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Conference organizers
Dr Giovanni Costantini
Dr Vasilios Stavros
Department of Chemistry
University of Warwick

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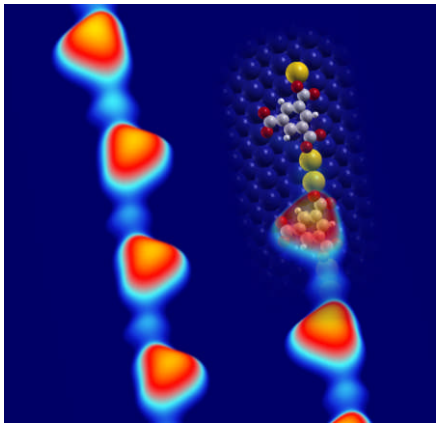
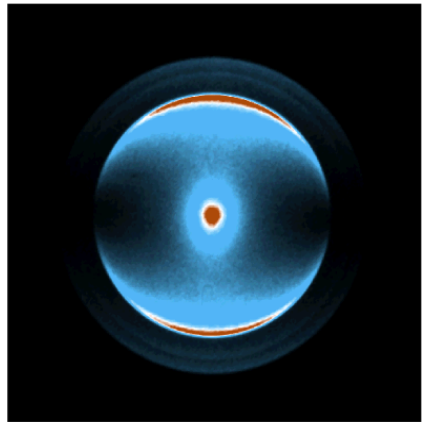
Meeting of recently appointed academics in physical chemistry

6-8 September 2010

Book of Abstracts





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PROGRAMME

Monday, September 6th (evening start)

17:00	Registration - *Radcliffe House foyer*
18:30	Prof. Mark Smith - *Welcome talk by the Deputy Vice-Chancellor*
18:45	Prof. Julie MacPherson - *The road to success in academia: things to do and things to avoid*
19:30	*Buffet dinner and wine reception*

Tuesday, September 7th

9:00	Prof. Mike Shipman - *Welcome by Head of Department of Chemistry*
9:15	Dr. Chris Veal - *How to write a successful research grant*
10:00	Dr. Katherine Holt - *Electrochemical Hydrogen Generation using Catalysts Inspired by the Hydrogenase Enzyme*
10:20	Dr. Jan Verlet - *Ultrafast dynamics of anions: from the gas- to the condensed-phase*
10:40	Dr. Cyrus Hirjibehedin - *The impact of the local environment on the Kondo screening of a high-spin atom*
11:00	Break
11:20	Dr. Mike Nix - *Directly probing ultrafast nuclear motion in solution phase photochemistry*
11:40	Dr. Paola Carbone - *From nano to meso: multiscale modelling of soft matter*
12:00	Dr. Neil Wilson - *Trying to understand chemically modified graphene*
12:20	Nick Barker - *Working with School Students - the next generation of scientists needs you!*
12:40	Lunch
14:00	Dr. Derek Wann - *Towards molecular movies: exploring reaction dynamics using electron diffraction*
14:20	Dr. Joshua Edel - *Molecular Isolation on the Micro and Nanoscale*
14:40	Dr. Wolfgang Theis - *Surface and Nanoscience*
15:00	Dr. Andrew Alexander - *Balancing research and teaching I*
15:20	Break
15:40	Dr. Philipp Kukura - *Novel tools for ultrafast and single molecule optics*
16:00	Dr. Bhavik Patel - *Electrochemical sensors to study biological signalling processes*
16:20	Dr. Marina Kuimova - *Molecular Rotors Measure Intracellular Viscosity*
16:40	Prof. Alessandro Troisi - *Starting Academics: the Rules and How to Break Them*
19:30	*Dinner*

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PROGRAMME

Wednesday, September 8th

9:00	Dr. Gareth Buchanan - *Funding opportunities for young investigators*
10:00	Dr. Iain Day - *Investigating Aggregation Phenomena using NMR Spectroscopy*
10:20	Dr. Renald Schaub - *Microscopy and Spectroscopy of Complex Materials*
10:40	Dr. Russell Minns - *Ultrafast and Ultrasmall: Molecular Movies at the Atomic Scale*
11:00	Break
11:20	Dr. Lars-Olof Pålsson - *Solvatochromism through the eye piece - Sensing of the physiological environment inside cells and other biological structures*
11:40	Dr. David Cheung - *Molecular simulation of nanoparticles at liquid interfaces*
12:00	Dr. Peter Portius - *Photochemistry of Nitrogen-Rich Compounds: TRIR and 2DIR Studies*
12:20	Dr. Ross Hatton - *Enhancing the Open-Circuit Voltage of Molecular Photovoltaics using Au Nanocrystals*
12:40	Lunch
14:00	Dr. Philip Earis - *How to write a successful research paper*
14:45	Prof. Susanne Ullrich - *The Photoprotective Properties of Adenine: Femtosecond Time-resolved Photoelectron Spectroscopy at Different UV Excitation Wavelengths*
15:30	Dr. Rebecca Notman - *Applications of molecular simulation in materials and biological science*
15:50	Dr. Cristina Flors - *Super-resolution fluorescence imaging of DNA topology*
16:10	Prof. Elizabeth Jones - *Balancing research and teaching II*
16:50	Break
17:30	Open discussion session
18:30	Prof. Mike Ashfold FRS - *Photochemistry, Diamonds and Nanorods: the past, present and future*
19:30	*Conference banquet*

Thursday, September 9th

End of Conference, departures

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Abstracts

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Electrochemical Hydrogen Generation using Catalysts Inspired by the Hydrogenase Enzyme.

Katherine B Holt

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With fossil fuel supplies running low and pressure to reduce emissions of greenhouse gases, there is increasing interest in identifying alternative fuel sources. Hydrogen is a promising new clean energy source as the product of its combustion is water. However there are problems with the generation, storage and transport of hydrogen which must be overcome if it is to find wide-spread acceptance as a useful fuel.

Hydrogenase enzymes are typically found in some bacteria and they can catalyse the reaction below with very high efficiency under mild conditions:

$$2H^+ + 2e^- \leftrightarrow H_2$$

The active site of the enzyme has been identified as an Fe-Fe cluster, which has structural analogues to well-known to inorganic compounds. In collaboration with synthetic chemists we are testing a range of complexes which mimic the structure of the active site of the hydrogenase enzyme. This presentation will show how we use electrochemical methods such as cyclic voltammetry to screen complexes for catalytic activity.

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Ultrafast dynamics of anions: from the gas- to the condensed-phase

Jan Verlet

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Our research focuses on the spectroscopy and ultrafast relaxation dynamics of anions that are pertinent to various branches of chemistry. We use a combination of time-resolved gas-phase and surface spectroscopy. In the gas-phase, anions are produced using electrospray ionisation and interrogated via time-resolved photoelectron imaging. In the condensed-phase, we study aqueous surfaces using second harmonic generation spectroscopy. Recent gas-phase experiments have focussed on the building blocks of organic conductors. Here we have elucidated the nature of the anionic excited states and lowest excited state of the neutral of the tetracyanoquinodimethane molecule and have measured the lifetime of the first excited state. Additionally, a new methodology for measuring ultrafast relaxation dynamics using photoelectron anisotropies has been used. This is particularly useful for larger and more complex molecules in which many spectroscopic features are overlapping. In the condensed-phase, we have studied the nature of the hydrated electron at the water/air interface, following recent observations from the gas-phase that excess electrons can reside on the water surface. We have shown however that at the ambient water/air surface, the electron is solvated below the dividing surface albeit within the first few nanometers of this surface.

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The impact of the local environment on the Kondo screening of a high-spin atom

Cyrus F. Hirjibehedin

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Kondo screening is a many-body phenomenon arising from the interaction between a localized magnetic moment and the conduction electrons in a metal. Spin 1/2 Kondo systems have been investigated extensively in theory and experiments. However the magnetic atoms that give rise to the Kondo effect in metals often have a larger spin, which makes the properties of the system more complex. Using a low-temperature scanning tunneling microscope, we explore the Kondo effect of individual high-spin magnetic atoms on surfaces. Using a combination of elastic and inelastic tunneling spectroscopy, we determine the spin of the atom and explore its impact on the Kondo resonance. We demonstrate that the local magnetic anisotropy plays a decisive role in the physics of Kondo screening [1]. In addition, we can tune the Kondo resonance through other parameters, such as coupling to a neighboring unscreened spin and a magnetic field [2].

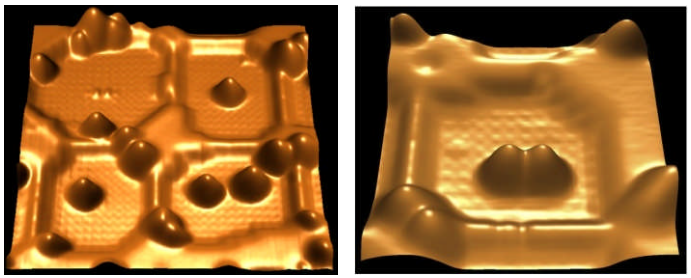

Figure: Individual Kondo screened Co atoms (left) and a spin-coupled Co-Fe dimer on a thin-decoupling Cu_2N surface on Cu(100) (after Refs. [1] and [2]).

References

[1] A.F. Otte et al., *Nature Physics* **4** (2008) 847
[2] A.F. Otte et al., *Phys. Rev. Lett.* **103** (2009) 107203

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Directly probing ultrafast nuclear motion in solution phase photochemistry

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Over the last 20 years or so it has become clear that the majority of interesting photochemistry involves non-adiabatic interactions, wherein electronic and vibrational energy are exchanged at or near points of degeneracy between potential energy surfaces. Such conical-intersections, as they are known, drive processes such as receptor isomerisation in human vision and photo-protection of DNA bases from UV radiation. In order to fully characterise such processes, it is necessary to have information about the multidimensional vibrational wavepacket as well as the electronic configuration of a system. Much progress has been made in making detailed measurements and understanding these interactions in the gas phase, but the necessary measurement in the more chemically and biologically relevant solution phase present particular challenges. It is necessary to employ ultrafast (sub-picosecond) timescales to eliminate collisional effects and to make measurements in the time domain, whilst attempting to preserve spectral resolution.

To this end, we are developing laser based methods to study nuclear motion in photochemistry, on the femtosecond timescale. The objective is to measure not only the vibrational spectrum, but also the population distribution amongst the various vibrational levels as a function of time. This new strategy takes the traditional laser based 'pump-probe' methodology and extends it using four-wave mixing probe techniques to gain specific information about the time evolution of vibrational energy in a molecular system. It has recently been shown [1] that a 2-D time vs. spectrum dataset contains all the information required for retrieval of the vibrational (nuclear) motion. The principle of recovery of the time-variant wavepacket is similar to that of 2-D phase retrieval as employed in frequency resolved optical gating (FROG) measurements of the full electric field of ultrafast laser pulses. We are currently assembling a new experiment to explore the possibilities of measuring nuclear wavepacket evolution in many degrees of freedom using this combination of techniques. We are also driving towards the generation of extremely short (sub-10fs) UV and visible laser pulses to explore photochemistry which occurs along high-frequency but chemically important bond stretching and breaking reaction coordinates.

I will give an overview of some of the principles involved and the potential for detailed nuclear dynamics in solution that this methodology promises.

References

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From nano to meso: multiscale simulations of soft matter

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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 in simulating realistic systems. 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 describes the chemical details, are often constrained in time scale up to 100 ns and limited in the number of atoms. In order to overcome this problem coarse-grained (CG) methods have been developed in the past 10 years to expand at the same time the size and the time scale of the simulations. These reduce the degrees of freedom of the model collecting several atoms in one superatom or bead.

The CG methods have showed to be a reliable way to investigate both structural and dynamical properties of complex liquids and polymer melts.

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Trying to understand chemically modified graphene

Neil Wilson

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The structure of single-atom thick materials such as graphene has implications for technological applications such as electronic and nanomechanical devices as well as for fundamental science. The chemical modification of graphene can impart functional properties such as aiding in dispersion and processing, or control over the electronic structure. The effect of chemical modification on the electronic, structural and mechanical properties of graphene is still being unravelled.

We are studying the structure and composition of chemically modified graphene as well as its electrical and mechanical properties. Despite being studied for over one hundred years the structure of graphene oxide, the source material for most chemically modified graphenes, is still far from clear. Experimental data appear to give conflicting pictures of its composition and properties. Unpicking the mystery of the structure of graphene oxide, and in particular the differences between graphene and chemically modified graphene, will be an important step in the continued development of the field.

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Towards molecular movies: exploring reaction dynamics using electron diffraction

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So much of our knowledge and understanding of the world around us comes from a consideration of the structures of molecules. But how do we know what is happening at a molecular or atomic level? Diffraction techniques can give us directly information such as the geometry that a molecule adopts, whether that geometry changes depending on the physical state of the substance, and what products are yielded when two or more molecules react. In the 21st century the new goal is to understand the dynamics of chemical reactions. This requires us not just to observe structures before and after reactions have occurred, but also to gain a deeper knowledge of how and why reactions proceed in particular ways and, ultimately, to use this information to control reactions.

The use of pump-probe experiments to study ultrafast events in chemistry, biology and materials science has already begun to revolutionise our understanding of chemical reactions. Until now the emphasis has been on using lasers for both the pump and probe phases or, more recently, using X-ray diffraction to probe the structures. Diffraction methods yield transient structures of molecules directly, which is greatly preferable to inferring structural information from spectroscopy.

My research takes this one step further and uses electron diffraction as a probe to study the structures of chemical species undergoing changes that occur on a variety of timescales. Electrons are particularly well suited to studying structures in the gas phase, where the lack of influence from neighbouring molecules (an issue with solid-state techniques) allows model systems to be studied. Electrons are efficient probes of molecular structure, with a high scattering cross section and a low proportion of inelastic scattering (which contains little or no structural information).

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Molecular Isolation on the Micro and Nanoscale

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Big advances in ultra sensitive detection of molecules in liquids at room temperature have been made since the first successful observation of single molecules. Over the past several years, high sensitivity detection has found increasing importance in biological and chemical analysis. This is a result of a need for rapid, on-line measurements at low concentrations. Importantly, most experimental observations of physical systems provide a measurement of ensemble averages, and yield information only on average properties. In contrast, single molecule measurements allow for the observation of how individual members of a molecular population behave and interact in real-time. The ability to perform such sensitive and selective measurements is extremely valuable in applications such as DNA analysis, immunoassays, environmental monitoring, and forensics where small sample volumes and low analyte concentrations are the norm. In this talk, novel micro and nanofluidic structures will be described for use in applications such as single molecule fluorescence spectroscopy within nanoporous membranes and multiphase flows.

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Surface and Nanoscience

Wolfgang Theis

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I will give a brief introduction to my research interests, which are in the fields of surface and nanoscience. One main theme is the study of epitaxial interfaces. An epitaxial interfaces is an interface between two different crystalline materials, typically a substrate and deposited film, which exhibits an atomic registry at the interface plane. These well-ordered and defect-free interfaces form the basis for high quality electronic devices, for example. My interest is both in fundamental aspects, e.g. the nature of epitaxial interfaces between quasiperiodic and periodic materials, as well as in applied aspects exemplified by a project to use epitaxial interfaces to stabilize thin films in non-equilibrium structures which can exhibit enhanced physical properties. In the later, epitaxial thin films of MnSb and related materials are stabilized in zinc blende crystal structure on semiconductor surfaces to achieve half-metallic ferromagnets for use in spintronics applications.

I conduct most experiments under ultra high vacuum conditions, exploring surfaces and film or island growth with a range of common surface science methods (low energy electron diffraction (LEED), electron spectroscopy (XPS), magnetic force microscopy (MFM)), as well as by ultra high vacuum scanning electron microscopy (UHV-SEM) and spin polarized low energy electron microscopy (SPLEEM). I have recently also started to study epitaxial interfaces by imaging cross-sectional samples with scanning transmission electron microscopy using aberration corrected instruments (ac-STEM).

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Novel tools for ultrafast and single molecule optics

Philipp Kukura

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We develop and apply optical techniques that allow us to see processes we often think about as (bio)chemists and physicists but currently cannot actually observe, measure and study experimentally. Our work can be roughly categorised into three main fields: ultrafast spectroscopy, non-linear imaging and single molecule optics.

We use a novel technique called femtosecond stimulated Raman spectroscopy to visualise structural dynamics on the femtosecond timescale. Of primary interest are aimed towards improving our understanding of the structural changes a molecule and its environment undergo after absorption of a photon. The same technique is also extended to create a broadband and background free alternative to non-linear vibrational imaging based on coherent Anti-Stokes Raman scattering. Finally, we are developing novel methodologies based on scattering interferometry aimed at significantly surpassing the temporal and spatial resolution limits in single particle tracking imposed by single molecule fluorescence. A brief introduction will be given to each of these topics.

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Electrochemical sensors to study biological signalling processes

Bhavik Anil Patel

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In biological process, small molecules such as serotonin and histamine are utilised to form a chemical communication between cells. These signalling processes are essential for the function or regulation of a biological system. They are released in small quantities (100s of molecules), in very localised regions (from 10 -30 nm fusion pores from cell membrane) in time domains of a few milliseconds [1,2]. This poses a difficult and challenging analytical problem, as the complex biological matrix is constantly evolving during the course or measurements [3]. Monitoring such signalling molecules is essential to understand biological physiology, but also in understanding how such processes alter during diseases and disorders [4,5].

In this presentation, I will focus on the development of stable and reproducible sensors for detection of serotonin release from the gastrointestinal tract. Serotonin is easily oxidised and thus is an attractive molecule for sensing, however oxidation by-products show high affinity for the electrode surface and reduced the lifespan of the electrode [6]. We have utilised various approaches including the application of boron-doped diamond electrodes as a means to overcome long-term electrode fouling [7-9]. The diamond electrode was able to detect serotonin release from isolated tissue samples during long-term recordings [7,8]. Based on initial measurements the sensors showed high stability and were able to show alterations in animal models of ulcerative colitis. I will also talk about new studies where we have also developed new experimental approaches to understand the signalling mechanism from sensor recordings by utilising a diffusion-reaction model to investigate key analytical parameters suitable for analysis.

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Molecular Rotors Measure Intracellular Viscosity

Marina K. Kuimova

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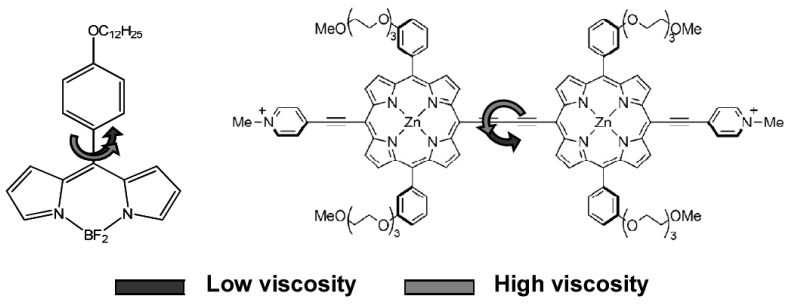
Viscosity is one of the main factors which influence diffusion in condensed media. In a cell viscosity can play a role in several diffusion mediated processes, such as drug delivery, signalling and mass transport. Previously, alterations in viscosity in cells and organs have been linked to malfunction; however, mapping viscosity on a single-cell scale remains a challenge.

We have imaged viscosity inside individual cells using fluorescent probes, called molecular rotors, Fig. 1, in which the speed of rotation about a sterically hindered bond is viscosity-dependent [1, 2]. This approach enabled us to demonstrate that viscosity distribution in a cell is highly heterogeneous and that the local microviscosity in hydrophobic cell domains can be up to 100× higher than that of water. These conclusions have been confirmed by monitoring the decay and reaction rates of short-lived excited state of molecular oxygen, singlet oxygen, $O_2(a^1\Delta_g)$, on a single cell level [3].

We have also shown that the intracellular viscosity increases dramatically during light activated cancer treatment, called Photodynamic therapy (PDT) [2]. We have demonstrated the effect of such viscosity increase on intracellular reactions by directly monitoring dynamic changes in the rates of formation and decay of a short lived toxic intermediate, crucial in PDT, singlet molecular oxygen, $O_2(a^1\Delta_g)$, in light perturbed cells [2].



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Investigating Aggregation Phenomena using NMR Spectroscopy

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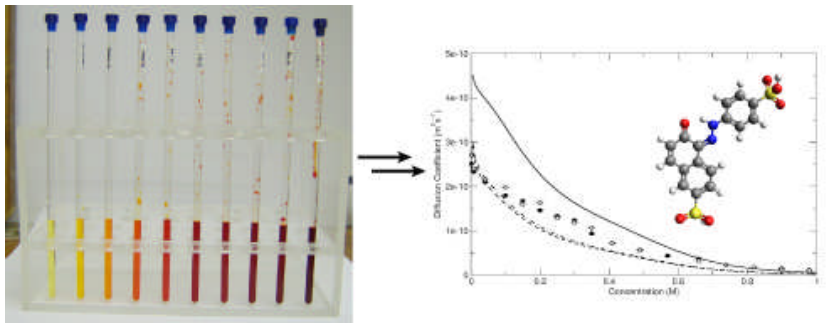
The formation of molecular aggregates from the association and assembly of smaller fragments is of key importance in a wide number of areas in chemistry and biology. For example, the assembly of peptides and proteins to form amyloid fibres is implicated in a number of disease pathologies, while the spontaneous aggregation of certain polymer molecules upon changes in physical parameters such as temperature, are finding application as novel drug delivery platforms.

In my group, we are interested in developing approaches to investigate a variety of molecular aggregation phenomena using solution-state NMR spectroscopy. Recently we have been studying the self association of the azo-dye sunset yellow. Using diffusion-ordered NMR spectroscopy and simple thermodynamic models of self assembly we have been able to characterise the size and nature of the aggregates as a function of sample composition [1].

On-going projects currently include the investigation of the interactions between dye molecules such as thioflavin T and amyloid fibrils, and the association of various aggregates, e.g. pharmaceutically active compounds, with biomimetic cell membranes.



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Microscopy and Spectroscopy of Complex Materials

Renald Schaub

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The objective of my research is to provide a better understanding of fundamental principles and mechanisms involved in the chemistry and physics of surfaces. This interest stems from a need for understanding the fundamental properties of materials in sufficient detail to be able to improve device performances for a variety of technological applications. This can be addressed by the use of scanning probe microscopies (STM, AFM) yielding high-resolution and real-space information on surface phenomena, supported by theoretical calculations (DFT). Strategies are devised to properly interrogate relevant systems at the atomic scale. For instance, surface nano-engineering is investigated with the aim of delivering concepts that can be used for the development of new devices used in, e.g., heterogeneous catalysis, photocatalysis, molecular electronics and architectures. Our application of ultra-microscopy aims at going beyond the traditional use (i.e. high-magnification topography) of such instrumentation by achieving the following: (1) local electronic and vibrational spectroscopy (STS and IETS) of single atoms/molecules; (2) atomic and molecular manipulation; (3) fast-acquisition (several tens of images per second) towards resolving dynamics at surfaces; and (4) high pressure measurements towards meaningful studies at the gas/solid interface (UHV-based). In this context, I will discuss recent studies focussing on the growth kinetics and chemical coupling of epitaxial graphene on transition metal surfaces.

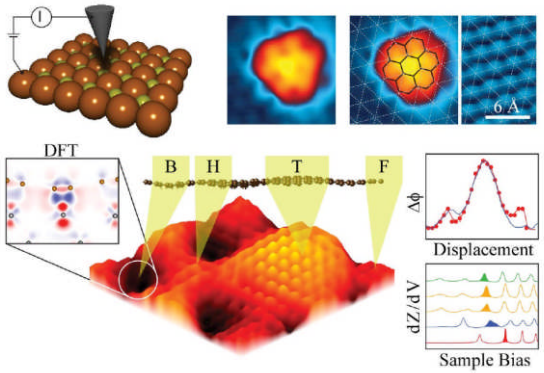

Figure: (top left) schematic representation of a tunnelling junction; (top right) size-selective carbon nano-clusters identified as precursors to the growth of epitaxial graphene; (bottom) combination of microscopy data, spectroscopy data and electronic structure calculations acquired for the graphene/Rh(111) system, illustrating the site-specific chemical coupling of the graphitic overlayer to the transition metal.

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Ultrafast and Ultrasmall: Molecular Movies at the Atomic Scale

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The fundamental motions that underlie all chemical and physical change occur on the atomic scale. With the atoms in molecules moving on the scale of a few Angstroms (1 Angstrom = 10^{-10} m) at speeds of several kilometers per second capturing these motions is technically challenging and has until recently been impossible. The advent of ultrafast laser technology made it possible to follow molecules as they react using a number of different techniques, creating its own sub-field known as femtochemistry. While the experiments have provided a wealth of knowledge and present great insight into the dynamical changes occurring during a reaction, obtaining a direct measure of how a molecule changes structurally has proven extremely difficult. The strict requirements for these measurements mean that no straightforward experimental approach currently exists and structural changes are often inferred from indirect measurements. This is far from satisfactory, leaving elementary questions in chemistry and biology unanswered. In this talk I will discuss previous work using photoelectron spectroscopy to show what information is currently attainable from femtochemistry experiments, before I discuss two emerging and complementary techniques which provide great promise for the direct measurement of how molecular structures change during a chemical reaction. The first is time resolved Coulomb explosion imaging (TR-CEI), a lab based method which combines conventional femtosecond lasers with ion coincidence imaging techniques, while the second is coherent diffractive imaging (CDI) where ultrafast scattering experiments are performed using lab or facility based ultrafast X-ray sources.

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Solvatochromism through the eye piece - Sensing of the physiological environment inside cells and other biological structures.

Dr Lars-Olof Pålsson

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Within biological systems there can be significant variations in the local environment. There are a number of different reasons behind these variations and furthermore, these are to some extent system dependent. For instance, phase separated regions in liposomes, bi-layer systems or cell membranes have very different local environments characterised by their hydrophobicity or hydrophilicity, or indeed by the presence of proteins. For bio-active systems such as intact cells the situation is very complex with many inherent variations in the physiological environment. These variations include differences in local pH, the presence and concentration of various an-ions and proteins (pX) and metals (pM), DNA etc in the different intra cellular compartments.

A full picture of the global variations in for instance bio-active cells, and the underlying factors that determine the specific local environment, is at present not available. For instance, the role of an-ions and their intra-cellular distribution is not well understood. Furthermore, the living cells response to stress and duress is likely to affect local environments and this impact is not well characterised or understood.

Any environmental change results in new or different dielectric medium. For an optical probe the impact on the chromophore is in the first instance a solvatochromic effect which could result in varying degrees of charge transfer. Secondly, more substantial impact on the excited state properties could be due to electron (ET) or electronic energy transfer (EET). This will modulate the excited state dynamics and an excellent way to monitor this is through various time-resolved emission methodologies.

In this contribution we will discuss some recent results in time-resolved microscopy obtained from different biological systems using functionalised optical probes.

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Molecular simulation of nanoparticles at liquid interfaces

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The behaviour of nanoparticles, such as synthetic quantum dots, macromolecules, and proteins, at soft (liquid) interfaces is of increasing importance in a number of disparate areas of science and technology. It has long been recognised that solid particles may adhere to liquid interfaces, which provides a convenient method for the preparation of dense nanoparticle structures, and, by using colloids or nanoparticles to modify interfacial properties, stabilise nanocomposite materials and supracolloidal structures. As the reduced dimensions of the particles makes experimental investigation challenging, molecular simulations provide a natural means for the study of these systems.

In this talk I will present my recent work using advanced Monte Carlo simulations to study the behaviour of nanoparticles near an ideal liquid-liquid interface. Comparison between the interaction determined from simulation and the predictions of macroscopic theories show that the latter provide a poor description of these interaction, underestimating both the interaction strength and range [1]. These theories become more accurate as the nanoparticle becomes larger and upon increasing the interfacial tension between the fluid components. Amphiphilic Janus particles are found to adhere more strongly to the interface [2].Such particles are also found to have significant rotational freedom and fixing the orientation of these particles, for instance through the application of an external field, is found to increase the adhesion strength further. Future work, aimed at studying the behaviour of complex nanoparticles and proteins at soft interfaces, will also be discussed.

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Photochemistry of Nitrogen-Rich Compounds: TRIR and 2DIR Studies

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Many nitrogen-rich compounds have a high energy density and produce mainly dinitrogen during their decomposition – an advantage over classical energetics such as nitro compounds, nitrates, perchlorates etc., which often generate undesired smoke and toxic decomposition byproducts. A challenge in nitrogen-rich chemistry lies in achieving the right combination of nitrogen-content and stability and gaining an understanding of the mechanisms of decomposition. Polyazido complexes of p- and d-block elements are promising candidates for efficient and controllable energy stores. Decomposition of energetic materials can be initiated by a variety of means, including mechanical shock, light and heat. The subject of our studies is to elucidate the underlying mechanisms leading to controllable photoinduced energy release and the nature of the photoproducts in nitrogen-rich hyper-coordinate p-block element ($E(N_3)_4(L_2)$, E = Si, Ge, L_2 = bidentate bpy and phen) and transition metal polyazides ($M(Cp^*)(PPh_3)(N_3)_2$, M = Rh, Ir) using time resolved spectroscopy on the ps to ns timescale.[1] The azido group (N_3) is a strong IR absorber in the mid infrared region 2200-2000 cm^{-1} (n_{asym}) and 1150-1250 cm^{-1} (n_{sym}) and hence TRIR spectroscopy is ideally suited to monitor temporal changes in solutions of these compounds. To develop an understanding of the dynamics of thermal decomposition it is necessary to investigate the redistribution of vibrational energy within a compound or complex following the triggering event. Two-dimensional infrared correlation spectroscopy, 2D IR, was used to determine the dynamics of vibrational energy distribution between different vibrational modes involving more then one energetic ligand.

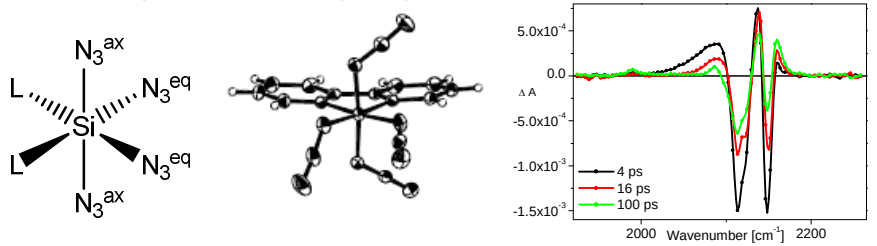

Figure: Silicon polyazide $Si(N_3)_4(bpy)$ (left), the X-ray structure (middle) and solution ps-TRIR spectrum (right).

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Enhancing the Open-Circuit Voltage of Molecular Photovoltaics using Au Nanocrystals

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For organic photovoltaics (OPVs) to realize applications effective strategies to maximize the open-circuit voltage must be developed. We show that solution processed Au nanocrystals (AuNCs) dramatically increase the open-circuit voltage (V_{oc}) of OPV cells based on phthalocyanine/C_{60} heterojunctions when incorporated at the interface between the hole-extracting electrode and the phthalocyanine donor layer. In addition, the cell-to-cell variation in V_{oc} is reduced by up to 10-fold combined with a large reduction in the light intensity dependence of V_{oc}, both of which are important advantages for practical application. This dramatic improvement in device performance is rationalized in terms of the unique properties of AuNCs.

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The Photoprotective Properties of Adenine: Femtosecond Time-resolved Photoelectron Spectroscopy at Different UV Excitation Wavelengths

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The UV photostability of biomolecules is determined by their excited state electronic relaxation mechanisms. To be effective, these mechanisms must operate on ultrafast timescales in order to dominate over competing photochemical processes that potentially lead to destruction of the biomolecule. Femtosecond time-resolved photoelectron spectroscopy (TRPES) provides unique capabilities for studying photoinduced processes in small polyatomic molecules. Changes in the PES, observed as the delay between the pump and probe pulses is scanned, can be associated with electronic configurational changes during the relaxation process. Analysis based on ionization correlations allows us to extract the electronic character of the excited states in addition to their lifetimes.

Details of the experimental setup and technique will be presented in this talk as well as our results on the deactivation pathways in the DNA base adenine following excitation by wavelengths between 200-266 nm.

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Applications of molecular simulation in materials and biological science

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Molecular simulation is a powerful tool which links the molecular-level properties of a system with its observable, macromolecular, behaviours and functions. Recent increases in computing power and developments in advanced sampling techniques mean that molecular simulation has become a valuable method that can complement and guide experimental studies. In this talk I will briefly present three case studies outlining recent and ongoing work that has applied molecular simulation to help address problems in materials and biological science.

(1) Modelling the Interactions of peptides with inorganic surfaces. The interactions of peptides and proteins with inorganic surfaces are of considerable interest due to the wide range of applications in materials science, and bio- and nanotechnology. An important goal is to fine-tune these interactions for the control of assembly of materials at the nanoscale. Recent research in this area has investigated the interactions of amino acid analogues[1] and strong and weak binding peptides with quartz surfaces.[2]

(2) Modelling the interactions of nanoparticles with biological membranes. The ability to predict how engineered nanoparticles interact with biological cells will help to address concerns of nanotoxicity and also in the design of functional nanoparticles for the controlled delivery of therapeutic molecules. It is well known that nanoparticle properties, such as size and surface chemistry, control the interactions with the membrane; however, these processes remain poorly understood. We are currently investigating the transit of silica and carbon nanoparticles across model lipid bilayers by means of free energy calculations and path sampling techniques.

(3) Molecular simulations of the skin barrier: The stratum corneum (SC, the topmost layer of the skin) represents the main barrier to the penetration of exogenous substances into the body. Work in this area aims to characterise the molecular structure and mechanical properties of the SC and investigate how this can be modulated by ingredients in a topically-applied formulation. This is of interest in the development of products that improve the appearance of the skin (personal care industry) and also for the transdermal delivery of pharmaceuticals. Much of the work to date has focused on the lipid component of the skin barrier[3,4] but we have recently begun to investigate the protein (keratin) component as well.

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Super-resolution fluorescence imaging of DNA topology

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Fluorescence microscopy is an essential tool in many aspects of science, in particular in biological and biomedical research. However, its spatial resolution is limited by light diffraction to about 200 nm, which precludes its application to the study of subcellular structures and its wide implementation in nanosciences.

Currently, approaches for improving the spatial resolution with far-field fluorescence microscopy are experiencing a spectacular expansion, and several imaging schemes have been successful in breaking the diffraction limit and achieving a spatial resolution of tens of nm. One alternative for super-resolution imaging is photoactivation-localization microscopy (PALM), also termed stochastic optical reconstruction microscopy (STORM). PALM, STORM and related techniques rely on the combination of photoswitchable fluorescent labels and a wide-field fluorescence microscope with single-molecule sensitivity. These techniques have mainly been applied to study the nanoscale organization of proteins. However, little progress has been seen to date on DNA imaging in the nanoscale.

In this talk, I will discuss my recent work on super-resolution imaging of isolated and cell DNA. A methodology to label DNA bases for these experiments using intercalating dyes and reducing buffers will be shown. In addition, by labeling chromosomal proteins with either fluorescent protein fusions or dye-labeled antibodies, I will show that it is possible to distinguish between the 10- and 30-nm chromatin fibers in vitro by using fluorescence microscopy. The results so far have important implications, as the exquisite sensitivity of fluorescence can now be combined with structural information at a very small scale

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Photochemistry, Diamonds and Nanorods: the past, present and future

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I will present an informal two part presentation. In part 1, I will recall selected personal highlights from my academic career, which serve to illustrate the important roles that (i) good fortune and (ii) recognition of opportunities have had in shaping the current research of my group. In part 2, I will outline a few of our recent research findings regarding: i) the photochemistry of gas phase heteroaromatic molecules, ii) the intricacies of diamond growth by chemical vapour deposition methods, and iii) the growth of ZnO nanorods by pulsed laser deposition methods. The presentation will end with a brief summary of future research ambitions, and a great many acknowledgements.

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