by a polarizable continuum medium and the molecule is placed in a vacuum cavity created within such medium, and (ii) to the approach, analogous to PCM, developed to describe the enhancement induced by plasmonic excitations in metallic nanoparticles surrounding the molecule on its spectroscopic properties (5); but it clearly highlights the connection between BEM-based and multipolar-based description of the molecule-environment interaction potential (3). Moreover, in the time-domain, our approach provides *equations of motion* for the fictitious degrees of freedom (polarization charges) generating the time-dependent interaction potential, that we derived both for a Debye (solvent) and a Drude-Lorentz (nanoparticle) response (1,2).
As a result we detail the effects of the environment polarization on the population of the molecular excited states, induced by an external electric-field short pulse, and on linear and non-linear spectroscopic properties of the molecule.

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A New Efficient Time Dependent Density Functional Algorithm for Large Systems: Theoretical Study and Applications to Plasmonic Systems

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A new algorithm to solve the TDDFT equations in the space of the density fitting auxiliary basis set has been developed and implemented in ADF.[1]In particular, the method extracts the spectrum from the imaginary part of the polarizability at any given photon energy, avoiding the bottleneck of Davidson diagonalization in Casida formulation. The original idea consists in the simplification of the double sum over occupied-virtual pairs in the definition of the complex dynamical polarizability, allowing an easy calculation of such matrix as a linear combination of constant matrices with photon energy dependent coefficients. This makes the present scheme very efficient.The method has been applied to very different systems in nature and size (from H_2 to $[Au_{309}]^-$)[2,3]. In all cases, the maximum deviations found for the excitation energies with respect to Casida approach are below 0.2 eV. The new algorithm has the merit to calculate the spectrum at whichever photon energy but also to allow a deep analysis of the results, in terms of Transition Contribution Maps,[4] plasmon scaling factor analysis[5], induced density analysis, and with a fragment projection analysis[6]. Circular Dichroism of large systems becomes also affordable.[7]

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Exploring Nuclear Photorelaxation and Photoreactivity by Excited State Ab-Initio Dynamics and Time Resolved Vibrational Analysis.

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Understanding at atomistic level the mechanism of photoinduced chemical reactions in terms of electronic/nuclear motions responding to the external perturbation is a challenging task from both experimental and theoretical point of view. Time resolved vibrational spectroscopies, such as femtosecond stimulated Raman spectroscopy (FSRS) (1), were shown to be a very powerful tool to investigate and follow in real time the nuclear motion of photoexcited chromophores. The interpretation of the often complex experimental spectra can benefit from the employment of a theoretical-computational approach. In particular, ab-initio molecular dynamics methods allow to simulate and accurately reproduce the behaviour of chromophore in solution in both equilibrium and far for equilibrium regime, i.e. after the interaction with light (2,3). The analysis of the signals extracted from dynamics allows to create a direct link electronic/nuclear structure and spectroscopic properties (2). The present contribution is focused on the photoreactivity of pyranine [8-hydroxypyrene-1,3,6-trisulfonic acid] in water solution (4). Pyranine is a popular photoacid molecule, upon irradiation with light an excited state proton transfer reaction (ESPT) takes place. We are interested in ultrafast reactivity, namely that occurring in the femtosecond to picosecond time scale. During this time pyranine shows a characteristic activation of low frequencies skeleton modes upon excitation that precedes the ESPT event (5). We adopted an integrated computational approach including ab-initio molecular dynamics and time resolved vibrational analysis based on Wavelet Transform (2). This latter allows us to localize any signal extracted from excited state trajectory in both time and frequency domain. In this way, we can follow the activation and relaxation of the key normal modes of the photoexcited pyranine, and to reproduce the reaction pathway before the reactive event itself.

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Lanthanoid(III) Ions: Transferable Lennard-Jones and Buckingham Pair Potentials from Aqueous to Complex Media

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Lanthanoid(III) ions, which are commonly denoted as Ln(III), represent the most extended series of chemically similar metal ions. The solvation properties of Ln(III) ions in solvents with different polarity are of special interest due to the huge number of possible applications, including industrial processes, separation in nuclear power technology, waste management, and liquid-liquid extraction processes. (1,2) Understanding the coordination properties of Ln(III) ions in different solvents and sheding light into the molecular interactions taking place in these solutions is therefore important to select the best performing solvents.

Here, for the first time, new sets of Lennard-Jones and Buckingham potentials have been developed for the whole lanthanoid series in water, by directly comparing the structural hydration properties obtained from classical Molecular Dynamics (MD) simulations and the extended X-ray absorption fine structure (EXAFS) experimental data. This joint MD-EXAFS approach is a powerful tool to assess the capability of the employed force field to correctly describe the structural properties of the investigated systems. (3,4) Starting from these sets of Ln-water parameters we have extrapolated generic Ln-Ln pair potentials to be used in combination with force fields available in the literature for studying the coordination of Ln(III) ions in different disordered systems, going from inorganic to bio-inorganic to organic systems.

The importance of developing a new set of Lennard-Jones parameters for Ln(III) ions is due to the fact that they are computationally efficient interaction potentials that can be readily used to perform classical MD simulations without explicit polarization. However, the transferability of a given potential to systems different from those for which they have been developed has to be verify case by case. To this end we will show examples of MD simulations of Ln(III)-containing systems, carried out using our developed Lennard-Jones parameters. In particular, we have investigated Ln(III) ions in water and acetonitrile, but in the presence of their counteranions, such as nitrate, triflate or bis(trifluoromethylsulfonil)imide ions. Finally, we will show the possibility of using the Ln-Ln Lennard-Jones pair potentials in MD simulations of a more complex and disordered Ln(III)-containing system: a diluted solution of $Ce(NO_3)_3$ in the protic ionic liquid (IL) ethylammonium nitrate. ILs may be ideal alternatives to standard solvents due to their excellent chemical and thermal stability, non-volatility and favorable solvating properties for a range of polar and non-polar compounds. In this case, for the first time polarizable effects have been included in the MD force field to describe a heavy metal ion in a protic IL, but they were found to be unessential.

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Unraveling Chiral Properties of Metal Complexes through Computational Vibrational Spectroscopy

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Transition metal complexes play a key role in asymmetric synthesis of fine chemicals and in the last year have drawn attention for their potential use as antitumoral agents. However, applying them for pharmaceutical purposes requires a correct and extensive characterization of their properties. In this respect, chiroptical methodologies are the only experimental techniques capable of directly probing the molecular chirality. In tangled systems like metal complexes, several stereogenic units can be present and it is often useful to find some features in the spectrum that could be referred to the specific contribution of each one of them. However, experimental spectra can seldom be interpreted on the basis of classical or phenomenological models and an accurate theoretical treatment is mandatory. In particular, vibrational analysis supported by Density Functional Theory (DFT) calculations have had considerable successes in assigning the absolute configuration (AC) and evaluating the conformational properties of many molecular systems. Nevertheless, the harmonic approximation, which is commonly used to simulate spectra, may be insufficient due to limitations in the accuracy and lack of features caused by the missing contributions from overtones and combinations. Thanks to the recent developments done in our group, it is now possible to simulate full anharmonic spectra with correction to both energies and intensities. In this contribution, we will show examples of accurate simulation of IR and vibrational circular dichroism (VCD) spectra beyond the harmonic approximation (1). Furthermore, a toolbox aimed at analyzing and interpreting the different features in the spectra will be presented. Due to the computational cost, full anharmonic calculations in systems of medium-to-large size can be very challenging. Therefore, an appealing alternative is to reduce the dimension of the system to a set of normal modes directly involved in the studied feature of the spectrum. Helped by user-friendly interfaces, a careful definition of the reduced dimensionality (RD) scheme can lead to very good results in target portions of the spectrum (2), at a fraction of the computational cost of the full calculations. Moreover, computations can provide extensive analysis on the origin of the band-shape and employing graphical tools can significantly aid the understanding of these phenomena. For example, transition current density (TCD) (3) maps, which allow an evaluation of the electron flow associated to the molecular vibration, provide insights in the origin of the intensities, that are generally lost when only numerical values are considered. All these aspects will be illustrated through a series of chiral ruthenium cyclopentadienyl carbonyl complexes, for which the carbonyl stretching has been recently proposed as probe of the chirality at the metal center (4). The relation between the chirality at the metal center and CO stretching will be deeper investigated with the presented ad hoc tools.

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Computational Study of Curcumin-Derivatives for Alzheimer's Disease Treatment

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The Alzheimer's disease (AD) is responsible of 60% of memory loss and cognitive disorders in people over their 65 due to the formation of amyloid plaques in the brain that modify or block nervous impulses. Amyloid plaques are made by the aggregation of amyloid-β fibrils that stack together through their β-sheets(1). Curcumin is used in traditional medicine in India and China due to its anti-inflammatory, anti-oxidants, chemopreventive and chemotherapeutic properties(2). In recent years, curcumin has been tested as an amyloid inhibitor finding that it is able to bind to small amyloid-fibrils and to block the aggregation and formation of fibrils *in vitro* and *in vivo*(3). In order to find curcumin-derivativeswith improved inhibition characteristics with respect to the Aβ(1-40) fibril aggregation, we have performed molecular docking(4) of curcumin-derivatives over full-length Aβ(1-40) fibrils obtaining for each compound 4 binding regions mainly located in the correspondence of the β-sheets. Then, each Aβ(1-40) fibril—curcumin configuration has been simulated by means of classical molecular dynamics in order to study the dynamics of the interaction and obtain the binding energies(5). This last step is of crucial importance to reproduce the fibril flexibility not taken into account in the docking procedure.From both computational approaches, we obtained an affinity ranking based on the binding energy of that molecule on each fibril region where the basic form of curcumin is used as a reference for others compounds. Data have been found to be in good agreement with experimental dissociation constants (DC50) of compounds on mature Aβ(1-40) fibrils measured in our lab.

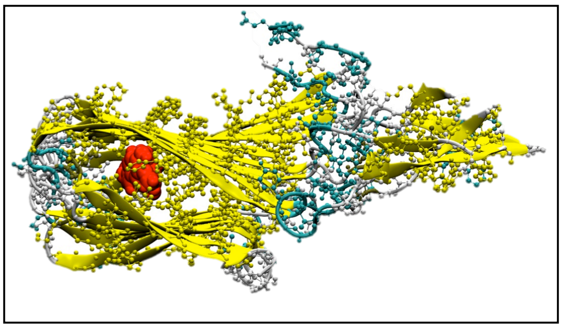

Figure 1: Docking of Curcumin to an Aβ(1-40) fibril.

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First-Principles Design of P-Type Semiconductor Oxides as Alternative to NiO in P-Type Dye-Sensitized Solar Cells

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Tandem Dye Sensitized Solar Cells (t-DSSCs), consisting of a n-type DSSC photoanode coupled with a p-type DSSC photocathode,have brought a lot of attention in the solar energy conversion scenario since they are capable to break the theoretical performance limits of the single devices. (1)Actually, tandem cells with a V_{oc} equal to the sum of that from the separate p and n devices have been reported. (2) The main limitation in this scheme is that p-DSSCs are underdeveloped with respect to their n-type counterparts. (3) This is in large part due to the choice of the semiconductor. Currently,the most efficient semiconductor in p-DSSCs is NiO, but presents several drawbacks: low electrical conductivity and redox potential, high visible light absorption and low hole mobility. Delafossites, showing a high p-type conductivity and a wide band gap around 3.6 eV, are a possible alternative to NiO for p-DSSCs. (4,5) Since the discovery of p-type conductivity in $CuAlO_2$ (6),many experimental and theoretical studies have focused on materials with delafossite-type structures, suggesting that these materials could outperform NiO as photocathodes. (7) The role of divalent cations (expecially Mg^{2+}) substitutions in the B site has been studied both theoretically and experimentally. (8) It is suggested that this kind of substitution reinforces the Cu^{+}/Cu^{2+} mixed valence and enhances the p-type conductivity by increasing the charge carrier concentration. (9) However, there are no studies that demonstrate the electronic and structural effects of Mg dopants on the delafossite bulk properties. Thus, here we report a first-principles investigation on the $CuBO_2$ (B = Al, Ga and Cr) delafossite oxides. $CuAlO_2$, $CuGaO_2$ and $CuCrO_2$ are among the most studied and synthesized delafossites, and record conductivities have been measured with p-doping on these materials. We investigated at the PBE+U and HSE06 levels of theory both the pristine materials and the p-type derivative with 8.3% of Mg doping. Our electronic structure and charge distribution analyses show that Mg doping creates Cu(II) acceptor states inside the band gap that can interfere the photoconversion process. Moreover, we also aimedat establishing the feasibility of $CuBO_2$ for DSSC devices. To this end, wepredicted the V_{oc} with respect to some of the most commonly used redox couples: we evaluated the absolute position of the valence band edges modelling the stoichiometric (100) orthorhombic surfaces and calculating the relative work-function (ϕ). From these results, we established the most convenient element at the B site to be exploited for p-type DSSCs.

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Toward a Rational Design of Half-Sandwich Group 9 Catalysts for [2+2+2] Alkynes Cycloadditions

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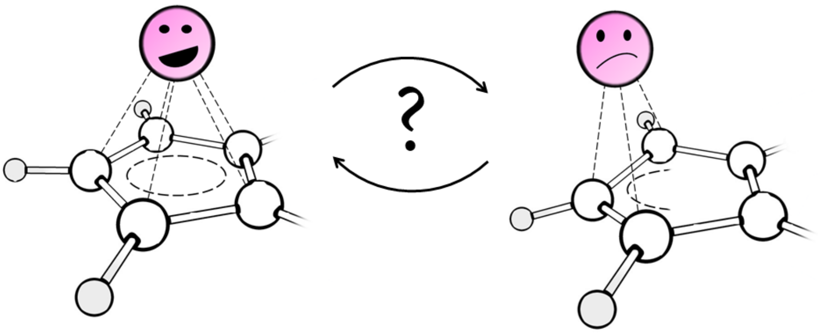
Filling the gap between molecular structure and reactivity is a well-known challenging task in chemistry. The rational design of catalysts may greatly benefit of computational aid, provided state-of-the-art methodologies are employed. The case of metal catalyzed [2+2+2] cycloaddition of alkynes/alkynes-nitriles to benzene/pyridine is investigated in detail, due to the paramount importance of these reactions for the synthesis of cyclic and polycyclic organic compounds.(1) Catalysts of general formula Cp'M are considered, where Cp' is the cyclopentadienyl anion or the cyclopentadienyl moiety of larger polycyclic aromatic/heteroaromatic ligands, and M=Co, Rh, Ir. Energy profiles of the whole cycles with a number of intermediates ranging from 5 to 9 connected by the corresponding transition states are computed and the catalyst performance is evaluated based on its turnover frequency (TOF), by implementing the equations of the energy span model.(2) TOF values are related to peculiar structural features of the Cp'M fragment, i.e. to the M-Cp' bonding mode which results in slippage phenomena during the catalytic cycle. In fact, the metal is never coordinated to the five carbon atoms ring in highly symmetric fashion (η^5), but is *slipped* and the amount of this distortion changes during the various steps of the catalysis.(3,4) This fluxionality is found to affect importantly the efficiency of the catalyst.



Scalar ZORA relativistic density functional methods are employed and activation strain analysis (5) is systematically performed to gain insight on the factors controlling the height of the relevant energy barriers.

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Ramachandran Energy Approach for Protein Folding

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Despite a tremendous effort to develop reliable models for the prediction of protein folding, and in spite of the results obtained so far, the quality of the geometry prediction remains quite poor for peptides longer than 60-80 residues (1). There are mainly two kinds of approaches: the *ab initio,* which relies simply on the amino acids sequence and on chemical-physical principles, and the homology, in which one starts from proteins with similar structure found in nature. In the present work, we will summarize the advances in the peptide folding research and we will offer a new approach that is promising to sensational results (2). The approach, falling in the realm of *ab initio* simulations, is largely inspired by biological and biochemical mechanisms (3). We have added two new terms to the Amber force field to drive the minimization toward the proper region in the Ramachandran plot (see Fig. 1). The method, entitled Ramachandran folding as a tribute to the great Indian biochemist, is capable to suggest the most realistic folding mechanism so far described.

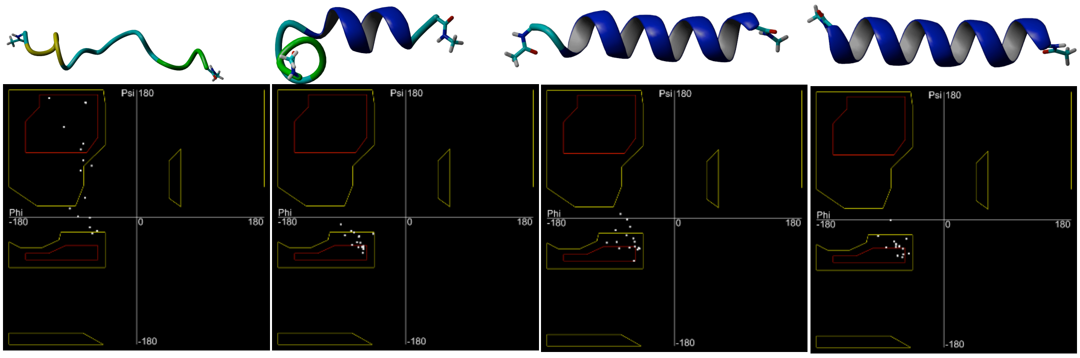

Figure 1 – Protein folding evolution in a Ramachandran plot

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Computational Design of $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO)-based Bifunctional Electrodes for Proton-Conducting Solid Oxide Electrochemical Cells

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Double perovskite $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ (SFMO) has attracted interest in the last few years as cathode material in intermediate temperature oxide-conducting (OC) solid oxide fuel cells (SOFCs) due to its good electrochemical activity, chemical stability in red-ox conditions, and resistance to coking and sulfur poisoning.(1) By means of state-of-the art first-principles calculations, we have unveiled SFMO structural, electronic, defect and catalytic properties and propose SFMO derivatives with promising performance also in proton-conducting (PC) SOFCs. SFMO excellent performance in the OC regime can be ascribed to the easy formation of oxygen vacancies and extraordinary low oxide migration barrier heights.(2)SFMO inherent non-stoichiometry(3) turns it into a good candidate for proton conduction provided that oxygen vacancies allow the incorporation of protons into the lattice via water dissociation.Our calculations show that aliovalent doping enables convenient hydration and effective proton transport in bulk SFMO, which opens the route toward new promising triple-conducting (proton/oxide/electron) oxides for use as single-phase electrodes in PC-SOFCs.(4) Moreover, we have analyzed different reaction pathways for the performance-limiting oxygen evolution and reduction reactions (OER/ORR) and evaluated the corresponding overpotentialswithin the theoretical standard hydrogen electrode (TSHE) framework.(5)Beyond discussion of specific SFMO applications, we use these results on SFMO and related systems within a general framework to discuss key structural and electronic properties/processes and easily-computable descriptors that can help to design new perovskite-based electrodes for OC- and PC-SOFCs.

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Hydrogen Defects in Diamond. A Quantum Mechanical Approach

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The investigation of native and radiation-induced point-defects in diamond (as well as in other semiconductors) has attracted large theoretical and experimental interest. Diamond is a wide-bandgap material characterized by well-known extreme physical properties (high Young's modulus and thermal conductivity, broad transparency range, high carriers mobility, etc.) with attractive applications in different fields, ranging from microelectromechanical systems to heatsinks, laser windows, particle detectors, etc (1). Hydrogen,with nitrogen, is the most important impurity in diamond. It is included during the growth of natural diamond as well as in chemical vapour deposition (CVD) processes. It is certainly present at the surfaces; a non minor fraction, however, is also thought to be incorporated in the bulk. H atoms are supposed to be involved in several defects combining vacancies and nitrogen aggregates(2). It is identified through its infrared(IR) active modes (stretching and bending), although probably not all hydrogen atoms present in diamond are IR active. Thesharp vibrational peaks at 3107 and 1405 cm^{-1} that appear in most natural diamonds (3) have been attributed in the past to various H containing defects. Experimental evidence suggest that His strongly bonded to a carbon atom, with weak perturbations due to nitrogen atoms (3).

Various H containing defects, in particular VN_3H (a vacancy surrounded by three N and one C atom, the latter being saturated with H),have been considered by using a quantum mechanical approach, a local gaussian-type basis set, hybrid functionals, the supercell scheme and the CRYSTAL code (4). The same scheme has recently been used for describing the vacancy (5) and interstitial (6). Various properties (structural, electronic vibrational) have been used for a complete identification of the defect. The Infrared spectra (wavenumbers and intensities, evaluated analytically through the Coupled Perturbed Hartree-Fock method) aregenerated and compared with experiments.

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A DFT Rationalization of a Two Metals Strategy to Tune Selectivity in Catalysis

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Selectivity is among the most important properties of an effective catalyst. In homogeneous transition metals catalysis this can be achieved by appropriate design of the ligand wrapped around the metal. In heterogeneous catalysis this is a more complex issue, since selectivity is often associated with different reactivity at different surfaces of the catalyst, as well as at steps, edges, and any type of defects that almost inevitably are present in any heterogeneous catalyst. Indeed, the less selective sites on a metallic catalyst are usually associated with low coordinated metals, such as those of rugged surfaces or defects, since these sites are considered as the most reactive. Under these conditions, a promising strategy to improve the selectivity of a metallic catalyst is alloying a second metal, less reactive and capable to occupy preferentially sites corresponding to low coordinated metals.(1) In this communication we will present some DFT insights in the dry reforming of methane promoted by Ni/Co catalysts.(2) In details, we performed DFT simulations aimed to elucidate the availability of the different active sites on the surface of the reduced CoNi particles to supplement the experimental techniques used that lack of atomic resolution.

Moreover, calculations allowed to rationalize the catalytic behavior of the alloy showing that the CoNi metal surface has an intermediate energy of oxygen chemisorption, between those of monometallic Co and Ni (see Chart 1).

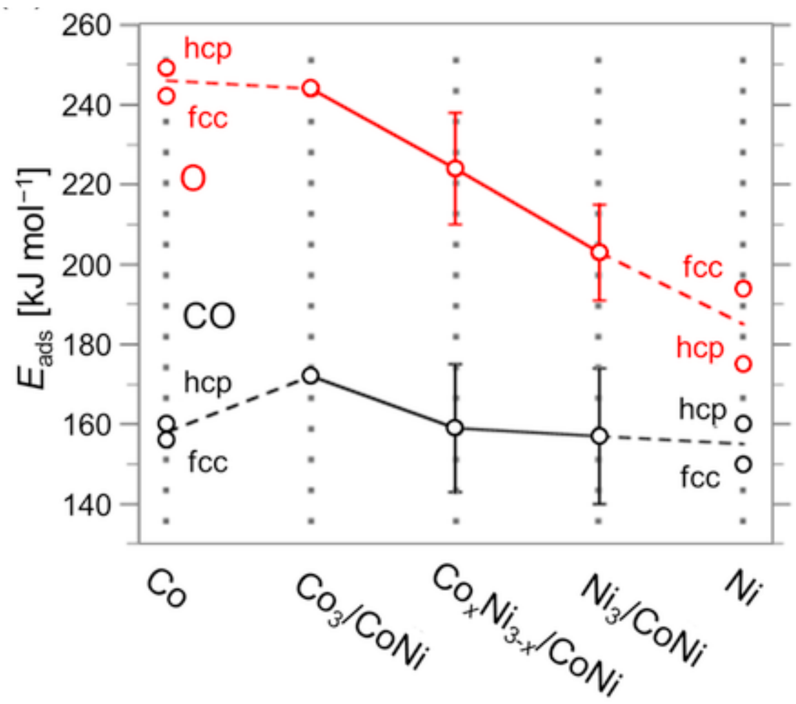

Chart 1.

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The Role of Metal Substitution in the Metallo-Enzymes: a Theoretical Point of View

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Quantum mechanical (QM) cluster model and quantum mechanical/molecular mechanical (QM/MM) calculations were performed on some metalloenzymes belonging to different classes. Insight is gained into the enzymatic activity upon metal-ion substitution.

The examined cases:

-Carbonic anhydrase (CA): Zn-, Co-, Cd-CA hydrating CO_2;(1,2)Rh-CA hydrogenating CO_2 to formic acid. (3)

-Methanol dehydrogenase (MDH): Ce(III)-MDH versus Ca(II)-MDH. (4)

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Back-Donation in d^0 Metal Complexes: does it Exist? The Case of Nb(V)

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Since the introduction of the Dewar-Chatt-Duncanson (DCD) model, which almost 70 years ago proposed an elegant framework to rationalize the coordination of an olefin to a transition metal, inorganic chemists expanded its use to the coordination of every ligands, including carbon monoxide, phosphines and carbenes, demonstrating its general applicability.

Particularly interesting is the bonding in d^0 metal complexes: in the simplest sense, they should not be able to back-donate electronic density to the ligand because their *d* orbitals are formally empty, but, obviously, things are more complex than this.For example, $[Cp^*{}_2M(H)_2CO]$ complexes (M = Zr, Hf) exhibit a classical behavior (υ_{CO} = 2044 and 2036 cm^{-1} for Zr(IV) and Hf(IV), respectively) (1) and it has been proposed that “back-donation” could come from a M-H orbital of appropriate symmetry.

Recently, various Nb(V)-carbene complexes have been structurally characterized(2) and all of them exhibit a peculiar metal arrangement: the halides *cis* to the carbene that lie almost perpendicular to the plane of the carbene are slightly bent toward the carbene itself. According to some authors, this is an evidence of Cl → carbene back-donation, but according to others, the Nb-carbene bond is a pure σ bond.

In this contribution, we shed some light on this controversial topic through a combined experimental/theoretical approach, studying complexes with appropriate ligands and analyzing their Nb-L bond by means of the Charge Displacement analysis, which recently demonstrated its potential in the detailed and quantitative characterization of coordinative bonds.(3)

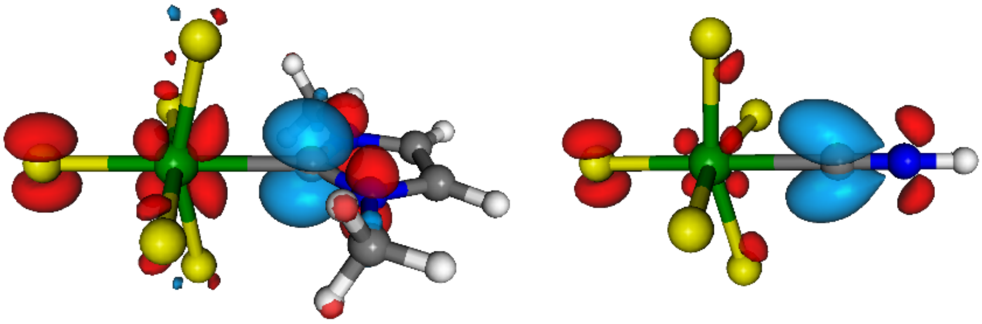

Figure: Isodensity surfaces (±0.001 e/a.u.) for the B1 component of the density deformation function upon the formation of the $[NbCl_5]$-L bond (L = 1,3-dimethyl-imidazol-2-ylidene, hydrogen isocyanate).

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Combination of Porphyrin and Ruthenium-arene Moieties for a Dual Anticancer Function. A Theoretical Investigation.

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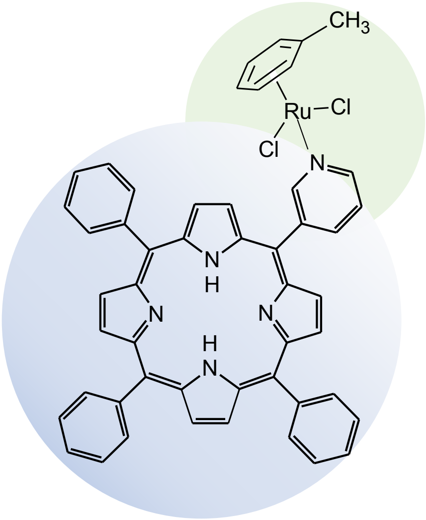
Combining therapies for the treatment of diseases has become a worthwhile strategy to improve efficiency and decrease side effects.In particular against cancer, a combination of chemotherapeutics with radiation is recently appeared as a common form of treatment. It requires the photosensitizing action of a molecule able to absorb a radiation with appropriate wavelength and a metal complex demanded to exert the chemotherapeutic function.

As regards the metal complex, several efforts have been devoted in the last years to find an alternative to cisplatin anticancer, whose clinical effectiveness has been greatly limited by drug resistance and significant side effects. In the search for new metal based anticancer agents ruthenium complexes have raised great interest, and their antitumor potential has been established over two decades ago. Thus, a huge variety of plausible complexes able to inhibit tumor cells growth have been proposed, some of them are under clinical trials.[1]



From the other hand, photosensitizers currently approved for clinical use in photodynamic therapy belong to the porphyrin-like class of molecules thanks to their low dark toxicity, thermodynamic stability, absorption properties in the Q band that can be modulated by varying π electrons and facility to form metal complexes or to include in their structures heavy atoms.

Recently some Ru-based complexes,as that depicted in figure, have been suggested as drug candidatestoward human melanoma cancer cells, due to their dual synergistic effect of thearene ruthenium chemotherapeutics and the porphyrinphotosensitizer.[2]

Previous studies have largely demonstrated that theoretical computationsbased on first-principles methods can reliably predict orreproduce and rationalize electronic transitions,[3-8] as well as can give further insight into the mechanisms involved in the drug action.[9,10]

Density Functional Theory and its time-dependent formulation (TD-DFT) have been used to shed light on the mechanism of action of these compounds, exploring their photophysical properties and the mechanistic features.

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Insight From DFT Simulations on the Collagen/Hydroxyapatite Interface: a Simple Model Based on the Poly-Proline Polymer

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Collagen protein (COL) is one of the most abundant protein in mammals. Its structural peculiarity is the geometrical motif in which three parallel polypeptides strands, in a poly-proline type II (PPII) fashion, coil about each other to form a triple helix (1). COL is also the main component of bone where is in strict interaction with the hydroxyapatite mineral (HAP). Large amount of Proline (PRO) and derivatives are found in COLs. It is known that the side chain conformations of PROs have a huge role in COL features. Conformational changes between PRO puckers can lead to the COL triple helix unfolding (2). Moreover, PRO side chain mobility induces structural flexibility to the COL protein (3). In our work, we focused on the very delicate conformations of the PRO ring embedded in the COL protein. We carried out the investigations by means of accurate *ab initio* calculations by employing a very simple COL model, e.g the PPII polymer (4-5). We characterized the free PPII polymer and we simulated its adsorption on the HAP surface. We computed the relative stabilities of the PPII as free and on the HAP surface. The comparison reveals that HAP adhesion guides the formation of puckering conformers which are un-accessible by the free polymer alone.

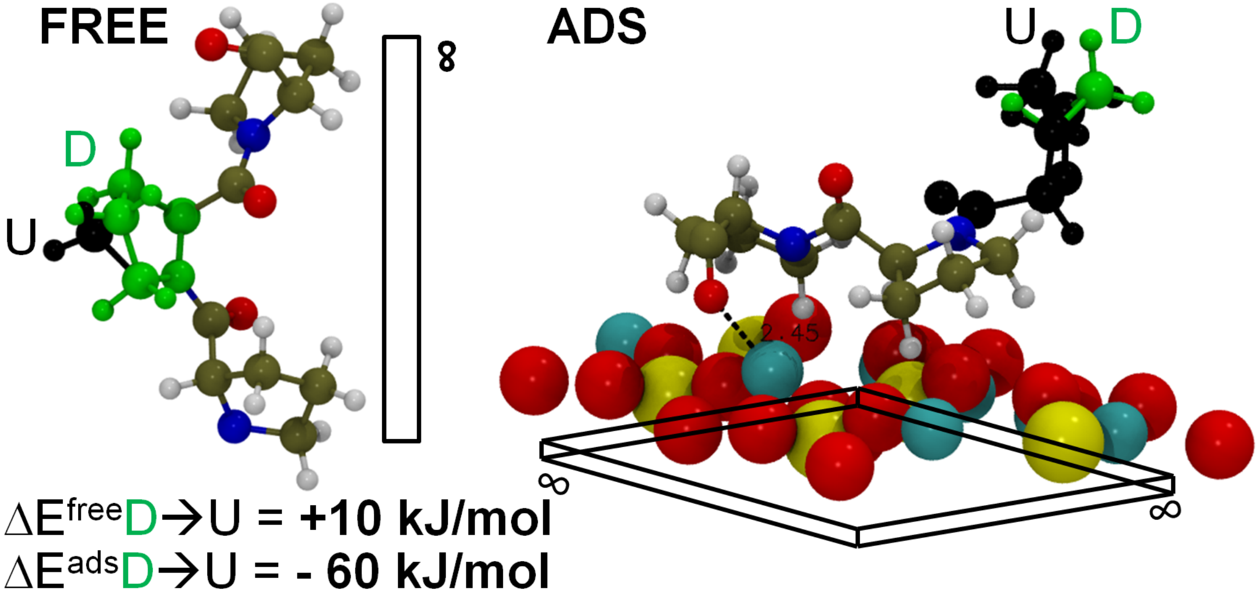

Figure **1.** *Difference in the relative stability for the U and D PPII conformers as free (FREE) and as adsorbed (ADS) on the HAP surface (by C=O···Ca electrostatic interaction).*

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Forsterite Surfaces as Models of Interstellar Core Dust Grains: Computational Study of Carbon Monoxide Adsorption

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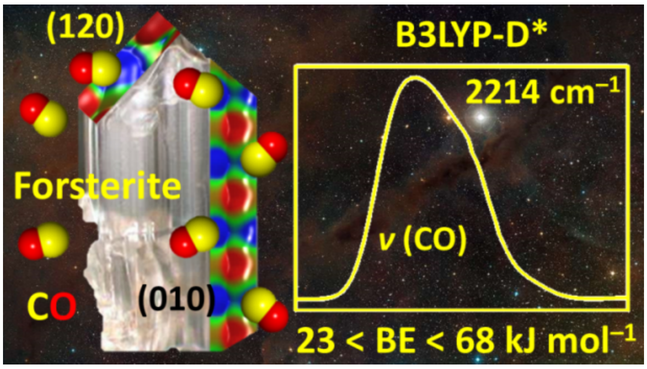
Carbon monoxide (CO) is thesecond most abundant gas-phase molecule (after hydrogen) of the Interstellar Medium (ISM) (1). In Molecular Clouds (MCs), regions of the ISM where star-forming processes occur, it adsorbs at the surface of grain cores – typically partially crystalline Mg/Fe silicates – or within the icy grain mantle and originate other molecular species through the catalytic power of surface active sites. More than 200 molecular species in the MCs have been observedso far by means of rotational spectroscopic, partly derived from reactions among molecules entrapped at the grains surfaces, while the presence of Mg-silicates has been inferred by IR spectroscopy (1,2,3).Laboratory studies can only partially reproduce the harsh conditions of the ISM (4), thus computational modeling can play a major role in the understanding of the chemical network charactering MCs. In this work, we performed and accurate analysis of the energetic and structural features of CO adsorption on different crystalline forsterite (Fo, Mg_2SiO_4) surfaces by means of DFT techniques. Data indicate that CO exclusively physisorbs on Mg exposed cations of Fo surfaces, with binding energies in the 23-68 kJ mol^{-1} range. Not only simple charge-dipole forces are involved, but also quadrupolar and dispersive ones are responsible of the CO adsorption. We also performed a full thermodynamic treatment of the CO adsorption at the very low temperatures and pressures typical of the MCs together with a full spectroscopic characterization of the CO stretching frequency. We proved the CO stretching frequency value to be extremely sensitive to the local nature of the surface active site of adsorption and showed results at variance with what is known about CO adsorbed on flat oxide surfaces due to the complex electrostatic and structural morphologies of the Fo surfaces.The detailed kinetic analysis of CO desorption at different low temperaturessuggested that desorption times are higher than the typical evolution times of the ISM, at least until 100 K when they become comparable.Our computed data could be incorporated in the various astrochemical models of interstellar grains developed so far and thus contribute to improve the description of the complex chemical network occurring at their surfaces.



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Prebiotic Molecules in Interstellar Space: Aminoacetonitrile and C-Cyanomethanimine

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The attempts to detect amino acids in the interstellar medium were so far unsuccessful even for its simplest form, glycine, despite that decades-long efforts have been devoted by many observational studies. From a chemical point of view, it is therefore important to identify the possible precursors of amino acids as well as the astronomical sources where they are abundant. Aminoacetonitrile (NH_2CH_2CN) is one of the possible precursors of glycine in the production process known as Strecker reaction, whose synthetic route is shown below:

$NH_3 + H_2C{=}O \rightarrow HN{=}CH_2 + H_2O$
$HN{=}CH_2 + HCN \rightarrow NH_2CH_2CN$
$NH_2CH_2CN + H_2O \rightarrow NH_2CH_2CONH_2$
$NH_2CH_2CONH_2 + H_2O \rightarrow NH_2CH_2COOH + NH_3$

Aminoacetonitrile has been already detected toward the giant molecular cloud Sagittarius B2 (1). Its vibrational ground-state rotational spectrum has been characterized in the laboratory up to 1.3 THz (2). Aminoacetonitrile has a few low-lying (below 400 cm^{-1}) vibrational excited states (3) and rotational transitions within these states may be observed in hot cores and circumstellar shells. In this study (4), the pure rotational transitions in the 3 lowest vibrational states have been assigned and analyzed in the range 80-450 GHz. It was found very important to include Coriolis coupling between the two lowest vibrational fundamentals, while the other one resulted unperturbed. The spectral data of these vibrational excited states are essential for future observations of the molecule in relatively high kinetic temperature conditions.

Another molecule of astrochemical interest is the dimerization product of hydrogen cyanide, C-Cyanomethanimine (HN=CHCN), that is thought to play an important role as intermediate in the prebiotic formation of purines and proteins. In fact, hydrogen cyanide tends to polymerize, giving biologically important molecules such as adenine (pentamer of HCN) (5). C-Cyanomethanimine exists in two isomeric forms, *Z* and *E*. Although the (*E*)-C-cyanomethanimine is about 210 cm^{-1} less stable than the (*Z*)-C-Cyanomethanimine (6), the former has been detected through radio-astronomical observation (7) in the star-forming region (Sgr)B2(N), while no detection for the latter has been claimed so far. For its astrophysical interest and because its rotational spectrum has been investigated only below 100 GHz, the study of this molecule is being extended to higher frequency (millimeter and sub-millimeter wave regions) in order to facilitate astronomical detection. The sextic centrifugal distortion constants for both isomers of C-Cyanomethanimine were evaluated by means of highly accurate *ab initio* calculations (8). Therefore, the assignment of the rotational spectrum above 200 GHz can rely on accurate predictions.

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Should we Introduce Pre-equilibria into Markov Models for Homogeneously Catalyzed Copolymerization?

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Polyolefin elastomers based on ethene and propene are important players in the field of synthetic rubbers and the molecular features that control bulk properties are strictly related to the monomer distributions along the chains (1). Usually, the chemical reactivity of a propagating chain is considered to depend only on the identity of monomer units at the growing end. Two reactivity ratios, $r_1$and r_2, were thus defined starting from the kinetic expressions for the uncontrolled radical mechanism in order to describe the radical copolymer micro-structure; mathematical models (e.g. Mayo-Lewis, Fineman-Ross and Kelen-Tudos) derived from such approach have also been exploited to characterize homogeneous catalyzed copolymers despite the latters could present a more complicated mechanism, involving coordination pre-equilibria (2,3).

In this study, we describe a theoretical study of E/P copolymerization by a C_2-symmetric metallocene catalyst, *rac*-Me_2C-Ind_2ZrCl_2 via a synergic DFT/kMC approach offering a robust alternative interpretation of homogeneously catalyzed copolymer process: the mechanism consists of at least two steps, equally important, namely coordination and insertion. If this holds, the application of Markovian models to copolymerization induced by homogeneous catalyst might request extreme care, as they hinge on the mechanism proposed for uncontrolled radical polymerization, which neglects coordination and pre-equilibria.

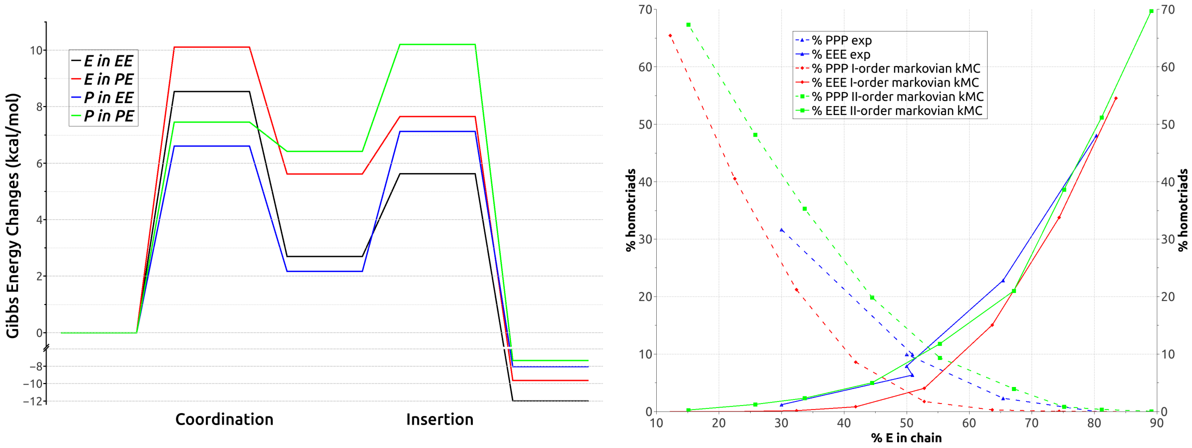

Figure 1. Left, a typical reaction pathway composed of coordination and insertion; right, comparison of experimental and kMC-simulated EEE and PPP triads.

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Intermolecular Energy Transfer in Real Time

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Essential state models (ESM) have been successfully used to describe low-energy optical properties (1,2,3) of different classes of charge-transfer (CT) chromophores, namely dipolar (D-A, where D=donor and A=acceptor of electrons), quadrupolar (D-A-D or A-D-A) and octupolar (A(-D)3 or D(-A)3) chromophores.

Here we introduce a truly dynamical and non-adiabatic model for resonant energy transfer (RET). More precisely, we consider two different dipolar chromophores, an energy donor ($\mathcal{D}$) and an energy acceptor ($\mathcal{A}$), their main resonating structures being used as electronic basis states and introducing the coupling to one effective molecular vibration per chromophore.

By means of a non-adiabatic dynamical calculation also accounting for energy dissipation, we follow in real time the complete $\mathcal{D}$-to-$\mathcal{A}$ energy transfer process (fig.1, panel a). Coherent oscillations of $\mathcal{D}$* as induced by an ultrashort light pulse are washed-out in the few hundred femtoseconds by fast intramolecular energy dissipation, while the $\mathcal{D}$*-to-$\mathcal{A}$ energy transfer process takes place in the following few picoseconds (fig.1, panel b). The whole process is followed through time-dependent fluorescence spectra (fig.1, panel c).

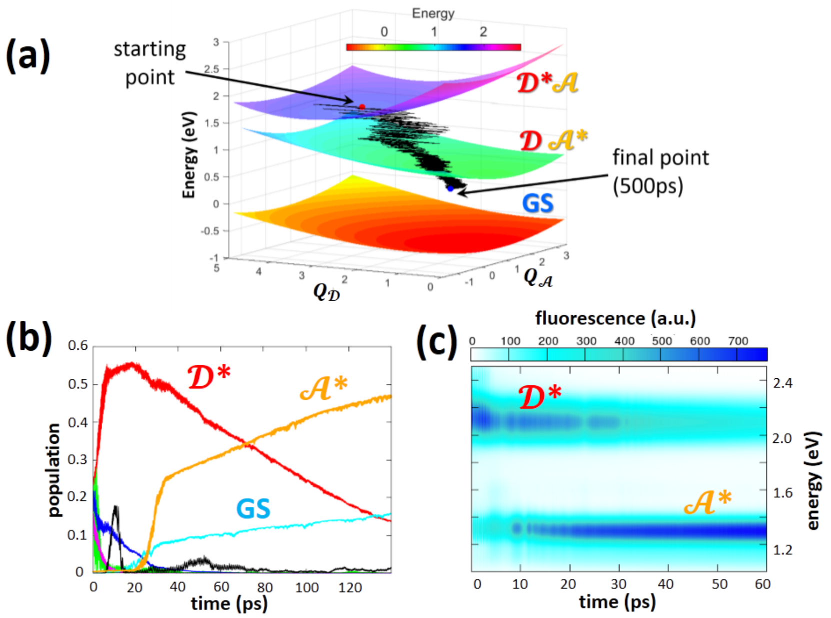

Fig. 1. Energy transfer in real time. Panel a: non-adiabatic $\mathcal{D}\mathcal{A}$ dynamics following impulsive excitation of $\mathcal{D}$; to help the eye, relevant adiabatic energy surfaces are also shown. Panel b: population time-dependence plotted for some relevant $\mathcal{D}\mathcal{A}$states. Panel c: time-dependent fluorescence spectra for the $\mathcal{D}\mathcal{A}$ system.

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Proton Mobility in Protic Ionic Liquids: New Results from Theoretical Calculations

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Ionic liquids (ILs) are salts made by bulky, sterically mismatched molecular ions that possess a low melting point because the electrostatic interactions are weakened by charge delocalization and lattice formation frustrated by geometric effects. In contrast to traditional organic solvents, ILs possess negligible flammability and volatility and represent a new class of "green" solvents that are inherently safer than conventional solvents. A Protic Ionic Liquid (PIL) is formed through an acid base reaction. When the difference of pKa between the acid and the conjugate acid of the base is large (>10 pKa units) the ensuing liquid is completely ionized. In this case, the acidic proton is transferred quantitatively from the acid to the base during the synthesis reaction and turns out to be strongly bound to the latter. Subsequent proton transfer is therefore not possible. Conduction in these liquids is therefore due to ion drift (Walden mechanism) and inversely proportional to the liquid viscosity. In order to have a larger conductivity one has to find a way to promote the formation of different charge carriers. One possibility is to have proton transfer from one molecular ion to another. Compounds where amino acids in their deprotonated (anionic) form are combined with inorganic cations such as [Ch][Asp] and [Ch][Cys] might have these features. The former has a weak acid terminal, while the latter has a weak basic proton attached to the sulphur atom. We will show evidences of a non-ordinary behavior of these two materials that have been obtained by carefully validated ab-initio and classical molecular dynamics simulations [1].

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Computational Tools for the Interpretation of Rotational Spectra within the Virtual Multifrequency Spectrometer

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Spectroscopic techniques provide a wealth of qualitative and quantitative information on the chemical and physical-chemical properties of molecular systems, in a variety of environments. However, the interpretation of experimental data is often a difficult task mainly because the observed spectroscopic properties depend on the subtle interplay of different effects, whose specific impact on the overall behavior is difficult to address. From this point of view, theoretical approaches are invaluable tools for guiding andcomplementing experiment as well as supporting the interpretation of spectra. For this reason, measurements are increasingly supported by theoretical studies, and computational spectroscopic techniques have become essential tools for understanding spectra in terms of basic physical-chemical process.The widespread use of computational spectroscopy has prompted the development of a virtual multifrequency spectrometer (VMS), which gives access to the latest developments in the field of computational spectroscopy also to non-specialists (1-4). In addition to the computational module (VMS-Comp), which provides the support for a wide range of spectroscopic techniques, it features VMS-Draw. This is a multiplatform graphical user interface (GUI), which offers to the user a powerful integrated environment for processing the outcomes of quantum-chemical calculations and visualizing the relevant information in an intuitive way. In addition, VMS-Draw includes a panel of advanced tools for the comparison of theoretical and experimental spectra, thus assisting their interpretation. In this contribution, we present VMS with particular attention to its newborn rotational spectroscopy module, VMS-Rot. VMS-Rot has been specifically designed for guiding the assignment and interpretation of rotational spectra: from the assignment of the observed transitions to a set of quantum numbers, as well as their fitting with a given model Hamiltonian, to the prediction and simulation of the whole spectrum. Given the general philosophy of VMS and the leading role played by quantum-chemical calculations in modern rotational spectroscopy, unlike other software supporting the analysis of MW spectra, VMS-Rot is intimately related to theoretical calculations, to be used as a starting point for guiding experiments and spectral interpretations. VMS-Rot is composed of four closely related modules, namely (i) the computational engine that allows spectroscopic parameters to be computed from first principles; (ii) the fitting-prediction engine that allows the refinement of the spectroscopic parameters, based on the assigned transitions, and the calculation of the simulated spectrum. (iii) the GUI that allows the comparison between theoretical and experimental spectra, aided by a number of advanced features for spectra manipulation and (iv) the assignment tool that takes care of the assignment of the rotational spectrum recorded experimentally by comparison with the simulated one. An overview of the range of applicability of VMS-Rot is given in order to demonstrate how this module of VMS represents a one-pot solution for the analysis of rotational spectra based on the interpretation of experimental measurements supported byquantum chemical simulations.

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A Spotlight on the Complex Hierarchical Structure of Some Ionic Liquid-Molecular Liquid Binary Mixtures

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Ionic Liquids (salts with melting point below 373K) are a class of compounds that are being intensively studied because of their peculiar properties(1). Being neat ions in the liquid phase, they exhibit almost zero vapour pressure, high viscosity, high conductivity, wide electrochemical window and low flammability. While it is possible to find a relatively wide literature for these neat chemicals, works on their mixtures are just about 14% of the total and only ~1% concerning structural properties. These mixtures are innovative materials that are recently reported as even more versatile and cheap than pure ILs. The structure of many neat ILs consists of two segregated micro-domains percolating each other: one is polar and the other is non-polar. This organization, often called "sponge like", is at the basis of the characteristic low-q peak in the SAXS patterns (~2-7 nm^{-1}) (2). Adding a second substance into the IL forces some rearrangement in its structure, affecting the domains, for example water enlarges the polar domain, while hexane does so in the apolar. The recent discovery (3) of a more complex structure hierarchy in some ethylammonium nitrate (EAN) + methanol mixtures, opened a new debate on the properties of ILs and the potential applications of such mixtures. A cluster-like organization was suggested then, while almost at the same time Atkin et al. (4) observed the same odd feature in other IL mixtures with longer n-alcohols. They interpreted the "Low q Excess" (LqE) as the fingerprint of self-assembled structures. Recently wehave shown that the LqE can be found not only when the co-solvent is amphiphilic (as reported so far), but also when it is highly symmetrical, regardless if the compound is polar or almost apolar. We had the experimental evidence of LqE in EAN+1,4-diaminobutane and EAN+1,2- dimetoxyethane mixtures(5). These molecules cannot self-assembly, thus confuting the hypothesis from Atkin et al.. The results collected using synchrotron radiation together with MD calculations enable us to state that the LqE arise when the mixture is preparing to demix, and is undergoing strong density fluctuations. This appears to be a general behaviour, and not strictly linked to the polar/apolar nature of the co-solvent. Our models are suggesting that some supramolecular structures can be found in the samples showing the LqE.The understanding of the driving force behind this large-scale hierarchical organization could open new landscapes for ionic liquids applications.

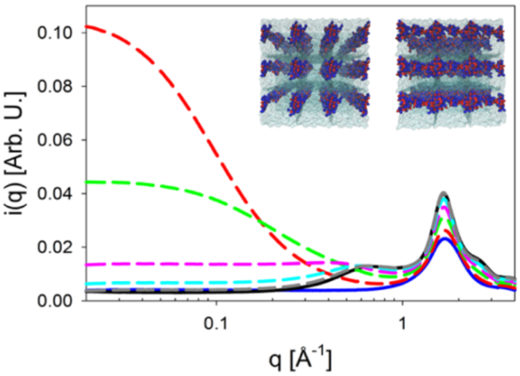

Figure 1: SAXS patterns for ethylammonium nitrate+acetonitrile mixtures. In the inset two snapshots of the simulation box for the mixture with the highest "Low q Excess".

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Fluorous Mesoscopic Domains in Room Temperature Ionic Liquids.

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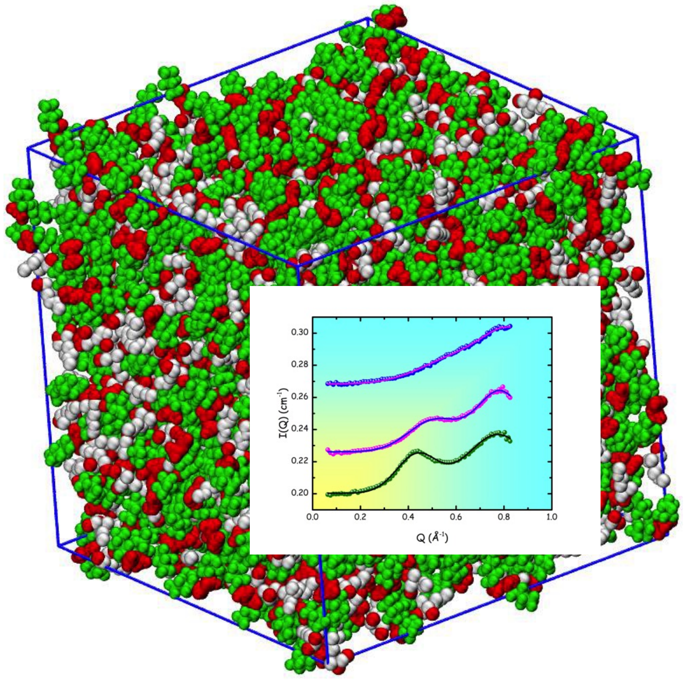
Room temperature ionic liquids (RTILs) are compounds composed solely of ionic species. Recently attention is focusing on the interesting properties of fluorinated RTILs that find application in separation, pharmacology, catalysis etc and show an appealing blending of ionic liquid specific properties and fluorous moieties induced features. Among the relevant properties highlighted in FRTILs, the possibility that fluorous moieties might segregate analogously to their alkyl counterparts in conventional RTILs has been proposed in the past [1–6]. So far however, no direct experimental evidence for such a behavior has been provided.



Simulation box of fluorinated RTILs, highlighting the different alkyl, fluorous and charged moieties.The inset data sets refer to neutron scattering data set collected as a function of the fluorous tail length. [Adapted from Ref. 7 with permission from the PCCP Owner Societies.]

Here we provide the first direct experimental evidence that RTILs bearing a long enough side fluorous chain are characterized by the occurrence of a well-defined mesoscopic organization, consistent with the segregation of the fluorous tails. [7] By exploiting the synergy between x-ray and neutron scattering coupled with state of the art Molecular Dynamics simulations, we will discuss several consistent examples where such a phenomenology has been observed.

We envisage an important role played by these self-aggregating domains of fluorous moieties in determining specific performances in the fields of separation, catalysis and related fields.

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Supramolecular Organization of Water–Ethanol Solution in Ferrierite under Pressure

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Turning disorder into organization is a key issue in science. In particular, supramolecular organization induced by external stimuli has opened new paths for the bottom-up fabrication of nanostructures. By using a combined strategy based on the synergy of X-ray powder diffraction experiments and modeling studies (1), we showed that high pressure - in combination with the shape and space constraints of a hydrophobic all-silica zeolite - separate an ethanol–water liquid mixture into ethanol dimer wires and water tetramer squares (Figure 1).

Separation of ethanol from water was accomplished in an all-silica ferrierite (Si-FER), by using as pressure transmitting medium a mixture of (1:3) ethanol and water in the 0.20 to 1.34 GPa pressure range. The system was studied in situ by high-pressure synchrotron X-ray powder diffraction at BM01 beamline at ESRF and refined via first principles modeling.

Upon separation, the confined supramolecular blocks alternate in a binary two-dimensional architecture that remains stable upon complete pressure release. These results support the combined use of high pressures and porous networks as a viable strategy for driving the organization of molecules or nano-objects towards complex, pre-defined patterns relevant for the realization of novel functional nanocomposites and highlight the need of appropriate modeling for an atomistic level understanding of complex phenomena.

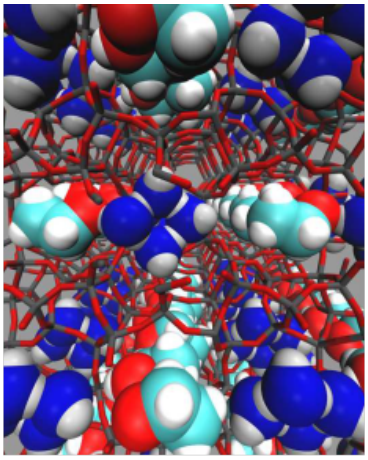

Figure 1.

(1)Arletti, R., Fois, E., Gigli, L., Vezzalini, G., Quartieri, S., Tabacchi, G. (2017) Angew. Chem. Int. Ed. 56, 2105,DOI: 10.1002/anie.201700219

Contributi Poster

Methods for Time-Resolved Vibrational Analysis from Ab-Initio Molecular Dynamics Simulations

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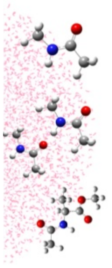
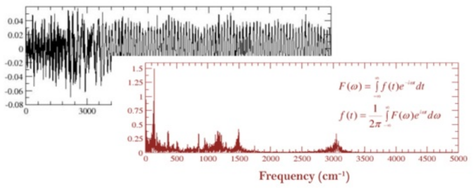
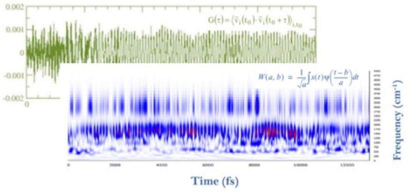
Advanced time resolved and non-linear vibrational spectroscopic techniques, such as time-resolved Fourier Transform Infrared, two-dimensional Infrared and Femtosecond Stimulated Raman Spectroscopy,(1,2) are powerful tools to characterize in detail the structure and the dynamics of molecular systems in condensed phase. Plenty of information is provided by interpreting trends in the time of vibrational features, which are subtle probes of structural motifs and reaction mechanisms. Indeed, the connection of the spectroscopic data with the structural and the dynamical features is far to be an easy task. The computational vibrational spectroscopy can provide a valuable support due to its predictive-interpretative character. However, standard techniques are aimed at the solution of the quantum vibrational problem, as alternative, very promising are those computational protocols based on the analysis of molecular dynamics simulations of large molecules in condensed phase and at finite temperature. In this contribution we present the development and the validation of a novel theoretical-computational method to perform time-resolved vibrational analysis on peptide benchmarks in aqueous solution. This method(3) is based on the Wavelet Transform(4) of suitable time dependent signals obtained through ab-initio molecular dynamics.(3,4) The Wavelet protocol, unlike the Fourier Transform, allows for the accurate localization in the time domain of a given vibrational band, thus monitoring frequency fluctuations, anharmonicity and vibrational modes coupling. We focused on three models presenting several vibrational fingerprints of peptides: the Methyl-2-Acetamidopropanoate,the trans-N-MethylAcetamide and the non-covalent dimer in both gas and explicit water phase.(5-9) Once sampled the AIMD trajectories in ground electronic state,(10,11) the time dependent signals were then Wavelet transformed to get generalized normal-modes and time-resolved vibrational spectra directly comparable to those provided from modern vibrational spectroscopies.(12,13) We were able to reproduce accurately many vibrational signatures of the systems (fundamental, overtone and combination bands), including the vibrational frequencies, the qualitative vibrational coupling, reproducing also the characteristic solvent-induced frequency shift and line broadenings. Importantly, we were able to interpret these features in terms of a clear correlation between structure and spectroscopic behavior. In conclusion, we obtained a very good agreement with both the experimental results and the data that is possible to calculate with standard approaches.(5-9)







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Experimental and Theoretical Investigation on the Catalytic Generation of Environmentally Persistent Free Radicals from Benzene

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Environmentally Persistent Free Radicals (EPFRs) are toxic products deriving from incomplete combustion processes and are able to generate DNA damage and pulmonary dysfunction. They are formed on particulate matter through interaction with aromatic hydrocarbons, catalyzed by transition metal oxides, and produce reactive oxygen species (ROS) in aquatic media. The processes are already described for substituted aromatic molecules, e.g. phenol (1), not for unsubstituted aromatic systems, such as benzene.

Here we present an experimental and computational investigation, based on cluster and periodic computational models, of the reaction of benzene with molecular oxygen in the presence of Cu_xO/SiO_2 (2).

The computational study was performed, at the Density Functional Theory (DFT) level with the hybrid functional B3-LYP, on a cluster model consisting in a Cu(I) center embedded in the silica matrix that mimics the case of totally dispersed metal centers on silica; the periodic calculations, performed at the DFT level with the PBE exchange-correlation density functional,investigated the reactivity of a whole crystalline surface of Cu_2O. Both approaches converge to the same picture of the reaction mechanism: the activation of O_2 by interaction with silica–coordinated Cu(I) centers leads to a peroxy species that yields the phenoxy radical upon reaction with benzene;dissociation of OH• radical eventually allows for the recovery of the catalyst.

The experimental characterization of the Cu_xO/SiO_2 catalyst regarded morphology, crystal structure, copper electronic state, and crystal field around Cu(II). Electron paramagnetic resonance (EPR) spectroscopy revealed the formation of phenoxy radical entrapped in the catalyst upon reaction between benzene and Cu_xO/SiO_2. Moreover, ESR investigation of ROS in aqueous solution evidenced the generation of OH• radicals by benzene–contacted Cu_xO/SiO_2. All the experimental results nicely fit the outcomes of the computational models.

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Hyperbranched Ethylene Oligomers by K2-(N,O)-Salicylaldiminato Ni(II) Complexes: DFT Investigation of Role of Remote Substituents

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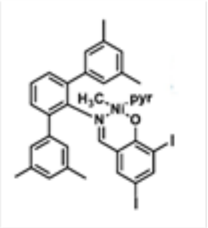
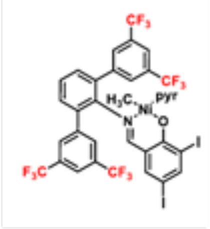
Beyond the extensively studied high molecular weight polyethylenes, ethylene oligomers are also of practical importance. Recently, neutral κ2-(N,O)-salicylaldiminato Ni(II) complexes showed to be promising candidates.(1,2) These Ni(II) catalysts convert ethylene to highly branched, low molecular weight oligomers. The microstructure of the polymer showed to be dependent on the catalyst structure and, in particular, on the size and on the nature of the ligand substituents (see Chart 1).(3)



1a
76 branches /1000 C; Mn = 1.1 × 10³ g/mol



1b
10 branches /1000 C ; Mn =1.6 × 10⁴ g/mol

Chart 1.

To clarify the role of the -CF3 groups, linear propagation, termination and branches formation mechanisms were studied theoretically.(4)

The results showed that the linear propagation and termination/branches formation mechanisms overlap until the ethylene coordinates with the chain in cis to the oxygen ligand. Then, the reaction proceed toward the new insertion or a monomer de-coordination. The de-coordination is the key step for a) B-H elimination and 2,1 re-insertion or b) chain transfer reaction. In the de-coordination transition state, the ethylene is replaced by η2 coordination of the ligand aromatic ring. Since the strength of the interaction between Ni and the aromatic ring strongly depends on the remote substituents of the ligand, by tuning these effects the structure of the polyethylene can be regulate.

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In Silico Identification of New Potential Antitubercular Drugs by The Multi-Target Approach

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The World Health Organization (WHO) reported that tuberculosis (TB) is one of the top 10 causes of death worldwide. In 2015 there were 10.4 million new TB cases, including 1.2 million among human immunodeficiency virus (HIV) positive people, and 1.4 million of deaths (1). The current therapy used to treat drug-susceptible *Mycobacterium tuberculosis* (Mtb) infection requires 2-month intensive phase of a four-drug cocktail containing rifampicin (RIF), isoniazid (INH), pyrazinamide (PZA) and ethambutol (EMB), followed by a longer continuation phase of RIF and INH. Infections with resistance to the two most efficacious frontline agents, RIF and INH, were classified as multidrug-resistant tuberculosis (MDR-TB) while the extensively drug-resistant tuberculosis (XDR-TB) is a form of TB which is resistant to at least four of the core anti-TB drugs. MDR-TB and XDR-TB require the use of second-line anti-TB drugs, which are more expensive and have more side-effects than the first-line drugs used for drug-susceptible TB. Moreover, a very common and deadly complication of TB is coinfection with HIV because RIF is a potent inducer of drug-metabolizing enzymes (e.g. CYP3A4) and patients are often forced to complete TB treatment before beginning HIV treatment (2).

It is evident the importance to discover and develop new antitubercular agents with novel mechanisms of action and a polypharmacological profile. *In silico* methods represent an alternative and innovative strategy to early identify new potential hit compounds. In particular, considering new promising antitubercular molecules under preclinical and clinical studies, a structure based virtual screening (SBVS) was performed using the most selective targets of Mtb deposited in the Protein Data Bank (3) with co-crystallized inhibitors. In order to discover new multi-target ligands (MuTaLig) the chemoinformatics platform of the homonymous European project (4) was taken into account for building the ligands library of the SBVS study. In addition, a database of FDA approved drugs was also screened, not excluding a possibility of discovering new antitubercular agents by a repurposing approach (**Figure 1**). For the promising hit compounds identified *in silico*, theoretical data of the binding affinity will be confirmed by enzymatic assays and *in vitro* test against Mtb models in order to confirm the ability to exert the predicted biological activity.

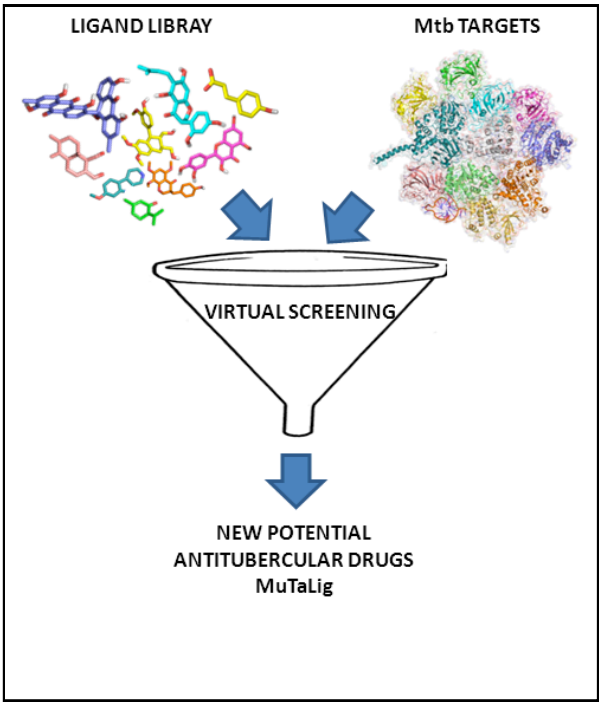

Figure 1. workflow of the *in silico* virtual screening study

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To Swell or to Shrink? Alkylammonium Alkanoates plus Molecular Solvents

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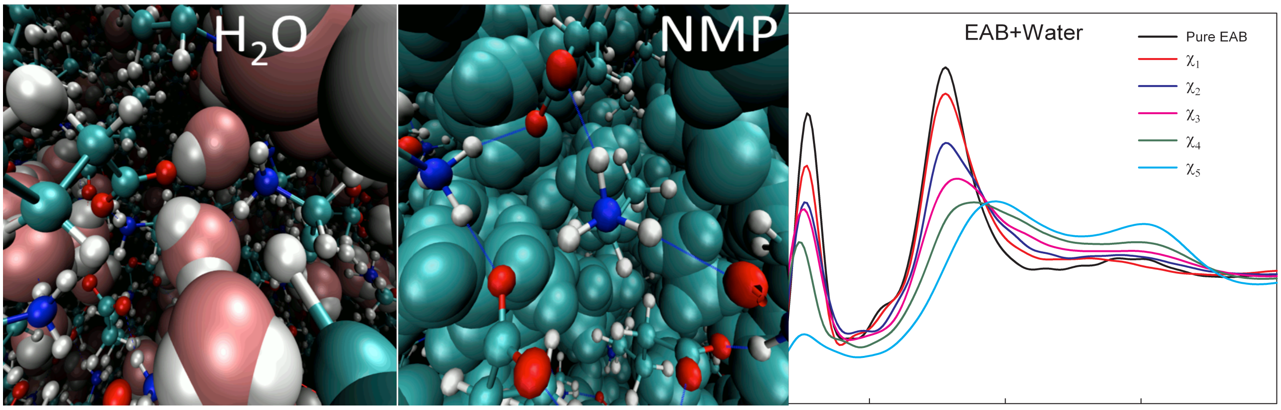
Aggregation in ILs is a phenomenon by which either or both the cations and anions interact with each other in solution to form local, highly charged phases. Most of the ionic liquids exhibit an intermediate range order ofsegregated polar and nonpolar domains, similar to surfactantaggregation, which can be pointed out in small-angle X-Ray scattering (SAXS)or neutron scattering (SANS) patterns in the form of pre-peaks. The scattering intensity of the pre-peak depends on the polarity alternation and is high when either cations or anions bear long alkyl chains, and becomes stronger when the alkyl chains are present on both ions. It has been noticed in **alkylammonium alkanoate**ionic liquids ($[N000_n][C_mCO_2]$) that ***mesoscopic*** order can be observed in the system when the alkyl chain ofcation and anion contains at least two or more carbon atoms (1).Theeffect of water and othercosolvents on ionic liquid structure has already been reported for 1,3-dialkylimidazolium ionic liquids (2), showing, for instance, that the liquid phase aggregates can be disrupted or broken at high shear rates orat high concentrations of water, that viscosity falls down very rapidly, and that the Newtonian behavior is recovered, showing that no aggregates are present. Recently, we have also shown that, at given concentration ratio, in the ethylammonium nitrate-DME solutions the peculiar critical phenomenon of "low-Q excess" shows up (3,4), indicating that the behavior of these systems is hardly predictable.



In this communication, we concentrate on the X-Ray properties of water solutions of different alkylammonium alkanoate liquids (n=3,4; m=2,3), that were compared with the nitrate analogous, and with the solutions of Ethylammonium butanoate ($[N_{0002}][C_3CO_2]$) with water and another polar solvent, N-methylpyrrolidone. In the first case, we show that: the scattering pattern is independent of the m-n sequence (4+3=3+4), and that the dilution of the alkanoate solution gives a marked system swelling, while a compaction is observed using the nitrate anion; in the second case, we point out how the different behavior of water vs NMP: water causes the swelling of the system (indicated by the shift of pre-peak towards lower Q values), NMP gives the opposite effect, signaling that the excluded volume of the big NMP molecule leads to the segregation of the ions.

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Can Ionic Liquids Support Grotthuss-like Proton Transfer? A Preliminary Study

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Ionic liquids (ILs) represent an interesting new type of solvents and have been the subject of a large number of studies in the last decade. The fact of being pure liquid electrolytes at room temperature gives them unique characteristics: thermal stability, negligible vapor pressure, hygroscopicity, extreme viscosity and low thermal and electric conductivity.

Various classes of ILs have been studied but we focus on a special subset of these compounds consisting of choline [Ch+] and anionic amino acids [AA-]. Some of these ILs showed an intriguing possibility that consists in the ability to transfer a proton between two anions (1). A condition is required: the side chain of AAs must have an "acid" proton (like Cys and Asp)
to allow the proton transfer (PT) to take place.

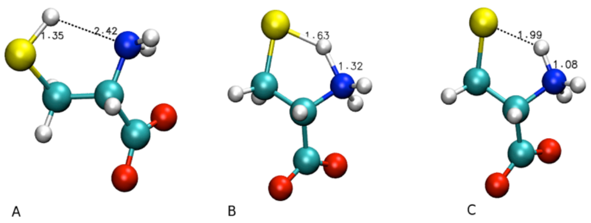

Figure 2.Example of structures for anion [Cys]. The Structure A represents the anionic form, B the transition state and C the final product (a zwitterionic anion).

The presence of this phenomenon suggested the possibility for an IL to improve its typical low conductivity through a controlled and concerted proton migration. In order to provide robust evidence for this behavior, we studied the physical condition under which the PT can take place. In this work, we focused on the study of stable geometries and energy barriers for an intramolecular and intermolecular PT. The starting molecules are the AAs with acid side chain (Cys, Sec, HomoCys, Asp and Glu). These type of calculations have been carried out at MP2 and B3LYP level (see Figure 1). The most promising results arise from Asp and Glu, where the transition state energy is only few kcal/mol.

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First-Principles Study of Co and Cu-based Electrolytesfor Dye-Sensitised Solar Cells

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Since the pioneering work by 'O Regan and Grätzel (1),dye–sensitized solar cells (DSSC) have attracted great academic and industrial interests as promising technology in solar energy conversion thanks to low manufactural costs, eco-friendly materials and high efficiency under diffuse light conditions. The chemical complexity of these devices, which is inherent to the electronic processes involved at semiconductor/dye/electrolyte interfaces, represents a great challengefor the effective design and engineering of DSSC devices with high photo-conversion efficiency (PCE) (2).

State-of-the-art devices have PCE at ~14% with metal-organic dyes on mesoporous ZnO or TiO_2 n-type semiconductor, but there is still room for improvement. Beside the optimization of the dye-electrode interface, several research groups are addressing the role of the electrolyte and possible alternatives to the most exploited I_3^-/I^- redox couple:latest efforts have focused on one-electron redox systems based on metal-organic complexes with Co(II/III) and more recently with Cu(I/II), which can overcome the problems of the twoelectron process of the triiodide/iodide: corrosiveness, competitive light absorption and large internal potential losses (3).

The aim of this work is providestructural and electronic insights at the dye–electrolyte interfacein DSSCs. We characterizedwith first-principles methods the new organometallic complexes as possible one-electron redox mediators (4) and their interactions with push–pull organic dyes. In particular, we investigated the structural and electronic features of several cobalt-based complexes(5) andcopper-based complexes, which have recently shown to outperform Co-based ones due to a minimum steric hindrance that avoids mass-transport limitations (6). Here wereport the computed redox potentials and reorganization energies for each Co(II/III) and Cu(I/II) couple in order to understand how the ligands can tune these important parameters for the electron transfer processes. These results are discussed together with the electronic properties of the push-pull dyes used in n-type and p-type DSSCs in order to predict and assess the most promising combinations of dye-electrolyte couple for the foreseen development of tandem-DSSCs.

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Molecular Dynamics Simulations of Amyloid-beta Fibrils for Alzheimer's Theranostic Applications

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Alzheimer's disease (AD) affects tens millions of people only in the US after their 65 causing to patients a progressive memory loss, cognitive deprivation and death(1). Extracellular proteic plaques formation on brain is the typical hallmarks of AD mainly made by amyloid-β (Aβ) fibrils. Aβ fibrils are peptides with a length from 39 to 43 amino acids and appear in two major isoforms that differ only for two amino acids on the C-terminus: Aβ40 and Aβ42(2). A single fibril monomer is structurally a region of amorphous residues followed by a β-sheet stretch, called "beta-1", an elbow and a second β-sheet called "beta-2" anti-parallel to beta-1 (obtaining an U-shape monomer), which is stabilized by a salt bridge between D23 and K28(3).The fibril is made by parallel β-strands where β-sheets are perpendicular to the fibril axis and adjacent monomers are stabilized by hydrogen bonds(4). Fibrillar amyloid-β structures grow in two distinct way: a growth along the fibrillar axis is obtained adding Aβ monomers to the ends(elongation) and the lateral binding of two fibrils along the fibril axis (thickening), which brings to a close packed fibril(4). However, other mechanisms have been found and a deep understanding of the tertiary fibrillar structure is still lacking(5).

We used classical Molecular Dynamics simulations to study how coated-nanoparticles and small molecules interact with long Aβ fibrils in order to gaining insight for the design of new agents for early diagnosis and therapeutic applications. The results obtained showthat their ability of binding to the β-sheets regions and to inhibit fibrillation depending on the coating, nanoparticle dimensions and the small molecules substituents.

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Vibrational Fingerprints of a Promising Mimic of the Oxygen Evolving Complex

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FTIR spectroscopy has been widely applied to the mechanistic characterization of both the Photosystem II (PSII) oxygen evolving complex (OEC) and the Mn-based water oxidations catalysts (WOCs) employed in artificial photosynthetic devices. In particular, the low-frequency (< 1000 cm^{-1}) region is able to provide direct electronic and structural information about WOCs Mn clusters, because it includes many Mn-ligand and Mn-substrate bands which are sensitive to cluster geometry and to the oxidation state of Mn metal centers. (1,2)

The spectroscopic characterization of the oxidized S_n intermediates (n = 2, 3, 4) of natural and artificial WOCs catalytic cycles has been proved quite challenging so far, due to the difficulty in obtaining and stabilising such states. Moreover, the assignment of the IR bands often turned out to be not simple. Therefore, a theoretical approach based on the simulation of IR spectra can be useful to support bands assignments and to validate the structures proposed for the S_n intermediates. In this work we have simulated the low-frequency IR spectrum of a synthetic calcium-tetramanganese $[CaMn_4O_4(t\text{-}BuCOO)_8(t\text{-}BuCOOH)_2(py)]$ complex (t-Bu: tert-butyl, py: pyridine) developed by Zhang and co-workers, characterized by a cubane-like $[CaMn_4O_4]$ cluster. (3) Beside the striking structural similarity with the native PSII OEC, also the main electronic features of the OEC reactivity appear to be well reproduced by this system, as shown by previous theoretical studies. (4)

A good reproduction of the experimental IR spectrum has been achieved, allowing a straightforward assignment of the observed low-frequency IR bands. In particular, in the 400-750 cm^{-1} spectral region, as expected, $[CaMn_4O_4]$ cluster vibrational modes have been observed, together with t-$BuCOO^-$ and py bending modes.

The evolution of $[CaMn_4O_4]$ cluster and Mn-ligand modes along the catalytic cycle has been then evaluated. IR spectra have been computed for every S_n intermediate (n = -1, 0, 1, 2, 3) in its high-spin state. The comparison of calculated spectra has shown that the position and intensity of most low-frequency IR bands are sensible to the oxidation state of the Mn metal centers. Moreover, IR bands active only for specific $S_n$states and so having a potential diagnostic relevance have been identified. The insights given by our theoretical approach suggest a structural flexibility of $[CaMn_4O_4]$ cluster along the OEC catalytic cycle and provide spectroscopic fingerprints of the different $S_n$intermediates, which can support the interpretation of experimental spectra.

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Brominated BODIPY as Possible Photosensitizers in Photodynamic Therapy

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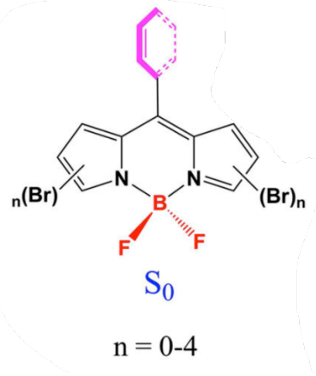
Photodynamic therapy (PDT) is an anti-cancer treatment modality, clinically approved, based on the interaction of light, a photosensitizing drug, and oxygen. PDT is commonly practiced in the treatment of a number of cancers (neck, lungs, bladder, and particular skin cancers)and is more selective (the drug can be given directly into the organ). Upon irradiation, the photosensitizer becomes excited and this energy is transferred to ground-state triplet oxygen ($^3O_2$). If the amount of transferred energy is higher than 0.98eV, highly reactive singlet oxygen ($^1O_2$)is formed, leading to cell death (referred to as Type II PDT mechanism). Different compounds are now used as photosensitizers, including phthalocyanine, chlorin, bacteriochlorin, porphyrin derivatives etc. A potential candidate induces light sensitivity in the region of 600-900 nm, the so called "therapeutic window", produces a good singlet oxygen quantum yield (Φ_Δ) and therefore a high intersystem spin crossing probability between the excited S_1 and the T_1 electronic states.In recent years, new sensitizers have been studied such as boron-dipyrromethane complexes (BODIPY) and their aza derivatives and, in order to enhance spin-orbit coupling, heavy atoms, as Br (1)andI, have been incorporated. In this study the role that can be played by heavy atoms (Br) in influencing the photosensitizing properties of BODIPY dye8-phenyl boron-dipyrromethane (Scheme) hasbeen investigated by means of density functional theory (DFT) and its time-dependent formulation (TDDFT).

Scheme



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Unveiling the Adsorption Interaction of Glycolaldehyde on TiO_2 - Anatase (1 0 1) by Quantum Chemical Calculations

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The knowledge of the chemical species that are present in the Universe and in the interstellar medium (ISM), as well as of the reactions involving them, is of fundamental importance for understanding the elementary reactive steps toward chemical evolution. Among the 200 molecules discovered up to now in interstellar and circumstellar shells, Glycolaldehyde (GA) is the smallest monosaccharide detected in the ISM. GA is an important prebiotic molecule, since it is an intermediate in the formose reaction that leads to the synthesis of sugars up to ribose, the principal constituent of RNA. Understanding how simple organic molecules may evolve toward the biochemical building blocks of life in space or in a primeval Earth is one of the main concerns of astrochemistry. For this purpose, it has been recognized that mineral surfaces play an important role in the synthesis of more complex molecules starting from simple precursors (1,2) and TiO_2 represents a catalytic substrate where these processes can take place (3).

In the present work, the adsorption of GA over the surface of TiO_2 - anatase (1 0 1) is deeply investigated from both theoretical and experimental points of view. Theoretically, six adsorption configurations are modeled by periodic density functional theory (DFT) calculations, and for each of them, structural, energetic and vibrational properties are calculated. The proposed configurations differ for both the orientation of the GA molecule with respect to the anatase (10 1) and for the atoms involved in the adsorbate – substrate interaction. Experimentally, infrared spectra of GA adsorbed on TiO_2 are recorded by Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy coupled to the use of a properly suited environmental chamber for *in situ* operations (4). Theoretical simulations are compared with experimental observations in order to get insights into the mechanism of GA adsorption on the TiO_2 surface. The interplay between theory and experiment shows that the interaction between GA and TiO_2 takes place provided that both carboxylic and hydroxyl groups of the molecule are involved in the anchoring to the TiO_2 - anatase (1 0 1) surface. Further, quantum mechanical simulations suggest GA activation through the formation of highly reactive species on the solid surface.

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First-Principles Study of the Lanthanum Ferrite Surface Chemistry Toward Oxygen Evolution/Reduction Reactions

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Perovskite oxides are object of considerable interests by academic and industrial research groups, especially those that show mixed ion-electron conductor properties (MIEC)(1) and can be used as air-electrode in intermediate-temperature solid oxide fuel/electrolyzer cells (SOFC/ECs) (2).

Here we present an *ab initio* study of the oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) at the (001) surface of the Fe-based perovskite $LaFeO_3$. In particular, we used density functional theory plus U (DFT+U) to analyze the factors governing the OER/ORR potential determining steps. We characterized the minimum-energy geometries of OER/ORR reactants, intermediates and products on the FeO_2-terminated $LaFeO_3$ (001) surface. Furthermore, we evaluated the role on OER/ORR catalytic mechanism of oxygen vacancies in the topmost layer of the $LaFeO_3$ (001) slab. To model the electrocatalytic reaction pathways, we considered proton-coupled electron transfer steps, according to the simple and effective approach based on the theoretical standard hydrogen electrode as proposed by Nørskov and co-workers.(3) With our *ab initio* results we have thus assessed the best model for the prototypical $LaFeO_3$ (001) surface.

In conclusion, we performed first-principles periodic DFT+U calculations to analyze the physic-chemical properties of a prototypical airelectrode. Our results pave the route toward the development and rational design of new Fe-based perovskite oxides for application as electrocatalysts for solid oxide electrochemical cells.

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