ScotCHEM 2015

Computational Chemistry Conference

26th June, 2015

Thomas Graham Building,
University of Strathclyde,
Glasgow, UK

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Programme

Friday 26th June 2015

09.30 Registration
10.30 Welcome and Opening Remarks

Reactivity. Chair: Hans Senn
10.40 **Jonathan Goodman** (Cambridge) *Plenary Talk*
11.30 Claire McMullin (Heriot-Watt)
12.00 Greg Anderson (Strathclyde)

12.30 Lunch

Biomolecules. Chair: John Mitchell
13.30 Antonia Mey (Edinburgh)
14.00 Jan Götze (St Andrews)
14.30 Tanja van Mourik (St Andrews)
14.50 Alexandra Simperler (NSCCS)

15.00 Tea & Coffee

Chemical Properties. Chair: Maciej Gutowski
15.30 Götz Bucher (Glasgow)
16.00 Steven Hunter (Edinburgh)
16.20 Barry Mant (Aberdeen)
16.40 Andres Moreno Carrascosa (Edinburgh)

Poster Session
17.00 Posters and Drinks Reception
17.50 Poster Prizes and Concluding Remarks

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Plenary Talk

Calculating Synthesis and Making Molecules

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Keywords: Organic Synthesis; NMR; Reaction Mechanisms

Millions of organic reactions have been reported in the literature [1] and details of the mechanisms are not always understood clearly [2]. We use computational methods to analyse reactions, to design syntheses and to interpret analytical data [3, 4], with the aim of improving our ability to rationalise reactivity, to predict molecular properties and to plan synthetic strategies with confidence.

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Contributed Talks

Investigating The Mechanism Of Ru(II)-Catalysed Direct Arylation With DFT

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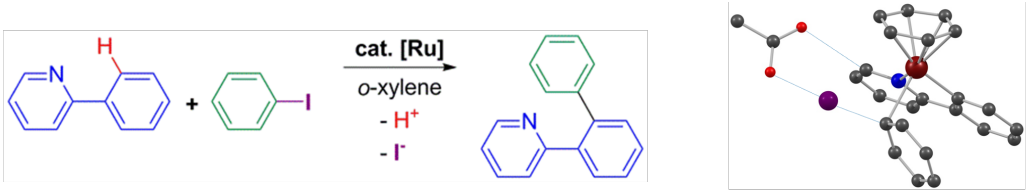
Keywords: DFT, mechanism, catalysis, C-H activation, direct arylation

C-C bond formation via cross-coupling based on initial C-H activation is termed "direct" aryl- or alkylation and Ru(II) catalysts have been shown to be particularly effective in mediating such transformations.[1,2] An example is the coupling of 2-phenylpyridine with phenyl iodide to give the direct arylation product shown in Scheme 1a.

Despite these synthetic advances, kinetic and mechanistic data are sparse on these catalytic systems, leading to speculation as to the precise order of the reaction steps. For example, is the C-H activation followed or preceded by oxidative addition of the aryl halide[3,4] and what is the nature of the oxidative addition step? We have used DFT calculations to study these processes, using a model catalyst, $[(C_6H_6)Ru(OAc)_2]$, for the reaction of 2-phenylpyridine with phenyl iodide in o-xylene.



Scheme 1; a) direct arylation reaction of 2-phenylpyridine and PhI with a Ru(II) catalyst; **b)** Acetate assisted C-I bond cleavage transition state

Our results suggest that C-H activation occurs prior to C-I activation. Moreover, the low polarity of the o-xylene solvent indicated that incorporating ion-pairs into the model was essential to produce viable energetics for the key bond activation steps. The presence of acetate in the outer coordination sphere also led us to propose a novel acetate-assisted process for C-I bond activation (Scheme 1b).

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The Role Of Organic Electron-Donors In Transition Metal-Free Biaryl Coupling Reactions: A Theoretical Investigation

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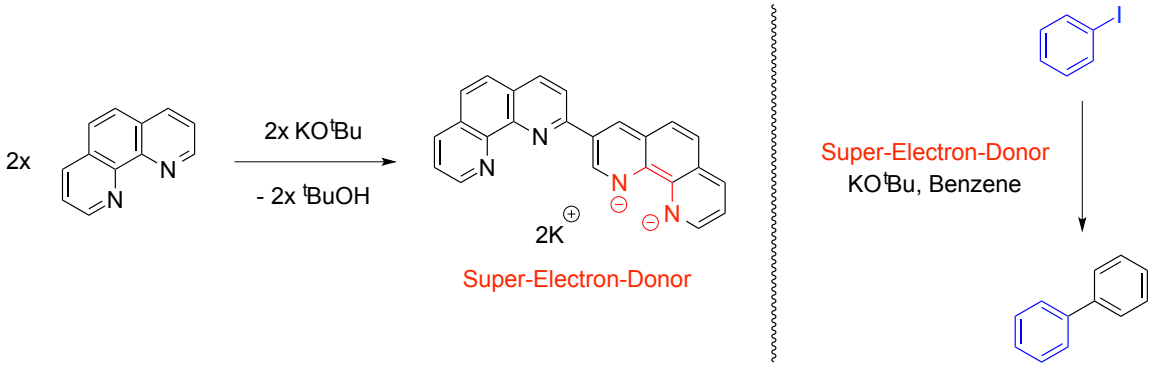
Keywords: DFT, electron transfer, biaryl coupling.

The synthesis of biaryl motifs is a transformation of keen interest both in academic and industrial settings. Traditionally, such chemical transformations are achieved through the use of ever-evolving transition metal catalysts. In recent years, it has been demonstrated that such motifs can be synthesized without the requirement for transition metal catalysts. [1] Instead, the combination of strong base, such as potassium *tert*-butoxide, and various organic molecules has been shown to be an efficient means of initiating a self-propagating base-promoted homolytic aromatic substitution (BHAS) reaction cycle. [2]

This presentation will give an overview on how a combined theoretical and experimental approach allowed us to elucidate the nature of the species responsible for the much-debated initiation step of these reactions. We have shown that, upon reaction with potassium *tert*-butoxide, a number of simple organic molecules are capable of generating organic super-electron-donors (SEDs) *in situ*. [3] These organic SEDs can reduce aryl iodides to their corresponding radical anions and, following loss of iodide, initiate the BHAS cycle to afford the desired biaryl product.



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Efficient Free Energy Estimations From Multi Ensemble Simulations

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Keywords: free energy, Markov state model, estimator, multi ensemble simulation

Estimating equilibrium properties of complex molecular systems bases on direct simulation data is often difficult, due to rare events plaguing the dynamics of these systems. This paved the way for a group of so called enhanced sampling simulation methods, under which the rare events are sped up, e.g. by coupling different temperatures or Hamiltonians as in parallel tempering; or by using biasing potentials as in umbrella sampling. The equilibrium properties of the thermodynamic state of interest (e.g. lowest temperature or unbiased potential) can for example be computed using reweighting estimators such as the weighted histogram analysis method (WHAM) [1] or the multistate Bennett acceptance ratio (MBAR) [2]. These estimators rely on the assumption that all data points are sampled from a global equilibrium for each thermodynamic state. Reaching global equilibrium can be very computationally expensive. Therefore we propose a new class of maximum-likelihood estimators, called transition-based reweighting analysis method (TRAM) estimators, which rely on conditional transition probabilities and can be used in conjunction with samples that were not necessarily generated at global equilibrium [3,4]. These estimators are a generalization of MBAR/WHAM and can be reduced to a traditional Markov state model (MSM) for simulations at a single thermodynamic state. Under certain conditions they can also be used to estimate kinetic properties. This talk aims to give an introduction to the class of TRAM estimators and their application to a range of molecular systems of varying complexity.

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The Photochemistry Of The Peridinin-Chlorophyll-Protein Using A New Carotenoid Model

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Keywords: Photobiology, light harvesting, carotenoids, chlorophyll, dipole coupling.

The peridinin-chlorophyll-protein (PCP) is a light harvesting complex found in organisms that often encounter light-depleted conditions [1]. In contrast many other light harvesters, PCP is brightly orange, due to the primary pigment not being chlorophyll (Chl). Instead, peridinin (Per) is the workhorse for acquisition of energy. How the actual Per → Chl energy transfer within PCP takes place has been a matter of debate for about two decades [2].

We conducted a series of QM/MM calculations using CAM-B3LYP and DFT/MRCI to analyse excited state minima, excitation and fluorescence energies and the charge transfer characters. We show that the protein is apparently supporting the generation of a transient excited charge transfer state that can couple strongly to the Chl acceptor state. For a second time we therefore observe that proteins can support excited state features in a function-enabling manner [3].

From our calculations, a new energy relaxation pathway that is consistent with all experimental measurements so far has been constructed. This mechanism reconciles apparently contradictory experimental findings and explains how the seemingly ultrafast internal conversion processes in carotenoids occur.

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DNA Base Stacking Studied With Density Functional Theory

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Keywords: base stacking, DNA, density functional theory, 2-aminopurine, bromouracil

The stability of DNA arises from a fine balance of hydrogen-bonding interactions between complementary bases on opposite strands and π-stacking interactions between bases on one strand. It is by now well established that intrastrand π-stacking is even more important than base pairing for the stability of DNA. In this presentation I will present results of several recent projects that involve base stacking, including stacked uracil/uracil, 5-bromouracil/uracil and stacking involving adenine and 2-aminopurine. Uracil/uracil (U/U) stacking has been employed as a benchmark system by several researchers, as uracil is the smallest nucleic acid base. Our results indicate that M06-2X/6-31+G(d) closely reproduces estimated CCSD(T)/CBS results [1]. 5-Bromouracil (BrU) is a thymine analogue and a known mutagen. The general model for its mutagenicity is that it mispairs with guanine in its enolised form. An alternative model has been suggested that explains the stability of the BrU-G mispair by enhanced stacking. However, our results do not show evidence for enhanced stacking of 5BrU compared to U [2]. The adenine analogue 2-aminopurine (2AP) is readily incorporated into DNA. Unlike adenine (A), 2AP is fluorescent, and this property has been used to experimentally investigate local nucleic acid structure. We have studied the potential energy surfaces of stacked A/A, 2AP/2AP and A/2AP to investigate whether 2AP behaves differently from A in base stacking [3]. All three projects show the complexity of the potential energy surfaces of these stacked structures, with many different minima, separated by low barriers. This shows the large conformational flexibility of these stacked structures, and provides further structural basis for the understanding of torsional flexibility in nucleotides.

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From Fleeting Intermediates to Strong Oxidants: New Aspects in the Chemistry of Carbonyloxy Radicals

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Keywords: free radicals, molecular dynamics, coupled cluster theory, density functional theory, carbon dioxide activation

Carbonyloxy radicals R-COO$^{\cdot}$ have been thought to decarboxylate too rapidly to be of any relevance in free radical chemistry, other than as fleeting intermediates, formed in quasistationary concentrations only.[1] Based on experimental work (performed using nanosecond laser flash photolysis), an in-depth computational study has been performed on a range of carbonyloxy radicals, from the highly labile formyloxy radical HCOO$^{\cdot}$ to a range of alkyl-, aryl-, vinyl-, and alkinylcarbonyloxy radicals, employing highly correlated coupled cluster methods and density functional theory, in geometry optimisations as well as in molecular dynamics simulations.
The results indicate that the kinetics of the decarboxylation of R-COO$^{\cdot}$ can range anywhere between a few femtoseconds and hours, with R-C≡C-COO$^{\cdot}$ showing the slowest kinetics. The calculations also show that p-complexation to arene chromophores should modulate the reactivity of R-COO$^{\cdot}$ to a considerable degree.

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High-Pressure Experimental and DFT-D Structural Studies of the Energetic Material FOX-7.

Steven Hunter, [1*] Paul L. Coster,[1] Alistair J. Davidson,[1] David I. A. Millar,[1] Stewart F. Parker,[2] William G. Marshall,[2] Ronald I. Smith,[2] Carole A. Morrison,[1] and Colin R. Pulham.[1]

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Keywords: DFT-D, FOX-7, high pressure, neutron powder diffraction, Inelastic Neutron Scattering.

This work reports the hydrostatic compression of the perdeuterated α-form of FOX-7 using neutron powder diffraction to follow the structural changes up to 4.58 GPa at room temperature. The equation of state for the hydrostatic compression of the α-form over the range 0 – 4.14 GPa has been determined and a phase transition was observed over the pressure range 3.63 - 4.24 GPa. On the basis of dispersion-corrected density functional theory (DFT-D) calculations performed on the γ-form over a range of pressures, the high-pressure form observed in the neutron diffraction experiments can unambiguously be identified as being different from the γ-form and should therefore be denoted as the ε-form. Based on similarities between the simulated and experimental powder diffraction patterns of the γ- and ε-forms, it is suggested that the ε-form adopts a planar, layered structure.[1]

The structural responses to pressure of the α-form observed experimentally are reproduced by DFT-D calculations, but in-depth analysis of the bond lengths, angles, dihedrals, and vibrational frequencies calculated in the DFT-D simulations identified a very subtle second-order phase transition at 1.9 GPa. This corroborates results obtained from previous far- and mid-IR vibrational spectroscopic studies.[2-6] These very small changes in molecular geometry do not manifest themselves in either the measured or calculated lattice parameters or unit-cell volumes, and are much smaller than can be detected by diffraction experiments. The results of phonon calculations were compared with experimental inelastic neutron scattering measurements and were used to investigate the effect of pressure on the heat capacities of α-FOX-7. The simulations predict very weak pressure dependencies (approximately -1 J K^{-1} mol^{-1} GPa^{-1}), in accordance with the conclusions reached in our previous studies of the energetic material RDX.[7]

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Antimatter Chemistry

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Keywords: Antimatter, Antihydrogen, Scattering, PES, Gaussians.

Experimental work into the properties of antimatter is set to answer fundamental questions in physics[1] and has inspired new theoretical work into matter-antimatter interactions[2]. These interactions are necessary for producing antimatter systems and are responsible for their destruction. Matter-antimatter chemical reactions such as

$$\bar{p} + H_2^+ \rightarrow Pn + H,$$

have been observed experimentally.[3] (Above $\bar{p}$ is an antiproton and Pn is protonium – that is, bound proton plus antiproton). Such reactions are a major cause of trapped antimatter destruction and a better understanding of these processes is important.

In the present work the primary focus is on antimatter collisions with molecular hydrogen species. The attraction between an antiproton and a molecule's nuclei gives rise to a highly anisotropic potential with no classically forbidden regions. This makes carrying out converged quantum scattering calculations challenging and special techniques are required.

We have developed a multidimensional Gaussian basis set for use in variational quantum scattering methods which is more efficient than conventional approaches for these potentials. Using the S-matrix version of the Kohn variational principle,[4] we have carried out calculations on low energy elastic scattering for antihydrogen atom-hydrogen molecule collisions. The potential energy surface used was constructed from highly accurate *ab initio* energies calculated at over 2800 geometries[5] which we have least squares fit to a functional form using a neural network approach.

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Inelastic Factors in Time-Resolved X-Ray Diffraction (TRXRD)

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Keywords: Scattering, Dynamics, Inelastic, X-Rays, Time-Evolution

We are here presenting a new factor to take into account within the time resolved X-ray diffraction (TRXRD) experiments: the inelastic effects.

Using TRXRD methods we are capable of measuring the evolution of a specific excited state in time by using the X-Ray scattering signal of its wavepacket. Usually, the experiments performed using the TRXRD only take into account the elastic scattering of the X-Rays to measure the position of the molecule in each step of time. This is because the inelastic terms are so small in comparison with the elastic ones and they can be disregarded by using the Waller-Hartree approximation.

However, due to the width of the pulses used, it is impossible to claim that all the interactions between the beam and the molecule will be coherent and elastic. For this reason it is important to calculate these inelastic factors to see if their contribution is remarkable when we perform experiments based in the aforementioned technique.

The method that we employ to obtain these matrix elements defining the inelastic factors is inside the frame of the Ab-Initio calculations of the Scattering factors. That is, we use wavefunctions built in terms of Slater Determinants and Gaussian functions to represent them. The results were compared in the case of atomic Hydrogen with exact wavefunctions showing a strong agreement with this data.

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Posters

P1: Study Of Potential Electron Transfer For A New Range Of Electron Donors For Transition Metal Free Synthesis

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Ever since Itami et al. discovered a transition metal free coupling between haloarenes and electron deficient heterocycles[1] neutral organic electron donors have been utilized in biaryl couplings, with advantages over current techniques that these methods do not utilize costly metal reagents, which contaminate final products.[2]

A new series of donors have been studied computationally using transition state analysis and Marcus-Hush theory[3] to determine whether or not the active donor would be formed and the probability of this being able to donate an electron to the substrate.

The donors have been studied in parallel experimentally and results compared to the computational studies.

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P2: Computational Analysis of the Proposed Allosteric-Activation Mechanism of Bovine Chymosin

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Keywords: chymosin, allosteric-activation, molecular dynamics, residue mobility.

Bovine chymosin is an aspartic protease that selectively cleaves the milk protein κ-casein. In industry the enzyme is extensively used to promote milk clotting for cheese manufacturing. Experimental studies have suggested that the apo enzyme can adopt a self-inhibited form in which the sidechain of residue *Tyr77* blocks the binding pocket. The self-inhibited form is proposed to undergo allosteric activation initiated by a *His-Pro* pentapeptide cluster in the κ-casein protein. Interrogation through computational molecular dynamics simulation have revealed a change in the conformation of *Tyr77* can be seen in the presence of the *His-Pro* cluster. Visual interpretation of the model suggests a repulsive interaction between the enzyme and *His-Pro* cluster results in a movement of *Tyr77* and the adjoining β-hairpin flap in the enzyme to result in the open conformation of chymosin. There is also evidence to suggest *Tyr77* conformation is dependent on the residues of a neighboring α-helix (residues 113-116), which occupies the space where open-*Tyr77* lies.

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P3: A DFT Investigation Into The Mechanism Of The Formation of 1,4-Azaborinines

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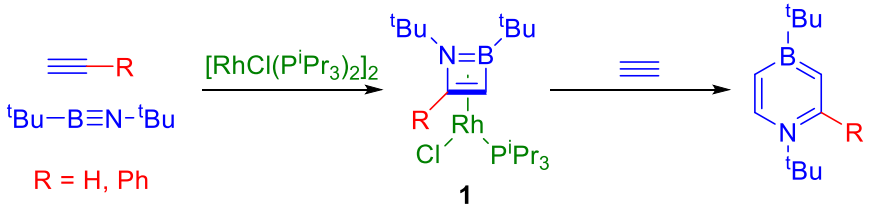
Keywords: Azaborinines, DFT, alkyne, iminoborane,

The synthesis of azaborinines is of interest because the B-N moiety causes different electronic properties to their isoelectronic C-C counterparts as well as their potential application in biomedical research and materials science.[1] Recent experimental work has demonstrated the synthesis of 1,4-azaborinines from alkynes and iminoboranes mediated by $[RhCl(P^iPr_3)_2]_2$.[2] The 1,2-azaborete complex **1**, was observed as an intermediate and could also be synthesised by carrying out the reaction with a single equivalent of the alkyne. Furthermore, with phenylacetylene an interesting regioselectivity is observed with the phenyl group situated next to the nitrogen in the final product.



We have used DFT calculations to investigate the mechanism of the formation of 1,4-azaborinines. We propose the 1,2-azaborete is formed through oxidative coupling of the bound acetylene and iminoborane to form a 5-membered rhodacyclic intermediate. This then undergoes N-C reductive coupling to form **1**. The 1,4-azaborinine is then formed through oxidative cleavage of the B-N bond before co-ordination and migratory insertion of the 2nd alkyne into the Rh-B bond. This forms a 7-membered rhodacycle from which reductive coupling forms the 1,4-azaborinine.

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P4: Binding Properties of the GBP1 Peptide to Gold

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Keywords: Molecular Dynamics, Free Energy, Peptides, Surfaces

Gold binding peptides have been successfully employed in the synthesis of gold nanoparticles; one of the first sequences to be identified for its gold-binding properties was MHGKTQATSGTIQS, known as GBP1.[1] Previous theoretical studies on GBP1's binding affinity have focused on examining the contribution of the individual amino acids[2] or, alternatively, the binding potential energies of the full peptide have been calculated through a thermodynamic cycle, which are unable to capture the entropic contributions and neglect the dynamic nature of the system. Here we utilize non-equilibrium thermodynamic integration (NETI)[3] with steered molecular dynamics (SMD) to compute the binding free energy of GBP1 with the Au (111) surface. Through strategic mutation of polar residues, we demonstrate the importance of considering the peptide as a whole (rather than the sum of the individual amino acids), as the binding strength of hydrophilic amino acids can change depending on their environment.

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ScotCHEM 2015

P5: 5- vs. 6-Membered Ring Formation in the Rh-Catalysed Coupling of Imines with Alkynes

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Keywords: C-H activation, functionalization, DFT, mechanisms, catalysis.

1-phenyl-*N*-R-methanimines (R = *i*Pr, *p*-tolyl) can undergo Rh-catalysed C-H functionalisation to give a range of organic products (Figure 1.).[1,2] The mechanism of the formation of these different heterocycles was investigated by DFT calculations in conjunction with experimental studies. The most accessible reaction pathway proceeded with C-C bond formation to form 5-membered rings, or C-N coupling to form 6-membered heterocycles. In acetic acid, protonation then leads to the indenamine, whereas with $Cu(OAc)_2$ a second acetate-assisted C-H activation gives indenimine.

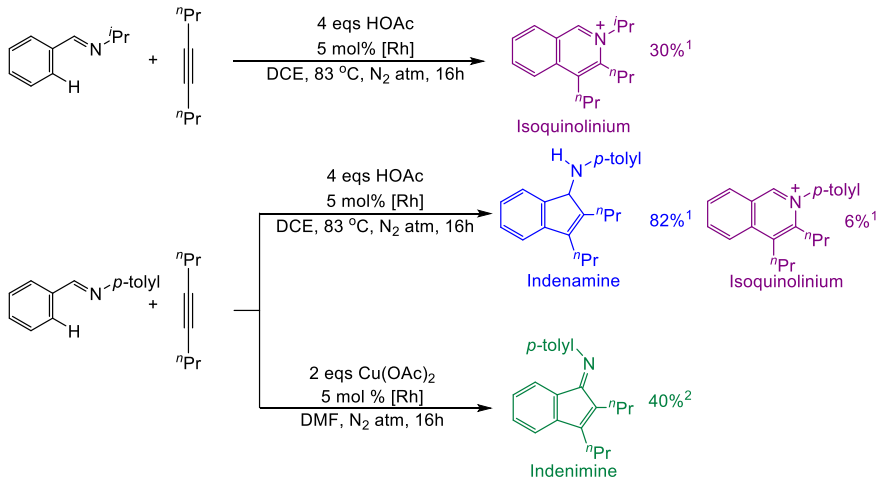

Figure 1. Experimental results for Rh-catalysed heterocycle formation.

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P6: Docking Novel Ratiometric Sensors for Guanine Quadruplex Structures

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Keywords: Molecular docking, Molecular dynamics, G-quadruplex

G-quadruplexes are non-canonical nucleic acid structures made up of stacked guanine tetrads (or G-quartets), composed of four Hoogsteen hydrogen-bonded guanines arranged in a cyclic fashion. G-quadruplexes have emerged as an attractive target for which to design site-specific drugs. Guanine-rich sequences, known to form polymorphic quadruplexes, can be found in the promoter regions of oncogenes, introns and human telomeres. A direct association of the formation of G-quadruplexes with the suppression of gene expression has been found [1]. Here, we report a docking study to predict the binding mode of *2-(2'-hydroxyphenyl)-3H-imidazo[4,5-b]pyridine* (HPIP-b), a fluorescent sensor, to G-quadruplex [2]. HPIP-b is the only known dual-wavelength ratiometric fluorescent sensor that binds to G-quadruplexes. Experimentally, HPIP-b behaves as an excited-state proton transfer probe and displays stronger interactions with the G-quadruplex than with single- or double-stranded DNA (dsDNA) [3]. In this study, firstly periodic boundary molecular dynamics was carried out to sample the conformational space of the targeted 22-mer telomeric parallel G-quadruplex, prior to the docking step. We then used Autodock 4.2.6 to perform dockings of HPIP-b to five snapshot structures of G-quadruplex extracted every 200ps from a 1ns production run. After that, two-layered ONIOM DFT/PM6 calculations were set up to assess the binding of HPIP-b to the G-quadruplex in the top ranking docked poses. We applied the same methodology to dsDNA and compared the predicted binding modes of HPIP-b to the G-quadruplex and dsDNA. This work yields a starting point for the design of lead compounds or of new G-quadruplex-specific probes.

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P7: Sum-over-states Property Calculations Using Monte Carlo Configuration Interaction

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Keywords: Polarizability, Hyperpolarizability, Monte Carlo, Configuration Interaction, Multireference.

It has been demonstrated[1] that multipole moments for a range of small molecules could generally be calculated to sufficient accuracy using Monte Carlo configuration interaction (MCCI).[2,3] These calculations only used a very small fraction of the full configuration interaction (FCI) space and could be implemented, even if the system was deemed to be multireference, without the need for chemical intuition. However the calculation of higher-order properties is more challenging, particularly for a stochastic method, when using derivatives up to fourth order in the energy with regards to the electric field.

We use state-averaged MCCI[4] for a small number of excited states to produce a tractable set of configurations that can capture enough of the ground and excited state aspects of the FCI wavefunction. We then investigate the use of these configurations in computationally viable sum-over-states calculations[5] for polarizabilities, hyperpolarizabilities and second hyperpolarizabilities. Results for a selection of small molecules, including those with wavefunctions considered multireference, are compared with other approaches including response methods.

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P8: Exploring the Self-Assembly Potential of Charged Aromatic Tripeptides

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Keywords: Self-assembly, tripeptide, molecular dynamics, coarse-graining

Self-assembly is governed by the tendency for molecules to spontaneously aggregate as a result of weak inter-molecular interactions to form various nanostructures. It has been shown that aromatic groups can promote aggregation[1] through the hydrophobic effect and π-stacking. In addition, charged amino acids can influence self-assembly through Coulombic interactions.[2]

In this work, the self-assembling properties of tripeptides containing both charged and aromatic residues are investigated to understand the nuances that shape aggregation of these species. Through coarse-grained molecular dynamics simulations and aggregation propensity algorithms, we explore the design landscape of more than 300 tripeptide mixtures through their ability to form nanostructures. The successful combinations will be tested further for suitability in industrial applications such as cosmetics and pharmaceuticals.

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P9: DFT Investigations and Improvements of Methyl Methacrylate Formation with Homogenous Pd(P,N) Complexes

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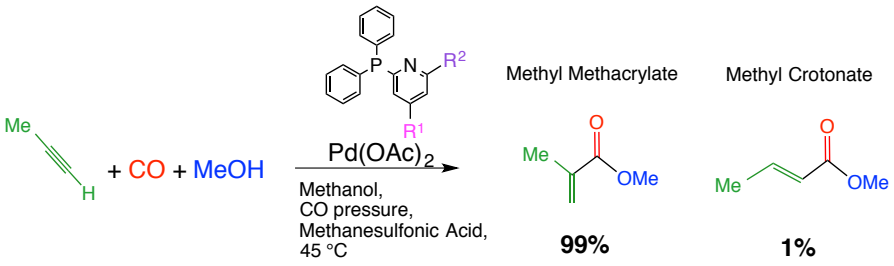
Keywords: density functional theory, homogenous catalysis, regioselectivity, ligand design, palladium

The methoxycarbonylation of propyne is a 100% atom efficient transformation for the production of acrylate esters. Using palladium tempered by hemilabile P,N ligands this reaction can achieve rapid turnover as well as high selectivity (>99%) for the branched product, methyl methacrylate (MMA)[1] (Scheme 1) the polymer of which is an important component in LCD displays and has a range of other uses.



Scheme 1: Production of MMA with Pd(P,N) complexes

Through density functional calculations we have found that an in-situ base mechanism wherein the hemilabile ligand acts in a co-catalytic fashion is the most congruent with experimental data. Our computations also furnished atomistic insight into subtle ligand changes that improve selectivity and may result in greater turnover[2,3]. We now report on the effect of modifications to the pyridyl ring – at locations R^1 and R^2 (Scheme 1) – and detail a new ligand structure we predict to increase regioselectivity and vastly improve turnover. The substrate scope of the final terminating step is also examined with and without this modification.

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P10: Alternative Bond Formations For Transition Metal-Free Reaction Conditions – BHAS *vs.* $S_{RN}1$ Pathways

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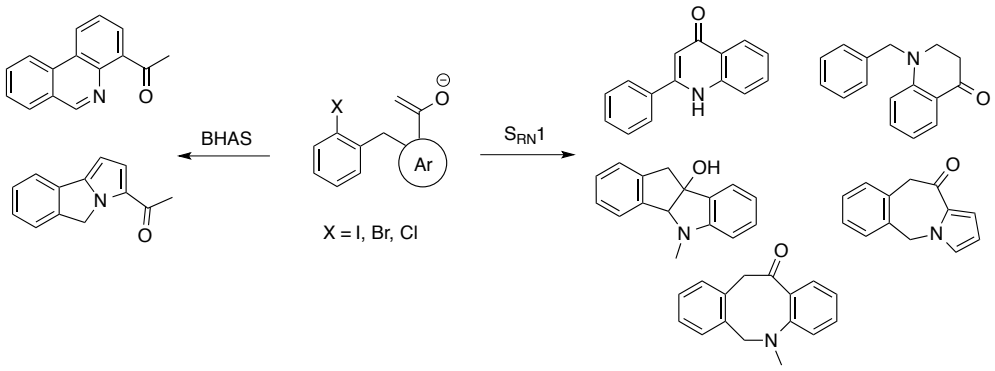
Keywords: free radicals, BHAS, $S_{RN}1$, cyclisations, DFT

Recently there has been an explosion of interest in the mechanism and scope of KOtBu-promoted C-C bond formations that are either $S_{RN}1$ reactions[1] or base-promoted homolytic aromatic substitutions.[2] Rossi *et al.* provided photoactivated approaches to $S_{RN}1$ reactions[1a] and this poster now compares the outcomes for similar substrates in polar and non-polar solvents under non-photoactivated conditions. Marked differences are now reported for some reactions, and new types of products identified and reaction mechanisms proposed, supported by computational analysis.[3] The success, direction and scope of these reactions are shown to depend crucially on the reaction conditions and on the mode of activation.



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P11: Towards molecular electronics: Inducing on-demand final-state control in a metal-bound single-molecule switch

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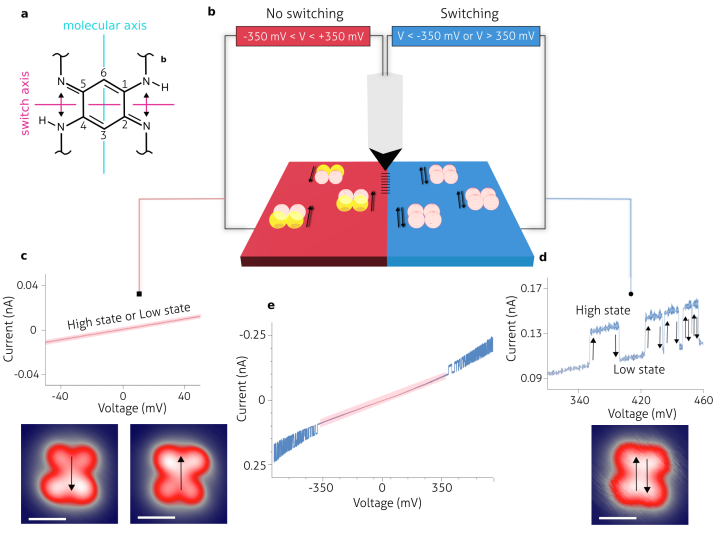
A potential end-point in the miniaturization of electronic devices lies in the field of molecular electronics, where molecules perform the function of single electronic components. Molecular switches display stability in two or more states[1,2]. To date, H-tautomerism in surface-bound molecular switches has only been observed in the macrocycle system of a porphyrin-type molecule[3,4]. The present work reveals how H-tautomerism is the mechanism for switching in substituted quinone derivatives[5] – a novel class of molecules with a different chemical structure.
STM measurements are carried out at 5K on azophenine - a prototypical quinone derivative. When adsorbed on a Cu(110) surface, the molecular switch remains in one of two stable H-tautomeric states and can be made to switch between them, at will, by applying a bias exceeding a threshold voltage of approximately 0.35 eV. Activation energy of the process is measured and shown to be induced by inelastic electron excitations. This property is retained upon functionalization by the addition of side groups, meaning that the switch can be chemically modified to fit specific applications.



Central functional unit of AP (a). Schematic switching behaviour of AP molecules depending on the bias applied (b). Recorded spectra while the molecules are stable (c) and switching (d), STM images of AP (bottom) at

By combining microscopy with single-molecule spectroscopy and theoretical calculations, we present two strategies (we demonstrate one experimentally, and

postulate the other one based on logical arguments) to allow for on-demand final-state control in our molecular switch whilst maintaining its bistability, without the need of an external perturbation source to the double-umbrella potential well[6].

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P12: An Investigation into Competition Between Halogen Bonding and Hydrogen Bonding in Microsolvated 1-methyl-5-halouracil

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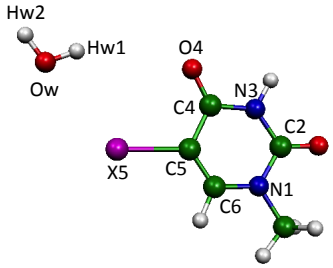
Keywords: Halogen bonding, DFT, microsolvation, 1-methyl-5-halouracil, hydrogen bonding



This investigation focused upon interactions between a 1-methyl-5-halouracil molecule and a single water molecule. In particular, X5-Ow (sigma hole), X5-Hw1, and O4-Hw1 interactions were the principal focus of this study. The geometries and interaction energies of minima stabilized by O4-Hw1 or X5-Ow interaction, and the transition state between those two minima were elucidated, allowing the strength and geometric influence of the halogen bonding and hydrogen bonding type interactions to be probed. This study was conducted for each of the five halogen elements, from fluorine to astatine inclusive. All calculations were performed using the M06-2X density functional with either the 6-31+G* basis set (for X=F, Cl, or Br) or the aug-cc-pVDZ-PP basis set with relativistic pseudopotential (for X=I or At). Full geometry optimisations were performed on the stationary points using the counterpoise correction procedure. Halogen bonding minima were found for X=Br, I and At, but not for X=F or Cl. Where halogen bonding was present, its strength increased down the halogen group.

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P13: High-Pressure Experimental and DFT-D Structural Studies of the Energetic Material FOX-7.

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Keywords: DFT-D, FOX-7, high pressure, neutron powder diffraction, Inelastic Neutron Scattering.

This work reports the hydrostatic compression of the perdeuterated α-form of FOX-7 using neutron powder diffraction to follow the structural changes up to 4.58 GPa at room temperature. The equation of state for the hydrostatic compression of the α-form over the range 0 – 4.14 GPa has been determined and a phase transition was observed over the pressure range 3.63 - 4.24 GPa. On the basis of dispersion-corrected density functional theory (DFT-D) calculations performed on the γ-form over a range of pressures, the high-pressure form observed in the neutron diffraction experiments can unambiguously be identified as being different from the γ-form and should therefore be denoted as the ε-form. Based on similarities between the simulated and experimental powder diffraction patterns of the γ- and ε-forms, it is suggested that the ε-form adopts a planar, layered structure.[1]

The structural responses to pressure of the α-form observed experimentally are reproduced by DFT-D calculations, but in-depth analysis of the bond lengths, angles, dihedrals, and vibrational frequencies calculated in the DFT-D simulations identified a very subtle second-order phase transition at 1.9 GPa. This corroborates results obtained from previous far- and mid-IR vibrational spectroscopic studies.[2-6] These very small changes in molecular geometry do not manifest themselves in either the measured or calculated lattice parameters or unit-cell volumes, and are much smaller than can be detected by diffraction experiments. The results of phonon calculations were compared with experimental inelastic neutron scattering measurements and were used to investigate the effect of pressure on the heat capacities of α-FOX-7. The simulations predict very weak pressure dependencies (approximately -1 J K^{-1} mol^{-1} GPa^{-1}), in accordance with the conclusions reached in our previous studies of the energetic material RDX.[7]

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P14: DFT Study of Selectivity and Mechanism in the Au(I)-Catalysed Direct Etherification of Allylic Alcohols

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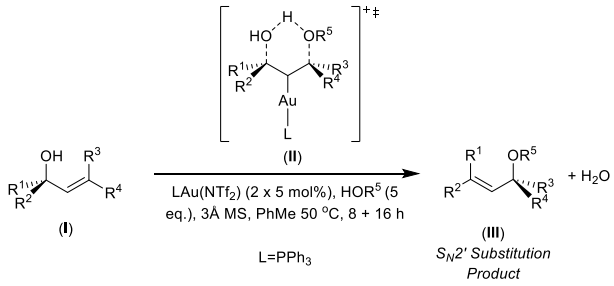
Keywords: Gold, computational, chiral, transfer, regioselectivity

The Lewis-acidic Au(I) centre is known to activate carbon-carbon multiple bonds allowing for nucleophilic attack, with previous work investigating the regioselective etherification of allylic alcohols with O-based nucleophiles[1] as well as thioetherification with S-based nucleophiles.[2] These processes both involve a formal S_N2' nucleophilic substitution with C-O (or C-S) bond formation at the C3 position (cf. **III**).



These S_N2' reactions are thought to proceed *via* a 6-membered intermediate (or transition state) such as **II**, involving proton transfer and loss of water. Under this mechanism enantiopure starting materials will react with transfer of chirality.[3] This result was seen in experiments with a range of enantiopure substrates, often showing excellent (>90% ee) chiral transfer. However it was noted that this outcome only occurred in the presence of molecular sieves that were also found to improve the reaction efficiency. In the absence of the sieves racemization occurred with most substrates.

This poster shall report on the DFT investigation of the mechanism of direct etherification and the potential reasons for the loss of the expected chiral transfer.

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P15: Determining Potential of Zero Charge from Density Functional Theory based Molecular Dynamics

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Keywords: PZC, Pt(111)/water interface, DFTMD, bulk water, CP2K/Quickstep

The potential of zero charge (PZC) is the potential at which no excess charge exists on the surface of the electrode. As a fundamental property of the electrode, PZC specifies the position where the electrical capacitance obtains its minimum, thus, determining the PZC has become a key requirement for studying the double layer phenomenon and other electrochemical processes occurring in the solid/liquid interfaces.[1]

This project aims at determining the PZC of the Pt(111)/water interface and understanding the effects of water orientation and charge redistribution on the workfunction of Pt(111) surface. We present a new method that couples the insertion of an electron to an electrode with the addition of a proton to the bulk water, the H^+ serves as the reference ion in this system so that we can directly estimate the PZC vs. SHE.

The Pt(111)/water interface is modelled by periodic Pt(111) 6 × 6 supercell slab of 4 atomic layers with fully filling the water molecules in between. The whole model contains 144 Pt atoms and 151 water, the density of the bulk water is 1 g/cm^3. Born Oppenheimer DFTMD simulations are carried out by the CP2K/Quickstep package, employing Perdew-Burke-Ernzerhof (PBE) functional to describe the exchange correlation effects.

The PZC of Pt(111)/water interface is determined to be 0.22 V after 5 ps simulation, which reproduces the experimental results[2,3] with a small uncertainty. We also find the charge-transfer phenomenon between Pt and water decreases the workfunciton of Pt(111) surface, while the water orientation has the opposite effect. In conclusion, a new method is developed by us to determine the PZC of the Pt(111) electrode in water, it gives an quite accurate result and avoids the expensive computation cost. In the future work, this method will be further applied to calculate the pK_a of the interfacial water and the capacitance of the electric double layer.

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P16: UV-Vis Spectra Of Methylene Blue Intercalated Between Specific DNA Base Pairs

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Keywords: DNA, Dyes, TD-DFT, Methylene Blue, Quantum Chemistry

Small Heterocyclic dyes are known to bind to polyanions through different mechanisms, which include π-stacking and electrostatic attraction. MethyleneBlue (MB) is a planar, aromatic cation, and as such intercalation between the base-pairs of DNA is a probable mechanism for its binding to this structure.[1] MB has many uses in both biological and non biological systems, which have been extensively studied.[2,3] However, its ability to intercalate between base pairs and the effect that this intercalation may have on the absorption spectra of the dye is not well-understood. Through the use of DFT ground state optimisations and TD-DFT excited state calculations, we aim to determine whether the intercalation of MB into DNA base pairs shifts the UV-VIS spectrum of the dye. Moreover, we establish whether there is an effect of the DNA sequence on the observed shift and as such, whether MB may be used as a probe in determining DNA sequences.

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P17: The Development of a Novel Force Field Based on Quantum Chemical Topology

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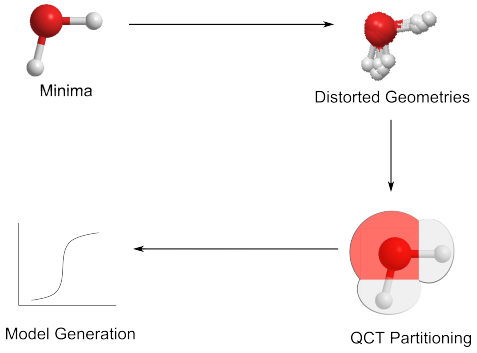
Keywords: Quantum Chemistry, Force field, Machine learning, Kriging

The Quantum Chemical Topology Force Field (QCTFF) is a novel polarizable force field combining rigorous quantum chemistry and machine learning. The force field is constructed from a bottom up approach with quantum chemistry providing a rigorous physical foundation. Quantum Chemical Topology (QCT) is used to define a molecule as a group of atomic basins with well-defined boundaries and hence energetics. Machine learning, using a method known as Kriging, is used to build models capable of predicting energetic changes as a function of the molecular geometry. Training data are provided to the Kriging method in the form of QCT energy contributions and geometries. A number of geometries are provided from normal mode distortions around a minimum. The figure below expounds this process.[1]



The method has been used successfully for a number of systems and energetic contributions.[1] Our current work focuses on extending this method for dynamic correlation, enabling the natural inclusion of correlation effects in a molecular forcefield. To this end we are developing the QCT program MORPHY01[2] to accurately capture dynamic correlation in the framework of QCT. Our final goal will be to apply machine learning to the dynamic correlation terms hence, enabling their prediction and inclusion as a function of atomic coordinates.

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P18: Hydration Thermodynamics of Small Organic Molecule using 3D RISM

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Keywords: Free energy, solvents, integral equations, chemical potential, correlation functions.

Hydration free energy, ΔG_{hyd}, is one of the most important properties in solution chemistry. It provides information about the equilibrium partitioning of a solute between gas and solution phases and, in computational chemistry, it is used in calculating properties such as solubility, acid-base dissociation constant, octanol-water partition coefficient, and protein-ligand binding free energy. We have developed a new model for computing hydration free energies based on the 3D Reference Interaction Site Model (3D-RISM) [2]. The new adjustment to 3D-RISM theory significantly improves hydration free energy predictions for various classes of organic molecules at both ambient and non-ambient temperatures. An extensive benchmarking against experimental data shows that, at least for uncharged compounds, the accuracy of the model is comparable to (much more computationally expensive) molecular dynamics simulations. The simulation protocol has been automated and a script is available on the web [3].

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P19: Computational Study Of Methylene Blue Aggregation

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Keywords: Methylene Blue, Aggregation, Dimers, Trimers, UV-Vis

Methylene blue is a compound commonly used as a stain or a dye.[1]The aggregation of methylene blue is computationally studied by UV-Vis spectroscopy in order to obtain shifts for the dimer and the trimer form of the dye. The spectra will allow to determine which form of the dye (in other words how it aggregates) is present inside the solution. In aqueous solution an equilibrium exists between the monomeric and the dimeric forms of methylene blue.[2] Firstly, dye aggregates are studied to determine which geometry is favored for the dimer, binding energies show that there is an equilibrium between the H and the J type aggregates in aqueous solution. Subsequently, trimers systems are then studied in the same way. UV-Vis spectra are compared to the experimental data from previous studies of methylene blue.

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P20: Using AIRSS To Probe Structural Disorder In Hydrous Fe-Free Wadsleyite, $Mg_{2-x}H_xSiO_4$

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Keywords: AIRSS, DFT, NMR, Materials

Wadsleyite makes up most of the Earth's transition zone and has the potential to act as a vast hydrogen reservoir. The inclusion of hydrogen, as hydroxyl groups, is charge balanced by the removal of Mg. With three distinct Mg sites in the structure and a number of possible substitution positions, despite extensive previous experimental studies,[1,2] the exact mechanism of hydrogen incorporation in Wadsleyite remains elusive. Though theoretical studies have also proved inconclusive,[3,4] *ab initio* random structure searching (AIRSS)[5] could represent a new approach for the structural investigation of hydrous Wadsleyite, particularly when combined with the subsequent DFT calculation of NMR parameters using codes such as CASTEP.[6]

Here, we present an AIRSS-based investigation into the structure of Fe-free Wadsleyite containing the equivalent of 1.6 wt% H2O. Initially, three series of structures were generated using AIRSS, with one Mg1, Mg2 or Mg3, respectively, being replaced by two hydrogen atoms per unit cell. The lowest energy structures were those with an Mg3 vacancy, with many structures with Mg1 and/or Mg2 vacancies being noticeably higher in energy. In the lowest energy structures, both hydrogen atoms were bonded to O1 sites close to the vacant Mg3 site, however, a series of alternative substitution sites, only slightly higher in energy were also observed. The predicted NMR parameters for these model structures were compared to previous experimental work, correlating well with a study of hydrous Fe-free Wadlseyite containing 3.3 wt% H2O, where structures with an Mg3 vacancy were also found to be the most energetically stable.[1]

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P21: Enzymatically Triggered Interfacial Nanofibre Networks as On-demand Stabilised Emulsions

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Keywords: Nanostructures, Self-Assembly, Peptides, Enzymatic, Emulsions

The biocatalytic self-assembly of Fmoc (9-fluorenylmethoxycarbonyl) dipeptide amphiphiles in aqueous/organic mixtures was used to create on-demand emulsifiers. An alkaline phosphatase was used to transform phosphorylated precursors into self-assembling aromatic peptide amphiphiles (Fmoc-tyrosine-leucine, Fmoc-YL), providing a route to trigger self-assembly of nanofibrous networks and gels. When in biphasic organic/aqueous systems, these networks form preferentially at the interface. This gives rise to the possibility of on-demand activation of emulsifying ability, producing switchable emulsions that may be activated by enzyme addition, even after storage of the biphasic mixture for several weeks. Experimental (Fluorescence and FTIR spectroscopy) and computational techniques (Atomistic Molecular Dynamics) are combined to show that the self-assembly process of Fmoc-YL occurs through aromatic interactions and hydrogen bonding to generate a nanofibrous network at the water/organic solvent interface.

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P22: Correlated Electronic Structure Approaches to the Excited States of TiO_2 Clusters

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Keywords: TiO_2, photochemistry, coupled cluster response theory, excited states

A thorough analysis of the singlet excited states of $(TiO_2)_n$ nanoclusters has been performed using linear response coupled cluster (CC) theory and equation-of-motion coupled cluster methods (EOM-CC), together with time-dependent density functional theory. The excitation energies of the low-lying electronic states are presented along with the oscillator strength of each excited state, the permanent electric dipole moment of each state, and the second moment of charge in order to characterize each state. The major orbital contributions of each excited state are also presented as determined by the response. We find major issues with reduced computational cost 2^{nd} order approaches such as CC2 for excitation energies that are not present for organic molecules, although molecular properties fair better. We are able to draw conclusions on convergence of excited state properties in terms of systematic electron correlation through the CC response hierarchy as well as one-electron basis set, and further to look at the physical convergence of these properties with cluster size.

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P23: Quantum Mechanics Study On PVDF (Poly-Vinylidenefluorine) Using DFT Theory And Van Der Waals Interactions

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Keywords: DFT, PVDF, Quantum Espresso, van der Waals, Molecular Dynamics

Several studies about PVDF where conducted to the Quantum Mechanics (QM) level, to understand the fundamental properties of this polymer, with different methods of calculation implemented in different software package like Hyperchem, Chemsoft, Material Studios and TeraChem, using different computational approach more or less far from the complete Schr¨odinger equation as MP2, DFT, BLYP, B3LYP and others (Broadhurst 1978, Bystrova 2013). What is still missing in computational research is an exhaustive study on PVDF taking account of Van Der Waals (vdW) interaction. DFT is the QM theory of calculation used in this project, where the use of vdWis planned and implemented, so technically possible. Putting vdW into the calculation process could be the last missing piece of force interaction calculation for being able to define the physical and chemical properties of PVDF. Thanks to the high electronegativity between fluorine and hydrogen, PVDF has a strong dipole moment that rise to ferroelectricity, piezoelectricity and pyroelectricity properties of this polymer [3]. A modelling study using DFT with vdW calculation on how the four phases of PVDF (a-b-d-g) interact with metals clusters and metals surfaces will be conducted [2]. The well known and unwanted property of PVDF that makes its crystallinity so low (transition glass temperature of -50ºC) at room temperature, could be better investigated with vdW interaction, giving more accurate data to be used in further computational research study. The interest beyond this polymer is mainly due as memory storage units [1], but many other application like energy harvesting, actuators, microphones, sensors, speakers, artificial muscles are under investigation, or already investigated.

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P24: Can Supramolecular Gel Be At Thermodynamic Equilibrium?

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Keywords: Gels, supramolecular, amphiphiles, thermodynamics, packing.

Low Molecular Weight Gelators are able to form nanostructure, typically fibres, which may entangle to form gel-phase materials, with a wide range of applications in biomedicine and nanobiotechnology. The possibility of changing their properties with simple modifications of their chemical structure along with their ability to form the final structures spontaneously in certain conditions through self-assembly makes them promising new materials. However, there is currently a significant disagreement on the thermodynamic nature of these systems - it is not clear if these structures are metastable states which do not allow the system to reach the actual thermodynamic minimum which is thought to be the crystalline state or if they can represent the global thermodynamic minimum. The metastable nature of gels is argued with the fact that a 3D extended structure (crystals) will be able to form more interactions than a 1D structure (fibres). This is supported by packing models based on spheres. In this study we propose a simple packing model based on prisms with faces of different nature to model the amphiphilicity of these molecules to demonstrate that this characteristic allows a 1D extended structure to be the global thermodynamic minimum. The model is developed based on experimental evidence and it depends on parameters which can be easily related with features of the amphiphiles and the system. We conclude that while many gels are metastable structures due to the restricted molecular dynamics in the gel state, one-dimensional fibres can represent thermodynamic equilibrium. This conclusion has critical implications for the theoretical treatment of gels.

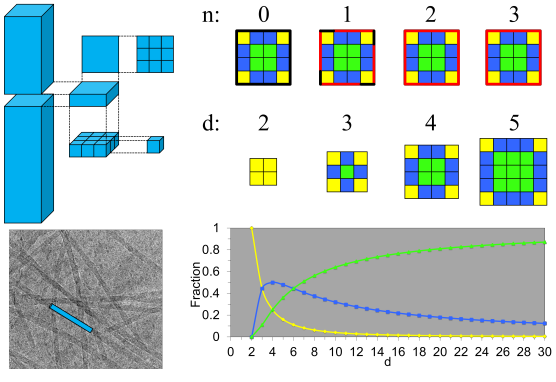

FIGURE 1. MODEL SCHEME, FROM FIBRES TO THE UNITS (LEFT) AND THE CROSS SECTIONS AS A FUNCTION OF *N* (SHOWING SOLVOPHILIC SURFACE IN RED AND SOLVOPHOBIC SURFACE IN BLACK) AND AS A FUNCTION OF *D* (RIGHT). THE CROSS SECTIONS SHOW BURIED UNITS IN GREEN, UNITS ON THE FIBRE FACES IN BLUE AND UNITS IN THE FIBRE EDGES IN YELLOW (M_{MAX}). THE GRAPH SHOWS THE EVOLUTION OF THE FRACTIONS OF THE DIFFERENT UNITS AS A FUNCTION OF *D*.

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P25: Discovery of Tri-peptide Emulsifiers Using Combined Computational Screening and Experimental Validation

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Keywords: Coarse-grained, peptide, self-assembly, emulsions

Peptide nanomaterials are an important class of material for the food, cosmetic and biomedical industries. Unfortunately, the self-assembling nature of peptides is often hard to predict. The use of very short (e.g. di- and tri-) peptides has advantages of cost, scalability and rational tenability however have been largely restricted to hydrophobic dipeptides, such as FF.[1] We previously reported the use of coarse-grained molecule dynamics (CG MD)[2-3] as a tool to predict self-assembly behaviour, which led to the discovery of a new class unprotected tripeptide gelators: KYF, KYY, KYW and KFF. The focus of the current work is to further develop this tool coarse-grained molecular dynamics to show that the introduction of organic solvents will allow the creation of emulsified systems. Results show that these tripeptide molecules can act as surfactants, where they assemble at the interface between the octane and water. Experimental methods, such as confocal microscopy, can allow the tracking of these systems, where labelling of the organic solvent with a fluorescent dye allows visualisation of the emulsion system. In addition, spectroscopic analysis (FTIR, fluorescence) is used to assess the peptide arrangements in the emulsions. We have therefore shown that CG MD can also be used for the identification of new emulsifiers comprised wholly of short unprotected peptides.

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P26: First principles static and dynamic calculations for the transition metal hydride series MH_4L_3 (M = Fe, Ru and Os; L = NH_3, PH_3 and PF_3)

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Keywords: Transition metal, hydrides, DFT, molecular dynamics, fluxionality.

Transition metal (TM) hydrides are at the heart of many chemical reactions that have found particular interest in catalysis, *e.g.* for the generation of molecular hydrogen from low molecular weight organic molecules, which is of great interest in the context of the hydrogen economy. For instance, [**Ru**H_4(**PPh$_3$**)$_3$] is a very efficient catalyst for hydrogen generation from alcohols.[1-3]

Herein, we present a first principles static and dynamical study of the transition metal hydride series **M**H_4**L**$_3$ (**M** = Fe, Ru and Os; **L** = NH_3, PH_3 and PF_3), with a view to arriving at an understanding of how the variation in the electronic properties of the metal sites and ligands can influence the dynamics of the resulting complexes. A broad range of behaviour was observed, encompassing stable classical minima (**M** = Os, **L** = NH_3 and **M** = Ru, **L** = PH_3) to stable η^2-H_2 non-classical minima (**M** = Fe, **L** = PF_3 and **M** = Ru, **L** = PH_3 or PF_3), with the other structures exhibiting dynamical behaviour that spontaneously converted between the classical and non-classical states during the molecular dynamics simulations. The importance of a small $\mathbf{L_{axial}}$–**M**–$\mathbf{L_{axial}}$ angle in stabilising the non-classical state is highlighted, as is a short η^2-H_2···H_{cis} distance in non-classical complexes that spontaneously convert to the classical form. We also investigated the changes in the electronic structure of the complex **Fe**H_4(**PH$_3$**)$_3$ during a η^2-H_2 bond breaking/bond making reaction and observed direct evidence of the 'cis effect', whereby a neighbouring hydride ligand acts to stabilise the intermediate classical state.[4]

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P27: A Computational Study of Matrix Metalloproteinase1Enzyme and its Mutants

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Keywords: Molecular Dynamics, enzymes, Structural Refinement, MMP1

MMP1 is involved mainly in degradation of collagen. The crystal structure of catalytically inactive mutant (E200A) of MMP1 complex with collagen molecule has recently been solved by [1] (Figure 1). The crystal structure consists of N terminal Catalytic domain (Cat), C terminal Hempexin domain (Hpx) and linker region comprising of sixteen amino acids residues which connect Cat and Hpx domain of MMP1 [1]. In spite of enormous research on collagenolysis there are still some open questions such as (1) how two domains of MMP-1 interact with collagen peptide, followed by destabilization and cleavage of collagen (2) detailed reaction mechanism of MMP-1. In order to provide understanding on the structure function relationships of this enzyme, we performed 300 ns molecular dynamics simulation on the wild-type MMP1 and 100 ns simulation on seven mutants. In this study we investigated the protein dynamics, flexibility of the linker region and the possible impact of the mutations on the protein structure and its function.

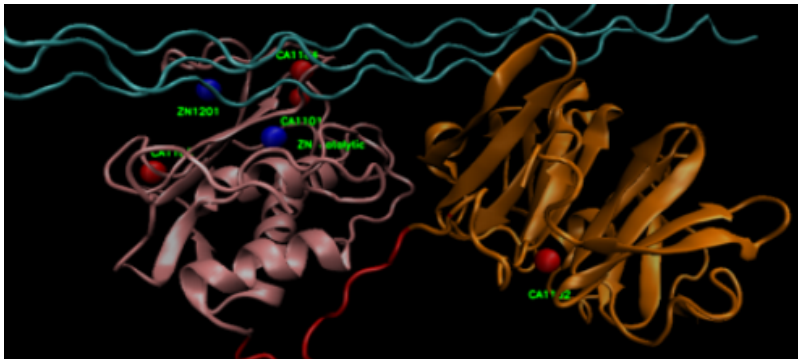

FIGURE 2 THE 3-D STRUCTURE OF WILD TYPE MMP-1 ENZYME. THE CAT DOMAIN OF THE ENZYME IS REPRESENTED IN PINK COLOUR AND THE HPX DOMAIN IN ORANGE COLOUR IN NEW-CARTOON REPRESENTATION USING VMD. THE LINKER REGION BETWEEN TWO DOMAINS IS SHOWN IN RED COLOUR FOLLOWED BY TRIPLE COLLAGEN MOLECULE IN CYAN COLOUR. THE

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P28: Cumulative Radial Distribution Functions of Organic Hydrates and Their Potential Applications

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Keywords: RDF, Organic, Hydrates, RISM, Solvation

Here, we present an example of a method development process with potential applications in solubility prediction, using large datasets of organic hydrate crystal structures. 3D-RISM models solution phase systems with classical statistical mechanics, and provides a half-way house between expensive explicit solvent models and inaccurate implicit solvent methods. This method relies on the calculation of site-site interaction potentials between solute and solvent. A number of functionals have been developed to allow a reasonable calculation of HFEs; however these methods have often proved to be biased from experimental data, with large standard deviation errors.

In order to improve errors associated with experimental bias, we have developed a method to extract large amounts of meaningful information from existing experimental data. Namely, we calculate radial distribution functions (RDFs), describing the probability of finding atom pairs as a function of distance. Atom typing is performed by an external routine, utilising a popular descriptive algorithm used primarily in describing protein environment, known as the AMBER forcefield. Application of these experimentally derived distribution functions to 3D-RISM may improve the quality and accuracy of solubility prediction with a traditionally theoretical method.

The use of popular atom typing algorithms and widely accessible datasets obtained from the CSD mean the information extracted and methods used are reproducible, allowing a multitude of potential applications; ranging from small molecule and protein crystallography to a variety of potential machine learning methods, all aimed at improving how we interpret and apply the large amounts of experimental data available to us as computational chemists.

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P29: Understanding Spectral Signatures of Cancerous Disease States

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Keywords: Cancer, Spectroscopy, 2D-correlation, Random Forest, Diagnostics.

Cancer is a leading cause of death and suffering across the modern world. Approximately 14 million new cases and 8.2 million deaths attributed to cancer occurred in 2012[1]. It is important that we have methods to quickly and easily diagnose various cancers, to ensure the best treatment is provided for patients. There are very few single medical tests (either in development, or in the clinic) which can distinguish between different types of cancerous disease states. We aim to provide new diagnostic methodology to address this problem. In order to achieve this, we have used IR data from serum samples, and applied various statistical methods to find distinguishing spectroscopic features between patients with differing diagnoses. Specific methods employed include Random Forest[2], and generalised 2D-correlational analysis[3]. From our dataset of 433 patients, we have identified several of these distinguishing features. The short-term aim for the project is to pin down what is causing these differences, using chemical reasoning. Following that, the development of a new clinical methodology for cancer diagnosis is the goal.

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P30: Enhanced Iridium(I) Complexes Bearing NHC-P Chelating Ligands: Synthesis, Activity and Application in Organic Processes

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Keywords: iridium, DFT methods, NHC-P ligands, HIE, percent buried volume.

The use of transition metals in the direct activation of C—H bonds represents a promising and very desirable method to perform transformations in organic chemistry.[1] Following our interest in the application of iridium(I) complexes as catalysts in selective hydrogen isotope exchange (HIE) reactions of compounds with pharmaceutical and biological relevance under mild conditions,[2] new systems were envisioned. Thus, iridium complexes bearing chelating ligands featuring phosphine substituted *N*-heterocyclic carbenes (NHC-P) were synthesised and theoretically evaluated using DFT methods. The percent buried volume model[3] was applied to assess steric hindrance around the metal centre, and its validity for chelating systems was scrutinised. Mechanistic evaluations on HIE and decarbonylation processes employing a simplified ligand set with benzaldehyde as a model substrate were conducted. Structure optimisation for intermediates and transition states were performed and notably low activation energies of 10.8 kcal mol^{-1} (13.3 kcal mol^{-1} for full ligand set) were determined, suggesting promising activity for the studied complexes in the activation of C—H bonds. Finally, insights into the solution behaviour of iridium(III) bis-hydride complexes were gathered by direct comparison of experimental ^{1}H NMR shifts and calculated shielding tensors of relevant structures. In summary, diverse theoretical evaluations on novel iridium(I) NHC-P complexes were performed and special attention was dedicated to the collection of physical chemical parameters in order to develop models to rationalise reactivity and behaviour of such species.

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P31: EPSRC UK National Service For Computational Chemistry Software

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Keywords: Mid-range Facility, Hardware, Software, Training, workshops

The EPSRC UK National Service for Computational Chemistry Software (NSCCS) at Imperial College London provides access to software, specialist consultation, computing resources and software training to support UK academics working across all fields of chemistry.

The NSCCS hardware is based and managed by our partner at the Rutherford Appleton Laboratory (RAL) of the Science and Technology Facilities Council (STFC). The NSCCS Cluster is called Slater. Slater is a 512-cores SGI UV 2000 and has a memory of 4TB. CPU: 64 x Intel E5-4620 v2, 2.6 GHz, and 8 core Ivybridge CPUs per node. At the moment the NSCCS hosts 30 software packages.

Our service can provide a complete service for experimentalists, including an initial scientific consultation to recommend appropriate methods and software packages for their problem, training on these packages and finally providing them with hardware resources on which to run their calculations.

Training is an important aspect of the Service. We provide workshops, one-to one training and group training sessions on our software packages. In addition to these, we also have a consultation service where users can receive advice on how to tackle specific chemical problems and the most appropriate software to use.

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P32: The RSC Theoretical Chemistry Group

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The Theoretical Chemistry Group (TCG) is one of the Royal Society of Chemistry (RSC)'s Special Interest Groups. Its aim is to promote the interests of theoretical and computational chemists and ensuring that the interests of its members are adequately represented in the activities of the RSC and other bodies. This poster details the activities of the TCG, which include the organisation of meetings and conferences as well as sponsorship of conferences in the UK. The benefits of TCG membership are also highlighted.