11th ScotCHEM
Computational Chemistry Symposium

University of Glasgow

16 June 2017

ScotCHEM

University of Glasgow | School of Chemistry

http://www.chem.gla.ac.uk/compscot/

Programme

Friday, 16 June 2017
University of Glasgow, School of Chemistry, Joseph Black Building, University Avenue, Glasgow G12 8QQ

9:30	Registration opens Coffee & pastries in the Conference Room
	Session I (Chair: Dr Hans Senn)
10:25	Dr Hans Senn: *Welcome and opening remarks*
10:30	**K1** Prof Fred Manby: *Quantum mechanics of light-matter and system-bath interactions in photosynthesis*
11:20	**C1** Paul Murphy: *Development of spin-orbit coupling for stochastic configuration interaction techniques*
11:40	**C2** Dr Benjamin D. Goddard: *Photo-dissociation: Mathematics meets quantum chemistry*
12:00	**C3** Dr Maria Tudorovskaya: *Time-resolved photoionization and high-harmonic generation by cyclohexadiene*
12:20	Lunch in the Atrium, Wolfson Medical School Building
	Session II (Chair: Dr Anna Stradomska)
13:30	**C4** Dr Ben Hourahine: *DFTB+ goes open source*
13:50	**C5** Paul Rapp: *Competitive adsorption for clean air applications*
14:10	**C6** Dr David McKay: *Investigating the hydration of inner Earth minerals through ab initio random structure searching and solid-state NMR spectroscopy*
14:30	**C7** Pattama Wapeesittipan: *Millisecond protein dynamics does not control catalysis in Cyclophilin A – evidence from molecular dynamics simulations*
14:50	**C8** Dr Zied Hosni: *Development of a novel computational method to identify key residues in protein structures*
15:10	Coffee & tea in the Conference Room

Session III (Chair: Dr Tell Tuttle)

15:30 **C9** Dr Fernanda Duarte: *Molecular recognition and solvent effect in asymmetric counteranion catalysis*

15:50 **C10** Renan Zorzatto: *Iridium(I) complexes bearing chelating NHC/phosphine ligands: synthesis and application in HIE processes*

16:10 **C11** Rebecca M. Nicolson: *Understanding rhodium solvent extraction: a mode of action study*

16:30 **C12** Maicon Delarmelina: *Carboxylation mechanism of alkylboronates with CO_2 catalysed by [Ni(NHC)(allyl)Cl] complexes: a DFT study*

Poster Session

16:50 **P1** – **P23** Posters & drinks in the Atrium, Wolfson Medical School Building

18:00 Announcement of poster prizes

Abstracts of Talks

K1 Quantum mechanics of light-matter and system-bath interactions in photosynthesis

F. Manby

School of Chemistry, University of Bristol, Bristol BS8 1TS, UK

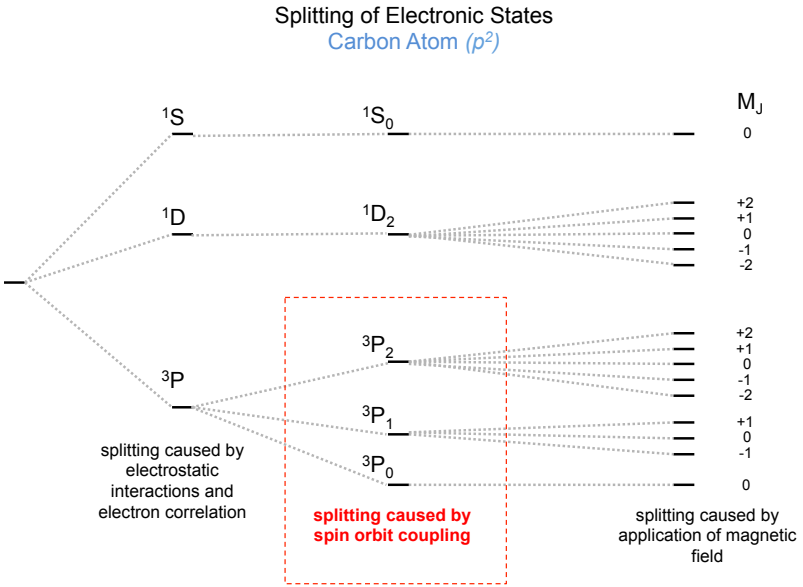
Almost all of the biomass in the world derives from the harvesting of solar energy through photosynthesis. A great deal is known about the structure and dynamics of the machinery responsible for this process, but mysteries remain. Photosynthesis in purple bacteria is amazingly efficient: chemical change is induced almost every time a photon is absorbed. This is curious because it implies very efficient transport of the energy through a disordered system. Here we will explore the quantum mechanics of the light-matter interaction, and of the energy-transport processes involved, to try to arrive at a clear picture of how photosynthetic light harvesting really works.

C1 Development of spin-orbit coupling for stochastic configuration interaction techniques

P. Murphy, J. P. Coe, M. J. Paterson

Heriot-Watt University, Edinburgh EH14 4AS

A discussion is presented of the software development of the Monte Carlo Configuration Interaction (MCCI) technique to allow spin orbit coupling calculations to be made using stochastic methods, with the aim of producing acceptable results using highly compact wavefunctions. In this first "proof of concept" work, the one-electron term from the Breit-Pauli Hamiltonian is used. Details of the development work along with results from a test-bed of atoms and diatomic molecules are presented. The splitting of degenerate energy levels of these test-bed species and the corresponding spin orbit coupling constants are compared with experiment and also with the one-electron results of other methods. A discussion of the difficulty of implementing the remaining two-electron terms of the Breit-Pauli Hamiltonian and the current progress towards a solution in this regard is also presented.



C2 Photo-dissociation: Mathematics meets quantum chemistry

Volker Betz[a], Benjamin D. Goddard[b], Uwe Manthe[c], Stefan Teufel[d]

[a] *TU Darmstadt, School of Mathematics*
[b] *University of Edinburgh, School of Mathematics*
[c] *University of Bielefeld, Faculty of Chemistry*
[d] *University of Tübingen, School of Mathematics*

Photo-dissociation is the break-down of molecules by light, e.g. during photosynthesis. Mathematically, its study involves transitions in a two-level partial differential equation. Given an initial wavepacket on the upper level, the challenge is to determine the wavepacket transmitted to the lower level at large times. This is typically very small with rapid oscillations, prohibiting accurate numerical calculations, especially in high dimensions. Fortunately, there exists a small parameter ε, the square root of the ratio of the electron and nuclear masses. In the standard adiabatic representation, the transmitted wavepacket is typically of order ε globally in time but exponentially small ($\sim\exp(-1/\varepsilon)$) for large times[1,2]. This strongly suggests that the adiabatic representation is not the right one for the problem. Using the more general superadiabatic representations, we obtain an explicit formula for the transmitted wavepacket[1,2,3]. Our results agree extremely well with high precision ab-initio calculations, in particular for real-world NaI[4].

[1] V. Betz, B. D. Goddard, S. Teufel, *Proc. R. Soc. A* **2009**, *465*, 3553-3580.
[2] V. Betz, B. D. Goddard, *Phys. Rev. Lett.* **2009**, *103*, 3553-3580.
[3] V. Betz, B. D. Goddard, *SIAM J. Sci. Comput.* **2011**, 33(5) 2247-2276.
[4] V. Betz, B. D. Goddard, U. Manthe, *J. Chem. Phys.* **2016**, 144 224109.

C3 Time-resolved photoionization and high-harmonic generation by cyclohexadiene

Maria Tudorovskaya, Adam Kirrander

School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ

In our work, we are trying to answer the question whether a new spectroscopic technique, namely, high-harmonic (HH) spectroscopy based on the photoionization induced by a strong infrared laser can be used to analyse a photochemical reaction. Our theoretical approach is based on the assumption that the features of the HH spectrum are determined by the photorecombination and the photoionization probabilities. The latter is calculated with the use of Dyson orbitals constructed as an overlap between the molecular and target wave functions [1,2].

We implement the method to investigate the UV-photon-induced ring-opening reaction of cyclohexodiene (CHD), which can be used a prototype for a large class of organic reactions. The dynamics following the pump has been recently described by Minniti et al.[2]. We take into account the relevant trajectories and the corresponding states population and show how the photoionization and HH output are varying as a function of time.

[1] C.M. Oana, A.I. Krylov, *J. Chem. Phys.* **2009**, *131*, 124114.

[2] S. Gozem, A.O. Gunina, T. Ichino, D.L. Osborn, J.F. Stanton, A.I. Krylov, *J. Phys. Chem. Lett.* **2015**, *6*, 4532–4540.

[3] M. P. Minitti, J. M. Budarz, A. Kirrander, J. S. Robinson, D. Ratner, T. J. Lane, D. Zhu, J. M. Glownia, M. Kozina, H. T. Lemke, M. Sikorski, Y. Feng, S. Nelson, K. Saita, B. Stankus, T. Northey, J. B. Hastings, P. M. Weber *Phys. Rev. Lett.* **2015**, *114*, .

C4 DFTB+ goes open source

Ben Hourahine[a], Bálint Aradi[b], Thomas Frauenheim[b]

[a]*SUPA, Department of Physics,University of Strathclyde, Glasgow*
[b]*Bremen Center for Computational Materials Science, University of Bremen, Germany*

Density functional based tight binding[1] is a fast semi-empirical approximation to DFT, typically being around 3 orders of magnitude faster, but capable of producing results that approach those of DFT to near chemical accuracy.[2]

The DFTB+ code[3] is a popular implementation of the DFTB1, DFTB2 and DFTB3 models for ground and excited state calculations, electronic transport and offering both multi-core and massive distributed parallelism. DFTB+ also contains features not found elsewhere for DFTB (both crystalline and molecular geometries, non-collinear spin, spin-orbit coupling, fast extended Lagrangian dynamics, interfaces for REMD and path-integral molecular dynamics, …).

The DFTB parameters have recently been released under Creative Common license [1] and the DFTB+ code is now moving to the open LGPL licence this year.

In this contribution, some of the features of DFTB and DFTB+, along with near term developments will be presented and discussed.

[1] http://www.dftb.org/
[2] X. Lu, M. Gaus, M. Elstner, Q. Cui, *J. Phys. Chem B* **2015**, 119, 1062−1082.
[3] B. Aradi, B. Hourahine, T. Frauenheim, *J. Phys. Chem. A* **2007**, 111, 5678–5684.

C5 Competitive adsorption for clean air applications

Ashleigh Fletcher, Karen Johnston, Paul Rapp

Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, UK

Environmental and health concerns from pollution are significant social economic drivers, which push legislation towards pollution prevention and sustainability. In addition to health concerns, the emission of the greenhouse gas carbon dioxide must be reduced to keep climate change below 2 °C. Therefore, it is essential to develop and test environmentally friendly materials that are highly optimized to remove specific pollutant species. Activated carbon is a well-known affordable carbon dioxide and pollutant adsorber. However, there are many types of activated carbons and these adsorb some species more effectively than others. To tailor activated carbons for different pollutant species, it is necessary to understand or control their chemical and structural composition. This project aims to identify which characteristics of activated carbon are optimal for removal of pollutants, such as carbon dioxide.

As a starting point we take graphite as a model system and study the adsorption of carbon dioxide using a combined computer simulation and experimental approach. Quantum calculations found that carbon dioxide adsorbs weakly on the graphite surface via physisorption (van der Waals interactions) with almost negligible preference for specific adsorption sites. Grand canonical Monte Carlo isotherms, with force fields based on quantum adsorption data were performed for graphite slit pores and amorphous carbon structures. Results revealed much higher adsorption for microporous structures compared to mesoporous slit pores at low pressure. Experimental results found graphite in powdered form has a significantly lower isosteric heat of adsorption compared to theoretical isotherms, which is attributed to a broader pore size distribution and larger pore sizes. Future work is aimed towards a) competitive adsorption of several pollutant species on graphite and b) adsorption on modified graphite to determine the most effective activated carbons.

C6 Investigating the hydration of inner Earth minerals through *ab initio* random structure searching and solid-state NMR spectroscopy

David McKay[a], Robert F. Moran[b], Daniel J. Twist[a], Chris J. Pickard[b], Andrew J. Berry[c], Sharon E. Ashbrook[a]

[a]*School of Chemistry, EaStCHEM Centre of Magnetic Resonance, University of St Andrews, St Andrews KY16 9ST, UK*
[b]*Department of Material Science and Metallurgy, University of Cambridge, Cambridge CB3 0FS, UK*
[c]*Australian National University, Research School of Earth Sciences, Acton ACT, Australia*

Nominally, anhydrous minerals (NAMs), ringwoodite and wadsleyite (Fe-free γ- and β-Mg_2SiO_4) make up the Earth's transition zone, a region of the mantle at depths of 410 - 660 km. NAMs can take up low levels of H_2O (some up to ~3.3 wt%), leading to transition zone hydration. The structures of many hydrated NAMs are not known, however, due to the inherent difficulty in locating H atoms and disordered vacancies by diffraction and synthetic challenges such as extreme synthesis conditions (1600 °C, 16-20 GPa), polymorphism and sample size limitations (~30 mg). Discovery of robust structural models would lead to a better understanding of the hydration mechanism and better modelling of the Earth's mantle.

Net hydration to is thought to involve the addition of $2n$ H^+, charge balanced by loss of n Mg^{2+} or $½n$ Si^{4+}. Herein we present models of ringwoodite and wadsleyite at two hydration levels: semi-hydrated γ/β Mg_2SiO_4 (~1.6 wt% H_2O) *via* $Mg^{2+}/2H^+$ exchange and fully-hydrated γ/β-Mg_2SiO_4 (~3.3 wt% H_2O) through either $2Mg^{2+}/4H^+$ or $Si^{4+}/4H^+$ exchange. H^+ ions do not sit on crystallographic sites in the hydrated structure. Therefore, *ab initio* random structure searching (AIRSS)[1] is used to randomly position H^+ ions near the vacancy, producing 100-1000s of candidate structures for optimisation *via* DFT.

Hydration of ringwoodite proceeds *via* Mg^{2+} and Si^{4+} vacancies (in agreement with neutron diffraction[2a]), with newly formed hydroxyl species forming hydrogen bonds along polyhedral edges. The fully-hydrated ground state results from 2 × $Mg^{2+}/2H^+$ exchange, with lowest energy $Si^{4+}/4H^+$ structure at just 0.1 eV higher. In wadsleyite, hydration *via* 2 × Mg^{2+}/H^+ exchange is substantially more accessible than by $Si^{4+}/4H^+$ exchange, discounting Si vacancies. However, the presence of three crystallographically-unique Mg^{2+} sites (and four O^{2-} sites), complicates the picture. The ground-state structure results from a 2 × Mg3/$2H^+$ hydration mechanism[3] and accessible higher energy structures (supported by solid-state NMR spectroscopy[4] and neutron diffraction studies[5]) involve a combination of Mg1 and Mg3 vacancies.

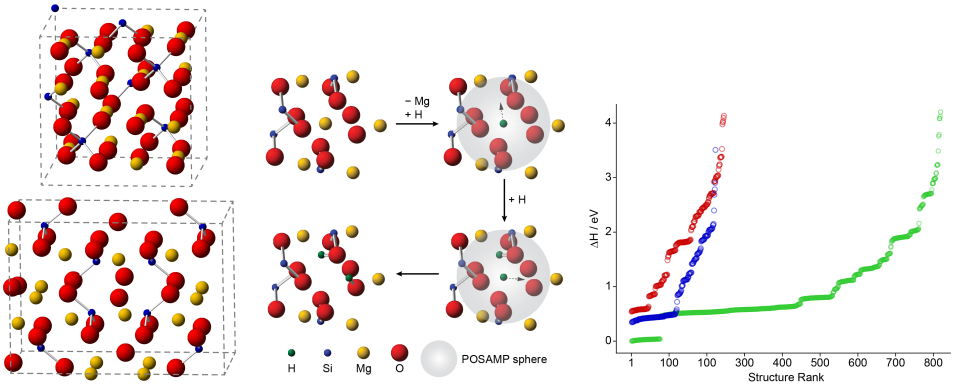


Figure 1 – Left, crystal structures of anhydrous ringwoodite (*Fd-3m*, top) and wadsleyite (*Imma*, bottom); middle, AIRSS H placement; right, energy rankings in semi-hydrated wadsleyite.

[1] C. J. Pickard and R. J. Needs, *Phys. Rev. Lett*. **2006**, *97*, 045504.
[2] N. Purevjav, et al., *Geophys. Res. Lett.* **2014**, *41*, 6718
[3] R. F. Moran, *et al.*, *Phys. Chem. Chem. Phys.* **2016**, *18*, 10173.
[4] J. M. Griffin *et al.*, *Chem. Sci*. **2013**, *4*, 1523.
[5] A. Sano-Furukawa, *et al.*, *Phys. Earth Planet. Inter.* **2011**, *189*, 56.

C7 Millisecond protein dynamics does not control catalysis in Cyclophilin A – evidence from molecular dynamics simulations

Pattama Wapeesittipan, Antonia S. J. S. Mey, Julien Michel

EaStCHEM School of Chemistry, University of Edinburgh, EH9 3FJ, UK

Cyclophilin A (CypA) is a member of the Cyclophilin family of peptidyl-prolyl isomerases which catalyzes the *cis-trans* isomerization of proline peptide bond. Previous biophysical studies have suggested that the CypA wild type (WT) active site interconverts between a 'major' catalytically active conformation and a 'minor' catalytically impaired conformation on millisecond timescales.[1] A serine to threonine (S99T) mutation distal (ca. 10 Å away) from the active site was devised to stabilize this minor conformation of CypA, leading to a dramatic 70 fold drop in catalytic turnover, similar in magnitude to activity changes upon mutation of key residues that make direct contacts with the substrate. Although such example is frequently cited in support of the importance of millisecond dynamics for enzymatic function, the details of how the S99T mutation reduces catalytic activity are still unclear.

In this research, molecular dynamic (MD) and biased MD simulations were carried out to investigate the link between conformational changes and catalysis in the WT and S99T mutant forms of CypA. In contrast to literature claims,[1] we observe conformational changes between the proposed 'major' and 'minor' active site conformations on nanosecond timescales. Yet in agreement with previous experimental data, free energy profiles from our simulations showed that the S99T CypA-catalyzed amide isomerization reaction has a larger activation barrier than in WT CypA. Further analysis indicates that this is a result of weakened hydrogen bonding interactions between Asn102 and the transition state. Additional simulations established that weakened transition state stabilisation is caused by an overall increase in fast (nanosecond) dynamics of active site residues due to poorer side-chains packing in the S99T mutant.

In summary, our study disputes literature claims of a link between slow (millisecond) protein dynamics and catalysis,[1] and suggests instead that changes in fast (nanosecond) dynamics are sufficient to explain the reduced catalytic power of the S99T Cyclophilin A mutant.

[1] J. Fraser, M. W. Clarkson, S. C. Degnan, R. Erion, D. Kern, *Nature* **2009**, *462*, 669–673.

C8 Development of a novel computational method to identify key residues in protein structures

Zied Hosni, Sreenu Vattipali

Bioinformatics Hub, Centre for Virus research, University of Glasgow, UK

Viruses are infectious agents that need host cells to replicate and survive. Virus-infected cells are recognised by host immune system with the help of the epitopes presented on the cell surface by MHC class-I molecules. MHC class-I epitopes are short (generally 9aa length) viral protein fragments that are recognised by immune cells (CD8 T-cells). Selection of a viral protein fragment as an epitope depends on the individual's HLA system. Recognition of an epitope by CD8 T-cells is a key in eliminating a virus from the host. To escape the host immune attack and survive, viruses often mutate their proteins. However, changing the structurally and functionally important residues in a protein will have a fitness cost on the virus. If an individual's immune system detects an important region of a protein as an epitope then it has a high chance of successfully eliminating the virus. Here we demonstrate a novel computational approach to identify structurally and functionally important residues in protein structures. We have developed a Python program that is capable of ranking residues' importance in a protein based on their non-covalent bonds, hydrogen bonds, salt bridges, disulphide bonds, hydrophobic and Van der Waals interactions. We are testing the program's efficiency by analysing epitopes sequences from Hepatitis C virus (HCV) proteins. We found key residues in HCV proteins using our program. HCV epitopes containing key residues were selected for further analysis. Spontaneous clearance of HCV in infected patients and the role of their epitopes is currently under investigations to test our program.

C9 Molecular recognition and solvent effect in asymmetric counteranion catalysis

Fernanda Duarte[a] and Robert S. Paton[b]

[a]*EaStCHEM School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ, UK*
[b]*Chemistry Research Laboratory, University of Oxford, Oxford OX1 3TA, UK*

Ion-pairing with a charged, chiral catalyst has emerged as a versatile strategy in asymmetric catalysis[1]. However, theoretical work on the stereoselectivities of these transformations remains a challenging task. This is due to the difficulties in identifying the most stable configurations in a given environment, where the predominantly electrostatic nature of these interactions make then less directional and more solvent dependent than *e.g.* hydrogen-bonding or dispersion interactions.

In this work we investigate the structures, dynamics and stabilities of the chiral ion-pairs in the condensed phase for the landmark anionic asymmetric PTC ring-opening reaction of *meso*-aziridinium and episulfonium cations[2]. We use both classical and quantum methods and explicitly and implicitly solvated models. We find that the stability of chiral ion-pairs, a pre-requisite for asymmetric catalysis, is dominated by electrostatic interactions at long-range and by CH···O interactions at short-range. The decisive role of solvent upon ion-pair formation and of non-bonding interactions upon enantioselectivity are quantified by complementary computational approaches. Our computational results rationalize the stereoselectivity for several experimental results and demonstrate a combined classical/quantum approach to perform realistic-modelling of chiral counterion catalysis in solution[3].

[1] (a) Phipps, R. J.; Hamilton, G. L.; Toste, F. D. *Nat. Chem.* **2012**, *4*, 603. (b) Brak, K.; Jacobsen, E. N. *Angew. Chem. Int. Ed.* **2013**, *52*, 534.
[2] Hamilton, G. L.; Kanai, T.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, *130*, 14984.
[3] F. Duarte, R S. Paton. Molecular Recognition in Asymmetric Counteranion Catalysis: Understanding Chiral Phosphate-Mediated Desymmetrization. Under Revision.

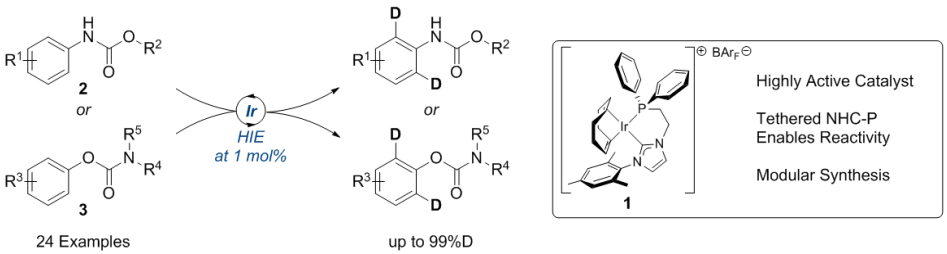
C10 Iridium(I) complexes bearing chelating NHC/phosphine ligands: synthesis and application in HIE processes

William J. Kerr, Tell Tuttle, Renan Zorzatto

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland, UK

Transition metal-catalysed C-H activation has become a valuable tool for the functionalisation of complex organic molecules.[1] In this context, hydrogen isotope exchange (HIE) allows expedient access to isotopically enriched compounds, crucial for the timely execution of adsorption, metabolism, excretion and toxicology (ADMET) studies,[2] and in mechanistic studies of organic reactions. Iridium complexes are commonly employed in HIE[3] due to their catalytic activity and specificity for labelling sites adjacent to directing groups.[4] However, the poor performance of existing Ir complexes with sterically-hindered directing groups constitutes an important limitation. Herein we report a new class of Ir(I) complexes (**1**) bearing a chelating *N*-heterocyclic carbene-phosphine (NHC-P) ligand, and their application in the HIE of substrates bearing sterically demanding carbamates (**2** – **3**), establishing a successful strategy to access two important classes of substrates.

A combined experimental and theoretical study was employed to evaluate the mechanism of this reaction. While DFT calculations suggest a low activation barrier of 20.7 kcal mol^{-1} for the key C-H bond cleavage, kinetic data revealed that an interesting interplay between substrate coordination and C-H activation operates in solution. Through comparison of calculated and experimental primary kinetic isotope effects (KIE), and evaluation of two directing groups with markedly distinct steric demands, it was possible to demonstrate a temperature-dependent balance between substrate coordination and C-H activation as the rate limiting process. Moreover, the observed reactivity could also be rationalised through evaluation of the interaction energy of selected substrates with the catalytically active iridium deuteride, which also constitutes an important step in the construction of tools to aid rational catalyst design.



[1] K. Godula, D. Sames, *Science* **2006**, *312*, 67-72.
[2] N. Penner *et al.*, *Chem. Res. Toxicol.* **2012**, *25*, 513-531.
[3] J. A. Brown *et al.*, *Adv. Synth. Catal.* **2014**, *356*, 3551-3562.
[4] A. R. Cochrane *et al.*, *J. Label Compd. Radiopharm.* **2013**, *56*, 451-454.

C11 Understanding rhodium solvent extraction: a mode of action study

Rebecca M. Nicolson[a], Ross J. Gordon[b], Jason B. Love[a], Peter A. Tasker[a], Carole A. Morrison[a]

[a] *School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ*
[b] *Johnson Matthey Technology Centre, Sonning Common, Reading RG4 9NH*

No commercial solvent extraction (SX) reagent currently exists for rhodium. Recent literature reported the promising recovery of Rh via SX using a new ligand system.[1,2] However, details concerning the structure of the extracted species and the interactions present – information key to developing a suitable commercial reagent – are not fully known.[1,2] This work has aimed to elucidate the mode of action.

Initial test extractions using one of the reported reagents, (N-n-hexyl-bis(N-methyl-N-n-octyl-ethylamide)amine (BisAA)),[1,2] and analyses of the resulting phases were conducted. Karl Fischer titrations showed that, though water appears to be extracted in association with chloride, negligible water is extracted with Rh, suggesting Rh extraction does not occur via a reverse micelle mechanism. ESI-MS suggested that either $[(RhCl_5(H_2O))(LH)_2]$ or $[(RhCl_5(LH))(LH)]$ is the main extracted species, and $[(Rh_2Cl_9)(LH)_3]$ is either extracted or forms in the organic phase. It also showed $[RhCl_3L]$ appears to form over long periods of time.

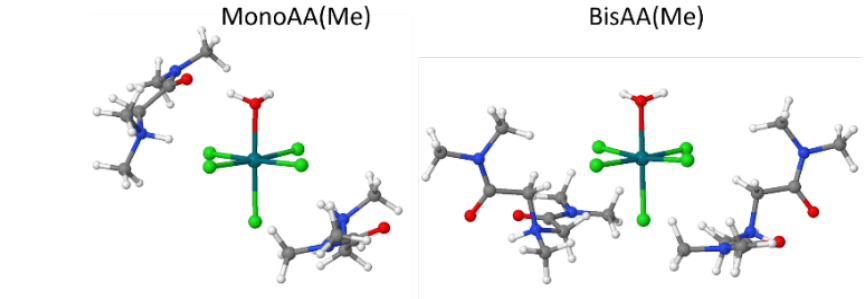


Figure 1. Minimum energy structures for $[RhCl_5(H_2O)]^{2-}$ with $[MonoAA(Me)H]^+$ or $[BisAA(Me)H]^+$, showing different binding modes.

Narita et al.'s findings suggest that extraction occurs via an ion-pair association rather than binding of the ligand in the inner-sphere.[1,2] The findings of this experimental work are not contradictory, therefore quantum mechanical modelling of ion-pair structures was pursued. Truncated R-group versions of BisAA and another two ligands developed by Narita et al,[1,2] N,N-di-n-hexyl(N-methyl-N-n-octyl-ethylamide) amine (MonoAA) and tris(Nmethyl-N-n-octyl-ethylamide) amine (TrisAA), were used.

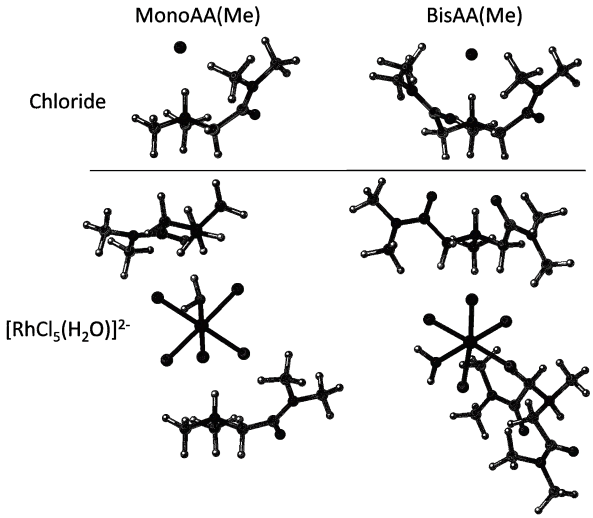


Figure 2. Minimum energy structures of $[MonoAA(Me)H]^+$ and $[BisAA(Me)H]^+$ with chloride and $[RhCl_5(H_2O)]^{2-}$, highlighting different binding sites.

The calculations show that complex formation with $[RhCl_5(H_2O)]^{2-}$ and exchange of associated chloride for $[RhCl_5(H_2O)]^{2-}$ is more favourable with protonated BisAA(Me) than MonoAA(Me), suggesting BisAA is a stronger, more selective extractant. The minimum energy structures of the assemblies suggest that $[MonoAAH]^+$ and $[BisAAH]^+$ interact differently with $[RhCl_5(H_2O)]^{2-}$ (see Figure 1). They also suggest that $[BisAAH]^+$ offers different binding sites for chloride and $[RhCl_5(H_2O)]^{2-}$, but both anions compete for the same binding site with $[MonoAAH]^+$ (see Figure 2). These results are in agreement with the findings reported by Narita et al.[2]

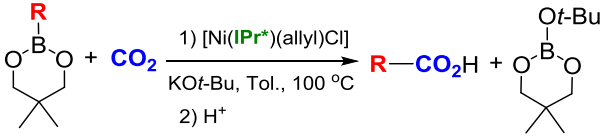
[1] H. Narita, K. Morisaku, M. Tanaka, *Chem. Commun.* **2008**, *45*, 5921–5923.
[2] H. Narita, K. Morisaku, M. Tanaka, *Solvent Extr. Ion Exch.* **2015**, *33*, 407–417.

C12 Carboxylation mechanism of alkylboronates with CO_2 catalysed by [Ni(NHC)(allyl)Cl] complexes: A DFT study

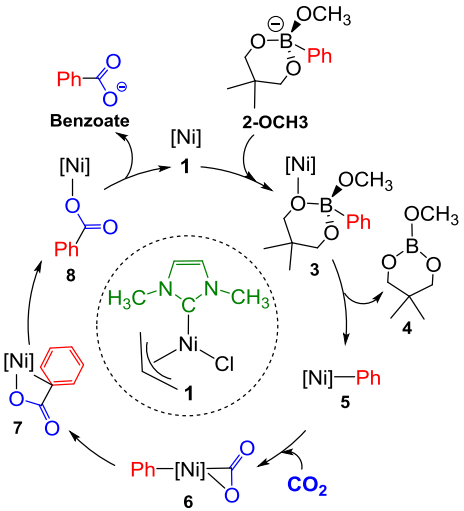
Maicon Delarmelina[a], Enrico Marelli[b], José Walkimar de M. Carneiro[a], Michael Bühl[b]

[a]*Instituto de Química, Universidade Federal Fluminense, Niterói, Rio de Janeiro, Brazil*
[b]*School of Chemistry, University of St Andrews, Fife, Scotland.*

Organoboronates can be carboxylated under mild condition using transition metal complexes as catalysts.[1] A recent highly efficient methodology (Scheme 1) uses Ni-NHC complexes (NHC = N-heterocyclic carbene) as catalysts.[2]



Scheme 1. Experimental condition for carboxylation of organoboronates.[2]



Scheme 2. Proposed catalytic cycle for carboxylation of organoboronates (Mec. D).

In order to rationalise these findings, we employed DFT calculations (PBE0-D3/ECP2//BP86/ECP1 level), using smaller congeners of the experimental ligand (IMe), boronate (phenylboronate) and base (methoxide anion). We have investigated a variety

of possible pathways for the catalytic conversion described in Scheme 1. The most favourable pathway identified is shown in Scheme 2, in which addition of the borate species **2**-OCH_3 to the catalyst **1** followed by transmetalations → oxidative addition of CO_2 → reductive elimination of the carboxylated product are the proposed sequential steps. Transmetalation is computed to be rate-determining (**3** → **4** + **5**, $\Delta G^{\ddagger}$ = 30.5 kcal mol^{-1}).

Future investigations will include evaluation of the effect of bulkier ligands and base on the efficiency of the catalysts, in order to facilitate rational catalyst design for this process.

[1] M. Brill et al., *Top. Organomet. Chem.* **2015**, *53*, 225–278.
[2] Y. Makida et al., *Chem. Commun.* **2014**, *50*, 8010–8013.

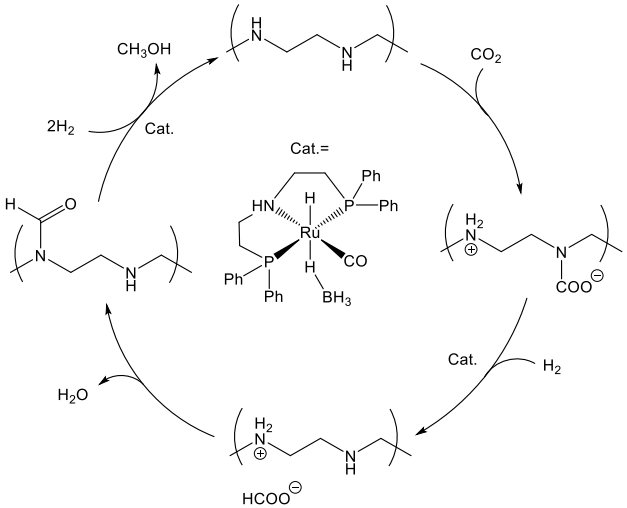
Abstracts of Posters

P1 Investigating Ru-catalysed CO_2 hydrogenation using DFT

Iain Prentice, Allan Young[a], Tell Tuttle[a]

University of Strathclyde, Thomas Graham Building, Glasgow, G1 1XL, UK

With recent rising CO_2 concentrations in the atmosphere, removal of CO_2 from the atmosphere has become an increasing field of interest not just in academia but also in industry. Alongside carbon capture and storage technologies, a carbon capture and recycle approach where CO_2 is converted to more useful fuels and feedstock's is appealing. Recently, Olah *et al*.[1] demonstrated a catalytic system for conversion CO_2 from air to methanol. This reaction utilised a Ruthenium catalyst and polyamine, with the proposed mechanism shown in Figure 1.



Here, we present results of an investigation into the role of only the Ruthenium catalyst in the hydrogenation of CO_2 in order to determine whether the reaction is able to occur solely in the presence of the catalyst. We include transition state barriers and relative energies for each step of the catalyst only mechanism and thus are able to provide an insight into the mechanistic steps where the polyamine molecule may be required to form alternative intermediates in the reaction mechanism.

[1] J. Kothandaraman, A. Goeppert, M. Czaun, G. A. Olah and G. K. S. Prakash, J. Am. Chem. Soc., **2016**, 138, 778-781.

P2 Carboxylation mechanism of alkylboronates with CO_2 catalysed by [Ni(NHC)(allyl)Cl] complexes: a DFT study

Maicon Delarmelina[a], Enrico Marelli[b], José Walkimar de M. Carneiro[a], Michael Bühl[b]

[a]*Instituto de Química, Universidade Federal Fluminense, Niterói, Rio de Janeiro, Brazil*
[b]*School of Chemistry, University of St Andrews, Fife, Scotland.*

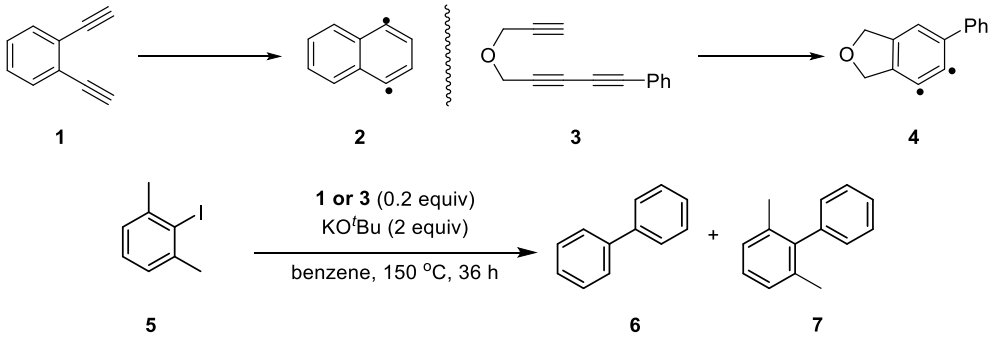
See abstract **C12**.

P3 Initiation of transition metal-free cross coupling reactions by biradicals formed under base-independent thermal conditions

Mark Allison, Tell Tuttle, John A. Murphy

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, UK

In recent years transition metal-free coupling of haloarenes to arenes, proceeding by the Base-promoted Homolytic Aromatic Substitution (BHAS) mechanism are widely reported in the literature.[1-4] These reactions work well when they are initiated by organic electron donors that are formed in situ from organic additives of various types. In the absence of the organic donor precursors, the coupling reactions can still proceed for many substrates, but at higher temperatures and at a much lower rate. A plausible mechanism that has been proposed for the initiation in these cases is that benzyne, generated in situ through potassium tert-butoxide(KOtBu) deprotonation of the haloarene, can act as a biradical and start the BHAS pathway.[3]



We now show that additives that afford arenediyls by base-independent routes, provide independent initiation of the coupling reactions for this substrate in the absence of electron donors, supporting a similar capability for benzyne generated by base-dependent means.

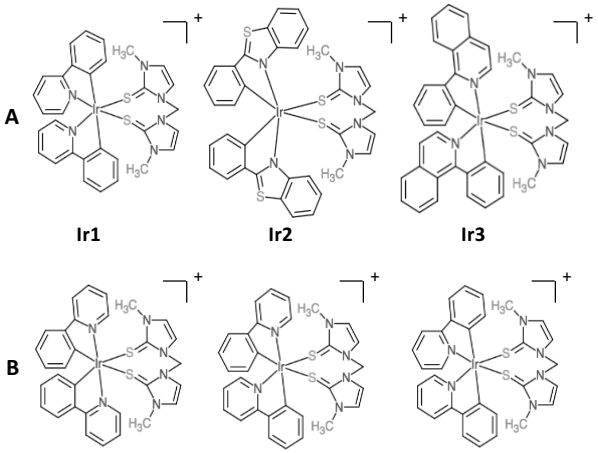
1. Yanagisawa, S.; Ueda, K.; Taniguchi, T.; Itami, K., *Org*. *Lett*., **2008**, *10*, 4673-6.
2. Studer, A.; Curran, D. P., *Angew*. *Chem*. *Int*., **2011**, *50*, 5018-22.
3. Zhou, S.; Anderson, G. M.; Mondal, B.; Doni, E.; Ironmonger, V.; Kranz, M.; Tuttle, T.; Murphy, J. A., *Chem*. *Sci*., **2014**, *5*, 476-482.
4. Shirakawa, E.; Hayashi, T., *Chem*. *Lett*., **2012**, *41*, 130-134

P4 The isomeric effect of the coordination sphere on the linear and non-linear optoelectronic properties of iridium(III) complexes

Thomas Malcomson, Martin Paterson

Heriot-Watt University, Edinburgh EH14 4AS

Here we present a computational investigation of the structural and optical properties of a series of Ir(III) complexes of potential use a photodynamic therapy agents using density functional theory. Detailed computations of several aspects of the photochemistry have been performed: isomeric effects via differential binding modes, lowest spin-states, linear single-photon absorption, and non-linear excited state absorption and two-photon absorption. An increase in the number of trans nitrogens produces a stabilising effect with increased geometry relaxation in the optimised triplet states, as well as providing a dampening effect to the main OPA peak in both the singlet and triplet excited states, and significant modification of the lower energy peaks of each complex. A red-shifted is observed in the lower energy singlet peak across each complex, corresponding to an increasing number of trans nitrogens, while no such trend is observed in the triplet spectra.



A) Three Iridium complexes under investigation. B) Isomers investigated for each complex represented in the **Ir1** complex: **cc**, **cn**, and **nn**, respectively, in reference to the atoms in the trans positions relative to the sulphur atoms.

[1] Z. Liu, I. Romero-Canelon, B. Qamar, J. M. Hearn, A. Habtemariam, N. P. E. Barry, A. M. Pizarro, G. J. Clarkson, P. Sadler, *Angew Chem Int Ed,* **2014**, *53*, 3941.
[2] V. Novohradsky, Z. Liu , M. Vojtiskova, P. J. Sadler, V. Brabec, J. Kasparkova, *Metallomics,* **2014**, *6*, 682.
[3] S. Stolik, J. A. Delgado, A. Perez, L. Anasagasti, *J Photoch Photobio B.* **2000***, 57,* 90.
[4] K. Hopmann, *Organometallics,* **2016**, *35*, 3795.
[5] P. Cronstrand, Y. Luo, H. Ågren, *Chem Phys Let,* **2002**, *352*, 262.

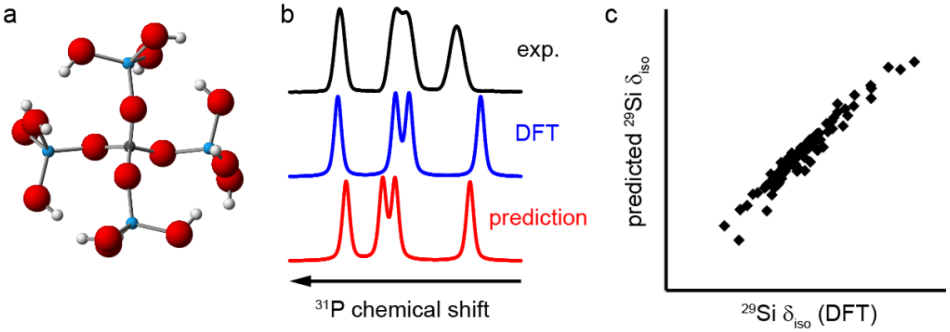
P5 Structure-based prediction of NMR parameters in zeolites

Daniel M. Dawson, Robert F. Moran, David McKay, Valerie R. Seymour, Scott Sneddon, Sharon E. Ashbrook

School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST

"NMR crystallography" is a philosophy that combines both nuclear magnetic resonance (NMR) spectroscopic and crystallographic experiments with the use of computation to provide a detailed picture of both the local and longer-range structures of materials. The approach has gained popularity in recent years, and has been applied particularly successfully to zeolites and zeolitic materials. However, many of these materials (particularly

in their most common and most interesting states) contain some element of disorder, whether that be compositional (*e.g.*, doping an SiO_2 framework to obtain an aluminosilicate zeolite), positional (*e.g.*, the presence of multiple possible orientations of a guest molecule in the pores), temporal (*e.g.*, motion of a guest or water molecule within the pores) or a combination of these (*e.g.*, during a catalysed reaction). This disorder may be inherent to the chemical and physical behaviour of the material, and can have significant effects on the local structure (as observed by NMR spectroscopy) but can go almost undetected by crystallographic methods, which typically provide a time- and length-averaged structure. In such cases, it can be challenging to generate a series of structural models capable of adequately describing the possible local structures present in the material, but these are a requisite for the density functional theory (DFT) calculations. Here, we use calculated NMR parameters for a series of ordered model systems (where the input structure corresponding to the NMR parameters is known exactly) to generate relatively simple structure-spectrum relationships (*i.e.*, depending only on bond lengths and angles) capable of predicting the NMR parameters that would be obtained by DFT calculations. We then demonstrate, for a series of aluminophosphates[1,2] and silicates,[3] that this semi-empirical approach opens up the possibility of a rapid estimation of the outcome of a hypothetical DFT calculation where the actual calculation would be either prohibitively costly or otherwise too challenging.



(a) Model of the local environment of a P atom in an aluminophosphate, (b) comparison of the experimental, calculated and semi-empirically predicted ^{31}P NMR spectra of calcined AlPO-14, (c) comparison of the calculated and semi-empirically predicted ^{29}Si chemical shifts for a series of silicate zeolites.

[1] D. M. Dawson, S. E. Ashbrook, *J. Phys. Chem. C* **2014**, *118*, 23285–23296.
[2] D. M. Dawson, D. McKay, V. R. Seymour, S. E. Ashbrook, *in preparation*
[3] D. M. Dawson, R. F. Moran, S. E. Ashbrook, *submitted*.

P6 NMR crystallography: probing cation distribution in mixed metal oxide ceramics

Arantxa Fernandes,[a] Dave McKay,[a] Scott Sneddon,[a] Daniel M. Dawson,[a] Karl R. Whittle[b], Sharon E. Ashbrook[a]

[a]*School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, University of St Andrews, St Andrews, Fife, KY16 9ST, UK*
[b]*School of Engineering, Centre for Materials and Structures, University of Liverpool, Brownlow Hill, L69 3GH, UK*

The ease of incorporation of cations with variable oxidation states into pyrochlore-based ($A_2B_2O_7$) oxide materials results in a range of applications, including nuclear waste encapsulation,[1] catalysis,[2] and energy materials.[3] There is, therefore, considerable interest in understanding the structure-property relationships in these materials, *i.e.*, investigating how cation/anion disorder and local structure vary with composition. However, substitution can bring about a structural change, with the pyrochlore phase predicted to be stable only when the relative ratio of the cation radii, r_A/r_B, is between 1.46 and 1.78 (*e.g.*, as is seen for $La_2Sn_2O_7$). Below this, a defect fluorite structure is formed, exhibiting disorder on the cation and anion lattices. When $r_A/r_B > 1.78$, a layered perovskite-based structure is observed, as is the case for $La_2Ti_2O_7$).

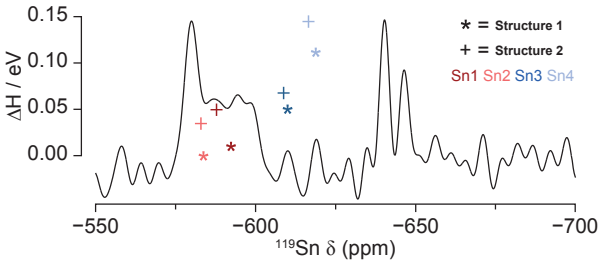


Figure 1. ^{119}Sn NMR of $La_2Ti_{1.8}Sn_{0.2}O_7$, showing pyrochlore and layered-perovskite phases present. The coloured points represent the DFT-predicted shifts for Sn substituted into the four Ti sites in the two very similar structures.

In this work, we exploit the sensitivity of solid-state NMR spectroscopy to the local structural environment to investigate the number, nature and composition of the two distinct phases formed in $La_2(Sn,Ti)_2O_7$ ceramics. Density Functional Theory (DFT) calculations (on both unit cells and supercells) are used to aid spectral assignment and interpretation, and provide information on cation ordering in both pyrochlore and layered perovskite phases. Calculations suggest that there is a random distribution of Ti cations in the Sn-

rich pyrochlore phase, although a limited solid solution is observed. However, comparison of experiment and calculation suggest a preferential substitution of Sn onto just 2 of the 4 possible Ti sites in the Ti-rich layered perovskite phase. $La_2Ti_2O_7$ itself is difficult to study by NMR, owing to the properties of the nuclides present. One option is to use ^{17}O NMR spectroscopy, after first enriching the sample with 70% $^{17}O_2$ gas. This resolves 14 crystallographic oxygen sites that can then be assigned using DFT calculations.

[1] J. M. Bae, B. C. H. Steele, *J. Electroceram.*, 1991,*3:1*, 37-46.
[2] R. C. Ewing, *Ceram. Int.*, **1991**, *17*, 287-293.
[3] S. Park, H. J. Hwang, and J. Moon, *Catal. Lett.* **2003**, *87*, 3-4.

P7 NMR Crystallography of a Disordered Gallophosphate Framework

Joseph E. Hooper,[a] Daniel M. Dawson,[a] Lucy Broom,[b] Mahrez Amri,[b] Nathalie Guillou,[c] Sharon E. Ashbrook,[a] Richard I. Walton.[b]

[a]*School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, Fife, UK, KY16 9ST*
[b]*Department of Chemistry, University of Warwick, Coventry, CV4 7AL*
[c]*Institut Lavoiser Versailles, Université de Versailles, UMR 8180, 78035 Versailles, France*

Gallophosphates (GaPOs) are a relatively underexplored family of zeolitic framework materials whose structures comprise alternating corner-sharing GaO_4 and PO_4 tetrahedra, with network topologies closely related to the better-known aluminosilicates and aluminophosphates. It is possible to prepare many such GaPOs, typically in the presence of fluoride and an organic structure-directing agent (SDA). The use of solid-state NMR spectroscopy for the characterisation of GaPOs can provide much structural information about the material, including the number of crystallographic species, the coordination number of Ga, the protonation state of the SDA and the types of fluoride-containing motifs present.

An unknown GAPO has been observed as a competing phase in the synthesis of GaPO-34, with both 1-methylimidazole and pyridine as SDAs.[1,2] After the development of a selective synthesis, to produce this material as a pure phase, a multinuclear solid-state NMR study has been undertaken. Partial structural models have been obtained from single crystal and power XRD measurements, but these do not agree with each other, or with the NMR experiments. In particular, NMR highlights the disorder present in the system, which is not reproduced well in the average structural models obtained using diffraction. DFT calculations have been employed to provide insight into the F^-/OH^- disorder

that NMR indicates is present, and to help assign and interpret the multinuclear and multidimensional NMR spectra obtained. The combination of NMR, XRD and DFT calculations should provide a powerful tool for obtaining a detailed structural picture of this unknown material.

1. M. Amri et al., J. Phys. Chem. C, 2012, 116, 15048
2. C. Schott-Darie et al., Stud. Surf. Sci. Catal., 1994, 84, 10

P8 Investigating the local structure of $Y_2(Ti,Sn)_2O_7$ ceramics using site occupancy disorder and NMR spectroscopy

Robert F. Moran[a], David McKay[a], Arantxa Fernandes[a], Paulynne C. Tornstrom[b], Ricardo Grau-Crespo[b], and Sharon E. Ashbrook[a]

[a] *School of Chemistry, EaStCHEM and Centre of Magnetic Resonance, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK*
[b] *Department of Chemistry, University of Reading, Reading, Berkshire, RG6 6AH, UK*

Pyrochlore materials ($A_2B_2O_7$) have recently seen significant interest as potential components of ceramic-based nuclear wasteforms, with the ultimate aim being the long-term storage of radioactive actinide species including U and Pu. As many ceramics are highly resilient to structural degradation caused by radioactive decay and can accommodate high waste loadings, pyrochlores are promising candidates to replace existing borosilicate glass wasteforms in the future. The 8-coordinate A site in pyrochlore materials is able to accommodate larger cations, such as Y^{3+} or La^{3+}, which are of comparable size to many actinides. The formation of a pyrochlore structure is governed by the ratio of the two cations ionic radii. If r_A/r_B is between 1.46 and 1.78 the pyrochlore structure is favoured, whereas an ionic radii ratio lower than 1.46 leads to the formation of a disordered defect fluorite (A_4O_7) structure, whereas above 1.78, a layered perovskite-type phase is observed.

Building on previous studies of the $Y_2Ti_{2-x}Sn_xO_7$ pyrochlore solid solution, where ^{89}Y and ^{119}Sn NMR, combined with X-ray diffraction and DFT calculations were used,[1-3] here we will focus on using first-principles calculations to investigate local structure and the effect of B-site cation mixing and variation in the next nearest neighbor (NNN) cation arrangements on the calculated ^{17}O, ^{89}Y and ^{119}Sn solid-state NMR parameters. We use different approaches used to generate possible structural models for the disordered $Y_2(Ti,Sn)_2O_7$ ceramic materials, from simple models where individual atoms, or a combination of atoms were substituted to model B-site cation mixing, to more complex approaches such

as the Site Occupancy Disorder (SOD) technique.[4] The use of SOD allows for every symmetry-unique arrangement of atoms for a given composition (value of x) to be determined, as well as the corresponding degeneracy of each of these structures, allowing an entropic, as well as an enthalpic term to be calculated for each arrangement. Using SOD, all symmetry-unique atomic arrangements for a series of compositions (x = 0, 0.25, 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2) were generated and models geometry optimized before NMR parameters were calculated, allowing a detailed investigation of the local ordering, B-site cation arrangement and structural variation in the ceramic materials to be undertaken. Comparing these results to experimental NMR spectra should allow us to deduce which, if any, of the SOD-generated structures contribute to the experimental spectra, providing more insight into the ordering B-site cations in the $Y_2(Ti,Sn)_2O_7$ pyrochlore solid solution.

[1] S. W. Reader, M. R. Mitchell, K. E. Johnston, C. J. Pickard, K. R. Whittle and S. E. Ashbrook, *J. Phys. Chem. C.*, 2009, **113**, 18874-18883.
[2] M. R. Mitchell, S. W. Reader, K. E. Johnston, C. J. Pickard, K. R. Whittle and S. E. Ashbrook, *Phys. Chem. Chem. Phys.*, 2011, **13**, 488-497.
[3] S. E. Ashbrook, M. R. Mitchell, S. Sneddon, R. F. Moran, M. de los Reyes, G. R. Lumpkin and K. R. Whittle, *Phys. Chem. Chem. Phys.*, 2015, **17**, 9049-9059.
[4] R. Grau-Crespo, S. Hamad, C. R. A. Catlow and N. H. de Leeuw, *J. Phys.: Condens. Matter*, 2007, **19**, 256201-256216.

P9 Exploring NMR properties of paramagnetic Cu phenolic oxime complexes using DFT

Zhipeng Ke, Daniel Dawson, Freddie Mack, Sharon Ashbrook, Michael Bühl

University of St. Andrews, EaStCHEM School of Chemistry and Centre of Magnetic Resonance, North Haugh, St Andrews, Fife, Scotland, UK

Copper (II) phenolic oxime complexes (shown in Figure 1) are important intermediates during liquid-liquid extraction of copper from ores, being an alternative to energy-intensive techniques involving smelting[1]. In conjunction with Density Functional Theory (DFT) calculations, solid-state nuclear magnetic resonance (NMR) can probe the local environment and give insights into the structure, symmetry and bonding in these materials.[2] The paramagnetism of the Cu(II) complexes poses a big challenge to both experiment and theory. We have been using state-of-the-art DFT methods (at the PBE0-⅓/IGLO-II level) to simulate the ^{1}H and ^{13}C chemical shifts in these complexes[3] and report on the detailed effect of temperature, intermolecular aggregation and substituents (R_1 and R_2 in Figure 1) on these parameters.

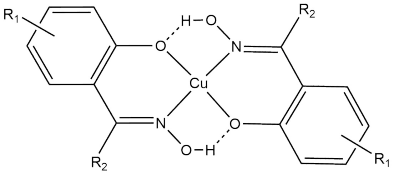


Fig. 1 Copper phenolic oxime complexes

[1] A. M. Wilson, P. J. Bailey, P. A. Tasker, J. R. Turkington, R. a Grant and J. B. Love, *Chem. Soc. Rev.*, **2014**, 43, 123–134.

[2] S. E. Ashbrook, D. M. Dawson and J. M. Griffi, in *Local Structural Characterisation: Inorganic Materials Series*, eds. D. W. Bruce, D. O'Hare and R. I. Walton, WILEY, West Sussex, 1st edn., **2013**, pp. 1–88.

[3] M. Bühl, S. E. Ashbrook, D. M. Dawson, R. A. Doyle, P. Hrobárik, M. Kaupp and I. A. Smellie, *Chem. - A Eur. J.*, **2016**, 22,15328-15339.

P10 Datamining semiconductor nanocluster structures

Susanne G. E. T. Escher, Tomas Lazauskas, Scott M. Woodley

Department of Chemistry, University College London

Nanoclusters are an avenue in materials design which allows for fine-tuning properties of a variety of materials, including structurally simple semiconductors (here: alkaline earth oxides). We previously investigated barium oxide clusters[1], i.e. $(BaO)_n$ with n = 4 to 18 and n = 24, using an evolutionary algorithm, and found that they tend to adopt structures resembling rocksalt cuts. Based on a large number of local minima found during this study, we have datamined corresponding structures for MgO, CaO and SrO clusters and determined their relative energies. As previously reported[2,3], MgO clusters tend to favour "barrel" shapes consisting of six-membered rings. We find that CaO and SrO clusters are more likely to adopt structures that resemble rocksalt cuts like found in BaO.

Based on this data, we have also confirmed smaller clusters where a unique structure is found in size-selected experiment[3] , and suggest synthesis targets based on this same criterion as well as which sizes are relatively more stable for each compound.

[1] S. G. E. T. Escher, T. Lazauskas, M. A. Zwijnenburg, S. M. Woodley, *Comp. Theor. Chem.* **2017**, *1107*, 74–81.

[2] M. R. Farrow, Y. Chow, S. M. Woodley, *Phys. Chem. Chem. Phys.*, **2014**, *39*, 74–81.

[3] K. Kwapien, M. Sierka, J. Döbler, J. Sauer, M. Haertelt, A. Fielicke, G. Meijer, *Angew. Chem. Int. Ed.*, **2011**, *50*, 1716-1719

P11 PRFFECT – a versatile tool for spectroscopists

Benjamin R. Smith[ab], Matthew J. Baker[b], David S. Palmer[a]

[a]*Department of Pure & Applied Chemistry, University of Strathclyde, Thomas Graham Building, 295 Cathedral Street, Glasgow G1 1XL*
[b]*Bionanotechnology, Technology and Innovation Centre, University of Strathclyde, 99 George Street, Glasgow G1 1RD*

The best choice of spectral pre-processing is an unresolved problem in the spectral diagnostic community. Often, pre-processing is a set local routine used by research groups across all datasets. However, the choice of the particular methods and parameters are not finely tuned to particular dataset types. With PRFFECT (Pre-processing & Random Forest Feature Extraction Combination Tester) we provide a robust methodology to decide on optimal choices for pre-processing spectral datasets. It is important to find these best-possible methods and parameters in order to build a strong routine for translation into clinical settings. PRFFECT accomplishes this through offering a large array of user-settable pre-processing methods and parameters. As well as pre-processing, the program can run a Random Forest classifier (previously found to be very effective for spectral datasets) and provide information on the importance of vibrational peaks in a classification. This allows the spectroscopist to easily identify areas of the spectrum which are important in distinguishing between classes of input data.

The pre-processing methods offered are in four main categories: Binning, smoothing methods, normalisation methods, and baseline correction. There are several methods offered in each category, with the ability to set parameters for each. These methods can then be chosen and combined to find the best possible pre-processing regime for the input data, to achieve the best classification and feature extraction.

P12 X-ray scattering: from static measurements to dynamics

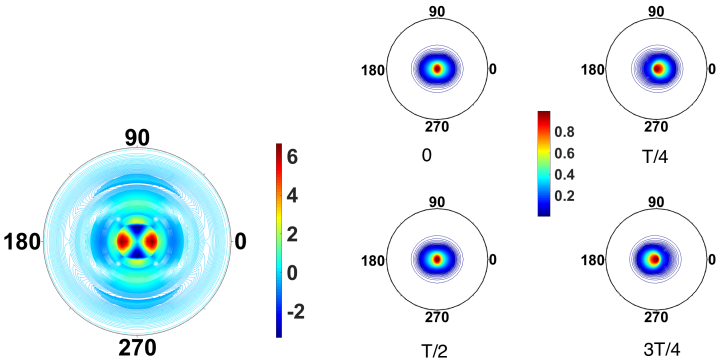
Andrés Moreno Carrascosa

University of Edinburgh, School of Chemistry, Edinburgh EH9 3FJ, UK

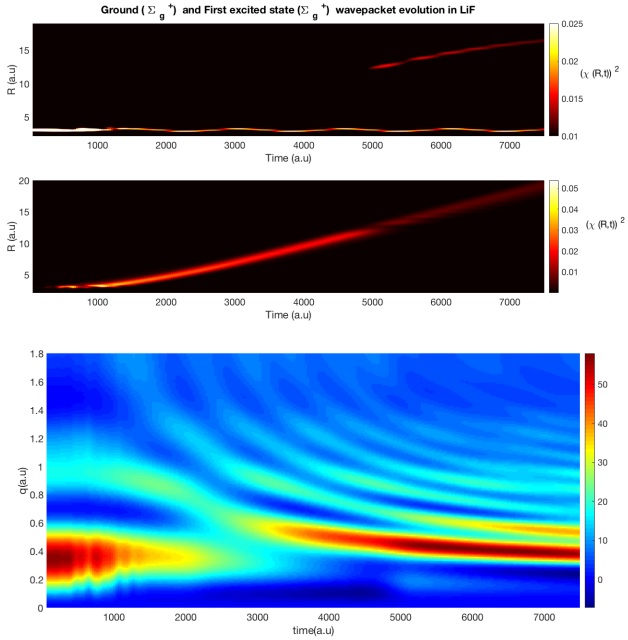
X-rays have been widely exploited to unravel structure of matter since their discovery in 1895. Nowadays, with the emergence of new X-ray sources with higher intensity and very short pulse duration, notably XFELs (X-ray Free Electron Lasers), the number of experiments available in the X-ray regime has increased dramatically, even allowing the characterization of gas phase atoms and molecules in space and time.

Our aim is to characterize ultrafast X-ray scattering theoretically. Based on electronic structure *ab-initio* calculations we have developed tools to predict the signatures of atoms and molecules in both elastic[1] and inelastic[2] scattering. The signal produced by the different rotational and vibrational states in diatomic[4] and polyatomic molecules[3] has been also characterized using this approach.

Our methods can be used to reproduce accurately how excited wave packets evolve in time in pump-probe X-ray scattering experiments. [5,6,7]



Left: Excitation of the (1,1,0) Rotational State in CS_2 (X). Right: X-ray evolution of a 3d-4f wave packet in Atomic Hydrogen; T = 6.3 fs.



Wave packet evolution and X-ray dynamics in LiF X and B states.

[1] T. Northey, N. Zotev and A. Kirrander, *J. Chem. Theory Comput.,* **2014**, 10, 4911.
[2] A.M. Carrascosa and A. Kirrander, *submitted to PCCP.*
[3] A.M. Carrascosa, T. Northey, A. Kirrander , *Physical Chemistry Chemical Physics*, **2017,**
[4] T. Northey , A.M. Carrascosa, S. Schëffer, A. Kirrander ,*The Journal of Chemical Physics*,**2016**,145,15,154304
[5] C. Vallance, *Phys. Chem. Chem. Phys.,* **2011**, 13, 14427.
[6] A. Kirrander, K. Saita and D. V. Shalashilin, *J. Chem. Theory Comput*., **2016**, 12, 957–967.
[7] Ulf Lorenz, Klaus B. Møller, and Niels E. Henriksen, *Phys. Rev. A*, **2010**, 81, 023422

P13 Ab initio surface-hopping simulations of CS_2 photodissociation dynamics

Darren Bellshaw and Adam Kirrander

EaStCHEM, School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, United Kingdom.

The rapid photodissociation dynamics of CS_2 following UV excitation into the $^1B_2(S_2)$ state is dictated by the complex interplay between multiple excited electronic states in a crowded manifold of potential energy surfaces. The reaction results in the production of a ground state CS($X\ ^1\Sigma^+$) molecular fragment alongside atomic sulfur in either an excited spin-allowed state (^1D) or the spin-forbidden ground state (^3P). The latter channel is mediated via the spin- orbit coupling arising from the presence of the sulfur atoms. Although the exact branching ratio has proven difficult to measure accurately, the spin-forbidden product is seen to dominate in most experimental studies [1], highlighting the importance of spin-orbit coupling in this photochemical process.

We present here the first simulations of CS_2 photodissociation that account for spin-orbit coupling. We use the SHARC code (Surface Hopping including Arbitrary Couplings) [2] interfaced with the Molpro suite of electronic structure programs [3]. Based on the fewest switches surface-hopping (FSSH) algorithm, SHARC accounts for spin-orbit coupling through a reformulation of the standard surface-hopping scheme in terms of a unitary transformation matrix and has previously been used to study the importance of spin-orbit coupling and branching ratios in systems such as IBr [2].

These simulations are compared to new time-resolved photoelectron spectroscopy measurements performed by experimental collaborators. This demonstrates that it is now possible to carry out on-the-fly dynamics calculations such that we are able to explain the shifting and narrowing of the photoelectron spectrum in terms of the bending motion of the vibrational wavepacket, and track population changes between the singlet and triplet manifold, with excel- lent agreement between experiment and theory [4].

[1] D. Xu, J. Huang, W.M. Jackson, J. Chem. Phys., 120:3051–3054, 2004.
[2] M. Richter, P. Marquetand, J. González-Vázquez, I. Sola, L. González, J. Chem. Theory Comp., 7:1253–1258, 2011.
[3] H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schütz, et al. Molpro, version 2015.1, a package of ab initio programs, 2015.
[4] D. Bellshaw, D. A. Horke, A. D. Smith, H. M. Watts, E. Jager, E. Springate, O. Alexander, C. Cacho, R. T. Chapman, A. Kirrander, et al. Chem. Phys. Lett.,2017.

P14 Implementation and testing of the JEDI collective variable to explore protein druggability

Joan Clark-Nicolas, Julien Michel

EaStCHEM School of Chemistry, Joseph Black Building, Edinburgh EH9 3FJ, UK

Protein druggability (i.e. the ability of a protein to bind a drug-like molecule) is a property that often depends on the conformational state of the protein of interest. Several studies have proven that di erent conformations of a protein pocket are able to bind di erent ligands with binding a nities that can di er from one to several orders of magnitude. Molecular Dynamics (MD) simulations allow to sample the conformational space of proteins, but very long simulation times are often required in order to detect conformational changes that can induce a relevant increase in druggability. A lot of e ort has been done to enhance the sampling by biasing a few carefully selected degrees of freedom, known as Collective Variables (CV). The JEDI (Just Exploring Druggability at protein Interfaces) CV[1] quanti es the druggablity of protein pockets with a good degree of correlation with the experimental druggability values compiled in the Druggable Cavity Directory dataset[2] and allows to monitor it during MD simulations. This CV can also be converted to a potential and a force, which allows to apply biasing potentials in order to explore regions of protein conformational space with a di erent druggability score. This work focuses on the stability and performance of simulations run using JEDI to monitor and bias the druggability. Directions for further improvement are also outlined.

[1] Cuchillo, R. et al, J. Chem. Theor. Comput. (2015), 11 (3), 1292.
[2] Schmidke, P.; Barril, X.; J. Med. Chem. (2010), 53 (15), 5858.

P15 Design and Biophysical Characterization of Novel Cyclophilin Inhibitors

Harris Ioannidis, Alessio De Simone, Jordi Juárez-Jiménez, Charis Georgiou, Arun Gupta, Julien Michel

EaStCHEM School of Chemistry, Joseph Black Building, Edinburgh EH9 3FJ, UK

Cyclophilins (Cyps) belong to a family of proteins known to catalyze the *cis-trans* interconversion of proline peptide bonds and are involved in various diseases, such as cancer,[1] Alzheimer,[2] HIV-1,[3] HCV[4] infections.[4] Due to the severe side effects of the known immunosuppressant Cyclosporin A,[5] there is a need for new drugs targeting Cyclophilins that can be selective towards one isoform.

A two-pronged strategy is pursued to discover novel isoform-selective ligands. The first approach exploits flexibility of the 70s loop (Fig. 1) neighbouring the known binding site that consists in the Abu and Pro pockets (Fig. 1). Diverse biophysical techniques (NMR Chemical Shift Perturbation, Saturation-Transfer Difference, and Isothermal Titration Calorimetry) were used to characterize the binding of ligands designed and synthesized by co-workers.

In parallel, the ligandability of the secondary three o'clock pocket (Fig. 1) is being explored with computational and biophysical techniques. This accessory pocket shows more structural variability between different isoforms, compared to the main binding site. To this end molecular dynamics simulations of cyclophilin isoforms A, B and D have been carried out to detect three o'clock pocket conformations that could accommodate drug-like fragments. Further steps will involve virtual screening of fragment libraries, and biophysical characterization of their binding. Ultimately we aim to incorporate three o'clock pocket binders into ligands that target the Abu/Pro pockets, leading to a new generation of cyclophilin ligands with enhanced isoform-selectivity.

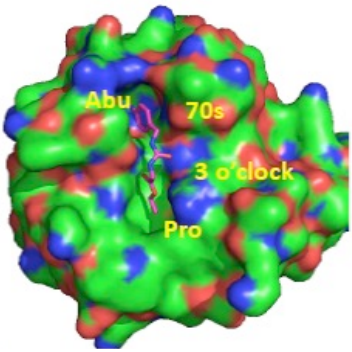


Fig. 1: Cyclophilin-compound complex (4XNC.pdb) showing the flexible 70s loop and the three different binding pockets (Abu, Pro and 3 o'clock) present in the Cyps isoforms.

[1] Q. Yao, M. Li, H. Yang, H. Chai, W. Fisher, and C. Chen, *World J. Surg.*, **2005**, *29* (3), 276–80.
[2] K. R. Valasani, J. R. Vangavaragu, V. W. Day, and S. S. Yan, *J. Chem. Inf. Model.*, **2014**, *54* (3), 902-912.
[3] J. Luban, K. L. Bossolt, E. K. Franke, G. V Kalpana, and S. P. Goff, *Cell*, **1993**, *73* (6), 1067–1078.
[4] F. Yang, J. M. Robotham, H. B. Nelson, A. Irsigler, R. Kenworthy, and H. Tang, *J. Virol.*, **2008**, *82* (11), 5269–5278.
[5] T. L. Davis, J. R. Walker, V. Campagna-Slater, P. J. Finerty, P. J. Finerty, R. Paramanathan, G. Bernstein, F. Mackenzie, W. Tempel, H. Ouyang, W. H. Lee, E. Z. Eisenmesser, and S. Dhe-Paganon, *PLoS Biol.*, **2010**, *8* (7), 1–16.

P16 Force field parameterisation and molecular dynamics simulation studies of cyclosporin A (CsA) and alisporivir (DEB025) to understand the differential dynamics of cyclophilin A (CypA) inhibition

Kanhaya Lal, Jordi Juárez Jiménez, Julien Michel

School of Chemistry, University of Edinburgh, Edinburgh EH9 3FJ,UK

The goal of this research is to contribute towards new methodologies to integrate experimental results of biomolecular NMR measurements with molecular dynamics (MD) simulations. The study involves understanding the differential dynamics of binding of cyclosporin A (CsA) and alisporivir (DEB025) to cyclophilin A (CypA) using MD simulation studies. Experimental studies in the literature have shown that the two cyclophilin A ligands CsA and DEB025 have similar structure and dissociation constant (K_D 11 nM and 7 nM respectively).[1] However, the dissociation rate (k_{off}) parameter is ca. 10 fold slower for CsA then for DEB025 (k_{off} 27 +/- 3 10^{-4} s^{-1} and 2.4 +/- 0.1 x 10^{-4} s^{-1} respectively).[2,3] Therefore, to understand the binding and unbinding mechanisms of both the cyclic peptides MD simulation approaches involving differential dynamics of the Csa-CypA and DB025-CypA complexes, Markov State Models (MSMs) and conformational dynamics of free CsA and DEB025 in aqueous solutions will be used. The study aims to understand the major and minor conformational preferences of CsA and DEB025 in solution and characterisation of their rate of exchange. The initial study involved force field parameterization to create a new residue template for 7 non-standard amino acid residues in both the peptides. The atomic partial charges were derived using R.E.D. (RESP and ESP charge Derive) software and backbone torsion parameters were fitted using Paramfit. The derived parameters were able to reproduce free energy plots for standard amino acids similar to the AMBER force field parameters. Finally, AMBER force field libraries were generated for non-standard amino acid residues of both the peptides. The results of MD simulations will be analysed to understand the binding mechanism.

[1] H. Launay, B. Parent, A. Page, X. Hanoulle, G. Lippens, *Angew Chem Int Ed Engl*. **2013**, 52, 12587-12591.

[2] D. Altschuh, W. Braun, J. Kallen, V. Mikol, C. Spitzfaden, J.C. Thierry, O. Vix, M.D. Walkishaw, K. Wüthrich, *Structure*. **1994**, 2, 963–972.

[3] R. Wenger, J. France, G. Bowerman, L. Walliser, A. Widmer, H. Widmer, *FEBS Letter* **1994**, 340, 255–259.

P17 Probing ligand binding affinities with alchemical free energy calculations

Antonia S J S Mey, Jordi Juárez Jiménez, Julien Michel

EaStCHEM School of Chemistry, University of Edinburgh, EH9 3FJ

Computer aided drug design has gained momentum in recent years, with the aim to reduce the overall cost of the development of a new drug. Therefore, the reliable prediction of binding poses and affinities of small/drug-like molecules to target proteins, with or without available crystal structures, is essential. However, despite the increase in available computational power and vast algorithmic improvements, this still remains a challenge. In particular, while there is a vast array of methods available for predicting protein-ligand interactions, until recently there has not been a systematic approach to compare different methods and assess their reliability on a set of blinded experimental data (IC50 values from FRET assays or similar). The drug design data resource (D3R) grand challenge tries to address this in form of a competition. Two rounds of the grand challenges were run in 2015 and 2016. Each challenge consisted of a blinded dataset of small molecules that serve as potential binders to a target protein. Participants were then given five months to predict the biding affinities of the small molecules to the protein as accurately as possible using any method of their choice. The accuracy of each of the predictions was then assessed after the release of the blinded data once the competition period was concluded.

Here I will present alchemical molecular dynamics (MD) simulation- and state-of-the-art analysis techniques to compute free energies of binding between ligands and proteins in the context of the D3R challenges. For this purpose, the semi-automated workflow used for ligand parameterization, simulation set up, production runs, and automated analysis will be introduced based on various freely available software packages, such as FESetup[1] and Sire[2]. The two D3R grand challenge datasets will serve as a basis to illustrate the workflow and highlight the successes and failures in the presented techniques used for predicting binding affinities[3]. The D3R datasets consist of compounds that serve as inhibitors to heat shock protein 90 (HSP90) and farsenoid receptor X (FSR X). Lastly, I will show how well the presented alchemical MD based workflow fares in comparison to other approaches such as biased MD simulations or quantum mechanical methods used by other participants of the challenge.

[1] Löffler, H. et al, *J Chem Inf Model.* **55**, 2485 (2015)
[2] Woods, C. J., **Mey, A**., Calabro, G., Michel, J. (2016). Sire molecular simulations framework.
[3] **Mey, A**. et al. *Bioorg. Med. Chem.* **24,** 4890 (2016)

P18 Understanding protein allostery: developing analysis methods for molecular dynamics

Lisa Patrick[a], Julien Michel[a], Ben Cossins[b]

[a]*The University of Edinburgh.*
[b]*UCB Celltech*

Although allostery was first discovered over 50 years ago, the molecular determinants underlying signal transduction are not yet completely understood. The ability to predict the activity of allosteric small molecules could have a huge therapeutic impact, as targeting allosteric sites in proteins potentially presents significant benefits over active site inhibitors, in both selectivity and efficacy. While some systems undergo fairly well understood structural changes, there is no overall model that satisfactorily describes how allostery works. Molecular dynamics simulations provide a tool to study protein dynamics at the atomistic level, however traditionally employed analysis methods have been proved inadequate to deliver a mechanistic description of allostery.

In this work, we present our approach to tailor MD simulation analysis methods to identify motions which may be significant to signal transmission in the case study of PDK1 (Phosphoinositide-dependent kinase-1). Long MD trajectories were run for PDK1 in complex with covalent activator and inhibitor small molecules, using the software Sire/Somd[1]. A geometrical analysis using the Kullback-Leibler divergence allowed comparison of probability distributions of various descriptors. Subsequently, an energetic comparison was performed using a per-residue decomposition of the interaction energy between the protein and the substrate. Mutual information was then used to determine whether particular structural changes correlate with changes in energetics, to identify motions which are important for the allosteric signal.

[1] Woods, C. J. and Michel, J., Sire/OpenMM, **2014**, (http://www.siremol.org/)

P19 3D-RISM for predicting water network

Lucia Fusani[a,b] Ian Wall,[a] David Palmer[b]

[a] *Computational & Modeling Sciences, GlaxoSmithKline, Stevenage, Herts. SG1 2NY, UK*
[b] *Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, G1 1XL, UK*

Water plays a key role in the recognition and stabilization of the interaction between a ligand and its binding site and as a consequence accurately modelling it has important application in drug design strategies.

Three-Dimensional Reference Interaction Site model (3D-RISM) theory combines a reasonable level of molecular description with low computational costs. It employs liquids integral equation to produce an approximate average solvent distribution around a rigid solvent without the need for long molecular dynamics or Monte Carlo simulations and only requires solute structure and solvent composition.[1]

In this study, 3D-RISM density functions are converted by the Placevent algorithm [2] to predict the well defined water network of several Bromodomains.[3] The sensitivity of the method has been extensively investigated to understand the approximations involved in using a single crystal structure. Initial results show that overall the method is good at predicting the water network, but in some areas, which may be key to ligand design, important water molecules can be missed.

The effects of averaging the results over multiple structures of the same protein, or over multiple snapshots from a molecular dynamics simulation have been investigated. Preliminary results suggest these approaches result in an overall improvement in reproducing the Bromodomains' water network, although at an experimental or computational cost.

[1] Ratkova, E. L.; Palmer, D. S.; Fedorov, M. V., *Chem. Rev.* **2015,** *115*, 6312-56.
[2] Sindhikara, D. J.; Yoshida, N.; Hirata, F., *J. Comput. Chem.* **2012,** *33*, 1536-1543.
[3] Crawford, T. D.; Tsui, V.; Flynn, E. M.; et al. *J. Med. Chem.* **2016,** *59*, 5391-402.

P20 A statistical investigation of chemical properties associated with conjugated organic systems generated from molecular dynamics simulations

Andrew W. Prentice[a], Martin J. Paterson[a], Jack Wildman[b], Ian Galbraith[b]

[a] *Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom*
[b] *Institute for Photonics and Quantum Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, United Kingdom*

Conjugated materials are of great interest due to the potential application in organic optoelectronic devices[1]. The effectiveness of these devices is governed by many different factors, one of which being a geometrical dependence which can be explored through molecular dynamics (MD) simulations, if appropriate force fields describing the systems are available. The overarching aim of this work is to investigate the sampling statistics of various chemical properties, such as ionisation energy, for oligo-fluorene and thiophene conformations generated by MD simulations employing a newly parameterised force-field[1]. The sampling landscape for each system was explored in terms of sample size and relative location in the MD simulation, with comparison to the ensembles. The preliminary results indicate that a lower limit sample size of 500 and 1000 conformations, for the fluorene and thiophene dimer systems respectively is needed to give an accurate comparison to the total ensemble ionisation energy.

[1] J. Wildman, P. Repiščák, M. J. Paterson and I. Galbraith, *J. Chem. Theory Comput.* 2016, 12(8), 3813-3824.

P21 Investigating guest uptake in Sc_2BDC_3 metal-organic framework using GCMC simulation

Jonathan Richardson[a], Stephen Moggach[a], Jorge Sotelo[a], Carole Morrison[a], Tina Düren[b], Claire Hobday[b]

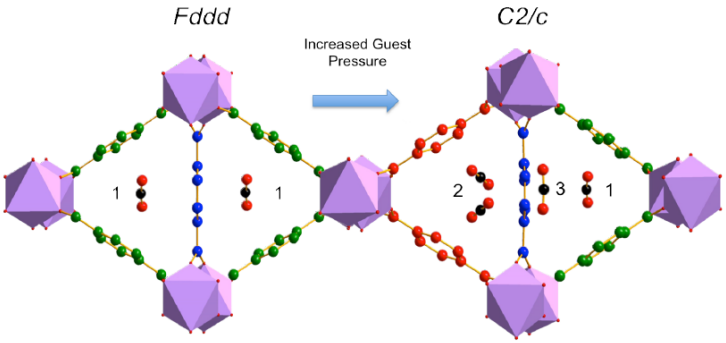
[a] *University of Edinburgh, School of Chemistry, Edinburgh, EH9 3FJ*
[b] *University of Bath, Department of Chemical Engineering, Bath, BA2 7AY*

Metal-organic frameworks, or MOFs, are a class of porous crystalline materials known for the high degree of structure variability, based upon the many possible combinations of metallic clusters and organic linkers. Despite their potential, very few MOFs have been utilised for application in gas storage and separation beyond the research environment.[1] One reason for this is the lack of understanding concerning the actual location of guest

molecules within the pores upon uptake and the nature of specific interactions between the guest molecules and the framework. If this understanding was more thorough, the process designing MOFs with enhanced or specific guest uptake would be improved significantly and aid the research-to-application transition.

The key aspect of this study, which investigates the uptake of guest molecules in the MOF Sc_2BDC_3 (where BDC = benzenedicarboxylate), is the collaboration between experimental methods and computation. Previous work in the group specifically focussed on the adsorption of CO_2 and CH_4 by use of high-pressure crystallography. [2,3] Upon uptake of CO_2, Sc_2BDC_3 was found to undergo a phase transition at approximately 3 bar, from its room temperature orthorhombic Fddd crystal structure to a monoclinic C2/c structure, as a result of the subtle rotation of a pair of organic linkers, which creates two symmetrically independent channels. A previously undiscovered third adsorption site was also located, supporting high-density gas storage.

The presented work has focussed on utilising the crystal structures from high-pressure crystallography experiments on Sc_2BDC_3 for computational Grand Canonical Monte-Carlo (GCMC) simulations, to verify and build upon the crystallographic results. GCMC is specifically designed to allow movement of guest molecules into the pores of the material and to stochastically probe all possible adsorption sites, and therefore determine the energies associated with these sites. The method has been successful in verifying the experimental CO_2 uptake in Sc_2BDC_3, as well as demonstrating that the guest-framework interactions are stronger in the C2/c structure, which could provide reasoning for why the phase transition occurs experimentally.



[1] *Nature Chemistry*, **2016**, 8, 987-987
[2] J. Sotelo, PhD thesis, University of Edinburgh, **2015**
[3] J. Sotelo et al., *Angew. Chem. Int. Ed.*, **2015**, 54, 13332-13336.

P22 Phase behaviour of self-assembled monolayers controlled by tuning physisorbed and chemisorbed states

Sara Fortuna[a,b], David L. Cheung[c], and Karen Johnston[d]

[a]*MOlecular NAnotechnology for LIfe Science Applications Theory Group, Department of Medical and Biological Sciences, University of Udine, Italy*
[b]*Center for biomedical sciences and engineering, University of Nova Gorica, Slovenia*
[c]*School of Chemistry, National University of Ireland, Galway, Ireland*
[d]*Department of Chemical and Process Engineering, University of Strathclyde, Glasgow, U.K.*

The self-assembly of molecules on surfaces into 2D structures is important for the bottom-up fabrication of functional nanomaterials, and the self-assembled structure depends on the interplay between molecule-molecule interactions and molecule-surface interactions. Halogenated benzene derivatives on platinum have been shown to have two distinct adsorption states: a physisorbed state and a chemisorbed state, and the interplay between the two can be expected to have a profound effect on the self-assembly and phase behaviour of these systems[1]. We developed a lattice model that explicitly includes both adsorption states, with representative interactions parameterised using density functional theory calculations. This model was used in Monte Carlo simulations to investigate pattern formation of hexahalogenated benzene molecules on the platinum surface[2]. Molecules that prefer the physisorbed state were found to self-assemble with ease, depending on the interactions between physisorbed molecules. In contrast, molecules that preferentially chemisorb tend to get arrested in disordered phases. However, changing the interactions between chemisorbed and physisorbed molecules affects the phase behaviour. We propose functionalising molecules in order to tune their adsorption states, as an innovative way to control monolayer structure, leading to a promising avenue for directed assembly of novel 2D structures.

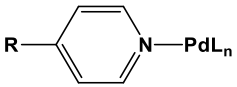
[1] R. Peköz, K. Johnston and D. Donadio, J. Phys. Chem. C **2014**, 118 6235-6241
[2] S. Fortuna, D. L. Cheung and K. Johnston, J. Chem. Phys. **2016**, 144, 134707

P23 A DFT study of palladium deposition onto a pyridine-terminated self-assembled monolayer

Zhen Yao, Manfred Buck, Michael Bühl

EaStCHEM School of Chemistry, University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, UK

Self-assembled monolayers (SAMs) are attractive systems for nanotechnology. There have been many efforts to generate a well-defined metal contact on top of a SAM[1-5] as these metal-SAM-metal systems are promising candidates for applications in, e.g., molecule-based electronics. Recent electrochemical experiments[4,5] have identified a highly practical two-step procedure to reliably deposit metal on top of a pyridine-terminated SAM. However, it remains a challenge to understand the mechanisms underlying metal nucleation and growth.



R=(Au)-S-$(CH_2)_3$-C_6H_4- (expt.)
R=H (calc.)

Here we present a density functional theory (DFT) study of Pd-SAM interfaces. Theoretical modeling allows us to investigate structural details of the surface at the atomic level. This information is important for elucidating the nature of Pd-SAM and Pd-Pd interactions in electrochemical environments and gaining insight into the mechanism of metal nucleation in the initial stage of deposition. Both Pd(II) and Pd(0) are found to bind to pyridine, which illustrates the importance of functional end groups in SAMs. Calculations also suggest that there is a substantial driving force towards the aggregation of Pd atoms.

[1] H. Haick, D. Cahen, *Prog. Surf. Sci.*, **2008**, *83*, 217-261.
[2] A. Hooper, G. L. Fisher, K. Konstadinidis, D. Jung, H. Nguyen, R. Opila, R. W. Collins, N. Winograd, D. L. Allara, *J. Am. Chem. Soc.*, **1999**, *121*, 8052-8064.
[3] W. J. Dressick, C. S. Dulcey, J. H. Georger, G. S. Calabrese, J. M. Calvert, *J. Electrochem. Soc.*, **1994**, *141*, 210-220.
[4] T. Baunach, V. Ivanova, D. M. Kolb, H.-G. Boyen, P. Ziemann, M. Büttner, P. Oelhafen, *Adv. Mater.*, **2004**, *16*, 2024-2028.
[5] C. Silien, D. Lahaye, M. Caffio, R. Schaub, N. R. Champness, M. Buck, *Langmuir*, **2011**, *27*, 2567-2574.

Sponsors of the 2017 Symposium

ScotCHEM

University of Glasgow | School of Chemistry

ROYAL SOCIETY OF CHEMISTRY

Glasgow & West of Scotland Local Section
Theoretical Chemistry Group