

Posters

Using Data-driven Models to Optimize Ethanol to Iso-butanol Conversion for Biofuel Application

Kushagra Agrawal*, Richard Wingad, Duncan Wass, Andrew Logsdai¹

Cardiff Catalysis Institute, Cardiff University, Cardiff, UK

discov-log

The Guerbet reaction has significant applications in biofuel production due to its ability to produce branched-chain alcohols producing fuel-grade hydrocarbons. However, the Guerbet reaction requires high temperatures exceeding 250°C, necessitating the use of catalysts to bring down the cost. Previous experimental studies have shown the ability to tune the design of homogeneous catalysts, consisting of transition metal complexes (Ir, Ru and Mn centres), to boost catalytic activities and selectivities, particularly in ethanol homologation to C4 alcohols. However, the underlying atomic-level mechanism remains a subject of debate despite concerted efforts due to a large number of variables. Therefore, advanced data-driven techniques could aid in extracting unknown non-linear trends and catalyst design rules from large datasets.

Here, machine learning tools are employed to draw out important features of the catalytic reaction to drive the conversion of ethanol towards iso-butanol conversion selectively. For this, the structural and electronic features were extracted along with the experimental parameters to generate a robust multi-fidelity feature space. The final dataset containing 400 data points and more than 200 descriptors was used for training. The sub-group discovery method was first employed to screen important descriptors, which were then fed through the Sure Independence Screening and Sparsifying Operation (SISSO) algorithm to find empirical correlations between the chosen descriptors and the selectivity and conversion towards iso-butanol.

The study identifies key characteristic features of the catalyst and its components, such as the importance of a carbon backbone with a nitrogen substitution in the ligands, towards iso-butanol production. Furthermore, empirical correlations relating these key characteristics with the output are also determined, providing us with physical insights into the system and allowing us to optimize the process for maximizing the yield. The physical insights from these models can help develop tailored catalysts towards this process and other processes with similar chemistry in a more efficient and targeted manner. Moreover, the co-optimization of catalytic properties and experimental conditions can lead to building a highly efficient system contributing towards a sustainable and renewable value chain in the energy industry.

DFT + *U* Study of Pu(IV) with Ferrihydrite Surfaces

Ryan L. Dempsey*, Nikolas Kaltsoyannis

*Department of Chemistry, University of Manchester

surfin-nik

The Enhanced Actinide Removal Plant (EARP) at Sellafield's nuclear decommissioning and spent fuel reprocessing site is one of the UK's most important radioactive effluent treatment plants. With the completion of operations at the Thermal Oxide Reprocessing Plant (THORP) and the Magnox reprocessing plant in 2018 and 2022 respectively, both facilities are now in Post-Operational Clean-Out (POCO). This POCO will provide the main feed to the EARP going forward, and will be more chemically diverse than during nuclear fuel reprocessing. Indeed, EARP chemistry is complex and not fully understood, and we here seek to address this knowledge gap using computational methods, linking with recent experimental observations.

Sequestration of actinides at the EARP occurs *via* a base induced hydrolysis mechanism. The EARP feed is highly acidic containing large quantities of Fe(III), and as the pH rises the Fe(III) precipitates out of solution in the form of nanocrystalline ferrihydrite particles. The formation of ferrihydrite itself is of great interest; recently it has been shown to form directly from molecular α -Fe₁₃ Keggin nanoclusters under aqueous conditions.¹ Under simulated EARP conditions, it was shown that Pu(IV) is removed from solution simultaneously as the Fe₁₃ Keggin forms, indicating molecular interaction between the nanocluster and actinide.² The Pu(IV) remains bound during transformation to ferrihydrite, most likely as a tightly bound tetradentate surface complex, and also remains bound through recrystallisation to hematite. In our recent work, we investigated the interactions of the early tetravalent actinides with the molecular α -Fe₁₃ Keggin, showing preference for uptake of Pu(IV), and noting that all of the tetravalent early actinides Th – Pu are strongly bound to the Keggin primarily through ionic interactions.³

We now extend our molecular work to investigate the interactions of Pu(IV) with different ferrihydrite surface models under the periodic boundary condition (PBC) and DFT + *U* formulism. Given that Fh is nanocrystalline the exact nature of the surface terminations is unknown, and so we selected two terminations, Fh{110} and Fh{100}, based on previous work in the literature. Considering that PBC calculation of Fh surfaces only approximates the complicated ensemble of Fh nanoparticles measured experimentally, the average Pu-O and Pu-Fe distances in the lowest energy adsorbed complexes show reasonable agreement ($\Delta r < 10\%$) with the EXAFS fitting. Initial results show that the substitution of Pu(IV) onto is Fh favourable, and the stability of the Pu@Fh surface complexes is driven by the ionic interactions of Pu with the hydrated surface water molecules.

[1] J. S. Weatherill et al., *Environ. Sci. Technol.*, 2016, **50**, 9333-0342.

[2] K. F. Smith et al., *ACS Earth Space Chem.*, 2019, **3**, 2437-2442.

[3] R. L. Dempsey and N. Kaltsoyannis, *Dalton Trans.*, 2024, **54**, 5947-5956.

Computational study of the adsorption of carbon and nitrogen oxides on the {110} surface of PuO₂

Jiali Chen^{*}, Nikolas Kaltsoyannis

The University of Manchester

enviro-nik

The presence of residual small molecules and their interactions with PuO₂ are important for the long-term safe storage of this material. The adsorptions of CO, CO₂, N₂O, NO and NO₂ on the PuO₂ {110} surface have here been studied using periodic boundary condition density functional theory with a Hubbard *U* correction. Different approaching pathways are analysed to locate physisorbed states. Starting from the most stable physisorbed structures, reaction paths leading to stable chemisorbed structures are determined. The chemisorptions of CO, CO₂, N₂O, NO and NO₂ are extensively studied and the following aspects are compared: molecule/surface structures, atomic magnetic moments, surface work functions, density of states, adsorption energies and reaction barriers. The interaction between N₂O and the PuO₂ surface is extremely weak. Physisorption of CO, CO₂, NO and NO₂ is also weak, but these species can then go on to form more stable chemisorbed states. The energy barrier to chemisorption decreases from CO and CO₂ to NO and NO₂, viz. 0.50 eV > 0.46 eV > 0.31 eV > none, so it is easier for NO_x to chemisorb than CO_x (*x* = 1,2). The latter have more stable final chemisorbed states than NO_x: -1.93 eV (CO₂) < -0.95 eV (CO) < -0.92 (NO₂) eV < -0.81 eV (NO), and the chemisorption of (C/N)O₂ is more energetically favourable than monoxides. By contrast, while dioxide chemisorption does not cause much distortion of the surface, CO₂ forming a stable [CO₃]^{*} group and NO₂ retaining its triangular structure, chemisorbed monoxides have larger influence on the adsorbed surface, such as elongated Pu-O bonds, and reduction of neighbouring surface Pu. The latter on the CO/NO chemisorbed surface has occupied *f* states at less negative energy than bare PuO₂ {110}, thereby providing an active site for co-adsorption of further incoming residual molecules.

Thermoelectric properties of the π -cubic phases of SnS and SnSe

Min Zhang*, Ioanna Pallikara, Joseph M. Flitcroft, Jonathan M. Skelton

Department of Chemistry, University of Manchester

power-ske

The tin chalcogenides SnS and SnSe are an important family of optoelectronic materials with applications to clean-energy technologies including photovoltaics (PV) and thermoelectric (TE) generators. In particular, SnS has been widely studied as a potential PV material, and orthorhombic *Pnma* SnSe is one of the current flagship high-performance TEs. The recently-discovered π -cubic phases of SnS and SnSe have similar local structures to the *Pnma* phases, have been shown to be both dynamically stable and close to the convex hull, and have been identified as potential high-performance TEs. However, the physical properties required to determine the TE figure of merit, ZT , have yet to be measured.

We have applied a fully *ab initio* modelling approach to determine the TE properties and ZT of π -cubic SnS and SnSe as a function of temperature and carrier concentration with both p- and n-type doping. Both materials show very low intrinsic thermal conductivity κ , and solution of the Wigner transport equation indicates that a substantial component of the heat transport is through wave-like tunnelling of energy characteristic of glasses. The n-type doping of π -cubic SnS and SnSe is predicted to yield high maximum ZT of 2.19 (860 K) and 2.83 (740 K), well above the industrially-viable threshold of $ZT > 1$, due to their favourable Seebeck coefficients. However, performance is limited compared to *Pnma* SnSe due to a relatively low σ , which might be improved by compositing with a conductive material such as graphene. Overall, our results indicate that the n-doped π -cubic SnS and SnSe are promising TE materials and motivate further exploration of the isostructural π -cubic Ge monochalcogenides.

Exploring formate adsorption on diluted Cu alloys

Z. Lu*, I. Kowalec, R. Catlow, A. J. Logsdail

Cardiff Catalysis Institute, School of Chemistry, Cardiff University

react-log

CO₂ reduction to alcohols, such as methanol and ethanol, is a crucial part of CO₂ utilization. Some Cu-based catalysts show high alcohol selectivity via CO₂ thermal reduction, but their alcohol yields are too low for commercial viability.¹ Cu-based alloy catalysts couples copper's ability of nondissociative activation of C-O bond with C-O scission or C-C coupling ability from other metals, allowing better alcohol yield. In search of promising Cu alloy catalysts, the single atom alloy (SAAs) of Cu² is employed as a simple model for the diluted Cu-based alloy. Formate adsorption is investigated on M-Cu (M: substituent atom) SAA surfaces as a descriptor for catalytic performance since formate is a pivotal intermediate defining alcohol selectivity³.

Two major binding configurations for monodentate formate were studied, both with and without a H...Cu/M bond (Figure 1). The latter configuration is more stable whose charge accumulation primarily localise on the O atoms. Os-, Ru-, and, Rh-Cu SAAs are most favourable for formate adsorption (Figure 2), and all have similar thermochemical electronegativity (X)⁴ (2.65-2.72) and stronger oxophilicity (Θ)⁵ (0.3-0.4) compared to Cu (X : 2.86, Θ : 0.2). Pt and Pd, with similar X (2.70-2.98) and low Θ (0.0-0.1), struggle to stabilize formate (Figure 2). These results suggest the dopant oxophilicity is crucial for formate adsorption. A metal with a moderate to strong Θ and a X comparable to Cu is likely to form a M-Cu diluted alloy to facilitate formate adsorption. This study indicates Os-, Ru-, and Rh-Cu alloy as potential catalysts for CO₂ reduction to alcohol.

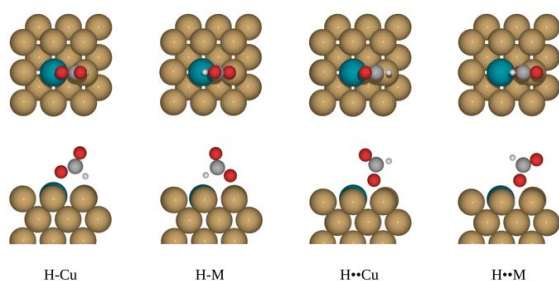


Figure 1. Binding configurations for monodentate formate on a PdCu SAA (100) surface. Brown, cyan, red, grey and white spheres refer to Cu, Pd, O, C and H atoms respectively.

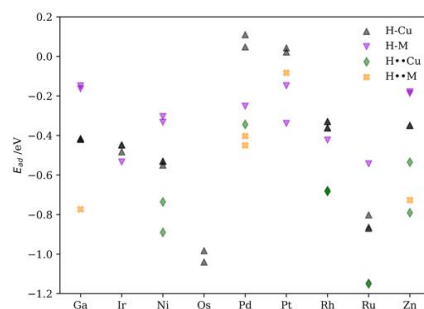


Figure 2. Adsorption energies of different monodentate formate configurations on various Cu SAA (110) surfaces. The x-axis is the metal atom substituent in the SAA model.

1. Xu, D., *et al.* (2021). *Chem*, 7(4), 849–881.
2. Hannagan, R. T., *et al.* (2023). *The Journal of Physical Chemistry Letters*, 14, 10561–10569.
3. Quan, J., *et al.* (2019). *Nature Chemistry*, 11(8), 722–729.
4. Tantardini, C., & Oganov, A. R. (2021). *Nature Communications*, 12(1), 1–9.
5. Kepp, K. P., *et al.* (2016). *Inorganic Chemistry*, 55(18), 9461–9470.

Thermal transport in TMDC heterostructures

Francis H. Davies, S. P. Hepplestone

Department of Physics and Astronomy, University of Exeter

power-hep

A critical factor influencing the vast majority of devices is heat management. This is largely dictated by the thermal conductivity of the host material. 2D materials continue to yield promising results and have shown huge potential in this field [1,2]. Transition metal dichalcogenides (TMDCs) represent an exciting category of 2D materials known for the large variety in their unique electronic properties [3]. However, unexplored areas still exist, such as the thermal properties of heterostructures and superlattices formed by stacking different TMDC layers.

We investigate the thermal properties of TMDC heterostructures from fundamental features of phonons and electrons, via ab initio calculations. We have investigated thermal transport in TMDC heterostructures in two ways. When using a constant coupling rate between all phonon modes and conservative parameter fitting, we show that the possible conductivity values are typically reduced below both the constituent materials. We however go further and perform 3-phonon calculations a variety of TMDC heterostructures. By perusing this higher level of theory, we provide a clear understanding of how the thermal transport varies in TMDC heterostructures. This study not only enhances our understanding of thermal behaviour in layered materials but also suggests practical pathways for optimizing thermoelectric performance by manipulating material properties.

1. Zhao, Jian, et al. *Nature* 625. 7993 (2024): 60-65.
2. Cai *et al.* *.Sci. Adv.* **5**. 6 eaav0129 (2019).
3. Geim, Andre K., and Irina V. Grigorieva. *Nature* 499.7459 (2013): 419-425.

Theoretical Simulations of Helium in Zirconolite

Anlu Wei. Presenter*, Nikolas Kaltsoyannis

**Department of Chemistry, The University of Manchester*

enviro-nik

Zirconolite is a prospective wasteform material for hosting plutonium, a highly radioactive component of spent nuclear fuel, within a geological disposal facility (GDF). However, the decay of plutonium generates helium, whose release within the wasteform can precipitate the formation of bubbles and consequent wasteform cracking, leading to diminished durability. Therefore, understanding the behaviour of helium in zirconolite is pivotal for reliably predicting the performance of this wasteform throughout the GDF's operational lifespan. We have investigated helium in zirconolite using periodic boundary condition density functional theory. A highly efficient random search technique known as the Ab initio Random Structure Searching method was employed to pinpoint the lowest energy conformation for interstitial helium. Findings from simulations involving multiple helium atoms per unit cell indicate a minimal propensity for helium interstitial clustering. Furthermore, diffusion barriers for helium in zirconolite were determined using the climbing image nudged elastic band method. It was observed that helium exhibits preferential migration along the $\langle 010 \rangle$ channel. Subsequently, the rates of helium migration and diffusion coefficients were calculated, also considering the influence of vacancies in the zirconolite lattice.

Challenges of Crystal Morphology Prediction – Hydration Effects on the Growing Halite Surface

John A. Hayton*, Stephen J. Cox

Yusuf Hamied Department of Chemistry, University of Cambridge

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Any attempt to understand crystal morphology begins with the kinetics of crystal facet growth. Given the expensive nature of directly sampling the growth of an entire face, this problem is regularly broken down further into attachment of single ‘growth units’ to a crystal. The rates of these elementary steps are then used to parameterise theoretical or stochastic models to obtain morphological predictions. Recent kinetic monte carlo methods aim to go further, reducing rate predictions to simple free energy measurements by applying the Bell-Evans-Polanyi principle, and have found success modelling several zeolites and molecular crystals.

Here, we explore the limits of such a method for ionic crystals, where long range electrostatic interactions and strongly bound solvent particles indicate that the rates of elementary steps may be challenging to predict. We find that it is both difficult to accurately predict the relative stability of sites without careful sampling of solvent, and that the application of the Bell-Evans-Polanyi principle in such systems appears limited. By comparing to less polar systems, we find that the majority of problems stem from the strong binding of polar solvents to an ionic crystal. Our results indicate a wealth of interesting ion/water interactions on the sodium chloride surface, and highlight the need to carefully model mechanistic pathways to obtain accurate attachment rates.

Understanding Organic Cocryystalsfor Room Temperature Phosphorescence

Kanyarat. Rueangboon*, María Eugenia. Sandoval-Salinas, Rachel. Crespo-Otero

Department of Chemistry, University College London

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Organic co-crystals offer a versatile platform for designing efficient room temperature phosphorescence (RTP) materials. Despite the growing number of reported organic co-crystals with RTP, there is a lack of understanding regarding how to exploit specific intermolecular interactions to achieve and enhance phosphorescence. Different strategies such as crystallisation, H-aggregation, and the heavy atom effect allow obtaining organic RTP with significant excited state lifetimes.¹ Recently, Abe et al.² used the heavy atom effect and rigid environment strategies to modulate the RTP in co-crystals of DITFB with Chry, Pyr, and Phen (Figure 1). To understand how specific intermolecular interactions and crystal packing affect the excited state mechanisms, we investigated the nature of the electronic transitions and the effects of the spin-orbit couplings in these co-crystals. Our calculations provide information about how to control photophysical properties in these systems through specific intermolecular interactions, which have an impact on the rational design of organic materials with a broad range of applications.

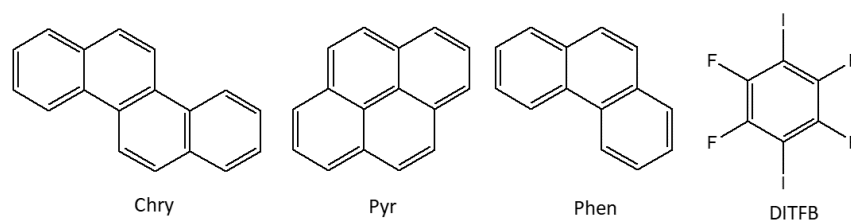


Figure 1: Components of the co-crystals with RTP under study

[1] M. Singh, K. Liu, S. Qu, H. Ma, H. Shi, Z. An, W. Huang, Recent Advances of Cocryystals with Room Temperature Phosphorescence. *Adv. Optical Mater.* 2021, 9, 2002197.

[2] A. Abe, K. Goushi, M. Mamada, C. Adachi, Organic Binary and Ternary Cocryystal Engineering Based on Halogen Bonding Aimed at Room-Temperature Phosphorescence. *Adv. Mater.* 2023, 2211160.

Point charge embedding approaches for simulating excited states in MOFs

Michael Ingham*, Amir Sidat, Alex Aziz, Devis Di Tommaso, and Rachel Crespo-Otero

Department of Chemistry, University College London

discov-rco

Metal-organic frameworks (MOFs) have significant photocatalytic and optoelectronic applications, many directly dependent on their excited states. However, simulating the excited states of MOFs remains highly challenging due to their large and complex unit cells, the inherent dual molecule/crystal nature of MOFs, and the unfavourable scaling of quantum chemical methods.¹ Crucially, this limits the application of traditional solid-state methods to MOF excited-state studies. For instance, band conduction is typically minimal in MOFs and transport follows a spatial-hopping scheme. Consequently, cluster models emerge as an effective approximation to take advantage of electronic structure localised on collections of sub-units at modest computational cost. By dividing a cluster model into multiple levels of theory, approaches such as ONIOM(QM:QM') massively expand the spatial dimensions of cluster models, at minimal added cost.^{2,3} Point charge-embedding incorporates environmental electrostatics of the crystal into models, but must be carefully constructed to avoid overpolarisation artefacts.⁴ Despite advances in its application to solids, ONIOM(QM:QM') with point charge embedding has rarely been utilised for MOF excited states. Here, we investigate the performance of the cluster, ONIOM(QM:QM'), and periodic approaches in the study of MOF excited states, with a special focus on the treatment of overpolarisation.

References

1. M. Ingham, A. Aziz, D. D. Tommaso and R. Crespo-Otero, *Materials Advances*, 2023, 4, 5388–5419.
2. M. Rivera, M. Dommett and R. Crespo-Otero, *Journal of Chemical Theory and Computation*, 2019, 15, 2504–2516.
3. M. Rivera, M. Dommett, A. Sidat, W. Rahim and R. Crespo-Otero, *Journal of Computational Chemistry*, 2020, 41, 1045–1058.
4. A. Sidat, M. Ingham, M. Rivera, A. J. Misquitta and R. Crespo-Otero, *The Journal of Chemical Physics*, 2023, 159, 244108.

The Impact of H₂O on WS₂ Oxidation

Katherine Milton*, Alex Shluger,

**Physics and Astronomy, University College London*

surfin-shl

The two-dimensional nature and semiconducting properties of transition metal dichalcogenide WS₂ make it a promising material for electronic devices. However, WS₂ is prone to oxidation at grain boundaries, edges, and defects when exposed to air, with the oxidation rate increasing with relative humidity. Despite extensive research, the precise mechanisms of WS₂ oxidation, particularly those involving water, remain unclear. This study employs density functional theory (DFT) to elucidate the interactions between water and WS₂ defects and edges, as well as the potential dissociation mechanisms contributing to oxidation.

Preliminary findings indicate that point defects with increased tungsten (W) exposure exhibit more favourable interactions with water, evidenced by charge distribution analysis and water adsorption energies. These sites are also more thermodynamically favourable for water dissociation. At the tungsten zigzag edges, water shows strong interactions, and a hydrogen hopping mechanism between water molecules leads to the spontaneous dissociation of water, forming H₃O⁺ molecules. Additionally, water can induce the spontaneous dissociation of oxygen molecules when they are adsorbed on the tungsten zigzag edges. This research enhances our understanding of the oxidation mechanisms of WS₂ in the presence of water and explains the increased oxidation rate with higher relative humidity.

Investigation of degradation mechanism of crystalline and amorphous Ga₂O₃

Chaiyawat Kaewmeechai*, Jack Strand, Alexander Shluger

* *Department of Physics and Astronomy, UCL*

bulk-shl

Ga₂O₃ is a promising material for power electronics devices, owing to its high breakdown electric field and wide bandgap (~5 eV). In devices based on Ga₂O₃, electron and hole injection from the metal contact occurs when the devices are operated. This intrinsic charge trapping leads to a polarons formation and subsequent device degradation. Therefore, understanding the mechanism behind defect creation and charge trapping in Ga₂O₃ is essential for designing high-performance devices. The Frenkel pairs (FPs) defects comprising one oxygen vacancy (V_o) and one oxygen interstitials (O_i) are considered as a consequence of charge trapping in Ga₂O₃. However, an unexplored question remains regarding the migration of the V_o⁺² to other sites once FPs defects are created.

In this study, we investigated the intrinsic charge trapping in crystalline β and amorphous Ga₂O₃ which, potentially induces defect creation. We modelled the 400-atom Ga₂O₃ by using the CI-NEB density functional theory (DFT) with PBEsol functional as implemented in CP2K. Our findings suggest that the potential initial cause of Ga₂O₃ degradation is the formation of a hole bipolaron, with an activation energy around 3 eV and 1.5 eV for β and amorphous Ga₂O₃ respectively resulting in the formation of a FP defect structure. This is a notable decrease from the 8.5 eV activation energy observed in the perfect pristine structure. Subsequently, the V_o⁺² can migrate to other sites in Ga₂O₃ with the migration energy around 1 eV. Therefore, we present a detailed demonstration of the degradation mechanism of β-Ga₂O₃ induced by charge trapping as a consequence of FP defects formation.

Modeling the Effect of OSDA on Nucleation Process of TS-1 Zeolite

Xu Zhang^{*}; Sokols, Alexey^{*}; Catlow, Richard^{*}.

^{}Department of Chemical, University College London*

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Zeolites are porous materials that come in many topologies and have multiple catalytic functions. The majority of zeolite synthesis relies on organic structure-directing agents (OSDAs). However, most OSDA designs are based on trial and error, chemical intuition, or large-scale screenings rather than rational design. This empirical, labor-intensive task makes the design of OSDA a significant technical threshold.

In this study, we analyzed the effects of over 80 different OSDAs on the nucleation process using TS-1 zeolite as an example. Through high-throughput computational simulations, literature mining, synthesis, and characterization, we revealed the energetic, geometric, and electrostatic descriptor effects of OSDAs on the entire nucleation process.

Furthermore, we extended our research to include TS-1, S-1, and NaSiAl zeolites, taking into account the influence of solvents. The final simulations and online Raman data provided validation for our findings. This comprehensive approach offers new insights into the rational design of OSDAs for zeolite synthesis, potentially reducing the trial-and-error nature of this process and enabling more efficient and targeted development of zeolite materials.

Semiconducting Materials from Analogy and Chemical Theory (SMACT) – Version 3

Panyalak Detrattanawichai,* Anthony Onwuli, Hyunsoo Park, Zhenzhu Li, Keith T. Butler, and Aron Walsh

Department of Materials, Imperial College London

algor-wal

The discovery of earth abundant, functional materials is critical for sustainable technological advancement. A variety of approaches are emerging that can reduce the time it takes to realise such materials via high-throughput experiment and first principles calculations. However, even the search space produced by forming four-component compounds from the first 103 elements – consisting of more than 10¹² potential combinations – is intractable to most methods. There is therefore a need for complementary sets of tools that can deal with such large search spaces.

I will present how a useful materials search space can be prepared rapidly using the open source SMACT package (<https://github.com/WMD-group/SMACT>) and describe how simple chemical rules can aid in restricting the space to chemically plausible compositions.¹ This space can then be fed into a hierarchical screening approach or to inform inverse design procedures based on artificial intelligence².

The new developments steps used fall broadly into three categories: (i) featuring compositions using machine learning embedding vectors³; (ii) the development of surrogate models that allow us to rapidly filter for target electronic properties such as bandgap; (iii) automated first-principles or universal force field calculations applied to leading candidates to verify stability, structure and target properties. At each stage, the size of the search space can be drastically reduced, ensuring that as computational cost increases, the number of candidate materials remains tractable.

1. D. W. Davies et al., *Chem*, (2016) 1, 617; <https://doi.org/10.1016/j.chempr.2016.09.010>
2. K. T. Butler et al., *Nature*, (2018) 559, 547; <https://www.nature.com/articles/s41586-018-0337-2>
3. H. Park et al., *Farad. Discuss.*, (2024) In Press; <https://doi.org/10.1039/D4FD00063C>

Machine-learning Aided simulation of Magnesium hydride dehydrogenation

Elena Uteva*, Sanliang Ling

*Advanced Materials Engineering Dept., Nottingham University

surfin-lin

There is a growing urgency in the scientific community to find novel ways to reduce global carbon dioxide emission levels and transition from fossil fuels to alternative green sources. Hydrogen is poised to play a substantial role in the future low- or no-CO₂ energy industry. However, the establishment of a hydrogen economy is currently bottlenecked by the technical issue of storing it. Solid-state storage has been a promising avenue. The most well researched hydrogen-storage material is magnesium hydride, which has a storage capacity of 8.6% wt, little safety risks and well-known production-routes. However, the sluggish desorption kinetics makes it currently unfeasible for widespread practical applications. Although catalytic doping has been shown to accelerate the uptake/release of hydrogen, more mechanistic information about the (de)hydrogenation reaction is required to optimize catalytic design. As this is too difficult to obtain experimentally and too computationally burdensome to obtain using ab-initio calculations, our research uses machine learning potentials trained on a limited set of DFT points to run the simulation at a fraction of the DFT-only simulation time. The research uses state-of-the-art transformer-based architecture with end-to-end learning through a SpookyNet model to simulate the dehydrogenation of a magnesium slab. SpookyNet scales better with the number of elements compared to the de facto Behler Parinello Neural Network (BPNN) and is better suited for modelling materials with catalytic dopants. We achieved an RMSE of 14.9 meV/atom and 49.2meV/Å for energy and force respectively, which is lower than the BPNN errors for energy and force of 23.4 meV/atom and 56.5meV/Å, despite having a lower number of symmetry functions.

Electron Spin Dynamics in Prospective MRI Contrast Agents

Toby R. C. Thompson*, Barak Alnami, Andrea Mattioni, Jonathan M. Skelton, Nicholas F. Chilton

*Department of Chemistry, The University of Manchester

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The electron spin dynamics of heavy metal complexes are key to their use as contrast agents in MRI as they drive nuclear spin relaxation. Recently, lanthanide-based PARASHIFT agents have been shown to be able to give simultaneous information on pH, temperature and agent location, vastly enhancing the information extractable from a single MRI scan.¹ These novel agents rely on the signal enhancement due to rapid, paramagnetically enhanced longitudinal nuclear spin relaxation.

Describing the electron spin dynamics in a fluid solution of lanthanide molecules is challenging for several reasons: i) the high-field limit does not apply when a large ligand field splitting is present, ii) the behavior of the stochastically varying ligand field is complex and poorly understood, and iii) the Redfield theory that makes nuclear relaxation tractable is invalid, due to the strength of the ligand field being large relative to the timescale on which it varies. Hence, simple phenomenological models have dominated the literature.² Prior attempts at approaching this problem with a molecular level of detail have been limited by available computational resources.

We have implemented a method to simulate electron spin dynamics explicitly, allowing the extraction of nuclear relaxation rates and hence an understanding of the chemical design features required to improve these agents. Our approach employs DFT molecular dynamics to obtain an approximation of the complex's vibrational degrees of freedom in fluid solution on the femtosecond timescale, including collisions with explicit solvent molecules. The electronic structure of the lanthanide complex is then considered at the CASSCF-SO level of theory, allowing us to directly determine the time-varying ligand field potential. With access to the time-dependent molecular Hamiltonian, we implement spin dynamics simulations to obtain unprecedented insight into the spin physics that drives nuclear relaxation.

References:

1. Finney *et al.*, *Chem. Eur. J.*, 2017, **23**, 7976.
2. Kowalewski *et al.*, *J. Magn. Reson.*, 2020, **314**, 106737.

Understanding the defect chemistry of CaAlSiN_3 inorganic red phosphor for solid state lighting applications

Maryia Shymanovich*, Alexander G. Squires, David O. Scanlon

*School of Chemistry, University of Birmingham

bulk-dos

One of the potential solutions to the global problem of increasing demand for energy is the reduction of electricity consumption from lighting. This can be achieved by replacing incandescent lights to phosphor-converted light-emitting diodes (pc-LED). Therefore, the development of efficient materials for inorganic phosphors has already attracted significant attention. CaAlSiN_3 (CASN) is a silicon-nitride inorganic phosphor host material and, when doped with rare-earth ion such as Eu^{2+} , produces red luminescence required for “warm-light” LEDs. Several studies have shown that doped-CASN serves as a promising inorganic red phosphor due to its high quantum output, good thermal and chemical stability, and low thermal quenching.¹⁻³ One of the important structural features of CASN is that Al and Si are randomly distributed among identical tetrahedral sites. The Al/Si distribution can influence the electronic and optical properties of host material^{4,5}. However, the defect chemistry in this material is not well understood and requires further research.

The goal of this project is the investigation of cation disorder in CASN and the analysis of the defect chemistry in this material. Vienna Ab initio Simulation Package is used to perform Density Functional Theory calculations. Generalised Gradient Approximation and hybrid functionals combined with plane-wave basis set are applied. The Al/Si ordering has been studied using Cluster Expansion (CE) method combined with Monte-Carlo (MC) simulations. Results from CE and MC as well as the density-of-states and band structure calculations of the CASN structures with various Al/Si ordering will be presented. Further steps toward understanding of the defects in this material will be proposed.

1. X. Piao, K. I. Machida, T. Horikawa, H. Hanzawa, Y. Shimomura and N. Kijima, *Chemistry of Materials*, 2007, **19**, 4592–4599.
2. K. Uheda, N. Hirotsuki, Y. Yamamoto, A. Naito, T. Nakajima and H. Yamamoto, *Electrochemical and Solid-State Letters*, , DOI:10.1149/1.2173192.
3. Z. Zhang, O. M. Ten Kate, A. C. A. Delsing, M. J. H. Stevens, J. Zhao, P. H. L. Notten, P. Dorenbos and H. T. Hintzen, *J Mater Chem*, 2012, **22**, 23871–23876.
4. M. Mikami, K. Uheda and N. Kijima, *Physica Status Solidi (A) Applications and Materials Science*, 2006, **203**, 2705–2711.
5. Z. Wang, B. Shen, F. Dong, S. Wang and W. S. Su, *Physical Chemistry Chemical Physics*, 2015, **17**, 15065–15070.

Catalytic Partial Oxidation of Methane using an Yttria-Stabilized Zirconia Catalyst

Erze Gao*, Alexey Sokol, Richard Catlow

*Chemistry, UCL

react-cat

This project is about discovering the catalytic cycle for Catalytic Partial Oxidation of Methane (CPOM) via using Yttria-Stabilized Zirconia (YSZ). The partial oxidation of methane is an important industrial process for upgrading natural gas into syngas, a mixture of CO and H₂ which is widely used in the industrial field. The reaction of CPOM occurs on the (111) plane of YSZ, in which the methane is physisorbed and oxidized into formaldehyde, before decomposing into syngas and other by-products. The surface model in this project is large symmetric slab model, which consists of 4*4 supercell with 96 ZrO₂ formula units. The thickness, width and vacuum separation of the slab are respectively 16.36Å, 14.6 Å and ~15Å. The concentration of Y₂O₃ is 14.3 mol% on the surface, which fits the experimental observation of 10-14 mol%.

The surface was firstly pre-oxidized via the removal of one lattice oxygen and absorption of the oxygen molecule in the atmosphere. Thus, the pre-oxidized 'YSZ+O' model was prepared for further reaction. Then the research discussed the process of methane absorption and oxidation into surface formaldehyde on the YSZ, with various routes and reactions being analyzed. To be specific, the results mainly indicated a possible method which led to the decomposition of surface formaldehyde through H-Zr interaction. Proper structures were discovered with lower potential energy compared with the initial structure, which suggested that CO may be desorbed firstly. When the CO was abstracted at first, the remaining hydrogen could form a surface hydroxyl and an isolated proton located at the surface vacancy. The electronic structures are simulated based on the Density Functional Theory (DFT) via VASP, to achieve its configuration and polarization if possible. Besides, other routes such as abstracting H₂ initially were also discussed, with higher energy barrier in the end.

Characterisation of Cu_2GeSe_3 for renewable energy applications

Philippa Cox*, David O. Scanlon, Alexander Squires

*School of Chemistry, University of Birmingham

power-dos

Photovoltaic (PV) technology is a critical solution to global energy challenges, offering a sustainable and renewable method for converting sunlight into electricity. Professor Scanlon's group at the University of Birmingham has recently characterised Cu_2SiSe_3 , a promising solar absorber material composed of inexpensive and non-toxic elements, showing potential efficiencies that may exceed those of leading materials such as CdTe^{1,2}. One identified limitation of Cu_2SiSe_3 is its larger than ideal bandgap. Alloying with Cu_2GeSe_3 , which has a narrower bandgap is one route to optimise this material. However, before proceeding with alloying, it is essential to comprehensively characterise the Cu_2GeSe_3 endmember to ensure its suitability as an energy material.

This project aims to provide a detailed characterisation of Cu_2GeSe_3 , focusing on its structure, thermodynamic and dynamic stability, optical absorption, and electron transport properties, thereby laying the groundwork for future alloying experiments. By thoroughly characterising Cu_2GeSe_3 , we aim to provide crucial insights for the development of high-efficiency, non-toxic, and cost-effective solar absorber materials, with a particular focus on laying the groundwork for future alloying with Cu_2SiSe_3 .

- (1) A. Nicolson, S. R. Kavanagh, C. N. Savory, G. W. Watson and D. O. Scanlon, *J. Mater. Chem. A*, 2023, 11, 14833–14839.
- (2) M. Green, E. Dunlop, J. Hohl-Ebinger, M. Yoshita, N. Kopidakis and X. Hao, *Prog. Photovoltaics.*, 2021, 29, 3–15.

Modelling of magnetochiral dichroism for lanthanide(III) complex

Maxime Grasser*, Jochen Autschbach, Boris Le Guennic

*Department of Chemistry, The University of Manchester

nano-chi

Since the pioneering work of van Vleck[1] it has been well established that crystal field splitting is at the origin of both magnetic and luminescent properties in lanthanide based complexes. Magneto-chiral dichroism (MChD) corresponds to the difference in absorption when the orientation of the magnetic field and the light beam are parallel and antiparallel [2]. This phenomenon could be responsible for the homochirality of life[3] and is envisaged for the optical reading of magnetic state of compounds with light[4].

The first MChD spectrum for a lanthanide-based complex has recently been reported for an ytterbium(III) ion (Figure 1a)[5]. The MChD phenomenon is described by the Barron and Vrbancich theory[6], while the electronic structure of lanthanide complexes requires multiconfigurational methods and the consideration of spin-orbit coupling for evaluating it. Based on CASPT2 calculations and self-made post-processing programs, the MChD spectrum of this complex has been successfully simulated (Figure 1b).

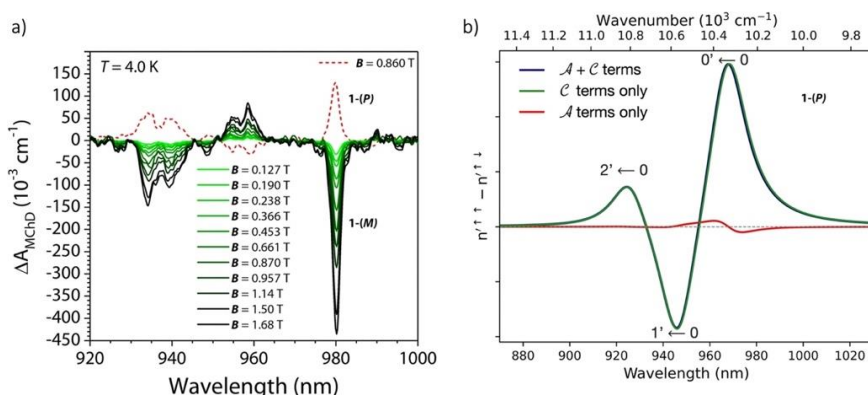


Figure 1. a) Field dependence of the MChD signal for $[Yb(hfac)_3(M-H6bpy)]$ (green curves) and at $B = 0.860$ T for $[Yb(hfac)_3(P-H6bpy)]$ at 4 K (red dashes); reprinted from [5]. b) Simulated MChD signal of $[Yb(hfac)_3(P-H6bpy)]$ at 4 K (blue curve) with decompositions of the Faraday terms.

References

- [1] van Vleck, J. H. *J. Phys. Chem.* **1937**, *41*, 67–80.
- [2] Atzori, M., Rikken, G. L. J. A. & Train, C. *Chem. Eur. J.* **2020**, *26*, 9784–9791.
- [3] Rikken, G. L. J. A. & Raupach, E. *Nature* **2000**, *405*, 932–935.
- [4] Barron, L. D. *Nature* **2000**, *405*, 895–895.
- [5] Atzori, M., Dhbaibi, K., Douib, H., Grasser, M. *et al. J. Am. Chem. Soc.* **2021**, *143*, 2671–2675.
- [6] Barron, L. D. & Vrbancich, J. *Mol. Phys.* **1984**, *51*, 715–730.

Ion-transport in Lithium Imide

Oskar G. Soulas*, Alexander G. Squires, David O. Scanlon

*School of Chemistry, University of Birmingham

power-dos

All-solid-state lithium-ion batteries are a large development in next-generation energy storage. Conventional lithium-ion batteries present safety concerns due to their flammable liquid electrolytes. Batteries with non-flammable ceramic electrolytes help to meet increasing safety requirements in the development of new portable devices and electric vehicles. Chemically-inert solid-electrolytes can potentially increase battery capacity by replacing traditional intercalation anodes with elemental lithium. As lithium metal is the densest form of lithium, this would maximise gravimetric efficiency.

Lithium imide (Li_2NH) has been extensively studied for use in hydrogen storage, but its high Li-ion conductivity has allowed it to be re-examined as a potential solid electrolyte.^{1,2} This is particularly interesting as the constituent elements are earth abundant and lightweight. Synthesis and processing are also cheap and require low energy input. Previous studies have identified a wide electrochemical stability window further suggesting that Li_2NH could be suitable for use as a solid electrolyte. Working with experimental collaborators, we are looking to understand the diffusion processes and validate as-yet-unpublished promising experimental results.

In this study, we investigate the nature of the ion-conducting properties found in members of the lithium-amide lithium-imide solid solution. This starts with the end members, Li_2NH and LiNH_2 . We observe atom dynamics on a femtosecond scale using high-quality bulk *Ab Initio* Molecular Dynamics (AIMD), allowing us to compare the bulk conductivities of the stoichiometric, lithium stuffed, and lithium deficient structures.

¹ Chen et al., Nat. 2002, 420, 302–304

² Paik et al., J. Phys. Chem. C 2019, 123, 3, 1619–1625

Effect of Nitrogen Incorporation on Charge Trapping and Defect Creation in Amorphous HfO₂

Isaac Mackley

*Department of Physics and Astronomy, University College
London*

bulk-shl

The nitridation of HfO₂ has demonstrated improvements in leakage current, bias temperature instability, and mobility of films. In this study, we aim to investigate the mechanisms underlying these enhancements by examining the effects of nitridation on charge trapping precursor sites. Amorphous HfO₂ is known to contain intrinsic charge trapping sites where electrons and holes can form strongly localised polarons and bipolarons. These bipolarons can lower the formation energy of O Frenkel pairs, which leads to degradation. We explore whether the incorporation of nitrogen into a-HfO₂ can mitigate trapping at these precursor sites, describe the mechanisms involved in its incorporation, and assess its potential to inhibit the degradation and dielectric breakdown of HfO₂-based devices. We also examine whether N can also provide unwanted effects, whether it can also facilitate the formation of O Frenkel pairs. To carry out this computational work, CP2K is used to perform Density Functional Theory calculations. Non-local functionals are used to provide more accurate values for the band gap allowing for better analysis of the electronic structure of defects.

Investigating point-defects in crystalline materials using a hybrid stochastic + Mott-Littleton method

Cyril Xu*, Alexey Sokols*, Scott Woodley*

*Department of Chemistry, University College London

algor-smw

The presence of point defects in ionic materials determines their ionic conductivity and many other bulk and surface properties, which is central to the discovery of novel materials for energy applications. The n-doped perovskite-structured barium stannate BaSnO_3 is a new generation transparent conducting oxide with excellent prospects in industrial applications. Its ability to sustain high levels of doping while maintaining its crystallinity, transparency, high carrier concentrations and mobility at ambient conditions are related to its defect properties, which are not yet fully understood. Manganese oxide, MnO_2 , has been widely recognised as an effective cathode material. Nevertheless, its polymorphic characteristics result in suboptimal performance in industrial applications, prompting the exploration of optimised designs. Using computer simulations, a variety of material properties can be accurately predicted in a time-efficient manner. An embedded approach, like that developed by Mott and Littleton, is a robust method for the investigation of point defects, based on interatomic potentials.

Employing the Mott-Littleton approach using Norgett's two-region strategy implemented in the General Utility Lattice Programme (GULP), we conducted simulations involving different types of point defects embedded in the perfect BaSnO_3 and ramsdellite- MnO_2 crystal lattices. This approach allows for an accurate and self-consistent description of the effects of the embedding crystal field around the defect and the polarisation. In addition, we used both stochastic and newly developed exhaustive sampling methods to explore the energy landscape of multiple charged defects. This approach will be demonstrated on both the perovskite and the ramsdellite materials. Our approach is shown to be more efficient than the supercell approach implemented in the periodic *ab initio* code.

By completing a thorough investigation of the convergence for modelling point defects, we encountered an unexpected behaviour: the defect energy unexpectedly drops periodically after initially showing signs of convergence. Our study revealed a correlation between this behaviour and the unusual anisotropic patterns observed in the defect polarisation field, which differs from patterns seen in simple cubic lattices like MgO . In this talk, I will present both the method developed for this project as well as the data and the analysis of our results.

Vibrational calculations in hybrid QM/MM: recent Py-ChemShell development for IR and Raman spectroscopic signatures

Jingcheng Guan*, Thomas W. Keal, You Lu, C. Richard A. Catlow and Alexey A. Sokol

*Department of Chemistry, University College London, UK

algor-sok

We present the development of methods for calculations of vibrational signatures for chemical systems modelled by hybrid QM/MM approaches. Our approach is based on the vibrational self-consistent field (VSCF) method applied to normal and local modes of chemically active sites, but also takes the effects of the chemical environment into account. The new facility has been implemented as a module in Py-ChemShell and is scalable using partitioned taskfarming parallelism. This work builds on recent extension to Py-ChemShell for calculations of infrared and Raman intensities using the double harmonic approximations. Our VSCF implementation tackles intrinsic anharmonicities, mode-mode couplings and delocalization of normal modes, which are recognized as key challenges for *ab-initio* calculations of vibrational properties.

Catalytic systems of interest include transition metal-containing zeolites, metallic oxide surfaces, and solvated biomolecules. We consider the assignment of band positions for intermediates in catalytic reactions using the new infrastructure, for example on pyridine adsorption at Brønsted acid sites in zeolite MFI and hydrogenation on polar ZnO surfaces and calculate anharmonic infrared and Raman signatures of active species. We conclude with a discussion of further intermodal correlation, thermal and evolution effects using VSCF in hybrid QM/MM.