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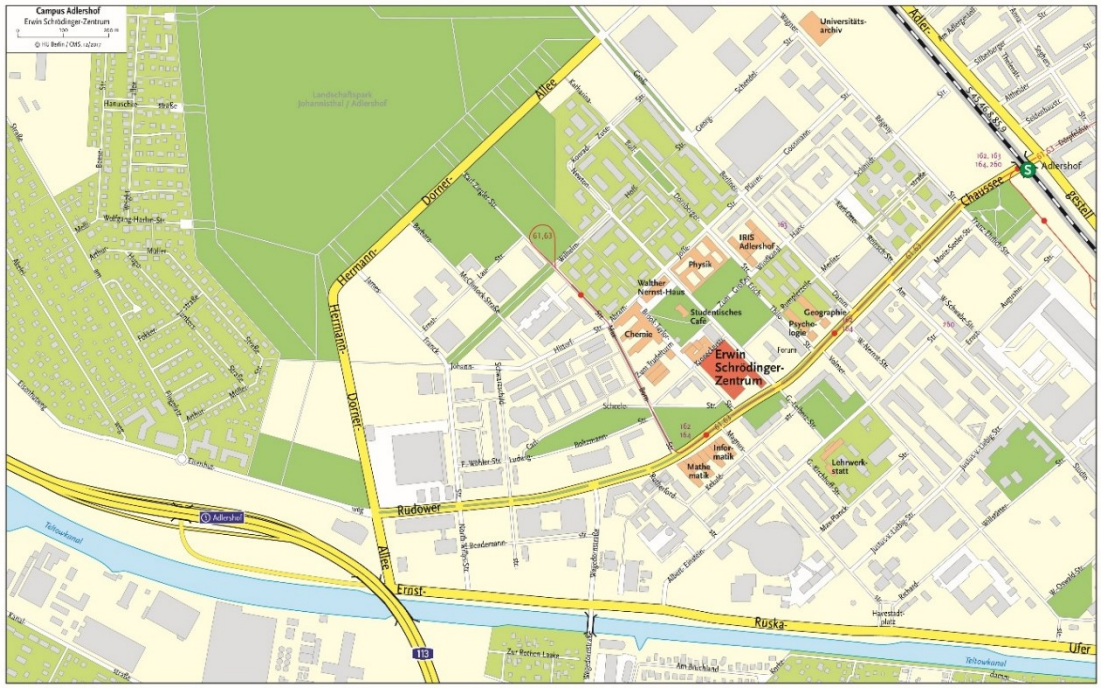
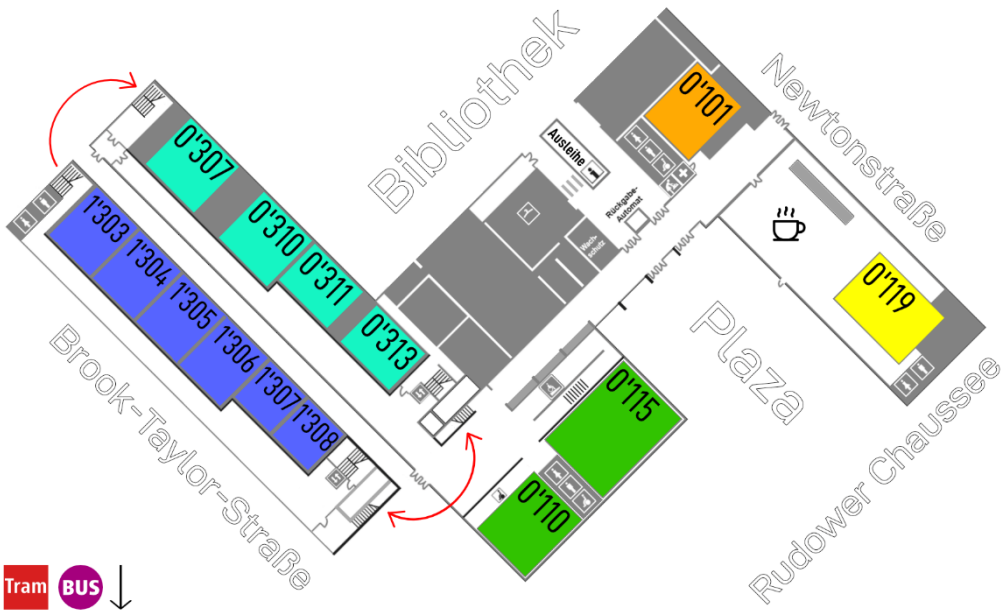
Venue

QBIC VII will take place at the **Erwin Schrödinger-Zentrum** of the Humboldt University of Berlin. It is close to the S-Bahn station Adlershof. You can simply walk down Rudower Chaussee until you see the big black building to your right. Alternatively, you can use the tram (61, 63, M17) and get off at station "Walther-Nernst-Str" or "Magnusstr". You will be provided with **internet access via eduroam**.



All oral presentations will be held in **Lecture Hall 0'115**, located on the ground floor of the Erwin Schrödinger-Zentrum (see site plan below). Breaks and the poster session will take place in the Foyer directly in front of the lecture hall which is also where you can find the Registration desk.



Program

Tuesday (26.8.)

	13:00 – 13:10	QBIC Organization Team	Opening remarks
K	13:10 – 14:00	Wonwoo Nam	Biomimetic Metal-Oxygen Intermediates in Dioxygen Activation and Formation Reactions
C	14:00 – 14:20	Per Siegbahn	Why is DFT so much better for larger systems?
C	14:20 – 14:40	Ran Friedman	Proteins and Heavy Metals: from Biology to Medicine
C	14:40 – 15:00	Markella Aliki Mermigki	Shape-Shifting Tetranuclear Manganese Clusters
	15:00 – 15:40		**Break**
I	15:40 – 16:10	Ainara Nova	From homogeneous to single-atom heterogeneous catalysis in C-H bond activation reactions
C	16:10 – 16:30	Gunasekaran Velmurugan	Iron catalyzed formation of methyl radicals as a common source of environmentally important volatile organic compounds
C	16:30 – 16:50	Kyung-Bin Cho	Examples of reaction mechanisms with synthetic biomimetic catalysts: NOx reduction and naphthalene di-oxygenation
C	16:50 – 17:10	Denis Poire	Does It Take Two CO? Unraveling ACS's True Stoichiometry
C	17:10 – 17:30	Esma Birsen Boydas	FAIR Quantum Chemistry using NOMAD
C	17:30		**Socializing**

Wednesday (27.8.)

I	09:00 – 09:30	Bhaskar Mondal	Electronic Structure and Reactivity of Metal-Bound Nitrene Intermediates
C	09:30 – 09:50	Peter Burger	Antiferromagnetic Coupling of Dimeric Iridium PDI Complexes
I	09:50 – 10:20	Max Holthausen	Nitrogen Fixation beyond Ammonia – Theoretical (Ad)Ventures and Frontiers
	10:20 – 10:50		**Break**
I	10:50 – 11:20	Erik D. Hedegård	Exploring the mysteries of metalloenzymes in mushrooms
C	11:20 – 11:40	Ragnar Bjornsson	ASH: a multiscale, multitheory modelling program
C	11:40 – 12:00	Umberto Terranova	Redox Potentials of Iron–Sulfur Clusters via QM/MM: From Synthetic Peptides to Viral Enzymes
C	12:00 – 12:20	Michael Stier	Reliable Redox Potential Calculations of Proteins
	12:20 – 14:00		**Lunch Break**
K	14:00 – 14:50	Heather J. Kulik	Machine learning and software for discovery in transition metal complexes and metalloenzymes
C	14:50 – 15:10	Ravi Kumar	Large cluster and QM/MM study of the fully oxidized state of the oxygen-tolerant [NiFe] hydrogenase from *Hydrogenophilus thermoluteolus*
C	15:10 – 15:30	Marius Horch	Probing [NiFe] Hydrogenases by Experimental and Computational 2D-IR Spectroscopy
C	15:30 – 15:50	Shalini Yadav	Carbon Monoxide Dehydrogenase: A Structural and Theoretical Perspective
	15:50 – 16:20		**Break**

I	16:20 – 16:50	Shengfa Ye	Electronic Structure and Reactivity of Dinuclear Bridging Nitrides
C	16:50 – 17:10	Andrea Madabeni	Exploring analogies and differences between coupled binuclear copper proteins via multiscale protocols
C	17:10 – 17:30	Erna K. Wieduwilt	Computing Enzymatic Reaction Mechanisms at Solvent-Exposed Copper Sites
I	17:30 – 18:00	Hélène Bolvin	Probing the magnetic properties of actinide complexes by paramagnetic NMR.
	18:00 – 19:30		**Poster Session**

Thursday (28.8.)

A	09:00 – 09:50	Anastassia Alexandrova	Enzymes as molecular capacitors
I	09:50 – 10:20	Adam Kubas	Towards an accurate description of (bio)molecules at catalytically active surfaces
	10:20 – 10:50		**Break**
A	10:50 – 11:40	Mariusz Radoń	Spin-state energetics of transition metal complexes: towards accurate prediction and benchmarking
I	11:40 – 12:10	Radek Marek	Paramagnetic effect in NMR spectroscopy of transition-metal complexes
C	12:10 – 12:30	Carlos Jimenez-Muñoz	Multi-scale modelling for an accurate prediction of redox potentials in iron coordination compounds
	12:30 – 14:00		**Lunch Break**

K	14:00 – 14:50	Kallol Ray	Small Molecule Activation at Transition Metal Centers: Structure-Function Correlations
C	14:50 – 15:10	Mayank Mahajan	Electronic Structure and Reactivity Correlation of Fe-Porphyrin-Nitrene Species in Nitrene Transfer Catalysis
C	15:10 – 15:30	James Shee	Correlated electronic structure modeling of polynuclear transition metal compounds with phaseless auxiliary-field quantum Monte Carlo
I	15:30 – 16:00	Celia Fonseca Guerra	G-Quadruplexes: Insights from Quantum Chemical Bonding Analyses
C	16:00 – 16:20	Christof Holzer	New versatile tools for complex molecules and materials
	16:20 – 16:30		**Break**
	16:30	QBIC society meeting	
	19:00		**Conference Dinner**

Friday (29.8.)

I	09:00 – 09:30	Michael Bühl	Modelling paramagnetic NMR chemical shifts of copper-based metal-organic frameworks
C	09:30 – 09:50	Lucas Lang	Field-Dependent NMR Shifts in Paramagnetic Molecules: Theory and Interpretation
C	09:50 – 10:10	Adam Šrut	Interplay of electronic, vibrational and solvent structure in aqueous solution of the Creutz–Taube ion
C	10:10 – 10:30	Zuzanna Wojdyla	Exploring the shift from proton-coupled to hydride-coupled electron transfer
	10:30 – 11:00		**Break**

I	11:00 – 11:30	Miquel Costas	Expanding the Reach of Selective C-H Oxidation Reactions with Bioinspired Catalysts via Cationic Mechanisms
C	11:30 – 11:50	Sergey I. Bokarev	Sub-fs electron dynamics in transition metal complexes
C	11:50 – 12:10	Olga S. Bokareva	Excited-State Dynamics of Cyclometalated Cobalt(III) Complexes
C	12:10 – 12:30	Niklas von Rhein	The temperature dependence of Mössbauer quadrupole splitting values: a quantum chemical analysis
	12:30	QBIC Organization Team	Poster Award Ceremony and Closing Remarks

Keynote Lectures

Biomimetic Metal-Oxygen Intermediates in Dioxygen Activation and Formation Reactions

Wonwoo Nam

Department of Chemistry and Nano Science, Ewha Womans University, Seoul 120-750, Korea

E-mail: wwnam@ewha.ac.kr

Dioxygen is essential in life processes, and enzymes activate dioxygen to carry out a variety of biological reactions. One primary goal in biomimetic research is to elucidate structures of reactive intermediates and mechanistic details of dioxygen activation and formation reactions occurring at the active sites of enzymes, by utilizing synthetic metal-oxygen complexes. A growing class of metal-oxygen complexes, such as metal–superoxo, –peroxo, –hydroperoxo, and –oxo species, have been isolated, characterized spectroscopically, and investigated in various oxygenation reactions. During the past several decades, we have been studying the chemical and physical properties of various reactive intermediates, such as high-valent iron- and manganese-oxo complexes of heme and non-heme ligands in oxo-transfer and C-H activation reactions, non-heme metal-peroxo complexes in nucleophilic/electrophilic reactions, and non-heme metal-superoxo complexes in electrophilic reactions. The effects of supporting and axial ligands on structural and spectroscopic properties and reactivities of metal-oxygen adducts have been extensively investigated as well. In this symposium, I will present the story of nonheme metal-oxo complexes and our new findings on the reactivities of mononuclear nonheme iron-peroxo species in electrophilic oxidation reactions, such as C-H bond activation, oxygen atom transfer, and cis-dihydroxylation reactions.

[1] Xue-Peng Zhang, Anirban Chandra, Yong-Min Lee, Rui Cao, Kallol Ray, and Wonwoo Nam “Transition Metal-Mediated O–O Bond Formation and Activation in Chemistry and Biology” *Chem. Soc. Rev.* **2021**, *58*, 4804–4811

[2] Virginia Larson, Beatrice Battistella, Kallol Ray, Nicolai Lehnert, and Wonwoo Nam “Iron and Manganese Oxo Complexes, Oxo Wall and Beyond” *Nat. Rev. Chem.* **2020**, *4*, 404–419.

[3] Shunichi Fukuzumi, Kyung-Bin Cho, Yong-Min Lee, Seungwoo Hong, and Wonwoo Nam “Mechanistic Dichotomies in Redox Reactions of Mononuclear Metal-Oxygen Intermediates” *Chem. Soc. Rev.* **2020**, *49*, 8988–19027.

[4] Wonwoo Nam “Hydrogen Atom Transfer Reactions by Metal-Oxygen Intermediates” *Acc. Chem. Res.* **2018**, *51*, 2014–2022.

[5] Kyung-Bin Cho, Hajime Hirao, Sason Shaik, and Wonwoo Nam “To rebound or dissociate? This is the mechanistic question in C-H hydroxylation by heme and nonheme metal-oxo complexes” *Chem. Soc. Rev.* **2016**, *45*, 1197–1210.

[6] Wonwoo Nam “Synthetic Mononuclear Nonheme Iron-Oxygen Intermediates” *Acc. Chem. Res.* **2015**, *48*, 2415–2423.
[7] Wonwoo Nam, Yong-Min Lee, and Shunichi Fukuzumi “Tuning Reactivity and Mechanism in Oxidation Reactions by Mononuclear Nonheme Iron(IV)-Oxo Complexes” *Acc. Chem. Res.* **2014**, *47*, 1146–1154.
[8] Jaeheung Cho, Ritimukta Sarangi, and Wonwoo Nam “Mononuclear Metal-O2 Complexes Bearing Macrocyclic TMC Ligands *Acc. Chem. Res.* **2012**, *45*, 1321–1330.
[9] Wonwoo Nam “High-Valent Iron(IV)-Oxo Complexes of Heme and Nonheme Ligands in Oxygenation Reactions” *Acc. Chem. Res*. **2007**, *40*, 522–531.
[10] Wonwoo Nam “Guest Editorial: Dioxygen Activation by Metalloenzymes and Models” *Acc. Chem. Res.* **2007**, *40*, 465.

Machine learning and software for discovery in transition metal complexes and metalloenzymes

Heather J. Kulik

Lammot du Pont Professor of Chemical Engineering, Department of Chemical Engineering and Chemistry, Massachusetts Institute of Technology

Machine learning (ML) in transition metal chemistry has lagged behind other areas of chemistry due to the combination of diversity of chemical bonding and limitations in high quality data sets, experimental or computational. Despite this limitation, the open-shell nature of transition metals means that intricate patterns in structure-property relationships are uniquely well-suited to the non-linear mappings that are possible with ML models. I will describe our efforts to overcome prior limitations to accelerate the discovery of novel transition metal containing materials using machine learning. I will review some of the software we have developed to address these challenges. I will also show how we have leveraged large datasets of synthesized materials to uncover those with novel function in polymer networks. I will demonstrate the success of our design strategy through macroscopically visible changes in network scale properties of polymers once our transition metal complexes are incorporated. Time permitting, I will also talk about our work to bring high-throughput screening and machine learning to uncovering structure-property relationships in metalloenzymes as well. The glue that ties all of these efforts together is open source workflows, and I will describe the key software elements we have developed that make these advances possible.

Small Molecule Activation at Transition Metal Centers: Structure-Functions Correlations

Kallol Ray

Department of Chemistry, Humboldt-Universität zu Berlin, Berlin (Germany).

kallol.ray@chemie.hu-berlin.de

Small molecule activation constitutes one of the main frontiers of inorganic and organometallic chemistry, with much effort directed towards the development of new processes for the selective and sustainable transformation of abundant small molecules such as dioxygen (O_2), water (H_2O), hydrogen peroxide (H_2O_2) or protons (H^+) into high-value chemical feedstocks and energy resources. Because nature mostly uses metal ions to activate these relatively inert molecules and modulate their reactivity, much inspiration for the field has come from bioinorganic chemistry. This talk will focus on some of the recent highlights from our group on homogenously catalyzed bioinspired activation of small molecules, as well as stoichiometric reactions that further our understanding towards such ends. It will cover many aspects of small molecule activation including: organometallic chemistry, spectroscopy, synthesis, and detailed mechanistic studies involving trapping of reactive intermediates. The demonstrated examples will help to emphasize the continuous effort of our group in uncovering the structure-reactivity relationships of biomimetic model complexes, which may allow vital insights into the prerequisites necessary for the design of efficient catalysts for the selective functionalization of unactivated C–H bonds, O_2/H_2O/H_2O_2 activations, or H^+ reductions by using cheap and readily available first-row transition metals under ambient conditions.

Award Lectures

Enzymes as molecular capacitors

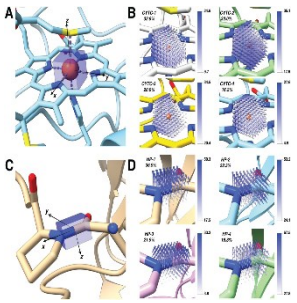
Anastassia N. Alexandrova

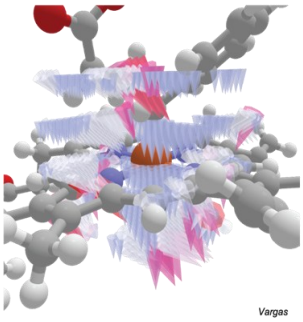
Department of Chemistry and Biochemistry, UCLA

E-mail: alexandrova@g.ucla.edu

Proteins have been shown to produce intramolecular electric fields, preorganized to help enzymatic catalysis. Using IR probes placed in proteins, and measuring their Stark shift, it became possible to assess the local fields at the location of the probe, and correlate those with the reactivity. The talk will show that in fact, 3-D fields in the entirety of the active site (as opposed to a particular bond) are relevant to catalysis. These fields are strongly heterogeneous and dynamic, and both properties are key to enzyme function. We therefore view protein dynamics from the point of view of the dynamics of the field that it creates, correlate global dynamical fields to reactivity, use these complex fields as protein design targets, and machine learn protein function form the portraits of the fields in their active sites. The talk will highlight several methods for field analysis, directly as a vector object, and indirectly via the scalar field of electronic charge density.

I will show that the diverging reactivity of the natural Fe-heme proteins is strongly regulated by the electric field from the protein, outside of the primary coordination sphere of the Fe. The diverse function of heme Fe proteins can be MLed from the fields alone, aka an image recognition problem. Furthermore, directed evolution in fact optimizes electric fields (Protoglobin evolved to catalyze carbene transfer being an example system). The evolved field is strongly heterogeneous and curvy, aligned opposite to the direction of the electron flow in the reaction. Even curvier fields can be seen in chorismite mutases – enzymes catalyzing pericyclic reactions. Yet excitingly, regardless of the protein class, size, and fold, the one unifying factor of chorismite mutases is their active site electrostatics.




Vargas


Picasso

[1] Chaturvedi, S. S.; Vargas, S.; Ajmera, P.; Alexandrova, A. N. *Directed Evolution of Protoglobin Optimizes the Enzyme Electric Field.* **2024**, J. Am. Chem. Soc., 146, 16670-16680.

[2] Bím, D.; Alexandrova, A. N. *Local Electric Fields as a Natural Switch of Heme-Iron Protein Reactivity.* **2021** ACS Catal.,11, 6534-6546.

[3] Bím, D.; Alexandrova, A. N. *Electrostatic Regulation of Blue Copper Sites.* **2021**, Chem. Sci.,12, 11406-11413.

[4] Eberhart, M. E.; Wilson, T. R.; Jones, T.; Alexandrova, A. N. *Electric fields imbue enzyme reactivity by aligning active site fragment orbitals.* **2024**, Proc. Natl. Acad. Sci., i121, e2411976121.

[5] Vargas, S.; Chaturvedi, S.; Alexandrova, A. N. *Machine-learning prediction of protein function from the portrait of its intramolecular electric field.* **2024**, J. Am. Chem. Soc., 146, 28375-28383.

[6] Vargas, S.; Gee, W.; Alexandrova, A. N. *High-throughput Quantum Theory of Atoms in Molecules (QTAIM) for Geometric Deep Learning of Molecular and Reaction Properties.* **2024**, Digital Discovery, DOI: 10.1039/D4DD00057A.

[7] Vargas, S.; Hennefarth, M. R.; Liu, Z.; Alexandrova, A. N. *Machine Learning to Predict Reaction Barriers from the Reactant State Electron Density.* **2021**, J. Chem. Theor. Comput., 17, 6203-6213.

[8] Eberhart, M. E.; Alexandrova, A. N.; Ajmera, P.; Bím, D.; Chaturvedi, S.; Vargas, S.; Wilson, T *Methods for Theoretical Treatment of Local Fields in Proteins and Enzymes.* **2025**, Chem. Rev., 125, 3772–3813.

Spin-state energetics of transition metal complexes: towards accurate prediction and benchmarking

Mariusz Radoń[a], Gabriela Drabik, Janusz Szklarzewicz

[a)] Faculty of Chemistry, Jagiellonian University, Kraków, Gronostajowa 2, 30-387 Kraków, Poland

Spin states of transition metal complexes are highly relevant in bioinorganic chemistry, but it is difficult to predict their energies reliably using available DFT and WFT (wave function theory) methods.[1] This talk will highlight some of our recent achievements in constructing efficient computational protocols[2] and benchmarking theoretical predictions with respect to curated experimental data.[3,4] The SSE17 benchmark,[3] which includes 9 adiabatic energies of spin-crossover complexes and 8 vertical energies derived from spin-forbidden absorptions, is used to assess the accuracy of spin-state energetics predicted by WFT and DFT methods for a diverse set of metals (Fe^{II}, Fe^{III}, Co^{II}, Co^{III}, Ni^{II}, Mn^{II}) and ligand field strengths, with the proper accounting for vibrational and environmental effects. The results demonstrate a high accuracy of the single-reference CCSD(T) method and some double-hybrid functionals (PWPB95, B2PLYP), and confirm the problem of non-universality in commonly used functionals. Some caveats of comparing theory with experiment will be discussed, including a curious case of $[Fe(H_2O)_6]^{3+}$.[5]

We acknowledge National Science Centre (grant no. 2017/26/D/ST4/00774), PLGrid Infrastructure (HPC Center: ACK Cyfronet AGH, grant no. PLG/2024/017815) and the European Union (project “ATOMIN 2.0”, POIR.04.02.00–00-D001/20).

[1] (a) M. Swart, In: Lledós, A., Ujaque, G. (eds) *Topics in Organometallic Chemistry*, vol 67. Springer, Cham, **2020**, vol. 67, pp. 192-226. (b) M. Radoń, *Phys. Chem. Chem. Phys.* **2023***, 25*, 30800.

[2] G. Drabik, M. Radoń, *J. Chem. Theory. Comput.* **2024**, *20*, 3199.

[3] M. Radoń, G. Drabik, M. Hodorowicz, J. Szklarzewicz, *Chem. Sci.,* **2024***, 15*, 20189.

[4] M. Radoń, *Phys. Chem. Chem. Phys.* **2024***, 26*, 18182.

[5] (a) M. Radoń, K. Gąssowska, J. Szklarzewicz, E. Brocławik, *J. Chem. Theory Comput.***, 2016**, *12*, 1592; (b) G. Drabik, J. Szklarzewicz, M. Radoń, *Phys. Chem. Chem. Phys.* **2021**, *23*, 151.

Invited Lectures

From homogeneous to single-atom heterogeneous catalysis in C-H bond activation reactions

Ainara Nova[1,2]

[1]Hylleraas Centre for Quantum Molecular Sciences and [2]Centre for Material Science and Nanotechnology, Department of Chemistry, University of Oslo, 1033 Blindern, Oslo, 0315, Norway

ainaran@kjemi.uio.no

Immobilizing well-defined molecular catalysts on solid supports, such as metal-organic frameworks (MOFs), is a promising strategy to merge the benefits of homogeneous and heterogeneous catalysis. To fully leverage the benefits of supported catalysts, we need a better understanding of how the reactivity of flexible, isolated active sites in solution is altered when they are immobilized in a rigid, confined environment where mass transfer is a limiting factor. Computational methods, combined with experiments, can assist in gaining this understanding.

Our group is using this strategy to develop efficient and selective single-atom heterogeneous catalysts for hydrogenation and C-H bond oxidation reactions.[1-5] In these studies, we have compared the reactivity of homogeneous catalysts, including Cu-biomimetic systems, with related or analogous single-atom heterogeneous catalysts. Computational methods have been employed to both understand the observed reactivity and support the characterization of the active sites. This presentation will summarize our key findings, revealing the specific changes in reactivity and the factors that may cause them.

[1] Cao, N.; Castro, A. C.; Balcells, D.; Olsbye, U.; Nova, A. *Inorg. Chem.* **2024**, *63*, 23082.

[5] Denjean, A. E. F.; Nova, A.; Balcells, D. *ACS Catal.* **2024**, *14*, 11332.

[2] Aunan, E.; Finelli, V.; Prodinger, S.; Cao, N.; Garetto, B.; Deplano, G.; Signorile, M.; Borfecchia, E.; Lillerud, K. P.; Nova, A.; Bordiga, S.; Olsbye, U. *J. Catal.* **2024**, *438*, 115722.

[3] Garetto, B.; Cao, N.; Finelli, V.; Aunan, E.; Signorile, M.; Olsbye, U.; Bordiga, S.; Nova, A.; Borfecchia, E. *J. Phys. Chem. C* **2025**, *129*, 3570.

[4] Centrella, B.; Pupo, R. C. S.; Rasheed, M. A.; Nejrotti, S.; Garetto, B.; Finelli, V.; Cao, N.; Bonomo, M.; Barolo, C.; Borfecchia, E.; Signorile, M.; Bertinetti, S.; Szilágyi, P. Á.; Nova, A.; Olsbye, U.; Bordiga, S. *ChemSusChem* **2025**, *18*, e202500149.

Electronic Structure and Reactivity of Metal-Bound Nitrene Intermediates

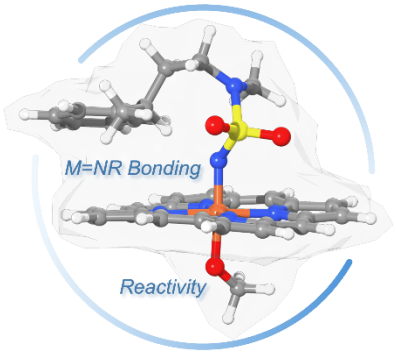
Bhaskar Mondal

School of Chemical Sciences, Indian Institute of Technology Mandi, 175075 Himachal Pradesh, India

e-mail: bhaskarmondal@iitmandi.ac.in

web: www.compcatlab.com

Metal-bound nitrenes are key intermediates in a variety of biocatalytic and synthetic nitrene-transfer reactions. One of the most intriguing aspects of metal-nitrenes is the complex bonding between open-shell transition metals and redox-active nitrenes, which significantly influences their nitrene-transfer mechanism and reactivity. However, determining the “true” electronic nature of the metal-nitrene bond–and thereby understanding the electronic origins of their reactivity–poses a significant challenge due to their high reactivity.



We utilize advanced quantum chemical techniques, such as density functional theory (DFT), ab initio multi-configurational CASSCF, and CASSCF/NEVPT2 methods, to precisely characterize the metal-nitrene bonding and its impact on reactivity. The first part of this talk highlights the fundamental differences in bonding and reactivity between Co- and Fe-porphyrin-nitrenoid species. The second part demonstrates how the subtle Fe-nitrene bonding interactions are influenced by the ligand environment, leading to unexpected nitrene-transfer reactivity. Finally, using a Co-catalyzed C–H amination reaction as an example, the discussion will emphasize how the metal–nitrene bond governs the reaction mechanism. Overall, our findings underscore the importance of a deep understanding of electronic structure-reactivity correlations in catalytic nitrene-transfer reactions. This knowledge not only unravels the complex electronic factors driving reactivity but also paves the way for the design of more efficient catalysts for targeted organic transformations.

[1] Mahajan, M.; Mondal, B. *Inorg. Chem.* **2023**, *62*, 5810–5821.
[2] Mahajan, M.; Mondal, B. *JACS Au* **2023**, *3*, 3494–3505.
[3] Aher, Y.; Ghosh, S.; Mondal, B.; Pawar, A. B. *JACS Au* **2025**, *5*, 2677–2688.

Innocent until proven guilty – assessing ligand descriptors for first row transition metals

Natalie Fey[a], Felix Mac-Fall[a], Sarah Valabhji[a]

[a)] School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.
Website: https://feygroupchem.wordpress.com/

Computational studies of homogeneous catalysis play an increasingly important role in furthering (and changing) our understanding of catalytic cycles and can help to guide the discovery and evaluation of new catalysts.[1-3] While a truly "rational design" process remains out of reach, detailed mechanistic information from both experiment and computation can be combined successfully with suitable parameters characterising catalysts[4,5] and substrates to predict outcomes and guide screening.[6]

The computational inputs to this process rely on large databases of parameters characterising ligand and complex properties in a range of different environments. [4,5] Such maps of catalyst space can be combined with experimental or calculated response data,[7] as well as large-scale data analysis,[8] and we are increasingly applying data science techniques for visualisation and prediction.

In this presentation, I will use examples drawn from our recent work, including the extension of one of our ligand property databases (LKB-bid)[9] to focus on ligand effects on complexes of first row transition metals, including the structural and energetic effects of different spin states.

[1] McMullin, C. L.;Fey, N.; Harvey, J. N. *Dalton Trans.*, **2014**, *43*,13545-13556
[2] Fey, N.; Garland, M.; Hopewell, J. P.; McMullin, C. L., Mastroianni, S.;Orpen, A. G.; Pringle, P. G., *Angew. Chem. Int. Ed*., **2012**, *51*, 118-122.
[3] Fey, N.; Lynam, J. M. *WIREs Comp. Molec. Sci*. 2021, e1509, DOI:10.1002/wcms.1590.
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Nitrogen Fixation beyond Ammonia – Theoretical (Ad)Ventures and Frontiers

Max C. Holthausen[a]

[a)] Institut für Anorganische und Analytische Chemie, Goethe-Universität Frankfurt, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany

The direct conversion of N_2 into nitrogenous products, like nitriles, amines, or nitro compounds, through catalytic C–N bond formation represents an ambitious challenge with the potential to reshape the nitrogen value chain by offering a sustainable alternative to ammonia-based processes. While this transformation has yet to be realized, significant progress has been made toward its enabling steps. In particular, the splitting of gaseous dinitrogen to form well-defined nitrido complexes under mild conditions has matured into a well-established field, and the chemistry of molecular nitrides is well developed.[1]

Further progress hinges on the identification of key intermediates involved in the elementary steps of potential catalytic cycles and correlating their electronic structure to reactivity. The talk outlines combined experimental and theoretical efforts along these lines, with a focus on the detailed understanding of electronic factors that control the metal-nitrogen bond continuum – from M≡N in nitrido complexes to M–N in metallonitrenes – as the associated bond strength is a key factor to balance the thermochemistry of plausible catalytic cycles. Highlights of this work will be presented from a theoretical perspective, such as the first characterizations of authentic metallonitrenes[2] and metallocarbenes[3] with triplet ground states, the boron-mediated catenation of N_2 to $[N_4]^{2-}$,[4] as well as the analysis of a striking failure of commonly used quantum-chemical methods in a seemingly innocuous case.[5]

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Exploring the mysteries of metalloenzymes in mushrooms

Erik D. Hedegård[1]

[1] University of Southern Denmark, Campusvej 55, 5230 Odense M, Denmark

erdh@sdu.dk

Lytic polysaccharide monooxygenases (LPMOs) belong to a copper-dependent family of enzymes, used by fungi and bacteria to boost polysaccharide degradation. The LPMOs oxidize the glycosidic bonds that link the monosaccharide subunits, breaking the recalcitrant polysaccharides. This oxidation is unique among polysaccharide-degrading enzymes and has the potential to overcome the present barriers for sustainable biofuel production from lignocellulosic sources.

Despite that it is now 15 years since the first discovery of LPMOs, the substrate oxidation mechanism of the LPMOs has remained elusive: Proposals employing either O_2 or H_2O_2 as co-substrate exist in the literature. Theoretical investigations on the AA9 LPMO *Ls*AA9 have previously supported both mechanisms [1], although this contrasts with recent experiments [2]. Moreover, the energetics of the rate-determining step has been predicted quite differently (see ref. [3] for an overview). A possible explanation is that the theoretical results critically depend on how the Cu active site is modeled.

We have recently investigated both the O_2- and H_2O_2-driven pathways, employing *Ls*AA9 as the underlying LPMO and a theoretical model based on a quantum mechanics/molecular mechanics (QM/MM) framework [4]. We ensure to consistently include all residues known to be important by using extensive QM regions of up to over 900 atoms. We also investigate several conformers based on molecular dynamics [5]. Here, I present the main results, namely that: (i) The O_2-driven reaction is unfeasible, in contrast to previous QM/MM calculations with smaller QM regions [1]. (ii) The H_2O_2-driven pathway is feasible, showing that for *Ls*AA9, only H_2O_2 is a viable co-substrate as proposed experimentally [2]. (iii) By including dynamics, all barriers are rather low, suggesting that the rate is not determined by substrate oxidation, but rather elsewhere in the mechanism (e.g. H_2O_2 formation).

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Electronic Structure and Reactivity of Dinuclear Bridging Nitrides

Shengfa Ye

School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China

Iron nitrides are key intermediates in the industrial nitrogen fixation Haber-Bosch process. Probing the correlation of geometric and electronic structures of high-valent iron nitrides with their varying reactivities is of significant importance for understanding the aforementioned industrial processes. We utilized ^{15}N solid-state NMR coupled to density functional calculations to explore the similarities and differences in hydrogenation reactivity between bent and linear dinuclear metal nitrides, M(μ-N)M. The former complexes can directly react with hydrogen or a combination of electron and proton and eventually release ammonia, while the vast majority of linear bridging nitrides cannot react with hydrogen or proton. Analysis of their ^{15}N chemical shielding tensors provided experimentally validated electronic structures that shed light on how the distinct geometry of bridging nitrides dictates their disparate hydrogenation activity.

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Probing the magnetic properties of actinide complexes by paramagnetic NMR.

Hélène Bolvin[a], Claude Berthon[b]

[a)] LCPQ, CNRS, Université de Toulouse, France b) CEA, Univ. Montpellier, Bagnols/Cèze 30207, France.

Paramagnetic nuclear magnetic resonance (pNMR) is a powerful tool for probing electronic structure and magnetic properties in paramagnetic systems. While pNMR has been extensively applied to transition metal and lanthanide complexes, its use in actinide chemistry remains relatively underexplored due to the radioactivity of the transuranide complexes. Understanding the pNMR signatures of actinide compounds requires a rigorous theoretical framework that accounts for spin-orbit coupling, magnetic anisotropy, and covalency, while maintaining close synergy with experimental data[1].

Paramagnetic NMR experiments on actinide complexes are performed by Claude Berthon (CEA Marcoule France). In this work, we apply advanced theoretical methods—based on relativistic quantum chemistry, density functional theory (DFT), and wavefunction-based approaches—to model and interpret the pNMR chemical shifts (^{1}H, ^{13}C, ^{15}N, ^{17}O, ^{19}F). of two series of actinide complexes, $[An(NO_3)_6]^{2-}$ and [AnDOTA]L An=U, Np, Pu and L=H_20, F^-.

In complexes with a strong anisotropy, it gives access to the anisotropic magnetic susceptibility $\Delta\chi$.[2,3] In complexes with a compact coordination sphere, it gives access to the spin density at the nuclei of the ligands, and consequently to the ligand hyperfine coupling constants.[3,4] The pathway of the spin density from the magnetic 5f orbitals to the nuclei will be discussed. The interplay between experiment and theory is essential in magnetic properties of actinides: theoretical models rely on experimental data for validation, while experimental results require theoretical interpretation to unravel the underlying electronic and magnetic interactions.[5]

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Towards an accurate description of (bio)molecules at catalytically active surfaces

A. Siklitskaya, T. Bednarek, J. Pogrebetsky, Adam Kubas

Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

The accuracy of quantum chemical calculations depends on two key aspects: the model chosen to represent the chemical problem and the computational method used. These choices are not independent, as the model's size determines the available computational methods. In this context, surface chemistry presents a particular challenge – on one hand, an appropriate surface model must account for its morphology and long-range interactions; on the other, the computational method must describe strong chemical bonds (e.g., covalent) and weak interactions (e.g., dispersion) with sufficient accuracy (ideally chemical accuracy, <1 kcal/mol).

In my presentation, I will introduce computational protocols, which we have successfully applied to study reactivity and spectroscopy of some biologically relevant molecules on periodic surfaces (e.g., titanium oxides or MXenes [1]) and aperiodic surfaces (e.g., graphene oxide [2]). The information derived from these calculations aids in the interpretation of experimental data.

Additionally, I will present promising first results for metals treated in a non-periodic manner.[3] Our newly developed method allows for the analytical calculation of the response of a metallic surface's electron density to the presence of a molecular model (dipole). Moreover, it enables the definition of an embedding potential for relatively small metallic surface cuts that permits accurate prediction of the adsorption site preference of CO at the Pt(111) surface with an arbitrary method of choice available for gas-phase calculations. We demonstrate that once embedding is applied, correct adsorption site preference can be recovered already with the well-known Perdew-Burke-Ernzerhof exchange-correlation density functional (PBE).

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Modelling paramagnetic NMR chemical shifts of copper-based metal-organic frameworks

Michael Bühl

EaStCHEM School of Chemistry and Centre of Magnetic Resonance, University of St Andrews,
North Haugh, St. Andrews, Fife KY16 9ST, United Kingdom; buehl@st-andrews.ac.uk

Paramagnetic NMR (pNMR) chemical shifts are computed for molecular models of extended metal-organic frameworks (MOFs) based on dinuclear Cu(II) paddlewheel dimer moieties (see Fig. 1 below).

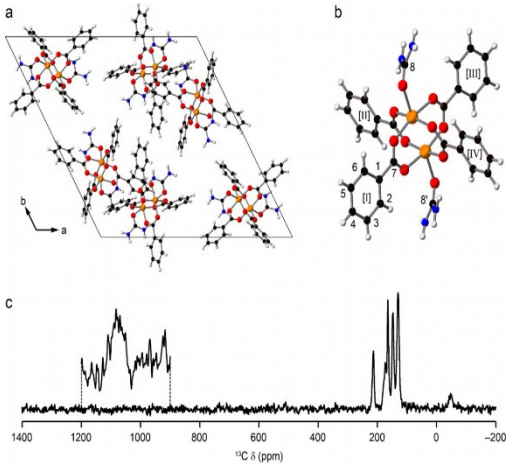

Figure 1: Cu(II) benzoate with two axial guests bound (from reference 1).

Using a methodology established for molecular crystals of such dimers,[1] and assuming a thermal equilibrium between diamagnetic, antiferromagnetically coupled, and paramagnetic, ferromagnetically coupled spins on the Cu centres, observed pNMR shifts of MOFs from the HKUST and STAM families, as well as their temperature dependence are well reproduced computationally at the CAM-B3LYP/IGLO-II//GFN2-xTB level of theory.[2] Effect of scaling as-computed DFT energy gaps between spin states, and the dependence of such scaling factor on the size of molecular models are discussed.

These results are encouraging for further applications to, e.g., MOFs loaded with different guest molecules (cf. Fig. 1), or identification of spin-½ defect sites with potentially unique chemical shifts.[3]

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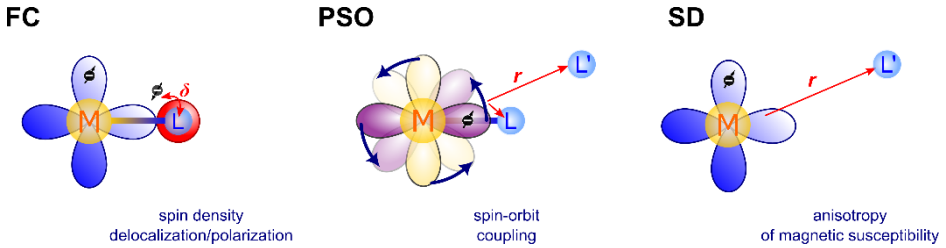
Paramagnetic effect in NMR spectroscopy of transition-metal complexes

Radek Marek[a]

[a)] CEITEC – Central European Institute of Technology, Masaryk University, Kamenice 5, 62500 Brno, Czechia

Presence of a paramagnetic center in a molecular or supramolecular system introduces an electron spin density that leads to large shifts in resonance frequencies in nuclear magnetic resonance (NMR) spectroscopy.

In the first part of my talk, the individual physical mechanisms of hyperfine NMR shifts in paramagnetic transition-metal compounds will be introduced (see figure).[1] The Fermi-contact term associated with the distribution of electron-spin density in the molecule[2-4] and the paramagnetic spin-orbit and spin-dipolar terms that give rise to the through-space (pseudocontact) shifts in supramolecular host-guest assemblies[5] will be interpreted using combined experimental and theoretical methods.



In the second part, an NMR approach to determine the head vs. tail host-guest binding between paramagnetic metallodrugs and macrocyclic carriers will be demonstrated.[6] Finally, an example of the effect of crystal packing on the NMR resonances of paramagnetic systems will be discussed.[7]

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G-Quadruplexes: Insights from Quantum Chemical Bonding Analyses.

C. Fonseca Guerra[a]

[a)]Department of Chemistry and Pharmaceutical Sciences, Vrije Universiteit Amsterdam, De Boelelaan 1108, 1081 HZ Amsterdam, The Netherlands

G-quadruplexes are biologically occurring non-canonical nucleic acid structures that self-assemble by forming stacks of successive quartets of guanine bases (the G-quartet), stabilized by hydrogen bonds, base stacking, and metal cation coordination. This presentation will demonstrate how experimental questions and phenomena regarding the structure and stability of G-quadruplexes and their interaction with metal ions can nowadays be understood from accurate quantum chemical computations. [1-6] Our computational analyses on G-quartets (G_4) shows that the experimental order of affinity of the guanine quadruplexes for the cations Li^+, Na^+, K^+, Rb^+, and Cs^+ can be reproduced computationally, revealing the equal importance of desolvation and the size of the alkali metal cation for the order of affinity.

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Expanding the Reach of Selective C-H Oxidation Reactions with Bioinspired Catalysts via Cationic Mechanisms

Miquel Costas

Institut de Química Computacional i Catàlisi, Universitat de Girona, Facultat de Ciències, Campus de Montilivi, 17003, Girona, Spain

C(sp^3)–H bond oxygenation is an important class of C–H functionalization reactions that is attracting increasing interest because of the ubiquity of oxidized aliphatic frameworks in molecules of biological and pharmaceutical interest and of the rich chemistry associated to C–O bond elaboration, amenable for broad product diversification.[1] C(sp^3)–H bond oxidation is performed by numerous iron-dependent enzymes that operate via high valent iron-oxo species.[2] The structures of these enzymes and the associated reaction mechanisms have served as inspiration motifs for the development of C–H oxidation catalysts.[3] Investigated for long, the current mechanistic consensus is that monoiron-dependent oxygenases and related small molecule catalytic systems hydroxylate C–H bonds by a similar radical rebound mechanism. The reaction is initiated by a hydrogen atom transfer (HAT) from a substrate C–H bond to generate a carbon radical that is then trapped by hydroxyl ligand transfer to form the hydroxylated product. Alternative mechanisms entailing cationic paths have been seldom considered.[4] However, cationic paths are interesting because they may diverge the chemoselectivity of the C-H oxidation reaction towards valuable products inaccessible via the canonical radical paths. This lecture will show examples of our recent work in C-H oxidation reactions with bioinspired catalysts where cationic intermediates are involved. Implications and examples of the utility of these paths will be discussed.

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Contributed Lectures

Why is DFT so much better for larger systems?

Per Siegbahn

Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91, Stockholm, Sweden

The hybrid DFT method B3LYP is probably the most popular functional used for actual chemical applications. That is so even though there are many examples of failures for small systems. Those failures have led to repeated warnings from the quantum chemical community saying that B3LYP should not be used. Still, the experience on applications have shown that B3LYP works very well for realistic organic systems. Even more remarkable is that B3LYP works so well for the most difficult systems. Applications on redox active enzymes such as Photosystem II and Nitrogenase have shown that it gives excellent results. In that case, inclusion of exchange is absolutely necessary. In the regular B3LYP 20 % exact exchange has been suggested, but in practice 15 % works even better. There are some additional requirements when B3LYP is used for those systems. For example, it is absolutely necessary that unrestricted B3LYP is used in the applications. On the other hand, the self-interaction is almost never a problem for large realistic systems. Examples will be given in this short talk for tests on the ten most important redox enzymes in nature, including explanations of these findings.

Proteins and Heavy Metals: from Biology to Medicine

Ran Friedman[a]

[a)] Department of Chemistry and Biomedical Sciences, Linnaeus University, Universitätsplan 1, SE-39 182 Kalmar, Sweden

Approximately one third of the proteins bind metals as cofactors. These are normally various ions that are utilised for holding the protein structure or for catalysis. Ions of metals heavier than Zn are rarely considered as biologically significant. In the recent years, however, it became apparent that even heavier ions are utilised in biology or have a role in medicine. Lanthanide ions (Ln^{3+}) are used in both and are native cofactors of enzymes in certain aquatic bacteria. Even heavier (and radioactive) ions, such as Ra^{3+} and Ac^{3+} are used in cancer medicine.

Theoretical considerations can be used to explain the preferential binding of ions to proteins, but can be challenging for heavy metals where relativistic effects are manifested. In my talk I will discuss the binding of Ln^{3+} ions to a bacterial enzyme that utilises them and show that middle-series lanthanides are thermodynamically preferred.[1] In the second part of my talk I will consider a relevant medical application and will provide details on the binding of Ra^{3+} and Y^{3+} ions in proteins. 226-Ra and 90-Y isotopes are used in cancer medicine, and it is necessary to consider potential interactions with proteins in the body. Fortunately, the calculations show that such risk is not high (at least for radium) [2] and suggest that targeted delivery of radium may be possible, which has great medical potential. The benefits of 223-Ra over other radioactive isotopes as therapy will also be discussed.

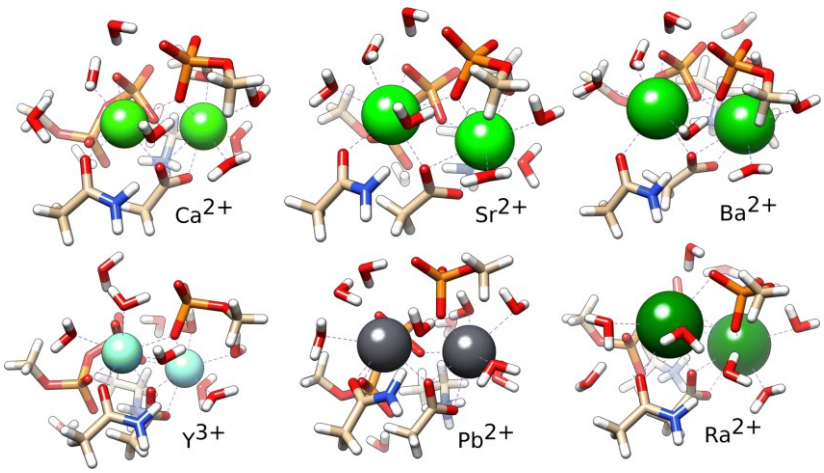

Figure: Protein kinase A (PKA) is active in the presence of alkali earth ions, from Mg^{2+} to Ba^{2+}.Calculations show that it can also bind yttrium, lead and radium ions. The figure shows the catalytic site in the presence of different ions that the protein binds.

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Shape-Shifting Tetranuclear Manganese Clusters

Markella Aliki Mermigki[a], William H. Armstrong[b], Dimitrios A. Pantazis[a]

[a)] Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

[b)] Chemistry Department, Boston College, 140 Commonwealth Ave, Chestnut Hill, MA 02467, USA

Synthetic models of metalloenzyme active sites have proven essential for probing the spectroscopic behavior and catalytic function of the metal clusters involved. Many models of the tetramanganese cluster in the Oxygen-Evolving Complex (OEC) of Photosystem II have been studied over the years, providing valuable insights into the magnetic and redox properties relevant for the catalytic cycle of water oxidation.[1] A unique type of model was presented by Armstrong and co-workers, who synthesized and characterized two isomeric forms with a $[Mn_4O_4]^{4+}$ core, one exhibiting a dimer-of-dimers structure and the other an adamantane-like geometry.[2-4] Importantly, the two structural forms can exist in multiple oxidation states and are interconvertible. They display differential stability in solution and in the solid state, as well as distinct redox and EPR properties. Here we investigate the relative energetics with DFT and DLPNO-CCSD(T) calculations to better understand their differential stabilization in solution and in the solid state, concluding that the adamantane-like structure is always more stable in solution, whereas the dimer-of-dimers can be preferentially stabilized upon crystallization. The mechanism of isomerization is also investigated to establish how this considerable structural transformation occurs in solution.

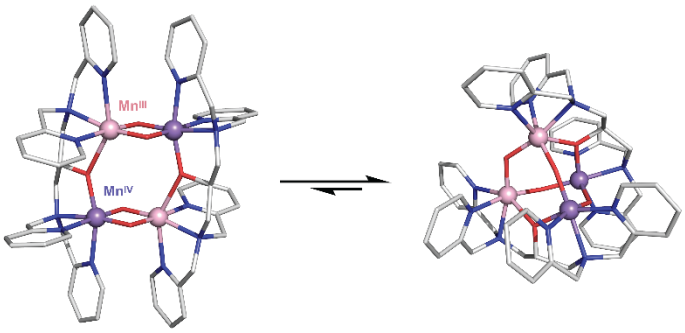

Figure 1: Structures of the two interconvertible tetramanganese complexes.

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Iron catalyzed formation of methyl radicals as a common source of environmentally important volatile organic compounds

Gunasekaran Velmurugan[a], Jonas Hädeler[b], Rebekka Lauer[b], Rejith Radhamani[a], Frank Keppler[b], and Peter Comba[a]

[a]Institute of Inorganic Chemistry, Heidelberg University, Heidelberg, Germany

[b]Institute of Geosciences, Heidelberg University, Heidelberg, Germany

E-mail: peter.comba@aci.uni-heidelberg.de

Methane (CH_4) is the most abundant organic trace gas in the atmosphere and has a significant role in tropospheric and stratospheric chemistry. Most natural sources are associated with microorganisms living under anaerobic conditions in wetlands, rice fields, landfills or the gastrointestinal tracts of ruminants and termites. However, recent studies have revealed direct CH_4 release from eukaryotes, including plants, animals, fungi, and lichens, even in the absence of microbes and in the presence of oxygen. These novel aerobic CH_4 production routes differ from the well-known anaerobic pathway that involves catalytic activity by methanogenic enzymes. We have explored a range of nonheme oxo-iron(IV) model systems with tetra- or pentadentate bispidine ligands that to produce methane from organic material with methyl-substituted heteroatoms, e.g., methionine.[1] This model reaction for the natural aerobic production of methane is shown to proceed via two sulfoxidation steps involving the oxo-iron(IV) complexes, with a bifurcation in the second step that either produces the sulfone or leads to demethylation with similar probabilities. The resulting methyl radicals lead to C_1 and C_2 compounds in all possible oxidation states. Together with ^{2}H, ^{13}C and ^{18}O labeling studies and product analyses, density functional theory (DFT) has helped to understand the reaction mechanisms. A main objective is to include all relevant substituted organic compounds as substrates for the formation of methane and other C_1 and C_2 compounds in various oxidation states. There are three possible pathways for the product formation, i.e. hydrogen atom abstraction (HAA), oxygen atom transfer (OAT) and outer sphere electron transfer. The combination of DFT shows that for thioethers and sulfoxides, methyl radicals are produced by OAT,[2] while other routes prevail for other substrates.[3] This study is shown to give deeper insights into the reaction mechanism for the formation of methane and other volatile organic compounds that are of importance in the carbon cycling and the atmospheric physics and chemistry.

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Examples of reaction mechanisms with synthetic biomimetic catalysts: NO_x reduction and naphthalene di-oxygenation

Kyung-Bin Cho

Department of Chemistry and Research Institute for Materials and Energy Sciences, Jeonbuk National University, Jeonju 54896, Republic of Korea

Our research group specializes in finding the reaction mechanisms of reactions involving catalysts and substrates found in a biomolecular or biomimetic settings, which is usually inorganic, first-row transition metal species interacting with some form of oxygen and an organic substrate. This talk will focus on two of these areas. First is a Ni-based pincer system that is shown to be able to reduce NO_3 and NO_2,[1,2] which in large enough scale would contribute to reducing the environmental contamination caused by industrialization. In the process, the contaminants are reduced to economically meaningful oximes (ON-R). The DFT calculations aim to unravel the exact reaction mechanism for this reaction. The second topic is about the reaction mechanism of naphthalene di-oxygenation by a high-valent Fe(IV)O heme species (Cpd II). We find that this Cpd II must be protonated (Fe(IV)OH) for the reaction to occur. The experimentally observed 1:6 (substrate:catalyst) stoichiometry is explained by finding the exact reaction mechanism involving a mix of hydrogen atom transfer, proton coupled electron transfer (PCET) and variations thereof.

Acknowledgement: National Research Council of Korea through Basic Science Research grant RS-2021-NR058689 and through G-LAMP program RS-2024-00443714.

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Does It Take Two CO? Unraveling ACS's True Stoichiometry

Denise Poire,[a,b] Cornelius C. M. Bernitzky,[a] Mathesh Vaithiyanathan,[a] Berta Martins,[c] Christian Lorent,[d] Tamanna M. Ahamad,[d] Igor Sazanovich,[e] Gregory M. Greetham,[e] James Birrell,[f] Ingo Zebger,[d] Holger Dobbek,[c] Maria Andrea Mroginski,[b] Marius Horch*[a]

[a] Freie Universität Berlin, Department of Physics, Ultrafast Dynamics in Catalysis, Arnimallee 14, 14195 Berlin, Germany. E-mail: marius.horch@fu-berlin.de

[b] Technische Universität Berlin, Department of Chemistry, Modelling of Biomolecular Systems, Straße des 17. Juni 135, 10623 Berlin, Germany

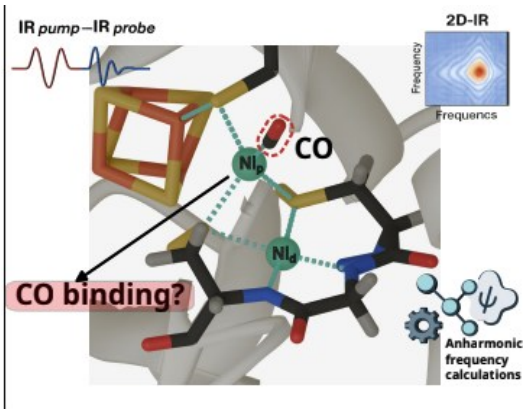
[c] Humboldt Universität zu Berlin, Department of Biology, Structural Biology / Biochemistry, Philippstraße 13, 10115 Berlin, Germany

[d] Technische Universität Berlin, Department of Chemistry, Spectroscopic Characterization of Metalloproteins, Straße des 17. Juni 135, 10623 Berlin, Germany

[e] STFC Central Laser Facility, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell Campus, Didcot, OX11 0QX, UK

[f] School of Life Sciences, University of Essex, Wivenhoe Park, Colchester, CO4 3SQ, UK

Acetyl-CoA synthase (ACS) plays a fundamental role in biology by converting carbon monoxide (CO) into acetyl-CoA, a central intermediate in the carbon fixation pathways of anaerobic organisms. Although prior studies identified a single CO molecule bound to the catalytic nickel center, recent cryogenic spectroscopic investigations suggested the possibility of dual CO coordination. [1]To resolve this ambiguity under biologically relevant conditions, we employed ultrafast nonlinear IR spectroscopy (IR pump-probe and two-dimensional IR), combined with anharmonic frequency calculations, to precisely characterize CO binding at ambient temperature. Our results demonstrate that ACS coordinates only one CO molecule at ambient conditions, thus clarifying its catalytic mechanism. Moreover, our findings underscore the effectiveness of integrating advanced spectroscopic techniques with quantum chemical calculations, offering a powerful strategy to investigate ligand coordination in complex bioorganometallic systems.



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FAIR Quantum Chemistry using NOMAD

Esma Birsen Boydas[a] and the FAIRmat team

[a)] Department of Physics and CSMB, Humboldt-Universität zu Berlin, Zum Großen Windkanal 2, 12489 Berlin, Germany

The past decade has seen quantum-chemical calculations transition from bespoke, project-specific runs to routine, high-throughput workflows capable of producing terabytes of structured output in a single campaign. This growth is driven by ever-cheaper high-performance computing and by the community's expanding ambition to screen vast chemical spaces, construct surrogate models, and extract statistically robust trends from heterogeneous data sets. Yet, despite the scientific progress, the practical task of organizing these results remains surprisingly ad-hoc: each electronic-structure package emits its own mixture of text files, binary blobs, and semi-structured logs, while downstream analysis codes rely on fragile parsers and one-off conversion scripts. The absence of a shared, machine-actionable data description is now a primary bottleneck to reproducible quantum-chemical data science.

A practical way forward is provided by NOMAD (nomad-lab.eu), an open-source, community-driven platform that implements FAIR research-data management.[1,2] Developed by FAIRmat, the NFDI consortium for condensed-matter physics and the chemical physics of solids, NOMAD has evolved considerably beyond its initial scope. Thanks to a modular, plugin-based design, users can add their own parsers, data schemas, and visualisation tools, adapting NOMAD to the requirements of each research workflow. In this talk, I will demonstrate how these capabilities transform scattered quantum-chemical outputs into a FAIR, machine-actionable corpus that can accelerate data-driven discovery.

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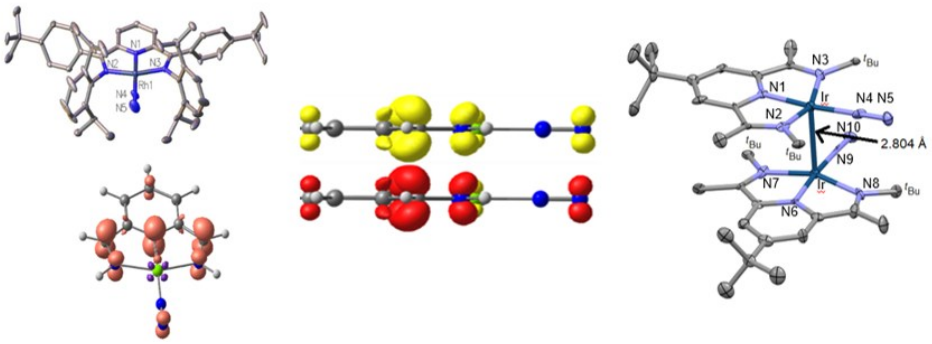
Antiferromagnetic Coupling of Dimeric Iridium PDI Complexes

Thomas Marx[a], Jan-Eric Fuhrmann[a], Peter Burger[a]

[a)] Institut für Anorganische und Angewandte Chemie, Fachbereich Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, 20146 Hamburg, Germany

Paramagnetic pyridine-diimine (PDI) metal complexes often feature non-innocent, reduced PDI ligands.[1,2] A representative example is the monomeric (PDI)Rh(N_2) complex (S = ½), best described as a [PDI^{-}]Rh^{I} (d^8, square-planar) species with spin density localized on the ligand, as confirmed by X-/Q-band EPR and ENDOR spectroscopy, and DFT studies (Fig.1 left).



S=1/2 closed shell, S=0

Figure 1: Example of monomeric rhodium dinitrogen complex (left), calculated spin density of PDI units (middle) and X-ray crystal structure of dimeric iridium dinitrogen complex (right).

We explored whether such spin density could couple antiferromagnetically via π-stacking ("pancake bonding"), known for organic radicals,[3] by designing PDI complexes with minimal steric hindrance. A series of (PDI)M-L complexes (M = Rh, Ir; L = N_2, CO, tBuNC, CN, NO) was synthesized and studied experimentally and computationally. Depending on the metal and ligand, the complexes exist as monomers or dimers.

Notably, the (PDI)Ir–N_2 complex forms a stable dimer, [(PDI)Ir(N_2)]$_2$, which is preserved in solution and exhibits a diamagnetic (closed-shell, S = 0) ground state, as supported by extensive MC-PDFT(tPBE)/CASSCF-DMRG (62e, 46o, n = 3000) calculations (Fig. 1, right). We examine trends in bonding, electronic structure, and reactivity. Additionally, local correlation methods, including LNO-CCSD(T), PNO-CCSD(T), and DLPNO-CCSD(T), are benchmarked against canonical CCSD(T) to assess their reliability in capturing monomer–dimer thermodynamics, specifically the equilibrium: 2 (PDI)M–L ⇌ [(PDI)M–L]$_2$.

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ASH: a multiscale, multitheory modelling program

Ragnar Bjornsson[a]

[a)] Laboratoire de Chimie et Biologie des Métaux, Univ. Grenoble Alpes, CNRS, CEA, IRIG, 17 Rue des Martyrs, F-38054 Grenoble, Cedex, France

We introduce ASH, a multi-scale, multi-theory modelling program for QM, MM and QM/MM calculations, written in the Python programming language. ASH is written in response to the increasingly diverse computational chemistry software landscape with more QM and MM programs than ever before and with new machine learning approaches expected to further complicate the way modern computational chemistry is performed. ASH is a Python library that intentionally separates computational chemistry jobs (geometry optimizations, frequency calculations, molecular dynamics, enhanced sampling MD, surface scans, reaction path optimizations etc.) from the Hamiltonian (calculated by the specialized QM or MM programs). By keeping the jobs separate from the Hamiltonian, a highly flexible computational chemistry environment emerges, that can be adapted to standard molecular chemistry QM calculations, MM, QM or QM/MM MD simulations, easy setup of biomolecular or solution QM/MM or ONIOM calculations, etc. ASH has already become a popular tool for driving classical simulations[1], complex QM/MM metalloenzyme investigations[2,3,4,5,6,7] and correlated wavefunction theory investigations[8,9].

ASH is an open-source project with repository hosted at https://github.com/RagnarB83/ash and documentation at https://ash.readthedocs.io.

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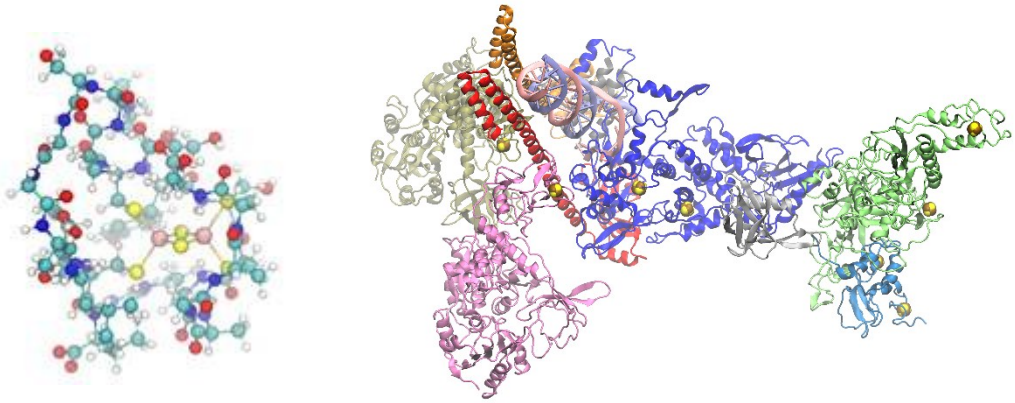
Redox Potentials of Iron–Sulfur Clusters via QM/MM: From Synthetic Peptides to Viral Enzymes

Umberto Terranova[a]

[a)] Faculty of Medicine and Health Sciences, University of Buckingham, Crewe Campus, Crewe, CW1 5DU, UK

Iron–sulfur (FeS) clusters are central to biological electron transfer. Understanding their redox properties is essential for elucidating their role in both natural and bioinspired systems. Here, I present QM/MM calculations under the linear response approximation of FeS clusters redox potentials in two distinct biological contexts: (i) ferredoxin-maquette peptides at the interface with hydrogenase and (ii) the SARS-CoV-2 replication and transcription complex (RTC) that governs the viral life cycle. In the first case, I will show that the redox potential of the peptides can be fine-tuned by single-residue mutations in the secondary coordination sphere of their FeS cluster. In particular, I have designed a variant of a canonical peptide that disrupts the hydrogen-bonding network between the cluster and water, causing a negative redox potential shift of 0.03 V [1]. In the second case, I will examine the four FeS cofactors of two essential proteins of the SARS-CoV-2 RTC [2]. The redox potentials of these clusters fall within the range –0.26 to 0.04 V, following a trend consistent with their measured electronegativities [3]. Together, these studies demonstrate the applicability of QM/MM methods based on the linear response approximation to a variety of FeS systems ranging from small peptides to large multiprotein assemblies.



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Reliable Redox Potential Calculations of Proteins

Michael Stier[a], Johannes Kästner[a]

[a)] University of Stuttgart, Institute for Theoretical Chemistry, Pfaffenwaldring 55, D-70569 Stuttgart, Germany

Various computational approaches have been developed to estimate the redox potentials of redox-active proteins, often employing hybrid quantum mechanical/molecular mechanics (QM/MM) methods.[1] However, a 2022 benchmark study on iron-sulfur proteins found that pure density functional theory (DFT) calculations on cluster models containing approximately 300 atoms outperformed QM/MM calculations with a similar QM region size.[2] Nevertheless, these methods exhibited significant systematic errors of approximately -0.5V, highlighting the need for reference calculations for calibration.[2] Building on these findings, we aimed to establish a more reliable computational approach for redox potential predictions that does not require calibration calculations. To this end, we investigated the influence of model system size on redox potentials. Cluster models ranging from 250 to 1500 atoms were computed using hybrid DFT across 10 different proteins, including iron-sulfur proteins, T1 copper proteins, and cytochrome c (see Figure 1). We found that around 500 atoms are sufficient, meaning that the corresponding cluster models yield results close to full protein DFT calculations. Since sampling at the DFT level remains computationally prohibitive for such large models, we propose a methodology based on Marcus theory, which uses QM/MM-optimized snapshots from classical molecular dynamics simulations to incorporate protein dynamics (see Figure 2). The proposed snapshot/cluster approach was tested on 8 different proteins and compared with experimental results. A mean absolute error of 0.10V was found. The mean signed error was close to zero indicating no systematic under- or overestimation.

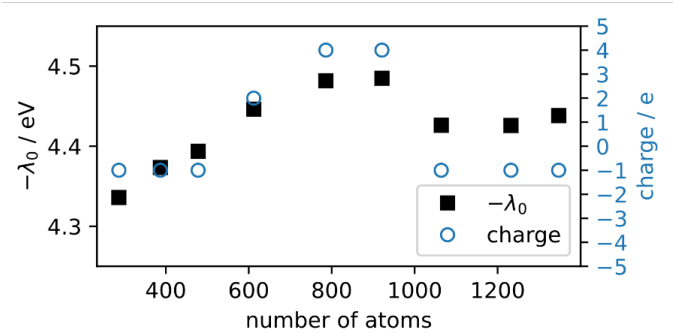

Figure 2: The Vertical reduction energy λ_0 was calculated with DFT for a snapshot with varying cluster model sizes. Analog calculations were performed on further 19 snapshots across 10 proteins.

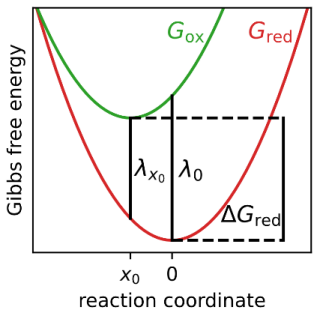

Figure 1: The Gibbs free energy of reduction ΔG_{red} is calculated from vertical reduction energies λ_{0/x_0}. The latter were calculated with DFT on QM/MM optimized snapshots.

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Large cluster and QM/MM study of the fully oxidized state of the oxygen-tolerant [NiFe] hydrogenase from *Hydrogenophilus thermoluteolus*

Ravi Kumar[a], Andrés M Escorcia[a], Matthias Stein[a]

[a)] Max Planck Institute for Dynamics of Complex Technical Systems, Molecular Simulations and Design Group, Sandtorstrasse 1, 39106 Magdeburg, Germany

Molecular hydrogen (H_2) is a promising next-generation energy carrier critical for achieving sustainable power and meeting global climate goals [1]. Hydrogenase enzymes, particularly [NiFe]-hydrogenases, catalyze the reversible proton reduction to H_2 with efficiencies comparable to noble metals [2]. However, their sensitivity to oxygen (O_2) limits industrial use [2]. Oxygen-tolerant variants, such as the [NiFe]-hydrogenase from *Hydrogenophilus thermoluteolus* (*Ht* SH), exhibit unique structural features that protect the active site under oxidative conditions [3].

This study employs quantum mechanical (QM) cluster and QM/MM calculations on a >300-atom model of the fully oxidized *Ht* SH active site to elucidate its electronic and structural properties [4]. Our results identify the ground state as a spin-coupled broken-symmetry Ni(III)Fe(III) open-shell singlet, contrasting earlier proposals of a closed-shell Ni(IV)Fe(II) state [4,5]. Ligand-mediated antiferromagnetic coupling stabilizes this state, supported by natural bond order analysis revealing an unusual three-center two-electron bond that likely enhances oxidative resilience [4,6].

Comparative evaluation of QM and QM/MM methodologies guides the model selection for metalloprotein studies. These insights advance understanding of oxygen tolerance mechanisms, guiding the design of robust bioinspired catalysts for sustainable hydrogen production.

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Probing [NiFe] Hydrogenases by Experimental and Computational 2D-IR Spectroscopy

Marius Horch[a], Yvonne Rippers[a], Cornelius C. M. Bernitzky[a], Catharina J. Kulka-Peschke[b], Anne-Christin Schulz[b], Christian Lorent[b], Ingo Zebger[b], Oliver Lenz[b]

[a)] Department of Physics, FU Berlin, Arnimallee 14, 14195 Berlin, Germany
[b)] Institute of Chemistry, TU Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

[NiFe] hydrogenases catalyse the conversion of dihydrogen (H_2) – a perfectly clean fuel – by utilizing a protein-embedded [NiFe] centre that carries CO and CN^- ligands. The function of these ligands is not well understood, but they can serve as structurally sensitive vibrational probes. Thus, infrared (IR) spectroscopy and harmonic vibrational analyses have long been used for studying hydrogenases. We have expanded this strategy by introducing two-dimensional (2D) IR spectroscopy in combination with anharmonic vibrational analyses.[1-4] Probing sequences of vibrational transitions, this approach yields solution-phase insights into bond lengths, strengths, and energies of the CO ligand.[1,2] Unexpected trends in these quantitates were observed, challenging the established understanding of organometallic bonding. In addition, a complex two-dimensional signature related to the CN^- ligands was probed experimentally and predicted by generalized second-order vibrational perturbation theory (GVPT2).[1,3] For the H_2-binding intermediate (Ni_a-S), this signature was fully captured by a small computational model of the active site,[3] highlighting the role of the [NiFe] core in shaping the enzymatic potential energy surface. Moreover, these calculations allowed experimentally inaccessible insights into spectrally encoded structural details, the localization of vibrational transitions, and (resonant) interactions of the ligand stretch modes.[3] Interestingly, we found that the computational prediction of the CN-stretch-mode pattern is more challenging for another catalytic state carrying a bridging hydride ligand (Ni_a-C).[3,4] While GVPT2 calculations on unconstrained small models predict significant differences between CN-stretch signatures of Ni_a-S and Ni_a-C,[3] calculations on constrained geometries accurately reproduce the nearly identical patterns obtained in the experiment.[4] This can be explained by the pattern's sensitivity to asymmetry in active-site charge distribution, which is overestimated in the unconstrained model of Ni_a-C. Thus, the combination of experimental and computational 2D-IR spectroscopy indicates that the protein scaffold constrains the [NiFe] active site during catalysis – not only regarding the molecular geometry but also in terms of electronic structure.[1,4] In total, these findings and strategies provide new perspectives for understanding structural, electronic, and dynamic properties of complex (bio)organometallic targets.

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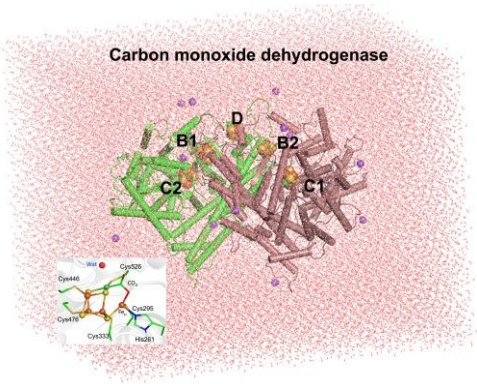
Carbon Monoxide Dehydrogenase: A Structural and Theoretical Perspective

Shalini Yadav, Dimitrios A. Pantazis

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



Carbon monoxide dehydrogenase (CODH) enzymes catalyse the reversible interconversion of carbon dioxide (CO_2) and carbon monoxide (CO), playing a central role in microbial carbon fixation and energy metabolism.[1, 2] This activity is mediated by a unique nickel- and iron-containing C-cluster [$NiFe_4S_4(Cys)_5His$].[3] Extensive studies using X-ray crystallography, spectroscopy, and computational methods have established its composition and the presence of gas channels facilitating substrate transport.[4, 5] Previous investigations have also highlighted the roles of key residues, such as His93 and Lys563, in substrate binding and proton transfer.[6] Despite these advances, the detailed electronic structure of catalytic intermediates and the dynamic behaviour of the active site remain poorly understood. Taking advantage of quantum computational methods combined with molecular dynamics (MD) simulations, we aim to bridge these gaps through a multiscale approach. MD simulations have been employed to model the full enzyme, capture its conformational flexibility, and verify system stability. Building upon this stable model, hybrid QM/MM calculations are performed to probe the electronic structure of the C-cluster and its changes during substrate activation and conversion. Additionally, this combined approach allows us to investigate how protein dynamics influence the electronic, magnetic (exchange coupling, spin states) and spectroscopic (EPR, Mössbauer) properties of the active site—a critical yet underexplored aspect of CODH catalysis. Insights gained from this study will contribute to a deeper mechanistic understanding and inform the design of bio-inspired catalysts for carbon conversion.

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Exploring analogies and differences between coupled binuclear copper proteins *via* multiscale protocols

Andrea Madabeni[a], Agnieszka Stańczak[a], Laura D. Elmendorf[b], Edward I. Solomon[b], Lubomír Rulíšek[a]

[a)] Institute of Organic Chemistry and Biochemistry, Flemingovo nam. 542/2, Prague, Czechia

[b)] Department of Chemistry, Stanford University, Stanford, CA 94305, USA

Coupled Binuclear Copper (CBC) enzymes are a wide family of proteins capable of oxygen binding and activation to perform regioselective oxidation reactions.[1] This reactivity is mediated by two Cu atoms in proximity to each other that can bind O_2 in the form of an antiferromagnetically coupled $[Cu_2O_2]^{2+}$ core. Six histidines, three per copper atom, coordinate the metal centers. The broad class of CBC proteins includes tyrosinase (*Ty*), catechol oxidases (*CaOx*) and *ortho*-amino phenol oxidases (*oAO*), which can react with monophenols (**1OH**), *ortho*-bisphenols (**2OH**) and *ortho*-amino phenols (**NOH**) respectively. To date, the molecular origin of the different chemoselectivity of CBC proteins for various substrates is not fully understood.

In this contribution, we employ multiscale quantum mechanics / molecular mechanics (QM/MM) approaches and broken-symmetry density functional theory to tackle this problem. Particularly, a large QM region (>300 atoms) is employed to accurately describe the first and the second coordination sphere of the $[Cu_2O_2]^{2+}$ catalytic core, and to identify analogies and differences across the three known types of CBC proteins. Great attention is given to the early stages of enzyme reactivity, i.e., to the reactive state of the protein after O_2 binding and to the nature and structure of the monophenol/O_2/protein ternary adduct, which is expected to dictate the different chemoselectivity between *CaOx* and *Ty*. [2,3] This study provides, i*nter alia*, an accurate account on the explicit solvation shell around the $[Cu_2O_2]^{2+}$ core for one archetypal *CaOx*. A careful comparison is made with *Ty*, to assess early-stage similarities and divergencies between different CBC proteins.

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Computing Enzymatic Reaction Mechanisms at Solvent-Exposed Copper Sites

Erna K. Wieduwilt[a], Marlisa M. Hagemann[a], Ulf Ryde[b], Erik D. Hedegård[a]

[a)] Department of Physics, Chemistry, and Pharmacy, University of Southern Denmark, Campusvej 55, 5230 Odense, Denmark

[b)] Department of Theoretical Chemistry, Lund University, Chemical Centre, P. O. Box 124, 221 00, Lund, Sweden

Lytic polysaccharide monooxygenases (LPMOs) are copper enzymes that play a crucial role in industrial enzyme cocktails for biomass conversion into sustainable biofuels. [1] By catalyzing the oxidative cleavage of glycosidic bonds, LPMOs significantly boost the degradation of polysaccharides such as cellulose and chitin. This process has sparked debate over whether molecular oxygen or hydrogen peroxide serves as the true co-substrate.[2] Growing evidence suggests that the true co-substrate for several LPMOs is hydrogen peroxide.[2-4] Intriguingly, LPMOs can generate hydrogen peroxide from oxygen in the absence of a substrate in an oxidase reaction.[5,6] Experiments conducted under typical monooxygenase conditions - without externally added hydrogen peroxide - rely heavily on this in situ production of hydrogen peroxide by either the LPMOs themselves[5,6] or free copper in solution. [7] This complicates mechanistic investigations and underscores the need to understand the precise pathways of hydrogen peroxide generation by LPMOs. In this presentation, I will share new computational insights from quantum mechanics/molecular mechanics (QM/MM) calculations into the mechanism of the oxidase reaction catalyzed by LPMOs. [8] I will highlight key challenges, pitfalls and solutions for calculating a mechanism that involves the transfer of two protons and two electrons, as well as the dissociation of charged species from the solvent-exposed active site.

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Multi-scale modelling for an accurate prediction of redox potentials in iron coordination compounds

Carlos M. Jimenez-Muñoza, Ragnar Björnsson[b], Vera Krewald[a]

[a] Department of Chemistry, Quantum Chemistry, TU Darmstadt, Peter-Grünberg-Str. 4, 64287 Darmstadt, Germany

[b] Laboratoire de Chimie et Biologie des Métaux, Univ. Grenoble Alpes, CNRS, CEA, IRIG, 17 Rue des Martyrs, F-38054 Grenoble, Cedex, France

Corresponding author: carlos.jimenez@tu-darmstadt.de

Accurately predicting the absolute redox potentials of molecular systems remains a challenge in computational chemistry. Redox-active iron complexes possess a complex electronic structure, with multiple accessible oxidation states that require high-level quantum mechanical protocols. Besides, the electronic structure of iron complexes is strongly influenced by ligand-field effects, spin crossovers and solvent interactions, increasing the complexity of an ideal model. For example, DFT approaches often struggle to recover the correct electronic structure for transition metal complexes and implicit solvation methods fail to capture short-range solute-solvent interactions and long-range bulk effects.

Recent studies have demonstrated that a multistep explicit solvation approach, combining quantum mechanics/molecular mechanics (QM/MM) molecular dynamics with the linear response approximation, can provide highly accurate redox potential predictions for organic molecules [1]. The inclusion of corrections like solvent polarization and bulk solvation through explicit solvation, significantly improves the agreement with experimental redox potentials compared to traditional implicit solvation models [2]. By extending this methodology to iron-based redox pairs, our study aims to explore its transferability and refine the computational framework to tackle the challenges posed by transition metal redox chemistry.

In this work, we develop a hybrid QM/MM molecular dynamics (QM/MM-MD) protocol to study redox reactions of mononuclear iron complexes in explicit solvation using the python-based multiscale modelling program ASH [3]. A calibration set of iron complexes with reported experimental redox potentials was used to benchmark the accuracy of different levels of theory for the MD trajectories and the linear response snapshots. The final computed redox potentials are expected to offer insight into the influence of explicit solvation and spin-state effects and will be used to assess the accuracy and limitations of the method in the context of transition metal redox chemistry.

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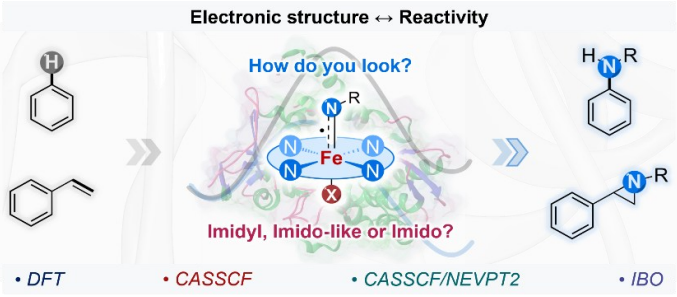
Electronic Structure and Reactivity Correlation of Fe-Porphyrin-Nitrene Species in Nitrene Transfer Catalysis

Mayank Mahajan[a], Bhaskar Mondal*[a]

[a)] School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh 175075, India.

e-mail: d20080@students.iitmandi.ac.in

Catalytic nitrene transfer enables the direct transformation of inert C–H and C=C bonds into reactive C–N bonds, via amination and aziridination reactions. At the heart of these transformations lies the metal-nitrene intermediate, a highly reactive species formed by the interaction of open-shell transition metal (M) and redox-active nitrene (:NR) ligand. These species display diverse M–N bonding motifs, from single bonds (M–•NR) in "imidyl" species to multiple bonds (M=NR, M≡NR) in "imido" species, with the nature of the M–N bond essentially governing their reactivity [1]. However, characterizing the M–N bond in metal-nitrene species remains challenging due to their transient nature and intricate metal-ligand covalency. To this end, we employ advanced quantum chemical methods, including density functional theory (DFT), ab initio complete active space self-consistent field (CASSCF), and N-electron valence perturbation theory up to second-order correction (NEVPT2), along with detailed molecular orbital analysis to elucidate the electronic structure-reactivity correlation of key Fe-porphyrin-nitrene species. Consequently, we have established the "true" electronic nature of the Fe–N bond in Fe-porphyrin-nitrene species and demonstrated how subtle changes in axial ligand coordination modulate Fe–N bonding and reactivity. Finally, we probe the role of Fe oxidation states in shaping Fe-nitrene bonding and reactivity. Together, these findings provide a detailed understanding of the nuanced electronic structure-reactivity correlation in the nitrene transfer catalysis, offering invaluable insights into the rational catalyst design and expanding the catalytic repertoire for targeted synthetic applications [2,3].



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Correlated electronic structure modeling of polynuclear transition metal compounds with phaseless auxiliary-field quantum Monte Carlo

James Shee[a]

[a)] Department of Chemistry, Rice University, Houston, TX, 77005-1892, USA

Phaseless auxiliary-field quantum Monte Carlo (ph-AFQMC) has, in recent years, emerged as a potentially transformative electronic structure technique to model chemical systems in an accurate and scalable way.[1] Energies and properties of ground and low-lying excited states can be stochastically estimated via an open-ended random walk in the space of non-orthogonal Slater determinants, guided by a “trial wavefunction” that enables low-polynomial scaling with system size at the expense of a bias. Use of an exact trial will yield exact energies and properties; however, in practice, the optimal choice of approximate trial wavefunction is an open research question. My group and others have demonstrated that active-space trial wavefunctions obtained from, e.g., CASSCF or selected Configuration Interaction approaches, can yield accurate ph-AFQMC energy differences (compared to experimental thermochemical measurements) for organic systems and a host of organometallic complexes containing a single transition metal center. Yet for multiple reasons, it would be desirable to define active-space-free ph-AFQMC models that are of polynomial cost (including the cost of trial wavefunction generation). Very recently, we have found that Generalized Hartree-Fock (GHF) trials, which can accommodate non-collinear spin configurations, yield highly accurate energies (corresponding to spin-symmetry-restored stochastic wavefunctions) for challenging molecular systems exhibiting strongly correlated ground states.[2] We have also explored the use of complex-valued GHF (cGHF) trials, which enable a mean-field description of non-coplanar spins. These ph-AFQMC protocols -- which are active-space-free, size-consistent, size-extensive, orbital-invariant, and of O(N^4) cost -- show remarkable accuracy for reduced structural/orbital models of, e.g., an [4Fe-4S] cluster. We are actively exploring other tri- and tetra-nuclear transition metal clusters of relevance to bioinorganic chemistry and catalysis.

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New versatile tools for complex molecules and materials

Christof Holzer[a,b], Yannick Franzke[c], Marjan Krstić[b], Carsten Rockstuhl[b], Florian Weigend[a]

[a)] Institut für QuantenMaterialien und Technologien, Karlsruher Institut für Technologie, Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

[b)] Institut für Theoretische Festkörperphysik, Karlsruher Institut für Technologie, Wolfgang-Gaede-Str. 2, 76131 Karlsruhe, Germany

[c)] Institut für Nanotechnologie, Karlsruher Institut für Technologie, Kaiserstr. 12, 76131 Karlsruhe, Germany

We will outline the latest technological developments in modern density functional theories[1,2], many-body perturbation theory[3], and advanced multiscale modeling of linear and nonlinear optical properties[4]. Thanks to recent developments, we can now perform simulations for large molecular systems, allowing for predictions with unprecedented accuracy. Relativistic effects are taken into account, with spin-orbit effects usually included from the outset, i.e., already at the self-consistent level of the theory. One focus is on applications for metal-organic compounds, such as SURMOFs, lanthanide-containing complexes, and the further investigation of nuclear excitations. All methodological advances are implemented in the Turbomole package[5], which has become a powerful tool for the theoretical spectroscopy of (bio)inorganic systems.

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Field-Dependent NMR Shifts in Paramagnetic Molecules: Theory and Interpretation

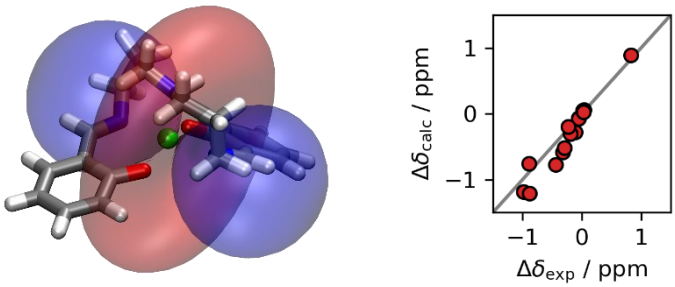
Lucas Lang[a], Letizia Fiorucci[b], Giacomo Parigi[c], Claudio Luchinat[c], Enrico Ravera[c]

a) Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

b) Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

c) Department of Chemistry “Ugo Schiff” and Magnetic Resonance Center (CERM), University of Florence, Via Luigi Sacconi 6, 50019 Sesto Fiorentino, Florence, Italy

Chemical shifts in NMR spectroscopy are typically assumed to be field-independent, but this assumption breaks down at high magnetic fields. While field-dependent shifts in diamagnetic compounds are well understood,[1] a general theoretical framework for paramagnetic systems has been lacking. Here, we present a detailed treatment of field-dependent chemical shifts for paramagnetic molecules in solution. We developed two complementary approaches:[2] a finite-field approach valid to all orders in the applied field B0, requiring numerical orientational averaging, and a second-order approach that allows the orientational average to be performed analytically. In the latter approach, the field dependence separates into two additive terms: the well-known “indirect” contribution from incomplete motional averaging and a “direct” contribution from the nonlinear magnetic response. The direct term involves a fourth-order tensor **τ**, whose elements are fourth derivatives of the electronic Helmholtz free energy, paralleling the diamagnetic case. Our second-order model shows good agreement with experimental field dependencies in both transition-metal and lanthanide complexes. It also allows decomposition into Fermi contact and pseudocontact contributions, helping to identify trends and mechanisms. These findings provide new insights into paramagnetic NMR at high fields and establish a framework for future experimental and theoretical studies in this area.



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Exploring the shift from proton-coupled to hydride-coupled electron transfer

Zuzanna Wojdyla[a], Jishnu Sai Gopinath[a] and Martin Srnec[a]

[a)] J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3, 18223 Prague, Czech Republic

This study explores an alternative mechanism to canonical proton-coupled electron transfer (PCET) - hydride-coupled electron transfer (HCET). HCET is a single barrier process, which involves hydride transfer coupled with electron transfer, as we observed in the set of reactions between a Cu^{III}–OH complex and various organic substrates.[1]

First, the propensity of Cu^{III}–OH complex towards HCET was identified based on the connection between the thermodynamic cycles describing the reaction and reactivity[2,3] and our recent finding that the mechanism (whether HCET or PCET) is dictated by the cycle with more favorable off-diagonal thermodynamics.[4]

The thermodynamic distinction between the mechanisms is evidenced by a match with electronic structure-based descriptors derived from atoms-in-molecule charges and volumes. In HCET, the hydrogen atom gains electron density and volume at transition state. which indicates hydride character, while in PCET, it loses electron density and volume signaling proton character. Moreover, intrinsic bond orbital analysis confirmed that HCET is a two-electron process (as opposed to one-electron PCET): it involves the complete transfer of the proton and the β-electron from substrate to the Cu ion while the α-electron undergoes a transient exchange, initially migrating to the Cu center before returning to substrate.

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Sub-fs electron dynamics in transition metal complexes

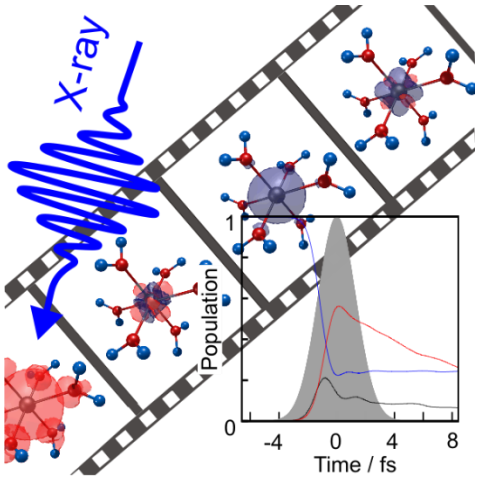
Sergey I. Bokarev[a,b]

[a)] Chemistry Department, School of Natural Sciences, Technical University of Munich, Lichtenbergstr. 4, Garching 85748, Germany

[b)] Institute of Physics, Rostock University, Albert-Einstein-Str. 23-24, 18059 Rostock, Germany

E-mail: sergey.bokarev@tum.de

The past decade has heralded a gradual shift in the ultrafast paradigm in physics and chemistry, from the femtosecond to the sub-femtosecond domain. The fascinating growth in the number of studies on ultrafast phenomena is due to the establishment of new sources, such as X-ray free-electron lasers and high-harmonic generation setups, which provide access to dynamics at electronic time scales. To keep pace with experiments, accurate and efficient theoretical methods need to be advanced.[1] In this contribution, I will present the development of the density-matrix-based time-dependent restricted active space configuration interaction method (ρ-TD-RASCI) for computing ultrafast electron dynamics.[2] The application of these theoretical tools will be exemplified by the ultrafast spin-flip dynamics in transition metal complexes excited by extreme ultraviolet and soft X-ray light.[2-4] The influence of the nuclear motion and (auto)ionization, as well as possible experimental detection methods, will also be discussed.



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Excited-State Dynamics of Cyclometalated Cobalt(III) Complexes

Olga S. Bokareva[a,b]

[a)] Leibniz Institute for Catalysis (LIKAT), Albert-Einstein-Str. 29A, 18057 Rostock, Germany

[b)] Institute of Chemistry and Department of Life, Light and Matter, University of Rostock, Albert-Einstein-Str. 27 and 25, 18057 Rostock, Germany

Transition-metal complexes exhibit rich photochemical and photophysical properties due to their ability to access long-lived electronically excited states. Replicating such behavior in first-row (3d) transition metals presents significant challenges that warrant further investigation. Recent progress in ligand-field photocatalysis, particularly with cobalt(III) cyclometalated complexes, has revealed novel excited-state reactivity. However, the photophysics and photochemistry of cobalt(III) complexes remain underexplored.

In this work, I present excited-state dynamical simulations using mixed quantum-classical non-adiabatic surface-hopping and quantum multi-layer MCTDH methods to unravel the excited-states dynamics of cobalt(III) photosensitizers. For polypyridyl cobalt(III) complexes, ground-state recovery occurs in the Marcus inverted region,[1] a notable deviation from typical first-row transition-metal behavior, such as that of isoelectronic iron(II) systems. This regime supports simultaneous enhancement of redox potential and excited-state lifetime, enabling light-to-chemical energy conversion, including activation of oxidatively resistant substrates in photoredox catalysis. Initial triplet population timescales are captured through simulated population dynamics, while long-time recovery is recovered using transition state theory.

As a second example, I discuss how alkyl substituent functionalization affects the photodynamics of newly reported cobalt(III) complexes with imidazole-based NHC ligands.[2] The simulations reveal that ultrafast relaxation is driven by spin-orbit coupling, vibrational coherence, and structural dynamics, all influenced by the ligand environment. Overall, our findings highlight the necessity of integrating mixed quantum-classical and quantum dynamical approaches to accurately describe excited-state processes in transition-metal complexes.

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The temperature dependence of Mössbauer quadrupole splitting values: a quantum chemical analysis

Niklas von Rhein[a], Vera Krewald[a]

[a)] Department of Chemistry, Quantum Chemistry, Technische Universität Darmstadt, Peter-Grünberg-Str. 4, 64287 Darmstadt, Germany

Mössbauer spectroscopy is a powerful tool for investigating iron in bioinorganic compounds or solid-state materials.[1] Its strengths lie in its isotope specificity, making it especially useful for amorphous systems, and its ability to connect spectroscopic information to spin state, oxidation state and symmetry considerations. For full structural elucidation, however, complementary techniques are needed. Often, experimental spectroscopic parameters are compared to those of model complexes calculated with quantum chemistry methods.[1]

Therein, however, lies a problem: While Mössbauer parameters exhibit a temperature dependence, quantum chemical calculations are formally performed at absolute zero. This limits the comparability to low temperature Mössbauer experiments, which are not only experimentally demanding, but also cannot probe reactive conditions.

In a recent work[2], we developed a method to a priori access temperature dependent information on the quadrupole splitting ΔEQ introduced by vibrational deformation (see Figure 1): We use Wigner sampling to create a temperature dependent ensemble of structures and calculate an average. Using the ensembles, we also gained a deeper insight into the relationship between quadrupole splitting and vibrational deformation: As the sign of the quadrupole splitting depends on the shape of the charge distribution around the iron nucleus, vibration can lead to sign swaps while retaining the absolute value. Hence, the temperature dependence of vibrational distortion leads to the temperature dependence of the quadrupole splitting.[2]

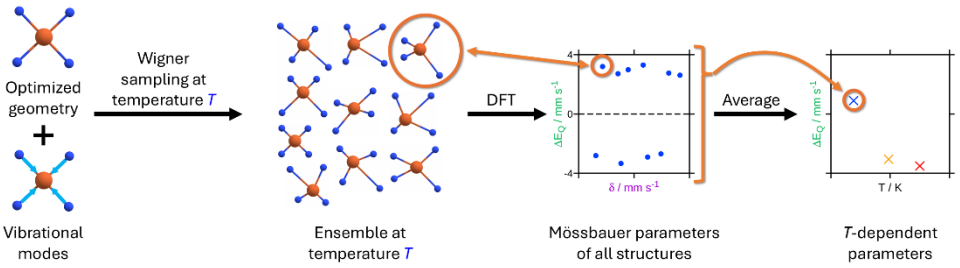

Figure 1: Schematic workflow of our sampling-based method for an exemplary FeN_4 center with Mössbauer quadrupole splitting ΔEQ and isomer shift δ.[2]

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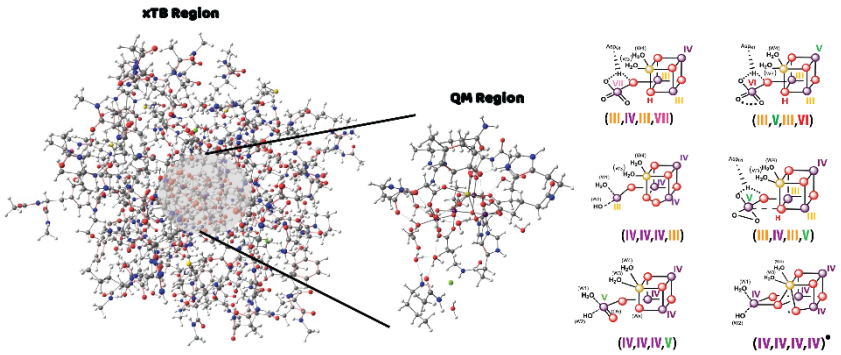
Posters

Redox Isomerism in the Final Catalytic Intermediate of Biological Water Oxidation

Tânia P. A. Sousa, Dimitrios A. Pantazis

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

The unique Mn4CaO5 cluster of the Oxygen Evolving Complex (OEC), located at the active site of photosystem II (PSII), has the capacity to efficiently catalyse one of the most fundamental biochemical processes on Earth, the light-driven four-electron water oxidation into dioxygen. This can be described by a catalytic cycle that involves successive progressions through one-electron oxidized intermediates Si (i = 0–4, known as the Kok cycle) with the final S_4 assigned to be the transient oxygen-evolving state. Over the years a lot of effort has been devoted to deduce features of the S_4 state using X-ray absorption (XAS) and electron paramagnetic resonance (EPR) spectroscopies, but direct information on the O–O bond formation step remains inaccessible. The OEC is an example where quantum chemical approaches are essential in order to explore aspects of the system that are often not directly accessible or easily decipherable from experiment. Theoretical studies have explored several possibilities and proposed various mechanisms for O–O bond formation. At the moment most proposed mechanisms fall into one of the following categories: *Oxo-oxyl radical coupling*[1]*; Concerted-Bond Switching*[2]*; Nucleophilic attack*[3] *and Single site with a* Mn^{VII}*-dioxo species*[4]. Depending on the oxidation state distribution among the Mn ions, there are 12 possible redox isomers as candidat structures for the S_4 state. With this work our goal is to build chemically accurate DFT-xTB models for all the possible redox isomeric forms of the S_4 state, as recently presented for the S_2 state[5], and evaluate their energetic landscape and electronic structure by using the gold standard of quantum chemical accuracy, the domain-based local pair natural orbital coupled-cluster method with singles, doubles, and perturbative triples (DLPNO-CCSD(T)) according to recently established protocols[6].



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Deciphering the Reaction Pathway of Aminophenol Dimerization to a Diazene Intermediate via a $[Cu_2O_2]^{2+}$ Core

Sumangla Arora, and Kyung-Bin Cho*

Department of Chemistry and Research Institute for Materials and Energy Sciences, Jeonju, Korea

E-mail: workforkyung@jbnu.ac.kr

NspF is a coupled binuclear copper protein. It catalyzes the oxidation of substituted *o*-aminophenols to nitrosophenols[1] (Figure 1a). Inspired by the Cu_2O_2-based active site of NspF, a wide range of biomimetic models have been synthesized to gain deeper insight into its enzymatic function. In the present work, we employed density functional theory (DFT) to study the conversion of aminophenol to a diazene intermediate via a biomimetic model based on $[Cu_2O_2]^{2+}$ unit, experimentally studied by Karlin and coworkers[2] (Figure 1b). However, to the best of our knowledge, no detailed reaction mechanism for diazene formation via a Cu_2O_2 core has been reported in the literature. Our calculations reveal that the reaction begins with proton transfer from a 4-methoxyaniline molecule to the Cu_2O_2 core, followed by O–O bond cleavage, leading to the formation of a μ-oxo-μ-hydroxo dicopper core. This species then interacts with a second 4-methoxyaniline molecule, which donates an electron and subsequently a proton in a barrierless process, yielding a stable bis-μ-hydroxo dicopper core. The two NH groups couple to form an NH–NH (hydrazine-type) intermediate. Finally, both NH groups transfer their protons to two μ-hydroxo ligands of the bis-μ-hydroxo dicopper core, leading to the generation of a diazene intermediate along with two water molecules. The active catalyst can be regenerated through reaction with molecular O_2. These results offer a detailed and energetically feasible pathway for N–N bond formation catalyzed via a Cu_2O_2-based model, providing computational support for the reactivity observed experimentally. The DFT method employed for the study is B3LYP/Def2-TZVPP/CPCM(THF)//B3LYP/Def2-SVP/CPCM(THF).

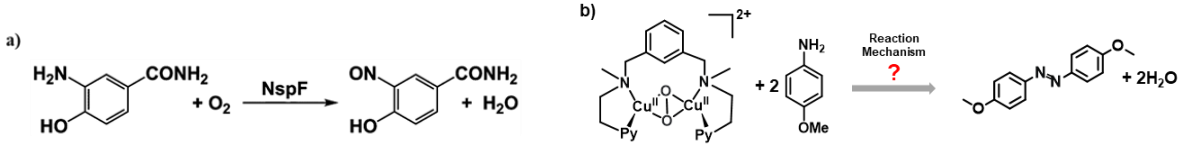

Figure 1. a) Oxidation of substituted *o*-aminophenols to nitrosophenols via NspF b) The conversion of aminophenol to a diazene intermediate via a $[Cu_2O_2]^{2+}$ core.

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Structural Insights Into [FeFe] Hydrogenase by Two-Dimensional Infrared Spectroscopy and Anharmonic Frequency Calculations

Cornelius C. M. Bernitzky[a], Mathesh Vaithiyanathan[a], Manon T. Lachmann[b], Igor Sazanovich[c], Gregory M. Greetham[c], Patricia Rodriguez Macia[b], James A. Birrell[d], Marius Horch[a]

[a)] Institut für Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany

[b)] School of Chemistry, University of Leicester, University Road, LE1 7RH Leicester, United Kingdom

[c)] STFC Central Laser Facility, Rutherford Appleton Laboratory, Harwell Campus, OX11 0QX Didcot, United Kingdom

[d)] School of Life Sciences, University of Essex, Wivenhoe Park, CO4 3SQ Colchester, United Kingdom

Molecular hydrogen (H_2) is a potential candidate for a clean and sustainable fuel. [FeFe] hydrogenases are notable for being noble-metal free and exhibiting the highest turnover rates of all known hydrogenases. A major drawback is their extreme oxygen sensitivity. By selective modification of the active site, oxygen-stable states are formed that can be probed by spectroscopic techniques.

Studies on the [FeFe] hydrogenases *Cr*HydA1 from the green algae *Chlamydomonas reinhardtii* and *Dd*HydAB form the gram-negative sulfate-reducing bacterium *Desulfovibrio desulfuricans* showed that [FeFe] hydrogenases from very different organisms can be converted to the oxygen-stable H_{inact}-like and H_{trans}-like states by addition of cyanide to the catalytically active H_{ox} state. Enrichment of these states was possible by altering a cysteine relevant for proton transport to a serine.[1]

While the infrared (IR) spectrum of the H_{inact}-like state exhibits a typical signature, the IR spectrum of the H_{trans}-like is unusual since only one terminal CO stretching signal can be observed. To resolve this puzzling observation, we have utilized two-dimensional (2D) IR spectroscopy together with computational modeling and anharmonic frequency calculations. By taking the reaction of H_{ox} with cyanide as a starting point, we have explored different structural scenarios that could explain the unusual IR properties by peculiarities of the electronic and vibrational structure of H_{trans}-like while still being consistent with the rather conventional nuclear geometry reflected by the crystal structure.[2] By this approach, we gained detailed insights into the structural sensitivity of experimental and computational 2D-IR spectroscopy.

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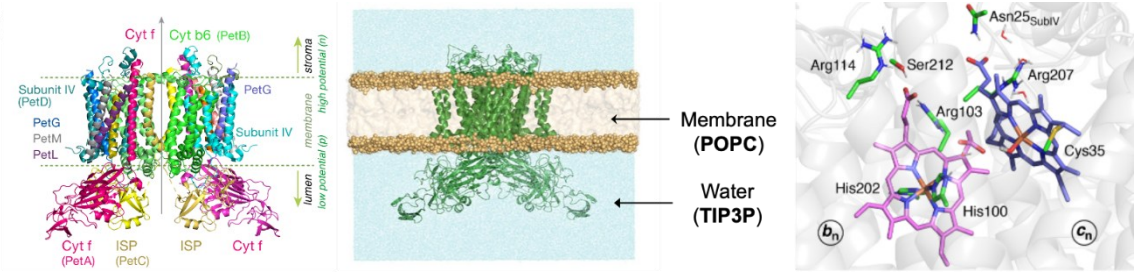
Conformational Dynamics Shape Redox Tuning in Cytochrome b_6f: Insights from MD and QM/MM

Sinjini Bhattacharjee[a] and Dimitrios A. Pantazis[a]

[a)] Department of Molecular Theory and Spectroscopy, Max-Planck-Institut für Kohlenforschung, Mülheim an der Ruhr, Germany

The membrane-bound Cytochrome b_6f (Cyt b_6f) complex is the central enzyme in oxygenic photosynthesis, mediating electron transport between Photosystem II and Photosystem I.[1,2] Cyt b_6f functions as a plastoquinol:plastocyanin oxidoreductase, contributing directly to the proton gradient that drives ATP synthesis. Uniquely, Cyt b_6f catalyzes both plastoquinol oxidation and plastoquinone reduction at opposite sides of the membrane (the Q_o and Q_i sites, respectively). A key feature of this system is electron bifurcation at the Qo site, which channels electrons along two distinct pathways: a high-potential branch involving the Rieske Fe_2S_2 cluster and cytochrome f, and a low-potential trans-membrane branch comprising two b-type hemes (b_p, b_n) and the unique c_n heme near the Q_i site.[3,4] While protein crystallography and cryo-EM [5,6] revealed the overall architecture and redox cofactor arrangement, the functional role of conformational dynamics within the protein matrix remains poorly understood. Here, we investigate the structural flexibility of Cyt b_6f using large-scale all-atom molecular dynamics (MD) simulations of the membrane-embedded complex. Our MD trajectories reveal alternative residue conformations and hydrogen-bond networks that may modulate the properties of the plastoquinone binding sites and redox cofactors. We further employ quantum mechanics/molecular mechanics (QM/MM) calculations to examine how local structural variations influence the electronic structure and redox properties of the cofactors. Our results highlight specific structural motifs implicated in plastoquinone binding and proton transfer at the Q_o and Q_i sites, as well as hydrogen-bonding interactions that fine-tune electron transfer along the high- and low-potential pathways. This work establishes an atomic-level understanding of the interplay between structural dynamics and electron transport in Cyt b_6f, providing new insights into the fundamental principles of photosynthetic energy conversion.



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Multireference-Multiscale Description of Photosynthetic Pigment-Protein Complexes

Maria Drosou[a], Mihkel Ugandi[b], Michael Roemelt [b], Dimitrios A. Pantazis[c]

[a)] Technische Universität Darmstadt, Peter-Grünberg-Straße 4, 64287 Darmstadt, Germany

[b)] Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

[c)] Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

A first-principles description of the primary photochemical processes driving Photosynthesis is a grand scientific challenge. These processes involve diverse pigment assemblies embedded in membrane protein complexes. Popular quantum chemical (QM) approaches based on density functional theory (TD-DFT) face key limitations, including non-transferability, imbalanced description of charge-transfer transitions, and inherent inability of single-reference approaches to describe double excitations. Multireference wavefunction methods can offer the highest level of insight by explicitly describing the wavefunction for each individual state, but they require informed user input and are computationally more intensive than "black-box" TD-DFT.

Here, we present a solid, transparent, and transferable methodological framework for the multireference description of low-lying excited states of protein-embedded chlorin-based pigments relevant to photosynthetic reaction centers and apply this protocol to the description of the reaction center of Photosystem II.[1] For the QM description of the pigment excited states, we use the complete active space self-consistent field (CASSCF) method, incorporating dynamic correlation effects with n-electron valence state perturbation theory (NEVPT2) to obtain accurate excited-state energies. We then integrate this multireference approach with molecular mechanics (MM) in a QM/MM framework to capture electrostatic effects from the protein matrix, which can uniquely diversify otherwise chemically identical pigments.[2] Our protocol extends to describe multichromophoric charge transfer states that define the primary charge separation events in the Reaction Center of Photosystem II. For CASSCF calculations on multichromophoric systems, we employ a dynamic-correlation-assisted approach, namely active space selection by 1st order perturbation theory (ASS1ST).[3] This optimized protocol is transferable to any photoactive embedded pigment system, marking the first step towards large-scale multireference studies of photosynthetic reaction centers and light-harvesting complexes.

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Photocatalytic H_2 evolution of [FeFe]-H_2ase mimic complex

Chizuru Kasahara[a,b], Micheal K. Farh[a], Katharina Rediger[c], Philipp Buday[a], Stefanie Gräfe[b], Mathias Micheel[c], Stephan Kupfer[b], Maria Wächtler[c,d], Wolfgang Weigand[a]

[a)] Institute of Inorganic and Analytical Chemistry, University Jena, Humboldtstr. 8, 07743 Jena, Germany

[b)] Institute of Physical Chemistry, University Jena, Lessingstr. 4, 07743 Jena, Germany

[c)] Chemistry Department and State Research Center OPTIMAS, RPTU Kaiserslautern-Landau, Erwin-Schrödinger-Str. 52, 67663 Kaiserslautern, Germany

[d)] Institute of Physical Chemistry and Kiel Nano, Surface and Interface Science (KiNSIS), Kiel University, Kiel, Max-Eyth-Straße 1, 24118 Kiel, Germany

[FeFe]-hydrogenase ([FeFe]-H_2ase) catalyses the H_2 evolution reaction efficiently using earth-abundant metal, i.e., butterfly shape [Fe_2S_2] cluster. Hence, numerous [Fe_2S_2] mimic complexes (**CAT**) have been reported[1]. For the photocatalytic application, **CAT** is combined with a light-harvesting moiety (photosensitiser, **PS**)[2]. The role of **PS** is to reduce the **CAT** after light absorption with a sacrificial electron donor (SED), and this (excited state) electron transfer pathway from **PS** to **CAT** enables the **CAT** moiety to reduce H^+ and produce H_2.

In this contribution, we present a novel molecular catalyst (**PS-CAT**) which builds on our previous joint synthetic-spectroscopic-theoretical studies.[3, 4] The **PS-CAT** structure can avoid diffusion control interaction between **PS** and **CAT**. The **PS-CAT** was investigated in terms of the electro- and photo-reduction properties, combining experimental and computational approaches to achieve a comprehensive understanding of the (photo) reduction mechanism of the dyad. Thereby, our computational focus was set on assessing the competitive excited state relaxation channels associated with ISC and subsequent relaxation into catalytically active charge-separated states (CS), ligand-centred state (LC) vs. deactivating metal-centred states (MC) (Figure 1).

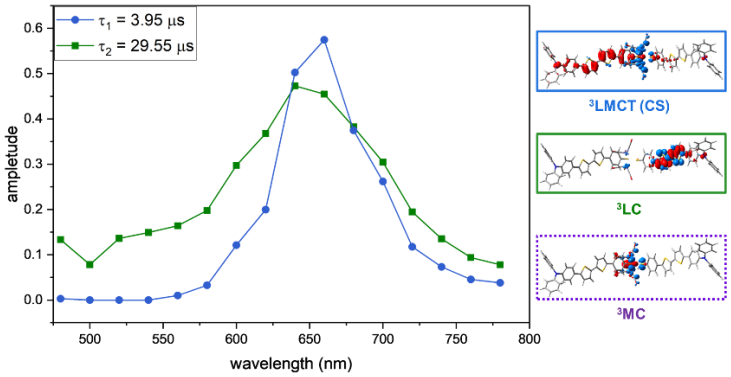

Figure1. ns-transient absorption spectra and charge density differences of **PS-CAT**.

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Nuclear quantum effects on electron transfer in organic mixed-valent systems

Roman Kornievskii[a], Adam Šrut[a], Johannes Kästner[b], Vera Krewald[a]

[a)] TU Darmstadt, Quantum Chemistry, Peter-Grünberg-Str. 4, 64287 Darmstadt, Germany

[b)] University of Stuttgart, Theoretical Chemistry, Pfaffenwaldring 55, 70569 Stuttgart, Germany

The conventional way of understanding electron transfer (ET) in moderately coupled mixed-valent systems is Marcus–Hush theory, where ET is achieved by overcoming a potential barrier in a double-well potential.[1] In the current work, we studied this model in more detail by investigating the role of nuclear quantum effects such as zero-point energy, delocalization and heavy-atom tunneling in ET. For this purpose, we built on the recently published method for reducing the number of dimensions relevant for ET.[2] We found that two dimensions are sufficient for the complete description of ET in 1,3-dinitrobenzene and 2,7-dinitronaphthalene radical anions: the so-called Marcus dimension, which is responsible for electron transfer itself; and another one allowing the system to relax to its minimum on the potential energy surface (PES). From these dimensions, we constructed the two-dimensional PES with DFT, using a local hybrid functional with strong static correlation (scLH23t-mBR)[3] which is particularly important for correctly describing the electronic structures in the transition state region, where static correlation is essential. We then obtained the nuclear vibrational states by solving the Schrödinger equation numerically on the generated PES. We found that these states are spatially highly delocalized with the energy at or above the barrier (see Figure 1). We thus observe an uncommon situation in which the ab initio scan yields a localized double-well potential, while the nuclear quantum effects force the systems to be delocalized.

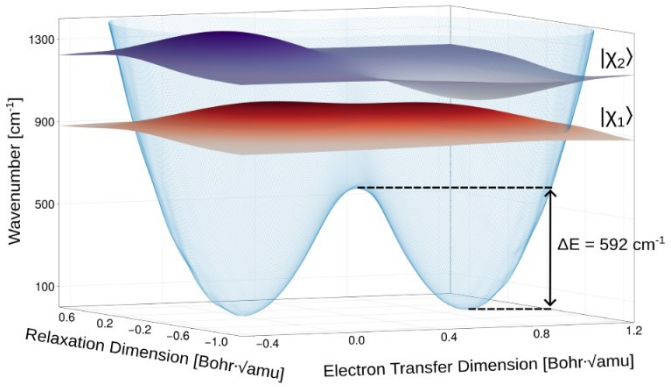

Figure 1: PES for ET in the 1,3-dinitrobenzene radical anion as well as the first two vibrational states. Both states lie above the barrier and are highly delocalized.

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Beyond Transition Metals: Comparing Cerium with group four Transition Metals on oxygen binding and electronic structure

Simon Raphael Kruse[a], Mayara da Silva Santos[a,b], João Pedro Massaria de Arcanto[a],

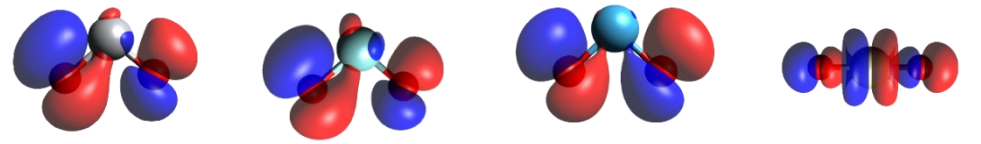
Konstantin Hirsch[a], Vicente Zamudio-Bayer[a], Tobias Lau[a]

[a)] Abteilung hochempfindiche Röntgenspektroskopie, Helmholtz-Zentrum Berlin, Albert-Einstein-Straße 15, 12489 Berlin

[b)] Universität Freiburg, Physikalisches Institut, Hermann-Herder-Straße 3, 79104 Freiburg

In a comparative study of molecular oxido and hydroxido cations of group 4 transition elements titanium, zirconium, and hafnium, including the lanthanoid cerium, we investigate the electronic structure of M^+, $[MO]^+$, $[OMO]^+$, and $[OMOH]^+$, M = Ti, Zr, Hf, Ce, by ion trap X-ray absorption spectroscopy, supported by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) computations.

For the [OMO]+ species of titanium, zirconium and hafnium, the measured oxygen K edge spectrum as well as TD-DFT computations identify a singly occupied molecular orbital (SOMO) of predominantly oxygen 2p derived orbitals, and oxygen-centered radical character.[1–3] In cerium, however, the SOMO only shows 38% of oxygen character but 62% cerium character in the antibonding SOMO because of strong hybridization with cerium-derived orbitals in the linear species.[4] This is in line with the findings of Heinemann et al., who observe hydrogen atom abstraction only for larger alkanes but not for CH_4 or C_2H_6.[5] As for the formal oxidation state, the metal edges show a linear shift of median excitation energy with formal oxidation state of 0.67eV for the titanium L_3 edge, 0.82eV for the zirconium M_3 edge, and 0.37eV for the hafnium N_3 edge. Cerium shows the same behaviour at the M_4 edge, with a shift of 1eV per formal oxidation state.



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The Role of π-Backbonding in Polypyridine Ligands for Electrocatalytic CO_2 Reduction

Florian Lemken[a,b], Lubomír Rulíšek[b]

[a)] Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská Cesta 9, 84536 Bratislava, Slovak Republic

[b)] Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences, Flemingovo Naměstě 2, 84536 Bratislava, Slovak Republic

Ever-increasing concerns about societal and ecological damage caused by climate change have brought measures for the decrease of greenhouse gas emissions like CO_2 to the forefront of research. A promising approach is the electrochemical reduction reaction of CO_2 (CO_2 RR) to syngas by polypyridine complexes of abundant Fe and Co. Many of the best performing members of this class of catalysts are known undergo ligand-centred reductions[1,2], during which strong π-backbonding effectively radicalises the aromatic ligand. The mobility of unpaired electron density has various fascinating implications for the catalytic performance.[3]

In our theoretical study we systematically analyse a subclass of 6 Fe and Co polypyridine complexes w.r.t. performance in the CO_2RR. All 6 displayed strong ligand-centred reduction waves, dominated by π-backbonding, which will be contrasted with their performance alongside insights into relevant π-system substituent effects.

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Time-resolved optical and X-ray spectroscopies applied on ultrafast valence tautomerism

F. Otte[a,b], E. B. Boydas[c,d], S. A. V. Jannuzzi[e], J. Rogalinski[a], T-K. Choi[a], F. Otto[e], M. A. Ribeiro[f], A. Riede[g], M. Nazari[g], M. Biednov[a], D. Khakhulin[a], C. Milne[a], S. DeBeer[e], A. Cannizzo[h], M. Roemelt[c,d], and F. Lima[a]

[a] European XFEL, Germany

[b] Fakultät für Physik, Technical University Dortmund, Germany

[c] Lehrstuhl für theoretische Chemie, Ruhr-Universität Bochum, Germany

[d] Institut für Chemie, Humboldt-Universität zu Berlin, Germany

[e] Max-Planck-Institute for Chemical Energy Conversion, Germany

[f] Universidade Federal do Espírito Santo, Brazil

[g] Institut für Angewandte Physik, University Bern, Switzerland

Bi-stable molecular systems can be used as molecular switches or in spintronic devices. These have motivated intense investigations of cobalt coordination compounds, in particular those presenting *Valence Tautomerism* (VT)[1-2]. A directional charge transfer associated with a change in the metal spin state is a marked characteristic of VT. Switching between two electronically distinct states can be done by external stimuli such as temperature or pressure changes, and also by visible/near-IR illumination[1-4]. The nature of the charge transfer and the metal-ligand magnetic exchange interaction in the VT process is still an open question[1-5]. In particular, the ultrafast dynamics of these processes remain elusive.

Here, we report on optical transient absorption (OTA) and transient X-ray Emission Spectroscopy (XES) measurements with ~100 fs resolution on a VT compound upon a metal-to-ligand charge transfer (MLCT) excitation. The OTA data indicates the presence of two components with about 880 fs and 8.3 ps time constants. The fs-resolved Co Kα and Kβ XES revealed a rich temporal evolution of the different Kα and Kβ spectral regions with two main components of 240 fs and 940 fs. Together, they indicate that a simple two-step process, derived from previous 100 ps-resolved OTA, provides an incomplete description of the ultrafast photo-induced VT process.

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Theoretical Investigation of the Reactivity of A Biomimetic Non-Heme Oxoiron(IV) Complex

Pragya Pudasaini[a], Michael Roemelt[a]

[a)] Institut für Chemie, Humboldt Universität zu Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

High-valent iron-oxo species are key intermediates in enzymatic oxidation processes, particularly within non-heme iron systems that mimic the activity of human catalase (CAT). A biomimetic non-heme oxoiron(IV) complex bearing the TMC-HOR ligand was recently synthesized and shown to form the 1-*anti* species upon oxidation.[1] 1-*anti* structurally resembles Compound I, the reactive intermediate formed during CAT-catalyzed decomposition of hydrogen peroxide.[2] Deprotonation of the complex prior to oxidation prevents the formation of 1-*anti*, suggesting that ligand protonation is crucial for stabilizing the oxoiron(IV) core.

In this study, we employed density functional theory (DFT) to investigate the reactivity of the oxoiron(IV) complex under oxidative conditions analogous to those in CAT's catalytic cycle. Calculations revealed that both, the quintet and triplet states are energetically accessible under experimental conditions. Axial coordination of the solvent, acetonitrile, is thermodynamically near equilibrium, indicating solvent binding. Deprotonation of the complex is strongly favored in the presence of water suggesting that hydrogen bonding significantly stabilizes the conjugate base and modulates the acidity of the coordinated hydroxyl group.

Two intermediate structures were studied as part of the redox reaction pathway, featuring either the protonated or the deprotonated TMC-HOR ligand. Calculations showed that the deprotonated form significantly stabilized the iron(IV)-oxo intermediate supporting experimental observations that deprotonation supresses the formation of the 1-*anti* product.

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Noble Gas Atoms as Ligands to Fe^+: Theory Meets Experiment

Marc Reimann, Dominik Jank, Milan Ončák, Martin K. Beyer

Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25/3, 6020 Innsbruck, Austria

The noble gases are well known for their small or even vanishing reactivity and while several Xe compounds have been prepared over the years, lighter atoms such as Ar or Ne are mostly considered to be chemically inert.

Complexes of 3d transition metals where all ligands are noble gas atoms may therefore be non-intuitive, and in standard (room temperature) condensed phase such complexes will most likely never be found. However, it is possible to obtain complexes such as $[VAr_4]^+$ and $[MAr_6]^+$ (M = Ti, Fe, Co) in the gas phase.[1-3] Apart from their existence, little is known about these systems -- most likely due to their limited chemical relevance.

In the context of quantum chemistry, on the other hand, such small complexes can be evaluated differently: Their limited number of atoms and high symmetry make them ideal candidates for benchmark studies using high-level methods. In this spirit, we have recently used the closely related complexes $[FeHe_6]^{2+/3+}$ for a pure theory benchmark based on MRCI+Q results.[4] However, the quality of these reference results can hardly be assessed, as the computational burden beyond MRCISD is immense.

The goal of this project is to combine the best of both worlds: Using photodissociation spectroscopy, the electronic excitations of $[FeAr_n]^+$ complexes (n = 1 − 4) are investigated in a broad energy window. As the systems are very well defined, the experimental results can easily be related to computed energy differences. Remaining effects such as spin-orbit coupling should not be too large and can be accounted for, e.g., by back-correction. Such high-quality benchmark data will then allow for a rigorous investigation of the quality of various quantum chemical methods, ranging from multi-reference approaches to DFT.

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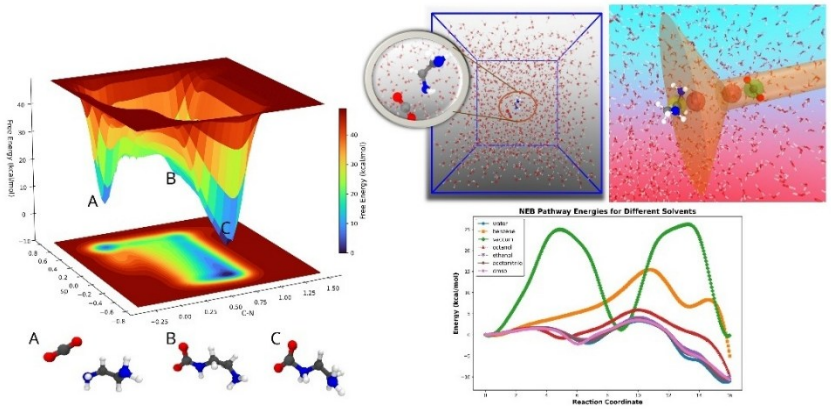
QM/MM Metadynamics Study of CO_2 Capture by Ethylenediamine:Toward an Accurate and Reliable Free Energy Protocol

Madhur Sharma[a] and Ragnar Bjornsson[a]

[a)] Laboratoire Chimie et Biologie des Métaux (LCBM), CEA-Grenoble, France, madhur.sharma@cea.fr

Direct CO_2 capture in aqueous solution using small amines such as Ethylenediamine (EDA) is a promising strategy in carbon capture technologies. However, accurately modelling the reaction mechanism and its free energy surface remains a computational challenge. Here, we present a QM/MM-Metadynamics (QM/MM-MTD) protocol designed to model similar systems in the most realistic manner and produce accurate reaction free energy surfaces. For an explicitly solvated system, we perform Well-tempered (WT) QM/MM-MTD and studied the free energy surface using carefully selected collective variables tailored for studying bond formation, tautomerism, and proton transfer in small-molecule systems [1] To prevent the unphysical diffusion of CO_2 far from EDA and to effectively sample both bound and unbound states, we introduced a funnel-shaped restraint potential [2]. Furthermore, we integrated delta machine learning (Δ-ML) corrections to enhance the accuracy of QM/MM energies and forces by bridging the gap between semiempirical methods and higher-level DFT [3]. The resulting protocol offers a transferable and computationally efficient framework for studying CO_2 capture reactions, combining the cost of semiempirical methods with the accuracy of DFT.



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Ligand Sphere Effects on Dinitrogen Activation in Bimetallic Complexes

Shweta Singh[a], Vera Krewald[a]

[a)] Technical University of Darmstadt, Department of Chemistry, Quantum Chemistry, Peter-Grünberg-Straße 4, 64287 Darmstadt/DE

Transition metal complexes can bind dinitrogen in various coordination modes and activate it further for the nitrogen functionalization N–X(X = C, Si, B, O), i.e. going beyond ammonia as the target product. The modes reported for mono- and di-nuclear transition metal complexes are linear end-on, bent end-on, and diamond coordination modes. In this work we investigate the factors affecting the reactivity of a linearly end-on bridged dinitrogen moiety in Mo, Ta and V dinuclear transition metal complexes in different ligand environments, similar to the nature of active site suggested for dinitrogen fixation in Nitrogenase. Among the three transition metal complexes, dinitrogen completely dissociates in the Mo[1] and Ta[2] complexes, whereas in the V[3] complex no dinitrogen activation is observed (Fig 1). The characteristic transition state for dinitrogen splitting to form nitride complex in dinitrogen end-on bridged complex is characterized of zig-zag shape. We have systematically explored the potential energy surfaces for the possible product formation paths using density functional theory and the more accurate DLPNO-CCSD(T1) extrapolated energies. We combine the study with electronic energy decomposition suggesting primarily the extent of dinitrogen activation is affected by the ligand sphere. We further rationalise the findings with qualitative molecular orbital analysis.

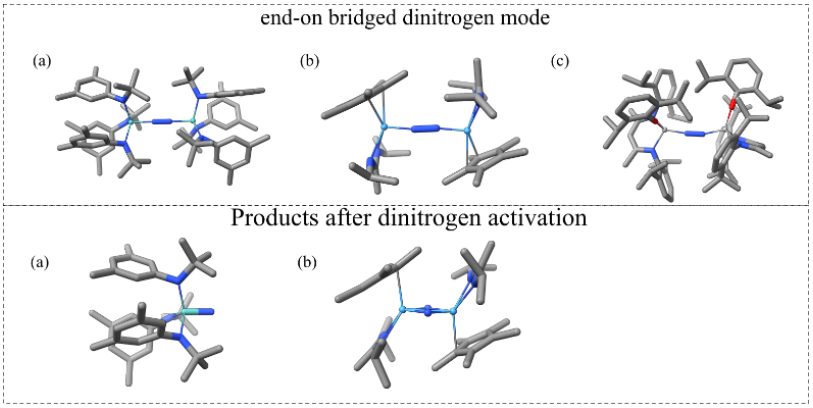

Fig 1: Dinuclear bridged complexes and the respective product formation reported for (a) Cummin's Mo complex, (b) Sita's Ta complex and (c) Mindiola's V complex.

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Computational insights into LPMOs dynamics across copper oxidation states

Katarzyna Szleper[a,b], Andres M. Escorcia[b], Ravi Kumar[b], Artur Góra[a], Matthias Stein[b]

[a)] Tunneling Group, Biotechnology Centre, Silesian University of Technology, Gliwice, Poland

[b)] Molecular Simulations and Design Group, Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany

Lytic polysaccharide monooxygenases (LPMOs) are copper-dependent enzymes that catalyse the oxidative cleavage of glycosidic bonds in recalcitrant polysaccharides such as cellulose and chitin, significantly enhancing biomass degradation in both natural and industrial settings. Their catalytic activity depends on a conserved “histidine brace” motif, where the copper ion is coordinated by the N-terminal amine and two histidine side chains. A key step in the LPMO catalytic cycle is the reduction from Cu(II) to Cu(I), which is essential for oxygen activation.

Beyond the active site, variations in residues forming the copper second coordination spheres, as well as those involved in internal electron transfer ("hole-hopping") pathways, are thought to fine-tune substrate specificity and modulate the reactivity and stability of LPMOs.

In this study, we investigated two structurally distinct LPMOs in both copper oxidation states using extensive molecular dynamics (MD) simulations and quantum mechanics/molecular mechanics (QM/MM) refinement. We focused on key parameters describing the active site environment as well as the dynamics of putative hole-hopping pathways.

Our results provide deeper insight into structural features that modulate LPMO reactivity, supporting efforts in enzyme engineering and redox tuning.

Solvation and Confinement of a Hydrogen Evolution Catalyst in Soft Matter

Simon Tippner[a,b], Leticia Gonzáleza,[c]

[a)] Institute for Theoretical Chemistry, Faculty of Chemistry, University of Vienna, Währinger Straße 17, 1090 Wien, Austria.

[b)] Doctoral School in Chemistry, (DoSChem), University of Vienna, Währinger Straße 42, 1090 Wien, Austria.

[c)] Vienna Research Platform on Accelerating Photoreaction Discovery, University of Vienna, Währinger Straße 17, 1090 Wien, Austria.

Embedding light-driven molecular components such as photocatalysts into structured soft matter offers promising routes for future applications.[1] We present a simulation model of a poly[2-(dimethylamino)ethyl methacrylate] (pDMAEMA) block copolymer membrane, characterized using molecular dynamics (MD) simulations across varying packing densities and geometries.[2]

A central focus is the incorporation of a manganese-vanadium cubane water oxidation catalyst, $[Mn_4V_4O_{17}(OAc)_3]^{3-}$, into the membrane. Our simulations provide insight into the catalyst's conformational behavior and emphasize its interaction with an acetonitrile-water solvent mixture, highlighting how solvent composition affects the microsolvation (see Figure 1). Complementary quantum mechanics/molecular mechanics (QM/MM) calculations were performed to determine redox potentials in the soft-matter environment,shedding light on how this environment might impact catalysis.

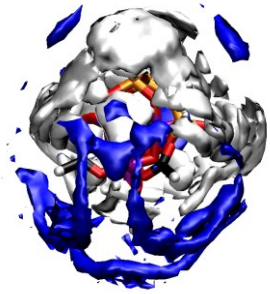

Figure 1: 3D Radial distribution functions of [Mn4V4O17(OAc)3]3− embedded in an acetonitrile/water mixture.

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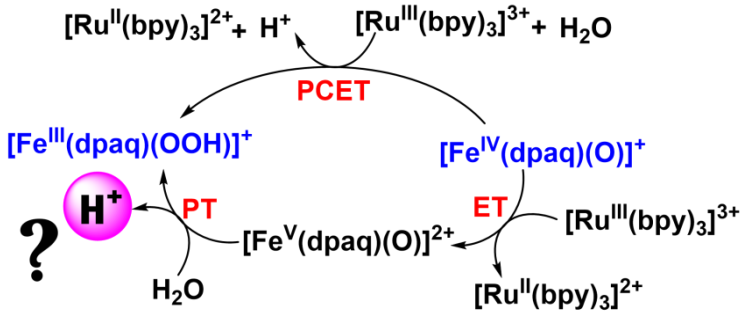
Mechanistic insights for water oxidation catalysis by non-heme Iron complexes: A DFT study

Vandana Kardam, Kyung-Bin Cho*

Department of Chemistry, Jeonbuk National University, Jeonju-si, 54896, South Korea.

Water oxidation is a fundamental step in artificial photosynthesis, emulating the function of the oxygen-evolving complex (OEC) found in Photosystem II of natural photosynthesis.[1,2] A promising synthetic analogue, the non-heme iron complex $[Fe^{II}(dpaq)]^+$, has recently shown catalytic activity in the presence of $[Ru^{III}(bpy)_3]^{3+}$ as an oxidant, where the authors successfully captured $[Fe^{IV}(dpaq)(O)]^+$ and $[Fe^{III}(dpaq)(OOH)]^+$ intermediates. However, the underlying reaction mechanism remains unexplored. To address this, we employed Density Functional Theory (DFT) calcuations to investigate the crucial steps of catalytic cycle, considering all relevant spin states to comprehensively capture the electronic structure throughout the reaction pathway. Our study reveals that the oxidation of $[Fe^{IV}(dpaq)(O)]^+$ to the high-valent, $[Fe^{V}(dpaq)(O)]^{2+}$ species is thermodynamically unfavourable. This computational result is consistent with experimental findings that did not observe the Fe(V)-oxo intermediate, suggesting its fleeting nature under reaction conditions.[3] The subsequent step involving the nucleophilic attack of water on the Fe(V)-oxo species has been identified as a key transformation, primarily due to its endothermic character. According to our DFT calculations, the Fe(IV)-oxo intermediate acts as a potential proton acceptor, facilitating the cleavage of the water molecule and enabling O–O bond formation. The thermodynamic driving force for the overall reaction arises from the exothermic hydrogen atom abstraction (HAA) by the resulting Fe(IV)–OH species which leads to the generation of Fe(III)–aqua and Fe(III)–superoxo as products. These mechanistic insights provide strong understanding for the design of more efficient non-heme iron-based catalysts in renewable energy applications.



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Debate of Nucleophilic versus Electrophilic Oxidative Aldehyde Deformylation by Mononuclear Nonheme Iron(III)-Peroxo and Iron(IV)-Oxo Complexes

Anran Zhou[a], Wenjuan Zhu[a,b], Yue Cui[a], Kallol Ray[b] and Wonwoo Nam[a]

[a)] Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea

[b)] Institut für Chemie, Humboldt-Universität zu Berlin, Brook-Taylor-Straße 2, 12489 Berlin, Germany

High-valent iron(IV)-oxo species are fleeting intermediates that perform vital reactions in enzymatic catalysis. In contrast, heme and nonheme iron(III)-peroxo intermediates usually act as nucleophiles[1,2]. Herein, we report a study on aldehyde deformylation reactions of 2-phenylpropionaldehyde (2-PPA) derivatives by iron(III)-peroxo complexes bearing tetramethylated cyclam (TMC) analogues, such as $[Fe^{III}(O_2)(12\text{-TMC})]^+$ (**1**), $[Fe^{III}(O_2)(13\text{-TMC})]^+$ (**2**), and $[Fe^{III}(O_2)(14\text{-TMC})]^+$ (**3**). Reactivity studies by employing deuterated substrates, such as α-[D_1]-2-phenylpropionaldehyde and aldehyde-[D]-2-phenylpropionaldehyde, demonstrate that deformylation of 2-PPA by the nonheme iron(III)-peroxo complexes occurs via abstraction of the stronger aldehyde C–H atom, rather than the expected nucleophilic attack or weaker α-C–H atom abstraction reactions. Interestingly, the preference for aldehyde C–H atom abstraction is retained during the deformylation of 2-PPA by iron(IV)-oxo complexes. DFT calculations reproduce the experimental trends in reactivity and reveal that the peroxide O–O bond is cleaved to form an iron(III)-dioxyl species that conducts aldehyde C–H bond abstraction. These new experimental and theoretical findings together with the previous demonstrations of the ability of **1**–**3** in hydrogen atom transfer, oxygen atom transfer, and *cis*-dihydroxylation reactions highlight that iron(III)-peroxo cores are not inherently nucleophiles and can have more important functions in chemical and biological oxidation reactions, rather than acting as transient species enroute to high-valent metal–oxo intermediates.

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Quantum Mechanical Mechanistic Insights into CPET-Mediated Ammonia Synthesis

Manjul Yadav[a], Ragnar Björnsson[a]

[a)] Laboratoire Chimie et Biologie des Métaux (LCBM), CEA-Grenoble, France

Converting dinitrogen (N2) to ammonia (NH3) electrochemically represents apromising sustainable alternative to the energy-intensive industrial Haber-Bosch process. Recent experimental advances have demonstrated that combining molecular transition metal complexes with co-catalysts for coupled proton-electron transfer (CPET) can overcome the selectivity challenges that plague conventional N_2 reduction catalysts [1]. However, the fundamental mechanisms of how these CPET mediators facilitate N_2 reduction remains poorly understood. Here, we present a quantum mechanical study to elucidate the mechanism of CPET-mediated N_2 reduction using Mo/W/Fe phosphine-based transition metal complexes , partnered with Co(II,NH) mediators. Using density functional theory (DFT) calculations via ORCA, driven by ASH [2], we investigate the relationship between N_2 binding/activation and the thermodynamics of the CPET steps. For the $W(N_2)_2$ system, we map complete reaction pathways considering multiple spin states and mechanistic scenarios, including distal, alternating, and mixed H-addition patterns. Transition state calculations employing nudged elastic band (NEB) methods are used to identify reaction barriers for both proton transfer (PT) and CPET pathways. Given the computational demands of NEB calculations for these large molecular systems, we have explored machine learning approaches to accelerate transition state searches, with a focus on a delta machine-learning correction approach.

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Free Energy Based Quantum Chemical Microsolvation in Arbitrary Solvents

Lukas Magenheim[a], Radu A. Talmazan[a], Maren Podewitz[a]

[a)] Technische Universität Wien, Institut für Materialchemie, Vienna, Austria

Much of chemistry takes place in solution. The physical and chemical behavior of the dissolved solute largely depends on the nature of the surrounding solvent. For an accurate description of the system at hand, it is therefore vital that solvent effects are taken into account. In quantum chemical descriptions, this can be done either by treating solvents implicitly, accounting only for bulk properties such as the electrical permittivity, or explicitly by describing an extended condensed phase system. As the latter strategy is often too computationally expensive, quantum chemical microsolvation, also termed cluster approach, has emerged, where only the most important solvent molecules around the solute are considered.

This, however, raises two issues:

a) Where should those solvents be placed?

b) How many are needed to capture the most relevant interactions?

We have developed a computational protocol that quantifies solute-solvent interactions using molecular dynamics simulations and Grid Inhomogeneous Solvation Theory (GIST).[1] Our algorithm automatically places and orients solvent molecules based on free energy solvation thermodynamics.[2]

Here, we present the completely revised and extended methodology, which is now capable of identifying favorable solvation sites for the most common (rigid) solvents, such as dichloromethane or DMSO.[3] We demonstrate the applicability of our method in a number of examples, from organic molecules to transition-metal complexes.

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Ligand Non-Innocence in a Cobalt CO_2RR Catalyst: MR Insights

Leon Gerndt[a], Michael Roemelt[a]

[a)] Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str 2, 12489 Berlin

We present a theoretical investigation of a Cobalt-bisbipyridine catalytic system for the CO_2 reduction reaction (CO_2RR). The catalyst system features bipyridine units linked by either an -NH- or -NMe- bridge. The former facilitates selective CO production through ligand non-innocence and proton shuttling via secondary coordination sphere interactions involving a hydrogen-bound proton donor cluster.[1]

Standard DFT functionals yielded conflicting results for the electronic ground state of the active intermediate, mandating a multireference approach. Subsequent CASSCF calculations confirmed the multireference nature, revealing near-degenerate low-lying electronic states. Intriguingly, the character of the computed ground state proved highly sensitive to the level of theory and the selection of starting guess orbitals for the CASSCF procedure. Only calculations employing large active spaces resulted in a state dominated by configurations with a formal Co(I) center featuring a ligand radical, a description consistent with experimental EPR spectroscopic signatures. Furthermore, dynamic electron correlation crucially affects the relative order of electronic states. These demanding investigations, requiring the treatment of dynamic correlation for large active spaces, were made feasible through the application of efficient modern MR techniques, including a spin-adapted variant of heatbath-CI (HCI)[2] and a yet unreported combination of second order Epstein Nesbet and N-electron valence state perturbation theory, denoted EN-NEVPT2.[3] Our findings underscore the limitations of DFT for such electronically intricate transition metal systems and demonstrate the power of advanced MR methods for accurately elucidating complex electronic structures relevant to catalysis.

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[3] https://hu.berlin/hummr

The Lord of the Rings: How Macrocycle Size Dictates Catalytic Reactivity.

Tran Ha My Nguyen[a], Wenjuan Zhu[a,b], Michael Roemelt[a], Wonwoo Nam[a,b]

[a)] Department of Chemistry, Humboldt-Universität zu Berlin, Brook-Taylor-Str 2, 12489 Berlin, Germany

[b)] Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760, Korea

Inspired by Rieske dioxygenase enzymes, this work presents a theoretical investigation of an iron-based catalytic system for alkene dihydroxylation. The system utilizes an Fe(II) center complexed with 12-, 13-, or 14-membered cyclam or its N-tetramethylated analogue (TMC).[1] Experimentally, Fe-TMC complexes are readily oxidized by hydrogen peroxide to form an active species that converts several alkenes into their corresponding cis-diol products, with reactivity reportedly increasing as the macrocyclic ring size decreases.[2] In contrast, the regular Fe-cyclam counterparts are found to be unreactive under identical conditions.

To help rationalize these disparate reactivities, this computational study explores the electronic structure of the active species. Employing a range of different DFT functionals, our analysis suggests the favored sextet ground state to possess significant Fe(II)-superoxo character, based on Löwdin spin population analysis and the shape of the spin density. This electronic description offers an alternative perspective to a previously proposed Fe(III)-peroxide formulation derived from experimental interpretations. Furthermore, the reaction mechanism for the dihydroxylation of styrene and cyclooctene was computationally explored. These calculations point toward the initial oxygen-oxygen bond cleavage to be the rate-determining step, which also showed to be sensitive to the ligand's ring size, giving a plausible explanation for the influence of the ring size on the reactivity. While the origin of the profound reactivity difference between the cyclam and TMC systems is not yet fully resolved, preliminary results suggest that explicit solvent interactions may exert a significant influence on the reaction pathway.

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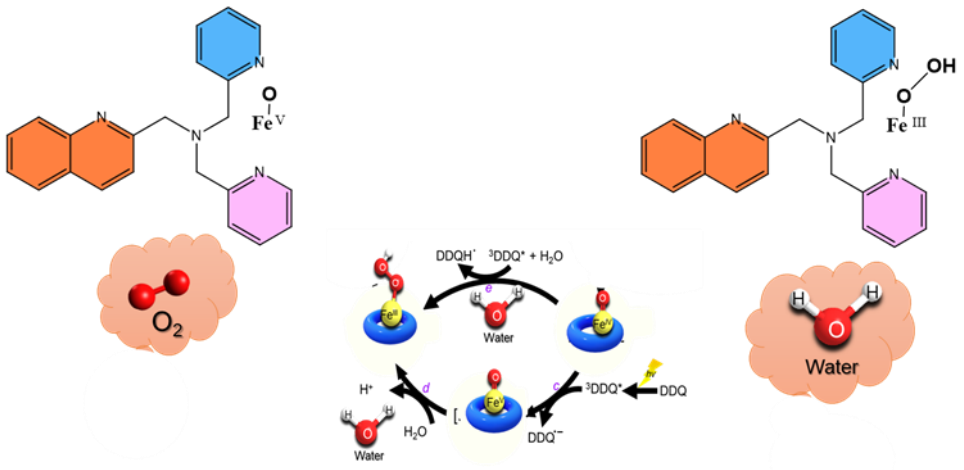
Mechanistic Elucidation of O–O Bond Formation in Iron-Catalyzed Water Oxidation: Theoretical Investigation into Reactive Intermediates Generated via Photocatalytic Activation

Steiny Russelisaac Premakumari[a], Kyung-Bin Cho[a]

[a)] Department of Chemistry and Research Institute for Materials and Energy Sciences, Jeonbuk National University, Jeonju, 54896, Republic of Korea

Inspired by the oxygen-evolving complex (OEC) in Photosystem II, devising a synthetic mimic system and elucidating the mechanistic pathways for the O–O bond formation remains a central challenge in photocatalytic water oxidation. make it two sentence. In this study, we employ density functional theory (DFT) to investigate the electronic structures, spin-state energetics, and transition state barriers associated with experimentally proposed conversion between iron-based intermediates, including iron(IV)-oxo ligand cation radical $[Fe^{IV}(dpaq^{\cdot+})(O)]^{2+}$ (dpaq =2-[bis(pyridin-2-ylmethyl)amino]-N-quinolin-8-yl-acetamide and $[Fe^{III}(dpaq)(OOH)]$ .These species are experimentally confirmed to be involved in a synthetic biomimetic system featuring water oxidation catalyzed by the photoexcited state of 2,3-dichloro-5,6-dicyano-p-benzoquinone (^{3}DDQ*).[1] In this ongoing detailed mechanistic analysis, we hope to be able to reveal plausible O–O bond formation routes, such as water nucleophilic attack (WNA) and radical coupling (RC), and provide insights into the spin-state crossings that govern the reactivity landscape. If successful, it would offer a molecular-level understanding of how ligand non-innocence, high-valent iron-oxo species, and excited-state oxidants cooperate to achieve efficient multi-electron water oxidation, thus contributing to the rational design of next-generation artificial photosynthetic systems.



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Characterization of size-selected platinum oxide cations in the gas-phase using X-ray absorption spectroscopy supported by theory

João Pedro Massaria de Arcanto[1,2], Robert Medel[2], Mayara da Silva Santos[1,3], Simon R. Kruse[1], Vicente Zamudio-Bayer[1], Konstantin Hirsch[1], Sebastian Hasenstab-Riedel[2] and J. Tobias Lau[1,3]

[1]Helmholtz-Zentrum Berlin für Materialien und Energie, Abteilung für Hochempfindliche Röntgenspektroskopie, Albert-Einstein-Straße 15, 12489 Berlin (Germany)

[2]Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 14195 Berlin (Germany)

[3]Physikalisches Institut, Universität Freiburg; Hermann-Herder-Straße 3, 79104 Freiburg (Germany)

joao.massaria_de_arcanto@helmholtz-berlin.de

In the transition metal block of the periodic table, the highest oxidation state (OS) equals the group number up to group 7 for 3d, group 8 for 4d, and group 9 for 5d metals[1]. Heavier 5d elements, particularly from the platinum group (osmium, iridium and platinum) stand out for their complex electronic structure and ability to reach high oxidation states[2,3]. For example, osmium can reach osmium(VIII) in the compound OsO_4, stable under room temperature conditions. Iridium has the highest OS of all elements being found iridium(IX) in $[IrO_4]^+$; platinum reaches an OS of +6 in $[PtF_6]$, yet its 10 valence electrons suggest potential for higher oxidation states[4]. This potential motivates further investigation. A combination of mass spectrometry and X-ray absorption spectroscopy (XAS) at the oxygen K-edge and platinum N_3-edge at the Ion Trap endstation (BESSY II, Berlin, Germany) with theoretical calculations at FU Berlin was carried out for gas-phase size-selected $[Pt,nO]^+$ (n=0-4) to determine their electronic states and identify their corresponding isomers. XAS is an ideal technique for this purpose as it is element specific and sensitive to the electronic structure[5,6]. $[Pt,3O]^+$ and $[Pt,4O]^+$ are two interesting species identified in the mass spectra. The XAS spectra of the two lowest-energy isomers of $[Pt,3O]^+$ were computed using TD-DFT (BP86 functional). Comparison with the experimental data shows agreement with the $[Pt(O_3)]^+$ structure, which also corresponds to the lowest energy species, and indicates a formal oxidation state of +7. This molecule contains only platinum–oxygen bonds. The molecular orbitals for $[Pt(O_3)]^+$ are assessed using CASSF(21,15)-NEVPT2/ZORA-def2-TVZP theory level. The assignment of an oxidation state from multireference calculations is challenging because of the high degree of covalency of the bonds. In contrast to $[Pt(O_3)]^+$, $[Pt(O_2)O]^+$ as a higher energy isomer of $[Pt,3O]^+$, as well as the lowest energy species of $[Pt,4O]^+$, each contain oxygen–oxygen bonds.

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