

Table of contents

Hylight, a new open-source tool for the luminescence simulation of inorganic materials., Théo Cavignac	3
Ab initio simulations of the hydration of organic compounds relevant to atmospheric aerosols, Rodolphe Pollet [et al.]	4
Frequency dependent conductivity and electrical current fluctuations of confined electrolytes., Minh-Thê Hoang Ngoc [et al.]	5
DFT screening of monovalent and divalent cation embedded faujasite on the selective entrapment of NO and NO ₂ in the presence of H ₂ O, Ioannis Karamanis [et al.]	7
Interpretation of NMR spectra of aqueous systems in porous carbons using lattice simulations, Anagha Sasikumar [et al.]	8
Chemistry and thermodynamic properties of protactinium (V) in aqueous phase by ab initio calculation, Hanna Oher	9
Why Ultrafast Photoinduced CO Desorption Dominates over Oxidation on Ru(0001), Auguste Tetenoire [et al.]	11
Ab initio screening of divalent cations embedded in chabazite for separation operations involving CH ₄ , CO ₂ , H ₂ and N ₂ , Jérôme Rey [et al.]	12
Modelling Absorption Spectra of Furimamide - Nanoluciferase System, Houda Moumene [et al.]	14
Molecular dynamics simulations unravelling the influence of light-activated drugs on a membrane cell model, Anastasiia Delova [et al.]	16
2D proton diffusion in model potentials and assessment of quantum MD methods, Niccolò Avallone	17

Prediction of Lewis acidity of borane derivatives with constrained ligands via Machine Learning, Juliette Fenogli [et al.]	18
Modelling bound and unbound RNA structures using molecular dynamics simulations to unravel the relationship between structure, flexibility and chemical reactivity, Elisa Frezza	19
Study of the bending relaxation of water by collision with Ar using the Rigid Bender Close Coupling treatment, Ricardo Manuel Garcia Vázquez [et al.]	21
Toward a molecular picture of thermal denaturation of RNA duplexes., Aimeric Dabin [et al.]	23
DFT QUANTUM CHEMICAL STUDIES OF LUMINESCENT COPPER (I) COMPOUNDS, Raquel Utrera Melero [et al.]	24
Organolanthanide complexes: ab initio study of electronic structures and rationalization of magnetic properties, Léo La Droitte [et al.]	25
Quantum Chemistry study of chromophores for OLED applications, Maxime Hodée [et al.]	27
Ab initio investigation of the mechanical and electronic properties of bismuth vanadate BiVO ₄ , David Vincent	28
Crucial Role of Conjugation in Monolayer-Protected Metal Clusters with Aromatic Ligands, Hans-Christian Weissker	29
(PdHCu ₁₁ {S ₂ P(OiPr) ₂ } ₆ (C≡CPh) ₄) a hydride-containing 2-electron superatom as electrocatalyst for hydrogen production, Hao Liang	30
Electronic structures and bonding properties of organometallic palladium nanoclusters, Jianyu Wei	32
Author Index	32

Hylight, a new open-source tool for the luminescence simulation of inorganic materials.

Théo Cavignac * ¹

¹ Institut des Matériaux de Nantes Jean Rouxel – Institut de Chimie du CNRS, Centre National de la Recherche Scientifique : UMR6502, Nantes université - UFR des Sciences et des Techniques, Nantes Université - Ecole Polytechnique de l'Université de Nantes – France

In the last ten years, the simulation of luminescence spectra for molecular system has become routine. Periodic solids, however, still stand out of the reach of most of these technics. In this poster we present a novel software, Hylight, that provides a panel of state-of-the-art techniques for the simulation of luminescence spectra in solids. In the form of a Python package, Hylight proposes turn key functions to simulate spectra from VASP outputs, including vibronic coupling in the harmonic approximation. The package also constitutes a toolbox of modular functionalities for methodological developments.

Keywords: Luminescence, Inorganic, Solid, Methodological development

*Speaker

Ab initio simulations of the hydration of organic compounds relevant to atmospheric aerosols

Rodolphe Pollet * ¹, Wutharath Chin

¹ Laboratoire Structure et Dynamique par Résonance Magnétique (LCF) – Nanosciences et Innovation pour les Matériaux, la Biomédecine et l'Énergie (ex SIS2M), Nanosciences et Innovation pour les Matériaux, la Biomédecine et l'Énergie (ex SIS2M) – France

Atmospheric aerosols have a strong impact on the climate and on human health: they can absorb or reflect solar radiations; they play an important role in cloud formation; they contribute to the formation of particle matter which badly affect human health. Carboxylic acids, especially glyoxylic acid and pyruvic acid, are very abundant in marine aerosols. In the aqueous phase, glyoxylic and pyruvic acids adopt two forms in equilibrium: The keto form with two carbonyl groups and the gem-diol form that bears two hydroxyl groups on the same carbon. While the gem-diol form is transparent to solar radiation, the keto moiety is light sensitive, thereby contributing through its photochemistry to the production of larger compounds involved in the formation of secondary organic aerosols. By means of ab-initio simulations well suited to the observation of rare events, our theoretical study on the keto/gem-diol equilibrium sheds light on the hydration mechanism of glyoxylic and pyruvic acids. Our investigation provides a description of the hydrogen-bond arrangements and of their conformational landscape in solution.

Keywords: ab initio molecular dynamics, CPMD, aerosols, dicarbonyl compounds

*Speaker

Frequency dependent conductivity and electrical current fluctuations of confined electrolytes.

Minh-Thê Hoang Ngoc * ¹, Gabriel Stoltz ^{2,3}, Benjamin Rotenberg ⁴

¹ PHysicochimie des Electrolytes et Nanosystèmes Interfaciaux (PHENIX) – Sorbonne Université, CNRS : UMR8234, Sorbonne Université – France

² Centre d’Enseignement et de Recherche en Mathématiques et Calcul Scientifique (CERMICS) – Université Paris Est (UPE), École des Ponts ParisTech (ENPC) – 6 et 8 avenue Blaise Pascal Cité Descartes - Champs sur Marne 77455 Marne la Vallée Cedex 2, France

³ MATHematics for MatERIALS (MATHERIALS) – Inria de Paris, Centre d’Enseignement et de Recherche en Mathématiques et Calcul Scientifique, Centre d’Enseignement et de Recherche en Mathématiques et Calcul Scientifique – France

⁴ PHysicochimie des Electrolytes et Nanosystèmes Interfaciaux (PHENIX) – Institut de Chimie du CNRS, Sorbonne Université, Centre National de la Recherche Scientifique : UMR8234 – Sorbonne Université, Case Courrier 51 4 place Jussieu – 72522 Paris Cedex 5, FRANCE, France

Recent advances in nanopore science and technology promise applications such as high performance batteries or ultra fast DNA sequencing (1-2), but understanding the underlying dynamics remains a crucial step to control the transport of water and ions at the nanoscale (3). Experimentally, the ionic current through single nanopores exhibits generic low-frequency fluctuations, yet a full explanation of the microscopic origins of this "1/f" noise remains elusive (4-5). The frequency dependent conductivity of electrolytes reflects the various timescales that govern the dynamics of the ions. Using Brownian dynamics simulations of model electrolyte solutions(6), we investigate features of nano-confined ionic conductivity spectrum $\sigma(f)$ (7), emerging from the interplay between thermal fluctuations, ionic interactions and nano-confinement. Using equilibrium and non equilibrium simulations techniques, we construct(8-9) frequency responses ranging from 0.1GHz to 1THz, that we compare to analytical predictions from continuous modeling. Brownian dynamics simulations allow us to explore considerably longer time scales than molecular dynamics while conserving sufficient details to understand macroscopic properties of confined ionic transport from microscopic interactions, and to go beyond the scope of approximations used in analytical methods. (1) L. Chanyuan et al., An all-in-one nanopore battery array

Nature Nanotechnology 9, 1031–1039 (2014)

(2) A. H. Laszlo et al., Decoding long nanopore sequencing reads of natural DNA
Nature Biotechnology 32, 829–833 (2014)

(3) N. Kavokine, R. R. Netz, L. Bocquet, Fluids at the Nanoscale: from continuum to sub-continuum, transport

Annual Review of Fluid Mechanics Vol. 53:377-410 (2021)

(4) S. J. Heerema, 1/f noise in graphene nanopores
Nanotechnology 26 074001 (2015)

(5) D. P. Hoogerheide, S. Garaj, J. A. Golovchenko, Probing Surface Charge Fluctuations with Solid-State Nanopores

Physical Review Letter 102, 256804 (2009)

(6) M. Jardat, O. Bernard, P. Turq, G. R. Kneller, Transport coefficients of electrolyte solutions

*Speaker

from Smart

Brownian dynamics simulations

The Journal of chemical physics 110, 7993 (1999)

(7) A. Chandra, B. Bagchi, Frequency dependence of ionic conductivity of electrolyte solutions
J. Chem. Phys. 112, 1876 (2000)

(8) B. Felderhof and R. Jones, Linear response theory of the viscosity of suspensions of spherical
brownian particles.

Physica A: Statistical Mechanics and its Applications 146, 417–432 (1987).

(9) R. Joubaud, G. Pavliotis, and G. Stoltz, Langevin

Keywords: Confined electrolytes, Nanopores, Ionic current, Electrical noise, Brownian dynamics

DFT screening of monovalent and divalent cation embedded faujasite on the selective entrapment of NO and NO₂ in the presence of H₂O

Ioannis Karamanis *^{2,1}, Ayoub Daouli^{† 2,3}, Hubert Monnier^{‡ 1},
Marie-Antoinette Dziurla^{§ 4}, Michael Badawi^{¶ 2}, Guillaume Maurin^{|| 5}

² Laboratoire de Physique et Chimie Théoriques – Université de Lorraine - LPCT UMR CNRS 7019 – France

¹ INRS – Institut national de recherche et de sécurité (Vandoeuvre lès Nancy) – France

³ LS2ME – Polydisciplinary Faculty of Khouribga – Sultan Moulay Slimane University of Beni Mellal – Morocco

⁴ IUT de Moselle-Est – IUT de Moselle-Est, Université de Lorraine, Saint-Avold – France

⁵ Institut Charles Gerhardt Montpellier - Institut de Chimie Moléculaire et des Matériaux de Montpellier – Institut de Chimie du CNRS, Centre National de la Recherche Scientifique : UMR5253, Université de Montpellier, Ecole Nationale Supérieure de Chimie de Montpellier – France

In previous years lots of resources have been invested in the exploration of ways to reduce NO_x (NO and NO₂) emissions from internal engine sources including means of transport. NO_x released by engines in a confined working environment lacking in ventilation and exhaust treatments, represent a major health and safety problem. Solutions have been proposed which can tackle the problem in higher temperatures (> 250 °C) but until that temperature is reached the fumes are free to be released.

To treat this issue, materials that can capture NO_x at low temperatures and release them at higher ones are introduced, the *passive NO_x adsorbers* (PNA). Among other materials, zeolites constitute an attractive contestant because of their good mechanical stability and their porous structures offering high adsorption capacities and capabilities.

In this work, F47 and F23 (FAU with Si/Al = 47 and 23 respectively), Y zeolite (Si/Al = 2.43) and X zeolite (Si/Al = 1.4) exchanged with monovalent and divalent cations have been investigated theoretically, using – the popular nowadays at designing adsorbents(1) – DFT with a sophisticated dispersion correction scheme. Adsorption energies have been obtained for, H₂O and NO_x at 0 K. The selectivity and efficiency of the different cation exchanged structures are explored and taking into consideration the current price of the materials we propose Fe²⁺ as the best option.

Keywords: Si/Al ratio, interaction energy, porous material, DFT, faujasite, cation exchange, NO_x

*Speaker

†Corresponding author:

‡Corresponding author: hubert.monnier@inrs.fr

§Corresponding author:

¶Corresponding author:

||Corresponding author:

Interpretation of NMR spectra of aqueous systems in porous carbons using lattice simulations

Anagha Sasikumar ¹, John Griffin ², Céline Merlet ^{*† 1}

¹ CIRIMAT – CNRS : UMR5085, Université Paul Sabatier - Toulouse III, Institut National Polytechnique de Toulouse - INPT – France

² University of Lancaster – United Kingdom

The performance of porous carbon materials in various applications is highly correlated with their structures and dynamics at the solid/fluid interface. However, the details of the behavior of the ions in the micropores at a molecular scale are not yet well understood. An in-situ NMR approach is a well-suited method to probe the fluids in porous carbons and follow the evolution of the interface at a local level. There are several factors influencing the spectra such as solvation of the species, fluid-carbon interactions, particle size etc, in addition to the structure of the carbon. These multiple factors complicate the process of interpreting the experimental data. Here, we use lattice simulations to predict the NMR spectra of alkali metal chloride aqueous systems in polymer derived carbons and to gauge the importance of various factors involved on the determination of the chemical shifts of the adsorbed species. A carbon particle with a realistic pore size distribution is represented as a collection of slit pores. Inputs from molecular dynamics simulations and density functional theory are used to describe the local adsorption of the fluid and shielding effects due to the carbon respectively. Our investigations show that the chemical shifts of less polarizable ions can be accounted for by the electronic structure of the carbon and ion organization in the pores. For more polarizable ions, the influence of the solvation of the of the ions on the chemical shifts are prominent.

Keywords: porous carbons, NMR, aqueous solutions, adsorption

*Speaker

†Corresponding author: celine.merlet@univ-tlse3.fr

Chemistry and thermodynamic properties of protactinium (V) in aqueous phase by ab initio calculation

Hanna Oher * ¹

¹ Univ Rennes – Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, F-35000 Rennes, France – France

It is of fundamental interest to understand and predict the chemistry of rare radioelements. In this work, we focus on protactinium ($Z = 91$), an element that is located between thorium and uranium in the periodic table. It might be considered as an unpredictable actinide because it behaves differently than any other actinide and in particular its immediate neighbours. For instance, in solution, the +V oxidation state dominates, and related complexes display a mono-oxo bond (thorium would not while uranium would display trans-di-oxo bonds). For the first study, we start with two series of protactinium(V) complexes of similar nature, that have been already experimentally investigated, and that successively form in sulfuric acid and oxalic acidic media (1-3). As experimental information, we may rely on the structure of one of the complexes, determined by EXAFS, and on apparent formation constants. Based on this information, research hypotheses and a preliminary methodological study, we aim at revealing the structure and coordination of all the complexes and at defining a computational strategy to derive relative complexation constants (corresponding to ligand-exchange reactions). For instance, if the formed 1:1, 1:2 and 1:3 (Pa:L) complexes all mutually have similar natures, we may simply derive the relative complexation constants from the global formation constants of both the relevant complexes. Note that owing to the few available computational studies of protactinium complexes and to the near degeneracy of the protactinium $5f$ and $6d$ shells, this study may prove to be quite challenging.

From our computational models, geometry optimizations performed both in the gas phase and in solution lead to a first view of the actual coordination sphere of protactinium(V). It involves an oxygen atom from the Pa=O mono-oxo bond and also oxygen atoms from the bidentate sulfate and oxalate ligands, and in some cases from water molecules. The deduced exchange-ligand formation constants showed good correspondence with experimental trends in the complexes of higher coordination, but our geometrical models could not bring the same accuracy to the values of the complexes of low coordination. This opened a gate for new possible considerations of different chemical compositions for the complexes of 1:1 and 1:2 coordination. The presence of one additional hydroxyl group is found to be very probable and moreover agreed well with the experimental condition of the speciation studies. The final trend in ligand-exchange formation constants showed excellent agreement with experimental trends and made proposed geometrical models to be considered for future experimental speciation studies.

(1) Le Naour C. *et al.* (2019) *Radiochim. Acta*, 107, 979-991.

*Speaker

(2) Le Naour C. *et al.* (2005) *Inorg. Chem.* 44, 9542.

(3) Mendes M. *et al.* (2010) *Inorg. Chem.* 49, 9962-9971.

Keywords: protactinium, formation constants, solvation

Why Ultrafast Photoinduced CO Desorption Dominates over Oxidation on Ru(0001)

Auguste Tetenoire ^{*} ¹, Christopher Ehlert ², J. I. Juaristi ^{1,3,4}, Peter Saalfrank ⁵, Maite Alducin[†] ³

¹ Donostia International Physics Center - DIPC (SPAIN) – Spain

² Heidelberg Institute for Theoretical Studies – Germany

³ Materials Physics Center — Centro de Fisica de Materiales – Spain

⁴ University of the Basque Country/Euskal Herriko Unibertsitatea – Spain

⁵ Institut für chemie, Universität Postdam – Germany

CO oxidation on Ru(0001) is a long-standing example of a reaction that, being thermally forbidden in ultrahigh vacuum, can be activated by femtosecond laser pulses.(1) In spite of its relevance, the precise dynamics of the photoinduced oxidation process as well as the reasons behind the dominant role of the competing CO photodesorption remain unclear.

Here we use ab initio molecular dynamics with electronic friction that account for the highly excited and nonequilibrated system created by the laser to investigate both reactions.(2) Our simulations successfully reproduce the main experimental findings: the existence of photoinduced oxidation and desorption, the large desorption to oxidation branching ratio, and the changes in the O K-edge X-ray absorption spectra attributed to the initial stage of the oxidation process.(3) Now, we are able to monitor in detail the ultrafast CO desorption and CO oxidation occurring in the highly excited system and to disentangle what causes the unexpected inertness to the otherwise energetically favored oxidation.

(1) M. Bonn, S. Funk, C. Hess, D. N. Denzler, C. Stampfl, M. Scheffler, M. Wolf, and G. Ertl, *Science* 285, 1042 (1999).

(2) M. Alducin, N. Camillone, S. Y. Hong, and J. I. Juaristi, *Phys. Rev. Lett.* 123, 1 (2019).

(3) H. Öström, H. Öberg, H. Xin, J. LaRue, M. Beye, M. Dell’Angela, J. Gladh, M. L. Ng, J. A. Sellberg, S. Kaya, G. Mercurio, D. Nordlund, M. Hantschmann, F. Hieke, D. Kühn, W. F. Schlotter, G. L. Dakovski, J. J. Turner, M. P. Minitti, A. Mitra, S. P. Moeller, A. Föhlisch, M. Wolf, W. Wurth, M. Persson, J. K. Nørskov, F. Abild-Pedersen, H. Ogasawara, L. G. M. Pettersson, and A. Nilsson, *Science* 347, 978 (2015).

Keywords: Computational chemistry, Desorption, Oxidation, Electronic friction

*Speaker

†Corresponding author:

Ab initio screening of divalent cations embedded in chabazite for separation operations involving CH₄, CO₂, H₂ and N₂

Jérôme Rey ^{*} ^{2,1}, Ayoub Daouli ^{3,4}, El Hassane Lahrar ⁵, Valentin Valtchev ⁶, Michael Badawi[†] ⁷, Rémy Guillet-Nicolas[‡] ⁸

² Laboratoire catalyse et spectrochimie – Université de Caen Normandie, Ecole Nationale Supérieure d'Ingénieurs de Caen, ENSICAEN CNRS – France

¹ LPCT – Université de Lorraine, CNRS : UMR7019 – France

³ Laboratoire de Physique et Chimie Théoriques (LPCT) – Université de Lorraine : UMR7019, Centre National de la Recherche Scientifique – Boulevard des Aiguillettes - B.P. 70239 F-54506 Vandoeuvre-les-Nancy, France

⁴ Laboratoire de recherche en Science des Matériaux, des Mathématiques et de la Modélisation (LS3M) – Faculté Polydisciplinaire de Khouribga, Khouribga, Morocco

⁵ LCS – Laboratoire Catalyse et Spectrochimie – France

⁶ Laboratoire Catalyse et Spectrochimie – Ecole Nationale Supérieure d'Ingénieurs de Caen – France

⁷ Laboratoire de Physique et Chimie Théoriques (LPCT) – Institut de Chimie du CNRS, Université de Lorraine : UMR7019, Centre National de la Recherche Scientifique – Boulevard des Aiguillettes - B.P. 70239 F-54506 Vandoeuvre-les-Nancy, France

⁸ Laboratoire catalyse et spectrochimie – Université de Caen Normandie, Ecole Nationale Supérieure d'Ingénieurs de Caen, Centre National de la Recherche Scientifique : UMR6506 / URA414 – France

Separation of gases is a crucial topic in the fields of CO₂ capture, or purification of renewable source of energies such as biogas or "green" dihydrogen. In this context, separations of CO₂, CH₄, H₂ and N₂ are of the utmost importance. Nanoporous materials are used for these applications, and among them, small pore zeolites are widely spread in the industry. Chabazite zeolite has large ellipsoidal cavities (of 6.7 10 Å) but they are accessible only through small 8 member rings (approximate dimension of 3.8 3.8 Å). Thus, chabazite is used for adsorption and separation of small molecules. So far, most of the experimental studies are based on trial and errors approaches. However, this is a time and resource consuming approach that can be dramatically improved using proper modeling tools.(1) To this end, we performed periodic DFT calculations, with the VASP code, at the PBE level and TS/HI dispersion correction.(2) Chabazite substituted with monovalent cations have already been investigated(3,4) and we present here a systematic study of chabazite exchanged with divalent cations (Ca²⁺, Mg²⁺, Fe²⁺, Cu²⁺, Zn²⁺, Sn²⁺): all possible locations of cations have been tested, and adsorption energies of CO₂, CH₄, H₂ and N₂ have been computed. Our results show that Mg²⁺ cation is the most appropriate divalent cation to separate CO₂ molecule from CH₄ while H₂/N₂ separation could be achieved using Ca²⁺, Mg²⁺ or Fe²⁺.

(1) Hessou; Jabraoui; Khalil; Dziurla; Badawi. *Applied Surface Science* **2021**, 541, 148515.

(2) Chibani; Chebbi; Lebègue, Bučko; Badawi *J. Chem. Phys.* **2016**, 144, 244705.

(3) Zhang; Singh; Webley. *Microporous and Mesoporous Materials* **2008**, 111 (1–3), 478–487.

*Speaker

†Corresponding author: michael.badawi@univ-lorraine.fr

‡Corresponding author: remy.guillet-nicolas@ensicaen.fr

(4) Shang; Li; Singh; Gu; Nairn; Bastow; Medhekar; Doherty; Hill; Liu; Webley. *J. Am. Chem. Soc.* **2012**, *134* (46), 19246–19253.

Keywords: DFT, zeolite, adsorption, separation

Modelling Absorption Spectra of Furimamide - Nanoluciferase System

Houda Moumene * ¹, Isabelle Navizet ², Etienne Mangaud ³

¹ Houda MOUMENE – Université Gustave Eiffel, F-77454 Marne-la-Vallée – France

² Laboratoire de Modélisation et Simulation Multi Echelle (MSME) – Université Paris-Est Marne-la-Vallée : UMR8208, Centre National de la Recherche Scientifique : UMR8208 – Université Paris-Est, 5 Bd Descartes, 77454 Marne-la-Vallée, Cedex 2, France

³ Laboratoire Modélisation et Simulation Multi-Echelle – Université Paris-Est Créteil Val-de-Marne - Paris 12 : UMR8208, Centre National de la Recherche Scientifique : UMR8208, Université Gustave Eiffel : UMR8208 – France

Bioluminescence is a biological phenomenon of light production by living species with many applications(1), notably for the detection of cancer cells(2).The present study deals with a ligand-protein system (furimazine – Nanoluciferase) derived from a shrimp called *Oplophorus gracilirostri* with a very high luminescence intensity(3). The protein catalyzes an oxidation reaction of furimazine by dioxygen, which leads to a new molecule, furimamide in its excited state. A better understanding of this system will provide insights to tailor new devices with emission of a photon with a red color, and thus a light signal more easily detectable inside the human body.

Simulations of the emission and absorption spectra are relevant tools(4) to comply this goal. We focus here on the absorption spectra of the light emitter system furimamide – Nanoluciferase. In order to take into account the protein environment and the system flexibility, we carry out classical molecular dynamics (MM) with AMBER software. Furimamide is a flexible molecule: standard force fields such as GAFF(5) (General Amber Force Field) are unable to reproduce correctly torsion angles potential energy when compared to in vacuo DFT computations. Thus, we perform a multidimensional fit using 1D and 2D potential energy surface scans with several torsion angles of the molecule in order to parameterize a new force field. Then, we compute electronic transitions at a QM/MM level of theory on a set of 100 snapshots extracted from each MM trajectory. We present analysis of the most important transitions and influence of the cavity. As a perspective, we plan to use the same methodology to simulate emission spectra.

References

(1) A. J. Syed et J. C. Anderson, *Chem. Soc. Rev.* 50 (2021) 5668-5705.

(2) M. A. Paley et J. A. Prescher, *Medchemcomm* 5 (2014) 255-267.

(3) M. P. Hall *et al.*, *ACS Chem. Biol.*, 7 (2012) 1848-1857.

(4) M. Sahihi, J. Sanz García, et I. Navizet, *J. Phys. Chem. B* 124 (2020) 2539-2548.

(5) J. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman, et D. A. Case, *Journal of Computational Chemistry* 25 (2014) 18.

*Speaker

Keywords: Bioluminescence, Force Field, Molecular Dynamics, QMMM, Absorption Spectra

Molecular dynamics simulations unravelling the influence of light-activated drugs on a membrane cell model

Anastasiia Delova * ¹, Raül Losantos[†] ^{2,3}, Antonio Monari[‡] ¹

¹ Université Paris Cité et CNRS, ITODYS – Université Paris Cité, CNRS-UMR : F-75006 – France

² Université Paris Cité et CNRS, ITODYS – Université Paris Cité, CNRS-UMR : F-75006 – France

³ Universidad de La Rioja, Departamento de Química, Centro de Investigación en Síntesis Química, 26006 Logroño, Spain. – Spain

This work examines how a biomimetic chromophore based on a cyclocurcumin derivative affects lipid bilayers composed of 1,2-dipalmitoyl-*sn*-glycero-3-phosphatidylcholine (DPPC) mimicking cellular membranes. The cyclocurcumin derivative can be used in light-activated chemotherapy to selectively induce cell death by disrupting and destroying cellular membranes due to its structural perturbation brought by the E/Z photoisomerization. This approach is an appealing alternative to conventional photodynamic therapy (PDT) because it is operative also in absence of oxygen, and hence could be efficient for hypoxic tumors.

Classical molecular dynamics simulations were used to investigate how the chromophore interacts with the lipid bilayer. We also used enhanced sampling simulations via the coupling of ABF and Metadynamics (meta-eABF) to determining free energy profiles for the penetration of the drug in the membrane. Thus, globally elucidating the complete process from penetrations of the chromophore to its effect on the membrane.

Additionally, the effects of different concentrations of chromophore on the perturbation of the membrane were investigated. We show that the interaction with the membrane is highly reliant on the concentration, furthermore we also evidenced a transition in the arrangement of the photoswitches from ordered to disordered state. We also confirmed that the structural parameters of the bilayer are differently affected by the two isomers, and hence can be modulated through photoswitching, offering interesting perspectives for future applications.

Keywords: molecular dynamics, cyclocurcumin, lipid membrane, light, activated chemotherapy, molecular modeling

*Speaker

[†]Corresponding author: raul.losantos-cabello@u-paris.fr

[‡]Corresponding author: antonio.monari@u-paris.fr

2D proton diffusion in model potentials and assessment of quantum MD methods

Niccolò Avallone * ¹

¹ Institut des NanoSciences de Paris – Sorbonne Universités, UPMC, CNRS – France

When considering systems containing light atoms, classical framework cannot provide an exhaustive description of the microscopic phenomena. However, the computation of time-dependent properties of light nuclei including Nuclear Quantum Effects (NQEs) remains a very important theoretical challenge. These dynamical properties can be probed through different experimental techniques such as infrared/Raman spectroscopy or measurement of rate constants.

This work is a comparative study of trajectory-based methods on the problem of proton diffusion on a lattice surface via a model interaction potential. NQEs expected to play an important role are zero-point energy and tunneling through a barrier (1). The methods under study are classical Langevin, Quantum Thermal Bath (QTB) (2) and its refined version Adaptive QTB (3, 4), Ring-Polymer Molecular Dynamics and its thermostatted version (5, 6). Moreover, we are able to solve the 2D time-independent Schrödinger in a fixed periodic lattice and compute the diffusion coefficient from the quantum velocity auto-correlation function, thus used as benchmark to assess the strengths and limits of MD methods.

References:

- (1) S. Schaack, P. Depondt, S. Huppert, and F. Finocchi. Quantum driven proton diffusion in brucite-like minerals under high pressure. *Sci. Rep.*, 10(1):8123, 2020.
- (2) H. Dammak, Y. Chalopin, M. Laroche, M. Hayoun, and J.-J. Greffet. Quantum Thermal Bath for Molecular Dynamics Simulation. *Phys. Rev. Lett.*, 103(19):190601, 2009.
- (3) F. Briec, Y. Bronstein, H. Dammak, P. Depondt, F. Finocchi, and M. Hayoun. Zero-Point Energy Leakage in Quantum Thermal Bath Molecular Dynamics Simulations. *J. Chem. Theory Comput.*, 12(12):5688–5697, 2016.
- (4) E. Mangaud, S. Huppert, T. Plé, P. Depondt, S. Bonella, and F. Finocchi. The Fluctuation–Dissipation Theorem as a Diagnosis and Cure for Zero Point Energy Leakage in Quantum Thermal Bath Simulations. *J. Chem. Theory Comput.*, 15(5):2863–2880, 2019.
- (5) J. E. Lawrence and D. E. Manolopoulos. Path integral methods for reaction rates in complex systems. *Faraday Discuss.*, 221:9–29, 2020.
- (6) M. Rossi, M. Ceriotti, and D. E. Manolopoulos. How to remove the spurious resonances from ring polymer molecular dynamics. *J. Chem. Phys.*, 140(23):234116, 2014.

Keywords: Nuclear Quantum Effects, Molecular Dynamics, Proton Diffusion

*Speaker

Prediction of Lewis acidity of borane derivatives with constrained ligands via Machine Learning

Juliette Fenogli *¹, Rodolphe Vuilleumier[†], Laurence Grimaud

¹ Pôle chimie théorique – PASTEUR, Département de chimie, École normale supérieure, PSL University, Sorbonne Université, CNRS, 75005 Paris – France

Ligand design around boron currently arises a lot of interest to finely tune the Lewis acidity of borane derivatives. Indeed, as Lewis acids, they can be used to catalyse or activate organic reactions. For example, the Lewis acidity of these derivatives can be enhanced either by the introduction of electron-withdrawing (perfluorinated) groups on the ligand or using constrained geometry ligands. These few promising structures have not yet really been evaluated in terms of reactivity. Yet, finding the ideal candidate for a given reactivity requires exploration of the vast chemical space of different possible structures, rendering this process not only costly but also time-consuming. This project aims at generating new boron Lewis acids, targeting the compounds to synthesize by a preliminary theoretical investigation. We have used machine learning (ML) to generate and study a large number of boron Lewis acids. The fluoride ion affinity (FIA), *i.e.* the reaction enthalpy between the studied Lewis acid and a fluoride ion, constitutes a well-established Lewis acidity scale that can easily be computed thanks to *ab initio* methods like density functional theory (DFT). Calculating the FIA of numerous borane derivatives differentially substituted by electron-withdrawing or -donating groups, we have constituted databases associating to a given molecular structure the corresponding FIA. Then, various ML models were trained and tested using different machine-understandable molecular descriptors as input: from the simple "fingerprints" to more sophisticated "quantum descriptors", gathering parameters extracted from DFT calculations. The models were able to predict efficiently the evolution of FIA for a dataset of similar molecules. They were also able, only trained on one type of molecular structure, to predict the trend of FIA for the dataset of another type of molecular structure. Besides, analysing the results, we were able to identify the key parameters of Lewis acidity in the electronic structure of molecules.

Keywords: ab initio calculations, machine learning, Lewis acidity, molecular descriptors

*Speaker

[†]Corresponding author: rodolphe.vuilleumier@ens.psl.eu

Modelling bound and unbound RNA structures using molecular dynamics simulations to unravel the relationship between structure, flexibility and chemical reactivity

Elisa Frezza * ¹

¹ Cibles Thérapeutiques et conception de médicaments – Université Paris Cité : UMR8038, CNRS : UMR8038 – France

Ribonucleic acid (RNA) molecules are involved in most steps of the genetic expression including catalysis of central cellular functions. RNA functions crucially rely on both the specific tridimensional (3D) folding of the molecule, which in turn depends on the sequence and on how nucleobases pair through hydrogen bonds (secondary structure), and its conformation. This relationship is even more crucial for protein-RNA complexes. Hence, determination of RNA tridimensional structures is fundamental for understanding their function. However, obtaining high-resolution 3D structures via X-ray crystallography and NMR is still a challenge. To overcome the lack of 3D structures, in the last decades, several low-resolution techniques have been developed, like chemical probing, whose data have been integrated in the prediction of secondary (2D) and 3D RNA structures with different levels of detail. In particular, the SHAPE (Selective 2 Hydroxyl Acylation analysed by Primer Extension) technology provides quantitative reactivity information for each nucleotide and has become the most popular among these techniques since it does not depend on the nature of the nucleotide unlike other chemical probing techniques and is amenable to high-throughput protocols. The probes are small-molecule electrophiles like 1-methyl-7-nitroisatoic anhydride (1M7) that acylate the 2'-hydroxyl group to form a 2'-O-adduct. Although this approach is very popular and it is known that the SHAPE reaction is dependent on the local structural properties of each nucleotide, it has not yet been understood why different reactivities can be obtained for the same nucleotide depending on the probe used and several questions associated with the relationship between structure, conformation, flexibility, and reactivity are still open. To overcome this with the aim to use SHAPE data to predict bound and unbound RNA structures, in the last years we have performed all-atom molecular dynamics simulations on a set of RNA molecules (unbound and bound to a protein or a ligand) for which their tridimensional structures are available and SHAPE data are accessible in the literature or have been obtained in our wet lab. We analysed the correlations between different geometrical parameters and the chemical reactivity. For the bound RNAs we also characterised the interfaces and their formation in relationship with the change of SHAPE reactivity. Our investigations confirm that SHAPE reactivity is guided by the local flexibility of the different chemical moieties and the ribose plays a crucial role and suggest that a multiscale approach based on different length scales seems to be necessary to understand and integrate chemical probe data in relation with RNA flexibility and structure.

*Speaker

Keywords: RNA, flexibility, chemical probing, molecular dynamics simulation, biochemical reactivity

Study of the bending relaxation of water by collision with Ar using the Rigid Bender Close Coupling treatment

Ricardo Manuel Garcia Vázquez * ¹, Lisan David Cabrera-González ²,
Thierry Stoecklin[†] ³, Otoniel Denis-Alpizar[‡] ⁴

¹ Institut des Sciences Moléculaires – Centre National de la Recherche Scientifique : UMR5255,
Université de Bordeaux (Bordeaux, France) – France

² Doctorado en Físicoquímica Molecular, Facultad de Ciencias Exactas, Universidad Andres Bello,
República 275, Santiago, Chile – Chile

³ Institut des Sciences Moleculaires, CNRS UMR 5255 – Université de Bordeaux (Bordeaux, France) –
France

⁴ Universidad Autónoma de Chile – Chile

Water is one of the most abundant molecules in the universe. It is the most abundant polyatomic molecule in our galaxy and the third most abundant molecule in the interstellar medium after H₂ and CO, where it plays an essential role in the chemistry of interstellar clouds. Transitions involving some of its ro-vibrationally excited levels have recently been detected and it becomes essential to know its collision rates with the most abundant elements in the interstellar medium (H₂, He, H, and e⁻). Such studies exist for the fundamental vibrational level and considering water as a rigid rotor (1,2,3). The methodology necessary to deal with the vibrationally excited levels which take into account the coupling between bending and rotation of the water molecule has recently been developed (4,5). It must now be tested against experiments and experimental data are already available for collisions with argon. This study presents a close coupling study of the bending relaxation of water by collision with Ar.

References:

1-Daniel, F., Dubernet, M.-L., and Grosjean, A. Rotational excitation of 45 levels of ortho/para-H₂O by excited ortho/para-H₂ from 5 K to 1500 K: state-to-state, effective, and thermalized rate coefficients, *A&A*, 536:A76, 2011

2- F. Daniel, A. Faure, P. J. Dagdigian, M.-L. Dubernet, F. Lique, and G. Pineau des Forêts. Collisional excitation of water by hydrogen atoms. *Monthly Notices of the Royal Astronomical Society*, 446(3):2312–2316, 11 2014

3-Alexandre Faure, Jimena D. Gorfinkiel, and Jonathan Tennyson. Electron-impact rotational excitation of water. *Monthly Notices of the Royal Astronomical Society*, 347(1):323–333, 01 2004.

4- Thierry Stoecklin, Otoniel Denis-Alpizar, Alexandre Clergerie, Philippe Halvick, Alexandre Faure, and Yohann Scribano. Rigid-bender close-coupling treatment of the inelastic collisions of H₂O with para-H₂. *The Journal of Physical Chemistry A*, 123(27):5704–5712, 2019. PMID: 31192600.

*Speaker

[†]Corresponding author: thierry.stoecklin@u-bordeaux.fr

[‡]Corresponding author: otonieldenisalpizar@gmail.com

5- Thierry Stoecklin, Lisán David Cabrera-González, Otoniel Denis-Alpizar, and Dayán Páez-Hernández. A close coupling study of the bending relaxation of H₂O by collision with He. The Journal of Chemical Physics, 154(14):144307, 2021.

Keywords: Close Coupling method, Bending relaxation, Inelastic collision, water

Toward a molecular picture of thermal denaturation of RNA duplexes.

Aimeric Dabin * ¹, Guillaume Stirnemann ²

¹ Laboratoire de biochimie théorique [Paris] – Centre National de la Recherche Scientifique : FRC550, Université de Paris : UPR9080 – *France*

² CNRS Laboratoire de Biochimie Théorique, Institut de Biologie Physico-Chimique, Univ. Paris Denis Diderot, Sorbonne Paris Cité, PSL Research University (CNRS-IBPC) – CNRS : UPR9080 – 13 rue Pierre et Marie Curie, 75005 PARIS, France

In the RNA world hypothesis, primitive RiboNucleic Acids (RNA) are assumed to act as the genetic and functional molecule at the origins of life. However, the template-directed synthesis of RNA remain challenging under abiotic conditions, for several reasons. One is the high melting temperature of RNA duplexes, which are the end-products of a template-directed synthesis. Our aim is to understand how melting depends on sequence using all-atom molecular dynamics simulations. Nearest-neighbor models provide a phenomenological, and usually accurate, prediction of the melting temperature, but they do not provide a detailed molecular picture of the underlying unfolding mechanism. We use a specific enhanced sampling scheme allowing to perform many simulations simultaneously along a temperature-ladder that allow to probe the thermal separation of the duplexes while accelerating conformational sampling. Our simulated melting curves of dodecamer duplexes are in remarkable agreement with available experimental data and the predictions of nearest-neighbor models. However, they shed unprecedented light on the unfolding mechanism, that is seen to significantly deviate from the 2-state picture that is usually employed to describe the folding/unfolding equilibrium of duplexes. Considering that primitive RNAs could have chemical defects in their backbone, we also investigate how modifications of the nucleic acid backbone (XenoNucleic Acids) influence the conformational landscape and unfolding behavior. This requires specific reparametrization of the molecular interaction models used for the simulations, and we show that these models are able to capture the dramatic effect of even minor changes of the backbone regarding the melting behavior of the duplexes.

Keywords: molecular dynamics, RNA, denaturation, enhanced sampling

*Speaker

DFT QUANTUM CHEMICAL STUDIES OF LUMINESCENT COPPER (I) COMPOUNDS

Raquel Utrera Melero * ¹, Constance Lecourt ¹, Chendong Xu ², Jana Schiller ¹, Valérie Marvaud ³, Christophe Lescop ¹, Karine Costuas ¹

¹ ISCR – Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes) UMR 6226, F-35000 Rennes, France – 263 Av. Général Leclerc, 35700 Rennes, France

² Institut des Sciences Chimiques de Rennes – ISCR UMR CNRS 6226, Institut National des Sciences Appliquées (INSA) - Rennes – France

³ Institut Parisien de Chimie Moléculaire – Université Pierre et Marie Curie (UPMC) - Paris VI, CNRS : UMR8232 – Université Pierre et Marie Curie (UPMC) 4 place Jussieu 75252 Paris Cedex 05 Bâtiment F/74, France

Cu(I)-containing compounds have been emerging as appealing alternatives to rare earth and heavy metal systems that are currently in use in the industry of OLEDs or lighting devices. Inspired by a general synthetic approach previously developed in our consortium of research, a series of new luminescent polymetallic assemblies of the general formula $(\text{Cu}_8\text{M}(\text{CN})_8\text{dppm}_8)_2^{2+}$ obtained by reacting a flexible and luminescent Cu(I) tetrametallic precursors with $\text{M}(\text{CN})_4$ -salts ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$).^(1,2) These discrete units are formed by a central square-planar "M(CN)₄" unit surrounded by a "Cu₈(CN)₄" metallacycle as shown in Figure 1 left. Interestingly, the central metal ion plays a role in the optical properties, some of the frontier orbitals having a substantial M character (ex: 12.7 % for $\text{M} = \text{Pt}$, see Figure 1 right). We thus investigate the introduction metal ions that possess intrinsic magnetic properties via the same synthetic route. It opened up the opportunity to integrate multifunctionality to the system in which one property can modify the other one. In this study, CuI, MoIV, WIV, and FeIII ions have been investigated that can have Prussian blue-like behavior.

Keywords: Copper, Magnetic properties, luminescent polymetallic assemblies, DFT

*Speaker

Organolanthanide complexes: *ab initio* study of electronic structures and rationalization of magnetic properties

Léo La Droitte * ¹, Boris Le Guennic ¹, Olivier Cador ¹

¹ Institut des Sciences Chimiques de Rennes – Ecole Nationale Supérieure de Chimie de Rennes, Université de Rennes 1, Université de Rennes, Institut National des Sciences Appliquées - Rennes, Institut National des Sciences Appliquées, Université de Rennes : UMR6226, Centre National de la Recherche Scientifique – France

Single Molecule Magnets (SMMs) are widely studied because of their potential impact in applications such as high-density information storage, quantum computing or spintronics.(1) Lanthanide ions can present strong anisotropy due to the unquenched orbital angular momentum of the unpaired electrons in their 4f orbitals, and this anisotropy can be maximized by the effect of a ligand field. Indeed, different strategies can be sought to enhance the SMM behaviour of a compound, i.e. to achieve a slow magnetic relaxation and the highest blocking temperature possible. Using organolanthanide complexes has proven to be one of the best ways to design performing SMMs.(2) In this context, tuning and understanding the impact of the ligands' geometry on the electronic structure of the complexes is essential.

In this work, recent computational results and magnetic measurements on different series of complexes will be presented, as well as the rationalization of the impact of complexes' geometry on their electronic structure and magnetic properties.(3-5) Different design strategies for organolanthanide SMMs are computationally explored via *ab initio* CASSCF/RASSI-SO methods, such as the use of cyclooctatetraenyl (Cot) and cyclononatetraenyl (Cnt) large ligands.

References:

(1) D. N. Woodruff, R. E. P. Winpenny and R. A. Layfield, *Chem. Rev.*, **2013**, 113, 5110–5148.

(2) A. Zabala-Lekuona, J. M. Seco and E. Colacio, *Coordination Chemistry Reviews*, **2021**, 441, 213984.

(3) J. Moutet, J. Schleinitz, L. La Droitte, M. Tricoire, F. Pointillart, F. Gendron, T. Simler, C. Clavaguéra, B. Le Guennic, O. Cador and G. Nocton, *Angew. Chem. Int. Ed.*, **2021**, 133, 6107-6111.

(4) M. Tricoire, L. Münzfeld, J. Moutet, N. Mahieu, L. La Droitte, E. Moreno-Pineda, F. Gendron, J. D. Hilgar, J. D. Rinehart, M. Ruben, B. Le Guennic, O. Cador, P. W. Roesky and G. Nocton, *Chem. Eur. J.*, **2021**, 54, 13558-13567.

(5) O. Stetsiuk, L. La Droitte, V. Goudy, B. Le Guennic, O. Cador and G. Nocton, *Organometallics*, **2022**, 41, 133–140.

*Speaker

Keywords: Single Molecule Magnets, Lanthanide, Quantum chemistry, Computational chemistry, Magnetometry, Organolanthanide complexes

Quantum Chemistry study of chromophores for OLED applications

Maxime Hodée * ¹, Claudine Katan ², Arnaud Fihey† ³

¹ Institut des Sciences Chimiques de Rennes – Université de Rennes 1, CNRS : UMR6226 – France

² Institut des Sciences Chimiques de Rennes (ISCR) – Université de Rennes 1, CNRS : UMR6226 – Campus de Beaulieu - Bât. 10 Avenue du Général Leclerc 35042 Rennes Cedex, France

³ Institut des Sciences Chimiques de Rennes – Université de Rennes 1, CNRS : UMR6226, Université de Rennes 1 – France

In the context of the ecological crisis in which we live, the development of new lighting systems is crucial. Indeed, lighting is now worth about 20% of global electricity consumption. The rise of organic lighting systems (OLEDs) in order to reduce energy costs has led to the development of different light production methods, allowing for example to obtain white light or to improve fluorescence properties through mechanisms such as Thermally Activated Delayed Fluorescence (TADF). In this context, theoretical calculations allow the rationalization of experimental results as well as the prediction of fluorescence-related characteristics. The tool of choice for these studies is generally TD-DFT, allowing access to optical properties (vertical absorption and emission) in a qualitative manner at a reasonable computational cost. However, this methodology may have its limitations, in particular with respect to the accuracy obtained or to mechanisms not taken into account by the classically used methodologies, in particular the non-radiative de-excitation mechanisms.

In this work, we are interested in diazinic derivatives functioning as fluorophores for 1st generation OLEDs, and chromophores potentially subject to TADF for 3rd generation OLEDs. The goal was to go beyond the simple study of vertical transitions obtained by TD-DFT, and to do so we are interested in vibronic calculation methods allowing to address the non-radiative de-excitation mechanisms, taking into account the electron-vibration coupling.

To obtain a quantitative approach of the quantities relevant to TADF, we will discuss the need to use a wave function approach with approximate Coupled Cluster calculations (CC2). For these diazine ring derivatives (pyrimidine, pyrazine, quinoxaline, ...), we will discuss the advantages and limitations of the different approaches used.

Keywords: OLED, TADF, photophysics, TD, DFT, CC2, vibronic

*Speaker

†Corresponding author: arnaud.fihey@univ-rennes1.fr

Ab initio investigation of the mechanical and electronic properties of bismuth vanadate BiVO₄

David Vincent * ¹

¹ Institut des Sciences Chimiques de Rennes – Université de Rennes 1 – France

Ab initio investigation of the mechanical and electronic properties of bismuth vanadate BiVO₄ Bismuth vanadate is a ternary compound which exhibits many attractive properties, such as ferroelasticity, ionic conduction, or photocatalysis. Its properties strongly depend on the allotropic form of BiVO₄. Here we have considered the monoclinic (m) and tetragonal (t) scheelite phases. Experimentally, the more stable phase is m-BiVO₄. Theoretically, the opposite is found when using density functional theory (DFT) within LDA or GGA functionals. Here we propose to discuss a series of tests allowing to define a theoretical approach allowing to properly describe the stability of m-BiVO₄ with respect to t-BiVO₄, their structural, electronic and vibrational properties. We have used the VASP code and tested the impact of (1) the pseudopotential, (2) the functional (including DFT+U, meta-GGA and hybrid functionals), (3) van der Waals corrections, (4) spin-orbit coupling. Among all these combinations, one appears to fulfill all the requirements without paying the price of hybrid functionals.

Keywords: materials energies characterizations modelisations

*Speaker

Crucial Role of Conjugation in Monolayer-Protected Metal Clusters with Aromatic Ligands

Hans-Christian Weissker ^{*† 1,2}

¹ European Theoretical Spectroscopy Facility (ETSF) – EU – www.etsf.eu, France

² Centre Interdisciplinaire de Nanoscience de Marseille – Aix Marseille Université : UMR7325 / UPR3118, Centre National de la Recherche Scientifique : UMR7325 / UPR3118 – France

In nanoscale objects, surface and interface effects often play a decisive role for all electronic and optical properties. For wet-chemically produced clusters, in particular, the interaction between the ligands and the metal core needs to be well described.

I will make use of the recently determined experimental structure of the Au₁₄₄ cluster compound(s) which turned out to have identical core structure in spite of their very different ligands (1). Using induced densities from real-time TDDFT calculations (2), I demonstrate that the conjugation between aromatic ligand rings and the metal core plays a primordial role for the optical properties (3). These findings are expected to have strong implications for ligand-protected clusters subjected to strong laser irradiation.

(1) R.L. Whetten, H.-Ch. Weissker, J. Jesús Pelayo, S.M. Mullins, X. López-Lozano, and I.L. Garzón, Chiral-Icosahedral (I) Symmetry in Ubiquitous Metallic Cluster Compounds (145A,60X): Structure and Bonding Principles. *Acc. Chem. Res.* 52, 34-43 (2019).

(2) R. Sinha-Roy, P. Garcia-Gonzalez, X. Lopez Lozano, R.L. Whetten, and H.-Ch. Weissker, Identifying Electronic Modes by Fourier Transform from δ -Kick Time-Evolution TDDFT Calculations, *J. Chem. Theory Comput.* 14, 6417-6426 (2018).

(3) R. Sinha-Roy, X. Lopez Lozano, R.L. Whetten, and H.-Ch. Weissker, Crucial Role of Conjugation in Monolayer-Protected Metal Clusters with Aromatic Ligands: Insights from the Archetypal Au₁₄₄L₆₀ Cluster Compounds, *J. Phys. Chem. Lett.* 2021, 12, 9262-9268.

Keywords: Metal clusters, ligands, TDDFT, conjugation, optical properties

*Speaker

†Corresponding author: hans-christian.weissker@univ-amu.fr

(PdHCu₁₁{S₂P(OiPr)₂}₆(C≡CPh)₄) a hydride-containing 2-electron superatom as electrocatalyst for hydrogen production

Hao Liang * ¹

¹ ISCR – Université de Rennes I – France

Abstract

The recently characterized (PdHCu₁₁{S₂P(OiPr)₂}₆(C≡CPh)₄) nanocluster exhibits an unprecedented metallic core made of an incomplete Cu₁₁ cuboctahedron encapsulating a Pd atom at its center. The hydride ligand is coordinated from the inside, principally to Pd and more weakly to three Cu atoms. This cluster shows excellent electrocatalytic properties in the hydrogen evolution reaction (HER). Our calculations confirm the experimental position of the hydride and indicate that this cluster is a 2-electron superatom(1-4) with 1S₂ 1P₀ configuration, despite the presence of a vacant vertex on the copper icosahedron. The hydride makes a bond with the central Pd, in which a 4ds(Pd) AO is involved. As a consequence, a PdH₂ unit is created, which provides one electron to the (Cu₁₁)₁₀+ polyhedron to complete the superatomic count. Thus, the presence of the hydride ensure stability to the incomplete cuboctahedron. This resulting incompleteness provides to the cluster with a void that calculations show to be a channel for an incoming hydrogen atom to access to the central Pd. This process constitutes the first step (Heyrowski step) of the HER catalytic cycle.

Reference

- (1) W. D. Knight, K. Clemenger, W. A. de Heer, W. Saunders, M. Y. Chou, M. L. Cohen, *Phys. Rev. Lett.* **1984**, *52*, 2141.
- (2) D. M. P. Mingos, T. Slee, Z. Lin, *Chem. Rev.* **1990**, *90*, 385.
- (3) S. Khanna, P. Jena, *Phys. Rev. Lett.* **1992**, *69*, 1664.
- (4) F. Gam, J. Wei, S. Kahlal, J-Y. Saillard, J-F. Halet. *Structure and Bonding* . **2021**, *188*, 69-102.
- (5) G. D. Liberto, L. A. Cipriano, G. Pacchioni. *J. Am. Chem. Soc.* **2021**, *143*, 20431-20441.
- (6) J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov, U. Stimming. *J. Electronchem. Soc.* **2005**, *152(2)*, J23-J26.

*Speaker

Keywords: superatom, DFT, HER

Electronic structures and bonding properties of organometallic palladium nanoclusters

Jianyu Wei * ¹

¹ Institut des Sciences Chimiques de Rennes – Université de Rennes 1 – France

The electronic structure and bonding properties of the Mackey icosahedral cluster Pd₅₅(P*i*Pr₃)₁₂(m³-CO)₂₀ (1) was analysed by using DFT calculations. The results show that it can be considered as a regular *superatom* (2) with the "magic" electron count of 20, characterized by a *jellium* configuration of 1S²1P⁶1D¹⁰2S². This configuration is attributed to an electron transfer from some 4d-type orbitals to 5s bonding combinations. This level crossing is assisted by the presence of the ligands. A similar behaviour was traced for other palladium clusters, such as the 2-electron *superatom* (Pd₁₃(μ₄-C₇H₇)₆)₂₊ (3). Our results show that the *superatom* concept can be used to rationalise the electronic structure of the spherical ligated group-10 transition metal clusters which are not 0-electron species as one could think at first sight.

Keywords: Palladium nanoclusters, electronic structure, Superatom

*Speaker

Author Index

- Alducin, Maïte, 11
Avallone, Niccolò, 17
- Badawi, Michael, 7, 12
- Cabrera-González, Lisan David, 21
Cador, Olivier, 25
Cavignac, Théo, 3
Chin, Wutharath, 4
Costuas, Karine, 24
- Dabin, Aimeric, 23
DAOULI, AYOUB, 7, 12
Delova, Anastasiia, 16
DENIS-ALPIZAR, Otoniel, 21
Dziurla, Marie-Antoinette, 7
- Ehlert, Christopher, 11
- Fenogli, Juliette, 18
Fihey, Arnaud, 27
Frezza, Elisa, 19
- Garcia Vázquez, Ricardo Manuel, 21
Griffin, John, 8
Grimaud, Laurence, 18
Guillet-Nicolas, Rémy, 12
- Hoang Ngoc, Minh-Thê, 5
Hodée, Maxime, 27
- Juaristi, J. I., 11
- KARAMANIS, IOANNIS, 7
katan, claudine, 27
- La Droitte, Léo, 25
LAHRAR, El Hassane, 12
Le Guennic, Boris, 25
Lecourt, Constance, 24
LESCOP, CHRISTOPHE, 24
LIANG, HAO, 30
Losantos, Raül, 16
- MANGAUD, Etienne, 14
Marvaud, Valérie, 24
Maurin, Guillaume, 7
- Merlet, Céline, 8
Monari, Antonio, 16
Monnier, Hubert, 7
Moumene, Houda, 14
- Navizet, Isabelle, 14
- Oher, Hanna, 9
- Pollet, Rodolphe, 4
- Rey, Jérôme, 12
Rotenberg, Benjamin, 5
- Saalfrank, Peter, 11
Sasikumar, Anagha, 8
Schiller, Jana, 24
Stirnemann, Guillaume, 23
STOECKLIN, Thierry, 21
Stoltz, Gabriel, 5
- TETENOIRE, Auguste, 11
- UTRERA MELERO, Raquel, 24
- Valtchev, Valentin, 12
Vincent, David, 28
Vuilleumier, Rodolphe, 18
- Wei, Jianyu, 32
Weissker, Hans-Christian, 29
- XU, Chendong, 24