

1st Faraday Joint Interest Group Conference 2017

Welcome from the Organisers

The Faraday Joint Interest Group Conference 2017 is a joint meeting of the Royal Society of Chemistry Faraday Division interest groups. This meeting is the first of its kind, and aims to bring the UK Physical Chemistry community together once every 2-3 years to highlight excellent research. It is our aim to increase the visibility of the UK Physical Chemistry community and encourage links with International Researchers as well as Industry.

This year, the Faraday Joint Interest Group Conference is composed of plenary lectures, RSC prize winner talks, poster sessions, a full exhibitions hall, and 7 parallel sessions of invited and contributed lectures organized by the following Faraday interest groups:

Astrophysical Chemistry Group
Biophysical Chemistry Group
British Carbon Group
Neutron Scattering Group
Photochemistry Group
Spectroscopy & Dynamics Group
Statistical Mechanics & Thermodynamics Group
Theoretical Chemistry Group

Thank you for making this what promises to be a very exciting meeting – we have an incredible line up of speakers and posters, and enormous support from our Industrial Sponsors. We hope that you enjoy yourselves, and we welcome you to the University of Warwick!



Dr. Ann Dixon
Conference Chair

On behalf of the co-organisers Dr. Carlos Avendaño, Prof. Wendy Brown, Dr. Sam Eden, Dr. Rachel Evans, Prof. Felix Fernandez-Alonso, Prof. Malcolm Heggie, Dr. Steven Lee, Prof. Martin McCoustra, Dr. Tanja van Mourik, and Dr. Jan R. R. Verlet



FaradayJIG Conf 2017
@FaradayMeeting

Our Sponsors

We have been very fortunate to have a number of Industrial Sponsors and exhibitors who have supported this meeting. We would like to sincerely thank our sponsors and encourage you all to visit the Exhibitors Hall (immediately adjacent to the Poster Session) throughout the meeting.

We would like to thank our **Supporting Sponsors** ...



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1st Faraday Joint Interest Group Conference 2017

Scientific Programme

Tuesday, April 11, 2017

- 12:00** Arrival and Registration (Register / Drop Luggage in Warwick Conferences Reception in Students Union and then come to Faraday Conference Reception in Chemistry and Science Concourse)
- 12:00-13:45** Lunch / Exhibitors Area Opens (Chemistry and Science Concourse)
- 13:45-14:00** Meeting Opens: Welcome from Conference Chair, Dr. Ann Dixon (University of Warwick) (Concourse Lecture Room 3 (L3))
- 14:00-15:00** Prof. Chris Dobson (University of Cambridge) "The Amyloid State of Proteins and its Significance in Biology and Medicine" (Concourse Lecture Room 3 (L3))
- 15:00-17:20** Parallel Sessions (see below)

Astrophysical Chemistry: AstroSurf 2017 (Chair: Prof. Martin McCoustra) (Social Sciences Room S0.11)

- 15:00-15:45** Prof. Alexander Tielens (Leiden University) "The Aromatic Universe: From PAHs to Fullerenes"
- 15:45-16:05** Dr. Alessandra Candian (Leiden University) "Deuterium-enriched Polycyclic Aromatic Hydrocarbons"
- 16:05-16:20** Coffee Break and Exhibitors Fair
- 16:20-16:40** Dr. Pernille Jensen (Aarhus University) "Deuteration and Hydrogenation of Coronene"
- 16:40-17:00** Dr. Tara Salter (University of Sussex) "Laboratory Investigations of Small Aromatic Molecules in Astrophysical Ices"
- 17:00-17:20** RAS/RSC Astrophysical Chemistry Group AGM

Biophysical Chemistry: Single Molecule Spectroscopy (Chair: Steven Lee) (Concourse Room B2.02)

- 15:00-15:45** Prof. Achillefs Kapanidis (University of Oxford) "Single-molecule fluorescence studies of bacterial transcription"
- 15:45-16:05** Dr. Alexander Roy Carr (University of Cambridge) "Three-dimensional Super-resolution Imaging and Single-Particle Tracking in Eukaryotic Cells Using a Double-Helix Point Spread Function"
- 16:05-16:20** Coffee Break and Exhibitors Fair
- 16:20-16:40** Dr. Charlotte Dodson (Imperial College London) "Dynamic equilibrium of Aurora-A kinase activation loop revealed by single molecule spectroscopy"
- 16:40-17:00** Dr. Maria Andreasen (University of Cambridge) "Propensity for autocatalytic amplification"
- 17:00-17:20** Dr. Lisa-Maria Needham (University of Cambridge) "FRET-enhanced photo-modulatable fluorophore for improved super-resolution microscopy and single-molecule tracking studies"

British Carbon: Novel Carbon (Chair: Malcolm Heggie) (Concourse Room B2.04/5)

- 15:00-15:45** Dr. Thuriid Gspann (University of Cambridge) "The role of carbonaceous coating for anchoring of carbon nanotube bundles"
- 15:45-16:05** Jonathan Rourke (University of Warwick) "Graphene oxide: a two component structural model"
- 16:05-16:20** Coffee Break and Exhibitors Fair
- 16:20-16:40** British Carbon Annual meeting
- 16:40-17:00** Jose Anguita (University of Surrey) "Carbon nanostructures for two-dimensional optical media"
- 17:00-17:20** Gavin Morley (University of Warwick) "Optical levitation of nanodiamonds in vacuum without heating"

Neutron Scattering: Energy & Security (Chair: Prof. Felix Fernandez-Alonso) (Social Sciences Room S0.19)

- 15:00-15:45** Prof. David Lennon (University of Glasgow) "The application of inelastic neutron scattering to investigate CO hydrogenation over iron based Fischer-Tröpsch synthesis catalysts"
- 15:45-16:05** Dr. Aidan Hindmarch (Durham University) "Magnetic thin-films: challenges for future applications in computing"
- 16:05-16:20** Coffee Break and Exhibitors Fair
- 16:20-16:40** Dr. Matthew Krzystyniak (ISIS Facility) "Energy dissipation in superconducting resonant cavities: lessons learnt from neutron scattering"
- 16:40-17:00** Dr. Judith Houston (Jülich Centre for Neutron Science) "Solvent- and surfactant-mediated self-assembly structures of diblock polythiophene polyelectrolytes for organic photovoltaic devices"
- 17:00-17:20** Dr. Krzysztof Dymkowski (STFC Scientific Computing) "AbINS: a modern software for INS interpretation"

Spectroscopy and Dynamics (Concourse Lecture Room 4 (L4))

15:00-15:45 Dr. Maria Sanz (King's College London)

15:45-16:05 Dr. Adam Smith (University of Southampton) "Measuring a Complete Reaction Coordinate: Windowless Observation of the Photodissociation Dynamics of CS₂"

16:05-16:20 Coffee Break and Exhibitors Fair

16:20-16:40 Dr. William Tuttle (University of Nottingham) "Vibration and vibration-torsion levels of the S₁ states of para-fluorotoluene and para-xylene"

16:40-17:00 Dr. Julia Lehman (University of Leeds) "Photoelectron Spectroscopy of the Thiazate (NSO⁻) and Thionitrite (SNO⁻) Isomer Anions"

17:00-17:20 Dr. Christopher Hansen (University of Bristol) "Multi-mass velocity-map imaging the UV photodissociation and VUV dissociative ionisation of 2-bromothiophene with a PlmMS2 camera"

Statistical Mechanics & Thermodynamics (Concourse Room B2.01)

15:00-15:45 Prof. Dirk Aarts (University of Oxford) "Directed self-assembly of Janus rods"

15:45-16:05 Anna Sofia Tascini (Imperial College London) "Thermal transport across nanoparticle-fluid interfaces"

16:05-16:20 Coffee Break and Exhibitors Fair

16:20-16:40 Adrian Sanchez-Fernandez (University of Bath) "Surfactant self-assembly in deep eutectic solvents"

16:40-17:00 Matthew Killeen (University of Sheffield) "Developing fundamental models of colloid transport and absorption in sand filters"

17:00-17:20 Prof. Andrew Masters (The University of Manchester) "An old chestnut: can the virial expansion describe the vapour-liquid phase transition?"

Theoretical Chemistry (Social Sciences Room S0.13)

15:00-15:45 Maria Ramos (University of Porto, Portugal) "S-S bonds in biological systems and other studies"

15:45-16:05 Gareth Richings (University of Warwick, UK) "Grid-based non-adiabatic quantum dynamics using potential energy surfaces constructed on-the-fly"

16:05-16:20 Coffee Break and Exhibitors Fair

16:20-16:40 Arend Dijkstra (University of Leeds UK) "Modeling 2DUV spectra of adenine in water"

16:40-17:00 Wilke Dononelli (University of Oldenburg, Germany) "Nanoporous gold - A selective catalyst for methanol oxidation"

17:00-17:20 Vagner Rigo (King's College London, UK) "Ethanol adsorption upon Pt-shell@M-core nanoparticles"

17:20 Parallel Sessions End / Evening Programme Begins

17:20-18:00 Collect Room Keys in Warwick Conferences Reception in Students Union

18:00-19:30 Evening meal

19:30-20:30 Sir Fraser Stoddart (2016 Nobel Laureate in Chemistry, Northwestern University) "The Mechanical Bond : Mingling Art with Science" (Concourse Lecture Room 3 (L3))

20:30-21:30 Drinks Reception and Mixer (Chemistry and Science Concourse)

Wednesday, April 12, 2017

09:00-10:00 Dr. Józef Lewandowski (University of Warwick) "Protein structure and dynamics through the lens of solid-state NMR" RSC Marlow Award for the development and applications of solid-state NMR methodology to study structure and dynamics of biomolecules. (Concourse Lecture Room 3 (L3))

10:00-12:20 Morning Parallel Sessions (see below)

Astrophysical Chemistry: AstroSurf 2017 (Chair: Dr. June McCombie) (Social Sciences Room S0.11)

10:00-10:45 Dr. Sandra Brünken (Cologne) "Hydrocarbon Radical Cations as Intermediates in Interstellar Carbon Chemistry"

10:45-11:05 Prof. Peter Sarre (University of Nottingham) "The Shapes of Diffuse Interstellar Bands"

11:05-11:20 Coffee Break and Exhibitors Fair

11:20-11:40 Dr. Benjamin Arenas (Max Planck Institute for the Structure and Dynamics of Matter) "Laboratory Spectroscopy of Astrochemically Relevant Molecules"

11:40-12:00 Dr. Giuliana Cosentino (University College of London) "Widespread SiO and CH₃OH Emission In Filamentary Infrared Dark Clouds"

12:00-12:20 Dr. Shaoshan Zeng (Queen Mary University of London) "15N Fractionation in Infrared Dark Cloud Cores"

Biophysical Chemistry: Physical Principles of Proteins (Chair: David Klenerman) (Concourse Room B2.02)

10:00-10:45 Prof. Tuomas Knowles (University of Cambridge) "Probing proteins in small volumes"

10:45-11:05 Dr. Adam Perriman (University of Bristol) "Reengineering protein surfaces for non-aqueous activity"

11:05-11:20 Coffee Break and Exhibitors Fair

11:20-11:40 Dr. Tilo Zollitsch (University of Oxford) "Magnetic field effect studies on radical pair reactions in artificial flavoproteins"

11:40-12:00 Prof. Christian Johannessen (University of Antwerp) "Towards a standardized characterization of solution phase protein structure using Raman optical activity: Implementation of comprehensive structural databases"

12:00-12:20 Dr. Zhuo Li (University of Nottingham) "Quantitative First Principles Calculations of Protein Circular Dichroism in the Near-Ultraviolet"

British Carbon: Diamond (Chair: Mark Newton) (Concourse Room B2.04/5)

10:00-10:45 The 9th British Carbon Group Ubbelohde lecture: Prof. Dr. Joerg Wrachtrup (University of Stuttgart) "The diamond quantum revolution"

10:45-11:05 Prof Ollie Williams (Cardiff), "Diamond reactivity and the nanoscale"

11:05-11:20 Coffee Break and Exhibitors Fair

11:20-11:40 Prof Andy Evans (University of Aberystwyth), "Epitaxial graphene growth by catalytic graphitisation of diamond"

11:40-12:00 Dr Matthew Markham (Element Six Ltd), "Diamond an Engineering Gem"

12:00-12:20 Prof Julie Macpherson (Warwick), "The Effect of Interfacial Electrode Temperature on Electrodeposited Metal Nanostructure Morphology"

Neutron Scattering: Environment (Chair: Dr. Katherine Thompson) (Social Sciences Room S0.19)

10:00-10:45 Prof. Jeffrey Penfold (University of Oxford and ISIS Facility) "The impact of neutron reflectivity in the study of surfactant adsorption in complex mixtures of technological importance"

10:45-11:05 Dr. John Holbrey (Queen's University Belfast) "Dialing in property sets - designing performance ionic liquid materials guided by neutron scattering"

11:05-11:20 Coffee Break and Exhibitors Fair

11:20-11:40 Ms. Marta Falkowska (University of Manchester) "Structural studies on aromatic and aliphatic liquids under confinement by total neutron scattering"

11:40-12:00 Mr. Oliver Hammond (University of Bath) "Constructing nanostructured metal oxides for sustainability using deep eutectic solvents and total scattering insights"

12:00-12:20 Dr. Richard Campbell (Institut Laue-Langevin) "New application of neutron reflectometry to resolve the dynamic interfacial composition of soft matter mixtures at the air/water interface"

Spectroscopy and Dynamics (Concourse Lecture Room 4 (L4))

10:00-10:45 Prof. Dr. Alec Wodtke (Max Planck Institute and University of Göttingen) "Building the World's Greatest Microscope: Revealing the atomic scale dynamics of surface chemistry"

10:45-11:05 Dr. Ethan Cunningham (University of Oxford) "Probing the Interaction of N₂O with Copper, Silver and Gold cations using Infrared Spectroscopy and Density Functional Theory Calculations"

11:05-11:20 Coffee Break and Exhibitors Fair

11:20-11:40 Dr. Graham Cooper (University of Newcastle) "Rotational Spectra and Nuclear Quadrupole Coupling Constants of 4-Bromo- and 4-Iodopyrazole"

11:40-12:00 Dr. Luke Hedley (University of Edinburgh) "Spectroelectrochemistry and Ultrafast Charge-Transfer in thin films of Prussian Blue Analogues"

12:00-12:20 Dr. Valentina Zhelyazkova (Imperial College London) "Controlling resonant energy transfer in atom-molecule collisions using electric fields"

Statistical Mechanics & Thermodynamics (Concourse Room B2.01)

10:00-10:45 Prof. Martin Trusler (Imperial College London) "Phase Behaviour and Thermophysical Properties of Fluids for Application in Carbon Capture and Storage Processes"

10:45-11:05 Silvia Di Lecce (Imperial College London) "Thermophoretic transport of LiCl solutions"

11:05-11:20 Coffee Break and Exhibitors Fair

- 11:20-11:40** Dr. Christopher D. Williams (The University of Manchester) "Ion Permeation in Graphene Oxide Membranes: a Molecular Simulation Perspective"
- 11:40-12:00** Jet-Sing Lee (University of Liverpool) "Hyperporous Carbons from Hypercrosslinked Polymers for Ultrahigh CO₂ and H₂ Storage"
- 12:00-12:20** Joshua E. S. J. Reid (University of York) "Statistical Thermodynamics of Ionic Liquid-water mixtures"

Theoretical Chemistry (Social Sciences Room S0.13)

- 10:00-10:45** Prof. Saiful Islam (Bath) "From Lithium Batteries to Perovskite Solar Cells: Atomic-Scale Insights into Energy Materials"
- 10:45-11:05** Dr. Herbert Fruchtl (University of St Andrews, UK) "Quinone based building blocks for molecular electronics"
- 11:05-11:20** Coffee Break and Exhibitors Fair
- 11:20-12:00** PCCP Lectureship Award Talk: Dr David Glowacki (University of Bristol) "Beyond gaming: virtual reality and real-time molecular dynamics for (bio)chemistry"
- 12:00-12:20** Dr. Antoine Carof (University College London, UK) "Electron Transfer in Organic and Biological Materials"
- 12:20** Morning Parallel Sessions End
- 12:30-14:00** Lunch and Poster Session / Exhibitors Fair (Chemistry and Science Concourse)
- 14:00-15:00** Prof. Ifor Samuel (University of St Andrews) "Time resolved spectroscopy of organic semiconductors: from solar cells to visible light communications" RSC Chemical Dynamics Award for pioneering studies of the dynamics of light emission and light harvesting in organic semiconductors (Concourse Lecture Room 3 (L3))

15:00-17:00 Afternoon Parallel Sessions (see below)

Astrophysical Chemistry: AstroSurf 2017 (Social Sciences Room S0.11)

- 15:00-15:45** Prof. Ian Sims (Institute of Physics, Rennes) "Synthesis of organic molecules in space – chemical reactions at low temperatures"
- 15:45-16:05** Dr. Kevin Douglas (University of Leeds) "Low Temperature Studies of the Removal Reactions of 1CH₂ with Particular Relevance to the Atmosphere of Titan"
- 16:05-16:20** Coffee Break and Exhibitors Fair
- 16:20-16:40** Dr. Guido Fuchs (University of Kassel) "Deep search for Hydrogen Peroxide towards Ppre- and Protostellar Objects - Testing the Pathway of Grain Surface Water Formation"
- 16:40-17:00** Dr. Sergio Ioppolo (The Open University) "VUV and Mid-IR Spectroscopy of Ices exposed to 1 keV Electrons"

Biophysical Chemistry: Biophysics of Membranes (Chair: Ann Dixon) (Concourse Room B2.02)

- 15:00-15:45** Prof. Bonnie Wallace (University of London) "Using Biophysical Methods to Characterise the Structure, Function and Drug Binding of Voltage-Gated Sodium Channels"
- 15:45-16:05** Prof. Karen Edler (University of Bath) "Polymer Stabilized Phospholipid Nanodiscs"
- 16:05-16:20** Coffee Break and Exhibitors Fair
- 16:20-16:40** Dr. Chandrashekhar V. Kulkarni (University of Central Lancashire) "Self-assembled Lipid Nanostructures and Dispersed Lipid Particles for the Delivery of Aspirin"

Photochemistry (Chair: Dr. Rachel Evans) (Concourse Room B2.04/5)

- 15:00-15:45** Prof. Richard Friend (University of Cambridge) "Molecular semiconductors for solar cells – designing around the Coulomb interaction"
- 15:45-16:05** Dr. Bo Hou (University of Oxford) "Highly monodispersed PbS QDs for outstanding QD optoelectronic applications"
- 16:05-16:20** Coffee Break and Exhibitors Fair
- 16:20-16:40** Dr. Elizabeth Gibson (Newcastle University) "Charge Transfer at Dye-Metal Oxide Interfaces for Solar Energy Capture, Conversion and Storage"
- 16:40-17:00** Dr. Alex Cowan (University of Liverpool) "Photochemical reduction of carbon dioxide in water"

Neutron Scattering: Health (Chair: Dr. Ian Tucker) (Social Sciences Room S0.19)

- 15:00-15:45** Dr. Simon Titmuss (University of Edinburgh) "Molecular scale microbiology with neutrons and x-rays"
- 15:45-16:05** Dr. Melissa Sharp (European Spallation Source) "Probing the structure and dynamics of proteins using neutron scattering"
- 16:05-17:00** Neutron Scattering Group Meeting

Spectroscopy and Dynamics (Concourse Lecture Room 4 (L4))

15:00-15:45 Dr. Susan Quinn (University College Dublin)

15:45-16:05 Dr. Stuart Crane (Heriot-Watt University) "Time-Resolved Photoion Yield Spectroscopy of Non-Volatile Biological Analogues"

16:05-16:20 Coffee Break and Exhibitors Fair

16:20-16:40 Dr. Edward Matthews (University of York) "Protomers of para-aminobenzoic acid: Can low-resolution UV action spectroscopy distinguish protomeric isomers formed via electrospray?"

16:40-17:00 Dr. Natercia Das Neves Rodrigues (University of Warwick) "Photophysics of the sunscreen ingredients methyl and menthyl anthranilate: a bottom-up approach to photoprotection"

Statistical Mechanics & Thermodynamics (Concourse Room B2.01)

15:00-15:45 Dr. Paddy Royall (University of Bristol)

15:45-16:05 Dr. David Quigley (University of Warwick) "Exploring the accuracy of solid-liquid interfacial free energies obtained via the capillary wave method"

16:05-16:20 Coffee Break and Exhibitors Fair

16:20-17:00 Dr. John Russo (University of Bristol and Winner of the SMTG Young Scientist Award) "Water: a matter for Soft Matter".

Theoretical Chemistry (Social Sciences Room S0.13)

15:00-15:45 Dr Francesca Baletto (King's College London) "Towards a rational design of metallic nano catalysts"

15:45-16:05 Dr. Pavlos Mouratides (Loughborough University, UK) "The peculiarities of dislocation behaviour in bilayer graphene"

16:05-16:20 Coffee Break and Exhibitors Fair

16:20-16:40 Dr. Scott Habershon (University of Warwick) "Automated reaction path sampling using random walks in chemical space"

16:40-17:00 Dr. Cate Anstöter (Durham University) "Conformational sensitivity of photoelectron angular distributions"

17:00 Parallel Sessions End / Evening Programme Begins

17:00-18:30 Drinks Reception and Poster Session (Chemistry and Science Concourse)

19:00 Conference Dinner and RSC Award Ceremony Presented by Prof. Eleanor Campbell (University of Edinburgh) (Panorama Room, Rootes Building)

Thursday, April 13, 2017

09:00-11:10 Morning Parallel Sessions (see below)

Astrophysical Chemistry: AstroSurf 2017 (Chair: Prof. Wendy Brown) (Social Sciences Room S0.11)

09:00-09:45 Dr. Anthony Meijer (University of Sheffield) "On the Ionization of PAHs in Molecular Ices"

09:45-10:05 Dr. Andrew Cassidy (Aarhus University) "Dipolar Molecules Spontaneously Organize to form Thin Films with Internal Electric Fields; Implications for CO-covered Dust Grains in the Interstellar Medium"

10:05-10:20 Coffee Break and Exhibitors Fair

10:20-10:40 Dr. John Thrower (University of Münster) "Femtosecond Laser-induced Desorption from Doped Ice and Hydrogenated Graphite"

10:40-11:00 Dr. Skandar Taj (Heriot-Watt University) "Surface Heterogeneity and Inhomogeneous Broadening of Vibrational Line Profiles"

Biophysical Chemistry: Frontiers of Biophysics (Chair: Dr. Nikola Chmel) (Concourse Room B2.02)

09:00-09:45 Dr. Corinne Smith (University of Warwick) "3D cryo-electron microscopy of multiple clathrin cage geometries"

09:45-10:05 Dr. Colin Campbell (University of Edinburgh) "Life and free-energy in 3D tissue models – a tool for drug discovery"

10:05-10:20 Coffee Break and Exhibitors Fair

10:20-10:40 Dr. Silvia Sonzini (MedImmune) "Efficient protein-drug supramolecular conjugation through host-guest chemistry"

10:40-11:00 Biophysical Chemistry Interest Group AGM

Photochemistry (Chair: David Worrall) (Concourse Room B2.04/5)

09:00-09:45 Prof. Luisa de Cola (Université de Strasbourg/ Karlsruhe Institute of Technology) "Luminescent metal complexes and their assemblies"

09:45-10:05 Prof. Anthony Harriman (Newcastle University) "Thermally-Activated Delayed Fluorescence in Strapped BODIPY Derivatives"

10:05-10:20 Coffee Break and Exhibitors Fair

10:20-10:40 Ms. Rachel Fisher (University of Edinburgh) "Photophysical Characterisation of Extended 6-Aza-Uridines – a Promising Class of Responsive, Fluorescent Nucleic Base Analogues"

10:40-11:00 Prof. Zoe Pikramenou (University of Birmingham) "Tailoring Luminescent Nanoparticles to Biomedical Applications Using Metal Complexes for Single and Two-Photon Luminescence Imaging"

Neutron Scattering: Healthcare (Chair: Dr. Elisabetta Canetta) (Social Sciences Room 0.19)

09:00-09:45 Prof. Jayne Lawrence (King's College London) "The characterisation of nanoparticulate drug delivery systems using small angle neutron scattering"

09:45-10:05 Dr. Matthew Blakeley (Institut Laue-Langevin) "Seeing H-atoms and protons: enzyme mechanisms and drug design"

10:05-10:20 Coffee Break and Exhibitors Fair

10:20-10:40 Dr. Maria Paula Marques (Universidade de Coimbra) "Probing breast cancer cells with neutrons: the impact of anticancer drugs on intracellular water"

10:40-11:00 Dr. Antonio Benedetto (University College Dublin) "The interaction of room-temperature ionic liquids with phospholipid bilayers"

Spectroscopy and Dynamics (Concourse Lecture Room 4 (L4))

09:00-09:45 Dr. Bas van de Meerakker (Radboud University) "Taming molecular collisions"

09:45-10:05 Dr. Daniel Horke (Center for Free-Electron Laser Science, DESY) "Controlling the motion of very large molecules and particles"

10:05-10:20 Coffee Break and Exhibitors Fair

10:20-10:40 Dr. Jack Eardley (Durham University) "Magnetic trapping of SH radicals"

10:40-11:00 Dr. Victoria Walpole (University of Oxford) "Towards a complete description of bond orientation in the inelastic scattering of NO(X)."

Statistical Mechanics & Thermodynamics (Concourse Room B2.01)

09:00-09:45 Dr. Paola Carbone (University of Manchester) "Multiscale Modelling of Polymer Aggregates"

09:45-10:05 Andrew R. McCluskey (University of Bath) "Simulations to understand reflectivity: how coarse can we go?"

10:05-10:20 Coffee Break and Exhibitors Fair

10:20-10:40 Xiao Han (Newcastle University) "Silica Aerogel: Synthesis and Application"

10:40-11:00 Khalil T. Hassan (Newcastle University) "Low cost superinsulation material via novel ambient pressure drying method"

Theoretical Chemistry (Social Sciences Room 0.13)

09:00-09:45 Prof Peter Saalfrank (Potsdam, Germany) "Light-driven processes in molecular systems: From photophysics to photochemistry"

09:45-10:05 Dr. Tanja van Mourik (University of St Andrews, UK) "Halogen bonding in molecules of biological interest"

10:05-10:20 Coffee Break and Exhibitors Fair

10:20-10:40 Dr. Angeles Pulido (University of Southampton, UK) "Computer-guided porous materials design: from rationalization to prediction"

10:40-11:00 Dr. Dmitry Shalashilin (University of Leeds, UK) "Efficient and accurate first principle on the fly quantum dynamics of ultrafast photoprocesses"

11:00 Morning Parallel Sessions End

11:00-12:00 Professor Peter Bruce (University of Oxford) "Storing energy with oxygen: oxygen redox chemistry in solids and aprotic solvents" Liversidge Award for his contributions to the chemistry of energy conversion and storage, particularly pioneering the lithium-air battery, the discovery of ionic conductivity in crystalline polymers. (Concourse Lecture Room 3 (L3))

12:00-12:30 Closing Comments / poster prizes announced, Dr. Ann Dixon (University of Warwick) (Concourse Lecture Room 3 (L3))

12:30 Meeting Closes – Thank you all for coming!

1st Faraday Joint Interest Group Conference 2017

Abstracts for Oral Presentations

Abstracts are listed in chronological order, following the Scientific Programme

The Amyloid State of Proteins and its Significance in Biology and Medicine

Christopher M. Dobson

University of Cambridge, Department of Chemistry,
Lensfield Road, Cambridge CB2 1EW, United Kingdom

Abstract

Interest in the phenomenon of amyloid formation by peptides and proteins has developed with extraordinary rapidity in recent years, such that is now a major topic of research across a wide range of disciplines. The reasons for this surge of interest arise primarily from the links between amyloid formation and a range of rapidly proliferating medical disorders such as Alzheimer's disease and type-2 diabetes, and also from the insights that studies of the amyloid state can provide about the nature of the biologically functional forms of peptides and proteins and the means of the maintenance of protein homeostasis within healthy living systems. Recent progress in understanding the factors affecting the stability of the amyloid state relative to that of the native state of a protein, along with the development of methods for defining the mechanism of the conversion between the different states, has led to a much more detailed understanding of the links between protein aggregation, amyloid formation and human disease. This talk will give an overview of recent advances in this field of study and discuss recent progress from our own laboratory towards understanding the structural and physical properties of the amyloid state, the kinetics and mechanism of its formation, and the nature and origins of its links with disease. In addition, the talk will discuss the ways in which protein aggregation and amyloid formation may be inhibited or suppressed, both to understand the nature of protein homeostasis in naturally functioning organisms and also to address the development of therapeutic strategies through which to combat the loss of homeostasis and the onset and progression of disease.

The aromatic Universe: From PAHs to fullerenes

Alexander Tielens

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Over the last 10-20 years, IR observations have demonstrated that the molecular universe is filled with large and complex species. In particular, observations with ESA's and NASA's infrared observatories have revealed the presence of polycyclic Aromatic hydrocarbons (PAHs) and C₆₀ molecules in space. Observed spectral variations reflect compositional changes in the family of molecules present in space, driven by the specific physical conditions of the emitting regions. Extensive experimental and theoretical studies have elucidated the intrinsic infrared properties of large PAH molecules and their dependence on the molecular characteristics. In addition, experimental studies and astronomical modeling have revealed the importance of top-down chemistry whereby large molecules are broken down to smaller species and isomerized to cages, fullerenes. I will review these different aspects of interstellar IR spectra and interstellar chemistry in the aromatic Universe.

References.

Keywords.

keyword1, keyword2, keyword3, keyword4, keyword5, keyword6, keyword7

Deuterium-Enriched Polycyclic Aromatic Hydrocarbons

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All cosmic deuterium (D) was produced during the Big Bang and has been subsequently destroyed by nuclear reactions in the interior of stars (Epstein et al. 1976). Thus, it is expected that the D/H ratio steadily decreases with the chemical evolution of galaxies. However, ultraviolet observations with FUSE have revealed a scatter in the D/H ratio in the local galactic disk, with $D/H=0.5-2.2 \times 10^{-5}$ (Linsky et al. 2006). To solve this issue, it has been proposed that carbonaceous dust grain and Polycyclic Aromatic Hydrocarbon (PAH) molecules may act as important deuterium reservoirs (Draine 2006). Recent AKARI observations (Doney et al. 2016) probed that deuterium-enriched PAHs are present, but in tiny amount, and appear to be very sensitive to the local physical conditions.

To investigate the condition for D enrichment in interstellar PAHs, a kinetic model is built (Andrews et al. 2016, 2017), that takes into account ionization, electron recombination of PAHs, multiphoton dissociation events, atomic (D/H) addition reactions, and Eley-Rideal abstraction mechanism of aliphatic groups on the prototypical coronene family. This model is then run in the physical conditions typical of the diffuse ISM ($G_0 = 1$, $n=500 \text{ cm}^{-3}$) and of a photodissociation region ($G_0 = 1000$, $n=10^6 \text{ cm}^{-3}$).

The result of the model suggests that, in the physical condition studied, deuteration of PAHs is scarce and dependent on the molecular size. Comparison of the model with observations and implications concerning the role of PAHs in the fractionation of D are discussed.

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Keywords.

Astrochemistry, PAHs, Deuterium, ISM, modelling

Deuteration and hydrogenation of coronene

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Polycyclic aromatic hydrocarbons are everywhere in interstellar space, and have been suggested to catalyse molecular hydrogen formation in photodissociation regions (Habart et al 2003, 2004). Previous experiments and theoretical calculations have shown that it is possible to hydrogenate the PAH molecule coronene very easily, with hot H atoms, and indirectly shown that molecular hydrogen can be formed in this reaction through abstraction (Rauls & Hornekær 2008; Mennella et al. 2011; Thrower et al. 2012, 2014; Skov et al. 2014). However, the hydrogen atoms used in the experiments were significantly hotter (2300K) than they are expected to be in the relevant regions of the interstellar medium.

We present temperature programmed desorption experiments showing deuterium and hydrogen addition to coronene, using colder atoms (~1000K). We find a double peak structure in the mass distribution, suggesting barriers for addition to certain sites.

Furthermore, in the case of hydrogen addition, we also find a clear preference for specific fragmentation products for specific masses, suggesting a preferred route for hydrogenation.

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Keywords.

Polycyclic aromatic hydrocarbons, hydrogen, astrochemistry, temperature programmed desorption

Laboratory investigations of small aromatic molecules in astrophysical ices

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Polycyclic aromatic hydrocarbons (PAHs) are thought to be present throughout the interstellar medium and account for around 20% of the galactic carbon. They have been proposed as the carriers of the diffuse interstellar bands (DIBs) and the unidentified infrared bands (UIRs). Benzene is the simplest building block of PAHs, and it has been detected in proto-planetary nebulae [1, 2]. Formation routes of toluene and xylene, precursors to methylated PAHs, have also been postulated in interstellar and circumstellar space [3, 4].

Here we present laboratory investigations of a series of simple aromatic molecules of increasing molecular weight and complexity: benzene, toluene and two isomers of xylene. Using an ultra-high vacuum chamber (at a pressure of 10^{-10} mbar) with a base temperature of 25 K, we are able to simulate the conditions of interstellar space. Molecular ices of benzene, toluene, xylene and water are grown upon highly oriented pyrolytic graphite, a carbonaceous dust grain analogue surface. We use temperature programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS) to investigate the interactions between these molecules and water, both in layered configurations and as co-deposited mixtures. These techniques allow us to probe the bonding and trapping in different environments, including those more representative of interstellar conditions. Although these molecules are similar in size and structure, their desorption behaviour and interaction with water are affected differently.

Desorption orders and energies have been calculated from data analysis of TPD traces. These parameters are incorporated into astrophysical models using non-linear interstellar heating rates. We present models for each aromatic molecule, as a pure ice and in the presence of water. These models help us to understand the implications of our work for interstellar chemistry.

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Keywords.

Astrochemistry, PAHs, laboratory investigations

Single-molecule fluorescence studies of bacterial transcription

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The talk will focus on the mechanisms of transcription by the bacterial RNA polymerase (RNAP) at the single-molecule level, both *in vitro* and *in vivo*.

Using *in vitro* methods, we recently captured real-time views of initial transcription by RNAP; the mechanism of this process has remained unclear mainly due to the presence of transient intermediates and heterogeneity, a landscape difficult to address using ensemble biochemical and conventional structural-biology approaches. To study the kinetics of initial transcription directly, we used single-molecule FRET to observe DNA scrunching and unscrunching on immobilized initial transcribing complexes for several minutes. Our work uncovered extensive RNAP pausing and backtracking during initiation, with region 3.2 of $\sigma 70$ being an important pausing determinant; such pausing is likely to have important regulatory roles. Current work focuses on the sequence-dependence and the mechanism of initiation pausing. Our work paves the way for further analysis of major conformational changes occurring from initiation to early elongation.

We will also present studies of the spatial organization of transcription at the single-cell level, a feature crucial for the control of gene expression. Specifically, we use *in vivo* photo-activated single-molecule tracking to discriminate between diffusing RNA polymerases and RNA polymerases specifically bound to DNA, either on promoters or transcribed genes. We find that transcription can cause spatial reorganization of the nucleoid, with movement of gene loci out of the bulk of DNA as levels of transcription increase. We also studied the degree and mode of interaction of RNAP with the DNA during on the promoter search process, showing that RNAP interacts substantially with non-specific DNA. Current work focuses on novel ways to study the non-specific interactions of DNA-binding proteins with chromosomal DNA, and the intracellular diffusion of protein molecules in the absence of the chromosome. Our work provides a global view of the organization of transcription and its interplay with chromosome organisation in living bacteria.

Keywords.

transcription, RNA polymerase, single-molecule FRET, single-particle tracking, PALM, transcriptional pausing

Three-dimensional Super-resolution Imaging and Single-Particle Tracking in Eukaryotic Cells Using a Double-Helix Point Spread Function

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The inherent 3D nature of biological systems has motivated the development of new physical methods achieving sub-diffraction localisation precision in three dimensions, one such technique is the double-helix point spread function (DHPSF) (1). Until recently, the application of the DHPSF approach has been limited to the study of, relatively small, prokaryotic cells (2) due to aberration effects present when imaging away from the coverslip. By extending previous work on axial aberration in confocal microscopy (3) to DHPSF localisation microscopy, we have developed and characterised a method to minimize aberration induced by a mismatch between the refractive index of the objective lens immersion liquid and the sample media.

We illustrate the capabilities of this method by imaging ~15 µm thick whole eukaryotic cell volumes in 3-5 imaging planes and explore large-scale membrane reorganisation in human T cells following receptor triggering and by using single-particle tracking to image several mammalian proteins in traditionally challenging areas of cells (4).

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Keywords.

Super-resolution, Three-dimensional, Single-particle tracking, Single-molecule, localisation

Dynamic equilibrium of Aurora-A kinase activation loop revealed by single molecule spectroscopy

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The conformation of the activation loop (T-loop) of protein kinases underlies enzymatic activity and influences the binding of small molecule inhibitors. We have used single molecule fluorescence spectroscopy to monitor the movement of the T-loop (activation loop) of Aurora-A kinase between two major conformations. Phosphorylated Aurora-A is in dynamic equilibrium between a DFG-in-like active T-loop conformation and a DFG-out-like inactive T-loop conformation and we have measured the rate constants of interconversion. We have directly measured the equilibrium between the two conformations and determined the free energy difference between them to be 0.7 ± 0.1 kcal mol⁻¹. Addition of activating protein (TPX2) shifts the equilibrium towards the active T-loop conformation, whereas addition of the inhibitors MLN8054 and CD532 favours an inactive T-loop conformation. Notably, 36% of Aurora-A still occupies an active T-loop conformation in the presence of saturating CD532. We show that TPX2 and MLN8054, whose binding modes are thought to be mutually exclusive, bind Aurora-A simultaneously. Our data is inconsistent with standard models of conformational change as part of an induced fit or conformational selection mechanism and we provide a new model for kinase conformational behaviour. Our approach will enable conformation-specific effects to be integrated into inhibitor discovery across the kinome and we outline some immediate consequences for structure-based drug discovery.

Keywords.

Aurora-A, protein kinase, activation loop, single molecule fluorescence, dye quenching, drug development, DFG-in, DFG-out

Propensity for autocatalytic amplification demarcates aberrant from functional protein self-assembly

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The majority of proteins exert their functional roles in living systems by self-assembling into supra-molecular complexes. In most cases these structures consist of a few molecules, interacting at specific sites, however, some proteins have the ability to aggregate into large filamentous structures made up of several thousand individual proteins. In recent decades the formation of such filaments has emerged as a key molecular event in the pathology of several diseases [1], including the formation of amyloid fibrils in neurodegenerative disorders and the aggregation of sickle haemoglobin in sickle cell anemia. Remarkably, structurally virtually indistinguishable forms of filaments also fulfil various biologically beneficial functional roles, in the context of cytoskeletal filaments or in bacterial biofilms [2-5]. The factors governing why some protein aggregation processes are crucial to the function of an organism, yet others have devastating effects, have remained challenging to define. Through a study of the aggregation mechanism of several proteins forming either functional or disease-associated aggregates, we identify the presence of molecular level positive feedback in the aggregation mechanism as a key characteristic which delineates functional protein self-assembly from its pathological counterpart. Our findings indicate that prevention of secondary nucleation may be an essential prerequisite in controlling aggregation and suggest that evolution may have selected against structures with this characteristic for use as functional materials in the cell.

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Keywords

Protein aggregation, self-assembly, aggregation kinetics, pathological vs. functional amyloids

FRET-enhanced photo-modulatable fluorophore for improved super-resolution microscopy and single-molecule tracking studies

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Super-resolution fluorescence microscopy and single-molecule tracking approaches have allowed us to study protein dynamics and localization in living cells at close to molecular resolution. Photo-modulatable fluorophores permit super-resolution imaging studies even in high-density samples but are often less photostable than traditional fluorophores¹. Recent research has focused on generating novel photo-modulatable fluorophores either to improve live-cell single-molecule tracking or to provide a broader colour palette for the tracking of protein complexes for which there are currently few options.

Here, we externally modified an existing genetically encodable, photo-modulatable fluorophore using Förster resonance energy transfer (FRET). We conjugated a bright, photo-convertible donor fluorophore (mEos3.2) with photostable HaloTag[®] acceptor dye (JF₆₄₆²) to yield a new ultra-photostable genetically encodable, photo-modulatable fluorophore. This resulted in a greater than 10-fold increase in the ensemble total on-state time of mEos3.2, with 5% of molecules showing a 60-fold improvement. As well as this, a 5-fold improvement in total photon emission and 3-fold increase in on-state time was observed. The increased on-state time of mEos3.2-HaloTag[®]-JF₆₄₆ compared to mEos3.2 permitted the tracking of single CHD4 protein molecules for longer in live mammalian cells. This resulted in better detection of transitions between diffusion modes and the revelation of previously unseen dynamics.

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Keywords.

Super-resolution, Photophysics, FRET, Single-protein tracking, Photostable, Fluorophore

The Role of Carbonaceous Coating for Anchoring of Carbon Nanotube Bundles

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Co-synthesized bundle coating has been shown to have key influence on the CNT fibre's properties, be it mechanical, electrical or thermal. Often over-simplified if not misunderstood as impurity, we aim to redefine the role of carbonaceous bundle coating in CVD spun carbon nanotube (CNT) fibres.

We will present the highest bulk CNT thermal conductivity to date, our know-how for achieving high mechanical strength at long gauge length, and the efficiency of post-process treatments in front of the background of those co-synthesized carbons, and relate their effectiveness not to say usefulness to the precursors and instrumentation used in the synthesis.

References.

Keywords.

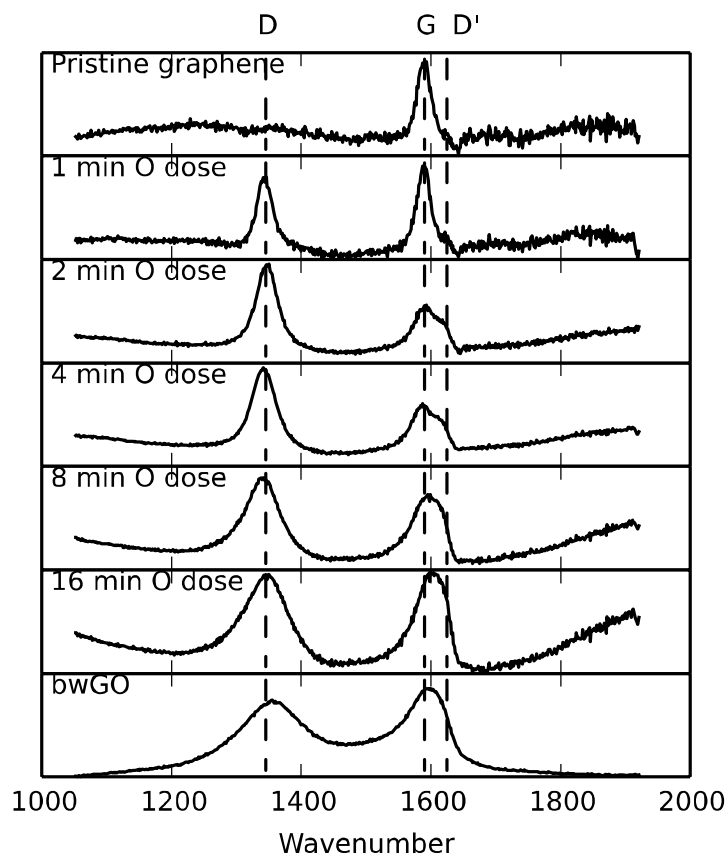
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Graphene Oxide A 2-component structural model

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There are many unanswered questions about the structure of Graphene Oxide (GO) and our 2-component model has been the subject of considerable discussion. Here we present new results on the functionalising of pure graphene with atomic oxygen. Atomic resolution TEM, XPS and Raman are used to show how graphene evolves into a structure indistinguishable from GO. Other work on the use of sulfur functionalities on the GO basal plane to anchor gold nanoparticles will also be presented.



Keywords.

graphene, GO, chemical functionalisation, Raman, XPS

Carbon nanostructures for two-dimensional optical media

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There is a requirement to eliminate the use of bulky and curved refracting lensing components from the optical components used in today's projection, imaging and sensing equipment. Replacing these with compact media is critical to enable optical system compactness. One means of achieving this miniaturization is by using a Veselago lens. However, this lens requires a material with a negative index of refraction. So far, the production of these for broadband operation at visible frequencies has proven technically challenging. Here we review these technical challenges, review the current status of the technology, and highlight the significant technical hurdles still remaining, before the commercial maturity of the technology can take place.

In order to overcome some of these limitations, here we introduce an alternative approach that relies on novel methods to produce carbon nanostructures. We show how these can be used to generate a highly-collimated, wide-diameter beam using compact optical medium in flat-slab form, without the use of negative-index materials. We base our approach on light collimation using nanomaterials in nanoscale patterns designed to provide a highly anisotropic absorption coefficient. The nanostructures are able to strongly absorb light rays travelling along unwanted off-axis directions, whilst transmitting the desired (on-axis) rays. Whilst non-lensing, this technique can be used to circumvent the technical challenges of current negative-index metamaterials. In addition, we show this nanostructure can be embedded into a flexible transparent polymer matrix.

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Doi:10.1038/srep18767

Keywords.

Carbon nanotubes, low temperature growth, optical nanostructures, optical lensing, nanostructures for optical collimation.

Optical levitation of nanodiamonds in vacuum without heating

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Optical trapping at high vacuum of a nanodiamond containing a nitrogen vacancy centre would provide a test bed for several new phenomena in fundamental physics [1-6]. However, the nanodiamonds used so far have absorbed too much of the trapping light, heating them to destruction (above 800 K) except at pressures above 10 mbar where air molecules dissipate the excess heat [7-10]. Here we show that milling diamond of 1000 times greater purity creates nanodiamonds that do not heat up even when the optical intensity is raised above 700 GW/m² below 5 mbar of pressure. For more details, see AC Frangeskou et al, arXiv:1608.04724 (2016). The large quantities of high purity nanodiamonds made in this way may also find applications in sensing.

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Keywords

Nanodiamond, quantum information, optical trapping

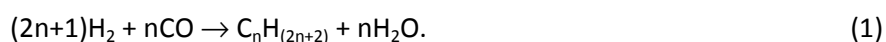
The application of inelastic neutron scattering to investigate CO hydrogenation over iron based Fischer-Tröpsch synthesis catalysts

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Abstract

Fischer-Tropsch synthesis (FTS) is making an increasing contribution to hydrocarbon production options; presently, it constitutes a most active area of heterogeneous catalysis research. The reaction may be presented by the following (deceptively) simple chemical equation:



Recent chemical plant commissions feature unit operations utilising cobalt based catalysts but there remains a significant research interest in iron based FTS catalysts, not least because these materials provide the opportunity for production of valuable unsaturated hydrocarbons [1].

The presentation concentrates on the surface chemistry surrounding iron based FTS catalysts, which, under FTS conditions, experience a “construction phase” in a process of self-organisation [2]. For example, a hematite precursor compound (α -Fe₂O₃) may be reduced to magnetite (Fe₃O₄), which then reacts to form various carbides [*e.g.* cementite (Fe₃C) and Hägg (Fe₅C₂)]; this combination of structural motifs then defines the active phase of the catalyst [1]. Whereas a variety of conventional analytical techniques are available to characterise such solid-state transformations (*e.g.* Mössbauer spectroscopy, X-ray diffraction and temperature-programmed oxidation, *etc.*), with reference to Equation 1, it is a non-trivial matter to evaluate how hydrogen is partitioned within the catalyst matrix.

One technique that is demonstrating increasing application for studying hydrogenous species in heterogeneous catalysis is inelastic neutron scattering (INS) [3]. In 2013 INS was used for the first time to obtain the vibrational spectrum (50-4000 cm⁻¹) of a commercial grade FTS catalyst extracted from a large-scale coal-to-liquids unit operation [4]; with the spectrum establishing a role for a hydrocarbonaceous overlayer in the process chemistry. Follow-up studies using CO hydrogenation as a test reaction over representative iron oxide catalysts suggest that the hydrocarbonaceous overlayer may play an active role in moderating the supply of reagents within the catalyst matrix during CO dissociative adsorption and CH_x chain propagation processes [5,6,7]. The presentation will describe how these novel INS measurements are providing new insight in to the operational phase of this economically relevant but complex catalytic system.

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Magnetic thin-films: challenges for future applications in computing

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In this talk I will present an overview of current and near-future applications of magnetic thin film nanostructured devices for computing. Electronic device functionality is currently based on the storage and flow of charge, but the field of ‘Spintronics’ provides the opportunity to also utilise the intrinsic magnetic moment, or ‘spin’, of the electron in addition to its charge. Computational logic, memory, and data storage device functionalities based on manipulating the electron spin can offer very low operating power consumption and high data density, in addition to possible novel computing architectures. After an introduction to spintronics I will cover the physics of how these various devices operate, how they compare with the current state-of-the-art in conventional electronics. I will describe the challenges in developing these future devices, and describe areas where magnetic scattering techniques provide valuable insight.

Keywords.

Magnetic thin-films, spintronics, data storage, computing

Energy dissipation in superconducting resonant cavities: lessons learnt from neutron scattering

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Increasing demand for state-of-the-art superconducting radio frequency (SRF) cavities requires good understanding of the performance-defining processes. In the absence of the external degrading factors, SRF cavity performance is fully defined by the quality of the superconducting material which can be tailored by the temperature and chemical treatments. Investigation of material structure and composition on nanoscale is vital for tailoring niobium-based material SRF optimization. Development of new niobium-based SRFs requires extended material characterization.

To complement the information obtained using a routinely applied set of characterization techniques, a concurrent measurement of neutron diffraction (ND) and Compton scattering (NCS) has been performed for the first time to investigate production-induced structural features of niobium-based SRFs. In our pilot neutron work employing VESUVIO+ spectrometer at ISIS neutron and muon spallation source we have concentrated on finding spectroscopic and structural signatures of multiple steps of mechanical, chemical and temperature treatments of niobium, the treatment that may eventually lead to SRF performance degradation, such as the hydrogen Q-disease and High Field Q-slope (HFQS) [1-4]. We have also attempted to find out why N-doping, a process discovered at Fermilab and applied to Linac Coherent Light Source-II Project at Stanford [5, 6], systematically improves the SRF quality factor up to a factor of three. ND spectra recorded at both temperatures showed hydrogen containing phases coexisting with the Nb main phase, in consistence with our previous electron-microscopy results indicating the coexistence of nano or micro domains of at least two H containing Nb phases embedded in Nb [1-4]. In particular, at least one phase showed superlattice peaks indicating a modulated structure. This latter observation may indicate a presence of spatial distributions of different crystalline domains of niobium hydrides, and possibly even niobium nitrides, that may be temperature dependent. Moreover, the longitudinal momentum distributions of Nb, obtained from NCS, showed marked systematic differences, most likely due to different sample preparation histories. To the best of our knowledge, this is the first demonstration of rather unprecedented sensitivity of the NCS method to the local structural disorder for such a high nuclear mass (93 amu).

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Keywords.

Niobium-based superconducting cavities, neutron Compton scattering, neutron diffraction

Solvent- and Surfactant-Mediated Self-Assembly Structures of Diblock Polythiophene Polyelectrolytes for Organic Photovoltaic Devices

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The performance of organic photovoltaic devices (OPVs) depends critically on simultaneous control of the optoelectronic properties and nanoscale morphology of conjugated polyelectrolytes (CPEs).¹ Recently, self-assembly strategies have emerged as an elegant approach for the design and fabrication of reproducible nanoscale aggregates from CPE building blocks.² Solvent-mediation and co-assembly with oppositely charged species are both attractive methods to control CPE architecture in solution. The challenge, however, is to determine the key structure-property relationships in these novel materials and demonstrate how structural order tailoring can be harnessed to deliver highly efficient OPVs.

Here we will demonstrate the solvent-mediated³ (methanol, water and methanol/water mixtures) and surfactant-mediated⁴ (SDS, *d*₂₅-SDS and PFOS) self-assembly of a series of amphiphilic diblock copolymers each containing a hydrophobic poly(3-hexylthiophene) (P3HT) block and a hydrophilic cationic P3HT block bearing different terminal ionic groups. Their optical properties and aggregate structures were studied in solution, and in subsequently prepared thin films, using photoluminescence, scattering and microscopic techniques. In particular, small-angle neutron scattering (SANS) was used to elucidate the nanoscale morphology and solvent content of the CPE and CPE-surfactant structures in solution. A variety of well-defined, solution-phase structures (*e.g.* rods, lamellar sheets) could be generated through careful modulation of the solvent polarity and surfactant charge ratio. In addition, direct comparison between the diblock copolymers and their analogous homopolymers revealed the significance of the hydrophobic P3HT block in controlling aggregate morphology. Solvent- and surfactant-mediated self-assembly of all-conjugated block CPEs may therefore provide a simple inexpensive route for obtaining nanostructured active interfaces suitable for OPV devices.

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AbINS: a modern software for INS interpretation

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Inelastic neutron scattering (INS) spectroscopy, in contrary to other vibrational spectroscopic techniques such as infrared or Raman spectroscopies, provides much richer microscopic insight into a material due to the absence of selection rules induced by the system's symmetry and via its dependence on both energy (E) and momentum (Q) transfer [1]. First-principles density functional theory (DFT) based calculations are now routinely used to interpret infrared and Raman spectra. These calculations can also be used to interpret INS spectra, however, the need to include the atomic neutron presence of scattering cross sections, overtones and combination modes, together with instrument specific E-Q windows make the data analysis challenging [2], [3].

Here we present AbINS: a new generation of software to interpret INS spectra using ab-initio phonon data. AbINS is an open-source package and can be used on Linux, Window and MacOS. It is implemented as a plugin to the neutron data analysis software, Mantid. AbINS can handle systems with up to 200 atoms, and offers the facility to plot the full (Q, E) map, with the option to extract individual atomic contributions. AbINS uses the phonon data calculated by DFT programs, such as CASTEP and CRYSTAL, to generate the calculated INS of a powder sample, making it easier to establish a connection between theory and experiments.

In this presentation we will discuss the implementation and different features of AbINS along with a few examples like croconic acid [4] which offers potential for metal-free organic electronic and non-linear-optical devices and caesium hydrogen sulfate which as a proton conductor is a promising candidate for fuel cells [5]. Since the work on this software is on-going, its scope and future outlook will also be discussed.

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Conformational Studies of Biomolecules by Rotational Spectroscopy

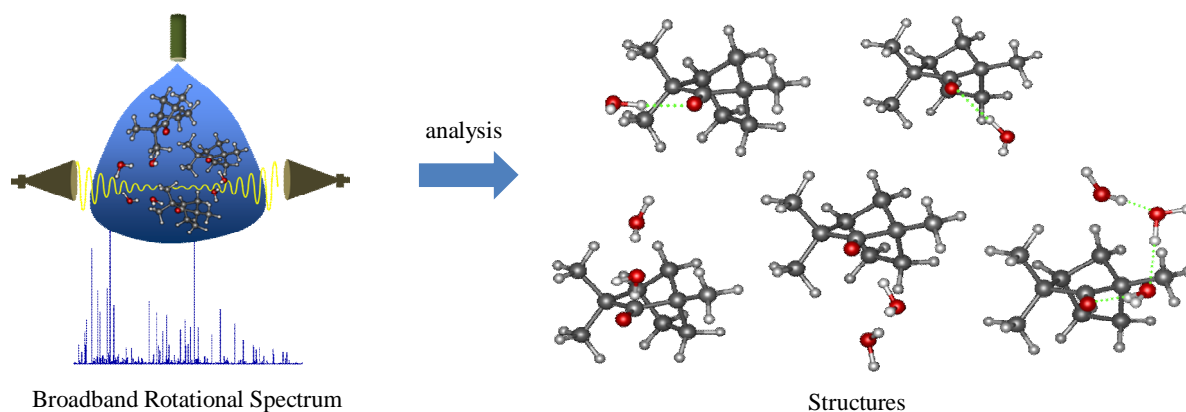
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Structure and function are intimately linked in biological systems. One of the important features of biologically-relevant molecules is that they are highly flexible and capable of adopting an immense array of conformations. However, for many biological processes a detailed knowledge of the structures of the biomolecules involved is lacking. What are the preferred conformations that a biomolecule adopts and why? What is the influence of the environment? Rotational spectroscopy is uniquely placed to answer these questions as it is directly related to molecular structure and its high resolution and sensitivity allows unequivocal identification of co-existing conformers and their stabilising interactions. Over the last decade, technical improvements had made possible to extend the range of biomolecules amenable to rotational studies. In this talk we will describe these advances and several examples of our recent work on isolated biomolecules and their clusters will be discussed. In all cases valuable information was obtained on the intra and intermolecular interactions determining molecular structure. Perspectives on future studies of biomolecules by rotational spectroscopy will be presented.

**Keywords.**

conformational analysis, microwave spectroscopy, non-covalent interactions, odorants

Measuring a Complete Reaction Coordinate: Windowless Observation of the Photodissociation Dynamics of CS₂

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Time resolved photoelectron spectroscopy (TRPES) shows exquisite sensitivity to both the electronic and nuclear dynamics of molecules. TRPES also provides, in principle, a windowless measurement of molecular structure as all states can be ionised. However, this windowless character is seldom achieved due to the limited energy range over which femtosecond lasers operate. The rapid development of femtosecond XUV sources at both free electron laser facilities and high harmonic generation (HHG) sources is set to remove this limitation with HHG sources offering advantages in terms of stability and accessibility. The relatively low flux of HHG sources has limited what can be achieved to date. We will present recent TRPES results on the photodissociation dynamics of CS₂. The experiments make use of a UV pump (6 eV) and XUV probe (21 eV) generated from a HHG source. The results allow for the unambiguous assignment of the full reaction pathway and allow us to capture the full dissociation dynamics including the ground state depletion, the multiple excited electronic states populated and the dissociation products in a single experiment. The experiments capture the dynamics in the initially excited singlet state, its subsequent conversion into the triplet manifold of states (Figure 1 A) as well as the production of the final dissociation products (Figure 1 B).

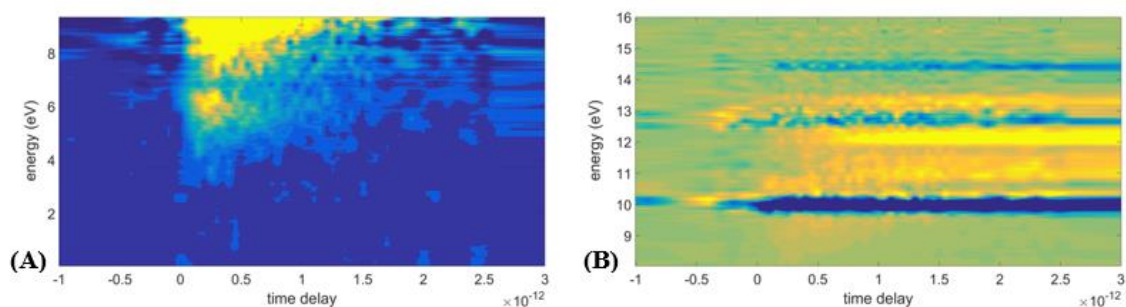


Figure. 1 TRPES surface plots of the binding energy ranges covered by the excited singlet and triplet states (A), and by the ground state depletion and final dissociation products (B).

Vibration and vibration-torsion levels of the S_1 states of *para*-fluorotoluene and *para*-xylene

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We have employed resonance-enhanced multiphoton ionisation (REMPI) spectroscopy and zero-kinetic-energy (ZEKE) spectroscopy to investigate the first excited electronic singlet (S_1) state and the cationic ground state (D_0^+) of *para*-fluorotoluene (*pFT*) and *para*-xylene (*pXyl*).^{a,b,c} Spectra have been recorded *via* a large number of selected intermediate levels, to support assignment of the vibration and vibration-torsion levels in these molecules and to investigate possible couplings.

The similarity in the activity observed in the excitation spectrum of the two molecules is striking, as is the comparison with toluene (methylbenzene), and the influence of the second methyl rotor in *para*-xylene on the onset of intramolecular vibrational redistribution (IVR) in the S_1 state is a point of interest.

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Keywords.

para-fluorotoluene, *para*-xylene, REMPI, ZEKE, torsion, vibration-torsion

Photoelectron Spectroscopy of the Thiazate (NSO^-) and Thionitrite (SNO^-) Isomer Anions

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The anion photoelectron spectra of the thiazate (NSO^-) and thionitrite (SNO^-) isomers were measured. Isomer-specific ion generation was achieved by the rational ion synthesis capability in our dual pulsed valve plasma entrainment ion source. The NSO^- photoelectron spectrum showed several well-resolved vibronic transitions from the anion to the NSO radical neutral. The electron affinity of NSO was determined to be 3.113(1) eV. The fundamental vibrational frequencies of NSO were measured and unambiguously assigned to be 1200(20) cm^{-1} (ν_1 , asymmetric stretch), 1010(30) cm^{-1} (ν_2 , symmetric stretch) and 300(30) cm^{-1} (ν_3 , bend). From the presence of vibrational hot band transitions, several vibrational frequencies of the NSO^- anion were also measured: 1280(85) cm^{-1} (ν_1 , asymmetric stretch), 990(70) cm^{-1} (ν_2 , symmetric stretch), and 480(35) cm^{-1} (ν_3 , bend). Combined with the previously measured $\Delta_{\text{acid}}H_{298\text{ K}}^\circ(\text{HNSO})$, the $D_0(\text{H-NSO})$ was found to be 4.4(2) eV. Unlike the results from NSO^- , the SNO^- photoelectron spectrum was broad with little structure, indicative of a large geometry change between the anion and neutral radical. In addition to the spectrally congested spectrum, there was evidence of a competition between photoelectron detachment from SNO^- and SNO^- photodissociation to form $\text{S}^- + \text{NO}$. Quantum chemical calculations were used to aid in the interpretation of the experimental data, and agree well with the observed photoelectron spectra, particularly for the NSO^- isomer.

Abstract ID (To be added by Conference committee)

Multi-mass velocity-map imaging the UV photodissociation and VUV dissociative ionisation of 2-bromothiophene with a PImMS2 camera

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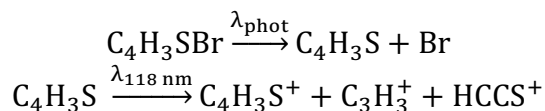
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The velocity-map imaging (VMI) apparatus at Bristol has been recently extended to incorporate a PImMS2 camera¹ for multi-mass imaging and a vacuum ultraviolet (VUV) laser source for ‘universal’ detection. This talk will provide a brief overview of these experimental enhancements before discussing the results of a study into the ultraviolet (UV) photochemistry of 2-bromothiophene (C₄H₃SBr).²

The UV photodissociation of 2-bromothiophene was investigated across the photolysis wavelength range $265 \geq \lambda_{\text{phot}} \geq 245$ nm with ionic fragments detected following VUV ionisation with 118 nm light:



At all wavelengths, the Br-loss photoproduct (C₄H₃S) was found to exhibit recoil velocities and anisotropies consistent with those reported elsewhere for the Br fragment [*J. Chem. Phys.* **142**, 224303 (2015)]. Velocity-map images for all lighter ions were also acquired simultaneously and include a C₃H₃⁺ channel that dominates the ion yield spectrum at $\lambda_{\text{phot}} \leq 255$ nm. Analysis of these images, alongside those for the REMPI-ionised Br fragment, reveal that these lighter ions arise from dissociative ionisation (from the VUV probe laser) of the most internally excited C₄H₃S fragments. This conclusion is supported by high level *ab initio* calculations.

References.

¹ <http://pimms.chem.ox.ac.uk/pimms2.php>

² Ingle *et al.* *J Chem. Phys.* Invited article - submitted (2017)

Keywords.

Gas-phase dynamics, velocity-map imaging, photodissociation, multi-mass imaging, universal detection, heterocycles

Prof. Dirk Aarts
University of Oxford
"Directed self-assembly of Janus rods"

Anisotropic Janus colloids are emerging building blocks for programmable self-assembly of materials. So far, experimental studies on the self-assembly of Janus particles have focused on the behavior of small clusters formed in dilute suspensions, mainly due to the scarcity of the available colloids. Here, we demonstrate a simple, yet versatile method yielding monodisperse colloids that possess anisotropy in both shape and chemistry. We observe that these particles exhibit hierarchical self-assembly: they first form inverse cylindrical "micelles", which subsequently stack into highly ordered lanes and ultimately form macroscopic structures. Computer simulations shine further light on the observed structures.

Thermal transport across nanoparticle-fluid interfaces

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The potential uses of nanoparticles in several biomedical applications, such as drug delivery, hyperthermia treatment, magnetic resonance imaging and tissue repair, have been recognized in previous works. Many of these applications involve transport of heat from the nanoparticles to the surrounding media and exploit the resulting increase in local temperature to, for example, destroy target cancer cells or to induce ion flux through biological membranes and nanoscale pores (1,2,3).

A full description of the mechanism of heat flow across the interface of solid nanoparticles and surrounding fluid requires an understanding of the complex interplay between various interfacial properties, such as surface free energies, interfacial curvature and microscopic structure. Specifically, at the nanoscale, the heat transport between two different phases is characterised by a temperature drop at the interface, quantified by a thermal boundary resistance, known as the Kapitza resistance, which offers a measure of the efficiency of heat transport.

Using non-equilibrium molecular dynamics computations, we have found that the thermal resistance of the interface depends strongly both on the wetting characteristics of the nanoparticle–fluid interface and on the nanoparticle size (4). Strong nanoparticle–fluid interactions, leading to full wetting states in the host fluid, result in high thermal conductances and efficient interfacial transport of heat. Moreover, the strength of the fluid–nanoparticle interactions has been found to influence the variation of the thermal conductance with particle size, with strongly hydrophilic particle showing the strongest curvature dependence. A general and effective equation has, therefore, been derived to describes the thermal conductance of nanoparticles in terms of curvature and interaction strength, with the aim to rationalize available computations and experimental data and motivate new investigations.

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Keywords:

Thermal transport, nanoparticles, Kapitza resistance, curvature, molecular dynamics.

Surfactant self-assembly in deep eutectic solvents

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Deep eutectic solvents (DES) are green solvents obtained through the complexation of a halide salt with a hydrogen bond donor at a certain mole ratio. Combinations of precursors allow myriad possibilities to be obtained in terms of physicochemical properties of the solvent, enabling solvent properties to be tuned for particular applications.[1] Our recent studies have shown the ability of DES to sustain self-assembly of surfactants.[2,3] Such alternatives bring the possibility to develop new, sustainable media for surfactant templating, microemulsion formation and synthesis of nanostructured materials. These results have shown the formation of micelles with different morphologies than those surfactants in water and other polar solvents, promoting shape transitions that are uncommon in water.[4]

Here we will explore the effects of headgroup solvation on micelle morphology and the role of surfactant-solvent interactions in the surfactant micellisation. Small-angle neutron and X-Ray scattering were used to investigate the behaviour of anionic and cationic surfactants in different DES. Our results provide a novel approach for surfactant aggregate manipulation in the absence of water. Selective charge screening at the headgroup region was found in particular systems. This change in the interfacial charge density and therefore in micelle morphology was found to depend on the surfactant concentration and solvent characteristics. Aiming to understand the fundamentals of amphiphile behaviour in these solvents, we will present details of surfactant self-assembly with varied physicochemical properties of the solvent, surfactant characteristics and the effects of counterion condensation.

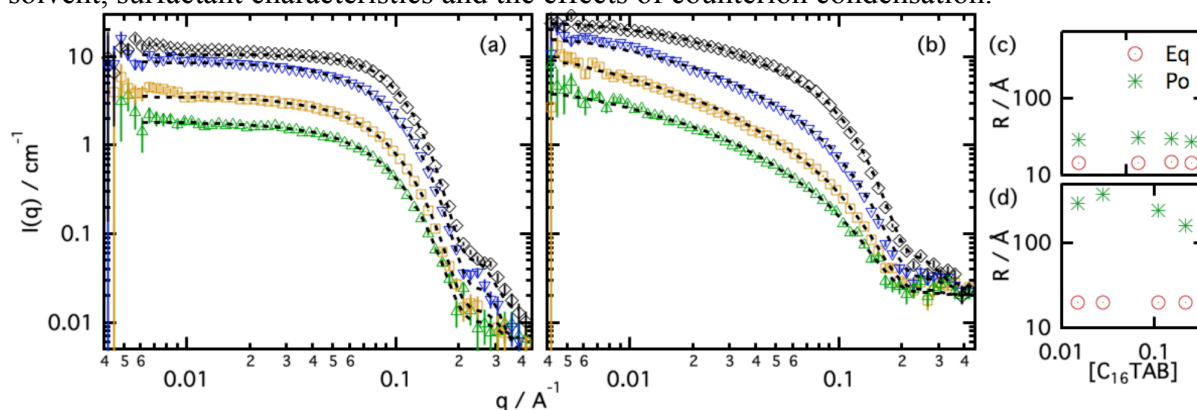


Figure small-angle neutron scattering data and fits of equivalent concentrations of $C_{16}TAB$ in (a) 1:2 choline chloride:glycerol and (b) 1:1 choline chloride:malonic acid. Equatorial (Eq) and polar (Po) radii of $C_{16}TAB$ micelles in (c) choline chloride:glycerol and (d) choline:malonic acid DES.

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Developing Fundamental Models of Colloid Transport and Absorption in Sand Filters

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The Site Ion Exchange Plant (SIXEP) at the Sellafield reprocessing site uses high-pressure sand bed filtration as part of the process to remove Caesium and Strontium from nuclear waste. As with all types of filtration, the filters eventually become clogged as colloids and other particulates accumulate within it. This causes a pressure drop and a decrease in permeability. The aim of this project is to improve the understanding of clogging in high-pressure sand bed filters by linking the currently empirical clogging parameter to fundamental properties of the sand bed and colloidal particles in the filtrate.

Smooth Particle Applied Mechanics (SPAM) is used to create a continuum scale model of the filtration process, using pseudo experimental information from Molecular Dynamics (MD) to provide the necessary parameters. The transport properties required for a continuum model are extracted from an MD simulation of the same process. The SPAM model is validated by comparison with both the MD simulation, and by an existing empirical model based on data gained from a time-lapse fluorescence imaging experiment hosted at Liverpool University. This model will be used to explore the effects on clogging by measuring properties such as pressure, velocity, and density across the system while varying factors such as the packing, shape, particle size distribution, and the nature of the colloidal interactions.

Keywords.

Molecular Dynamics, Smooth Particle Applied Mechanics, Colloids

Modelling the extraction of rare earths with ionic liquids

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Rare earths play an important role in much modern technology. They are used in catalysts for petroleum refining, are used in mobile phones and computer monitors and they are vital ingredients in the high power magnets used in laptops and lasers and also in new offshore wind turbines and electric vehicles. Currently China supplies 95-97% of world demand, but has been reducing supply and increasing prices to foreign consumers. It is thus clearly desirable for the UK to reduce its dependency on these imports. The nation lacks its own mineral resources but what it can do is to improve its recycling of rare earths [1].

Ionic liquids provide an attractive, environmentally friendly way of extracting these metals from waste [2]. This has been demonstrated experimentally as a viable approach but if one were to do this on a large, industrial scale, the process would need full optimisation. We use a multi-scale approach to do this, combining molecular dynamics simulation and the SAFT equation of state [3] with flow-sheet modelling using the gPROMS package developed by PSE[4]. Our current focus is on the reasonably well-characterised process of separating Co/Ni using the ionic liquid Cyphos IL 101 [5], so we may develop the protocol for dealing with real rare earths.

We present simulation results on the properties of the metal ions both in aqueous and ionic liquid phases and compare these data with SAFT modelling [3]. We then use these data to create a flow-sheet model and we also present results from this, comparing where possible with available experimental data. We finish up with a conclusion and an outlook for future work.

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Keywords.

Rare earths, ionic liquids, recycling, molecular dynamics, SAFT, flow sheet modelling

S-S bonds in biological systems and other studies

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I will begin by summarizing the areas of research currently developed in our group, which are mainly enzymatic catalysis, computational mutagenesis and drug discovery. Subsequently, the establishment of enzyme reaction mechanisms in systems with S-S bonds, using QM/MM techniques (1,2) will be addressed, emphasizing the methodological aspects that have to be taken into consideration to achieve accurate and reliable results. The role of enzyme flexibility on catalytic rates will be discussed too.

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Keywords.

S-S bonds, enzyme reaction mechanisms, QM/MM.

Grid-Based Non-Adiabatic Quantum Dynamics Using Potential Energy Surfaces Constructed On-The-Fly

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Recent advances in the field of theoretical quantum dynamics have made the study of molecules of non-trivial size feasible (1,2). However, the bottleneck in terms of effort is the construction of the potential energy surface (PES) on which the nuclear wavefunction evolves. In order to minimise effort, and make methods usable by non-experts, the PES should ideally be constructed on-the-fly, that is while the nuclear dynamics is proceeding. As quantum dynamics is inherently non-local, this is an issue. One solution is the DD-vMCG method which uses Gaussian functions as the basis of the nuclear wavefunction, allowing a local harmonic expansion of the PES around the centres of the Gaussians to be calculated, from which Shepard interpolation, for example, is used to construct a global representation of the PES (3). This method suffers from numerical difficulties in the dynamics due to the non-orthogonality of the basis and requires the calculation of energy gradients and Hessians; a significant computational effort for large molecules. In this work we present a recently developed method to integrate construction of the PES, on-the-fly, using Gaussian Process Regression (GPR) (4) with grid-based quantum dynamics methods, in particular the MCTDH method (1). These well developed dynamics methods use orthonormal basis functions and the GPR expansion of the PES only requires the evaluation of electronic energies. In addition to allowing dynamics on a single PES, the GPR expansion has been allied with a pragmatic diabatisation scheme (5), and hence the method can also cope with dynamics on multiple, non-adiabatically coupled PESs (6). Along with an exposition of the method, illustrative results will be presented showing the method's efficacy.

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Modeling 2DUV spectra of adenine in water

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The nucleobases strongly absorb UV radiation. Studying the electronic dynamics after UV irradiation is difficult because of the ultrafast time scales involved. Recently, new experimental techniques have enabled the collection of two-dimensional spectra in the UV part of the spectrum [1]. We have modeled such spectra of the nucleobase adenine in water. By comparing our model with experimental results, we conclude that an intermediate dark state is involved in the energy relaxation process.

Our model of electronic dynamics in solution is based on the hierarchy of equation of motion method, which is here extended to treat a system with a conical intersection between electronic states. The method fully includes quantum decoherence and dissipation induced by the solvent. Thus, our method provides a link between model potential energy surfaces and sensitive experimental observables. We expect that our work will renew interest of quantum chemists in understanding the photophysics of nucleobases, guided by experimental data.

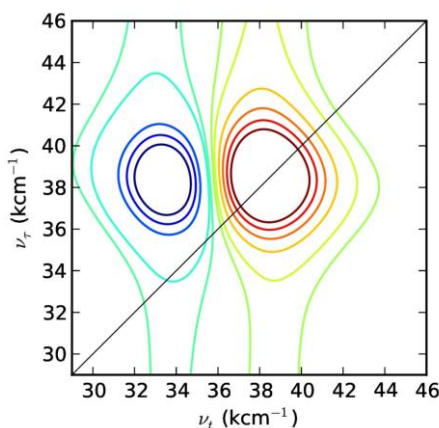


Figure: calculated 2DUV spectrum of adenine in water at a waiting time of 500 fs.

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Nanoporous Gold - A Selective Catalyst For Methanol Oxidation

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Bulk gold is an inert material which is not known for any special catalytic activity. On the other hand nanostructured gold can be remarkably active and selective for a range of chemical reactions, especially for those involving molecular oxygen. Au-based catalysts can be used for fuel cells, the synthesis of esters or the selective oxidation of alcohols. [1] There is a high interest in this gold based catalysts because the selectivity of gold to partial oxidation products is higher than the selectivity of other metal catalysts. [2] Especially Nanoporous gold (np-Au)

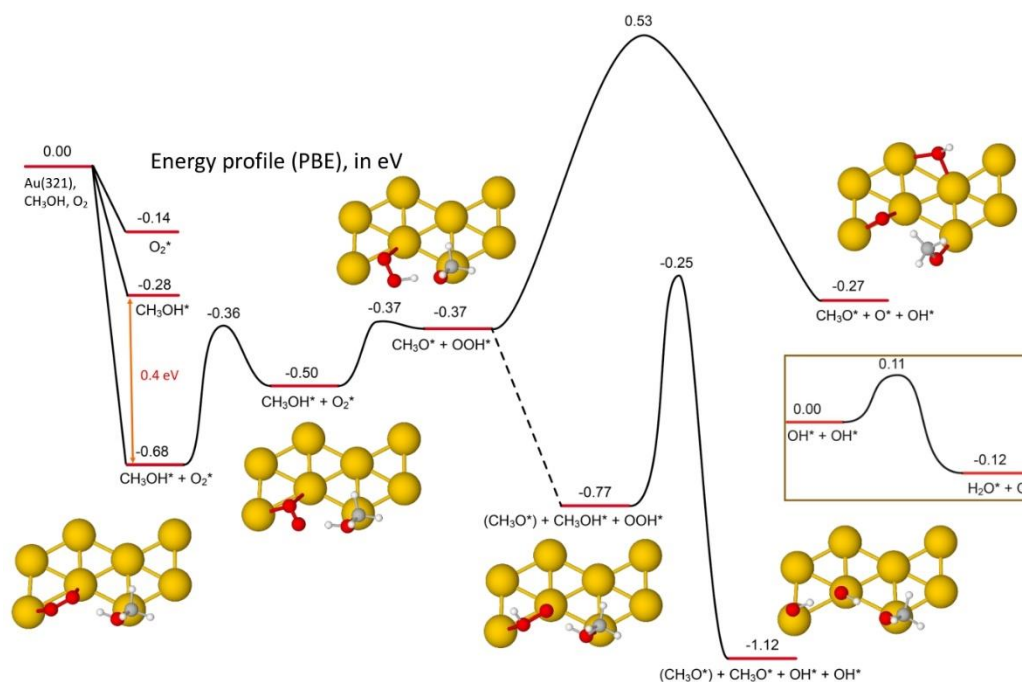


Figure 1: Pathway for Methanol oxidation with molecular oxygen on Au(321) [4]

has recently attracted considerable interest due to its potential use in catalysis. This Au-based catalyst can be used for the selective oxidation of methanol. The bottleneck of this oxidation reaction is the activation of oxygen on the surface.

For this study, a kinked Au(321) surface introduced by Moskaleva [3] represents one of the reactive surfaces of the nanoporous gold. It consists of (111) terraces and zigzag-shaped steps, which may be favourable as possible adsorption positions for methanol in partial oxidation reactions. The aim of our work is the elucidation of the detailed mechanisms for total and partial oxidation of methanol on this model surface. So far we analysed the process of the oxygen activation and were able to present a first theoretical mechanism that explains the first steps of this oxidation process, where first a methoxy species and in a next step formaldehyde is formed. The first step of this pathway is shown in figure 1. For reasons of simplification just the terrace of the Au(321) surface is shown.

These catalytic surface reactions are analysed using the exchange-correlation functional PBE implemented in the plane-wave based Vienna ab initio simulation package (VASP) [5] within the supercell approach. PAW Potentials are used. [6]

In order to validate the reaction paths on a higher level of theory, we will validate the activation barriers using an embedded cluster model for Coupled-Cluster calculations.

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Ethanol adsorption upon Pt-shell@M-core nanoparticles

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The uncompleted ethanol oxidation reaction is one of the major sources of efficiency loss in direct ethanol fuel cells [1]. Alternatives to have the full 12 e⁻ production during the ethanol oxidation reaction (EOR) are needed, where highly efficient catalytic materials can be coined by surface design. Here, we address the effect of the miniaturization and the alloying effect as alternative to improve the EOR. The energetic, geometrical, and electronics properties of ethanol adsorbed onto Pt-shell@M-core (M=Au, Pd, Ni, Ag) nanoparticles are evaluated by means of van der Waals corrected density functional theory simulations. Our results show that ethanol is more strongly bound to the metallic nanoparticles than the Pt-monolayer/M nanofilms by 0.2-0.3 eV [2]. Although the adsorption happens always through the oxygen atoms, and that it attaches preferentially atop a vertex or edge Pt-atoms, a variety of configurations is found depending on the relative position of the CH₃ and CH₂ groups with respect to the cluster, with or without the formation of an elongated bond between a hydrogen of the CH₃ and the cluster. Furthermore, a geometrical analysis show that the deformation induced by the ethanol into the nanoparticle depends on its chemical composition, with more significant distortions in the pure Pt and Pt@Au than in the Pt@Pd system. Although the charge transfer between surface and sub-surface metallic atoms depends on both the chemical composition and the adsorption site, the ethanol donates charge to the cluster and both the oxygen and its docking Pt are losing charge. The reported data can open new routes along the design and selection of nanomaterials for ethanol catalysis and our data shows that Pt@Au nanoparticles have promising adsorption properties [3]. The effect of many ethanol molecules will be addressed.

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Keywords.

Ethanol, Catalysis, Fuel Cell, Nanoparticle, DFT

Protein structure and dynamics through the lens of solid-state NMR

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Solid-state NMR is a powerful, complementary to other biophysical techniques, approach for studying at atomic resolution structures and dynamics of proteins in various forms from fibrils and membrane proteins to large protein complexes. In this presentation, I discuss several developments in methodology and applications concerning protein structure and dynamics in the solid state with examples illustrating advantages and challenges of the above-mentioned approach.

Keywords.

solid-state NMR, magic angle spinning, proteins, dynamics, structure

Hydrocarbon Radical Cations as Intermediates in Interstellar Carbon Chemistry

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Small hydrocarbon molecules play an important role in the astrochemistry of the inter- and circumstellar medium leading to the formation of large organic molecules, and ultimately to PAHs and carbonaceous dust. Whereas neutral hydrocarbons are commonly used as probes for physical and chemical conditions in astrophysical environments, observations of reactive hydrocarbon cations, important intermediates in carbon chemistry, are very limited, mostly due to a lack of accurate laboratory spectroscopic work. Here I will present first laboratory data on the gas phase spectra of several hydrocarbon cations (e.g., C_2H^+ , C_3H_2^+ , and C_3H^+), made possible by our recent development of sensitive methods for vibrational and rotational action spectroscopy in cryogenic ion traps [1-4]. Details of high-resolution studies using narrow-band continuous-wave radiation sources (OPOs, mm-wave multiplier chains) as well as broadband data obtained at the infrared free electron laser facility FELIX will be given. An outlook on how to extend these studies to larger organic species, including PAH ions, will be presented.

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The shapes of diffuse interstellar bands

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The longest standing challenge in astronomical spectroscopy is to identify the carriers of the *c.* 500 diffuse interstellar bands (DIBs) [1] - absorption features seen in optical and near-IR spectra towards stars with significant foreground material. The band carriers are thought to be carbonaceous molecules such as polycyclic aromatic hydrocarbons (PAHs) and fullerenes, one of which was recently identified as a DIB carrier. The DIB carriers represent a significant fraction of the cosmic carbon quota, and once identified, will make them a powerful tool to probe the chemistry and conditions in the interstellar medium.

The bands have a range of widths, strengths and shapes ranging from relatively sharp features with widths of *c.* 1 Å to the broadest and strongest with a width of *c.* 23 Å. Some of the sharper DIBs have distinct shapes and exhibit fine structure. In this presentation I will describe an example, the λ 6614 DIB, the shape of which varies between lines-of-sight [2], and a wider study of diffuse bands one group of which, previously classified as correlating with the presence of the C₂ molecule [3], does not show a change in profile. When local effects such as multiple absorbing clouds can be discounted, most of the profile difference can be interpreted in terms of differing levels of 'hot-band' contributions due to excitation from low-lying vibrationally excited levels of the carriers. This contrasts with an alternative interpretation of band profiles in terms of rotational contours [4].

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Laboratory Spectroscopy of Astrochemically Relevant Molecules

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The interplay between laboratory spectroscopy and observational astronomy has allowed for the chemical complexity of the interstellar medium (ISM) to be explored. Our laboratory studies involve the measurement of the rotational spectra of smaller, but complex organic molecules (complex in the sense that they have nonlinear structures or contain several substituents) in the region 75-110 GHz, thus covering a portion of Band 3 of the Atacama Large Millimeter/submillimeter Array (ALMA). Up until recently, we have concentrated on medium-sized (5 to 9 heavy atoms) nitrogen- and oxygen-containing molecules and their vibrationally excited states. Examples include cyanides, such as *iso*-propyl cyanide, dialcohols, such as 1,2-propanediol, and amino alcohols, such as alaninol (2-amino-1-propanol). Further, we have extended the capabilities of our segmented chirped-pulse spectrometer [1] with an electrical discharge apparatus. With this modification, unstable, transient molecules, as well as stable molecules, can be formed and investigated. We present here the recent results from our set-up. These experimental results have yielded transitions that will facilitate the detection of these molecules in the ISM with ALMA, and the discharge experiments planned should allow us to consider formation pathways of organic molecules from smaller building blocks.

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Keywords.

spectroscopy, astrochemistry, interstellar medium, millimeter-wave spectroscopy

Widespread SiO and CH₃OH Emission in Filamentary Infrared Dark Clouds

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Infrared-Dark Clouds (IRDCs) are cold ($T \leq 25$ K), dense ($n(\text{H}_2) \geq 10^5 \text{ cm}^{-3}$) and highly-extinguished regions ($A_V \geq 10$) believed to be the birthplace of high-mass stars (≥ 8 solar masses) and stellar clusters. The physical mechanisms that lead to the formation of these IRDCs are not completely understood and it is thus important to study the kinematics of the molecular gas and the chemical content of IRDCs to search for any signature/fossil record of their formation process. We have obtained parsec-scale maps of the emission of dense gas tracers (H₁₃CO⁺ and HN₁₃C) and of typical shock tracers such as silicon monoxide (SiO) and methanol (CH₃OH) toward a sample of three filamentary IRDCs, G028.37+00.07, G034.43+00.24 and G034.77-00.55 (hereafter Clouds C, F and G, respectively), believed to be at an early stage in their evolution. We have used the SCOUSE analysis tool to study the kinematics of the molecular gas in these clouds and, consistently with previous works toward other IRDCs, Clouds C, F and G show complex kinematic structures with several velocity coherent molecular filaments separated in velocity space by a few km/s. Correlated with the presence of these complex kinematic structures, widespread (parsec-scale) emission of SiO and CH₃OH is present in all clouds of our sample. For Clouds C and F, known to be actively forming stars, widespread SiO and CH₃OH is likely associated with on-going star formation activity. However, for Cloud G, a quiescent cloud with very low star formation activity as inferred from the lack of 8 μm , 24 μm sources or H₂ 4.5 μm shock-excited emission, the detected widespread SiO and CH₃OH emission may have originated in a gentle large-scale shock interaction.

Keywords. Stars: formation; ISM: individual objects G28.37+00.07, G034.43+00.24, G034.77-00.55; ISM: molecules

^{15}N Fractionation in Infrared-Dark Cloud Cores

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Nitrogen is one of the most abundant elements in the Universe and its $^{14}\text{N}/^{15}\text{N}$ isotopic ratio has the potential to unveil the initial chemical composition of the protosolar nebulae (PSN) from which the Solar-system formed. Recent findings suggest that the Solar-system may have formed in a massive cluster since the presence of short-lived radioisotopes in meteorites can only be explained by the influence of a supernova. Infrared-Dark clouds (IRDCs) are cold, dense regions of giant molecular clouds and they are believed to represent the initial conditions of high-mass star formation. Therefore, IRDCs are unique laboratories where to test the ^{15}N fractionation processes in an environment similar to that of the PSN.

In our study, isotopologues of HCN and HNC were used to probe the $^{14}\text{N}/^{15}\text{N}$ ratio toward a sample of 22 dense cores within 4 IRDCs (namely clouds C, F, G and H^[1]). The J=1-0 rotational transitions of H^{13}CN , HC^{15}N , HN^{13}C and H^{15}NC were observed with the IRAM-30m telescope. Assuming optically thin emission and LTE conditions with a constant temperature of 15K, the nitrogen ratios were derived from the integrated intensities by substituting the estimated $^{12}\text{C}/^{13}\text{C}$ ratio from independent measurements.

The $^{14}\text{N}/^{15}\text{N}$ ratios measured toward IRDCs range from ~ 70 to ≥ 954 in HCN and from ~ 200 to ~ 540 in HNC. Amongst the 4 IRDCs, lower nitrogen ratios were measured in cloud G which are comparable to those measured in small Solar-system bodies and protoplanetary disks. In contrast, the results from clouds C, F and H showed relatively higher values which are consistent with the Terrestrial (TA) value (~ 272) and the PSN value (~ 450). Such difference between star-forming IRDCs (clouds C, F and H) and non-star forming IRDCs (cloud G) was further confirmed by measuring the $^{14}\text{N}/^{15}\text{N}$ ratios directly between HCN and HC^{15}N , as well as by taking into account the time dependence of $^{12}\text{C}/^{13}\text{C}$ derived from modelling^[2]. Our results support the idea that this difference could be due to the lower average gas density of cloud G with respect to the other clouds, and suggest that the gas density may be the key parameter in determining the initial nitrogen isotopic composition in the young PSN. As a result, our Solar system may have originated in a low-density IRDC.

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Probing proteins in small volumes

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The self-assembly of protein molecules into functional structures underlies core aspects of biological activity in living systems. When this process doesn't occur correctly, however, misfolded and misassembled species are formed, which can have deleterious activity, including compromising the viability of neurons and thus leading to neurodegeneration in the context of Alzheimer's and Parkinson's diseases. This talk outlines our efforts to develop and apply new physical chemistry approaches to probe and understand protein self-assembly and misassembly, and their roles in biological function and malfunction. A particular focus will be on probing protein behaviour using microfluidic tools, and I will discuss a number of cases where experiments in ultra-small volumes allow key aspects of protein behaviour to be quantified that remain challenging to obtain from conventional bulk experiments.

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Keywords.

Microfluidics, protein aggregation, neurodegenerative disorders

Reengineering protein surfaces for non-aqueous activity

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Biological macromolecules, such as proteins, have evolved to synergistically utilise the ensemble of forces that arise in an aqueous environment. Such forces help to drive protein folding and modulate dynamical behaviour, which in turn facilitates biological function. Although some enzymes can retain limited activity when extracted into anhydrous solvents, we have demonstrated that completely solvent-free (molten) functional protein liquids can be produced by remodelling the surface of a protein with a polymer surfactant. The electrostatically-grafted surfactant molecules act to extend the range of the intermolecular interactions, which allows the protein molecules to access an anhydrous liquid phase that is amenable to protein folding¹, dynamics² and function³.

These findings challenge the existing dogma that describes the role of water molecules in determining protein structure and function, and the robustness of this facile approach for achieving protein fluidity indicates that it could readily be developed for a wide range of biomolecules. Moreover, the development of the methodologies surrounding these novel hybrid constructs will not only provide insights into the role of water in protein folding, dynamics and function, but will also provide a gateway to the development of new technologies that will impact on industrial biocatalysis⁴ and regenerative medicine⁵.

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Keywords.

protein, surfactant, scattering, regenerative medicine, enzyme.

Magnetic field effect studies on radical pair reactions in artificial flavoproteins

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Magnetic field effects (MFE) on the photochemistry of novel artificial flavoproteins (flavomaquettes) have been investigated by cavity ring-down spectroscopy (CRDS). The simple, robust, and adaptable design of the flavomaquettes facilitates MFE studies by circumventing the complexity and diversity of their natural counterparts (cryptochromes) which are believed to play an important role in animal magnetoreception.

We have recently demonstrated that photoinduced electron transfer occurs in these artificial proteins leading to the formation of a spin-correlated radical pair which exhibits MFEs at room temperature.¹ In this work, the profound effect of the donor-acceptor distance on the MFE is demonstrated using flavomaquettes with distinctive flavin-tryptophan distances. CRDS was used to detect MFEs as a function of time and wavelength with a sensitivity two orders of magnitude greater than conventional single pass transient absorption techniques.

This innovative approach using purposefully designed artificial flavoproteins in combination with highly sensitive cavity enhanced spectroscopy opens up new pathways to explore MFEs in biologically relevant environments.

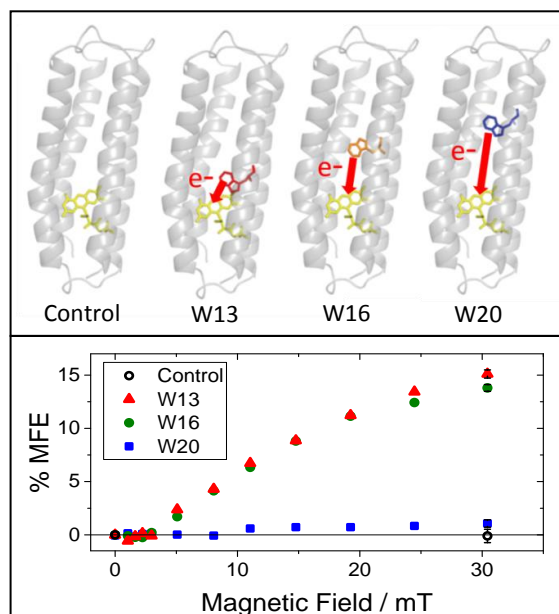


Figure 1. Flavomaquette designs with one tryptophan at increasing distance to the flavin (top). Percentage change in differential absorbance upon application of a magnetic field (%MFE) measured as a function of magnetic field strength (bottom).

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Towards a standardized characterization of solution phase protein structure using Raman optical activity: Implementation of comprehensive structural databases

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Over the last 20 years, Raman optical activity (ROA) spectroscopy has shown much promise as an alternative candidate for the structural analysis of proteins.¹ The technique, measuring a small intensity difference in right- and left-circularly polarized photons Raman scattered by chiral molecules, is extraordinarily sensitive to differences in the backbone torsion angles of peptides and proteins and thus gives a direct indication of the secondary structure of the protein being studied. The main limitation of ROA, traditionally, has been the general requirement for optical spectroscopic methods to be supported by quantum mechanical calculations, limiting detailed structural analysis to smaller molecules. This limitation is now being pushed back by advances in computational chemistry and computer power, which means that larger peptides²⁻³, or even whole proteins⁴ can be studied in detail by a combination of theoretical and experimental ROA.

Here, we outline the first large scale systematic study of ROA spectral signatures and how these are related to protein conformation.⁵ By generating libraries of peptide models long enough to adapt secondary structure motifs, all with repeating backbone torsion angles, and subsequently calculating the ROA property tensors of each of these peptides, the influence of the backbone conformation on the ROA profile can be studied in detail. Furthermore, the predicted Raman and ROA spectra in this database can, by means of similarity indices, be compared to experimental Raman and ROA data of peptides with known secondary structure. This allows for an unprecedented insight into the actual solution phase conformational landscape of these peptides.

The library approach to generating ROA data also allows us to include regions of the Ramachandran plot that are hard to come by experimentally, e.g. in regions that are not associated with the traditional definition of “order”. The addition of these disordered protein regions has the potential to redefine the structure-function paradigm, by including protein motifs usually thought of as “non-functional” and thus adding to our understanding of protein misfolding in neurodegenerative diseases.

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Keywords.

Raman optical activity, structural biology, protein chemistry, computational chemistry

Quantitative First Principles Calculations of Protein Circular Dichroism in the Near-Ultraviolet

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Vibrational structure in the near-UV circular dichroism (CD) spectra of proteins is an important source of information on protein conformation and can be exploited to study structure and folding.^{1,2} A fully quantitative theory of the relationship between protein conformation and optical spectroscopy would facilitate deeper interpretation and insights into biophysical and simulation studies of protein dynamics and folding. We have developed new models of the aromatic side chain chromophores toluene, *p*-cresol and 3-methylindole, which incorporate *ab initio* calculations of the Franck-Condon effect into first principles calculations of CD using an exciton approach.³⁻⁶ The near-UV CD spectra of 40 proteins are calculated with the new parameter set and the correlation between the computed and the experimental intensity from 270 to 290 nm is much improved. The contribution of individual chromophores to the CD spectra has been calculated for several mutants and in many cases helps rationalize changes in their experimental spectra. Considering conformational flexibility by using families of NMR structures leads to further improvements for some proteins and illustrates an informative level of sensitivity to side chain conformation. In several cases, the near-UV CD calculations can distinguish the native protein structure from a set of computer-generated misfolded decoy structures.

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Keywords.

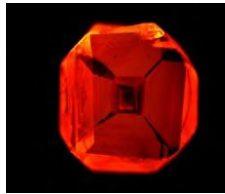
circular dichroism spectroscopy, near-ultraviolet, aromatic amino acid, vibrational structure

The Diamond Quantum Revolution

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Quantum coherence and entanglement were long thought to be observable only under exotic conditions. Hence, the discovery of quantum coherences and even nanoscale quantum correlations in diamond under ambient conditions have brought up entirely new opportunities in quantum science in technology. The precision of any measurement e.g. is limited by quantum mechanics. Yet, in practice, hardly any measurement reaches its quantum limits. This is because dephasing typically influences the measurement device, thus rendering sensitivity below its physical limits. Quantum sensors based on spin defects in materials like diamond, however, reach quantum-limited precision even under ambient conditions. Such sensors, e.g. allow for very precise detection of quantities like magnetic and electric fields, temperature, and pressure. By using multispin entanglement, quantum algorithms or quantum memories, Heisenberg scaling of sensitivity is achieved. While the physics of engineering optimum quantum states is subject to intense research in laboratories around the world, diamond quantum sensors start to venture into applications. First proof of principle work has demonstrated their use in material science, biology, medical imaging, and even industry.

Diamond Reactivity at the Nanoscale

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Nanodiamond particles are fundamental low dimensional diamonds with extreme surface to volume fractions, as high as 400m²/g. This surface to volume fraction has a profound effect on the properties of these particles, with 20% of the carbon atoms residing at the surface. The reactivity of these particles differs substantially for bulk diamond and considerable effort is required to disperse them from their aggregated commercial source. Their applications are as diverse as the seeds for diamond film growth through drug delivery to single photon sources.

In this work we will show how the reactivity of nanodiamond particles is substantially different to bulk diamond particles. Specifically, we will show how nanodiamond can react with molecular hydrogen at temperatures as low as 300 °C. This is particularly surprising as the bond dissociation energy of hydrogen is 4.5 eV. We will also show that this process renders the surface positively charged (zeta potential) in aqueous solutions over a wide pH range. Positive zeta potentials are rarely seen on bulk diamond surfaces and we attribute this to the nanostructure of the surface as observed by Transmission Electron Microscopy and Fourier Transform Infrared Spectroscopy.

References.

Keywords.

diamond, nanocarbon, zeta potential,

Epitaxial graphene growth by catalytic graphitisation of diamond

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There is considerable interest in the fabrication and electronic properties of graphene and related 2d materials for low-dimensional materials engineering. Graphene is most commonly produced by CVD growth and exfoliation^[1]; here we show that epitaxial films can be produced by controlled metal-catalysed graphitization of diamond.

Advantages of metal-catalyzed graphitization of diamond include the lower temperature in comparison with metal-free graphitization and CVD growth ($\sim 500^{\circ}\text{C}$) and the use of the substrate as a source of material in addition to its use as a lattice-matched substrate. Using photoelectron-based methods^[2], we have shown that epitaxy is maintained throughout the process as illustrated schematically in Fig. 1 for graphene growth on the (111) face of diamond.

The graphene grows from below rather than above as in CVD and therefore it is possible to controllably grow single and multilayer films. In a bilayer structure, the inner layer is bound strongly to the metal catalyst, but the second layer exhibits the electron dispersion characteristic of quasi-free graphene with Dirac points at the Fermi level.

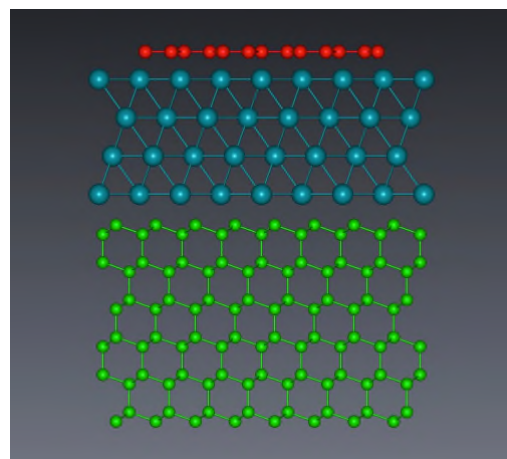


Fig. 1. 2-D growth of graphene (top layer) on a diamond substrate with an interlayer metal catalyst

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Keywords

2d materials; BN; photoemission

Diamond an Engineering Gem

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Diamond has long been recognized that, aside from its extreme hardness, that it is a remarkable material with many properties – optical, thermal, electrochemical, chemical, electronic – that outclass competing materials. When combined, these properties offer the designer an engineering material with tremendous potential to create solutions that can shift performance to new levels or enable completely new approaches to challenging problems.

One such area where diamond has provided significant advantages over existing technology is that of quantum technologies. Diamond based quantum technology utilising the nitrogen vacancy (NV) centre in diamond has seen rapid growth in research over the past decade. This initial growth was driven by the fact the NV centre provides an ‘easy’ to manipulate quantum system along with opening up the possibility of a new material to deliver a solid state quantum computer.

The NV defect is now moving from a quantum curiosity to a commercial development platform for a range of applications such as gyroscopes, timing and magnetometry as well as the more traditional quantum technologies such as quantum encryption and quantum simulation. These technologies are pushing the developmental needs of the material, and the processing of that material. This paper will discuss the synthesis control of diamond and the methods to process diamond for quantum technologies.

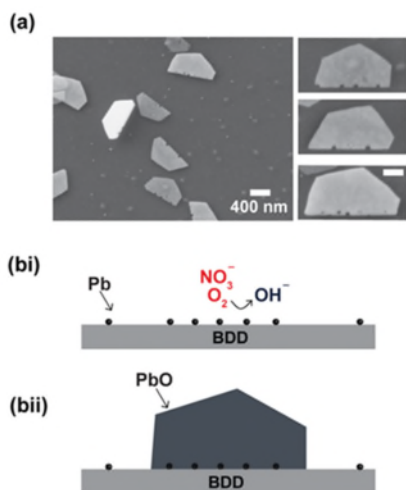
The Effect of Interfacial Electrode Temperature on Electrodeposited Metal Nanostructure Morphology

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There are many reasons to use diamond doped with sufficient boron so that it shows metal-like properties, in electrochemical applications. For example, diamond has an exceptionally high heat diffusivity, a product of a high thermal conductivity of $600 \text{ W m}^{-1} \text{ K}^{-1}$ at 300 K, a low heat capacity ($\sim 500 \text{ J Kg}^{-1} \text{ K}^{-1}$) and a high oxidation temperature ($\sim 700^\circ \text{C}$) in air. When combined with the excellent electrochemical properties of boron doped diamond (BDD), such as extended potential window, low background currents and insensitivity to oxygen reduction, BDD offers an excellent platform for investigating the role of the interfacial electrode temperature on metal electrodeposition and the resulting structures formed.

Electrodeposition is an extremely useful strategy for plating metallic structures onto electrode surfaces directly for use in electrocatalytic applications. We illustrate the role temperature plays in the electrodeposition process by considering the electrodeposition of Pb from Pb^{2+} in aqueous solution. The local temperature of the interface is controlled using an IR pulsed laser which heats from the rear side and not the solution facing side of the BDD.¹ Using such approaches it is possible to raise the interfacial temperature in a controllably way without introducing chaotic mixing / mass transport in the fluid. Temperatures above 100°C in aqueous solution are even possible without boiling the liquid. We show how by controlling the deposition potential, temperature and understanding the role of oxygen in the process we can switch electrodeposition from Pb nanoaggregates to predominantly crystalline PbO structures (Figure 1).² We also present preliminary data on the effect of temperature on the morphology of electrodeposited Pt nanostructures and the affect of the resulting structure on improving electrocatalytic performance properties.



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Figure 1: Different Pb structures formed on the surface of BDD during electrodeposition under elevated temperatures

The impact of neutron reflectivity in the study of surfactant adsorption in complex mixtures of technological importance

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Neutron reflectivity, in combination with H/D isotopic substitution, has in recent years made a major contribution to our understanding of the structure and composition of surfaces and interfaces in many aspects of Soft Matter. The impact of this approach is illustrated through examples of surfactant and mixed surfactant adsorption, which demonstrate the significant contribution and advances this approach has enabled. In the examples presented an emphasis will be placed upon systems of technological relevance and the contribution to the development of more efficient, lower energy usage and biosustainable products which have the potential for reduced environmental impact.

Keywords.

Neutron reflectivity, Surfactant and mixed surfactant adsorption, Biosustainability

Dialing in property sets - designing performance ionic liquid materials guided by neutron scattering

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Ionic liquids have been extensively investigated over the last 20 years as *designer solvents*. However, despite the extraordinary levels of interest, penetration into commercial markets has been slow. This is changing; uses of ionic liquids in liquid chromatography for separations, for cellulose processing, mercury control in the oil and gas sector, acid catalysis for petrochemical olefin alkylation to eliminate the use of HF, and as electrolytes in dye-sensitised solar cells and super-capacitors have all been successfully commercialised. The diversity of uses demonstrates how, given sufficient understanding of the fundamental chemistry and physics of this still relatively understood class of materials, ground-breaking advances can be delivered.

Neutron scattering combined with isotopic substitution has proven to be the key tool for studying the structure of ionic liquids at the atomic scale, enabling key ion-ion and ion-solvate interactions that define the behaviours of specific systems to be identified and characterised.¹ Moreover, crucial experimental data is gained that can be used to test the validity of molecular dynamics code, further extending capabilities for modelling and structural analysis.

This talk will summarise some recent, emerging developments where neutron scattering studies (performed using the SANDALS and NIMROD disordered materials diffractometers at ISIS) provide key guidance into the use of ionic liquids as extractants for aromatics, acid and heavy metals from oil and gas, light olefin/paraffin gas separations, and urban mining and recovery of key elemental resources.

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Keywords.

Ionic liquids, neutron scattering, isotopic substitution

Structural studies on aromatic and aliphatic liquids under confinement by total neutron scattering

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Confined liquids are subject of research in many areas such as geology, biology, food and drug preservation, and heterogeneous catalysis. Due to reduced dimensionality and large surface interface effects, liquids that are subjected to some geometric constraints, usually on nanoscale, can have different properties than in standard bulk conditions. Understanding the structure of confined liquids can explain why these properties change. Comprehending the local environment of liquids in catalyst pores will also reveal information necessary to understand the behaviour of the reacting system during the heterogeneous process.

Molecular-scale structure of three complex disordered systems comprising liquid reagents, *i.e.* benzene- d_6 , cyclohexene- d_{10} and cyclohexane- d_{12} , confined in porous catalyst has been studied by total neutron scattering. MCM-41 was used as the catalyst support. Its use simplifies the analysis of neutron scattering data, because it is an amorphous material with highly-ordered hexagonally arranged cylindrical pores. The model of MCM-41, as well as three 3D models for liquids under confinement were constrained by the experimental data by utilisation of Empirical Potential Structure Refinement (EPSR), and were used for study on local ordering in the system. The structural information expressed by radial, site-site and spatial density functions for confined liquids were compared with the corresponding bulk phases. Additionally, cylindrical distribution functions showing the arrangement of atoms and molecules across a pore and orientational cylindrical distribution functions showing the preferred orientations of molecules with respect to the pore walls were calculated.

Analysis of the cylindrical distribution functions showed that all chosen confined liquids form layers across a pore. Molecules form seven coordination layers counted across the pore diameter, from which the closest ones were better pronounced. Analysis of radial distribution functions indicates the disruption of local ordering when compared to the bulk liquid, which is pronounced by change in the function shape. This is particularly observed for benzene- d_6 . This is confirmed by an analysis of the spatial density functions, which, for benzene, shows different preferable positions for surrounding parallel molecules. Orientational cylindrical distribution functions in general show a tendency for molecules to orient with the plane of the ring flat against the pore wall.

For the first time, to our knowledge, three liquid reagents in confinement have been fully examined by total neutron scattering. This study shows that it is possible to model the pure reactant and the final product within a pore, and is the primary step for modelling snapshots of the heterogeneously catalysed liquid-phase reacting system where a mixture of product and reactant molecules will occur.

Constructing Nanostructured Metal Oxides for Sustainability using Deep Eutectic Solvents and Total Scattering Insights

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Deep Eutectic Solvents (DES) are a new class of alternative solvents, formed by the complexation of various H-bonding compounds to make a stable, room-temperature, pseudo-ionic liquid.¹ DES are rapidly gathering interest because of their low environmental impact and tuneable nature. This allows them to replace conventional solvents, offering enhanced functionality whilst helping to make processes greener. We have used DES to develop a ‘designer’ synthesis of nanostructured metal oxides. Our recent work has focused on using the choline chloride-urea DES (reline) to synthesise nanocerium to be used as improved automobile catalytic converter materials. The novel deep eutectic-solvothermal methodology allows tuning of nanoparticle shape, size, porosity, and hence the activity of the catalysts.² We have found that this method is particularly green, allowing the preparation of active nanorod catalysts at very mild conditions (~100 °C).

Further, we have developed a microwave-assisted solvothermal preparation of nanostructured iron oxides to be used as green energy storage materials. The nanoparticles are solution-cast as photoanodes for the splitting of water to hydrogen.³ We found that the reline-based process again allows for greener nanoparticle design by control of shape, size, and phase (either α -Fe₂O₃ or γ -Fe₂O₃), simply by modifying the reaction temperature and solvent composition. Pure DES produces small nanoparticles (~3 nm), and hydrated DES make nanoshards or rhombohedra, with magnetic properties and photoactivity varying accordingly. The photoanodes had competitive photocurrent densities of up to 0.7 mA cm⁻² at 1.23 V vs RHE, that is strong for a non-intensive preparation (10 min. microwave, 150 °C).⁴

Throughout, neutron total scattering and EPSR modelling are used to gain fundamental insights into DES nanostructure. With this combined approach, we are able to demonstrate that the mild conditions are enabled by a unique solvent-driven pre-structuring of the reactants. Therefore, we show how neutron scattering can guide the development of novel green chemistry to address modern challenges in sustainability and nanomaterials.

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Keywords.

Green chemistry, neutron scattering, empirical potential structure refinement, nanomaterials

New Application of Neutron Reflectometry to resolve the Dynamic Interfacial Composition of Soft Matter Mixtures at the Air/Water Interface

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Neutron reflectometry has been used extensively over the last few decades to determine the structure and composition of mixtures in soft matter and biology at the air/water and solid/water interfaces. The technique exploits the acquisition of data in multiple isotopic contrasts to resolve the amounts and locations of different components in a system [1]. The approach typically involves several measurements down to ppm in the reflectivity, so to resolve information about one sample usually takes a couple of hours even on the highest performing reflectometers [2]. As measurements are rather slow most of the published data concern steady state measurements of equilibrated samples.

Recently we have developed a new approach to resolve the composition of binary mixtures at the air/water interface by exploiting the high flux at low momentum transfer values of the FIGARO reflectometer at the Institut Laue-Langevin (Grenoble, France) [3]. Simultaneous equations of the scattering excesses of a mixture recorded in two different isotopic contrasts, but both in a mixture of H₂O and D₂O that has zero scattering length density, are solved to give the surface excess of each component. The approach minimizes influence on the data of the interfacial structure while maximizing sensitivity to the composition [4].

We demonstrate that this new approach provides more accurate compositions in a much shorter time than was previously possible. Indeed data are presented that are about 60 times faster than those using the traditional approach [5]. This improvement in the time resolution has now allowed us to apply the approach to dynamic systems for the first time.

Results are presented from 4 different projects: polyelectrolyte/surfactant films subjected to compression/expansion cycles [5], the kinetics of penetration of antimicrobial peptides in lipid monolayers [6], the interaction between oil vapour and surfactant monolayers, and the squeeze out of a drug from lipid monolayers by changing the surface pressure. These examples demonstrate the high potential of this new application of an established technique to contribute to a range of problems in soft matter science over the years to come.

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Keywords.

Air/water interface, neutron reflectometry, composition, soft matter, kinetics, dynamics

Building the World's Greatest Microscope: Revealing the atomic scale dynamics of surface chemistry

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In 1929, Nobel Laureate Paul Dirac made comments to the effect that Chemistry had been solved. With the advent of quantum mechanics “The underlying physical laws necessary for the mathematical theory of... ..the whole of chemistry are... ..completely known.... However, on a practical level computational chemistry is still in an early stage of development. Dirac went on: “the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” Despite electrifying advances in computational power since that time, Dirac is still right. The theory of chemistry requires approximations before theoretical descriptions and predictions of chemical reactions can be made.

The advent of the Born-Oppenheimer Approximation led to the development of the standard model of chemical reactivity where the electronically adiabatic potential energy surface for nuclear motion is derived and quantum motion of the nuclei on that surface can be calculated. For simple gas phase reactions, this approach has become an extraordinarily useful and reliable tool. For surface chemistry, additional approximations are commonly made: 1) classical mechanics for describing nuclear motion, 2) density functional theory (usually at the generalized gradient level) for calculating electronic states, 3) reduced dimensionality approximations and as before 4) the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom. I call this collection of approximations the provisional model for surface chemistry as we in the field are still testing and improving it.

In this talk, I will describe how a fruitful interplay between experiment and theory can lead to accurate atomic-scale simulations of simple reactions at metal surfaces. I will describe the very significant challenges surface chemistry presents including the problems of high dimensionality and the common failure of the Born Oppenheimer approximation. I will present two concrete examples. In the first, results of a full dimensional experimentally validated theoretical approach to hydrogen atom adsorption at a metal surface that includes the effects of Born-Oppenheimer failure leads to an atomic scale view of H-atom adsorption at a noble metal as well as an explanation for chemicurrents. In the second, energy loss dynamics occurring on a 25-fs time scale can be inferred from the scattering of hydrogen atoms from a graphene surface where a transient C-H chemical bond is formed. The H interaction on graphene is strongly influenced by the choice of metal substrate upon which the graphene is grown.

Keywords.

Quantum Mechanics, Density Functional Theory, Born-Oppenheimer Approximation, Dynamics of Surface Chemistry, H-atom Adsorption, Graphene, H-atom Scattering,

Probing the Interaction of N₂O with Copper, Silver and Gold cations using Infrared Spectroscopy and Density Functional Theory Calculations

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Metal cations and their electrostatic interactions with ligands are ever present in chemistry. Transition metal-ligand complexes are prototypes for bonding in inorganic and organometallic chemistry, playing a pivotal role in catalytic processes. There is much interest in investigating gas-phase metal ion complexes in the hope of better understanding fundamental metal-ligand interactions and metal ion solvation, both of which contribute to fundamental processes in chemistry, biology, geochemistry and astrophysics.¹ Clusters in the gas-phase have been studied extensively both experimentally and theoretically^{2,3} as they serve as models for reaction intermediates in chemical reactions. The molecule of interest in this work is nitrous oxide, a potent greenhouse gas,⁴ causing depletion of stratospheric ozone.^{5,6} The atmospheric concentration of N₂O is estimated to be increasing between 0.5-0.9 parts per billion per volume per year owing largely to anthropogenic sources such as fossil fuel usage and agriculture.⁴ As such, methods attempting to reduce N₂O sources, in particular metal-catalyzed N₂O decomposition, have been investigated.⁷ Significant importance lies in the reactivity of N₂O with metal centers, with the most attention directed towards reduction of N₂O to N₂. In this instance, N₂O acts as a clean and highly-selective oxygen donor for catalytic oxidation processes. Isolated Copper, Silver and Gold nitrous oxide cation complexes (M⁺(N₂O)_n-Ar (M = Cu, Ag, Au) n = 2-7) have been studied with infrared laser photodissociation spectroscopy in the region of the ν₃ stretch of N₂O using inert gas tagging. Infrared active bands are assigned with the help of density functional calculations. These clusters are characterized in terms of N₂O ligands binding *via* the N atom or the O atom resulting in unique shifts in the ν₃ stretch (N-N) of the N₂O. The N-N stretching frequencies of the M⁺(N₂O)_n-Ar clusters are all blue shifted with respect to the free ν₃ stretch of N₂O providing an insight into the M⁺-N₂O binding. Metal-nitrous oxide binding involves the synergetic donation of electrons in the 7σ orbital of the N₂O to a vacant σ orbital on the metal and the back donation of the metal π orbitals to the π* orbital of the N₂O. The 7σ orbital donation from N₂O to metal is the dominating factor causing a blue shift in the N-N stretching frequency.

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Rotational Spectra and Nuclear Quadrupole Coupling Constants of 4-Bromo- and 4-Iodopyrazole

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The microwave spectra of the heteroaromatic molecules 4-bromopyrazole and 4-iodopyrazole have been recorded for the first time, along with their *N*-deuterated isotopologues. These species have recently been shown to be useful in structural determination of proteins due to their ability to attach at a variety of binding sites.¹ The nuclear quadrupole coupling constants have been fitted, and these have been used to determine the nature of the C-X bond, and related to the strength of the halogen bonds formed by the molecules.

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Keywords.

Microwave Spectroscopy, Nuclear Quadrupole, Structural Determination, Halogen Bonding

Spectroelectrochemistry and Ultrafast Charge-Transfer in thin films of Prussian Blue Analogues

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Switching the physical properties of functional molecular materials to metastable states using external perturbations is of great interest for future electronic and information storage technologies. The V^{II/III}-Cr^{III} analogue of Prussian blue (V-Cr PBA) is a promising candidate for combining optical and magnetic properties of thin films as it displays ferrimagnetism at room temperature¹ and has a deep blue colour. We will present a spectroelectrochemical study of this material and compare these results to ultrafast transient absorption measurements where photo-induced charge-transfer transitions give rise to comparable spectral changes as were observed in the spectroelectrochemical measurement.

In a recent study on the V-Cr PBA using transient absorption and magneto-optical (MO) techniques², it was found that exciting at the ligand-to-metal charge-transfer (LMCT) band resulted in a transient reduction of the Cr^{III} ions to Cr^{II}. However, back electron transfer occurred within 250 fs and Cr^{III} was subsequently formed in a doublet state via fast intersystem crossing (ISC) from a quartet state. The MO measurements could detect the formation of this doublet state on the Cr ion from the change in the super-exchange interaction taking place as a result of the corresponding spin flip associated with the ISC. Our recent spectroelectrochemical study³ revealed that the electrochemical reduction of the Cr oxidation state in the V-Cr PBA lattice, from Cr^{III} to Cr^{II}, resulted in an increased absorption in the blue region of the spectrum. Motivated by this finding, we have carried out transient absorption measurements with an emphasis on this region of the spectrum. We were able to observe a transient absorption centred at 460 nm, which is consistent with the spectroelectrochemical measurements. The measured lifetime was in the region of 100 fs, in agreement with the short lifetime previously assigned to the LMCT state^{2, 4}.

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Controlling resonant energy transfer in atom-molecule collisions using electric fields

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Energy transfer via resonant electric dipole interactions plays an important role in a wide range of atomic and molecular systems. Förster resonance energy transfer, in which the radius of interaction is smaller than the wavelength of the radiation, is one such type of interaction, and is exploited as a framework to study excitation energy transfer in light-harvesting complexes [1] and single-molecule spectroscopy [2]. In the gas phase, Rydberg atoms are an attractive model system with which to study Förster resonances in collisions with other Rydberg atoms or polar molecules [3] as their energy levels can be tuned with external electric fields to be resonant with the energy transfer channel.

Here we present the results of experiments in which helium atoms, produced in a supersonic source and excited to $|ns\rangle$ Rydberg states with $n=36-41$, undergo collisions with NH_3 molecules in the $A\ ^1X_1$ electronic state emanating from an effusive beam. For the Rydberg atoms with these values of n , electric dipole transitions between the states that evolve adiabatically to the $|ns\rangle$ and $|np\rangle$ states in zero electric field can be tuned through resonance with the inversion transitions in ammonia using weak electric fields, with the energy transfer occurring via Förster resonance. The energy transfer process for a range of electric fields and values of n was identified by state-selective pulsed electric field ionization. The electric field dependence of the experimental data is in excellent agreement with a model in which the dipole-dipole coupling between the collision partners was accounted for. The large transition dipole moments of the Rydberg atoms, e.g. $\langle ns|\hat{\mu}|np\rangle > 1000ea_0$ for $n > 36$, the transition dipole moment associated with the NH_3 inversion, 1.468 D, and the relative speed of the two collision partners lead to typical energy transfer cross sections of $\sigma \sim 10^{-11} \text{ cm}^2$, while the estimated energy transfer rate is 10^4 s^{-1} . These results open the possibilities for future investigations of chemical dynamics in which long-range dipolar interactions are exploited to regulate access to short-range Penning ionization processes at low temperatures [4].

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Keywords. Rydberg atoms, Förster resonance, Stark effect, long-range interactions, scattering of atoms and molecules.

Phase Behaviour and Thermophysical Properties of Fluids for Application in Carbon Capture and Storage Processes

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In order to design safe and effective systems for carbon capture and storage (CCS), it is necessary to have quantitative understanding of the phase behaviour and thermophysical properties of the key fluid mixtures that appear in these processes. A variety of models are available for this purpose but all require some degree of calibration and/or validation against experimental data. Since CCS involves combinations of substances and conditions that are relatively poorly studied from the experimental perspective, new measurements are especially important. This paper follows the process of post-combustion capture, pipeline transportation and geological sequestration of CO₂ from the perspective of the thermophysical properties and phase equilibria involved. The current state of knowledge is reviewed with emphasis on requirements for experimental measurements of thermophysical properties and phase equilibria. Measurements techniques and results are described for several key properties including mutual solubility,¹ density,² interfacial tension,^{3, 4} viscosity⁵ and diffusion coefficients.⁶ Uncertainties in the experimental data are discussed and also areas in which the available models require refinement.

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Keywords.

Carbon dioxide, density, diffusion, interfacial tension, phase behaviour, viscosity.

Thermophoretic transport of LiCl solutions

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The application of thermal gradients to aqueous electrolyte solutions gives rise to several interesting coupling phenomena, such as the Soret effect [1,2], in which thermal gradients induce concentration gradients. The Soret effect and the thermophoretic response of the solution can be quantified by using the Soret coefficient (s_T). Particles that move from hot to the cold regions, showing a thermophobic response, have positive Soret coefficients ($s_T > 0$), while thermophilic solution, in which the solute migrates towards hot regions, have negative coefficients ($s_T < 0$). It has been found that the thermophoretic response of aqueous solutions is extremely sensitive to physical [3] and chemical [4] factors. The former are the atomic mass, size, and moment of inertia of the molecules, while the latter involves solvent-particle and particle-particle interactions. Experimental studies of LiCl reported changes in the sign of the Soret coefficient [5] as well as a minimum [6] in this coefficient at specific salt concentrations and temperatures. At the minimum, the thermodiffusive response of the solution is enhanced significantly.

The Soret coefficient has been interpreted using the concept of heat of transport [7,8], which is the amount of heat absorbed or released to keep constant the temperature of the solution when the solute migrates in thermal gradients. Although there are early estimates of the heat of transport of electrolytes solutions [8], the computation of heat of transport of individual ions is an outstanding question both experimentally and theoretically.

We have performed non-equilibrium molecular dynamics simulations of LiCl solutions to quantify the dependence of the sign change and minimum of the Soret coefficient with salt concentration and temperature. We find that the ion mass plays a secondary role in determining the magnitude of the Soret coefficient, while the diameter of the cation has a significant impact on the coefficient and on the observation of the minimum [9]. Our simulations show that the ordering of water around Li^+ plays a key role in determining the Soret coefficient of LiCl salts. We propose a new computational approach to calculate the heat of transport of the ions. We find that the heat of transport can be significantly different from the estimates at infinite dilution [10].

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Keywords.

Soret coefficient, LiCl, Soret effect, heat of transport, thermophoretic, thermophilic, thermophobic, minimum

Ion Permeation in Graphene Oxide Membranes: a Molecular Simulation Perspective

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When graphene oxide (GO) membranes are immersed in water the interlayer spacing between GO flakes increases and the membrane swells. In this swollen state, water and ions are thought to permeate through the membrane via a network of interconnected unoxidised 2D pores.¹ Careful control of the swelling has now been realised, enabling ion permeation selectivity through the membrane.² This breakthrough means that GO membranes could be used for the water purification by nanofiltration in the future.

In this work, the ion-rejection properties of GO membranes were investigated using molecular dynamics simulations and the umbrella sampling technique.^{2,3} The simulations have demonstrated, using simple 2D pore models, that relative permeation rates are determined by the free energy associated with ion dehydration upon entering the pore. The implications of this finding are discussed in the context of desalination and the removal of problematic radioactive contaminants, such as ⁹⁹Tc.

In order to resolve quantitative differences in permeation energy barriers between experiment and simulation, we propose alternatives to the widely assumed permeation pathway of ions through GO membranes.

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Hyperporous Carbons from Hypercrosslinked Polymers for Ultrahigh CO₂ and H₂ Storage

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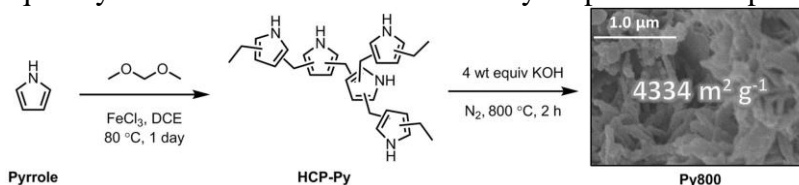
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Porous carbonaceous materials have been of interest for many decades because of their broad range of applications, easy preparation, high surface areas, thermal and mechanical stability, electrical conductivity, and good processability. A number of microporous solids have been used as precursors for carbonaceous materials to improve their properties; these include zeolitic imidazolate frameworks, metal-organic frameworks, porous aromatic frameworks, and conjugated microporous polymers. While these materials can show superior performance with respect to carbons produced from non-porous precursors, there is a major disadvantage in terms of the increased cost of the microporous precursors, some of which require rigorous anhydrous and anaerobic conditions that may preclude scale-up.

Hypercrosslinked polymers (HCPs) are microporous materials synthesized from cheap organic monomers such as benzene, toluene, and many other simple aromatics. HCPs are industrially scalable and show potential for synthetic diversification. They can be prepared through a simple one-step Friedel-Crafts reaction, which opens the approach to a large library of polymers derived from simple aromatic monomers.¹

Here, we present a route for the preparation of highly porous carbonaceous materials with remarkably high carbon dioxide and hydrogen uptakes using inexpensive HCP precursors – benzene, thiophene, and pyrrole (Scheme 1).² Upon optimisation, a surface area of 4334 m² g⁻¹ was achieved with HCP pyrrole precursor, that is, the highest reported to date for an organic-derived carbonaceous material. The material shows remarkably high CO₂ uptakes of 22.0 mmol g⁻¹ (298 K / 10 bar) and H₂ uptakes of 5.6 wt% (77 K / 10 bar) outperforming other leading materials such as MOF-205, PPN-4, Maxsorb, CN 2800, COF-102, and zeolite-, carbide-, and MOF-derived carbons. There are over 25 million aromatic molecules in the REAXYS database, many of which are susceptible to Friedel-Crafts alkylation to form HCPs and subsequently carbonaceous materials that may surpass those reported here.



Scheme 1. Synthesis of HCPs and resultant porous carbons.

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Keywords.

Porous, carbon, hypercrosslinked polymers, carbon dioxide capture, hydrogen storage

Statistical Thermodynamics of Ionic Liquid-Water mixtures

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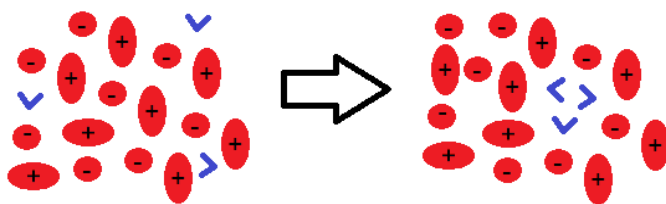
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The use of ionic liquids as solvents for a multitude of applications has been well documented in recent times.¹ Research into this area has been driven by the potential to tune solvation properties of an IL by modifying either anion or cation, mixing with another ionic liquid or by mixing with a molecular solvent. In particular, the use of a molecular solvent as an antisolvent or cosolvent with ionic liquids could lead to new extraction processes based on ionic liquids. But how does the presence of molecular solvents affect the interactions in ionic liquids? Numerous spectroscopic and thermodynamic experiments fail to make clear the effect of added solvent to ionic liquid properties.⁴

Herein we showcase the use of Kirkwood Buff theory of solutions to describe the interactions in the case of water-in-ionic liquids. The Kirkwood Buff theory has a proven track history of clarifying mechanisms of solvation, from pharmaceutical formulation to biochemical processes.^{2,3} Utilizing water activity and density data, we can extract without approximation the average pairwise interactions between species and information on the liquid structure. This allows us to answer with confidence the questions posed from the literature on the effect of water on ionic liquid properties. The theory is not limited to this system; any ionic liquid-cosolvent system can be studied in this way if the required thermodynamic data is available.



Change in water behaviour in ILs with composition and ion structure rationalised through statistical thermodynamics

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Keywords.

Ionic Liquids, Water, Statistical Thermodynamics, Solution Theory, Binary Mixtures.

From Lithium Batteries to Perovskite Solar Cells: Atomic-Scale Insights into Energy Materials

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Major breakthroughs in lithium batteries and perovskite solar cells require advances in new materials and underpinning science. It is clear that a complete understanding of energy materials requires fundamental knowledge of their underlying structural, transport and surface properties on the atomic- and nano-scales. In this context, advanced materials modelling [1] combined with structural and electrochemical techniques are now powerful tools for investigating such properties. This presentation will highlight recent studies [2] in two principal areas: (i) structural and electrochemical insights into Li-rich oxide and silicate electrode materials for lithium-ion batteries; (ii) defect chemistry and ion transport in perovskite solar cell materials (based on methylammonium lead iodide $\text{CH}_3\text{NH}_3\text{PbI}_3$), which have shown rapidly rising power-conversion efficiencies.

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Quinone based building blocks for molecular electronics

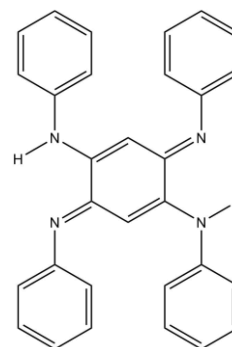
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It has been shown that azophenine (1,4-diamino-3,6-diimino-1,4-cyclohexadiene) adsorbed on a Cu-(110) surface displays controlled switching behavior between tautomeric conformations when exposed to a current through an STM tip. Thus it could be used as a molecule-sized memory element.

The prerequisites of such behavior are:

- Two states of similar energy, separated by a not too high barrier.
- Different electronic behavior, such as conductivity, between the two states.



If such behavior could be reproduced away from the surface, similar molecules, based on a quinone-like core, could be used as switches or transistors for molecular electronics.

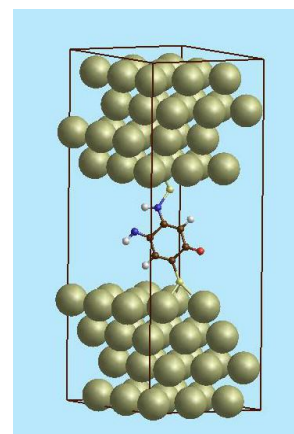
We will present initial results for tautomerisation barrier and electron transport properties of candidate molecules between electrodes to assess their suitability as components in more complex molecular electronic networks.

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Keywords

Surface Science, Molecular Electronics



Beyond Gaming: Virtual reality and real-time molecular dynamics for (bio)chemistry

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The use of large tangible models has a long history within both chemistry and biochemistry, perhaps most famously captured by Watson and Crick's model of DNA. Room-sized “Kendrew” models¹ were popular within protein modelling and visualization in the 1950s/60s (prior to widely available commodity computational machinery), allowing researchers to understand the first protein crystal structures. Models like these have played an important role in chemical research, allowing us to visualize the design intricacies of complicated nano-architectures across both biology and materials science.

Driven by the consumer market, state-of-the-art virtual reality (VR) hardware now allows us to carry out broad new classes of video-gaming tasks which were previously impossible: wielding light-sabres, making 3d sculptures, and even simulating surgery. Applying these technologies to the molecular sciences allows us to re-engage with the sorts of large, immersive, tangible models that were once popular in molecular research.² Along with state-of-the-art advances in high performance computing (HPC), we can even go one step further: whereas the older models were time stationary objects that could only capture a single conformation of a molecule (e.g., a protein or DNA crystal structure), it is now possible to construct room-sized tangible models of molecular structures which are “animated” by rigorous dynamics, building on the significant progress that has been made in computational molecular physics over the last 60 years.³

I will discuss (and hopefully demo) the work we have carried out to design a new environment which fuses commodity VR and GPU-accelerated HPC to allow (up to 8) researcher(s) to natively inhabit a fully interactive 3d virtual molecular simulation environment. Using wireless ‘atomic tweezers’, it is possible to fluidly chaperone a real-time research-grade biomolecular MD simulation in a fully co-located 3d space *with surgical precision*. This platform opens up a new domain of “interactive simulation”, allowing researchers to tackle a range of biomolecular design problems as they interactively explore dynamical pathways and conformational states in hyperdimensional biomolecular systems. I will discuss some initial applications of our multi-person VR-HPC environment, including our attempts to understand the fundamental kinetic mechanisms and dynamical pathways whereby small molecular ligands (e.g., a drug or substrate) dock with a larger molecular receptor (a protein or enzyme).⁴

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Electron Transfer in Organic and Biological Materials

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Charge transfer processes are ubiquitous and play a prominent role in biology and material science. While experiments give valuable information on certain kinetic and thermodynamic properties of charge transfer events, they usually do not offer a molecular-level insight into these phenomena. Adequate simulations can bridge the gap between microscopic processes and macroscopic charge transports. For instance, a combination of Marcus theory, classical molecular simulation and master equation formalism can estimate complex charge transfer processes involving multiple redox sites in large systems [1]. But such rate-based approaches usually only work for localized charge carriers and in situations where the charge transfer is a rare event in the time scale of other molecular motions. To surpass these limitations, we have recently implemented a fast non-adiabatic molecular dynamics approach (based on Tully's surface hopping) where the wavefunction of the charge carrier is explicitly propagated in the time-dependent potential created by (classical) nuclear motion [2,3]. First applications to hole transfer in the ethylene dimer successfully reproduced exact results from the theory [3] and applications to a chain of ethylene molecules successfully predicted a crossover from activated to band-like transport [2]. Here we present a new implementation of the method into the CP2K software that enables us to model fast charge transfer in larger, application relevant organic crystals consisting of thousands of atoms. We will present applications as well as a detailed analysis of the charge transfer mechanism predicted by our surface hopping approach.

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Keywords.

Charge transfer, non adiabatic dynamics, organic crystal

Synthesis of organic molecules in space – chemical reactions at low temperatures

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I will give an overview of the importance of determining temperature dependent rate constants for elementary chemical reactions for understanding the creation and destruction of organic matter in space. In particular I will focus on studies of the reactivity of carbon-containing radical species with organic co-reagents leading to efficient molecular growth even at the low temperatures of dense interstellar clouds (10—20 K) or of the atmospheres of planets and their moons, such as that of Titan (70—180 K), studied using the CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme, or Reaction Kinetics in Uniform Supersonic Flow) technique¹⁻⁴ coupled with a range of state-of-the-art detection methods including vacuum ultraviolet laser-induced fluorescence (VUV LIF) and chirped-pulse Fourier transform microwave (CPFTMW) spectroscopy.⁵

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Keywords.

chemical kinetics, low temperatures, astrochemistry, planetary atmospheres

Low Temperature Studies of the Removal Reactions of $^1\text{CH}_2$ with Particular Relevance to the Atmosphere of Titan

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The photolysis of methane by UV photons is the primary source of hydrocarbon radicals in the atmospheres of Titan and the giant planets. Although there is still significant uncertainty in the branching ratios of products, the production of the first singlet excited state of methylene, $^1\text{CH}_2$, is thought to be a significant channel. In the atmosphere of Titan, reactions of $^1\text{CH}_2$ with methane and hydrogen are a significant source of methyl radicals, CH_3 , the recombination of which is the primary route to ethane. The reaction of $^1\text{CH}_2$ with acetylene is also a source of propargyl, C_3H_3 , the recombination of which is the primary route to benzene. Additionally, $^1\text{CH}_2$ may also be removed by electronic relaxation to ground state triplet methylene, $^3\text{CH}_2$. Triplet methylene is much less reactive, and cannot undergo the complex insertion elimination reactions of singlet methylene. Instead, the main reactions of $^3\text{CH}_2$ occur with other radical species such as H and CH_3 , leading (directly or indirectly) to formation of ethylene, C_2H_4 . Thus both states of methylene are important to different aspects of Titan's photochemistry, and understanding the competition between the two removal channels of $^1\text{CH}_2$ is important to understanding the chemistry of Titan's atmosphere. Despite this there are no measurements of any rate constants for $^1\text{CH}_2$ at temperatures relevant to Titan's atmosphere (60 – 170 K).

Using pulsed laser photolysis laser-induced fluorescence, we have studied the reaction kinetics for the removal of $^1\text{CH}_2$ with N_2 , H_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , and O_2 as a function of temperature. Low temperatures between 43 and 135 K were obtained using a pulsed Laval nozzle apparatus, while data at 160 K was obtained using a low flow reaction cell with cryogenic cooling. In addition to measuring total removal rates, the fraction of $^1\text{CH}_2$ removed via electronic relaxation versus chemical reaction to products has also been investigated for H_2 and CH_4 at 160 and 73 K. Results show that that removal of $^1\text{CH}_2$ by electronic relaxation increases with decreasing temperature.

These experimental results indicate that the majority of $^1\text{CH}_2$ formed in Titan's atmosphere will be rapidly relaxed to its ground state via collisions with both reactive and non-reactive species, and thus is likely to play a less significant role in the formation of larger hydrocarbons than previously thought. However, for a full understanding of the implications of these results, the new measurements have been included in a 1D model of Titan's atmosphere. The model results show a significant reduction in ethane concentrations (10 – 50 %), due to the reduction in CH_3 produced from reactions of $^1\text{CH}_2$. We also observe an increase in ethylene concentrations, the result of an increase in $^3\text{CH}_2$ reacting with other radical species.

Additional work is also underway to determine branching ratios between reaction and relaxation of $^1\text{CH}_2$ with ethane, ethylene, and acetylene. Model results have shown that if a similar trend to reactions with H_2 and CH_4 is observed, there would be significant reductions in benzene production on Titan.

Deep search for hydrogen peroxide towards pre- and protostellar objects - Testing the pathway of grain surface water formation

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How does the water in young stellar objects (YSOs) form? It is believed that for a large fraction of the water content the formation of these molecules takes place on grain surfaces during the star formation process. Hydrogen peroxide (HOOH) is an intermediate product in the grain surface water formation pathway. Like H₂CO and CH₃OH it is believed to form within interstellar ices. Once the molecule desorbs from the icy grains it can be detected in the gas-phase and has already been found towards ρ Oph A (Bergman *et al.* 2011). However, further searches for the molecule in other sources proved difficult. The molecule plays a fundamental role in the understanding of solid state water formation and the overall water reservoir in YSOs. Without further HOOH detections it is difficult to develop suitable grain gas-phase chemical models. In addition to the chemical aspects also the physical structure of the YSOs needs to be considered to fully understand the HOOH occurrence in these sources. To find the molecule HOOH in YSOs and thereby testing the grain surface water formation hypothesis a model has been developed that combines a previously available grain - gas-phase chemical model by Du *et al.* (2012) with a simple physical model of YSOs. According to the model and other considerations the sources R CrA-IRS5, NGCC1333-IRAS2a, L1551, and L1544 were identified as suitable sources for HOOH detection. Observations using the APEX12m and IRAM30m telescopes have been performed using long integration times to search for HOOH. In addition, other molecules like HO₂, H₂CO and CH₃OH have been investigated to better understand the local conditions in these sources and to test the physical-chemical model. None of the sources showed clear signs of HOOH. Thus, in all cases the model overestimated the abundance of HOOH. In case of the other molecules under investigation (H₂CO and CH₃OH) the model made reliable predictions and rather underestimates the abundances (except for the pre-stellar object L1544). Thus, the failure of the HOOH predictions seems to be rather molecule related, i.e. how hydrogen peroxide is treated in the gas-grain chemical model, and is not so much caused by the physical model of the YSO. The formation of HOOH on surfaces has been well studied in the laboratory (Ioppolo *et al.* 2010), however the desorption mechanism of HOOH is still highly controversial. In this work we argue against the recent view (Cazaux *et al.* 2016) that chemisorption is sufficient to explain the HOOH observations.

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VUV and mid-IR spectroscopy of ices exposed to 1 keV electrons

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Laboratory work shows that energetic processing (e.g., photons, cosmic rays, electrons, X-rays) of interstellar ice grain analogues lead to a higher molecular complexity. In space, solid molecules are formed and destroyed by (non-)energetic mechanisms throughout the evolution of star forming regions. In the Solar System (e.g., in the magnetospheres of giant planets within which many icy satellites are embedded), ices are continuously exposed to energetic processing by photons, electrons and ions. At the OU Astrochemistry Laboratory (UK) and at the synchrotron facility ASTRID² (DK), we have recently investigated the interaction between 1 keV electrons and ices of astrophysical interest such as oxygen (O₂), nitrogen (N₂), and carbon dioxide (CO₂) also mixed with water ice in the VUV (110-340 nm; at ASTRID²) and mid-IR (4000-600 cm⁻¹; at the OU) spectral ranges and for temperatures including 22-200 K. Mid-IR data is used to quantify the amount of new species formed upon irradiation, while VUV spectra of processed ices are acquired in support of past (e.g., Hubble Space Telescope) and future (e.g., JUICE - JUpiter ICy moons Explorer; <http://sci.esa.int/juice/>) astronomical observations. The observed changes in relative intensities, peak position and shape of the VUV absorption bands as well as spectral reddening upon e⁻ irradiation of the ice will be discussed in light of their relevance in astrophysical environments.

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"Using Biophysical Methods to Characterise the Structure, Function and Drug Binding of Voltage-Gated Sodium Channels"

Voltage-gated sodium channels (Navs) play essential roles in excitable tissues, with the activation and opening of these channels resulting in the initial phase of the action potential. The cycling of sodium channels through closed and inactivated states, and their closely choreographed relationships with the opening and closing of other ion channels lead to exquisite control of intracellular ion concentrations in both prokaryotes and eukaryotes.

Our new high resolution crystal structure of the NavMs prokaryotic sodium channel¹, has provided the first view of a complete sodium channel structure, enabling visualisation of the interactions of the voltage sensor (VS), S4-S5 linker, pore, and C-terminal domains, and forms the physical basis understanding the relationship between activation and opening. The structure has a canonical activated conformation for its VS S4 helix, with a novel S4-S5 linker conformation that leads to an open selectivity filter which in turn leads to an open activation gate at the intracellular membrane surface. This ends in a C-terminal domain (CTD) that acts as a “glue” between the monomers that comprise the tetrameric channel. The activated VS conformation produces a heretofore unseen extensively-hydrogen bonded and salt-bridged interaction motif involving the sodium-channel specific S3 Trp, the S4-S5 linker, the end of the S6 transmembrane region and the top of the CTD.

I will discuss the synergy between the use of various biophysical methods such as X-ray crystallography, circular dichroism² and EPR-DEER³ spectroscopies, bioinformatics⁴ and molecular dynamics calculations⁵, and drug binding studies⁶ to characterise the structure, function and drug interactions of voltage-gated sodium channels. By complementing these with functional studies, we have been able to define a new model for not only drug blocker interactions but also for how the gating and activation processes enable these channels to translocate sodium ions across biological membranes.

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Polymer Stabilized Phospholipid Nanodiscs

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Phospholipid bilayer nanodiscs are novel self-assembled model membrane structures composed of a bilayer of phospholipids with the hydrophobic disc edges surrounded and stabilized by a polymer^{1,2} or protein³ belt. They can be used to solubilise membrane proteins, allowing structural and functional studies of this class of proteins, which are otherwise difficult to study outside of the native cell membrane. The polymeric stabilizers can be made in bulk quantities, more cheaply than the protein belt, enabling large quantities of discs to be prepared. Polymer-stabilized nanodiscs are also made directly from cell membranes simply by adding polymer and shaking, without requiring addition of detergent or ultrasound to assist dispersion, so are useful for membrane protein purification and separation,^{1,2} as well as for studies of membrane protein function.⁴

We are working to understand the formation mechanisms and properties of lipid nanodiscs stabilized by acid and amine derivatives of poly(styrene-co-maleic anhydride) using small angle neutron and X-ray scattering (SANS/SAXS), DLS, cryo-TEM and by variation of the polymer structure using RAFT synthesis methods to control the polymer molecular weight and structure. In this presentation I will discuss the effects of polymer chemistry, molecular weight and structure on disc formation. I will also report our *in situ* studies of polymer-lipid nanodisc formation processes, using stopped flow mixing with SANS and fluorescence for studies of polymer interactions with lipid vesicles and high flux neutron reflectivity measurements for time-resolved studies of polymer interactions with lipid films at the air-solution interface.

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Keywords.

Lipids, poly(styrene-co-maleic acid), nanodiscs, self-assembly, small angle scattering

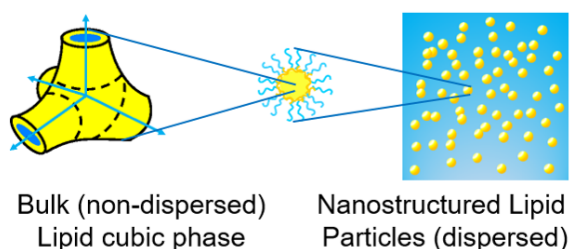
Self-assembled Lipid Nanostructures and Dispersed Lipid Particles for the Delivery of Aspirin

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Lipid molecules self-assemble into remarkable range of nanostructures in an aqueous environment¹. Lamellar, hexagonal and cubic phases are formed, correspondingly, by 1-, 2- and 3- dimensional nanoscale arrangement of lipid molecules¹. These lyotropic liquid crystalline phases have demonstrated their potential in various biotechnological applications including drug delivery². Owing to the availability of large surface area, large hydrophobic volume and high level of tunability, these nanostructures are becoming popular for solubilizing a broad range of active molecules². To enhance the applicability of some of the lipid nanostructures, especially highly viscous cubic phases, they are dispersed into particle based oil-in-water emulsions³. By this, the original self-assembly is retained inside the cores of the lipid particles; moreover, their fluid form is easy to handle for physical operations, and thus for various modes of drug delivery².



Aspirin is a vital drug with analgesic, antipyretic and anti-inflammatory activities; moreover, it increases the solubility of cholesterol when in membranes⁴. However, its main side effects include the toxicity to the gastrointestinal (GI) tract and its rapid conversion into less desired products⁵. Therefore, its encapsulation into some sort of carrier becomes advantageous⁵. Here we

employed two types of nanocarriers: bulk (non-dispersed) lipid nanostructures and their dispersed lipid particles for the delivery of aspirin. Drug release was monitored by UV-Vis spectroscopy whereas nanoscale characterization of lipid phases was performed using small angle X-ray scattering (SAXS) technique. Several researchers have separately reported the drug delivery from bulk and dispersed lipid nanostructures, while we are reporting their comparison for aspirin release, for the first time.

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Keywords

Lipid self-assembly, nanostructured lipid particles, emulsions, drug delivery, nanocarriers.

Molecular semiconductors for LEDs and solar cells:
designing around the Coulomb interaction

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π -conjugated organic molecules and polymers now provide a set of well-performing semiconductors that support devices, including light-emitting diodes (LEDs) as used in smart-phone displays and lighting, field-effect transistors (FETs) and photovoltaic diodes (PVs). These are attractive materials to manufacture, particularly for large-area applications where they can be processed by direct printing, so that the cost of materials and processing can be very low. This practical success is made possible by breakthroughs in the understanding and engineering of the underlying semiconductor science. The physics of organic semiconductors is often controlled by large electron-hole Coulomb interactions and by large spin exchange energies. Management of excited state spin is fundamental for efficient LED and solar cells operation. I will discuss in particular recent progress in the control of emissive spin singlet excited states and non-emissive spin triplet excited states.

Highly monodispersed PbS QDs for outstanding QD optoelectronic applications

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The infinitesimal semiconducting nanocrystals, which are called ‘quantum dot’ (QD) have been shining the light to the next generation optoelectronics and electrochemical energy harvesting. The advantage of employing the photoactive semiconductor in the state of QD is due to the band gap (ϵ_{gap}) tuning accessibility and solution-processed reproducibility. Due to the size-dependent quantum confinement effect, the QD ϵ_{gap} can be easily adjusted by tuning the size. Owing to the merit of developing colloid synthetic chemistry and synthetic mechanism study, most of the semiconductor crystals can be readily fabricated into nano-scales through the economical solution process. Lead sulfide (PbS) QDs is considered as one of the most promising candidates for QDs optoelectronic applications due to wide ϵ_{gap} adjustability from its extremely big Bohr radius (20nm). PbS QDs have been deployed into different types of energy harvesting or conversion systems, such as DSSC type solar cell, Schottky junction or p-n junction photodiodes and organic dye hybrids solar cells. PbS QDs solar cell (QDSC) has been improved their light harvest efficiency dramatically in recently years. Up to now, the lab scale cell efficiency has been achieved by around 10%. Recently, we elucidate effective and reliable synthesis protocols for fabricating high-quality PbS QDs. Through adjusting the precursor concentration systematically, in a fixed reaction time, a wide range of different sizes of colloidal PbS QDs is produced with a narrow size distribution and high reproducibility.¹ A rationalization analysis between the quantum-confinement effect and surface functionalization of PbS QDs is also carried, which are used for QD size and ligand effect study.^{2,3} Different sizes PbS QDs are selected and tentatively fabricated into Cascaded-junction solar cells.¹ The elaborately designed devices show impressive high PCE (9.05%) and short circuit current density (32.51mAcm⁻²) compared with previously reported devices.¹ Moreover, through a ‘heterogeneous’ synthesis approach, we also fabricate red green blue (RGB) emissive PbS QDs which eventually bring PbS QDs into the visible emission QD family and also set a new open-circuit voltage record (0.8V) for PbS QD solar cells. This will encourage future works on their use in solar cell technologies as well as the enhancement of quantum yield for light emitting applications.⁴

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Keywords.

Quantum dot, Colloidal, Solar cells, Emissive, RGB, Monodisperse, Heterogeneous

Charge Transfer at Dye-Metal Oxide Interfaces for Solar Energy Capture, Conversion and Storage

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Efficient dye-sensitized photocathodes offer new opportunities for converting sunlight into storable energy cheaply and sustainably. We are developing dye-sensitized NiO cathodes for tandem solar cells and the photo-reduction of carbon dioxide or water to high energy products (solar fuels). Despite the infancy and complexity of this research area, we have brought about a number of exciting developments which have improved our understanding of the system. We are tackling the main limitations to p-type dye-sensitized solar cells, by improving the quality of the NiO electrodes and engineering new dyes specifically for the p-type system, to increase the quantum efficiency of the device. The electron-transfer dynamics are key to the performance and a major challenge is slowing down charge recombination between the photoreduced dye and the oxidised NiO so that chemistry can take place. Highlights from recent work examining charge-transfer at the interface between NiO and new porphyrin and bodipy-based photosensitizers using transient absorption spectroscopy, time-resolved infrared spectroscopy and resonance Raman spectroscopy will be presented.

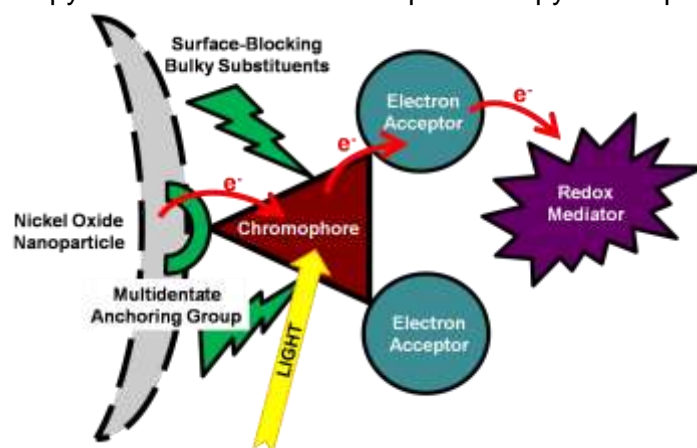


Figure 1. Schematic illustration of a dye-sensitized NiO cathode for H^+ reduction.

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Photochemical reduction of carbon dioxide in water

A. J. Cowan

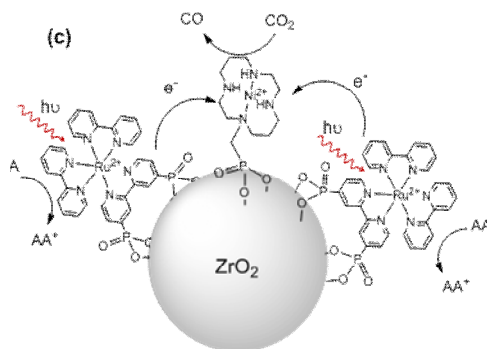
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Using solar energy to drive the production of a storable chemical fuel offers a route to addressing the intermittency of the energy resource. Our research explores the photochemical and photoelectrochemical reduction of CO₂ to useful fuels (e.g. methanol) and fuel precursors (e.g. carbon monoxide). Despite recent progress within the field relatively few systems that operate in water are known. This is significant as to make the reduction of CO₂ into fuels a viable process it is necessary to use a sustainable electron source, for example from the oxidation of water.

Here I will present recently developed^{1,2} visible light photocatalysts that are able to selectively reduce CO₂ to CO in water. To achieve selectivity we have coupled molecular electrocatalysts to light absorbing semiconductors and dyes that are able to generate sufficiently reducing photoelectrons for transfer to the catalytic centre. Using transient UV/Vis absorption spectroscopy the mechanism of sensitization has been studied and we demonstrate how immobilisation of the electrocatalyst in close proximity, or onto, the sensitizer both improves charge separation and catalytic efficiency.

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Keywords.

Photocatalysis, Carbon dioxide, Solar Fuels, Transient spectroscopy

Molecular scale microbiology with neutrons (and x-rays)

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In 2013 the UK's Chief Medical Officer placed the development of antimicrobial resistance by bacteria and the failure to develop novel antimicrobials on the UK Risk Register, painting a scenario in which even trivial operations will become hazardous due to the risk from hospital acquired infections.

We have been using neutron (and x-ray) reflectivity to bridge the structural gap between microbial growth experiments and molecular dynamics simulations to try to understand at the molecular scale various interfacial aspects of bacterial life & death.[1]

Working from the inside of the bacterial cell outwards, we have examined the following systems, which will be considered in this talk.

(i) The interaction of the membrane-targeting sequence (MinD-mts) of the MinD protein that is crucial for bacterial cell division with models for the inner cell membrane of Gram negative bacteria. As cell division is a pre-requisite for growth of bacterial populations and biofilms, understanding the factors that control it at the molecular scale, may help us to understand how best to control such growth. As transmembrane potential is intimately linked to bacterial metabolism, I will also describe our efforts to examine the influence of such a potential on our model bilayers.

(ii) The interaction of the antimicrobial peptide pexiganan with models for the inner and outer bacterial cell membranes, including the influence of the polymer brush-like LPS layer. Antimicrobial peptides are a part of the innate immune system, towards which bacteria have been less successful at developing resistance, and so are seen as a possible means to replace or complement antibiotics. To date, there is no consensus as to how they kill bacteria at the molecular scale. We think our data can shed some light on a possible mechanism.

(iii) In collaboration with the MacPhee group in Edinburgh, we have also examined the formation of BslA protein layers at the air-water interface. In nature these layers act as a form of bacterial cling-film at the air-water interface of a biofilm. If time allows, I will show how reflectivity data can complement the wealth of information [2] that MacPhee and co-workers have assembled into their mode of assembly.

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Probing the structure and dynamics of proteins using neutron scattering

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To fully understand the function of proteins it is necessary to consider both their structure and dynamics. Neutron spin-echo spectroscopy (NSE) has been shown to be ideally suited to probe the slow dynamics of materials, making it a very powerful tool when combined with other techniques.

In this talk I will show how we have used NSE and backscattering spectroscopy to probe the dynamics of biologically relevant systems, such as human serum albumin, a protein abundant in blood, which plays a key role in the transport of compounds such as nutrients, hormones and drugs. We are able to detect small changes in the internal dynamics of the protein upon binding of small molecules such as heme and myristic acid under physiologically realistic conditions.

A New VMI Spectrometer for the Study of Bimolecular Collisions

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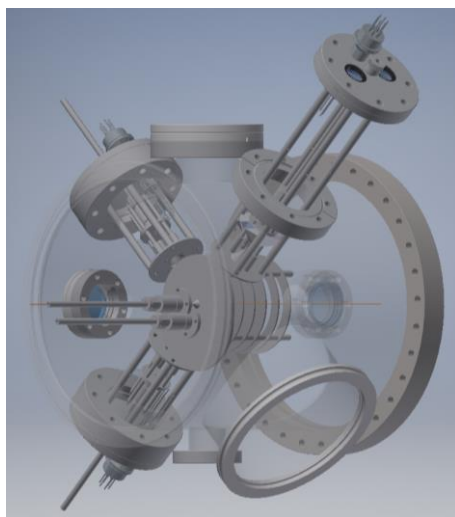
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A velocity map ion (VMI) imaging spectrometer has been constructed with the capacity to study a variety of bimolecular collision reactions in the gas phase. The new chamber allows for significant control over collisional conditions through the use of three different types of reactive scattering techniques involving jet-cooled molecular beams. Specifically the chamber can study reactions between parallel, crossed and counter-propagating molecular beams (see figure below). The latter two forms of reactive scattering allow for the greatest control of the relative velocities of the molecular beams based upon nozzle conditions. We hope to study the reactivity between closed shell molecular species and open shell species to uncover more details into the effect of rotational excitation on rates of reaction (e.g. $\text{CN} + \text{CH}_4$)[1] and to further elucidate the criterion for roaming reactions in bimolecular collisions (e.g. $\text{Cl} + \text{CH}_3\text{CCCH}_3$).[2]

The chamber has been further upgraded with the addition of a Pixel Imaging Mass Spectrometry (PImMS) camera.[3] This camera contains a fast imaging sensor that allows for time resolved (up to 25 ns) particle imaging over the entire time of flight mass-spectrum. Thus permitting the simultaneous collection of VMI images of multiple fragments arising from a collisional reaction. Additionally we demonstrate that the camera can record VMI images of non-cylindrically symmetric ion velocity distributions.



A cross-section of the source chamber of the VMI apparatus.

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Time-Resolved Photoion Yield Spectroscopy of Non-Volatile Biological Analogues

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Gas-phase spectroscopic techniques provide valuable insight into the fundamental dynamics of biological chromophores following ultraviolet (UV) absorption, free of intermolecular and solvent effects^[1]. These rapid and efficient energy redistribution processes are believed to be vital to the understanding of biological photoprotection. Many large molecules of interest, however, have low vapour pressures, with a tendency to decompose under vigorous heating, making gas-phase spectroscopy difficult.

This talk introduces a soft thermal desorption technique^[2], incorporated within a time-of-flight mass spectrometer (TOFMS), facilitating studies of the UV-photoprotection in non-volatile model biological chromophores. Back irradiation of a thin metallic foil by a CW laser produces neutral plumes of the molecule of interest. Numerous biologically relevant molecules will be discussed, including preliminary studies on uracil and 2-thiouracil.

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Keywords.

Time-Resolved Spectroscopy, Molecular Dynamics, Non-Volatile Molecules

Protomers of *para*-aminobenzoic acid: Can low-resolution UV action spectroscopy distinguish protomeric isomers formed via electrospray?

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The sites at which protonation or deprotonation occur following electrospray ionisation of even small molecular systems remains controversial. It is therefore important to develop new in-situ approaches to identifying protomers and deprotomers. In this work, we test whether low-resolution, UV laser action spectroscopy can be applied within a laser-interfaced commercial mass spectrometer to identify the gaseous protomers of *para*-aminobenzoic acid (PABA) formed following electrospray.

PABA is a biologically active molecule that displays two possible protonation sites: an amine group (**PABA-NH₃⁺** protomer) and a carboxylic group (**PABA-OH⁺** protomer). Importantly, the protonation characteristics of PABA are well established, so it represents an excellent prototype system for testing the efficacy of our method.^{1, 2} We report the gaseous electronic absorption spectra, recorded via photodepletion and photofragmentation, for PABA electrosprayed from solutions of water and acidified acetonitrile. We find that the two protomers can be straightforwardly identified, with the **PABA-OH⁺** protomer is associated with strong absorption bands centred between 3.6-3.8 and 4.9-5.2 eV, while the **PABA-NH₃⁺** protomer absorbs between 4.5-4.9 and above 5.4 eV. The results show that PABA electrosprayed from water produces **PABA-OH⁺** as the sole protomer, while **PABA-NH₃⁺** and **PABA-OH⁺** are observed in a 90:10 ratio from acetonitrile.

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Keywords.

Aminobenzoic Acid, Structural Isomers, Protomers, UV Photodissociation Spectroscopy.

Photophysics of the sunscreen ingredients methyl and menthyl anthranilate: a bottom-up approach to photoprotection

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The ultrafast dynamics of the sunscreen ingredient menthyl anthranilate (MenA, trade name Meradimate)¹ and its precursor methyl anthranilate (MA) were studied in the gas-phase (using time-resolved ion yield and photoelectron spectroscopy) and solution-phase (using transient electronic absorption spectroscopy). Experimental results were complemented with computational studies, in order to garner further details on the electronic landscape of these molecules. Both MenA and its precursor showed long lived dynamics in the gas- and solution-phase, revealing a persistence of excited states upon absorption of UV radiation that is undesirable in sunscreen molecules.² Computational results suggest that a shallow proton transfer state is accessed upon photoexcitation, where population is trapped and from which fluorescence occurs as the main decay pathway. This is in accordance with previous studies which have reported luminescence in both MA and MenA.^{1,3} This work demonstrates how a molecule's photophysics – and hence its photoprotective capabilities – may not be drastically influenced by molecular structure or solvent environment alone. Rather the combination of these factors and how they affect the chromophore's electronic landscape needs to be understood in order to uncover the key to photoprotection. A *bottom-up approach* is therefore essential in the efforts towards a new generation of tailor made, more effective sunscreens.⁴ Future work in this field will involve an evaluation of how intrinsic photoprotective capabilities change with molecular structure.

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Keywords.

sunscreens, photophysics, photodynamics, bottom-up approach

Fivefold Symmetry in the Glass Transition and Crystallisation

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That fivefold symmetry should play a crucial role in the non-equilibrium behaviour of condensed matter was proposed in the 1950s [1]. Six decades later, the basic mechanism of the solidification of liquids remains unexplained, either in the case that the material crystallises, or that it forms an amorphous solid, a glass [2]. We will explore the implications of fivefold symmetry in the solidification of liquids and discuss two recent developments.

Crystallisation is among the most common everyday physical phenomena. Yet in the only material in which quantitative comparison has been made between experiment and theory — hard spheres — predictions of crystal nucleation rates are up to 20 orders of magnitude slower than measurements, the “second worst prediction in physics” [3]. This discrepancy casts doubt upon the theoretical methods concerned — importance sampling — which is important not only for crystallisation, because these methods are used to tackle a very wide range of problems, such as drug uptake in cells and chemical reaction pathways. We show that fivefold symmetry may hold the key to resolving this long-standing puzzle [4].

The nature of amorphous solids — glasses — is not understood: the possibility of a phase transition to a thermodynamically stable “ideal glass” is a contentious and challenging issue. Unlike everyday non-equilibrium glasses, such an ideal glass has a vanishing entropy — like a crystal — yet remains amorphous. The geometric frustration approach to the glass transition posits an avoided phase transition in a curved space inaccessible to experiment [5]. Here we show that such a “crystallisation” to a state comprised of fivefold symmetric icosahedra indeed occurs and consider its implications [6].

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Keywords.

Glass transition, Geometric Frustration, Crystallisation, Nucleation, Colloids

Exploring the accuracy of solid-liquid interfacial free energies obtained via the capillary wave method

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The metastability of a supercooled liquid arises from the interfacial free energy penalty which must be overcome to form a solid-liquid interface. Selection of nucleation pathways can depend critically on how this penalty varies between the crystalline polymorphs involved. In this work, we revisit calculation of solid-liquid interfacial free energies from analysis of capillary waves, using the mW coarse-grained model of the ice-water interface as an exemplar. We critically explore limits of accuracy, and compare results to those obtained via more involved methods [1]. By extending our study to metastable ice phases, we can distinguish between two possible explanations for the low temperature nucleation behaviour seen in this model.

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Keywords.

ice, polymorphism, molecular dynamics, interfaces

Water: a matter for Soft Matter

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Water is the most common and yet least understood material on Earth. From an anthropic viewpoint, many of its unique properties appear as if they were fine tuned, and originate from complex interactions that, despite the simplicity of the molecule, are responsible for unique structural and dynamical behaviour. In this contribution we will show how some ideas borrowed from Soft Matter can be applied to the study of water, often with surprising results. Starting from the observation that the properties of water seem to appear fine-tuned, we are going to "untune" water, changing its interactions in a continuous manner, i.e. as if it behaved like a Soft Matter system. This allows us to study how the properties of water change going from "real" water to models which behave like other simple liquids.

In particular, we will show how: 1) mixture models provide the easiest (and often most accurate) way to understand the complex thermodynamic and dynamic anomalies of liquid water [1,2]; 2) metastable phases can play an important role in the microscopic pathway of ice nucleation [3]; 3) a classical Soft Matter model with three-phase metastable equilibria can provide microscopic insight into the process of rain formation [4].

The possibility to observe the emergence of anomalous behaviour with Soft Matter models, opens the way to a fundamental understanding of the properties of water by gradually reducing its complexity to that of a simple liquid.

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Keywords.

water, nucleation, crystal growth, glass formation

Towards a rational design of metallic nanocatalysts

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Nanoclusters are today of widespread use in various applications, ranging from nanomedicine, to memory storage, nanooptics, nanoplasmonics, and nanocatalysis. Such a wide range of applications is possible because of a large variety of their peculiar chemo-physical properties can be tuned by playing with size, shape, and chemical composition of the nanoparticle itself. Indeed, the properties of a cluster depend on their geometry, although the structure-activity relationship is not fully understood yet. In this talk, we will try to elucidate this link with examples taken from nanomagnetism [1] and nanocatalysis [2]. The general idea is to deliver a fingerprint based on geometrical quantities, that can be used to predict the qualitative behaviour of a metallic nano catalyst with a diameter up to 12 nm. We will discuss the effect of thermal stability and the role of structural transitions [3].

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Keywords.

Nanocatalysis, Pt-alloy, nanoparticles

The peculiarities of basal dislocation behaviour in bilayer graphene

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In the last decade the behaviour of dislocations in graphite has been examined theoretically, and the following conclusions were reached: (a) interlayer bonding occurs in the cores of prismatic dislocations, (b) basal dislocations have a Peierls stress of zero and hence move reversibly, (c) basal dislocation motion is inhibited by interactions with point defects, impurities or each other, and (d) where the interaction is strong it can give rise to buckling and folding of layers. The latter conclusion has recently been interpreted by others as a new defect called the ‘bulk riplocation’.

Here we present new Density Functional Theory calculations of basal dislocations in bilayer graphene using the AIMPRO code. We focused on the dipole of basal dislocations in bilayer graphene in a long, thin supercell. In order to introduce a pair of opposite sign on dislocations the displacement field predicted by elasticity theory is imposed on the perfect structure, and four atoms are held fixed in order to preserve the basal slip equal to the dislocation Burgers vector and prevent annihilation.

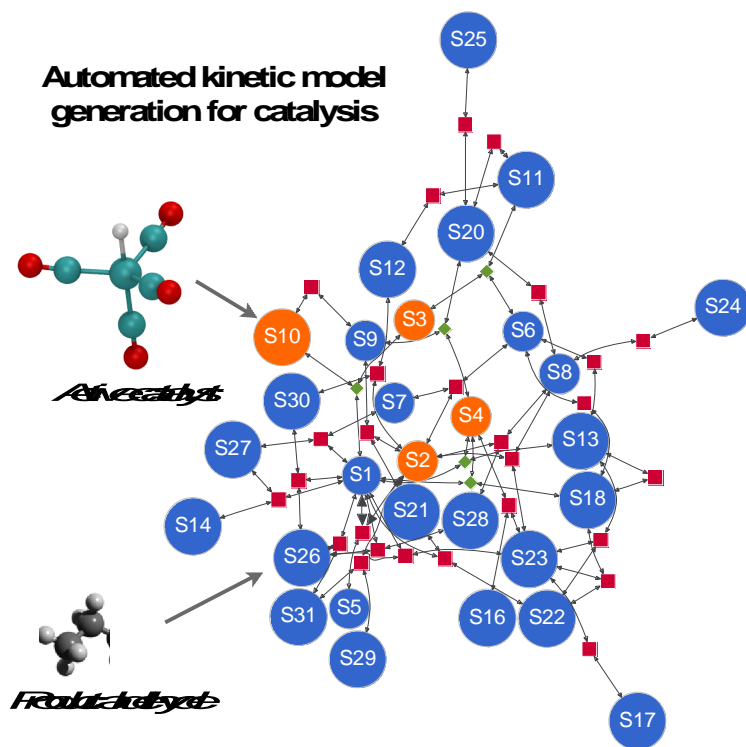
The supercells are examined for tensile and compressive strains (ε) up to 6% in the long dimension, in order to optimize superlattice vectors as well as internal coordinates. The results reveal a complex many-valued relationship, $E(\varepsilon)$, between energy (E) and strain (ε), with branches corresponding to different wavelength buckling and delaminations.

Automated reaction path sampling using random walks in chemical space

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I will describe recent development of a methodology for automated (“black box”) sampling of chemical reaction paths in complex systems [1,2]. This method exploits the simple idea of using connectivity (or bonding) matrices to drive exploration of chemical space; the output of these simulations is a set of chemical reaction paths connecting different sets of reactants and products. These output reaction paths can subsequently be used to construct a kinetic model (e.g. based on rates calculated using transition state theory and standard quantum chemistry) describing the full chemical reactivity of the system; direct kinetic simulations then allow determination of mechanism and rate law. To demonstrate this approach, we consider direct computational determination of the rate law of cobalt-catalyzed ethane hydroformylation; recent results investigating carbon nanotube growth on iron nanoparticles will also be highlighted.

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Keywords

Catalysis; Reaction rates; Reaction paths

Conformational sensitivity of photoelectron angular distributions

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Photoelectron images of a series of para-substituted phenolate anions at a range of photon energies have been recorded. Para-methylphenolate, para-ethylphenolate, and para-vinylphenolate show two direct detachment channels leaving the neutral radical in its ground or first excited state. The photoelectron angular distributions as a function of the electron kinetic energy for the two channels were extracted and interpreted using the relevant Dyson orbitals obtained from EOM-IP-CCSD calculations. Photoelectron angular distributions calculated using eZ-Dyson¹⁻³ were compared with experiment and obtained very good agreement for all three molecules in a planar geometry except the para-ethylphenolate channel leaving the radical in its ground state. Rotation of the ethyl out of the phenolate plane results in a dramatic change in predicted angular distribution for the lowest energy channel. Ground state calculations show that the out-of-plane geometry is the lowest energy conformation, although at 300 K, complete rotation is possible. The observed angular distribution is therefore a sum of photoelectron distributions for all possible conformations, allowing the observed anisotropy to be rationalized from the calculated Dyson orbitals.

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Keywords.

Photoelectron angular distributions, anion spectroscopy, Dyson orbital

On the ionization of PAHs in molecular ices

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Chemistry in the interstellar medium (ISM) is complex and varied. Initially, it was assumed that most molecules form in the gas phase. However, more recently it has become clear that gas-surface chemistry involving interstellar dust grains and interstellar ices has a crucial role to play in the formation of molecules in the ISM. In particular, interstellar ices are ubiquitous in dense (molecular) clouds, where much of the chemistry is taking place. It has also become increasingly clear over the last decade or so that these grains and ices do not just function as a third-body to take away reaction energy, but also as catalysts and reaction mediums, e.g. in the formation of complex organic molecules. Therefore, it is of interest to investigate how the properties of molecules change as they are embedded in interstellar ices, since this will influence any subsequent reactivity.

In this talk we will report on our work on the properties of polycyclic-aromatic hydrocarbons (PAHs) in interstellar (water)-ices. Experimentally, it has been shown that embedding such PAHs into water ice will lower the ionization energy, which has consequences for the availability of cationic species in dense molecular clouds.¹ We have investigated a variety of PAHs in different models of interstellar ices using density functional theory, in particular focussing on their excited state properties in order to explain the experimental observations.

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Dipolar molecules spontaneously organize to form thin films with internal electric fields; implications for CO covered dust grains in the interstellar medium

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It has recently been proposed that nanoscale molecular films can spontaneously assemble to generate static internal electric fields that permeate the film and can exceed 10^8 V/m. These electric fields originate from polarisation charges in the material that arise when the films self-assemble to align molecular dipole moments. This “spontelectric effect” has been observed for molecular species as diverse as nitrous oxide, carbon monoxide, methyl formate, several of the freons and other small, dipolar molecular species.¹

The effect has been illustrated directly by measurement of the residual charge that develops at the surface of molecular films as they grow. Infrared spectroscopy and, most recently, neutron scattering techniques have also been brought to bare. In situ neutron scattering measurements reveal the phase behaviour and density of nitrous oxide as a function of temperature. They were produced by condensation of polarized films directly onto a cold head with line of sight to a neutron beam, under high vacuum conditions, at the spallation neutron source in ORNL.²

Here I discuss the results from the structural characterisation of spontelectric solids, and introduce a model that accurately describes the intermolecular forces at play in stabilising the organized structures. The results are of particular interest in cold, dense molecular clouds, thought to be star forming regions in the interstellar medium. Our experiments show that CO films, similar to those that coat cold dust grain surfaces, are also dipole aligned and exhibit polarization charges at their surface.³ The implications of this for ion recombination pathways in collapsing molecular clouds will be discussed.

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Keywords.

Astrochemistry, neutron scattering, molecular solids, spontaneously organised

Femtosecond laser-induced desorption from doped ice and hydrogenated graphite

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The interaction of photons with species adsorbed on grain surfaces plays an important role in the chemistry of accretion disks and the photon-dominated regions (PDRs) at the edges of interstellar clouds. This energetic input can both drive solid state chemistry as well provide a non-thermal route for the return of species to the gas phase [1]. Laboratory measurements of photodesorption from model grain surfaces employing femtosecond (fs) laser sources provide insights into the desorption process, including the underlying ultrafast dynamics [2,3].

Using fs-laser pulses at 400 nm we have investigated the associative desorption of H₂ from a hydrogenated HOPG surface, using (1+1) REMPI *via* the C ¹Π ← X ¹Σ transition to probe the internal state populations. The detected rotational populations exhibit a non-thermal distribution whilst the vibrationally excited v''=1 state is more highly populated than the ground v''=0 state, demonstrating efficient partitioning of energy into molecular vibration. Kinetic energy measurements indicate a moderate partitioning into the translational degree of freedom. The observed laser fluence dependence is non-linear, permitting the use of two-pulse correlation measurements to provide insights into the underlying desorption mechanism. The observed FWHM of 450 fs suggests an electronically driven process.

We have also used fs XUV pulses from the Free-Electron Laser in Hamburg (FLASH) to probe desorption from molecular ices. Multilayer CO ice held at 18 K was irradiated with 40.8 eV photons. Desorbing neutral CO was detected using (2+1) REMPI *via* the B ¹Σ ← X ¹Σ transition. Vibrational temperatures of T_{vib} ~ 1500 K suggest a desorption mechanism involving a short lived CO⁺ intermediate. We also irradiated mixed CH₄:D₂O ice, resulting in the desorption of simple fragment ions, methane photoproducts up to C₃H_x⁺ and, most strikingly, C_n⁺ clusters up to n = 11. These clusters display a highly non-linear laser fluence dependence (m=5) with two-pulse correlation measurements pointing towards an electronically driven desorption mechanism.

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Keywords.

astrochemistry, interstellar ice, laser desorption, ultrafast dynamics, femtosecond pulses

Abstract

The surface heterogeneity of amorphous silica (aSiO_2) has been probed using coverage dependent temperature programmed desorption (TPD) of a simple probe molecule, carbon monoxide (CO). The resulting distribution of interaction energies is the foundation from which an environmentally broadened vibrational line profile synthesis has been undertaken. These simulations are compared with measured line profiles recorded at 0.1 cm^{-1} resolution using reflection–absorption infrared spectroscopy (RAIRS).

3D cryo-electron microscopy of multiple clathrin cage geometries.

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New electron detectors for cryo-electron microscopy and improved methods of single particle image processing are revolutionizing structural biology, resulting in structures of proteins at below 4 Å resolution from images of individual molecules. We have sought to understand clathrin structure and function by combining cryo-EM methods with kinetic studies to investigate the mechanism of clathrin cage assembly and disassembly. Clathrin cages adopt different geometries both as part of their biological function when forming clathrin-coated vesicles during endocytosis and when purified. Our analysis of some of these geometries has revealed the structure of five unique clathrin cage arrangements. In addition we have determined a higher resolution structure of a tetrahedral 'mini coat' cage at below 6 Å resolution revealing secondary structure elements. Our studies on clathrin cage disassembly have suggested a role for clathrin light chains in structural rearrangements occurring after Hsc70 is recruited to the clathrin cage and in increasing the efficiency of auxilin-facilitated disassembly. I will discuss the implications this new information has for our understanding of clathrin cage assembly and disassembly mechanisms.

Life and free-energy in 3D tissue models – a tool for drug discovery

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From a physical-chemistry perspective, life could be considered as a system that can maintain itself in a non-equilibrium state. Pretty simple really, but it's not a way that we typically think about biological systems.

Similarly life as it applies to us (humans) is a 3D phenomenon, but most therapies are still tested using monolayers of cells growing on a plastic plate – that's not very physiological so it's not surprising that therapies discovered using 2D cell culture don't always translate well *in vivo*.¹

We have developed 3D tumour models that incorporate optical nanosensors that report on their immediate environment. The 3D models recapitulate aspects of tumour tissue such as oxygen gradients, metabolic changes and pH gradients. The nanosensors are gold nanoparticles decorated with reporter molecules whose surface enhanced Raman (SERS) spectrum report on local pH and redox potential. The targeted incorporation of nanosensors allows *in situ* 3D mapping of redox potential gradients whilst retaining 3D morphology and function. The magnitude of the redox potential gradient can be quantified as a free energy difference (ΔG) and used as a measurement of the viability of the 3D tumour model.² We found that by delivering different doses of radiotherapy to MTS we could correlate loss of ΔG with increasing therapeutic dose.³ In addition, we found that resistance to drug therapy was indicated by an increase in ΔG . This robust and reproducible technique allows interrogation of an *in vitro* tumor-model's bioenergetic response to therapy, indicating its potential as a tool for therapy development.

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Keywords.

SERS, bioenergetics, redox biology, 3D tissue models

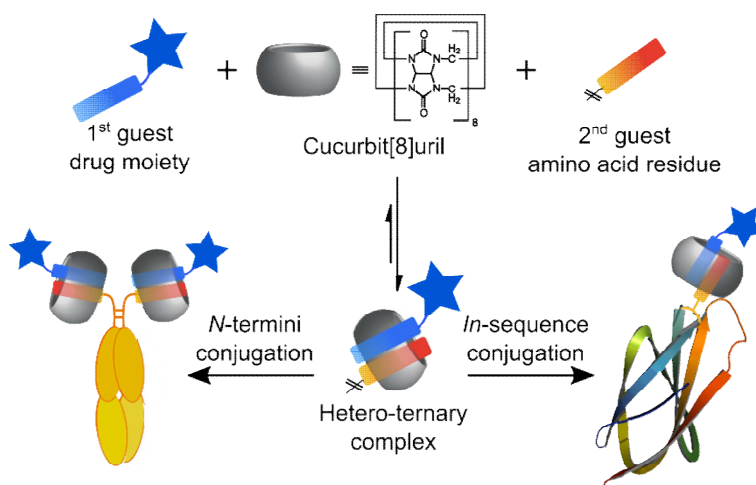
Efficient protein-drug supramolecular conjugation through host-guest chemistry

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The conjugation of small molecule drugs and peptides to biologically active proteins is one of the today's most innovative strategies in drug delivery. This process enables greater *in vivo* stability and drug targeting properties. However, it also presents two major drawbacks: (i) the involvement of difficult and low yielding chemical modifications of proteins and (ii) the likely loss of potency on account of the



covalent fusion of small molecules to large domains. We present a novel and powerful approach to selectively and efficiently conjugate protein domains with drugs, without the need for chemical modification of the protein domain. Our strategy takes advantage of specific sequences of natural amino acid residues, either at the N-terminus¹ or within protein domains,² which show tight binding interactions to a macrocycle, cucurbit[8]uril. This peculiar construct acts as a host and is able to include two guest molecules at the same time, forming a hetero-ternary complex that can simultaneously bring together both a protein domain and a drug moiety. Hence, our host-guest chemistry approach yields protein-drug conjugates which are non-covalently bound/chemically modified while retaining targeting and potency.

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Keywords.

Supramolecular Chemistry, Protein, Phage Display, Cucurbit[8]uril, Host-Guest Chemistry

Self-assembly of Luminescent Compounds for Imaging and Sensing

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Luminescent molecules that can undergo self-assembly are of great interest for the development of new materials, sensors, biolabels.... The talk will illustrate some of the recent results on soft structures based on metal complexes able to aggregate in fibers, gels and soft mechanochromic materials [1]. The use of platinum complexes as building block for luminescent reversible piezochromic and mechanochromic materials will be illustrated. The emission of the compounds can be tuned by an appropriate choice of the coordinated ligands as well as of their aggregation in different structures. The formation of soft assemblies allows the tuning of the emission color, by pressure and temperature leading to a new class of materials possessing reversible properties. We demonstrate how even small changes in molecular design can completely inhibit or enhance the formation of organized supramolecular architectures, leading to a deep understanding of the key factor affecting the whole self-assembly process.

The monitoring of the different emission properties, used as fingerprint for each of the assembled species, allowed an unprecedented real-time visualization of the evolving self-assemblies [2]. Interesting the assembly also occurs in living cells allowing the use of the complex as imaging tools of different cell compartments

Finally the discussed self-assembly can be used as platform for sensing. We have recently demonstrated that a platinum precursor complex can be efficiently employed to detect drugs and toxins in water. The coordination of the analyte to the Pt precursor afford a supramolecular emission-switch-on of the chemosensor and different colors or emission excited lifetimes allow the discrimination of several tenths of analytes [3].

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Keywords.

Platinum complexes, self-assembly, biosensing, chiral structures

Thermally-Activated Delayed Fluorescence in Strapped BODIPY Derivatives

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Thermally-activated delayed fluorescence (TADF) has long been recognized as a simple strategy for increasing the fluorescence yield in cases where prompt emission is weak. The key feature responsible for TADF in organic compounds is the availability of a dark state lying at an energy slightly below that of the emitting excited-singlet state. This dark state, which must be weakly coupled to the ground state, is usually a triplet-excited state. Many examples are known, however, whereby the dark state is reached through intramolecular charge transfer. The rate of repopulation of the emitting state is temperature dependent provided this process competes with direct deactivation of the dark state to the ground state. As such, a characteristic of TADF is that the overall fluorescence yield increases with increasing temperature over a certain range. A second property concerns the dynamics for decay of the emitting state. Here, prompt fluorescence is usually short lived but the decay records contain a contribution from delayed emission that occurs on a much longer timescale. In recent years, much attention has focused on the likelihood for multiple cycles between emissive and dark states as a means to amplify fluorescence, especially for OLEDs. Earlier work reported TADF from a boron dipyrromethene (BODIPY) based molecular dyad able to undergo light-induced intramolecular charge transfer. We now describe a novel form of TADF where the dark state is created by a conformational effect unconnected with either triplet or charge-transfer states. The effect is unique to BODIPY derivatives where the lower rim of the dipyrroin unit is constrained in a small macrocycle.

Thus, a small series of boron dipyrromethene (BODIPY) dyes has been synthesized whereby the boron atom is constrained in a 5-membered ring formed from either *ortho*-dihydroxypyridine or *ortho*-aminophenol. In the latter case, the amino group has been converted into the corresponding amide derivative so as to curtail the possibility for light-induced charge transfer from strap to BODIPY. These compounds are weakly emissive in fluid solution but cleavage of the strap, by treatment with a photo-acid generator, restores strong fluorescence. Surprisingly, the same compounds remain weakly fluorescent in a rigid glass at 80K where light-induced charge transfer is most unlikely. In fluid solution, the fluorescence quantum yield increases with increasing temperature due to a thermally-activated step, but does not correlate with the thermodynamics for intramolecular charge transfer. It is proposed that the strap causes rupture of the potential energy surface for the excited state, creating traps that provide new routes by which the wave-packet can return to the ground state. Access to the trap from the excited state is reversible, leading to the delayed emission. Analysis of the temperature-dependent emission intensities allows estimation of the kinetic parameters associated with entering and leaving the trap.

Photophysical Characterisation of Extended 6-Aza-Uridines – a Promising Class of Responsive, Fluorescent Nucleic Base Analogues

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Fluorescent nucleic acid base analogues are widely used to study the structure and dynamics of DNA and RNA (1). 2-aminopurine (2AP) has long been the most widely used fluorescent base analogue (2) and is one of the few base analogues that are commercially available. A variety of new fluorescent base analogues are being synthesised, with a view to expanding the current range of use and remedying the deficiencies of 2AP (1). A crucial property of 2AP is its extreme sensitivity to inter-base interactions, from which derives its value as a probe of nucleic acid conformation. Recently, considerable progress has been made in the development of new base analogues that, like 2AP, are responsive to their molecular environment (3). One such family is the extended, 5-modified-6-aza-uridines (4). These compounds, analogues of uridine, have large Stokes shifts and absorption and emission spectra that are red-shifted in comparison to 2AP; their quantum yields as free bases have been demonstrated to exceed that of 2AP and their environmental sensitivity has been demonstrated (4). We will report a comprehensive analysis of the photophysical properties of these extended 6-aza-uridine fluorophores and an assessment of their potential as favourable alternatives to 2AP. We will also demonstrate how DFT calculations can be used to rationalise their experimentally determined fluorescence properties.

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Tailoring Luminescent Nanoparticles to Biomedical Applications Using Metal Complexes for Single and Two-Photon Luminescence Imaging

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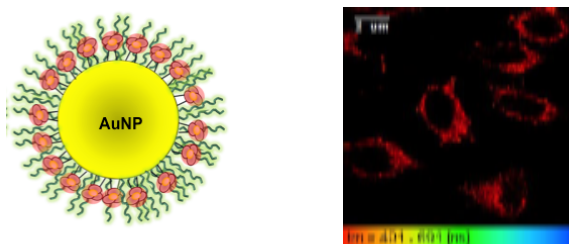
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Gold nanoparticles offer a unique opportunity to incorporate multiple molecular luminescent metal complexes into a single nanoscale architecture for signal detection without engaging in lengthy synthetic procedures for incorporation of multiple labels. We have developed luminescent metal complexes based on lanthanides and transition metals attached on nanoparticles for imaging and sensing applications.^{1,2} The visible luminescence with long lifetimes of the metal provide ideal detection of nanoparticles in cells.^{3,4} Lifetime-based imaging techniques, such as fluorescence and phosphorescence lifetime imaging microscopy (FLIM and PLIM, respectively) are ideal gating out unwanted cellular autofluorescence and transition metals are good candidates for PLIM imaging.⁵

Most recently we developed iridium complexes to coat gold nanoparticles to monitor blood flow in microchannels and obtain increased resolution in imaging of blood velocities.⁶ In this presentation we will show the detection of iridium coated nanoparticles by two photon lifetime imaging in cancer cells and highlight the advantages of using nanoprobe in single and two photo imaging.



Nanoparticles coated with iridium complexes and PLIM image of cancer cells

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Keywords.

luminescence, nanoparticles, luminescence lifetime imaging.

The characterisation of nanoparticulate drug delivery systems using small angle neutron scattering

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An understanding of the detailed molecular architecture of nanoparticulate systems intended for use in drug delivery is essential if such delivery systems are to be effectively exploited as medicines. Small angle neutron scattering (SANS) in combination with contrast variation has proven to be invaluable in gaining such an understanding. This talk will describe the use of contrast variation SANS to characterise a variety of nanoparticulate drug delivery systems including nanocomplexes composed of lipid, peptide and DNA/SiRNA¹ intended for gene delivery, nanosuspensions of high-dose poorly water-soluble drug² and nanoemulsions and microemulsions containing poorly-water soluble drug as well as novel combination formulations comprised of nanosuspensions of drug and nano/microemulsions. Particular emphasis will be placed on the problems experienced with the characterisation of such 'real world' systems.

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Seeing H-atoms and protons: Enzyme mechanisms and drug design

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Neutron crystallography is an important complementary technique to X-ray crystallography because it provides details of the H-atom and proton (H^+) positions in biological macromolecules, and given the absence of radiation damage with neutrons the resulting structures are ‘damage-free’, even at room temperature. Knowledge of the positions of the H-atoms and protons is important because details of protonation and hydration are often necessary for determining enzyme reaction pathways. Moreover, since H-atoms are involved in drug binding, via directional H-bonding and non-directional hydrophobic and electrostatic interactions, knowledge of their location and movement, can also help guide structure based drug design.

Although historically the study of biological macromolecules using neutron crystallography had been limited due to the requirement for extremely large crystals, recent advances in instrumentation and sample preparation now allow much smaller crystals ($\sim 0.1\text{mm}^3$) and the study of larger, more complex systems ($\sim 150\text{ \AA}$ on cell edge). Here I will describe the on-going studies of Human immunodeficiency virus type-1 protease (HIV-1 PR), an essential enzyme for the HIV virus life-cycle and therefore an important target for the development of more effective protease inhibitors in HIV therapy. Neutron crystallography studies have been performed using both the wild-type enzyme and drug-resistant mutant variants, in complex with different clinical inhibitors (amprenavir, darunavir) and at various pH values [1-3]. This ensemble of neutron structures are providing advances in our comprehension of the catalytic mechanism for the enzyme and are allowing us to suggest ways to improve the design of the next-generation of anti-retroviral drugs.

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Keywords.

Hydrogen, protonation, enzyme mechanisms, drug design, neutron crystallography

Probing Breast Cancer Cells with Neutrons The Impact of Anticancer Drugs on Intracellular Water

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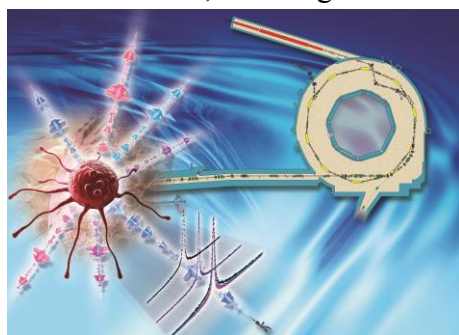
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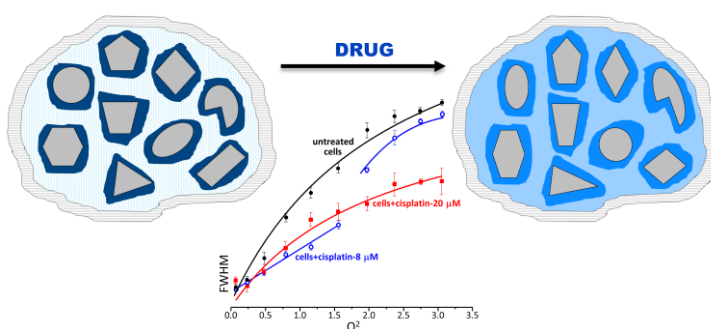
The first neutron scattering study of whole human cells is reported, addressing the subject of solvent-slaving to a drug by probing intracellular water to ascertain structural and dynamical variations upon drug exposure [1]. This study is based on the assumption that the behaviour of cytoplasmic water determines both the conformation and function of biomolecules. Inelastic and quasi-elastic neutron scattering spectroscopy experiments with isotope labelling were performed, for monitoring interfacial water response to metal-based chemotherapeutic agents in cancer cells. This is an innovative way of tackling a drug's pharmacodynamics, searching for alternative targets of drug action to improve chemotherapeutic efficiency.

The widely used cisplatin drug as well as a dinuclear Pd(II) complex extensively investigated by the team [2-5] were probed, at 8 and 20 μM , in human metastatic breast adenocarcinoma cells (MDA-MB-231, a low prognosis cancer with a very poor survival rate).

Intracellular water was found to behave differently in untreated and drug-exposed cells: concentration-dependent structural changes coupled to a progressive mobility reduction were unveiled, concurrent with variations in the native organisation of water within the intracellular medium as a consequence of drug action. This constitutes the first reported experimental evidence of a drug's impact on the cytomatrix by neutron techniques, and will hopefully lead to a better understanding of the *in vivo* mode of action of antitumour compounds, at a molecular level, allowing a rational design of improved chemotherapeutic agents.



(from ref [1])



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Keywords

Pt/Pd anticancer drugs; neutron scattering; breast cancer; intracellular water; drug targeting.

The Interaction of Room-Temperature Ionic Liquids with Phospholipid Bilayers Investigated by Neutron Scattering, Atomic Force Microscopy, and Molecular Dynamics Simulations

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The interaction between room-temperature ionic liquids (RTILs) and biomolecules is an emerging area of research as apparent from the number of publications that appeared in the literature in the past few years¹. Among biological structures, model biomembranes such as phospholipid bilayers and vesicles have been the first to be investigated in relation with RTILs, primarily because of safety and environmental concern but also for opportunities in pharmacology and in nanotechnology. The recognised affinity of RTILs for phospholipid bilayers, first revealed in a short series of pioneering experiments² and later confirmed by computer simulations³ and by neutron scattering experiments⁴, opens a vast new playground to investigate the interaction of organic ionic liquids with paradigmatic biological structures. The subject is of apparent interest for environmental safety, but also for pharmacology, and, eventually, it might impact nanotechnology applications of RTILs and phospholipid bilayers deposited on semiconducting and metal electrodes. In this context, the comprehensive characterisation of the structure and dynamics of both DMPC and POPC in RTIL/water solutions at equilibrium and across phase transformations provides a conceptual and practical tool to understand and predict the properties of a vast class of similar systems. I will show that this far-reaching goal can be achieved by using neutron scattering as a structure- and dynamics-sensitive technique, by exploiting selective deuteration, by using complementary sample configurations, and, last but not least, by resorting to atomic force microscopy (AFM) and molecular dynamics simulations to visualise the system behaviour at the atomistic level. I will present recent experimental results on the microscopic mechanisms that allow RTILs to penetrate lipid bilayers. This process is driven by the Coulomb interaction between the head of the lipids and the cations charges, and it is stabilized by the dispersion forces between their tails. Whereas neutron scattering allows to determine the characteristic time of the absorption of the single cations in the lipid region, which is of order of nanoseconds, AFM allows to determine that cations penetrates first into the bilayer defect by following a power law distribution in time ($\beta=1.2$). Moreover, AFM allows to probe the mechanical properties of the lipid bilayers doped with RTILs, which result more rigid than the net ones. Whereas the neutron structural data have been published, the dynamics data collected at NIST, ILL and MLZ, and the AFM study have not published yet. In my contribution I will also outline few important directions for further experimental and computational developments, as well as for applications, especially in drug delivery and in biomedical applications.

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Taming Molecular Collisions

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The study of molecular collisions with the highest possible detail has been an important research theme in physical chemistry for decades. Over the last years we have developed methods to get improved control over molecules in a molecular beam. With the Stark decelerator, a part of a molecular beam can be selected to produce bunches of molecules with a computer-controlled velocity and with longitudinal temperatures as low as a few mK. The molecular packets that emerge from the decelerator have small spatial and angular spreads, and have almost perfect quantum state purity. These tamed molecular beams are excellent starting points for high-resolution crossed beam scattering experiments.

I will discuss our most recent results on the combination of Stark deceleration and velocity map imaging. The narrow velocity spread of Stark-decelerated beams results in scattering images with an unprecedented sharpness and angular resolution. This has facilitated the observation of diffraction oscillations in the state-to-state differential cross sections for collisions of NO with rare gas atoms [1-3], and the observation of scattering resonances at low-energy inelastic NO-He collisions that reveal the influence of individual partial waves to the scattering dynamics [4].

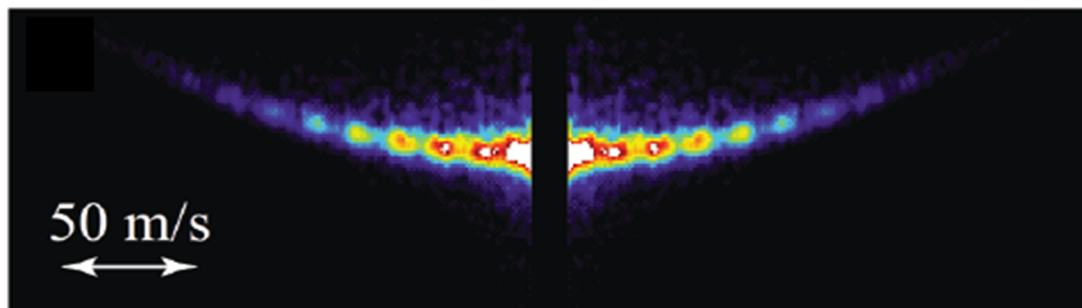


Fig. 1 Velocity mapped ion image for inelastic NO-Ar collisions, featuring a rich diffraction oscillation pattern. Adapted from Ref. [5].

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Controlling the motion of very large molecules and particles

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Recent years saw the development of several techniques to control and confine various degrees of freedom of neutral molecules. We can now routinely select single structural isomers of small molecules, disperse rotational quantum-states, and in certain cases create single-quantum-state samples [1]. Here, we report on the COMOTION project, which aims to extend the available approaches to significantly larger systems, from (poly-)peptide molecules to entire cells or viruses and, furthermore, to develop methods to inject these controlled samples into the interaction region of x-ray free-electron lasers (XFELs) to enable truly single-species single-particle diffractive imaging.

Using soft vaporisation techniques, such as laser or acoustic desorption, allows the production of large volatile (bio)molecules in the gas-phase. We present first results from our new laser desorption setup, designed specifically for incorporation into x-ray free-electron lasers, and show the production of dense and cold beams of intact dipeptides in the gas-phase. For nanoparticle-sized systems, we are developing novel aerodynamic lens stacks [2] and convergent-nozzle focusing injectors [3] to produce controlled particle beams. We have developed a numerical simulation infrastructure that allows the quantitative simulation of isolated particles within complex aerodynamic lens setups. This is used to build aerosol injection systems optimized for a specific particle size and producing the highest density particle beams to optimize XFEL hit rates. Produced particle beams can subsequently be further manipulated using optical techniques, such as hollow-core vortex laser beams [4,5]. The produced cold and controlled samples of large (bio)molecules and nanoparticles will not only benefit diffractive imaging experiments at XFELs, but furthermore are of interest in studies of ultrafast electron dynamics across extended biological systems, or in testing the fundamental size limits of quantum mechanics.

Besides DESY, this work was supported by the ERC through grant ERC-Küpper-614507.

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Keywords.

Molecular Physics, Controlled Molecules, Cold Molecules, Diffractive Imaging, Structure Determination

Magnetic Trapping of SH Radicals

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We have demonstrated and will present results showing the magnetic trapping of cold SH radicals, produced via the photostop technique.¹ H₂S in a skimmed, supersonic molecular beam was photodissociated to produce SH inside a magnetic trap.

The molecular beam speed was matched to the recoil velocity of the SH photofragments and some SH radicals were produced with near-zero laboratory-frame velocity inside the trap allowing them to be confined by the magnetic field. The density of SH radicals in the ground-state was followed by probing using (2+1) resonance-enhanced multiphoton-ionisation (REMPI) over seven orders of magnitude of signal intensity.

The trapped SH density is being investigated further by an enhanced absorption spectroscopy technique called cavity-enhanced laser induced fluorescence (CELIF) to provide robust absolute density measurements.² We are also starting experiments to trap ground state triplet oxygen atoms,³ from the dissociation of NO₂ in our magnetic trap. This should result in orders of magnitude increases in trapped species density. As our trap does not require opening to be loaded with cold species we also intend to observe trap density accumulation from multiple molecular beam pulses.

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Keywords.

Photodissociation, photoionisation, cold molecules, magnetic trapping, molecular beam, spectroscopy.

Towards a complete description of bond orientation in the inelastic scattering of NO(X).

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The three vector $\mathbf{r}\text{-}\mathbf{k}\text{-}\mathbf{k}'$ correlation (where \mathbf{k} and \mathbf{k}' are the initial and final relative velocities of the system respectively) of the inelastic scattering of NO(X) with a rare gas describes the effects of initial bond-orientation of the NO bond axis (defined by \mathbf{r}) on the final angular scattering distribution observed after the scattering event. Experimentally [1,2], the NO bond axis may be oriented, using an electric field, such that the 'N' or 'O' end or the flatter side of the molecule is oriented towards the incoming atom (fig 1.). The effects of such bond-axis orientation on the resulting angular scattering distribution may be shown to be quantum mechanical in nature for all but the case in which large rotational angular momentum transfer between the collision partners is achieved, when classical torque type arguments become important [1-3].

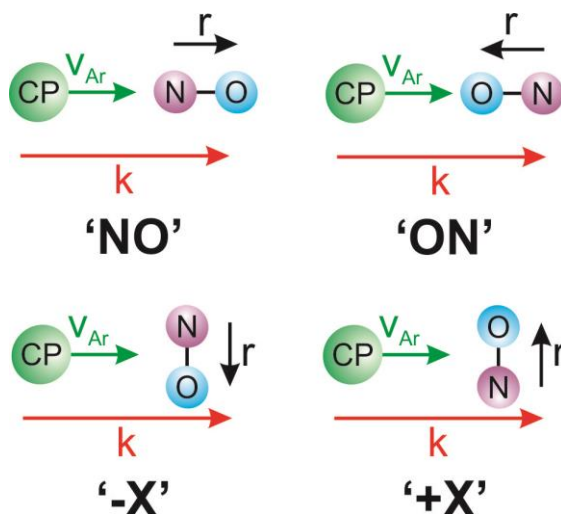


Fig 1. Diagrams to show the orientation of the NO(X) bond axis prior to collision for the 4 possible orientations.

Whilst much is known about collisions at either end of the molecule [1-3], the effects of collisions at the sides of the molecule are much more subtle. Preliminary results show that the observed integral ($\mathbf{r}\text{-}\mathbf{k}$) and differential ($\mathbf{k}\text{-}\mathbf{r}\text{-}\mathbf{k}'$) effects for collisions on the two sides of the molecule may be rationalized using similar arguments to the 'end-on' case. Again, quantum interference effects are shown to be important.

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Multiscale modelling of polymer aggregates

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The ability to combine a detailed description of the chemistry of a molecular model with an efficient exploration of the conformation space is a key point and a real challenge in material science. This is particularly true in the case of soft materials where phenomena taking place at different length scales (ranging from few picoseconds to microseconds and beyond) are responsible for their global properties. Due to the current computational power, all-atom (AA) simulations, which naturally describe the chemical details, are often constrained in time scale up to hundreds of nanoseconds and limited in the number of atoms. In order to overcome this problem, coarser or continuous models can be developed to expand at the same time the size and the time scale of the simulations. [1]

In this talk we will present two different approaches to combine continuous (specifically Computational Fluid Dynamics) or systematic CG with all-atoms force fields to efficiently model polymer aggregates in melt and solutions keeping the atomistic details only where they should be explicitly modelled. We will present results on test models of polyacaprolactone [2], polyethylene and polystyrene [3] and recent developments on nylon [4]. We will also present a simple method to implement a multiple time step algorithm for the simulation of such models. [5]

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Simulations to understand reflectivity: how coarse can we go?

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As the complexity of the systems studied with neutron and X-ray reflectivity increases, so must the methodology applied to the analysis. The current analytical procedure that is widely used for the interpreting reflectivity measurements involves the use of layer models, which are unsuitable for highly complex systems. For this reason, all-atom and coarse-grained molecular dynamics simulations have been investigated to aid in the calculation of reflectivity profiles [1-3]. These have involved the use of research group-specific code to slice snapshots of the simulation box into layers and apply the Abelès method; generating a reflectivity profile.

In this work, we have produced the open-access software, falass [4] which has been used to determine reflectivity profile from a lipid system at various levels of coarse-graining. This involved the simulation of a DSPC monolayer at a water-air interface, using a series of force fields; including all-atom and Martini coarse grained. Using this we have been able to assess the effectiveness of each force field to reproduce the reflectivity from the DSPC monolayers. This knowledge will inform the level of simulation resolution required to ensure the accurate modelling of systems of higher complexity, such as tethered lipid bilayers, or protein-lipid interactions.

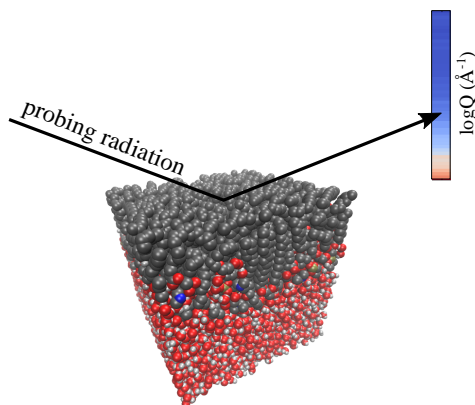


Figure 1. Reflectivity from a MD trajectory.

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Keywords.

molecular simulation, neutron reflectivity, X-ray reflectivity, coarse-graining

Silica Aerogels: Synthesis and Application

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Silica aerogel is a typically inorganic polymer with highly porous property. When the silica wet-gels are formed by polymerisation from precursors, there are various drying methods, such as supercritical drying (SCD), freeze drying (FD) and ambient pressure drying (APD), could be subsequently utilised to replace the liquid inside the pores of the silica gels by gas with causing the minimum capillary shrinkage to produce the silica aerogels. In order for the solvent in the pores of the wet-gels to reach supercritical or freezing point, SCD and FD are all require specially designed equipment which is high energy consumption and costly. APD is a lower-cost process with less requirement of equipment, relying on using organic low-surface-tension (LST) solvent (such as hexane, heptane, octane, and nonane) as drying solvent, and able to fabricate continuous aerogel product [1]. However, the use of organic LST solvent is still costly.

Through 5-year-development, we have invented a novel APD method [2] which eliminates the demand of using organic LST solvents and applied this method to the production of silica aerogels from various precursors, for instance of tetraethoxysilane, waterglass, methyltrimethoxysilane and bridged silsesquioxane (BS). Therefore, the various silica aerogels have been synthesised via our novel APD method for diverse applications, such as thermal insulation and liquid absorption. The BS-based silica aerogel, our most recent research, was synthesised by our novel APD method, and analysed by nitrogen adsorption/desorption isotherm for its specific surface area and pore sizes, and its porous structure was characterised by scanning electron microscope. In order to compare the capability of absorption, the hydrophobic methyltrimethoxysilane-based aerogel and the hydrophilic BS-based aerogel that were both produced by our novel APD method were tested with water. An extraction experiment was carried out following the absorption test and utilising centrifugation to recover the absorbed water from the BS-based aerogel. These tests reveal that BS-based silica aerogel could potentially be an ideal sampling material for water-based solution.

The future scope of our research is to continue the optimisation of our novel method, as this method provides an alternative way of synthesising aerogels with low cost and can be potentially applied to fabricate other aerogels (such as alumina aerogels, fibre-reinforced aerogels and silica-based aerogel composites) in the future.

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Keywords.

aerogel, sol-gel, inorganic, polymer, ambient pressure drying

Low cost superinsulation material via novel ambient pressure drying method

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Abstract

Conventional insulators such as polymeric foams and fibrous materials have common use as insulation materials. However, conventional insulation materials are limited. The reduction of thickness lowers the effectiveness of the materials insulating properties. A solution is the use of highly insulating materials with thermal conductivities lower than (25 m W/m.K) [1]. At room temperature, silica aerogels have a very low thermal conductivity (even lower than air); the values can be as low as 0.015 m W/m.K. The commercialisation of silica aerogels is inhibited due to poor mechanical properties, fragility under low stresses, moisture sensitivity and high production costs [2]. In this study, silica aerogels have been synthesised via a novel economical ambient drying method and are reinforced by ceramic fibre blankets (CFB) or ceramic short fibres (CFS) [3]. A few milligrams of CSF increased the compressive strength of the composite by ten times with little decrease in the surface area and an increase of the thermal conductivity. Ceramic blanket-silica aerogels (CBSA) produced with a small weight percentage of silica aerogels was found to reduce the thermal conductivities. Despite of the small amount of the CSF, ceramic short fibres-silica aerogels composites (CSSA) exhibit a low thermal conductivity while still maintain high surface areas.

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Keywords.

Silica aerogel, Thermal conductivity, CFS, CBSA, CSSA

Light-driven processes in molecular systems: From photophysics to photochemistry

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Modern laser technology and ultrafast spectroscopies have pushed the timescales for detecting and manipulating dynamical processes in molecules from the picosecond over femtosecond domains ($1 \text{ fs} = 10^{-15} \text{ s}$), to the so-called attosecond regime ($1 \text{ as} = 10^{-18} \text{ s}$). This way, real-time dynamics of electrons and nuclei after their photoexcitation became accessible experimentally. On the theory side, powerful (quantum) dynamical tools have been developed to rationalize experiments on photon-driven molecular species. In the talk, light-induced processes in molecular systems, ranging from “photophysics” and “photochemistry” – will be studied with the help of modern quantum chemistry and molecular quantum dynamics.

In a first, “photophysical” part laser-driven ultrafast electron dynamics will be followed with the help of wavefunction-based ab initio methods such as time-dependent configuration interaction (TD-CI) and the multi-configurational time-dependent Hartree-Fock (MCTDHF) method. Specific examples will be given for state-to-state transitions, creation of electronic wavepacket, and non-linear molecular response and their control.

In a second part the vibronic spectroscopy of molecular systems will be considered. For species such as diamondoids the vibronic finestructure in electronic absorption and emission spectra is determined within a time-dependent correlation function approach. This approach has been suggested several decades ago by Heller and coworkers, and is now an efficient method for spectroscopy in complex molecular systems. Also, non-radiative transitions can be treated in this way. Finally, the step to “photochemistry” is made by considering photoswitching of azobenzene and bis-azobenzene molecules. Here, non-adiabatic molecular dynamics with surface hopping allow for detailed insight into the mechanism of photoinduced *trans*-to-*cis* isomerization.

Halogen bonding in molecules of biological interest

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A halogen bond (X-bond) is a type of noncovalent interaction similar to a hydrogen bond (H-bond), but with a halogen atom taking the role of the donor. In a halogen-bonded complex, the positive σ -hole at the end of the halogen atom in one molecule interacts favourably with the negative site (a lone pair, for example) of another molecule. In this presentation I will discuss halogen bonding systems studied recently in our group. These include complexes of halogenated methyluracil (XmU) with water and halogen bonding in thyroxine-protein complexes. In the XmU-H₂O (X = F, Cl, Br, I, At) complexes the water can bind to the XmU molecule through a halogen or a hydrogen bond, leading to competition between these two types of interaction (1).

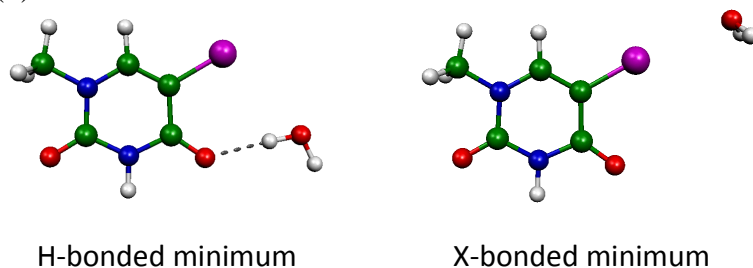


Figure 1. H-bonded and X-bonded interactions in BrmU-H₂O.

The thyroid hormone thyroxine contains iodine atoms, which have the potential of forming stabilising halogen bonds. We have extracted model halogen-bonding systems from X-ray crystal structures of thyroxine—protein complexes and are investigating their stability and geometry.

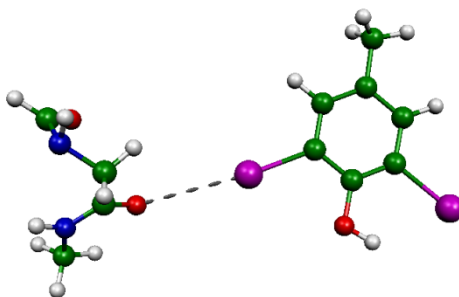


Figure 2. Model system showing the C-I...O halogen bond in a complex of a human serum albumin mutant and thyroxine

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Keywords

Halogen bond, hydrogen bond, density functional theory, M06-2X

Computer-guided porous materials design: from rationalization to prediction

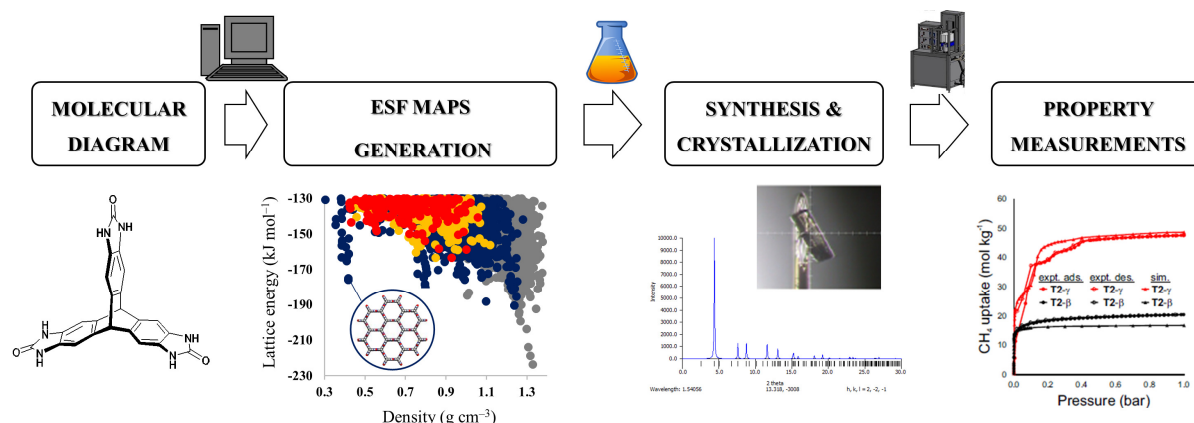
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Organic molecules will tend to pack in dense crystal structures, avoiding the formation of voids. However, the generally less energetically favorable arrangement of molecules into porous crystal structures show important advantages in applications such as gas storage, separation or catalysis. Weak –electrostatic and dispersive– intermolecular interactions dominate molecular packing and are the origin of the unpredictability that seems to surround their crystallization. Thus, the rational design of new materials for technological applications will be limited by the ability to reliably anticipate: (i) the final crystal structure formed and (ii) the physico-chemical properties of such a material.

In this contribution we show how computational techniques and, in particular, crystal structure prediction (CSP) can be successfully used to get a better understanding of the crystal packing preferences of covalently bonded tubular porous organic cages (over 200 atoms); which could be only partially understood experimentally. CSP was used to show how small structural modifications of the molecular cages lead to drastic modifications of crystal packing preferences and help rationalize experimental crystallization outcomes^[1].

Moreover, it will be shown how CSP enabled the identification of a highly porous organic molecular crystal, with the lowest crystal density reported so far; which was subsequently synthesized^[2]. It will be discuss how using the molecular diagram as the only input, CSP and property prediction were combined to build energy-structure-function (ESF) maps (see Scheme 1), and used to reveal the potential of materials for methane storage or alkane separation, which were experimentally confirmed. The potential of ESF maps for computer-guided crystal engineering will be also discussed.



Scheme 1. Representation of the strategy used for computer guided organic molecular crystals design.

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Efficient and accurate first principle on the fly quantum dynamics of ultrafast photoprocesses.

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Previously it was shown that the methods of Coupled Coherent States [1] and Multiconfigurational Ehrenfest (MCE) [2,3] are capable of treating large number of nuclear quantum degrees of freedom (DOF) on a fully quantum level. Well converged and accurate results have been obtained for a number of model systems comprised of tens and in some cases hundreds of DOF, such as spin-boson model for example. Recently an “*ab initio* on the fly” version of the approach has been developed and applied to wavepacket dynamics of photo excited polyatomic molecules [4,5]. Our Multiple Cloning MCE treats all electrons and all nuclei on a fully quantum level and is capable of reproducing accurately ultrafast photodynamics imaging experiments [6]. High level of convergence has been achieved because our “on-the-fly” approach uses sampling techniques developed and tested on model systems.

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Storing energy with oxygen: oxygen redox chemistry in solids and aprotic solvents.

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Oxygen is one of the most important elements in the periodic table. It is available everywhere on our planet and its consumption and evolution lie at the heart of biology. As a result, oxygen reduction and oxygen evolution in aqueous media have been studied extensively for many decades. However such processes in non—aqueous media have received much less attention until recently. The Li-air (O_2) battery has the highest theoretical specific energy of any battery, 3500 Wh kg^{-1} . It could revolutionise energy storage, enabling electric vehicles with a long driving range. The processes of oxygen reduction and evolution in aprotic solvents are fundamental to the reactions taking place at the positive electrode of this battery on discharge and charge, yet almost nothing was known about these processes until interest in the Li-air battery developed. The mechanisms of oxygen reduction at the positive electrode in a Li- O_2 cell will be discussed, highlighting the important role of the solvent in determining the pathway of oxygen reduction, which can be via a surface or solution mediated route. The implications of the new understanding of O_2 reduction in aprotic solvents is that by using redox mediators as electron-hole shuttles to decouple the interfacial electrochemistry from the O redox processes on discharge (O_2 reduction) and charge (O_2 evolution) it is possible to enable high discharge and charge rates, with high capacity to store charge and continuous cycling.

One of the important challenges in Li-ion batteries is how to increase the energy storage at the positive electrode (cathode). The cathode is a lithium transition metal oxide, from which Li^+ and e^- are removed on charge and reinserted on discharge, the electrons being stored on the transition metal ions (transition metal redox). Recent work has highlighted the possibility of storing electrons not only on the transition metal ions, as is the case in LiMn_2O_4 , but also on oxygen, i.e. of oxygen redox processes in solid oxide-based intercalation compounds. This opens up the possibility of cathodes with charge storage exceeding the limit imposed by conventional thinking. O redox in transition metal oxides will be considered, including the nature of the metal-oxygen bond in such materials. The metal-oxygen bond has a key role in switching on O redox in the solid state and controlling whether the holes on oxygen are localized or not and whether the electron deficient O is stable or evolves from the lattice. Work on characterising the nature of the electron-holes on oxygen in cathode materials such as, $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}]\text{O}_2$ and $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{Mn}_{0.6}]\text{O}_2$ will be discussed.

1st Faraday Joint Interest Group Conference 2017

Abstracts for Poster Presentations

ID	Presenter	Title	Poster competition
P1	Camille Blayo	Specific design of photoswitchable surfactants to elaborate smart materials	Yes
P2	Chris Medcraft	Laser Vaporization of nitrogen containing molecules, studied by broadband rotational spectroscopy	Yes
P3	Delaram Ahmadi	Neutron Diffraction Studies of Membrane Rafts	Yes
P4	Andrew Cassidy	Dipolar molecules spontaneously organize to form thin films with internal electric fields; implications for CO covered dust grains in the interstellar medium	Yes
P5	Branislav Dzurnak	Exciton dynamics in non-covalently bound tetracene dimers	No
P6	Catherine Higgins	Desorption from amorphous carbonaceous dust analogues: enhanced binding with respect to graphite	Yes
P7	Emily Slate	Methyl formate formation in the ISM	Yes
P8	Frederik Doktor S. Simonsen	Investigating Superhydrogenated Polycyclic Aromatic Hydrocarbons as catalysts for Interstellar H ₂ formation	Yes
P9	James W. Stubbing	Reflection Absorption Ultraviolet/Visible Spectroscopy as a Tool for Experimental Surface Astrochemistry	Yes
P10	Nigel John Mason	Reversible Phase Change Observed in Astrochemical Ethanethiol Ices	No
P11	Rachel James	Mid-IR spectroscopy of electron irradiated interstellar ice analogues	Yes
P12	Alexandra Martin	Effect of Anionic Phospholipid Doping on the Structure and Dynamics of Zwitterionic Phospholipid Bilayers in Electric Fields	Yes
P13	Angela Garcia Perez	Biophysical Study of Siglec8 ligand binding	Yes
P14	Christine Lockey	An NMR Investigation of Potential Ligands for a Sensor Histidine Kinase involved in Acquired Antibiotic Resistance	Yes
P15	Christopher William Thoroughgood	Antibiotic Resistance in Enterococcus faecalis: Influences from a Serine/Threonine Kinase	Yes
P16	Marc Mora	Protein S-sulfonation and S-thiosulfonation regulates non-enzymatic oxidative folding.	Yes
P17	Marleen Wilde	Exploring Interactions of PAMAM Dendrimers with Membrane Lipids - A Biophysical Approach	Yes
P18	Rachael M. Smith	Spatial Distribution Analysis of the Constitutive Components of a Cell Membrane Mimic	Yes
P19	Safa Damiati	In-vitro and in-silico exploration of hydrotropy to improve drug aqueous solubility	No
P20	Shafaq Muzammal	Molecular interactions of protein-based materials with ionic liquids	Yes
P21	Nadeem Raza	Quantification of photo-induced superoxide anion radicals (O ₂ ⁻) via ZnO nanoparticles	No

P22	Alina Talmantaite	Influence of surface treatment on CVD growth of graphene on polycrystalline copper	Yes
P23	Chris Bloomer	The use of single-crystal CVD diamond as a synchrotron X-ray monitor	Yes
P24	Haytham E. M. Hussein	Electrochemical Synthesis of nano-porous Pt nanoparticles for Enhanced Electrocatalytic Performance	Yes
P25	Jiabin Wang	Study the electrochemical properties of graphene/bismuth composite	Yes
P26	Lidija Siller	Bi ₂ O ₂ CO ₃ nanoparticles decorated on graphene as electrode materials	Yes
P27	Malcolm Ian Heggie	Interlayer vacancy defects in AA-stacked bilayer graphene	----
P28	Michael Hunt	Silagraphenes: stability, transport and synthesis	No
P29	Muhammad Zulqurnain	Reclaiming the third dimension: towards van der Waals heterostructures with tunable optical absorption and emission	Yes
P30	Oznur Kaya	Synthesis of water-glass based silica aerogels reinforced with graphene oxide	Yes
P31	Sam Cobb	Laser micromachining as a route to spatial control of sp ² carbon in boron doped diamond electrodes: pH electrode fabrication and application in unbuffered solutions	Yes
P32	Shams B. Ali	Carbon nanotube-conductive polymer films as gas sensors	Yes
P33	Sharon Strawbridge	A Carbon Electronics World	Yes
P34	Andi Di	Polyelectrolyte-Surfactant Templated Mesoporous Silica Films Grown from Sodium Silicate Solution Precursors	No
P35	Julien Schmitt	Formation of cellulose-starch gels using various cellulose sources	Yes
P36	Marcelo Alves da Silva	Alcohol-induced gelation of cellulose nanofibrils dispersions	No
P37	Naomi Elstone	Investigation into the effect of mixing amino acid surfactants on their structure and physical properties	Yes
P38	Robin Lea	Structural Analysis of Starch Suspensions with Heating Using Laboratory Based SAXS	Yes
P39	Simona Kolarova	Non-aqueous Microemulsions for the Delivery of Drugs	Yes
P40	Anna Riabtseva	Self-assembly of fluorinated polyoxazolines: SAXS and SANS comparative studies	No
P41	Ian Silverwood	Measuring the Surface diffusion of Cyclic Hydrocarbons on Nickel with Quasielastic Neutron Scattering	No
P42	Jonathan F. Gebbia	INS spectroscopy and DFT simulations for 2-adamantanone	Yes

P43	Louis Forto Chungong	Atomic structure of novel chlorine containing calcium silicate glasses for dental applications	No
P44	Orathai Loruthai	The Effect of Testosterone Propionate on Physico-chemical Properties of Triolein Nanoemulsions	Yes
P45	Peixun Li	Deuteration for neutron scattering	No
P46	Stewart F. Parker	Inelastic neutron scattering studies of bone	No
P47	Xing Chen	Properties and Structure of Non-Ionic Surfactant Micelles containing Non-Steroid Anti-Inflammatory Drugs	No
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P51	Alfredo Quinto-Hernandez	Fragmentation Processes of Model Peptide Bonds	No
P52	Ben Jarman	Light-Harvesting Antennae using the Host-Guest Chemistry of Mesoporous Organosilica	No
P53	Jordan Shaikh	Transient Absorption Spectroscopy of a D-A Polymer containing a covalently bound Zinc Porphyrin	Yes
P54	Joshua Karlsson	Intercomponent Exciton Delocalization in a Bispentacene Derivative	Yes
P55	Junwang Tang	Polymer Photocatalysts for Water Splitting	No
P56	Owen Woodford	Photophysics of BOPHY Chromophores	Yes
P57	Pedro Nunes	Ultrafast electron diffraction of small cyclic disulfides	Yes
P58	R. Guy Grantham	Velocity Dependency in Photochemistry	No
P59	Rosaria Cercola	Photochemistry of CO-releasing molecules	Yes
P60	Heather Mutch	Magnetic Frustration in Double Perovskites	Yes
P61	Jessica McGlynn	Controlling Hydrogen Evolution Activity by Phase Transition in MoTe ₂	Yes
P62	Zoe Jones	Development of Offline and Online Methods for Neutron Experiments	Yes
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P66	Mario Gonzalez Jimenez	Tracking the origin of DNA transcriptional bubbles with terahertz spectroscopy	Yes
P67	Sanghamitra Mukhopadhyay	Structure and Vibrations of Hydrogen Bonds in Organic Anti-ferroelectric Squaric Acid	No
P68	Lingli Zeng	Towards Photochemical Interruption of Mitochondria Using Ruthenium Photosensitizers	No
P69	Ada Chiara Capuano	Photon Counting for CELIF	Yes
P70	Adrian Gainar	The Electronic Structure of Para-Aminobenzoic Acid (PABA) in Water: A Spectroscopic Approach Combining UV with Near-Edge X-ray Absorption Fine Structure (NEXAFS) and Resonant Inelastic X-ray Scattering (RIXS)	Yes
P71	Alexandra Tyson	Time-resolved phase second harmonic spectroscopy of ambient liquid interfaces	Yes
P72	Alice Green	Infrared Photodissociation of Metal-Ligand Complexes	No
P73	Alice Henley	Electronic Structure and Dynamics of Conformationally-Locked Photoactive Yellow Protein Chromophores	Yes
P74	André Rebelo	Uracil and uridine photodynamics probed by multi-photon ionisation	Yes
P75	Andrew J Musser	Intermolecular Interactions in BODIPY Films: Aggregates vs Excimers	Yes
P76	Bingxing Wang	Resonance-enhanced photoelectron spectroscopy of phenol in the gaseous and aqueous phases	Yes
P77	Chris Rennick	Potential for long-term, high-frequency, high-precision methane isotope measurements to improve UK emissions estimates	No
P78	Conor Rankine	Non-Adiabatic Multiconfigurational Molecular Dynamics Reveals Ultrafast Structural Change and Internal Conversion in 1,2-Dithiane and 1,2-Dithiine	Yes
P79	Cornelia Heid	Inelastic scattering of state-selected and oriented NO with Ar in the side-on geometry	----
P80	Danica Glenda Pinto	Transportable CELIF Set-up Design	Yes
P81	Daniel Polak	Characterisation of the singlet fission process in protein-stabilised carotenoids aggregates	Yes
P82	David Heathcote	Theoretical total ionisation cross sections of interstellar molecules	No
P83	Ed Greenough & Michael Staniforth	tbc	No
P84	Hansjochen Koeckert	Investigation of CH ₂ BrI charge transfer dynamics using time-dependent and site-selective Coulomb Explosion Imaging on a femtosecond timescale	Yes

P85	Huda AlSalem	Chemically Functionalised Graphene Studied by Time Resolved- Sum Frequency Generation Spectroscopy	Yes
P86	James D. Pickering	Time resolved excited state dynamics of 1-Iodonaphthalene molecules studied inside helium droplets	Yes
P87	James Fletcher	Collisional quenching of excited NO A2Σ+ studied by time-resolved FTIR emission spectroscopy	Yes
P88	James Oliver Frank Thompson	Finite Slice Analysis (FINA) – A General Reconstruction Method for Velocity Mapped and Direct Current Sliced Imaging	Yes
P89	Jamie Gibson	The Excited State Dynamics of Thermally Activated Delayed Fluorescence Emitters	Yes
P90	Jamie Riley	Resonance-enhanced photoelectron spectroscopy of phenol in the gaseous and aqueous phases	Yes
P91	Jana Bocková	Multi-photon ionisation studies of 3-aminophenol: metastable dissociation and Stark deflection.	Yes
P92	Joanne Woodhouse	A Combined Photoelectron Spectroscopy and Quantum Chemistry Study of Luciferin Chromophores	No
P93	Joe Leng	Pair-correlated stereodynamics for diatom-diatom rotational energy transfer: NO(A2Σ+) + N2	Yes
P94	John Mullaney	Weak interactions of thiourea and urea complexes examined by rotational spectroscopy and ab initio calculations	Yes
P95	Joshua Rogers	Hunting for a correlation-bound state: frequency- and time-resolved photoelectron spectroscopy of (C6F6) _n • I– clusters	No
P96	Jutta Toscano	Cold state-selected radicals for the study of low temperature chemistry	Yes
P97	Katherine Buckton	Magnetic field effects on cryptochromes and related model systems	No
P98	Kevin Lovelock	Electronic Structure of Ionic Liquids Using X-ray Spectroscopy: Probing Reactivity	No
P99	Laura Blackburn	LIF is too short	Yes
P100	Laura E. Whalley	Probing intramolecular vibrational energy redistribution using picosecond timeresolved photoelectron imaging.	No
P101	Lisa Saalbach	Time-resolved photoelectron imaging using vacuum ultraviolet pump pulses	Yes
P102	Lorenzo Petralia	Cold reactive collisions between neutral molecules and cold, trapped ions	Yes
P103	Simon Purcell	Probing the surface structure at the vacuum-liquid interface of fluoroalkyl ionic liquid mixtures using reactive O-atom scattering	Yes
P104	Marta Duchi	Following the Femtosecond to Nanosecond Dynamics of Photoinduced Methyl-ammonium Lead-Halide-Perovskite Thin Films	Yes
P105	Mathew Hawkrige	Fundamental Gas Phase Spectroscopy of Geologically Relevant Metalloporphyrins	Yes

P106	Michael Horbury	One- and Two-Photon Activation of [Ru(bpy) ₂ (Nicotinamide) ₂] ²⁺	Yes
P107	Jeni Toland	A reactive extraction strategy to transform biobutane-2,3-diol into platform chemicals	Yes
P108	Minas Stefanou	A Femtosecond Laser Photoelectron Spectroscopy and Computational Study of the Super-atom Molecular Orbital Electronic States of Li@C ₆₀	Yes
P109	Nathan Goodfriend	Blister-Based Laser-Induced Forward-Transfer of Molecules and Nanoparticles	Yes
P110	Neil Cole-Filipiak	Ultrafast Dissociation Dynamics of Aromatic Heterocycles	Yes
P111	Nicholas Smith	In-airway molecular flow sensing: developments and applications	Yes
P112	Ravi Kumar Venkatraman	Intermolecular Hydrogen Bonding Controlled Intersystem Crossing Rates of Benzophenone	Yes
P113	Robert Bianchini	Molecular-beam scattering of OD radicals from atmospherically relevant liquid surfaces	Yes
P114	Steven Parslow	A Magnetic Resonance Disruption (MaRDi) Technique for the Detection of Surface Immobilised Magnetic Nanoparticles	Yes
P115	Stuart R Mackenzie	Velocity Map Imaging Studies of Metal-Containing Molecules	No
P116	Stuart Thompson	TADF in Coinage Metal Complexes for Organic Light Emitting Diodes	Yes
P117	Thomas Northey	Time-resolved X-ray Spectroscopy using Direct Quantum Dynamics	Yes
P118	Tom Sharples	Experimental testing of ab initio potential energy surfaces: stereodynamics of NO(A ² Σ ⁺) + Ne inelastic scattering at multiple collision energies	Yes
P119	Victoria Taylor	Investigating charge carrier dynamics in formamidinium lead iodide perovskites using time-resolved infrared spectroscopy	Yes
P120	Weiwei Zhou	Electron impact total and partial ionization cross sections and kinetic energy releases for hydrocarbon species relevant to fusion edge plasmas	Yes
P121	Esma Birsan Boydas	Probing Optical Properties of Thiophene-Derivatives for Two-Photon Absorption	No
P122	Fu Song	Atomic Structure, Stabilities and Dynamics of Molecular Clusters of Cement	Yes
P123	Golda Mensa-Bonsu	Investigating the Electron Impact Resonances of PAHs	No
P124	Maximilian Saller	Progressive minimal basis set sampling for quantum dynamics using short-time trajectories	Yes
P125	Olga Ershova	Basis Sets for Explicitly Correlated Calculations for Heavy Group 1 (K – Fr) and Group 2 (Ca – Ra) Elements	No
P126	Rasha W. M. Al-saedi	Theoretical analysis of liquid exfoliation of copper based metal organic frameworks	No
P127	Simon Hogan	An Investigation into Competition Between Halogen Bonding and Hydrogen Bonding in Microsolvated 1-	Yes

methyl-5-halouracil

P128	Benedykt Biezanek	tbc	No
P129	Christopher Robertson	A novel Path integral Monte-Carlo approach for general Quantum correlation functions.	No

Specific design of photoswitchable surfactants to elaborate smart materials

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Photosurfactants (PS) are amphiphilic molecules which contain a light-responsive chromophore, such as an azobenzene group. PSs demonstrate the combined ability to form supramolecular structures past a critical concentration and change their shape upon irradiation with light. Light-induced changes in the size, polarity or shape of these amphiphilic molecules are accomplished through reactions such as *trans-cis* isomerisations or photodestructions.¹ However, in order to effectively design the next generation of smart materials, the challenge is to be able to accurately predict and control the aggregate nanostructure formed.

This study aims to demonstrate that by varying the position of the azobenzene core the resulting shape and size of micelles can be controlled for a series of cationic azobenzenes photosurfactants (AzoTAB, Fig. 1a). The structure and the *trans-cis* photoisomerisation of AzoTABs leads to the formation of a variety of self-assembled structures, which can be resolved by small-angle neutron (SANS) and X-ray (SAXS) scattering.^{2,3} The results show that *trans*-AzoTABs with long alkyl chains ($R_1 = 8$) form larger, more stretched ellipsoidal micelles than short alkyl chains ($R_1 = 4$), suggesting that the relative position of the azobenzene core drives the resulting shape of the aggregates. The *trans-cis* photoisomerisation leads to a reorganisation of the nanostructure to form smaller, more hydrophilic spherical micelles (Fig. 1b). Our study shows that, by astute changes in the molecular structure, one can control the nanoscale organisation of the global system. Such nanostructural differences associated with the isomerisation process make these materials potentially interesting for phase transfer catalysis or light-controlled delivery applications.

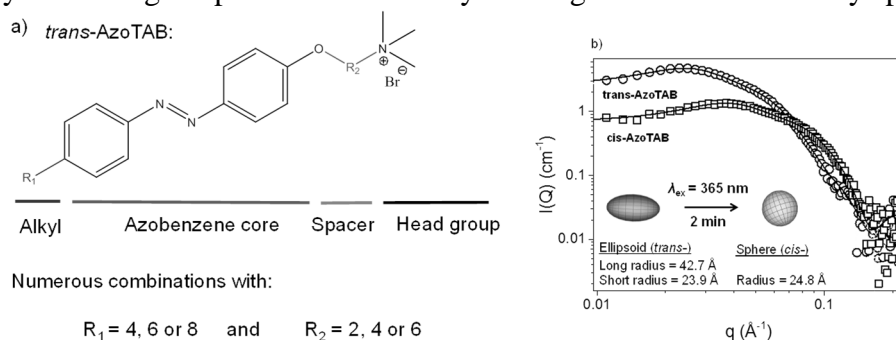


Fig. 1 (a) Chemical structure of the AzoTABs studied. (b) SANS profile of the *trans* (circle)-*cis* (square) isomerisation of AzoTAB ($R_1 = 4$, $R_2 = 6$) in D_2O (20 mmol dm^{-3}) and 20 °C. The schematic representations of the proposed shapes of the micelles are shown for visual support.

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Keywords.

Self-assembly, Photosensitive surfactants, Small-angle neutron scattering.

Laser Vaporization of nitrogen containing molecules, studied by broadband rotational spectroscopy

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The vast majority of molecules that have been detected in space were verified in the laboratory by rotational spectroscopy.^[1] Through recent advancements in high speed electronics it is now possible to record many gigahertz of rotational spectra, at kilohertz resolution, nearly instantaneously. The technique of chirped pulse Fourier transform microwave (CP-FTMW) spectroscopy is not only highly accurate in frequency, but also in relative intensities. The combination of broad bandwidth, accurate intensities, isomer selectivity and near universality of detection makes CP-FTMW spectroscopy an ideal tool for studying chemical reactions and short lived species.

The Newcastle CP-FTMW spectrometer operates from ≈ 2 -19 GHz and uses laser vaporization to seed molecules into a supersonic expansion. This molecular source is used to produce metal containing compounds (e.g. Y---MX where Y=a Lewis base; H₂S, H₂O, M=Cu, Ag, Au, X=F, Cl, I) and also to bring organic compounds (e.g. urea and substituted imidazoles and pyrazoles) into the gas phase. These small organic compounds produce a large range of interesting fragmentation and complexation products, many of which have astrochemical relevance. Experimental details and the spectroscopic results from the laser vaporization of urea and 2-methylimidazole will be presented along with the observed fragmentation products. Possible astrochemical implications of these fragmentation pathways and future research directions will be discussed.

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Keywords.

Microwave spectroscopy, structure determination, gas phase, chirped pulse

Neutron Diffraction Studies of Membrane Rafts

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The lateral organisation of lipids and proteins in the eukaryotic cell membrane has been the focus of intense research. Of special interest is how the lipid components of the membrane can be triggered to phase-separate and form highly dynamic, nanoscale structures known as “rafts” (1). It has been well-established that under physiological conditions in membranes composed of phospholipid (PL), cholesterol (Chol) and sphingolipid (SL), phase separation occurs forming distinct liquid ordered (L_o) domains containing Chol and the highly saturated, conformationally ordered SLs (2,3), “floating” within a bed of “liquid-like” unsaturated and conformationally disordered PLs in a liquid disordered (L_d) phase (4, 5). Significantly, recruitment of certain proteins within these lipid domains has led to the so-called “raft hypothesis” wherein rafts are seen to be key in a variety of biological processes such as cell signalling and membrane trafficking (6).

To date, there have been a number of fluorescence microscopy and X-ray scattering studies of raft formation that have been conducted on biologically relevant ternary lipid mixtures involving dioleoylphosphatidylcholine (DOPC), mixed with dipalmitoylphosphatidylcholine (DPPC) and Chol (7, 8). There have been no studies yet conducted, however, that have allowed a direct determination of the molecular architecture of these raft-forming systems.

In the studies reported here, we aimed to rectify this deficiency, using the technique of lamellar neutron diffraction to study the formation of rafts in lipid multilayers comprising 2:2:1 ternary mixtures of DPPC, DOPC, and Chol. The multilayers were studied as a function of temperature, and the experiments conducted on the D16 diffractometer at the Institut de Laue Langevin, Grenoble, France.

Diffraction patterns were successfully recorded for the lipid multilayers at 25 °C, 20 °C, and at 15 °C, with a relative humidity of 80%. At 25 °C, the diffraction patterns showed a single lipid phase with d -spacing of 53.8 Å. As the temperature was lowered to 15 °C, two phases appeared with d -spacings of 53.9 Å and 59.2 Å. The diffraction patterns were recorded with varying D₂O:H₂O solvents, and the neutron scattering length density profiles for the system computed by Fourier summation using the calculated structure factors. The scattering length density profiles for the two phases existing at 15 °C were successfully modelled assuming one phase comprising a L_o domain of DPPC with Chol, and the second phase comprising a L_d domain of DOPC.

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Dipolar molecules spontaneously organize to form thin films with internal electric fields; implications for CO covered dust grains in the interstellar medium

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It has recently been proposed that nanoscale molecular films can spontaneously assemble to generate static internal electric fields that permeate the film and can exceed 10^8 V/m. These electric fields originate from polarisation charges in the material that arise when the films self-assemble to align molecular dipole moments. This “spontelectric effect” has been observed for molecular species as diverse as nitrous oxide, carbon monoxide, methyl formate, several of the freons and other small, dipolar molecular species.¹

The effect has been illustrated directly by measurement of the residual charge that develops at the surface of molecular films as they grow. Infrared spectroscopy and, most recently, neutron scattering techniques have also been brought to bare. In situ neutron scattering measurements reveal the phase behaviour and density of nitrous oxide as a function of temperature. They were produced by condensation of polarized films directly onto a cold head with line of sight to a neutron beam, under high vacuum conditions, at the spallation neutron source in ORNL.²

Here I discuss the results from the structural characterisation of spontelectric solids, and introduce a model that accurately describes the intermolecular forces at play in stabilising the organized structures. The results are of particular interest in cold, dense molecular clouds, thought to be star forming regions in the interstellar medium. Our experiments show that CO films, similar to those that coat cold dust grain surfaces, are also dipole aligned and exhibit polarization charges at their surface.³ The implications of this for ion recombination pathways in collapsing molecular clouds will be discussed.

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Keywords.

Astrochemistry, neutron scattering, molecular solids, spontaneously organised

Exciton dynamics in non-covalently bound tetracene dimers

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Singlet fission (SF) is a process during which the excited singlet state is split in a pair of triplet excitons. In this way, one absorbed photon can produce two charged carriers hence increase the efficiency of potential photovoltaic devices. SF occurs in several organic materials such as carotenoids or polyacenes [1]. In tetracene the energy of triplet state is approximately double the energy of singlet therefore it is a promising molecule to study the process of SF [2]. It has been shown that covalently bound dimers of tetracene in solutions exhibit SF, however the efficiency was low compared to crystalline tetracene [2, 3]. Possible SF has also been observed in covalently bound tetracene in thin films [4, 5].

Here we study solutions of tetracene in protein maquette. This maquette consists of hydrophilic exterior and hydrophobic interior which creates a pocket capable of trapping tetracene dimer molecules without forming a covalent bond.

We present time-resolved photoluminescence measurements which show two independent emissive states decaying with different time-constants on a scale of hundreds ps. We also present results on transient absorption experiments which can provide identification of triplet states formed by SF. We also investigate the stability of our samples by studying the degradation of absorbance spectra.

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Keywords.

singlet fission, polyacenes, exciton dynamics, ultrafast spectroscopy, transient absorption

Desorption from amorphous carbonaceous dust analogues: enhanced binding with respect to graphite

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The space between stars, the interstellar medium (ISM), is not empty but rather filled with clouds of gas and dust. These interstellar clouds can collapse to form stars. Of particular interest are the “dense clouds” in the ISM, where the gas and grain temperatures are low (approximately 10 K). These regions are shielded from UV radiation by the surrounding gas and dust particles. This shielding protects the complex molecules formed in the cloud *via* gas-grain interactions and standard gas phase routes.¹ In order to account for the observed molecular abundances, astronomers are particularly interested in identifying the possible gas-grain interactions that may be taking place within these denser clouds.

Dust grains account for 1 % of the mass of interstellar clouds and the grains are composed of amorphous carbonaceous material and amorphous silicates. The grains are believed to be between 0.1 μm - 0.001 μm in size and are elongated in shape with irregular surfaces. These surfaces possess a large number of physisorption sites with a wide range of binding energies which can facilitate gas-grain interactions.¹⁻² When a gas is incident upon the surface of a dust grain it can be adsorbed onto the cold surface. Adsorbed species can then be brought together to react, meaning the dust grains act as a “reservoir” for gases. Discrepancies (or so-called depletions) between the observed gas-phase abundances of certain molecules and the abundances predicted in astronomical models can be explained if the grains can “store” gases on their surface and synthesis new molecules.

Experimentally, the most common dust grain analogues are olivine (for siliceous material) and graphite (for carbonaceous material). In the experiments presented here, we will focus on the carbonaceous material. The desorption characteristics of gases from graphite as well as the results of various reactions upon the surface have been studied in great detail.¹⁻³ However, it is unlikely that graphite, with its ordered structure, is an accurate representation of the amorphous surfaces in the ISM. In this poster, we present preliminary results showing the desorption of various gases from an amorphous carbonaceous surface (ACS). The ACS was formed *via* a laser ablation technique at the University of Jena.⁴ From the desorption data, we can conclude that the amorphous surfaces show enhanced binding at higher temperatures, compared with graphite, indicating a greater proportion of high-energy binding sites are present on the ACS. This observation means that various simple molecules could remain adsorbed onto the dust grains at temperatures higher than was previously anticipated using the data obtained from desorption studies on graphite. This graphitic data has been used to model the desorption of ice mantles during the warming of interstellar clouds.⁵ Our data may indicate that an upgrading of these models is necessary to accurately describe the desorption of lower coverages of simple molecules from amorphous surfaces.

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Methyl formate formation in the ISM

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For many years methyl formate, and its isomers glycolaldehyde and acetic acid, were thought to have a gas-phase formation route in the Interstellar Medium (ISM).[1] However, it has become increasingly apparent that this is not feasible given the extremely low temperatures found in the ISM.[2] It is now thought that methyl formate is made via surface reactions on icy interstellar dust grains.[3]

This work uses computational means to investigate the role of interactions between the icy mantle of the dust grain and radical component species in facilitating the formation of methyl formate. Formation of methyl formate from radical pairs has been investigated both in the presence and absence of water ice. It has been found that hydrogen bonding interactions with the water molecules can facilitate the formation of both methyl formate and glycolaldehyde. The target species are not observed in the absence of an ice structure.

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Investigating Superhydrogenated Polycyclic Aromatic Hydrocarbons as catalysts for Interstellar H₂ formation

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Scanning tunneling microscopy and temperature programmed desorption techniques have been used to investigate adsorption and abstraction of hydrogen atoms on the polycyclic aromatic hydrocarbon, coronene. The coronene molecules were exposed to different hydrogen fluences at a dosing temperature of 1000K. Large fluences of hydrogen leave superhydrogenated coronene molecules, which reveal stable configurations and indications of H₂ formation

In certain regions of the interstellar medium (ISM), like photodissociation regions (PDRs), unexpectedly high abundances of molecular hydrogen, H₂, are observed. Because of relatively high H₂ destruction rates in these regions, the presently accepted formation routes on dust grains cannot exclusively account for the observed abundances [1]. Therefore, new formation routes are needed and lately attention has been drawn towards molecules called polycyclic aromatic hydrocarbons (PAHs). PAHs are believed to account for up to 20% of the available carbon in the ISM and have been observed, with significantly large abundances, alongside H₂ [2].

Here we investigate the adsorption pattern of hydrogen/deuterium on coronene, C₂₄H₁₂. Both scanning tunneling microscopy (STM) and temperature programmed desorption (TPD) techniques have been used. Coronene monolayers were prepared on highly ordered pyrolytic graphite (HOPG) and exposed to different fluences of hot (2300K) or cold (1000K) H or D atoms. STM images show bright spots on the coronene monolayers after hydrogenation indicating adsorption to coronene.

TPD measurements show an exponential decay of pristine coronene with increasing D fluence again showing the adsorption process. TPD also reveals formation of fully deuterated coronene (C₂₄D₃₆), hence the original H atoms are substituted with D atoms i.e. by Eley Rideal abstraction reactions forming HD [3].

Density functional theory (DFT) calculations made for H-addition to coronene molecules predict that the barrier for adsorption is lowest at the outer edge of the coronene molecule [4]. Further predicted was that competing abstraction and adsorption channels with 0eV barriers should be present after only 3 H-additions to the coronene molecule. These tendencies can be recognized by both the STM images and the TPD measurements.

We observe superdeuterated coronene species which appear stable against further hydrogenation at intermediate D fluences. These stable configurations indicate energy barriers for certain adsorption sites.

DFT cautions made on desorption of H from a fully hydrogenated coronene molecule reveal a favorable desorption route and stable configurations consistent with our TPD measurements [5].

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Reflection Absorption Ultraviolet/Visible Spectroscopy as a Tool for Experimental Surface Astrochemistry

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The interstellar medium (ISM) is known to have rich chemistry, in spite of the low pressures and temperatures that occur there ($\sim 10^{-4}$ molecules cm^{-3} and ~ 10 K respectively). This chemical diversity is in part due to the presence of dust grains, which offer a surface on which processing and reactions of molecules occur.

We present a newly installed ultraviolet/visible (UV/vis) spectroscopy apparatus with a variable reflection geometry. Ultimately, using the Fresnel equations to analyse the spectra obtained, we will be able to determine optical parameters of highly oriented pyrolytic graphite (HOPG) and amorphous silica (aSiO_2) surfaces and thin films of adsorbates on these surfaces. The accurate determination of these parameters will allow UV/vis spectra of interstellar ices to be predicted, and will allow a direct comparison with observational data. This technique for determining optical parameters of ice films has already been demonstrated in the infrared region.¹

Initial test data collected using the new instrument is presented for small aromatic molecules, namely benzene and toluene, for a range of ice thicknesses and incidence angles. Benzene has been detected in the ISM^{2,3} and formation routes for toluene are postulated⁴. Benzene can be considered a building block of larger polyaromatic hydrocarbons (PAHs) and toluene presents an interesting comparison due to its slight increase in size and its small dipole. The behavior of these molecules on a HOPG surface has been the focus of recent work undertaken in our laboratory, and the data presented in this poster is the next step in this investigation.

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Keywords.

Ultraviolet/visible spectroscopy, astrochemistry, PAHs

Reversible Phase Change Observed in Astrochemical Ethanethiol Ices

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Thiol molecules are known to be present in the InterStellar Medium (ISM) since 1970's. The recent discovery of ethanethiol ($\text{CH}_3\text{CH}_2\text{SH}$) in the ISM suggests that even larger thiols might be synthesized as part of complex chemical processes in these regions (Gorai et al., 2017). Therefore we have performed a series of experimental investigations to explore the morphology of thiols, such as methanethiol (CH_3SH), ethanethiol and propanethiol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{SH}$) under astrochemical conditions.

These experiments were carried out at the Physical Research Laboratory (PRL) in India and at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The experimental conditions employed in both the laboratories are similar where an ultrahigh vacuum chamber is used to cool down ZnSe/KBr substrates to between 10 K and 4 K. After cooling the substrate to these low temperatures, thiol molecules were let into the chamber to freeze onto the substrate. Temperature cycling was carried out from 10 K until a phase change was observed and then these ices were cooled back down, infrared spectra were recorded throughout this temperature cycle.

For methanethiol, spectra obtained at lower (10 K) and higher temperatures (110 K) revealed that a phase change occurs in the ice which is consistent to those reported by Hudson (2016). In the case of propanethiol, a shoulder band in the S-H stretching region is an indication of phase change to have occurred in the ice before sublimation. However, for thin ethanethiol ice films there was no phase change until sublimation whereas a thick ice was found to change phase from amorphous to crystalline around 115 K followed by another phase change from crystalline to amorphous at 125 K (Pavithraa et al., 2017). This *reversible phase change* was found to be repeated by subjecting the sample to temperature cycling until the sample is thinned below a critical value by losing molecules during every phase change after which no phase change was observed again.

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Keywords.

Interstellar medium, laboratory simulations, ethanethiol, reversible phase change

Mid-IR spectroscopy of electron irradiated interstellar ice analogues

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With temperatures as low as 10 K to temperatures as high as 10^6 K and densities spanning over nine orders of magnitude, the interstellar medium (ISM) is a diverse place for molecular formation. Although a variety of molecules have been detected in the ISM, the formation routes for most of these molecules is still not fully understood. Gas-phase chemical reactions can account for the formation of some molecules, but surface reactions must also play a pivotal role in molecular formation. In the ISM, the surfaces are in the form of dust grains covered in icy mantles and these ice-covered dust grains are subjected to energetic processing (e.g. cosmic rays, electrons, UV photons, X-rays) which can lead to more complex molecules. Processing from secondary electrons is relatively abundant in the ISM due to the interaction of ionising radiation, such as cosmic rays, with solids releasing large numbers of electrons. At the OU Astrochemistry Laboratory, we investigate electron induced reactions by mimicking ISM conditions and irradiating interstellar dust grain analogues with 1 keV electrons from an electron gun. We monitor the formation of molecules with mid-IR ($4000 - 600 \text{ cm}^{-1}$) spectroscopy and can quantitatively determine the final yields of molecules in solid-phase. Current studies of ices of astrophysical interest being conducted at the OU include water ice mixed individually with carbon dioxide (CO_2), oxygen (O_2) and nitrogen (N_2).

Effect of Anionic Phospholipid Doping on the Structure and Dynamics of Zwitterionic Phospholipid Bilayers in Electric Fields

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The effect of molecular structure on macroscopic structure and behaviour of phospholipid bilayers has been investigated. Mixed bilayers of dimyristoyl phosphatidylethanolamine (DMPE) and dimyristoyl phosphatidylserine (DMPS) were prepared on Au(111) electrodes by Langmuir-Blodgett and Langmuir-Schaeffer deposition and investigated with a combination of electrochemical measurements and *in situ* Polarisation Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS). Bilayer capacitance is observed to increase as the proportion of DMPS content increases, which is likely to result from an increase in overall hydration of bilayers. Infrared measurements show that the structural response to increasing anionic lipid content is complex: the chain tilt of 9:1 DMPE:DMPS bilayers experiences a distinct reorientation as the applied electric field is varied, which is different from behaviour exhibited by either DMPE or DMPS. The extent of hydrogen-bonding of the carbonyl moiety in the lipid headgroup with water molecules is shown to depend on the proportion of anionic lipid present in the bilayers, as does its dependence on the applied potential. The changes in orientation and hydration are discussed in terms of the packing of the constituents and the biological relevance of mixed bilayers.

References.

Keywords.

keyword1, keyword2, keyword3, keyword4, keyword5, keyword6, keyword7

BIOPHYSICAL CHARACTERIZATION OF SIGLEC8 LIGAND BINDING

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Lectins are cell surface carbohydrate binding proteins that play a significant role in cellular events such as cell-cell communication, cellular self recognition, cell migration, apoptosis or immune system response. Sialic Acid Immunoglobulin-like lectins (Siglecs) are highly promising biological targets for development of new therapeutic treatments for several chronic human diseases such as Lymphomas, Rheumatoid Arthritis or Alzheimer's disease [1]. Siglec 8 is specifically expressed in eosinophils, the main cellular effectors involved in asthma [2, 3, 4]. Previous *in vitro* studies have demonstrated that the interaction between Siglec 8 and its glycan ligand, the sialic acid 6'-sulpho sialyl Lewis X, leads to eosinophil programmed cell death and could reduce inflammation and tissue damage in the lungs during an asthma crisis [5, 6, 7]. The aim of this work is structure-based design of mimetic molecules that bind Siglec 8, utilising the recently resolved 3D structure of the Siglec8 carbohydrate binding domain in complex with its ligand 6'-Sulpho Sialyl Lewis X. The structure has revealed the molecular features of the protein-ligand interaction, which will form the basis for our design of new Siglec 8 ligands [8]. We have cloned and expressed soluble Siglec 8 carbohydrate binding domain in *E. coli* in order to test ligand binding by means of glycan array [7] and biophysical techniques such as solution state NMR. Therefore this work could form the basis of development of new therapeutic molecules that target Siglec 8 in order to treat asthma.

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An NMR Investigation of Potential Ligands for a Sensor Histidine Kinase involved in Acquired Antibiotic Resistance

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The antibiotic vancomycin induces cell death in Gram-positive bacteria, including clinically significant *Enterococci*, by binding to precursors of the bacterial cell wall after they are passed through the membrane, and prior to their integration into the peptidoglycan matrix^[1]. Vancomycin targets the d-Alanyl-d-Alanine terminus of the pentapeptide stem of the precursor^[2], and this binding event prevents incorporation of the precursors into the cell wall, leading to deterioration of the wall, and cell death.

A resistance mechanism has arisen, whereby bacteria may synthesise a modified peptidoglycan precursor whose pentapeptide stem terminates d-Alanyl-d-Lactate^[3]. This modified precursor cannot be bound by vancomycin, but may still be integrated into the cell wall. In this way, the action of vancomycin is circumvented. Substitution of this modified precursor is coordinated by several enzymes, the expression of which is induced by the regulatory protein VanR. VanR is activated through phosphorylation by VanS, a receptor histidine kinase, in the presence of vancomycin. The precise activation mechanism of VanS has yet to be elucidated, with conflicting evidence in the literature to suggest that binding of vancomycin^[4] or peptidoglycan precursors^[5] to VanS may induce kinase activity. Direct observation of ligand binding to VanS has yet to be reported. This work investigates the ligand-binding characteristics of VanS from two sources (*Enterococcus faecium* and *Streptomyces coelicolor*) through solution-state NMR and other biophysical techniques.

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Keywords.

Peptidoglycan, vancomycin, VanSR, antibiotic resistance, ligand binding

Antibiotic Resistance in *Enterococcus faecalis*: Influences from a Serine/Threonine Kinase

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The regulatory control of gene expression by external stimuli in bacteria is poorly understood but is fundamental to bacterial signaling, environmental response and antibiotic resistance. It has been known for sometime that almost all bacteria use multiple membrane bound histidine kinases and cytoplasmic response regulator proteins to form two-component systems (2CS) to respond to external stimuli. However, the nature of these protein-ligand interactions and how that interaction is transmitted through the membrane is still largely unexplored. It is becoming increasingly clear that many bacteria also contain single Serine-Threonine kinase (STK) proteins similar to those found in eukaryotes, which are responsible for more global extracellular signal responses.

Between groups at Columbia (USA) and Warwick (UK), we have identified IreK as a unique STK in pathogenic *Enterococci* that appears to have a highly significant role in peptidoglycan and related antibiotic resistance. The aim of this project is to dissect the molecular architecture and interaction of the *Enterococcal* IreK. We have already assembled a molecular tool kit of proteins, ligands and chemical probes to explore this system. We are interrogating IreK extracellular domain ligand interactions using a range of biophysical techniques including SPR and NMR structural characterization of these domains to monitor the ligand interaction. We aim to describe IreK ligand recognition to intracellular signaling and its relationship to antibiotic resistance.

Keywords.

Anti Biotic Resistance, NMR and SPR

Abstract ID (To be added by Conference committee)

Protein S-sulfonation and S-thiosulfonation regulate non-enzymatic oxidative folding

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Disulfide bonds are a widely employed strategy used by nature to regulate the mechanical stability of proteins. Importantly, the presence of disulfide bonds is often reversible through chemical reactions, a process known as post-translational modifications (PTM's). This ability of sulfur to undergo PTM's is due to the external empty d-orbital from sulfur ($[\text{Ne}]3s^23p^43d^0$) available for bonding. While the general effect of mechanical forces on protein unfolding is now well understood, how mechanical forces regulate the reduction and reformation of individual disulfide bonds is largely elusive. Here we use a combination of protein engineering and single molecule force spectroscopy to investigate how different nucleophiles - sulfite and thiosulfate- regulate the reactivity of protein disulfide under force, thus severely impacting on the nanomechanics of the protein. Our measurements reflect the broadly different role of the intimately related S-sulfonation and S-thiosulfonation on protein's elasticity, and focus on the importance of force-induced exposition of cryptic disulfide bridges on the regulation of protein nanomechanics through PTM's.

Keywords.

Biophysical chemistry, chemical modification, protein folding, single-molecule biophysics

Exploring Interactions of PAMAM Dendrimers with Membrane Lipids – A Biophysical Approach

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Structurally well-defined PAMAM dendrimers have been developed as potential drug and gene delivery systems¹. Cationic dendrimers (e.g. G5) efficiently internalise genes and drugs into cells; and have shown antibacterial and antiviral activity (*in vitro*, *in vivo* and in clinical studies)^{2,3} but their therapeutic application is still limited by their toxicity. Furthermore, they are generally reported to be more toxic than the structurally similar anionic PAMAMs (e.g. G4.5)^{1,4}. This study aims to provide mechanistic insights to the PAMAMs interaction with both eukaryotic and prokaryotic lipid membrane models using biophysical methods.

Phospholipid monolayers were employed as simple, but well-established models⁵ for studying the impact of lipid, dendrimer and solution properties on PAMAM binding at the air/water interface. Neutron reflectometry on supported bilayers was used to study PAMAM adsorption at the solid/liquid interface and explore structural effects of the dendrimer binding. Zwitterionic phosphocholine (DPPC) and anionic phosphoglycerol (DPPG) (predominant in eukaryotes and prokaryotes respectively) were selected for our study as simple model lipids. Langmuir surface pressure (SP) measurements at pH 7 revealed a concentration-dependent penetration of both, PAMAM G4.5 and PAMAM G5, into both monolayers. Both PAMAM species showed a binding preference to DPPG displaying a surface pressure increase of $4.3 \pm 0.3 \text{ mN m}^{-1}$ for PAMAM G5 and $5.7 \pm 0.6 \text{ mN m}^{-1}$ for PAMAM G4.5 at 0.06 mg mL^{-1} , whereas little to no penetration into DPPC monolayers was observed (SP change for PAMAM G5: $0.8 \pm 0.1 \text{ mN m}^{-1}$, for PAMAM G4.5: $1.3 \pm 0.3 \text{ mN m}^{-1}$).

Neutron reflectometry studies on lipid bilayers supported the results observed with the monolayer experiments. Furthermore, the fitted model data provided useful structural information of the lipid bilayers and the location of the PAMAM dendrimers in relation to the membrane.

Strong electrostatic attraction between the cationic PAMAM surface groups and the anionic head group of DPPG could explain the interactions of PAMAM G5, whereas interactions with the lipid tail and changes in lipid packing might be the cause for the penetration behaviour observed for PAMAM G4.5.

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Keywords.

Neutron reflectometry, PAMAM, dendrimers, membranes, lipids, Langmuir trough, surface pressure

Spatial Distribution Analysis of the Constitutive Components of a Cell Membrane Mimic

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Clustering of cell membrane components is a widely accepted model to explain cell membrane functionalities; sphingomyelin, cholesterol and proteins involved in signal transduction, have been shown to form lipid raft micro-domains. Lipid raft formation can result in altered membrane biochemistry and topography at their locality due to the altered membrane composition ^[1,2]. The study of such clustering effects has been limited however due to the limited analytical technique compatibility of cellular membranes. Therefore, adaptation of analytical techniques to study membrane component distributions are required. Here, we developed a supported lipid bilayer (SLB) model suitable for analysis with Atomic Force Microscopy (AFM) and Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) to establish the capability to study the topographical and chemical distribution of ligands within a lipid bilayer.

SLBs were formed in a composition mimicking that of an epithelial cell membrane; comprised of phosphatidylcholine, phosphatidylserine, phosphatidylethanolamine, phosphatidylinositol sphingomyelin, cholesterol and a polymer with a cholesterol anchor with varying chain lengths to mimic a wider range of membrane ligands. AFM of these SLBs revealed regions of greater height, 2.16 ± 0.31 nm, consistent with the height increase when comparing a sphingomyelin and cholesterol bilayer to a phospholipid bilayer. It is within or bordering these taller regions that incorporated polymers are distributed, with some polymers accumulating together (Figure 1). ToF-SIMS was used for chemical spatial mapping of the lipids and ligands, on the micron-scale (resolution limit). Despite the highly similar structures of the components of the membrane, distinction between them was gained via this analysis, allowing for examination of the distribution of lipid species, enabling the identification of lipid species clustering. Furthermore, ToF-SIMS proved invaluable as a proof of incorporation, allowing the attribution of tall SLB regions as found by AFM (Figure 1) to ligand.

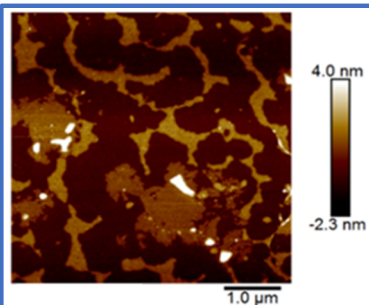


Figure 1: Atomic Force Microscopy image of a cell membrane mimicking supported lipid bilayer. Three distinct layers of varying height may be attributed to the base (dark) phospholipid membrane, with the middle (orange) layer being the sphingomyelin/cholesterol rich regions protruding from the base membrane and the tall (white) regions being due to ligand.

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In-vitro and *in-silico* exploration of hydrotropy to improve drug aqueous solubility

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Background. Around 80 % of drug candidates fail to reach the market (and therefore the patient) due to problems of poor water solubility. Solubilisation using hydrotropes offers a possible solution to this problem. A hydrotrope is an amphiphilic compound that can enhance the apparent solubility of poorly water-soluble (hydrophobic) compounds. Despite their potential for increasing drug solubility, however, relatively little work has been performed exploring the potential of hydrotropes to increase solubility. The aim of this work was therefore to study - both *in-vitro* and *in-silico* - the capacity of a range of potential hydrotropes to improve the aqueous solubility of a poorly water-soluble non-steroidal anti-inflammatory drug, indomethacin.

Methods. The apparent aqueous solubility of indomethacin was studied in the presence of eleven structurally related potential hydrotropes. Excess drug was added to aqueous hydrotrope solutions prepared at a range of concentrations. Excess drug was removed from the equilibrated solutions and the amount of drug dissolved quantified using high performance liquid chromatography with UV detection. Subsequently, *in-silico* modelling using Artificial Neural Networks (ANNs) was performed using experimental data on indomethacin solubility, together with various computed physicochemical descriptors for the hydrotropes. The trained ANN was thereafter used for *in-silico* screening of untested hydrotrope systems for indomethacin.

Results. The enhancement of the apparent aqueous solubility of indomethacin varied using the tested hydrotropes from ~3 to ~260 fold (at 0.5 M hydrotrope concentration) and the trained ANN was found to give highly accurate predictions of indomethacin solubility in the presence of the hydrotropes tested experimentally. The ANN was also used to explore the hydrotrope characteristics required for optimum enhancement of indomethacin solubility - the four most important features thereby identified as molecular complexity, heavy atom count, hydrogen bond acceptor count, and pK_a . With the insights thus provided, the commercially available compounds, catechol and resorcinol, were identified as superior hydrotropes for indomethacin, each yielding predicted solubility enhancements for indomethacin of the order of 2000-fold.

Conclusions. ANNs with hydrotrope molecular descriptors as inputs provide an accurate means of screening drug/hydrotrope systems *in-silico*, and offer great potential for use in optimisation of drug formulations.

Molecular Interactions of Protein-based materials with Ionic Liquids

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Ionic liquids (ILs) are solvents consisting purely of ions. The properties of ionic liquids such as low vapor pressure, low flammability and their ability to dissolve polar and nonpolar organic, inorganic and polymeric compounds are a result of a complex interplay of intermolecular interactions between constituent ions, their geometry and charge distribution.

Proteins are polyamides having amino acids (AAs) as building blocks and are essential macromolecules in biological systems. The dissolution and processing of such polymers by standard molecular solvents is hindered by their complex nature and the presence of strong inter and intra-molecular hydrogen bonds. ILs have shown favorable solvation properties for polar substrates, including carbohydrates¹ and proteins^{2,3} but apart from the beneficial effects found for the use of biocompatible ILs in connection with proteins, remarkably little is known about the molecular basis of the IL–solute interactions.

Here we present our latest results, determined from computational methods showing the microscopic organisation of ionic liquids around amino acid and peptide-based solutes, to help explain the ionic liquid-peptide interactions and to develop a predictive understanding and optimisation of macroscopic processes including solubility and reactivity of proteinaceous materials in ionic liquids.

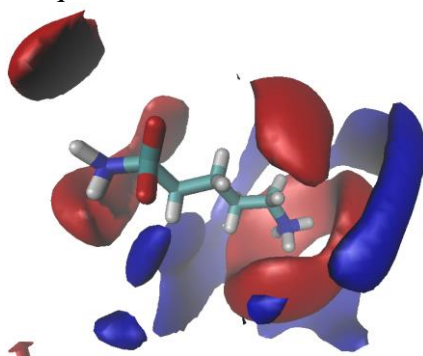


Figure 1. Organisation of the ionic liquid ions [C2C1Im]⁺ (blue) and Cl⁻ (red) around the zwitterionic lysine cation, shown as a spatial distribution function.

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Quantification of photo-induced superoxide anion radicals (O_2^- via ZnO nanoparticles

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The optical and electronic properties of zinc oxide are exploited in sunscreen formulations. ZnO nanoparticles (NPs) impart both aesthetic value and UV light absorption capabilities to sunscreens. However, potential adverse effects on human skin make it interesting for investigations. This work demonstrates detection and quantification of superoxide anion radicals (O_2^-). These radicals can have deleterious effects on skin tissues. In this work, 50 mg/L ZnO-NPs in aqueous solution are subjected to UV irradiation in the presence of molecular probe (XTT tetrazolium salt). XTT tetrazolium salt is converted to XTT formazan which is detected and quantified using absorption spectroscopy. Our findings show that 49% of superoxide anion radicals are produced per unit mass of ZnO- NPs. Average sizes of 295.3 nm and 616.5 nm are observed for irradiated and non-irradiated ZnO-NPs respectively. Zeta potential values of -24.4 mV and 0 mV are recorded for irradiated and non-irradiated ZnO-NPs respectively. Photocatalysis of ZnO-NPs induce superoxide anion radicals and generate fine nanoparticle suspension.

Influence of surface treatment on CVD growth of graphene on polycrystalline copper

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Chemical vapour deposition (CVD) is an attractive technique for the scalable production of graphene [1]. However, the condition of the substrate surface can play a key role in growth, with poor surface condition potentially leading to the formation of defective, multilayer graphene islands with degraded electrical, optical and mechanical properties [2].

In this work we have studied the effect of surface preparation of copper substrates on the morphology, size and nucleation density of graphene islands. Two surface treatment procedures were adopted: electropolishing and a more conventional treatment with acetone, isopropanol and acetic acid. Ambient pressure CVD was then employed, using methane, to grow graphene on the resulting substrates. The quality of graphene islands was examined using Raman spectroscopy and scanning electron microscopy (SEM). The data have shown that there is no significant difference between the two treatment methods on graphene quality as measured by Raman scattering, nor on treatment time; however, preliminary results from SEM reveal dendritic island growth on the etched substrates, while compact island shapes are observed on the electropolished substrates indicating a higher mobility of carbon-containing precursors.

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Keywords.

Graphene, CVD, Raman, SEM

The use of single-crystal CVD diamond as a synchrotron X-ray monitor

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Diamond Light Source (DLS) delivers highly intense, focused X-rays beams for scientific users, tunable in energy, and orders of magnitude brighter than a traditional laboratory X-ray source. Synchrotron X-rays can be focused down to micrometer spot-sizes to examine microscopic crystals, or to enable high resolution mapping of larger samples [1]. This light is used in scientific fields from archeology to protein biology, and everything in-between.

Common to all of the experiments conducted at synchrotrons are the requirements to monitor and maintain the stability of the X-ray beam upon the sample: in spatial position, in intensity, in photon energy; and to do so over the whole range of timescales exploited by the synchrotron users, nanoseconds [2] up to months [3]. Monitoring instruments that can make (nearly) non-destructive measurements of the incident X-ray beam position and intensity are thus of the utmost importance for the operation of synchrotron beamlines.

CVD diamond is shown to be an excellent X-ray monitoring material for synchrotron beamlines. It's unique mechanical, thermal, optical, and electrical properties make it well suited to the non-destructive monitoring of intense X-ray beams, and it has been demonstrated that such detectors can provide a measurement of the incident X-ray beam position with resolutions of a few 10nm at kHz bandwidths [4]. CVD diamond X-ray position and intensity monitors far surpass the performance of the previous generation of instruments, giving beamlines and synchrotron users unprecedented access to high resolution, quantitative information about their X-ray beam stability. This technology is revolutionary in enabling improvements to synchrotron beamline stability.

The use of CVD diamond monitors installed at DLS is presented here, demonstrating how they are used in beamline development and commissioning, in day-to-day troubleshooting, and most importantly in real-time feedback loops used to fix the position of the X-ray beam at the sample point. These feedback loops are a vital step in stabilizing the X-ray beam, and giving DLS users the best possible X-ray beams with which to run their experiments.

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Electrochemical Synthesis of nano-porous Pt nanoparticles for Enhanced Electrocatalytic Performance

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Nanosized particles of platinum (Pt) supported on a substrate surface are pivotal for oxidation-reduction reactions in proton exchange membrane fuel cells that operate at elevated temperatures.¹ Among many shapes and structures, nano-porous platinum nanoparticles (Pt NPs) have gained interest due to their high catalytic activity features, however, synthesizing such structures is challenging. Electrodeposition is proving to be a promising technique to fabricate NPs. It is a one-step method of both producing the nanostructure and ensuring it remains in intimate electrical contact with the underlying electrode substrate.

Over the past decade, boron doped diamond (BDD) has proven to be an interesting NP support material due to its excellent electrochemical and physical properties such as stable surface, high thermal conductivity, wide solvent window and low background currents.² Recently we demonstrated that by controlling the interfacial electrode/electrolyte temperature by heating the surface locally (non-isothermally) via illuminating the backside of the electrode surface with an IR laser, changed in material structure / composition could be achieved.³ Thus temperature gives us further control of the structure and the associated reactions, in addition to those parameters normally associated with electrodeposition i.e. current, voltage, time. In this work we show how the use of a pulsed IR laser to locally heat, in combination with electrodeposition results in porous Pt NPs (Figure 1). By heating, smaller particles with more quasi spherical and spherical structures were produced, at significantly higher NPs densities and coverages than those produced under ambient conditions, as shown in Figure 1. The electrocatalytic activity of Pt NPs formed via temperature heated versus ambient temperature was compared for methanol oxidation and it was found to be 40% more reactive. This was attributed to the porous structure of Pt NPs made under laser pulse heating.

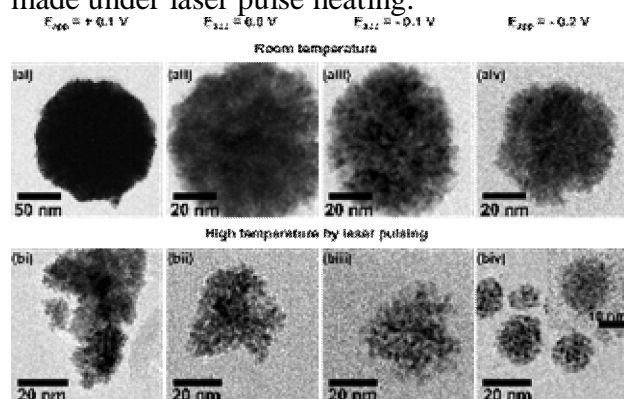


Fig 1. A representative HR-TEM images of Pt NPs obtained under (a) room and (b) high temperature from different driving forces +0.1 V, 0 V, -0.1 V and -0.2 V for t_{dep} = 5 s.

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Study the electrochemical properties of graphene/bismuth composite

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Bismuth was one of the most extensively studied elements in solid-state physics because of its electronic properties, such as a long Fermi wavelength (around 30 nm) and high Hall coefficient ^[1,2]. With the thickness of bismuth film reduced, it develops a high density of states crossing the Fermi level, which leads to the failure of band gap opening. A particularly attractive feature of bismuth is that, in spite of its heavy metal status, it is considered a safe and non-toxic material. Moreover, a large amount of bismuth is produced as a by-product of the copper and tin refining industry. All these make bismuth a promising candidate as electrode used in energy storage devices.

However, it has been observed previously that bismuth metal nanostructures, such as nanowires or nanoparticles, readily oxidize when exposed to air at atmospheric pressure. Metallic bismuth wires typically have an oxide layer ~1 nm thick after 4 h exposure to air ^[3]. High temperature hydrogen and ammonia environments were found to reduce the oxide without damaging the bismuth metal after a sufficient amount of time, but the oxide was found to reform in less than 1 min of exposure to air.

Graphene sheets act as impermeable atomic membranes to many gases therefore it is likely to protect bismuth from oxidation. In this work ^[4], a reduced graphene oxide/bismuth (rGO/Bi) composite was synthesized for the first time using a polyol process at a low reaction temperature and with a short reaction time (60 °C and 3 hours, respectively). The as-prepared sample is structured with 20–50 nm diameter bismuth particles distributed on the rGO sheets and protected by rGO sheets from oxidation. The rGO/Bi composite displays a combination of capacitive and battery-like charge storage, achieving a specific capacity value of 773 C g⁻¹, which is in its theoretical value range, at a current density of 0.2 A g⁻¹ when charged to 1 V. This material also has good stability in cycling tests with a high current density of 5 A g⁻¹ ^[4].

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energy, electrochemistry, electrode materials

Bi₂O₂CO₃ nanoparticles decorated on graphene as electrode materials

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Nanosized metallic particles attract much interest because of their considerably changed physical and chemical properties compared to micron sized bulk materials ^[1]. In addition, by using nanosized transition metal oxide particles with high surface area carbon materials, composite materials with readily accessible mesoporous can be obtained ^[2]. Hydrothermal synthesis methods, which require autoclave and high reaction temperature, are generally used to prepare nanosized composite materials. However, the high cost of initial materials, requirement for the special equipment, need for high reaction temperatures and toxic nature of these materials limit their scale up preparation and applications. With the concern of CO₂ emission and environmental protection, searching for materials with low cost production and innocuous to nature attracts tremendous interest in the study of electrode materials.

In this work, we proposed a novel one step method to prepare rGO/Bi₂O₂CO₃ nanocomposite material. Bi₂O₂CO₃, as one of the bismuth components, shares the non-toxic and environmental friendly properties of bismuth. In this work, we successfully synthesized nanosized Bi₂O₂CO₃ particles (5-10 nm) at room temperature within 3 hours. Bi₂O₂CO₃ particles uniformly decorated on the reduced graphene oxide surface. With only 6% of Bi₂O₂CO₃ used in this composite material, a specific capacity of 280 C g⁻¹ at the current density of 1 A g⁻¹ was obtained. This composite material shows stable cycling performance for ~ 4500 cycles under the current density of 3 A g⁻¹.



Figure. EDS results of rGO/ Bi₂O₂CO₃ composite material a) a typical SEM image b) carbon element in this area c) bismuth element in this area.

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Interlayer vacancy defects in AA-stacked bilayer graphene

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In AA stacking all atoms are in registry in the direction perpendicular to the layers. This can occur when graphene folds to make a bilayer or, in an approximate sense, in rotated layers with a small angle of relative rotation. In previous work, it has been shown that vacancies can bind to each other across the interlayer gap in graphite¹, and also that some patterns of aggregation must arise where the bonds so formed between vacancy aggregates in different layers give rise to a ramp of graphene connecting graphene layers together². Here we present the results of *ab initio* Density Functional Theory calculations of complexes of various morphologies that are formed from the binding of vacancy oligomers across neighbouring layers in AA stacked bilayers. As with AB stacking, the carbon atoms surrounding lattice vacancies can form interlayer structures with sp^2 bonding that are lower in energy than in-plane reconstructions. This applies even to the case of a pair of highly stable 5-8-5 divacancies in registry: interlayer bonding is still energetically favoured. The sp^2 interlayer bonding of adjacent multi-vacancy defects in registry creates a type of stable sp^2 bonded 'wormhole' or tunnel defect between the layers. We also identify a new class of 'mezzanine' structure characterised by sp^3 interlayer bonding, resembling a prismatic vacancy loop. The hexavacancy mezzanine variant, *i.e.* V_6 arising from V_3 in each layer, has six sp^3 carbon atoms sitting midway between the two carbon layers which each bond to both layers. It is substantially more stable than any other vacancy aggregate in AA stacked layers.

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Silagraphenes: stability, transport and synthesis

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Despite the great excitement generated by the isolation of graphene [1], the absence of a band gap limits the application of this material in logic and opto-electronic devices. Although there are two-dimensional solids which display possess a band gap, such as the transition metal dichalcogenide molybdenum disulphide (MoS₂), these are often characterised by low carrier mobility [2]. The synthesis of silagraphene (Si_xC_y) materials has recently been reported [3] providing another, potentially valuable, member of the family of two-dimensional solids.

In this work density functional theory (DFT) is used to study the structural stability, electronic and optical properties of siligraphenes of a range of compositions. Silagraphenes with a Si:C ratio of up to 3:1 are found to be planar whilst buckling occurs at higher silicon content due to tilting of rigid Si₃C units. Electronic band gaps are seen only in structures for which the sub-lattice symmetry is broken. Upper limits to the intrinsic carrier mobility of these solids are calculated using deformation potential theory and are found to be higher than those calculated for the transition metal dichalcogenides. Solid phase synthesis of two-dimensional islands from silicon-containing precursors is demonstrated with Raman spectroscopy, scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) suggesting silagraphene growth has been achieved.

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Keywords.

Graphene, 2D materials, Transport, ab-initio calculations, growth, Raman, XPS

Reclaiming the third dimension: towards van der Waals heterostructures with tunable optical absorption and emission

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The family of two-dimensional solids has expanded rapidly since the discovery of graphene in 2004 [1] and offers a broad palette of materials for the creation of novel heterostructures [2]. In such ‘van der Waals heterostructures’ the absence of dangling bonds and weak interlayer interactions create abrupt interfaces with minimal perturbation of the physical and chemical properties of the constituent materials. Hence, it is possible to create structures with tunable electronic structure and optical absorption with potential applications in areas as diverse as electronic devices, sensors, absorber materials for solar cells [3].

In this work, shear exfoliation [4] is used to produce suspensions of monolayer to few layer platelets of graphene and molybdenum disulphide (MoS_2), which have been among the most widely studied two-dimensional solids. Thin films and heterostructures of these solids have been successfully deposited from these suspensions on to a range of both hydrophilic and hydrophobic substrates and characterized by Raman scattering, Scanning Electron Microscopy, Optical Absorption spectroscopy and X-ray reflectivity. The resulting films and heterostructures are shown to be continuous with tunable layer thickness, providing the basis for the development of new materials and devices.

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Synthesis of water-glass based silica aerogels reinforced with graphene oxide

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Silica aerogels are the most highly porous nanostructured materials, discovered in 1931 by Kistler [1]. They could have remarkable properties such as low bulk density ($\sim 0.03 \text{ g/cm}^3$), high specific surface area ($\sim 1200 \text{ m}^2/\text{g}$), high porosity (80-90%) and the extreme low thermal conductivity (0.005 W/mK) [2]. Because of these properties, they are considered as excellent thermal insulators, energy materials, dielectric materials and adsorbents [3, 4]. Despite long standing history and their promising applications, the high production costs have so far prevented their wide commercial use.

To further reduce the cost, the sodium silicate (an inexpensive precursor) based aerogel has been synthesized. In addition to this, when cheaper water based solvents are used instead of costly organic solvents in ambient pressure drying (APD), it enables to be an alternative, less energy intensive route with possibility of continuous production [5]. Another problem in aerogel production is their inferior mechanical property if they are used solely as monoliths, therefore the reinforcement is considered to be promising strategy. Graphene can improve comprehensive performance of host materials due to excellent mechanical properties, but the poor solubility of the graphene prohibits homogeneous dispersion in common solvents [6]. Therefore, the graphene oxide is a wonderful alternative.

In this study, composite silica aerogels with different additions of graphene oxide were made by Newcastle's novel low cost APD method. The prepared silica aerogels composites were then characterized in terms of the morphology, microstructure, the elemental/ composition, structure, specific surface areas, pore volume and pore size distribution. Improvements in properties of aerogels will be presented.

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Laser micromachining as a route to spatial control of sp^2 carbon in boron doped diamond (BDD) electrodes: application to pH electrode sensing in unbuffered solutions.

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High power laser micromachining systems are used to cut diamond and have previously been used to manufacture all diamond electrochemical devices, including disk electrodes, band electrodes and ring disk electrodes¹. The machining process also leaves non diamond (sp^2) carbon behind. Recently, we have shown how we can use this approach to functionalise the BDD surface with sp^2 sites, which are more catalytically active than the surrounding sp^3 BDD surface. The nature of this sp^2 carbon is still not completely understood, but has been shown to contain quinone-like moieties (QLM's) which demonstrate a quantitative pH response² and can be used as a measure of the surface sp^2 content³.

Previous carbon pH sensors based on the electrochemical reduction/oxidation of surface bound quinone groups have been shown to have significant limitations, often struggling at high pH⁴ and in unbuffered solutions. The latter is due to the fact that by making the measurement protons are removed from solution resulting in a changing proton concentration at the surface of the electrode. The surface attachment of these molecules has also been shown to fail in extreme environments^{4,5}.

QLM's produced on the surface of BDD by laser micromachining have a significant advantage over previous approaches. The QLM's are incredibly stable, being resistant to mechanical abrasion, extremely high temperatures and extreme environments. However, the challenge is to maintain the proton level constant at the surface during the electrochemical measurement. To this regard, we investigate ways in which we can either increase the flux of protons to the electrode surface or decrease the number of protons being turned over at the electrode surface. In particular, we explore how the laser micromachining parameters influence the number of QLMs on the surface and the effect of the sp^2 functionalisation pattern on the performance of the pH electrode.

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Carbon nanotube-conductive polymer films as gas sensors

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This research concerns the physical and structural properties of carbon nanotube/ conductive polymer composites and their use in gas sensors. In particular we provide information on the sensing mechanism by observing the temperature-dependence of the sensing response. A good sensor should be sensitive, reliable and low cost, with fast response and a short recovery time¹. Carbon nanotubes (CNTs) are well-suited because of their unique properties; small size, large surface area, good electric conductivity and change in electrical properties when in the presence of different gases at different temperatures². However, it has been shown that bare carbon nanotubes CNTs have a low response for volatile organic compounds, therefore we attempted to improve this property of CNTs by templating pyrrole on CNTs. Polypyrrole is simple to prepare by oxidation of the monomer and its resistance is very sensitive to organic vapours, although much greater than that of CNTs. TEM of polypyrrole/CNT composites prepared from single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) show polypyrrole coated the CNTs successfully. There are significant changes in the range of diameters of nano tubes for SWCNTs from (3-5) nm to (8-35) nm and from (8-9.9) to (21-50) nm for MWCNTs. The nanocomposites were tested for the variation in their resistance upon exposure to a range of organic vapours (chloroform, methanol, ethanol and acetone). The sensing devices comprised simple two-terminal devices over which a layer of the composite was applied by drop-coating. We investigated the effect of the CNTs:polypyrrole ratio on the sensor response, $S=(R-R_0)/R_0$ where R_0 is the resistance in an air atmosphere and R is the resistance at steady-state after exposure to an air/analyte mixture³. In general, bare CNTs show a rapid response time, but very low response (typically $S<0.1$). As the amount of polypyrrole in the composite is increased, the sensitivity increases, but the response time deteriorates. Interestingly, the response of the composites may even change sign as a function of target analyse concentration; this suggests that a simple mechanism based on swelling and its effect on the percolation behaviour of CNTs in the polypyrrole matrix is insufficient to explain the data. The response of the film also changed with the temperature: increases in temperature generally decreased the size of the response. This effect was analysed in terms of an adsorption equilibrium of the analyte on the polymer/CNT composite and the enthalpy related to the swelling of the conductive polymer especially with a high concentration of of adsorption/desorption could be extracted from the data by plotting $\ln S$ against $1/T$.

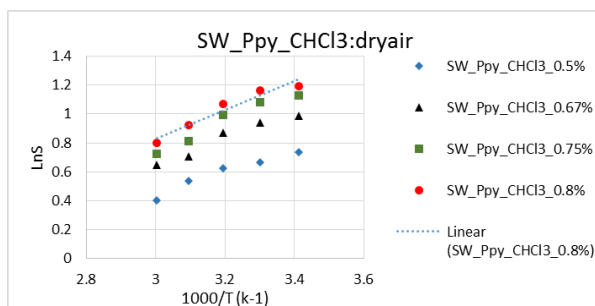


Fig (1) the relation between $\ln S$ and temperature for the different concentration of the mixture (CHCl₃: dry air)

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Keywords.

Carbon nanotubes gas sensors, gas sensors, CNTs/Polypyrrole, for volatile organic compounds

A Carbon Electronics World

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From the extended super-aromatic systems such as graphene and nanotubes to smaller polyaromatic molecules, pure carbon systems together with functionalised carbon based molecules present the possibility of ultimate electronic/functional miniaturisation.

It will require a high degree of sophistication and technical prowess to fully achieve this vision and despite the great advances we have made during the last decades, we are still very much in the foothills of this 'carbon' revolution.

The poster will explore the current practical limitations to developing carbon electronics and how some these limitations may be overcome.

It is very clear from experiment that graphene is not the clean pristine carbon film of the theorists, graphene is hampered by the absorption of dopants and contaminants onto the surface, resulting in a huge variability between sample devices. Graphene/CNT surfaces are very "sticky". However, this "stickiness" is not all bad news, in controlled conditions this property can be used to functionalise graphene and CNTs via non-covalent interactions.[1] We have shown that some simple hydrocarbons such as toluene can *n*-dope graphene, through a mechanism that is more complex than we initially expected.[2] There are synthetic limitations to building defined extended aromatic systems [3], although, there have been some remarkable bottom-up synthetic methodologies developed [4].

The generation of more complex organic molecules that are able to act as components in electronic systems is synthetically possible, however, assembling systems of components in a controlled way is the real challenge [5]. When nature does this with such elegance, one has to ask, what can we learn from nature? Finally, how will these systems be integrated into other existing technologies such as silicon [6].

This poster presents some ideas for discussion within the community of carbon scientists, exploring the potential of carbon/molecule based electronics in the future.

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Keywords. graphene, doping, synthesis, molecular electronics, carbon electronics

Polyelectrolyte-Surfactant Templated Mesoporous Silica Films Grown from Sodium Silicate Solution Precursors

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Mesoporous thin silica films are of great interest since they have potential applications in separation [1], catalysis [2] and specialist areas such as positron to positronium converters [3]. Previous research [4] has developed a water/air interface method to make free standing mesoporous silica film with surfactant-polyelectrolyte complexes. However the silica source, TMOS used in this earlier work, although convenient as a model system, is not suitable for scale up due to its toxicity and expense. It generates methanol during hydrolysis and condensation of silica which also disrupts micelle organisation, affecting our ability to control mesostructure and film thickness/strength as adding more TMOS to provide further silica to strengthen the network generates enough methanol to dissolve the micelles.

A more environmentally-friendly and lower cost silica source, sodium silicate, has therefore been applied to synthesize silica films at the solution/air interface exploiting the co-assembly of cetyltrimethylammonium bromide (CTAB) and high molecular weight polyethylenimine (LPEI). Using sodium silicate solution allows film formation to occur successfully at the interface between the air and the alkaline solution and makes the structure of the prepared hybrid film more controllable since this precursor does not produce alcohol during condensation compared to tetramethoxysilane (TMOS). After removal from the solution interface and drying, these films show relatively sharp diffraction peaks measured on in house SAXS. The mesostructure of silica/CTAB/LPEI hybrid films can be controlled by changing the composition ratio of the solutions on which the silica/CTAB/LPEI hybrid films grow. Nitrate ion addition improves the stability of the mesostructure and film thickness increases from 0.142 mm to 0.162 mm. Water wash treatments before calcination protect the mesostructure from collapsing during calcination at 600 °C, however the calcined silica films have relatively poor long-range order compared to ambient dried silica/CTAB/LPEI hybrid films. Nitrogen adsorption and desorption characterization proves that the BEI surface area of the calcined silica films is 660.43 m²/g.

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Keywords.

Free-standing; mesoporous silica films; sodium silicate

Formation of cellulose-starch gels using various cellulose sources

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Cellulose, the most abundant natural polymer¹, is biocompatible² and environmentally friendly. Diverse sources of cellulose exist, such as wood-pulp fibers or bacterial cellulose, which, after oxidation using the TEMPO-oxidation process, form nanofibrils dispersible in water and present shear-thinning properties³. Starch is also an abundant natural polymer,⁴ and is frequently a waste product from food processing. In this project, in collaboration with universities (Exeter, Bath, Norwich) and industrial partners, we aim to study interpenetrating cellulose-starch hydrogels, with possible applications in personal care or agrochemicals.

Two sources of cellulose were studied: anionic cellulose (AC) nanofibrils obtained from wood-pulp (manufactured by Croda) and oxidized bacterial cellulose (BC) from *Acetobacter xylinum* culture. At 1wt%, partially oxidized cellulose nanofibril suspensions present a weak

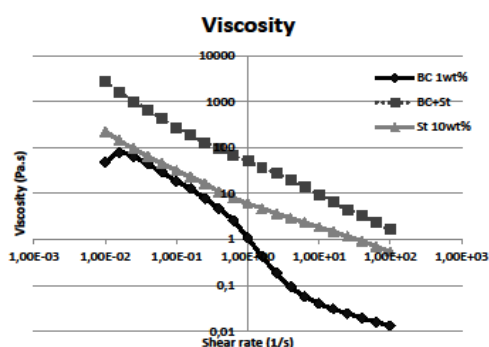


Figure 1

Viscosity upon shearing of BC 1 wt% gel (black diamonds), Starch 10 wt% (pale grey triangles) and corresponding cellulose-starch gel (grey squares).

gel behavior, with shear-thinning properties. Starch, either corn or potato starch, can also form shear-thinning gels at high weight fraction (>5wt%). We have prepared starch-cellulose mixtures, with a fixed weight fraction of cellulose (1wt% of AC or BC) and different starch weight fractions (1, 5, 10, 15 wt%). Samples have been studied via rheology measurements, small-angle X-ray scattering, light scattering and electron microscopy. For both cellulose sources, at low weight fractions of starch, the rheological properties are completely dominated by those of the cellulose fibrils. At higher starch concentration, samples behave as strong shear-thinning gels, with enhancements of viscosities, elastic and loss moduli, but with noticeable differences in viscosity values and loss factor upon

strain for the two types of cellulose, related to the structural differences of the nanofibrils.

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Keywords.

Cellulose, starch, gels, interpenetrating networks, rheology, SAXS

Alcohol-induced gelation of cellulose nanofibrils dispersions

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Cellulose nanofibrils (CNF) are nanoscale sized fibrils obtained from cellulosic materials, especially wood pulp. Due their biological nature, they are inherently green materials, renewable and biodegradable, also abundant, cellulose being the most abundant natural polymer. CNFs, due the colloidal dimensions, present a versatile material to form films, nanocomposites or dispersions.¹ TEMPO-oxidized CNFs, negatively charged flexible fibrils, can be easily dispersed in water, and caused to aggregate and gel by physical-chemical modifications of the dispersing media, salt, co-solvents, etc.² In this work, we focused on CNF gelation induced by addition of co-solvents, namely methanol, ethanol, 1-propanol and 2-propanol. These systems were investigated both at macroscopic level, via rheology, and at nanoscale level, via small-angle X-ray scattering.

Rheological data showed that all the alcohols studied are capable of inducing CNF gelation. The addition of alcohol leads to an increase of viscosity, producing shear-thinning fluids, up to a certain critical alcohol concentration at which the gel forms. This critical concentration, and the gel's shear modulus, depends on the type of alcohol, the more hydrophobic alcohols (log P) have a lower gelation onset and higher shear modulus. Preliminary analysis of the SAXS data suggests the alcohol affects the cross-section of the scattering centred at higher-q end instead of changing the structure of the larger structures observed at the lower-q range. That could suggests that the gelation is driven by fibrils aggregating aligned along their longitudinal axis resulting in thicker fibrils, but still forming long, flexible objects.

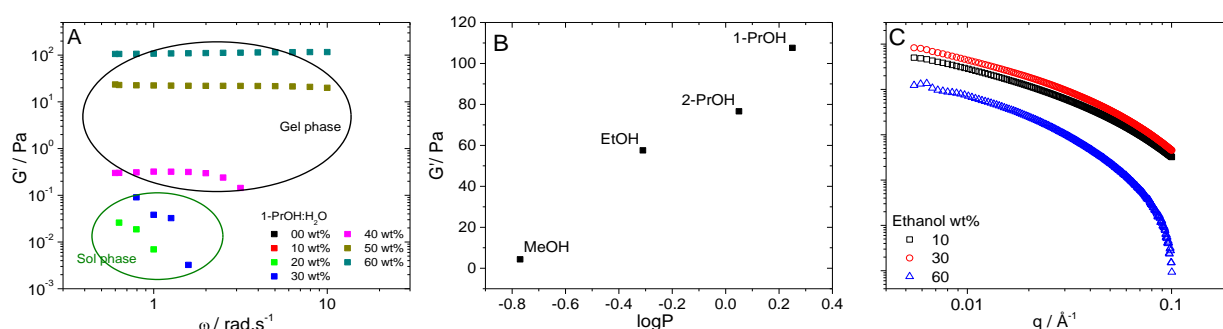


Figure (A) Small-amplitude oscillatory frequency sweeps of anionic CNFs dispersed in water/1-propanol mixtures, data from sol and gel phases are highlighted (B) Storage modulus (G') dependence as function of the lipophilicity as measured by log P for anionic CNFs gels in water/alcohol mixtures. (C) Small-angle scattering X-ray data from anionic CNFs gels in ethanol/water mixtures.

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Keywords.

cellulose nanofibrils, rheology, small-angle scattering, rheological modifiers

Investigation into the effect of mixing amino acid surfactants on their structure and physical properties

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The potential of amino acids as surfactant headgroups has been recognized and investigated since their discovery in the early 1900's.¹ There has been a resurgence in interest in surfactants prepared from amino acids and other naturally occurring compounds in recent years due to their green credentials, including renewability and biodegradability.^{1,2}

The amino acid surfactants of interest for this work are N-acyl amino acid surfactants, which have been prepared using saturated fatty acids for the surfactant tails and glycine, proline and glutamine for the headgroups. These amino acids have been used in this work as the aim is to use a mixed amino acid waste source from grain residues in the brewing industry to directly synthesize surfactants without the requirement to separately purify each component.

Initial work to determine the effect of producing surfactants from a mixed source has been carried out using pure surfactants mixed in controlled molar ratios. In this work both soluble and insoluble surfactants have been used to allow the structural variation achieved through mixing at interfaces and in bulk solutions to be better resolved. Pressure-area isotherms for insoluble surfactants show interesting variation between the pure surfactant data and that for 1:1 molar mixtures, with shifts in the positions of the mixed phase plateau observed. Further investigation into the insoluble surfactant monolayers was carried out using neutron reflectivity. This data suggests that the structure of the mixed monolayer tended to be more similar to one of the components pure structure than the other, indicating that one species dominates the surface behavior for insoluble species.

Soluble surfactants have also been investigated, CMC results for a mixture of two surfactants were used to probe ideality of mixing of the components, with a slightly lower adsorbed surface pressure being observed for the mixture. SANS data has been collected for pure and molar mixtures of these surfactants, and as with the reflectivity data, it was found that the aggregates observed mixtures tended to be more similar to one of their components than the other.

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Keywords.

Surfactant, SANS, Reflectivity, Renewable

Structural Analysis of Starch Suspensions with Heating Using Laboratory Based SAXS

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As part of the expansion of the Materials Characterisation Laboratory at ISIS, Rutherford Appleton Laboratory, a new small angle X-ray scattering instrument has been added to the lab. During the commissioning of this instrument I have been taking SAXS spectra of starches in water with temperature changes to observe the semicrystalline structure of starch and the known processes of gelatinisation and retrogradation, previously studied using synchrotron based SAXS. The aim of this has been to test the performance of the instrument and it's capabilities with kinetic experiments.

I have now begun to take this further than previous studies by looking at the structure of reheated retrograded starch and plan to expand this work to starches that haven't previously been studied using SAXS at all.

Non-aqueous Microemulsions for the Delivery of Drugs

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Background. In recent years microemulsions (MEs) have been widely studied for their potential as delivery systems for water-insoluble drugs, possessing a number of advantageous properties including thermodynamic stability, optical clarity and ease of preparation. Nonetheless, the commercial applications of these nano-sized structures have been limited by the lack of pharmaceutically acceptable systems, mainly attributed to the need to incorporate toxic co-surfactants in most water-surfactant-oil systems to promote ME formation. To address this issue the current project explores the potential of non-aqueous systems employing lecithin as surfactant as drug delivery systems as such systems have been previously shown to form stable MEs in the absence of co-surfactants.¹

Methods. A range of polar solvents (PSs) - short chain diols, polyols and carbonates, and a selection of non-polar solvents (NPSs) - single chain fatty ester and triglycerides, were selected to study the effect of solvent structure and properties on ME formation in lecithin-based systems. The phase state of the different PS-lecithin-NPS mixtures at varying mixing ratios, *i.e.* ME, macroemulsion or liquid crystalline phase, was determined *via* turbidity and birefringence assessments and mapped on ternary phase diagrams. The results of these phase behaviour studies together with a set of computed chemical and structural properties of the solvents were used to create an artificial neural network (ANN) model employed in predicting the phase behaviour of unknown non-aqueous lecithin-based systems.

Results. The changes in phase behaviour observed in the presence of different PSs and NPSs suggested a relationship between the amphiphilicity and molecular volume of the solvents and their ability to penetrate into the surfactant layer to modify its flexibility and curvature and promote the formation of extended ME areas of existence in the phase diagrams. The ANN model was used to predict the phase behaviour of three unknown non-aqueous lecithin systems and achieved an overall precision of 97.9%, recall of 75.8% and F-measure of 85.4%

Conclusions. The study explored the effect of various PSs and NPSs on the formation of pharmaceutically acceptable lecithin-based MEs to identify the structural and physico-chemical properties of the solvents which govern the size and position of the areas of existence of the different phase states. An ANN model was successfully developed and employed in predicting the phase behaviour of unknown non-aqueous lecithin systems.

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Keywords. Microemulsion, non-aqueous, lecithin, amphiphilicity, artificial neural network.

Self-assembly of fluorinated polyoxazolines: SAXS and SANS comparative studies

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Poly(2-alkyl/aryl-2-oxazoline)s (PAOx) are widely studied as materials for biomedical applications such as drug, protein, radionuclide or gene delivery due to their biocompatibility and nontoxicity. Varying the ratio and the order of hydrophilic and hydrophobic blocks constitutive of amphiphilic PAOx leads to a plethora of self-assembled structures such as spheres, vesicles, rod- or worm-like micelles, cylinders and corresponding aggregates in solution. Especially interesting are the so-called polyphiles - triblock terpolymers that combine hydrophilic, hydrophobic and fluorophilic blocks. Recently we reported on the synthesis and solution properties of a novel quasi-triblock fluorine-containing terpolymers based on 2-oxazolines¹. Preliminary investigations of the self-assembly of the so-synthesized polymers in water using dynamic light scattering and cryo-TEM revealed the coexistence of bilayer and multi-layer vesicles as well as worm-like micelles. The aim of present work is the detailed study of the internal structure of nanoparticles formed by the self-assembly of quasi-triblock fluorine-containing terpolymers, namely PMeOx-POctOx-C₈F₁₇, PMeOx-POctOx-C₁₀F₂₁, PMeOx-POctOx-C₁₂F₂₅ (where PMeOx-POctOx - poly(2-methyl-2-oxazoline)-block-poly(2-octyl-2-oxazoline), as well as non-fluorinated PMeOx-b-POctOx diblock copolymers. Detailed information about the shape and the internal structure of self-assembled nanoparticles depending on their composition and fluorine content was obtained using SAXS and SANS and compared with previously obtained cryo-TEM data. Nanoparticles formed by diblock PMeOx-b-POctOx were described with a bilayered vesicle form factor in combination with a Percus-Yevick structure factor. SANS and SAXS experiments revealed the morphological transition of micelles from bilayered vesicles to worm-like micelles with increasing length of perfluorinated fragment of triblock PAOx. It was further found that the preparation method influences nanoparticles shape and internal structure: with solvent displacement it becomes independent of the fluorine content and PAOx SAXS curves may be fitted with a core-shell-shell form factor. Additional ordering was identified within the inner layer of bilayered vesicles, core of worm-like micelles as well as inside of the core of spheres, probably due to the crystallization of octyl and perfluorinated chains, and was described with a Voigt peak model.

Acknowledgements. This work was supported by the Czech Science Foundation GACR (grant 17-00973S).

References.

L.I. Kabarov et al. / European Polymer Journal 88 (2017) 645–655

Keywords. Polyoxazolones, self-assembly, small-angle neutron scattering, small-angle X-ray scattering, polymersomes, worm-like micelles.

Measuring the Surface diffusion of Cyclic Hydrocarbons on Nickel with Quasielastic Neutron Scattering

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Surface diffusion is of interest in heterogeneous catalysis as it has relevance to the Langmuir-Hinshelwood reaction mechanism and the concept of spillover. Despite this importance, the difficulty in experimental measurement, particularly under realistic conditions, means that the literature is sparse. Investigating atomically thin layers in the presence of interference from bulk solid and fluid phases is immensely challenging. Diffusion measurements with catalytically relevant materials are therefore mostly confined to either guest molecules in zeolites or to model systems that are on the wrong side of the pressure and materials gap. Neutron scattering has been used to measure adsorption processes since 1964, due to the contrast in interaction between different elements and isotopes. Quasielastic neutron scattering (QENS) investigates energy transfers on the scale of translation processes and can therefore provide a quantitative measure of diffusion of organic molecules on inorganic sorbates.

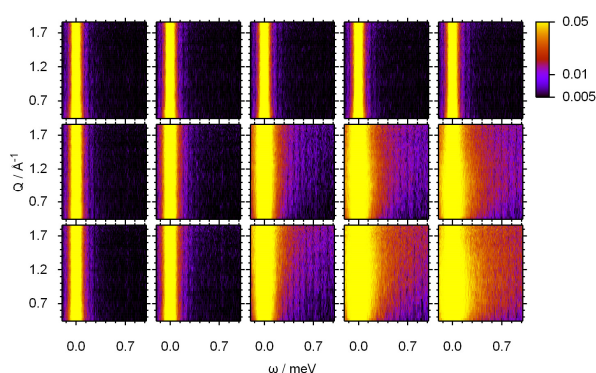


Figure 1: QENS spectra for Ni (top), Ni-benzene and Ni-cyclohexane (bottom) at base temperature, 77, 152, 227 and 302 K, increasing from left.

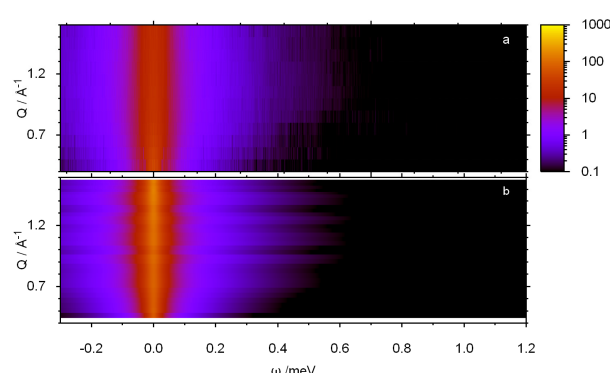


Figure 2: Simulated (a) and experimentally fitted (b) inelastic component for Ni-benzene system. Intensity is scaled.

QENS spectra were obtained between 77 and 302 K for benzene and cyclohexane adsorbed on a high surface area Raney nickel catalyst, as shown in Fig. 1. The diffusion was fitted to a Chudley-Elliott jump diffusion model, which provided the calculation of activation energies of 3.8 and 4.2 kJ/mol for benzene and cyclohexane respectively. Initial molecular dynamics simulations to further elucidate the diffusion process showed qualitative agreement (Figure2).

Keywords.

Catalysis, Quasielastic neutron scattering, Diffusion

INS spectroscopy and DFT simulations for 2-adamantanone

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The interest in 2-adamantanone (C₁₀H₁₄O) stems from its role as a model to study glassy phenomena which arise from the action of well-defined degrees of freedom concerning the occupational disorder^{1,2,3}. The most striking characteristic of the low-temperature monoclinic phase (P2₁/c) is the existence of statistical disorder concerning the occupancy of the oxygen atom along 3 different sites (occupancies are 50%, 25% and 25%). The existence of the fully ordered (orthorhombic, Cmc2₁) phase makes available to us a ground state to be taken as a reference for any fundamental physical property.

We performed an Inelastic Neutron Scattering (INS) experiment using the indirect geometry spectrometer TOSCA to get the spectral frequency distribution over a wide range of energies for 2-adamantanone of the fully ordered orthorhombic phase and the occupational disordered monoclinic phase. The experimental results demonstrate the relevance of the presence of the intrinsic disorder to the vibrational density of states likewise affecting to other physical properties as the specific heat and thermal conductivity. The main differences between the spectra of the orthorhombic and the monoclinic phases are found to be below 500 cm⁻¹, and even more, it shows an excess of vibrational modes at very low frequencies^{4,5}, typically called Boson Peak in glasses, in the disordered monoclinic phase respect to the fully ordered one. Finally, *ab-initio* DFT calculations⁶ were performed to shed some light on the understanding of vibrational spectra.

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Keywords.

2-adamantanone, disordered systems, glassy phenomena, vibrational density of states

Atomic structure of novel chlorine containing calcium silicate glasses for dental applications

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Abstract

This study reports the first detailed structural investigation of novel bioactive chloride containing glasses. Bioactive glasses are of great importance for medical and dental applications. In order to understand, model and predict the behaviour of these materials, and ultimately improve their design, it is important to understand the structure of these glasses. Dissolution of ions from these glasses under physiological conditions is known to be the crucial first step in bioactivity. This dissolution is strongly dependent upon the atomic scale structure, network connectivity and cross linking. Whilst significant progress has been made understanding the structure of traditional oxide based glasses relatively little is known about the structure of bioactive glasses containing halides. Fluoride ions have been widely incorporated into bioactive glasses for dental applications however the use of fluoride ions is heavily regulated. Recently a series of novel chloride based bioactive glasses has been developed for dental applications. Chlorapatite is known to convert to hydroxyapatite, the mineral phase of teeth, on immersion in water but structural information about these glasses are limited. Therefore to fully understand these materials and to be able to further rationalise their design and optimisation, a compositional - structure - property relationships using neutron diffraction, solid state NMR, have been undertaken in this study to elucidate the structure of these novel materials at the atomic scale.

The Effect of Testosterone Propionate on Physico-chemical Properties of Triolein Nanoemulsions

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Background Nanoemulsions (NE) containing an oil dispersed in a water phase and stabilized by a surfactant have been increasingly explored as vehicles for the delivery of poorly-water soluble drugs. The interest in these systems stems from the ability of NE to increase the apparent aqueous solubility of such drugs. The aim of the study was to investigate the molecular architecture and physico-chemical properties of NE to establish their suitability for the delivery of the poorly-water soluble drugs. Here the hydrophobic steroid, testosterone propionate (TP), was used as drug.

Methods Oil-in-water (o/w) NE stabilised by the non-ionic surfactant, C_{18:1}E₁₀, and containing triolein (GTO) were prepared by the phase inversion temperature (PIT) method. An excess of TP was added to NE containing 20 wt% C_{18:1}E₁₀ which were then equilibrated at room temperature for up to 1 week, after which excess drug was removed by centrifugation. TP solubilisation was determined by UV spectroscopy while the size and shape of GTO NE was assessed using small angle neutron scattering (SANS). SANS experiments were performed on 10 x diluted NE to minimize interparticle interactions and as a consequence, concentrations of GTO in the final NE ranged from 0.05% to 1.5% w/v, while the surfactant concentration was fixed at 2.0% w/v.

Results The existence of NE, which were stable for 1 month, was established between 5-30 % w/w C_{18:1}E₁₀, with a maximum oil incorporation of 15 % w/w GTO at 20 % w/w C_{18:1}E₁₀. While a significant increase in TP solubilisation was seen with C_{18:1}E₁₀ content in the region of clear and slightly hazy NEs, there was a dramatic decrease in TP solubilisation in the cloudy or milky NEs region. After fitting the SANS data obtained for the 'drop contrast' of GTO NE, it was clear that the model which consistently provided the best fit to the SANS data was that of an oblate ellipsoid with the radius of core of the NE increasing with GTO content. Surprisingly, the SANS results indicated that shape of the particle become more elongated as the oil content increased. This change in NE morphology with GTO content can explain the decrease in TP solubilisation seen in the cloudy or milky NEs.

Conclusions The SANS studies suggest that GTO forms a distinct core of oil in the NE. The neutron scattering studies suggest that the GTO-containing NE are suitable as drug delivery vehicles for poorly-water soluble drugs which exhibit a good level of solubility in GTO. In addition, the changes in morphology seen in the SANS studies explain the decrease in solubility of TP in cloudy or milky GTO NE.

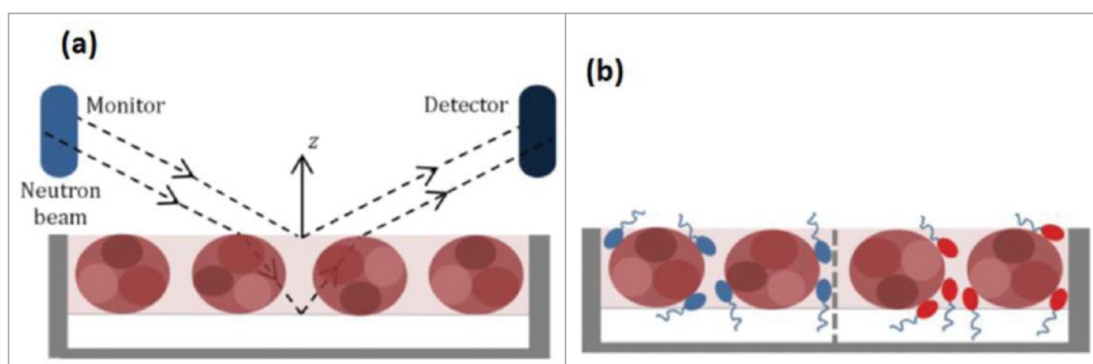
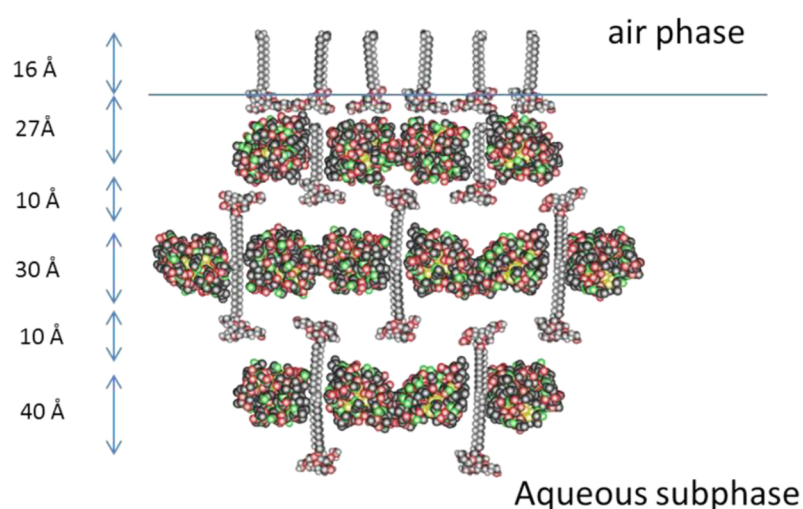
Keywords.

nanoemulsion, triolein, testosterone propionate, SANS

Deuteration for Neutron Scattering

Peixun Li

The ISIS Deuteration Facility aims to provide isotopically labelled chemicals for ISIS users for their ISIS experiments. The poster will introduce the access scheme for the routine deuterated materials, as well as details on how to request non-routine materials on a collaborative basis. A recent science highlight is also presented on soft matter research utilising deuterated materials supplied by the facility.



Inelastic neutron scattering studies of bone

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Bone is a composite material that consists of a mineral, hydroxyapatite, $(\text{Ca}_5(\text{PO}_4)_3\text{OH})$, in a mainly collagen matrix. The hydroxyl ions reside in channels that run along the *c*-axis and this ready access to the external environment means that substitution of hydroxyl or phosphate by carbonate commonly occurs under physiological conditions. On the basis of infrared spectroscopic studies, it has been suggested that complete substitution of the hydroxyl ions occurs in mature bone. Vibrational spectroscopy with neutrons (inelastic neutron scattering, INS) is particularly sensitive to hydrogen motion and INS studies of defatted and deproteinated bone, unambiguously show the presence of hydroxyl ions, even though the infrared spectra of the same sample shows no evidence for hydroxyls. Comparison with a stoichiometric hydroxyapatite reference material, indicates that ~40% of the hydroxyls remain in the bone [1].

In a novel application, INS has been applied to the study of burned human skeletal remains. The examination of unburned skeletal remains is routinely carried out by either bioarchaeologists or forensic scientists to provide identification of the deceased, as well as the circumstances of death. Unfortunately, the analysis of bones affected by high temperatures encounters serious problems, as heat induces significant changes in the skeleton which interfere with the reliability of the available methods. INS spectra recorded as a function of the temperature at which the bone was burned, show progressive loss of the organic component and increasing crystallinity of the hydroxyl librational mode at $\sim 650\text{ cm}^{-1}$. The spectra also showed a burning temperature dependent shift of the hydroxyapatite O–H libration and stretch modes. This effect was found to be different for the two types of bone studied (femur and humerus), being larger for femur [2].

The spectroscopic results lead to a complete assignment and a thorough interpretation of the vibrational profile of human bone, for distinct conditions – unburned (intact), unburned subject to defatting and deproteination, and burned (for distinct temperatures and times) – as well as for different types of bone (humerus and femur).

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Properties and Structure of Non-Ionic Surfactant Micelles containing Non-Steroidal Anti-Inflammatory Drugs

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The viscosity and micelle size and structure of two structurally related non-ionic surfactants, namely Triton X-100 and its closely polymeric counterpart, Tyloxapol, have been measured in the absence and presence of two poorly-water soluble, non-steroidal anti-inflammatory drugs (NSAIDs), i.e. ibuprofen and indomethacin. In addition, the level of solubilization of the two poorly-water soluble NSAIDs in the surfactant micelles has been determined. Significantly, both surfactants possessed a higher ability to solubilize ibuprofen, which has a very similar structure to the surfactant hydrophobes, while indomethacin which has a very different structure was solubilized by both surfactants to a much lower extent. Viscosity measurements in the presence of a saturation amount of drug showed that the presence of both drugs increased the viscosity of the surfactant solutions, with ibuprofen increasing the viscosity of the Triton X-100 solution to the greatest extent. Small-angle neutron scattering of the surfactants in the absence of drug indicated that the structure of the micelles are core-shelled ellipsoids. However, the presence of a saturation amount of drug altered the structure of the micelles by increasing their length with the presence of ibuprofen increasing the length of the Triton X-100 micelles to produce worm-like micelles: a result that corresponded with the large increase in viscosity of the micelles in the presence of the drug. The results suggest that matching the structure of the drug with the hydrophobe of the surfactant is likely to lead to a considerable increase in solubilisation of that drug.

Keywords.

Solubilization, Micelle, Viscosity, Neutron Scattering, Structure Similarity

Interaction of steroidal drug-like molecules with sodium dodecyl sulphate monolayers: the effect of time

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Background Micelles formed by the surfactant, sodium dodecyl sulphate (SDS), have been determined to be an excellent solubiliser of steroidal, drug-like molecules, such as 4-cholesten-3-one ($C_{27}H_{44}O$, 4-CHOL) and adrenosterone ($C_{19}H_{24}O_3$, ADRENO). As the distribution of a 'drug' in the monolayer is related to its distribution in the corresponding micelles, it is considered that determination of this profile will provide valuable information about the micellar solubilisation of drug. Ultimately this information should aid in the design of new surfactant that form micelles with increased drug solubilisation. Surprisingly solubilisation and surface tension measurements showed that 4-CHOL required a long time for equilibrium to be obtained in SDS micelles and monolayers, respectively.

Methods Specular neutron reflectivity (SNR) measurements in combination with contrast variation were performed on SDS monolayers at a concentration of twice the critical micelle concentration both in the presence or absence of a saturation amount of either 4-CHOL and ADRENO. SNR measurements were repeatedly performed until equilibrium (i.e. not change in scattering) was reached. Each sample was measured over time until no significant change in the SNR curve was seen. After equilibrium had been obtained, an aliquot of a solution of either 4-CHOL or ADRENO in hexane was carefully spread on the surface of the SDS monolayer and left for at least 20 minutes to ensure that all hexane had evaporated, after which time the SNR profile of the SDS monolayer was re-measured.

Results The SNR curves of SDS in the presence of 4-CHOL were seen to change over a period of 12 h while no such change were seen in the SDS monolayer in the absence of drug-like molecule or in the presence of ADRENO over the same time period. Analysis of the SNR curve in the presence of 4-CHOL, indicated that the SDS monolayer became thicker over time, corresponding with an increase in the surface excess of 4-CHOL, suggesting the slow penetration of more 4-CHOL into the SDS monolayer. In addition, SDS in the monolayer was seen to be replaced by 4-CHOL. The stoichiometry of the SDS:4-CHOL was 2:1. After extra 4-CHOL was added to the surface of SDS in hexane, the SDS monolayer became even thicker, exhibiting a stoichiometry of $\sim 1:1$.

Conclusions The SNR results support the extremely equilibrium of 4-CHOL in the SDS monolayer, possibly as a consequence of its very low aqueous solubility.

Keywords.

Sodium dodecyl sulphate, steroid, Time effect, Specular neutron reflectivity

^1H -Detected NMR Measurements of $^{13}\text{C}^\alpha$ Relaxation in Fully Protonated Proteins in the Solid State

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Detailed characterisation of protein dynamics is vital for our understanding of protein functions and stability; this knowledge is critical throughout the biological sciences.¹ Solid-state NMR experiments, more specifically relaxation measurements, are an extremely powerful tool for the investigation of structural protein dynamics since they allow the simultaneous, quantitative characterisation of both the timescales and the amplitudes of protein dynamics in a site-specific manner.^{2,3}

Here, the $^{13}\text{C}^\alpha$ spin-lattice relaxation rates (R_1) in fully protonated, uniformly labelled crystalline proteins are accurately measured using state-of-the-art equipment which allows magic angle spinning (MAS) of up to 100 kHz. The main challenge for these relaxation measurements on the $^{13}\text{C}^\alpha$ nuclei is eliminating the rate-averaging effects of proton driven spin diffusion (PDSD). Previously these measurements have only been possible by deuterating or partially ^{13}C labelling the protein sample; both techniques limit the polarisation transfer pathways by which PDSD can occur.^{4,5} However, removal of most of the protons results in a significant loss in sensitivity, and partial ^{13}C labelling limits which $^{13}\text{C}^\alpha$ nuclei are observable. Additionally, not all proteins can be easily produced in these labelled forms in large quantities which may result in such samples being prohibitively expensive to make.

A series of $^{13}\text{C}^\alpha$ R_1 measurements at various spinning speeds clearly show that MAS \leq 90 kHz successfully eliminates the rate-averaging effects of PDSD in fully protonated, uniformly labelled proteins. Further benefits of the fast spinning are an improvement in resolution and that only a small amount of sample (<0.5 mg) is required to fill the 0.7mm diameter rotors used at such speeds.

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SHARPER-J: A new method for the measurement of scalar and residual dipolar coupling constants of small molecules

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A novel pure shift NMR method is proposed that allows accurate measurement of scalar and residual dipolar couplings of small molecules, providing important structural information. It is based on an NMR experiment that we have recently developed for reaction monitoring by NMR, under the acronym SHARPER (Sensitive, Homogeneous And Resolved PEaks in Real time).¹ SHARPER-J reintroduces modulation of the signal due to one selected coupling constant. It benefits from all attributes of the SHARPER pulse sequence: i.e. removal of homonuclear and heteronuclear couplings without the use of a second channel, magnetic field inhomogeneity compensation and signal linewidths determined by the spin-spin relaxation, T₂. SHARPER-J involves excitation of a single spin by an initial selective pulse field gradient spin-echo and subsequent acquisition periodically interrupted by double-selective 180° pulses surrounded by low level pulsed field gradients (PFGs). Here we explore the effects of lengthening the time period between the inversion pulses and consequent up-scaling of coupling constants on the sensitivity of the experiment and accuracy of coupling constant determination.

Keywords.

¹SHARPER - a magnetic field inhomogeneity compensating, single channel pure-shift NMR method. Application to reaction monitoring. Ariana B. Jones, Guy C. Lloyd-Jones and Dušan Uhrín, submitted for publication.

Fragmentation Processes of Model Peptide Bonds

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Mass spectrometry techniques are widely used to study biomolecular structure and function; nevertheless, the molecular fragmentation processes that lead to the observed ions have not been well understood up to now. Using ultrafast imaging sensors, velocity-map imaging (VMI) – an experimental technique that combines time-of-flight (ToF) mass spectrometry with a measurement of the velocity distribution of each observed fragment ion - may provide a wealth of information on the detailed dynamics of the molecular fragmentation process for such molecules.

We are currently performing VMI studies on a number of model peptide-bond containing molecules (formamide, methylformamide, and dimethylformamide) in a ‘bottom-up’ approach to understanding the complex molecular fragmentation processes exhibited by larger peptides. By using a universal ionization scheme to enable every fragment to be ionized and therefore detected, and the PImMS (Pixel Imaging Mass Spectrometry) sensor, we record images for multiple fragments on every ToF cycle.

Once we identify the fragments formed, we evaluate their relative abundances, the partitioning of energy amongst the various translational and internal degrees of freedom of the products, and the product angular distributions, yielding important information about the evolution of the species under this study from parent molecule to fragment ions.

Keywords.

PImMS, Dipeptide, Mass Spectrometry, VMI, Photodissociation

Light-Harvesting Antennae using the Host-Guest Chemistry of Mesoporous Organosilica

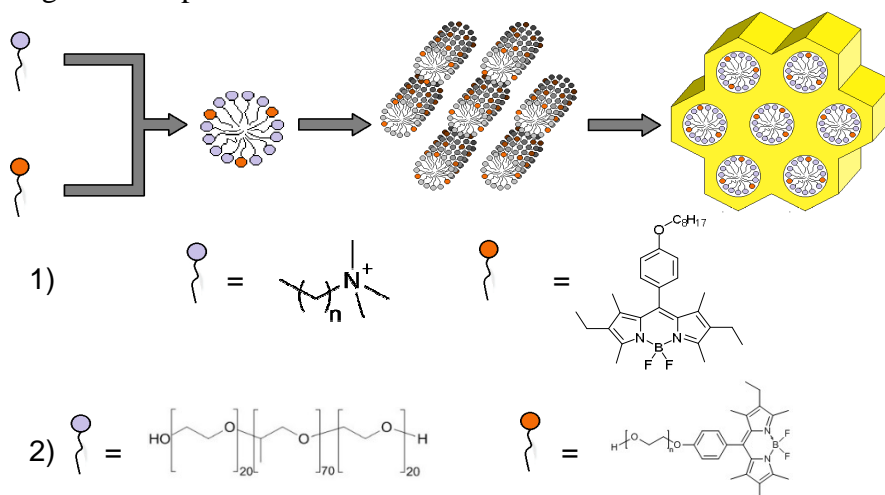
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Supramolecular host-guest systems offer exciting avenues towards fundamental understanding of photochemical processes and their promising applications. Here we present a system where the high chemical, thermal and mechanical stability of mesoporous silica has been combined with the excellent photophysical properties of BODIPY dyes. The use of amphiphilic dyes as templates for the silica eliminates the need for removal of the micelles while retaining the mesoporous structure of the framework.



Synthesis of dye-loaded mesoporous silica using two differing procedures.

Two well-known approaches were used as outlined in Figure 1 (MCM-41 and COK-12)[1],[2]. Approach 1) resulted in silica that, while regularly porous at low dye-loading, lose crystallinity at higher content of the dye, which perturbs the mesophase structure. A high-energy species was also observed which has been attributed to H-aggregation, probably due to the dyes insolubility in water. This interplay between monomer and aggregate species within the silica could give rise to tunable emission[3]. Approach 2) was devised using a water-soluble PEG-based BODIPY which takes place under mild conditions. This procedure resulted in the mesophase being retained up to much higher dye-loading and exhibited no aggregation behaviour. These approaches will be expanded by coupling it with metal complexes accommodated within the silica walls themselves to afford novel photosensitisers for light conversion and catalysis.

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Intercomponent Exciton Delocalization in a Bispentacene Derivative

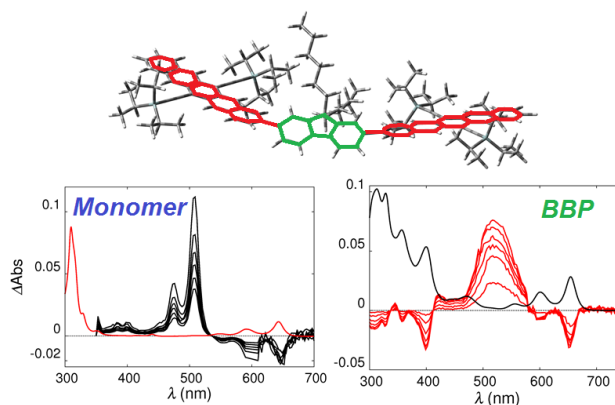
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Singlet exciton fission¹ has gained considerable interest over the past five years as a means by which the number of charge carriers per absorbed photon could be doubled in an organic solar cell. Singlet fission (SF) generates two triplets from the singlet excited state where a pair of coupled organic chromophores satisfying the energy requirement $E S_1 \geq 2 \times T_1$ interact. SF sensitizers have become a more practical proposition for solar cells as additional singlet fission chromophores have emerged. First discovered in crystals of acenes, SF has also been observed in concentrated solution for TIPS-pentacene². Recently intramolecular SF (iSF) in covalently linked SF bichromophores has been reported³.

Pentacene in particular is a well-studied SF chromophore both in crystals and in solution. Triplet quantum yields of up to 200 % have been seen in solution for pentacene derivatives³. Recent reports suggest SF sensitizers can be incorporated into existing organic solar cell designs⁴, but more work is required to fully understand the mechanism.

The study here presents a new bridged bispentacene chromophore (BBP) where two TIPS-pentacene units have been linked by a fluorene bridge, a spatial separation of ~ 10 Å. A study of the photophysics of this system in solution has attempted to shed more light on how the rate of intersystem crossing is enhanced. Nano- and picosecond transient absorption spectroscopy suggests there is strong communication between pentacene moieties in the bichromophore, showing an unusually long-lived delocalized triplet state.

It has been shown that charge transfer may play a critical role in the SF mechanism⁵. Preliminary data for BBP suggest prevailing conformations between the two TIPS-pentacene units may affect charge transfer. Molecular modelling shows a far from rigid structure for BBP. Molecular orbital calculations suggest super-exchange also plays a role in the communication between the pentacene units. Additional bands in the absorption spectrum of BBP compared to TIPS-pentacene might be attributed to charge transfer. The energy gap law predicts a short-lived triplet.



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Polymer Photocatalysts for Water Splitting

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As the most abundant renewable energy sources available on the Earth, solar energy has the potential to meet the increasing global energy demands. Therefore solar energy conversion and storage, via water splitting has been attracting substantial interest over the last ten years, which can provide renewable H₂ fuel with a strong potential to replace fossil fuel. This zero carbon process can not only provide a renewable fuel but also dramatically reduce CO₂ emission.

The key in the technology is an efficient photocatalyst which can convert a photon to a pair of charge carriers and then utilise them to drive the expected chemical reactions. The current low efficiency in water splitting to H₂ fuel process is contributed to both fast charge recombination and large bandgap of an inorganic semiconductor.¹

Stimulated by our recent research outcomes on the charge dynamics in inorganic semiconductor photocatalysts,¹ we developed novel materials strategies for solar driven hydrogen synthesis. One is to mitigate the charge recombination by improving the degree of polymerization of a polymer e.g. C₃N₄. With respect to it, one successful example of pure water splitting in a suspensions solution under visible light has been demonstrated for the first time (Figure 1).^{2,3} The other strategy is to narrow the bandgap of C₃N₄ (g-CN) by bandgap engineering. The material prepared via an oxygen rich organic precursor has a brown color, indicating a longer range absorption in the visible region, resulting into a quantum yield (QY) of 10% at 420 nm.⁴

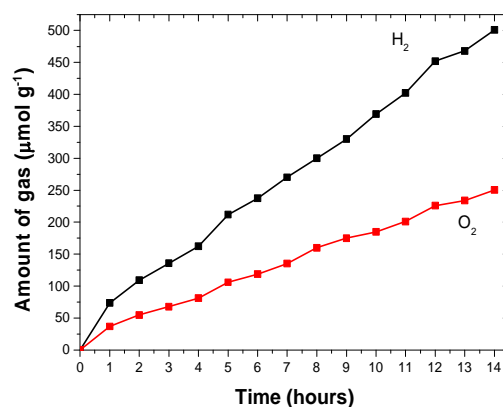


Figure 1 Stoichiometric water splitting by g-C₃N₄ (3 wt% Pt) - NaI - WO₃ (0.5 wt% Pt) at pH 8.3.

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Keywords.

Water splitting, photocatalysis, polymer, charge dynamics

The Photophysics of BOPHY Chromophores

There is, it seems, an insatiable desire for new highly fluorescent chromophores. A new class of compounds have recently been developed and are known by the general acronym BOPHY. These chromophores are similar to the well-known and studied BODIPY chromophores and at first glance have similar photophysical properties.

However, BOPHY molecules show some promise in that they present synthetic opportunities to build up very long, almost linear molecules. BOPHY shows strong internal electronic communication so the potential for creating energy harvesting arrays is clear.

Additionally BOPHY molecules show some interesting photophysical quirks such as geometry dependent transitions which we have studied.

Ultrafast electron diffraction of small cyclic disulfides

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The Wann group has recently commissioned the UK's first time-resolved electron diffraction (TRED) apparatus at York, allowing for the photo-induced motion of small molecules to be imaged with sub-picosecond temporal resolution. This apparatus uses a compact electron gun to produce sub-picosecond electron bunches using the third harmonic of a Ti:Sapphire femtosecond laser.^{1,2}

Ahead of any ultrafast electron diffraction (UED) experiments, the photo-induced dynamics of the sample are extensively explored using non-adiabatic molecular dynamics. The results of these simulations are then used to identify the temporal resolution requirement of the experiment, and to develop reliable data analysis routines, to allow structural information to be extracted from time-dependent diffraction data.

Non-adiabatic molecular dynamics simulations of 1,2-dithiane, post-illumination with mid-UV light, have revealed a novel "Newton's Cradle" ring-opening motion.³ Due to the sub-100 femtosecond timescale of its motion, 1,2-dithiane could not be experimentally studied using York's TRED apparatus. Instead, the photo-induced dynamics of 1,2-dithiane were studied using the MeV UED apparatus at the SLAC National Accelerator Laboratory, where the use of relativistic electrons produced using a MeV RF electron gun allows the sub-100 femtosecond dynamics of small molecules to be temporally resolved.

In this poster, experimental results will be presented alongside simulated diffraction data, demonstrating the Wann group's capability to simulate, record and interpret UED data. In our UED data analysis package tried-and-tested analytical routines used to retrieve structural information from gas electron diffraction data are combined with dynamical information generated using contemporary computation methods, to deconvolute and extract experimental data, reconstructing molecular motions from time-dependent diffraction data.

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- ³ C. D. Rankine, J. P. F. Nunes, M. S. Robinson, P. D. Lane, D. A. Wann, *Phys. Chem. Chem. Phys.*, 2016, **18**, 27170-27174.

Keywords

Ultrafast electron diffraction, Non-adiabatic molecular dynamics, Photo-induced, Disulfide.

Velocity Dependency in Photochemistry

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The Fine-structure Constant of space, alpha (where $\alpha \approx 1/137$), was first derived by Arnold Sommerfeld (1916) as the ratio of the orbital speed of the ground state electron in a hydrogen atom to the speed of light in vacuum, assuming the Bohr model of the atom. Alpha is shown to conform to the CODATA value by our formula updating the de Broglie-Bohr concept and incorporating a relativistic transformation, causing the ground state 1s electron shell to take the shape of an oblate spheroid^{Ref.1}. The implied velocity of the atom is found to correspond to the peculiar velocity of the Solar System (Vp). The measured value of Vp, 361+/-54 kms⁻¹ in a direction towards the constellation of Leo, was determined by George Smoot et al. (1980)^{Ref.2} and was detected as temporal and spatial variations of alpha by Webb and others.

The proton nucleus of a hydrogen atom is shown by standard data to travel at Vp across the difference of the shells' radii during the period of the 10.2 eV Lyman-alpha radiant wave emitted on collapse of the excited 2s electron to the ground state.

A model of the active vacuum^{Ref3} is portrayed, predicting velocity dependence of ionisation potentials and periodicity of nuclear decay rates. The stability of nuclei for Earth's heaviest primordial elements is shown to depend upon their de Broglie wavelengths and thus upon speed. Details and implications are displayed for the model as an elastically bound polycrystalline chemical lattice of electrons and positrons.

An experiment is proposed for the ISS or other satellite in near Earth orbit (e.g. E.S.A. CubeSat) to investigate change of ionisation potentials with velocity towards Leo.

The illustrated results of our ongoing experiment during these last four years, monitoring radioactive decay rates, indicate annual periodicity and correlations to gravitational potential. Collaboration and more advanced analysis of the raw experimental decay data are invited.

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Photochemistry of CO-releasing molecules

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The use of CO as a potential therapeutic agent (due to its anti-inflammatory, vasodilation, and anti-apoptotic effects) has increased the interest in the synthesis of CO-RMs (CO-releasing molecules).^{1,2} Among the essential characteristics, the controlled release of CO at a specified wavelength is required together with low toxicity and tissue specificity.²

Gas-phase photodepletion and action spectroscopy can allow us to monitor the CO release after the irradiation.

In this study, we analyzed two possible CO-RMs via action spectroscopy to explore the potential of the technique (in both positive and negative mode) with these molecules.

A modified Bruker AmaZon ESI mass spectrometer that allows a tunable laser in the ion trap was used for this purpose.³

Preliminary results are shown and are compared with solution phase spectra.

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Magnetic Frustration in Double Perovskites

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Frustration is a phenomenon which affects magnetic systems, such as double perovskites, which contain metallic cations interacting via equilateral triangles or tetrahedra. [1] In geometrically frustrated compounds the structure can prevent the antiparallel arrangement of magnetic spins and instead drives the formation of exotic spin states. [1] In particular we are focused on how geometrical frustration affects the antiferromagnetic double perovskite series $\text{Ba}_{2-x}\text{Sr}_x\text{LuMoO}_6$, $0 \leq x \leq 2.0$. $\text{Ba}_2\text{LuMoO}_6$ was found to exhibit strong antiferromagnetic coupling; however, it does not remain paramagnetic on cooling from ambient temperature down to 2K, [2] but instead resembles the valence bond glass Ba_2YMoO_6 . [3] These compounds show strong antiferromagnetic coupling at ambient conditions, but the structure prevents the long range ordering of the magnetic moments at low temperature. [2], [3]

Here, we explore how the $\text{Ba}_{2-x}\text{Sr}_x\text{LuMoO}_6$ series behaves as the fractional occupancy of Sr^{2+} increases and will explain how this alters both the structure and magnetic behaviour and the role of geometrical frustration in these compounds.

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Keywords

Geometric Magnetic Frustration, Double Perovskites, Valence Bond Glass

Controlling Hydrogen Evolution Activity by Phase Transition in MoTe₂

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Transition metal chalcogenides (TMCs) have attracted significant interest as hydrogen evolution catalysts in recent years.¹ Currently, much attention has been given to MoS₂ as a potential replacement for platinum, the current HER catalyst of choice. In the bulk form, MoS₂ exists only as the semiconducting (hexagonal) 2H-MoS₂ phase, with chemical exfoliation *via* lithium intercalation required in order to access the metallic (monoclinic) form.² However, this lithium intercalation may compromise the composition of the material, and hence it is unknown if the superior electrocatalytic performance of the metallic phase is attributed to its conductive properties or change in composition / structure. In this work, we propose a reliable method of assessing this theory by employing MoTe₂ which can be accessed in both hexagonal (semiconducting) and monoclinic (metallic) forms. Both phases can be produced by a solid state approach with a phase transition being achieved by a simple change in reaction temperature,³ allowing for the controlled synthesis of both phases. Moreover, in the course of this work we found that MoTe₂ demonstrates good electrochemical performance in acidic condition and can act as a hydrogen evolution catalyst with the monoclinic (metallic) phase showing better performance than the hexagonal counterpart.

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Development of Offline and Online Methods for Neutron Experiments

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The ISIS Neutron and Muon source is a user facility providing both online neutron scattering techniques and a variety of offline techniques, such as XRD and DSC for research into a diverse range of materials. The development of online methods includes commissioning experiments for a new volumetric rig on TOSCA, an inelastic neutron scattering beamline. The offline development involves method development of pressure DSC to exploit the instrument's full capability and improve accuracy and precision of measurements. Following this, my research project presents XRD and PDSC data for the temperature induced phase transitions of Phenanthrene under pressures of up to 69 bar.

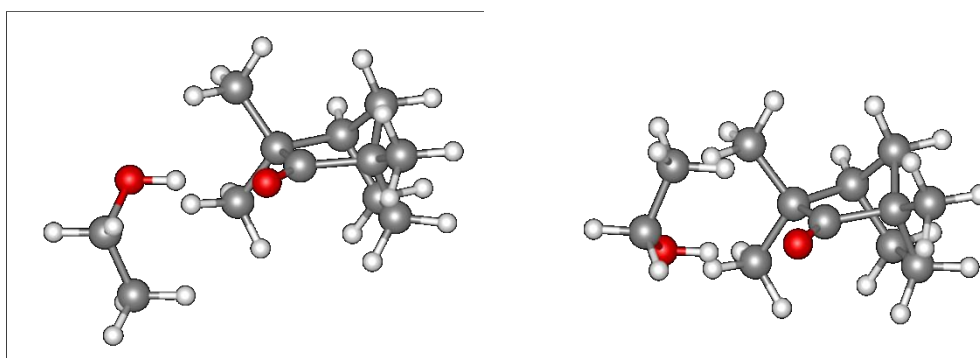
Interactions between odorants and mimics of amino acid side chains: the fenchone-ethanol complex

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Although significant advances in understanding the human olfactory system have taken place over the last two decades, detailed information on how the interactions between odorants and olfactory receptors occur at the molecular level is still lacking. To achieve a better understanding on the molecular mechanisms involved in olfaction, we are investigating several odorants and their interactions with mimics of amino acid residues in olfactory receptors.

We present here the structural characterisation of fenchone (a component of the essential oil of fennel) and its complexes with ethanol (a mimic of the side chain of serine) using a broadband microwave spectrometer built at King's College London. Three different conformations of fenchone-ethanol have been observed in the rotational spectrum. In all the complexes the ethanol molecule binds to the carbonyl group through an O-H \cdots O hydrogen bond and secondary C-H \cdots O interactions. Surprisingly, the potential energy surface of the complex is quite flat, with different arrangements of ethanol around fenchone having very similar energies.



Reversible heat induced sol-gel transition of anionic cellulose

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Cellulose is an abundant polymer in agricultural wastes, thus, representing an excellent candidate for eco-sustainable components. It is biocompatible, has good mechanical properties¹ and has the ability to stabilize oil-in-water emulsions via Pickering stabilization². As such, cellulosic materials can provide functional properties in multiple commercial products (e.g. cream, lotion, food).

Anionic cellulose (AC) fibrils have a negative charge (ζ -potential of -60 ± 2 mV) which allows a prompt dispersibility and a high stability of dispersed fibrils in polar media³. Cation-induced gelation is observed for AC fibrils due to charge screening^{3,4}. It results in shear thinning gels with good network recoverability upon breakage (weak thixotropy) and a long term stability¹.

We present the possibility to form heat-induced hydrogels using AC fibrils in absence of salt (**Figure 1**). The rheological characterization of the gels shows a strong gel structure irreversibility upon breakage (strong thixotropy) with a permanent gel-liquid transition upon vigorous shaking.

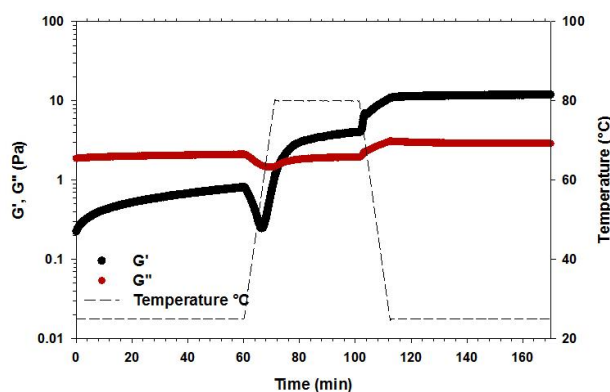


Figure 1. Heating ramp of anionic cellulose (AC) at 1.3 wt%. Storage and loss modulus (G' and G'') respectively are monitored at constant frequency (1Hz) and strain (0.1%) as function of time.

UV-vis spectroscopy and conductivity analysis suggested weak interfibrillar aggregation while differential scanning calorimetry (DSC) confirmed the absence of covalent crosslinks between AC fibrils upon heating. Further characterization of fibril aggregation was conducted via small angle X-ray scattering (SAXS). In addition, hydrophobic interactions of the AC fibrils before and after heating were probed via fluorescent probe PRODAN.

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Keywords.

Cellulose, heat induced aggregation, rheology.

Abstract ID (To be added by Conference committee)

Hydrogen Bonding in Ribitol

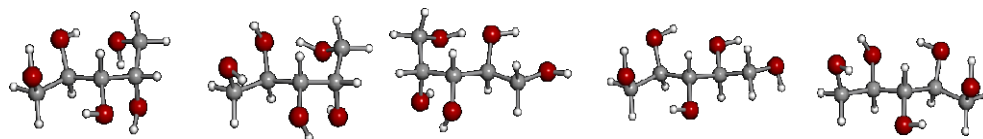
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The conformational behaviour of D-ribitol, a constituent of flavins, has been determined for the first time. Five different conformations have been identified by broadband rotational spectroscopy after vaporization of the crystalline pentose alcohol by laser ablation. All conformers show networks of either five or four cooperative intramolecular hydrogen bonds with clockwise or anticlockwise arrangements of the OH groups. The detected conformers are compared with those observed in flavins using X-ray crystallography.



Keywords.

flavin, microwave spectroscopy, laser ablation, conformational analysis, sugar alcohol

Structure and Vibrations of Hydrogen Bonds in Organic Anti-ferroelectric Squaric Acid

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Hydrogen bonds influence structure-property relations in a large number of functional materials. This is the driving factor for considerable effort dedicated in understanding the nature of hydrogen bonds both experimentally and computationally. Squaric acid is a simple hydrogen bonded organic material manifests anti-ferroelectricity at low temperature and paraelectricity at 373 K. Apart from this low temperature phase transition squaric acid derivatives have found applications in medicines. Croconic acid having a similar hydrogen bonded structure with just an extra carbon atom in the ring, on the other hand, is ferroelectric until its melting point at 450 K. The main difference between these structures is their hydrogen bond network. Squaric acid has a layered structure where the structure of croconic acid is three dimensional due to the presence of interlayer hydrogen bonding. The structure and dynamics of hydrogen bonding in croconic acid has been reported recently [1-3]. In the current presentation we will extend that investigation to squaric acid for analysing its functional properties microscopically.

We have performed neutron diffractions and inelastic neutron scattering experiments to understand the structure and dynamics of hydrogen bonds of squaric acid. To understand the dispersion of hydrogen bonds, two dimensional maps of energy and momentum transfer are measured on a sample of squaric acid single crystal in the MERLIN instrument at ISIS. The inelastic neutron scattering experiments are performed on Lagrange instrument at ILL. First principles density functional based lattice dynamics simulations are performed to calculate the phonon dispersion. The calculations are performed using plane-wave basis set using norm-conserving pseudo-potentials and dispersion corrected generalized gradient approximate functionals as implemented in CASTEP code.

Calculated lattice structures and bond lengths compared within 1% of the experiments. A strong hydrogen-bond-character is observed in the vibrational peaks of the stretching frequency of hydroxyl bonds observed around 2200 cm^{-1} . These hydrogen bonds show large dispersions which is compared well with neutron experiments. In this talk we will present the microscopic analysis of hydrogen bonds using neutron spectroscopy and correlate with the structure and the functional properties of squaric acid.

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Towards Photochemical Interruption of Mitochondria Using Ruthenium Photosensitizers

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Mitochondrial dysfunction causes intracellular Reactive Oxygen Species (ROS) levels to be out of balance. In recent years, mitochondria has been a target site for tumor treatment through a number of methods including interruption of its redox signaling and balance, bioenergetic capacity etc.

This research has focused on trying to find a way to disrupt how mitochondria function using a photoactivation approach based on the following observations: 1. H_2O_2 and ROS are generated by mitochondrial metabolism; 2. The function of H_2O_2 is to promote cell proliferation so that ROS do not overly accumulate in the cell and thus prevent oxidative stress; 3. ROS levels in tumor cells are high when compared to a normal cell.¹

Thus, our idea was to use the novel photosensitizers Δ and Δ -[Ru(bipy)₂(1-hydroxyanthra-9,10-quinone)]PF₆ (**1**) (Scheme 1) to consume H_2O_2 by way of a light-activated reaction. Under these

conditions cell proliferation ability would be limited, and ROS would accumulate, especially in a tumor cell, and this would induce oxidative stress and tumor cell apoptosis.

The current study represents a significant step forward to understand the preliminary reaction mechanism *in vitro* through a series of stability tests in CH_3CN , H_2O , buffer solution and with H_2O_2 by using UV-Visible spectroscopy, ¹H-NMR spectroscopy and mass spectrometry. The results demonstrate the compounds are stable in CH_3CN , H_2O and slightly acid or basic conditions under white light irradiation. With H_2O_2 present the complexes degraded under white light irradiation over time from inspection of the UV-Vis NMR and ESI-MS spectra (Figure 1). Two different reactions (fast and slow) appear to take place. The Ru(II) complexes lose their quinone-based ligand under irradiation, resulting in Ru(III) and Ru(V) species plus hydroxyanthra-9,10-quinone.

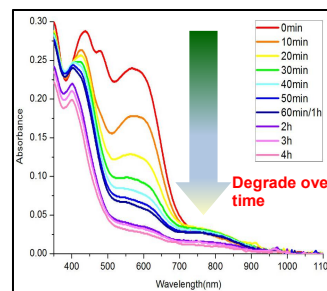
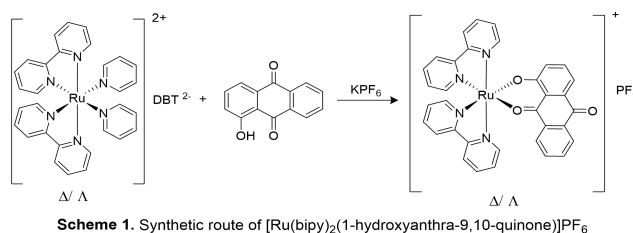
Next stage studies are underway to see if the complexes **1** are incorporated in mitochondria, and to see if they disrupt chemical processes.

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Keywords.

Ruthenium, Photosensitizer, Mitochondria, Redox System.



Photon Counting for CELIF

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➤ Knowing the Fluorescence Quantum Yield of Acetone (FQY) is necessary to determine the compound concentrations in different mixtures (with relevance in atmospheric studies, DKA diagnosis and photochemistry). To measure FQY, we use Cavity Enhanced Laser Induced Fluorescence (CELIF). This technique consists of the normalization and absolute calibration of the LIF signal through the CRD signal¹ ($S^{\text{CELIF}} = \frac{S^{\text{LIF}}}{S^{\text{CRD}}}$ (1)), leading to an enhancement of both techniques: this allows us to extend the CRDS sensitivity by at least three orders of magnitude. As CELIF only provides the number of photons that reach the detector, it lacks wavelength resolution. It is thus necessary to combine it with a wavelength resolved Acetone spectrum measurement (by itself, the spectrum measurement would provide only a qualitative picture of the photons emitted at each wavelength). In our experiments, we use mixtures of known Acetone concentrations and N₂ Rayleigh scattering as a calibration factor, in order to determine the fluorescence quantum yield of the compound (it can be

shown from (1) that $\Phi_{\text{Acetone}}(\lambda) = \frac{S^{\text{CELIF}}_{\text{Acetone}+\text{BG}} - S^{\text{CELIF}}_{\text{BG}}}{\alpha_{\text{Acetone}} K_{\text{N}_2, \text{R}} K_{\text{Acetone}}}$. $K_{\text{N}_2, \text{R}}$ and K_{Acetone} are respectively the above-mentioned Rayleigh scattering and Acetone spectrum calibration factors).

➤ When Acetone concentration is very low, the S/N ratio becomes smaller than the detection limit. Rather than using the LIF signal integration, as in S^{LIF} , we determine the number of photons that fluoresce in the Acetone mixture, and divide it by the integrated CRD signal to obtain the photon counting CELIF.

➤ We chose to develop a software-based photon counter, to achieve the most efficient technique possible for the characteristics of our specific setup. In fact, we use a pulsed laser to excite the compound, rather than a CW source, making it much easier to couple light inside the cavity. Although this results in a rather weak fluorescence signal, it allows us to cross-correlate the fluorescence photons emitted with the exponential decay of the laser shot within the cavity, on a shot to shot basis. Thus, as mentioned before, it is possible to normalize and calibrate the photon counting LIF signal through the CRD signal. This makes the CELIF signal independent from shot-to-shot fluctuations, and also makes it unnecessary to know the instrument dependent factors that contribute to the measurement. This calibration is particularly robust, being the laser shots and the sample the same in both CRD and LIF cases.

➤ Stray light and PMT noise are responsible for polluting the count of photons. To discriminate against the latter, we determine a threshold. Increasing the value of said threshold to improve the S/N ratio is ineffective for stray light, and could lead to the loss of actual fluorescence signal. While the problem of stray light seems to be solvable by simply using a blackout fabric, electronic noise is much harder to get rid of.

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The Electronic Structure of *Para*-Aminobenzoic Acid (PABA) in Water: A Spectroscopic Approach Combining UV with Near-Edge X-ray Absorption Fine Structure (NEXAFS) and Resonant Inelastic X-ray Scattering (RIXS)

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Fundamental understanding of the physicochemical properties of organic compounds is essential to advancing the development of new materials and products. A specific example is *para*-aminobenzoic acid (PABA) with therapeutic and sunscreen properties¹ due to its capability to absorb UV radiation as a result of electronic conjugation of the *para* orientated amino and carboxylic acid groups through the aromatic ring. This study reflects the effect of pH in aqueous solutions and focuses on showing how laboratory UV and synchrotron combination of near-edge X-ray absorption fine structure (NEXAFS) – resonant inelastic X-ray spectroscopy (RIXS) complement each other in providing access to a more complete picture around the electronic structure of solvated PABA molecules. Both UV and NEXAFS are absorption techniques that probe electronic transitions from occupied states to unoccupied molecular (MO) levels (such as the lowest unoccupied MO, LUMO), while RIXS involves the valence MOs (such as the highest occupied MO, HOMO). The HOMO↔LUMO energy gap in the density functional theory (DFT) calculations associated with the experimental NEXAFS–RIXS² identify well with the orbital gap observed in the time-dependent density functional theory (TD-DFT) simulations that reflects the main absorption peaks in the UV, thus bridging the synchrotron X-ray core-level spectroscopies NEXAFS and RIXS with the laboratory UV technique. Monitoring the electronic transitions in the UV range for PABA in water at intermediate, high and low pH, and interpreting the results with TD-DFT calculations provides us with a spectroscopic identification of PABA species in water.

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Keywords.

UV, NEXAFS, RIXS, pH, *para*-aminobenzoic acid, HOMO, LUMO, DFT, TD-DFT

Infrared Photodissociation of Metal-Ligand Complexes

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Isolated metal ion nitrous oxide complexes, $M^+(N_2O)_n-Ar$ ($M = Cu, Ag, Au, Nb, n = 2-7$), have been studied with infrared laser photodissociation spectroscopy in the region of the ν_3 stretch of N_2O using inert gas tagging. Infrared active bands are assigned with the help of simulations based on density functional theory. The structures are discussed in terms of N_2O ligands binding *via* either the N atom or the O atom, each resulting in characteristic shifts in the ν_3 stretch (N-N) of the N_2O .^{1,2}

For the coinage metal cations, the blue shift in the N-bound complexes from the free N_2O correlates directly with the σ accepting character, whereby the N_2O donates electron density from its 7σ HOMO into the s -orbital of the metal centre. From valence orbital calculations, gold accepts the most σ character, exhibiting the strongest blue shift, followed by copper and silver respectively.

Laser ablation of a niobium target in the presences of N_2O leads to $NbO_2^+(N_2O)_n$ complexes whose infrared spectra feature additional bands strongly blue shifted from the free N_2O . These are tentatively assigned as overtones of the N_2O symmetric stretch.

The infrared spectra of gas-phase gold-methane complexes, $Au^+(CH_4)_n$, have also been investigated to study potential C-H activation. An inner coordination sphere of two methane molecules is observed with additional methane molecules forming the second coordination sphere. In an intriguing observation, vibrationally exciting the T_2 mode of methane prior to ablation of the metal target appears to markedly enhance the methane dehydrogenation.^{3,4}

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Electronic Structure and Dynamics of Conformationally-Locked Photoactive Yellow Protein Chromophores

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Photoactive yellow protein (PYP) is responsible for a photocycle upon irradiation of blue light that signals its host bacterium, *Halorhodospira halophila*, to move away from potentially harmful UV light. The first step of the photocycle involves a *trans-cis* isomerisation of the covalently bound chromophore, deprotonated *para*-coumaric acid (*pCA*). It has been found that PYP derivatives reconstituted with a chromophore rotation-locked at the single bond adjacent to the phenol ring reduced the isomerisation yield by up to ~60%.¹ On the other hand, studies of the isolated chromophore have indicated that a role of the protein environment surrounding the chromophore might be to hinder rotation about this single bond to impede radical formation.² Thus the various torsional pathways involved in the initial isomerisation event are still not understood fully. Studies investigating changes in the molecular structure of the chromophore such as substitution at the coumaryl tail³ or different isomers,² have shown to be valuable in our understanding of the intrinsic excited state dynamics of the chromophore and hence the role of the protein in controlling the photocycle. Similarly, altering the molecular structure to inhibit torsion motions while keeping the backbone and functionality of the chromophore consistent allows for a methodical study of the role of torsional motions on the excited state dynamics.

Here, we present anion photoelectron spectra and quantum chemistry calculations for four model chromophores: *pCA*, its methyl ester (*MpCA*), and two analogues of *MpCA* with aliphatic bridges hindering single-bond torsional motion at either site adjacent to the unsaturated bond. We have found that the rotation-locked chromophore restricting rotation at the single bond between the alkene moiety and the ester follows similar excited state dynamics to the reference chromophores. However, the chromophore with the locked single bond adjacent to the phenol ring (*NpCA*) shows very little indirect photodetachment following photoexcitation in the range 310 nm–346 nm, indicating that the indirect pathways to S_0 become less accessible.

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Keywords.

biological chromophore, photochemistry, photoactive yellow protein, anion spectroscopy, photoelectron spectroscopy, computational chemistry

Uracil and uridine photodynamics probed by multi-photon ionisation

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Here we report on the UV wavelength (220-270 nm) dependence of fragment ion production from multi-photon ionized uracil and uridine in the gas phase. Uridine is one of the nucleosides in RNA and uracil is its base unit. Our aim is to better understand how the radiostabilities of key biological building blocks such as nucleobases are modified in biological environments (notably within condensed macromolecules). Comparing the radiation response of sequentially more complex biomolecules in the gas phase provides a natural approach to tackling this problem and complements our parallel studies of clustering effects [1, 2].

In order to bring nucleosides into the gas phase without thermal decomposition or reactivity, we have adopted the laser thermal desorption approach developed at Queen's University Belfast (Greenwood and co-workers) and Heriot Watt University (Townsend and co-workers) [3]. The absence of thermal damage in uridine was confirmed by testing that the fragment ion branching ratios were independent of the heating laser fluence. The standout results of our experiments were photon energy thresholds for two prominent fragment ion channels: the (sugar unit)⁺ and the (nucleoside less CO)⁺. Photon energy thresholds of this kind in the present MPI experiments provide strong indicators of critical processes in neutral excited states (notably structural changes and / or neutral dissociation) prior to ionization. The CO loss channel is particularly intriguing as we observed an analogous (but blue-shifted) photon energy threshold for CO loss from multiphoton ionized uracil, possibly associated with a previously calculated ring-opening S₂/S₁ conical intersection [1, 4]. We are currently carrying out electron impact ionization experiments and thermochemical, DFT, and dynamical calculations in order to refine our interpretations.

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Intermolecular Interactions in BODIPY Films: Aggregates vs Excimers

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Boron-dipyrromethene (BODIPY) derivatives are among the most versatile molecular dyes, with immense potential in wide-ranging applications. They are known for very high PL quantum yields, narrow absorption and emission linewidths, broad solvent compatibility and high thermal and photochemical stability. With established routes for chemical functionalization and bandgap tuning, they have seen extensive application in bio-imaging, photovoltaics, lasing and fundamental photophysical studies. Recently they have also been applied as the active material in organic microcavities, exhibiting strong coupling with the formation of new lower and upper polariton states [1]. However, like many organic chromophores BODIPYs exhibit a propensity for π - π stacking, resulting in PL quenching by states variously described as excimers or aggregates. Even when molecules are dispersed in neutral host matrices, photoluminescence quantum yields decrease sharply with increased concentration, pointing to efficient intermolecular non-radiative decay pathways that remain poorly understood. Here we study the nature of the intermolecular states formed in dispersions the prototypical BODIPY dyes. Using temperature-dependent and time-resolved photoluminescence measurements, we describe the processes of energy transfer into excimer states (Fig. 1, left) and, in materials with suitable chemical structure, exciton-coupled dimers (Fig. 1, right). These dimer states exhibit remarkable near-unity quantum yield.

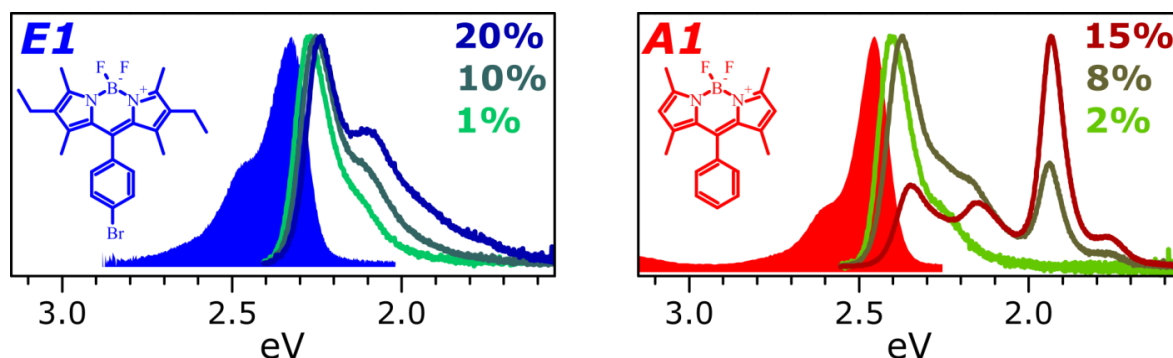


Fig. 1. Concentration-dependent PL spectra of BODIPY dispersions showing (left) excimer formation in E-type and (right) strongly red-shifted J-aggregated dimer formation in A-type dyes.

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Resonance-enhanced photoelectron
spectroscopy of phenol in the gaseous
and aqueous phases

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The extensive use of efficient light-induced processes in nature is inspiring efforts to exploit similar processes in functional synthetic systems. For example, biological imaging has been revolutionised by biological fluorophores, such as the Green Fluorescent Protein (GFP).¹ Isolated biological fluorophores are ideal starting points for studying key elementary processes following light-absorption. However, it is important to understand the role of the environment in determining electronic structure and dynamics. We take a bottom-up approach to unravelling the role of the environment, by using photoelectron spectroscopy to make analogous measurements of the chromophores *in vacuo*, in aqueous solution and in protein. Here, we begin with phenol – one of the molecular units of the chromophore for GFP – where we present our first systematic study to compare photoelectron spectra of phenol between gas-phase and aqueous solution. We also introduce our new liquid jet spectrometer, a novel technique for photoelectron spectroscopy of liquids.²

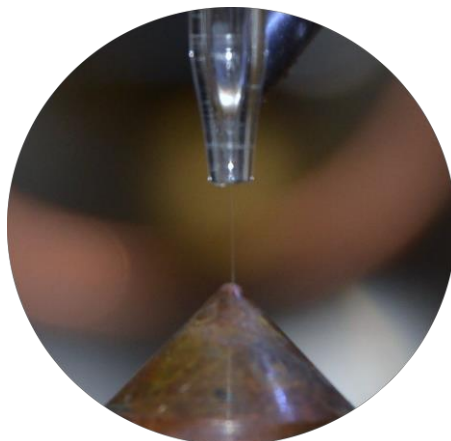


Figure: A 20 μm continuously flowing laminar liquid microjet formed *via* a fused-silica nozzle. A catcher is situated downstream to recirculate the liquid through our system.

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Keywords.

liquid microjet, photoelectron spectroscopy, phenol, green fluorescent protein, photochemistry, biological chromophore, fluorophore

Potential for Long-Term, High-Frequency, High-Precision Methane Isotope Measurements to Improve UK Emissions Estimates

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On the global scale methane (CH_4) concentrations have more than doubled over the last 150 years, and the contribution to the enhanced greenhouse effect is almost half of that due to the increase in carbon dioxide (CO_2) over the same period. Microbial, fossil fuel, biomass burning and landfill are dominant methane sources with differing annual variabilities; however, in the UK for example, mixing ratio measurements from a tall tower network and regional scale inversion modelling have thus far been unable to disaggregate emissions from specific source categories with any significant certainty. Measurement of the methane isotopologue ratios will provide the additional information needed for more robust sector attribution, which will be important for directing policy action

Here we explore the potential for isotope ratio measurements by diode laser spectroscopy, and describe current analytical work at the National Physical Laboratory that will realise deployment of such measurements. These measurements will improve the interpretation of atmospheric mixing ratios beyond calculation of total UK emissions. We simulate isotopic variations at the four UK greenhouse gas tall tower network sites to understand where deployment of the first isotope analyser would be best situated. We calculate the levels of precision needed in both $\delta\text{-}^{13}\text{C}$ and $\delta\text{-D}$ in order to detect particular scenarios of emissions.

Spectroscopic measurement in the infrared by quantum cascade laser (QCL) absorption is a well-established technique to quantify the mixing ratios of trace species in atmospheric samples and, as has been demonstrated in 2016, if coupled to a suitable preconcentrator then high-precision measurements are possible. The current preconcentration system under development at NPL is designed to make the highest precision measurements yet of the standard isotope ratios via a new large-volume cryogenic trap design and controlled thermal desorption into a QCL spectrometer.

Finally we explore the potential for the measurement of clumped isotopes at high frequency and precision. The doubly-substituted $^{13}\text{CH}_3\text{D}$ isotopologue is a tracer for methane formed at geological temperatures, and will provide additional information for identification of these sources.

Keywords.

Methane, Isotope, diode laser absorption spectroscopy, greenhouse gases, atmospheric measurement

Non-Adiabatic Multiconfigurational Molecular Dynamics Reveals Ultrafast Structural Change and Internal Conversion in 1,2-Dithiane and 1,2-Dithiine

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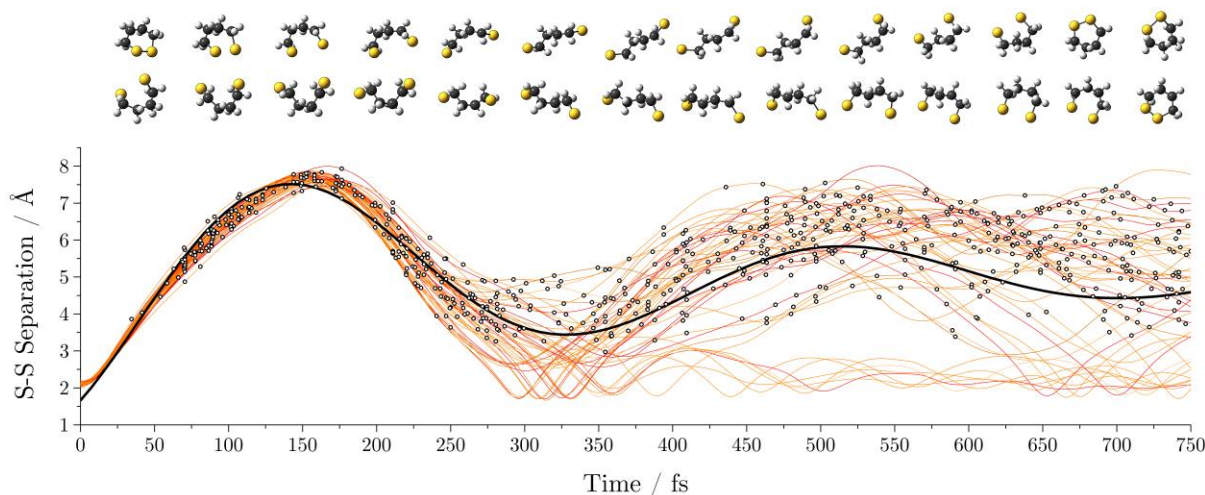
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The disulfide bond is ubiquitous in the natural world and key to the survival of specialised proteins and Archaea in some of the most extreme environments on Earth.

1,2-dithiane and 1,2-dithiine – two small cyclic disulfides – have been studied computationally using an SA3-CASSCF(10,8)/CASPT2 approach coupled with on-the-fly non-adiabatic multiconfigurational molecular dynamics (NAMMD) simulations. The theory outlined on this poster inspired recent ultrafast gas-phase electron diffraction experiments at the SLAC National Accelerator Laboratories (Stanford, US) aiming to understand the origin of the photostability of cyclic disulfides to harsh solar radiation in the near-UV.

In 1,2-dithiane, an ultrafast “Newton’s Cradle”-like motion is revealed^[1] that activates upon illumination by light in the near-UV, allowing us to make a classically-intuitive reinterpretation of early experimental observations^[2,3] that challenges the contemporary understanding of the system. It is demonstrated that subtle changes to the atomic and electronic structure have an appreciable impact on the character and coherency of the motion, ultimately leading to the destruction of the cyclic system in 1,2-dithiine and the observation of a number of photoproducts.



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Keywords.

Computational Chemistry, Non-Adiabatic Dynamics, Ultrafast Dynamics, Ultrafast Electron Diffraction, Disulfides

Inelastic Scattering of State-selected NO(X) with Ar in the Side-on Geometry

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We use a crossed molecular beam apparatus in combination with a hexapole state selector and a static electric field to select NO molecules in their low-field seeking $|\Omega=0.5, j=0.5, f\rangle$ state and to orient their bond axis before colliding them with Ar atoms. A (1+1') Resonance Enhanced Multiphoton Ionization (REMPI) scheme and velocity-map imaging are then employed to selectively ionize and detect the scattered NO molecules in a final rotational state (j'). While previous experiments have focused on collisions in which the rare gas atoms hit the NO at either the N- or the O-end (z-direction[1]), the current work is concerned with collisions in which the atoms approach the NO molecules from the side (x-direction). Preliminary velocity-map images show a change in the sign of the integral steric asymmetry, the preference for scattering to the left or the right of the initial relative velocity vector, as a function of the final j' state. This trend is confirmed by a newly developed quantum-mechanical treatment that may be applied to any arbitrary orientation of a diatom-atom collision system.

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Keywords.

Crossed-molecular beam scattering, bond-axis orientation, stereodynamics, hexapole state-selection, velocity-map imaging

Transportable CELIF Set-up Design

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The motivation to build this new set-up is to carry out in-situ measurements of trace gas species like acetone and glyoxal. Acetone has been gaining importance in the field of atmospheric chemistry, photochemistry and is used as a biomarker in breath analysis measurements. Glyoxal has importance in the field of atmospheric chemistry because of its role in aerosol formation and as an indicator for oxidative chemistry.

In 2013, the groups of Nahler and Wrede developed the Cavity Enhanced Laser-Induced Fluorescence (CELIF) technique, a combination of Laser Induced Fluorescence (LIF) and Cavity Ring-Down Spectroscopy (CRDS). This technique combines the analysis of fluorescence and ring-down transients in a way that enhances both the techniques. The ring-down time obtained from CRD measurement provides absolute calibration for LIF measurement.¹ The new set-up is a variant of CELIF with an Incoherent Broadband (IBB) light source such as a Light Emitting Diode (LED) being used in place of a coherent monochromatic light source (LASER) as in the case of CELIF. Thus, this new set-up will combine IBB Cavity Enhanced Absorption Spectroscopy (IBBCEAS) and LIF.

The advantages of using LED light source over a pulsed LASER are its compact size, low cost, lower energy consumption, robustness to temperature variations and vibrations. While the advantages over a CW-diode LASER include measurements in wavelength range down to about 230 nm and its broadband nature that will make it possible to analyse samples containing a mixture of trace gases that absorb at different wavelengths and samples with varying composition. Overall, this new set-up will have major advantage of being a compact transportable device and will be cost-effective, environmentally robust and energy efficient. In our experiment, we will carry out the detection of glyoxal in the background of NO₂, wherein the CELIF component of the measurement will be very sensitive to glyoxal fluorescence while the CEAS component will be for broadband NO₂ absorption.

The set-up will have two chief modes of operation: (i) the combined technique of IBBCEAS and LIF to determine trace gas species in the sample from their absorption features, and (ii) phase shift cavity ring-down spectroscopy (PSCRDS) to determine the reflectivity of cavity mirrors. Furthermore, as these modes will be utilising the same light source and optical alignment, it minimizes the probable systematic errors in the measurements.²

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Characterisation of the singlet fission process in protein-stabilised carotenoids aggregates

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As energy consumption continues to rise year on year, we still obtain the majority of our energy from fossil fuels. Clearly it is hugely important for us to create clean and sustainable energy in the near future. While renewable energy production is growing, it's a slow process with the 227GW produced by solar cells, accounting for only 1.2% of energy produced in 2015. While silicon solar cells continue to improve, in recent years alternative design philosophies have flourished. A promising method is exciton multiplication via singlet fission. Singlet fission converts a singlet (spin = 0) exciton to two bound triplet (spin = 1) excitons. Splitting the energy into two lower energy carriers reduces energy absorbed above the band gap and hence reduces loss from thermalisation. Singlet fission has been demonstrated with a 100% internal quantum efficiency and could increase the maximum power conversion efficiency limit by 11% (from 33 to 44%).

A class of singlet fission materials, Carotenoids, are pigments found in photosynthetic materials and have been shown to undergo singlet fission *in vivo* [1], where its function is still under debate. These materials show promise for solar cell production, with high cross sections of absorption ($\times 10^{-16}$) (an order of magnitude higher than other singlet fission materials) and near unity singlet fission yields *in vitro* [2]. A limitation to carotenoid research is instability and unpredictability in sample preparation. Aggregate production, which is required for singlet fission, is uncontrollable and creates very unstable samples. Here I present samples sequestered in man-made proteins (Maquettes) [3] which are used to control sample production and increase stability. Ultrafast transient absorption allowed for an in depth study of the effect of excitation conditions and molecular structure on the singlet fission process. We additionally present a plan for future study of singlet fission in the context of solar cell technology and lend evidence for current theories of its function in photosynthetic materials.

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Theoretical total ionisation cross sections of interstellar molecules

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Electron-induced chemistry is thought to play an important role in the chemistry of the interstellar medium.¹ We have undertaken theoretical studies to calculate total electron ionisation cross sections for molecules found in the interstellar medium or circumstellar shells, as listed in The Cologne Database for Molecular Spectroscopy.^{2,3} By using the binary-encounter Bethe model,^{4,5} these cross sections can be calculated using an expression relying on two molecular parameters, namely the binding and average kinetic energy for each occupied molecular orbital. These parameters are calculated here using the method developed by Bull *et al.*⁶

The binary-encounter Bethe model combines a modified version of Mott theory⁷ with Bethe theory,⁸ and shows a good agreement with experimental cross sections for non-relativistic electron energies. By applying this method to astrochemical molecules, ionisation cross sections can be obtained both for molecules that can be studied experimentally, and for molecules that would present a challenge to study on Earth, whether due to low vapour pressures or lack of terrestrial stability.

A selection of calculated total ionisation cross sections are presented, and are compared with experimental data from our laboratory and available literature.

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Investigation of CH₂BrI charge transfer dynamics using time-dependent and site-selective Coulomb Explosion Imaging on a femtosecond timescale

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The mechanism of charge transfer is key to understanding a broad range of biochemical processes, such as those involved in the respiratory chain. To gain a deeper insight, we have studied intramolecular charge transfer between dissociating photofragments in the model system CH₂BrI in a series of pump-probe spectroscopy experiments carried out at the FLASH free-electron laser facility. The UV pump pulse at $\lambda = 267$ nm induces photodissociation along one of the halide bonds. The products are probed by an intense, femtosecond XUV pulse from the free-electron laser after a pump-probe delay that is varied from -3.0 ps to 3.0 ps. Probe wavelengths of $\lambda = 18.6$, 17.7 , or 8.9 nm were employed, which predominantly ionise an electron from either the iodine 4d or the bromine 3d inner-shell orbitals. The subsequent Auger relaxation yields a highly charged ion that undergoes Coulomb explosion. In some of the dissociating molecules, an electron is transferred from a neutral co-fragment to the departing multiply charged halide atom.

In order to probe the charge transfer dynamics, the scattering distributions of the ions, Auger electrons, and primary photoelectrons are imaged in each pump-probe cycle, using a double-sided velocity-map imaging spectrometer equipped with a multi-mass detection setup. As a result of this study, we are able to present recent insights into the CH₂BrI charge transfer dynamics and to comment on the wavelength-dependent site-selectivity of XUV induced Coulomb explosion in comparison to non-selective IR strong-field ionisation.

Chemically Modified Graphene Studied by Time Resolved Sum-Frequency Generation Spectroscopy

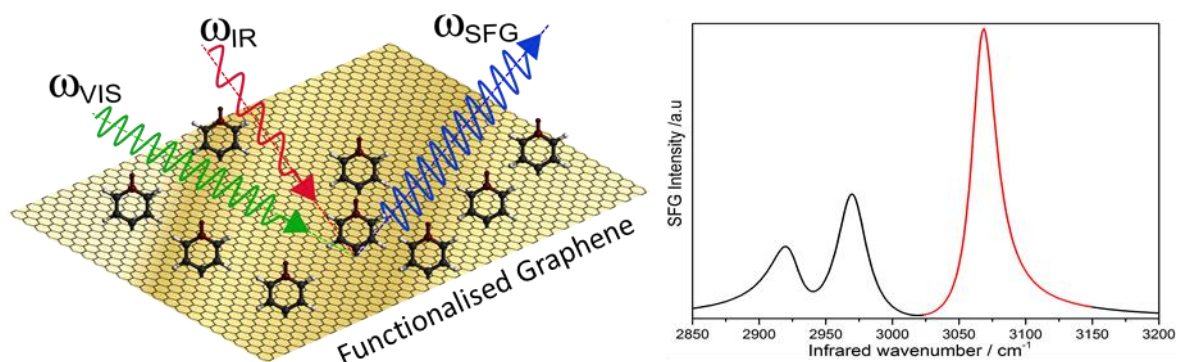
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Vibrational sum-frequency generation (SFG) employing femtosecond infrared (IR) laser pulses is used to probe CVD graphene on gold surface after a) chemical functionalization using a benzene diazonium salt and b) chemical hydrogenation using Birch reduction method. Distinct resonances were observed at 3064 cm^{-1} and 2720 cm^{-1} which can be assigned to an aromatic C-H stretch and hydrogenated graphene C-H stretch, respectively. Not only does sum-frequency generation spectroscopy allow one to characterise functionalised graphene with higher sensitivity and better specificity than many other spectroscopic techniques, but it also opens up the possibility to assess the coverage of functional groups on graphene and allowing time resolved experiments to be employed to gain insight into energy transfer processes through graphene sheets.

Time resolved excited state dynamics of 1-Iodonaphthalene molecules studied inside helium droplets

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The dynamics of electronically excited 1-iodonaphthalene (Inaph) molecules inside helium droplets have been studied using time-resolved ion yield spectroscopy (TRIY). A 120fs 266nm pump pulse was used to excite the Inaph from the ground state to the excited state. The population in the excited state was monitored by measuring the ion yield of singly ionized molecules as a function of time delay between the pump pulse and a nonresonant 40fs 800nm probe pulse. By keeping the intensity of the probe pulse low enough not to ionize from the ground state, we are selective to only the excited state. The decay in ion yield from molecules excited outside and inside helium droplets reveal different timescales, thus the excited state decay inside helium droplets is modified by the environment. These experiments pave the way for better understanding the excited states in the time domain where little is known compared to the frequency domain.

The TRIY measurements performed here is a first step towards more elaborate time resolved excited state experiments. For isolated molecules time-resolved photoelectron spectroscopy has proven to be an extremely powerful technique to study the evolution of excited states of molecules [1]. By using the photoelectron as an observable more information can be extracted. In particular if the molecules are prealigned and the photoelectron angular distributions are measured [2].

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Collisional quenching of excited NO ($A^2\Sigma^+$) studied by time-resolved FTIR emission spectroscopy

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Time-resolved FTIR emission spectroscopy has been used to determine the fate of electronically excited NO following collisions with a number of quenching species. Quenching of NO ($A^2\Sigma^+$ $v=0$) by atomic xenon results in emission from NO ($X^2\Pi$, $v=1-22$), but yields a vibrational distribution unlike that seen following quenching by any other rare gas atom (see figure 1). In stark contrast to the vibrational distributions observed following quenching of electronically excited NO by He, Ne, Ar and Kr, quenching by Xe produces a far greater fraction of vibrationally excited NO in the ground state. A series of experiments observing the IR emission from NO ($X^2\Pi$) in different conditions provide evidence of an alternative process involving the formation of NO ($a^4\Pi$) which we predict will produce vibrationally excited NO.

Collisional quenching of NO $A^2\Sigma^+$ ($v = 0, 1$) by O_2 has been studied using the same technique. Non-reactive quenching of NO $A^2\Sigma^+$ ($v = 0$) produces a vibrational distribution in NO $X^2\Pi$ which has been quantified for $v = 2-22$, and is found to be bimodal. The results are consistent with two quenching channels. The first forms the ground $X^3\Sigma_g^-$ or low-lying $^1\Delta_g$ electronic state of O_2 with a distribution including high vibrational levels of NO $X^2\Pi$ which is slightly hotter than statistical. Two possibilities are identified for the second channel: i) formation of highly electronically excited state (*e.g.* O_2 $c^1\Sigma_u^-$) with low vibrational levels in NO $X^2\Pi$ which are inverted with a distribution resembling that resulting from a sudden or harpoon mechanism; ii) ground state oxygen is formed with low vibrational energy partitioned into NO $X^2\Pi$. Vibrationally excited NO_2 is also observed, but at intensities which indicate that it is formed in low quantum yield. Quantitatively unobservable processes (defined as those which do not form ground state NO ($v \geq 2$)) are found to have a branching ratio of at most $25 \pm 5\%$. The results are compared with those of previous studies and the most consistent interpretation suggests that dissociation of O_2 to form ground state O (3P) atoms and ground vibrational state NO $X^2\Pi$ ($v = 0$) is the main reactive process rather than NO_2 formation. Qualitatively similar results are seen for the quenching of NO $A^2\Sigma^+$ ($v = 1$).

Finite Slice Analysis (FINA) – A General Reconstruction Method for Velocity Mapped and Direct Current Sliced Imaging

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Since the advent of ion imaging, one of the key issues in the field has been creating methods to reconstruct the initial 3D distribution of particles from its 2D projection. This has led to development of a number of different numerical methods and fitting techniques to solve this fundamental issue in imaging. In recent years, slice-imaging methods have been developed that permit direct recording of the 3D distribution, i.e., a thin slice of the recoiling fragment distribution. However, in practice, most slice imaging experiments achieve a velocity slice width of around 10 – 25% around the center of the distribution. This still carries significant out-of-plane elements that can blur the spectrum, lose fine resolution, and underestimate the contribution from slow recoiling products. To overcome these limitations we developed a new numerical method to remove these out-of-plane elements from a sliced image. The FINite sliced Analysis (FinA) method models the off-axis elements of the 3D particle distribution through the use of radial basis functions. Once applied, the method reconstructs the underlying central slice of the 3D particle distribution. The approach may be applied to arbitrarily sliced or unsliced data and has the further advantage that it neither requires nor enforces cylindrical symmetry of the data. We demonstrate this reconstruction approach with a broad range of synthetic and experimental data that, at the same time, allow us to examine the impact of finite slicing on the recovered distributions in detail.

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Keywords.

Image Reconstruction, Velocity Map Imaging, DC Slice imaging, photodissociation,

The Excited State Dynamics of Thermally Activated Delayed Fluorescence Emitters

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Organic Light-Emitting Diodes (OLEDs) are increasingly being used in novel technologies such as displays in electronic device and light sources in agriculture. However in typical organic molecules the lowest triplet state, T_1 , is not strongly dipole coupled to the ground state, S_0 . Consequently, the triplet excitons cannot relax radiatively meaning that the efficiency is limited to 25%. This limit is imposed by the spin-statistical nature of electrical excitation. An exciting new way to overcome this efficiency barrier is to exploit Thermally Activated Delayed Fluorescence (TADF).

In this work we study the mechanism by which reverse intersystem crossing (rISC) occurs in metal-free organic TADF emitters, as $T_1 \rightarrow S_1$ population transfer is crucial for TADF. [1]. To capture the core photophysics important in rISC, a Donor-Acceptor molecule Phenothiazine Dibenzothiophene-S,S-dioxide (PTZ- DBTO2) [2] was used to develop a linear vibronic coupling Hamiltonian based upon 3 excited state and 3 normal modes. [3] The Multi-Configurational Time-Dependent Hartree (MCTDH) method was used to simulate the wavepacket dynamics of this system, both with a wavefunction and a density operator formalism. The excited state dynamics calculations show the importance of vibronic coupling, between the T_1 and T_2 , for fast rISC, and that population is transferred to the S_1 through an efficient second order pathway in addition to a slower first order pathway. This suggests that when designing molecules for TADF, it is important to consider which vibrational modes enhance non-adiabatic coupling and how they correlate with those that drive non-radiative decay [3, 4]. This mechanism can also lead to non Arrhenius behavior [5].

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Keywords.

Thermally activated delayed fluorescence, nonadiabatic coupling, excited states, quantum dynamics.

Resonance-enhanced photoelectron
spectroscopy of phenol in the gaseous
and aqueous phases

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The extensive use of efficient light-induced processes in nature is inspiring efforts to exploit similar processes in functional synthetic systems. For example, biological imaging has been revolutionised by biological fluorophores, such as the Green Fluorescent Protein (GFP).¹ Isolated biological fluorophores are ideal starting points for studying key elementary processes following light-absorption. However, it is important to understand the role of the environment in determining electronic structure and dynamics. We take a bottom-up approach to unravelling the role of the environment, by using photoelectron spectroscopy to make analogous measurements of the chromophores *in vacuo*, in aqueous solution and in protein. Here, we begin with phenol – one of the molecular units of the chromophore for GFP – where we present our first systematic study to compare photoelectron spectra of phenol between gas-phase and aqueous solution. We also introduce our new liquid jet spectrometer, a novel technique for photoelectron spectroscopy of liquids.²

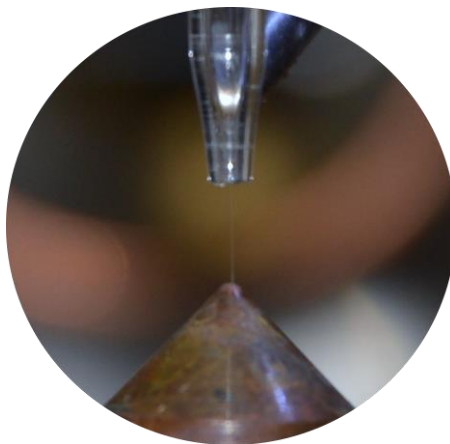


Figure: A 20 μm continuously flowing laminar liquid microjet formed *via* a fused-silica nozzle. A catcher is situated downstream to recirculate the liquid through our system.

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Keywords.

liquid microjet, photoelectron spectroscopy, phenol, green fluorescent protein, photochemistry, biological chromophore, fluorophore

Multi-photon ionization studies of 3-aminophenol: metastable dissociation and Stark deflection.

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This contribution reports on metastable dissociation pathways of 3-aminophenol (3-AP), a model system for amino acids as well as the neurotransmitter dopamine [1]. 3-AP molecules were ionised using ns-timescale UV laser pulses (220-270 nm) and the resulting ions were detected using a reflectron time-of-flight mass spectrometer. The voltage on the reflection electrode could be adjusted to test for metastable dissociation (several μ s after ionization). Exceptionally strong MPI signals, suggesting efficient access to long-lived electronic excited states, enabled 17 distinct metastable dissociation pathways have been detected. Analyzing metastable dissociation in parallel with *ab initio* quantum chemical can provide new insights into the complex sequential fragmentation processes of ionized biomolecules.

In addition to its biological relevance, 3-AP is interesting as a test-case for methods aimed at separating out the spectroscopies of structural conformers in gas-phase molecules as it exists in two conformational configurations in typical experimental targets: cis- and trans- with significantly different permanent dipole moments. Stark deflection has been used to completely separate these conformers in pulsed supersonic helium beams [3]. Such beams are suitable for diverse action spectroscopy experiments but are much less applicable to studies of collision-induced processes with relatively low cross sections. We are developing an experiment at the Open University that uses a Stark deflector built by Küpper and co-workers (DESY) to manipulate CW beams with the ultimate aim of probing dissociative electron attachment processes in selected tautomers and clusters of biological building blocks. To demonstrate the current capabilities of our experiment, we present Stark deflection results for nitromethane and for 3-AP in CW beams of helium and krypton.

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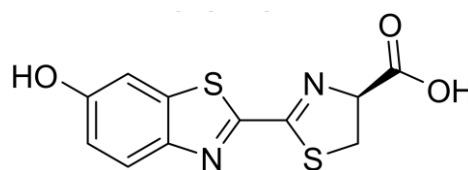
Acknowledgments.

EPSRC fellowship (EP/J002577/1); Fundação para a Ciência e Tecnologia (FCT-MCTES); Radiation Biology and Biophysics Training Programme of the Universidade NOVA de Lisboa (PD/00193/2012, PD/BD/114449/2016, SFRH/BD/52538/2014); CNRS PICS grant (07390); EU Horizon 2020 research and innovation programme (grant 692335 - *ELEVATE*)

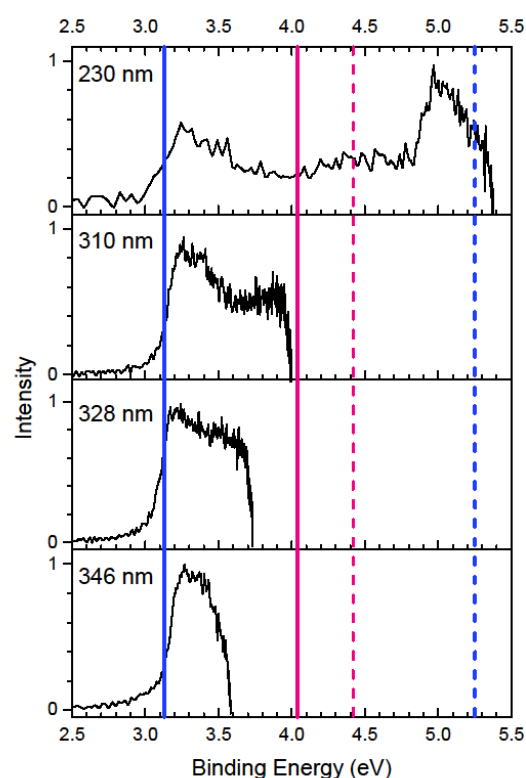
A Combined Photoelectron Spectroscopy and Quantum Chemistry Study of Luciferin Chromophores

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Firefly luciferin is the molecule responsible for the luminescence of the big dipper firefly, *Photinus pyralis*. Catalysed by the luciferase enzyme, luciferin reacts with Mg^{2+} , ATP and oxygen to produce the oxyluciferin phenolate anion in an excited state, which then emits yellow-green light ($\lambda_{\text{max}} = 558 \text{ nm}$).¹ All bioluminescent beetle species use the same substrate molecule (D-luciferin, right) to produce light, but the emission wavelength varies with the structure of the luciferase enzyme, resulting in different bioluminescence colours ranging between green and red.²



In order to unravel how the complex structure of the enzyme binding site influences the electronic structure and excited state dynamics of the chromophore, an understanding of the intrinsic excited state dynamics of the isolated chromophore is required. To this end, we present photoelectron spectra (PES) of the luciferin chromophore anion *in vacuo*, supported with equation-of-motion coupled-cluster method with single and double excitations (EOM-IP-CCSD) calculated ionisation potentials.³ We also present PES of a near infrared emitting synthetic luciferin chromophore, infraluciferin, which is used in multiparametric imaging of cells *in vivo*.⁴



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Keywords.

Photoelectron Spectroscopy, Dynamics, Firefly luciferin

Pair-correlated stereodynamics for diatom-diatom
rotational energy transfer: $\text{NO}(\text{A}^2\Sigma^+) + \text{N}_2$ Joseph G. Leng, Thomas F. M. Luxford, Thomas R. Sharples,
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We present the results of a crossed molecular beam velocity map imaging (CMB-VMI) study of the stereodynamics of state-to-state rotational energy transfer (RET) of $\text{NO}(\text{A}^2\Sigma^+, v=0, N=0, j=0.5) + \text{N}_2$ at a mean collision energy, $\langle E_{\text{col}} \rangle$, of 797 cm^{-1} . We have measured rotational angular momentum polarisation dependent images of scattering into product $\text{NO}(\text{A})$ rotational levels ($N' = 3, 5-11$), which show evidence for rotational excitation in the unobserved N_2 collider.

$\text{NO}(\text{A}^2\Sigma^+)$ was prepared by pulsed excitation in the crossing region of the CMB-VMI apparatus and the products of RET were subsequently probed state-selectively using $(1+1')$ REMPI on the $\text{NO}(\text{E}^2\Sigma^+ - \text{A}^2\Sigma^+)$ transition. Images were recorded with vertical (V) and horizontal (H) probe polarizations, in order to measure the collision-induced alignment.

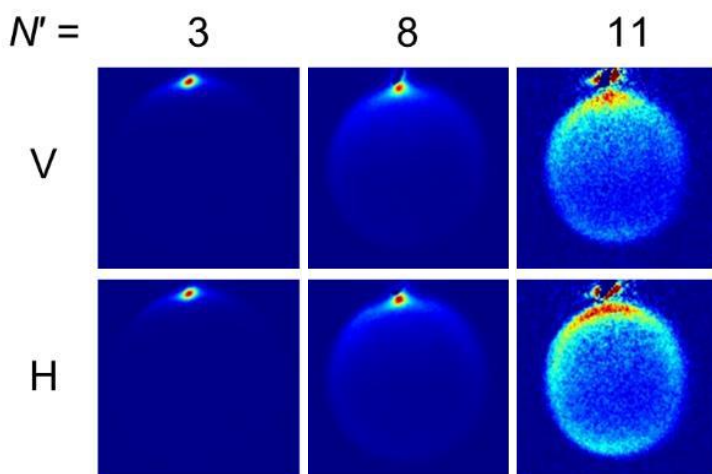


Figure 1. Experimental images for the collisions of $\text{NO}(\text{A})$ with N_2 at $\langle E_{\text{col}} \rangle = 797 \text{ cm}^{-1}$, for final $\text{NO}(\text{A})$ rotational levels $N' = 3, 8$ and 11 , for both vertical (V) and horizontal (H) probe laser polarisations.

The state-to-state differential cross-sections (DCSs) and scattering-angle dependent angular momentum alignment moments for $\text{NO}(\text{A})$ levels ($N' = 3, 5-11$) are reported as a function of the rotational excitation of the coincident N_2 partner. We discuss the dependence of the scattering dynamics on the degree of rotational excitation of the two colliders, inferring details of the previously unknown $\text{NO}(\text{A})\text{-N}_2$ potential energy surface (PES) through detailed comparison with previous measurements and calculations of the scattering dynamics of $\text{NO}(\text{A}) + \text{rare gas RET}$.^{1, 2}

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Keywords.

Crossed Molecular Beams, Velocity Map Imaging, Molecule-Molecule Scattering, Differential Cross Section

Weak interactions of thiourea and urea complexes examined by rotational spectroscopy and *ab initio* calculations

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The rotational spectra of thiourea-water, thiourea-argon, urea-argon and urea isocyanic acid were measured in this work, using a Chirped-pulse Fourier transform microwave spectrometer (CP-FTMW)¹. A laser ablation source was used to generate the species from rods containing thiourea or urea. A comparison of their structures and energies is presented, alongside species that were not observed, such as the urea water complex.

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Keywords.

Microwave spectroscopy, structure determination, hydrogen bonding, laser ablation

Hunting for a correlation-bound state: frequency- and time-resolved photoelectron spectroscopy of $(\text{C}_6\text{F}_6)_n \bullet \Gamma$ clusters

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It has been proposed that C_6F_6 may host a channel for low energy electron capture via a correlation-bound state, a diffuse non-valence orbital stabilised only by dispersion interactions with the valence electrons¹. In an attempt to observe such a state, we have measured frequency- and time-resolved photoelectron spectra of $(\text{C}_6\text{F}_6)_n^-$ and $(\text{C}_6\text{F}_6) \bullet \Gamma$ clusters on a new photoelectron spectrometer in the photon energy range of 1.8 – 5.9 eV (700 - 210 nm).

The direct detachment feature of $(\text{C}_6\text{F}_6)_n^-$ is broad and Gaussian-shaped with a vertical detachment energy of 1.45 eV for the monomer ($n = 1$), increasing by ~ 200 meV per n . The electron affinity is not observed experimentally but has been calculated to be 0.55 eV. This discrepancy arises from the poor Franck-Condon overlap between the anion and neutral ground states, which is confirmed by electronic structure calculations. These calculations show that the anion ground state adopts an out-of-plane buckled structure while both the correlation-bound state and the neutral ground state adopt a planar geometry. There was no direct observation of the correlation-bound state in the initial frequency-resolved study but evidence of resonance dynamics was present².

In order to generate the weakly-bound planar correlation-bound state, a clustered electron donor was employed in order to transfer the charge in situ onto the C_6F_6 molecule in its planar form. Firstly, clusters of $(\text{C}_6\text{F}_6)_n^-$ and then $(\text{C}_6\text{F}_6) \bullet \Gamma$ clusters were explored. The $(\text{C}_6\text{F}_6)_n^-$ clusters for $n = 2 - 5$ yield similar frequency-resolved spectra as $n = 1$. However, there are additional features present that correspond to the release of very low kinetic energy electrons. This suggests that there are resonances that act as a pathway to delayed electron loss that would be consistent with a correlation bound anion. The frequency-resolved spectrum of $\text{C}_6\text{F}_6 \bullet \Gamma$ shows that the direct detachment channel is shifted to higher electron binding energy relative to atomic Γ by 400 meV. There is also a weak-intensity atomic line of Γ present at a binding energy corresponding to unclustered Γ , suggesting that charge transfer between the Γ and the C_6F_6 can occur below the threshold for direct detachment and leads to pathways including disintegration of the cluster. Current experiments are exploring the time-resolved photoelectron spectra following charge injection in an attempt to probe the correlation bound state directly.

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Cold state-selected radicals for the study of low temperature chemistry

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In Zeeman deceleration, time-varying spatially-inhomogeneous magnetic fields are used to create packets of translationally cold, quantum-state-selected paramagnetic particles with a tuneable forward velocity, which are ideal for cold reaction dynamics studies. Here, the covariance matrix adaptation evolutionary strategy (CMA-ES) is adopted in order to optimise deceleration switching sequences for the operation of a Zeeman decelerator. Using the optimised sequences, a 60% increase in the number of decelerated particles is observed compared to standard sequences for the same final velocity. Furthermore, we demonstrate that it is possible to reach final velocities that are 60% lower than those experimentally accessible with standard sequences. Three-dimensional particle trajectory simulations are employed to reproduce the experimental results and to investigate differences in the deceleration mechanism adopted by standard and optimised sequences. It is experimentally verified that the optimal solution uncovered by the evolutionary algorithm is not merely a local optimisation of the experimental parameters – it is a novel mode of operation that goes beyond the standard periodic phase stability approach typically adopted. Ultimately, we seek to combine the decelerator with an ion trap to undertake collision studies between paramagnetic species and trapped ions. The design of a new magnetic guide to select decelerated particles travelling at a specific velocity whilst filtering out the rest of the beam is presented. The guide, made of a series of permanent hexapole magnets, is predicted by numerical particles trajectory simulations to yield a pure beam of state-selected particles.

Magnetic field effects on cryptochromes and related model systems

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The ability of birds to orient themselves during migration using the Earth's magnetic field is hypothesised to involve cryptochrome proteins located in their retinæ. Photochemical radical pair reactions within these proteins have product yields that are sensitive to the magnitude and direction of the external magnetic field, and have been proposed as the starting point for a more complex signalling cascade that allows birds to visualize the Earth's field. Cryptochromes are currently the only candidate magnetoreceptor for a biological, chemical compass based on radical pair mechanism (RPM), but the relationship between the photochemistry and signal transduction in these proteins is largely unexplored. The work presented here involves a combination of fluorescence spectroscopy and hydrogen-deuterium exchange (HDX) experiments to investigate the photochemistry and photosignaling mechanisms, respectively, occurring in cryptochrome.

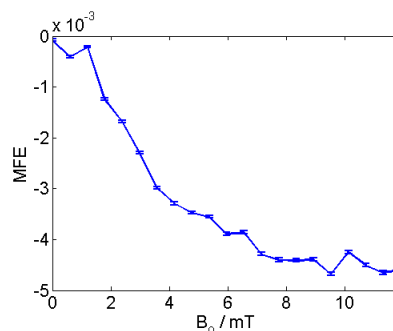


Figure 1. Magnetically Altered Reaction Yield (MARY) plot obtained *via* fluorescence spectroscopy for 10 μ M FMN / 1mM W (a model system for cryptochromes).

Fluorescence spectroscopy provides significant sensitivity gains over the traditional absorption based techniques and has been used to study magnetic field effects (MFEs) in a variety of chemical systems related to cryptochrome to increase our understanding of the fundamental photophysics.[1] Future work will exploit this enhanced sensitivity to investigate cryptochrome photochemistry within a cellular environment. In complementary studies, HDX studies with mass spectrometric detection has allowed us to monitor blue-light induced conformational changes around the C-terminal tail (CTT) in the wild-type protein which may be key to the signal transduction pathway in cryptochromes.

Support: EMF Biological Research Trust

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Electronic Structure of Ionic Liquids Using X-ray Spectroscopy: Probing Reactivity

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Ionic liquids (ILs), liquids composed entirely of mobile ions, provide a novel liquid environment different from traditional neutral molecular liquids or high temperature molten salts. ILs have the potential to impact upon a broad range of technologies: electrochemical applications,^{1, 2} photochemical applications,^{1, 2} nuclear fuel processing,³ deconstruction of lignocellulosic biomass,⁴ and gas separation/capture/storage⁵. The valence electronic structure of ILs controls chemical reactivity, electrochemistry and electronic interactions with light, and therefore underpins all of these applications.^{6, 7} The identity and energy of the frontier orbitals, *e.g.* the highest occupied molecular orbital (HOMO), is very important, particularly whether the HOMO is from the anion (expected) or the cation (surprising).

X-ray spectroscopy is regularly used to study the valence band of solids. ILs are sufficiently involatile that standard apparatus can be used to study the liquid phase at room temperature.⁸ Studying the valence bands of volatile liquids, *e.g.* water-IL mixtures, is far more challenging, and a liquid microjet is usually used.⁹ We used X-ray photoelectron spectroscopy (XPS), resonant Auger electron spectroscopy (RAES) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy to probe the electronic structure of both neat ILs and solutes in ILs. Experiments were carried out on a lab-based XPS apparatus, and a range of synchrotron beamlines. We compared our experimental results to DFT and time-dependent DFT calculations for a range of systems.

We experimentally identified the HOMO for seven ILs. For six ILs the HOMO was from the anion; for one IL the cation gave the HOMO. Excellent agreement was found between the experimental and calculated HOMOs for all seven ILs. For calculations, the system size was found to be particularly important. The HOMO energy for [C₄C₁Im][SCN]-water mixtures was found to vary with the water concentration, and was significantly smaller (and therefore less stable) for the mixtures compared to neat water. Lastly, the valence band structures of metal ion complexes in ILs were probed, and the HOMOs were identified. These results have significant implications for reactivity of IL-based systems.

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LIF is too short

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The absolute densities of SD radicals exiting a Stark decelerator [1] have been measured using a direct, single-beam combination of laser-induced fluorescence (LIF) and cavity ring-down spectroscopy (CRDS), a technique we call cavity-enhanced laser-induced fluorescence (CELIF). The CRDS aspect provides the calibration of the LIF signal such that absolute densities below the limit of detection of CRDS can be measured in a simple setup [2]. The analysis of the concurrently recorded laser-induced fluorescence and ring-down transients has been adapted to measure molecular densities that change significantly over the course of a single measurement. CELIF can be used to monitor molecular densities changing significantly over a microsecond time scale under a variety of conditions relevant to cold molecules, reaction dynamics, photodissociation, combustion and atmospheric chemistry.

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Keywords.

LIF, CRDS, cavity-enhanced laser-induced fluorescence, absolute density measurements.

Probing intramolecular vibrational energy redistribution using picosecond time-resolved photoelectron imaging.

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We present results on the intramolecular dynamics of excited state *p*-fluorotoluene (*p*FT). Two vibrational states, 13^11^1 and $7a^11^1$, have been excited in S_1 with a picosecond laser in order to study the intramolecular dynamics using time-resolved photoelectron imaging.¹ These two states are very close in energy in the S_1 , lying at 1990 cm^{-1} and 2026 cm^{-1} respectively. The dynamics resulting from excitation of these vibrational states are similar, being mediated by strongly coupled doorway states, however the lifetimes differ by a factor of three. We conclude the vibrational character of the modes involved influences the dynamics due to enhanced torsion-vibrational coupling which will be discussed.² In current work we are studying aniline for comparison with the intramolecular dynamics seen in *p*FT.

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Time-resolved photoelectron imaging using vacuum ultraviolet pump pulses

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Biological chromophores are light absorbing sites that have been found to efficiently dissipate excess energy gained through the absorption of ultraviolet (UV) light. This photoprotection mechanism ensures that crucial biological molecules (such as DNA) remain able to carry out their biological function. In order to gain insight into this inherent photostability, we investigate the evolution of the wavepacket in the excited state, on ultrafast timescales using the time-resolved photoelectron imaging (TRPEI) pump-probe technique¹⁻³. TRPEI provides extremely differential measurements, yielding time-, energy- and angle resolved information. The technique can be further enhanced and provide a more detailed dynamical picture by the use of vacuum-ultraviolet (VUV) femtosecond pulses.

Our TRPEI setup has been recently extended to support the generation of ultrashort pulses in the VUV region, by the process of non-collinear four wave mixing in an argon filled gas cell⁴. We present preliminary results of measurements made on 1,3-butadiene using VUV (160 nm) pump and UV (267 nm) probe pulses, along with excited state theoretical calculations in the vertical Franck-Condon region. Furthermore, we present a numerical model investigating the influence of excited state lifetime and instrument response function on detection efficiency in TRPEI studies.

Acknowledgments.

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Keywords.

Ultrafast gas phase spectroscopy, vacuum-ultraviolet, time-resolved photoelectron imaging

Cold reactive collisions between neutral molecules and cold, trapped ions

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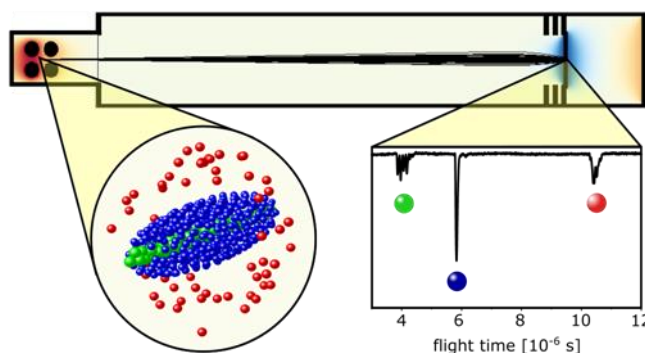
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With the ultimate goal of exploring the quantum dynamics of ion-neutral reactions in cold conditions, we employ two sources of cold neutral molecules in combination with ions held in a linear ion trap and cooled by lasers. The two sources of cold neutral molecules we adopt are a Stark decelerator and a quadrupole guide velocity selector combined with a buffer gas cooling system [1]. Laser-cooled atomic ions within the trap undergo a phase transition, adopting an ordered structure called a Coulomb crystal [2]. Other non-laser cooled species can be sympathetically cooled into the Coulomb crystal, enabling a range of ionic targets to be prepared. Reactions are investigated by monitoring the change in the morphology of Coulomb crystals over time and by performing time-of-flight mass spectrometry measurements [3,4]. In this way, we can examine the progress of ion-molecule reactions within Coulomb crystals.

We also report on the extent to which the spatial orientation of cold polar molecules can be controlled as molecules pass through various electric field regions of the experimental apparatus involving the quadrupole guide velocity filter [5].



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Probing the surface structure at the vacuum-liquid interface of fluoroalkyl ionic liquid mixtures using reactive O-atom scattering

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Room temperature ionic liquids offer a tunable reaction medium whose physical properties can be tailored by altering the constituent ions, or by mixing with other ionic liquids. Our aim is to understand the surface structure of ionic-liquid mixtures such that gas-phase interactions can be optimised for surface-specific applications such as multiphase catalysis.

Figures 1 a) and b) illustrate our technique:¹ O(³P) atoms are generated by laser photolysis of NO₂ above an ionic liquid, the O-atoms react *via* hydrogen abstraction with the CH₂-subunits of the alkyl sidechains to form OH; the nascent OH recoils into the gas-phase and is then detected using laser-induced fluorescence.

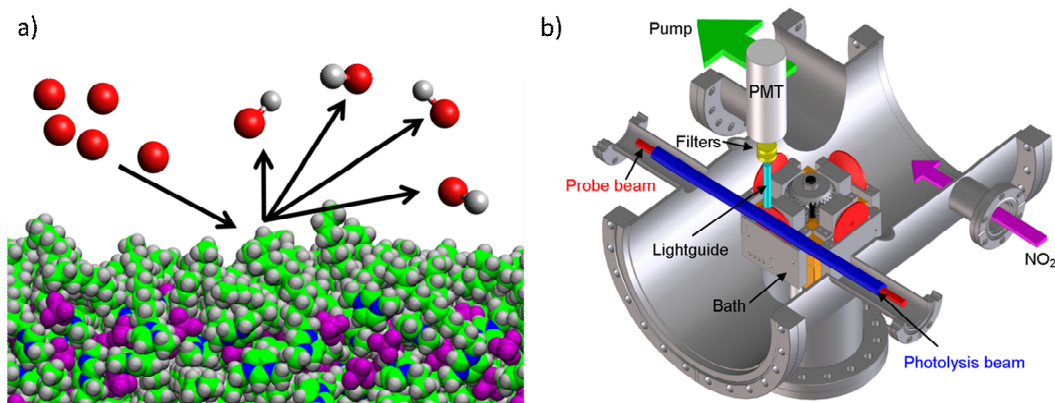


Figure 1: a) Illustration of reactive O-atom scattering from an ionic liquid to form OH *via* hydrogen abstraction from alkyl groups. b) Schematic of experimental apparatus.

Our recent experiments have focused on the surface structure of cation mixtures of 1-alkyl-3-methylimidazolium [C_nmim], and a partially fluorinated cation [C₈mim-F], where the C₈ chain has six fluorinated carbon atoms, (with the common anion, bis(trifluoromethylsulfonyl)imide ([NTf₂])). We have shown that for [C_nmim]_x[C₈mim-F]_{1-x}[NTf₂] mixtures, the presence of the partially fluorinated cation strongly depletes the surface of secondary hydrogens, indicating that the fluorinated cation is highly surface active. This suggests that by choosing cations, anions or possibly solutes that contain fluorinated groups, they can be selectively chosen to preferentially occupy the gas-liquid interface.

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Following the Femtosecond to Nanosecond Dynamics of Photoinduced Methyl-ammonium Lead-Halide-Perovskite Thin Films

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Photovoltaic cells and devices incorporating methyl-ammonium lead iodide perovskites such as, $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI₃), have been intensively studied because of their ease of production and high power conversion efficiencies, which has increased from 4% to 20% in the last 4 years. [1-2]

We investigated the photoexcited relaxation dynamics of two different hybrid organic-inorganic perovskite samples with time resolved infrared (TRIR) spectroscopy using the state-of-the-art ultrafast time-resolved multiple probe spectroscopy (TRMPs) experiment at RAL. This permits us to seamlessly follow the evolution of transient species from 100 femtosecond to 1 millisecond [3]. Two samples were studied MAPbI₃ and a sample where MAPbI₃ was sandwiched between titanium oxide (TiO₂) and the hole transporting material (HTM) 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD). The data were collected for two different pump wavelengths: 750 and 540nm. The former wavelength is near to the band edge, while the latter is close to the maximum of the solar spectrum. Broadband IR probe pulses were centred at $\sim 1500\text{ cm}^{-1}$ to investigate the NH_3^+ symmetric stretch of the methyl-ammonium cation (1466 cm^{-1}). Both pump wavelengths are known to excite above the band-gap, creating charge carriers immediately in the perovskite semiconductor. All data display a broad structureless absorption with sharper features on top. The broad feature, spanning all probe wavelengths ($1200\text{--}1800\text{ cm}^{-1}$), has been assigned to intra-band transitions, *i.e.* excited state absorptions between bands in the conduction band (CB). [1] The kinetics of the intra-band transitions for the MAPbI₃ can be fitted with a biexponential when excited at 750 nm, returning two time constants of ~ 0.4 and 2.5 ns . For 540nm excitation the longest lifetime is $\sim 3\text{ ns}$. For the sandwich structure, our analysis returned longer associated lifetimes $\sim 1\text{--}5\text{ ns}$ and $\sim 1\text{--}8\text{ ns}$ for the two excitation wavelengths 750 and 540nm, respectively. The longer lifetimes extracted from experiments on the TiO₂|MAPbI₃|spiro-OMeTAD sample is indicative of a longer-lived perovskite excited states. This may be because the HTM and TiO₂ can extract photo-carriers and thereby reduce the probability for geminate recombination processes. [1] The sharp features festooned on top of the intra-band transitions are associated with the methyl-ammonium⁺ symmetric stretching vibration, and display Fano-type line shapes due to strong coupling between the CB and the methyl-ammonium modes.

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Keywords.

Time-resolved spectroscopy, electronic-vibrational spectroscopy, nanomaterials, electron-phonon coupling, charge-carriers, photovoltaics

Gas Phase Photodissociation Spectroscopy of Geologically relevant Metalloporphyrins

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Porphyrins are ubiquitous through biology and hence are present in 100-1000 PPM quantities in oil,^{1,2} where they are known as pteroporphyrins. Whilst commonly found in biology with iron or magnesium centers, and long side chains, these pteroporphyrins are found with Ni, VO, and Mn centres, and have simple methyl or benzyl side chains. Despite their relatively low concentrations, these pteroporphyrins can adversely affect the performance of hydrocarbon cracking catalysts and hence make certain sources of oil unusable.³ The typical strong electronic absorption shown by porphyrins is much weaker and broader than expected in oil for the given concentrations.⁴ Using a laser interfaced mass spectrometer, we report an initial gas phase photodissociation study of a model iron tetraphenyl porphyrin system. This will guide future work on these pteroporphyrins to explore how the electronic absorption spectra change as the porphyrins interact with other species found in oil.

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Keywords.

Metalloporphyrins, pteroporphyrins, Photodissociation spectroscopy

One- and Two-Photon Activation of $[\text{Ru}(\text{bpy})_2(\text{Nicotinamide})_2]^{2+}$

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The unique photochemical properties of ruthenium-pyridyl complexes have been exploited for a plethora of technological and medicinal applications. One of the more novel uses of these complexes is as photoactivatable prodrugs, where light induces formation of an active species from a stable, inert precursor molecule; a technique known by the term photodynamic therapy. One potential photoactivatable prodrug is $[\text{Ru}(\text{bpy})_2(\text{NA})_2]^{2+}$ (NA = Nicotinamide, pyridine-3-carboxamide), which undergoes NA ligand loss upon excitation. However, like many ruthenium-pyridyl complexes, their absorption lies out of the photodynamic therapy window (620 – 1000 nm); limiting their potential. Serendipitously, these molecules can undergo two-photon absorption within this window.

Normally a molecule can be photoexcited by an ultraviolet/visible photon that is equal to the energy gap between the ground electronic state and the excited electronic state. However, it is possible to induce the same transition using two photons whose combined energy is equal to the energy gap between the two states. Yet, this requires large photon densities to be achieved, such as those found in femtosecond laser pulses.

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A reactive extraction strategy to transform biobutane-2,3-diol into platform chemicals

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Green chemistry encourages the development of innovative processes combining biorenewable, sustainable resources with non-hazardous, minimal energy and waste generating transformations in order to produce useful chemical products.

2,3-Butanediol is a commodity chemical with a wide range of applications as a precursor to plastics and pesticides. Although industrially, it is produced by hydrolysis of 2,3-butene oxide, optically pure (2R,3R)-butanediol can be generated through large scale fermentation processes that were first investigated during the 1940s. More recently, it has been shown that 2,3-butanediol can be synthesised by fermentation from industrial waste carbon monoxide using clostridium bacteria. However, a challenge to the fermentation process is that recovery of the diol (bp 177 °C) from water by either solvent extraction or by distillation is energy intensive, costly and environmentally damaging.

Here we describe a strategy to enable reactive extraction of the diol from the fermentation broth using in-situ trans-esterification to generate butylene carbonate that can be readily separated as a liquid-liquid biphasic system. This overcomes the energy barriers associated with fractional distillation and simultaneously upgrades the diol to a valuable platform intermediate with many existing commercial applications.

Keywords.

Reactive extraction, fermentation, trans-esterification

A Femtosecond Laser Photoelectron Spectroscopy and Computational Study of the Super-atom Molecular Orbital Electronic States of Li@C₆₀

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Due to their highly symmetric nature and elemental purity, fullerenes are ideal model systems for studying and understanding the excitation and ionisation mechanisms of large complex systems. An intriguing characteristic that they possess is the atom-like nature of the diffuse excited electronic states known as “super-atom molecular orbitals” (SAMOs). SAMOs are described as low lying Rydberg-like states where the charge distribution is centered on the center of the hollow carbon cage. These states have been observed in gas-phase photoelectron spectroscopic (PES) studies of fullerenes, such as C₆₀ and C₇₀, and endohedral fullerenes, such as Sc₃N@C₈₀.^{1,2} The PES are characterized by a thermal electron background and a peak structure superimposed on it at kinetic energies lower than the photon energy. Based on the PADs and TD-DFT calculations,³ the peak structure can be assigned to a one-photon ionisation of the SAMO states.

Recent work has focused on exploring the electronic properties of Li@C₆₀ in the gas phase, together with STM/STS experiments and DFT calculations. Comparisons with the empty C₆₀ provide information about the influence that the encapsulated atom has on the electronic system. This is particularly valuable for the endohedral C₆₀ since, unlike the more commonly studied endohedral molecules with larger carbon cages, the C₆₀ cage isomer is the same for the empty and filled species. From our comparisons we have seen that the Li@C₆₀ shows a lower ionisation potential and an increased binding energy for the lowest-lying s-SAMO while the p- and d-SAMOs are largely unaffected. This has also been demonstrated in STS experiments and DFT calculations.

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Keywords.

Endohedral fullerenes, Li@C₆₀, Super-atom molecular orbitals, Velocity map imaging, DFT

Blister-Based Laser Induced Forward Transfer of Molecules and Nanoparticles

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It is often very challenging to eject large molecules or small nanoparticles cleanly into the gas phase without introducing any impurities in the form of matrix material or inducing thermal degradation. In this poster we will present our recent work on the development of a laser-based technique that allows nanoparticles to be transferred cleanly between substrates or provides a reasonably dense gas phase target of large, thermally labile molecules. The technique is related to the more commonly used LIAD (laser induced acoustic desorption) where an intense laser pulse impinges on the back of a thin metal foil and removes any molecules deposited on the front surface. Although originally attributed to acoustic wave desorption, it is now more commonly accepted that the method relies predominantly on thermal desorption of the molecules.¹ In our approach, we use a very thin metal film deposited on a glass substrate (in place of the metal foil) and study the effect of both ns and fs laser pulses on the deformation of the metal film and subsequent material ejection.² We have shown that ns laser pulses predominantly heat the metal film inducing a thermal blister deformation of the film leading to release of molecules with predominantly thermal velocity distributions. On the other hand, fs laser pulses induce vaporization of the metal at the glass-metal interface and induce the formation of a blister caused by gas expansion at the interface. This releases molecules with lower, non-thermal velocity distributions.

The measured velocity distributions will be shown for fullerene molecules and we will illustrate the possibility of changing the velocity distribution by altering the thickness of the metal film. In addition we will show that, even although the ns-laser-induced mechanism is predominantly thermal in nature, it is possible to cleanly remove functionalized fullerenes (PCBM) without the molecules undergoing thermal fragmentation or temperature-induced isomerization. Finally, we will show the usefulness of the technique in transferring low dimensional (1D and 2D) materials between substrates.

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Keywords.

LIFT, BB-LIFT, laser-induced desorption

Ultrafast Dissociation Dynamics of Aromatic Heterocycles

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The aromatic heterocycles of many biologically relevant systems have attracted significant attention from spectroscopists, as photoexcitation to the lowest lying electronic excited singlet state [1] results in prompt H-atom loss. As the prototypical chromophore in biomolecules such as tryptophan or tyrosine, the photodissociation of pyrrole (*c*-C₄H₅N) and phenol (*c*-C₆H₅OH) have thus been extensively studied in the gas phase (see, for example, Ref. 2), where H-atom loss dynamics depend strongly upon the photon energy [3]. Towards the development of a “bottom-up” understanding of biomolecule photochemistry, the effects of ring substitution on the H-atom photofragment translational energies have been extensively investigated (see, for example, Ref. 4). However, the effects of substitution on the ultrafast photochemistry of these aromatic systems has received less attention. Recently, our group has investigated the time-resolved photodissociation of several pyrrole derivatives [5], finding subtle changes in the N–H dissociation dynamics due to alkylation. Herein, we report on our current work to continue exploring the structure-dynamics relationship of the ultrafast photochemistry of pyrrole and phenol derivatives.

Acknowledgements. This work has the support of the Leverhulme Trust, the EPSRC, the Royal Society, and the University of Warwick.

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Keywords.

femtochemistry, ultrafast, dissociation, dynamics, lifetime, pyrrole, phenol

In-airway molecular flow sensing: developments and applications

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A laser based device has been developed that provides highly accurate measurements of flow and O₂, CO₂ and water vapour concentrations every 10 ms. The flow is determined by a novel flow meter within which laser absorption spectroscopy is utilized to determine the concentrations of the gases. The CO₂ and H₂O concentrations are evaluated using direct laser absorption spectroscopy on overtone/combination transitions, whilst the reduced absorption cross sections associated with the X-A transitions of O₂ dictate that off-axis cavity enhanced laser spectroscopy is required in order to achieve the necessary sensitivity.

The purpose of this device is twofold. Firstly, this device provides, for the first time, easy, accurate, noninvasive measurement of O₂ consumption for intubated patients within critical care. The flow meter used here represents a precision improvement of an order of magnitude when compared to other respiratory flow meters. This precision, coupled with the accurate alignment of gas concentrations and flow, makes possible the determination of O₂ consumption by direct integration over time the product of O₂ concentration and flow. The precision of this device is illustrated by integrating the balance gas (N₂ plus Ar) flux and showing that this exchange is near zero. Clinical capability has been illustrated by recording O₂ consumption during an aortic aneurysm repair, with clear and discernable physiological changes being observed for the first time^[1].

The second area of application for this device resides in its capacity to generate data from which valuable parameters of respiratory health could be determined. Coupled with a mathematical model of the lung, data from this device can be used to assess inhomogeneity within a patient's respiratory system. Inhomogeneity arising from lung disease significantly impairs gas exchange; however, standard lung function tests do not assess this inhomogeneity. Our measurements of respiratory inhomogeneity are easy to make, non-invasive, and involve neither ionizing radiation nor expensive/scarcely reagents. This device therefore represents a potential screening option for mild or early onset lung disease for which current methods, such as spirometry, have been found to lack the required sensitivity.

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Keywords.

Respiration, oxygen consumption, gas exchange, medical technology, laser spectroscopy

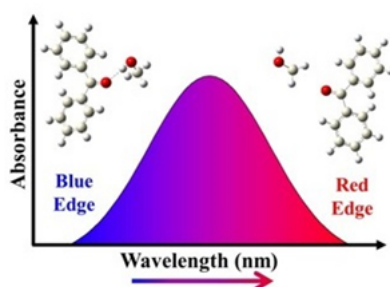
Intermolecular Hydrogen Bonding Controlled Intersystem Crossing Rates of Benzophenone

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Benzophenone (Bzp), a paradigmatic aromatic ketone, has been comprehensively studied for its intriguing photophysical and photochemical properties. Bzp shows interesting solvatochromic behaviour, in both electronic and vibrational spectroscopy [1]. The $1^1n\pi^*$ electronic transition undergoes a blue shift while the carbonyl (C=O) stretching frequency shows a red shift with increasing solvent polarity. Furthermore, in protic solvents the C=O stretching frequency shows two peaks, assigned to: i) free; and ii) hydrogen bonded (HB) carbonyls. A linear correlation was obtained for the $1^1n\pi^*$ electronic and the C=O vibrational solvatochromism, which indicates that excitation of the Bzp at different wavelengths within the $1^1n\pi^*$ electronic absorption band probes different solvation environments as seen in Fig. 1. Resonance Raman study of Bzp in protic solvents shows selective excitation of HB carbonyls at the blue side of the $1^1n\pi^*$ electronic band. This is in agreement with the **Fig. 2.** Schematic representation of electronic ($1^1n\pi^*$) excitation wavelength dependent



solvation states of Bzp in methanol (protic) solvent.

proposed hydrogen bonded mechanisms for aromatic ketones in the excited state [2]. This hypothesis is further supported by excitation wavelength dependent intersystem crossing dynamics of Bzp in methanol, as observed in femtosecond (fs) time-resolved electronic absorption spectroscopy.

Ultrafast time-resolved infrared spectroscopic [3] experiments were carried out to assign the nature of the different species formed upon photoexcitation unambiguously. Their implications for the photophysics and photochemistry of Bzp in solution will be discussed in the presentation.

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Acknowledgements: RKV acknowledges Royal Society-SERB Newton International Fellowship.

Keywords: Ultrafast Spectroscopy, Hydrogen Bond Dynamics, Photophysics, Photochemistry, Solvation.

Molecular-beam scattering of OD radicals from atmospherically relevant liquid surfaces

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The aim of the work is to study the inelastic scattering of rotationally cold OD radicals from a series of continuously refreshed liquid surfaces of interest in atmospheric chemistry using a molecular-beam source. OD radicals are produced by a pulsed DC electrical discharge of D₂O seeded in a carrier gas, and scattered at normal incidence from the liquid surface. The radicals are detected via laser-induced fluorescence (LIF) using a photo-multiplying tube and liquid light guide set-up at a fixed point above the liquid surface. This probes the internal energy distribution of the pre-collision and scattered species and the initial and final translational energies via time-of-flight. The liquid surfaces studied are the potentially reactive surfaces squalane (C₃₀H₆₂, 2,6,10,15,19,23-hexamethyltetracosane) and squalene (C₃₀H₅₀, trans-2,6,10,15,19,23-hexamethyltetracos-2,6,10,14,18,22-hexaene), with a perfluorinated polyether (PFPE, Krytox[®] 1506) used as an inert reference.

The collision energy of the incoming radicals was modified by changing the carrier gas in the molecular beam. Ne and He carrier gases were used in this experiment, which gave lab-frame collision energies of 6.1 kJ mol⁻¹ and 26 kJ mol⁻¹, respectively. Integrated OD survival probabilities from the potentially reactive surfaces were obtained by assuming 100% of OD scatters from PFPE, and taking into account the rotational distribution of the scattered species. The results were compared with previous measurements in our group, which used a photolytic source of OH at a higher lab-frame collision energy (54 kJ mol⁻¹).¹⁻³ The survival probability of squalene increases with increased collision energies, which is consistent with more thermally accommodated OD reacting via an addition mechanism at the vinyl sites on the surface. Surprisingly, the survival probabilities for squalane are relatively insensitive to collision energy over the measured range, indicating that OD at lower collision energies is more thermally accommodated at the surface, giving it more chance to react via secondary interactions, and counteracting the expected higher reactivity in primary abstraction reactions at higher energies. Further insights into the properties of the scattered species, obtained from the appearance profiles and rotational distributions of the scattered species, and from realistic Monte Carlo simulations of the appearance profiles, will be discussed.

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Keywords.

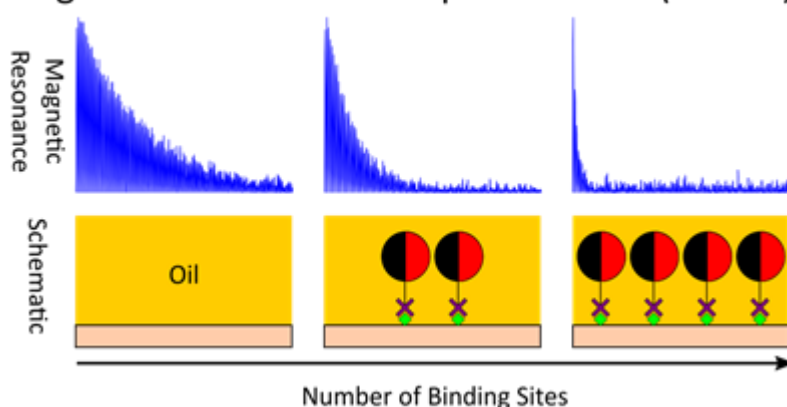
Gas-liquid interface, molecular beam, DC discharge, atmospheric chemistry,

A Magnetic Resonance Disruption (MaRDi) Technique for the Detection of Surface Immobilised Magnetic Nanoparticles

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There are numerous assays that result in a surface with bound magnetic nanoparticles (MNP) whose number is proportional to the concentration of the analyte of interest. The techniques used to explore such assays are typically complex and costly. Since the presence of such MNP disrupts the pulsed magnetic resonance signal that would normally be detected from a fluid covering the surface, we present a measurement technique to quantify such assays. In this work we identify and characterise a suitable fluid for such measurements, namely 10 cSt viscosity PDMS oil of thickness 250 μm . We demonstrate that the T_2^{eff} relaxation time from the PDMS reduces as the proportion of the surface area covered with MNP increases. Most significant however, is a linear decrease in the signal amplitude from the PDMS as a function of MNP coverage. This is observed both for the integral over 4096 echoes and also in the first echo, promising simplified console electronics for rapid measurements.

Magnetic Resonance Disruption Sensor (MaRDi)



References.

S.T. Parslow, T. Hughes-Riley, M.I. Newton, R.H. Morris, *Anal. Methods*, 2017, **9**, 1681.
DOI: 10.1039/c7ay00039a

Keywords.

Magnetic Nanoparticles; MNP; Spin-Spin Relaxation Time; T_2 ; T_2^{eff} ; Magnetic Resonance; Point of Care.

Velocity Map Imaging Studies of Metal-Containing Molecules

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Neutral metal-containing molecules and clusters present a particular challenge to velocity map imaging techniques. Common methods of choice for producing these species in the gas-phase, such as laser ablation or magnetron sputtering, typically generate a wide variety of metal-containing species, clusters and complexes. Without the possibility of mass-selection, even determining the identity of the dissociating moiety can represent a significant challenge. In recent years, this group has developed a velocity map imaging spectrometer equipped with laser ablation source explicitly for studying neutral metal-containing and other gas-phase cluster species.

Here we present an overview of our recent studies together with new photofragment imaging data for a range of transition metal-oxides including VO, CrO and MoO. Analysis of the kinetic energy release spectra at a range of photon energies allows precise determination of the ground state dissociation energies.

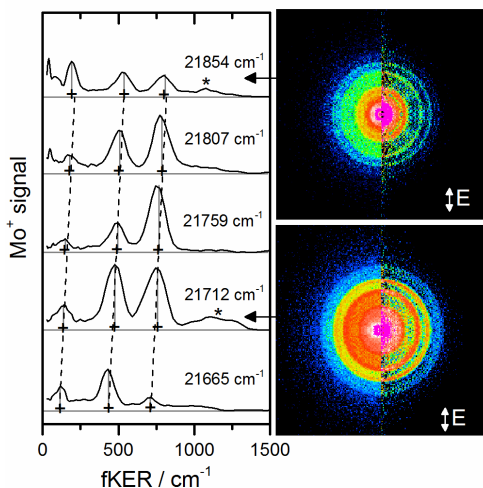


Figure 1. Mo* atom photofragment images and kinetic energy release spectra following multi-photon dissociation of MoO

TADF in Coinage Metal Complexes for Organic Light Emitting Diodes

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Heavy metal complexes containing platinum and iridium have been heavily researched owing to their application in phosphorescent organic light emitting diodes (PhOLEDs). However, their main drawback is the low abundance of these metals and consequently, alternatives are being urgently sort. This has been a recent increase in popularity of organic systems exploiting thermally activated delayed fluorescence (TADF) in the literature. Alternatively, the d¹⁰ coinage 'heavy metal' trio of gold, silver and copper offer a different route to achieving efficient TADF OLEDs.

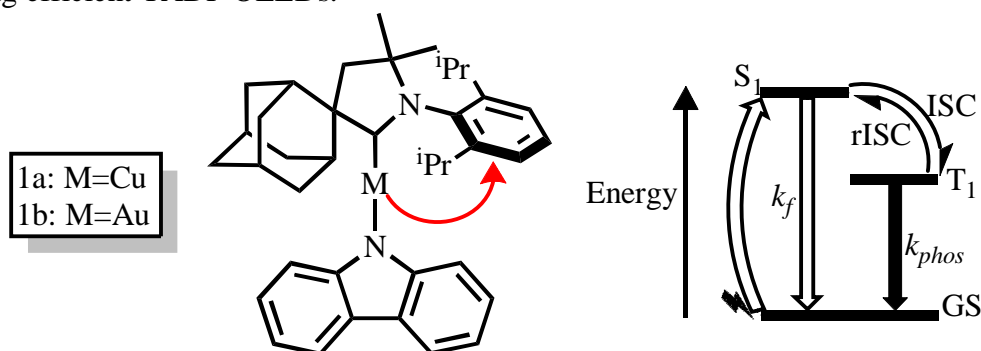


Figure 1: A schematic of the TADF process.

Here we show the results of recent work on various complexes of these coinage metals aimed at shedding new insight in the mechanism of TADF in these systems. In contrast to many organic systems, spin orbit coupling (SOC) between the lowest singlet and triplet is sufficient to describe TADF. Some complexes also show dual TADF and phosphorescence. Finally, for a specific copper and gold complex we observe a strong vibronic contribution and SOC between the S₁, T₁ and T₂. These observation are promising TADF emitters exploiting the advantages of the relativistic effects associated with heavy metals and the vibronic contribution observed in organic systems.

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Keywords.

TADF, Metal Complexes, Organic Light Emitting Diodes, Spin Orbit Coupling.

Time-resolved X-ray Spectroscopy using Direct Quantum Dynamics

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Probing ultrafast dynamics became possible with the advent of ultrafast time-resolved linear and non-linear optical spectroscopies. These studies have had a huge impact on our understanding of chemical reactions, biological functions and phase transitions in materials owing to their ability to probe, in real-time, the nuclear motion within these different types of systems. However, spectroscopy performed in the ultraviolet and visible spectral regions only probes the delocalised valence states and consequently the link between the spectroscopic observable and structure is ambiguous for systems composed of more than one nuclear degree of freedom, i.e. >2 atoms. To overcome this, the last decade has witnessed a significant research effort aimed at exploiting short wavelength probe pulses to achieve direct structural sensitivity in time-resolved pump-probe experiments. This has led to the development of time-resolved diffraction methods using X-rays or electrons and core level spectroscopies using either X-rays or electrons.

The advent of X-ray Free electron lasers (X-FELs)¹ and VUV or XUV-light generated through the process of high-order harmonic generation (HHG) is opening new opportunities for time-resolved core-hole spectroscopy. But crucially theory must keep pace with these developments². In this poster we present recent results using the direct dynamics variational multi-configurational Gaussian (DD-vMCG) method to calculate time-resolved core-hole spectra *on-the-fly*. This is applied to study the dissociation of CF₄⁺ and SF₆⁺ as recently performed experimentally³ and the photoexcited decay of pyrazine using the Nitrogen K-edge.

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Keywords.

Femtosecond X-ray Spectroscopy, Quantum Dynamics, DD-vMCG.

Experimental testing of *ab initio* potential energy surfaces: stereodynamics of $\text{NO}(\text{A}^2\Sigma^+) + \text{Ne}$ inelastic scattering at multiple collision energies

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We present the results of a crossed molecular beam velocity map imaging (CMB-VMI) study of $\text{NO}(\text{A}^2\Sigma^+) + \text{Ne}$ scattering. State-to-state resolved measurements of the stereodynamics of rotational energy transfer (RET) at mean collision energies, $\langle E_{\text{col}} \rangle$, of 523 cm^{-1} and 1309 cm^{-1} are used to test *ab initio* potential energy surfaces (PESs) for this system calculated by Pajón-Suárez *et al.* [i] and by Cybulski and Fernández [ii] (henceforth referred to as the PRRH and CF PESs, respectively). $\text{NO}(\text{A}^2\Sigma^+; v=0; N=0, j=0.5)$ is prepared by pulsed laser excitation in the crossing region of a CMB-VMI apparatus and the products of RET subsequently probed with N' -state selectivity using $1 + 1'$ REMPI via the $\text{E}^2\Sigma^+$ state. Images are recorded with the electric vector of the probe laser switched between horizontal (H) and vertical (V) polarization in order to measure the collision-induced alignment.

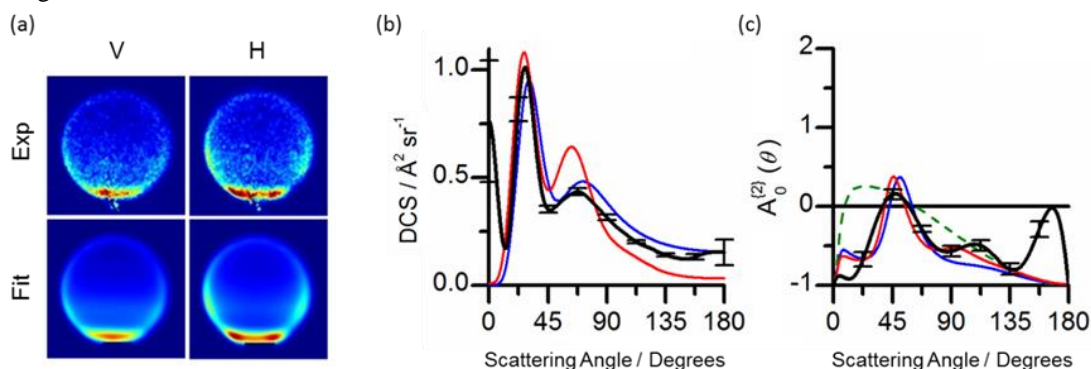


Fig 1: (a) Example experimental scattering images for probing $N' = 7$ following scattering at $\langle E_{\text{col}} \rangle = 523 \text{ cm}^{-1}$ with fits to these images. (b) DCS measured from fits to experimental data (black) with quantum scattering calculations using the PRRH (blue) and CF (red) PESs. (c) Experimentally measured $A_0^{(2)}(\theta)$ moment of the rotational angular momentum distribution (black) with quantum scattering calculations using the PRRH (blue) and CF (red) PESs. The classical hard shell 'Kinematic Apse' model prediction is also shown (green). Errors in (b) and (c) represent 95 % confidence limits obtained from fits to 8 replicate measurements.

The state-to-state differential cross sections (DCSs) and scattering angle dependent moments of the rotational angular momentum distribution have been compared with the results of close-coupled quantum scattering calculations on the two PESs. Both PESs yield calculated DCSs that qualitatively reproduce the rotational rainbow structures measured experimentally, but the scattering angles at which the rainbow maxima occur are better reproduced by the CF PES. The positions of these maxima are sensitive to the angular variation of the PES for the energies accessed experimentally suggesting that the CF PES provides a better description of the repulsive wall than does the PRRH PES. The level of agreement at $\langle E_{\text{col}} \rangle = 1309 \text{ cm}^{-1}$ is less good than for $\langle E_{\text{col}} \rangle = 523 \text{ cm}^{-1}$ in both sets of calculations, suggesting that the angular variation in the PES is less well described for the closer approaches accessed at this higher energy.

Forward scattered peaks in the DCS are experimentally measured for a range of final states, while being completely absent from the quantum scattering calculations on either PES. These features indicate the existence of an attractive well on the $\text{NO}(\text{A}) - \text{Ne}$ PES which is absent from the electronic structure calculations.

The measured and calculated moments of the rotational angular momentum distribution display deviations from a classical hard shell model of the scattering. These deviations may arise because of the significant angular variation in the gradient of the PESs for these systems.

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Investigating charge carrier dynamics in formamidinium lead iodide perovskites using time-resolved infrared spectroscopy

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Hybrid organic-inorganic halide perovskites have been the subject of intense study since the first proposal of their use as photovoltaic materials in 2009.¹ This effort has resulted in rapid progress in methodologies for the production of high quality perovskite films and increased understanding of the mechanisms behind such properties, culminating in reports of perovskite films with efficiencies of greater than 20%.² However, despite these advances, the ultrafast dynamics and mechanisms behind charge separation and transport are still contended and discrepancies in data interpretation persist in literature. Ultrafast spectroscopy is an ideal tool to elucidate the initial events in such thin films and the influence on phenomenological processes. Much of this work has focused the dynamics in methylammonium lead halide perovskite (MAPbI₃), one of the first hybrid organic halide perovskites to be used as a light harvesting and charge-separation medium. It has been demonstrated, however, that incorporation of less studied cations, such as formamidinium (CH(NH₂)₂⁺), results in narrower band gaps penetrating further into the near-IR and therefore theoretically higher efficiencies.³

We report the use of a time-resolved multiple probe spectrometer in the ULTRA facility at RAL,⁴ to probe the excited state dynamics of formamidinium lead iodide perovskite (FAPbI₃) films with and without the presence of hole and electron transport materials (spiro-MeOTAD and TiO₂), from femtosecond to microsecond timescales. 540 nm or 760 nm pumps were used to excite FAPbI₃ perovskite films followed by a 1250–1840cm⁻¹ broadband IR probe. Our samples exhibited fast (≤ 1 ns) and longer (10s of ns) lifetime components. All observed differences between the two excitation wavelengths are attributable to higher intra-band transitions for the higher energy pump. Vibrations associated with the molecular formamidinium cation showed a shorter 10s of ns lifetime component when deposited with the spiro-MeOTAD and TiO₂, indicative of faster relaxation due to charge extraction by the transport media.

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Keywords: Perovskite, Ultrafast spectroscopy, Electronic-vibrational spectroscopy, Photovoltaic materials

Electron impact total and partial ionization cross sections and kinetic energy releases for hydrocarbon species relevant to fusion edge plasmas

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The Electron Ionization Cross Section (EICS) quantifies the probability that an atom or molecule will be ionized in a collision with an electron. Accurate absolute electron ionization cross sections are needed for modelling a range of plasma processes, including fusion and industrial plasmas, as well as naturally occurring plasmas such as those found in the upper atmosphere and interstellar space [1]. We have recently upgraded an existing instrument (Figure 1 left) for measuring electron total ionization cross sections [2], and will report recent progress on these measurements, such as experimental total ionization cross section (TICS) data for an important interstellar molecule, Acetonitrile (Figure 1 right).

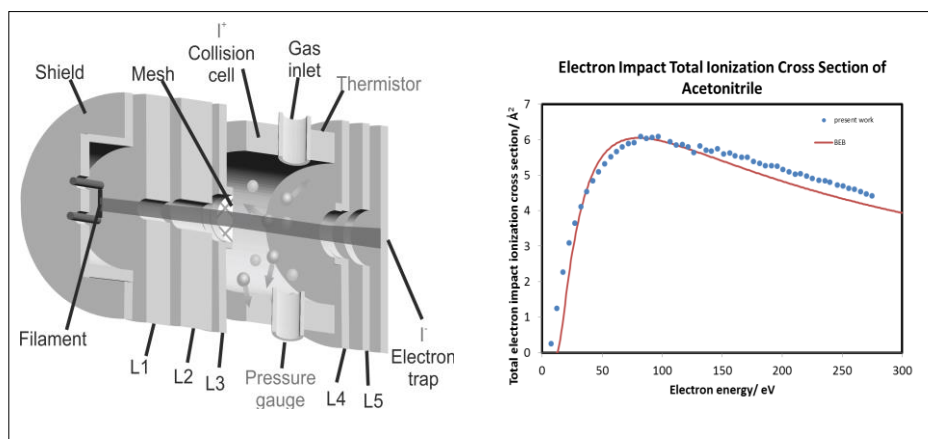


Figure 1 Left: Schematic representation of ionization cell. Right: Present experimental TICS data (dots) for Acetonitrile, together with theoretical data (line).

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Keywords.

Ionization cross-section, Electron impact ionization, Plasma modelling, Interstellar medium

Probing Optical Properties of Thiophene-Derivatives for Two-Photon Absorption

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A novel class of organic dyes, emerging as promising donor substituents in D- π -A sensitizers for DSSCs¹, were appraised in terms of linear and nonlinear optical properties. An extensive conformational analysis was performed on 2,5-dithienylpyrrole (DTP)² dyes. The absorption spectra was obtained at Time Dependent Density Functional Theory (TD-DFT) while including dynamical effects via a Wigner distribution³ in the ground vibrational state. Excited state topologies and charge transfer character of the dyes were quantified with recently developed methodologies: calculations of Φ_s index⁴⁻⁶ and Natural Transition Orbitals (NTOs)⁷. Finally, Two-photon absorption (TPA)⁸ abilities were also reported, which show significantly high cross-sections in the IR region, thus making the two organic dyes good candidates for non-linear optical applications.

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Keywords.

Two-photon absorption (TPA), 2,5-Dithienylpyrrole (DTP), Time Dependent Density Functional Theory (TD-DFT), Wigner distribution

Atomic Structure, Stabilities and Dynamics of Molecular Clusters of Cement

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Abstract

The work involves characterising the microscopic and mesoscopic structure, dynamics and mechanical properties during and after setting of ordinary (Portland) cement OPC. Cement is currently the most manufactured material worldwide and growing, as is the diversity of application for all cementitious materials in engineering, construction, medical sciences and beyond. Despite this, true understanding of the atomic-level structure and function remains scarce, particularly with respect to observed mechanical properties. Molecular cluster models based on DFT methods (Fig-1a) have generated encouraging synergies between experiment and computation. These non-periodic cluster models have no geometric restrictions, therefore are truly amorphous and dynamic (Fig-1b). The approach has successfully predicted interfacial structure and dynamics of bioactive dental cements. Hence a battery of neutron and coherent-THz techniques are being employed, guided by the theoretical results, to track the changes in structure, dynamics and functional properties over setting time, OPC and other cementitious systems.

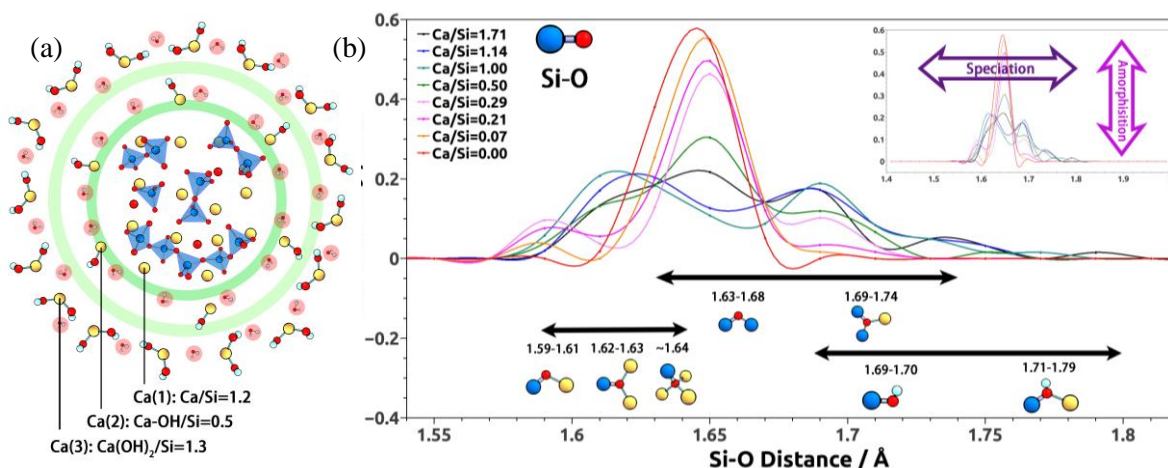


Fig. 1: (a) A cluster model of the disordered structure of the Ca-Si-Hydrate phase of cement (Ca/Si = 1.67); in agreement with structures derived from neutron scattering. (b) Radial distribution functions of the Si-O pair, for models with differing Ca/Si ratios; raised Ca-content results in increased speciation of the Si environs and effective amorphisation of the cluster.

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Keywords.

Cement, C₂S, C₃S, dynamic models, RDF, hydration, neutron scattering

Investigating the Electron Impact Resonances of PAHs

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Polyaromatic hydrocarbons (PAHs) are of significant interest because of their application to a variety of research areas including organic, medicinal and environmental chemistry. Due to their abundance in the interstellar medium (ISM), PAHs and their anions are also frequently studied within astrochemistry,¹ though questions still remain regarding the mechanism of formation and lifetimes of these ions.² By studying the excited state properties of PAHs, a greater understanding of the mechanism and dynamics of these systems can be achieved.

Theoretical methods that can be employed to study the excited states of PAHs include Time Dependent Density Functional Theory (TDDFT) and a corrected Koopmans approach. Using both methods, the excited states of neutral and anionic anthracene were characterised. The vertical excitation energies of anthracene were calculated and the lowest energy $\pi\pi^*$ states were identified. From these calculations, the accuracy and reliability of the Koopmans method and TDDFT could be evaluated. Additionally, a basis set stabilisation approach (Stabilised Koopmans Theorem) was used to differentiate between shape resonances and discretised continuum states.³

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Keywords.

TDDFT, PAHs, Excited States, Resonances

Progressive minimal basis set sampling for quantum dynamics using short-time trajectories

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Methods for solving the time-dependent Schroedinger equation basis set expansion of the wavefunction can generally be categorised as having either static (time-independent) or dynamic (time-dependent) basis functions. We have recently introduced an alternative simulation approach which represents a middle road between these two extremes, employing dynamic (classical-like) trajectories to create a static basis set of Gaussian wavepackets in regions of phase-space relevant to future propagation of the wavefunction. Here, we propose and test a modification of our methodology which aims to reduce the size of basis sets generated in our original scheme. In particular, we employ short-time classical trajectories to continuously generate new basis functions for short-time quantum propagation of the wavefunction; to avoid the continued growth of the basis set describing the time-dependent wavefunction, we employ Matching Pursuit to periodically minimize the number of basis functions required to accurately describe the wavefunction. Overall, this approach generates a basis set which is adapted to evolution of the wavefunction whilst also being as small as possible. In applications to challenging benchmark problems, namely a 4-dimensional model of photoexcited pyrazine and three different double-well tunnelling problems, we find that our new scheme enables accurate wavefunction propagation with basis sets which are around an order-of-magnitude smaller than our original trajectory-guided basis set methodology, highlighting the benefits of adaptive strategies for wavefunction propagation.

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M.A.C.Saller and S. Habershon, *J. Chem. Theo. Comput.*, **11**, 8 (2015)

Keywords.

Quantum Dynamics, Nuclear Dynamics, Computational Chemistry, Photophysics

Basis Sets for Explicitly Correlated Calculations for Heavy Group 1 (K – Fr) and Group 2 (Ca – Ra) Elements

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The slow convergence of correlated electronic structure methods with respect to the one-particle basis set can be ameliorated by the inclusion of terms that depend on the inter-electronic distance into the wavefunction [1]. Such explicitly correlated (F12) methods are becoming routine for high accuracy studies of molecules from the first two rows of the periodic table. With the Coulomb cusp described by a non-linear correlation factor, e.g., $\exp(-\gamma r_{12})$, it has been possible to optimise new basis sets specifically for F12 methods that further improve convergence and ensure that errors in the Hartree-Fock reference energy do not dominate those in the correlation treatment [2].

Developments in ultracold (<1 mK) chemistry mean accurate calculations on molecules containing heavy alkali and alkaline earth metals, such as RbCs [3], are of interest to both theoretical and experimental groups working in this area, yet there is a limited choice of basis sets for such molecules.

We report on the progress in development of basis sets for explicitly correlated calculations for the group 1 atoms K – Fr and group 2 atoms Ca – Ra. Basis sets to be used in conjunction with small-core pseudopotentials of the Stuttgart-Massey variety [4], denoted cc-VnZ-PP-F12 ($n = D, T, Q$), have been optimised. The validation of the resulting basis sets on the diatomics M₂, MO, MF and MH ($M = K, Rb, Cs, Fr, Ca, Sr, Ba, \text{ and } Ra$), at the CCSD(T)-F12b level of theory, is also presented. It is evident that correlation of the outer core electrons is vital for computed spectroscopic constants to approach existing experimental data and the basis sets developed include functions for the description of core-valence electron correlation.

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Theoretical analysis of liquid exfoliation of copper based metal organic frameworks

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The exfoliation of layered materials, metal-organic framework as a typical example, in a liquid environment is a very promising method for their performance in wide applications, for instance, energy storage and sensors. In this work, a theoretical analysis including a detailed IR intensities and vibrational frequencies has been made to study the effect of exfoliation into different coordinating solvents on copper paddlewheel motif. The theoretical calculations have been performed using Gaussian 09 density functional B3LYP method with 6-311G (d, p) basis set. The infra-red spectra measurements are compared with the corresponding experimental spectra¹. The paddle wheel systems have the formula of $[\text{Cu}_2(\text{L}^1)_4\text{X}_2]$ and $[\text{Cu}_2(\text{L}^2)_4\text{X}^2]$ where $\text{L}^1 = 2\text{-(3-methoxypropoxy) benzoic acid}$, $\text{L}^2 = 2,5\text{-bis(3-methoxypropoxy) benzoic acid}$, $\text{X} = \text{dimethylformamide, acetone, acetonitrile, water or ethanol}$. A series of investigations were employed. First, IR analysis is characterized to compare the spectra of the materials utilizing a substitution of alkyl ether chains in position 2 and 5 (linkers L^2) and the alkyl ether derivative in position 2 (linkers L^1). The results show that the differences are rather indistinct between the two substitution pattern. Therefore, the MOF utilize linker L^1 was set up for the following investigations. Second, a comparison of IR spectra of copper based motif with and with solvent exchange has been identified. The latter include exchanging the solvent molecules at the axial positions with one of the methoxy-terminated substituents as it has been hypothesized experimentally. The calculated frequency of paddlewheel motif with solvent loss is in good agreement with experiment, where there are no bands of solvents in the spectra. Moreover, replacing the $-\text{O}-\text{CH}_3$ ether side chain with alkyl groups of type $-\text{CH}_2-\text{CH}_3$ shows that the hydrophobic pattern does not agree with the experiment raising the solvent exchange hypothesis. Other studies were performed by replacing the $\text{O}-\text{CH}_3$ chain terminated with $\text{NH}-\text{CH}_3$ and $\text{S}-\text{CH}_3$ side chain.

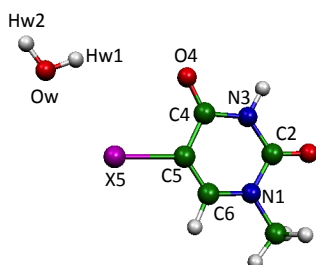
References: J. A. Foster, S. Henke, A. Schneemann, R. A. Fischer and A. K. Cheetham, Chem. Comm.2016, 52, 10474-10477

Keywords: Density functional theory, exfoliation, layered materials, Metal organic frameworks, structural flexibility, theoretical chemistry.

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

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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. Calculations were also performed in which two water molecules were present (XUr-2w). In the case of XUr-2w, halogen bonds formed for all cases except where X=F. Again there was a trend towards stronger halogen bonding down the halogen group.

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Keywords.

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

A novel path-integral Monte-Carlo approach to quantum correlation functions.

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In recent years a number of Monte-Carlo (MC), short-time Path integral strategies (1,2,3) have been devised to calculate complex-symmetrised quantum-correlation function between two operators. The so-called 'sign problem' when evaluating the phase component using MC makes the integral difficult to converge for long euclidean-times. We shall present a novel approach which replaces the phase of the correlation function by an approximate function which has only positive components and can therefore be included into the sampling function, obviating the sign-problem all together. The approximation is shown to work satisfactorily for 1D $x^n(0) x^n(t)$ correlation functions with different model system potential and which can be extended to a larger number of degrees of freedom.

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Keywords.

PIMC, complex-symmetrised correlation function.