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Book of Abstracts

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From the high spin to low spin in mono- and bidentate Fe(II) spin-crossover complexes

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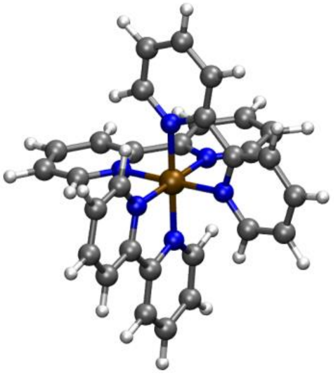
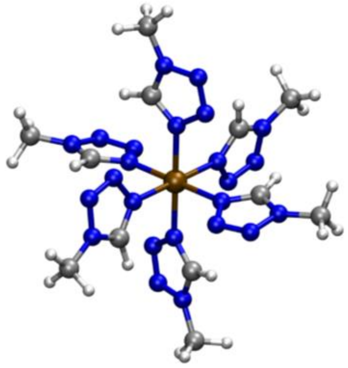
Transition metal complexes offer a wide range of possible applications because of the stability of their excited states. They can play a role as a catalysts in different chemical reactions such as H_2 production[1] or asymmetric chemical syntesis[2]. They also can show magnetic bistability because of spin-crossover (SCO). Spin-crossover is a phenomena experimented usually for d^4-d^7 TM complexes such as Fe^{2+}. It can be induced by different perturbations of the system such as temperature, pressure or light-induction[3]. This last mechanism is called light-induced excited spin-state trapping and it is known as LIESST which has been largely studied from both experimental and theoretical point of view[4-6]. In the current project, we study the inverse mechanism, reverse-LIESST, for a bidentate complex $[Fe(bipy)_3]^{2+}$ and a monodentate one $[Fe(mtz)_6]^{2+}$. It is studying the photodeactivation pathway from the ^5E, after absorbing a photon from the $^5T_2$, to the ^1A ground state or coming back to the metastable $^5T_2$. It is studied from a static point of view through the Fermi's golden rule which take into account the adiabatic electronic energy difference, the vibration overlap and the coupling between states[7]. It is also studied the thermal spin-crossover for the $[Fe(bipy)_3]^{2+}$ complex through the same methodology. Both studies are carried out at the topological points of interest (minima or crossing points) but also along different snapshots of the dynamic calculations because thermal distortions were proved to strongly affect spin-orbit coupling between some states[8].





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Properties of molecules in weak and strong magnetic fields

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Weak magnetic fields act as a perturbation to the electron density and induce current vortices in atoms and molecules. The current density is high in the vicinity of atoms due to the response of the core electrons. There are ring current tracing the perimeter of the whole molecule, the direction of which is determined according to classical electrodynamics. However, in molecular rings there are also non-classical current pathways, flowing the opposite direction. According to the ring-current model, net diatropic currents are associated with aromatic character, whereas net paratropic currents signify antiaromatic properties. We investigated B_2N_2-dibenzopentalenes to evaluate the influence of the heteroatoms on the aromatic character of the molecule. [1] We also investigated the topology of $C_{40}H_{40}$ annulenes and showed that both the twist of the carbon skeleton and the writhe – the spatial twisting of the molecular ring – affect the aromaticity. [2] In another study we constructed a chiral toroidal carbon nanotube with helical current flow, which is expected to give rise to magnetically induced anapole moment. [3] As the magnetic field strength grows, it can no longer be treated perturbatively. Wave functions become complex and new quantum-chemistry codes are needed. Conventional basis sets turn out to be unsuitable and the basis-set truncation error in magnetic fields stronger than 10^5 T ranges from about 10 kcal/mol to more than 1000 kcal/mol at field strength of 10^6 T at the Hartree-Fock level and a triple-zeta uncontracted correlation-consistent basis set. [4] We further showed that small CH_x molecules exist as bound high-spin systems in magnetic field of 10^5 T, however there is no defined molecular structure.

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SPIN-STATE ENERGETICS OF SELECTED METALLOCENES FROM CORRELATED WAVE FUNCTION AND DFT CALCULATIONS

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Metallocenes are metal-organic sandwich compounds, with ferrocene as the best recognizable, and probably one of the most extensively studied chemical system since its discovery in 1951. In this work, we focus on the spin-state energetics (relative energies of different possible spin states) of metallocenes, which are challenging for reliable theoretical computation and hence the estimates inferred from the experimental data often serve as valuable benchmarks for theory [1]. Surprisingly, in spite of extensive research material available, the spin-state energetics of ferrocene and other metallocenes is still uncertain.

The present study takes under scrutiny the spin-state energetics for a representative choice of metallocenes with d^6 or d^5 configuration: ferrocene, ruthenocene, cobaltocenium ion and manganocene (the last one being a SCO system). We perform DFT and correlated wave function calculations (including single-reference coupled cluster and multireference methods) targeting vertical (absorption and emission) and adiabatic energies of different spin states, and benchmark the results against the quantitative experimental data of spin-state energetics available for these metallocenes. The most detailed comparison is possible for the singlet and triplet states of ruthenocene due to the abundance of spectroscopic data [2,3]. Here, an important methodological outcome of our analysis is developing a back-correction to the experimental “vertical energy” (taken from a maximum of an absorption or emission spectrum) with the aim of approximately accounting for vibronic effects. With high-level wave function methods, such as CCSD(T), we are able to reach a reasonable agreement with the experimental data for ruthenocene and manganocene. By contrast, for ferrocene and cobaltocenium, our detailed analysis suggests that weak spin-forbidden bands might be misassigned in their experimental spectra.

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Elucidating the Mechanism of Proton Reduction Catalysed by Heteroleptic Nickel Thiolates

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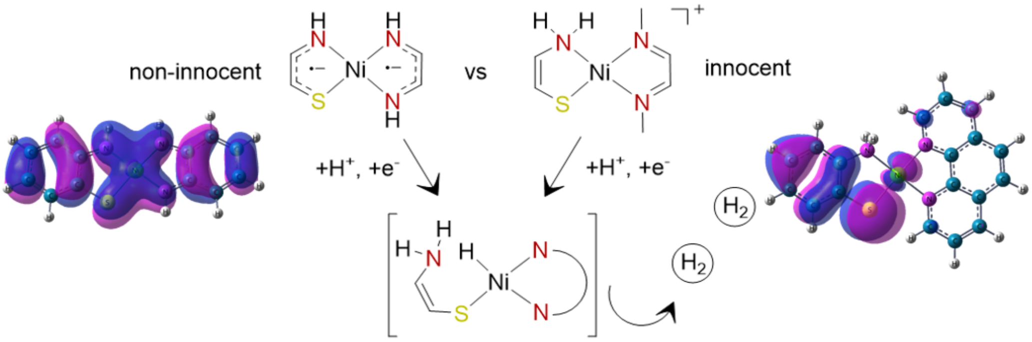
Abstract

An important step towards sustainable solar energy conversion is the development of earth-abundant metal complexes as promising candidates for photocatalytic proton reduction.[1] Metal dithiolenes and thiolate complexes have long been recognized as a special type of multifunctional molecular systems, partly due to the non-innocent nature of dithiolene ligands.[2, 3] Efficient strategies for the synthesis of new molecular catalysts requires deep understanding of how the nature of the ligands affects the locus of redox activity, spin density and the H_2 formation mechanism.[4] Herein, two heteroleptic square planar nickel complexes bearing the non-innocent o-aminobenzenethiolate ligand,[5] which serve as efficient photocatalysts for H_2 evolution, were investigated and compared experimentally and computationally to determine how ligand-centered redox properties change when the redox active o-phenylenediamine ligand is replaced with redox-innocent phenanthroline. These results will provide the foundation necessary to evaluate how electronic structure variations modulate metal−ligand cooperation in heteroleptic nickel thiolates.



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Photophysical properties of the triangular $[Au(HN{=}COH)]_3$ complex and its dimer

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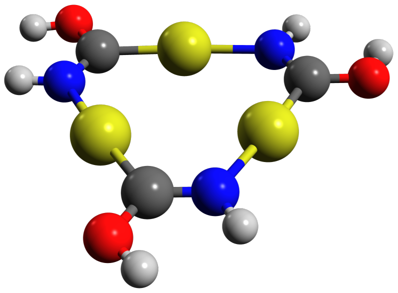
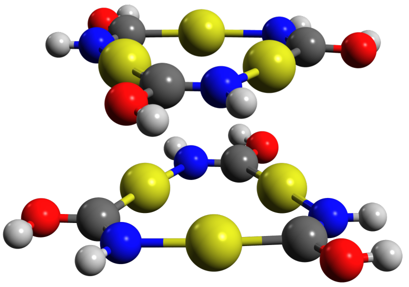
Radiative and non-radiative rate constants of the $[Au(HN{=}COH)]_3$ complex and its dimer were calculated within the Herzberg-Teller approximation based on quantum mechanical principles. For the monomer a triplet quantum yield of 0.74 has been estimated. Internal conversion (IC) was found to be the major competing process to the intersystem crossing (ISC) from S_1 to T_1. ISC and IC from the spin-mixed state also dominate the triplet relaxation process resulting in negligible phosphorescence quantum yield for the monomer. The IC and ISC rate constants of the dimer are considerably smaller due to much lower Franck-Condon factors. This can be explained by strong intermolecular aurophillic interactions that lead to dimer formation, which hinders the out-of-plane vibrational modes and therefore inhibits vibrational relaxation. The triplet quantum yield of the dimer was estimated to be 0.70 with fluorescence as the major competing process. The ISC and IC processes are insignificant for triplet relaxation resulting in unity phosphorescence quantum yield. The $[Au(HN{=}COH)]_3$ complex can be used as a model system for the $[Au(RN{=}COR')]_3$ group of compounds. The high triplet and phosphorescence quantum yields of the $[Au(HN{=}COH)]_3$ dimer make the $[Au(RN{=}COR')]_3$ dimer and its higher oligomers potential candidates as dopants for phosphorescent organic light emitting diodes and as down-converters in solid state lighting applications.



Monomer



Dimer

Fullerene-Based Switching Diodes Controlled by Oriented External Electric Fields

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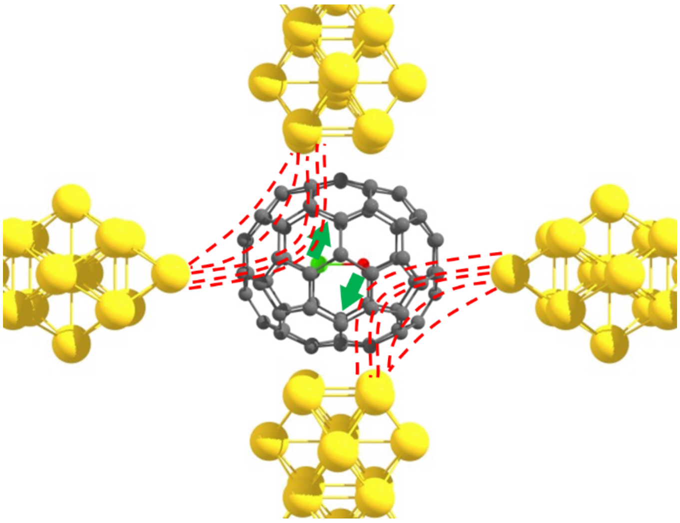
We propose switching molecular diode based on endohedral fullerene systems ($MX@C_{70}$). Encapsulated molecules with general formula MX (M - metal, X - fluorine, chlorine, oxygen) were used. We show that relative orientation of enclosed molecules can be controlled by oriented external electric field. We suggest a four-terminal system of electrodes, in which two electrodes (main) are used to help current pass through the system while the other two electrodes (gate) lower the barrier of rotation by stabilizing the transition state of rotation. Non-equilibrium Green's function was used together with density functional theory (DFT-NEGF) to study the dependence of conductivity on orientation of the enclosed molecule. Based on our results, orientation of the MX can be both enforced ("written") and retrieved ("read") by applied voltage. The studied systems thus behave like voltage-sensitive switching molecular diodes suitable for application in random access memories for short-term or memristors for long-term data storage. This depends on the energy barrier for the MX switching in the absence/presence of an external electric field, i.e. the lifetime of the states.



Relativistic correction of core excitations from *GW*

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We present a simple relativistic correction to improve the accuracy of *GW* 1s core level energies. The *GW* method is a Green's function-based approach to calculate the quasiparticle spectrum, typically as a post-processing step to a mean field theory calculation[1]. *GW* has become the method of choice for the calculation of addition and removal energies for valence electrons [2], and recently it has been shown to also provide good accuracy for core states[3]. However, even for light (2nd period) elements, relativistic effects begin to dominate the error in core state quasiparticle energies, leading to a species dependence in the magnitude of the overall error.

We solve the radial Kohn-Sham (KS) and 4-component Dirac-Kohn-Sham equations self consistently for a free neutral atom on a fully numeric real-space grid, and evaluate the difference ΔE_{1s} between their 1s eigenvalues [4]. We examine the dependence of ΔE_{1s} on molecular environment and on the amount of exact exchange in the exchange correlation functional, and find it to be within the range of experimental error ($\leq$ 0.1 eV). We then investigate the effect of shifting the KS eigenvalues prior to an eigenvalue-self-consistent *GW* calculation (evGW_0) by this corrective term for a benchmark set of 65 2nd period core states. We similarly consider the effect of applying this correction to the quasiparticle energies subsequent to an evGW_0 calculation. The mean absolute error (MAE) is calculated as the mean absolute difference between the 1s eigenvalue extrapolated to the basis set limit and the negative ionization potential. The MAE is reduced by either corrective procedure from 0.5 to 0.3 eV, and the species dependence of the MAE is eliminated.

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A dynamic microkinetic model for the catalytic reduction of ester to alcohol

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Microkinetic modelling is an important tool to translate the information gained in computational homogenous catalysis to the experimental world.[1] Free energy barriers obtained by DFT calculation are easily converted to rate constant and can together with concentration data provide reaction rates that are acquired in experiments. However, during a reaction the conditions are constantly changing, providing different environments for the catalyst to function in.[2] Therefore, it is not sufficient to model our reaction pathway solely with the starting conditions of our experiments. We have developed a dynamic microkinetic model that adapts to changes in the reaction environment and is therefore able to predict the reaction pathway more realistically. In this case study, the pathways of the non-pincer manganese complex were investigated for the hydrogenation of ester to alcohol.[3] In the course of the reaction the local environment becomes more polar, which effects the function of the catalyst. We have described these effects with the COSMO-RS method[4] and subsequently integrated in the microkinetic model.

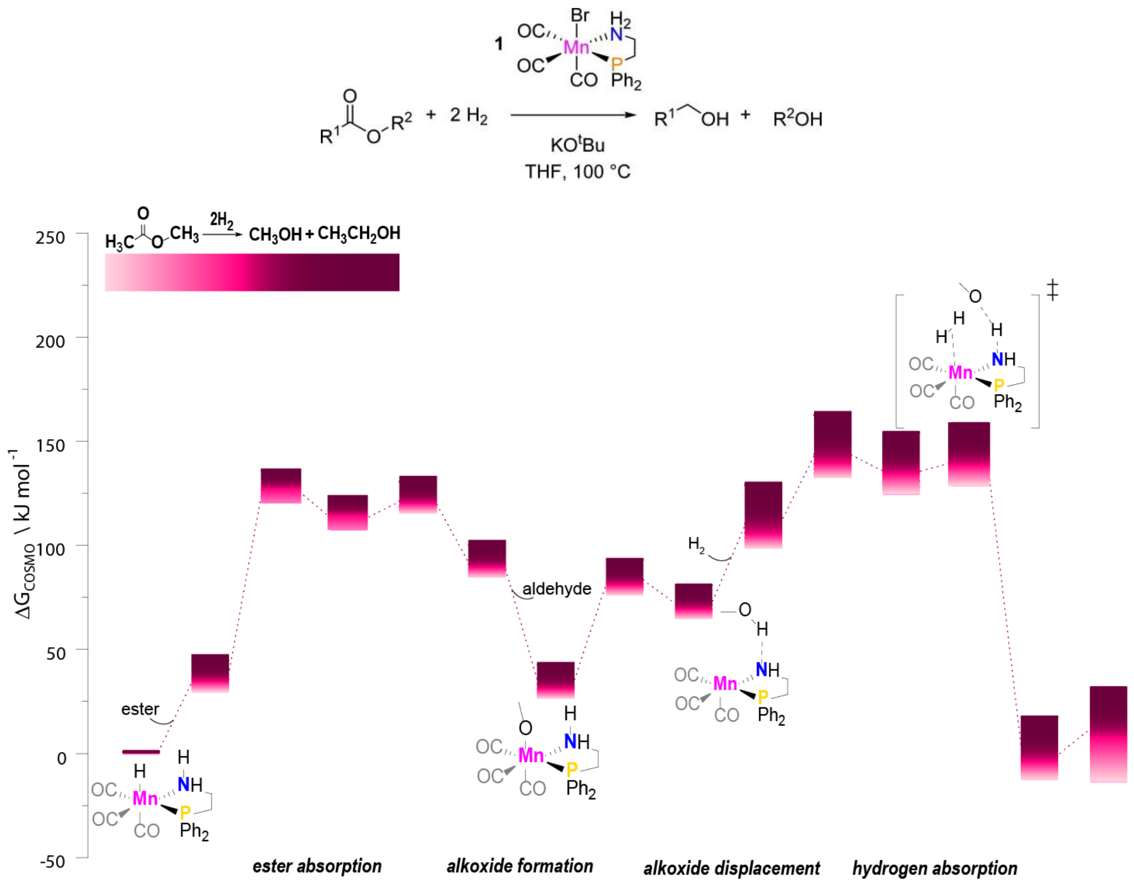

Figure: Hydrogenation of ester[5] (above) and concentration dependant free energy diagram (below)

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Theoretical Investigation of Thermochromia in Laterally Diborylated Teraryls

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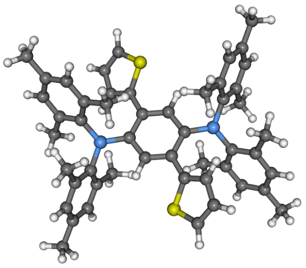
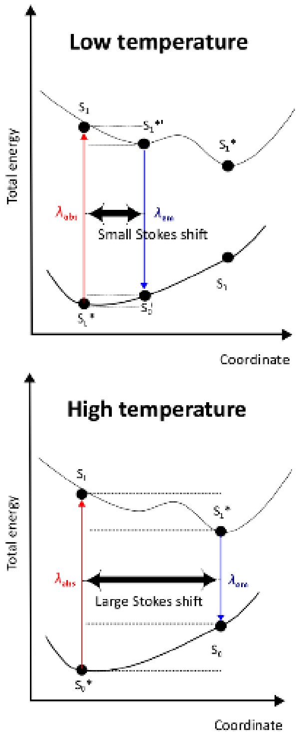
2,5-Bis(dimesitylboryl)-1,4-dithiophenyl benzene is a thermochromic dye molecule representing a novel class of diborylated teraryls with a series of potential applications in the fields of organic semiconductor lasers and photo sensory devices, due to their high fluorescence quantum yield in the solid state. In-depth knowledge on the thermic tunability of photochromic abilities (i.e. its exploitation or suppression) can be expected to play an essential role in every potential application.





We attempted to develop a theoretical method for the prediction of thermochromic properties in our sample molecule, which we assume to be applicable to similar dye molecules as a template.

The starting point of this development was the calculation of vertical excitation energies and their relaxation analogues at the DFT and TD-DFT level with various functionals, which were compared to experimental spectra. The accompanying geometry optimisations of the ground and first excited singlet state were used for the evaluation of structural transitions the molecule is subjected to upon photoexcitation.

We utilised the common praxis of feeding high quality DFT data on the EHS into classical force field (FF) parameters to enable accurate MD simulations on reasonable time scales. This approach was further facilitated by limiting DFT calculations on the EHS to those molecular structures, which are affected the most within the vertical excitation, while we used values provided by the OPLS-AA standard FF parameter library for less affected structures. We will demonstrate that with these punctual modifications FF based MD simulations are eligible to qualitatively predict the dye's thermochromic behaviour.

In silico optimization of a high-valent Ni oxidant

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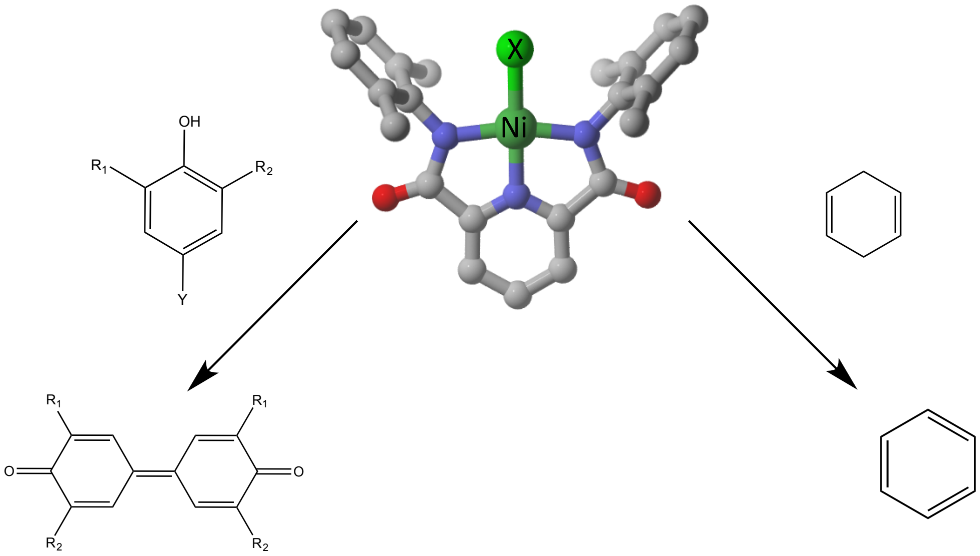
The activation of C-H bonds with high bond dissociation energies (BDEs) is of the utmost importance for the chemical industry due to the chemical space exploration that it allows; one of the most efficient methods for its achievement is resorting to transition metal complexes.[1] While some of the most iconic C-H activation reactions are performed with noble metal catalysts,[2] their high cost and environmental footprint led to the development of more sustainable catalysts, a field which is dominated by bio-inspired iron-oxo complexes.[3]

More recently, however, McDonald and coworkers reported another sustainable catalyst candidate, a high-valent Ni^{III}-Chloride complex which is capable of activating both C-H and O-H bonds through an apparent hydrogen atom transfer (HAT) mechanism.[4] The bonds activated had BDEs up to ca. 85 kcal mol^{-1} and exhibited varying reaction rates, depending on the BDE. They postulated that tuning the halogen ligand in the catalytic species could lead to better performing catalysts.

In this work, we use DFT with a functional that excels in spin-state description[5] to characterize the reactivity of the Ni complex reported by McDonald *et al.* and dive further into the chemical space to probe for more efficient derivatives.



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The aromaticity and spectroscopy of weakly coupled tetranuclear square-planar complex of Cu(II) with a tetraporphyrin sheet

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The index of aromaticity and electronic excitation energies of free tetranuclear square-planar a tetraporphyrin and tetraisophlorin, and their complex with Zn, Cu were calculated using the magnetically induced current density method and TDDFT/B3LYP/def2-TZVP, respectively. The results show that the free tetranuclear square-planar a tetraporphyrin, its complex with Zn and Cu are strongly antiaromatic with the current density -36 nA/T, -72 nA/T and -75 nA/T. The first electronic transition (0→1) is a strongly magnetic dipole electronic transition with the energy 0.6-0.85 eV and transition moment 5.0 a.u. for them. The current density is 0.8 nA/T for the free tetranuclear square-planar a tetraisophlorin and it is nonaromatic. The 0→1 is located higher with the 1.7 eV and with the transition moment 10.0 for this molecule.

Thus there is a correlation between current density and energy of magnetic dipole electronic transition for them. It corresponds to the criteria of aromaticity and antiaromaticity for hetero[8]circulenes and poprhyrinoids which was obtained in the Ref. [1,2] where the correlation is described by

$$I_{paratropic} \sim \sum_i \frac{<\psi(S_i)\,|\,\hat{L}\,|\,\psi(S_0)>}{E(S_i)-E(S_0)}, \qquad (1)$$

where $<\psi(S_i)\,|\,\hat{L}\,|\,\psi(S_0)>$ is the matrix element of the angular momentum operator for the transition between the *i-th* singlet excited state (S_i) and the electronic ground state (S_0). $E(S_i)-E(S_0)$ is the vertical ground-state excitation energy to the S_i state.

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Conductivity as a Function of Individual Molecular Redox States for a Lindqvist-type polyoxovanadates

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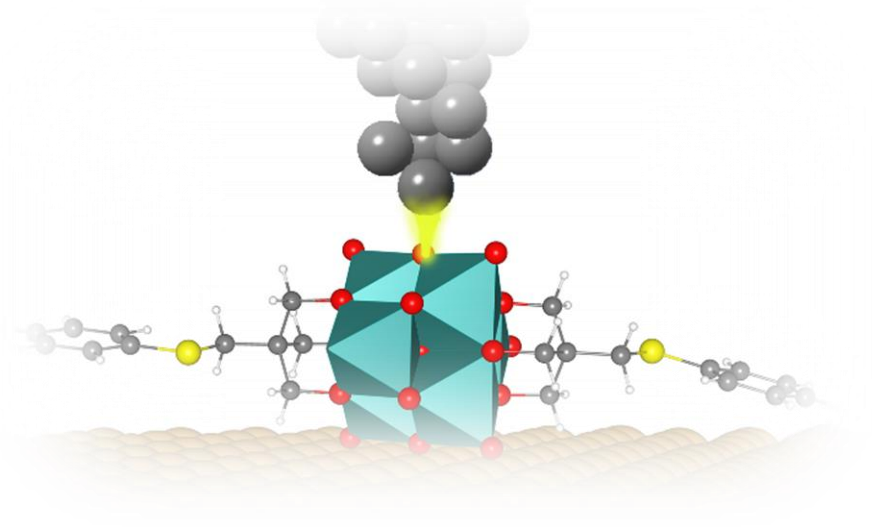
Deposition of the Lindqvist-type polyoxovanadate (POV) functionalized with R organic groups, $[V_6O_{13}\{R\}_2]^{2-}$, on the Au(111) surface gives a physisorbed structure, which features a random orientation on the surface and preserves its structural and electronic characteristics. By applying an external voltage to this arrangement at room temperature, the valence state of the single POV molecule could be changed multiple times through the injection of up to 4 electrons. The calculated density of states shows that the injected electrons partially fill the vanadium *d*-band. Furthermore, the molecular electrical conductivity is dependent on the number of vanadium 3*d* electrons, resulting in several discrete states with increasing conductivity.[1]



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The study of KIE in MAO A Catalyzed Decomposition of Benzylamin derivatives.

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Biogenic amines are an important group of naturally occurring biologically active compounds, most of which act as neurotransmitters–endogenous chemicals that allow the transmission of signals from a neuron to target cells across synapses. Many of them are derivatives of Benzylamine (e.g. Dopamine).[1] The most physiologically important biogenic amines and their level in the central nervous system are prerequisite for homeostasis. It should be noted that control the dopamine level in our brain as well as reaction with the Monoamine Oxidase A (MAO A) is crucial for neurodegeneration. MAO A is flavoenzyme (Fig. 1.) that catalyzes the oxidative deamination of a broad range of biogenic and dietary amines into their corresponding imines.

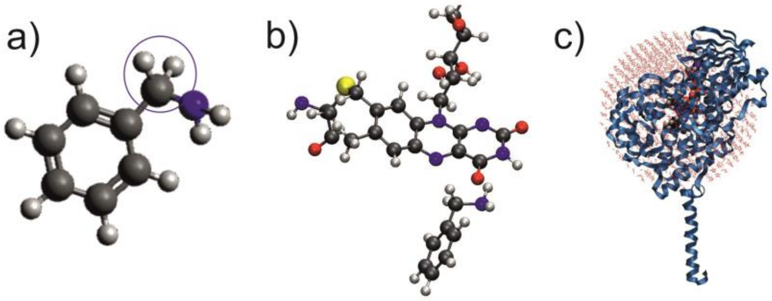

Fig 1. The structures of a) benzylamine, b) flavin moiety, c) complex of MAO A, benzylamine and watter.

We focus on the two steps mechanism for the benzamine decomposition (Fig. 2). In this studied SN2 reaction proton transfer take place between α-CH_2 group in benzyloamine and N-5 in MOA A. It should be pointed out that considered proton transfer is a limiting step of the decomposition process.[2]

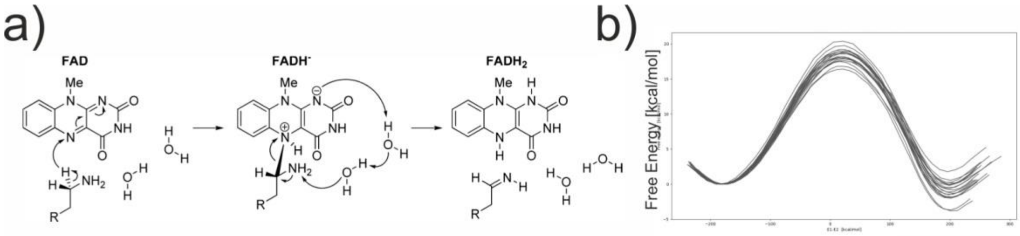

Fig.2 a) Two-steps Mechanism for MAO-Catalyzes Amino Degradation[2]. b) Free Energy profiles.

We use QM/MM methods as a base for umbrella sampling. The path integral quantization (QCP) has been applied for benzylamine DERIVATIVES as well as flavin moiety. The whole enzyme with solvent has been investigated with the QM/MM treatment on the Empirical Valence Bond (EVB) level and OPLSAA force field. The simulations have been performed in the Q6 package[3]. The H/D KIE results have been compared with the experimental kinetic data[4].

The calculated H/D KIE is in the reasonable good agreement with experimental data. Additionally, our results elucidate the influence of the methoxy group in the *para-* position of benzylamine on the activation energy of considered SN2 reaction as well as the KIE.

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On the aromaticity of 1,2,3,5-tetrazine

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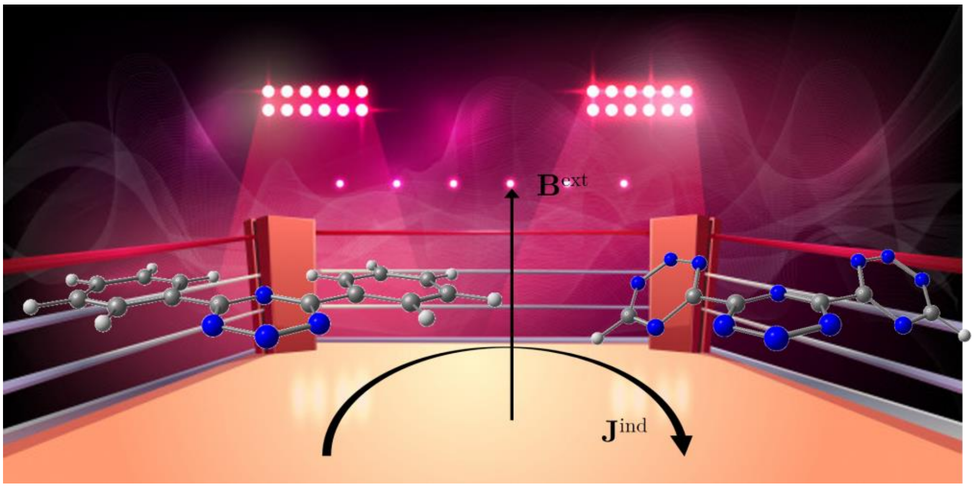

Analysis of the magnetic response is performed for the 1,2,3,5-tetrazine and a set of derivatives including the newly synthesized 4,6-diphenyl-1,2,3,5-tetrazine by calculating the magnetically induced current densities and by dissecting induced magnetic field in its molecular orbital components.[1,2] The calculations show that 1,2,3,5-tetrazine is aromatic but less than benzene. In the derivatives, the electron delocalization of the tetrazine core is affected by the substitution, leading to a less aromatic character than for 1,2,3,5-tetrazine. 4,6-diphenyl-1,2,3,5-tetrazine was found to be the least aromatic one of the studied molecules.[3] In the experimental study, it is mentioned that 4,6-diphenyl-1,2,3,5-tetrazine contains an aromatic tetrazine core, whereas the present calculations show that it is indeed aromatic but not more aromatic than than 1,2,3,5-tetrazine. We propose that 4,6-[1,2,3,5]-ditetrazinyl-1,2,3,5-tetrazine is a substituted 1,2,3,5-tetrazine with a core that has very similar magnetic properties as unsubstituted 1,2,3,5-tetrazine.

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Modelling of SAM formation on silica

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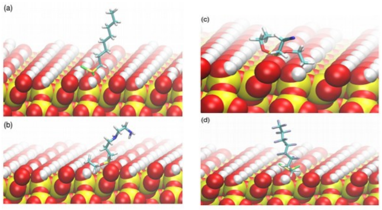
Abstract

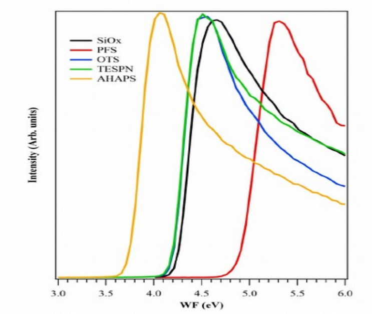
The modification of surfaces with organic molecules represents a promising approach for the incorporation of new functionality into semiconductors. In this work, we study, by periodic density functional theory, the change in work function of the silica surface upon formation of self-assembled monolayers (SAMs) consisting of four different molecules.

Objective

The molecules under consideration changes the work function of the silica (lower energy for AHAPS, almost no change for TESPN and OTS and higher energy for PFS). Our goal is to confirm from the theoretical point of view the observed shifts.



Chemisorption of SAMs molecule on native surface. (a) OTS molecule, (b) AHAPS , (c) TESPN moleculs, (d) PFS molecule.



Results

The work function Φ was calculated for the native surface as well as for each of the four chemisorption structures with one Si–O–Si bridge which were calculated to be most stable. Φ was obtained by subtracting the Fermi energy E_F from the asymptotic vacuum value of the *(xy)*-averaged Coulomb potential. Due to the simplifications made when constructing the surface model used in the calculations (as e.g. the finite number of silica layers), the intrinsic part of the work function is only poorly described by our calculation, and the calculated absolute work functions can therefore not be compared with the experimental values. By contrast, the surface dipole contribution to the work function is very well captured by our model. In general the contribution of the surface dipole moment to the change in work function is :

$$\Delta\Phi = \frac{e\Delta\mu_z}{A\epsilon_0} \qquad (1)$$

		Calculated						Experiment		
Adsorbate		Φ[a]	ΔΦ[a]	$\Delta\mu_z$[b]	μ_z[c]	$\Delta\mu_z$[c]		Φ	ΔΦ	
None (native surface)		6.55	0.00	0.0	1.01	0		4.7	0	
OTS		6.45	-0.10	-0.08	0.86	-0.15		4.5	-0.2	
PFS		7.16	0.61	0.53	1.55	0.53		5.3	0.6	
TESPN		6.00	-0.54	-0.43	0.82	-0.19		4.5	-0.2	
AHAPS		5.06	-1.48	-1.28	0.86	-0.15		4.1	-0.6	

[a] Calculated using the (xy)-averaged Coulomb potential . [b] calculated based on the calculated ΔΦ (eq. 1) [c] Directly calculated dipole moments.

Theoretical Approach of Electronic Structure and DFT of (Sb_2O_5) in Aqueous Medium Molecular Design, Glucose and Cysteine Activity of Inhibitors Probed in Antilieshmanial Activity

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Abstract:

Molecular structures are performed to probe the relative stabilities of the different $(Sb_2O_5)n.H_2O$ clusters at *DFT* levels. Extended basis sets for the treatment of Sb atoms with effective core potentials, which are available in the literature, were used. Hydroxylated Antimony clusters are predicted to be more stable with proton mobility. Analysis of ΔG, ΔS, BSSE and binding energies shows high interaction strengths of Sb-O with Cyclic glycose. Cysteine adsorption through H–proton bond and Sulfur-attached cluster were analyzed. Elucidation of stability-dependent of different hydroxylated Antimony oxides clusters and their interaction with organic molecules (glucose) were determined.

HPC-Europa3: Chemists’ goto source for travel grants

A. Sillanpää
CSC - IT Center for Science Ltd., P.O. Box 405, 02101 Espoo, Finland
e-mail: atte.sillanpaa@csc.fi

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HPC-Europa3 receives funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No.730897

References

[1] https://hpc-europa.cineca.it/researcher/login
[2] http://www.hpc-europa.eu/
[3] http://www.hpc-europa.eu/visitors
[4] https://hpc-europa.cineca.it/host/login

Accurate *ab initio* calculations for ionic alkali and alkaline-earth dimers and trimers

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Molecular ions formed in cold hybrid ion-atom experiments may find interesting applications ranging from precision measurements to controlled chemical reactions. Using *ab initio* electronic structure methods, such as the coupled cluster and configuration interaction ones with small-core relativistic energy-consistent pseudopotentials and large Gaussian basis sets, we calculated potential energy curves and surfaces for all diatomic AB^+ and most of triatomic A_2B^+ molecular ions consisting of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba and Yb atoms [1]. Different geometries and wave-function symmetries of the ground state were found for different classes of molecular ions. We analyzed intermolecular interactions in the investigated systems including additive two-body and nonadditive three-body ones (Fig. 2). Additionally, we investigated electronic structure of the Sr_2^+ molecular ion in detail and shown that alkaline-earth dimer ions despite of their apparently simple structure with three valence electrons only are challenging for state-of-the-art quantum chemistry methods due to their multireference nature and high density of states [2] (Fig. 1).

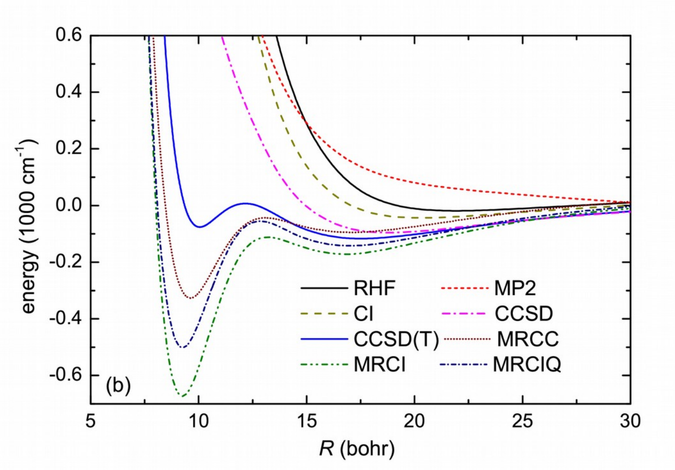

Fig. 1. The lowest-energetic $^2\Sigma_g$ excited electronic state of the Sr_2^+ molecular ion calculated at different levels of theory.

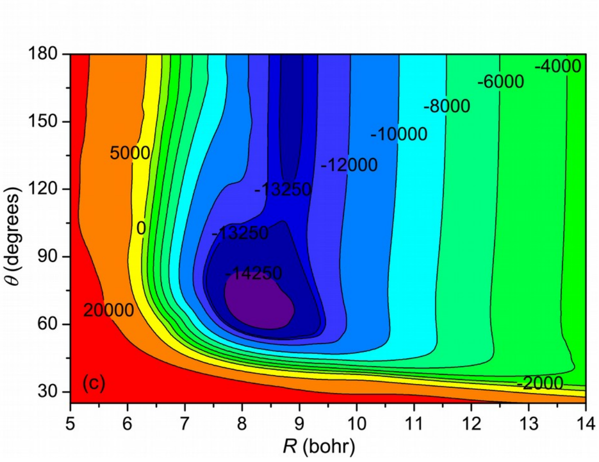

Fig. 2. Two-dimensional cuts through the ground-state potential energy surfaces of Ba_3^+ in the A_1 electronic electronic state.

Literature

[1] M. Śmiałkowski, M. Tomza, Interactions and chemical reactions in ionic alkali and alkaline-earth diatomic AB^+ and triatomic A_2B^+ systems, *submitted to Phys. Rev. A / arXiv:1910.14016* (2019)

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Investigating hydrogen bonding of room-temperature hybrid perovskites $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ through N 1s XAS spectra

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Affiliation: Department of Physics, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden
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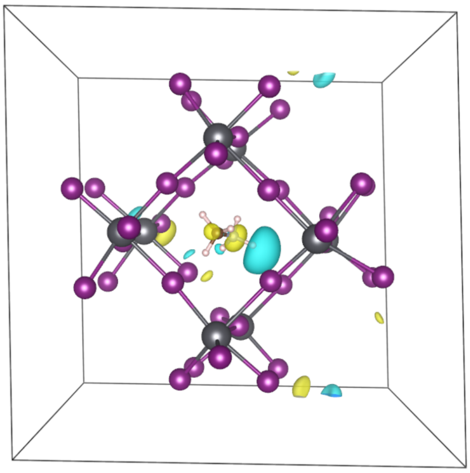
Hybrid perovskite solar cells are a type of photovoltaic material with the general formula ABX_3, consisting of an organic molecule A in an inorganic BX_3 lattice. These materials are relatively new, but have been the focus of much research and shown conversion efficiencies of over 20%. Some of the prototypical hybrid perovskites are $CH_3NH_3PbI_3$ – methylammonium lead iodide (MAPI) – and its bromide cousin MAPBr. These materials were simulated using molecular dynamics for 50 ps and had N 1s XAS spectra calculated at various time points. Hydrogen bonding between the MA molecule and the inorganic lattice is expected to influence the electronic structure and therefore the XAS spectra of the N atoms. The MAPI and MAPBr spectra look qualitatively similar, except the MAPBr spectral features are blueshifted by approximately 0.25 eV. Ordering the individual XAS spectra according to various geometric coordinates shows clear spectral trends based on intramolecular N-H and C-N distances, and intermolecular H-X distances and asymmetry, for both MAPI and MAPBr, which help explain the shape and sharpness of spectral features.



Spectroscopic evidence for hydrogen bonding to Au(I)

Michal Straka,[1] Erik Andris,[2] Jan Vícha,[1] Lubomír Rulíšek,[1] Jana Roithová,[2] Aleš Růžička[3]

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Despite substantial evidence of short Au···H–X contacts derived from a number of X-ray structures of Au^{I} compounds, the nature of Au^{I}···H bonding in these systems has not been clearly understood.[1,2] Herein, we present the first spectroscopic evidence for an intramolecular Au^{I}···H–N hydrogen bond in a [ClAuL]$^{+}$ complex, where L is a protonated N-heterocyclic carbene. The complex was isolated in the gas phase and characterized with helium-tagging infrared photodissociation (IRPD) [3] spectra, in which H–N-mode- derived bands evidence the intramolecular Au^{I}···H–N bond. Quantum chemical calculations reproduce the experimental IRPD spectra and allow to characterize the intramolecular Au···H–N bonding with a short $r_{\mathrm{Au\cdots H}}$ distance of 2.17 Å and an interaction energy of approximately –10 kcal/mol. Various theoretical descriptors of chemical bonding calculated for the Au···H–N interaction provide strong evidence for a hydrogen bonding.[4]

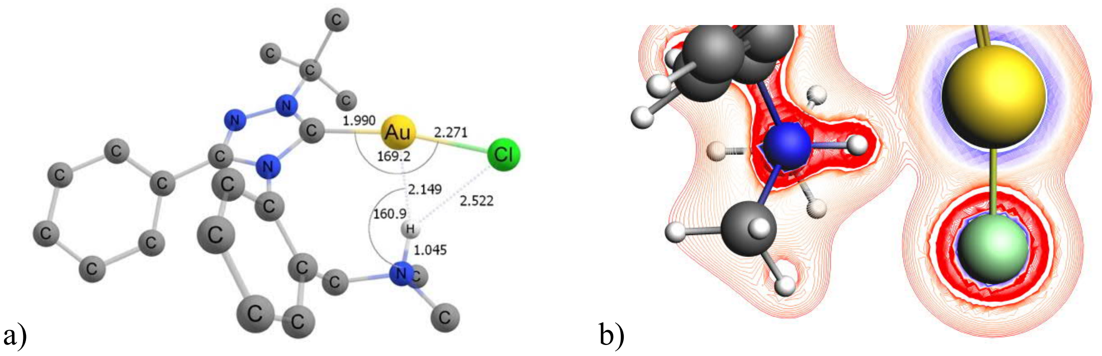

Figure 1: a) Studied system with Au…H bond. Selected geometrical parameters are shown. Angles in degrees, distances in Ångstroms. b) Gradient of energy density reveals interactions between NH and Au.

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Notes

Computational Study of the Transformation of gamma-Valerolactone over Ruthenium Catalyst

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Environmentally friendly approach and shrinking crude oil resources are some of the reasons to study biomass valorisation for production of chemicals [1]. Employment of catalysis makes it possible to convert biomass derived feedstock like gamma-nonalactone (GNL) to various products including hydrocarbons [2] that may be used as fuel. The selectivity pattern of GNL conversion hints towards complex reaction mechanism that could be resolved with the support from computational modelling. In this work we investigate the reaction mechanism of an analogous compound - gamma-valerolactone (GVL) over Ru(0001) surface with an emphasis on reaction selectivity. Exploration of the Potential Energy Surface of Ru-catalyzed GVL conversion is done by means of computational chemistry: density functional theory and projector augmented wave method. Subsequently microkinetic modelling is used to simulate reaction kinetics of a complex reaction network of GVL transformation.

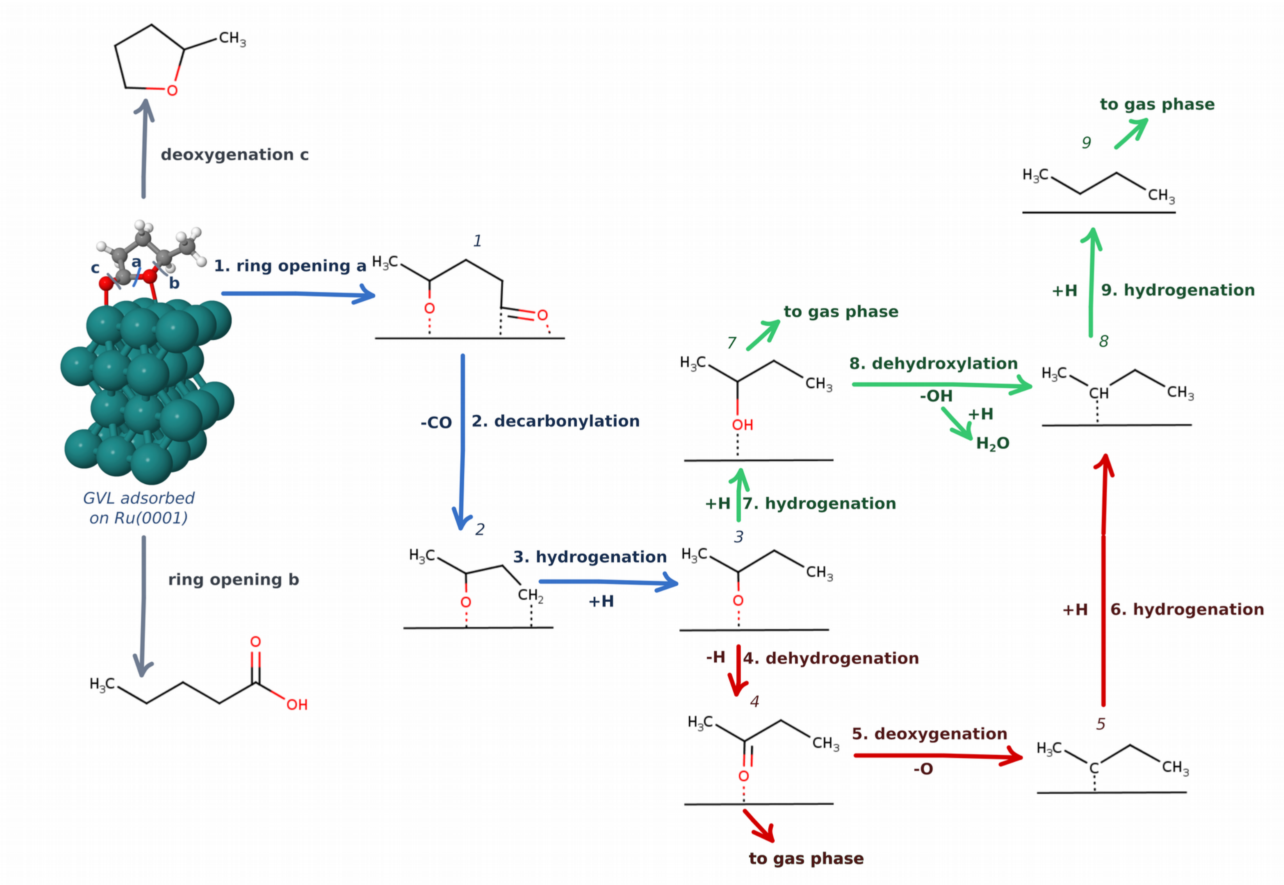

Figure 1. Reaction network of GVL conversion over ruthenium surface.

References

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[2] J. L. González Escobedo, E. Mäkelä, A. Braunschweiler, J. Lehtonen, M. Lindblad, R. L. Puurunen, R. Karinen, *Top Catal* 62: 724 (2019).

Which one fits the best? A search for the ideal $MX@C_{70}$ (M = metal, X = halogen, chalcogen) electric field-driven molecular switch

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A recent study has shown that systems consisting of a molecular dipole MX, encapsulated inside a C_{70} fullerene cage, are molecular switches operable by an external electric field (EEF).[1] Such systems are promising for potential applications in data storage. Our premise (schematically shown in Fig. 1) is based on the existence of two energetically favourable states separated by an energy barrier; switching between these two energetic minima can be controlled by the applied EEF. Furthermore, the orientation of the encapsulated molecule affects the conductivity of the whole molecule, therefore the binary state of this two-level system can be easily "read" due to the distinct conductivity of the two minima.[2]

The aim of this study is to find the most appropriate systems for creating electric field-driven fullerene-based switches with desired switching and transmission properties. To identify the ideal candidate(s), we used density functional theory (DFT) methods to study series of $MX@C_{70}$ systems and their properties, such as the energy barrier between the two minima and its response to the EEF (i.e., how much is the energy barrier lowered when the EEF is applied), dipole moment of MX etc. Our main objective was to determine how the response to the applied EEF correlates with the electronic structure of the studied molecules, and therefore to identify the ideal MX molecules for the $MX@C_{70}$ switch. Based on the results obtained, we propose several molecules as suitable candidates for further studies of their conductivity and usage as EEF-driven nanodevices.

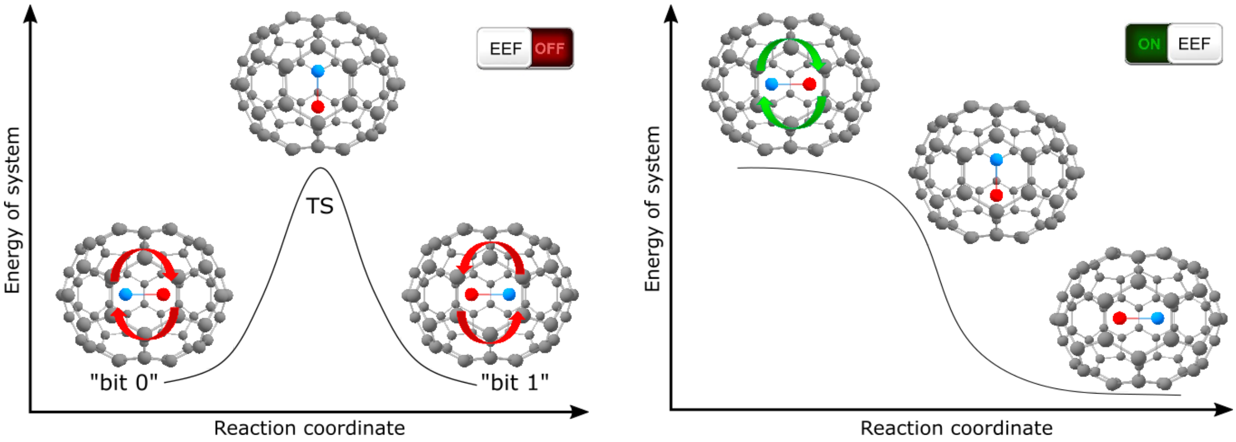

Figure 1: The principle of switching - change of the reaction coordinate with respect to the energy of the system as a response to having the external electric field (EEF) turned either off (left) or on (right)

[1] Foroutan-Nejad, Cina; Andrushchenko, Valery; Straka, Michal; *Physical Chemistry Chemical Physics* **2016**, *18,* 32673-32677

[2] Jaroš, Adam; Bonab, Esmaeil Farajpour; Straka, Michal; Foroutan-Nejad, Cina; *In revision for Journal of the American Chemical Society*

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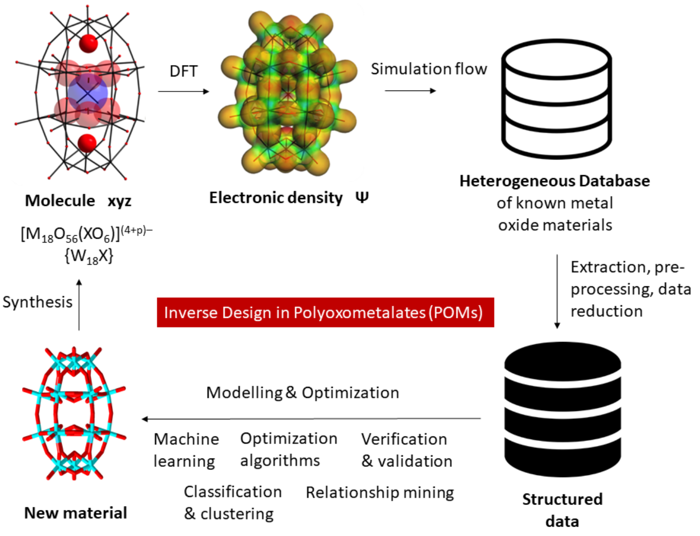
ResearchGate (link) LinkedIn (link) Google Scholar (link) MRSC

Metal oxide chemistry, self-assembly and applications, what does theory say?

Project: I am a newly appointed lecturer at the School of Chemistry in the University of Glasgow. My aim is to apply the concept of 'materials by design' in metal oxide chemistry synthesis. Computationally exploring the combinatorial space generated by the self-assembly of known metal oxides to predict new ones is a challenging task. In my independent research I propose to discover new tailored metal oxide materials using inverse design, see Scheme 1 below. The new materials will be targeted from the beginning searching for a real-world application (e.g. redox flow batteries, memory devices, porosity, selectivity, *etc.*). With the final aim of achieving rational design of prospective oxide materials I aim to apply deep generative models to this class of materials.



Scheme 1. Description of the worflow proposed research in the project. I am a co-author in the following publications, in which theoretical calculations were key to understand metal oxide chemistry reactivity:

a) *J. Am. Chem. Soc.,* **2016,** 28, 8765–8773. (link)
b) *Angew. Chem. Int. Ed.,* **2015,** 54, 7895–7899.(link)
c) *Angew. Chem. Int. Ed.,* **2015**, 51,15708–15712. (link)
d) *Nature,* **2014**, 515, 545–549. (link)
e) *Angew. Chem. Int. Ed.*, **2009**, 48, 5452–5456. (link)

Background: Polyoxometalates (POMs) are discrete molecular structures composed of metal ions bridged by oxide anions.[i] POMs are primarily constituted of early-transition-metal (*d-block*) elements in their highest oxidation states, a great majority of these structures are anionic and consequently salts with obligatory cations. They are composed of between 6 to 368 metal ions in a single molecule and are commonly assembled under 'one-pot' reaction conditions. POMs, especially tungsto- and molybdophospates and silicates, are highly used in industry for catalysis.[ii] First principles multiscale modelling has allowed a deep understanding of materials by enabling accurate prediction of electronic properties of materials at a low computational cost,[iii] for instance, band gaps that are crucial for memory device applications.[iv] Theoretical estimates for new polyoxometalate (POM) materials and their properties lead to a deeper understanding faster, and more efficiently than with test and experimentation alone.

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[iii] S. Grimme, P. R. Schreiner, *Angew.Chem. Int.Ed.* 2018, 57,4170–4176.

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Probing the adsorption of CO_2 from flue gas on metal nitride/phosphide monolayers

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In response to the ever increasing calamity of global warming, the capture and storage of carbon dioxide (CO_2) released by burning of fossil fuels will be an essential technology in the context of energy and environment [1]. Thus, identifying stable materials with improved capability for CO_2 capture has become an important target for capture and storage technologies [2].

In present work, we performed ab initio calculations [3,4] to investigate the structural stability, electron and phonon properties, and CO2 separation and capture ability of mono-layered group III nitrides (XN) and phosphides (XP) (X= Al, Ga, In). Using HSE functional, we found that all the nanostructures show indirect band gaps that varies from 1.35 eV for InP to 4.02 eV for AlN [**Figure 1.]**. The mobility calculations performed using deformation potential theory shows that the mobility is dominated by holes compared to electrons and approaches to the order of 10^3 (in units of $cm^2\ V^{-1}\ s^{-1}$) for AlN and AlP. Also, from phonon band dispersion, soft modes were seen in XP whereas no such modes were observed in XN nanostructures. Additionally, the Raman peak frequency [**Figure 2.**] was seen to show red shift as the mass of metal ion increases [5].

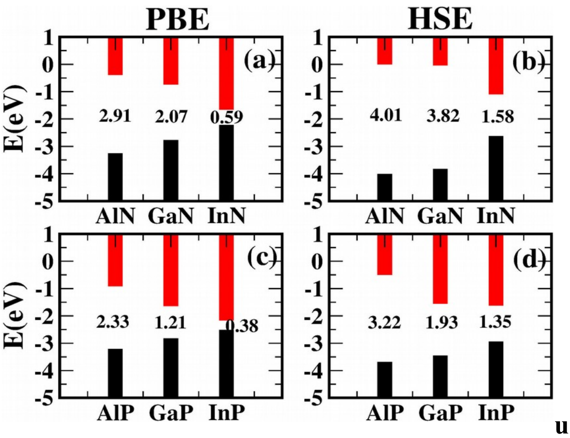

Figure 1. Bandgap of monolayers.

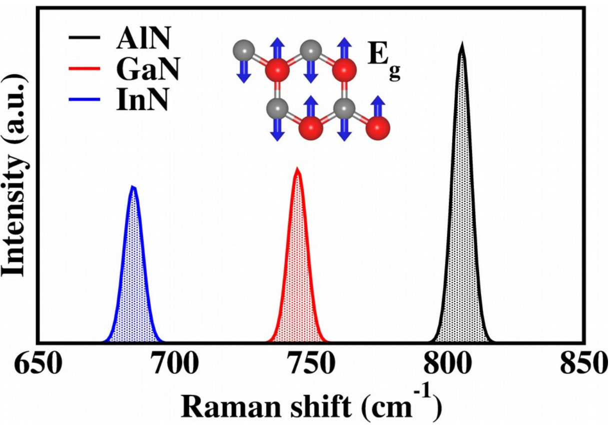

Figure 2. Raman spectra of metal nitrides monolayers.

The calculated binding energy of AlP and GaP was -0.43 eV and -0.37 eV, which is approx. two times as compared to XN nanostructures and the binding energy (-1.06 eV) was found maximum for InP. The adsorption energy of CO_2 on XN and XP follows the order as $E_{GaN} > E_{InN} > E_{AlN}$ and $E_{InP} > E_{AlP} > E_{GaP}$. Moreover, it was found that N_2 show significantly weaker interaction with the XN and XP, which indicates high selectivity of these nanostructures towards CO_2 separation and capture in a flue gas of CO_2 /N_2 [**Table 3**].

We conclude that, the cohesive energy per atom is maximum for AlN (-4.83 eV) and minimum for InN (-2.65 eV) and follows the order as AlN > GaN > InN, i.e. cohesive energy per atom decreases as the size of metal ion increases. Likewise, cohesive energy, the bandgap of both XN and XP were found to decrease as the size of metal ion increases. The carrier mobility was found maximum for AlN (1734.5 $cm^2\ V^{-1}\ s^{-1}$) and minimum for InP (61.2 $cm^2\ V^{-1}\ s^{-1}$) and was found to be dominant by holes for all nanostructures.

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Computation of transition probability approximated absorption spectra (TPA - Abs) of azulene and azulene chloride in Expanded Hartree-Fock (ExHF) Method

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Abstract :

In this poster , a new method is described to calculate dynamical electron correlation effect without adding any computation cost which is termed as Expanded Hartree-Fock (ExHF) method.We also report a new technique to compute absorption spectra of a compound without time dependent calculation.For this purpose the idea of transition probability approximation of TPA-CI is used.This method is termed as Transition Probability Approximated Absorption Spectra (TPA-AbS). TPA-AbS combined with ExHF is found the best for computation of absorption spectra of a compound with respect to accuracy, computation time and storage capacity. Both ExHF and TPA-AbS are found very handy to implement for larger systems. Using these two methods absorption spectra of azulene and azulene chloride are computed.