

WINTER MODELING

on Valentine's Day

SECOND EDITION - February 14-15, 2022

Winter Modeling on Valentine's Day (... and the day after)

Complesso SS. Marcellino e Festo

Largo S. Marcellino, NAPOLI

BOOK of ABSTRACT



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8:30 Registration

9:00 Opening Speech – Luigi Paduano & Nadia Rega
Università degli Studi di Napoli Federico II

DAY 1
14/02

Session I – Session chair : Nadia Rega

9:10 **MARIA CRISTINA MENZIANI** – Università di Modena e Reggio Emilia
Keynote A *Understanding Crystal Nucleation in Glasses by Computational Simulations*

9:50 **FRANCESCA TONOLO** – Alma Mater Studiorum Università di Bologna
Talk 1.1 *Extending the Applicability of the Semi-experimental Approach by Means of “Template Molecule” and “Linear Regression” Models on Top of DFT Computations*

10:10 **FEDERICA LODESANI** – Università di Modena e Reggio Emilia
Talk 1.2 *Mixed Alkali Effect in Aluminosilicate Glasses: Assessing the Best Interatomic Potential Models*

10:30 **ANDREA DELLA LIBERA** – Politecnico di Milano
Talk 1.3 *Automation of Variable Reaction Coordinate Transition State Theory and Application to Methyl-Vinyl Ketone, 2- and 3- Butenal Decomposition*

10:50 **MARIAGRAZIA FORTINO** – Università "Magna Græcia" di Catanzaro
Talk 1.4 *Multi-replica Biased Sampling for the Design of Photoactive Chiral Nanomaterials*

11:10 *Coffee Break*

DAY 1
14/02

Session II – Session chair : Mattia Melosso

11:30 **SILVIA ALESSANDRINI** – Scuola Normale Superiore
Talk 2.1 *Simulating the Gas-Phase Reaction between Oxirane and the CN Radical in Interstellar Conditions*

11:50 **ANGELA PARISE** – Università della Calabria
Talk 2.2 *Attosecond Dynamics Simulations of Glycine and Poliglycine Irradiated by α -Particle*

12:10 **FULVIO PERRELLA** – Scuola Superiore Meridionale
Talk 2.3 *New Computational Approaches for Molecular and Electronic Dynamics*

12:30 **MASSIMO CHRISTIAN D'ALTERIO** – Università di Salerno
Talk 2.4 *Moving from α -olefins Transition Metal Catalysis to Biodegradable Materials: Insight from DFT Calculations*

12:50 **ANNA ROVALETTI** – Università di Milano - Bicocca
Talk 2.5 *Unravelling the CO Oxidation Reaction Mechanism of Mo/Cu CO Dehydrogenase by Means of QM/MM Calculations*

13:10 **IDA RITACCO** – Università degli Studi di Salerno
Talk 2.6 *A DFT Investigation of Substitutional and Interstitial Nitrogen (N)-Doping Effects on a ZnO(100)-TiO₂(101) Heterojunction*

13:30 *Lunch Break*

DAY 1
14/02

Session III – Session chair : Vincenzo Barone

- 15:00
Keynote B
LUCA BIZZOCCHI – Alma Mater Studiorum Università di Bologna
Modelling the Rovibrational Energy Manifold of Cyanoacetylene (HC₃N): a Key Molecule for Astrochemistry
- 15:40
Talk 3.1
FEVEN ALEMU KORSAYE – École Nationale Supérieure de Paris, Chimie ParisTech
Following the Density Evolution Using Real Time Density Functional Theory and Density Based Indexes
- 16:00
Talk 3.2
GRETA DONATI – Università degli Studi di Napoli Federico II
Exploration of Human vs. Murin PD-L1-Small Molecules Interactions through Molecular Dynamics Simulations
- 16:20
Talk 3.3
MICHELE NOTTOLI – Università di Pisa
Energy, Structures, and Response Properties with a Fully Coupled QM/AMOEBA/ddCOSMO Implementation
- 16:40
Talk 3.4
GIANLUCA SABELLA – Università degli Studi di Napoli Federico II
A High-Performance Computing Hybrid Cluster: Testing the I/O Performances
- 17:00
Coffee Break
- 17:30
–
19:30
Round Table: *The role of high performance scientific computing: The present and the future. (moderator: Nadia Rega). – with the participation of **Carlo Adamo** (Chimie ParisTech), **Diego Di Bernardo** (TIGEM), **Giordano Mancini** (Scuola Normale Superiore), **Domenico Nicodemi** (Università di Napoli Federico II), **Cristina Puzzarini** (Alma Mater Studiorum Università di Bologna), **Guido Russo** (INFN, Napoli)*
- 20:30
Social Dinner

DAY 2
15/02

Session IV – Session chair : Cristina Puzzarini

- 9:00
Keynote C
CARLO CAVALLOTTI – Politecnico di Milano
Automation of Chemical Kinetics: Perspectives, Status, and Challenges
- 9:40
Talk 4.1
FEDERICO LAZZARI – Scuola Normale Superiore
Continuous Perception in Feature Spaces: the Proxima Paradigm for Representation and Computation
- 10:00
Talk 4.2
STEFANO PANTALEONE – Università degli Studi di Torino
Water Reactivity on Schreibersite: a Reservoir for Prebiotic Living Phosphorus
- 10:20
Talk 4.3
ANDREA NOBILI – Politecnico di Milano
On the Radical Behavior of Large Polycyclic Aromatic Hydrocarbons in Soot Formation and Oxidation
- 10:40
Talk 4.4
FORTUNA PONTE – Università della Calabria
Pt(IV) Prodrugs Reduction, What Do We Know Currently? The Contribution of Computational Investigations
- 11:00
Coffee Break

- 11:30
Talk 5.1
ALESSIO MELLI – Alma Mater Studiorum Università di Bologna
Accurate Spectroscopic Characterization of Unsaturated Carbon-Chains of Astrochemical Importance
- 11:50
Talk 5.2
MARCO MENDOLICCHIO – Scuola Superiore Meridionale
New Challenges in Theoretical Vibrational Spectroscopy
- 12:10
Talk 5.3
FRANCESCA FASULO – Università degli Studi di Napoli Federico II
Reactivity of Vinylene Carbonate at Lithium Metal Anode Interface: New Insights from Density Functional Embedding Theory
- 12:30
Talk 5.4
MATTEO CAPONE – Università degli Studi dell'Aquila
Multi-scale Modeling of Spectroscopic Features for Electron Donor Acceptor Complexes
- 12:50
Talk 5.5
LUIGI CRISCI – Università degli Studi di Napoli Federico II – Scuola Normale Superiore
Photophysics of Tetracene Derivatives in Monomeric and Dimeric Forms through Ab-Initio Methods
- 13:10
Talk 5.6
SANDRA MONICA VIERIA PINTO – Scuola Normale Superiore
Glutamine as an Infrared Probe to Understand Local Environment Properties of Fibril Structures: the Perturbed Matrix Method
- 13.30
Closing Remarks



Understanding crystal nucleation in glasses by computational simulations

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Crystal nucleation is highly relevant to many industrial and technological applications of glasses.[1,2]

Devitrification, mostly observed on the glass surface, is an undesired phenomenon in glass manufacturing because the formation of crystals in the glass products often deteriorates their transparency and strength.

On the other hand, technologies for controlling crystallization have contributed to society since they enable us to develop glass–ceramics products with exceptional optical and mechanical properties. A deep knowledge of the mechanism governing the process of crystal nucleation and crystallization in oxide glass is thus fundamental to design a glass–ceramic system that exactly fulfils the requirements for desired applications.

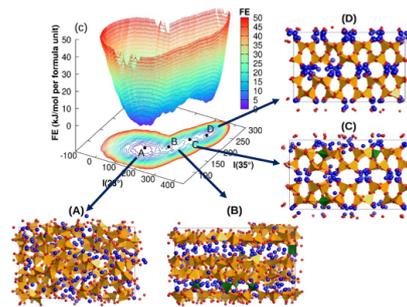


Figure 1. Potential free energy surface (FES) and 3D structure of lithium disilicate at characteristic points. Blue atoms represent lithium, red ones are oxygen, and yellow and green tetrahedral are silicon.

I will show in this talk the results obtained for the glass lithium disilicate by metadynamics simulations.[3,4] The accelerated atomistic simulation revealed a two-step mechanism of the nanoscale crystal formation (Figure 1). First, a partially layered silica embryo appeared, and then a more ordered crystalline layer with size larger than the critical nucleus size was formed. Subsequently, lithium ions piled up around the silicate layer and triggered stacking of adjacent silicate layers, which eventually built a perfect crystal. Contrarily to previous hypotheses, no lithium metasilicate crystal is observed as a precursor of the homogeneous crystallization of lithium disilicate.

References

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Extending the Applicability of the Semi-experimental Approach by Means of “Template Molecule” and “Linear Regression” Models on Top of DFT Computations

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When looking to better understand the stereo-electronic, thermodynamic and spectroscopic properties of isolated molecules, the accurate determination of their equilibrium structure is a mandatory step. However, for medium- to large- sized molecules and/or flexible systems, the computational cost to achieve high accuracy might be unaffordable. In these cases, cheaper yet accurate approaches need to be defined.

In a recently published work [1] a benchmark study, based on the availability of accurate semi-experimental equilibrium rotational constants for 21 molecular species, tested and validated a new approach which relies on a “Lego bricks” model. This approach is rooted in the idea that a molecular system can be seen as formed by different fragments (i.e. the “LEGO bricks”), whose accurate semi-experimental (SE) equilibrium geometries are available [2]. To join together the different “LEGO bricks”, this approach relied on: (i) the template molecule approach (TM) [2] in order to account, at the rev-DSD-PBEP86-D3/jun-cc-pVTZ level, for the changes occurring when moving from the smaller fragment to the larger molecular system; (ii) the linear regression model (LR) to correct the inter-fragment parameters [3].

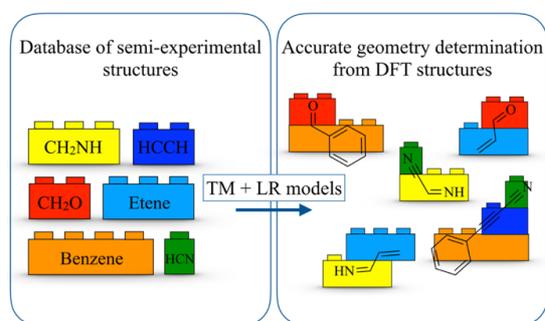


Figure 1 Graphical description of the TM-SE_LR approach.

The molecular systems considered for benchmarking the resulting structure, denoted as TM-SE_LR, are those obtained from addition/elimination reactions of nucleophilic unsaturated radicals (e.g., CN, \bar{C}_2H , and phenyl) to alkenes, imines, and aldehydes. The TM-SE_LR scheme has thus been validated by comparison with their semi-experimental equilibrium structures (when available) and rotational constants (which straightforwardly depend on the equilibrium geometry).

The main outcome of this study is the reliability, robustness and accuracy of this novel approach, showing structural differences of about 0.001 Å for bond lengths and 0.1° for angles and an average relative deviation with respect to the accurate semi-experimental equilibrium rotational constants of ~0.2%.

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Mixed alkali effect in aluminosilicate glasses: assessing the best interatomic potential models

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Ionic mobility in oxide glasses plays a fundamental role in understanding the behavior of properties such as chemical durability, glass transition temperature, viscosity and ionic conductivity. According to the glass composition, this feature can be optimized by exploiting the mixed alkali effect (MAE) on those glasses, which affect the mentioned properties and others in a non-linear way [1].

The mixed alkali effect, which appears when one alkaline ion is replaced with another, has been extensively studied for silicate glasses from a molecular dynamic point of view [2,3]. Whereas, it has received less interest in the case of mixed alkali aluminosilicate glasses. In the latter case, the role of the two alkali ions is controversial between acting as a modifier, forming non-bridging oxygens and percolation channels, or as charge compensator of the AlO_4^- units present in the network. The effect that different roles have on ionic mobility is thus interesting to understand.

In this contribution, we have compared five major interatomic potentials of classical molecular dynamics including the latest one developed by our group (BMP) [4] for explaining the mixed alkali effect in the presented systems. The comparison is based on simulating and reproducing experimental trends of ionic conductivity and glass transition temperature of different compositions of Na, K aluminosilicate glasses.

Among the tested potentials, the core-shell polarizable force-field and the last developed BMP best reproduce MAE by capturing the typical non-linear behavior of studied properties, obtaining good agreement with available experimental data. The highest resistivity is shown for the mixed alkali glass and the effect of the temperature on the conductivity of the single alkali glasses is also well controlled: higher conductivity of single Na-glass at low temperature and higher conductivity of single K-glass at high temperature. The latter feature, which is reproduced only by core-shell model, is explained by the greater flexibility of percolation channels in the single K-containing glass at high temperatures. Additionally, in core-shell simulations, the mixed alkali effect is due to the suppression of hopping events between dissimilar sites in the percolation channels hosting both sodium and potassium, as widely described in experimental studies [5].

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Automation of Variable Reaction Coordinate Transition State Theory and application to Methyl-Vinyl Ketone, 2- and 3- Butenal Decomposition

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The theoretical investigation of the reactivity on singlet potential energy surfaces (PES) is a challenging task [1], since it requires characterization of all stationary points that can be accessed from the entrance well. These are all the isomers that can be reached from the entrance well and the saddle points by which they are connected. A further obstacle to the exploration of singlet PESs is the possible diradical nature of saddle points, which is badly described by black box single reference ab initio methods routinely adopted to investigate PESs, such as density functional theory (DFT). Finally, the fastest exit channels are usually barrierless. These rate constants can be determined using Variable Reaction Coordinate Transition State Theory (VRC-TST), which requires multireference ab initio techniques.

In this work, we use the automation tools implemented in EStokTP [3] to investigate the reactivity on the C_4H_6O isomers singlet PES and overcome the afore-mentioned hurdles. This is of interest for the atmospheric and combustion kinetics communities both from a fundamental and an applied perspective. On the fundamental side, this is an important PES as it is accessed following the addition of atomic oxygen in its ground state, $O(^3P)$, to 1,3 butadiene, the simplest unsaturated conjugated alkene, and the successive fast intersystem crossing (ISC) to the singlet state. From an applied perspective, it is known that $O(^3P)$ addition to 1,3 butadiene is one of the most sensitive reactions in 1,3 butadiene oxidation [4].

The approach we followed consisted in the study of the isomerization reactions that become active following $O(^3P)$ addition to 1,3 C_4H_6 , and the determination of decomposition kinetics for the most stable isomers, methyl-vinyl ketone (MVK), 2-butenal (2-BUT), and 3-butenal (3-BUT), as shown in Figure 1. The decomposition rate constants of seven reaction were determined using our recent partially automated VRC-TST protocol.

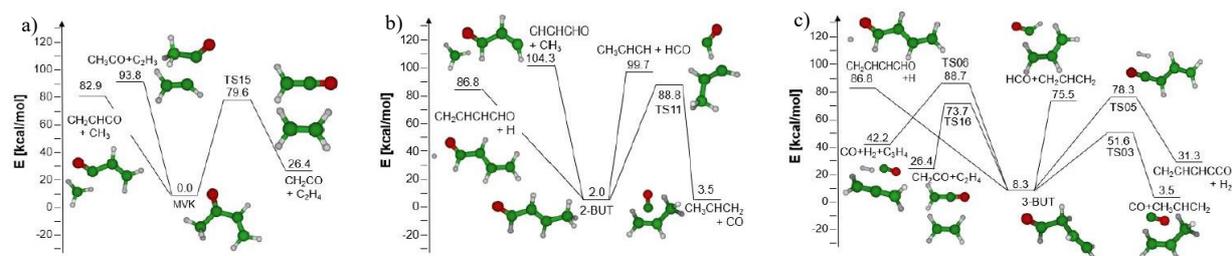


Figure 1 Decomposition pathways of a) MVK, b) 2-BUT, and c) 3-BUT.

While we are aware that the adopted approach leads to the investigation of a restricted portion of the C_4H_6O PES, it is nevertheless an important step forward in the comprehension of the reaction kinetics for systems that are important in combustion and atmospheric kinetics.

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Multi-replica biased sampling for the design of photoactive chiral nanomaterials

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Asymmetric organic and inorganic materials are constantly gaining a significant interest due to the opportunity of reaching tunable chiral signatures. In this background, asymmetric π -conjugated polymers are attracting considerable interest in view of their light-dependent torsional reorganization around the π -conjugated backbone, which determines peculiar light-emitting properties. More specifically, polyfluorene derivatives are of wide interest in the field of organic electronics, because their typical photo-induced helix-sense switching, enabling a specific molecular response after light-irradiation.

Motivated by the interest in designing asymmetric frameworks with tunable photoelectronic properties, a bespoke simulation method has been recently proposed to enhance the sampling of the torsional conformational space and, at the same time, to estimate ground to excited-state free energy differences^{1,2}. This scheme is based on a combination of Hamiltonian Replica Exchange Method (REM)³, parallel bias metadynamics (PBMetaD)⁴ and free-energy perturbation theory (FEP)⁵ and it has been applied on a pentamer of 9,9-dioctylfluorene by biasing multiple torsions. We found that, upon irradiation, our simulation strategy predicts ground and excited state free-energy surfaces, together with emission spectra, showing a good agreement with the experiments.

The proposed simulation scheme allowed us to enhance the sampling of switchable conjugated polymers and to estimate the free-energy gap between ground and excited states. This is a general scheme that can be used to predict large-scale rearrangements occurring upon light-irradiation and it allows designing new systems with enhanced chiral signatures.⁶

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Simulating the gas-phase reaction between oxirane and the CN radical in interstellar conditions

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The increasing molecular complexity of the interstellar medium (ISM) is testified by the large number of new detections of 2021 [1]. These new observations claim for a rationalization from the point of view of chemical networks and formation routes, which should be able to explain the formation and abundances of these astrochemical species.

Here, the *ab initio* investigation of the gas-phase pathways involved in the bimolecular reaction between oxirane (c-C₂H₄O) and the CN radical is presented. The relevance of this mechanism in astrochemistry is twofold: (i) both species have been detected in the ISM with high abundances, thus the reaction is a promising formation route for molecules of astrochemical interest; (ii) possible products are species belonging to the C₃H₃NO family of isomers. The latter is an interesting family of compounds containing prebiotic species like propiolamide, cyanooxirane or vinyl isocyanate but at the same time seems elusive in the ISM, since none of the species with this chemical formula has been detected up to date [1].

To simulate such reaction in the interstellar conditions and understand the possible products that could be formed, the mechanism has been explored from the energetic and kinetic point of view and the results are reported in a recently published paper [2]. The reactive potential energy surface (PES) has been investigated employing the rev-DSD-PBEP86 double-hybrid density functional in conjunction with the jun-cc-pVTZ basis set. The thermodynamically allowed products are showed schematically in fig. 1 and are (in order of increasing stability): cyanoacetaldehyde+H·, oxazole+H· and, formaldehyde+H₂CCN. In competition with the formation of these products there is also the H-abstraction process that leads to the formation of HCN and the 2-oxiranyl radical. From kinetical simulations in the low-limit pressure of the reaction at a temperature of 60 K, the preferred reaction pathway is the H-abstraction, with a rate constant in the order 1×10^{-11} cm³molecules⁻¹s⁻¹. This path is followed by the production of H₂CO+H₂CCN and cyanoacetaldehyde+H·, which have a rate constant in the order of 10^{-12} cm³molecules⁻¹s⁻¹. The rate constants obtained have a meaningful order of magnitude for ISM conditions and are useful information to consider for future chemical modelling of the ISM.

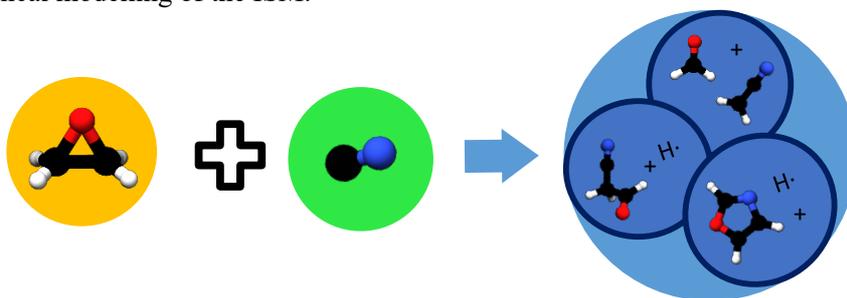


Figure 1 Schematic representation of the reaction between oxirane and the CN radical showing also the thermodynamically allowed products

References

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Attosecond dynamics simulations of Glycine and Poliglycine irradiated by α -particle

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The interest for electronic dynamics is growing in recent years due to the continuous progress in optics and laser technologies that made the realization of pump-probe experiments on the attosecond regime a reality. Such techniques have started to shed unprecedented light on the details of the electronic dynamics in intimate relationship with chemical structure and dynamic. The propagation of time-dependent Kohn-Sham equations provides a mean to access the realm of attosecond electron dynamics. Recently, a RT-TDDFT module has been implemented in deMon2k [1]. In this contribution we present some details of this methodology and its validation through the cross-section calculation for the interaction between α -particle with water [2]. In addition, we show the effect induced by radiation to the electron cloud on glycine and protein back-bone (poliglycine) [3], focusing on energy profiles and the redistribution of charge in the first femtoseconds of the interaction. It can represent a promising tools to investigated cosmic rays energies range from 1 to 10^4 MeV and that are essentially formed by H^+ (85%) and He^{2+} (13%) particles.

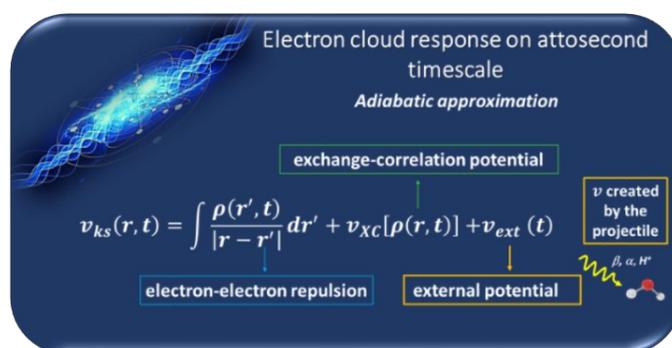


Figure 1 Schematic representation of RT-TD-DFT induced ionization on systems by alpha-particle radiation.

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New computational approaches for molecular and electronic dynamics

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Ab initio molecular dynamics is widely employed for the prediction of molecular equilibrium and non-equilibrium properties. [1] In particular, the so-called extended Lagrangian methods offer a good compromise between accuracy and computational cost. In the Atom-centered Density Matrix Propagation (ADMP) approach, the one-electron density matrix is treated as a (classical) dynamical variable and propagated along with the nuclei. [2-4] Therefore, a fictitious electronic mass has to be introduced. This parameter has a fundamental role in governing the degree of adiabaticity between the (fictitious) electronic and (real) nuclear degrees of freedom. A rational method to evaluate the mass-matrix is here shown. In particular, fictitious electronic normal modes are defined and a common frequency (compatible with the chosen time step) is imposed to them. The corresponding mass-matrix is then derived. The analysis of the performances and limits of such approach reveals an enhanced adiabaticity and therefore an increased accuracy in the predicted vibrational dynamics. [5]

At the same time, electronic relaxation phenomena on an ultra-fast time scale require the direct, real, propagation of the electronic density starting from a given excited electronic state. In this regard, the so-called real-time time-dependent density functional theory (RT-TDDFT) approach allows a propagation in time of the electronic structure, according to the TDDFT equations of motion. [6] This method has been successfully applied to simulate the electronic density evolution upon vertical excitations in systems of both fundamental and technological interest. [7] In particular, the dynamic evolution of metal-to-ligand charge-transfer (MLCT) states has been investigated in interesting Ru(II) complexes, such as Ru[(dcbpy)₂(NCS)₂]⁴⁺ (“N3”). Following a strong absorption in the 370-500 nm region, N3 photophysics is characterized by a peculiar excited-state relaxation dynamics, involving an intersystem crossing (ISC) from the initially excited singlet ¹MLCT states to triplet ³MLCT ones. [8] The ultra-fast (< 100 fs) electronic dynamics of the N3 ¹MLCT states more involved in the following ISC reveals the different hole and electron behavior in the molecular donor and acceptor moieties after photo-excitation, also suggesting the possibility of inter-ligand electron transfer processes. Moreover, the effect of solvent polarization on charge carriers mobilities has been investigated.

The comprehension from first principles of the electronic density reorganization following light absorption in molecular dyes is fundamental for the interpretation of time-resolved spectroscopic data and for a rational design of improved light-harvesting systems.

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Pt(IV) Prodrugs Reduction, what do we know currently? The contribution of computational investigations

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In the development of new platinum-based anticancer drugs, able to overcome the well-known drawbacks of cisplatin and its derivatives, a great interest is concentrated on the class of Pt(IV) prodrugs that, upon reduction by cellular reducing agents or by photoactivation, release the corresponding four-coordinate active Pt(II) species and the relative axial ligands.

A detailed understanding of the mechanism of action of these prodrugs and the influence of the ligands in axial and equatorial position on the reduction mechanism, should allow to obtain useful guidelines for the subsequent design of more potent Pt(IV) complexes with improved anticancer properties.

In a 2012 paper Wexselblatt and Gibson [1] asked the question “What do we know about the reduction of Pt(IV) pro-drugs?”. It is still matter of debate the kind of mechanism that allows the activation by reduction of Pt(IV) prodrugs. Both inner- and outer-sphere mechanisms are considered viable and were both computationally and experimentally investigated adopting several strategies. In the former case, the two-electron transfers occur through a direct contact of the platinum complex with the reducing agent and new bonds are formed, while in the latter the electrons are transferred without any direct interaction. However, theoretical investigations carried out recently by us[2,3] allowed to further classify the reduction mechanisms of Pt(IV) prodrugs, when the reducing agent is ascorbic acid, as i) ligand bridged, ii) ligand-bridged H-transfer and iii) enolate β -carbon attack. While, concerning the outer-sphere mechanism, the adoption of the decomposition scheme proposed by Baik and coworkers[4] allows the estimation of the standard redox potential of the investigated complexes.

Here, the outcomes of detailed investigations of the activation mechanism of numerous Pt(IV) prodrugs, carried out by means of density functional theory (DFT), are reported. On the basis of the collected results, we try to rationalize the differences in behavior experimentally observed for the selected Pt(IV) complexes (some stable in dark) as a function of the nature of the ligands both in axial and equatorial position.

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Unravelling the CO oxidation reaction mechanism of Mo/Cu CO dehydrogenase by means of QM/MM calculations

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In Nature, bio-oxidation of carbon monoxide to CO₂ occurs thanks to bacteria living in the soil. Such microorganisms exploit specific CO dehydrogenase (CODH) enzymes to catalyse the reaction through the presence of multimetal active sites. So far, only one aerobic CODH enzyme has been reported, which takes advantage of the redox abilities of a bimetallic Mo/Cu center [1].

Despite numerous experimental and theoretical studies described in the literature over the last twenty years, many key aspects of the Mo/Cu CODH catalytic mechanism are still object of debate. Among the others, open points even include uncertainties whether a solvent water molecule can act as a nucleophile in the course of CO oxidation, this being a plausible alternative of the extensively investigated possibility that one of the Mo-bound oxo ligands exerts such crucial role. Notably, neither options have been associated to quantum mechanical or hybrid quantum/classical (QM/MM) catalytic energy profiles that, to date, appear to be fully satisfactory when compared to the available experimental evidences.

By means of a QM/MM model of the whole enzyme developed in our laboratories, we gained insights on several of the currently debated key points in CODH reactivity. This allowed us to propose a new mechanism for the oxidation of CO that fits well with the experimental data published so far on the Mo/Cu CODH catalytic activity. Our novel results will be discussed also in the light of previous theoretical studies we recently carried out on complimentary issues regarding the chemistry of such enzymes [2-5].

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A DFT investigation of substitutional and interstitial nitrogen (N)-doping effects on a ZnO(100)-TiO₂(101) heterojunction

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Understanding the mechanism of the heterojunctions is fundamental in order to generate systems with high photocatalytic power. To this aim, we have theoretically investigated the effects of substitutional, interstitial nitrogen (N) doping, both in absence and presence of oxygen vacancies (Ov), on the electronic and structural properties of the wurtzite (ZnO) and anatase (ATiO₂) heterojunction by means of Density Functional Theory (DFT). Our structural analysis provides a key information on the nature of the interaction between these two non-polar surfaces, showing that i) the substitutional N doping is favored in TiO₂ region, ii) the interstitial N doping prefers the ZnO portion of the heterojunction and iii) the energy required to generate substitutional (interstitial) N-doped sites decreases (increases) farther from the interfacial zone. In addition, both at low and high N dopants concentrations, the photocatalytic activity of the system increases compared to the undoped heterojunction [1]. In fact, substitutional and interstitial N-doped sites improve the visible light adsorption of the heterojunction due to the introduction of gap states. These states, which act as deep electronic traps, improve the charge separation delaying electron-hole recombination [2]. Furthermore, the N-dopants presence facilitates the Ov formation causing a decrease in the formation energy (E_{FORM}) of the vacancy. Finally, we have shown that the band alignment of the N-doped models, compared to the undoped system, is not affected neither by the N presence nor by the N concentration nor by the presence of oxygen vacancies. Therefore, the N-doped sites are useful in order to generate the higher energy gap states, which presence increases the photocatalytic activity of the system delaying electron-hole recombination. For these reasons, photocatalytic processes can be improved by using the following strategy: N-doped heterojunction with oxygen vacancies.

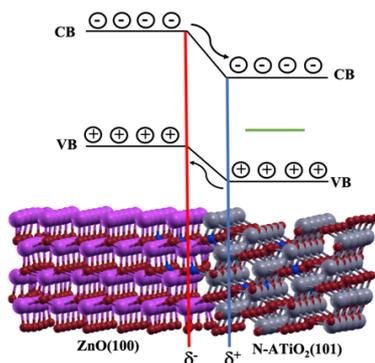


Figure 1. N doped ZnO(100)-TiO₂(101) heterojunction

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Modelling the rovibrational energy manifold of cyanoacetylene (HC₃N): a key molecule for astrochemistry

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Cyanoacetylene (HC₃N) is the simplest member of the cyanopolyynes family (HC_{2n+1}N) and is ubiquitous in Space, from external galaxies to Galactic interstellar clouds, star-forming regions, and planetary atmospheres [1]. Owing to its large permanent dipole moment and the prominent infrared spectrum, emission lines of HC₃N are easily observed by ground-based and space-born facilities in a broad wavelength interval, ranging from the microwave to the mid-infrared regions. Such observational data provide crucial information on the physical and chemical structures of the targets.

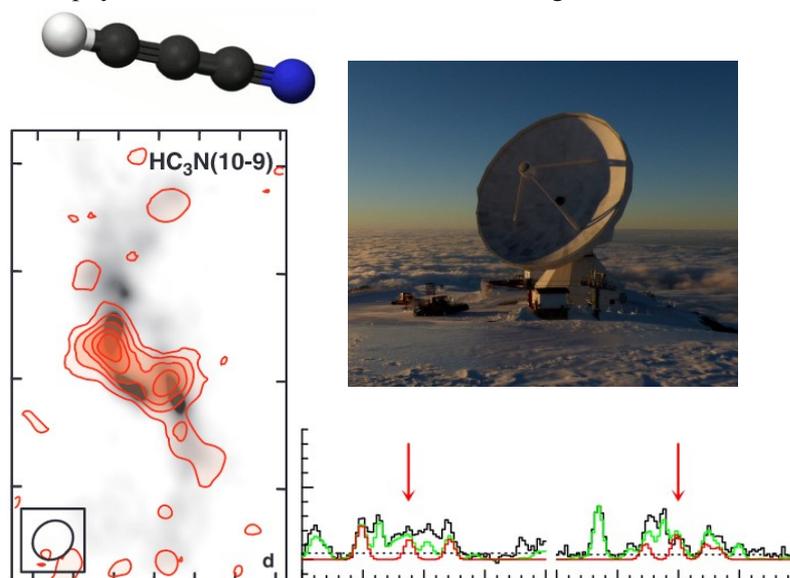


Figure 1 map of HC₃N in IC342 (left); spectrum of vibrationally excited HC₃N in SgrB2 (bottom right); IRAM 30m telescope in Sierra Nevada (Spain, top right).

As a matter of facts, observations of HC₃N in extraterrestrial environments very often involve excited vibrational states [2] and, in the context of planetary sciences, a precise model of the observed infrared band profiles must include the associated hot bands [3]. A very detailed knowledge of the molecular rovibrational pattern is thus a prerequisite for a correct interpretation of the astronomical data.

In a couple recent comprehensive studies, all existing laboratory data for the vibrational states of HC₃N located below 1200 cm⁻¹ have been analysed in a global model fashion [1,4]. These included — besides extensive literature data — new far- and mid-infrared spectra recorded at SOLEIL (Paris Sud) and Bologna, plus further measurements in the millimeter- and submillimeter-wave range performed in laboratories located in Garching, Cologne and Bologna, for a total of some 18 000 entries. The model Hamiltonian included the *l*-type resonance effects in bending states and the various anharmonic resonances which affects the polyads of levels $\nu_4 = m \sim \nu_6 = m + 1 \sim (\nu_5 = 1, \nu_7 = m) \sim \nu_7 = 3 + m$, for $m = 1, 2, 3$. A particular care has been exerted in treating subtle interaction effects in order to retrieve a set of spectroscopic parameters with accurate value and unambiguous physical meaning.

In this contribution I describe the features of this global approach, I present the results and discuss the implications for astrochemistry and planetary sciences.

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Following the Density evolution using Real Time Density Functional Theory and Density Based indexes.

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Density functional theory (DFT) and time-dependent (TD)DFT allow to compute the ground and excited state properties with a simple formalism and a good accuracy to computational cost ratio. Nevertheless, it is well documented in literature the intrinsic drawback of TDDFT theory in modeling the excited states with long-range charge transfer (CT) character. In particular, DFT based approaches fail to reproduce the correct $1/R$ asymptotic behavior (with R the distance between the transferred electron and the generated hole) due to the approximated nature of the exchange and correlation functional (XC) used to express the total energy of the system. As consequence, some of the XC functionals may predict the presence of unphysical states at very low energies and thus providing a misleading picture of the photophysics of the molecules considered [1]. In this scenario the usage of indexes as diagnostic tool to characterize and assess the reliability of TDDFT methods becomes helpful. In particular, the density based D_{CT} index [2] provides for a qualitative measure of the degree of locality of a CT processes by computing the distance of the charge transfer on the basis of the density distribution and the M_{AC} index [3] allows to predict if the excited states obtained at TDDFT level of theory derives from a good or erroneous energy prediction. In this context, with the aim of analyzing the CT states evolution in time we have performed electron dynamics simulations with real-time (RT)TDDFT method. This approach allows to directly propagate the electronic density in time domain enabling to investigate the time-dependent molecular response and modeling the electronic dynamic of excited states in the femtoseconds timescale. In this work the M_{AC} index has been implemented for the RT simulations ($M_{AC}^{RT}(t)$) taking into account the density reorganization during the dynamic and, together with the D_{CT} index, they have been applied to characterize and assess the reliability of excited states dynamics of molecules with CT character in relation to the XC functional used.

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Exploration of Human vs. Murine PD-L1-Small Molecules Interactions through Molecular Dynamics Simulations

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In the oncologic field, the relationship between tumor cells and the immune system has been widely demonstrated in the last years [1,2]. In this context, the prevention of the binding between programmed cell death receptor 1 (PD-1) with its ligand (PD-L1) represents an important goal in cancer immunotherapy [3,4] and has inspired the design of several small molecule inhibitors. [5,6]. For clinical translation of these compounds, *in vivo* experiments on animals are a decisive step; however, some promising inhibitors have shown loss of activity in murine PD-L1.[7]

In this work, a computational approach based on molecular dynamics simulations on the microsecond timescale, is proposed to understand the main chemical reasons behind the observed distinct ligands' behaviors with human and murine PD-L1. In particular, three inhibitors showing different degree of affinity for these receptors are investigated. Our results highlight that some residues are crucial to stabilize the formation of a ligand-induced PD-L1 homodimer and that such interactions can be compromised in murine case because of some crucial mutations at the binding interface. Moreover, our indications suggest that an atomistic inspection of the ligand-protein interactions can give precious hints for future drug design campaigns targeting the PD-1/PD-L1 interaction.

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Energy, Structures, and Response Properties with a Fully Coupled QM/AMOEBA/ddCOSMO Implementation

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The accurate computational modeling of molecules embedded in complex (bio)matrices, and of their properties, requires the use of a hybrid quantum/classical description of the system. In this way, the interesting region is described through quantum mechanics (QM), while accounting for the surrounding environment in a computationally affordable way through molecular mechanics (MM) [1] or polarizable continuum models (PCMs) [2].

Both QM/MM and QM/PCM descriptions present strengths and weaknesses. Models of the first kind are particularly suited for the description of specific interactions (such as hydrogen bonds and coordinations) and anisotropic environments, such as the inner region of proteins. However, for proper modeling of the long-range electrostatic interactions, a large amount of MM atoms have to be included in the calculation. Models of the second kind, on the other hand, naturally take into account both long-range electrostatic effects and statistical sampling. However, their description of the specific short-range interactions is missing.

A possible strategy to further improve the modeling is carried out by combining atomistic and continuum approaches in a multilayered fashion. This strategy is promising because it benefits from the strengths of the two kind of models, allowing for a good description of the specific interactions and a cheap and simple description of the long-range electrostatic.

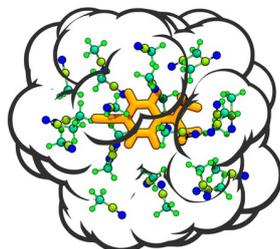


Figure 1 System described using the 3-layer QM/MM/Continuum model.

In this contribution, we present the implementation of a fully coupled polarizable QM/MM/continuum model based on the AMOEBA polarizable force field and the domain decomposition implementation of the conductor-like screening model[3]. Energies, response properties, and analytical gradients with respect to both QM and MM nuclear positions are available, and a generic, atomistic cavity can be employed. The model is linear scaling in memory requirements and computational cost with respect to the number of classical atoms and is therefore suited to model large, complex systems. Using three variants of the green-fluorescent protein, we investigate the overall computational cost of such calculations and the effect of the continuum model on the convergence of the computed properties with respect to the size of the embedding. We also demonstrate the fundamental role of polarization effects by comparing polarizable and nonpolarizable embeddings to full QM calculations.

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A High-Performance Computing Hybrid Cluster: Testing the I/O Performances

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The growing computational complexity of the problems justifies the use of resources for High-Performance Computing (HPC) [1]. Thanks to its characteristics of high bandwidth, flexibility, support for different types of messages and above all low latency, InfiniBand is a connection technology suitable for High Performance Computing.

We present a hybrid cluster, set up in the Monte Sant'Angelo complex of the University of Naples Federico II and funded by the IBISCO (Infrastructure for Big Data and Scientific Computing) project, a combination of both network connections [2]: a 100 Gb/s InfiniBand connection and a 10/25/100 Gb/s Ethernet connection (See Figure 1).

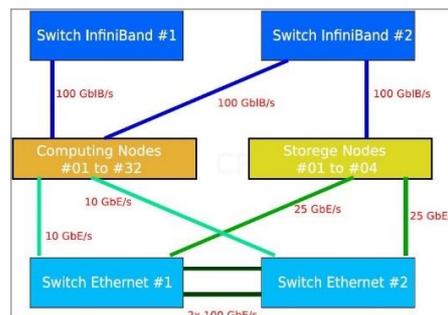


Figure 1: Network Configuration of HPC Hybrid Cluster

The characteristics of InfiniBand allow a low latency and therefore efficiency in terms of connection, but many applications are still based on the classic TCP/IP protocols over Ethernet, like NFS, FTP and the TCP sockets. It is best to use both networking standards and organize them to get the most out of both of their characteristics [3]. Our cluster provides a hybrid network, with two connections for both standards, InfiniBand and Ethernet.

We decided to duplicate each switch, configuring it with an automatic fail-over mechanism, to ensure the operation of network traffic even in the event of a switch failure. This makes the cluster more reliable.

We used the Link Aggregation Group (LAG) protocol over Ethernet to double the transfer efficiency, thus increasing redundancy when both switches are running. We were able to use the Link Aggregation Group (mLAG) multi-chassis protocol to allow the aggregation of the two 25 Gb/s ports of the Huawei CE-8861-4C-EI Ethernet switches present in the infrastructure since we were connected with a stack - 2x100 Gb/s links in a ring topology.

We decided to use different InfiniBand connections for inter process communication and data access communication.

A set of benchmarks was used to measure the I/O performances.

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ROUND TABLE

THE ROLE OF HIGH-PERFORMANCE SCIENTIFIC COMPUTING: THE PRESENT AND THE FUTURE

Moderator: Nadia Rega (Università di Napoli Federico II)

with the participation of

Carlo Adamo (Chimie ParisTech):

HP computing is at the core of Theoretical Chemistry, a domain that, not being necessary one of the most resource-demanding in Science, has by definition a need of powerful informatic infrastructures for its application. However, a cleavage can be observed in the last years between the development of large HP facilities and the real needs of the Theoretical Chemists. Is this a peculiar case where, in contrast with other scientific disciplines, the development of hardware facilities is orienting the fundamental research? This question will be analyzed starting from my personal experience in France.

Diego Di Bernardo (TIGEM):

I will discuss how HPC in genomics has become an essential tool for the welfare of the human being and the planet at large, and its importance will increase even more in the future. Advancements in DNA sequencers have decreased the cost of sequencing and at the same time dramatically increased the amount of data that needs to be analyzed. Real-time analysis is required to track mutations in cancer for personalized treatments, the emergence of new viruses and strains, and to assess the safety of food and in the environment.

Giordano Mancini (Scuola Normale Superiore):

Who is afraid of the big (bad) black boxes? The recent developments in artificial intelligence, deep learning and data lakes and the accompanying hardware advances in GPU computing, networking, and storage have boosted automation and the development of deep pipelines in all fields of research, including computational chemistry. Molecular modeling is seemingly on the verge of a big-data revolution. How can we steer it towards real knowledge and not just predictions?

Domenico Nicodemi (Università di Napoli Federico II):

New technologies in molecular biology have made available quantitative data about functionality of life, whose richness and complexity need the use of sophisticated simulation and analysis methods in chemical, physical, mathematical and informatics sciences in order to be interpreted and understood. For this reason, the boundary between biology and hard sciences is currently considered a strategic scientific area, which advances can revolutionize biomedicine. This is the subject of my brief contribution.

Cristina Puzzarini (Alma Mater Studiorum Università di Bologna):

Let us start from the oft-quoted words of Richard Feynman: "Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum-mechanical". This suggests that all the aspects of chemistry, also those that are more practical by tradition, need to be modeled at a quantum level if a deep understanding is aimed. However, to get quantitative descriptions or even good qualitative pictures, we need to reduce simplifications and approximations. This, in turn, means powerful computers, means to push scientific computing to the limit. We have seen huge advances in the power of high-performance computers in the last decades. Do we need more?

Guido Russo (INFN, Napoli):

The need for HPC is changing: very complex computation algorithms used in meteorology, aerodynamics, chemistry and oil and gas industry used to run on single parallel computers, but now most of these applications can run on smaller systems. This has led to a plethora of new medium-sized Data Centers devoted to HPC. In these Data Centers, the goal is achieved with both vertical scalability and horizontal scalability. The first refers to the parallelization of a task within a single many-core server, using a hundredth of simultaneous threads. The latter refers to using several servers in parallel, with a very efficient network connection. In both cases, GP-GPUs can give substantial speed-up in the execution times. The new quantum computing paradigm will perhaps change again the world of HPC, but without replacing older paradigms. Each application will have its own optimal infrastructure, thus leading us to a world with specialized Data Centers of any size.

Automation of Chemical Kinetics: Perspectives, Status, and Challenges

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Driven by synergic advancements in high performance computing and theory, the capability to estimate rate constants from first principles has evolved considerably recently [1]. When this knowledge is coupled with a procedure to determine a list of all reactions relevant to describe the evolution of a reacting system, it becomes possible to envision a methodology to predict theoretically the reaction kinetics. A scheme towards this goal is highlighted in Figure 1. However, if a thorough examination of all possible reaction channels is desired, the number of reactions for which a rate constant estimate is needed can become quite large. This determines the need for rate constant estimation automation.

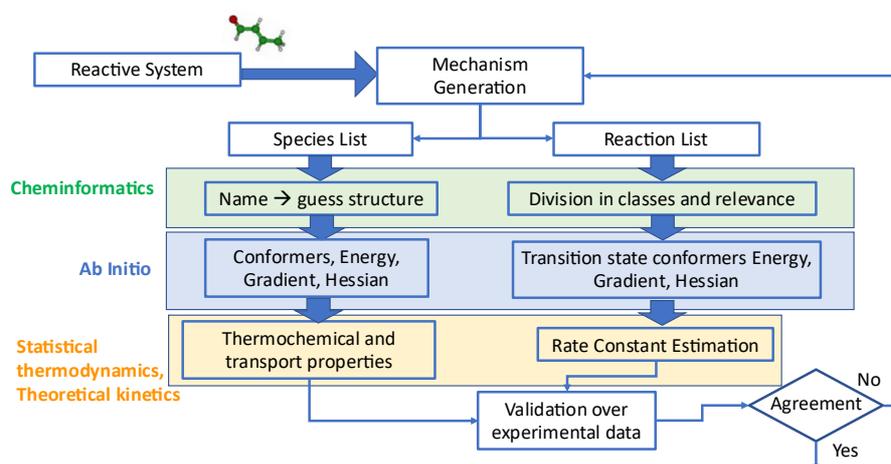


Figure 1. Key steps involved in the development of a theoretical mechanism

In this presentation, the status of this rapidly evolving field is reviewed and examples are given, with emphasis on recent advancements and present challenges. Thermochemistry is the field where automation is most advanced. Entropies, heat capacities, and enthalpies can be determined efficiently with accuracy comparable to experiments for chemical species containing a limited number of atoms, while machine learning can be used to improve the computational predictions for large chemical species using reduced computational resources. Several approaches have been proposed to automatically investigate the reactivity over complex potential energy surfaces, while rate constants for elementary steps can be determined accurately for several reaction classes, such as abstraction, addition, beta-scission, and isomerization [2]. Kinetic mechanisms can be automatically generated using methodologies that differ for level of complexity and required physical insight [3]. Among the challenges that are still to be met are the estimation of rate constants for intrinsically multireference reaction classes, such as barrierless processes, the containment of the number of reactions to screen in mechanism development, and the integration of the existing automated software.

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Continuous Perception in Feature Spaces: the Proxima Paradigm for Representation and Computation

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We introduce a new paradigm for molecular perception, which is based on continuous rather than discrete indexes providing a conceptual link between traditional chemical concepts and the quantum chemistry world. Starting from atoms in molecules we employ electrons and holes to build localized and delocalized nearly-independent fragments. In this stage, after automatic detection of cycles and chiral centers, full lists of diastereoisomers, isomers and tautomers can be built. Next, a semi-empirical tight-binding scheme [1] based on the molecular topology is employed to derive charges and bond-orders, which are at the foundation of a so-called feature space that can be employed to derive physical-chemical properties in an intuitive yet accurate way. As a result of the "feature-space", it is possible to move from an Indirect Perception (which is based on atom types), to a Direct Perception which allows to treat atomic parameters (e.g. force field) in a continuous fashion. A formal perturbative approach is finally used to define inter-fragment interactions (both intra- and inter-molecular) in terms of simple many-body functions. This procedure has a two-fold purpose: to be used with immersive molecular viewers and to be integrated in workflow managers thus providing the functionalities needed for molecular modeling studies. It thus stands as an effective tool for reconciling accuracy and interpretability for both visualization and computation.

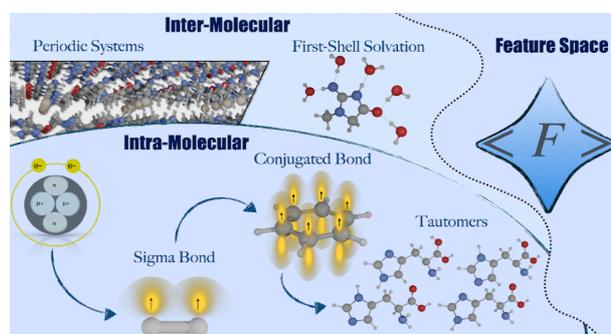


Figure 1 The Proxima [2] Perception Paradigm.

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Water reactivity on Schreibersite: a reservoir for prebiotic living phosphorus

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Phosphorus is an element of primary importance for all living creatures, being present in many biological activities in the form of phosphate (PO_4^{3-}). However, there are still open questions about the origin of this specific element and on the transformation which allowed it to be incorporated in biological systems. The most probable source of prebiotic phosphorus is the intense meteoritic bombardment during the Archean era, few million years after the solar system formation, which brought tons of iron-phosphide materials (schreibersite) on the early Earth crust.¹ It was recently demonstrated that by simple wetting/corrosion processes from this material various oxygenated phosphorus compounds are produced.² In the present work, the wetting process of schreibersite (Fe_2NiP) was studied by computer simulations using density functional theory, with the PBE functional supplemented with dispersive interactions through a posteriori empirical correction ($\text{D}^*\text{0}$).^{3,4} Therefore, the two stable (110) and (001) Fe_2NiP surfaces were used simulating different water coverages, from which structures, water binding energies and vibrational spectra have been predicted. The computed (ana-)harmonic infrared spectra have been compared with the experimental ones, thus confirming the validity of the adopted methodology and models (see Figure 1).^{5,6} Moreover, water reactivity was inspected in several possible deprotonation reactions, also increasing the number of water molecules in order to lead to the formation of phosphonic and phosphoric acids and their corresponding deprotonated forms.

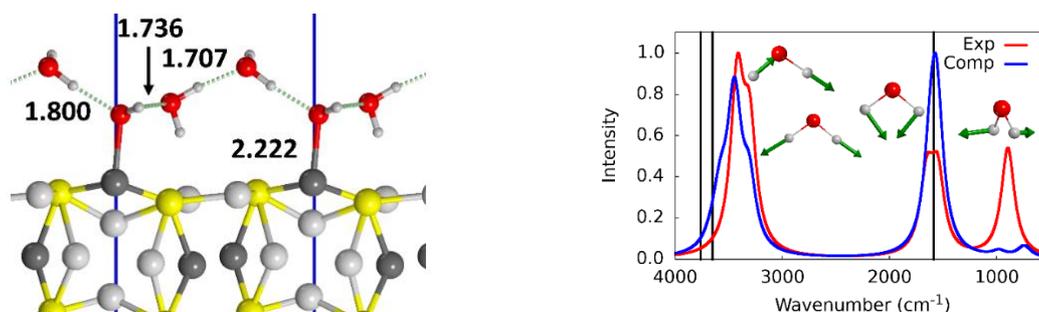


Figure 1 PBE-D*0 optimized geometry of water monolayer on the (110) Fe_2NiP surface (left) and simulated vs experimental IR spectrum (at 125 K). Atom color legend: H in white, O in red, P in yellow, Fe in light grey, Ni in dark grey.

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On the Radical Behavior of Large Polycyclic Aromatic Hydrocarbons in Soot Formation and Oxidation

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The mechanism of evolution of polycyclic aromatic hydrocarbons (PAHs) into carbonaceous particles in combustion, atmosphere, and interstellar space has been the subject of intense debate. Recently, there has been emerging evidences [1,2] supporting resonantly-stabilized radicals as key players in PAH growth. In our latest study [3], we built on this hypothesis and proposed that, beyond a critical size, PAH reactivity can be assimilated to that of persistent radicals. We found that, with the increase of their size, odd-C-numbered PAHs embedding 5-membered rings rapidly lose a hydrogen atom to form π -radicals, while even-C-numbered PAHs react as open-shell triplet radicals rather than closed-shell molecules, as shown in Figure 1, where acenes were used as prototypes of larger aromatic structures.

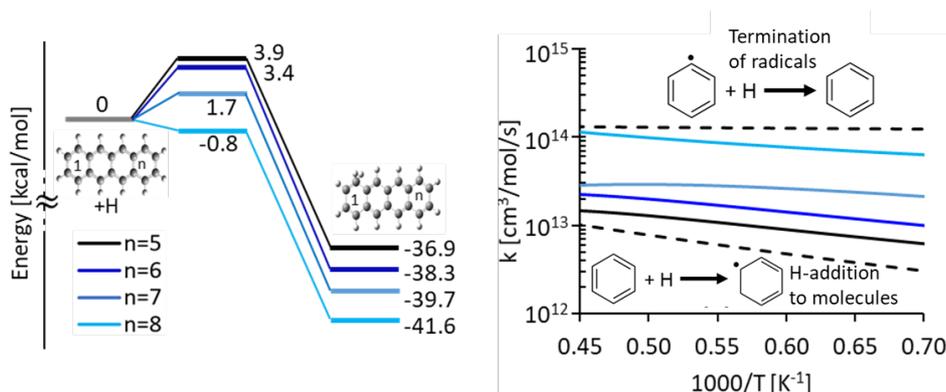


Figure 1. Radical character of linear acenes toward H addition. Left panel: potential energy surface (PES) of H atom addition reactions to the external ring zigzag site in linear acenes with increasing number (n) of six-membered rings. Right panel: per-site high pressure rate constant for H atom addition to acenes compared with $H+C_6H_6$ and $H+C_6H_5$ rates.

Since singlet-triplet intersystem crossing (ISC) may enhance considerably even-C-numbered PAHs reactivity, we investigated in detail the kinetics of this process using nonadiabatic transition state theory (NA-TST) [4], as recently implemented in the EStokTP framework [5], which was used for all the calculations performed in this work. The NA-TST crossing rates highlight a significant dependence on molecular size. The characteristic reaction time computed for singlet-triplet interconversion in octacene and, quite likely, larger acenes, is at all temperatures abundantly below the lifetime of PAHs containing a hundred or more atoms calculated through the kinetic simulations, thus indicating that PAHs triplet and singlet populations are likely to reach equilibrium during soot growth. This analysis of the reaction kinetics of even-C-numbered PAHs clearly indicates that their reactivity is best described as that an open-shell singlet diradicals or triplets, rather than as closed-shell singlets.

By accounting for the open-shell character of large PAHs, it was also possible to explain why large aromatic structures are often found to be alkylated [2], despite the fact that H ipso-substitution reactions, exothermic (by ~ 10 kcal/mol) and entropically favored, should rapidly lead to the loss of the alkyl group. Indeed, our calculations reveal that following methyl addition and H loss, methylated acenes rapidly eject

a hydrogen atom to form stable benzylic radicals, that are more stable than the closed-shell counterparts in typical soot growth conditions. As such, ipso-substitution reactions are not possible as they can take place only if the alkyl chain is not a radical center, since otherwise recombination would prevail.

The construction of a kinetic model including these findings allows to interpret experimental soot oxidation data otherwise irreconcilable with existing chemical kinetic mechanisms.

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Moving from α -olefins transition metal catalysis to biodegradable materials: insight from DFT calculations

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The research of bio-based thermoplastic materials able to replace the petrochemically derived plastics maintaining similar performances is one of the more ambitious goals of the circular economy. The substitution of the monomer feedstock from the α -olefins to renewable ones lead to a change of polymerization mechanisms (e.g. ring opening polymerization (ROP), in a place of classical Ziegler-Natta (ZN)) with several unknowns. As a matter of fact, the control of polymer microstructure, that is the key of material properties, achieved with ZN catalysis is not yet reached by any other metal-catalysis. In this presentation we would like to report on two selected test cases that is: 1) the stereoselective polymerization of lactide and 2) the stereoselective ring opening copolymerization (ROCOP) of CO₂/epoxides [1] yielding respectively poly(lactic acid) and polycarbonates that are attracting increasing interest as polymeric materials.

In particular in first case study we will show how DFT calculations revealed that the chiral catalyst control shows unusual features, including active site reorganization on the reaction path, which add complexity and need to be taken into account when addressing the challenge of chiral catalyst recognition [2,3].

In the second case study we will present some unpublished results on "in silico" catalysts modification to achieve very high stereoselective CO₂/*meso*-epoxide ROCOP.

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Accurate spectroscopic characterization of unsaturated carbon-chains of astrochemical importance

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The molecular universe of Astrochemistry is expanding at a surprisingly rapid pace. Currently, most of the astronomical identifications are achieved by observation of rotational transitions, exploiting radioastronomical large-scale surveys of the interstellar medium (ISM). However, to univocally identify the transitions of the studied molecule within a survey – which are, typically, densely packed with lines – an extremely accurate knowledge of the rotational frequencies is required. This can be achieved only with laboratory techniques. Moreover, even if the spectral prediction is based on experimental data but relies on the extrapolation from low-frequency experiments, ambiguities or discrepancies can arise [1].

Therefore, an accurate spectroscopic characterization of *E*- and *Z*-cyanovinylacetylene (CVA), allenylacetylene (AA) and propadienone (PD) has been carried out to guide their detection in the interstellar medium, thus providing to the astronomers accurate rotational frequencies up to 400 GHz.

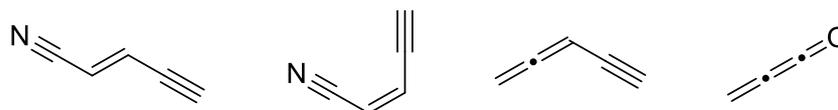


Figure 1 The four investigated species: from left to right, *E*-CVA, *Z*-CVA, AA, and PD.

An eventual first detection, as it would be for PD and *Z*-CVA, as well as new findings (on *E*-CVA and AA, which have been recently identified in the prestellar core of Taurus molecular cloud, TMC-1 [2,3]) in different astronomical regions, can be of great help in the refining of the models of the interstellar objects. Indeed, PD is the only isomer of the [H₂C₃O] family which has not been observed in the ISM [4], while unsaturated N-bearing carbon chains like CVA and pure hydrocarbons like AA can play important roles in reactivity, e.g., the pathways leading to the formation of aromatic molecules [3, 5].

In this work, we relied on a solid computational study to complete the experimental data available in literature. The accurate equilibrium geometries of the four species have been determined, exploiting composite schemes rooted in the coupled-cluster theory. Harmonic and anharmonic force field calculations gave access to the set of centrifugal distortion parameters; the importance of an accurate estimate of the sextic ones is presented. Exploiting a pyrolysis system to generate the four species in the gas-phase and using a frequency-modulation spectrometer working in the millimeter/sub-millimeter wave range, we were able to record and analyze the rotational spectrum up to 400 GHz, providing a thorough characterization of the spectroscopic parameters. In addition, a state-of-the-art energetic characterization of the [H₃C₅N] and [H₂C₃O] families has been carried out.

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New challenges in theoretical vibrational spectroscopy

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Vibrational and rotational spectroscopies are very powerful tools for investigating the physical-chemical properties of molecular systems, since they allow one to obtain a remarkable set of information related to structure and dynamics [1]. However, experimental spectra are tuned by several intertwined effects which can make the interpretation of experimental data very challenging without the support of reliable *in silico* simulations. In this respect, the second-order vibrational perturbation theory (VPT2) [2] has shown to offer a very effective balance between accuracy and computational cost.

A current hurdle is that the standard implementation of VPT2 is fragmented between asymmetric tops (no degeneracy) and symmetric/linear rotors (presence of doubly-degenerate vibrations), which means that any work carried out on VPT2 needs to be duplicated. The first part of this contribution concerns the extension of the VPT2 for Abelian groups to non-Abelian groups without employing specific equations for two- or three-fold degenerate vibrations but rather handling properly all the degeneracy issues and deriving the peculiar spectroscopic signatures of non-Abelian groups (e.g. *l*-type doubling) by a *a posteriori* transformation of the wavefunctions [3]. Comparison with the results of previous conventional implementations [4] shows a perfect agreement for the vibrational energies of linear and symmetric tops, thus paving the route to the transparent extension to the energies of spherical tops and the infrared and Raman intensities of molecules presenting degenerate vibrations. The whole procedure has been implemented in our general engine for vibro-rotational spectroscopy and will be presented through selected test-cases.

The next part focuses on the treatment of molecules presenting highly-anharmonic, floppy large amplitude motions (LAMs), and thus unsatisfactorily described at the purely VPT2 level due to the quartic approximation of the potential energy. It is noteworthy that for such systems a pure variational treatment would be prohibitive, and even reaching an accuracy comparable to VPT2 could only be performed at several times the cost of the perturbative model. Therefore, the best course of action is the formulation of a strategy based on an interplay between both computational methods, in order to take full advantage of each one. From a practical point of view, this operation can be carried out by separating the normal modes, or more generally a set of coordinates, and then treat the resulting groups separately. For this purpose, a description of molecular vibrations based on internal coordinates is more suitable. In this work, a theoretical derivation of the VPT2 framework has been carried out starting from the available literature [5]. The main difference with respect to the Cartesian-based formulation is that the kinetic energy operator has to be expanded as well, leading to additional terms. It is worth mentioning that each expression derived in the internal-based framework, can be written as a generalization of the corresponding Cartesian-based counterpart, implying a remarkable simplification at the implementation level. In this contribution, the theoretical derivation will be described in some detail, and preliminary analyses of the vibrational couplings in both formulations will be presented.

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Reactivity of vinylene carbonate at lithium metal anode interface: new insights from density functional embedding theory

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A strategy to achieve durable and effective anodes for Lithium metal batteries is by engineering the solid-electrolyte interphase (SEI) with purposely designed molecules [1].

To this end, some recent experiments proved that addition of vinylene carbonate (VC) in conventional electrolytes promotes the formation of a stable and protective SEI between Li metal and electrolyte [2,3]. However, it is difficult to control such complex process that involves both dissociation and polymerization of VC molecules at the electrode surface.

To dissect the tangled VC reactivity, here we present new atomistic insights on VC-Lithium SEI formation via first-principles calculations: Density Functional Embedding Theory (DFET)[4] has been applied to combine the best feasible approaches for molecular species (hybrid DFT for VC molecules and derivatives) and Li metal electrode (semi-local GGA density functional).

Our results highlight different VC dissociation pathways, with formation of reactive radical species and localized cluster of Li_2O and Li_2CO_3 , in close agreement with experiments [3]. The energetics and structural features of these intermediates improve the current understanding of SEI formation process and can be exploited to drive the reactions toward the desired interfacial properties.

Moreover, beyond these findings, our study highlights the potentialities of DFET for modeling complex reactions at hybrid interfaces in electrocatalysis

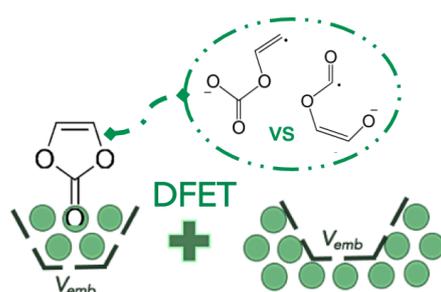


Figure 1 DFET model for VC-Li interface.

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MULTI-SCALE MODELING OF SPECTROSCOPIC FEATURES FOR ELECTRON DONOR ACCEPTOR COMPLEXES

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An Electron Donor Acceptor Complex (EDAC) is a transient species formed by two molecules, one electron donor and the other electron acceptor. Excitation under visible light of an EDAC can be used to catalyze chemical functionalization also of non-activated substrates [1]. A protein-based EDAC is an ideal kind of catalyst due to the intrinsic regio- and stereo-selectivity. Additionally, in the excited state the protein-based EDA complexes can fulfill reactions that are precluded to the ground state of the protein, as for example in Flavin mononucleotide (FMN) enereductases [2]. The transient nature of a protein-based EDAC and its dependence on the fluctuating and anisotropic protein environment makes its characterization very challenging.

Herein, we employ a multiscale methodology based on molecular dynamics simulation and the Perturbed Matrix Method [3,4] to study the first stages of the enantioselective radical cyclization of α -chloroacetamide- (1) within a FMN-dependent enereductase and a triple-mutant that shows a faster catalytic rate [2]. With this approach we are able to characterize the UV-VIS fingerprint of the involved EDA complexes, with a particular focus on the charge-transfer excited states. In particular, we aim at identifying how the protein dynamics affects the character and distribution of these states and how they differ in the wilde-type and mutated enzymes. We also plan to study the subsequent photo-induced catalytic mechanism in order to possibly predict substrates with enhanced catalytic rate and/or yield.

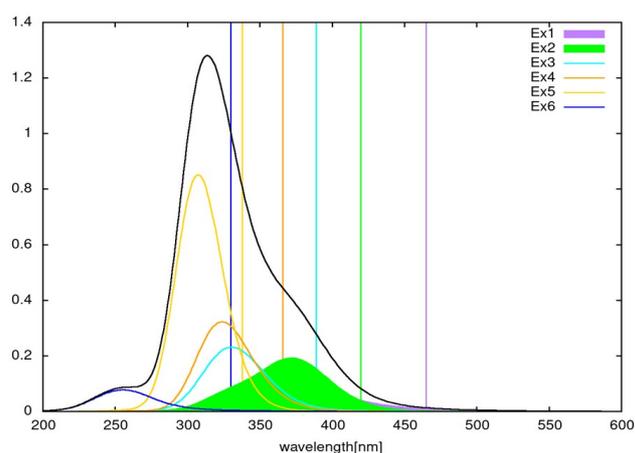
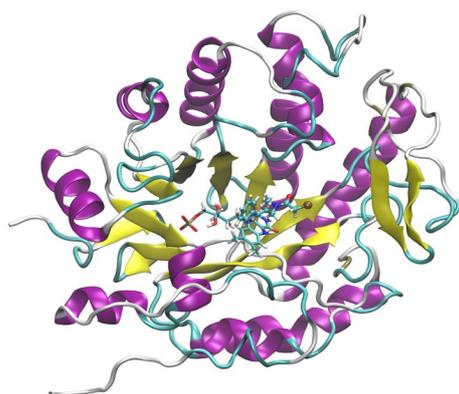


Fig.1: Secondary structure of the GluER protein with FMN cofactor and docked substrate.

Fig.2: UV-VIS spectrum under protein environment perturbation. Vertical lines represent the unperturbed energies of the excited states.

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Photophysics of tetracene derivatives in monomeric and dimeric forms through ab-initio methods

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The access to economically viable renewable energy sources is essential for the development of a globally sustainable society. Solar energy, besides fusion, has the largest potential to satisfy the future global need for renewable energy sources.[1] Single junction devices have a calculated thermodynamic efficiency limit of 31%: this so called *Shockley-Queisser* limit can be overcome by the use of various types of third generation solar cell devices.[2] A valid strategy to deal with such theoretical limit is to exploit photophysical processes, known as *multiple exciton generation*, which are able to give a $1 \rightarrow 2$ conversion, boosting the overall efficiency up to 100%. *Singlet Fission (SF)* falls into this category, a process in which an organic chromophore in an excited singlet state shares its excitation energy with a neighboring ground-state chromophore and both are converted into triplet excited states.[3, 4] One class of molecules that satisfies the requirements to observe SF is a new organic n-type material based on indene scaffold already used in organic photovoltaic devices.[5, 6, 7] In this work we carried out a theoretically and computational study of the photoinduced pathway and related spectroscopies of two indenotetracene derivatives of 9,10-diphenylindeno[1,2,3-fg]tetracene, an asymmetrically substituted indenotetracene (Dimethoxy ASI) molecule. To this aim we exploited the *density functional theory (DFT)*, its *time-dependent* version (*TD-DFT*) [8, 9] and real time propagation of electronic density, a first step for non adiabatic molecular dynamics.[10] First, an accurate calibration of the potential was performed, finding the best potential that minimizes the computational cost without losing accuracy for the description of all of the electronic states considered. In addition, a detailed balance of the environmental effects was obtained by the introduction of the implicit solvent,[11, 12] while non-covalent interactions were accounted by employing empirical dispersion methods.[13, 14, 15, 16] The benchmarked level of theory was obtained comparing our results with the experimental spectroscopic studies.[17] We obtained a reference structure by optimizing the monomer of Dimethoxy ASI extracted from the crystallographic structure. On this geometry we evaluated effects on the electronic excited states characterized by different exchange correlation *DFT* kernels, implicit solvent, dispersion corrections and basis sets by performing several *TD* calculations. Relying on this preliminary step, we evaluated the influence of different substituents (electron donor vs. acceptor) on the ground and low lying excited states. Then, since the *Singlet Fission* is a multichromophoric phenomenon,[18] we extended our study to the dimeric form. In particular, analyzing the X-Ray structures we discovered multiple spatial conformations.[17] We started from these to obtain two reference structures by *DFT* optimization. We then performed a detailed excited state analysis by *TD-DFT*, evaluating the presence of charge transfer states and the effects of the dimeric form on the transitions. Finally we collected non-equilibrium real time electronic dynamics in order to take into account explicit properties of electronic density on the Dimethoxy ASI and Dimethyl ASI structures. In particular we analyzed the evolution of the bright charge transfer states that can be crucial in mediating the singlet fission first step that leading to $^1(TT)$ state. Results give numerous insights on the *SF* process involving these indenotetracene derivatives.

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Glutamine as an infrared probe to understand local environment properties of fibril structures: the perturbed matrix method

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Glutamine containing proteins can form amyloid fibrils, which are known to be present in Alzheimer's and Parkinson's patients. The experimental isotopic labeled infrared (IR) bands of the two glutamines (Q4 and Q5) in a microcrystal of the yeast prion Sup35-derived peptide, GNNQQNY, with a fibrillar structure have been investigated by Wu *et al* [1]. Experimental IR signals arising from the two glutamines indicate that both residues experience different hydration environments. We studied the hydrogen bonding network of this fibril (see Figure 1) using molecular dynamics simulations and we calculated their IR spectra using a computational methodology called molecular dynamics – perturbed matrix method (MD-PMM) [2]. Our analysis clarified the molecular origin of the different spectroscopic signatures observed experimentally, that arise from the different local electric field experienced by the two glutamine residues, which is in turn determined by a different hydrogen bonding pattern [3].

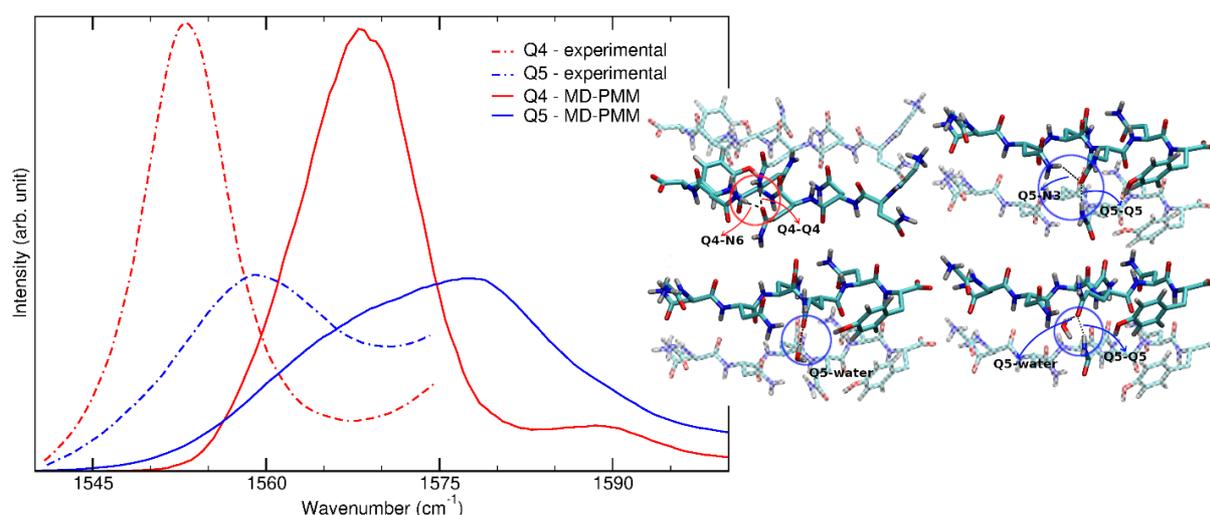


Figure 1: Left: Experimental and computed IR spectra of the C=O stretching of the two glutamine residues (Q4 and Q5) in the GNNQQNY peptide; Right: Hydrogen bonding networks responsible for the main differences in the IR signals between Q4 and Q5.

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