

Chimica Teorica e Computazionale

CTC-KN-01 The polarizability and hyperpolarizability of C and BN nanotubes.

A quantum-mechanical simulation.

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The polarizability, the first and second hyperpolarizability of BN and Carbon nanotubes of the (n,0) family have been evaluated by using a quantum-mechanical approach, a Gaussian basis set and the CRYSTAL code [1]. The Coupled Perturbed Hartree-Fock or Kohn-Sham Self Consistent perturbative schemes [2-3] have been implemented and applied to tubes of increasing radius (from (6,0) to (60,0)) [4,5]. The pure electronic and the ionic contributions have been evaluated, the latter through the FF-NR (finite field nuclear relaxation) scheme proposed by Bishop and Kirtman [6,7]. Longitudinal and transverse components of the three tensors are considered. Five different Hamiltonians (Hartree-Fock, LDA, PBE, PBE0 and B3LYP) are compared. The evolution with the tube radius is considered, and the trend towards the limit of infinite radius (that is, the hexagonal BN or the graphene monolayer) explored.

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CTC-KN-02 Steady-state and time-resolved spectroscopy by excited state ab-initio dynamics

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We discuss our recent progress in simulating steady-state and time resolved spectroscopy by equilibrium and non equilibrium excited state ab-initio dynamics. In particular, we debate the capability of excited state Born-Oppenheimer dynamics[1,2] to properly describe the solvent reorganization following a sudden change of the local electric field, due to electronic excitation of a solute. The focus is on optical spectroscopy and on the potentiality of solvatochromic fluorophores to act as molecular probes.[3,4] Study cases are illustrated.

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CTC-KN-03 Modeling molecule-based devices using Density Functional Theory

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The performances of Density Functional Theory (DFT) and Time-Dependent DFT (TD-DFT) for the prediction of photophysical properties of molecule based devices are here reviewed taking as an example two classes of compounds used either as Photochemical Molecular Devices (PMDs) or as dyes in dye-sensitized solar cells (DSSCs). In the case of PMDs the topology adopted for the novel systems proposed derives from that of acceptor dyads devised to produce charge separated states constituted by an electron withdrawing moiety (A) covalently linked to a photosensitizer (P). Both the properties of existing dyads as well as those of new acceptor units eventually functionalized with magnetic substituents, will be analyzed. In this case various mechanisms of magnetic coupling, as a function of the topology of the acceptor units, will be discussed. The performances of different approaches in reproducing both magnetic coupling and spectral properties will be reviewed. [1-5]. In the case of DSSCs, the performances of DFT and TD-DFT for the study of the photophysical properties of dyes in complex environments (i.e. when adsorbed on semiconductor, such ZnO and TiO₂) are shown via two examples [6-7]. A general protocol for the in-silico optimization of dyes for DSSCs applications is proposed [8].

Finally, some possible methodological developments based on the use of a Spin Flip approach will be discussed.

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CTC-KN-04 Oxygen activation by oxides at the nanoscale

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The properties of materials change when the dimensions are reduced at the nanometer level. This is true also for oxide materials in the form of ultrathin films on metals or of nanoparticles. Here we discuss three cases, all related to the capability to activate oxygen molecules and facilitate oxidation processes by nano-oxides. In doing this we combine DFT calculations with sophisticated experiments. The first two cases deal with oxide ultrathin films. We report recent results which show the spontaneous formation of superoxo radical anions, O_2^- , by simple adsorption of molecular oxygen on 2-3 layers of MgO grown on Mo(100) [1]. The process involved is the spontaneous tunnelling of electrons through the MgO thin film and the process is of general importance in the field of oxidative catalysis.

The second example is related to monolayer FeO(111) films grown on Pt(111) which efficiently promote low temperature CO oxidation [2,3]. The proposed mechanism includes adsorption of O_2 , formation of O_2^- , and oxidation of the bilayer FeO film to a trilayer O-Fe-O film. Under CO and O_2 pressures, this system catalyses CO oxidation to CO_2 via a Mars – van Krevelen type mechanism. The reaction is possible only thanks to the high flexibility of the FeO thin layer, a typical property of ultrathin oxide films not present in bulk surfaces.

The last example is related to oxygen activation on stoichiometric and reduced CeO_2 nanoparticles. The interaction of O_2 with the regular $CeO_2(111)$ surface is very weak, while a strong bond occurs with O vacancies (reduced ceria). On O vacancies (two-electron centers), however, only peroxo, O_2^{2-} , and not superoxo species form. We show that superoxo ions can form on reduced ceria nanoparticles where single excess electrons are localized on low-coordinated Ce^{3+} ions. The interaction of O_2 with these one-electron centers leads to the formation of paramagnetic O_2^- ions [4,5].

These three examples show the importance of dimensionality on the catalytic properties of oxide materials.

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CTC-KN-05 The Excited State Decay in DNA: Quantum Mechanical Calculations on Realistic Polynucleotide Models

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The dynamical properties of the excited states of DNA and of nucleobases have been extensively investigated in the last years, triggering a very lively scientific debate, especially concerning the decay in single and double DNA strand [1,2]. In the last years we have tried to describe, at a Quantum Mechanical level, systems as close as possible to those studied by experimentalists.[3-8] For example, we have studied the excited state decay of a meaningful model of polyAde-polyThy double strand (the Ade₂-Thy₂ tetramer) in aqueous solution.[6,7]

By characterizing the main excited state decay routes of a tetra-nucleotides (dA)₄Na₃, fully treated at the QM level, we have recently obtained an unifying description of the dynamics in A-based polynucleotides, giving account of all the main available experimental results, showing that their behaviour is ruled by the equilibrium between 'neutral' and 'charge transfer' excimers.

The study of the most significant decay routes in dinucleotides of Thymine (dT)₂ provides instead useful insights on the effects ruling the formation of cyclo-butane dimers and of 6-4 adducts, i.e. the most significant lesions formed in DNA following the UV absorption.

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CTC-KN-06 Computer Simulation Study of Dynamic Crossover Phenomena in Supercooled Nanoconfined Water

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In order to study the dynamic crossover phenomena in nanoconfined water, we performed a series of molecular dynamics (MD) computer simulations of water clusters adsorbed in zeolites, which are microporous crystalline aluminosilicates, whose channels and cavities are of nanometric dimensions.

We used a sophisticated empirical potential for water, including the full flexibility of the molecule and of the aluminosilicate framework was included in the calculations [1,2].

The results of the simulations of water confined in a variety of zeolites (worm-like clusters in silicalite[1], spherical nano-clusters in zeolite A [3], cross-linked nanowires in NaX and ice-like nanotubes in $\text{AlPO}_4\text{-5}$ and SSZ-24 [1]) at different temperatures and coverage (*loading*) are discussed in connection with the experimental data. Preliminary results of Car-Parrinello MD simulations of water in vermiculite clay are also shown.

In particular, dynamic crossover phenomena are found for the adsorbed water in all the considered cases, in spite of the different shape and size of the clusters, even when the confinement hinders the formation of tetrahedral hydrogen bonds for water molecules. They were evidenced by inspecting the trends of rotational relaxation constants and of spectral contributions to vibrational spectra *vs.* temperature.

Dynamical crossover temperatures were detected around 220 K and 160 K, corresponding to those found experimentally in many hydrated systems, such as aqueous solutions, oxide surfaces, clays, proteins and cement paste. Based on a detailed analysis of the single-molecule dynamical behaviour, hypotheses about the possible dynamic crossover mechanisms are proposed.

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CTC-KN-07 Theoretical Modelling of Electron Transfer Reactions in Complex Molecular Systems.

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Modeling of electron transfer (ET) reactions in complex atomic-molecular environment have always represented a challenge for computational-theoretical physical chemistry. The main reason for that probably resides in the fact that many of the experimental observations regarding ET thermodynamics and kinetics usually involve purely quantum events, i.e. the electron dynamics, somewhat coupled with the classical and semi-classical atomic-molecular degrees of freedom.

As a consequence a physically coherent modeling of this kind of reactions should take into account different events occurring on very different energy and time scales. If one wants to avoid brute-force dynamical calculations to this problem, which are still far from providing reasonable numbers for molecular systems with more than a couple of atoms with few electrons, alternative theoretical and computational tools are necessary. The most popular and efficient approach to address ET reactions rely on the seminal work of Marcus and much of the kinetics is modeled within the framework of the Fermi Golden rule. In this respect a huge amount of computational data have been, and are still being produced. However, despite the successes of Marcus theory, probably further efforts are still necessary for improving our ability of reproducing the complexity of the experimental observable. In particular the coupling with the atomic-molecular fluctuations might be not always reducible to simple analytical forms.

In the last few years we have been working for developing a new computational-theoretical methodology, somewhat complementary to Marcus model, essentially based on a joint application of Molecular Dynamics simulations and Quantum-Chemical calculations and making use of the basic concept of the Diabatic Perturbed Energies to approximate the evolution of the Electron Transfer. In this talk the theoretical basis of the method and two applications, one concerning the equilibrium properties of ET reaction and the other one focused on the modeling of non-equilibrium (kinetics) observables, will be illustrated and commented.

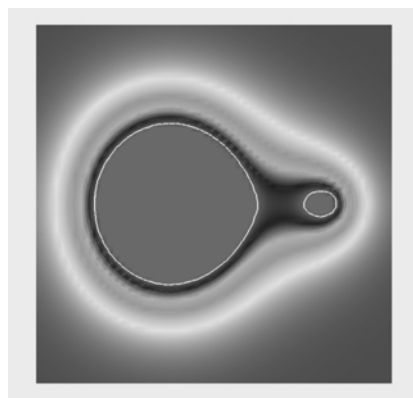
CTC-OR-01 Roto-vibrational Characterization of Heavier Protonated Argonons by the Relativistic CCSD(T) Method

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Already in 1933 Pauling inferred the existence of a peculiar chemistry for the heavier inert gas, [1] namely for Kr and Xe and potentially for the radioactive Rn. He also suggested to name them *argonons* (*Rgs*), to move out their claimed nobility and/or inertia. In fact, the first ionization energies of the heavier *Rgs* are in-between those of B and N, being that of H smaller than that of Kr but larger than that of Rn and Xe. *HRgX* species, with X non-hydrogenic atoms, have been characterized spectroscopically, [2] showing a significant although not dominant RgH^+ component, further investigated deeply. [3]



The electronic structure and the spectroscopic roto-vibrational properties of protonated heavier *Rg* species (RgH^+) have been here calculated, employing a fully relativistic coupled-cluster approach with single and double excitations and a perturbative treatment for triple excitations [CCSD(T)]. Roto-vibrational constants have been obtained by the Dunham analysis performed on the calculated potential energy curves, showing a very good agreement with the available KrH^+ e XeH^+ experimental data. This clearly allows for confidence in the calculated results obtained for the experimentally not characterized RnH^+ species that, as a consequence, could be used for designing spectroscopic experiments, never realized so far. The parameters calculated at relativistic level were compared to the corresponding ones, got without considering relativistic effects. In addition to the expected behavior – concerning the dissociation paths ($Rg + H^+$ and $Rg^+ + H$) characterizing the different RgH^+ species ascribable to the *argononic* potential energy behavior and spin-orbit coupling – the comparison among the protonated *Rgs* also reveals relativistic effects i) on the fundamental vibration frequencies, ii) on the dipole moments and finally iii) on various higher order spectroscopic properties, referable to the differences present in the potential energy curves.

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CTC-OR-02 Carbon dioxide internal energy exchange in earth and planetary atmospheres and hypersonic flows

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The vibrational energy exchange occurring in collisions involving small molecules is largely responsible for energy relaxation and state population of gas phase, and therefore plays a key role in determining the energy balance of planetary atmospheres (see e.g. [1]).

Carbon dioxide is an important component of planetary atmospheres. Being a triatomic molecule, the exchange of internal energy upon collision can be relevant and is a key step in its contribution to the energy balance of the atmospheres. Therefore the behaviour of CO₂ in inelastic collisions with itself or other species such as N₂ and CO deserves considerable interest and finds interesting applications in plasma chemistry and hypersonic aerodynamics.

The first step of the study has been concerned with the assemblage of an appropriate Force Field. To this end electronic structure calculations have been performed at a CCSD(T) level to integrate previous MP2 results [2]. Related information has been used to build a semiempirical potential energy surface (PES) that makes use of a recently introduced bond-bond approach [3].

Due to the important effects of long range interactions on vibrational relaxation and excitation, intermolecular interactions have been formulated using a well tested bond-bond interaction model [3], which reproduces with accuracy short and long range parts of the intermolecular interactions.

The resulting PES has been exported into the VENUS [4] program, and extended ensembles of quasi-classical trajectories (QCT) have been run for the CO₂ + CO₂ collisions in a wide range of energies. Results are targeted to calculate state-to-state vibrational exchange cross sections and thermal rate coefficients. These quantities are the necessary input of kinetic models of use in gas dynamics, aircraft re-entry studies, and many other technological applications.

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CTC-OR-03 ONIOM calculations for electronic excited states.

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The accurate evaluation of electronic transition energies and properties requires the use of computationally expensive methods like the equation of motion coupled cluster singles and doubles (EOM-CCSD). However, the scaling of such methods often makes the study of molecules larger than 10–15 heavy atoms prohibitive, and more approximate approaches must be pursued. The ONIOM (Our own N-layer Integrated molecular Orbital molecular Mechanics) hybrid method, where the system is partitioned into regions which are treated with different levels of theory, represents a promising approach to completely characterize valence excited states of large molecules that cannot be entirely studied with a conventional high-accuracy method. In this contribution we present a series of results that validate the ability of ONIOM(QM:QM) to compute accurate transition energies and oscillator strengths compared to EOM-CCSD [1-3]. We test the effect of various choices of partitioning, low level methods and basis sets, as well as how the link atom bond length can affect the results. ONIOM is compared to conventional calculations with the CIS, TDHF and TDDFT methods. It is shown that the best accuracy-computational time combination is obtained with ONIOM(EOM:TDDFT).

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CTC-OR-04 NMA in aqueous solution using a portable intermolecular potential

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Molecular Dynamics were carried for N-methylacetamide (NMA) in water out using a modified DL_POLY 2.20 molecular modeling package¹. The system was investigated by running a series of simulations on a different X_{NMA} .

The MD simulations were performed with AMBER² charges for the NMA system and for the water we have used the intermolecular potential for non rigid molecules³.

Initial configurations for each of the concentrations were obtained by placing the correct numbers of *trans*-NMA and water molecules randomly on approximately

30 Angstroms lattice. The total intermolecular interaction was assembled by adding the corresponding electrostatic (V_{el}) and non electrostatic (V_{nel}) contributions. V_{el} is expressed in terms of Coulomb potential of the punctual charge distribution of different molecules while V_{nel} is expressed in terms of effective potentials formulated as an Improved Lennard Jones (ILJ) function⁴:

$$V_{\text{ILJ}} = \varepsilon \left[\frac{m}{m - n(r)} \left(\frac{r_m}{r} \right)^{n(r)} - \frac{n(r)}{m - n(r)} \left(\frac{r_m}{r} \right)^m \right] \quad n(r) = \beta + 4.0 \left(\frac{r}{r_m} \right)^2$$

in which the additional β parameter, with respect to the usual formulation of the Lennard Jones (LJ) potential, removes most of inadequacies of the LJ function.

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CTC-OR-05 Structure and Dynamics in Y:BaZrO₃ Protonic Conductor

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Yttrium-doped barium zirconate protonic conductor seems to be a good candidate as electrolyte ceramic materials for high technological devices [1]. *Ab initio* computational models of singly and doubly substituted Y:BaZrO₃ structure have been built and tested. Only in presence of two nearest neighbour yttrium atoms, the relative energy differences of stable protonic sites reproduced the correct order of magnitude of activation energy values related to the proton hopping.

Ab initio results on BaZrO₃ derivatives were the basis of MD simulations performed on yttrium-doped barium zirconate. Dynamics simulations showed a peculiar oxygen sub-network that changed its characteristics up to a temperature value, which depended on the yttrium content. Protonated models having neighbouring yttrium atoms were able to mimic the experimental activation energies characterizing protonic conduction, while oxygen atoms could be grouped into three clusters with peculiar structural features. In particular, two clusters behaved like a multilevel trap for the proton, delaying the diffusion of the latter across the material bulk. A characteristic of these traps was the very large number of proton hopping events, occurring per time unit among oxygens surrounding yttrium atoms.

These results, finally, suggest that yttrium clustering, inferred for Y:BaCeO₃ systems [2], seems to also occur for the Y:BaZrO₃ derivatives; eventually, protonic conduction in these materials could be improved avoiding such clustering, that is preventing the formation of protonic traps.

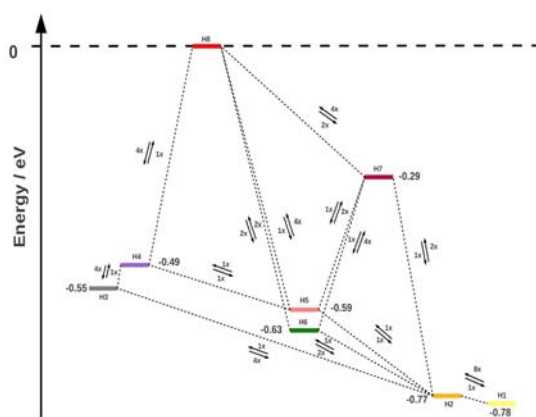


Figure 1. Energy diagram for doubly doped systems.

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CTC-OR-06 Coverage-dependent reactivity toward oxygen of Iron Phthalocyanine on Ag(110)

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In the last decade, non-precious metal compounds able to catalyze the oxygen reduction reaction (ORR) have attracted a great deal of attention as a consequence of their potential technological application as cost-effective replacement for Pt-based catalysts in low-temperature fuel cells. Actually, it is well known that Iron porphyrins (P) and phthalocyanines (Pc) can promote the reduction of O₂ to H₂O, even though their catalytic activity is lower than that of precious metal compounds and they are almost inert when supported on a substrate other than edge-plane graphite [1].

In this communication, we present a combined experimental and computational study of an ordered network of FePc adsorbed on Ag(110), able to react with O₂. The system was characterized by means of XPS, XAS and STM techniques as well as by Density Functional calculations on slab models of the adsorbed phases. The FePc molecules self-organize on the Ag(110) surface at room temperature. Two different assemblies were observed: the FePc submonolayer exhibited a c(10×4)/p(10×4) arrangement whilst, in the proximity of one monolayer, a more compact (1 4, 4 -3) phase emerged [2]. Furthermore, it was found that, at low-coverage, the FePc units react with O₂ inducing a dramatic change of the STM intramolecular features. Interestingly, such a reaction did not take place at higher coverages. The theoretical modeling of the FePc/ Ag(110) interface ultimately shows that the reactivity of FePc toward oxygen is ruled by the Fe local environment.

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CTC-OR-07 Modeling proton transfer in Proton Exchange Membrane Fuel Cells: a combined DFT/MD approach

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The performances of Proton Exchange Membrane Fuel Cells (PEMFCs) are strongly influenced by the proton conductivity of the solid electrolyte. The N-heterocycles based polymers are today the most promising materials to improve the effectiveness of these systems. A protocol based on Density Functional Theory (DFT) to study azole-based systems is proposed [1]. A detailed theoretical investigation performed on Poly(4-vinyl-imidazole) (P4VI) indicates that the commonly accepted mechanism (Grotthuss) could be hindered in this system because of the backbone constraint. Classical Molecular Dynamic simulations support an alternative mechanism of conduction hypothesized. This latter involves a rotation of the protonated imidazole, constituting the rate-limiting step, before each proton transfer reaction between adjacent azole-moieties can take place (Figure 1). These new insights into the mechanism of conduction are relevant for a rational design of modified azole-based systems used in PEMFCs.

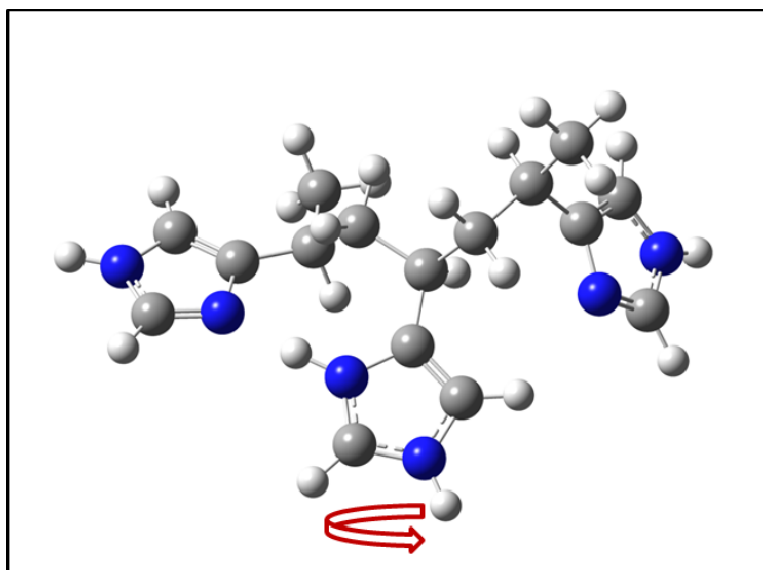


Figure 1

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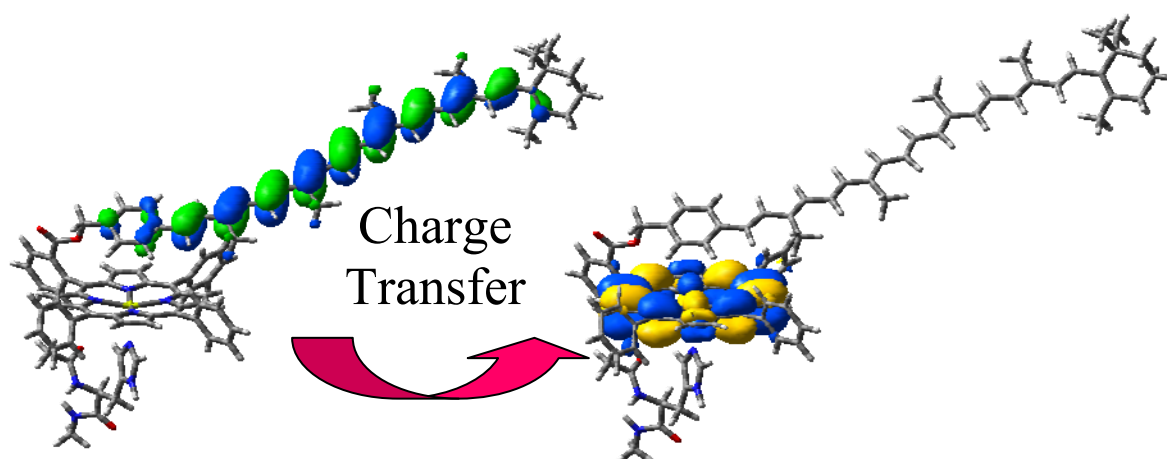
CTC-OR-08 Tuning charge transfer in model bio-inspired porphyrin-carotene dyads

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We present a computational study on model bio-inspired donor-acceptor (DA) dyads formed by a carotenoid (C) covalently linked to a tetraphenylporphyrin (TPP) at the *ortho* position of one of the TPP phenyl rings [1]. The mutual orientation of the components and their distance closely resembles the geometry of the dyad chlorophyll-peridinin in PCP [2]. Dyadic systems are intensively studied for potential application in the construction of organic solar cells and development of efficient photocatalytic systems for the solar energy conversion for the unique advantages they offer with regard to synthetic feasibility. The recent progress in computational methodologies, especially the development of DFT rooted methods suitable to describe charge transfer (CT) processes, allow to perform systematic investigations *in silico* of those molecular features which might be important to design high performance bio-inspired artificial devices.



Focused on CT process, this study aims (i) at better understanding the effect of slight chemical modifications on the absorption spectra, in particular on the lowest CT bands, as well as (ii) at gaining deeper insight on the role of H₂O and histidine (Hys) in the biological system. The coordination of H₂O or Hys might occur in two different positions: it can be sandwiched between the carotene and the porphyrin ring or can be coordinated to the metal under the porphyrin plane. The effect of different metals of biological interest is also investigated to rationalize the fine tuning of the CT process.

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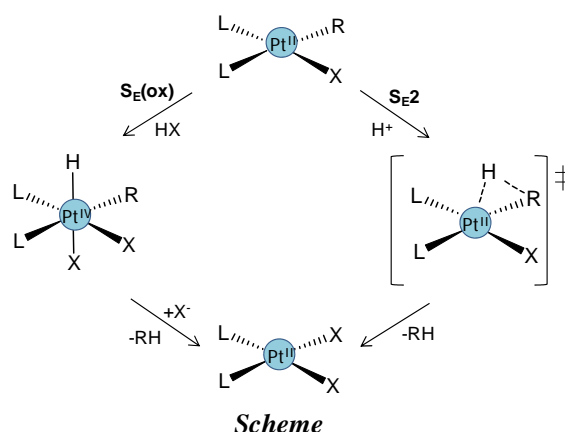
CTC-OR-09 Mechanistic Insight into Protonolysis of Dimethylplatinum Complexes. A DFT Study

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Development of catalysts able to selectively transform hydrocarbons to value-added products is among the most fundamental challenges in chemistry. The understanding of the mechanism of the protonolysis of the Pt-C bond of alkyl Pt(II) complexes, as the *microscopic reverse* of C-H bond activation process, can be considered a part of the efforts devoted to shed light on the mechanistic aspects of alkane C-H bond activation. To date it is still a difficult challenge to obtain experimentally direct and accurate insight in the mechanistic pathways of chemical reactions due to the very short lifetime of key intermediates. Obviously this holds also for the reaction we are addressing here. Computational studies do not suffer from these limitations and provide therefore a valuable complementary tool with respect to experimental studies. The outcomes of a detailed theoretical investigation, aiming to give a contribution to the debate on the mechanism of the electrophilic cleavage of the Pt-C bond, are presented. Energy profiles have been calculated, and compared with experimental observations, for the protonation and subsequent methane elimination reactions of a series of dimethylplatinum(II) complexes as a function of the nature of the ancillary ligands and solvent. The possibility to rationalize and predict the preference for a stepwise oxidative, $S_E(\text{ox})$, or a concerted, S_E2 , route has been examined. Theoretical calculations suggest that HOMO nature, d metal based or σ -bond localized, is the main factor in determining the preferred protonation site, platinum or carbon atom, and then the preferred protonolysis mechanism.



CTC-OR-10 Possible mechanistic paths of the enzymatic activity of GPx

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Glutathione peroxidases (GPx, Fig. 1) belong to a widespread family of proteins that, over the years, have been discovered in almost all kingdoms of life.[1] They catalyze the reduction of H₂O₂ or organic hydroperoxides to water or corresponding alcohols, thus mitigating their toxicity.[2] The global reaction is ROOH+2GSH → GSSG+ROH+H₂O, where GSH indicates glutathione. In the GPx family the active site SeCys or Cys is surrounded by highly conserved residues (Asn, Gln and Trp) forming the catalytic tetrad. One of the main open questions is about the specific role of either SeCys or Cys in the catalysis: it is not yet clear why selenium rather than sulphur has been chosen by nature selection given that a complex and energetically very expensive co-translational insertion machinery for SeCys is needed.

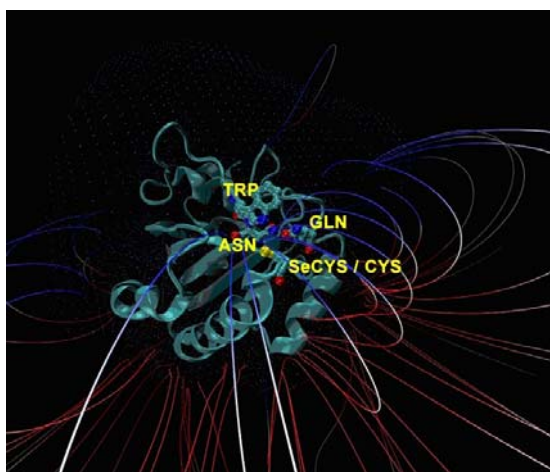


Fig. 1 GPx

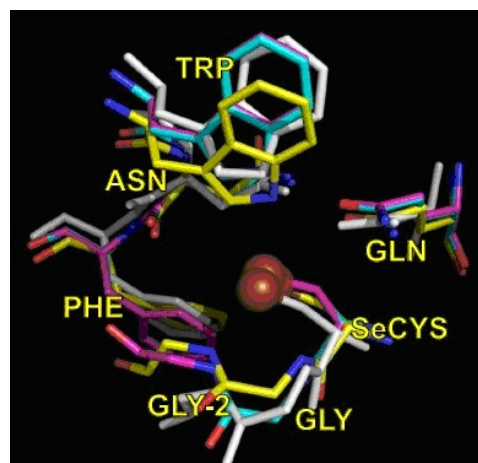


Fig. 2 Model catalytic site

The basic catalytic scheme involves three main steps, i.e. (i) O-O bond cleavage and formation of selenenic/sulphenic acid Se/S-OH and ROH; (ii) formation of a seleno-sulfide (disulfide) intermediate and elimination of H₂O; (iii) formation of the disulfide product and regeneration of the catalyst.

We present a detailed investigation of different possible paths of the reduction of H₂O₂ catalyzed by Se-based as well as S-based GPxs with the aim of validating at quantum chemistry (DFT) level the experimental findings obtained by recent mass spectrometry and biochemistry methods (enzymatic kinetics); a core of seven aminoacids has been identified, which suitably represents the GPx core (Fig. 2). From our results a complex energy landscape emerges, where novel mechanistic paths are possible and novel perspectives on the intriguing behaviour of GPx can be outlined.

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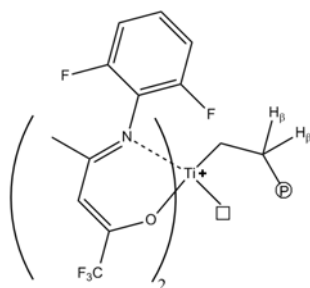
CTC-OR-11 H_{β} -termination mechanisms in living catalysis of polyolefin at *ab-initio* level

Vincenzo Villani and Gaetano Giammarino

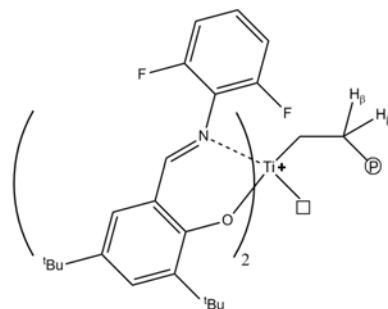
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Fujita¹ has been the first to highlight the living behavior of Ti-bis(phenoxyimine) catalysts in the polymerization of ethylene, and proposed the role of an hydrogen-bond between aromatic *o*-fluorine and H_{β} of the growing chain in the H_{β} -transfer inhibition. Coates² demonstrated the living behavior of non fluorinated catalysts, showing an active role of the chelating ligands in this context.



Recently, Mecking³ showed that the simpler catalyst Ti-bis(enolatoimine) with *o*-fluorinated aryl groups is able to achieve a living behavior and proposed via NMR studies a key role of the H-bonds between *o*-F and either H_{β} atoms or Ti in the suppression of the H_{β} -termination. In our recent works^{4,5}, we analyzed via DFT a number of models for Ti-bis(phenoxyimine) and Ti-phenoxyarylpyridine catalysts and studied the insertion mechanism and the role of F interactions.

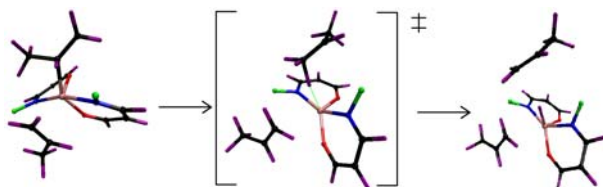


Currently, we are investigating the mechanism of H_{β} -transfer inhibition, necessary to achieve the living polymerization behavior. We studied both Fujita's and Mecking's catalysts with living or non-living behaviors.

Ab-initio calculations were performed on parallel platform using GAUSSIAN09.

Minimum energy profiles have been computed, in which one or two selected internal coordinate(s) are scanned. In all cases, the stationary points (minima and transition states) were localized and energy barriers of activation determined.

A deep investigation of the different termination mechanisms has been performed, and insight about the reasons for each of them taking place is proposed.



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CTC-OR-12 Natural and Artificial Photosynthesis: Computational Studies

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Nature has solved the difficult problem of efficient light-driven, four-electron oxidation of water to O₂, by means of a Mn-based catalyst embedded in the Photosystem II (PSII), a ~350 kDa complex of 20 proteins. The Mn₄CaO₅ cluster of the oxygen-evolving complex (OEC) of PSII is composed of inexpensive earth-abundant metals (Mn and Ca) and features high turnover rates that are still unmatched by artificial water splitting systems. Elucidating its detailed molecular structure and the catalytic mechanism of photosynthetic water oxidation is crucial for developing new biomimetic catalysts for renewable solar-energy conversion.

Computational modeling studies, including density functional theory (DFT) combined with quantum mechanics/molecular mechanics (QM/MM) hybrid methods, have proposed chemically satisfactory models of the fully ligated OEC Mn-cluster that are maximally consistent with experimental results [1]. Mechanistic investigations of the water-splitting reaction of the OEC have been fundamentally informed by structural studies of oxomanganese complexes. In particular, the [H₂O(terpy)Mn(O)₂Mn(terpy)OH₂](terpy is 2,2':6',2''-terpyridine) complex, is a multi-turnover homogeneous water-oxidation catalyst and an excellent functional model of the OEC [2].

This talk summarizes our recent advances on studies of PSII and biomimetic oxomanganese complexes for artificial photosynthesis. Our computational studies [3,4], including DFT, QM/MM methods, classical Molecular Dynamics (MD) and Monte Carlo simulations, are based on the recent crystal structure of PSII at 1.9 Å resolution [5]. We have introduced a novel model for the OEC resting state [3] and elucidated the structural/functional role of chloride cofactor in PSII [4]. The implications of these findings on the water-splitting mechanism in both homogenous and enzymatic reactions will be discussed.

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CTC-OR-13 Monomeric and Collective Deactivation Mechanisms in Photoexcited DNA Investigated by a Quantum Dynamical Approach.

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Sunlight is essential to life but it is also a potential carcinogenic agent, and evolution has selected highly photostable molecules to encode the genomic information. Their photostability is ensured by highly efficient decay pathways that are able to transform the electronic excitation into vibrational energy and finally into heat. The deactivation mechanisms of the single nucleobases after the $\pi\pi^*$ excitation has been deeply investigated experimentally and show multi-exponential features ranging from fs to ps timescales [1]. Here we report the results of our recent static [2] and quantum dynamics investigation of the role of $\pi\pi^*$ in the decay of Uracil derivatives both in gas-phase [3] and in different solvents [4-5]. Potential energy surfaces have been characterized by TD-DFT, while solvent effect has been accounted by mixed atomistic/continuum models.

The understanding of the dynamics of isolated nucleobases is the necessary pre-requisite for a full comprehension of the deactivation processes in the real bio-polymers, where nonetheless inter-bases interactions modify the efficiency of the single-base decays and open new competitive pathways. In fact long-living excited states, up to the nanosecond timescale have been identified in DNA oligomers, while they are absent in single nucleobases [6]. Recently, we performed TD-DFT studies in water solution of the excited states of adenine stacked dimers [7], and of tetramers made up of adenine-thymine base-pairs [8]. From these data we derived a vibronic Hamiltonian to study, at quantum dynamical level, the interplay between excitonic and charge-transfer states in the decay mechanism, and we applied it to dimers and oligomers [9]. Quantum dynamical calculation have been carried through traditional Lanczos based propagation schemes and/or a self-made implementation of MCTDH method [10]

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ORG/CTC-KN-01 Bridging the Gap between Theory and Experiment: Modeling Chiroptical Properties and Spectroscopies

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The tremendous progress of ab-initio quantum chemistry in the last decades has led to an increasing number of applications of quantum mechanical (QM) approaches to the calculation of chiroptical properties [1-7].

The progress has been so large that a “renaissance” in chiroptical methods due to the accuracy and computational efficiency achieved by ab initio QM methods in reproducing experimental data and predicting new ones has been invoked [8].

In this contribution, some peculiar aspects of the computation of chiroptical properties and spectroscopies are remarked through the analysis of case studies, with special emphasis towards the gaining of calculated data directly comparable to experiments, by the inclusion of solvation and vibrational effects.

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Protein lysine acetylation is a key mechanism in the epigenetic control of gene expression, the regulation of cell metabolism[1,2], and protein deacetylases are potential targets for treating cancer and a range of autoimmune and neurodegenerative diseases[3]. In this context, the HDAC inhibitors have attracted the attention of the researchers as promising anticancer agents [4,5]. Based on sequence phylogeny and function, there are four distinct classes of HDAC: class I (HDAC1, 2, 3 and 8), class IIa (HDAC4, 5, 7 and 9), class IIb (HDAC6 and 10) and class IV (HDAC11) represent Zn²⁺-dependent amidohydrolases, whereas class III comprises the mechanistically diverse NAD⁺-dependent sirtuins [6]. In this contribute, we have traced out the structural elements responsible of selective binding in the whole landscape of the HDAC isoforms considered interesting therapeutic targets. In particular, we have rationalized experimental observations and tried to systematically add new insights for a targeted design of selective inhibitors for the different HDAC isoforms. In detail, we have focused our attention on all HDACs zinc dependent enzymes, except HDAC5 and HDAC9-11, for which few information on expression, function in tumor cells, and ligand inhibitory profile are available in literature. The structural analysis was performed by molecular docking calculations, using as ligands known pan and class selective HDAC inhibitors [4]. Based on the obtained structural guidelines, we designed, synthesized and experimentally tested selective inhibitors for HDAC2.

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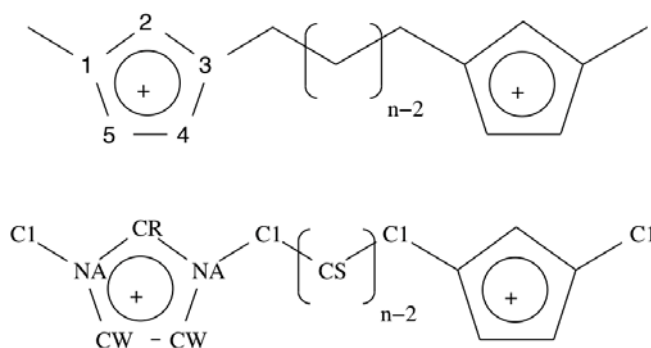
ORG/CTC-OR-01 The Structure of Ionic Liquids Based on Geminal Imidazolium: a Theoretical Study

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Among the most exciting and successful materials developed and studied in the last twenty years, ionic liquids [1] are among those that can certainly claim one of the most rich field of applications in industry and in applied technological research. A special class of ILs is have recently been obtained using geminal imidazolium dications [2] that represent a very interesting variation of the cationic partner and that may present various advantages over the traditional mono-cationic ionic liquids in applications such as lubricants, catalyst, solvents and as separation media.



A schematic view of the molecular structures is reported above: we have a linkage chain (whose length can be 3, 6, 9 or 12 for the compounds analyzed in the present work) that connects two imidazolium rings with a net positive charge on them and that are substituted with a methyl group. We have recently [3] analyzed the behavior of such compounds by calculating the structures of the gas phase complexes. We will report these and further results obtained by means of MD simulations.

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ORG/CTC-OR-02 Chemoinformatic strategies in the design of new antibacterials active against multidrug resistant Gram-positive pathogens.

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Chemoinformatic strategies possess great potentialities in modelling the interactions between biopolymers and ligands. Molecular recognition plays in fact a fundamental role in drug-receptor interactions.

Due to the lack of pharmacological targets, in previous studies [1] we adopted a Virtual Receptor Site (VRS) approach, where ligands interact with a complex receptor of unknown structure, aimed at identifying pieces of the structure which could be valuable for improving the antibacterial activity.

In the design of new drugs it is also very important that they exhibit ADME (Adsorption, Distribution, Metabolism, Elimination) properties warranting an acceptable bioavailability. For this purpose, a new method, called VOLSURF [2], able to correlate 3D molecular structures with physico-chemical properties, and highly efficient in predicting the biological activities, appears to be appropriate.

According to the advances achieved in the past two years due to the availability of the x-ray structures for a few drug targets, molecular modelling by docking of new ligands to the receptor active sites appears nowadays an appropriate strategy in the design of new antibacterials against multidrug resistant strains.

In this context, we adopted a recently developed algorithm called Fingerprints for Ligands and Proteins (FLAP) that can be used to describe proteins and ligands based on a common reference framework [3]. FLAP is able to explore the 3D-pharmacophoric space of ligands and proteins and to provide quantitative information for the complementarity of their interactions to allow ligand-ligand, ligand-protein, or protein-protein comparison. By means of all these chemoinformatic tools, we studied the interactions between synthetically accessible compounds and the crystallographic structure of Linezolid binding protein to identify a scaffold that we could modify introducing different substituents to improve the *in vitro* antibacterial activity.

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ORG/CTC-OR-03 Revisiting Nucleophilic-Electrophilic Mechanisms in Oxidation Reactivity

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Oxidation chemistry has always been one of the most important playgrounds for the interpretation and mastering of reactivity.[1] The interest of scientists has been driven not only by the strong implications that this reactivity plays in biological systems, but also because it represents an essential tool in functional groups transformation. These studies have also deeply contributed to the development of the basic principles of reactivity.

In recent years we have been involved in the study of metal catalysts for oxygen transfer reactions.[2] The experimental results have offered us the possibility to investigate in detail the mechanism of oxidation reactions, and in particular to study the effect of intermolecular interactions in catalysis.[3]

The evaluation of these experimental results, with the support of theoretical calculations, have led to a reinterpretation of the concept of nucleophilic and electrophilic reactivity in oxidation chemistry. This analysis can have implications that go beyond oxidation chemistry

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ORG/CTC-OR-04 L-Arabinose adsorption on a Ru cluster

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Use of bio-mass for energy, chemicals and material supply is one of the key issues of sustainable development, because bio-based resources are both CO₂-neutral and renewable, at variance with fossil fuels. Carbohydrates are the main source of renewables employed for the production of bio-based products. Therefore, chemistry know-how on industrial processes, involving carbohydrates is a subject of basis importance. Adsorption of the monosaccharide L-Arabinose on a ruthenium nanocluster is here presented as an example of a catalytic system of potential industrial interest [1]. L-Arabinose can be found in aqueous solution in 5 tautomeric forms (*i.e.* α or β pyranose, α or β furanose and acyclic species) in equilibrium with each other. All these tautomers show a very large conformational flexibility, which previously has been also analyzed.

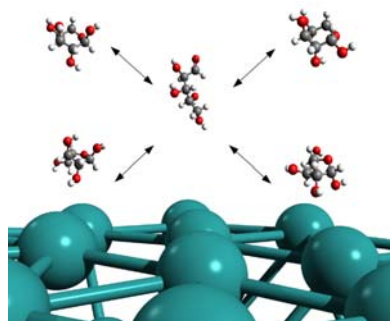


Figure 1. L-Arabinose on Ru surface

The L-Arabinose/Ru system has been investigated into the frame of the density functional theory (DFT). Calculations have been actually performed, using the DFT approach as implemented in SIESTA [2]. This employs linear combination of pseudoatomic orbitals as basis set. The atomic core is replaced by a non-local norm-conserving relativistic Troullier Martins pseudopotential, factorized in the Kleinmann-Bylander form.

The adsorption of different conformers, per each tautomers, on a Ru (0001) surface of the nanocluster have been modeled and analyzed in order to characterize the adsorption points both on the ruthenium surface and in the tautomeric species and to characterize if some of the latter are especially stabilized by the adsorption processes. Since adsorption phenomena could be affected by the adsorbate orientation, three different ways of binding per each conformers were investigated, considering either pyranose or furanose forms, and two for the acyclic forms.

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CTC-PO-01 Computation of the lineshape of electronic spectra in solution within polarizable continuum models: Accounting for both vibrational structure and inhomogeneous broadening

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Starting from the Marcus's relationships connecting the inhomogeneous broadening with the solvent reorganization energy and exploiting recent developments in Polarizable Continuum Model [1] and PCM/TD-DFT calculations namely state-specific (SS) treatment [2], we propose a procedure to estimate the polar broadening of optical transitions. When applied to a representative molecular probe, coumarin C153 in different solvents, our approach provides for the polar broadening values fully consistent with the experimental ones. For the first time fully ab initio vibrationally resolved absorption spectra in solution (Figure 1) are computed (including both Duschinsky and Herzberg Teller effects, with a method developed in our group [3]) and obtaining spectra for coumarin C153 in remarkable agreement with experiments [4]. Such an agreement allows us to critically compare the relevance of all the vibrational and medium effects that produce the observed lineshapes in gas phase and in different solvents.

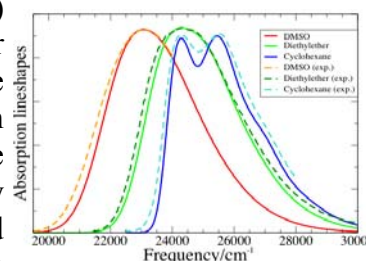


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CTC-PO-02 Theoretical investigation of magnetic properties in Cu(II) complexes with bridging azide ions

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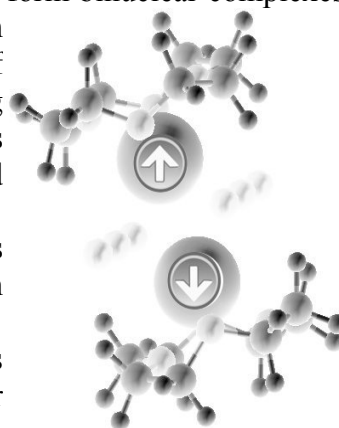
The property of the azide ion to act as a bridging ligand has been recently exploited in the formation of crystals of crown ether complexes, such as those formed by $[\text{Cs}([18]\text{-crown-6})(\text{N}_3)_2]$, where two azide ions form a linkage between two cesium cations each coordinated by crown ether [1].

In this work, using a computational approach at DFT level, we report some preliminary results obtained in investigating the possibility of forming similar complexes in which, instead of the cesium ion, is present the copper(II) ion.

It is known indeed that the azide ion can bind transition metal atoms to form binuclear complexes, such as $[\text{Cu}_2(\text{tetramethylethylenediammine})(\text{N}_3)(\text{OH})(\text{ClO}_4)_2]$, which show different magnetic properties depending on the kind of coordination [2]. In particular, when the azido group acts as bridging ligands with end-on coordination the resulting binuclear complexes show a ferromagnetic behavior and, conversely, when it is coordinated in an end-to-end fashion an antiferromagnetic coupling results.

Therefore, for these complexes the exchange coupling constant J has been estimated as the energy difference between the state of high spin and a broken symmetry singlet state [3].

All results obtained here may be useful for designing new compounds with magnetic properties applicable in the field of single molecular magnets.



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CTC-PO-03 Computational modelling of *de novo* formation of DibenzoFuran: investigation of oxidative pathways of Pyrene and BenzoDibenzoFuran

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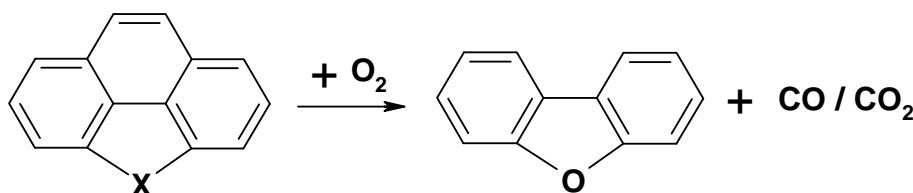
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Municipal solid waste (MSW) incineration leads to the production of significant amounts of polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF).¹

PCDD/Fs are formed in the combustion processes through two main pathways: one involving reactions in the gas phase of precursors, such as chlorinated phenols and chlorobenzenes, in the 400-800 °C range; the second one operates in the 200–400 °C range and mainly involves the so called *de novo* synthesis, which proceeds through burn off of a carbonaceous matrix present in the fly ash with simultaneous oxidation and chlorination reactions. The *de novo* synthesis is the dominating route in the PCDD/F formation in flue gas cooling sections of industrial scale incinerators.²

Here we present a theoretical investigation of the oxidative pathways of Pyrene (**1**) and Benzo DibenzoFuran (**2**) that can lead to DibenzoFuran formation. These two systems have been chosen as model compounds of the carbonaceous matrix present in the fly ash.



- (1) X: CH=CH Pyrene
(2) X: O Benzo DibenzoFuran

Optimized geometries and harmonic vibrational frequencies of reactants, intermediates, products and transition states have been calculated at the PBE1PBE/6-311G** level. IRC calculations have been used to link reactants and products with their transition states. On the basis of previous theoretical studies on benzene³ and dibenzofuran⁴ oxidation, the investigated mechanism involves the initial formation of a radical species (**R**[•]) that, reacting with molecular oxygen, yields a peroxy radical (**R-OO**[•]). In (**1**) and (**2**), this key-intermediate evolves toward the products following similar paths but involving different energetic barriers.

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CTC-PO-04 Role of IRMOF-3 Zn₄O Vertices in Knoevenagel Condensation

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The Knoevenagel (*Knvgl*) condensation, employed to produce alkenes, involves couple of molecules singly having carbonyl groups and α acidic hydrogen atoms. It has been recently reported that the third member of the Isoreticular Metal Organic Framework family (IRMOF-3) [1] may behave as a basic catalyst, active in the *Knvgl* condensation [2]. The lattice structure of this family of solids is based on Zn₄O moieties (inorganic vertices) and poly-topic linkers, derived by functionalizing 1,4 Benzendicarboxylate (BDC) derivatives.

Within the density functional theory (DFT) framework we already studied structural and basic properties of IRMOF-3 derivatives. Moreover, the mechanism of the catalytic cycle for the *Knvgl* condensation of benzaldehyde and ethyl cyanoacetate was analyzed. The investigation of local chemical properties and of a plausible reaction route for the aniline and dimethyl-2-aminoterephthalate (DM2AT) *Knvgl* catalytic condensation has been also performed, in order to clarify the effects of the inorganic vertices on the amine moieties. Aniline and DM2AT, were chosen for modeling the effects of increasing complexity around the basic sites, characterizing the IRMOF-3 system.

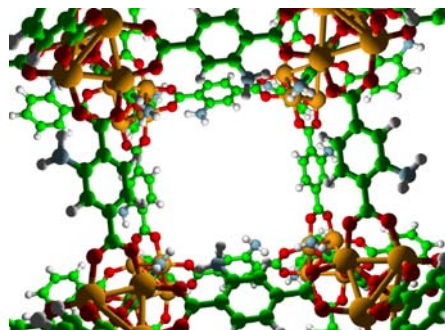


Figure 1. IRMOF-3 cage

The basicity of aniline-like amino moieties grew, along with the catalytic activity, when incorporated into MOF structures. However, the basicity of this class of catalysts did not depend on the charge density present on the nitrogen atom of the aminic group. On the contrary, the basicity was for the most part referable to the IRMOF-3 conjugate acid stabilization, determined by interactions involving the inorganic vertices. Besides this, a direct involvement of the inorganic vertices in the catalytic mechanism could be also pointed out.

These findings, highlighting the active role of the inorganic vertices in the IRMOF-3 activity, are here discussed.

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CTC-PO-05 Time Dependent Density Functional Theory of X-Ray absorption spectroscopy of metal oxides

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The Time Dependent Density Functional Theory (TD-DFT) has been employed to calculate the core electron excitations in metal oxides. From a computational point of view the simulation of the X-Ray Absorption Spectra (XAS) in such systems is an open problem both as concerns the best computational approach and the modelling of the system. Here we present the TD-DFT results obtained for the series of the alkaline-earth oxides (MgO, CaO, SrO e BaO) and the closed shell transition metal oxides TiO₂ and V₂O₅. The XAS spectra have been calculated at the metal K, L and Oxygen K edges. Cluster models to mimic the bulk are considered, embedded within an array of point charges to simulate the Madelung potential. Comparison with experimental data allows a precise assessment of the performances of the method, which appears competitive and suitable to reproduce the measurements. The configuration mixing explicitly included in the TDDFT scheme appears mandatory for a correct reproduction of the oscillator strength distribution in the metal 2p spectra. The origin of the theoretical spectral features is investigated with the help of the partial density of the virtual states (PDOS) calculated to each core hole considered, allowing to discuss the spectral features in terms of the nature of the virtual final states.

CTC-PO-06 Investigating the ion conduction mechanism of the hERG potassium channel

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The hERG channel (Kv11.1) encoded by the human *ether-à-go-go*-related gene KCNH2 [1] is an inward rectifier voltage-gated potassium channel which displays a remarkable low conductance at physiological voltage and K⁺ concentrations [2]. In this study, the ion conduction mechanism of hERG was investigated at a fully atomistic detail on a state of the art homology model of the channel [3] by means of the Umbrella Sampling method [4] combined with Path Collective Variables [5]. In apparent disagreement with previous findings based on studies performed on high and moderate conductance channels, no knock-on mechanism was observed in our simulations, and a relatively high energetic barrier (of about 6 kcal mol⁻¹) was found instead (Fig. 1). This barrier is indeed in accordance with a low conductance behavior, and it can be explained in terms of a series of distinctive structural features displayed by the hERG channel.

The achieved results might be useful to provide a predictive framework to assess the impact of point mutations on the conduction functionality of the channel.

To investigate such a possibility, the wild-type ion conduction energetics was compared with that of the G628S mutant, which is known to cause a congenital form of arrhythmia by impairing the ion permeation of the channel.

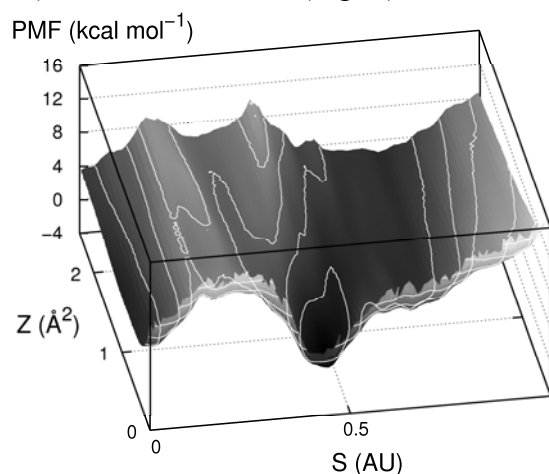


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CTC-PO-07 Combined Docking and Molecular Dynamics of agonists and antagonists 5-HT_{2C} G-coupled Receptor

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Serotonin (5-hydroxyptamine or 5-HT) through its various class of receptors regulates body temperature, sleep, mood, appetite, pain, anxiety, sex, cognition, smooth muscle growth, gastrointestinal and cardiovascular activities and peripheral secretions [1].

Thus these receptors are target for a variety of drug therapies, including antipsychotic principles.

Among this class, there is the 5-HT₂ family (5-HT_{2a}, 5-HT_{2b}, 5-HT_{2c}). In particular, 5-HT_{2C} receptor, which is mainly expressed in brain, is target of drugs for schizophrenia, depression and glaucoma and it plays an active role in regulating the sleep-wake cycle [2].

5-HT_{2C} receptor variants, due to genetic polymorphisms causing aminoacidic changes, affect treatment efficacy and are involved in treatment-induced side effects as metabolic syndrome and bodyweight gain.

By using a combined automated docking/molecular dynamics protocol [5], we want to assess if polymorphic receptor variants could have altered ligand binding affinity. These changes could explain at molecular level the results obtained in association studies and even help to resolve contradictory associations.

In particular, we docked the natural ligand and several agonists and antagonists to the wild type homology modeled 5-HT_{2C} receptor [3-4]. Then, we repeated the docking using the mutated receptor and comparing the relative agonists' and antagonists' binding energy, pointing out the differences in the corresponding non-covalent interactions at the active site.

This study will be also extended inserting the complexes 5-HT_{2C} receptor-drug into the lipid bilayer of the cellular membrane.

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CTC-PO-08 A theoretical model for the study of the time-resolved fluorescence

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The development of ultrafast laser techniques promoted the study of inherently dynamical phenomena. Nowadays we are able to freeze a far-from-equilibrium system, to observe several snapshots of a chemical reaction and to study the solvent reorganization on both the nuclear and the electronic time scales. Femtochemistry is now a reality.[1] Moreover, advances in the molecular design and bio-sensoristic applications encouraged the development of ad hoc modeled molecules to probe peculiar properties of the environment.[2]

In this new scientific area the computational and theoretical chemistry is essential to analyse and guide the experiment. Relating the spectroscopic behavior to the atomistic re-organisation of a far-from-equilibrium system becomes one of the principal aims of the modern theoretical chemistry. Here we present an integrated theoretical approach to study the time evolution of solute-solvent interactions, or, more in general, of a molecular probe environment. Our approach is based on excited states ab-initio molecular dynamics performed by time-dependent density functional theory.[3-5] In our opinion, this model can provide an invaluable support to the description of ultrafast phenomena (sub-ps time scale), when the Born-Oppenheimer approximation is still suitable.

As study case, we focussed on the solvation dynamics of the N-methyl-6-oxyquinolinium betaine, in particular on the simulation of its time-resolved Stoke-shift.[6] In spite of a complex solvent dynamics, we observe that the first solvation shell molecules dynamics is ruled by high frequency collective bulk motions. Our results are in good agreement with the experimental counterparts.

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CTC-PO-09 Hydroxymatairesinol Oxidation to Oxomatairesinol on Gold

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The natural product 7-hydroxymatairesinol (HMR) is a member of lignans. The latter form a class of phenolic compounds possessing 2,3-dibenzylbutane skeleton. HMR is abundant in the knots of Norway spruce (*Picea Abies*), both as (7R,8R,8'R)-(-)-7-allo-hydroxymatairesinol (RRR-HMR) and (7S,8R,8'R)-(-)-7-allo-hydroxymatairesinol (SRR-HMR) diastereoisomers, undergoing isomeric equilibria [1]. HMR can be selectively oxidized to another lignan, oxomatairesinol (oxoMAT) that, due to its antioxidative activity and UV-protection properties, is valuable in cosmetic, pharmaceutical and textile industry. Either RRR-HMR or SRR-HMR can be transformed by oxidative dehydrogenation to oxoMAT. SRR-HMR is the most reactive species [2]. Clearly, the reaction of HMR to oxoMAT is a selective oxidation of a secondary alcohol to the corresponding ketone. Nano-sized gold clusters exhibited excellent activity and selectivity in this kind of reaction [3]. In this work, with the aim of understanding the elementary steps governing the aerobic dehydrogenation of HMR to oxoMAT on gold, adsorption of molecular species – such as O₂, RRR-HMR, SRR-HMR and oxoMAT – on a Au₂₈ gold cluster, has been studied by using a DFT approach. The computed kinetic and structural results, related to the binding process, show that molecular oxygen adsorb on the Au₂₈ cluster, acting as an electron acceptor able to activate the HMR dehydrogenation. In this context, a reaction mechanism is proposed, especially considering structural and steric properties of the HMR diastereoisomers adsorbed over the gold cluster, which are able to point out and explain their, experimentally found, different reactivity.

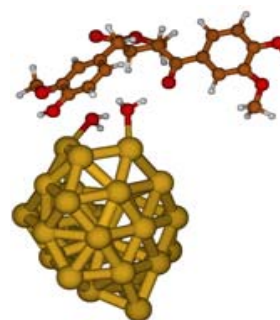


Figure 1. oxoMat on gold

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CTC-PO-10 C K-edge NEXAFS Spectra of Model Systems for C₂H₄ on Si (100): a DFT Simulation

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Adsorption of organic molecules on semiconductor surfaces has been attracting a growing attention for its importance in emerging technologies. Since the properties of the resulting materials are largely dependent on the organic/semiconductor interface, fundamental research on the covalent bonding of molecules with the surface can provide useful information. Problems that have been addressed include the structure of the resulting systems and the spectroscopic measurements, often in concert with theoretical calculations, can assess the orientation and geometry of the molecular adsorbate. NEXAFS spectroscopy is widely used to characterize adsorbate structures on surfaces since it allows to investigate the adsorption mode as well as the extent of the adsorbate-substrate interaction, through the comparison between the spectra of the free and adsorbed molecules. Here we present a DFT simulation of the NEXAFS spectra of ethylene adsorbed on a regular Si (100) surface, considering several adsorption models. Cluster models have been employed to mimic the molecule-surface system for the spectra simulation. Surface models with and without the adsorbed molecule have been optimized by means of periodic slab DFT calculations. Angle dependent spectra have been also calculated and compared with available polarization dependent NEXAFS experiments, revealing the suitability of this technique to derive the adsorption configuration of the molecule on the surface.

CTC-PO-11 Dyes for fluorescence encoding: lifetimes and quantum yields by a combined experimental and theoretical study.

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Due to the advance of techniques based on fluorescence encoding, a renewed interest in synthesis strategies [1] and spectroscopic characterization of common fluorophores [2,3] has been recently shown in literature.

Although the most important features of the optical behaviour, including fluorescence quantum yield and lifetime, are usually well known for commercially available chromophores, a deep understanding of the photophysical behaviour is not fully assessed. On the other hand, an high degree of comprehension is nowadays required for a full control/design of modern optical devices.

In this combined experimental and theoretical work we analyze the fluorescence signatures (lifetime, quantum yield and band peak) of several commonly used rhodamine and pyronin dyes.

In particular we combine Fluorescence Lifetime Imaging Microscopy [4] data with calculations based on the Time-Dependent Density Functional Theory [5] to analyze and interpret the fluorescence signatures (lifetime, quantum yield and band peak) of the chromophores under study.

Our procedure is validated by calculated quantum yields values in good agreement with the experimental counterparts. [6]

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CTC-PO-12 Theoretical study of near edge x-ray absorption fine structure spectra of metal phtalocyanines at C and N K-edges

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Copper phtalocyanine (CuPc), nickel phtalocyanine (NiPc) and metal-free phtalocyanine (H₂Pc) have been considered in this work. Density Functional calculations have been performed in order to assess the relationships between the electronic structure and the most salient NEXAFS spectral features. We have first addressed the description of the electronic structure of the systems under study at the ground state level, in order to establish the nature of the virtual valence molecular orbitals involved in the core excitations, in particular as concerns the relative contributions of ligand and metal atomic sites. Second, we have calculated the NEXAFS spectra, including the relaxation effects upon formation of the core hole by means of the Transition State (TS) scheme, with the aim to compare the results with respect to the experiment as well as to discuss the effect of the presence and the nature of the metal on the spectra.

CTC-PO-13 Theoretical study on the wt-GFP absorption

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Our work is included among the studies of biological macromolecules with specific chemical-physical properties in order to use them in biological, biotechnological or medical applications.[1] In this field GFPs are non-invasive biosensors ideal to be used in biological systems thanks to their main features.

Our contribution regards the theoretical study of wt-GFP absorption in both its neutral and anionic form and the analysis of the protein environmental influence on the isolated chromophore.

In order to gain these results we used the time-dependent density functional theory (TD-DFT) to describe the electronic excited states of GFP and a quantum mechanical-molecular mechanics approach to study the relationship between the protein structure and the optical properties. For the isolated chromophores we have conducted TD-DFT calculations both in vacuum and in solvents using the conductor-like polarizable continuum model (CPCM).

First of all, as ambiguous conclusions emerge from previous works,[2] we have verified that TD-DFT can accurately describe the S_0 - S_1 transition in wt-GFP giving results comparable with the more well-established multi-determinantal methods.

Our results support the idea that the protein environment has a fundamental role in GFP absorption, determining a not negligible red shift with respect to the isolated chromophore. The reliability of our analysis is proven by results in good agreement with the experimental counterparts.[3]

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CTC-PO-14 A theoretical protocol for the determination of the metal-site structure in metalloprotein superfamilies

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NMR spectroscopy is a powerful experimental tool used for the determination of protein structure [1]. NMR chemical shifts accurately reflect the local chemical environment at atomic resolution and are sensitive to many different factors including contacts between residues, hydrogen bonding and proximity to aromatic rings. Several papers have appeared which suggest that reasonably accurate protein structures can be determined directly from chemical shifts [2-4].

In the present work we aim at developing a protocol that employs ab initio computation of chemical shifts as a tool for the structural validation of metal binding site(s) in metalloproteins. EF-hand calcium-binding proteins represent a suitable test application, since accurate databases of structural and NMR properties are available. We have adopted a hybrid quantum mechanical (QM) / molecular mechanical (MM) approach, namely the ONIOM method as implemented in the Gaussian package. In essence, the system is partitioned into two “layers”: the molecular region which is immediately adjacent to NMR-active nucleus under investigation is treated at the QM (DFT) level of theory, whereas the rest of the biomacromolecular system is modeled by partial charges from the Amber force field. The frontier between the two layers is based on a hydrogen link-atom scheme and electrostatic interactions between the two layers are accounted for by means of an electronic-embedding implementation. A prototypical EF-hand calcium-binding protein, Calbindin D9k, was employed to perform a systematic exploration of the convergence of computed NMR chemical shifts with respect to the number and nature of residues included in the QM partition. This allows to determine an optimal balance between the high accuracy issuing from the choice of a sufficiently large QM region and the computational costs.

Once a satisfactory partition scheme has been devised, more realistic computations were sought by including motional averaging effects. The procedure requires to perform a classical MD simulation of the biomacromolecule (in explicit solvent); snapshots are extracted at regular time intervals and the results of QM/MM calculations performed on each frame are averaged.

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