BOOK OF ABSTRACTS

EUCO-TCC 2017

11th European Conference on Theoretical and Computational Chemistry

BARCELONA
4-7 September

SOCIETAT CATALANA QVÍMICA
INSTITVT D'ESTVDIS CATALANS

EuCheMS
European Chemical Sciences

WELCOME

The local organizing committee of the Catalan Chemical Society (SCQ) cordially invites you, on behalf of the Division of Computational and Theoretical Chemistry (DCTC) of the European Association of Chemical and Molecular Sciences (EuCheMS), to participate at the 11th European Conference on Theoretical and Computational Chemistry, September 4 – September 7, 2017, in Barcelona.

The conference will reflect recent advances, developments and trends in the field and its impact on related molecular sciences and technology. EuCO-TCC 2017 will provide a unique information and communication platform and will cover a wide range of subjects related to computational chemistry, theoretical chemistry, material sciences, biology and drug design, and from fundamental academic research to industrial applications.

This invitation is addressed to scientists in academia, industry and in governmental institutions. You are all warmly welcomed to share your most recent findings and ideas and to continue the tradition of EuCO-CC conferences (Nancy 1994, Lisbon 1997, Budapest 2000, Assisi 2002, La Londe le Maures 2006, Tale 2006, Venetia 2008, Lund 2010, Sopron 2013, Fulda 2015).

Outstanding keynote speakers will outline recent trends in fields of interest. The scientific program will be completed by exhibitors presenting latest methods and applications in the field of computational chemistry.

On behalf the Local Organizing Committee

Carles Bo
11EuCO-TCC Chair

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Ramon Crehuet (CSIC)
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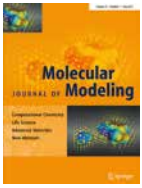


JOURNAL OF CHEMICAL INFORMATION AND MODELING

GENERAL INFORMATION

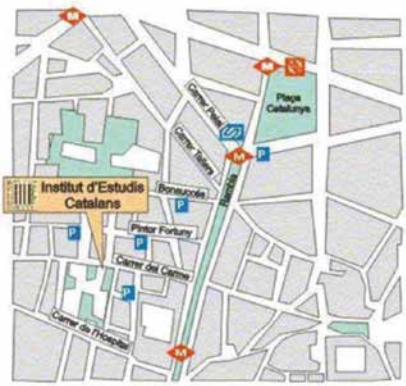
The **11the European Conference on Theoretical and Computational Chemistry (EUCO-TCC)** conference will be celebrated in Barcelona, 4-7th September 2017.

Venue

Institut d' Estudis Catalans
Carrer del Carme, 47; 08001 Barcelona

Institut d'Estudis Catalans (Institute for Catalan Studies, IEC), founded in 1907, is an academic institution whose main goals are high level scientific research and the promotion of knowledge. The Institut has affiliated societies which work in a wide variety of cultural, scientific and technological fields. One of the societies is the Catalan Chemistry Society.

The Casa de Convalescencia de Sant Pau (Saint Paul's Convalescent Home), the historical and current headquarters of the IEC, is a magnificent XVII century civic building built for the convalescence of the sick at the neighboring Hospital de la Santa Creu (Hospital of the Holy Cross) (1401-1926). In the XVII century both buildings were on the outskirts of Barcelona.



Registration and general information

The secretariat and registration desk will be located at the hall of the Institut d' Estudis Catalans.

Open every day during lectures' time.

Registration fees

Regular fees include access to conference sessions and exhibition area, link to book of abstracts, welcome reception, lunches, coffee breaks and conference dinner.

One day ticket

The One day ticket includes access to conference sessions and exhibition area, lunches and coffee breaks during the day, as well as a link to book of abstracts. For any accepted communication as first author, a regular fee is required.

Only one day ticket is permitted per attendee. If you wish to attend more than one day, then the Regular participant fee will be required.

Student fee

Student fee registration is only available for students that are not professional teachers or researchers. Regular participant fee is also required if they are the first author of any communication.

Accompanying person fee includes welcome reception, lunches and coffee/tea during session breaks, conference dinner.

All fees exclude accommodation, which needs to be booked separately.

Conference Dinner (September, 6th, 2017) included except in the One day ticket fees .

Liability:

ECRICE and the congress venue accept no liability for personal injuries sustained, loss or damage of property belonging to Conference participants, either or as a result of the Conference. Please check the validity of your own personal insurance before travelling.

CONFERENCE SECRETARIAT (Registration and abstracts collection)

PACIFIC WORLD
World Trade Center
Moll de Barcelona, s/n
North Building, 8th floor
08039 Barcelona, Spain
11euco-tcc@pacificworld.com

Conference Dinner

1881 per SAGARDI is a traditional Mediterranean restaurant set up around a large outdoor terrace boasting a unique and privileged view of the Barcelona skyline.

Located in upper levels of the Museum of History of Catalonia, a building that was built following the English style found in ports around the world, where history and culture bring together countries and people.

SAGARDI makes of this unique location a place of gastronomy, sensibility and emotions.

Wednesday, 6th September 2017
20:30 hrs

How to get there
1881 RESTAURANT
(at the top floor of MUSEU D'HISTÒRIA DE CATALUNYA) "Palau de Mar"
Address: Pl. Pau Vila, 3
Zone: Barceloneta
District: Ciutat Vella
Code: 08003
How to get: BUS D20, 64,59,45, 39 Metro L4 Barceloneta

Sunday, September 3, 2017	
18:00-21.00	Registration Welcome Cocktail

Monday, September 4, 2017	
08:00	Registration
08:45-09:00	Opening
09:00-09:40	K1- Thiel
09:40-10:00	O1- Andricioaei
10:00-10:20	O2- Cherkasov
10:20-10:40	O3- Young
10:40-10:50	RT1- Sárosi
10:50-11:00	RT2- Fianchini
11:00-11:30	Coffee Break
11:30-12:10	K2- Corral
12:10-12:30	O4- Evangelisti
12:30-12:50	O5- Handley
12:50-13:10	O6- Besora
13:10-14:30	Lunch
14:30-15:10	K3- Fernandes
15:10-15:30	O7- Vela
15:30-15:50	O8- Nilges
15:50-16:10	O9- Bandeira
16:10-16:20	RT3- Gierada
16:20-16:30	RT4- Solé-Daura
16:30-17:00	Coffee Break
17:00-18:30	Poster session 1

Tuesday, September 5, 2017	
09:00-09:40	K4- Mennucci
09:40-10:00	O10- Anglada
10:00-10:20	O11- Blonsk
10:20-10:30 10:30-10:40	RT5- Via RT6- Sansone
10:40-10:50	RT7- Dral
10:50-11:00	RT8- Álvarez Barcia
11:00-11:30	Coffee Break
11:30-12:10	K5- Maseras
12:10-12:30	O12- Hellström
12:30-12:50	O13- Hirst
12:50-13:10	O14- Filippov
13:10-14:30	Lunch
14:30-15:10	K6-Fonseca-Guerra
15:10-15:30	O15- Habershon
15:30-15:50	O16- Pielak
15:50-16:10	O17- Coe
16:10-16:20	RT9- Francese
16:20-16:30	RT10- Alonso
16:30-17:00	Coffee Break
17:00-18:30	Poster session 2
18:30	DCTC Meeting

Wednesday, September 6, 2017	
09:00-09:40	K7- Corminboeuf
09:40-10:00	O18- González-Lafont
10:00-10:20	O19- Salvador
10:20-10:40	O20-Fruchtl
10:40-10:50	RT11-González-Fabra
10:50-11:00	RT12- Fischer
11:00-11:30	Coffee Break
11:30-12:10	K8- Harvey
12:10-12:30	O21- Reguero
12:30-13:10	Special Session Local Companies Nonell / Barril
13:10-14:30	Lunch
14:30-14:50	O22- van Mourik
14:50-15:10	O23- Moreira
15:10-15:30	O24- Bhati
15:30-15:50	O25- Coletti
15:50-16:10	O26- Curpan
16:10-16:20	RT13- Golov
16:20-16:30	RT14- Zivanovic
16:30-17:00	Coffee Break
17:00-18:30	Poster session 3
20:30	Conference Dinner

Thursday, September 7, 2017	
09:00-09:40	K9- Paton
09:40-10:00	O27- Lombardi
10:00-10:20	O28-Yánez
10:20-10:40	O29-Tchougreeff
10:40-10:50	RT15- Vidal
10:50-11:00	RT14- Cebrián
11:00-11:30	Coffee Break
11:30-11:50	O30- Lüthi
11:50-12:10	O31- Alcamí
12:10-12:30	O32- Gelabert
12:30-13:30	EuCheMS Award K10- Roethlisberger Closing
13:30	Lunch

Sunday, September 3, 2017

Cloister (Ground floor)

19:00 – 21:00 Pre-Registration // Welcome Cocktail

Monday, September 4, 2017

08:00 REGISTRATION

08:45–09:00 **OPENING CEREMONY**:
11th European Conference on Theoretical and Computational Chemistry

Keynote lecture

09:00–09:40 KL1 Quantum Chemistry: Status and Perspectives
Walter Thiel, *Max-Planck-Institut für Kohlenforschung*, Mülheim, Germany

Oral Communications:

09:40 – 10:00 O01 Scaling Strategies for Enhanced Sampling of Kinetic Properties via Stochastic Path Integrals and Extrapolation
Ioan Andricioaei, *University of California, Irvine*, Irvine, USA

10:00 – 10:20 O02 Best Practices of Computer-Aided Drug Discovery (CADD): Lessons Learned from the Development of a Preclinical Candidate for Prostate Cancer with a New Mechanism of Action
Artem Cherkasov, *University of British Clumbia*, Vancouver, Canada

10:20 – 10:40 O03 An Investigation into the Mechanism of Transition Metal-Free Formation of 1,2,4-Triarylbenzene from α,γ-Diarylpropanones
Allan Young, *University of Strathclyde*, Glasgow, United Kingdom

Research Telegrams:

10:40 – 10:50 RT01 Molecular modeling of carborane-containing drug molecules
Menyhárt-Botond Sárosi, *Leipzig University*, Leipzig, Germany

10:50 – 11:00 RT02 Wittig olefination, an old reaction with new perspectives
Mauro Fianchini, *The Institute of Chemical Research of Catalonia (ICIQ)*, Tarragona, Spain

11:00 - 11:30 Coffee Break – Cloister (Ground floor)

Keynote lecture

11:30 – 12:10 KL2 Outwitting DNA's photostability: novel photosensitizers based on natural nucleobases thiosubstituted derivatives
Inés Corral, *Universidad Autónoma de Madrid*, Madrid, Spain

Oral Communications:

12:10 – 12:30	O04 Electron localization in a one-dimensional system Stefano Evangelisti, *Laboratoire de Chimie et Physique Quantiques, Université de Toulouse Paul Sabatier and CNRS*, Toulouse, France
12:30 – 12:50	O05 Novel Potentials for Methylammonium Lead Iodide and Related Hybrid Organic-Inorganic Halide Perovskites. Christopher Handley, *University of Sheffield*, Sheffield, England
12:50 - 13:10	O06 Free energy barriers are not always enough. A computational study on aromatic C-H bond functionalization Maria Besora, *Institut Català d'Investigació Química (ICIQ)*, Tarragona, Spain
13:10 – 14:30	Lunch – Cloister (Ground floor)

Keynote Lecture:

14:30 – 15:10	KL03 Advances and Pitfalls on the Study of Enzymatic Reaction Mechanisms using QM/MM Methods Pedro Alexandrino Fernandes, *Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto*, Porto, Portugal

Oral communications:

15:10 – 15:30	O07 Solvent-dependent Cooperativity in Spin Crossover Systems from First Principles Sergi Vela, *University of Strasbourg*, Strasbourg, France
15:30 – 15:50	O08 Inorganic SnIP-type double helix semiconductors – A DFT approach to new representatives Tom Nilges, *Technical University of Munich*, Garching b München, Germany
15:50 - 16:10	O09 Insights into polynuclear Gold(I) cyclisation catalysis of 1,6-enyne substrates Nuno Bandeira, *Faculdade de Ciências, Universidade de Lisboa,* Lisbon, Portugal

Research Telegrams:

16:10 – 16:20	RT3 Computational insights into reactivity of the phillips cro_x/sio_2 catalyst – role of amorphous silica model Maciej Gierada, *Cracow University of Technology*, Kraków, Poland
16:20 – 16:30	RT4 Molecular dynamics-based structure-activity relationships for the affinity of polyoxometalates towards proteins Albert Solé-Daura, *Universitat Rovira i Virgili*, Tarragona, Spain
16:30 – 17:00	Coffee Break – Cloister (Ground floor)
17:00 – 18:30	Poster Session 1

Tuesday, September 5, 2017

Keynote Lecture:

09:00 – 09:40 KL4 Modeling linear and nonlinear optical spectra of multichromophoric biosystems: a multiscale strategy
Benedetta Mennucci, *Department of Chemistry, University of Pisa*, Pisa, Italy

Oral communications:

09:40 – 10:00 O10 Oxidation of atmospheric trace gases by radicals. Proton coupled electron transfer versus hydrogen atom transfer reaction mechanisms
Josep M Anglada, *IQAC-CSIC,* Barcelona, Spain

10:00 – 10:20 O11 From substitution to sp3 functionalization - various avenues toward magnetic ordering in graphene
Piotr Blonski, Regional *Centre of Advanced Technologies and Materials, Palacky University Olomouc*, Olomouc, Czech Republic

Research Telegrams:

10:20 – 10:30 RT5 Splitting the coulomb hole into its dynamic and nondynamic parts
Mireia Via, *Donostia International Physics Center (DIPC) & Euskal Herriko Unibertsitatea (EHU)*, Donostia-San Sebastián, Spain

10:30 – 10:40 RT6 Toward an accurate estimate of the exfoliation energy of black phosphorus
Giuseppe Sansone, *Università degli Studi di Torino*, Torino, Italy

10:40 - 10:50 RT7 Towards next-generation semiempirical QM methods and reliable machine learning-based techniques
Pavlo Dral, *Max-Planck-Institut für Kohlenforschung*, Mülheim an der Ruhr, Germany

10:50 - 11:00 RT8 QM/MM study of atom tunneling in the hydroxylation process of taurine/ A-ketoglutarate dioxygenase (TauD)
Sonia Álvarez Barcia, *University of Stuttgart*, Stuttgart, Germany

11:00 - 11:30 Coffee Break – Cloister (Ground floor)

Keynote Lecture:

11:30 – 12:10 KL5 Microkinetic models can be an important complement to DFT calculations
Feliu Maseras, *Intitute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology*, Barcelona, Spain

Oral communications:

12:10 – 12:30	O12 Proton transfer mechanisms in basic solutions and at the oxide/water interface revealed by neural networks Matti Hellström, *Georg-August-Universität Göttingen*, Göttingen, Geramny
12:30 – 12:50	O13 Computing protein circular dichroism spectroscopy in the near-ultraviolet, Jonathan Hirst, *University of Nottingham*, Nottingham, England
12:50 – 13:10	O14 Proton and hydride transfer – two faces of dehydrocoupling via dihydrogen bonds Oleg Filippov, *A.N.Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences (INEOS RAS)*, Moscow, Rusia
13:10 – 14:30	Lunch – Cloister (Ground floor)

Keynote Lecture:

14:30 - 15:10	KL6 Explaining Chemistry with Repulsive Frontier Orbitals Célia Fonseca-Guerra, *Department of Theoretical Chemistry and Amsterdam Center for Multiscale Modeling VU University Amsterdam*, Amsterdam, The Netherlands

Oral communications:

15:10 – 15:30	O15 Automated reaction path sampling using random walks in chemical space Scott Habershon, *University of Warwick*, Coventry, England
15:30 – 15:50	O16 Second nonlinear optical responses of indolino-oxazolidine switches: a multiscale numerical investigation Kornelia Pielak, *University of Namur*, Namur, Bélgica
15:50 - 16:10	O17 Modelling molecules with challenging spin: a 'black-box' DMRG and MCCI approach Jeremy Coe, *Heriot-Watt University*, Edinburgh, England

Research Telegrams:

16:10 – 16:20	RT9 Magnetic Fingerprint of Dithiazolyl-based Molecule Magnets Tommaso Francese, University of Barcelona, Barcelona, Spain
16:20 - 16:30	RT10 Molecular dynamic simulations of oil-water wetting on mineral surfaces Gerard Alonso, *University of Barcelona*, Barcelona, Spain
16:30 – 17:00	Coffee Break – Cloister (Ground floor)
17:00 – 18:30	Poster Session 2
18:30	DCTC Meeting

Wednesday September 6, 2017

Keynote Lecture:

09:00 – 09:40 KL7 An Old Principle Applied to Homogeneous Catalysis
Clémence Corminboeuf, *Ecole polytechnique fédérale de Lausanne (EPFL)*, Lausanne, Switzerland

Oral communications:

09:40 – 10:00 O18 Is the ALA/GLY residue a regio- stereodeterminant in lipoxygenase catalysis? A theoretical study of coral 8*R*-lipoxygenase
Àngels González Lafont, *Universitat Autònoma de Barcelona*, Barcelona, Spain

10:00 – 10:20 O19 Can wavefuntion analysis support the (new) definition of oxidation state?
Pedro Salvador, *Universitat de Girona*, Girona, Spain

10:20 - 10:40 O20 Quinone based building blocks for molecular electronics
Herbert Fruchtl, *University of St Andrews*, St Andrews, England

Research Telegrams:

10:40 – 10:50 RT11 Selective Cyclic Carbonate Formation from CO_2 and Epoxy-Alcohols: Mechanistic Elucidation via DFT Analysis
Joan González Fabra, *Insitut Català d'Investigació Química (ICIQ)*, Tarragona, Spain

10:50 – 11:00 RT12 Carbon Dioxide Reduction on Sodium and Potassium Hydroxide activated Graphitic Carbon Nitride
Julia Melisande Fischer, *The University of Queensland*, Brisbane, Australia

11:00 – 11:30 Coffee Break – Cloister (Ground floor)

Keynote Lecture:

11:30 – 12:10 KL8 Accurate computational modelling of the kinetics of homogeneous catalysis: Progress and Challenges
Jeremy Harvey, *KU Leuven, Department of Chemistry*, Leuven, Belgium

Oral communications:

12:10 – 12:30 O21 The challege of elucidating photoreaction mechanisms: the cis-trans photoisomerization of azobenzene
Mar Reguero, *Rovira i Virgili University*, Tarragona, Spain

12:50 – 13:10 Special Session: Turning computational chemistry into a bussines opportunity: what does it take?
Alfons Nonell, *MindtheByte, Barcelona;* Xavier Barril, *ICREA & University of Barcelona*

13:10 – 14:30 Lunch – Cloister (Ground floor)

Oral communications:

14:30 – 14:50 O22 DNA with unnatural base pairs studied by density functional theory
Tanja van Mourik, *University of St Andrews*, St Andrews, England

14:50 - 15:10 O23 TI(IV)-ENOLATES can act as nucleophilic or birradical reagents: new reactivity induced by valence tautomerism
Ibério de P. R. Moreira, *Universitat de Barcelona*, Barcelona, Spain

15:10 - 15:30 O24 Rapid, accurate, precise and reliable relative free energy prediction using ensemble based thermodynamic integration
Agastya P. Bhati, *University College London*, London, England

15:30 - 15:50 O25 Long range potential effects on the reactive and inelastic scattering in $OH+H_2$ collisions: a quantum-classical study
Cecilia Coletti, *Università G. d'Annunzio Chieti-Pescara*, Chieti, Italy

15:50 - 16:10 O26 *IN-SILICO* modeling of promiscuous compounds in high-throughput screening
Ramona Curpan, *Institute of Chemistry Timisoara of the Romanian Academy*, Timisoara, Romania

Research Telegrams:

16:10 – 16:20 RT13 MOFs decomposition and the database of secondary building units
Andrey Golov, *Samara Center for Theoretical Materials Science (Samara University)*, Samara, Rusia

16:20 – 16:30 RT14 Multi-level strategy for analysis of bioactive drug conformations
Sanja Zivanovic, *IRB Barcelona*, Barcelona,Spain

16:30 – 17:00 Coffee Break – Cloister (Ground floor)

17:00 – 18:30 Poster Session 3

20:30 Conference Dinner

Thursday, September 7, 2017

Keynote Lecture:

09:00 – 09:40 KL9 Chiral ion-pairs: dissociation, dynamics and asymmetric catalysis
Robert S. Paton, *Chemistry Research Laboratory, University of Oxford,* Oxford, England

Oral communications:

09:40 –10:00 O27 Energy transfer in gaseous mixtures for atmospheric and astrochemical modelling
Andrea Lombardi, *Università di Perugia*, Perugia, Italia

10:00 – 10:20	O28 Beryllium Bonds Outstanding features: Spontaneous formation of radicals, design of anion sponges, and Be-Be one-electron bonds Manuel Yáñez,Universidad Autónoma de Madrid, Madrid, Spain
10:20 – 10:40	O29 Deductive Molecular Mechanics of Crystalline Water Polymorphs Andrei Tchougréeff, *Moscow Center for Continuous Mathematical Education, A.N. Frumkin Institute of Physical Chemistry and Electrochemistry of RAS, Institute of Inorganic Chemistry of RWTH - Aachen University* Aachen, Germany

Research Telegrams:

10:40 – 10:50	RT15 Potential energy landscape and spectroscopical characterization of aza-nanohoops: promising structures for gas capture Angel Vidal, Universidade de Vigo, Vigo, Spain
10:50 – 11:00	RT16 Undertanding the synthesis of Prostaglandin G2 from Arachidonic Acid catalyzed by Cyclooxygenase-2: A molecular dynamics/QM/MM approach Anna Cebrián, Universitat Autònoma de Barcelona, Barcelona, Spain
11:00 – 11:30	Coffee Break – Cloister (Ground floor)

Oral communications:

12:10 – 12:30	O30 Stability Prediction of Hypervalent Compounds Based on Data-Centric Modeling Hans Peter Lüthi, *ETH Zürich*, Zürich,Switzerland
12:10 - 12:30	O31 Key factors governing the relative stability of charged, endohedral and exohedral fullerenes Manuel Alcami, *Universidad Autónoma de Madrid*, Madrid, Spain
12:10 – 12:30	O32 Ultrafast Action Chemistry in Slow Motion: Atomistic Description of the Excitation and Fluorescence Processes in an Archetypal Fluorescent Protein Ricard Gelabert, *Universitat Autònoma de Barcelona*, Barcelona, Spain
12:50 –13:10	EuCheMS Award

Keynote Lecture:

12:50 – 13:10	KL10 When Computational Chemistry Meets Artificial Intelligence Ursula Röthlisberger, *Ecole polytechnique fédérale de Lausanne. Institut des sciences et ingénierie chimiques.* Lausanne (Switzerland)
13:10 – 14:30	Lunch – Cloister (Ground floor)

Keynote
Lectures

Quantum Chemistry: Status and Perspectives

Walter Thiel

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim, Germany

Theoretical calculations and computer simulations continue to gain importance in chemistry. Due to the synergy between improved computational methods and increasing hardware performance, the computations become ever more accurate and can be applied to ever more complex systems so that chemical problems can nowadays often be solved by the interplay of experiment and theory. [1-3]

The lecture will present an overview over these developments and address the current status and the perspectives of quantum chemistry. Current applications include highly accurate ab initio calculations on the spectroscopy of small molecules, density functional studies of transition metal catalyzed reactions, semiempirical excited-state dynamics simulations, and QM/MM modeling of enzymatic reactions. The lecture will cover selected such applications using examples from our own research [3-7] to illustrate the merits and limitations of the available methods.

References

(1) W. Thiel, *Angew. Chem. Int. Ed.* **50**, 9216-9217 (2011).
(2) H. M. Senn, W. Thiel, *Angew. Chem. Int. Ed.* **48**, 1198-1229 (2009).
(3) W. Thiel, *Angew. Chem. Int. Ed.* **53**, 8605-8613 (2014).
(4) S. Shaik, S. Cohen, Y. Wang, H. Chen, D. Kumar, W. Thiel, *Chem. Rev.* **110**, 949-1017 (2010).
(5) M. Leutzsch, L. M. Wolf, P. Gupta, W. Thiel, C. Farès, A. Fürstner, *Angew. Chem. Int. Ed.* **54**, 12431-12436 (2015).
(6) A. Owens, S. N. Yurchenko, W. Thiel, V. Spirko, *Phys. Rev. A* **93**, 052506 (2016).
(7) Y.-T. Wang, X.-Y. Liu, G. Cui, W.-H. Fang, W. Thiel, *Angew. Chem. Int. Ed.* **55**, 14009-14013 (2016).

Outwitting DNA's photostability: novel photosensitizers based on natural nucleobases thiosubstituted derivatives

Inés Corral

Departamento de Química. Módulo 13. Facultad de Ciencias. Universidad Autónoma de Madrid. Campus de Cantoblanco. 28049. Cantoblanco. Madrid. Spain. ines.corral@uam.es

Thionucleobases, or nucleobases where a single or several carbonyl groups have been substituted by thiocarbonyl groups, have a long tradition as photolabels in structural biology studies [(1)] and have been recently proposed as prototypes for chemotherapeutics [(2)] to be used in medicinal applications. The extraordinary photosensitizing properties of these sulfur-functionalized nucleobases leads to the generation of reactive oxygen species and/or photocrosslinking lesions, that would infringe structural and functional damage to the biomolecules of the cells where they are produced. In fact, their structural resemblance to canonical nucleobases facilitates their incorporation in small proportions into natural DNA. Also importantly, the red shifted absorption spectrum of these chromophores compared to natural nucleobases significantly increases the sensitivity of the DNA macromolecule to UVA light. [(3)]

The origin for these phototherapeutic properties relies on the dramatically different photophysics and photochemistry of these chromophores compared to canonical nucleobases. At contrast to natural nucleobases, where, for the spectroscopic state, a barrierless profile connects the Franck-Condon region with an internal conversion funnel with the ground state, the topology of the excited potential energy surfaces in thiobases is imprinted with one or several minima that would trap and eventually divert the population to other deactivation routes, preventing the ultrafast and efficient return of the excited molecules to the ground state.

In this contribution, we combine femtosecond transient absorption experiments with multiconfigurational ab initio calculations and singlet-triplet semiclassical molecular dynamics simulations [(4)(5)(6)(7)] to understand how does the sulfur-substitution pattern on the purine and pyrimidine rings direct the photophysics and photochemistry, and ultimately determine the prospective chemotherapeutic properties of these chromophores.

References:

(1) A. Favre, et al., *J. Photochem. Photobiol. B: Biol.* **42** (1998) 109-124.
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Advances and Pitfalls on the Study of Enzymatic Reaction Mechanisms using QM/MM Methods

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This talk will address our most recent works devoted to understand enzyme reaction mechanisms using QM/MM methods [1-3]. The talk will not focus on specific applications but instead in will give an overview of the fields we are working in, with selected examples to illustrate the concepts. We will focus on the choice of the QM region and on the consequences in might have to the predicted reaction mechanism; on the choice of the theoretical levels, in particular the density functionals, and the expectable accuracy they might bring [4]. The role of enzyme flexibility on catalytic rates will be discussed as well [5-6]. Overall, we pretend to highlight the most recent advances and pitfalls of the method and the way we intend to follow to move forward in this field.

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Modeling linear and nonlinear optical spectra of multichromophoric biosystems: a multiscale strategy

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In Nature, electronic interactions among different chromophoric units are used to tune the optical properties of supramolecular complexes and control the photo-induced processes at the basis of their biological function [(1)]. As a result, the linear and nonlinear optical spectra of each complex become a unique fingerprint, which, in principle, can be used to obtain detailed information about its structural and electronic nature. Unfortunately, such an analysis is extremely difficult due to the complex network of interactions between the electronic and nuclear degrees of freedom of all the chromophoric units as well as their coupling with a heterogeneous environment (the protein matrix, the membrane and the solvent). Here it will be shown that an "ab initio" strategy can be successfully used by integrating molecular dynamics with quantum chemical descriptions combined to polarizable classical models [(2)]. Examples of antenna complexes from different photosynthetic organisms will be presented and discussed.

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Microkinetic models can be an important complement to DFT calculations

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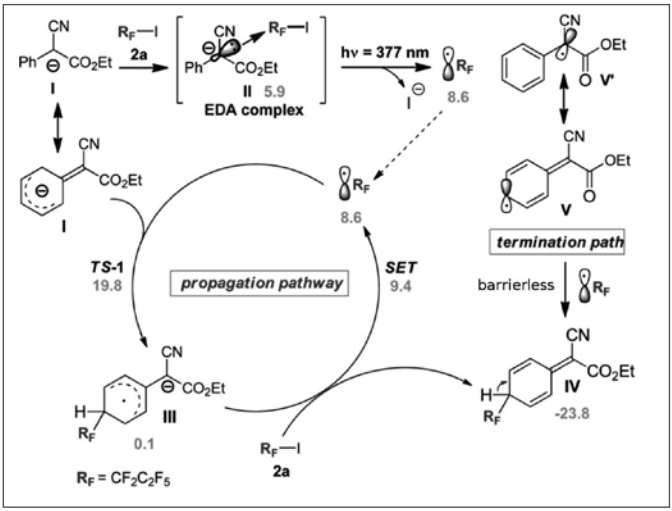
Calculations based on density functional theory (DFT) and density functional theory / molecular mechanics (DFT/MM) are a well-established approach in the treatment of a variety of problems in chemistry, and in particular those in homogeneous catalysis.[1] Calculations lead to a free energy profile, from where the feasibility of reactions can be ascertained, and the competition between different paths can be evaluated.



The information on rate constants in the free energy profile is sufficient to predict the reactivity of systems in most cases, but there are notable exceptions when very different concentrations or complicated reaction cycles are involved (see Figure). Microkinetic models provide in these cases a computationally affordable complement that improves substantially agreement with experiment. In this communication we will present selected examples from work in our group showing the importance of these corrections.[2] [3]

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Explaining Chemistry with repulsive Frontier Orbitals

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For the explanation of chemical phenomena, chemists quite often rely on old concepts as Lewis structures or on very rudimentary, and therefore often misleading, molecular orbital theory, which explains chemical bonds exclusively with stabilizing donor-acceptor and/or electron-pair bonding interactions between frontier orbitals. However, occupied frontier orbitals also contribute via a repulsive interaction, which is a manifestation of the Pauli exclusion principle. This quantum chemical phenomenon can overrule the attractive electrostatics and charge-transfer interactions and become decisive for the chemistry that we observe. In this presentation, quantum chemical investigations are presented with evidence for the importance of the Pauli repulsion in three different well-known chemical observations, namely: the direction of electrophilic aromatic substitution in benzene [(1)], the preference of guanine quadruplexes for potassium cations [(2)] and the hydrogen bonds between the mismatched DNA base pairs Guanine-Guanine and Cytosine-Cytosine [(3)].

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An Old Principle Applied to Homogeneous Catalysis

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In this talk, we will demonstrate the utility of volcano plots, which are common tools used by the heterogeneous/electrochemistry communities, into the realm of homogeneous catalysis. These plots pictorially represent Sabatier's principle, which states that the interaction between a substrate and a catalyst should be neither too weak nor too strong. [(1)] Despite their inherent ability to identify attractive catalysts and to facilitate understanding of the roles that metal and ligand choice have on cycle energetics, "molecular volcano" plots describing homogeneous catalytic processes have only recently been realized. [(2)] To meet the unique challenges of homogeneous catalysis, these plots must be further extended beyond the simple thermodynamic picture.[(3)] Most recently, we have sought to systematically gauge the impact of multiple factors (*e.g.*, a transmetallation partner, electrophile) that influence catalytic cycle energetics through the creation of three-dimensional volcano plots.[4] Using cross-coupling reactions as a prototypical model, these 3D plots allowed us to uncover a kind of "cross-coupling genome" that not only enhances fundamental understanding of this important class of chemical reactions, but also outlines strategies for developing new catalytic systems.

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Accurate computational modelling of the kinetics of homogeneous catalysis: Progress and Challenges

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In this talk, I will describe recent work from our group aimed at exploring the mechanisms of organic and organometallic reactions relevant for catalysis. As well as using standard computational methods to yield qualitative insight into the characteristics of individual elementary reaction steps, we have tried to use accurate ab initio methods combined with transition state theory to make predictions concerning the overall kinetic features of the reactions. This requires careful consideration not only of the electronic potential energy surface, for which modern local versions of coupled-cluster theory enable benchmark accuracy to be obtained, but also of solvation and of enthalpic and entropic thermal corrections. In my talk, I will give an overview of our progress and on remaining challenges, with a focus on the organocatalytic Baylis-Hillman reaction and on alkene hydroformylation by cobalt catalysts.

Although my talk will focus on recent unpublished results, the following papers provide some relevant background:

Homologation of Boronic Esters with Organolithium Compounds: A Computational Assessment of Mechanism
S. Essafi, S. Tomasi, V. K. Aggarwal and J. N. Harvey
J. Org. Chem., 2014, 79, 12148 – 12158.

Computational Kinetics of Cobalt-Catalyzed Alkene Hydroformylation
Laura E. Rush, P. G. Pringle and J. N. Harvey
Angew. Chem., Int. Ed., 2014, 53, 8672 – 8676 (and Angew. Chem., 2014, 126, 8816 – 8820).

Computed Ligand Effects on the Oxidative Addition of Phenyl Halides to Phosphine Supported Palladium(0) Catalysts
C. L. McMullin, N. Fey and J. N. Harvey
Dalton Trans., 2014, 43, 13545 – 13556.

Chiral ion-pairs: dissociation, dynamics and asymmetric catalysis

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Asymmetric catalysis through ion-pairing is used on a large-scale. But it is also challenging to compute: contact ion-pairs are bound through multiple non-covalent interactions and solvation effects influence structure and stability. We explore this phenomenon with quantum and classical methods to understand mechanism and selectivity in several transformations proceeding via ion-pairing. [2]

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When Computational Chemistry Meets Artificial Intelligence

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The combination of traditional computational chemistry approaches with techniques from artificial intelligence not only enables the unbiased analysis of high dimensional simulation data but also opens new possibility for efficient exploration of chemical and sequence space, an indispensable requisite for inverse design applications. In this talk, some illustrate examples of such combinations will be presented ranging from the application of genetic algorithms for the design of biomimetic systems to the use of machine learning algorithms for the analysis of spectral shifts and the development of machine learning models for force prediction in next generation ab initio based molecular dynamics.

Oral
Communications

Scaling Strategies for Enhanced Sampling of Kinetic Properties via Stochastic Path Integrals and Extrapolation

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Enhanced sampling techniques that reduce barriers of potential energy landscapes are useful strategies to increase the frequency of "rare events" during computer simulations of complex molecules. Although re-weighting methods exist that allow accurate thermodynamics to be recovered from enhanced simulations, recovering kinetics is more challenging. I shall present two approaches towards enhanced sampling of kinetics [(1)]: a trajectory reweighting method for Langevin dynamics based on the Wiener formalism of stochastic path integrals yielding general time-correlation functions and [(2)] an extrapolation approach that allows kinetics to be recovered from potential-scaled MD simulations based on Kramers' rate theory. The mean first passage time estimates obtained are in agreement with exact values on the unscaled potentials performed over times that are orders of magnitude longer. Both methods are tested to determine the kinetics of barrier crossing between two metastable states of model systems as well as complex biomolecules such as proteins and RNA. Applications are presented in the context of single-molecule manipulation techniques and, in the realm of fluctuation theorems, for the decomposition of entropy and enthalpy from non-equilibrium free energy calculations.

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Best Practices of Computer-Aided Drug Discovery (CADD): Lessons Learned from the Development of a Preclinical Candidate for Prostate Cancer with a New Mechanism of Action

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Small-molecule drug design is a complex and iterative decision-making process relying on pre-existing knowledge and driven by experimental data. Low molecular weight chemicals represent an attractive therapeutic option as they are readily accessible to organic synthesis and can easily be characterized. Their potency, as well as pharmacokinetic and pharmacodynamic properties can be systematically and rationally investigated, and ultimately optimized via expert science behind medicinal chemistry and methods of computer-aided drug design (CADD).

In recent years, significant advances in molecular modeling techniques afforded a variety of tools to effectively identify potential binding pockets on prospective targets, to map key interactions between ligands and their binding sites, to construct and assess energetics of the resulting complexes, to predict ADMET properties of candidate compounds, and to systematically analyze experimental and computational data to derive meaningful structure-activity relationships leading to the creation of a drug candidate. This perspective paper describes a real case of a drug discovery campaign accomplished in a relatively short time with limited resources.

The study integrated an arsenal of available molecular modeling techniques with an array of experimental tools to successfully develop a novel class of potent and selective androgen receptor inhibitors with a novel mode of action. This project exemplifies the importance of team science, integrative approach to drug discovery, and the use of best practices in CADD. We posit that lessons learned and best practices for executing an effective CADD project can be applied, with similar success, to many drug discover projects both in academia and industry.

An Investigation into the Mechanism of Transition Metal-Free Formation of 1,2,4-Triarylbenzene from α,γ-Diarylpropanones

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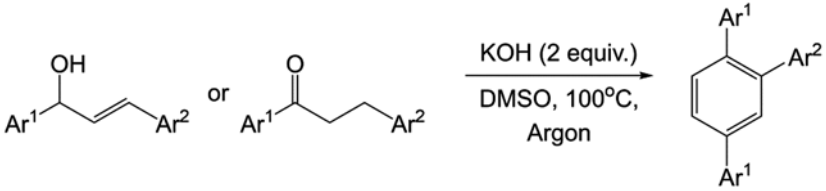
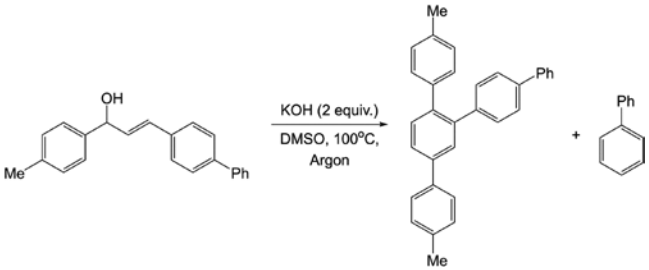
Keywords: DFT, DMSO, KOH, Transition Metal-Free, C-C Bond Cleavage

In 2016 Ghorai *et al* [1] reported the formation of homo- and hetero-1,2,4-triarylbenzenes from α,γ-diarylpropanones or α-aryl cinnamyl alcohols, under thermal conditions using potassium hydroxide and dimethylsulfoxide. Interestingly, formation of hetero-1,2,4-triarylbenzenes was shown to exhibit exclusive selectivity for retention of both α-aryl moieties of the starting α,γ-diarylpropanones, with loss of one γ-aryl moiety.



Ghorai *et al.* were able to isolate biphenyl from the reaction of 1-biphenyl-3-(4-methylphenyl)-prop-2-en-1-ol:



Here, we report the results of DFT investigations into the mechanism of the reaction reported by Ghorai ***et al.***, as well as our alternative mechanistic proposal. We also report experimental and computational evidence for the role of potassium hydroxide in dimethylsulfoxide in such reactions where C-C bond cleavage has been observed.

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Electron localization in a one-dimensional system

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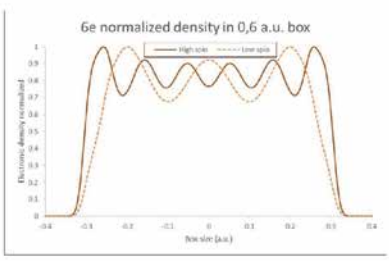
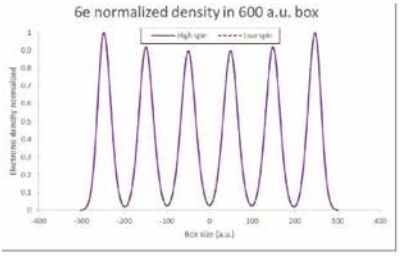
When electrons are confined to one dimension (1D), they exhibit a remarkable physics. Well-known examples are quantization of the conductance, fractional conductance, spin-charge separation, and many others. In particular, an enhanced localization of electrons at low densities is expected. When only few electrons are involved, these 1D systems are often referred to as Wigner atoms or molecules, because of the similarity with the low-density electron-crystallization phenomenon, theoretically predicted by Eugene Wigner long time ago [(1)]. Recently, a two-electron Wigner molecule has been observed experimentally. [(2)]

In this work, we make use of a Quantum-Chemistry approach to study the localization of a set of few electrons (2-8) confined in a 1D arrangement. In particular, we make use of Full Configuration Interaction (FCI) and CAS-SCF expansion of the wavefunction. The orbitals are chosen as equally spaced gaussian orbitals of *s* type having a single exponent, and whose centers are placed on the region of the *z* axis where the electrons are to be confined. Beside the one-electron density, two basic quantities are used to monitor the electron behavior: the Total-Position Spread (TPS) tensor, and the Total Electronic Entropy (TEE).

The wavefunction structure depends critically on the electron density, and hence the Wigner-Seitz radius r_s of the system. For small values of r_s we are in presence of a Fermi liquid, and the electrons are delocalized in space and well described by a single Slater determinant. Between r_s=0.5 and r_s=5.0 bohr, there is a complete revolution of the wavefunction structure: the electrons change to a state where they are localized in fixed space positions. This phenomenon is is reminiscent of a Wigner crystallization.





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Novel Potentials for Methylammonium Lead Iodide and Related Hybrid Organic-Inorganic Halide Perovskites

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Methylammonium Lead Iodide (MALI) is one of the most actively investigated materials for use in photovoltaic devices. MALI is a promising material as it displays critical properties, notably a band gap that makes it usable as a photoabsorber, and a significant light extinction coefficient that makes the material ideal for the fabrication of solid state thin film solar cells [(1) (2) (3)]. Futhermore, MALI is an excellent charge carrier, and so unlike most organic dyes used in photovoltaics, it does not require a mesoporous charge conducting substrate. While a great deal of computational effort has been directed at modelling the electronic structure of MALI [(4) (5) (6)], and determining how the band gap may be tuned to create an optimal photoabsorber [(7)], little effort has been directed towards understanding the mechanism of formation of MALI and the solid solution it forms with the related materials, formamidinium lead iodide, and caesium lead iodide.

We present the results of molecular dynamics simulations for MALI, FALI, and combinations of the two, demonstrating the formation of distinction domains within the materials.

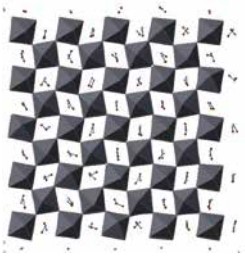

Figure 1. A slice through a snapshot of MALI simulation of a 5x5x5 supercell, at 50K. Methylammonium cations are represented as just C-N rods to better see the ordering that emerges on quenching the simulation from 400K.

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Free energy barriers are not always enough. A computational study on aromatic C-H bond functionalization

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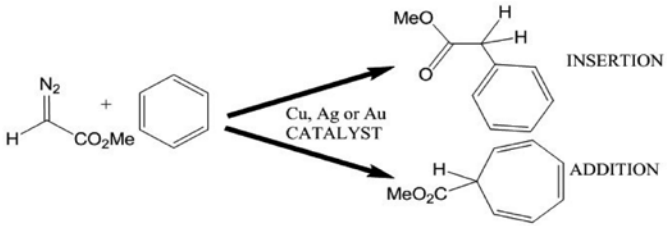
The transfer of carbene units from diazo compounds to different types of nucleophiles has been exploited to catalytically generate new value-added products [1]. The functionalization of aromatic C-H bonds by carbene transfer and catalyzed by coinage-metal complexes bearing an N-heterocyclic carbene based ligand can follow insertion into an aromatic C-H bond or addition to the aromatic ring. [2]



We have computationally investigated the reaction mechanisms for which these processes take place, providing information on the nature of the intermediates, the role of the catalyst as well as the other species present in the reaction media. The competition between addition and insertion has its origin in two low energy transition states close in energy with a common shallow intermediate. Direct application of Transition State Theory (TST) to these barriers cannot explain the experimental results. TST assumes redistribution of internal energy among the vibrational modes and internal rotations previous to any reaction step. We conducted Born–Oppenheimer molecular dynamics (BOMD) calculations that show that this is not the case and explain the experimental results.

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Solvent-dependent Cooperativity in Spin Crossover Systems from First Principles

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[(b)] *Institut für Physik, Universität zu Lübeck, Ratzeburger Allee 160, 23562 Lübeck, Germany*

Spin Crossover (SCO) compounds are molecular materials that can be stable in two electronic states with different magnetic response, and whose relative stability can be interconverted by the application of external stimuli such as light, heat or pressure, among others [(1)]. This quality makes them ideal candidates to be exploited in new electronic and spintronic devices, especially if the system features sufficient cooperativity to open an hysteresis loop, which creates a bistability region. [(2)]

We present the study of the compound $[Fe^{II}(2\text{-pic})_3]Cl_2$ [(3)], which features significantly different spin transitions depending on the lattice solvent molecules. The use of ethanol, leads to an abrupt two-step phase transition at 120 K, whereas the use of methanol solvate leads to a gradual transition at *ca.* 154 K, and the use of t-butanol leads to a blocking of the HS state. This intriguing behavior has been analyzed by means of periodic DFT calculations (GGA+*U*+*D2*), and discussed in terms of the Slichter-Drickammer and Ising models. We analyze how (i) the structural distortion of the SCO molecules in the presence of the different solvent molecules, and (ii) the intermolecular interactions, contribute to over-stabilize either the high- or the low-spin state of the material, and how these effects are related to the opening of an hysteresis loop.

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Inorganic SnIP-type double helix semiconductors – A DFT approach to new representatives

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Recently, the first inorganic, atomic-scale double helix compound SnIP was reported [(1)]. A $^{1}_{\infty}$[SnI^{+}] and a $^{1}_{\infty}$ [P^{-}] helix form a hexagonally rod packing of double helices being only weakly bonded via van der Waals interactions (see Figure 1). Chiral right and left-handed double helices are present forming an ideal racemic mixture of this material represents a 1.8 eV semiconductor with extraordinary mechanical properties and a strong tendency to be delaminated into nanometer fibers with large aspect ratios. DFT calculations, diffuse reflectance and photoluminescence has been applied to verify and measure the band gap of this compound. Bending tests of micrometer (diameter) needles showed that this material can be bent 180° without disintegration. DFT calculations including Grimme D2 corrections were used to determine the electronic structure of bulk material and nano fibers. We found only a weak modulation of the band gap upon delamination down to the single double helix.

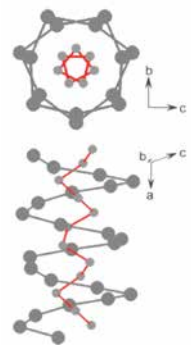

Fig. 1. Outer [SnI^{+}] (grey bonds and dots) and inner [P-] helices (red bonds) of a right handed double helix in SnIP. [(2)]

DFT was also used to predict new MXPn homologues with M = group 14, X = group 17 and Pn = group 15 elements [(2)]. In total 31 different SnIP-analogues structure models have been evaluated and more than 20 promising candidates with a SnIP structure type have been found, covering a band gap range of 1-2.5 eV. Additional properties like crystal structures, band structures, and vibrational spectra will be presented. Based on our results from quantum chemical calculations we will report on the latest efforts to prepare new double helix main group semiconductors.

These inorganic double helix materials represent a new substance class of one-dimensional semiconductors with a certain perspective in bulk and nano-particular form for energy conversion, water splitting and sensor applications. [(3)]

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Insights into polynuclear Gold(I) cyclisation catalysis of 1,6-enyne substrates

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The chemistry of Gold(I) complexes offers interesting catalytic routes to obtain pharmaceutically desired [(1)], cyclic organic molecules from 1,6-enynes [(2)]. In one recent example[(3)] a hexanuclear cluster of the type $[Au6L4]^{2+}$ ($L=PPh_2C_6H_4^-$) (**Figure 1**) was shown to cyclise the linear substrate $HC^{o}CCH_2C(COMe)_2CH_2CH=CMe_2$ into a five member ring. This dication is iso-electronic with the one previously characterised by Schmidbaur[(4)] $[C@(AuPPh_3)_6]^{2+}$ (**Figure 1.b**).

DFT analysis of this new $[Au_6L_4]^{2+}$ dication reveals a 3c-2e bond between the bridging phenyl groups and the gold centres which determine the structural deviation from pure octahedral symmetry. The mechanistic steps of the 1,6-enyne cyclisation are analogous to that known from the mono-nuclear triphenylphosphine-gold(I) [(5)], with the exception of some nuances. The initial substrate adduct is only very weakly bound to the $[Au_6L_4]^{2+}$ cluster and this interaction is akin to physisorption on metal surfaces. This is in contrast to the binding of triphenylphosphine-gold(I) with the substrate which is much stronger due to charge concentration in one single gold moiety.

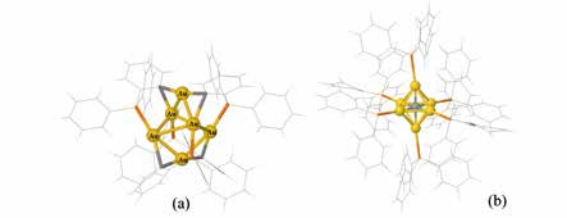

Figure 1. Optimised geometry of $[Au_6L_4]^{2+}$ (a) the isoelectronic Schmidbaur complex (b).

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Oxidation of atmospheric trace gases by radicals. Proton coupled electron transfer versus Hydrogen atom transfer reaction mechanisms

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Oxidation reactions are ubiquitous in the Earth's atmosphere. They are mainly driven by the OH and NO_3 radicals although other radicals can also play an important role. These radicals react, in great part, by abstracting one hydrogen atoms from organic species, and it is generally accepted that the hydrogen abstraction by the radical R proceeds through the concerted breaking and making of the covalent bond as it is indicated in equation 1.

$$X\text{-}H + R \rightarrow X + RH \qquad (1)$$

In this case, the radical R approaches the X-H bond with its unpaired electron and forms the H-R bond whereas the X-H bond is broken. This process is called hydrogen atom transfer (*hat*) and it is schematized in Figure 1a. It is known that the associated energy barrier is related to the bond dissociation energy of the X-H bond, which depends on the triplet repulsion energy for the X•/R• pair at the transition structure.[1] Depending on the nature of X (for instance, having a terminal atom Z with a lone pair of electrons) the radical R can approach in a different way the X-H reactant, undergoing a proton coupled electron transfer (*pcet*) process. This mechanism is schematized in Figure 1b, where an electron is transferred from the lone pair of the Z terminal atom to the radical R, and, simultaneously, the hydrogen atom bonded to X is transferred as a proton to the R moiety.[2,5]

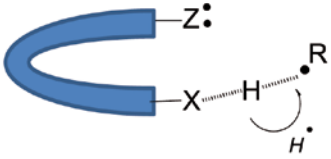

Fig. 1a). Hydrogen atom transfer.

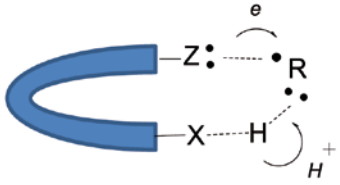

Fig. 1b). Proton copled electron transfer.

The relevance of the *hat versus* the *pcet* processes will be discussed by considering the oxidation of atmospheric trace gases by atmospheric radicals.

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From substitution to sp^3 functionalization - various avenues toward magnetic ordering in graphene

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Heteroatom doping of graphene by light elements opens a doorway to tailor electronic properties of graphene, and, hence, its physical properties, meeting thus the requirements of a given application. Recently, it has been proved [1] [2], that doping of graphene lattice with non-carbon atoms offers a promising approach for imprinting the magnetic ordering into graphene. Graphene doped with 4.2 at% of sulfur shows [1] ferromagnetic properties below ≈62 K with a saturation magnetization reaching ≈5.5 emu g−1, which is among the highest values reported so far for any graphene-based system. Electronic-structure calculations indicate that in a narrow concentration window (4-6 at%) magnetic interactions mediated by the π-electrons emerge between the substitution-generated paramagnetic centers resembling the gamma-thiothiapyrone motif leading to the ferromagnetic ordering. Ferromagnetic graphene can also be achieved by controlled doping with graphitic, pyridinic, and chemisorbed nitrogen [2]. The magnetic properties depend on both the nitrogen concentration and type of structural N-motifs in the host lattice. Graphene doped at 5.1 at. % of nitrogen exhibits transition to a ferromagnetic state at ≈69 K and displays a saturation magnetization reaching 1.09 emu/g. Calculations further proved the existence of exchange coupling among the paramagnetic centers mediated by the conduction electrons.

Finally, development of room temperature carbon magnets [3] prepared by a simple and controllable route based on the substitution of fluorine atoms in fluorographene with hydroxyl groups and containing exclusively *sp* orbitals will be discussed. Depending on the chemical composition (an F/OH ratio) and sp^3 coverage, these new graphene derivatives show room temperature antiferromagnetic ordering, which has never been observed for any *sp*-based materials. Such 2D magnets undergo a transition to a ferromagnetic state at low temperatures. The theoretical model addresses the origin of the room temperature magnetism in terms of sp^2-conjugated diradical motifs embedded in an sp^3 matrix and superexchange interactions via –OH functionalization.

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Proton transfer mechanisms in basic solutions and at the oxide/water interface revealed by neural networks

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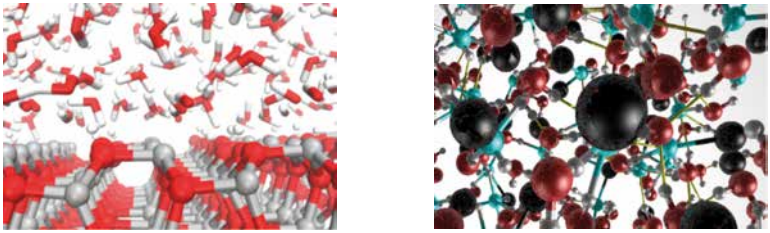
Proton transfer (PT) reactions play an important role in many fields of chemistry, for example during homogeneous and heterogeneous catalysis. Here, we develop high-dimensional neural network potentials [(1)] (NNPs) to elucidate the predominant PT mechanisms for water dissociation at the ZnO/liquid-water interface [(2)] and in NaOH(aq) solutions of different concentrations [(3)]. NNPs are computationally inexpensive and can accurately reproduce ab initio potential energy surfaces.

NNP-based molecular dynamics simulations reveal that PT reactions are coupled to fluctuations in the hydrogen-bonding environment around the proton donors and acceptors. We find that there is an unexpected similarity for the most predominant PT mechanisms at the ZnO/liquid-water interface and in NaOH(aq) solutions of high concentrations, which we explain by the influence that the cations (Zn2+ and Na+) have on the hydrogen-bonding environment around the dissociating water molecules.



Different systems but similar proton transfer mechanisms.
Left: The ZnO/liquid-water interface, and right: 15 mol/L NaOH(aq).

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Computing protein circular dichroism spectroscopy in the near-ultraviolet

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A fully quantitative theory of the relationship between protein conformation and optical spectroscopy would facilitate deeper insights into biophysical and simulation studies of protein dynamics and folding. Our web-server DichroCalc (http://comp.chem.nottingham.ac.uk/dichrocalc) allows one to compute from first principles the electronic circular dichroism spectrum of a (modelled or experimental) protein structure or ensemble of structures. The regular, repeating, chiral nature of secondary structure elements leads to intense bands in the far-ultraviolet. The near-UV bands are much weaker and have been challenging to compute theoretically. We report some advances in the accuracy of calculations in the near-UV, realised through the consideration of the vibrational structure of the electronic transitions of aromatic side chains and the influence of the electrostatic environment on the electronic excitation energies [1]. The improvements have been assessed over a set of diverse proteins, with just one example shown in Figure 1 below.

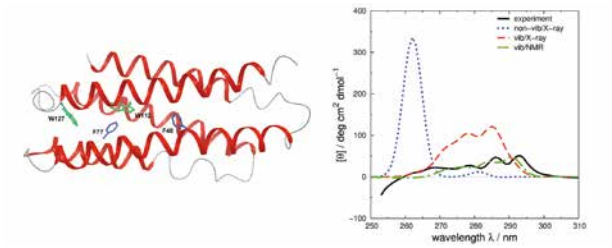

Figure 1. Structure and experimental (black solid line) and computed (blue dotted line: previous parameters; red dashed line: new parameters + X-ray structure; green line: new parameters + NMR structure) near-UV CD spectra of apolipophorin III.

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Proton and hydride transfer – two faces of dehydrocoupling via dihydrogen bonds

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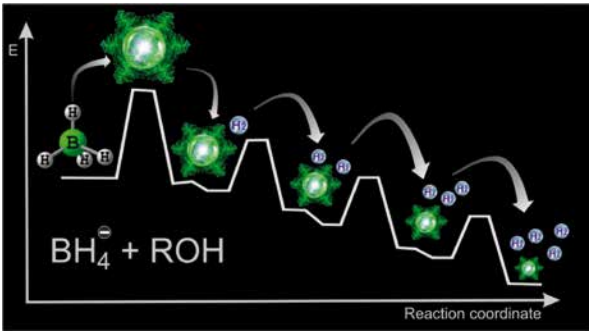
The reaction mechanism for the step-wise alcoholysis of anionic and neutral boron hydrides BH_4^-, $THF{\cdot}BH_3$, $Me_2NH{\cdot}BH_3$ and BH_3 was studied by DFT [1] [2]. The dihydrogen bonded complexes BH···HOR are the key intermediates of the cascade borohydride alcoholysis, which set the proper orientation of the reactants molecules and direct their further activation. The consecutive introduction of RO groups instead of hydride ligands in $[(RO)_nBH_{(4-n)}]-$ (n = 0–3) decreases the dihydrogen bond strength. Nevertheless, the B–H bond polarization and thermodynamic hydricity increase with the substitution, leading to the decrease of the reaction barrier. The H–H bond formation can be considered as a result of concerted proton and hydride transfer in the transition state.



The highest activation barrier was found for the first reaction step: $BH_4- + HOR \rightarrow H2 + [(RO)BH_3]-$, meaning the reaction is self-accelerating. Notably, for different hydrides (e.g. $THF{\cdot}BH_3$, $Me_2NH{\cdot}BH_3$) only the first proton/hydride transfer step is crucial because they can undergo subsequent ligand exchange switching to the kinetically more favorable $[(RO)BH_3]- + 3ROH \rightarrow [(RO)_4B]-$ process. The latter scheme is relevant for many processes, including amine boranes catalytic dehydrocoupling. [3]

ACKNOWLEGMENTS: This work was financially supported by the Russian Science Foundation (grant number 14-13-00801).

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Automated reaction path sampling using random walks in chemical space

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I will describe recent development of a methodology for automated ("black box") sampling of chemical reaction paths in complex systems [(1) (2)]. This method exploits the simple idea of using connectivity (or bonding) matrices to drive exploration of chemical space; the output of these simulations is a set of chemical reaction paths connecting different sets of reactants and products. These output reaction paths can subsequently be used to construct a kinetic model (*e.g.* based on rates calculated using transition state theory and standard quantum chemistry) describing the full chemical reactivity of the system; direct kinetic simulations then allow determination of mechanism and rate law. To demonstrate this approach, we consider direct computational determination of the rate law of cobalt-catalyzed ethane hydroformylation; recent results investigating carbon nanotube growth on iron nanoparticles will also be highlighted.

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Second nonlinear optical responses of indolino-oxazolidine switches: a multiscale numerical investigation

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The elaboration of molecular switches that undergo large contrast of second-order nonlinear optical (NLO) properties [at the molecular level, of the first hyperpolarizability (β)] is attracting considerable interest because of their potential applications in molecular-scale memory devices with multiple storage and nondestructive capacity. In this talk, we will illustrate the role of numerical simulations to provide a fundamental understanding of these NLO effects and to design new compounds with improved properties. In particular, we study an indolino-oxazolidine derivative, that switches between a non-conjugated closed form and a π-conjugated open form (Figure 1). The reaction is triggered by a decrease of pH (addition of trifluoroacetic acid), leading to the formation of a cation that interacts with its counterion (trifluoroacetate). [(1)]

To do this, we adopt a multiscale approach, which consists of i) molecular dynamics (MD) simulations of the indolinooxazolidine, in presence of solvent molecules (including the counterion when the chromophore is protonated) and ii), for a selection of snapshots, of the calculation of the first hyperpolarizability using quantum chemical calculations (DFT in this case). The results provide information on various factors governing the efficiency of the switches that are not directly accessible experimentally, including donor/acceptor contributions, photo-induced charge transfers, frequency dispersion, and solvent effects. Then, the results are compared with experimental data obtained using the electric field induced second harmonic generation and Hyper-Rayleigh scattering techniques.

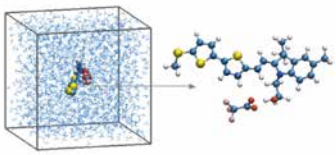

Figure 1. Snapshot from the molecular dynamics simulations.

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Modelling molecules with challenging spin: a 'black-box' DMRG and MCCI approach

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Molecules with multiple low-lying spin states can represent a serious challenge for methods in quantum chemistry. Open-shell methods bring the possibility of spin contamination, and these molecules often incorporate transition metals which can present the added difficulty of strong multireference character.

Multireference methods are becoming increasingly important. However they often require serious choices when setting up a calculation. Monte Carlo configuration interaction (MCCI) [(1)] seeks to stochastically build up a sufficiently accurate wavefunction where the calculation is controlled by the cut-off for removal of configurations. The density matrix renormalization group (DMRG) for quantum chemistry [(2)] maps the problem to one-dimensional system and builds up the Hamiltonian using states predicted from blocks of this system.

We first consider the spin gap in CH and employ a genetic algorithm for orbital ordering in DMRG. This system is used to benchmark appropriate accuracy levels in the two methods.

These approaches are then applied in a more 'black-box' manner to systems and basis sets beyond exact calculation. We look at high-spin states of the iron dimer and then transition metal carbonyls. Generally, we demonstrate agreement in the ordering of states between MCCI and DMRG, and also with RCCSD for the metal carbonyls. A contemporary multireference indicator [(3)] is used to assess the difficulty of these problems and contrasted with a coupled cluster diagnostic.

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Is the ala/gly residue a regio- stereodeterminant in lipoxygenase catalysis? A theoretical study of coral 8*R*-lipoxygenase

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Lypoxygenases (LOXs) are a family of enzymes that catalyze the highly specific hidroperoxidation of polyunsaturated fatty acids, like arachidonic acid. Different stereo- or/and regioisomer hydroperoxidation products lead later to different metabolites that exert opposite physiological effects in the animal body and play a central role in inflammatory processes. The Gly-Ala switch of a single residue is crucial for the stereo- and regiocontrol in many lipoxygenases. Herein, we have combined molecular dynamics simulations with quantum mechanics/molecular mechanics calculations to study the hydrogen abstraction step and the molecular oxygen addition step of the hydroperoxydation reaction of arachidonic acid catalyzed by both wild-type Coral 8*R*-LOX and its Gly427Ala mutant. We have obtained a detailed molecular understanding of this Ala-*versus*-Gly concept. After abstraction of pro-*R* H_{10} the oxygen addition occurs following a channel in the active site cavity that leads to C_8 of arachidonic acid (with an *R* stereochemistry) rather than to C_{12}, whose oxygen approach is hindered by Leu385. In the mutant, Ala427 pushes Leu385, blocks the region over C_8, and opens a new oxygen access channel now directed to C_{12}, where molecular oxygen is added with an *S* stereochemistry. Thus, the specificity turns out to be dramatically inverted. Since Leu385 is highly conserved among many lipoxygenase isoforms, this mechanism can be general, and we propose that the presence of such type of bulky and hydrophobic residues can be key in controlling the extreme regio- and stereospecificity of lipoxygenases and, as a consequence, their physiological effects.

Can wavefuntion analysis support the (new) definition of oxidation state?

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Oxidation state (OS) is a concept of utmost relevance in Chemistry that has been lacking a proper, clear cut definition. IUPAC's Gold Book still discusses a set of "agreed upon" rules, but no definition (it does provide one for oxidation number, restricted to compounds with central atoms). Consequently, considerable debate can be found in the literature discussing over inconsistencies and alternative OS assignation in non-trivial bonding situations.

Quite recently, Karen lead a IUPAC's Report [(1)] on the revision of the OS concept, providing a new generic definition, namely "*The OS of a bonded atom equals its charge after ionic approximation*", as well as algorithms for OS assignation and a vast number of illustrative examples, ranging from simple organic molecules to complex molecules and solids. Despite OS is intrinsically related to the distribution of electrons around atom, the report tiptoes around the role of quantum-chemical calculations for OS assignation, essentially pointing out that the partial atomic charges cannot be put into correspondence with the OS. The wavefunction of the system, however, should contain this type of information; one just needs to devise *proper* schemes to retrieve it.

Almost at the same time as Karen's work, we had introduced [(2)] a new and general scheme to derive OS from wavefunction analysis (more precisely from the first-order density matrix), the so-called effective oxidation state (EOS) analysis. It is formally applicable to any molecular system (i.e. not restricted to transition metal atoms) and for any level of theory. Thus far, EOS analysis has been successfully applied to a considerable number of systems, with quite consistent results. [(3)]

Here we present a systematic analysis of the molecular examples described in (or related with) Karen's report (more than 80 systems) using the EOS approach [(4)]. Remarkably, the results of the quantum mechanical approach can be reconciled with the improved OS definition in most cases, even though the EOS analysis considers explicitly neither bonds nor Lewis structures. Moreover, no special provisions are needed when the practical application of Karen's algorithms comes with exceptions or leads to ambiguities (e.g. when the more electronegative atom is bonded as a Lewis acid, or when the molecule cannot be described by a single Lewis structure).

Discrepancies occur and are expected in those cases where the individual bond polarization, tuned by the chemical environment, does not match with the tabulated pairwise atomic electronegativities. Karen's algorithms introduce exceptions to the rule in some specific cases, but the EOS approach does not require any external input, and therefore does not foresee whether or not an exception is to be applied. Also, the rule [...] *bonds between two atoms of the same element are divided equally* cannot always be recovered from first principles, unless the involved atoms are symmetry-equivalent. In general, when multiple homonuclear bonds occur in a system, the assignation of OS is less intrinsically reliable with the present algorithm of the EOS analysis.

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Quinone based building blocks for molecular electronics

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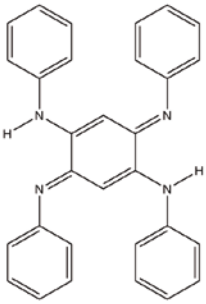

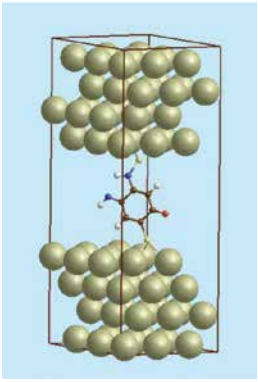

It has been shown that azophenine (1,4-diamino - 3,6 - diimino - 1,4 - cyclo - hexadiene) adsorbed on a Cu-(110) surface displays controlled switching behavior between tautomeric conformations when exposed to a current through an STM tip. Thus it could be used as a molecule-sized memory element.

The prerequisites of such behavior are:

– Two states of similar energy, separated by a not too high barrier.

– Different electronic behavior, such as conductivity, between the two states.

If such behavior could be reproduced away from the surface, similar molecules, based on a quinone-like core, could be used as switches or transistors for molecular electronics.

We will present initial results for tautomerisation barrier and electron transport properties of candidate molecules between electrodes to assess their suitability as components in more complex molecular electronic networks.

Keywords

Surface Science, Molecular Electronics.

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The challege of elucidating photoreaction mechanisms: the cis-trans photoisomerization of azobenzene

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The theoretical determination of the mechanisms of chemical reactions is not an easy task, but the difficulty increases enormously when the reactions are photochemical. The methodology used to develop this kind of studies must be able to describe photophysical and photochemical phenomena, account properly for very different structures, scan large areas of the potential energy surfaces, deal with ground and excited states of different nature at the same level of accuracy, be able to describe interactions between states, and be fast when dynamics studies want to be developed. These studies become, in fact, a serious challenge for computational methods.

In this contribution we present an example of such an application of computational chemistry: the study of the mechanism of a well-known and long-studied photochemical reaction, that continue being a subject of debate, the photoisomerization of azobenzene.

Azobenzene is an organic compound that has a singular behaviour due to the possibility of switching between *cis* and *trans* isomers using particular irradiation wavelengths. Experimental observations suggests that two different isomerization mechanisms operate on excitation to S_1 (n-π^*) or S_2 (π-π^*) excited states, but the reaction mechanisms are still a subject of hot debate.

The study presented here revisits the mechanism of photoisomerization of azobenzene on its S_1 (n-π^*) and S_2 (π-π^*) excited states from the computational point of view. We have determined the topology of the potential energy surfaces (PES) of these low-energy states by means of an ab initio methodology that includes dynamic electron correlation. Specifically, we have used the CASSCF/CASPT2 (Complete Active Space Self Consistent Field/CAS second-order multiconfigurational perturbation) combined methodology.

We have also performed a study of the dynamics of this photoisomerization reaction that confirms the mechanistic hypothesis suggested by the stationary study.

DNA with unnatural base pairs studied by density functional theory

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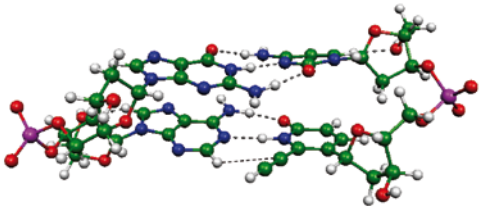
DNA is one of life's most important molecules, as it carries all genetic information. DNA uses a four-letter alphabet to encode genetic instructions: A (adenine), T (thymine), G (guanine) and C (cytosine). T selectively pairs with A and C with G, ***via*** specific hydrogen bonds. Specific pairing is essential for the correct transmission of the genetic information. Over the last few decades, nucleotide analogues have been used to increase the DNA alphabet, forming unnatural base pairs. This increases the genetic information that can be encoded by DNA. We have been studying several DNA structures containing unnatural base pairs with density functional theory methods:

- DNA containing 6-ethynylpyridone, E (replacing thymine in a thymine-adenine base pair). The incorporation of E into a DNA duplex leads to DNA duplexes that are more stable than the corresponding T:A-containing duplexes [(1)]. Our calculations suggest that the observed increased stability of E:A-containing duplexes is due to the combined effects of stronger base pairing and enhanced stacking of the E:A base pair. [(2)]
- DNA containing a hydrophobic base pair (5SICS-NaM), which forms no hydrogen bonds [(3)]. So unlike in normal DNA, the base pair is only stabilised by stacking interactions, and not by hydrogen-bonding interactions between the two bases.
- A DNA-like duplex of pyrene and anthraquinone pseudo base pairs [(4)]. The pyrene/anthraquinone duplex does not contain (deoxy) ribose and there are no hydrogen bonds between the pyrene and anthraquinone "bases" but, instead, the pairing is stabilised by donor-acceptor interactions.

These artificial base pairs can all be incorporated into functioning DNA. It is therefore of interest to investigate how they affect the stability and structure of DNA duplexes.



Duplex dinucleotide containing a C-G and E-A base pair.

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TI(IV)-enolates can act as nucleophilic or birradical reagents: new reactivity induced by valence tautomerism

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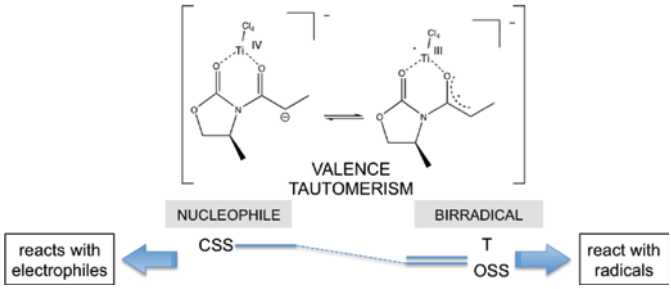
Quantum chemical calculations have unveiled the unexpected biradical character of Ti(IV) enolates from *N*-acyl oxazolidinones and thiazolidinethiones. The appropriate description of the electronic structure of the Ti(IV) enolates derived from these compounds includes a *valence tautomery* equilibrium that involves a closed shell (CSS) and two open shell (OSS and T) configurations. As the energy gap between the closed and the open shell configurations is small, subtle changes to the Ti–O distance in oxazolidinones (or Ti-S bond in thiazolidinethiones) makes the OSS configuration the more stable with a thermally accessible triplet state T. These open shell configurations are formally Ti(III) enolates and reveal the biradical character of these intermediates [(1)] in line with previous studies on similar Ti(IV) enolates [(2) (3)]. The biradical character has been observed in EPR studies and has been established as the source of radical-like reactivity, which is complementary to the most common nucleophilic profile [(4)]. The mechanism of the aminoxylation reaction of Ti(IV) enolates from oxazolidinones with TEMPO has been satisfactorily explained on radical grounds and the resulting model accounts for the regio- as well as the diastereoselectivity of such a transformation, strongly supporting the calculations. The present results establish a new paradigm of the structure and reactivity of enolates of Ti(IV) and, potentially, of other metals.



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Rapid, accurate, precise and reliable relative free energy prediction using ensemble based thermodynamic integration

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The accurate prediction of the binding affinities of ligands to proteins is a major goal in drug discovery and personalised medicine. The use of *in silico* methods to predict binding affinities has been largely confined to academic research until recently, primarily due to the lack of their reproducibility, as well as lack of accuracy and time to solution. In the last few years, an ensemble based molecular dynamics approach, called ESMACS, has been proposed that provides a route to reliable predictions of free energies meeting the requirements of speed, accuracy, precision and reliability [(1-3)]. Here, we describe our approach to thermodynamic integration, known as TIES, which substantially improves the speed, accuracy, precision and reliability of calculated relative binding free energies [(4)]. We report the performance of TIES when applied to a diverse set of protein targets and ligands. The results are in very good agreement with experimental data (90% of the predictions agree to within 1 kcal/mol) while the method is reproducible by construction. Statistical uncertainties of the order of 0.5 kcal/mol or less are achieved. Work is ongoing to extend the application of TIES to calculate the relative binding affinites of protein mutations (TIES_PM). This methodology, which is being pursued in the CompBioMed Centre of Excellence (http://www.compbiomed.eu/), has the potential to positively impact the drug design process in the pharmaceutical domain as well as in personalised medicine, with concomitant major industrial and societal impact. TIES is an automated workflow that can be completely run in 8 hours or less, depending on the architecture and hardware available. To exhibit this feature as well as the excellent scalability of TIES, in an unprecedented study we harnessed the combined power of Phases 1 and 2 of PRACE's Tier-0 SuperMUC at the Leibniz Rechnzentrum in Garching, resulting in accurate relative binding affinity predictions of more than 50 biomolecular systems [(5)] at a sustained performance in excess of 1 petasflop throughout.

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Long range potential effects on the reactive and inelastic scattering in OH+H_2 collisions: a quantum-classical study

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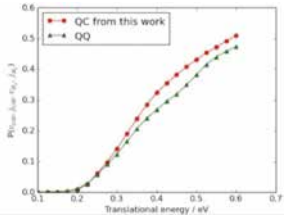
We carried out a study of OH + H_2 scattering using a quantum-classical (QC) method, to obviate the heavy computational demand associated with full quantum calculations, treating vibrations according to quantum mechanics and both translations and rotations classically [(1)]. Furthermore, the largely decoupled nature of the classical mechanics component of the QC code and the compactness of the quantum one make the code highly distributable, so that a high speed gain was achieved through parallelization.

The good agreement between the state specific quantum-classical reactive probabilities and the corresponding quantum ones prompted the extension of the study to state to state probabilities for non reactive vibrational energy exchange. [(2)]



The study showed that H_2 reactive dynamics depends on the vibrational excitation, whereas the non reactive one is mainly vibrationally adiabatic. On the other hand, OH reactive dynamics is much less affected by its vibrational excitation.

Preliminary calculations on internal energy redistribution processes upon non reactive collisions showed that the QC code can be efficiently used to investigate quantum effects in inelastic scattering. However, in order to get reliable results in this respect, the potential energy surface has to take into account long range effects, which are essential to accurately evaluate the exchange of vibrational quanta.

To this end, the potential energy surface [(3)] first employed in the study was modified by adding a long range tail, formulated according to an improved Lennard-Jones model [(4)], and its effect on reaction probabilities and rate constants as well as on vibrational energy exchange probabilities and rate constants has been evaluated and will be discussed.

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In-silico modeling of promiscuous compounds in high-throughput screening

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In high capacity biological testing or high-throughput screening (HTS) large libraries of small-molecules are evaluated in short time stages against one and/or multiple targets to discover new bioactive structures. A major challenge in HTS campaigns is to analyze the outcomes and clearly separate true active compounds from those interfering with the assay format or technique, i.e., false actives or false-positives [(1)]. This phenomenon is mediated via non-specific mechanisms, e.g., the compounds tested in HTS can chemically react with the target, interfere with the assay detection signal (fluorescent compounds or luciferase inhibitors), or form colloidal aggregates. [(2)]

Our latest efforts regard the development of new computational methods to clear chemical libraries from promiscuous compounds and enhance the quality of HTS outcomes. Using the largest open-access repository of HTS data, PubChem Bioassay [(3)] [(4)], we defined datasets of frequent hitters. These were used to build and validate predictors for highly biologically reactive compounds, fluorescent compounds, luciferase inhibitors and functional aggregators, using state-of-the-art modelling algorithms. These models can assist decision-making in HTS and accelerate chemical developments.

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Energy transfer in gaseous mixtures for atmospheric and astrochemical modelling

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The development of realistic kinetic models of gaseous systems is a fundamental issue in the study of Earth and planetary atmospheres, plasma chemistry, gas flows and astrochemistry. Particularly, the adoption of a state-to-state level of detail in the description of the molecular energy transfer [(1) (2)], a desirable and necessary improvement, requires much insight into the dynamics of the inelastic collisions and the prompt availability of state-specific energy transfer probabilities and rate coefficients. Approximated theories of the energy transfer, such as the Schwartz-Slawsky-Herzfeld one, currently used to obtain rate coefficients on wide temperature ranges, are not really state-specific and have limited validity. Therefore probabilities and cross sections have to be calculated directly by simulation of the dynamics of the molecular collisions. The reliability of the simulations is conditional to the availability of accurate descriptions of the intermolecular interactions occurring between pairs of the molecular species present in the gas mixture. Here, we present examples of calculation of rate coefficients of energy transfer in mixtures containing CO_2 and N_2 [(3-6)] obtained applying a semiempirical approach to the interaction modelling, based on (i) a physically meaningful partition of the contribution to the interaction, (ii) the use of data from molecular beam experiments and (iii) ab initio calculations. An extension of such an approach can be also applied to the modelling dynamics and kinetics of gas-surface systems, also required in astrochemical modelling.

Acknowledgments

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Beryllium Bonds Outstanding features: Spontaneous formation of radicals, design of anion sponges, and Be-Be one-electron bonds.

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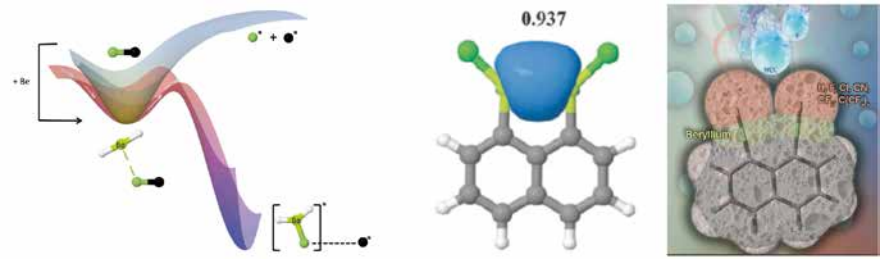
Beryllium bonds are a new type of non-covalent interactions described for the first time some years ago [(1)], in which BeXY molecules, behaving as Lewis acids, interact with conventional Lewis bases, leading to highly stabilized complexes, in which the electron densities of both interacting moieties are significantly distorted. In this communication we will show, through the use of high-level ab initio and density functional calculations, that these electron density redistributions lead to the exergonic and spontaneous formation of radicals through the homolytic bond fission of Y–R (Y=F, OH, NH_2; R=CH_3, NH_2, OH, F, SiH3, PH2, SH, Cl, NO) molecules upon association with BeX_2 (X=H and Cl) derivatives. [(2)]

We have also showed that even though the Be–Be bond is extremely weak in Be_2 dimers, the electron attachment to 1,8-diBeX-naphthalene derivatives leads to rather strong Be–Be one-electron sigma bonds, reflected in a dramatic shortening of the Be–Be distance with respect to the corresponding neutral molecule [(3)]. A similar effect is behind the behavior of 1,8-diBeXnaphthalene (X=H, F, Cl, CN, CF3, C(CF_3)$_3$) derivatives as *anion sponges* [(4)] (see Figure 1c) very much as 1,8-bis(dimethylamino) naphthalene derivatives behave as proton sponges.



(a) (b) (c)

Figure 1. (a) Potential energy curves associated to the exergonic formation of radicals from BeH_2FR complexes. (b) one-electron localized MO and its population for 1,8-diBeCl-naphthalene radical anion. (c) 1,8-diBeX-naphthalene derivatives acting as anion sponges.

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Deductive Molecular Mechanics of Crystalline Water Polymorphs

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We apply previously developed *Deductive Molecular Mechanics* [(1)] based on (i) representing the molecular electronic structure through antisymmetrized products of the group functions of the observable parts of the molecule - generalized chromophores, and (ii) determining the form and orientation of the hybrid orbitals spanning the carrier subspaces for these chromophores from the minimum condition for the total energy. This approach have been implemented by us in the SLG method [(2)], which allowed us to reduce the dependence of the computational costs on the molecule size down to O(N). The suggested combination of the assumptions yields not only numerical efficiency, but also permits to prove statements (theorems) concerning electronic structure either general or related to concrete molecules. Very recently we have proven the nonexistence of the "banana" bonds in the C_2 molecule and formulated the conditions when this particle can exist as an aggregate of either two divalent or two tetravalent carbon atoms [(3)]. In the present work we apply a similar approach to studying the origin of the phase diagram of ices. We start from establishing the energy expression for highly symmetric form of non-molecular ice (ice X) as for a system of oxygen atoms connected by hydrogen bonds and prove mathematically the stability of this polymorph under external pressure above critical. For pressures below critical we derive the expressions describing the pressure dependence of the interaction energy of the effective dipoles emerging in the system when the symmetric lay-out of the hydrogen atoms among the oxygen atoms, characteristic for ice X, breaks down. This dependence allows us to reproduce qualitatively and understand the characteristic and unusual (as compared to the others) form of the boundary between the existence areas of the ordered and disordered ices VIII and VII. We also discuss the possibility of describing the differences between the ices existing at lower pressures (down to normal) on account of terms dependent on global structure including the long-range electrostatic contributions.

This work is supported in the frame of initiative of joint trilateral German-Russian-Ukrainian research in the area of Natural Science by the Volkswagenstieftung.

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Stability Prediction of Hypervalent Compounds Based on Data-Centric Modelling

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Hypervalent iodine compounds have become widely used reagents for the transfer of electrophilic substituents to donors. However, being very reactive by definition, many of these compounds are stable only because of a high barrier protecting them from transformation to chemically inactive forms.

In this study we explore hundreds of reagents of the general type shown in Figure 1 in view of their stability, i.e. the possibility of their use for the transfer of the substituent marked L.

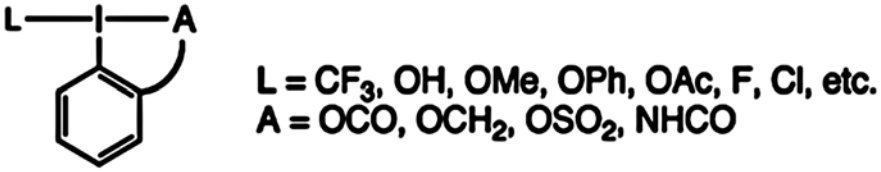

Figure 1. Scaffold of the hypervalent iodine regents explored in this study. L marks the electrophilic substituent transferred to nucleophiles, ranging from aromatic compounds all the way to peptides.

For that matter, a support vector machine (SVM) was trained using simple descriptors based on the molecular structure and the atomic charges observed in the reactive center. The SVM, a popular machine learning tool for yes/no-type classification, one trained properly, was shown to successfully predict (in)stability of these compounds based on the descriptors selected.

In this talk we will focus on the selection of descriptors, the training of the SVM and its application to a large array of know and (still) unknown compounds. Relative to the explicit determination of the kinetic and thermodynamic stability, this approach allows a prediction at a small fraction of the cost since only the molecular structures and the atomic charges need to be available.

We will also show that in machine learning the availability of "negative" information, i.e. information on non-existing compounds, is essential. The fact that negative information is much more difficult to find, presents a challenge and calls for rethinking of the existing, success-based publication culture.

Key factors governing the relative stability of charged, endohedral and exohedral fullerenes

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Fullerene anions and cations, as well as endohedral and exohedral fullerenes, have unique structural, electronic, and chemical properties that make them substantially different from pristine neutral fullerenes. The theoretical prediction of the most stable structures is a very challenging task due to the large number of isomeric forms accessible in such hot environments (e.g., more than 20 billion isomers for C60X8). In this talk, we present a simple model [1] [2], exclusively based on topological arguments, that allows one to predict the relative stability of these fullerene species without the need for electronic structure calculations or geometry optimizations. This model allows also identifying the key structural motifs that explain the fullerene stability [3] [4]. We show that the subtle interplay between π delocalization, cage strain, and steric hindrance is responsible for the stability of these compounds. The most stable structures predicted by the model are in good agreement with those found in synthetic experiments performed in high-energy conditions.

We have also performed Molecular Dynamics (MD) simulations to understand the interaction of charged fullerenes with He atoms in a He nanodroplet environment. Combination of these results with a simple model that describes the polarizability induced by the He atoms on the fullerene cage allows us to interpret the absorption line shifts as a function of the number of He atoms observed in recent experiments. [5]

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Ultrafast Action Chemistry in Slow Motion: Atomistic Description of the Excitation and Fluorescence Processes in an Archetypal Fluorescent Protein

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Extensive quantum mechanical/molecular mechanical non-adiabatic molecular dynamics simulations have been performed on the electronic excited state of Green Fluorescent Protein Variant S65T/H148D to find out the driving force of the ultrafast ($\tau < 50$ fs) KIE-less process of excited-state proton-transfer unleashed by absorption of the A band at 415 nm as well as the atomic description of the two dynamical regimes experimentally reported (1). The different regimes are explained in terms of two sets of successive dynamical events: First the proton transfers quickly from the chromophore to the acceptor Asp148. Second, geometrical parameters change in the cavity of the chromophore. Among these the distance between chromophore and Asp148, the planarity of the excited-state chromophore and, lastly, the distance between chromophore and Tyr145 undergo evolution on a slower time scale than the proton motion. Two different non-radiative relaxation channels have been found that are operative for structures where the process is at the reactants' region and that can explain the mismatch between the decay of the emission of A* and the rise of the emission of I*, including the temperature dependence of the non-radiative reaction path rate. Significantly, the method used and the results obtained set the grounds for understanding the molecular laws of the time evolution of fluorescence spectra in proteins.

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Research
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Molecular modeling of carborane-containing drug molecules

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Carborane clusters and their derivatives have recently become the focus of intense research in medicinal chemistry and drug design. The substitution of organic ring systems with carboranes proved to be a successful strategy towards novel and improved drug molecules [(1)]. Molecular modeling studies were able to predict the correct binding mode of the nido-carborane-containing derivative of indomethacin methyl ester (1, Figure 1) and helped rationalize the role of the planar chirality of the nido-dicarbaborate(−1) cluster in influencing binding affinities [(2)] [(3)]. The same computational tools have also been employed to gain insight into the binding modes of the ortho-carboranylphenoxy derived inhibitor of heat shock protein 60 (HSP60) chaperone activity (2, Figure 1) [(4)] and the carboranyl analogues of the 5-lipoxygenase-activating protein (FLAP) inhibitor Rev-5901 (3 and 4, Figure 1). [(5)]

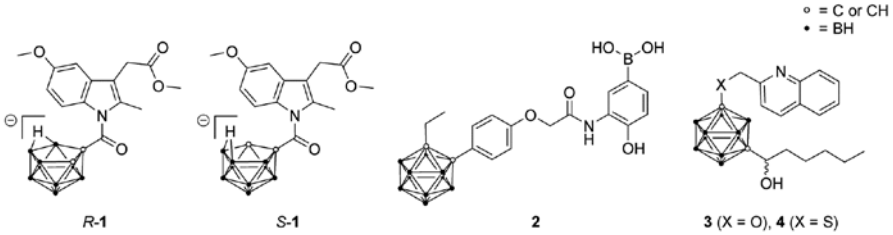

Figure 1. Structural formulas of cyclooxygenase inhibitor 1, inhibitor of HSP60 chaperone activity 2 and FLAP inhibitors 3 and 4.

Acknowledgements: This work was supported by the German Research Foundation (DFG, SA 2902/2-1).

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Wittig olefination, an old reaction with new perspectives

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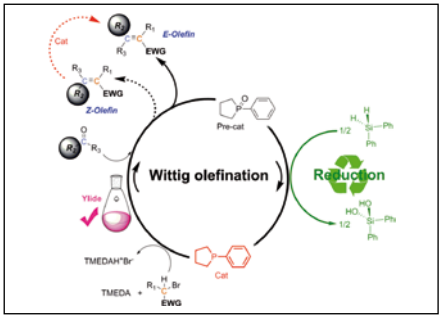

The formation of carbon-carbon double bonds is very important in organic chemistry. Classic Wittig reaction is one of the most famous and successful olefination reported in literature [(1)]. Organocatalytic Wittig reaction protocols have been recently proposed and optimized for different ylides [(2)]. Since theoretical models reproducing experimental findings with a high degree of confidence have tremendous impact in the future of rational synthesis, this paper presents to the audience state-of-the-art approaches in modern computation aiming to shed definitive light on the formation and reactivity of stabilized phosphorus ylides in condensed phase (in figure). A combined theoretical approach will be presented, summarized here as follows:

- Kinetic Model: thermodynamic data, extrapolated from electronic structures (M06-2X-D3/def2-TZVP/SMD) and integrated deterministically via simple kinetic laws, mimic the complex network of equilibria underlying the reaction. The rate determining step(s), the importance of fast reduction cycles and the E/Z-diasteroselective resolution are discussed.
- Statistical analysis: techniques enabling dimensionality reduction (i.e. principal component analysis), applied to a statistical sample of catalytic analogs to 3-methyl-1-phenyl-phospholane 1-oxide [(3)] with different electronic and steric properties, aim to uncover the catalytic motifs behind E/Z-diasteroselective experimental footprints. An interesting dependence of reactivity/selectivity upon 'deformability' of the reactants at the transition state is carefully addressed.

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Computational insights into reactivity of the phillips cro$_x$/sio$_2$ catalyst – role of amorphous silica model

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The Phillips CrO_x/SiO_2 catalyst is one the most commonly used catalytic systems to perform ethylene polymerization. Since the discovery of its unique activity in 1950's [(1)]many efforts have been made to unravel mysteries of its reactivity towards ethylene, as well as to determine structure of the active centers and theirs precursors. Nevertheless, the most fundamental questions still remain unanswered.

Here, we are presenting thorough theoretical studies, in which two different families of the models of the amorphous silica surface are applied, i.e., (i) structures derived from b-cristobalite framework [(2)] and (ii) amorphous silica structure from previous periodic simulations [(3-5)]. The cluster models developed reproduce accurately heterogeneity of the surface. Geometry optimization were performed using the PBE0 functional combined with the def2-SVP basis sets. Dispersion interactions were included in the single point calculations at the PBE0(D3)/def2-TZVPP level of theory. In some of the reaction pathways studied multiple spin-state changes occur. To this end, we calculated minimum energy crossing points (MECPs) between two potential energy surfaces following the methodology developed by Harvey and co-workers. [(6)]

In our simulations [(7)] [(8)], we included many different Cr surface species on various oxidation states, in order to comprehensively evaluate reactivity of different oxide precursors towards ethylene. Such extensive theoretical calculations were done for the first time for the CrOx/SiO2 system. Among others, we have proposed hydroxylated two-fold bounded Cr(III) oxide species as the active site precursor and found that such a structure can be the active species, as evidenced by the calculated activation parameters.[(7)] The obtained results are supported by the experimental data [(7)]. In addition to this, using the advanced models of amorphous silica, we have found that surface defects may play a role in one-electron Cr(II) to Cr(III) transformation [(8)]. Hence, our results show how important is to apply models that adequately represent complex structure of the surface.

Acknowledgments

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Molecular dynamics-based structure-activity relationships for the affinity of polyoxometalates towards proteins

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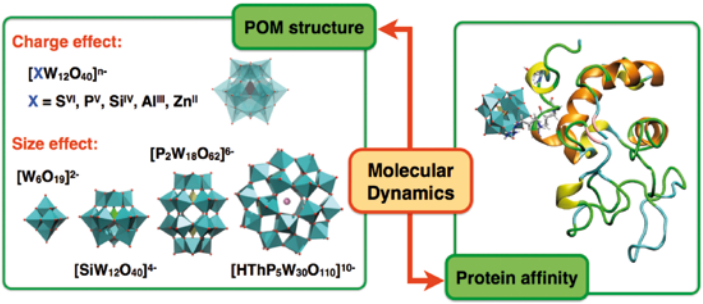
Polyoxometalates (POMs) are anionic polynuclear metal oxide clusters with promising applications in the fields of biochemistry and medicine [(1)] including antiviral, antibacterial or antitumor properties. Although it is widely accepted that the affinity of POMs to biological systems plays a crucial role in their biological activity, little is known about how to rationally modify their structure to set up, for instance, new inorganic drugs with enhanced bioactivity.

Initially, we probed and characterized computationally the physicochemical origin of the POM···protein interactions [(2)] Herein, we present a systematic Molecular Dynamics (MD) study aiming to evaluate the individual effects of POM composition on POM···protein interactions, in order to establish clear structure-affinity relationships. We performed simulations of lysozyme protein with two series of POMs whereby the charge density or the size of the cluster is modified systematically (see Figure). The comparison between the percentages of simulated time in which each POM is attached on HEWL surface was used to determine relative protein affinities. We concluded that efficient POM···protein contacts require a large enough POM size and the right shape to fit the protein cationic pockets, and more importantly, a moderate charge density of the POM to balance the interaction strength with the protein with its hydrophilicity. Finally, we were able to build a mathematical model with predictive ability between the protein affinity and two computational descriptors: the charge per metal ratio as a measure of the charge density (ρ_q) and the volumetric shape (V_S), which accounts for the POM size and shape.



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Splitting the coulomb hole into its dynamic and nondynamic parts

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The account of electron correlation in quantum calculations is a most important challenge in current computational chemistry. Whereas the dynamic part of electron correlation accounts for the interactions due to the movement of the electrons, the nondynamic correlation is important in systems where the ground state cannot be described by a single determinant.

The wavefunction includes information regarding electron-electron interactions. However, it becomes more intuitive to use the pair probability (or reduced two-electron density matrix). The intracule density [(1)], a contraction of the pair probability, is the probability function for the interelectronic vector that retains the information of electron correlation, but with the advantage of working with functions of lower dimensionality.

The introduction of electron correlation decreases the probability of finding two electrons close to each other, and in turn the probability of finding them in longer interelectronic distances increases. This consequence of electron repulsion can be easily assessed by means of the Coulomb hole, defined as the difference between the exact or FCI (correlated reference) intracule and the HF (uncorrelated reference) intracule densities [(2)]. In our approach, we use the Hartree-Fock-like (HFL) density matrix functional as a qualitative separator between the dynamic and nondynamic correlation parts. [(3)]

In this context, a systematic study over a group of diverse diatomic molecules has been performed with the aim to assess the magnitude of the electron correlation, and to reveal the nature of the type of correlation present in the molecule.

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Toward an accurate estimate of the exfoliation energy of black phosphorus

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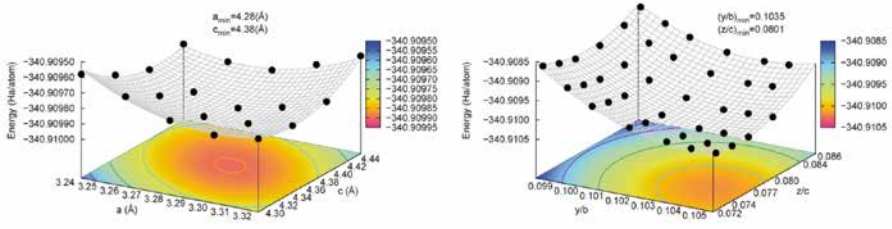
In the attempt to find a valid alternative to silicon-based electronics, phosphorene is definitely one of the most promising materials. Phosphorene can be seen as a 2D allotrope or phosphorus or, more simply, as a single layer extracted (exfoliated) from the black phosphorus (black-P) bulk structure.

The understanding and control of the exfoliation process is key to the fabrication of phosphorene. However, although few layers of phosphorene have been already fabricated [(1)] there is no available experimental measurement of the exfoliation energy between layers yet, defined as the energy required to extract (peel) one layer from the solid black-P. The assessment of such quantity is also a tough challenge for quantum chemical methods, since it is results from a delicate balance of several physical effects such as covalent bonds between Phosphorus atoms in the same layer, long- and mid-range dispersive interactions between layers, and so on. Such challenge calls for the adoption of high-level (state of the art) quantum chemical techniques, since even dispersion-corrected functionals yield contradictory results.

We adopted periodic local electron correlation methods (such as MP2 [(2)] and RPA [(3)]) combined with high- level Coupled-Cluster calculations on molecular clusters in order to estimate the exfoliation energy of the black-P [(4) (5)]. We performed a structural optimisation (see figure) of black-P at p-LMP2 level [(4)], that was made possible thanks to the Orbital-Specific Virtuals (OSV) approach adopted to describe the virtual manifold. [(6)]

We finally managed to obtain an accurate estimate for the exfoliation energy, that is in substantial agreement with Quantum-Monte Carlo estimates from other groups [(7)] and describes black-P as more difficult to exfoliate with respect to graphite. The accurate assessment at the post-HF level allows to benchmark the performance of different Density Functional approximations, that opens the way to extend the study to other effects like thermal lattice expansion.



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Towards next-generation semiempirical QM methods and reliable machine learning-based techniques

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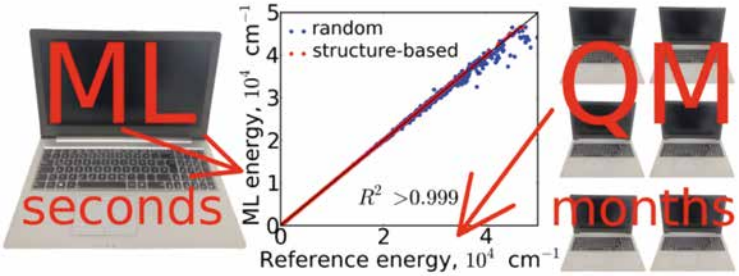
Our research is focused on developing next-generation semiempirical quantum mechanics (SQM) methods and techniques for reliable application of machine learning (ML) for calculating QM properties.

New SQM methods called orthogonalization- and dispersion-corrected methods (ODM***x***) [(1)] are based on the OM***x*** methods [(2)] and include explicit D3 dispersion corrections. The OM***x*** methods are among the most accurate SQM methods for calculating ground- and excited-state properties, while the D3-corrected OM***x*** methods are among the best for describing noncovalent interactions [(3)] [(4)]. In the ODM***x*** methods, heats of formation are calculated using the harmonic-oscillator and rigid-rotor approximations in contrast to older SQM methods. We also aim at the minimization of the error in electronic excitations.



We have proposed structure-based sampling and self-correcting ML to calculate precise potential energy surfaces based on a greatly (up to 90%) reduced number of the required reference ab initio calculations [(5)]. This approach allows the calculation of rovibrational spectra with errors of less than 1 cm−1 relative to the reference ***ab initio*** spectrum. We also mitigate the disadvantages of SQM and ML methods by exploiting their advantages in hybrid QM/ML methods with an automatic parameterization technique [(6)] and Δ-ML [(7)].

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QM/MM study of atom tunneling in the hydroxylation process of taurine/ α-ketoglutarate dioxygenase (taud)

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Enzymes of the class of α-ketoglutarate dependent dioxygenases (αKGDs) are vital in many biochemical and pharmacological processes, while details of their reaction mechanism remain poorly understood. This study focuses on one of the most studied αKGDs: the Taurine/α-ketoglutarate Dioxygenase (TauD) [(1) (2)].More concretely, we are interested in clarifying one of the key steps in the catalytic cycle of the αKGDs, the hydrogen atom transfer (HAT) process. We have studied the HAT process in TauD by QM/MM simulations (see Figure 1). Analysis of the charge and spin densities during the reaction demonstrates that a concerted mechanism takes place, where the H atom transfer happens simultaneously with the electron transfer from taurine to the Fe=O cofactor.

In addition, the rate constants of this step have been studied by employing TST, including tunneling by means of the Eckart barrier. We have found that the reaction is significantly enhanced by atom tunneling, which increases the rate constant by a factor of 40 at 5 ºC. This causes a KIE of about 60, which is in excellent agreement with the experimental value of about 58 [(3)]. These results influence our understanding of the whole class of αKGDs.

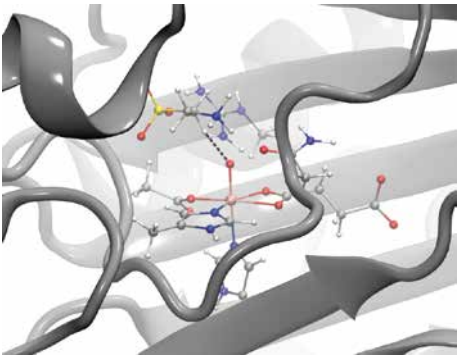

Figure 1. Schematic representation of one snapshot (reactant complex structure) of the TauD enzyme after a QM/MM optimization. The QM part is represented by the ball and stick model.

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Magnetic fingerprint of dithiazolyl-based molecule magnets

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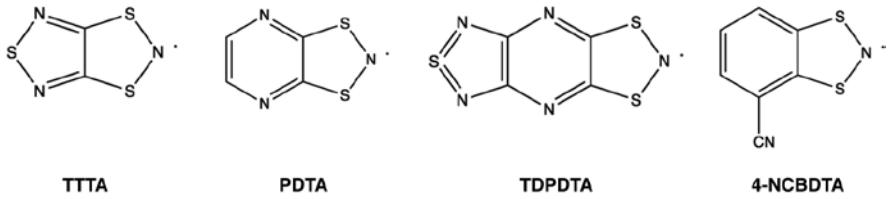
Theoretical predictions of magnetic properties of bistable purely organic molecule-based magnets have experienced an incredible progress during the last years. Yet some of these compounds present peculiarities that cannot be explained with the current *state-of-the-art* theoretical models. Our attention is devoted to dithiazolyl (DTA) compounds, namely TTTA [(1)], PDTA, TDPDTA, and 4NCBDTA [(2)], because they are promising candidates for potential technological applications (e.g. storage devices, sensors and quantum computers). The four selected DTA compounds present a common trend in the solid state: the planar DTA radicals pile up forming stacks.



Our first goal is to evaluate which pairs of radicals are magnetically non-negligible in order to identify the magnetic topology of the molecule-based crystals [(3)], by means of the First-Principles Bottom-Up working strategy. Next, our objective is to assess whether structural (geometrical) as well as electronic (DTA-ring, substituent interactions) factors affect the magnitude of the overall radical···radical J_{AB} magnetic coupling. Finally, we aim at providing a magneto-structural correlation map as a function of the substituents of the DTA-moiety to highlight the static ferromagnetic fingerprint region. At this point, we would like to stress that this magneto-structural map could become a practical tool to help experimentalists to design more stable and efficient purely organic radicals with ferromagnetic properties in the solid state.

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Molecular dynamic simulations of oil-water wetting on mineral surfaces

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Oil reservoirs are composed by microporous and mesoporous rocks filled with brine and crude oil. The remaining oil saturation, is currently more than 60% after the application of oil recovery techniques. Wettability has an important influence in oil recovery as well in production, for which the governing forces among the fluids and the rock of a reservoir are important to be studied. This property is related to the interfacial tension (IFT) of a brine/oil system and the contact angle of an oil droplet deposited on a surface immersed in brine. Experimental measurements of these properties are possible at lab conditions but measurements at reservoir conditions, high temperatures and pressures, are very challenging. For this reason, computational modeling became interesting on this field, allowing to obtain reliable values working both at lab and reservoir conditions.

In this presentation, we will review the calculation of the main properties that determine wettability (i.e., IFT and contact angle) via molecular dynamics simulations. Liquid-liquid interfacial tension can be determined indirectly by several methods [(1) (2)], advantages and disadvantages of these methods will be exposed comparing the resulting IFTs with available experimental measurements. On the other hand, contact angle calculations are currently performed by letting evolve in time through an oil droplet placed on a substrate and surrounded by water or brine [(3) (4)]. Although the method seems simple, it is important to be aware of the droplet size and shape, the size of the simulation box and the droplet equilibrium distance with respect the surface, among others. We will review the effect of these factors on the obtention of an equilibrium contact angle.

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Selective cyclic carbonate formation from CO_2 and epoxy-alcohols: mechanistic elucidation via dft analysis

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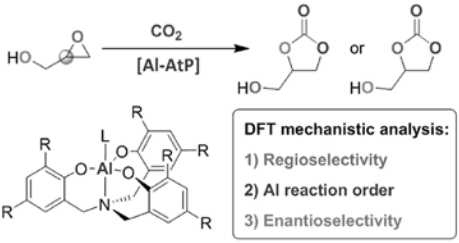
Carbon Capture Utilisation and Storage (CCUS) is indispensable to decrease CO_2 concentration in the atmosphere and consequently, mitigate the relentless global warming. Our group has studied computationally several processes to yield valuable chemical products like cyclic carbonates [1] [2] or polycarbonates [3] [4] through CO_2 fixation. These reactions were catalysed by an Al{amino-tri(phenolate)} [**Al-AtP**] complex and a nucleophilic co-catalyst (NBu_4**X** or **PPNX**).



This new approach (see Figure above) to convert CO_2 to cyclic carbonates begins with the deprotonation of the epoxy-alcohol by the phenolate ligand of **[Al-AtP]**, providing a nucleophile that leads to an unusual activation of CO_2 for intramolecular epoxy ring-opening under mild reaction conditions. We have elucidated the reaction mechanism through DFT-based methods shedding light to the origin of regioselectivity and enantioselectivity of the process and showing full consistency with the obtained experimental results.

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Carbon dioxide reduction on sodium and potassium hydroxide activated graphitic carbon nitride

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For carbon dioxide (CO_2) reduction, nanostructured two dimensional (2D) carbon nitrides appear to be a sustainable alternative to semiconductors containing metals such as CdS or TiO_2 [(1)]. In experiments, graphitic carbon nitride (g-C_6N_8) has shown potential for the photocatalytic reduction of CO_2 into carbon monoxide (CO) and acetaldehyde (CH_3CHO). The g-C_6N_8 material is made of nitrogen connected heptazine-units (C_6N_7), building a periodic porous 2D sheet.

An important experimental observation was the activation of the surface with different chemicals. While there was no change in performance with addition of potassium carbonate (K_2CO_3) and potassium bicarbonate ($KHCO_3$), an increase in yield was noted with sodium hydroxide (NaOH) and potassium hydroxide (KOH). Of these hydroxides, KOH showed the best performance for the CO_2 reduction. [(2)]

We endeavour to understand the origin of the enhanced performance of KOH over NaOH using computational methods [(2)]. The difference in charge density and a wide range of binding possibilities were examined with density functional theory. We ascertained a different adsorption for Na^+ and K^+. While both are coordinated with pyridinic nitrogen in the middle of the pores, Na^+ is smaller in size and fits more closely into the g-C_6N_8 pores. In contrast, K^+ sits on top of the pore. This behaviour does not affect the CO_2 adsorption directly, but K^+ stabilises the H_2CO_3 and HCO_3- adsorption more than Na^+ (see Figure 1). Both of these species are in an equilibrium with CO_2 and were identified as intermediates in the reduction.

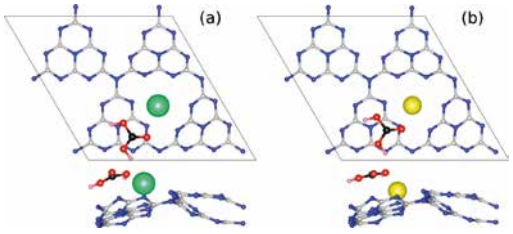

Figure 1. Most stable adsorption sites for H_2CO_3 on g-C3N4 with K (a) and Na (b). (Grey, black – carbon atoms, blue – nitrogen atoms, red – oxygen atoms, pink – hydrogen atoms, green – potassium atoms and yellow – sodium atoms.)

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MOFS decomposition and the database of secondary building units

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Metal-organic frameworks (MOFs) are porous crystalline materials that are formed by metal cations and organic ligands [1]. Over the past two decades, a lot of MOF structures have been proposed and synthesized [2]. The interest in this class of compounds is due to their potential application as catalysts, gas storage and chemical sensors [3] as well as the possibility of their directed synthesis based on the strategy of reticular design [4]. The main concept of reticular design is to use structural building units (SBUs) for assembling structures [5]. The design is carried out by decoration of a periodic net with a given topology by some SBUs (Fig. 1). There are a few program implementations of the algorithm for assembling of MOFs structures from SBUs [6]. These programs allow to generate large databases of hypothetical MOFs to search for structures with special properties. In general, the input information for MOF builders is the geometry and connectivity of SBUs and the topology of the underlying net. While there is a large database underlying nets for MOFs [7], we are not aware of any extensive database of MOF SBUs.

The main goal of this work is to create a database of SBUs that includes all required information for MOF builders. To do this, we have developed a universal algorithm for decomposition of MOF structures into SBUs. The algorithm is based on the clusters representation that is implemented in ToposPro program package [8]. A sample of more than 20000 coordination polymer structures were decomposed into SBUs. The information about occurrence, geometry, and connection type of SBUs as well as geometry and topology of the underlying net were stored.

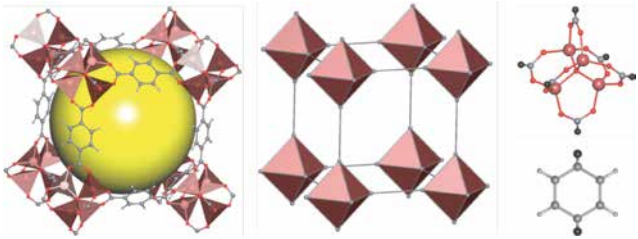

Figure 1. The fragment of MOF-5 structure, its augmented net and secondary building units. The black balls correspond to points of connection.

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Multi-level strategy for analysis of bioactive drug conformations

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Exploring the conformational preferences of small flexible ligands plays an increasingly important role in drug design. Estimating the relative free energy of a ligand in its target-bound state (i.e. the bioactive conformation) is necessary to understand the process of molecular recognition, to optimize the potency of bioactive molecules and to improve the accuracy of structure-based drug design methods [(1) (2)]. A set of 100 crystal structures of pharmaceutically relevant drug-like molecules was tested using multi-level computational strategy [(3)]. We combined low-level (LL) method for sampling the conformational minima and high-level (HL) ab-initio calculations for estimating their relative stability. [1] The method was automated and tested on various ligands with different numbers of atoms, charge and rotatable bonds. The analysis show that is necessary to perform Hamiltonian Replica Exchange simulations in order to explore all possible states of energy landscape of given dihedrals. Our findings suggest that the method is an effective way to improve the conformational sampling of the drug-like molecules. In the most cases, we found that the cluster representatives of the ligands have less than 1.0 Aº RMSD difference with respect to the bioactive conformation bound in complex. Moreover, our quantum mechanical results report that the bioactive conformation is around 2 kcal/mol higher in potential energy than the lowest-energy conformation. It is worth noting that present framework for multilevel strategy is a complex and long-term task, which requires a lot of rehearsals and implementations. Taking into account the flexible nature of molecules, protonation state and tautomeric forms, make our task even more challenging. The proposed strategy may represent an efficient tool for predicting the conformational landscape of drugs while keeping a reasonable balance between chemical accuracy and computational cost.

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Potential energy landscape and spectroscopical characterization of aza-nanohoops: promising structures for gas capture

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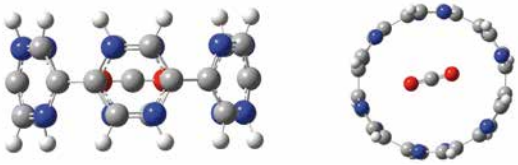
Nanohoops, chemically known as [***n***]Cycloparaphenylenes, possess a unique rigid architecture composed of n-benzene rings linked at para positions to form a 3D fully sp^2 conjugated cylindrical structure which, in solid state, from long-range channels with multiple π-π interactions [(1)]. These cyclic structures have attracted the attention of numerous investigations due to the advantageous properties that they feature with respect to their linear counterparts. The cyclic conjugation has been shown to be crucial to enhance the unique properties that nanohoops show and it also renders them to be electronic hybrids between polymers and small molecules. It is worth mentioning that these cylindrical motifs involve radially oriented pi electron densities from which very interesting electronic behavior arise. [(2)]

Significant effort has been devoted to tune the electronic properties of these carbon-based materials to enhance specific properties. One of the most common approaches is based on the inclusion of doping atoms such as boron, silicon, phosphorus and even nitrogen [(3)]. Aza-doped carbon nanohoops enable both the introduction of novel reactivity into these materials and fine tuning of their electronic properties. Electron-poor molecules such as C60 has been used as guest molecules in the hydrophobic electron-rich cavity of this nanohoops. Since the cavity size can be synthetically modified other molecules may be used as potential guests.



This work explores the possibility of forming donor-acceptor complexes between CO_2, and nanohoops with different degrees of nitrogen doping. First, the potential energy surface of the structure is analyzed to know which are the preferential CO_2 orientations within this structure. Once the most favorable configuration is known UV-Vis and Raman spectroscopy studies were carried out to identify the characteristic spectroscopic signals that allows their structural elucidation, prospectively also allowing the determination the degree of occupation. This computational study was carried out at the M06-2X /def2-TZVPP level of theory.

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Understanding the synthesis of prostaglandin G2 from arachidonic acid catalyzed by cyclooxygenase-2: a molecular dynamics/QM/MM approach

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Cyclooxygenases (COXs) are heme-containing bi-functional homodimeric enzymes. These enzymes catalyze the prostaglandin (PG) biosynthesis by the addition of two molecules of oxygen to Arachidonic Acid (AA) forming the hydroperoxy endoperoxide PGG2, that is reduced to PGH2, a precursor of different prostaglandins and thromboxanes. Three isoforms of COXs exist: COX-1 (a constitutive enzyme), COX-2 (the expression of the enzyme is induced during inflammatory states) and COX-3.

In this work, we have explored the conformational landscape of AA:COX-2 Michaelis complex by means of 100 ns classical Molecular Dynamics (MD) simulation, and we have compared the AA conformation with the one adopted in the active site of Lipoxygenases.

Subsequently, some MD snapshots were selected to calculate the potential energy surface by a QM(DFT)/MM approach, in order to study all the steps of the catalytic mechanism. The reaction mechanism that transforms AA into PGG_2 is constituted by six steps: the abstraction of the 13-proS hydrogen from AA by the Tyr385 radical; the addition of oxygen (O_2) at C_{11} in an antarafacial way; two cyclizations: the first one at C_9 pro-R position with a radical oxygen, and the second one between the C_8 – C_{12} atoms of AA; the addition of another oxygen at C15 pro-S position and the back hydrogen transfer from Tyr385, to finally yield PGG_2.

The main goal of this project is to analyze each one of the steps mentioned above and determine which is the rate limiting step. The understanding of the catalytic mechanism using a QM/MM approach can be useful in designing new selective inhibitors that might control inflammatory activity.

Posters

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QUANTUM CLUSTER APPROACH TO DEACETYLATION REACTION MECHANISM OF O-ACETYLPEPTIDOGLYCAN ESTERASE	P2	Z.Aksakal, M.M. Tataroğlu, F.A.Sungur, N.Tüzün	Turkey
CONFORMATIONALLY INDUCED PARAMAGNETISM IN ARYL-SUBSTITUTED 2-IMINO THIAZOLE DERIVATIVES	P3	Carlos Heras, Rosendo Valero, Guillermo Albareda, Francisco López-Calahorra, Ibério de P. R. Moreira, and Josep Maria Bofill	Spain
THREE COMPONENT SYSTEM OF DYE, QUANTUM DOT AND GOLD NANOPARTICLE	P4	Anuar Aldongarov, Irina Irgibaeva, Artur Mantel and Mukataev Iskander	Kazakhstan
THE IOCHEM-BD PLATFORM: A BIG DATA SOLUTION FOR COMPUTATIONAL CHEMISTRY	P5	M. Álvarez-Moreno, C. Bo, C. de Graaf, N. López, J. M. Poblet and F. Maseras	Spain
PUBCHEMDFT: A LIVE EXPERIMENT THAT COMPUTES AND TWEETS MOLECULES	P6	Joan González-Fabra, Moises Álvarez-Moreno, Martin Gumbau, Ana Mateo, Enric Petrus, Carles Bo	Spain
INVESTIGATION OF HYDROGEN BOND STABILITY ON N'-(7-CHLORO-4-QUINOLINYL)-N- (CYCLOPROPYLMETHYL)-N-PROPYL-1,3-PROPANEDIAMINE – PFATP6 COMPLEX IN WATER USING MOLECULAR DYNAMICS SIMULATION	P7	Ria Armunanto, Iqmal Tahir, Kurniawan Eka Satrya	Indonesia
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QUANTUM CHEMICAL DESCRIPTORS OF THE SULFONAMIDES BY DFT	P10	Seyda Aydogdu and Arzu Hatipoglu	Turkey
A COMPARATIVE DFT STUDY OF INTERACTIONS OF AU AND SMALL GOLD CLUSTERS AUN (N = 2 – 4) WITH CH3S AND CH2 RADICALS	P11	Martin Blaško, Tomaš Rajský, and Miroslav Urban	Slovakia
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ANALYSIS OF TITANIUM DIOXIDE SURFACES IN THE WATER SPLITTING PROCESS	P29	Amanda Fernandes Gouveia, Mateus Meneghetti Ferrer, Júlio Ricardo Sambrano, Elson Longo[a] and Juan Andrés	Spain and Brazil
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MOLECULAR MODELING OF CARBORANE-CONTAINING DRUG MOLECULES	RT1	Menyhárt-Botond Sárosi	Germany
WITTIG OLEFINATION, AN OLD REACTION WITH NEW PERSPECTIVES	RT2	Mauro Fianchini, Maria Besora, and Feliu Maseras	Spain
COMPUTATIONAL INSIGHTS INTO REACTIVITY OF THE PHILLIPS CrOx/SiO2 CATALYST – ROLE OF AMORPHOUS SILICA MODEL	RT3	Maciej Gierada, Jarosław Handzlik	Poland
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ELECTRONIC STRUCTURES OF THE HALOGENATED ORGANOPHOSPHORUS COMPOUNDS: A DFT STUDY	P33	Arzu Hatipoğlu and Didem Civan	Turkey
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SUBSTITUENT EFFECT ON THE REDUCTION TENDENCY AND CONFORMATION OF FLAVIN RING: A DFT STUDY	P56	Safiye Sağ Erdem and Arzu Topal	Turkey

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TOWARDS NEXT-GENERATION SEMIEMPIRICAL QM METHODS AND RELIABLE MACHINE LEARNING-BASED TECHNIQUES	RT7	Pavlo Dral and Walter Thiel	Germany
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BINDING OF POTENTIAL LEAD COMPOUNDS TO *PLASMODIUM FALCIPARUM* GLUCOSE-6-PHOSPHATE DEHYDROGENASE	P74	Antonio Viayna, David Vílchez, Diego Muñoz-Torrero, F. Javier Luque	Spain
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A DFT STUDY ON THE ELECTRONIC STRUCTURE AND ANTI- / PROOXIDANT PROPERTIES OF FLAVONOIDS: 3,5-DIHYDROXYFLAVONE AND ITS Cu^{+}, Cu^{2+} AND Zn^{2+} COORDINATION COMPLEXES	P78	Francisco Partal Ureña, Mª Carmen Ramírez Avi, and Ana África Márquez García	Spain
MOLECULAR DYNAMICS STUDIES OF A COMPLEX SYSTEM TO UNDERSTAND THE MODUS OPERANDI OF AN INTRINSICALLY DISORDERED PROTEIN	P79	Susana Barrera-Vilarmau, Alfredo De Biasio and Ramon Crehuet	Spain
A PROGRAM TO SEARCH FOR ADSORPTION SITES IN MOFS	P80	Pavel N. Zolotarev, Vladislav A. Blatov, Davide M. Proserpio	Russia and Italy
THE STATE OF IRON ATOMS AND EXCHANGE INTERACTIONS IN $BI_3NB_{1-X}FE_XO_{7-A}$	P81	Nadezhda Zhuk, Nataliya Chezhina, Vladimir Lutoev, Boris Makeev, and Lyba Rychkova	Russia
PINPOINTING DFT PERFORMANCE IN THE SIMULATIONS OF TWO-PHOTON ABSORPTION SPECTRA OF ORGANIC CHROMOPHORES	P82	Joanna Bednarska, Robert Zaleśny, Wojciech Bartkowiak, Hans Ågren	Poland and Sweden
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SELECTIVE CYCLIC CARBONATE FORMATION FROM CO_2 AND EPOXY-ALCOHOLS: MECHANISTIC ELUCIDATION VIA DFT ANALYSIS	RT11	Joan González-Fabra, Jeroen Rintjema, Nuno A. G. Bandeira, Arjan W. Kleij and Carles Bo	Spain
CARBON DIOXIDE REDUCTION ON SODIUM AND POTASSIUM HYDROXIDE ACTIVATED GRAPHITIC CARBON NITRIDE	RT12	Julia M. T. A. Fischer, Marlies Hankel, and Debra J. Searles	Australia
MOFS DECOMPOSITION AND THE DATABASE OF SECONDARY BUILDING UNITS	RT13	Andrey A. Golov, Vladislav A. Blatov, Davide M. Proserpio	Russia and Italy
MULTI-LEVEL STRATEGY FOR ANALYSIS OF BIOACTIVE DRUG CONFORMATIONS	RT14	Sanja Zivanovic, Adam Hospital, Modesto Orozco	Spain
POTENTIAL ENERGY LANDSCAPE AND SPECTROSCOPICAL CHARACTERIZATION OF AZA-NANOHOOPS: PROMISING STRUCTURES FOR GAS CAPTURE	RT15	Ángel Vida-Vidal, Olalla Nieto Faza, and Carlos Silva López	Spain
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Phototoxicity of non-steroidal anti-inflammatory drugs insight through in-silico calculations

Neus Aguilera-Porta [(a) (b) (c)], Giovanni Granucci [(c)], Jordi Muñoz-Muriedas [(b)] and Inés Corral [(a)]

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It is very important to evaluate the sensitivity of drugs to light as electronic photoexitation may lead to a loss of potency or production of toxic reactive species. The photosafety of pharmaceuticals is outlined in the International Council for Harmonization (ICH) S10 guidance [(1)], where the characterization of the UV-visible absorption spectrum is recommended.

Our research aims to investigate the photophysics and the photoreactive paths activated in drugs upon photon absorption in order to assess whether In Silico experiments can help to assess their photostable or phototoxic potential.

We have modelled the absorption spectra of non-steroidal anti-inflammatory drugs (NSAIDs), such as aspirin and ibuprofen in gas phase as well as in solvent. Multistate second order perturbation theory on state average complete active space self-consistent field wavefunctions MS-CASPT2//SA-CASSCF [(2) (3) (4)] protocol and time dependent density functional theory (TD-DFT) [(5)] were the computational protocols used.

Starting from the spectroscopic state, we have mapped the principal deactivation funnels and located the main stationary points along the singlet manifold. At the position of the minima, we have also located the closest triplets that would allow the transfer of population to manifolds of different multiplicity than that of the ground state.

These calculations provide an idea of the photophysical deactivation mechanisms that will next serve as a reference to obtain a time resolved picture of the evolution of the system upon its electronic excitation by means of non-adiabatic molecular dynamic simulations. [(6)]

Our goal with these results will be to develop phototoxicity alerts based on the drug photophysical properties that can be introduced at early stages of the drug discovery process and help to mitigate risks associated with photon absorption.

References:

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Quantum cluster approach to deacetylation reaction mechanism of o-acetylpeptidoglycan esterase

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The O-acetylpeptidoglycan esterase (Ape1) from N-Gonorrhoeae has an important role in the bacterial Oacetylation/deacetylation pathway. The O-acetyl modification in the peptidoglycan increases resistance to lysozyme and lytic enzymes which are essential for bacterial life cycle. At this point, bacterial cell growth and controlled division entails deacetylation of the cell wall. O-acetylpeptidoglycan esterase (Ape1) enzyme which belongs to SGNH family catalyze the deacetylation of peptidoglycans and hence, was proposed to be a potential target for antibiotic development.[(1)]

In this study, the deacetylation reaction performed by APE1 enzyme is elucidated in detail. For this purpose, the deacetylation reaction of APE1 enzyme with p-nitrophenyl acetate as a substrate was investigated with the quantum cluster approach using DFT. To mimic the enzyme enviroment, the residues that play a crucial role around the active site were included in the three different model clusters that varied in size (Figure 1), based on the X-ray crystal structure of the enzyme. In the smallest model (C0), SER80, ASP366 and HIS369 residues belonging to the catalytic triad of Ape1 were included. In the second model (C1), two important residues that were found in the oxanion hole and GLY324 and VAL325 residues surrounding the active site were also included to the system. The QM region was extended to 209 atoms for the last model (C2) and the reaction profile was found. In calculations, the geometrical structures of all stationary points in the energy profile were optimized at B3LYP/6-31G(d,p) level in the gas phase and D2 correction was added to include dispersion interactions. Accurate energies were calculated at higher level with single-point calculations on the optimized geometries. Solvation effects at various dielectric constants (ε=4 and ε=80) were evaluated with single point energies on the optimized structures.

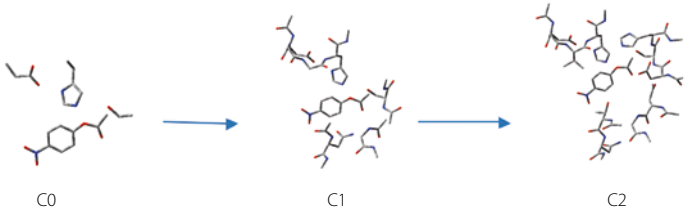

Figure. Schematic representation of the three different size DFT models of the active site of Ape1.

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Conformationally induced paramagnetism in aryl-substituted 2-imino thiazole derivatives

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Thermally accessible triplet electronic states are observed in members of a new family of neutral even-electron enamine- or imine- substituted thiazole compounds by EPR spectroscopy (Fig. 1) and magnetization experiments. The presence of paramagnetic species is also supported by reaction with radicals and the ability to sustain dynamic nuclear polarization. The paramagnetic species are assigned to the fraction of molecules adopting non-planar conformations around imine-enamine linker connecting two aromatic rings. We propose a mechanism based on a low energy triplet state originating from the weak double bond character of the bridging C=N bond and the capacity of the adjacent aromatic systems to stabilize the unpaired electrons (Fig. 2). This mechanism is currently under study by using high-level quantum chemistry calculations at the density matrix renormalization group (DMRG) level. Only in this way are we able to handle very large active spaces including the relevant sigma and pi molecular orbitals, which we believe are involved in the hypothesized mechanism.

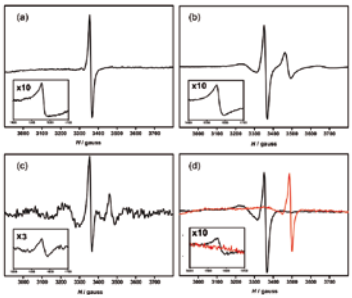

Fig. 1. X-band EPR spectra for Δms = 1 and Δms = 2 (inset) transitions for a) microcrystalline 1 at 4 K; b) microcrystalline 2 at 4 K; c) frozen CH2Cl2 solution of 2 at 4 K; d) microcrystalline 2 at 30 K (black line) and 300 K (red line). The same intensity scale has been used for a), b) and d) whereas for c) has been increased by one order of magnitude. The non-crystalline sample gives weaker EPR spectra and a Fourier Transform filtering of low frequency components has been applied. The higher complexity of the EPR spectra of 2 is tentatively assigned to the presence of multiple isomers.

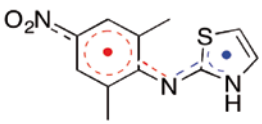

Fig. 2. The central scheme highlights the different localization of the unpaired electrons with the centers of higher density marked by green and red dots, respectively.

Three component system of DYE, quantum dot and gold nanoparticle

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We have considered luminescent properties of polymer system based on PMMA coumarin dye C-440, semiconducting quantum dots (QDs) CdSxSe1-x/ZnS and 3 nm gold nanoparticles (GNPs). Experimental results show that for this three component system presence of GNPs may increase emission intensity of QDs while for two component system of QDs and GNPs no such increase is observed. In the three component system increase of QDs emission happens at the expense of decrease of C-440 emission intensity. Based on the obtained results the model of three component system was considered at DFT level of approximation. In this model we have considered single C-440 molecule, two Au5 and Zn_6Se_6 clusters. Theoretical results show that addition of GNPs may provide increase of absorption rate of C-440 in two component system (C-440+GNPs) and in three component system (C-440+QDs+GNPs). While for QDs GNPs provide decrease of absorption probability. It is shown that relative positions of QDs and C-440 do not make an effect on their absorption properties.

The ioChem-BD platform: a Big Data solution for computational chemistry

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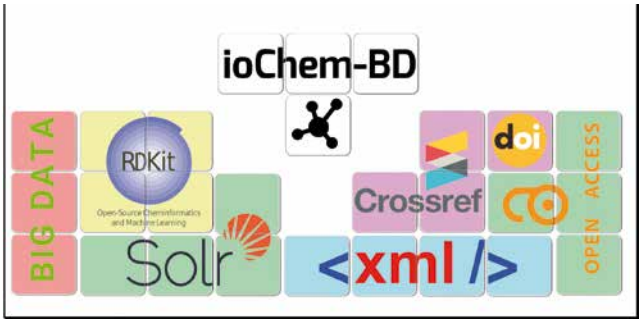
The use of automated processing tools and workflows, the need to feed machine learning algorithms, and the exponential increase of computing power are favouring the generation of large datasets in the field of theoretical chemistry and materials science. Managing such datasets is becoming a major challenge.

Nowadays, scientific research demands data services that allow chemists to store results, to convert into other formats, to visualise, to reuse, and eventually to share results so to increase their research visibility and social impact. ioChem-BD [(1)] is a web-based platform (http://www.iochem-bd.org) that stores scientific data and provides a solution to the aforementioned challenges, which is flexible to adapt to future requirements by its modular design. Three main modules cover the whole data lifecycle: creation, processing, visualisation, publishing and sharing. A new module called Find will be presented, which integrates the Apache Solr [(2)] indexing framework and the RDKit toolkit [(3)]. This enables searching by molecular substructure through millions of indexed entries in few milliseconds.



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(2) Apache Solr search platform, official webpage: http://lucene.apache.org/solr/
(3) RDKit Open-Source Cheminformatics Software, official webpage: http://www.rdkit.org

PubChemDFT: a live experiment that computes and tweets molecules

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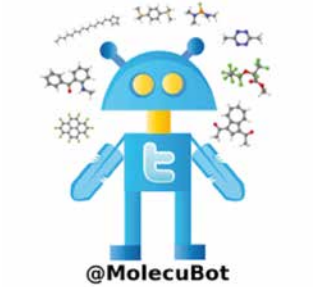
In this communication we are presenting PubChemDFT [1], a live experiment that aims at using spare computer time in low-cost machines to compute, process, store, and publish open-access DFT results of molecules contained in the PubChem database [2]. For each entry, we provide its optimized geometry, energies, atomic charges, vibrational frequencies, cube files for the electron density and the electrostatic potential, etc ... Average rate is close to 1000 molecules/day.

The system relies on Fireworks [3], which is a robust workflows system, and on our ioChem-BD platform [4] specialized in managing and publishing computational chemistry Big Data. Results are finally stored at BSC (Barcelona Supercomputer Center) ioChem-BD instance as soon as they are generated. A Twitter bot embedded within the workflows, @MolecuBot, tweets links to the data every time a new molecule is uploaded.

The experiment serves for disseminating computational chemistry among the general public so we expect it will become a funny teaching resource. Also, it demonstrates the robustness of all the technologies that we set up for this project, and it let us analyze their weaknesses. @MolecuBot **also** allows monitoring the health of all systems involved, from our own old cluster nodes till the servers at BSC.



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Investigation of Hydrogen Bond Stability on N'-(7-Chloro-4-Quinolinyl)-N- (Cyclopropylmethyl)-N-Propyl-1,3-Propanediamine – PfATP6 Complex in Water Using Molecular Dynamics Simulation

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Investigation of hydrogen bond stability on N'-(7-Chloro-4-Quinolinyl)-N- (Cyclopropylmethyl)-N-Propyl-1,3-Propanediamine (CCPP) – PfATP6 complex in water has been carried out using moleculer dynamics simulation. Antimalarial activity of CCP compound was predicted by molecular docking using ligand standard. Then, best pose of the complex obtained from molecular docking was used for initial configuration of molecular dynamics simulation. Dynamics of hydrogen bonds was evaluated using radial distribution function, hydrogen bond distribution, plot distances, and visualization, to compare with the ligand standard.

Two hydrogen bonds at amino acid residue of ASN101 and GLN56 with distances of 1,9 and 2.5 Å, respectively, were obtained from the moleculer docks of the CCPP – PfATP6 complex showing binding energy of -87.82 kJ/mol. During the MD simulation of the complex in water, a broken hydrogen bond at ASN101 residue was observed for a simulation time of 300 ps whereas GLN56 still stable indicating for a predicted antimalarial activity of CCPP compound due to the stability of hydrogen bond at GLN56.

Density functional study of the C_{60}-acetylene [2+2+2] cycloaddition promoted by the wilkinson's catalyst

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Since the discovery of C_{60} in 1985 [(1)], fullerenes have attracted the attention of chemists due to their unique structure, properties and reactivity, along with their potential applications in a variety of fields from materials science to biomedicine [(2-5)]. Many functionalized fullerene derivatives resulting from the structural modification of the fullerene cage have been reported over the last 30 years. C_{60} fullerene can react with nucleophiles and its [6,6] bonds are good dienophiles. Moreover, several cycloaddition reactions involving [6,6] junctions of C_{60} have also been reported [(6)]. The preparation of cyclohexadiene-fused C_{60} derivatives can be achieved by [2+2+2] cycloaddition reactions of C_{60} with alkynes [(7-9)]. These compounds have been found to be important intermediates in the synthesis of so-called open-cage fullerenes [(10)]. However, no mechanistic studies have been reported yet concerning this specific kind of reactions. We report density functional calculations at the M06L/B3LYP level of the [2+2+2] intermolecular cyclotrimerization of C_{60} and two acetylene molecules. The results obtained show that the process is both thermodynamically and kinetically favorable through two different reaction paths and, as expected, the reaction shows high regioselectivity at the [6,6] bond. This theoretical study suggests the feasibility of new catalytic methods for obtaining of cyclohexadiene-fused C_{60} cycloadducts.

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Development of reliable prediction models for the efficient profiling of kinase inhibitors

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Computational chemistry is an indispensable requisite in modern drug discovery and design. In the quest to develop safer drugs, *in silico* methods can drive forward the efficient identification of molecules with improved biological profiles, as required for kinase inhibitors. Given the large size of the human-kinome (> 500 kinases) [(1)] and the conserved catalytic site, the development of new drugs targeting selectively kinases is a challenging task.

In this study, we aimed to improve the predictors for kinase inhibitors, starting from the target sets published recently by Bora et al [(2)]. (www.chembioinf.ro/). Here we emphasize a harsher selection of the bioactivity data used to build random forest models. These are externally validated with computed error intervals for classification and virtual screening. In the latter case, we use eROCE (exponential receiver operating curve) [(3)] to compare the early enrichment capacity of the predictors. Overall, the approach leads to more reliable predictors capable to identify promiscuous compounds in large chemical libraries and guide the rational discovery of novel molecules with desirable kinome-wide profiles.

Acknowledgements: this work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-0422 and by the ERA.NET RUS PLUS, European and International Cooperation-Subproject 3.2-Orizont 2020 grant, project number 6/2016, PN-III-P3-40/19.04.2016.

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Quantum chemical descriptors of the sulfonamides by DFT

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Antibiotics are widely used as human and veterinary medicines, as well as in the feeding of animals (1). Sulfonamides (SAs), N-substituted derivatives of the p-aminobenzenesulfonic acid, are the major class of antibiotic drugs in the world owing to their low cost, low toxicity and excellent activity against bacterial diseases (2,3). SAs are used as therapeutic agents against specific bacterias which cause some diseases such as urinary infections, skin infections and respiratory track infection (4).Over the last decade, due to the extensive and unregulated SAs usage, many SAs and their metabolites dispersed into the environmental compartments (water, soil and atmosphere). Thus the presence of these compounds in the environment has detrimental consequences for public health (5).

In this study, 22 sulfonamide compounds were investigated theoretically. Conformational analyses and geometry optimizations of all the structures were performed to determine the most stable structures. All quantum chemical calculations were performed with Density Functional Theory (DFT) method. The DFT calculations were carried out as implemented in GAUSSIAN 09W, using the exchange-correlation functional B3LYP, which combines HF and Becke exchange terms with the Lee–Yang–Parr correlation functional, in combination with the 6-311++G(d,p) basis set. **The solvation effects were computed using COSMO as the solvation method**.

Based on the quantum mechanical calculations, frontier orbitals, energetic parameters, Mullikan atomic charges and electron densities of the molecules were calculated. These results were used to calculate the DFT reactivity descriptors of molecules such as chemical hardness, chemical potential, electrophilicity index for all molecules.

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A comparative DFT study of interactions of Au and small gold clusters Au_n (n = 2 – 4) with CH_3S and CH_2 radicals

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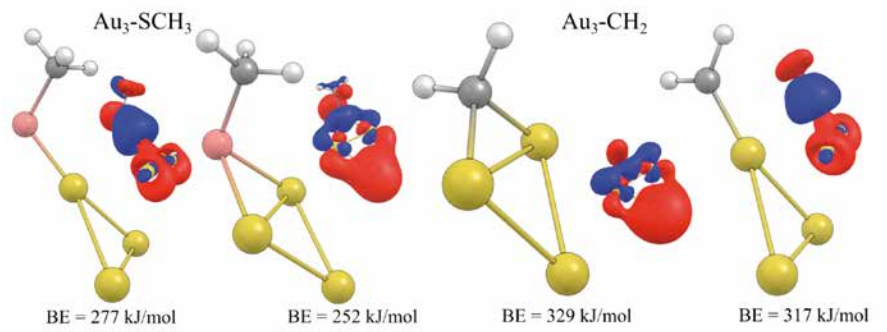
We compared DFT binding energies (BEs) of Au and small gold clusters interacting with CH_3S and CH_2 ligands (Au_n–L complexes, n = 1–4). Au_n–SCH_3 and Au_n–CH_2 complexes serve as a model for understanding the binding mechanism of the Au atom and small Au_n clusters interacting with open shell ligands. The spin state and the binding mechanism in Au_n–L varies with the participation of singly occupied non-bonding orbitals or doubly occupied lone-pair orbitals of a ligand and on the number of atoms (even or odd) of Au_n. Crucial role in the Au_n–CH_2 bonding play two singly occupied orbitals in CH_2 which leads to much higher BEs in Au_n–CH_2 complexes than in Au_n–SCH_3. For Au_n – ligand complexes having the same number of gold atoms are BEs with CH_2 by 57 to 175 kJ/mol higher than BEs with CH_3S as a ligand. With respect to *n*, the highest BEs in Au_n–SCH_3 complexes were calculated for Au_3–SCH_3 (singlet) followed by Au_4–SCH_3 (doublet), Au–SCH_3 (singlet) and Au_2–SCH_3 (doublet). For complexes with the same multiplicity are BEs higher for those having larger number of gold atoms. Singlet complexes have higher BEs than triplets. With CH_2 as a ligand the highest BE exhibits Au_3–CH_2 (doublet) closely followed by Au_4–CH_2 (singlet) and Au_2–CH_2 (singlet). In Au_2–CH_2 and Au_4–CH_2 complexes have singlets higher BEs than triplets. In line with interaction mechanisms go geometries of Aun–L complexes. With a few exceptions CH_2 prefers the bonding of the carbon atom with two gold atoms of Au_n (bridge structures) while in most stable Au_n–SCH_3 complexes is the sulphur atom bound to a single Au atom (on top interactions).



Minimizing false-positive rates in high-throughput screening (HTS): prediction of luciferase inhibitors

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The discovery of new chemical entities with targeted biological activity is highly reliant on large scale high-throughput screening (HTS) [(1)]. Firefly luciferase (FLuc), a bioluminescent enzyme, is used as a reporter in a large number of assays to monitor the effect of compounds against specific targets and/or cellular pathways [(2)]. However, the false active rates of luciferase-based assay is relative high due to the direct interaction of the compounds with FLuc which leads to enzyme inhibition [(3)]. Consequently, early and reliable identification of such compounds is highly needed to clean up the screening libraries of these structures and minimize the costs of HTS campaigns.

In this work, we describe robust models for the prediction of luciferase inhibitors. The models were developed using machine learning algorithms based on large-scale specific bioactivity data publicly available from PubChem database [(4)] [(5)]. The performance of the models was evaluated in classification and virtual screening experiments, using well-established metrics. The best model classified correctly more than 80% of the actives (inhibitors), while in virtual screening more than 40% of the actives were retrieved in the first 1% of the evaluated database.

Acknowledgements: this work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-0422 and by the ERA.NET RUS PLUS, European and International Cooperation-Subproject 3.2-Orizont 2020 grant, project number 6/2016, PN-III-P3-40/19.04.2016.

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Structure- and Fragment-based Design of Novel Diaminopyrimidine Derivatives Inhibitors for Human Myt1 Kinase

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Membrane-associated inhibitory kinase Myt1 belongs to Wee1-kinase family and regulates the cell cycle at G2/M transition [1]. Myt1 is responsible for inhibitory Cdk1 phosphorylation [(1)]. As result, the cell cycle is restricted until DNA damage is repaired [(2)]. A new strategy for cancer treatment is to keep the cell going in the cell cycle with unrepaired DNA damage in premature mitosis. The abrogation of the G2 checkpoint results mitotic catastrophe and immediately causes apoptotic or non-apoptotic cell death [(3)].

In the current project we used a combination of ***in silico*** and ***in vitro*** screening to identify novel Myt1 inhibitors. The ***in silico*** screening was done using the available Myt1 crystal structure (PDB 3P1A) and several docking methods [(4)]. As databases for screening we used in-house libraries of already tested inhibitors as well as focused kinase inhibitor libraries (e.g. Selleckchem and GSK kinase inhibitor dataset I and II). The docking solutions were analyzed and re-scored using binding free energy calculations. The tested inhibitors were used to derive a quantitative structure-activity relationships (QSAR) including different descriptors and scoring methods. The QSAR models were validated using external test sets and showed good predictivity. Several scaffolds were identified as starting point for the development of novel Myt1 inhibitors. To optimize the identified hits we used the fragment-based approach. The most promising docking solutions were used to identify putative binding groups for the individual binding pockets of Myt1. The first set of inhibitors was synthesized and submitted to the biological evaluation. Novel active Myt1 kinase inhibitors have been identified.

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Experimental and theoretical insights on $BaW_{0.5}Mo_{0.5}O_4$ scheelite solid solution prepared by co-precipitation methods

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The morphology of a material is related to the stability of their corresponding exposed surfaces, which can be rigorously described by their surface energies. In this context, first principle calculations have been gradually developed and employed for the study of crystal morphology [(1)]. This has enabled the understanding of the atomic and electronic properties of a crystal surface, which has provided some insight into the features of single crystal facets relevant to subsequent technological applications. Our group are engaged in a research project devoted to develop and apply a working methodology, based on the joint use of experimental findings and first-principles calculations, to obtain the electronic, structural and energetic properties controlling the morphology and the transformation mechanism of complex crystals [(2) (3)], as $BaW_{0.5}Mo_{0.5}O_4$ used in this work. Barium tungstate ($BaWO_4$) and Barium molybdate ($BaMoO_4$) crystals have attracted a great interest of several research groups, since they are important materials that present a potential application as scintillating, battery, capacitor, photocatalyst and especially as photoluminescent materials, as well as different synthetic methods have been used to obtain them, such as co-precipitation (CP), sol–gel, modified Pechini, solid state reaction, solution route, Czocharski, sonochemical and hydrothermal conditions.

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Computational modeling of versatile photosensitizers

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Nowadays, the most available renewable energy source on the planet is sunlight. Therefore, one of the most prolific chemical research lines in photovoltaics cells consists in the search for dyes, molecules to be used in the so-called Dye-Sensitized Solar Cells (DSSC). Solar cells are a promising alternative to the silicon photovoltaic cells because they are easier to build and very economical. The challenge today is to improve the yield of DSSC (figure 1) in the transformation of sunlight into electricity [(1)]. Dyes used in DSSC can also be used in Organic Light Emitting Diodes (OLEDs) devices and in the water splitting process. [(2)]

In this project, we have studied the electronic structure of sixteen copper photosensitizers (three have been synthetized and characterized in the lab) using different density functionals in the framework of Time-Dependent Density Functional Theory (TDDFT) [(3)]. We have analyzed LC-ωPBE functional by optimizing the attenuating parameter (ω) [(4)]. Our results show the importance of the improvement of several properties upon optimization of ω, such as the simulation of UV-Vis absorption spectra and REDOX potentials. Research is underway in our laboratories to improve the adjustment of the computationally simulated absorption spectra and find new molecules that present a wider range of absorption.

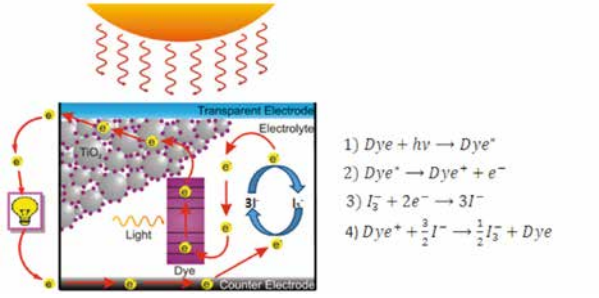

Figure 1. Scheme of DSSC operation process and the corresponding reactions.

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Theoretical estimate of charge-separation and -recombination rate constants in donor-acceptor buckybowl-based supramolecular complexes

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Fullerenes and their derivatives are one of the most important electron-acceptor (A) compounds in organic electronics [(1)]. In particular, fullerene and fullerene fragments (buckybowls) in combination with the electron-donor (D) truxene-tetrathiafulvalene (truxTTF) form donor-acceptor supramolecular complexes that undergo an efficient photoinduced electron transfer process (Figure 1a) [(2) (3)]. In this contribution, we present a theoretical protocol to estimate charge-separation and charge-recombination rate constants in D-A buckybowl-based supramolecular complexes (Figure 1b). The theoretical protocol makes use of the Marcus-Levitch-Jortner equation [(4) (5)] in which the relevant parameters are evaluated from Density Functional Theory (DFT) and time-dependent DFT (TDDFT) calculations. The theoretical protocol allows us to identify the most relevant effects (electronic coupling, reorganization energy and energy difference between the electronic states involved in the transfer process) that determine the charge-separation and charge-recombination rates.

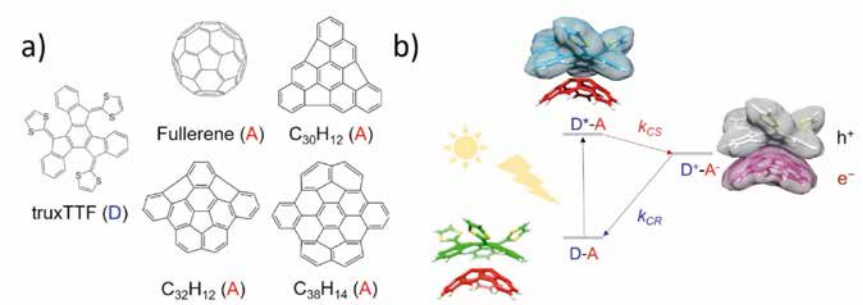

Figure 1. a) Chemical structures of the donor (truxTTF) and acceptor (Fullerene and buckybowls) systems. b) Diagram of the supramolecular organization between truxTTF and $C_{30}H_{12}$ and the photoinduced electron transfer events.

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Polar flattening and charge transfer contributions to halogen bonded complexes

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A deep understanding of the halogen bond (XB) at molecular level is an important goal with potential implications for fields ranging from biochemistry to materials science. In XB, the halogen atom X is shared between a donor D and an acceptor A(A-X···D interaction). The XB is usually interpreted in terms of σ-hole and polar flattening. The former refers to the presence of a region of positive charge along the extension of the A-X bond, which interacts electrostatically with the incoming Y moiety. The latter refers to the flattening of the electron density around the halogen atom covalently bound to A. The flattening of the electron density at the opposite side of the A-X bond leads to a reduction of the Pauli repulsion in the interaction with Y. Accordingly, the X and D partners, with a high polarizability, come very close to each other, so that the halogen bond interaction is not merely an electrostatic effect, but also the dispersion and the charge transfer terms may significantly contribute to the overall energetics. The size of the σ-hole and polar flattening concur to determine the strength of the halogen bond and can be modulated by substitution of suitable chemical groups close to the halogen site. We carried out high level quantum mechanical calculations to deeply investigate and characterize the halogen bond interaction both in prototypical and more complex systems, with special attention devoted to the charge transfer contribution to the interaction. The effect of the chemical environmental has also been considered, by replacing one chemical species near the halogen atom. Our approach allows us to unambiguously identify and quantify the electron charge displaced upon formation of the halogen bond between X and D partners.

Selective Oxidation of Methane Catalyzed by Soluble Platinum Species in Oleum: Density Functional Theory Study

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The selective conversion of methane into methanol in an economically competitive process is one of great challenges in catalysis. The functionalization of methane is of significant practical interest, but methane is relatively unreactive. The first important homogeneous catalytic system for selective methane functionalization is Shilov system with aqueous solutions of Pt^{II} salts to produce alcohol and alkyl chloride [(1)]. However, use of Pt^{IV} as a stoichiometric oxidant in this system has been a problem. So Periana has developed an alternative system with $(bpym)_2PtCl_2$ (bpym=2,2′-bipyridine) in concentrated or fuming sulfuric acid (oleum) to oxidize methane to methyl bisulfate (MBS) using sulfur in the +6 oxidation state (SO_4^{2-} or SO_3) as the oxidant [(2)]. The limitation of this catalyst is the volumetric production of functionalized product < 1 M. Recently Schüth has shown that simple platinum salts are stable, selective, and unprecedently active, and under most conditions superior to Periana system. [(3)]

Here we have performed the hybrid density functional theory (DFT) calculations in conjunction with the conductor-like polarizable continuum solvent model to gain molecular-level insight into the intricate features of catalytic behaviour of a simple soluble platinum species towards methane activation. We have determined the full potential energy profiles for plausible catalytic pathways along the major phases of the catalytic cycle. From the calculated results important insight is gained into the mechanism of selective oxidation of methane.

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Water-Gas Shift Reaction cocatalyzed by $K_3PM_{12}O_{40}$ and Au(111): The magic role of polyoxometalates

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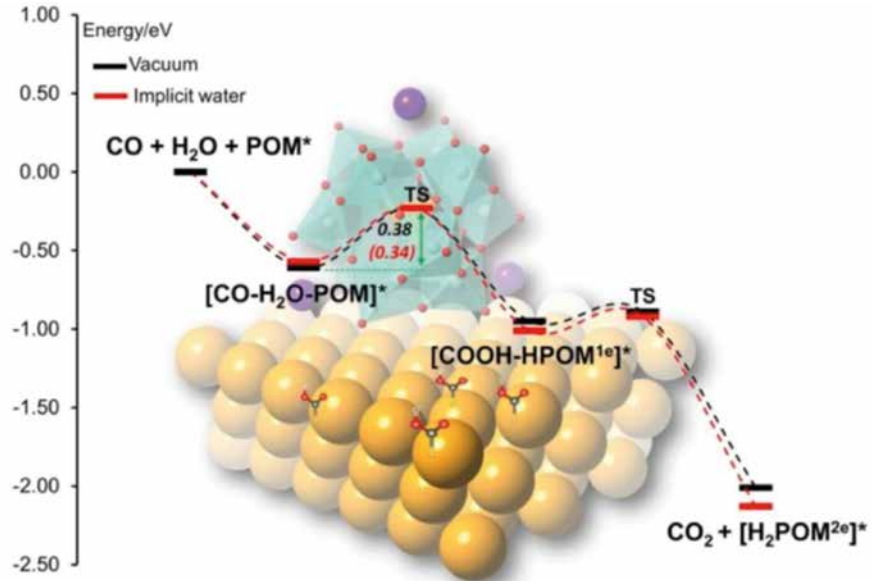
Water-gas shift reaction (WGSR) has been extensively investigated because of its relevance in industry.

$$CO + H_2O \rightarrow CO_2 + H_2$$

Ab initio density functional theory calculations combined with the periodic continuum solvation model were applied to provide a mechanistic network of WGSR cocatalyzed by Au(111) and a polyoxometalate (POM), $K_3PMo_{12}O_{40}$ (PMo_{12}), in aqueous solution. The contributions of Mo(d) and O(sp) bands near the Fermi level of PMo_{12}-Au(111) were found to be responsible for the activity of POM modified gold catalyst, serving as both electron and proton acceptors. We show that the interfacial water can easily dissociate at room temperature in the presence of CO and a PMo_{12} adsorbed on the surface, via proton transfer to the O of the POM and electron transfer from the surface to the POM. A detailed mechanism study will be presented. Furthermore, we will show that PMo12-Au(111) catalyst exhibits an enhanced catalytic activity compared to PW_{12}-Au(111) catalyst.



Minimizing false-positive rates in high-throughput screening: predictors for fluorescent compounds

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High-throughput screening (HTS) is widely used in drug discovery to screen large chemical libraries for active compounds against protein-targets implicated in various diseases. During the last decade, several reports drew attention towards the high incident of false-positives in HTS outcomes. For instance, the interference with the signal detection system is one major source of error in fluorescence-based assays [(1)]. In this case, the removal of autofluorescent molecules, embedded in the screening library, can significantly reduce false-positives rates in HTS results.

Here, we report the generation and evaluation of robust predictors for fluorescent compounds. Data sets were extracted from one of the largest collection of publicly available bioactivity database, PubChem Bioassay [(2) (3)]. A machine learning algorithm, i.e. Random Forest [(4)], was used to develop models for classification and virtual screening. The external evaluation indicates that 75% of the fluorescent compounds were correctly classified, and up to 40% of them can be retrieved in the top 1% of the ranked dataset.

Acknowledgement: this work was supported by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS – UEFISCDI, project number PN-II-RU-TE-2014-4-0422.

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The dark side of aluminum chelation therapy: characterization of the al(III) – ligand binding features

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In the last century, human intervention has made aluminum highly bioavailable [(1)]. However, there is increasing evidence that aluminum could be behind of a variety of toxic effects in biological systems, with significant risks for human health. In this context, the goal of chelation therapy is the removal of toxic metal ions from the human body or attenuation of their toxicity by transforming them into less toxic compounds.

Such a situation has led several groups to focus the attention and to make efforts toward the identification of aluminum-specific chelating agents, with a need to rationalize the effect of different substituents (such as electron donating groups or electron withdrawing groups) toward the modulation of the Al(III)-ligand binding affinity.

Accordingly, the aim of our work is to set-up a *state-of-the-art* theoretical approach that would help to characterize the structural features and the nature of the aluminum-chelator interactions, as well as to unveil the substituents effect.

Our theoretical protocol is based on DFT calculations at the B3LYP-D3(BJ)/6-311++G(3df,2p) level of theory, validated with respect to experimental data and other levels of theory. In order to rigorously characterize the aluminum-chelator interactions, the Bader's Quantum Theory of Atoms In Molecules (QTAIM), the Natural Bond Orbital (NBO) theory and the Energy Decomposition Analysis (EDA) scheme by Ziegler and Rauk have been applied.

Moreover, since some chelating agents contain many degrees of freedom, MonteCarlo-based conformational searches and QM/MM Replica Exchange Molecular Dynamics (REMD) simulations have been performed in order to identify minima structures of interest.

Among many interesting aluminum chelators, our interest is focused on those that have been shown to form highly stable complexes with Al(III) [(2)] [(3)], such as catechol, salicylic acid, ethylenediaminetetraacetic acid (EDTA), the commercial drugs Deferiprone and Deferoxamine, and a new family of Mimosine-based chelating agents.

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Theoretical and spectroscopic investigation on charge-transfer complex between N-sulfamoyloxazolidinone and picric acid

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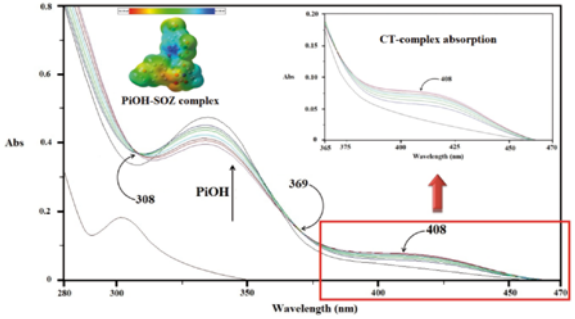
Charge-transfer complex formation between N-(4-methoxyphenyl)-2-oxooxazolidine-3-sulfonamide (SOZ) as electron donor and picric acid (PiOH) as electron acceptor with stoichiometry ratio 1:1 has been studied spectrophotometrically in chloroform and dichloromethane at room temperature. Various important parameters such as formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), thermodynamic standard reaction quantities ($\Delta G°$, $\Delta H°$, $\Delta S°$), energy of interaction (E_{CT}), ionization potential (I_D), oscillator strength (f) and transition dipole moment (μ_{EN}) were calculated and the effect of polarity on these parameters was also discussed. Fourier transform infrared (FT-IR) spectral study has been carried out to confirm the presence of various functional groups present in the complex.

The experimental studies were complemented by quantum chemical calculations by DFT and TD-DFT at B3LYP level. The theoretical UV visible and the simulated IR spectra were carried out using B3LYP/6-311G (d,p) and compared with those obtained experimentally. The Mulliken charges, MEP calculations, the electronic properties HOMO and LUMO energies and NBO analysis were performed on the optimized charge transfer complex.

Graphical abstract



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Unraveling the mechanisms of the so-called "pericyclic reactions". A molecular electron density theory study

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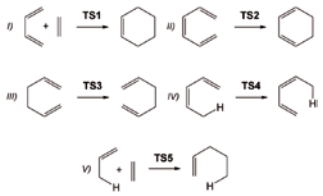
The molecular mechanisms of five relevant organic reactions classified as "pericyclic reactions" have been studied within the Molecular Electron Density Theory (MEDT) using quantum-chemical DFT calculations at the MPWB1K/6-311G(d,p) computational level (see Scheme 1). The Bonding Evolution Theory [1] (BET) analysis of the mechanisms of these five non-polar organic reactions indicates that the bonding changes along these reactions are neither concerted nor take place in a cyclic movement, as proposed by Woodward and Hofmann [2] [3], but they take place symmetrically to the plane crossing the molecular plane orthogonally.

Formation of the new C-C single bonds in these *pseudocyclic* reactions takes place following the same pattern [4]: i) rupture of the C-C double bonds, ii) formation of a *pseudoradical* center at each interacting carbon, and iii) formation of the new C-C single bonds through the C-to-C coupling of the two corresponding *pseudoradical* centers.

Most of these *pseudocyclic* reactions [5] do not take place experimentally due to the high activation energies associated to the corresponding TSs. The present MEDT study allows explaining the high activation energies experimentally determined. The computed high activation energies can be related with the energy cost associated with the rupture of the C-C double bonds in the reagents, which is demanded for the creation of the *pseudoradical* centers required for formation of the new single bonds.

Both electron locasitation function (ELF) and atoms in molecules (AIM) topological analyses of the electron density at the corresponding TSs indicate that at least in four of the five studied TSs the formation of the new C-C single bonds has not yet begun.[5]

The present MEDT study permits to reject the pericyclic mechanisms$_2$ proposed within the Frontier Molecular Orbital (FMO) theory.



Scheme 1. Studied *pseudociclic* reactions.

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Electronic structure analysis of key organogold transformations

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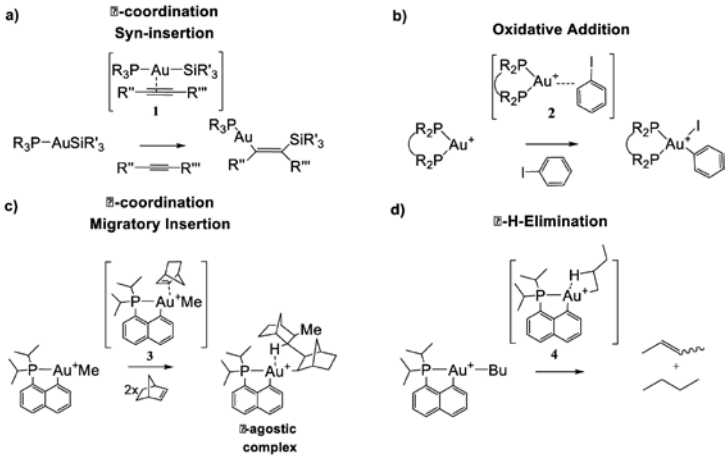
New gold-mediated processes have been reported demonstrating that gold offers many opportunities in catalysis well extend beyond π-activation. Still, several elementary steps of organometallic chemistry were considered highly disfavored for gold complexes [(1)]. In a joint experimental and theoretical approach, we have unequivocally substantiated the ability of gold complexes to undergo some of the key organometallic transformations such as migratory insertion [(2)(3)], oxidative addition [(4)] and β-Hydride elimination.[5]

In this poster communication, we will depict the DFT mechanistic studies of the elementary transformations drawn in Scheme 1 and the electronic structure analysis carried out on key intermediates (1-4) by means of NBO and QTAIM analyses. All together has allowed us to get a deeper understanding on gold chemistry.



Scheme 1. Fundamental organometallic transformations with Gold complexes.

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Ultrafast Excited-State Decays in $[Re(CO)_3(N,N)(L)]^{n+}$: Non-Adiabatic Quantum Dynamics

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The ultrafast luminescent decay of $[Re(CO)_3(phen)(im)]^+$ [(1)], representative of Re(I) carbonyl-diimine photosensitizers, is investigated by means of wavepacket propagations based on the multiconfiguration time-dependent Hartree (MCTDH) method [(2)]. On the basis of electronic structure data [(3) (4)] obtained at the time-dependent density functional theory (TD-DFT) level the luminescence decay is simulated by solving a 14 electronic states multimode problem including both vibronic [(5)] and spin-orbit coupling (SOC) up to 15 vibrational modes. A careful analysis of the results provides the key features of the mechanism of the intersystem crossing (ISC) in this complex. The intermediate state, detected by means of fs-ps time-resolved spectroscopies, is assigned to the T_3 state corresponding to the triplet intraligand (^{3}IL) transition localized on the phen ligand. By switching off/on SOC and vibronic coupling in the model it is shown that efficient population transfer occurs from the optically active metal-to-ligand-charge-transfer ^{1,3}MLCT states to T_3 and to the lowest long-lived phosphorescent ^{3}MLCT (T_1) state. The early ultrafast SOC-driven decay followed by a T_3/T_1 equilibration underlies the photoluminescent properties of $[Re(CO)_3(phen)(im)]^+$. [(6)]

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Modeling of ring distortion in hexopyranoses

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The conformational rearrangements occurring within the hexopyranose ring are often neglected degree of freedom, due to the assumption that ring-inversion equilibrium is greatly shifted toward one of the chair conformers ($^4C_1$ in the case of hexopyranoses of the d series). This is not necessarily true considering both unfunctionalized hexopyranose monomers (e.g. altrose and idose), functionalized, biologically-relevant hexoses as well as residues in the chain for which there is no quantitative information regarding ring-inversion properties. Although there are many computational methods aimed at determining the favorable conformation of carbohydrates, most of them are not optimized with respect to the shape of the ring. The poster will concern several issues related to the use of computational methodologies that can be applied to accurately determine the ring conformation of various hexopyranoses. First, the comparison of the carbohydrate-dedicated force fields (GROMOS $56a6_{CARBO/CARBO\_R}$) in the context of ring-inversion properties of both monomers and residues in a chain reveals a large quantitative and qualitative diversity between their predictions. Secondly, the application of the semi-empirical potentials (including those carbohydrate-dedicated) in molecular dynamics simulations leads to the results that are in disagreement with both available experimental data and predictions of the biomolecular force fields. Finally, presentation of simple computational approach that combines the data derived from classical molecular dynamics simulations with the high-level DFT calculations in order to provide the results that are in agreement with both the NMR measurements and the semi-empirical schemes by Angyal and Rao. The results are in the context of the topology of the hexopyranose residue and how this topology affects ring-inversion properties of the considered residue.

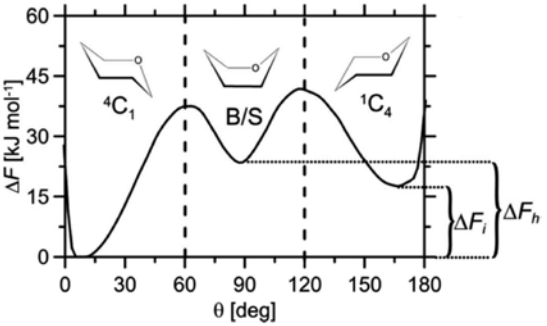

Figure 1. Illustrative free energy (D*Fi*) profile, along the Cremer-Pople θ parameter corresponding to the unfunctionalized α-d-glucopyranose monomer, calculated within the $56A6_{CARBO}$ force field. The course of the profile (three free energy minima and two free energy barriers) is typical for all hexopyranoses; the dashed vertical lines at θ = 60° and 120° separate the three free-energy basins corresponding to the regular chair ($^4C_1$), boat/skew-boat (B/S) and inverted-chair ($^1C_4$) conformers.

Clarifying the Mechanism of the 2-Hydroxypyridine/2-Pyridone Photo-tautomerization.

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The tautomeric mechanisms have been subject to extensive research. Particularly the lactim-lactam tautomerism has been widely studied because of its presence in many biological systems such as nucleic acids. In fact, due to the possibility of photo-chemical damage in the secondary structure of the DNA and RNA, the understanding of this intramolecular proton-transfer (PT) subjected to radiation becomes essential [(1)]. The photo-tautomerism of the 2-Hydroxypyridine/2-Pyridone (2HP/2PY) has been used as a model for those PT reactions unassisted by intramolecular hydrogen bonds and with large energy barriers.

The mechanism for the 2HP/2PY proton transfer proposed by Sobolewski and Adamowicz [(2)] has been assumed to explain this reaction in similar systems [(1) (3)]. They consider this process as a photo-induced PT reaction (PIPT), in which an excited state dissociation of the N-H and O-H bonds along the dark state $\pi\sigma^*$ is followed by a ground-state association. Although the dissociation path, in which the proton moves away from the structure, is well described, its rearrangement has not been deeply explained.

In order to clarify the characteristics of this process, a theoretical analysis of the $\pi\sigma^*$ PES was performed with the MOLCAS software [(4)], using CASSCF and CASPT2 levels of theory and testing different active spaces. A new alternative mechanism was obtained along the hydrogen dissociation, discovering a connection between the $\pi\sigma^*$ PES of both isomers. In our proposed mechanism there is a direct transference of the hydrogen that takes place only when the hydrogen has begun its dissociation along the $\pi\sigma^*$ state. This new proposal provides answers for the obscure aspects of the process, giving a new perspective for the treatment of PT reactions without intramolecular hydrogen bond.

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Mechanistic investigation Pd catalyzed C-N cross-coupling using ammonia

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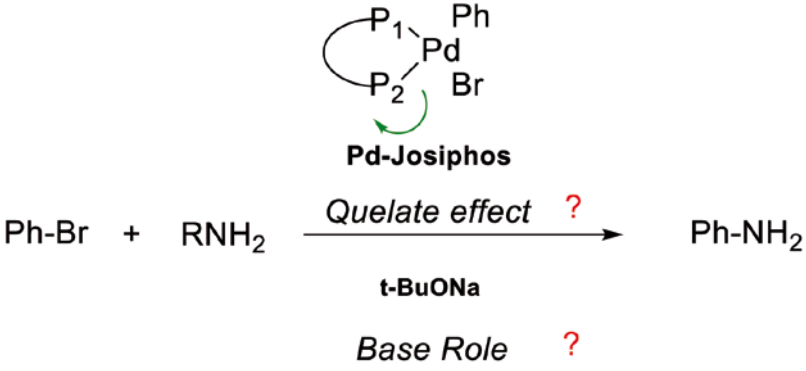
The Buchwald-Hartwig amination[1,2] has been developed to generate N-containing compound. The commonly reactants are primary and secondary amines, whereas the use of ammonia is rather scarce. This is mainly due its high basicity, strong bond N-H bond and small size, but Hartwig group developed a process for the use of NH_3 as reactant. The reaction mechanism for the C-N cross-coupling has been analyzed from both the experimental[3] and theorical[4] point of views.

Following the research line to our group[5,6] about the C-N bond formation, in this work, we studied the reaction mechanism for the Buchwald-Hartwig amination for the particular case of NH3 as reactant. We want to undertand the differences for the reactivity of the primary and secondary amines. The mechanism is analyzed using a Pd bidentate (Josiphos) as catalyst and t-BuONa as base. The challenge is to understand the extent of the chelate effect on the mechanism, which role a strong base is able to play, the behavior of the ammonia and a secondary amines in this particular reaction and comparission of their results.



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Analysis of titanium dioxide surfaces in the water splitting process

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The scenario of environmental and energy issues are important topics at the global level [1]. Several groups have focused their studies on clean and renewable energy, mainly in obtaining hydrogen, to use as fuel, from water splitting [2]. The process of photocatalytic water splitting is very simple, and this is its remarkable point. This simplicity of the process makes it advantageous and attractive for large-scale application, which contributes to sustainable green chemistry. [1]

Titanium dioxide, TiO_2, is a multifunctional semiconductor, which has been used in several areas [3] [4]. At atmospheric pressure exhibit three polymorphs stable: rutile, anatase and brookite. Theses polymorphs show different degrees of chemical reactivity and studies demonstrated that anatase is more reactive when employed for catalysis and photocatalysis applications. In addition, TiO_2 has been also applied in the water splitting [5] and several types of surfaces present in the photocatalyst influence this process. Therefore, a highly detailed study of the different surfaces is necessary to understand the surfaces activities during the process.

In this work, a systematic study of the TiO_2 anatase surfaces and the interaction with water were carried out. The calculations were performed by CRYSTAL14 associated with DFT and B3LYP. The results of water interaction and activity of the surfaces were correlated with experimental data obtained by our group and those found in the literature.

This work was supported by FAPESP (process number 2017/07240-8).

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The catalytic role of water clusters in the formation of acid rain [(1)]

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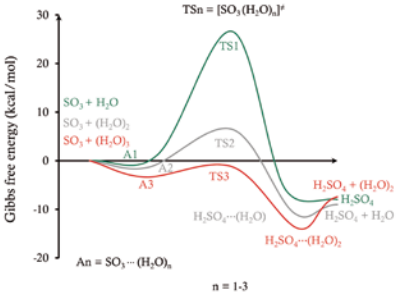
Hydrogen Bond (HB) cooperativity can strongly affect the energetics and structure of molecular clusters. In this work we show that HB cooperative effects, as quantified by modern chemical bonding analyses in real space, can also have a strong influence on reactivity by considering the formation of acid rain through the chemical reaction of SO_3 with the water monomer, dimer and trimer. Our results indicate that surrounding H_2O molecules increase the respective nucleophilic and electrophilic character of the O and S atoms in the Lewis acid base reaction between water and sulphur trioxide which ultimately leads to H_2SO_4. Moreover, our techniques show that the chemical bonding scenario in the reacting molecular cluster and the corresponding transition state is more similar as additional water molecules are included in the system, reducing thereby the activation energy of the rate-limiting step of the whole process. Altogether, this work improves the understanding of the formation of acid rain, a very important phenomenon in atmospheric chemistry.



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Mapping the chemical space of kinase inhibitors

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In the recent years, drug discovery programs rely more-and-more on chemogenomics to systemically screen chemical libraries of small molecules against families of targets. The approach is very costly, therefore, *in silico* methods are strongly desired to predict a compound's virtual biological profile. These tools can be employed to tackle important challenges, such as the discovery of kinase inhibitors with a desirable polypharmacology.

Here, we used a set of carefully designed predictors [(1)] of individual kinase inhibitors to compute biological kinase profiles (BKPs) for large datasets of compounds. The predicted BKPs were used to generate a self-organizing map, allowing the easy navigation through chemical space areas with similar kinome-wide inhibitory activity, and to explore bio-selectivity and highlight promiscuous chemotypes. This novel technology aims to guide the discovery and development of safer and more efficient drugs.

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Assessment of DFT methods for studying olefin metathesis catalysed by molybdenum and tungsten systems

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Computational chemistry is nowadays routinely applied in the field of heterogeneous catalysis. It is helpful in interpretation of experimental results and usually provides complementary description of surface sites and reactions, still not fully available by spectroscopic techniques [(1)] [(2)]. DFT methods, offering a good balance between the accuracy and the cost, are still the best choice for computational catalysis. However, because of so many density functionals available presently, a selection of an adequate DFT method for a given problem is not a trivial task, especially in the case of systems containing transition metals. [(3)] [(4)]

Olefin metathesis is a catalytic reaction of a great importance. Large-scale metathesis processes are carried out over heterogeneous molybdenum or tungsten catalysts [(5)]. The mechanism of olefin metathesis involves breaking and formation of transition metal-carbon and carbon-carbon bonds. Hence, the accurate theoretical description of the catalytic process requires methods which perform well for both transition metals and main group elements.

In this work, a benchmark of DFT methods for energetics of olefin metathesis catalyzed by molybdenum and tungsten systems has been done. In selected cases, the DFT-D3 dispersion corrections are included. The active Mo and W sites of the heterogeneous catalysts are represented by model systems. The key propagation step for ethene metathesis, an addition of ethene to metal methylidene species resulting in metallacyclobutane formation, has been chosen as the test reaction. The reference energy values are calculated on the CCSD(T) level. It is shown that large discrepancies in reaction energies are obtained using different density functionals. On the other hand, among all classes of the DFT methods considered (GGA, meta-GGA, hybrid GGA and hybrid meta-GGA) there are functionals which perform well for the reactions studied.

Acknowledgments: This work was supported by the National Science Centre, Poland, Project. No. 2015/19/B/ST4/01836, and by the PL-Grid Infrastructure.

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Electronic structures of the halogenated organophosphorus compounds: a DFT study

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Organophosphorous compounds (OP) constitute an important class of pesticides. Pesticides and other organic halogenated compounds are known as major environmentally hazardous chemicals. It is estimated that only 5% of the consumed pesticides reach the target pest, the rest is dispersed into the environment [(1)]. The increasing amount of use is significantly increasing the risks of environmental contamination of groundwater, food, plants, water resources and human beings. An increased understanding of the physicochemical and electronic properties involved in the reactions of OP compounds with potential destructants could lead to superior pesticides with greater safety margins [(2)]. Therefore, there is a need for certain molecular descriptors to predict the toxicity of OPs. Quantum-chemical descriptors have become quite popular recently and are widely used to the reliability and accuracy, as well as capability to characterize electronic properties of the molecules. [(3)]

In this study, the structures of 30 halogenated organophosphorous pesticides were investigated theoretically with the intention of finding certain molecular descriptors to predict the toxicity for both gas and aqueous phases. Conformational analyses and geometry optimizations of all the structures were performed to determine the most stable structures. All quantum chemical calculations were carried out at DFT/ B3LYP level of the theory with 6-31G(d) basis set in Gaussian 03W program package. The solvation effects were computed using COSMO as the solvation model. The electronic energies, electron densities, Mullikan charge distributions of the molecules and the DFT reactivity descriptors such as chemical hardness, electronegativity and electrophilicity index for all the molecules were calculated.

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Nuclear quantum effect on hydrogen fluoride trimer studiedby ab initio path integral molecular dynamics simulation

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Hydrogen bonded complexes of the hydrogen fluoride were investigated in various experimental [(1)] and theoretical [(2)] studies of the structures and vibrational spectrum at the equilibrium geometry. However, the effects of quantum fluctuation and thermal activation are not considered in these theoretical studies. In present study, thus, we performed *ab initio* path integral molecular dynamics (PIMD) simulation for the hydrogen fluoride trimer $(HF)_3$ to discuss both the thermal effect and quantum effect.

The *ab initio* PIMD simulation was done in essentially the same way as in the previous works [(3)]. The forces were calculated by MP2/6-31+G(d,2p) level. The PIMD calculation was carried out at temperature T=300 K with the imaginary time slices P=32 (i.e. number of beads) and the step size Dt=0.1 fs. The *ab initio* classical MD simulation has been also executed by the same setting except *P*=1.

Figure 1 (a), (b), and (c) show the equilibrium structure, the representative snapshots for classical MD, and for PIMD, respectively. To see a nuclear quantum effect, we compare the distribution of intermolecular FFF angle (q_{FFF}) in PIMD with that in classical MD in Figure 2(a), truncated in the range from 0 to 120 degrees. The graphs indicate that the nuclear quantum effect enhances the localization with respect to the intermolecular structure at the equilateral triangle as in Figure 1(a), and less distribution of the shape as in Figure 2(b).

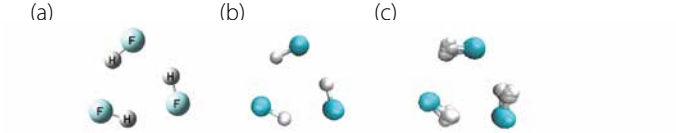

Figure 1. Schematic illustration of HF trimer by (a) conventional MO, (b) classical MD, and (c) ab initio PIMD.

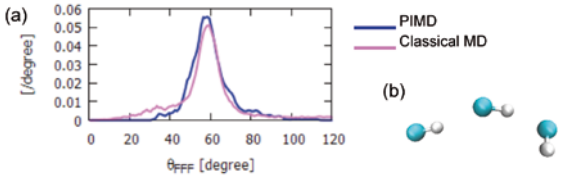

Figure 2. (a) Distribution of q_{FFF} in PIMD and classical MD. (b) A snapshot at q_{FFF} =20° in classical MD.

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DFT computations on the mechanism of flavin oxidative half-reaction

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Flavoproteins are the class of oxidoreductases that catalyze oxidation-reduction reactions and play important roles in the body. For example, monoamine oxidase enzyme (MAO) is a flavoenzyme that regulates the concentrations of neurotransmitter amines such as dopamine, norepinephrine, epinephrine, and serotonin by catalyzing the oxidative deamination of these compounds in the brain. The inhibition of MAO activity prevents the degradation of such amines and provides antidepressant and anti-parkinsonian effects. Like other flavoenzymes, flavin adenine dinucleotide (FAD) is reduced during MAO catalysis. In order to re-activate the enzyme, FAD is re-oxidized by molecular oxygen according to the following reaction.

$E\text{-}FADH_2(reduced) + O_2 \rightarrow E\text{-}FAD(oxidized) + H_2O_2$

Hydrogen peroxide formed as a result of FAD oxidation is known to cause oxidative stress which is an important problem leading to cell function deterioration and even cell death.

The mechanism of flavin reduction in MAO and other flavoenzymes has been studied extensively by experimental and computational methods previously [(1)]. However, information on flavin oxidation mechanism is quite limited [(2) (3)]. The aim of this work is to elucidate the mechanism of oxidation of $FADH_2$ in flavoenzymes by oxygen. Regarding to literature reports, we proposed various singlet and triplet mechanisms on *re*-face and *si*-face of flavin. The stationary points belonging to each step of these mechanisms were optimized and characterized with M06-2X/6-31+G(d,p) method. Based on the calculated activation energies plausible pathways were determined. Understanding the details of the mechanism may help to design future therapeutic approaches about oxidative stress and neurodegeneration.

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Combined plane wave and localized orbital electronic structure calculation

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The demand is growing for more accurate first-principles calculations that are applicable for larger and realistic systems. The hybrid quantum mechanical/molecular mechanics (QM/MM) method (which is used in quantum chemical calculations based on the localized orbital (LO) approach) enables the investigation of chemical processes in larger molecular systems. However, sometimes this approach does not fully reproduce the electronic structure and geometry, such as surface or bulk systems. A large number of application have been reported for plane wave (PW) based first-principles calculations with periodic boundary condition (PBC) for bulk, surface, and interface models. Compared with the LO based approach, the PW based approach can be applied to large systems and can describe the delocalized electrons in a PBC framework. However, it is sometimes difficult to calculate the local electronic structure to the necessary degree of accuracy. In this study, we verify the use of the combined PW and LO approach. As an example, we analyzed the hydrogen adsorption on a Pd(111) surface. [1]

The concept of the combined PW and LO approach is illustrated in Fig. 1. The adsorption properties can be calculated as shown in Eq. (1).

$$E(PW+LO,surface)=E(PW,surface)-E(PW,cluster)+E(LO,cluster) \quad (1)$$

Figure 2 shows the potential energy surface of the hydrogen adsorption on the Pd(111) surface. We clearly demonstrated that the combined PW and LO approach is both effective and necessary to determine local surface phenomena. We expect that the proposed approach will be effective for a broad range of applications in the material science field.

The activities of Advanced Automotive Research Collaborative Laboratory at Hiroshima University are supported by Mazda Motor Corporation, Japan.

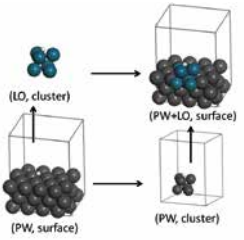

Figure 1. Concep ilustration of the combined PW and LO approach.

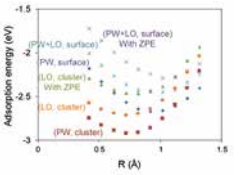

Figure 2. Potential energy surface of a hydrogen atom adsorption onto a fcc site on a Pd(111) surface.

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Palladium catalysed conversion of cyclic vinyl carbonates to allylic amines: a DFT study

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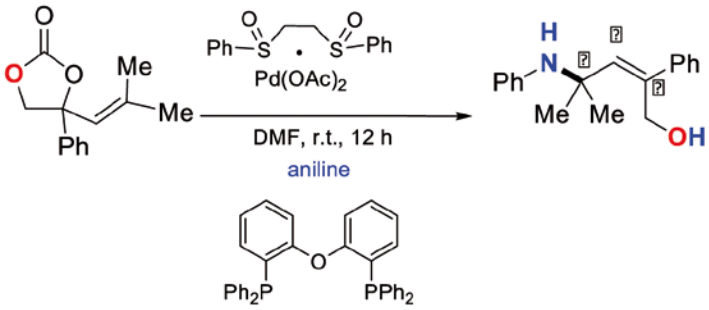
Allylic amines, representing a class of functional olefins, are fundamental building blocks in organic chemistry, and their synthesis is an important industrial and synthetic goal.[1] Significant progress has been observed in recent years in the synthesis of allylic amines which has limited potential to introduce three or four different substituents.[2]

Pd-catalyzed conversion of allyl surrogates which are readily obtained from cyclic vinyl carbonates to multisubstituted allylic amines are characterized by excellent stereoselectivity, operational simplicity, mild reaction conditions, and wide scope in reaction partners.[3] DFT studies were performed to rationalize the stereocontrol in these allylic amine formation reactions, and evidence is provided that the formation of a six-membered palladacyclic intermediate leads toward the formation of (Z)-configured allylic amine products.



Scheme 1. Conversion of cyclic vinyl carbonates to allylic amines

The detailed mechanism for the palladium catalyzed conversion of cyclic vinyl carbonates to allylic amines will be presented.

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Electronic excited states equilibrium geometries of molecules presenting an excited state proton transfer

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In recent years, the performance of TDDFT for the calculation of the vertical excitation energies and oscillator strengths has been extensively studied but huge differences can be found between different exchange-correlation functionals. On the other hand, few studies were carried on the quality of this method for the description of properties of electronically excited states. In the current work, we present a comparison of excited state geometries of 3 molecules: the salicylideneaniline (SaOH), the 2-(2'-hydroxyphenyl)benzothiazol (HBT), the 3-hydroxychromone (3-HC). All of them are characterized by intramolecular proton transfer at the excited state (ESIPT). A comparison is carried out at the CC2 and at TDDFT level with the B3LYP, B3LYP-35 (B3LYP with 35% HF-exchange), M06, M06-2X, CAM-B3LYP and LC-BLYP exchange correlation functionals.

Chymotrypsin-like activity inhibition model of human 20s proteasome

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Proteasome is a major component of a non-lysosomal proteolysis system. Eukaryotic proteasomes are unusually large protein complexes with characteristic sets of subunits and have been classified into two isoforms with apparent sedimentation coefficients of 20S and 26S, respectively. The eukaryotic 20S proteasome has the molecular mass of about 700 kDa and consists of 28 protein subunits, which are organized as four stacked rings of seven subunits each. The β chains contain a total of six catalytic sites with three distinct substrate specificities: caspase-like (β1), trypsin-like (β2), and chymotrypsin-like (β5) [(1)]. The goal of this project is to create all-atom dynamic models of the substrate- and inhibitor-bound chymotrypsin-like activity center. For these studies, molecular dynamics simulations with the all-atom AMBER16 force field and AUTODOCK 4.0 program were used. The simulations were started from the human proteasome crystal structures [(2)] [(3)] [(4)] determined recently. The possible inhibition mechanism deduced based on the simulations with selected inhibitors will be presented and discussed.

Acknowledgments: Supported by grant BMN 2017 from the University of Gdańsk. The calculations were carried out on the 488-processor Beowulf cluster at the Faculty of Chemistry, University of Gdańsk and in the Academic Computer Centre (TASK) in Gdańsk, Poland.

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Ab initio Molecular Dynamics Studies of Hydrated Magnesium, Calcium and Strontium Hydroxides

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An important problem in the nuclear power industry in the UK is the reprocessing of the legacy waste storage ponds at Sellafield in Cumbria. Understanding the solvation structure of the radionuclides present in these ponds, as well as the stability of their hydroxide and carbonate complexes is vital for effective reprocessing [(1) (2)]. Our work improves on our current understanding of these complexes, previously only studied with gas phase or implicitly solvated density functional theory (DFT), through the use of *ab initio* molecular dynamics simulations, thereby aiding the characterisation, and potentially reprocessing of, the waste present in the storage ponds.

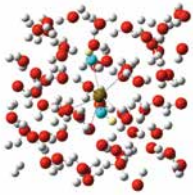

Figure 1. Snapshot of a solvated strontium dihydroxide complex. Two OH^- ions are highlighted.

To establish an accurate solvation model, this study employed *ab initio* molecular dynamics to investigate the interactions of Mg^{2+}, Ca^{2+} and Sr^{2+} ions with water. The properties of the first solvation shell have been categorised, including average metal oxygen bond length, total coordination number and the accompanying residence times. When compared to current experimental and computational literature excellent agreement is found, justifying the solvation model developed.

Additionally, two hydroxide ions were introduced into the hydrated ion system to mimic the alkaline properties of the storage ponds. Previous DFT simulations found little energetic difference between mono and di-hydroxide systems, with only a small (~ 3kJ/mol) barrier between the two.[3] Our results indicate a preference for a mono-hydroxide structure for magnesium, while the hydroxide ions prefer to exist outside of the first coordination shell for calcium and strontium. We have also studied the movement of hydroxide via proton transfer through these systems, finding that proton transfer occurs frequently and is more likely outside of the first coordination shell.

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Theoretical investigation of CO catalytic oxidation by Fe-$PtSe_2$ monolayer

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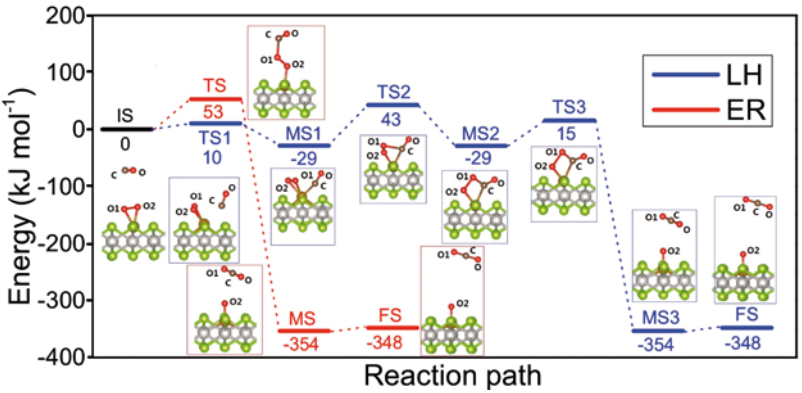
The CO oxidation under mild conditions [(1)] is investigated computationally for the catalysts based on a single transition metal (Sc-Zn) embedded at the Se vacancy of $PtSe_2$ monolayer [(2)]. The iron-embedded Fe-$PtSe_2$ monolayer is identified as the most suitable catalyst among the investigated systems. Both, Langmuir-Hinshelwood (LH) and Eley-Ridel (ER) reaction paths were considered for the CO oxidation by adsorbed O_2 molecule and by adsorbed O atom. The CO oxidation by O atom bound to Fe-$PtSe_2$ proceeds via the ER mechanism in the single reaction step with small activation barrier (21 kJ mol^{-1}). Both LH and ER reaction mechanisms can take place for CO oxidation by adsorbed O_2 molecule. Whereas the barrier for rate-determining step of the LH reaction path (72 kJ mol^{-1}) is higher than that for the ER path (53 kJ mol^{-1}), the kinetics analysis shows that both processes have comparable rate constants at 300 K. Langmuir-Hinshelwood mechanism becomes dominant at a lower temperature. Results reported here indicate that the Fe-$PtSe_2$ catalyst can efficiently catalyze CO oxidation under mild conditions.



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Phenylacetylene and styrene adsorption on Pd(111): a relativistic DFT study

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Phenylacetylene (PA) removal by semihydrogenation is a process of great industrial importance because PA is a poisoning impurity in styrene (St) feedstock, causing deactivation of the St polymerization catalyst. Palladium is one of the most frequently used metals in the semihydrogenation because of its high ability to selective hydrogenation of alkynes to alkenes. Quantum chemical calculations can be very useful in understanding the interaction of PA and St molecules with metal surfaces. An advantage of theoretical studies is that they allow for the straightforward determination of binding energies for a range of different adsorption structures, information that is difficult to measure experimentally. This information can be used to achieve the better understanding of reactant-catalyst interactions, which in turn can help explain trends in catalytic behavior. In this work we present a theoretical study of PA and St adsorption on Pd(111) surface.

All-electron DFT calculations were performed with the PRIRODA software[1]. The PBE96 functional and L11 basis set[2] were used. Relativistic effects were taken into account in terms of a scalar-relativistic approach. The Pd (111) surface model was built using a two-layer Pd_{30} cluster.

The calculations indicate that the most stable PA adsorption structure is a threefold perpendicular-bridge configuration. The PA molecule can interact with Pd surface with benzene ring participation and without it. The adsorption of PA on the Pd(111) both in the presence and in the absence of preadsorbed hydrogen is thermodynamically more preferable than the adsorption of St.

The work was supported by the Russian Foundation for Basic Research (Project No. 16-33-60190).

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Enantio- and Regioselectivity of Arylation Reactions with Sulfoxides: Computational Studies Shed the Light on the Mechanism

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The quantum chemical calculations suggest a mechanism for the newly reported arylation of ynamides and thioalkynes with chiral sulfoxides [1]. The first example of a general 1,4-chirality transfer from sulfur to carbon via [3,3]-sigmatropic rearrangement is explored by modern theoretical methods in the present study. The computations explain the experimentally observed correlation of the enantioselectivity with both the catalyst and the substrate. The dependence of the regioselectivity on the tested sulfoxide is also clarified. Moreover, the suggested theoretical model can be applied to design new arylation reactions of chiral sulfoxides with higher enantio- and regioselectivity.

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On the role of the base in the nickel-catalyzed borylation reaction of aryl fluorides: a computational and microkinetic study

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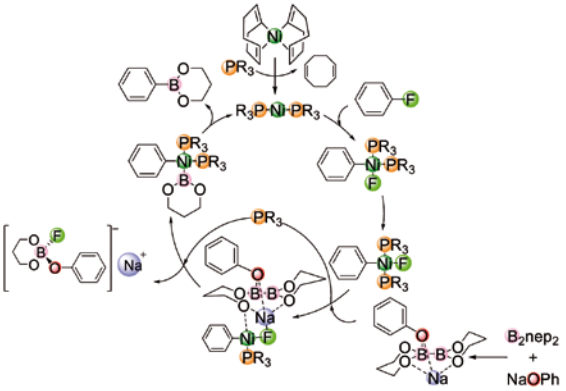
Martin and coworkers reported recently an efficient Ni catalyzed C-B bond formation reaction through C-F bond activation of aryl fluorides [(1)]. The reaction mechanism is basically understood as the well-known Cross-Coupling mechanism [(2)]: thus C-F oxidative addition, F/B transmetallation, and C-B reductive elimination steps. However, the subtle reaction requirements in terms of phosphine, diboron reagent, and sodium phenolate as a base suggested the possibility of a more complex situation.

We have carried out a DFT study with different methods in order to shed light to this mechanism computationally. Also, we have developed the microkinetical model for this reaction. Our results (see Figure below) confirm that the system is more sophisticated than they have been proposed previously. There are a previous diboron activation with the base forming and adduct that gives stability to all the posterior complexes. This type of adduct have been reported by some authors recently. [(3-5)]



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Photoelectron spectra from optimally tuned TDDFT and Dyson orbital formalism

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Photoelectron spectroscopy is a popular tool to probe the electronic structure of matter in different states of aggregation. To assign and understand experimental photoelectron spectra, which are usually rich of features, application of advanced theoretical modelling is required. In the present work, we compare the popular approach for interpretation of spectra considering the molecular orbital density of states based on Koopmans' theorem with the Dyson orbital formalism. The latter is applied both in the sudden approximation[1] as well as the in the form where full integration with outgoing photoelectron wave function is employed[2, 3].

As the electronic structure theory we use linear-response time-dependent density functional theory (TDDFT) and thus the underlying exchange-correlation functional is important for the quality of the results. We study its influence by comparing results of the widely used functionals BLYP and B3LYP against those obtained with optimally-tuned long-range separated density functional[4]. In the latter scheme, two range-separation parameters tuning the contributions of the DFT-exchange and Hartree-Fock exchange are optimized in an ab initio-scheme to fulfilKoopmans' theorem and the derivative discontinuity condition[5]. The performance of different methods is exemplified for (in)organic and metallo-organic molecules belonging to various classes possessing notably different electronic structure.

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Development Of Interaction Potentials For Designing New Heterocycle-Containing Molecular Rings For Carbon Capture And Storage

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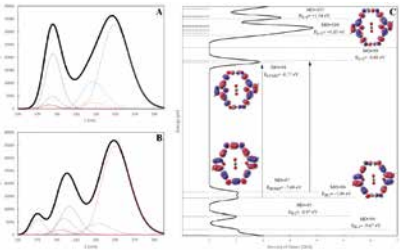
The selective adsorption and capture of CO_2 is a critical issue in both environment and petrochemistry-related technological processes. Traditionally amine sorbents were used for this purpose, requiring high operational costs to regenerate them due to the considerable amount of energy required . To avoid the use of amines, new porous crystalline materials such as MOFs and ZIFs, covalent organic structures and other structures with exceptionally rich host-guest chemistry have been designed[(2)(3)]. In order to have materials with high CO_2 uptake properties, strong interactions must arise between the gas molecule and the solid framework and this can only be efficiently achieved by gaining deeper knowledge of the electronic structure of the complexes.



Based on our recently developed interaction potentials between CO_2 and different heterocycles derived from furan, thiophene and pyrrole substituted with different number of N atoms, and knowing the orientations and distances that are more favorable, in the present work we have designed a series of molecular rings aimed at the capture and storage of CO_2. The binding energies for these complexes have been calculated with highly accurate methods and their trends rationalized in terms of aromaticity, charges or topology of the electron density. Likewise, we have analysed their selectivity against 18 common gases including the most abundant industrial pollutants (NO_2, CS_2, H_2S...). Finally, the use of UV-Vis spectroscopy is evaluated in order to be able to differentiate between the different rings and also to discriminate the presence of a guest inside them.

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Tuning Electronic Factors Controlling Oxidative Addition of Ammonia N-H Bond to Ir(I) PXP Pincer Complexes

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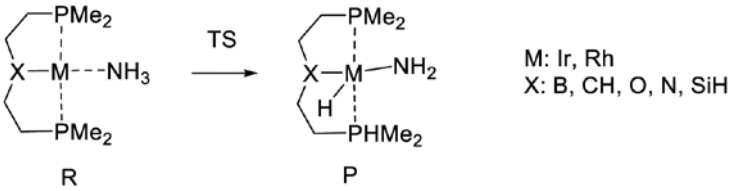
The oxidative addition of ammonia by transition metal complexes is a challenging reaction that would open new catalytic ways for olefin hydroamination processes under mild conditions. Although some paradigmatic examples are reported in the literature [(1) (2)] the formation of metal-amido parent species are rare and scarce and their electronic features have not been characterized properly.

In this work, a comprehensive analysis of the electronic factors controling oxidative addition of ammonia to the metal (Ir or Rh) for some pincer PXP complexes (X = B, Si, C, O, N) is presented using different theoretical methodologies. The electron localization analysis (ELF) provides an understanding for the sequence of bond formation/cleavage by revealing the changes on electron pairing along the reaction path. Hence, it is found that metal oxidation from M(I) to M(III) takes place at the transition structure influencing the calculated activation energies. The electrostatic interaction between the X atom and the metal is a key factor controlling the energetic barrier as shown by the interacting quantum atoms (IQA) method. The reaction energy depends on the trans influence of the X atom. The formed metal-amido product presents some degree of double bond character, depending on the nature of the X atom, as it is shown by NBO or bond order indices.



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Chemical and structural efects of inhibitor molecules on influenza a virus m2 protein channel

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M2 protein of *influenza A* virus plays a vital role in virus' life cycle. N-terminal residues (amino acids 1-23) enable the virus to interact with host, C-terminal amino acids are needed for proliferation, and amino acids 23-46 form the trans membrane helical region functioning as proton channel, which assists the protonation of virus interior and the transfer of virus DNA into (human) host [1-3]. In the channel His37 residues act as a pH sensor, changing their protonation states at low/high pH leading to opening and closing of channel, and Trp41 and Asp44 residues operate as proton gates. [4]

Binding sites for two commercial inhibitors of this channel, rimantadine (RIM) and amantadine (AMA), chemical and structural effects of binding on the proton channel are still under debate. Recent RIM bound NMR structure revealed structure with ligand bound outside of the channel, opposite of previously identified binding pocket inside the channel,[4] intensifying the debate. Chemical effect of inhibitor binding on protonation states of His37 residues has not been clearly observed, as well.

By combination of molecular docking, classical molecular dynamics (MD), and constant pH MD simulations, we identified novel binding sites for RIM and AMA molecules on M2 channel structural alterations occurred upon ligand binding. Furthermore, we investigated the change in the protonation states of His37 and Asp44 residues upon ligand binding and observed the chemical effect of ligand binding directly, which will improve our understanding on the channel inhibition and lead to design of more efficient next generation influenza inhibitors.

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Pyranose ring puckering in aldopentoses, ketohexoses and deoxyaldohexoses. A molecular dynamics study

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An overwhelming majority of the theoretical studies concerning the shape of pyranose ring is focused on the eight standard aldohexoses of the D series (including their derivatives and particular anomers). However, there exists a number of other compounds that contain pyranose ring in their structures (e.g. ketohexoses in pyranose form, aldopentoses or deoxy- and dideoxy- derivatives of aldohexopyranoses). See **Fig. 1.** for the structures of the considered compounds. Here we apply the enhanced-sampling molecular dynamics simulations within the GROMOS 56a6CARBO force field to quantitatively assess the ring-inversion properties of these compounds. These properties are expressed in terms of both the chair-chair and chair-boat/skew-boat inversion free energies. We concluded that in the case of deoxy- and dideoxy aldohexopyranoses the preferred ring shape is determined by the series of the considered compound (i.e. D vs. L). The expected relation between the favorable ring conformation and the chemical structure is not always fulfilled in the case of ketohexopyranoses (where β-D-sorbopyranose prefers the $^4C_1$ ring shape instead of the $^1C_4$ one) as well as for aldopentoses (where most of the compounds exhibit a very large degree of ring flexibility). The results are complemented by calculations of the rotamer populations with respect to the exocyclic lactol and hydroxymethyl functional groups and the anomeric equilibria in aqueous solution.

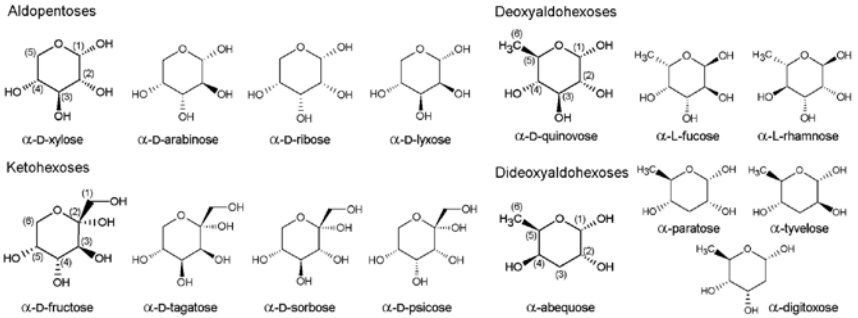

Fig. 1. The chemical structure of compounds considered in the study. Only the α anomers are shown for the same of clarity.

Peptide bond formation catalysed by tio$_2$ (101) anatase surface

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The interaction of biomolecules with mineral surfaces is a topic of extraordinary relevance, due to its broad application in many fields [1]. In particular, the adsorption of amino acids on mineral surfaces is of interest in the prebiotic chemistry field, because they can protect and concentrate amino acids, and also catalyse the condensation reaction among them to form oligopeptides [2]; both experimental and computational works confirm this theory [3] [4]. Within this context titania acting as adsorbent surface plays a fundamental role due to its natural large abundance [5]. Several reactions about the peptide bond formation between two glycine molecules adsorbed on the TiO_2 (101) anatase surface were studied, by means of periodic DFT calculations using the VASP code (see Figure 1). In particular, we decided to focus on three main aspects: i) the effect of the surface as reaction catalyst, ii) the presence of water molecules that may assist the proton transfer between the amino group and the carboxyl group and iii) the adsorption states of the initial amino acids.

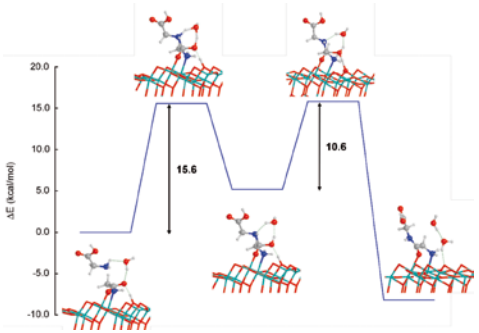

Figure 1. PBE-D2* optimized geometries for the water assisted reaction: Gly +Gly + H_2O → Digly + $2H_2O$.

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A DFT study on the electronic configuration and optical properties of apigenin and its Cu^{2+} coordination complex

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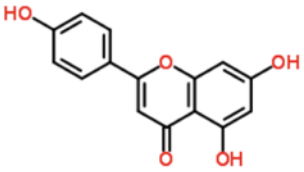
Flavonoids are a class of secondary plant phenolics with significant antioxidant properties [(1)]. They are colored compounds, and have specific absorption bands in the UV/Vis region. These absorption bands are attributed to HOMO-LUMO energy gaps. After coordination with metal cations, the UV spectra change, displaying a bathochromic shift that is attributed to strong Ligand to Metal Charge Transfer (LMCT) or to a decrease in the HOMO-LUMO gas, depending on the author. [(2)]

In the current work, a study on the photophysics of one flavonoid, apigenin (5,7-Dihydroxy-2-(4-hydroxyphenyl)-4H-chromen-4-one, see figure below) is done and its UV/Vis spectra is obtained.

Molecular structures of apigenin and its possible ESIPT tautomer are optimized at the ωB97X-D/6-311++G(2d,2p)//C-PCM (water) level [(3)], and the electronic configuration and optical properties are studied with Time-Dependent Density Functional Theory (TD-DFT). [(4)]

The effect of chelation with Cu^{2+} on the photophysical properties of apigenin is analyzed as well, and experimental UV/Vis spectra are compared with theoretical ones.



Acknowledgements: Authors are grateful to University of Jaén (UJA) and *Andalusian Government (Junta de Andalucía)* for financial support, and to *Centro de Servicios de Informática y Redes de Comunicaciones (CSIRC)*, for computational time and facilities.

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Modelling the interactions at surfaces

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Metal surfaces of beryllium and tungsten feature in important parts of nuclear fusion devices currently being build (ITER) and planned (DEMO). They can undergo various transformation and alloys of these metals can form upon operation of the devices. It is therefore of interest to look at these materials from the perspective of theoretical atomistic materials science. This starts with quantum chemical calculation and can go up the multiscale ladder to differential equation codes [(1)] or kinetic Monte Carlo [(2)] and other higher-level treatments that incorporate realistic geometries and environments.

Binding energies of surface atoms are related to materials stability. Quantum chemical calculations give values of 4.08-5.63 eV for beryllium and 6.81-10.04 eV for tungsten were obtained [(3)] from large scale calculations using plane-wave DFT calculations with the VASP code. An analytical force field of the bond order potential type [(4)] agrees with these values for beryllium, but some of the tungsten surface atoms are too strongly bound. Alloys are naturally more complicated. Be and W atoms on the (001) surface of $Be_{12}W$ are slightly less bound than on the pure Be and W surfaces, respectively. For higher tungsten content, i.e. for Be_2W (figure 1) the situation different surface terminations with several sites each are possible. For some surface sites of this alloy the surface binding energies are enhanced while for others they are diminished, compared to the pure metal surfaces. The cohesive energy of the material is the equivalent of these energies inside the bulk. It is found that its dependency on the mole fraction follows an almost linear relationship.

The complexity of these systems is discussed by giving examples from experimental data and a brief overview of modelling efforts taking place at many laboratories is given.

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DFT study on the structure of Cobalt(II)/(III)-citrate-water coordination complexes

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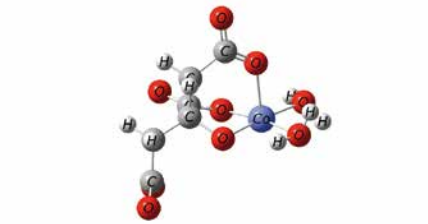
Many biological processes involve metal-ligand coordination complexes where the metal cation can adopt different spin states. In general, the switch from low to high spin states is usually accompanied by a change in metal–ligand bond lengths, in spectroscopic observables, in reactivity and other properties. [(1)]

In the present work, a study within the Density Functional Theory (DFT) of cobalt-citrate-water coordination complexes with different cobalt spin states is carried out. Molecular structures of complexes with a molar ratio of 1:1 metal-ligand are optimized using the B3LYP, M06-2X and ωB97X-D functionals and the Pople's type 6-311++(2d, 2p) basis set [(2)]. In order to simulate aqueous medium three continuum solvation models, PCM-IEF, SMD and C-PCM, are used [(3)], as implemented in Gaussian09 package. [(4)]

Changes in coordination numbers and polyhedra are found (figure below displays one optimized structure), as well as effects on the reactivity of metal cation in Fenton and Haber-Weiss type reactions involved in cellular oxidative stress processes. [(5)]



Acknowledgements. Authors are grateful to *University of Jaén (UJA)* and *Andalusian Government (Junta de Andalucía)* for financial support, and to *Centro de Servicios de Informática y Redes de Comunicaciones (CSIRC)*, for computational time and facilities.

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How does the global electron density transfer diminish $\Delta E^{\neq}$ in polar cycloaddition reactions? An MEDT study

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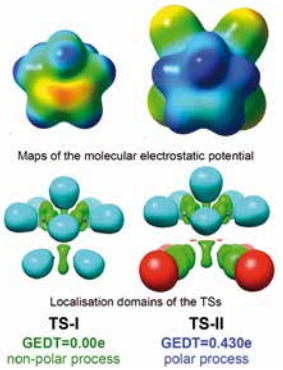
The key role of the global electron density transfer (GEDT) [1] in polar cycloaddition reactions is analysed within the Molecular Electron Density Theory (MEDT) [2] using Density Functional Theory (DFT) calculations at the MPWB1K/6-311G(d) computational level [3]. A comparative MEDT study of the non-polar Diels-Alder reaction between cyclopentadiene (Cp) and ethylene and the polar Diels-Alder reaction between Cp and tetracyanoethylene makes it possible to establish that the GEDT taking place in the direction of the transition state structures (TSs) favours the bonding changes required for the formation of the new C-C single bonds along polar cycloaddition reactions. Analysis of the reactivity indices defined within the conceptual DFT [4] at the ground state of the reagents makes it possible to predict the reactivity of organic molecules in polar reactions.



The GEDT taking place along a polar reaction favours the bonding changes required for the formation of the new C-C single bonds.

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Design of new bioengineered glycosidases for the synthesis of oligosaccharides. Insights from computational calculations

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Glycans are the most abundant organic molecules on Earth and are used in a variety of biotechnological applications. Carbohydrates also play an essential role in many biological processes and modulate the physicochemical properties of the molecules they are linked to.

However, glycans applicability is hindered by their poor availability. Their complex structure (linear or branched) and the similar reactivity of their hydroxyl groups make their chemical synthesis a challenge as it requires meticulous control of both regio- and stereoselectivity. For these reasons, the use of enzymes is very desirable as they can catalyse highly regioselective reactions in water solution, which is very important, especially in the food and pharmaceutical/ cosmetic industries. In Nature, glycan synthesis is mainly performed by glycosyltransferases, but their use is limited by the difficulty of accessing activated sugar donors. Thus, important efforts have been made to design new enzymes for glycan synthesis. These have been mainly based in the modification of glycosidases, which normally catalyse the hydrolysis of the glycosidic bond but, under certain conditions, can be used in the 'reverse' mode for synthesis (transglycosidation). Mutation of glycosidases has produced a series of tranglycosidases or glycosynthases (depending on the mutation strategy followed) [1] [2]. Although their substrates are cheaper to produce and easy to express and purify, transglycosilation usually lacks the high regioselectivities desired.

Our goal is to perform a deep QM(DFT)/MM computational study combined with MD simulations, to understand the molecular basis of these designed synthetic enzymes and to be able to propose new mutations that improve its transglycosylation reaction. We will first focus on GH1 *Thermus thermophillus ß*-glycosidase (TtßGly), as it has been previously shown an increase of 40-50% of its transglycosylation activity in two mutants (N282T, F401S). [3]

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Substituent effect on the reduction tendency and conformation of flavin ring: a DFT study

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Flavin is found in many flavoenzymes and acts as a cofactor in biological redox processes. The mechanism of flavin reduction in several flavoenzymes such as monoamine oxidases (MAO), N-methyltryptophan oxidase, *D*-aminoacid oxidase and lysine-specific demethylase attract attention in recent years because the details of the chemical mechanism of some flavoenzymes are still debated [(1) (2)]. Flavoenzymes have many non-covalent interactions with the isoalloxazine ring of flavin. In 10% of all flavoproteins, flavin ring is covalently bound to protein and the role of covalent flavin is not completely understood [(3) (4)]. In this study, we explore the effect of substituents on the reduction tendency and conformations of the flavin ring to provide new insights into flavin redox chemistry of flavoenzymes. The substituents were chosen so as to represent the flavin C8a covalent linkage in MAO and the N10-covalent bond to triol moeity in FAD.

The oxidized and reduced states of the isoalloxazine rings having different substituents on C8a and N10 were optimized with M06-2X/6-3+1G(d,p) method. Reduction tendencies of substituted flavins were modelled based on the Gibbs free energy of hydrogenation reactions. Optimized conformations of the oxidized and reduced states of the isoalloxazine rings were compared with the experimental crystal structures of various flavoproteins.

The results revealed that the large substituents on N10 decrease the reduction tendency of isoalloxazine ring. Flavin with no N10 substituent but C8a covalent bond to Cys-Tyr linkage exhibits the greatest reduction tendency. Ring conformation is also influenced by the nature of the substituent.

Marmara University Scientific Research Project Commission BAPKO is greatly acknowledged.

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Investigation of rubidium(I) ion solvation in liquid ammonia using qmcf-md simulation and nbo analysis of first solvation shell structure

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Solvated of Rb^+ ion in liquid ammonia has been studied by an ab initio quantum mechanical charge field molecular dynamic (QMCF-MD) simulation. Simulations was performed in 29 Å of side box length at 235,16 K and quantum mechanical calculation employed for 6.4 Å area. Structure of the first solvation shell was evaluated by NBO analysis using LANL2DZ ECP and DZP (Dunning) basisset for Rb^+ ion and ammonia. RDF shows two region of solvation. At the first solvation region, Rb^+ ion can be coordinated by six to ten ammonia molecules. The average distance ion-ligand in solvation shell is of 3.1 Å in accordance with experiment. Within simulation time of 12 ps, frequent exchange processes is occurred. Mean residence time of ligands that less than 2 ps in first solvation shell are indicate for a very labile structure. Wiberg Bond index of NBO of ion-ligand less than 0.05 confirms that interaction is weak.

Keyword: *lability, solvation, simulation , QMCF, NBO.*

Prediction of the Char Formation of Polybenzoxazines: The Effect of Heterogeneities on the Prediction Accuracy

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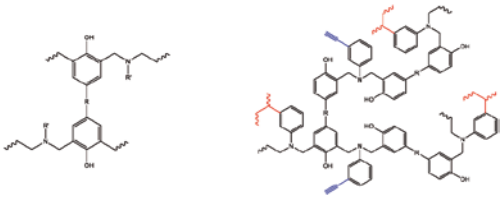
There has been a great demand for improving the thermal stability of materials used for aerospace applications. A report from the National Transportation Safety Board in New York in 1999 revealed that from 1970-1995, 72.5 % of the total fatalities in air crash died from the post-impact incidents with almost all (95.4 %) resulting from smoke inhalation and/or burns. Polybenzoxazines are a relatively new addition to the family of thermoset polymers, but with great potential in fire resistance applications. It can form char yields (the residue remaining when combustion reaches 800 °C) of up to 81 %, compared to only 30-55 % formed by phenolic resins (traditionally used in many aircraft interiors) and 5-15 % char yield formed by epoxies. Benzoxazines polymerise through a ring opening polymerisation reaction to form a highly crosslinked network and the presence of an additional polymerisable functional group in some of the bezoxazines provides further crosslinks in the polymer system (Scheme 1).



Scheme 1. Possible crosslinked system in (left) polybenzoxazines and (right) polybenzoxazines with polymerisable functional group (R and R' = alkyl or phenyl).

A dataset that contains both benzoxazines with and without extra polymerisable functionalities will introduce heterogeneities in the model.The Quantitative Structure-Property Relationships (QSPR) technique (an analogue of Quantitative Structure-Activity Relationships (QSAR)) has been used in this work to investigate the effect of these heterogeneities on the polybenzoxazine char yield prediction model. It was found that the error between a general model, GM (containing both benzoxazines with and without additional polymerisable functional groups) and the specific model (Ace-M and Ani-M) is very small (4.81% *vs.* 3.15%). The ability of GM model prediction was also tested on an additional series of benzoxazines and it performs better than the Van Krevelen group contribution prediction. The GM model is therefore an additional contribution to the polybenzoxazines char yield prediction tool to work along with the well known Van Krevelen method.

Preferential solvation and dynamical properties of Cu^+ ion in 18.6% Aqueous ammonia solution: ab initio quantum mechanical charge field (QMCF) molecular dynamics study

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Preferential solvation and dynamical properties of Cu^+ ion in 18.6% aqueous ammonia solution have been studied using quantum mechanical charge field molecular dynamics (QMCF-MD) simulation. Hartree-Fock (HF) level was used to calculate ion-ligands and ligands-ligands interactions in QM region with LANL2DZ-ECP basis set for the ion and DZP-Dunning for the ligands. QM radius was set to 6.7 Å including a smoothing zone of 0.2 Å. Simulation system was equilibrated at 298.15 K for 4 ps. Simulation trajectory was collected every fifth step during simulation time of 20 ps. The radial distribution function in the first solvation shell showed the maximum probability of the Cu^+-NH_3 and Cu^+-H_2O distances at 2.20 and 2.31 Å respectively. Four NH_3 molecules forming $[Cu(NH_3)_4]^+$ complex was dominated with tetrahedral geometry whereas a distorted tetrahedral $[Cu(NH_3)_3H_2O]^+$ occurred in short time. Mean residence time of NH_3 and H_2O ligand in the first solvation shell were 15.31 ps and 1.09 ps respectively indicating for the stability of NH_3 and high intensity of H_2O ligand exchange processes. Power spectrum of Cu^+-N in first solvation shell was calculated via Fourier transformed velocity auto-correlation function showing maximum of Cu-N peak located at 248.5 cm^{-1} which correspond to the force constant of 41.48 Nm^{-1}. These structural and dynamical properties were found in good agreement to experimental data. [1] [2]

Keywords: 18.6% ammonia solution, Cu^+ ion, QMCF-MD, preferential.

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On the way to finding novel photoinitiated drugs: revealing relaxation mechanisms of modified nucleobases

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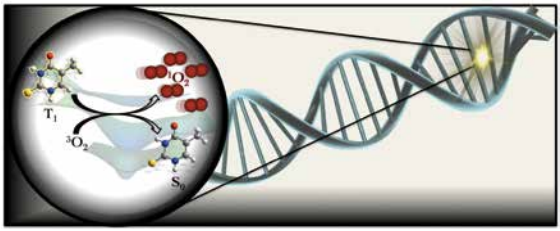
DNA/RNA canonical nucleobases are considered highly photostable systems for their capacity to dissipate absorbed energy, via ultrafast internal conversion to the ground state, preventing possible harm to cells. [1]



A large number of theoretical and experimental studies have, however, demonstrated that minor structural modifications on the substitution pattern of purine or pyrimidine heterocyclic rings, such as carbonyl-by-thiocarbonyl replacement, may lead to radical differences on the photophysical and photochemical properties [2]. In particular, the characteristic topography of the potential energy surfaces of thiobases, favors the population of the triplet manifold with high efficiency upon UV light absorption. From their triplet states, these systems are able to generate DNA-damaging reactive oxygen species which are cytotoxic to cells [3], and thus have been suggested as prototypes for photosensitizers to be used in photodynamic therapy against cancer.

This contribution focuses on the mapping of the decay pathways of thiopyrimidines using state-of-the-art quantum chemical calculations and surface hopping molecular dynamics simulations. Special attention will be paid to the role played by degree and position of the substituents on the relaxation pathways of these systems.

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Influence on antioxidant properties of hydroxyl group substitution in flavone scaffold: a DFT insight

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Flavonoids are a family of secondary metabolites that present protection against cellular oxidative stress by the sequestration of free radicals, as peroxyl, hydroxyl, and methoxy radicals among others [(1)], following the overall reaction

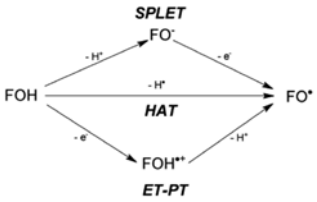
$$FOH + R^{\cdot} \rightarrow FO^{\cdot} + RH$$

This reaction can be divided into three individual mechanisms, the Hydrogen Atom Transfer (HAT), the Electron Transfer–Proton Transfer (ET–PT) and the Sequential Proton Loss Electron Transfer (SPLET) [(2)] (see figure below).

In this work six flavonols, 3,5-dihydroxyflavone, galagin, kaempferol, datiscetin, quercetin, and myricetin, that present hydroxyl substitutions in different positions on the flavone scaffolds, are studied to determine their antioxidant power.

Molecular structures of flavonoids and their anion and radical derivatives are optimized at the ωB97X-D/6-311++G(2d,2p) level in the gas, aqueous and lipidic phases (within the C-PCM solvation model), using Gaussian09 software package. [(3)]

Thermodynamics of the three possible antioxidant channels of flavonoids are studied at the same level of theory.



Acknowledgements. Authors are grateful to *University of Jaén (UJA)* and *Andalusian Government (Junta de Andalucía)* for financial support, and to *Centro de Servicios de Informática y Redes de Comunicaciones (CSIRC)*, for computational time and facilities.

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Effect of central metal ion on the photophysical properties of metallophthalocyanines: a DFT/TDDFT study

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Metallophthalocyanines are effective photocatalysts for the photooxidation of different substrates by molecular oxygen. The key stage of the mechanisms of these processes is the intersystem crossing (ISC), the nonradiative transition between two electronic states of different multiplicity. As is known, ISC rates depend on the energy gap between a given pair of states as well as on the strength of the spin–orbit coupling (SOC), which can be estimated quantitatively by the evaluation of SOC matrix elements.

In this work we report the results of a theoretical study of some photophysical properties for metallophthalocyanines: PcM (M = Zn, Pd) and PcMX (M = Al, Ga, In, X = Cl, OH). Geometry optimization of the metallophthalocyanines in the ground (S_0) and excited (S_1 and T_1) states have been carried out by using the PRIRODA [1] program at DFT and TDDFT levels. The matrix elements of the SOC operator for $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ were calculated in the DALTON program.

On the basis of our results, the following conclusions can be drawn: for all the investigated metallophthalocyanines the computed ΔE_{S-T} energy gaps are sufficient (> 0.98 eV) to excite the molecular oxygen; the triplet excited states T_1 and T_2 are located 0.47-0.73 eV lower than the energy of S_1 state; the sum of square of spin–orbit Cartesian components for the radiationless $S_1 \rightarrow T_1$ and $S_1 \rightarrow T_2$ coupling depends on the nuclear charge of central atom and decreases in the order:

$$PcInX > PcPd > PcZn \sim PcGaX > PcAlX > PcH_2$$

The computational results are in good agreement with experimental data for the singlet oxygen quantum yields.

The work was supported by the Russian Foundation for Basic Research (Project No. 16-29-10674).

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Tuning the strength of the resonance-assisted hydrogen bond in o-hydroxybenzaldehyde by substitution in the aromatic ring

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Intramolecular resonance-assisted hydrogen bonds (RAHBs) are stronger than conventional hydrogen bonds (HBs) thanks to the extra stabilization connected with the partial delocalization of the p-electrons within the HB motif containing conjugated formally single and double bonds. When these conjugated bonds are part of an aromatic ring, there is an interplay between resonance-assisted hydrogen bonding and aromaticity of the ring. The less aromatic the ring, the stronger the RAHB [(1)]. Main aim of the present work is to analyze changes in RAHB strength by substitution in the aromatic ring. For this purpose, we use density functional theory methods to study all possible mono- and di-substitutions in the four free positions of o-hydroxybenzaldehyde considering three electron donating groups (EDG: NH_2, OH, and F) and three electron withdrawing groups (EWG: NO_2, NO, and CN). We show that it is possible to tune the HB bond distance in the RAHB by locating different substituents in given positions of the aromatic ring. Indeed, certain combinations of EDG and EWD result in a reduction or increase of the HB distance by up to 0.06 Å. We also found a direct relationship between the change in the aromaticity of the benzene ring and the strength of the HB. Our results can be explained by considering the existence of a resonance effect of the p-electrons within the HB motif.

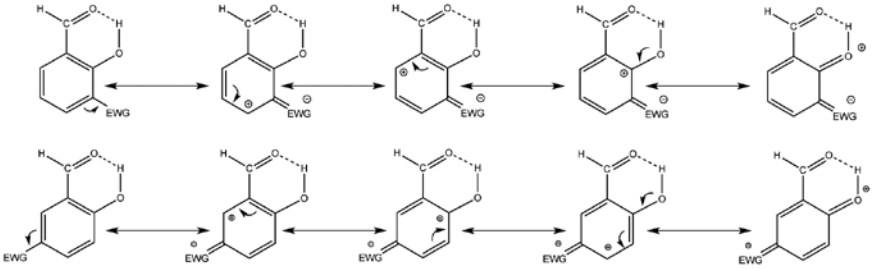

Figure 1. Resonance canonical structures for *o*-hydroxybenzaldehydes substituted in C3 and C5 for EWGs *(meta activation).*

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In silico binding analysis of PGC-1α interaction with peroxisome proliferator-activated recptorα modulaltors

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PPARs (Proliferator-Activated Receptor) have three subtypes of PPARα, PPARγ and PPARδ. Each subtype has a different physiological function. PPARα is a regulator to activate fatty acid oxidation and improve hypertriglyceridemia [(1)]. K-877 is a novel selective PPARα modulator (SPPARMα) to activate PPARα transcriptional activity [(1) (2)]. Here, we theoretically analyzed the complex structure of the ligand binding domain (LBD) of the human PPARα with K-877 and fenofibrate (Feno) based on the first-principles calculations using the Fragment Molecular Orbital (FMO) method [(3) (4)]. The LXXLL motif in PGC-1α consisting of Leu144-XX-Leu147-Leu148 has been described as critical in the PPARγ···PGC-1α interaction [(5)]. Val306 binds directly with several amino acids from PGC-1α via dispersion dominated van der Waals intercations. Interestingly, our first principles interaction analysis reveals quantitative differences in the PGC-1α binding to Val306 depending on whether Feno or K877 are in the LBD of PPARα.This finding may be related to experimntal observation of the importance of Val306 in mutation assays.

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Effect of Stacking Interactions and Conformation Changes on Polymer Polarizability

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The Long-Range Corrected density functionals (LC-DF)[(1)] represent dynamical polarizabilities of medium-sized organic and metal-organic compounds with very good accuracy [(4) (5)]. The functional with 100% of Hartree–Fock (HF) exchange at long-range, LC-BLYP[2], performs best for aromatic compounds and CAM-B3LYP[3] for saturated compounds. These very good benchmark results motivated us to consider optical properties of polymers. If repeat unit models are corrected for end-effects, refractive index and Abbe number of large number of non-conjugated polymers is represented with very good accuracy, for example, for polystyrene (PS), poly(methyl methacrylate) and CYTOP wavelength-dependent refractive indices exceptionally good agreement (rmsd within 0.004) [(6)]. The latter results, as well as some tendency to overestimate refractive index in polymers rich in large aromatic moieties, prompted us to investigate how stacking between aromatic moieties affects polarizability [(7)]. We consider diads (dimers) with aromatic substituents containing six to fourteen π electrons. The stacking of aromatic substituents in meso-*$t\overline{g}$,* racemo-*$t\overline{g}$* and racemo-*tt* conformers causes polarizability reduction relative to meso-***tg*** conformer, in which substituents are situated far away. The polarizability reduction is more pronounced in larger aromatic systems. In PS, the experiment [(8)] and simulations [(9)] suggest that meso-*tg*, racemo-*tg* and racemo-*tt* diads are favored, in which no stacking of phenylenes is observed. Consequently, the refractive index based on (simulated and experimental) diad populations, is practically the same as the monomer-based refractive index, with both values in excellent agreement with the experimental value of 1.592 [(6)]. We extend this analysis to, among others, poly(ethylene terephthalate), for which a nonbonded dimer model similar to that of parallel displaced benzene dimer predicts refractive index in excellent agreement with experiment. From the knowledge of polarizability changes upon stacking, and conformer population, estimation of this effect in condensed systems appears to be possible.

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Mechanistic aspects of the palladium-catalyzed stereoselective synthesis of methylene oxindoles

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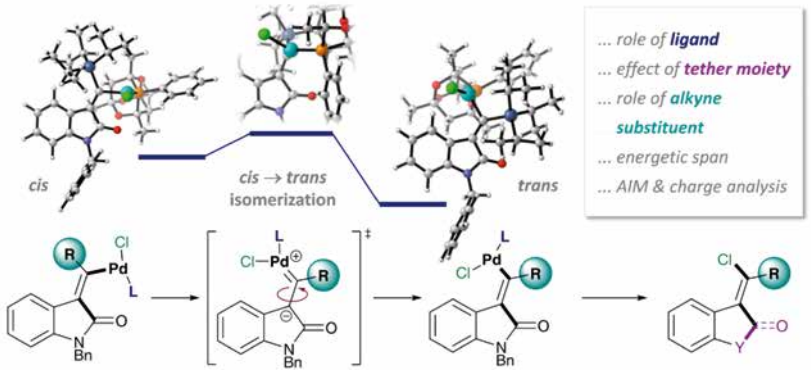
The mechanism of the highly stereoselective Pd-catalyzed synthesis of various methylene oxindoles has been studied computationally and with selected mechanistic test experiments[1-3]. Lautens and co-workers have developed a Pd(0)-catalyzed (*E*)-selective synthesis [1] [2] as well as a complementary (*Z*)-selective Pd(II)-catalyzed method [3] to access the highly valuable methylene oxindole motif. In this presentation we will present our thorough mechanistic analysis of these highly stereo- and regioselective methodologies. Focus is set on elucidating the origins of selectivities. Unique roles of the ligand, tether moiety and alkyne substituents in the substrate were uncovered. State-of-the art QM methods were applied [4-6] and were assisted by experimental tests and verifications of the computational predictions.



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Properties of sigma-hole

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The present study deals with complexes containing halogen bond. In complexes under investigation, halogen bond is formed between positively charged σ-hole on I or Br, and negatively charged O or S atoms. Our trial set contains trifluoroiodomethane formaldehyde and iodobenzene methanethiol and their Br analogues. The structures were taken from work of Řezáč et al. [(1)]

We have focused our attention on the impact of scalar relativistic effects on properties of σ-hole on I and Br atoms, as well as the effect of use of particular atomic orbital basis set. The investigated σ-holes properties were the so-called magnitude and the size, calculated from the correlated electrostatic potential of monomers.

Bromine, and especially Iodine are heavy atoms, thus (scalar) relativistic effects can have non-negligible impacts on various (molecular) properties. Results were obtained using MP2 method. Relativistic effects were treated at DKH2 level, or alternatively (for Iodine) using the effective core potential.

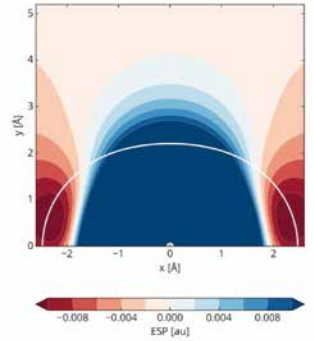

Figure 1. Projection of the electrostatic potential on Iodine.

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Increasing reactivity of aluminum Al_{13}^- clusters towards water by doping with transition metal elements

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Mass spectrometry studies of sodium clusters three decades ago have shown that stability of clusters is fluctuating with size, when some "magic" clusters showed increased stability. This phenomenon was explained by simple shell model [(1)], in which clusters possess electronic shells resulting from quantum confinement of the nearly free valence electrons. An increased stability of the magic clusters can then be explained by closing the incomplete electronic shells (n=2, 8, 18, 20, 34, 40, 58, 68, 70, 92...). Among the Al clusters, anionic icosahedral Al_{13}^- with 40 valence electrons corresponding to closed electronic shell and large HOMO-LUMO gap resembles an inert gas atom [(2)]. In the present DFT study we have investigated how doping elements can change its electronic structure and influence reactivity of $Al_{12}X^-$ clusters towards water. It turned out that crucial parameter to watch is the energy level of LUMO (LUMO+1) of corresponding cluster. Doping by p-elements on right from aluminum does not increase reactivity, since electrons start to fill shells much higher in energy, even though the HOMO-LUMO gap is smaller. On the contrary doping by s-elements on left from aluminum increases reactivity as the 40 electrons shell is still not closed. The largest effect of doping is seen for transition metals which introduce the d-orbitals lower in energy. These predictions might be useful for designing a catalysts for H2 release.

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Path integral simulation on the hyperfine coupling constants of the muoniated and hydrogenated acetone radicals

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A considerable amount of knowledge for muonium (Mu; complex of positive muon and electron) chemistry has been accumulated for over 30 years [1]. Compared with a proton, positive muon (μ+) has a smaller mass and larger magnetic moment. Because of these unique features, Mu is used as the muon spin resonance/rotation/relaxation (μSR), where hyperfine coupling constant (HFCC) is a good index for the magnetic interaction between electron and muon spins.

For instance, the HFCC value of muoniated acetone radical (Mu-ACE, Figure 1) is measured by Percival et al [2] as 10.27 MHz at 300 K (reduced using the proton magnetic moment). However, the reduced HFCC value for Mu-ACE is calculated as -5.8 MHz with the conventional DFT calculation [3], where the quantum effect of nuclei and thermal effect are excluded. In this study, thus, we performed on-the-fly ab initio path integral molecular dynamics (PIMD) simulation [4, 5], which can include these effects, to reproduce the HFCC value of Mu-ACE. We also calculated hydrogenated acetone radical (H-ACE) to compare with Mu-ACE.

Our HFCC values for Mu-ACE and H-ACE are calculated as 32.1 and 3.97 MHz, respectively, which are in reasonable agreement with the corresponding experimental values of 10.3 and 1.51 MHz. Such mass-dependence on HFCC values is due to the large quantum effect of muon. We will also show other results for other muoniated molecular species.

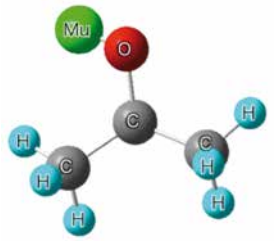

Figure 1. Structure of Mu-ACE.

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A computational study on potential new inhibitors of o-acetylpeptidoglycan esterase

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The mechanism of bacterial resistance to antibiotics has been shown to be an urgent problem by WHO [1]. Peptidoglycan that consists of N-acetylglucosamine (GlcNAc) and N-acetylmuramic acid (MurNAc) monomers linked by a glycosidic β-1-4 linkage is a main component of bacteria cell. The recycling process of a peptidoglycan components of bacterial cell walls is inevitable for their growth. O-Acetylpeptidoglycan esterase 1 (Ape1) enzyme is responsible for the growth and division activities of the bacterial cell wall recycling process. Ape1 enzyme is a member of SGNH hydrolase family where Ser, Gly, Asn and His residues are found absolutely in the catalytic sites of the enzymes. In recent studies, several antraquionone compounds are proposed to be possible inhibitors of Ape1 enzyme [2]. In order to understand the inhibitory effects of several molecules on Ape1 enzyme, a collection of 9 active inhibitor of Ape1 were selected. Molecular docking was performed to study the behaviour of these protein-ligand interactions. Computational docking analysis was performed using AutoDock Vina based on scoring functions [3]. Residues such as Asp79, Ser80, His81, Gly236, Thr267, Asn268, His369 which play important roles in ligand binding was investigated in details. Rescoring of protein ligand interactions using several extracted frames of receptor structure from Molecular Dynamic simulations of 100 ns produced binding scores that were better than the initially docked conformations. The docking scores are in harmony with the experimentally determined K_i values of tested compounds. Furthermore, a ligand library was generated based on quionone structure from Pubchem, Zinc, Chembl Databases. The preparation of multiple-molecules in the library was done by the Software Raccoon [4] and docking scores were calculated with Autodock Vina.

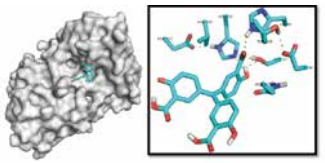

Figure. 3D. Representation of protein-ligand interactions.

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Ab initio calculations on polymononucleotide and polydinucleotides as model of b-type dna polymers

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As an attempts at the electronic structure calculations of the B-type model-DNA, polymononucleotide (poly-(deoxyguanosine) poly-(deoxycytidine)) double helix chain neutralized by Sodium cation Na^+, where the base pair is guanine and cytosine, hereafter referred as (poly-(dG) poly-(dC)), double helix model polymer is performed by means of *ab initio* crystal orbital method adapting the screw axis-symmetry [(1-3)] which results in great reduction of computational efforts. All sugar backbones and ions are included in the calculations. Energy band structures are calculated at 3-21G and 6-31G levels, where the cell wise cutoff method is used for the cutoff method for two electron integrals and all the integrals are exactly calculated up to the nearest 10th neighbors. We also performe almost the same calculations on the four polydinucleotides, (poly-(dA-T) poly-(dA-T)), (poly-(dA-C) poly-(dG-T)), (poly-(dA-G) poly-(dC-T)), and (poly-(dG-C) poly-(dG-C)).

Fig. 1. View of structure of (poly..(dG) polymononucleotide.

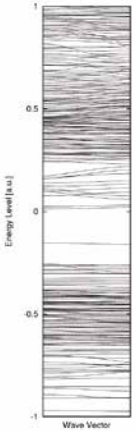

Fig. 2. The energy babnd structure of (poly-(dC) polymono-nucleotide at HF/6-31G level.

Figure 1 shows the structure of (poly-(dG) poly- (dC)) polymononucleotide used for the calculation. The 6-31G energy band structure of this polymer is shown in Fig.2.

It is significant that the bottom of the lowest conduction band at the Gamma point of the first Brillouin zone has almost zero energy value. The effective masses of the hole and electron at the Gamma point is 13.7 and 9.53. Both values are relatively large, therefore, the band conductions are expected not to be effective in this model-DNA backbone.

The effective masses of hole and electron of four polydinucleotides have almost the same values of those of polymononucleotide (poly-(dG) poly-(dC)), therefore, the band conductions are also expected not to be effective in these model-DNA backbones.

We will present more detail of the results at the presentation time.

Acknowledgment: This work was supported by JSPS KAKENHI Grant Number 16K05666.

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Novel Computational Workflow to the Rational Design of PPI Inhibitors. The Challenge of Inhibiting E-cadherin/N-cadherin interactions

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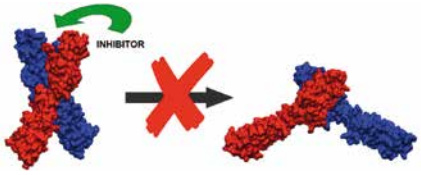
Protein-protein interactions (PPIs) are of importance in biological processes because these interactions play key role in understanding the protein functions and different pathways. The study of protein-protein interactions (PPIs) has been growing for some years now, as well as the rational design of inhibitors, and modulators in general, against them. With this purpose, several computational approaches have been developed, some of them being structure-based. The three-dimensional structure of proteins offers an opportunity for the rational design of small molecules to modulate protein-protein interactions

E-cadherin/N-cadherin interactions can drive cancer processes. Recent findings have shown how these interactions could drive metastasis processes supported by cancer-associated fibroblasts [(1)]. Thus, a molecule suppressing these interactions could become a potential anti-cancer therapy. Up to now, some attempts have done to design new drugs, mostly peptidomimetics, against the interaction between E- and N-cadherins. The most of them were rationally designed using CADD techniques, however, no human E-N cadherin dimer model has been used in the previously conducted studies, partly because of the lack of a human N-cadherin crystallographic model. The absence of a correct model of interaction between human E- and N-cadherins might explain why the drugs proposed to date do not continue moving forward on clinical trials.



Here, we present an accurate an easy-to-use computational workflow to model PPI interactions and to rationally design small-molecule inhibitors against them. This model has been successfully tested in the case of human E-cadherin/N-cadherin interactions.

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Experimental and computational investigations on the Cu(I)-catalysed enantioselective alkynylation of α-ketoesters

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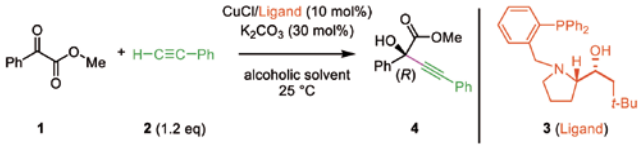
Directionalysed hydrogen bonds often play a key role in stabilizing not only intermediates, and products, but also transition states. Thus, they are very important factors in developing new catalysts for asymmetric synthesis.

This study presents evidence for the enantioselectivity of the reaction of α-ketoesters 1 with terminal alkynes 2, which produces a chiral quaternary carbon center. The synthesis is controlled by copper catalysis utilizing hydroxy amine phosphine ligands 3 to selectively form the product 4 with the *R* stereo center. Reaction yields are up to 99% with enantiomeric excess up to 94%. Potassium carbonate is added to deprotonate the alkyne. The reaction is carried out in alcoholic solvents.

To elucidate the stereo-selective bond formation we have performed a computational study employing density functional theory, which has been evaluated to yield good results in our previous studies. [(1) (2)]

Gibbs activation energies for the most economic reaction pathways are about 11-12 kcal/mol, a reasonable value for a reaction at room temperature. The formation of the *R*-product is favored over the formation of the *S*-alcohol, which is in good agreement with the experimental data (DF-BP86-D3(BJ)-PCM/def2-TZVPP//DF-BP86/def2-SVP). Intramolecular O–H–O hydrogen bonding plays a key role into stabilizing the transition state conformations. A notable secondary interaction arises from a non-classical C–H–O hydrogen bond, which leads to a preference for only a few reaction pathways. This can be quantified with an analysis in terms of the quantum theory of atoms in molecules. The *S* transition state is slightly disfavored compared to the corresponding *R* state, because of the interactions between the phenyl moieties of the reactants.



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Binding of potential lead compounds to *plasmodium falciparum* glucose-6-phosphate dehydrogenase

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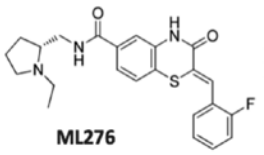
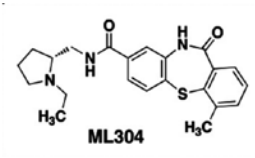
Malaria is a severe infectious disease that caused 212 million cases and 429,000 deaths worldwide during 2015,[1] which makes it necessary to search for novel therapeutic strategies to fight this disease. In this context, we recently started a research project focused on the glucose-6-phosphate dehydrogenase enzyme as a potential target for development of antimalarial agents. Since oxidative stress is a central process in the intraerythrocytic cycle of *Plasmodium falciparum* (*Pf*), the pentose phosphate pathway (PPP) is crucial for both the host and the parasite to neutralize the reactive oxygen species (ROS) through the generation of NADPH.[2] The parasite contains a bifunctional enzyme to catalyze the conversion of glucose-6-phosphate (G6P) to 6-phosphogluconolactone (6PGL) with the concomitant generation of NADPH. This bifunctional enzyme contains a glucose-6-phosphate dehydrogenase domain (G6PD) linked to a 6-phosphogluconolactonase (PGLS) domain, which catalyzes the conversion of G6P to 6PGL.

The presence of a specific mutation (R365D) in the binding site of *Pf*G6PD relative to the human enzyme prompted us to build up a 3D structural model of this domain, which was useful to design a series of a chemically modified substrate analogues that proved to inhibit selectively the parasite enzyme. On the basis of these findings, we pursued the development of novel drug-like compounds with better pharmacological profile. In particular, we determined the binding mode of two compounds described in the literature, ML276 and ML304,[3,4] with known inhibitory activity against the parasite enzyme, and a remarkable selectivity between parasite and human enzymes.





Determination of the binding mode was performed by combining docking and molecular dynamics simulations. This strategy has led to the proposal of a specific binding mode, which permits to provide a rationale for structure-activity relationships in related compounds. This information will be valuable to design novel drug-like selective inhibitors of *Pf*G6PD.

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Conformational distributions of linear alcohols from *ab initio* calculations

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Alcohols show a rich conformational variety associated with internal rotation about C--O and C--C bonds. The conformation problem of alcohols has been investigated over the years using various experimental and theoretical methods, albeit on a molecule-by-molecule basis. Different from previous studies, the present work is conducted from a comparative and systematic perspective, mapping out the low-lying conformers of alcohols with up to 5 carbon atoms. Geometry optimization was performed at the MP2(FC)/cc-pVTZ level of theory, with single-point energies evaluated using CCSD(T)/cc-pVTZ and basis-set corrections at the quintuple-zeta level of complexity. Vibrational contributions to enthalpy and entropy, excluding soft modes, were estimated in the harmonic approximation from potential energy surfaces computed using MP2(FC)/cc-pVTZ. The resulting conformational free energies are of high accuracy, affording useful estimates of conformational populations. For the linear alcohols, it is helpful to consider the relationship between conformations of alcohols that differ by only one CH_2 unit in chain length, exemplified by n-propanol and n-butanol. Such a comparison is facilitated by adopting a systematic notation that specifies the orientation of each dihedral angle along the OC_m chain, in terms of *trans* (abbreviated *t*, corresponding to a dihedral angle near 180°) and *gauche* (abbreviated *g* and *g´*, corresponding to a dihedral angle near plus or minus 60°). In general, we find that relative populations form an inheritary pattern, cf Figure 1. Moreover, although the *trans* orientation is generally favored over *gauche* for each new CCCC angle, the all-trans conformer becomes increasingly irrelevant as the chain length increases, demonstrating conformational entropy at work.

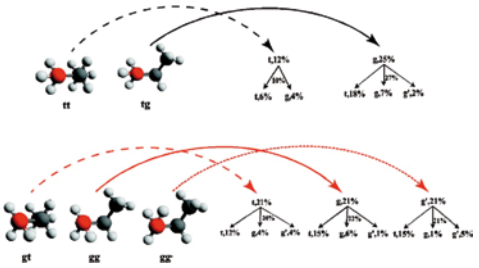

Figure 1. Conformation populations (%) of n-alcohols [1], with the 5 conformers of *n*-propanol shown explicitly. Relative populations in percent are indicated in the right-hand part of the figure.

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In silico binding analysis of novel seective peroxisome proliferator-activated RECPTORα modulaltors (SPPARMA)

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Peroxisome Proliferator-Activated Receptor (PPAR) is a ligand-dependent transcription factor and a member of the nuclear receptor superfamily. PPARs have three subtypes of PPARα, PPARγand PPARδ. Each subtype has a different physiological function. PPARα is a regulator to activate fatty acid oxidation and improve hypertriglyceridemia [(1)]. K-877 is a novel selective PPARα modulator (SPPARMα) to activate PPARα transcriptional activity [(1) (2)]. Here, we theoretically analyzed the complex structure of the ligand binding domain (LBD) of the human PPARα with K-877 and fenofibrate (Feno) based on the first-principles calculations using the Fragment Molecular Orbital (FMO) method [(3) (4)]. Interaction energy analysis between amino acids in the PPARα-LBD and ligands were performed at the level of the RI-MP2/cc-pVDZ to estimate correctly hydrophilic/hydrophobic interactions. Thermodynamic interaction energies between the PPARα and ligands were also evaluated by the molecular dynamics (MD) simulations at the Poisson–Boltzmann Surface Area (PBSA) and Generalized Born Surface Area (GBSA) methods. The binding energy of K-877 to the PPARα is almost twice that of traditional agonist, Fenofibrate. It should be noted that K-877 could bind to the ligand binding pocket of PPARα by using effectively three spherical pharmacophores, while Fenofibrate uses only two.

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Description of PubChemkinina: a comprehensive dataset of kinase inactive compounds

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In many cases, modelling studies suffer from class imbalances [(1) (2)]. Usually, in drug discovery the number of actives against a protein-target is much higher compared to the inactives and several tricks are applied, e.g., to reduce the number of actives by selecting the most potent ones, or the most diverse ones. Also, in validation approaches mimetic or random decoys are used. These approaches are widely encountered and commonly accepted. However, a consistent set of inactives would enhance both modelling and validation.

In a recent study, Bora et al [(3)] compiled a set of 38957 compounds considered generally inactive against kinases. The set has been extracted from PubChem High Throughput Screening (HTS) [(4) (5)] data and has been denominated as PubChemKinIna (freely available in the supporting information of the paper) [(3)]. The authors, employed PubChemKinIna to model and validate kinase inhibitors for classification and virtual screening (www.chembioinf.ro/).

Here, we describe PubChemKinIna inactives in comparison to kinase inhibitors. We show that in terms of simple physico-chemical properties the two sets are similar. PubChemKinIna offers a consistent and chemically diverse set of compounds (6179 chemotypes) which can be used to develop and evaluate virtual screening methods targeting kinases.

Acknowledgments: this work was supported by Project 1.2, Theme 1.2.2 of the Institute of Chemistry Timisoara of the Romanian Academy and by a grant of the Romanian National Authority for Scientific Research and Innovation, CNCS-UEFISCDI, project number PN-II-RU-TE-2014-4-0422.

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A DFT study on the electronic structure and anti- / prooxidant properties of flavonoids: 3,5-dihydroxyflavone and its Cu^{+}, Cu^{2+} and Zn^{2+} coordination complexes

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Flavonoids are a class of secondary plant phenolics with significant antioxidant properties [(1)]. Flavonoids are able to scavenge free radicals directly following the overall reaction

$$FOH + R^{\cdot} \rightarrow FO^{\cdot} + RH$$

This reaction can be divided into three individual mechanisms, the Hydrogen Atom Transfer (HAT), the Electron Transfer–Proton Transfer (ET–PT) and the Sequential Proton Loss Electron Transfer (SPLET) (Figure 1) [(2)]. In literature have been shown that, on one hand, flavonoids-metal cation complexes have better antioxidant activity than parent flavonoids, but, on the other hand, in some cases they present prooxidant activities. [(3)]

In the current work, a study on the electronic structure of one flavonoid, 3,5-dihydroxyflavone (Figure 2), and its oxidation intermediates is presented, and an attempt is made to relate electronic structure and anti-/prooxidant activity. Molecular structures are optimized at the ωB97X-D/6-311++G(2d,2p)//C-PCM (water) level, and electronic structure is described applying NBO methodology and QTAIM [(4)] at the B3LYP/6-311G(d,p) level. The effect of chelation with Cu^{+}, Cu^{2+} and Zn^{2+} metal cations is analysed as well.

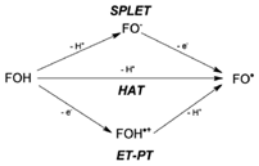

Figura 1

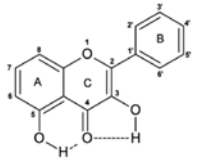

Figura 2

Acknowledgements: Authors are grateful to *University of Jaén (UJA)* and *Andalusian Government (Junta de Andalucía)* for financial support, and to *Centro de Servicios de Informática y Redes de Comunicaciones (CSIRC)*, for computational time and facilities.

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Molecular dynamics studies of a complex system to understand the *modus operandi* of an intrinsically disordered protein

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The Proliferating Cell Nuclear Antigen (PCNA) sliding clamp encircles DNA and tethers together polymerases and other proteins to assemble the DNA replication and repair machinery. One of these proteins, the proliferating-cell-nuclear-antigen-associated factor p15PAF is an intrinsically disordered protein (IDP) in solution but only a very restricted conformational space can sample an interaction with PCNA. We are investigating the PCNA-DNA system [(1)] with p15 to shed light on the universe of IDPs and help redefine the proteins' structure-function paradigm.

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A program to search for adsorption sites in MOFs

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Reticular chemistry approach [(1)] gives the possibility to design porous crystalline solids like MOFs and COFs with valuable physico-chemical properties for applications like separation of gas mixtures, gas storage and catalysis. These potential applications raised a great deal of interest on these compounds during the last two decades [(2)]. The geometry and topology of a pore system define which molecules can be absorbed but to know how strong a molecule will be retained one have to know the strength of intermolecular interactions in the given system. To get knowledge about active centers of sorption, i.e. the sites of a crystalline adsorbent where a molecule forms the strongest interaction, we developed a program written in Python that generates molecular configurations and runs calculation of intermolecular interaction energy using the PIXEL [(3)] method. The results were used for visualization of intermolecular interactions map and subsequent identification of the adsorption sites. The program was successfully applied to the search of adsorption sites in several MOF structures including MOF-5 (Fig.1).

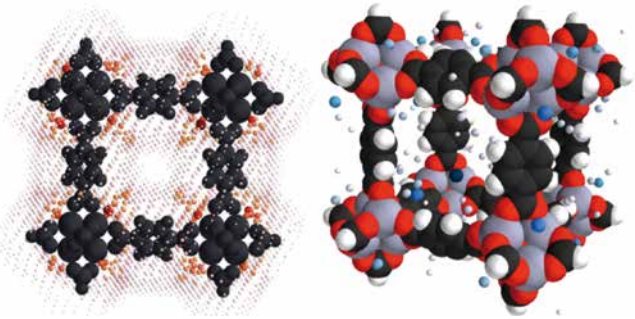

Fig 1. (Left) A visualized interaction energy map of MOF-5 cage fragment with N_2 molecule as adsorbate. Each point corresponds to the position of the N_2 molecule. The size and color of a point are proportional to the calculated interaction energy. (Right) Identified adsorption sites of MOF-5 relative to N_2 molecule. The size and color of the point are proportional to the calculated interaction energy at given adsorption site.

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The state of iron atoms and exchange interactions in $Bi_3Nb_{1-x}Fe_xO_{7-\delta}$

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On the basis of the results of magnetic susceptibility and ESR studies of the $Bi_3Nb_{1-x}Fe_xO_{7-\delta}$ solid solutions iron atoms in the solid solutions of cubic modification of bismuth niobate were found to exist as Fe(III) monomers and exchange bound Fe(III)-O-Fe(III) dimers with antiferro- and ferromagnetic type of superexchange. The exchange parameters and the distribution of monomers and dimers in the solid solutions were calculated as a function of paramagnetic atom content.

Pinpointing DFT performance in the simulations of two-photon absorption spectra of organic chromophores

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Two-photon absorption is the process of simultaneous absorption of two photons via the intermediate state.1 The property in question can be estimated by using the quantum-chemical calculations combined with the accurate response theory2 or the sum-over-states formalism, including various few-level models.3 The latter approaches can be helpful in elucidating the physics behind the nonlinear absorption phenomenon by analyzing the magnitude and orientation of transition dipole moments between particular intermediate states. Therefore, the simulations with the aid of few-level models allow to gain insight into the role of particular excited states in the two-photon activity of a molecule, which constitutes a significant hint in the molecular design of effective two-photon absorbers. Few-level models are most frequently combined with the TD-DFT formalism. However, the vast majority of exchange-correlation functionals suffer from poor predictive power in the field of molecular nonlinear optics.

In this work, we present the assessment of a palette of exchange-correlation functionals in the calculations of two-photon properties for the set of organic chromophores against the coupled-cluster reference data. The focus is put on both electronic and vibrational contributions to the two-photon absorption strengths.4

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The best computational indices for intramolecular hydrogen bond studying, confirmed by experimental observation

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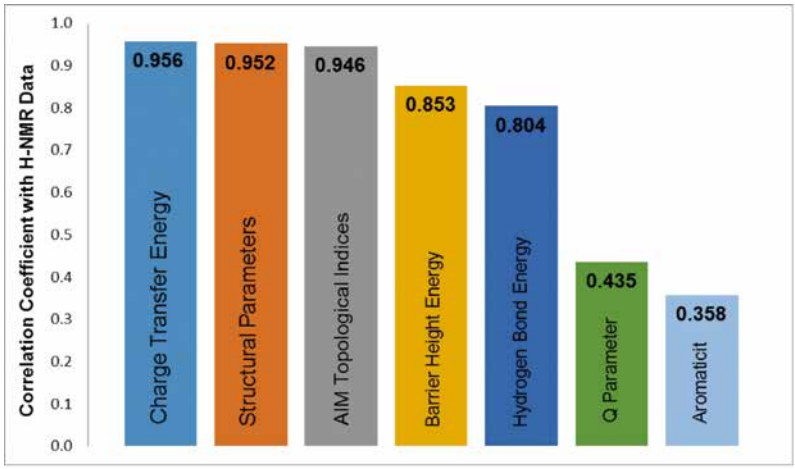
We have analyzed the RAHB (resonance assisted hydrogen bond) concept in enol forms of a series of 16 β-diketone compounds by DFT and AIM computations. Several aromaticity indices as representative for π-electron delocalization (such as HOMA, ATI, FLU, PDI, and multicenter DI) have been computed using different methods and programs. Moreover, variety of indices related to the strength of intramolecular hydrogen bond (IHB), such as, structural parameters, HB energy, energy of barrier height for proton transfer, Gilli's Q parameter, charge transfer energy, inter-orbital interactions, electron density and its laplacian, have been computed. All correlations between different aromaticity and IHB strength indices, showing insufficient coefficient, obviously express that this could not be said that IHB is assisted by electron resonance. These computational results are well confirmed by analyzing H-NMR experimental observation for enolic proton. Investigation on variety of correlations between many different indices shows that there are more efficient parameters, such as, σ-skeleton of compound and inductive effect of functional groups, which influence the IHB strength. The results of our studies, which are confirmed by experimental observations, shows that the best indices for studying IHB, according to the following diagram, are NBO charge transfer energy, structural parameters, and AIM topological indices, showing the best correlation coefficients with observed H-NMR data of enolic proton.



Small molecule binding pathway and kinetics with htmd

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Recent advances in molecular simulations, like efficient sampling and harnessed GPU based simulations, have allowed scientists to investigate slower biological processes than ever before. At Acellera, we have developed powerful tools and protocols for target based drug discovery. **HTMD** is a python based programmable interface for medicinal and computational chemistry groups. Data generation and machine learning analysis are organized in **workflow** increasing reproducibility and providing a **complete workspace** for simulation-based discovery. We show a case study: the small molecule ML056 binding to a Lipid G protein-coupled receptor, using **HTMD** for files preparation/trajectories analysis and **ACEMD** to enhance Molecular Dynamics speed on GPU.

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