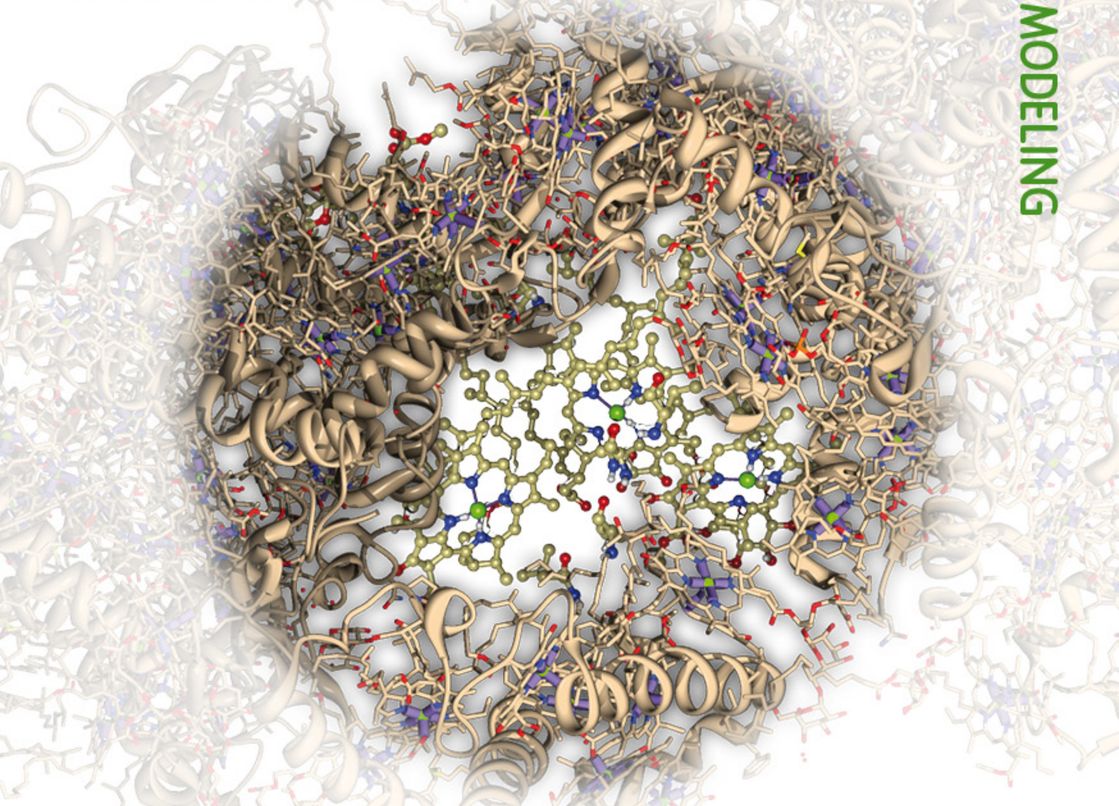
IN THE FRAMEWORK OF DREAMS

WINTER 2015 MODELING



18 DECEMBER 2015

WINTER MODELING 2015

Complex Systems:
Accuracy and Interpretation

Sala Azzurra
Palazzo della Carovana
Piazza dei Cavalieri, 7 - Pisa

BOOK OF ABSTRACTS

Elaborazione a cura del Servizio Comunicazione e Relazioni Esterne | SNS

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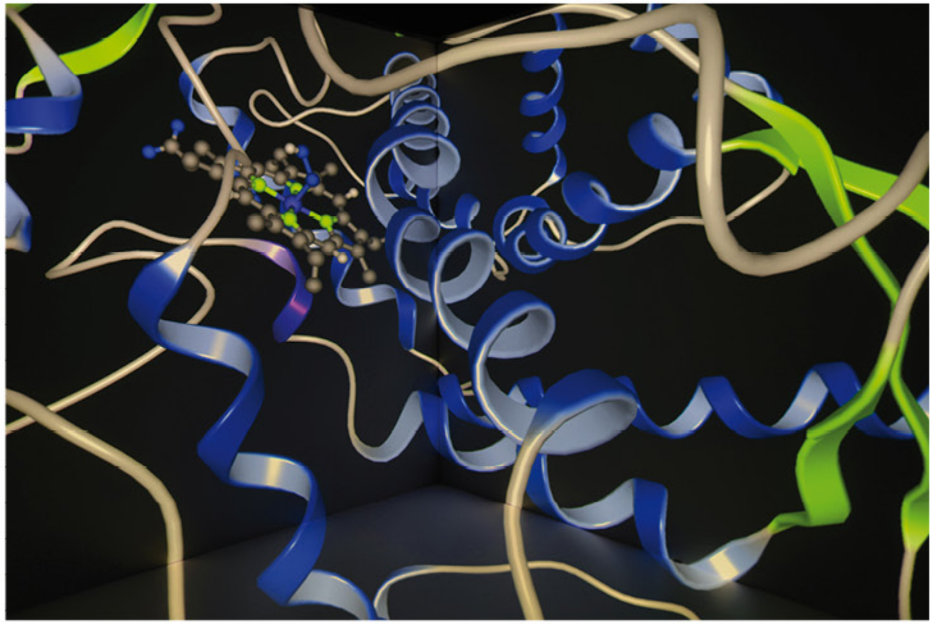
Arrived at its nine edition, the Winter Modeling workshop has become a "classical" meeting for the Italian community in Theoretical and Computational Chemistry, a not-to-be-missed annual *rendez-vous*.

The focus of this edition is the description of complex systems coupling accuracy and interpretation, and it will be also the occasion to present the scientific activities carried out in the mid-term ERC Research Period on DREAMS (Development of a Research Environment for Advanced Modelling of Soft matter) project. DREAMS (http://dreamserc.sns.it/) aims at developing integrated theoretical-computational approaches for the efficient description of linear and non-linear spectroscopies of several classes of organic probes, isolated and embedded in complex environments.

In the Invited Lectures and Oral Presentations of this edition, the interaction of radiation with matter is a central theme, including various forms of spectroscopy such as infrared, microwave and UV-VIS. Effects such as nuclear spin relaxation in NMR as well as chiroptical properties will be discussed. Apart from the purely spectroscopic aspects, the dynamics of complex systems (both photoinduced or not) is going to be treated, both from the more common nuclear point of view as well as the electronic one. Solid state structure (especially at interfaces) and complex organic reaction mechanisms are also treated.



FRIDAY 18 DECEMBER 2015

9.15 Registration

10.15 Conference opening

Chair: MAURO STENER — 1st SESSION

10.25 **STEFANO BARONI**
A multi-scale protocol for simulating the color optical properties of complex molecular species in solution

11.05 **CRISTIANA DI VALENTIN**
Charge Carriers Separation at the Graphene/TiO2 Interface

11.20 **ANA B. MUÑOZ-GARCÍA**
Dye-electrode interfacial features in p-type photoelectrochemical cells:
a quantum chemical perspective

11.35 **GIOVANNI TALARICO**
New polymerization catalysts discovered by high throughput screening techniques: a further challenge for computational methods

11.50 **EMILIA SICILIA**
Organoiridium(III) catalysts as anticancer agents with a new mechanism of action.
Some indications from DFT calculations

12.05 **FRANCESCO ZERBETTO**
Living cells as soft matter

12.45 Conference Lunch

Chair: ORLANDO CRESCENZI — 2nd SESSION

14.30 **MICHAEL A. ROBB**
Electron and Nuclear Dynamics Driven by a Coherent Superposition of Electronic Wavefunctions

15.10 **CRISTINA PUZZARINI**
Quantum Chemistry Meets Spectroscopy for Astrochemistry:
Increasing Complexity toward Prebiotic Molecules

15.25 **NICOLA TASINATO**
Modeling the adsorption of glycolaldehyde over titanium dioxide by coupling quantum chemical calculations and DRIFT spectroscopy

15.40 **ALBERTO BAIARDI**
DVR-based approaches for the simulation of vibronic spectra of flexible systems

15.55 **MARIA CRISTINA MENZIANI**
Understanding Protein–Nanoparticle Interaction by Computational Simulations

16.10 Coffee Break

Chair: MAURIZIO CASARIN — 3rd SESSION

16.40 **CHIARA CAPPELLI**
Towards a Reliable Virtual Modeling of Chiroptical Properties and Spectroscopies

17.20 **MIRCO ZERBETTO**
Conformational Mobility in Monolayer-Protected Nanoparticles:
from Torsional Free Energy Profiles to NMR Relaxation

17.35 **CLAUDIO GRECO**
Theoretical investigation of the Spectroscopic properties of Europium complexes

17.50 **STEFANO CAPRASECCA**
Excitonic states and plasmonics: a multiscale approach

18.05 **CHRISTIAN SILVIO POMELLI**
The mechanism of the aerobic oxidation of aldehydes catalyzed by N-heterocyclic carbenes

18.20 Conclusions

A multi-scale protocol for simulating the color optical properties of complex molecular species in solution

Marco Micciarelli, Marta Rosa, Iurii Tomrov, Alessandro Laio, and Stefano Baroni
SISSA – Scuola Internazionale Superiore di Studi Avanzati, 32136 Trieste
baroni@sissa.it

The UV-vis optical properties of molecular solutions result from a complex interplay between conformational isomerism, thermal fluctuations, and the intrinsic optical responsivity of the solvated molecules, all of these factors being strongly influenced by the interactions between the solute and the solvent. We propose a multi-scale approach to cope with this problem and apply it to the color optical properties of anthocyanins, a class of natural dyes that are responsible for the coloration of many fruits and flowers, and that are of current interest in the food and pharmaceutical industries. In our method the most relevant molecular conformers are first identified by a combination of large-scale classical molecular dynamics (MD) simulations and a recently proposed clustering algorithm [1]. The free energies thus obtained are then refined perturbatively by sampling the DFT energies within each conformer using a QM/MM approach, and the corresponding populations modified accordingly. The optical activity within each conformer is determined as the time average of the spectra computed on the fly over ab-initio MD trajectories [2], using a newly developed effective-medium approach to TDDFT [3]. In order to enhance the statistics, we have developed a "learn-on-the-fly" technique that allows us to repeatedly compute spectra of TDDFT quality at a nearly independent-electron cost. The overall spectrum of the solution is finally evaluated by averaging the contributions from individual conformers, weighted with their relative populations. In this talk I will review all of the above, and present a few preliminary results on the color optical properties of cyanidin 3-glucoside (cyanin).

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Towards a Reliable Virtual Modeling of Chiroptical Properties and Spectroscopies

Chiara Cappelli
Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa (Italy)
chiara.cappelli@sns.it

Effective *in silico* simulations of response and spectroscopic properties of chiral molecular systems in their natural environment is among the most significant tasks of contemporary theoretical and computational chemistry in view of the increasing reliability of the results coupled to the quite straightforward disentanglement of the role of different effects. However, the production of calculated spectroscopic data directly comparable to their experimental counterparts is particularly tricky in the case of solvated systems. In fact, the models should reliably represent the experimental sample, i.e., the physical model should be as realistic as possible, which in practice means that all the physical interactions in the sample and between the sample and the probing field have to be taken into account in the model.
The simultaneous accounting of solvent effects [1-4] and anharmonicity [5-7] is among the most difficult tasks, coupled with the modeling of strong interacting environments [8-11]. I will give an overview of the computational methods recently developed in this field [12].

This work was supported by the Italian MIUR (PRIN 2012 NB3KLK 002).

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Electron and Nuclear Dynamics Driven by a Coherent Superposition of Electronic Wavefunctions

Michael A. Robb, Morgane Vacher, Andrew J. Jenkins, Michael J. Bearpark
Imperial College London, London SW7 2AZ, United Kingdom
Mike.Robb@imperial.ac.uk

Attosecond spectroscopy has opened up the possibility of observing the motion of electrons on their natural timescale (few attoseconds). We have been studying such electron dynamics together with coupled nuclear motion, using our implementation of the Ehrenfest method [1,2]. The initial electronic wavepacket is chosen as a superposition of eigenstates to model the effects seen in attosecond spectroscopy. We will discuss two types of application with some examples: 1) pure electron dynamics [3,4,5], and its subsequent decoherence [5] driven by nuclear motion and the natural zero point distribution in geometries, and 2) the electronic control [6] of nuclear dynamics.

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Living cells as soft matter

Marco Dallavalle, Francesca Lugli, Stefania Rapino, Francesco Zerbetto
Dipartimento di Chimica "G. Ciamician", Universita' di Bologna, V. F. Selmi 2, 40126,
Bologna, Italia
E-mail: francesco.zerbetto@unibo.it

Neuro-electronics is a rapidly developing field that interfaces the living with electronic devices. In its simplest form it couples cells, actually neurons, to the working of devices such as transistors with the intent of modifying the response of the organisms themselves or of detecting some of their activities by the variation of the device response. Further complexity is added by the medium of operation necessary to keep the cells viable. The combination of these systems generates something that, by any standard, is exceedingly complicated to apprise quantitatively. And yet, in order to understand the overall behavior, simulations appear to be desirable. The issue is whether they are at all possible and if they are what can be done in terms of computer chemistry.

In this communication, I review the effort that is being carried out in my group aimed at understanding various features of the interaction of cells with organic surfaces and devices. Simulations are carried out at different levels of computational theory that include mesoscopic modelling and finite differences approaches. The collaboration with experimental groups is also described.

DVR-based approaches for the simulation of vibronic spectra of flexible systemsle

Alberto Baiardi[1], **Julien Bloino**[2] **and Vincenzo Barone**[3]
[1] Scuola Normale Superiore, Piazza dei Cavalieri 7, Pisa
[2] Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR, Via G. Moruzzi 1, I-56124 Pisa, Italy
e-mail alberto.baiardi@sns.it

Electronic spectroscopy is among the most powerful tools for the study of molecular systems, and a correct interpretation of the spectra relies more and more on quantum mechanical (QM) computations, for both interpretative and predictive aspects. In this connection, the inclusion of vibro-electronic (vibronic) effects in the computational simulations is usually crucial for a correct reproduction of the experimental data, both for the interpretation of high resolution data showing a detailed vibrational structure, as well as for low-resolution spectra, whose asymmetric peaks cannot be reproduced by a single symmetric distribution function [1-3].

Most of the vibronic models, which are commonly used are based on the harmonic approxiation in cartesian coordinates. However, medium- and large-size systems usually display several flexible degrees of freedom, which are poorly described at the harmonic level. An effective solution is offered by block-based computational procedures, where a limited number of modes is treated separately using ad-hoc procedures, whereas the remaining modes are treated at the harmonic level. Within those approaches, the coordinate system, used in the simulation must be chosen carefully in order to minimize the coupling between different blocks of normal modes. Regarding this matter, Cartesian coordinates are generally unsatisfactory, whereas curvilinear internal coordinates are better suited. However, a significant drawback of internal coordinates is the definition of non-redundant coordinates, which can be cumbersome for large-size systems [4,5].

In this contribution, different fully-automatized algorithms for the generation of natural internal coordinates, supporting also systems with complex topologies, will be presented. Based on the use of those coordinate systems, a block-based approach will be described, where the potential energy surface along the large-amplitude motion is obtained after an explicit scan, whereas the vibrational wavefunctions are computed using a DVR-based approach.

This theoretical framework will be applied to the simulation of vibronic spectra, both at the time-independent (TI) and at the time-dependent (TD) level, of flexible systems, where a single degreee of freedom is treated using the DVR approach. The further extension to the treatment of more complex systems, where multiple flexible degrees of freedom are present, will be discussed.

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Excitonic states and plasmonics: a multiscale approach

Stefano Caprasecca, Ciro A. Guido , Benedetta Mennucci
[1] Department of Chemistry, University of Pisa, Via G. Moruzzi 13, 56124, Pisa (ITALY).
Email: Stefano.caprasecca@for.unipi.it

Photoinduced processes of (multi)chromophoric systems can be greatly affected by the presence of plasmonic devices. Particularly, light-harvesting systems show a marked enhancement of their fluorescence and absorption properties when placed close to metal nanoparticles (NPs). Computationally, an accurate description of such processes is challenging, because the system spans different lengthscales. We studied the effect that gold NPs have on the LH2 light-harvesting pigment-protein complex present in bacteria. Because of the electronic nature of such processes, a quantum-mechanical (QM) description is mandatory: we employed an excitonic approach to study them. The rest of the protein is described classically, with a discrete polarizable approach, allowing to account for the structured interaction between the QM and classical subsystems. The NP is described using a continuum model. We analysed the absorption, quantum yield and fluorescence enhancements behaviour of LH2 at different distances and orientations with respect to the NP, with particular attention to the hot- spot configuration, where a large enhancement of the electric-field induces a strong response of the LH2 system. Our study proves valuable not only to interpret and analyse the experimental results available to dissect the metal-induced effects on the excitonic states.

Charge Carriers Separation at the Graphene/TiO_2 Interface

Cristiana Di Valentin
Università di Milano Bicocca, Milano, 20125, Italy .
cristiana.divalentin@mater.unimib.it

Graphene/TiO_2 nanocomposites are successfully applied both in photocatalysis and photovoltaics.[1,2,3] The enhanced performances are attributed to their improved interfacial charged transfer and charge separation, reducing the recombination rate of photoexcited electron and hole pairs. In this talk we show that only density functional methods which provide corrections for the spurious self-interaction and for the Van der Waals forces can correctly describe the electronic structure, the adhesion energy and the atomic distances of this hybrid interface. We also discuss the role played by residual O atoms trapped at the interface during preparation. Their presence largely enhances the binding energy and causes further electronic states hybridization between G and TiO_2, which is expected to favour interfacial electron transfers. Finally, we provide evidences that electrons are preferentially trapped at subsurface layers of TiO_2, while holes are preferentially delocalized on the G sheet. This opposite tendency is proposed to be at the basis of the lower recombination rate leading to the observed improved outcomes in photocatalytic and photovoltaic applications. [4]

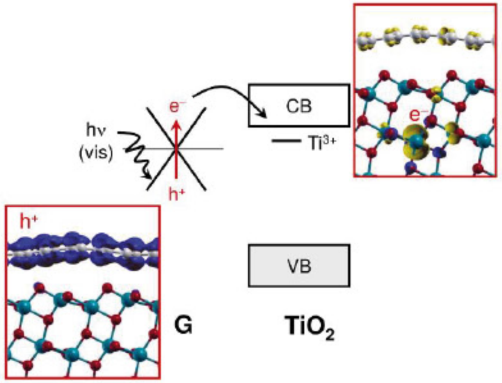

Figure 1 Photoexcited electron and hole separation at the graphene/anatase (101) TiO_2 interface.

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Theoretical investigation of the Spectroscopic properties of Europium complexes

Claudio Greco,[1] Ugo Cosentino,[1] Damiano Gerosa,[1] Giorgio Moro[1]
Alberto Baiardi,[2] Vincenzo Barone[2]
[1] Milano-Bicocca University, Milan, 20126, Italy
[2] Scuola Normale Superiore, Pisa, 56126, Italy
claudio.greco@unimib.it

Due to their photophysical properties, Lanthanide complexes with π-conjugated ligands can act as light antennae, and thus find applications in several technological fields. [1] One of the most studied class of ligands is constituted by β-diketonate ligands (β-DK) in view of their noticeable emission properties due to the effectiveness of the energy transfer (ET) from this ligand to the Ln(III) ion. In particular, europium β-DK complexes have attracted special interest in optoelectronic applications because of their strong and narrow red emission.

We will present the results obtained for a series of β-diketonate Europium complexes [2], the photophysical characterization of which has been recently reported in literature. [3, 4] Our attention was focused on the calculation of spectrophotophysical properties relevant for the photoluminescence process, such as the lowest triplet state energy, a critical parameter in determining the photoluminescence quantum yields of these systems, and the vibrationally resolved phosphorescence spectra of the corresponding Gadolinium complexes (Figure 1).

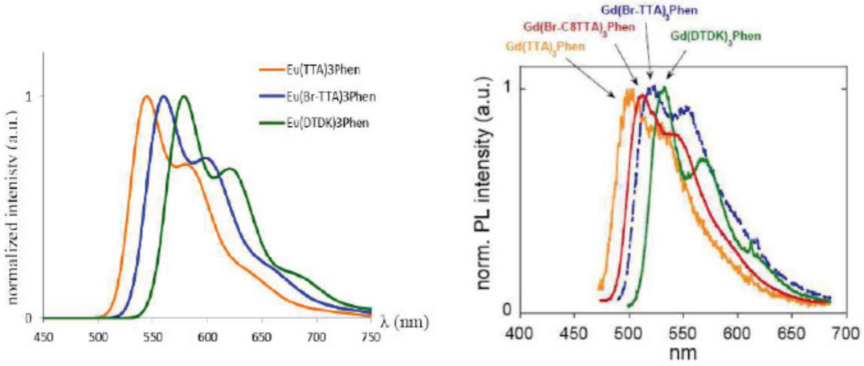

Figure 1. Calculated [2] and experimental [3] phosphorescence spectra in solution of the investigated β-diketonate lanthanide complexes.

The adiabatic transition energies from the lowest triplet states of the investigated compounds have been determined in solution by the ΔSCF method at the DFT theory level, using the PBE1PBE and the CAM-B3LYP hybrid functionals. Calculations have been done by using for the Europium ion a large-core quasi-relativistic effective core potential (ECP) in combination with the related [5s4p3d]-GTO valence basis set, and the 6-31G* basis for the ligand atoms. The vibrationally resolved phosphorescence spectra were calculated in the framework of the Franck-Condon (FC) approximation using the adiabatic Hessian (AH) model.

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Understanding Protein–Nanoparticle Interaction by Computational Simulations

Francesco Tavanti, Alfonso Pedone, Maria Cristina Menziani
Dipartimento di Scienze Chimiche e Geologiche, Università di Modena e Reggio Emilia, Via Campi 103, Modena, Italy; mariacristina.menziani@unimore.it

In the last years, the interest in the interaction of nanoparticles (NPs) with biological medium is grown due to the huge number of possible applications in nano-medicine and nano-technology.(1)
It is well known that the contact between NPs and biological medium triggers a competition between different biological molecules to adsorb on the surface of the nanoparticles.
Notwithstanding the phenomenon has been explored with a variety of experimental and computational techniques, there is still limited knowledge about the binding modality and stability of the protein-NPs complexes and the subsequent impact.
In fact, the interaction mechanism is still poorly understood being a complex process that depends on many parameters, such as the physicochemical properties of the NP (size, shape, composition, surface decoration, and surface charges), the nature of the physiological environment (blood, cell cytoplasm, etc.), and the duration of exposure.

In my lab coarse-grained computational simulations have been used to describe the structural and dynamic characteristics of the interactions between several proteins and citrate-coated Au-NPs. (2,3) The results obtained will be discussed as a function of protein heterogeneity, concentration, conformational stability, and NP dimension, coating, and concentration.

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Dye-electrode interfacial features in p-type photoelectrochemical cells: a quantum chemical perspective

<u>Ana B. Muñoz-García</u> and Michele Pavone
Department of Chemical Sciences, University of Naples Federico II, Naples, 80126, Italy
anabelen.munozgarcia@unina.it

Recent interest in photo-electrochemical catalysis of water splitting have boosted studies on p-type dye-sensitized photo-cathodes for the hydrogen evolution reaction [1]. In these devices, the sunlight harvesting is carried out by p-type dye-sensitized solar cell (p-DSSC), which is the complementary photocathode to the well-studied n-type DSSCs (Grätzel cells) [2]. However, their low performances have hindered the development of convenient tandem solar cells based on cost-effective n- and p-type DSSCs [3]. Experimental investigations have demonstrated that electronic processes at the dye-electrode interface are responsible of the low p-DSSC efficiencies [4]. The most exploited p-type semiconductor used as p-DSSC solid electrode is nickel oxide (NiO), where the electronic features at the dye-electrode interface are strongly dependent on the dye anchoring group and binding modes on NiO surfaces [5].

Here we report state-of-the-art first-principles calculations on the interfaces between NiO surface and two different sensitizers: a prototypical coumarin-based dye (C343) and recently proposed push-pull dyes [6]. From our results, we derive structure-property-function relationships that can help to develop further the p-type DSSC photocathode materials toward improved performances.

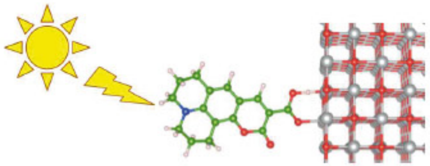

Figure 1 Coumarin dye (C343) adsorbed on p-NiO

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The mechanism of the aerobic oxidation of aldehydes catalyzed by N-heterocyclic carbenes

<u>Christian Silvio Pomelli,</u>[1] Cinzia Chiappe[1], Olga Bortolini[2]
[1]Dipartimento di Farmacia, Università di Pisa, Via Bonanno, 33 – Pisa;
[2]Dipartimento di Scienze Chimiche e Farmaceutiche, Università degli Studi di Ferrara, Via Fossato di Mortara 17 – Ferrara.
christian.pomelli@unipi.it

The aerobic oxidation of aldehydes catalysed by *N*-heterocyclic carbenes presents a complex reaction mechanism. At least two reaction paths, having a common key event represented by the oxidation of the Breslow intermediate, exist: one, leading to the corresponding carboxylic acid upon reaction with an additional aldehyde, the other, to the corresponding ester after trapping by methanol. Aromatic aldehydes can follow a different path depending on substituents and substituent position on the phenyl ring.

To obtain information on the reaction mechanism, carbene catalysts have been recently synthetized using the charge-tag strategy [1] starting from dicationic ionic liquids (*i.e.* 3,3'-dimethyl-1,1'-(hexane-1,6-diyl)diimidazolium salts) [2], which can provide carbenes having a charged moiety (*i.e.* imidazolium cation) on the sidechain. This feature has allowed the individuation of important reaction intermediates, via ESI-MS experiments. These measures have been integrated with *ab-initio* DFT calculation [3] in order to rationalize some relevant aspects of the mechanism. In particular,

- The nature and the role of the Breslow intermediate.
- How differently substituted aldehydes resolve in a different way the dichotomy of the reaction path.
- The geometric and electronic structure of the complex arising from the Breslow intermediate and $^3O_2$ and its relation to the reaction path at the point of bifurcation.

The computational results presented in this contribution answer to these questions and furthermore provide evidences of the active role of the solvent (methanol) in the reaction mechanism.

Figure 1: One of the last steps of the oxidative path: HOO^- elimination.

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Quantum Chemistry Meets Spectroscopy for Astrochemistry: Increasing Complexity toward Prebiotic Molecules

<u>C. Puzzarini</u>[1], V. Barone[2], M. Biczysko[3]
[1] Dipartimento di Chimica "Giacomo Ciamician", University of Bologna, I-40126 Bologna, Italy.
[2] Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy.
[3] Consiglio Nazionale delle Ricerche, Istituto di Chimica dei Composti OrganoMetallici (ICCOM-CNR), UOS di Pisa, Area della Ricerca CNR, Via G. Moruzzi 1, I-56124 Pisa, Italy.
cristina.puzzarini@unibo.it

For many years, scientists suspected that the interstellar medium was too hostile for organic species and that only a few simple molecules could be formed under such extreme conditions. However, the detection of approximately 180 molecules in interstellar or circumstellar environments in recent decades has changed this view dramatically. A rich chemistry has emerged, and relatively complex molecules such as C_{60} and C_{70} are formed. Recently, researchers have also detected complex organic and potentially prebiotic molecules, such as amino acids, in meteorites and in other space environments. Those discoveries have further stimulated the debate on the origin of the building blocks of life in the universe.

Spectroscopic techniques play a crucial role in the investigation of planetary atmosphere and the interstellar medium. Increasingly these astrochemical investigations are assisted by quantum-mechanical calculations of structures as well as spectroscopic and thermodynamic properties to guide and support observations, line assignments, and data analysis in these new and chemically complicated situations. However, it has proved challenging to extend accurate quantum-chemical computational approaches to larger systems because of the unfavorable scaling with the number of degrees of freedom (both electronic and nuclear). In this contribution [1], it is shown that it is now possible to compute spectroscopic and physicochemical properties of building blocks of biomolecules with an accuracy rivaling that of the most sophisticated experimental techniques. Representative building blocks of DNA bases (uracil and thiouracil) and of proteins (glycine and glycine dipeptide analogue) are considered as case studies.

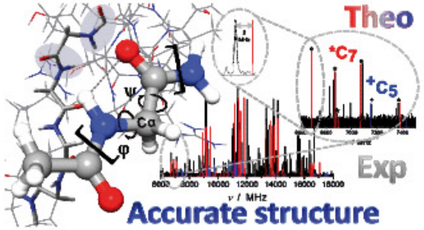

Figure 1. Molecular structure and rotational spectrum of glyine-dipeptide analogue.

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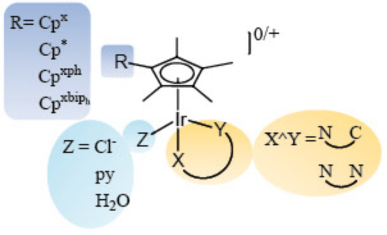
Organoiridium(III) catalysts as anticancer agents with a new mechanism of action. Some indications from DFT calculations

<u>Emilia Sicilia</u>, Ida Ritacco and Nino Russo
Università della Calabria, Arcavacata di Rende (CS), 87036, Italy.
Emilia.sicilia@unical.it

Impetus to the design of organometallic transition metal-based complexes as anticancer agents is due to a need to produce compounds with higher potency, a wider spectrum of activity, higher cancer cell selectivity, lower resistance, and reduced side effects in comparison with conventional, already used in the clinic, antitumor metal-based (platinum) complexes. Quite recently, novel half-sandwich organometallic Ir(III) cyclopentadienyl complexes have introduced as potent cytostatic and cytotoxic anticancer agents.[1-4] The activity of such pseudo-octahedral complexes of general formula (Scheme 1) $[(\eta^5\text{-}Cp^x)Ir(III)(X^\wedge Y)Z]^{0/+}$ where Cp^x = Cp*, Cp^{xph} (tetramethyl-(phenyl)cyclopentadienyl), or Cp^{xbiph} (tetramethyl(biphenyl)-cyclopentadienyl), X^Y = bidentate ligand with nitrogen, oxygen, and/or carbon donor atoms, and Z = Cl, H_2O, or pyridine (py), can be modulated by properly choosing ligands and substituents. It has been shown that these complexes exhibit higher potency than conventional cisplatin and, very importantly, that the mechanism underlying their biological effects, involving ROS production, does not correlate with that of cisplatin. With the aim to elucidate the MoA of such class of iridium complexes and to rationalize a great deal of experimental data, we have performed DFT calculations, which can provide valuable information exploitable in optimizing the design of this class of anticancer complexes. For the chlorido complex, $[(\eta^5\text{-}Cp^{xbiph})Ir\text{-}(phpy)(Cl)]$, **1-Cl**, and its pyridine analogue, $[(\eta^5\text{-}Cp^{xbiph})Ir\text{-}(phpy)(py)]$, **1-py**, the mechanism of the hydrolysis reaction, H_2O_2 ROS production by hydride transfer from NADH to molecular oxygen, interaction with gluthatione and purine nucleobases adenine and guanine alongside the reaction mechanism for the oxidation of the formed sulfur-coordinated thiolate to the corresponding sulfenato complex have been theoretically investigated in detail. The comparison between kinetic and thermodynamic parameters calculated for all the involved processes shows that, according to the hypothesis based on experimental findings, the interaction with the tripeptide glutathione causes deactivation of **1-Cl**, whereas **1-py**, in both its aquated and non-aquated form, can induce cell apoptosis in a dual manner: DNA damage and H_2O_2 ROS production to increase oxidative stress.



Scheme 1

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New polymerization catalysts discovered by high throughput screening techniques: a further challenge for computational methods

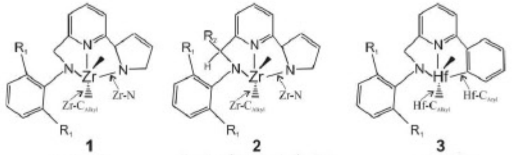
Giovanni Talarico, Claudio De Rosa and Rocco di Girolamo
Dipartimento di Scienze Chimiche, Università degli Studi di Napoli Federico II,
Complesso Monte S'Angelo, Via Cintia, 80127, Napoli, Italy
giovanni.talarico@unina.it

In the last ten years, the more relevant catalysts for stereoselective olefin polymerization have been discovered by high throughput screening techniques (HTS) [1,2]. The catalyst discovery workflow using the HTS infrastructure reached such a level [3] that the "familiar" concept of "catalyst ligand design" by basic principles [4] seems to play a marginal role at the present stage. By using this approach a greater number of pyridyl-amine ligands with enhanced structural diversity were synthesized (see Figure 1). In designing the expanded ligand array, three convenient positions for structural amplification were identified, labeled in the Figure as R_1, R_2 and the presence of unusual reactivity of metal-aryl bond (see Hf-C_{Aryl} and Hf-C_{Alkyl} bonds in system 3 of Figure 1). However, the stereoselectivity mechanism of propene polymerization promoted by such systems is still unknown [1,2].

In this communication, by means of computational methods, we investigated the enantioselectivity of propene insertion for systems **1-3** reported in Figure 1. Surprisingly, the generally accepted model of "chiral growing chain orientation" [5] was ineffective for this class of catalysts and a new model for the propene enantioselectivity has been sorted out.

Despite the computational results tuned by DFT methods combined with dispersion and solvent corrections [6], there are two aspects that we would like to stress: a) our model is able to explain the subtle interplay between the steric and electronic effects as well as the reactivity of metal-aryl bond; b) it appears a general model, able after 35 years to reconnect the Ziegler-Natta catalysis to the more general asymmetric catalysis [7].

Let us make a final comment: we are well aware that discoveries of such systems were possible thanks to experimental HTS technologies because of the huge number of variables involved; nevertheless, we are still convinced that a rational catalysts design is not over the game as soon as new models are developed.



1 $1 = R_1 = {}^iPr$

2 $2 = R_1 = {}^iPr; R_2 = 2,6{}^iPrC_6H_3$

3 $3 = R_1 = {}^iPr$

Figure 1 Catalyst systems analyzed in this study for the propene polymerization catalysis.

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Modeling the adsorption of glycolaldehyde over titanium dioxide by coupling quantum chemical calculations and DRIFT spectroscopy

Nicola Tasinato
Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155,
I-30172 Venezia Mestre, Italy.
tasinato@unive.it

In the last years glycolaldehyde (CH_2OHCHO, GA) has been the subject of notable interest, mainly motivated by its first identification in the interstellar space toward the Galactic center cloud Sagittarius B2(N). GA is the simplest α-hydroxy aldehyde, and being a sugar-related prebiotic molecule involved in formose reaction to ribose, this detection provides fascinating clues about the origins of life. Besides, GA is also of atmospheric relevance, as it belongs to the class of oxygenated volatile organic compounds and it has been proposed to play a role in heterogeneous processes, like the formation of secondary aerosols.

The present contribution reports the earliest outcomes about the study of the adsorption of GA over titanium dioxide (TiO_2) performed by coupling periodic quantum chemical calculations rooted into density functional theory and Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy. Molecular modeling has been carried out at B3LYP-D2 level according to five interaction models, differing for either the molecular orientation and the anchoring functional groups involved in the interaction. The surface has been described as a 6-layer slab cut from the anatase crystal structure along the (1 0 1) plane and for each adsorption configuration, the structures, binding energies and vibrational frequencies of the adsorbed molecule have been determined. Experimentally, the vibrational spectra of GA adsorbed on a commercial TiO_2 powder have been obtained by DRIFT spectroscopy coupled to the use of a properly tailored environmental chamber for *in situ* measurements.

The main experimental findings, derived from the analysis of the differential spectra of GA in interaction with TiO_2, point to a red shift of the C=O and O—H stretching frequencies. These are theoretically reproduced by a model in which the GA molecule adsorbs on the anatase (1 0 1) surface by means of the carbonyl oxygen atom and the hydroxylic hydrogen interacting, respectively, with a five-fold coordinated titanium and a two-fold coordinated oxygen of the surface.

The results of the work provide the first insights into the adsorption of GA on TiO_2 and they represent the starting point for further developments aiming at a more refined modeling of the interfacial interaction, in order to achieve a better accuracy with experimental observations. For the purpose, future direction of study will also be addressed.

Conformational Mobility in Monolayer-Protected Nanoparticles: from Torsional Free Energy Profiles to NMR Relaxation

Andrea Piserchia[1], Mirco Zerbetto[2], Marie-Virginie Salvia[2], Giovanni Salassa[2], Luca Gabrielli[2], Fabrizio Mancin[2], Federico Rastrelli[2], Diego Frezzato[2]
[1] Scuola Normale Superiore, piazza dei Cavalieri 7, I-56126 Pisa, Italy.
[2] Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Padova, 35131, Italy.
mirco.zerbetto@unipd.it

We present an integrated computational approach that proved to be a self-consistent route to inspect and interpret the conformational mobility of single alkyl chains in gold nanoparticles (AuNP) passivated with a monolayer of decanethiols.

Experimentally, the overall dynamics of an alkyl chain can be indirectly accessed by nuclear magnetic resonance spectroscopy (NMR). In particular, ^{13}C T_1 and T_2 relaxation times are modulated by the complex, global plus internal, dynamics of the system. However, the interplay of the molecular details in affecting the relaxation process makes it necessary to employ an appropriate modeling to quantitatively bridge between the single-molecule description and the bulk response. To this aim, we employ a stochastic description of only relevant, slow coordinates. In particular, we selected the global tumbling of the AuNP and the probe alkyl chain torsion angles. The remaining degrees of freedom constitute a thermal bath that imposes fluctuation-dissipation on the dynamics of the relevant coordinates. Two ingredients are required to fully parameterize the stochastic equation: the potential of mean force acting on the selected coordinates, and the friction, which describes how the bath opposes to a change of the system configuration. We setup a multiscale modeling scheme in which the system is treated at different levels of detail based on the different molecular properties entering the stochastic equation that need to be evaluated. In particular, a united-atom description of the whole molecular system is employed to build-up the free energy profiles along the alkyl chain torsion angles, while hydrodynamics modeling is employed to access the generalized friction (rotational and conformational). Then, stochastic, Brownian dynamics simulations are carried out to evaluate the spectral densities that enter in the calculation of NMR relaxation data.

Our results show a good agreement with relaxation times as function of the distance of the ^{13}C atom from the surface of the AuNP. It emerges that the mobility of the single chains resembles that of an ideal chain made of connected *n*-butane-like bonds. Since no free parameters have been employed, the proposed computational protocol, tailored to the study of the dynamics of flexible coatings of AuNP's, showed to be predictive when employing *ad hoc* theoretical tools suited for the problem. Specially, the employment of a novel strategy to calculate free energies (based on Jarzynski's equality [1]) recently introduced by some of us [2,3] turned out to be efficient to construct torsion free energy profiles which may display barriers even of several k_BT units. Our belief is that the proposed protocol, coupled to the information that can be obtained from NMR experiments, may become of particular help in the design of functionalized nanomaterials.

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Niccolò Albertini	Scuola Normale Superiore
Alberto Baiardi	Scuola Normale Superiore
Jacopo Baldini	Scuola Normale Superiore
Shiladitya Banerjee	ICCOM-CNR, UOS di Pisa
Vincenzo Barone	Scuola Normale Superiore
Stefano Baroni	Scuola Internazionale Superiore di Studi Avanzati
Paolo Calligari	Università degli Studi di Padova
Chiara Cappelli	Scuola Normale Superiore
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Javier Cerezo Bastida	ICCOM-CNR, UOS di Pisa
Claudio Cosentino	Università degli Studi di Milano-Bicocca
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Cristiana Di Valentin	Università degli Studi di Milano-Bicocca
Alessandro Fortunelli	CNR-ICOM, UOS Pisa
Damiano Gerosa	Università degli Studi di Milano-Bicocca
Tommaso Giovannini	Scuola Normale Superiore
Claudio Greco	Università degli Studi di Milano-Bicocca
Jerryman Appiahene Gyamfi	Scuola Normale Superiore
Yanli Liu	ICCOM-CNR, UOS di Pisa
Marina Macchiagodena	Scuola Normale Superiore
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Michael A. Robb	Imperial College London
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Fabrizio Santoro	ICCOM-CNR, UOS di Pisa
Emilia Sicilia	Università della Calabria
Dimitrios Skouteris	Scuola Normale Superiore
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Nicola Tasinato	Università Ca' Foscari Venezia
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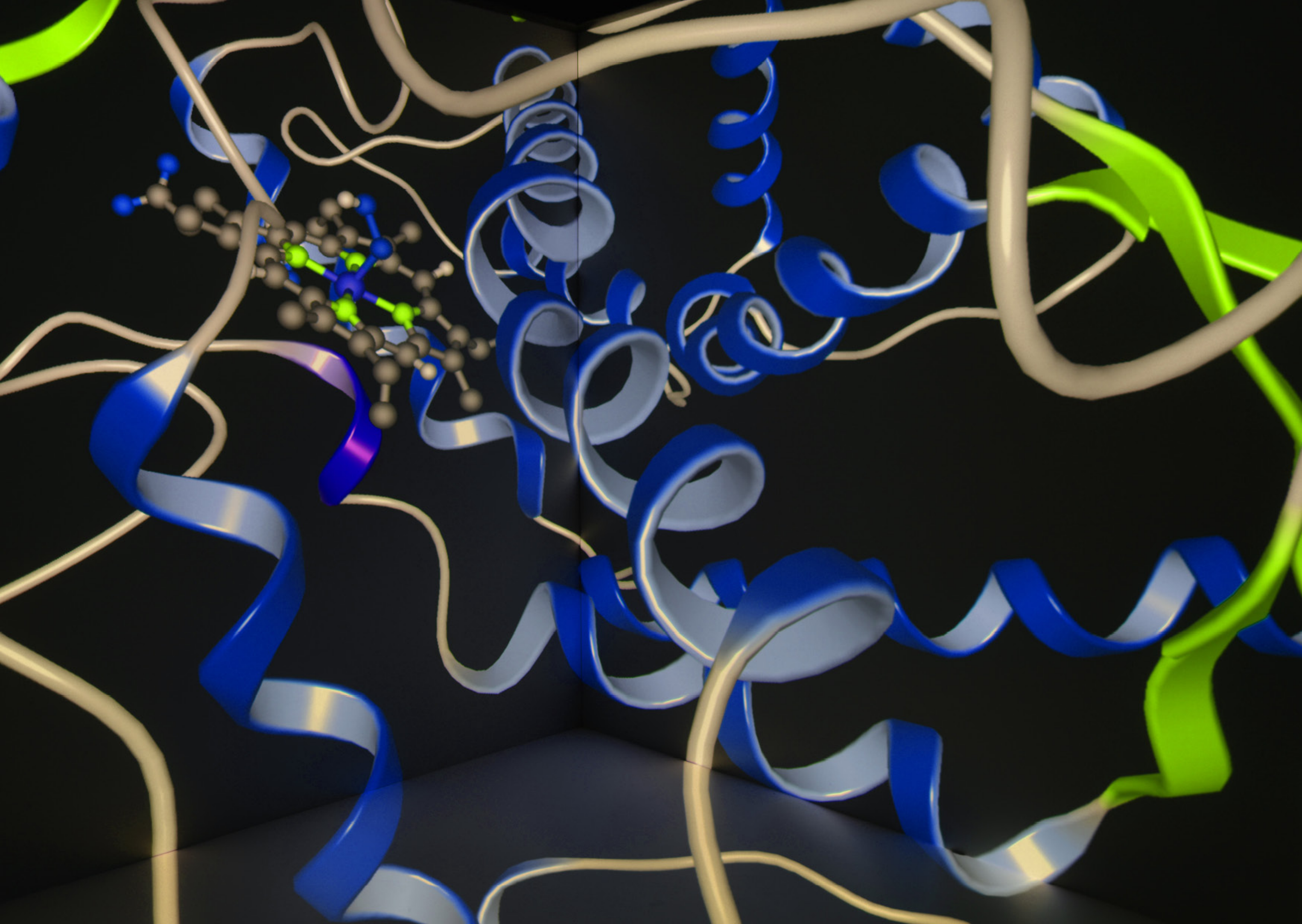
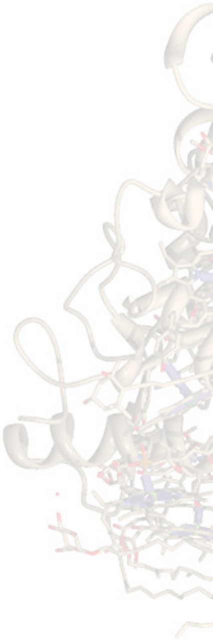
Francesco Zerbetto	Università degli Studi di Padova
Mirco Zerbetto	Università di Bologna





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