

XXXII ANNUAL MEETING OF REFERENCE
NETWORK OF R+D+I ON THEORETICAL AND
COMPUTATIONAL CHEMISTRY

BOOK OF ABSTRACTS

JULY 4th and 5th 2016
Universitat Autònoma de Barcelona
FACULTAT DE CIÈNCIES
Bellaterra, Catalonia, Spain

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UAB

Universitat Autònoma de Barcelona

MONDAY JULY 4th

9:00-9:30	Registration
9:30-9:50	Opening session and welcome: Excm. Sr. José A. Aguilera, vicerector Universitat Autònoma de Barcelona Il·lm. Sr. Antoni Méndez, degà de la Facultat de Ciències UAB Dra. Rosa Ortuño, Directora del Departament de Química UAB
Session 1	Chairwoman: Annapaola Migani (ICN2)
9:50-10:30 Plenary Session	Large Scale QM Simulations of Periodic Systems: The Cases of Mesoporous Silica and Protein Crystals. Piero Ugliengo, Professor, Università di Torino, Dipartimento di Chimica.
10:30-10:45	Prebiotic Reactions based on Titan's Atmosphere Chemistry. Estefania López (UB)
10:45-11:00	Four-component Relativistic ³¹ P-NMR calculations in trans-Platinum(II) Complexes and the importance of the Solvent and Dynamics in Spectral Simulations. Abril C. Castro (UdG)
11:00-11:15	Study of the Interactions Between Ruthenium Oxide Surface and Water Molecules. Javier Heras (UAB)
11:15-11:45	Coffee Break
Session 2	Chairwoman: Maria Besora (ICIQ)
11:45-12:00	Rh-catalyzed hydroamination reactions: LUMO's shape drives regioselectivity. Almudena Couce (UAB)
12:00-12:15	Thermal energy storage in nanofluids: what can simulations teach us? Francesca Costanzo (ICN2)
12:15-12:30	Density functional theory description of the electronic structure of realistic models of TiO ₂ nanoparticles. Oriol Lamiel (UB)
12:30-12:45	Molecular Sieving of H ₂ and D ₂ in a Carbon Nanotube: kinetic vs thermodynamic effects. Manel Mondelo (UB)
12:45-13:00	Predictive DFT-based QSAR model for the nucleophilic reactivity of trivalent boron compounds. Diego García (URV)
13:00-13:15	On the mechanism of bistability in prototype pdta molecule-based magnets. Tommaso Francese (UB)
13:15-14:45	Lunch

Session 3	Chairman: Fermín Huarte (UB)
14:45-15:25 Plenary Session	Quantum coherent control of chemical processes: some perspectives. Fabien Gatti, Professor, Institut Charles GERHARDT, Université Montpellier.
15:25-15:40	Conditional Born–Oppenheimer Dynamics. Efrem Bernuz (UB)
15:40-15:55	Mo Carbides for the Conversion of CO ₂ : The Metal/C Ratio as a Key Factor. Sergio Posada (UB)
15:55-16:15	Coffee Break
Session 4	Chairman: Jordi Carbó (URV)
16:15-16:30	Elucidation of the mechanism of activation of oxygen by Iron (II) polypyridylamine complexes in water. Davide Angelone (UdG)
16:30-16:45	Using open-shell molecules to design 2D covalent networks with controllable properties. Isaac Alcón (UB)
16:45-17:00	Computational study of the Si/Al ratio effect in FAU-type zeolites for CO ₂ post-combustion capture. Daniel Bahamón (UB)
17:00-17:15	Of triangles and squares: hierarchical self-assembly of interlinked polyoxometalates. Stefano Serapian (ICIQ)
17:20	REUNIÓ DEL CONSELL CIENTÍFIC XRQTC

TUESDAY JULY 5th

9:15-9:30	Registration
Session 5	Chairwoman: Silvia Osuna (UdG)
9:30-10:10 Plenary Session	Dynamics and Reaction Mechanism of Phosphate Catalytic Enzymes. Edina Rosta, Professor, Department of Chemistry, King's College London.
10:10-10:25	Theoretical study of a new class of nuclease using a metal/histidine catalytic machinery for DNA cleavage and ligation. Hansel Gomez (IRB)
10:25-10:40	α 1,4-N-Acetylgalactosaminyltransferase EXTL2: The Missing Link for Understanding Glycosidic Bond Biosynthesis with Retention of Configuration. María Fernanda Mendoza (UAB)
10:40-10:55	Thermodynamics of ligand binding in CRBPs: Linking protein flexibility and binding affinity. Carolina Estarellas (UB)

10:55-11:25	Coffee Break
Session 6	Chairwoman: Laura Masgrau (UAB)
11:25-12:05 Plenary Session	Exploring Free Energy Surfaces in Enzymatic Reactions. Iñaki Tuñón, Professor, Departamento de Química Física, Universidad de Valencia.
12:05-12:20	Predicting the interactions of metallic compounds with bio-scaffolds. Jaime Rodriguez-Guerra (UAB)
12:20-12:35	Joining carbohydrates with nature-modified enzymes. Insights into the design of new glycosyl hydrolases with synthetic abilities. Lluís Raich (UB)
12:35-12:50	Effect of mixed crowded media on the diffusion processes of proteins in intracellular media by Brownian dynamics simulations. Pablo M. Blanco (UB)
12:50-13:05	A computational approach to reveal the sliding mechanism of PCNA on DNA. Susana Barrera-Vilarmau (CSIC)
13:05-14:30	Lunch
Session 7	Chairman: Jordi Poater (UB)
14:30-15:10 Plenary Session	Unexpectedly large solvation effects on photochemical reaction rates at the liquid water-vapor interface. Manuel F. Ruiz-López, Professor, SRSMC, University of Lorraine
15:10-15:25	Unraveling the energy ladder in cryptophyte light-harvesting proteins. Marina Corbella (UB)
15:25-15:40	Revisiting the ribose 2'-hydroxyl group orientation in RNA: insights from the Protein Data Bank and molecular simulations. Leonardo Darré (IRB)
15:40-16:00	Coffee Break
Session 8	Chairman: Sergi Madurga (UB)
16:00-16:15	Charge-density- wave state manipulation in TiSe ₂ single-layers. Bogdan Guster (ICN2)
16:15-16:30	Modulating the Absorption Band Maximum in Fluorescent Proteins: A Molecular dynamics and QM/MM TD-DFT description. Pau Armengol (UAB)
16:30-16:45	Towards ab-initio Molecular Dynamics without Born-Oppenheimer Potential-Energy Surfaces. Guillermo Albareda (UB)
16:45-17:00	Reaction Mechanism and Kinetic Simulation for the photoinduced C-H Arylation of Amines: Role of the Counterion in the Rate of Photoredox Catalyzed Reactions. Víctor Fernández (ICIQ)
17:00	Cloenda: Professor Francesc Illas, director de la XRQTC

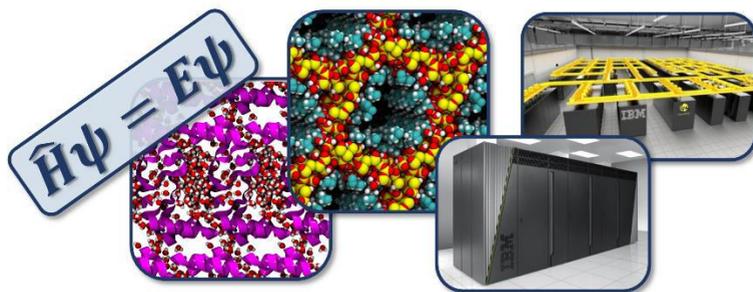
Large Scale QM Simulations of Periodic Systems: The Cases of Mesoporous Silica and Protein Crystals

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Recent evolutions in High Performance Computing (HPC) architectures and the concurrent development of more efficient quantum-mechanical software have dramatically increased the size and complexity of the systems that can be modeled by fully ab initio methods, at a high accuracy level. One of the areas that greatly benefits from these advancements is materials science: surfaces and interfacial phenomena, defective solids, biomaterials and nano-particulate systems, all require models hardly handled by desktop computing architectures due to the large system size. We show two recent applications of periodic large-scale ab initio simulations: the investigation of drugs encapsulated into mesoporous silica materials for drug delivery purposes¹ and the first fully B3LYP modeling of a protein² crystal, inclusive of lattice water molecules.



References

1. Delle Piane, *et al* J. Phys. Chem. C 2014, 118, 26737-26749
2. Delle Piane, *et al* Chem. Sci. 2016, 7, 1496-1507

Prebiotic Reactions based on Titan's Atmosphere Chemistry

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Titan, the largest moon of Saturn, is characterized by the presence of a dense and stable atmosphere around its surface. Titan's geography is similar to the primitive Earth, and the meteorological conditions in the satellite remember the prebiotic conditions in our planet millions of years ago. Experimental and computational studies of Titan's atmosphere chemistry make us to understand prebiotic mechanisms that remind the reactions involved in the beginning of life on Earth, and moreover show us the current evolution of Titan's atmosphere and other surface processes. N₂ and CH₄ are the most abundant gases on Titan[1], resulting in a nitriles chemistry predominant in its atmosphere[2]. In the present studies we have found computationally several organic mechanisms to explain the formation of cyclic organic compounds and other interesting adducts that are in good agreement with the gas phase experimental results obtained in Trento's laboratory. Characterized compounds and structures resemble such important molecules as some essential amino acids or nitrogenous bases clearly involved in the presence of life on earth.

References:

[1]: Chemistry of Titan's atmosphere, V.Vuitton, O. Dututi, M.A. Smith and N. Balucani.

[2]: Ion chemistry and N-containing molecules in Titan's upper atmosphere, V. Vuitton, R.V. Yelle, M.J. McEwan, Icarus 191 (2007) 722–742

Acknowledgments: Thanks are due to MINECO Project CTQ2013-41307-P, AGAUR Project 2013 SGR 25 and FCR-CSUC for supercomputer time.

Four-component Relativistic ³¹P-NMR calculations in trans-Platinum(II) Complexes and the importance of the Solvent and Dynamics in Spectral Simulations

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Our investigation focuses on the theoretical determination of the NMR chemical shifts using both “static” and “dynamic” approaches of the *trans*-[PtCl₂(dimethylamine)PPh₃] complex and the species derived from its hydrolysis, in a first attempt to understand its mechanism of action as anticancer platinum drug.^[1]

The ³¹P-NMR chemical shifts were computed using *ab initio* molecular dynamics (AIMD) simulations, followed by DFT-NMR calculations on a large series of snapshots. The relativistic calculations were performed with the ReSpect (*Relativistic Spectroscopy*) program, using a full four-component Dirac-Coulomb (DC) Hamiltonian (including both scalar and spin-orbit corrections)^[2] and also with the ADF program, using the spin-orbit zeroth-order-regular approximation (SO-ZORA). Comparing with the experimental spectra,^[1] we will show the importance of the relativistic effects, dynamics, and inclusion of explicit solvent molecules for the accurate modeling of the ³¹P-NMR chemical shifts.

References

[1] F. J. Ramos-Lima, A. G. Quiroga, B. García-Serrelde, F. Blanco, A. Carnero, C. Navarro-Ranninger, *J. Med. Chem.*, **2007**, 50, 2194.

[2] V. G. Malkin, O. L. Malkina, R. Reviakine, A. V. Arbuznikov, M. Kaupp, B. Schimmelpfennig, I. Malkin, M. Repiský, S. Komorovský, P. Hrobárik, E. Malkin, T. Helgaker, and K. Ruud, *ReSpect program*, **2007**.

Study of the Interactions Between Ruthenium Oxide Surface and Water Molecules

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The water oxidation reaction is the most challenging step in water splitting process. To catalyze this critical semi-reaction, heterogeneous catalyst such as ruthenium oxide, with unique surface chemistry and versatile behaviours in oxidative reactions are promising. Existing only one stable solid phase, RuO₂ is widely applied in chemistry due its ability to dehydrogenate small molecules at low temperature and as electro-catalyst for the chlorine alkali industry.

In this contribution, DFT calculations with periodic boundary conditions as implemented in VASP are performed. In particular, full structural relaxation and surface energy calculation of the most relevant crystallographic orientations (110), (100), (001), (101) of RuO₂ are accomplished. After that, water molecules from 1 per unit cell to the formation of a water monolayer are adsorbed onto these surfaces. This allows to determine the interactions between the highly reactive under-coordinated atom and the adsorbed small molecules, as well as to predict the degree of water deprotonation as function of water coverage. Moreover, Nudged Elastic Band studies are performed to evaluate the structure of possible transitions states and the energetic barriers associated with proton transfer between water molecules of the monolayer and the solid surface.

Preliminar results show that water coverage has a high influence in the degree of water dissociation on the surface than the nature of the surface. Formation of H₃O⁺ - units appears to be a driving force for water dissociation and this seems to be regardless of the nature of the surfaces.

References

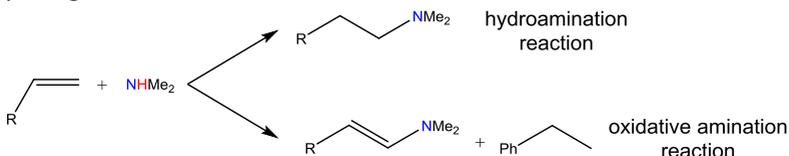
- 1)M.D. Kärkas, E.V. Johnston, O. Verho and B. Åkermark, *Acc. Chem. Res.*, 2013, **47**, 100-11.
- 2)H. Over, Y.D. Kim, A.P. Seitsonen, S. Wendt, *et al.*, *Science*, 2000, **287**, 1474-1476.
- 3)R. Mu, D.C. Cantu, V.A. Glezakou, I. Lyubinetsky, *et al.*, *J. Phys.Chem. C*, 2015, **119**, 23552-23558.

Rh-catalyzed hydroamination reactions: LUMO's shape drives regioselectivity

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The hydroamination reaction is very important due to its industrial and pharmaceutical applications. The number of articles containing this topic has been increased during last years being the anti-Markovnikov hydroamination one of 10 challenges for homogeneous catalysis.¹

The reaction mechanism for the hydroamination reaction catalyzed by a cationic Rhodium complex² was studied as well as the mechanism for the competing side reaction, the oxidative amination reaction.



Two mechanisms were proposed for the hydroamination reaction: the amine activation mechanism and the alkene activation mechanism.³ The most plausible mechanism was found to be the alkene activation mechanism which involves the coordination of alkene to metal center, a metal center protonation and a reductive elimination steps.

The origin of the regioselectivity for the nucleophilic addition (Markovnikov vs anti-Markovnikov) was shown to be orbitally driven, depending on the LUMO's shape. Moreover, regioselectivity can be correlated with some structural parameters of reactants.⁴

References

1. Haggin, J. *Chem. Eng. News* **1993**, 71 (22), 23-27
2. Utsunomiya, M.; Kuwano, R.; Kawatsura, M.; Hartwig, J.F. *J. Am. Chem. Soc.* **2003**, 125, 5608-5609
3. Beller, M.; Trauthwein, H.; Eichberger, M.; Breindl, C.; Müller, T. E. *Eur. J. Inorg. Chem.* **1999**, 7, 1121-1132
4. Couce-Rios, A.; Lledós, A.; Ujaque, G. *Chem. Eur. J.* **2016**, 22 In press (DOI: 10.1002/chem.201504645)

Charge-density-wave state manipulation in TiSe₂ single-layers

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The field of 2D materials is increasingly attracting more researchers due to the new and interesting properties of materials already studied in bulk that now can be studied in the 2D limit. We focus in this work on the single-layer transition metal dichalcogenide 1T-TiSe₂. There has been a perpetual debate over the origin of the transition from the semi-metallic phase to the charge-density-wave phase that this material suffers in bulk. We present here our results for single-layers based on density functional theory calculations. We explain the transition of the single-layer TiSe₂ as a result of electron-phonon coupling and, moreover, the recovery of the conductivity lost in the phase transition as a function of charge doping.

References

[1] PRB, 14, 10, 1976, 4321-4328

[2] Nature. 2016 Jan 14;529(7585):185-9

[3] ACS Nano, 2016, 10 (1), pp 1341–1345

Density functional theory description of the electronic structure of realistic models of TiO₂ nanoparticles

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Titanium dioxide (TiO₂), usually known as titania, is one of the most studied inorganic oxides due to its unique catalytic and photocatalytic properties. Hence, titania is involved in many technological applications such as self-cleaning surfaces, water and air cleaning systems, and specially, for H₂ and O₂ obtention through photocatalytic water splitting.^{1,2} In spite of the long time transurred since photocatalytic water splitting by TiO₂ nanoparticles under ultraviolet radiation was reported, there are many unknown details such as the influence of size and shape of the nanoparticles in the resulting electronic structure and related properties. To contribute to unveil these unknowns, we performed all electron relativistic density functional theory (DFT) based calculations using GGA and hybrid functionals on several TiO₂ nanoparticles models containing up to 1365 atoms. The nanoparticles studied encompass different sizes up to 6 nm and different structures initially derived from Wulff construction. Results will be presented that analyzed the energetic stability and electronic structure as a function of size and morphology and discuss possible implications regarding the photocatalytical activity of this material.

References

- (1) Hashimoto, K.; Irie, H.; Fujishima, A. *Jpn. J. Appl. Phys.* 2005, 44, 8269–8285.
- (2) Fujishima, A.; Zhang, X.; Tryk, D. A. *Surf. Sci. Rep.* 2008, 63, 515–582.

Molecular Sieving of H₂ and D₂ in a Carbon Nanotube: kinetic vs thermodynamic effects

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The development of nanostructured materials with good adsorption properties for gaseous substances is an attractive research field due to its industrial applications for gas separation and its obvious environmental impact^{1,2}. Among these materials, some present pores small enough to induce a *quantum confinement* of the adsorbed molecules³. This effect can be taken advantage of to separate even different isotopologues, such as H₂ from D₂.

Quantum molecular sieving is usually studied from the point of view of selective adsorption of one species with respect to the other⁴. Isotope separation using this process requires very low temperatures, below 100 K. At such low temperatures, kinetic effects must be taken into account, and the *kinetic sieving* of the molecules, *i.e.* the separation obtained due to the different diffusion rates in the molecular sieve, becomes important. Under suitable conditions, a *reverse kinetic sieving* effect, with the heavier molecule diffusing faster than the lighter, has been reported⁵. Works on this field have focused on selected zeolites and carbon molecular sieves, so more studies are needed to fully understand the process.

¹ G. E. Ioannatos and X. E. Verykios, Int. J. Hydrogen Energy 35, 622 (2010).

² X. Ren, C. Chen, M. Nagatsu, and X. Wang, Chem. Eng. J. 170, 395 (2011).

³ J. J. M. Beenakker, V. D. Borman, and S. Y. Krylov, Chem. Phys. Lett. 232, 379 (1995).

⁴ H. Kagita, T. Ohba, T. Fujimori, H. Tanaka, K. Hata, S. Taira, H. Kanoh, D. Minami, Y. Hattori, T. Itoh, H. Masu, M. Endo, and K. Kaneko, J. Phys. Chem. 116, 20918 (2012).

⁵ A. V. A. Kumar and S. K. Bhatia, Phys. Rev. Lett. 95, 1 (2005).

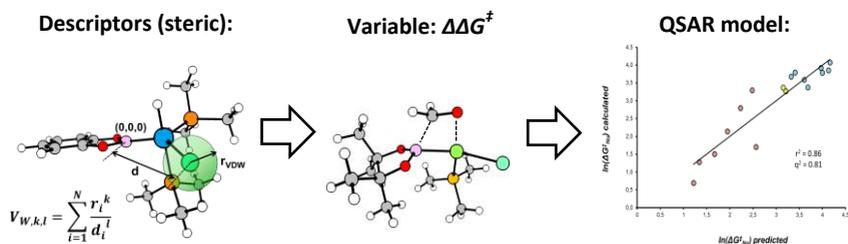
Predictive DFT-based QSAR model for the nucleophilic reactivity of trivalent boron compounds

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Although most trivalent boron compounds are electrophiles, they can switch their reactivity from an electrophilic character to a nucleophilic behaviour by changing the nature of the substituents on the boron atom.¹ Our goal is to set a quantitative relationship between the stereoelectronic properties of boryl compounds and their nucleophilic reactivity. For that purpose, we used previously defined electronic descriptors² and a novel steric descriptor, the distance-weighted volume (V_W).³ To determine a quantitative dependent variable that measures the nucleophilic activity, we made use of the boryl addition to formaldehyde and computed its free energy barrier, covering a wide range of boryl fragments. Using multivariate regression techniques, we were able to generate QSAR models that correlate well with computed reactivity and that show predictive ability.



1. Cid J., Gulyás H., Carbó J. J., Fernández E., *Chem. Soc. Rev.* **2012**, *41*, 3558.
2. Cid J., Carbó J. J., Fernández E., *Chem. Eur. J.*, **2012**, *40*, 12794.
3. MolQuo: <http://rodi.urv.es/~carbo/quadrants/index.html>

On the Mechanism of Bistability in Prototype PDTA Molecule-Based Magnets

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In this work we want to verify that the pair-exchange dynamics model¹ proposed for the TTTA bistable neutral radical can be generalized to the DTA (azodithiazolyl) radical family. In order to explore this applicability, we analyzed the PDTA ([1,3,2]-pyrazinodithiazol-2-yl) bistable neutral radical molecule. PDTA presents a first-order phase transition between the LT and HT phases, encompassing room temperature. LT crystals belong to the triclinic space group ($P1$), and consist of diamagnetic π -stack dimers. In contrast, HT crystals belong to the monoclinic space group ($C2/c$), and consist of paramagnetic π -stacks radicals². The magnetic susceptibility data, $\chi(T)$, of PDTA crystals show the presence of a strong antiferromagnetic behavior for the LT phase, whereas the HT phase is associated with a quenched paramagnetic behavior. We analyzed PDTA from a static point of view, defining its electronic structure both in solid state and for isolated pairs, and by means of *First Principle Molecular Dynamics* simulations, in order to unveil if the phase transition structure and magnetic properties of PDTA are generated by the same physical principles operating in TTTA³.

References

- 1) Vela, S. et al. *Chem. Sci.* (2015), 6, 2371;
- 2) Brusso, J. L. et al. *JACS* (2004), 126, 8256;
- 3) Fujita, W. et al. *Science* (1999), 286, 261.

Quantum coherent control of chemical processes: some perspectives

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Industrial processes involving chemical reactions are typically controlled by macroscopic parameters, such as temperature or pressure, which usually results in a huge waste of energy and the massive production of unwanted by-products leading to energy consumption and pollution. To overcome these problems, one possibility is to control the chemical reactivity at a microscopic level via the systematic use of quantum phenomena such as quantum coherence induced by laser. On the experimental front, it becomes possible to control the motion of electrons and nuclei, molecular vibrations and rotations, each of them on its natural time scale [1, 2]. In this context, we will present different strategies of control of chemical processes exploiting the Multi-Configuration Time-Dependent (MCTDH) approach [3] that allows one to propagate coherent wave-packets one one or several potential energy surfaces.

References :

- [1] M. Drescher, M. Hentschel, R. Kienberger, M. Uiberacker, A. Scrinzi, U. Heinzmann, and F. Krausz., *Nature* 419 (2002) 803.
- [2] Jakob Larsen, I. Wendt-Larsen, and H. Stapelfeldt, *Phys. Rev. Lett.* 83 (1999) 1123.
- [3] H.-D. Meyer, F. Gatti, and G. A. Worth, Eds. *MCTDH Theory and Applications*, Wiley-VCH, Weinheim, 2009.

Conditional Born–Oppenheimer Dynamics

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We report a new theoretical approach to solve adiabatic quantum molecular dynamics halfway between wave function and trajectory-based methods. The evolution of a N-body nuclear wave function moving on a 3N-dimensional Born–Oppenheimer potential-energy hyper-surface is rewritten in terms of single-nuclei wave functions evolving nonunitarily on a 3-dimensional potential-energy surface that depends parametrically on the configuration of an ensemble of generally defined trajectories. The scheme is exact and, together with the use of trajectory-based statistical techniques, can be exploited to circumvent the calculation and storage of many-body quantities (e.g., wave function and potential-energy surface) whose size scales exponentially with the number of nuclear degrees of freedom. The resulting propagation scheme lends itself as a rigorous starting point for developing new algorithms based on a new class of “quasi-on-the-fly” molecular dynamics. We thus expect it to be of particular interest in scenarios where the involved number of nuclear degrees of freedom is large and quantum effects both complex and conspicuous. As a proof of concept, we present numerical simulations of a 2-dimensional model porphine where switching from concerted to sequential double proton transfer (and back) is induced quantum mechanically(1). We also show results for the reactive scattering of the chlorine methane proton transfer, still a 2-dimensional model (2).

References

1.- Albareda G., Bofill J. M., Tavernelli I., Huarte-Larrañaga F., Illas F., Rubio A.; Conditional Born–Oppenheimer Dynamics: Quantum Simulations for the Model Porphine, *J. Phys.Chem. Lett.*,

2.- Bernuz E., Bofill J. M., Illas F., Albareda G.; A conditional wave function approach to reactive scattering (in progress)

Mo Carbides for the Conversion of CO₂: The Metal/C Ratio as a Key Factor

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The ever growing increase of CO₂ concentration in the atmosphere is one of the main causes of global warming. Thus, CO₂ activation and conversion towards valuable added compounds is a major scientific challenge. Transition metal carbides (TMCs) are efficient catalyst for CO₂ conversion towards CO with possible subsequent selective hydrogenation towards methanol.¹

Sophisticated experiments and periodic DFT calculations have been used to study the unique behavior of β -Mo₂C (orthorhombic) and δ -MoC (cubic) surfaces and of Cu clusters supported thereon. Experiments and theory highlight the impact of the metal/carbon ratio in the resulting catalysts.^{2,3} Additionally, CO₂ hydrogenation on Cu/MoC and Cu/Mo₂C systems leads to increased CO and methanol production; selectivity towards CO is drastically enhanced for Cu/MoC.

REFERENCES

1. J. A. Rodríguez, J. Evans, L. Feria, A. B. Vidal, P. Liu, K. Nakamura, F. Illas, *J. Catal.* 2013, 307, 162.
2. S. Posada-Pérez, P. J. Ramírez, R. A. Gutierrez, D. J., Stacchiola, F. Viñes, P. Liu, F. Viñes, F. Illas, and J. A. Rodríguez, *Catal. Sci. Technol.* DOI: 10.1039/c5cy02143j.
3. S. Posada-Pérez, P. J. Ramírez, J. Evans, F. Viñes, P. Liu, F. Illas and J. A. Rodríguez, submitted

Elucidation of the mechanism of activation of oxygen by Iron (II) polypyridylamine complexes in water

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The activation of oxygen by Fe(II) polypyridylamine complexes is crucial, in particular, to understand the factors that determine their activity in achieving substrate oxidation (such as the oxidative cleavage of double strand DNA).[1] In this contribution, we explore, the reaction of these complexes with oxygen and the pathways which are involved in achieving substrate oxidation. The major focus will be on the generation of superoxide radical from the reaction of Fe(II) polypyridylamine based complexes and oxygen and in particular the enhancement in reaction rates observed by irradiation with visible and UV light.[2] This will be complemented by state-of-the-art density functional studies using methods[3] that have been proven[4,5] to work well for spin-state properties that play a major role here.

References

[1] T. A. van den Berg , B. L. Feringa and G. Roelfes, *Chem. Commun.* **2007**, 180–182

[2] A. Draksharapu, Q. Li, G. Roelfes and W. R. Browne, *Dalton Trans.* **2012**, 41, 13180-13190

[3] M. Swart, *Chem. Phys. Lett.* **2013**, 580, 166-171

[4] M. Swart, *Chem. Commun.* **2013**, 49, 6650-6652

[5] J. Prakash, G.T. Rohde, K.K. Meier, A.J. Jasniewski, K.M. van Heuvelen, E. Münck, L. Que Jr., *J. Am. Chem. Soc.* **2015**, 137, 3478-3481

Using open-shell molecules to design 2D covalent networks with controllable properties

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Triarylmethyls (TAMs) are stable open-shell molecules composed of three aryl rings bonded to a central methyl carbon atom, where their unpaired electron mainly resides. TAMs have played a prominent role within the research field of molecular magnetic materials and have a range of practical applications.^[1] Moreover, very recently the potential of TAMs for use in molecular spintronics has been firmly established experimentally.^[2] Using accurate *ab initio* density functional calculations we have shown that the spin localization within any TAM derivative, regardless of the chemical functionalization and temperature, can be controlled by the torsion angles of the three aryl rings.^[3] To exploit such a powerful feature, we have designed a range of chemically viable TAM-based 2D covalent organic frameworks (2D-COFs) where, in full agreement with our previous study,^[3] the spin localization can be finely controlled by applying external strain. As a consequence of the strain-induced structural and spin localisation changes, other very important properties of these 2D materials (e.g. ferromagnetism, optical bandgaps, electrical conduction) can also be finely tuned in a reversible way.

- [1] I. Ratera and J. Veciana, *Chem. Soc. Rev.*, 2012, **41**, 303–49.
- [2] R. Frisenda, R. Gaudenzi, C. Franco, M. Mas-Torrent, C. Rovira, J. Veciana, I. Alcon, S. T. Bromley, E. Burzurí and H. S. J. van der Zant, *Nano Lett.*, 2015, **15**, 3109–3114.
- [3] I. Alcon and S. T. Bromley, *RSC Adv.*, 2015, **5**, 98593–98599.

Computational study of the Si/Al ratio effect in FAU-type zeolites for CO₂ post-combustion capture

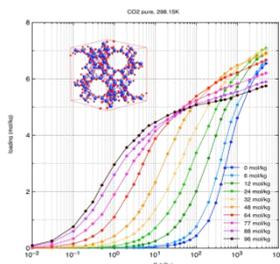
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Since in the short-term power plants will continue operating with fossil fuels, the development of a cost-effective CO₂ capture system is critical to reducing global carbon dioxide emissions.^{1,2} In this regard, solid adsorbent based systems have received significant attention as alternatives to amine solutions, showing high CO₂ capacities and high selectivities for CO₂ over N₂, thus demonstrating potential toward reducing energy penalties and improving efficiency.^{3,4} Among these materials, zeolites deserve special attention, since they are inexpensive porous materials already produced on a large scale for many commercial applications. The different ways in which they can be connected lead to a rich variety of structures,⁵ and their adsorption properties can be controlled in a very straightforward way by modifying the aluminum content in the framework.⁶ In this work, a series of FAU-type zeolites with sodium cations have been evaluated by Grand Canonical Monte Carlo simulations for potential application in post-combustion CO₂ capture, screening from zeolite topology to the mixture adsorption properties. The methodology used provides a general means for comparing the efficacies of the different structures, including transient breakthrough curves as well as energetic cost calculations, in order to evaluate in a more realistic way the operating conditions of swing adsorption cycles. Results show that better performances can be afforded by using medium Si/Al ratio zeolites than the traditionally used structures with a higher Al content.

References

- 1 E.D. Bloch et al., *J. Am. Chem. Soc.*, **2011**, 133, 14814.
- 2 J. Wang et al., *Energy Environ. Sci.*, **2014**, 7, 3478.
- 3 J. Liu et al., *J. Chem. Soc. Rev.* **2012**, 41, 2308.9.
- 4 Z. Zhang et al., *Energy Environ. Sci.*, **2014**, 7, 2868.
- 5 M.E. Davis, *Nature*, **2002**, 417, 813.
- 6 A. Corma, *Chem. Rev.*, **1997**, 97, 2373.



Of triangles and squares: hierarchical self-assembly of interlinked polyoxometalates

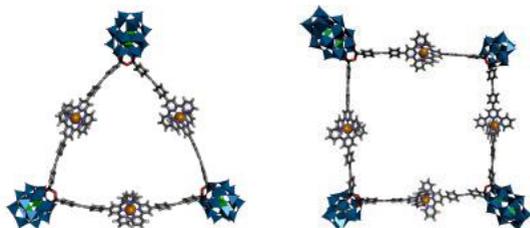
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In this communication,¹ we illustrate our computational efforts to support the characterisation of recently synthesised *coordination oligomers*,^{2,3} incorporating catalytically active lacunary Wells-Dawson anions (WDA; formally $[P_2W_{17}O_{61}]^{10-}$). Once equipped with two long organic alkynyl-phenyl-terpyridine arms, the resulting hybrid WDAs ($[P_2W_{17}O_{61}\{O(SiC_{29}H_{18}N_3)_2\}]^{6-}$; **1**) are driven by Fe^{II} to self-assemble into oligomeric units $[Fe_x\mathbf{1}_x]^{4x-}$ (see Figure). Further self-assembly of $[Fe_x\mathbf{1}_x]^{4x-}$ into higher, finite-size nanoparticle-like structures is entirely controllable and reversible by altering solvent conditions. Using two distinct multi-level *in silico* approaches, we are here able to show that such units coexist in solution both as triangles ($x = 3$) or squares ($x = 4$).



References

- (1) G. Izzet *et al.*, *J. Am. Chem. Soc.* **2016**, *138*, 5093
- (2) M.-P. Santoni *et al.*, *Coord. Chem. Rev.* **2014**, *281*, 64
- (3) G. Izzet *et al.*, *Chem. - Eur. J.* **2015**, *21*, 19010

Dynamics and Reaction Mechanism of Phosphate Catalytic Enzymes

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The formation and cleavage of phosphate bonds is essential in most biological processes including nucleic acid processing. Many enzymes that catalyze phosphate hydrolysis require bound Mg^{2+} ions. Here we focus on two such enzymes that carry out NTP cleavage: dUTPases¹ and RAF kinases.² dUTPases produce pyrophosphate as the cleavage product, and have essential roles in nucleotide metabolism and preventive DNA repair for most organisms. Intriguingly, they also possess additional moonlighting functions in viral signalling including gene expression, regulation and pathogenesis processes. RAF kinases are key participants in the MAPK/ERK pathway, fundamental in the regulation of many cellular processes related to cell growth and division. Their mutations, such as V600E for BRAF, are present in melanomas, colorectal, ovarian, and thyroid cancer. In RAF protein dimers, an activator protomer forms a binary molecular complex with a receiver protomer, and thus significantly enhances RAF catalytic activity.

We present atomistic MD and QM/MM simulation results, experimental mutational studies providing structural and biochemical insights into these phosphate catalytic enzymes.

References

1. Lopata, A.; Jambrina, P. G.; Sharma, P. K.; Brooks, B. R.; Toth, J.; Vertessy, B. G.; Rosta, E., *ACS Catalysis* **2015**, *5* (6), 3225-3237.
2. (a) Jambrina, P. G.; Bohuszewicz, O.; Buchete, N. V.; Kolch, W.; Rosta, E., *Biochem. Soc. Trans.* **2014**, *42* (4), 784-90; (b) Jambrina, P. G.; Rauch, N.; Pilkington, R.; Rybakova, K.; Nguyen, L. K.; Kholodenko, B. N.; Buchete, N.-V.; Kolch, W.; Rosta, E., *Angewandte Chemie International Edition* **2016**, *55* (3), 983-986.

Theoretical study of a new class of nuclease using a metal/histidine catalytic machinery for DNA cleavage and ligation.

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MobM belongs to the HUH endonuclease superfamily, which members depend on a single metal ion (e.g. Mn²⁺) for the activation of the scissile phosphate bond and on a catalytic residue (i.e. typically a tyrosine), that performs a nucleophilic attack to form a protein-5'-DNA adduct.[1] However, an initial visual analysis of MobM suggested that a histidine - which is assumed to be a weak nucleophile- would actually be in position to form the covalent protein/DNA complex.

We performed a Quantum Mechanics/Molecular Mechanics study to describe the catalytic mechanism followed by MobM, including ab initio QM(DFT)/MM free energy calculations. According to our results, His22 nucleophilically attacks on the scissile phosphate group through a concerted SN₂-like mechanism and an energy barrier of ~15-20 kcal/mol. Moreover, we have proposed that the nearby glutamate 129 is acting as a general acid that protonates the leaving O3' group and facilitates the nucleolytic reaction.

References

[1]. Chandler, M.; de la Cruz et al. (2013) Nat. Rev. Microbiol., 11, 525-38.

α 1,4-N-Acetylgalactosaminyltransferase EXTL2: The Missing Link for Understanding Glycosidic Bond Biosynthesis with Retention of Configuration

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Glycosyltransferases (GTs) are a prominent family of enzymes that play critical roles in a diversity of cellular processes. EXTL2 is a GT which catalyzes the transfer reaction with retention of the configuration of both sugars, the N-acetylgalactosamine (GalNAc) and the N-acetylglucosamine from the respective UDP-sugar to the [glucuronic acid] β 1-3[galactose], a natural common linker of various glycosylaminoglycans.

Two different reaction mechanisms have been suggested to explain the stereochemical outcome of retaining GTs, the Double Displacement mechanism that involves the formation of a Covalent Glycosyl Enzyme (CGE) intermediate employing a nucleophilic residue ^[1,2], and the Front Side Attack mechanism which can occur either by a Single Displacement mechanism with an oxocarbenium ion-like transition state (TS) ^[3] or via a two-step mechanism with an oxocarbenium ion par (IP) intermediate ^[1,5]. Thus, this topic has been strongly debated for long.

Here we present a full QM/MM mechanistic study of EXTL2 with one of its donor substrates, UDP-GalNAc. The intriguing dyad Asp-Arg featured by this enzyme on the nearby region of the anomeric carbon and its effects on the reaction mechanism are analyzed. The implications of this model for the understanding of retaining glycosidic bond formation and the catalytic mechanism of other members of the GT-A family are discussed.^[4]

References

- [1] Gómez, H.; Lluch, J.M.; Masgrau, L. *J. Am. Chem. Soc.* **2013**, 135, 7053.
- [2] Rojas-Cervellera, V.; Ardèvol, A.; Boero, M.; Planas, A.; Rovira, C. *Chem. Eur. J.* **2013**, 19, 14018.
- [3] Gómez, H.; Polyak, I.; Thiel, W.; Lluch, J.M.; Masgrau, L. *J. Am. Chem. Soc.* **2012**, 134, 4743.
- [4] Mendoza, F.; Gómez, H.; Lluch J.M.; Masgrau L. *ACS Catal.* **2016**, 6, 2577.
- [5] Alvesa-Jové, D.; Mendoza, F.; et al. *Angew. Chem. Int. Ed.* **2015**, 54, 9898.

Thermodynamics of ligand binding in CRBPs: Linking protein flexibility and binding affinity

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Retinoids are essential for many physiological processes like cell growth and differentiation, among others.¹ In order to exert their biological roles, they have to be transported to the appropriate site in the cell by specific proteins, namely, Cellular Retinol-Binding Proteins (CRBPs). The 3D structures of the most abundant CRBPs (isoforms I and II) have been solved by NMR^{2a} or X-ray crystallography.³ Although both isoforms share the ligand-binding motif and the structural superposition of both forms reveals no significant differences between them, CRBP-I binds retinol with approximately 100-fold higher affinity than CRBP-II. This fact has been ascribed to its different flexibility, as NMR experiments indicate that amide protons exchanged much faster in CRBP-II than in CRBP-I.^{2b} These trends are well reflected in the configurational sampling obtained from molecular dynamics (12 μ s/system) simulations for the apo and holo forms of both isoforms. The analysis indicates that apo-I is more flexible than apo-II, and that holo-I is more rigid than holo-II. It is worth noting that the differences in protein flexibility are primarily found in the “portal” domain that gives access to the interior of the protein. In particular, this area is found to be less flexible in apo-II compared to apo-I, suggesting that ligand association could be favoured in this latter isoform.

With the aim of understanding the nature of the factors that modulate retinol binding and the different affinity for both proteins, we have performed parallel tempered-metadynamics simulations to study the opening of the portal site in both isoforms, and the ligand binding and unbinding processes. The results provide a better understanding of the events implicated in ligand binding, including the role of entropy/enthalpy balance⁴ and solvent reorganization, and allow us to identify the molecular basis of the factors that regulate the distinct affinity for retinol.

References

1. Blomhoff, R., Blomhoff, H. K. *J. Neurobiol.* **2006**, *66*, 606.
- 2a. Franzoni, L., et al. *J. Biol. Chem.* **2002**, *277*, 21983. b) Franzoni, L., et al. *J. Lip. Res.* **2010**, *51*, 1332.
3. Tarter, M., et al. *Proteins* **2007**, *70*, 1626.
4. Chodera, J.D., Mobley, D.L. *Ann. Rev. Biophys.* **2013**, *42*, 121.

Exploring Free Energy Surfaces in Enzymatic Reactions

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Chemical reactions in complex environments can be studied using hybrid QM/MM approaches, which provide adequate Potential Energy functions for their analysis considering simultaneously the electronic reordering inherent to the bond breaking/forming process and the influence of the environment. However, differently to gas phase reactions, tracing a Potential Energy Surface is not enough to consider the complexity of chemical processes involving a large number of degree of freedoms and temperature-dependent Free Energy Surfaces must be considered. We will discuss several computational approaches for the exploration of such surfaces and the determination of Transition State ensembles in enzymatic reactions. New methodologies will be illustrated with several examples including hydride transfers and DNA methylation.

Predicting the interactions of metallic compounds with bio-scaffolds

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With about a third of Nature's biomolecules containing metal ions, efforts are constant to understand and manipulate biometallic interactions synthetically. From the development of biosensors based on non natural metallopeptides to the design of artificial metalloenzymes, an increasing number of bioinorganic studies are focused on fine tuning the interaction of biological scaffolds with coordination systems (either naked ions or coordination complexes).

While protein-ligand dockings are the common place to predict the binding of chemical compounds with proteins, standard methods in this field are extremely limited when it comes to predict how a metallic species could bind to a biological partner. From the complexity to generate accurate enough scoring functions accounting for metals to the challenge of predicting changes in the first coordination sphere of the metal during binding, novel strategies need to be developed.

In the recent years, we developed several workarounds to perform docking studies on metal compounds with inert scaffold upon binding. [1] Here we present our most recent advances in order to predict the interaction of metallic species with bio-scaffolds that explicitly consider coordination features of the metal and direct interactions with the protein amino-acids.

[1] Ortega - Carrasco E., Lledós A. And Maréchal J.-D. *J. Comput. Chem.* **2014**, 35 (3) 192 – 198

Joining carbohydrates with nature-modified enzymes. Insights into the design of new glycosyl hydrolases with synthetic abilities

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The conversion of glycoside hydrolases (GHs) into transglycosylases (TGs), *i.e.*, from enzymes that hydrolyze carbohydrates to enzymes that synthesize them, represents a promising solution for the large-scale synthesis of complex carbohydrates for biotechnological purposes.¹ However, the lack of knowledge about the molecular details of transglycosylation hampers the rational design of TGs. Here we present, by means of quantum mechanics/molecular mechanics (QM/MM) simulations, the transglycosylation mechanism of a membrane-anchored TG, finding crucial substrate-enzyme interactions that affect both the free energy barriers and the conformational distortion of the substrate during catalysis.^{2,3} Our results suggest that changes in these interactions could have an impact on the transglycosylation activity of several GHs.

References

- [1] (a) Mackenzie, L. F.; Wang, Q.; Warren, R. A. J.; Withers, S. G. *J. Am. Chem. Soc.* **1998**, 120, 5583. (b) Malet, C.; Planas, A. *FEBS Lett.* **1998**, 440, 208. (c) Teze, D.; Hendrickx, J.; Czjzek, M.; Ropartz, D.; Sanejouand, Y. H.; Tran, V.; Tellier, C.; Dion, M. *Protein Eng., Des. Sel.* **2014**, 27, 13.
- [2] (a) Davies, G. J.; Planas, A.; Rovira, C. *Acc. Chem. Res.* **2012**, 45, 308–316. (b) Ardèvol, A.; Rovira, C. *J. Am. Chem. Soc.*, **2015**, 137, 7528–7547.
- [3] Raich, L.; Borodkin, V.; Fang, W.; Castro-López, J.; Aalten, D. M. F.; Hurtado-Guerrero, R.; Rovira, C. *J. Am. Chem. Soc.*, **2016**, 138, 3325–3332.

Effect of mixed crowded media on the diffusion processes of proteins in intracellular media by Brownian dynamics simulations

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The cellular cytosol is a very dense medium, with huge concentrations of biological macromolecules that, by means of non-specific interactions, has a considerable effect in intracellular diffusion processes. Therefore, theoretical models that describe these processes in homogeneous media are no longer valid in crowded conditions [1,2].

Diffusion processes could be studied by computer simulations using on-lattice [3] and off-lattice algorithms. In this study, we develop an off-lattice Brownian dynamics code to perform simulations of mixed crowded media in order to identify the key factors affecting the diffusion in in-vivo-like experiments.

We examined possible mechanism responsible for the great reduction in diffusion constants of macromolecules in vivo from that at infinite dilution. The role of crowded size, polydispersity, nonspecific and hydrodynamics interactions is analyzed.

References

1. I. Pastor, E. Vilaseca, S. Madurga, J.L. Garcés, M. Cascante, F. Mas: J. Phys.Chem. B 114, 4028 (2010) & erratum 114,12182 (2010).
2. E. Vilaseca, I. Pastor, A. Isvoran, S. Madurga, J.L. Garcés, F. Mas: Theor. Chem. Acc. 128, 795 (2011).
3. E. Vilaseca, A. Isvoran, S. Madurga, I. Pastor, J.L. Garcés, F. Mas: PhysChem-ChemPhys 13, 7396 (2011).

A computational approach to reveal the sliding mechanism of PCNA on DNA

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Highly processive chromosomal replication requires ring-shaped sliding clamp factors that encircle the DNA and anchor polymerases and other proteins of the replisome, preventing polymerase release from the genomic template (1). Proliferating cell nuclear antigen (PCNA), the protein fold of sliding clamps, is an evolutionarily well-conserved protein in all domains of life and acts as a processivity factor of DNA polymerases (2). The fast diffusion of the eukaryotic PCNA clamps involves transient clamp-DNA interactions that are so weak that they have so far escaped direct observation. As a consequence, the molecular mechanism of PCNA sliding and its functional implications remain obscure. In this work, we combined crystallography and NMR data with Molecular Dynamics (MD) simulations to visualize the interactions, at atomic resolution, between human PCNA and DNA, and to follow the time evolution. We used GROMACS for the MD simulations (3) because is a free and open source package and for its versatility and extremely high performance compared to all other programs. This work shows that the residue side chains rapidly switch between adjacent phosphates in a non-coordinated manner, supporting a clamp bi-directional “cogwheel” mechanism for DNA backbone tracking.

References

(1) Mailand et al. Regulation of PCNA-protein interactions for genome stability. *Nature Reviews Molecular Cell Biology*, 2013 May; 14 (5): 269-82.

(2) Dieckman et al. PCNA structure and function: insights from structures of PCNA complexes and post-translationally modified PCNA. *Subcellular Biochemistry*, 2012; 62: 281-99.

(3) Pronk et al. GROMACS 4.5: a high-throughput and highly parallel open source molecular simulation toolkit. *Bioinformatics*, 2013; 29: 845-854.

Unexpectedly large solvation effects on photochemical reaction rates at the liquid water-vapor interface.

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Current atmospheric models underestimate the observed concentrations of OH radicals in the troposphere. Several studies have suggested that these models, which are mainly based on gas-phase chemistry, are probably missing a source of such radicals. Accordingly, a variety of possible additional sources have been proposed in the literature. In this work, we have examined the role of solvation effects at the surface of cloud water droplets. Computer simulations using the QM/MM Molecular Dynamics approach [1] have allowed us to show that solvation effects at the air-water interface may produce significant modifications of the electronic properties of adsorbed molecules and radicals [2-3]. Ozone photolysis, which is the main source of OH radicals in the troposphere, is significantly accelerated [4] and similar effects are predicted for other key photolytic processes occurring around the tropospheric cutoff (290 nm) [5].

[1] M.T.C. Martins-Costa, M.F. Ruiz-López, Chem. Phys., 332, 341-347 (2007)

[2] M.T.C. Martins-Costa, J.M. Anglada, J.S. Francisco and M.F. Ruiz-López, Angew. Chem. Int. Ed. 51, 5413–5417 (2012)

[3] M.T.C. Martins-Costa, J.M. Anglada, J.S. Francisco, and M.F. Ruiz-Lopez, J. Am. Chem. Soc. 134, 11821–11827 (2012).

[4] J.M. Anglada, M. Martins-Costa, M.F. Ruiz-López, and J.S. Francisco, Proc. Natl. Acad. Sci. USA 111, 11618–11623 (2014).

[5] M. T. C. Martins-Costa, F. F. García-Prieto and M. F. Ruiz-López, Org. Biomol. Chem., 13, 1673-1679 (2015).

Unraveling the energy ladder in cryptophyte light-harvesting proteins

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In photosynthesis, specialized light harvesting pigment-protein complexes (PPCs) are used to capture incident sunlight and funnel its energy to reaction centers. The PPCs of cryptophyte algae use eight tunable linear tetrapyrrole chromophores (bilins) covalently bound to the protein scaffold, which structure and disposition inside the protein have evolved to increase the spatial and spectral cross section for absorption of incident light, specially reduced in marine and freshwater environments. It is thus of interest to elucidate the principles that govern cryptophyte light harvesting, and in particular assess the role of coherent energy transfer effects recently observed.¹ The uncertainty regarding the precise exciton levels in these complexes, however, complicates the interpretation of spectroscopic data as well as precludes the possibility to understand the basis of the coherence effects observed in terms of structure.² In this contribution we present recent work aimed at unravelling the energy ladder on several cryptophyte PPCs by adopting a combined MD-QM/MMpol strategy³ as well as a three-layer QM/MMpol/ddCOSMO scheme⁴, both of which are able to consistently account for protein and solvent polarization in the calculation of site energies and electronic couplings, the key ingredients needed to predict the exciton states in a multichromophoric complex.

References

1. Harrop, S. J. *et al. Proc. Natl. Acad. Sci. U. S. A.* **111**, ES2666-75 (2014).
2. Curutchet, C. *et al. Chem. Rev.* (2016), in press.
3. Curutchet, C. *et al. J. Phys Chem. B* **117**, 4263-73 (2013). Caprasecca, S. *et al. J. Chem. Theory Comput.* **8**, 4462-4473 (2012); Caprasecca, S. *et al. J. Chem. Theory Comput.* **11**, 694-704 (2015).

Revisiting the ribose 2'-hydroxyl group orientation in RNA: insights from the Protein Data Bank and molecular simulations

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The RNA conformational realm is characterized by a great diversity in three dimensional structures critical to their function, including protein synthesis, RNA self-splicing and gene expression regulation, thus at the basis of the cell machinery production. A major determinant of RNA architecture is the formation of stabilizing stacking and backbone interactions that serves to bring strands together and stabilize adjacent local substructures. Besides base specific contacts, a major player in the stabilization of several tertiary interactions, i.e. tetra-loop receptors, kissing-loops or S-turns, is the ribose 2'-hydroxyl group. Being able to act both as donor and acceptor of a hydrogen bond and to contribute ~1-2 kcal/mol of interaction free energy within a tertiary interaction network,^{1,2} the 2'-hydroxyl moiety adds an extra layer of complexity to the interactions network, thus enhancing conformational diversity.

In the present work the focus is placed on the orientation of the 2'-hydroxyl group as observed from the structural sampling provided by the Protein Data Base and complemented with molecular and quantum mechanics simulations. Three main orientations are observed, in agreement with previous reports based on short molecular dynamics simulations,³ which are influenced by the sugar puckering, local hydrogen bond networks and the interaction with specific amino acids in protein-RNA complexes.

References

1. Abramovitz, D.L.; Pyle, A. M. *J. Mol. Biol.* 1997, 266, 493-506
2. Bevilacqua, P.C.; Turner, D.H. *Biochemistry* 1991, 30, 10632-10640
3. Auffinger, P. Westhof, J. *Mol. Biol.* 1997, 274, 54-63

Thermal energy storage in nanofluids: what can simulations teach us?

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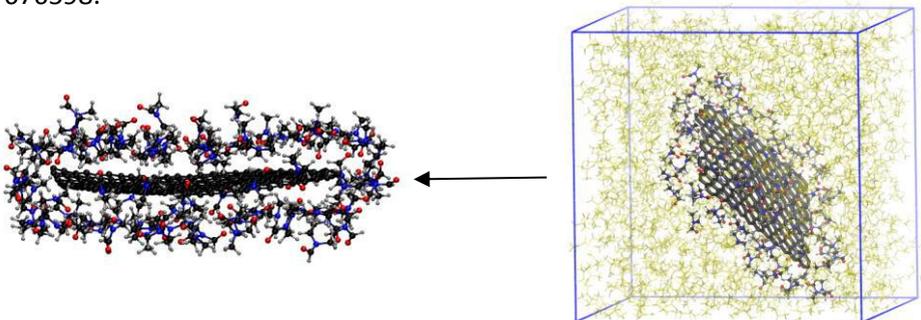
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Ionic Liquids are one of the preferred options used by the industry for the storage of thermal energy in solar energy plants. Improving their thermophysical properties is an important goal to achieve more efficient heat storage and transportation media. A promising approach for improving these properties is to introduce nanoparticles dispersed in the ionic liquid or the molten salt, the so-called nanofluids. However, how thermophysical properties such as the heat capacity, self-diffusion, or heat conductivity depend on the microstructure of the nanofluids is still rather unknown.

Molecular simulation, therefore, can play a major role in this research, as producing reliable experimental data for these systems is difficult and expensive. We have calculated by classical molecular dynamic simulations, thermal properties of disk-like graphene nanoflakes dispersed in dimethylformamide. In this talk, I will discuss how the heat capacity and the thermal conductivity depend on the shape, the size and the density of the dispersed carbon nanoflakes. With our classical model, we are able to shed light and gather basic understanding on the dependence of thermal transport properties on the nature of solute-solute and solute-solvent interaction.

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Modulating the Absorption Band Maximum in Fluorescent Proteins: A Molecular dynamics and QM/MM TD-DFT description.

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The development of FPs has set a milestone in modern bioimaging techniques, as they can be used as noninvasive labels for protein observation in living cells. There's an special interest in developing FPs which absorb in the living mammal transparency window (between ~600 nm and 1000 nm). Rationalizing how the absorption maximum can be affected is needed to do this. In this regard we have studied two cases, comparing 2 proteins for each one: Two GFP mutants for the first case, and two RFPs for the second one which presents an intense band at ~600nm. By means of the statistical treatment of extensive MD simulations and using QM/MM TD-DFT calculations, we have been able to reproduce the absorption spectra experimentally reported.^{2,3} Having characterized the excitation taking place, we could rationalize the reasons for the change in the band positions, being able to modulate it by placing charged residues in specific places near the chromophore.

References

- (1) R. Y. Tsien, *Annu Rev Biochem*, 1998, 67, 509-44.
- (2) P. Armengol, R. Gelabert, M. Moreno and José.M. Lluch, *Org. Biomol. Chem.*, 2014, 12, 9845-9852.
- (3) P. Armengol, R. Gelabert, M. Moreno and José.M. Lluch, *Pysh. Chem. Chem. Phys.* DOI:10.1039/C6CP01297C

Towards ab-initio Molecular Dynamics without Born-Oppenheimer Potential-Energy Surfaces

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The correlated motion of electrons and ions is a challenging problem yet one that is increasingly topical due to the advent of experimental techniques that allow to visualize the “molecular movie”. Theoretical methods rely on the Born-Huang expansion of the molecular wavefunction. Hence, the concepts of Born-Oppenheimer potential-energy surfaces (BOPEs) and nonadiabatic couplings (NAC) arise naturally, suggesting the picture of a nuclear wavepacket evolving on many static BOPEs. This approach is, however, very expensive due to the need of all BOPEs and NACs involved in the dynamics. We propose an alternative approach to molecular dynamics based on the use of conditional wavefunctions [1]. This approach allows for the use of trajectory-based techniques to circumvent the calculation of the BOPEs and NACs [2]. Further, we have proposed a universal mechanism for the explanation of quantum nonadiabatic effects [3]. Finally, the combination of this approach with the inherent scalability of other techniques such as TDDFT could lead to a breakthrough in the efficiency of ab-initio molecular dynamics methods.

References

[1] G. Albareda et al., Phys. Rev. Lett. 113, 083003 (2014).

[2] G. Albareda et al., J. Phys. Chem. Lett. 6, 1529 (2015).

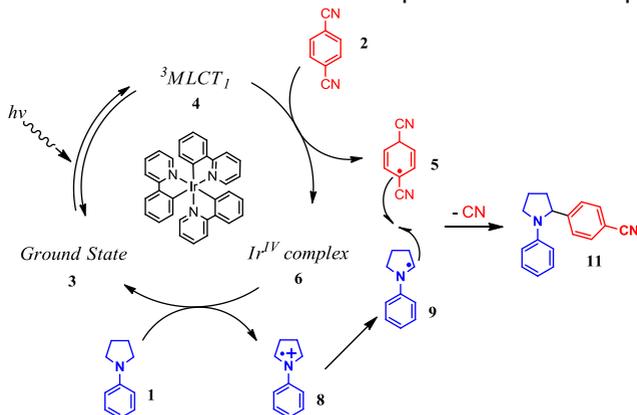
[3] G. Albareda et al., arXiv:1512.08531 (2015).

Reaction Mechanism and Kinetic Simulation for the photoinduced C-H Arylation of Amines: Role of the Counterion in the Rate of Photoredox Catalyzed Reactions

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The mechanism of the photocatalyzed C-H arylation of amines proposed by MacMillan *et al.*¹ has been studied at the DFT level of theory in combination with a microkinetic model. Calculations support the proposed mechanism consisting of two consecutive single electron transfers (SET) followed by radical-radical coupling. Kinetic simulations of the calculated steps accurately reproduce the experimental yields. The rate of the reaction was found to depend strongly on the competition between the first single electron transfer, and the different decay pathways that the excited photoredox catalyst can undergo. In addition, the counterion of the base was found to have an impact on the overall rate of the reaction when the substrate is a poor electron acceptor.



McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science* 2011, 334, 1114–1117.

