4GLS
Science Landscapes

http://www.4gls.ac.uk/

2007

Executive Summary

The small lengths and fast timescales governing many of the leading 21st century technologies means that there is now a fundamental necessity to understand the *dynamic* behaviour of physical and living matter, often in very small (nm) units, on very fast (fs) timescales.

The international scientific community recognises a need not just to determine *structure* with high precision (as may be done with a 3rd generation synchrotron radiation source), but to understand *how these structures work*.

The extraction of this dynamic information is far from trivial; it will necessitate cutting-edge experiments using multiple, synchronised sources of ultra-bright and ultra-short pulses of light. The pulse lengths need to be short enough to study bond formation and scission while the energy of the pulses must be low enough to allow very high resolution spectroscopy of vibrational and electronic motions, while limiting damage e.g. to biological material. The need is thus for an ultra-high brightness *low energy* facility that allows the use of pulsed sources in combination, built into the design of the facility from the start for the primary purpose of addressing these issues.

4GLS is thus designed to meet this science need, distinguishing it from, and yet complementing, other hard X-ray sources. It will produce short pulses of long-wavelength light up to soft X-rays with enormously high brightness. The pulse lengths will be comparable with the time taken to make or break a chemical bond, making it possible in principle to study any dynamic process occurring on a timescale as short as this fundamental step (or longer). In world terms, 4GLS will have a unique capability for these 'pump-probe' experiments, arising from built-in synchronisation of pairs of high quality pulse trains.

Following the submission of the 4GLS Science Case in 2001, continued close interaction with potential users of the source has led to the identification of five key areas of science where 4GLS will make unique contributions. These are outlined below.

- Understanding the function of biomolecules in living systems and membrane transport. Ultra-high brightness in the IR and THz will allow development of nonlinear and multidimensional spectroscopic probes capable of studying membranes and their interfaces in naturally aqueous environments.

  Examples of scientific impact: 4GLS will revolutionise our understanding of the relationship between the structure, dynamics and function of proteins, in particular membrane proteins. This will lead to a better understanding of the processes of molecular recognition and drug binding and enable the UK to exploit its strong position in genomics. In collaboration with pharmaceutical enterprises such as AstraZeneca, this will allow the UK to dominate the development of internationally competitive post-genomic applied science.

- Determining reaction pathways (in areas as diverse as enzyme processes, reactions contributing to atmospheric pollution or occurring in the interstellar medium). Multiple synchronised sources in the VUV, XUV and THz will allow reaction

initiation, the creation of short-lived transients and the study of their evolution on the timescales of bond-breaking and bond-making.

Examples of scientific impact: The mechanisms of catalytic reactions in a range of enzyme and chemical processes will be established for the first time, producing a step change in our fundamental understanding. It will be possible to monitor reactions occurring in real time on fs and ps timescales, and thus provide experimental data over timescales that match those of computer simulation techniques. It will provide insight into the design of enzymes for biotechnological exploitation, methods for manufacturing cheap clean bio-fuels, photosynthesis, flame chemistry and the management of environmental CO_2. A new understanding of free radical reactions will be obtained that will inform strategies for bioremediation. Understanding of the chemistry of transient atoms, molecules and ions and of gas-grain equilibria in the interstellar medium will be obtained that will revolutionise our understanding of the evolution of the universe.

- Studies of electron motion in atoms and molecules under extremely high electromagnetic fields and on ultrafast time scales, developing 'coherent control' of reactions and intense laser-matter interaction leading to new physics. These are enabled by seeded XUV-FEL and VUV-FEL radiation, allowing for pulse shaping, in combination with synchronised, variably polarised, VUV and XUV spontaneous radiation. High field regimes are accessed with the extremely high EM fields of up to 10^{17} W cm^{-2} generated by the XUV FEL, going beyond what is possible with high power, short wavelength, conventional lasers today.

  Examples of scientific impact: Control of competing reactive and non-reactive relaxation channels in molecular systems will be achieved through exploitation of phase, amplitudes, and polarization. A new understanding of the electron dynamics and electron-nuclear couplings that influence observed chemical outcomes will be achieved. Profound insight into the influence of the surrounding media on quantum selectivity (of importance to coherent control in biological systems) will be obtained. Experimental data will be gathered to test theoretical models of intense laser-matter interaction with impact in laboratory astrophysics, energy production and defence.

- Developing new nanoscale devices through understanding electron charge and spin transport. High brightness synchronised sources in the IR, VUV and XUV enable pump-probe interrogation and measurements of electron and spin dynamics and allow nanoscale dynamic imaging.

  Examples of scientific impact: An atomic scale correlation of chemical and electronic structure in advanced materials for electronics and photonics will be achieved. It will be possible to determine (for example) the spin-resolved electronic structure of a single nanoparticle. The mechanisms of ultra-fast charge and spin transport across boundaries will be determined, advancing the development of excitonic solar cells, optoelectronic nanomaterials such as high *k*-dielectrics and hybrid materials for spintronics.

- Development of new dynamic sub-cellular imaging techniques to improve the early recognition of changes induced in living cells by disease and cell response to

pharmaceuticals. This is made possible by the ultra-high brightness of the FEL sources and of the spontaneous THz radiation, combined with the ability to generate short-pulsed X-rays by laser-electron beam interaction.

Examples of scientific impact: This will provide insight into the mechanisms by which viruses enter cells, determine the safe limits of human exposure to THz radiation and may lead to novel therapies based on the use of THz to modify cell behaviour and to new methods of protein separation and analysis based on non-destructive ablation using high power THz radiation. It will open a new window in the understanding of a wide range of human disease including: arthritis, cancer, Alzheimer's disease, Creutzfeldt-Jakob disease, inflammation and congenital disorders, HIV and malaria. Such investigations will inevitably involve the medical community and research physicians across the community towards working collectively towards disease prevention, therapy and cure.

These areas span the key challenges facing us today in energy, lifelong healthcare and nanotechnology.

In addition to the above five key areas, there are speculative yet potentially high-impact areas of sub-atomic physics enabled by the 4GLS facility allowing for serendipitous discoveries. One such possibility is finding the origins of 'hidden dark matter' in the universe by allowing intense polarised electromagnetic fields from the 4GLS facility to couple, in presence of a high static magnetic field, to the candidate fundamental particles (e.g. axions) responsible for the hidden mass of the universe.

In world terms, 4GLS is complementary in its scientific compass to Diamond, the ESRF, XFEL and to tabletop laser sources. In terms of the European 'mid-range' FEL projects, 4GLS is unique in offering multiple sources of light, and in particular, short-pulse SR from an ERL for use in combination with seeded FEL sources. The science programme of 4GLS is substantially broader (particularly in the biological sciences), arising from the wider photon energy range and ability to combine sources of widely different frequency.

The extraction of dynamic information from systems undergoing change is far from trivial, and will require cutting-edge experiments using precisely synchronised light sources. It is necessary to begin building a user community with the right technical skills long before 4GLS is delivered. To this end, members of the community who wish to carry out the science programme of 4GLS are actively exploiting FEL sources around the world as they come on stream. These include FLASH at Hamburg, the JLab energy recovery IR FEL, the Vanderbilt IR FEL, and the European IR FELs (CLIO and FELIX). Some early results of key importance to the 4GLS science programme have been generated.

The user base of 4GLS when fully developed is estimated to be some 920 scientists. The proposal brings together two previously rather independent communities, the 'SR' community and the 'laser' community, and allows the synergies between SR and laser sources to be exploited to the full in dynamics experiments. It is envisaged that the international usage of the 4GLS source will be at least 25%. Throughout its genesis, the 4GLS proposal has enjoyed support from a wide community of UK and international scientists. Three annual 4GLS User Consultation Meetings and numerous more

specialist workshops (including industry conferences) have been held; details may be found at www.4gls.ac.uk. This has led to a process of continuous updating and evolution and of the science case, accompanied by some refinements in the source design to accommodate the new scientific compass. A number of Flagship Science Proposals for the source have been developed, and a précis of each is presented in Part B of this volume.

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1. Introduction

1.1 Background and context

In this volume, we present a summary of the anticipated science impact of the UK's Fourth Generation Light Source Project, 4GLS.

The 4GLS proposal arises from the fundamental requirement to understand the *dynamic* behaviour of matter, often in very small (nm) units, on very fast (fs) timescales. 4GLS is a suite of accelerator-based light sources designed to meet this science need. It will provide state-of-the-art free electron laser (FEL) and *short pulse* synchrotron radiation covering the THz to soft X-ray regime. The 4GLS proposal is the first world proposal to combine energy recovery linac (ERL) and FEL technology in a multisource, multiuser facility. The facility is uniquely suited to *pump-probe* experiments, probing dynamics on timescales down to 100 fs or better. This is because of the natural synchronization that arises from combining sources that originate from the same electron bunch, and is a significant advantage over 'stand-alone' FEL sources. The emphasis is on providing high quality output (in terms of stability, pulse-to-pulse reproducibility *etc*.) from synchronised multiple sources.

The Science Case for 4GLS was presented by the UK and international scientific community in December 2001, and is available at www.4gls.ac.uk. It passed through Peer Review (organised by EPSRC acting on behalf of RCUK) in April 2002, and the project was allowed to pass to Gateway 1 (Business Justification) of the UK OGC 'Gateway Process' for assessing large-scale projects. The documentation prepared for the business justification assessment is summarised in the 4GLS Business Case, presented in October 2002. Following OGC assessment in November 2002, the project was given a 'green light' to proceed to the next stages of the Gateway Process. In April 2003, funds were awarded by DTI and CCLRC for the construction of an energy recovery linac prototype source, ERLP. This project is currently nearing completion at STFC Daresbury Laboratory.

The scientific programme that is proposed for 4GLS has been continuously developed since 2001 in the light of advice from the 4GLS International Advisory Committee and in close consultation with the user community through regular meetings of the 4GLS Steering Committee. A series of focused workshops and annual meetings of the potential user community have also been held. Details of these meetings are available at the 4GLS website www.4gls.ac.uk. Useful advice on aspects of the scientific programme relevant to the needs of industry has been obtained from 4GLS industry conferences in 2004 and 2007, and from the 4GLS Industrial Advisory Board. These developments have led to a process of continuous updating, evolution and refinement of the science case, accompanied by matching refinements in the source design to accommodate the new scientific compass. In particular, through the 4GLS Steering Group, various consortia of users have presented proposals to their peers for the key science to be carried out at 4GLS, and a number of these have been developed into Flagship Science Proposals for the facility.

A summary of the current Flagship Proposals is contained in this volume. The document is thus not intended as a complete statement of all that can be accomplished

with 4GLS - as some of this is as yet unimagined - but rather to give a vision of the scientific impact of 4GLS.

Developments in the science programme have been carried out synergistically with the design of the source. In April 2005, funds were made available to commence design work for the 4GLS facility, and in April 2006 the first output of this process, the 4GLS Conceptual Design Report was published. This is available at www.4gls.ac.uk. The outline of the design concept contained in the CDR will be followed by a detailed Technical Design Report (TDR), planned for March 2008. In the TDR document, we will move on from the concept developed in the CDR to a proposal that includes experimental details of specimen beamlines, endstations and detector developments.

1.2 The structure of this volume

This document is presented in two parts. In Part A, we give a summary of the scientific impact of 4GLS in five main areas, and indicate the correlation of the Flagship Programmes to these themes. We discuss the complementarity of the science programme with that at other existing and planned sources and the ways in which the 4GLS community is already making use of new sources as they come on stream to carry out 'precursor' experiments. In Part B, we give a précis of each of the current Flagship Programmes. Each is supported by more extensive documentation, available online through the 4GLS Project Office.

2. Science Overview

2.1 The Scientific Impact of 4GLS

The small lengths and fast timescales governing many 21st century technologies means that there is now a fundamental need to understand the *dynamic* behaviour of matter, often in very small (nm) units, on very fast (fs) timescales.

For example, semiconductor device structures based on silicon are set to become so small that they will operate normally in a non-equilibrium regime which makes *dynamic* carrier distribution measurements essential for their further exploitation. The development of spintronic logic and sensors will require nanoscale characterisation of electron spin distributions of magnetic clusters. Dynamic measurements of protein folding in realistic solutions on fast timescales are necessary to complement the 'static' structure information provided by protein crystallography in the post-genomics world. The ability to manipulate molecules using tailored light pulses is essential for exploitation of the coherent control of reactions, while the ability to follow reaction pathways and pinpoint reaction intermediates is necessary to improve our understanding of all types of industrial catalysis, particularly pharmaceutical synthesis.

The international scientific community recognises a need not just to determine *structure* with high precision (as may be done with a 3rd generation synchrotron radiation source), but to understand *how these structures work*.

The extraction of this dynamic information is far from trivial; it will necessitate cutting-edge experiments using multiple, synchronised sources of ultra-bright and ultra-short pulses of light. The pulse lengths need to be short enough to study bond formation and scission while the energy of the pulses must be low enough to allow very high resolution spectroscopy of vibrational and electronic motions, while limiting damage e.g. to biological material. The need is thus for an ultra-high brightness *low energy* facility that allows the use of pulsed sources in combination, built into the design of the facility from the start for the primary purpose of addressing these issues.

4GLS is thus designed to meet this science need, distinguishing it from and yet complementing other hard X-ray sources. It will produce short pulses of long-wavelength light up to soft X-rays with enormously high brightness. The pulse lengths will be comparable with the time taken to make or break a chemical bond, making it possible in principle to study any dynamic process occurring on a timescale as short as this fundamental step (or longer). In world terms, 4GLS will have a unique capability for these 'pump-probe' experiments, arising from natural built-in synchronisation of pairs of high quality pulse trains.

Following the submission of the 4GLS Science Case in 2001, continued close interaction with potential users of the source has led to the identification of five key areas of science where 4GLS will make unique contributions. These are described below.

2.1.1 *Understanding the function of biomolecules in living systems and membrane transport.*

Ultra-high brightness in the IR and THz will allow development of nonlinear and multidimensional spectroscopic probes capable of studying membranes and their interfaces in naturally aqueous environments.

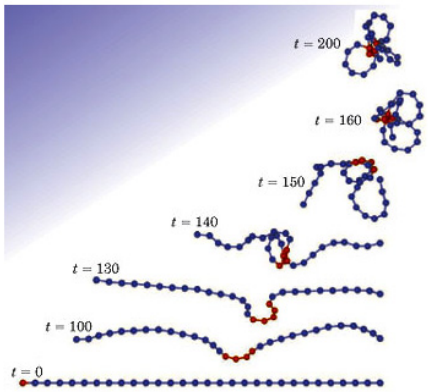

Figure 2-1 A biopolymer chain buckles and folds on itself due to an instability produced by a nonlinear localized mode (see S. F. Mingaleev et al. Europhys. Lett. 59 403 (2002)). These modes can be generated using high field THz light. (Reprinted with permission from Physics Today Jan. 2004 p49, copyright 2004, American Institute of Physics)

Examples of scientific impact: 4GLS will revolutionise our understanding of the relationship between the structure, dynamics and function of proteins, in particular membrane proteins. This will lead to a better understanding of the processes of molecular recognition and drug binding and enable the UK to exploit its strong position in genomics. In collaboration with pharmaceutical enterprises such as AstraZeneca, this will allow the UK to dominate the development of internationally competitive post-genomic applied science.

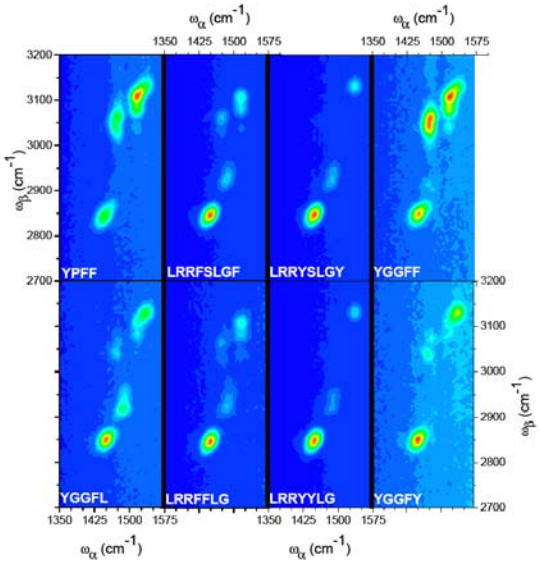

Figure 2-2 A demonstration of 2-dimensional infrared spectroscopy (2DIR) in yielding the fingerprint of some small fragments of peptides. The intensity of these features corresponds to the proportion of phenylalanine or tyrosine composition of the peptides referenced against the number of methylene groups in the peptide. Reproduced with permission of D Klug.

Flagship programmes:

- Biocatalysis, photosynthesis and membrane proteins (section B-7)
- The relationship between protein structure, protein dynamics and protein function (section B-8)
- Molecular assemblies in the extra-cellular matrix and cell signalling (section B-9)

- Reaction dynamics of excited states and free radicals in chemistry and biology (section B-6)

2.1.2 Determining reaction pathways.

This encompasses areas as diverse as enzyme processes, reactions contributing to atmospheric pollution and occurring in the interstellar medium. Multiple synchronised sources in the VUV, XUV and THz will allow reaction initiation, the creation of short-lived transients and the study of their evolution on the timescales of bond-breaking and bond-making.

Examples of scientific impact: The mechanisms of catalytic reactions in a range of enzyme and chemical processes will be established for the first time, producing a step change in our fundamental understanding. It will be possible to monitor reactions occurring in real time on fs and ps timescales, and thus provide experimental data over timescales that match those of computer simulation techniques.

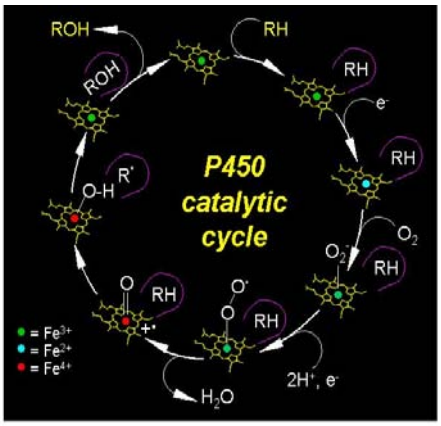

Figure 2-3 The proposed catalytic cycle of cytochrome P450 redox enzyme. RH represents an organic substrate, ROH the product of hydroxylation. Two electrons and two protons are delivered to the P450 haem at strategic points in the cycle. (N Scrutton, University of Manchester, reproduced with permission.)

It will provide insight into the design of enzymes for biotechnological exploitation, methods for manufacturing cheap clean bio-fuels, photosynthesis, flame chemistry and the management of environmental CO_2. Reactions of transients (such as free radicals and ions) contributing to pollution creation and removal in the biosphere will be understood at a mechanistic level hitherto impossible, allowing the development of strategies for pollution removal and reduction, bioremediation and improvement in the efficiency of hydrocarbon combustion.

*Figure 2-4 Improving the efficiency of hydrocarbon combustion: molecular beam mass spectrometry combined with VUV photoionisation in the study of transient species in flames at the ALS, LBNL (Science **308**, 24th June 2005, reproduced with permission of Science and Sandia National Laboratories).*

A new understanding of the interactions of gas molecules and ions with intense photon fluxes will be obtained that will revolutionise our understanding of stellar coronae, massive star evolution, planetary nebulae, cooling flows in galaxies, active galactic nuclei and the accretion disks around black holes. Fundamental parameters will be provided for theoretical models, allowing direct comparison between calculated astrophysical parameters and data from spectroscopic missions. An understanding of gas-grain equilibria in the interstellar medium will be obtained that will revolutionise our understanding of the evolution of the universe

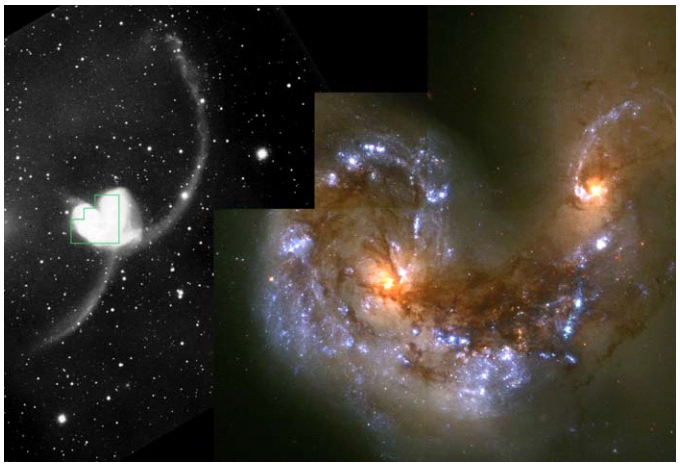

Figure 2-5: Left panel: A ground-based telescopic view of the collision between the Antennae galaxies (known formally as NGC 4038/4039) - so named because a pair of long tails of luminous matter, formed by the gravitational tidal forces of their encounter, resembles an insect's antennae. The galaxies are located 63 million light-years away in the southern constellation Corvus.
Right panel: A Hubble Space Telescope image of the galaxy cores. The sweeping spiral-like patterns, traced by bright blue star clusters, shows the result of a firestorm of star birth activity which was triggered by the collision. Much of the oxygen and carbon in the Universe is produced in such regions. The young, massive stars cause the regions to be dominated by highly ionizing far-UV radiation. Credit: Brad Whitmore (STScI), and NASA

Flagship programmes:

- Reaction pathways in catalytic chemical processes (section B-5)
- Reaction dynamics of excited states and free radicals in chemistry and biology (section B-6)
- Biocatalysis, photosynthesis and membrane proteins (section B-7)
- Origins (section B-3)
- Probing the low energy photoresponse of atomic nuclei (section B-4)

2.1.3 Studies of electron motion in atoms and molecules

This includes studies of electron dynamics under extremely high electromagnetic fields and on ultrafast time scales, developing 'coherent control' of reactions and intense laser-matter interaction leading to new physics. These studies are enabled by seeded XUV-FEL and VUV-FEL radiation, allowing for pulse shaping, in combination with synchronised, variably polarised, VUV and XUV spontaneous radiation. High field regimes are accessed with the extremely high EM fields of up to 10^{17} W cm^{-2} generated by the XUV FEL, going beyond what is possible with high power, short wavelength, conventional lasers today.

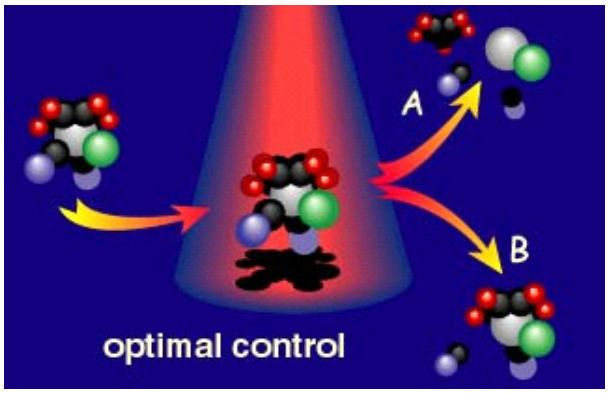

Figure 2-6 Influencing chemical reactions: shaped light pulses may be used to direct the course of a chemical reaction by quantum chemical control. (Gustav Gerber, University of Würzburg)

Examples of scientific impact: The ability to control chemical reactions, by creating coherent state populations and exploiting quantum interference effects will be developed. Control of competing reactive and non-reactive relaxation channels in molecular systems will be achieved through exploitation of phase, amplitudes, and polarization. A new understanding of the electron dynamics and electron-nuclear couplings that influence observed chemical outcomes will be achieved. The ability to control chemical reactions, by creating coherent state populations and exploiting quantum interference effects will be developed. 4GLS offers unique opportunities for pre-alignment and state selection of large molecules in this work that could ultimately lead to new routes to chiral biomolecules. Profound insight into the influence of the surrounding media on quantum selectivity (of importance to coherent control in biological systems) will be obtained. Experimental data will be gathered to test theoretical models of intense laser-matter interaction with impact in laboratory astrophysics, energy production and defence.

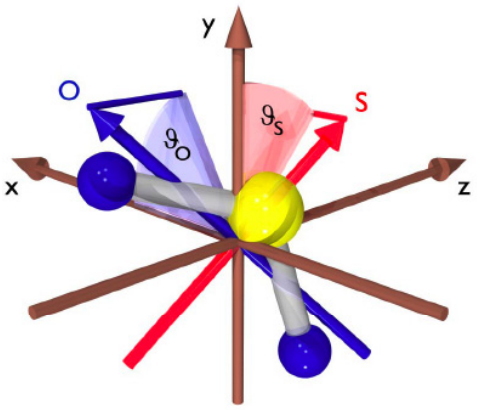

Figure 2-7 Field-free molecular alignment of SO_2 molecules using two time-separated fs laser pulses of perpendicular polarisation – the first produces 1D alignment of the most polarisable axis of the molecule, at which point the second produces a torque about this axis that brings the seond most polarisable axis of the molecule into alignment with the field of the second laser pulse. Adapted from Lee et al., Phys. Rev. Lett., **97**, 173001 (2006), *reproduced with permission of J Underwood.*

Flagship programmes:

- Electron dynamics of the chemical bond (section B-1)
- Quantum chemical control (section B-2)

2.1.4 Developing new nanoscale devices through understanding electron charge and spin transport.

High brightness synchronised sources in the IR, VUV and XUV enable pump-probe interrogation and measurements of electron and spin dynamics and allow nanoscale dynamic imaging.

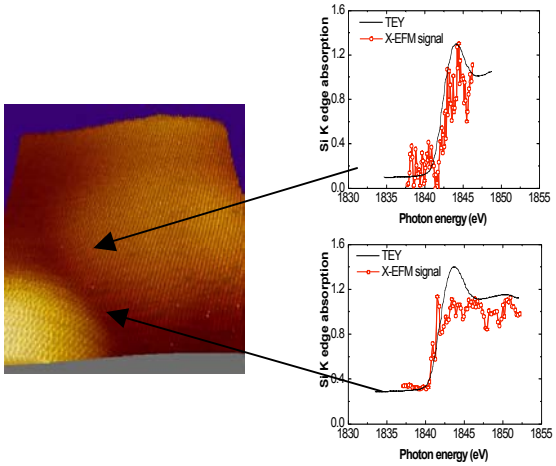

Figure 2-8: Local variations in chemistry in a 2 nm thick Hf silicate (a high k-dielectric), probed using a scanning probe microscope tip in recent experiments at the APS. The marked locations are separated by 4 nm. These so-called '3rd generation oxides' are contenders for use as gate dielectrics in CMOS technology as the Moore's law technology 'brick wall' is reached. (B Hamilton, reproduced with permission.)

Examples of scientific impact: An atomic scale correlation of chemical and electronic structure in advanced materials for electronics and photonics will be achieved. It will be possible to determine (for example) the spin-resolved electronic structure of a single nanoparticle. The dynamics of charge and spin carriers in microdevices and their transport across boundaries will be probed in real time on ps and fs timescales. This will allow, for example, fast charge dynamics at critical wide-gap interfaces (such as Si/SiO_2 or 3rd generation oxides, such as Hf silicate) to be understood in a way not currently possible. This understanding is essential to continued future exploitation of silicon technology as miniaturization continues and will advance the development of excitonic solar cells, optoelectronic nano-materials and hybrid materials for spintronics.

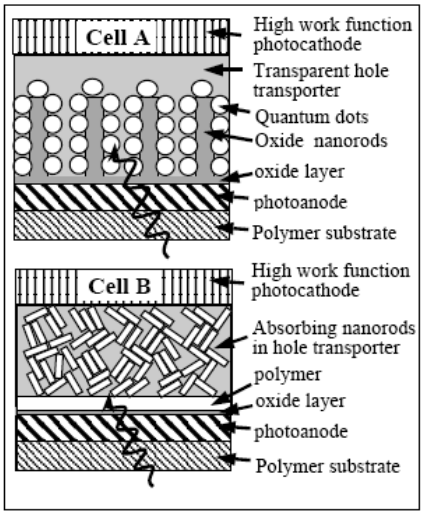

Figure 2-9 Examples of so-called 'third generation' hybrid polymer solar cell designs for rooftop microgeneration, illustrating the complexity of the next generation of microdevices. (David Binks, reproduced with permission).

Flagship programmes:

- Atom scale correlation of chemical and electronic structure in solids (section B-12)
- Spin@4GLS (section B-11)
- Many-body properties of solids (section B-13)

2.1.5 Development of new dynamic sub-cellular imaging techniques to improve the early recognition of changes induced in living cells by disease and cell response to pharmaceuticals.

The imaging of sub-cellular structures in *live* cells is made possible by the ultra-high brightness of the FEL sources and of the spontaneous THz radiation, combined with the ability to generate short-pulsed X-rays by laser-electron beam interaction.

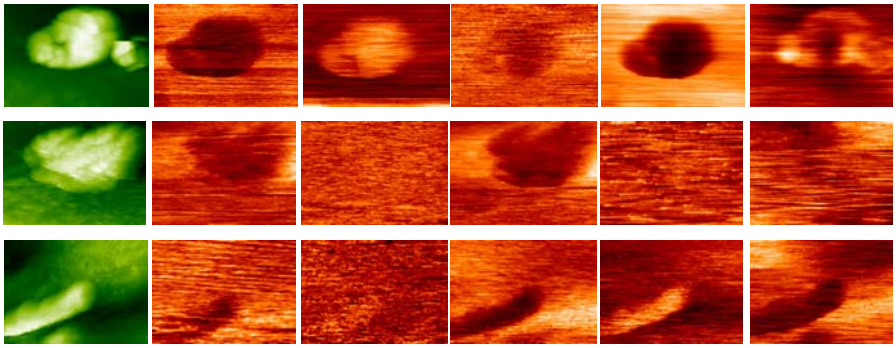

Figure 2-10: Scanning near-field techniques used with the Vanderbilt University IR-FEL source to analyze the distribution of functional groups in a single cell with a resolution well below the diffraction limit. The lefthand column shows topography images for HaCat (top), pancreatic (middle) and Cos 7 (bottom) cells, with the corresponding IR images at frequencies from 6.1 μm (amide C=O stretch) to 8.05 μm (phosphorus stretch) shown to the right. (Antonio Cricenti, ISM-CNR, Roma-Italy and Vanderbilt University, Nashville, USA, reproduced with permission.)

Examples of scientific impact: Functional dynamic imaging of *live* cells will be possible at 30 – 50 nm resolution allowing mechanisms of cell differentiation, apoptosis, and interaction with pharmaceutical agents to be understood at a sub-cellular level. This work will provide insight into the mechanisms by which viruses enter cells, determine the safe limits of human exposure to THz radiation and may lead to novel therapies based on the use of THz to modify cell behaviour and to new methods of protein separation and analysis based on non-destructive ablation using high power THz radiation. It will open a new window in the understanding of a wide range of human disease including: arthritis, cancer, Alzheimer's disease, Creutzfeldt-Jakob disease, inflammation and congenital disorders, HIV and malaria. Such investigations will inevitably involve the medical community and research physicians across the community towards working collectively towards disease prevention, therapy and cure.

Flagship programme:

- Cell imaging and spectroscopy (section B-10)

2.2 Further programmes under development

The science case of a revolutionary facility such as 4GLS can never be static. New programmes are always under development. Two of these are summarised below.

2.2.1 Particle physics at 4GLS

In addition to the five key areas described, there are speculative yet potentially high-impact areas of sub-atomic physics enabled by the 4GLS facility allowing for serendipitous discoveries. One such possibility is finding the origins of 'hidden dark matter' in the universe by allowing intense polarised electromagnetic fields from the 4GLS facility to couple, in presence of a high static magnetic field, to the candidate fundamental particles (e.g. axions) responsible for the hidden mass of the universe. This proposal stems from the experimental observation in 2006 of optical rotation generated in vacuum by a magnetic field [1], leading to speculation that this might be used experimentally as a signature of a light, neutral, spin-zero particle. Experiments to probe this phenomenon, taking advantage of the high average power, coherence, low emittance beam, tunability and high polarisation of FEL beams, have already been proposed at JLab. The concept is that the FEL photon will couple to virtual photons in a high field magnet to create the spin-zero particles. These weakly interacting bosons will travel through a light shield to a second high field magnet where photons of light are regenerated. 4GLS will offer significant advantages in average power and tunability that could be exploited in a programme of low energy scale particle physics at 4GLS. This programme is under development by Professor J Dainton FRS.

2.2.2 Monitoring and therapy of diseased cells deep inside live tissue

This potential Flagship Programme is currently undergoing technical assessment and is headed by Professor O H Petersen FRS, Vice President of the Royal Society. The immediate focus of the proposal will be to study cellular processes that are important in acute pancreatitis and cancer of the pancreas and to develop new therapies for these and other conditions. There are currently no effective treatments for these diseases. Acute pancreatitis is an often fatal condition that affects about 20,000 people each year in the UK and carries an overall death rate of 5-10%. Cancer of the pancreas is the fourth leading cause of cancer death in the United States. This year approximately 32,000 Americans will die from pancreatic cancer, which has been called 'the challenge of the twenty-first century'. The proposing team currently probe diseased cells using a lab-based two-photon technique where the radiation from the photon sources is made to cross in a narrow region of the specimen giving rise to fluorescence. This geometry gives the technique its high spatial resolution and also the ability to probe cells lying deep in the tissue. The key capability that 4GLS will bring to this research programme will be the provision of intense radiation from the infrared FEL at wavelengths in the range 0.1 to 10 μm. This can considerably extend the range and tunability of the two-photon spectroscopy technique used to image cells located deep in the tissue. The extended range will dramatically increase the depth to which cells can be studied from around 500 μm using lab-based sources up to ~3000 μm. This extension of the depth that can be probed will allow future development of optical surgery with the potential to kill dangerous/cancer cells without harm to surrounding healthy cells.

2.3 Addressing 21st Century Challenges

The issue of *how to control global climate change and secure energy supplies for the future* is one of the most important questions facing us today. 4GLS can contribute both to our efficient use of fossil-based resources, and to the creation of new energy sources in several ways including:

- improving our understanding of flame chemistry leading to more efficient hydrocarbon combustion;
- providing a revolutionised understanding of enzyme catalysis leading to better biofuels and biochemical solar energy conversion;
- developing new photovoltaics and solar cells through atomic scale understanding of charge separation and
- characterising short-lived intermediates and reaction pathways of importance to the nuclear industry.

Possibly the next most important challenge facing us concerns *the lifelong healthcare of an increasingly ageing population*. Here the contribution of 4GLS may include:

- improved understanding of wound healing through conformational dynamics of the extra-cellular matrix;
- the development of new approaches to the early diagnosis of diseased states.

Maintaining the *security of our population* is an increasing challenge. Here, the huge THz output of an ERL source offers unique possibilities for the development of new approaches to THz spectroscopy, leading to sensitive detectors of drugs and explosives. Work to establish the safe limits of human exposure to THz radiation can also be carried out.

Electronics and photonics technologies currently account for 60% of the world's economy, and this figure is increasing. However, *the industry faces the so-called 'Moore's Law' brick wall*, where miniaturisation cannot continue without a radical change in technology. 4GLS provides a tool with the power to produce an atomic-scale correlation between chemistry and electronic structure and to measure the processes of fast charge and spin transport in complex devices. This will contribute to the development of new high *k*-dielectrics, UV-LEDs, excitonic solar cells and spintronic devices.

The value of manipulating intense light pulses in addressing key scientific challenges of the future has been raised in a number of recent reports. These include the US DOE Basic Energy Science 2006 'Science Grand Challenges' [2] for example:

- How do electrons move in atoms, molecules and materials?
- How does matter behave beyond equilibrium?
- How do particles cluster?

- Can we control the essential architecture of nature?
- How do we learn about small things?

These are all questions addressed by the science programme of 4GLS. These challenges are also aligned with the US National Academy of Sciences 2006 report in 'Controlling the Quantum World' [3] that lists

- Can we control the inner workings of a molecule?
- How do we control and exploit the nanoworld?

In the UK, the importance in innovation of this field was highlighted in the 2004 DTI Foresight report 'Exploiting the electromagnetic spectrum'[4]. In addition to recognising the importance of 'manufacturing with light', the report also stresses the importance to the future economy of electromagnetics in the near field and non-intrusive imaging (via THz radiation), all themes that resonate strongly with the vision for 4GLS.

2.4 4GLS – a unique capability for pump-probe experiments

A key question that currently excites the international community is to what extent femtosecond light pulses may be used controllably to initiate a specific reaction and to follow its reaction pathway. At present, the mechanisms of very few reactions are understood in any detail – measurement techniques are usually too slow to monitor the intermediates formed. In order to be able to measure properly along a reaction trajectory, we need ultra-fast (femtosecond scale) pairs of *synchronised* light pulses – one to start the reaction, and another (at a fixed time delay) to measure what has happened (figure 2-11). By varying the time delay between the pump and the probe pulse, we can measure the reaction pathway directly.

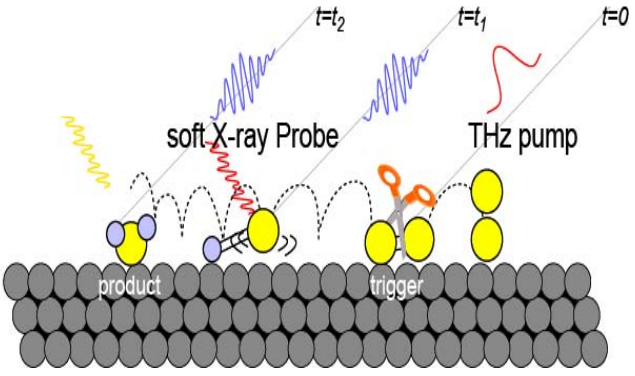

Figure 2-11: An example of a pump-probe measurement at a surface. A very low energy half-cycle terahertz (THz) pulse causes initial dissociation of a molecule (yellow) at a surface at time t_0. The reaction is followed at times t_1 and t_2 using synchronised soft X-ray photons (blue) that monitor the reaction of the dissociated atoms with new species to form the product. (Adapted from original figure by Anders Nilsson and colleagues at SLAC).

The generic term 'pump-probe' encompasses a vast range of dynamic experiments. The pump pulse may range in frequency from THz, with energies of the order kT (for example in initating a room temperature surface reaction as shown in figure 2-11, or in promoting proton transfer in enzyme catalysis [5]) to those in the VUV or XUV (for example in investigating hydrocarbon combustion [6] or reactions in the interstellar medium). The probe pulse may range in frequency from THz (for example in

measuring the time evolution of the excitonic states of a semiconductor [7]) to soft X-ray (giving chemical specificity in probing molecular intermediates, as in figure 2-11). A key advantage of 4th generation sources over tabletop sources in this application is that they offer laser-like radiation in important frequency regimes that are not well-covered by tabletop lasers. In the case of 4GLS, this includes the VUV and XUV, and the far-IR and THz parts of the spectrum. However, a far more significant advantage of 4GLS in international terms is its capability to combine pairs of naturally synchronised light sources (arising from the same electron bunch where possible), over a wide range of frequencies from THz to soft X-ray. This means that in world terms, 4GLS will have a unique capability for these pump-probe measurements, and hence for dynamic measurements. The complementarity of 4GLS with other sources is explored in more detail in the next section.

2.5 Complementarity with science at existing and planned sources

4GLS is complementary to the Diamond Light Source and the European Synchrotron Radiation Facility (ESRF) that are both based on storage rings and optimised for time average spectral brilliance at higher photon energies. The science programmes envisaged for 3rd and 4th generation facilities are very different. The main function of 3rd generation X-ray sources like Diamond and ESRF is to determine *structure* with high precision (largely through diffraction), whereas the domain of 4th generation light sources like 4GLS is to determine *how these structures function* (largely through spectroscopy). This relies on the much shorter pulse lengths that are achieved in 4th generation instruments (typically 20 - 100 fs, compared with some tens of ps from a 3rd generation source). It is very difficult to shorten the electron bunch length in a 3rd generation storage ring (to achieve short photon pulses) without sacrificing intensity. Since 'function' often implies an aggregation of moieties in the microscopic world, larger wavelengths, longer than atomic resolution hard X-rays, are needed to interrogate collective motion contributing to function - hence the complementarity to hard X-ray sources.

The 4GLS science programme is similarly complementary to those proposed for hard X-ray FEL facilities such as XFEL. The XFEL project concentrates on the creation of new states of matter, on radiation damage studies, on time-resolved X-ray diffraction, and in particular the goal of single molecule diffraction. In contrast, in 4GLS, the emphasis is on precisely controlled pump-probe measurements probing fs dynamics largely through spectroscopic (vibrational and electronic) means, in a variety of phases including aqueous environments. 4GLS can also produce non-damaging fluxes of short-pulsed radiation at energies below UV, and thus offers the potential, for example, for real-time studies of live cells with sub-cellular resolution.

In addition to FLASH (operating in the XUV), a number of linac-based soft X-ray FEL projects are in their initial stages in Europe. These include FERMI@elettra (anticipated in 2009), and FEL proposals from the BESSY and PSI laboratories. A tabulation of the parameters of the European 'mid-range' FEL projects is shown in Table 2-1. 4GLS is unique among these projects in offering multiple sources of light, and in particular, short-pulse SR from an ERL for use in combination with seeded FEL sources. It also offers clear advantages in repetition rate over most of the planned facilities, which, for example, makes possible a range of coincidence experiments aimed at exploring

electron dynamics (as illustrated in sections B-1 and B-2) that cannot be accomplished at lower repetition rate sources.

Name	Wavelength range	Repetition rate	Pulse duration	FEL concept	No. of users per year	Beamlines	No. of 8-hour shifts for users per year
FLASH	~ 6.5 - 60 nm	1 MHz pulse trains at 10 Hz	~10 - 100 fs	SASE; self seeding in prep.	~100	4	currently ~400
4GLS	SR: 0.1 cm-1 - 4 kV, IR FEL 2.5 - 200 μm, VUV FEL 124-410 nm, XUV FEL 150 - 12nm (to 4 nm in 3rd harmonic)	SR 1.3 GHz and nx4.33 MHz, IR FEL 13 MHz, VUV FEL nx4.33 MHz, XUV FEL 1 kHz	SR: 0.2 - 2 ps, IR FEL 1.8 - 5.6 ps, VUV FEL 170 fs, XUV FEL 50 fs	IR FEL: high Q cavity, VUV FEL low Q cavity, XUV FEL seeded HHG	~300	8 initially	~600
ERLP	0.1-100 cm-1 (CSR THz), IR FEL 4.3 μm	81 MHz in 100μs trains, train rate 20 Hz	1.4 ps (THz), 500 fs(IR FEL)	cavity	demonstrator ~20	2 initially	~100
FERMI	FEL1: 100-40 nm FEL2: 40-10 nm	50 Hz	~50 - 1000 fs	Seeded HG	~100's	5	> 500
BESSY-FEL	1.24 - 51 nm	25 kHz (linac CW)	< 20 fs RMS	HGHG	ca. 200	3 FEL lines with 3 beamlines each	ca. 625
STARS	40 - 70 nm (13 nm on third harmonic)	100 Hz (linac CW)	35 fs FWHM	HGHG	ca. 30	1	ca. 100
Max IV-FEL	~1-50 nm	<1kHz	~100 fs	Seeded HGHG	50-100	2-4	300
SPARX	~1-13 nm	10-50 Hz	10-100 fs	SASE - SEEDING HGHG	100	4	260
PSI-FEL	Initially 1-10 nm; upgrade to 0.1-10 nm	10-100 Hz	50 fs	Seeding	100	3 at the beginning; upgrade: 9	500

Table 2-1: Comparison of the parameters of the European FEL projects that cover the XUV and soft X-ray ranges as at May 2007 [8].

The European 'mid-range' projects have in common a capability for high fluence studies of nonlinear behaviour, multiphoton ionisation and imaging applications taking advantages of the coherence of the sources. However the science programme of 4GLS is substantially wider in scope than any of the other projects (particularly in the biological sciences, B-7 – B-10). This arises from the wider photon energy range (particularly to low energy) and ability to combine sources of widely different frequency and pulse length. The latter point is of key importance for high resolution spectroscopy, as the Uncertainty Principle provides a fundamental limit on the energy resolution that may be attained for any pulse length. For example, for a 10 fs pulse, this gives an energy broadening of 33 meV, far too large, for example, for high resolution valence band photoemission. A further complication is the space-charge effects that are encountered in attempting to use low repetition rate FELs in such experiments on solids (already encountered in attempting W 4f photoemission at FLASH [9]). The high repetition rate ps-length and lower intensity ERL synchrotron radiation pulses from 4GLS provide a much more natural choice for high resolution spectroscopy, particularly where this is dispersive. The combination with FEL radiation allows the advantages of

both to be extracted in experiments that use the FEL as a pump and synchrotron radiation as a spectroscopic probe.

The spectral range of laser radiation, which tabletop systems are able to deliver in the visible and near visible, will be greatly extended by 4GLS in the far IR, extending into the THz, and for wavelengths in the VUV and shorter. The FELs will also be very widely tunable, unlike conventional laser sources, and will offer higher repetition rates and average power levels. The science programme of 4GLS is synergetic to those proposed for ultra-fast laser facilities, for example the Astra-Artemis and ULTRA facilities at STFC's CLF. In essence, 4GLS can provide average brightness and scannability in the THz and XUV parts of the spectrum to enable studies of molecular conformational dynamics, electron dynamics and reaction pathways outside the compass of tabletop facilities. However, 4GLS has much to gain from exploitation of routes developed at these facilities to generate ultra-short (attosecond) and phase-stabilised pulses, for example in coherent control of reactions. The development of high power HHG sources is crucial to the 4GLS project and will be jointly exploited at CLF and 4GLS.

2.6 The development and evolution of 4GLS Science Case

In 1993, the Woolfson Report resulting from a review of Synchrotron Radiation in the UK [10] recommended a 'three source scenario' for the UK. High energy X-ray radiation would be provided by the UK's share in the ESRF, the bulk of X-rays for the UK would be provided by a home-based medium energy source (Diamond), and VUV radiation would be provided by a home-based low energy source. The first two recommendations of this report have now been funded, but the provision of *low energy* radiation has not so far been addressed.

Rapid developments in accelerator technology during this period have produced a 'technology pull' that exactly complements the 'science push' described above. This enables us to realise scientific goals that far surpass the original expectations for a low energy source as outlined by Woolfson [10]. Detailed consultation with potential users of low energy photons led in 2001 to the development of a Science Case [11] (available at www.4gls.ac.uk) drawing on contributions from over 200 scientists. In order to deliver this science case, the following were identified at the Business Case assessment of 4GLS in 2002 as key targets for the UK low energy SR and FEL communities [12]:

- Optimised continuous radiation in the IR to XUV region of the spectrum;
- Optimised pulsed sources of radiation in the IR, VUV and XUV regions of the spectrum;
- Multiple, synchronised sources to enable pump-probe and two-colour experiments;
- Both ultra-high brightness and ultra-high flux to enable the study of very dilute or nanoscale samples, and to allow the development of new nanoimaging techniques;

- Pulse lengths which are variable from the ps to the fs regime, with variable pulse spacing for investigation of dynamic processes.

In the five years following the peer-review of the 4GLS Science Case [11], the field has been far from static. Indeed there have been a number of key developments that have led to proposed enhancements in the 4GLS science programme and which impact on the key targets. These are summarised below:

- Increased scientific excitement in exploitation of the THz (far-IR) part of the electromagnetic spectrum in areas as diverse as coherent manipulation of semiconductor qubits, imaging and spectroscopy of biological molecules (particularly of H-bonding), and security applications. This has been coupled with the realisation that linac-based accelerators provide the world's most intense sources of broadband THz radiation [13].

- The advent of phase-stabilised few cycle attosecond pulses from tabletop lasers [14] has led to increased scientific activity in the use of photons for coherent control of processes in atoms and molecules. There is an increased demand both to combine the advantages of tabletop attosecond pulses with the power and energy ranges accessible with FEL sources and to seek progressively to shorten the pulse lengths that are provided by FEL sources.

- An increased demand from the user community for provision of soft X-rays in combination with other 4GLS sources, for example for studies of surface dynamics by soft X-ray absorption and emission initiated by a THz pump and for combined IR/soft X-ray spectroscopy to address environmental problems.

- An appreciation that short pulse broad-bandwidth hard X-rays may be readily produced in modest fluxes by interaction of electron bunches from a linac-based accelerator with pulses from a FEL or table-top laser [15].

These developments have led to a process of continuous updating and evolution and of the science case, accompanied by some refinements in the source design to accommodate the new scientific compass. The science case for a major international facility such as this can never be static. In Part B of this document we summarise the current science programmes proposed for 4GLS by the UK and international community.

2.7 Effect of phasing the 4GLS proposal on the science that can be delivered

One option currently being explored for delivery of the project is phased construction in two parts. Potential users of the 4GLS facility were consulted about the proposed phased delivery of the project at the most recent user consultation meeting on 6th July 2007, and the impact on the science programme of various phasing options was considered.

A consensus was achieved that a Phase 1 project operating with a reduced current energy recovery loop (with a VUV FEL) and a far IR FEL, but no XUV FEL would retain some world-class capability in macromolecular dynamics (Flagship proposals B-

7, B-9), sub-cellular imaging (B-10), spin/charge dynamics and many body properties (B11-B13), nuclear astrophysics (B-4), catalysis (B-5), astrochemistry (B-3) and general reaction dynamics. All these programmes would be affected by reduced flux, but in general the reduction in capability would be proportionate to the reduction in current. It would, however, be necessary for radiation in the mid-IR part of the spectrum to be provided by tabletop lasers, and even so, studies of spin injection and coherence in semiconductors (parts of B-11), multidimensional spectroscopy (such as 2DIR, B-8) and biological spectroscopy in general would be adversely affected.

The programmes in electron dynamics (B-1) and coherent control (B-2) would be severely curtailed without an XUV FEL. Neither of these high-profile programmes would be possible. This can be alleviated by the phased delivery of the XUV FEL, with operation at energies up to 30 eV in phase 1.

The user community across all areas of the 4GLS science progamme were unanimous in their support for such a Phase 1 option illustrated in Figure 2-12 that includes a reduced energy ERL loop, and low energy operation of the XUV FEL.

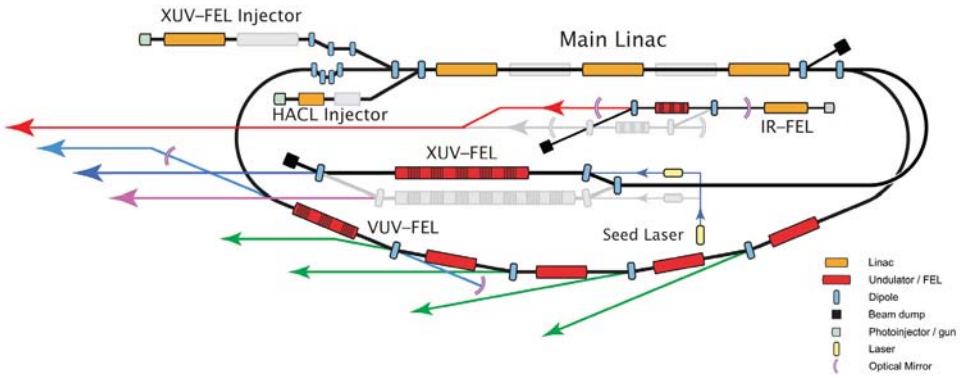

Figure 2-12: An option for phased delivery of 4GLS that retains the essential vision of combined source science. The parts of the accelerator to be delivered in phase 2 are shown greyed out. A reduced number of linac cavities is used, resulting in reduced current (10 mA) phase 1 operation of the ERL loop. The mid IR-FEL and high energy part of the XUV FEL are delivered in phase 2, together with 3 of the undulators shown in red.

2.8 Precursor experiments by the 4GLS community

The extraction of dynamic information from systems undergoing change is far from trivial, and will require cutting-edge experiments using precisely synchronised light sources. It is necessary to begin building a user community with the right technical skills long before 4GLS is delivered. To this end, members of the community who wish to carry out the science programme of 4GLS are actively exploiting FEL sources around the world as they come on stream. These include FLASH at Hamburg, the JLab energy recovery IR FEL, the Vanderbilt IR FEL, and the European IR FELs (CLIO and FELIX). Some examples of the early results generated that are of key importance to the 4GLS science programme are illustrated below.

Currently the only short wavelength FEL in operation in the world is the FLASH facility at the DESY laboratory near Hamburg, operating in the range 6.5 – 60 nm. It

will remain so until 2009 when LCLS in Stanford, USA, and FERMI@ELETTRA are expected to start operation. It is already being used for important tests of theory – for example, in the very first results from the precursor TTF-II machine, published in 2002, clusters of Xe atoms were shown to undergo a Coulomb explosion in the huge field provided by the FEL pulses at much lower fluence than is predicted by available theory [16]. More recently, Michael Meyer and his co-workers including Eugene Kennedy (4GLS International Advisory Committee) have been able to carry out pump-probe experiments of the ionisation of He using XUV photons from FLASH synchronised with a ps optical table-top laser (Figure 2) [17]. When the two pulses overlap, new 'sideband' peaks appear in the photoemission spectrum, due to the dressing of the continuum electrons with one or more optical photons. This effect may be used as a pulse diagnostic to identify the time delay between the pump and probe pulses as the intensity of the side bands varies with the degree of temporal overlap between the XUV and dressing pulses [18].

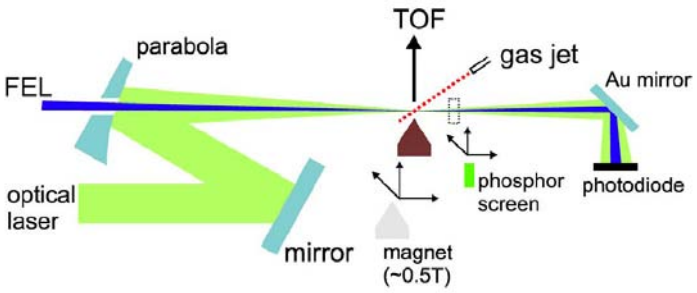

Figure 2-13: Schematic experimental arrangement for a gas-phase pump-probe experiment using the FLASH facility at the DESY Laboratory in Hamburg in combination with an optical laser. 'One-shot' experiments are possible using time-of-flight (TOF) detection of the electrons produced. M Meyer, with permission.

In more recent experiments, these workers use this approach in two-colour above-threshold ionisation of He and Xe to determine the jitter between the two independent photon sources; 20 fs XUV FEL pulses from FLASH and a 120 fs 800 nm Ti:sapphire laser. A 250 fs rms jitter is found [19].

The progress made already at FLASH is occurring at a time when rapid advances are being made in pulse-shaping using adaptive control [20] and molecular alignment using table-top lasers [21]. Field-free molecular alignment of SO_2 molecules has recently been demonstrated using two time-separated fs laser pulses of perpendicular polarisation at 815 nm – the first produces 1D alignment of the most polarisable axis of the molecule, at which point the second produces a torque about this axis that brings the seond most polarisable axis of the molecule into alignment with the field of the second laser pulse. This work has been carried out by Jonathan Underwood (co-author of sections B-1 and B-2) and his collaborators, and leads to the exciting prospects for molecular alignment at 4GLS that are discussed in these sections. Using pairs of fs pulses whose relative phase is locked on attosecond timescales, together with another fs probe pulse, Kiyoshi Ueda (4GLS IAC and collaborator in section B-2) and co-workers have observed the quantum interference of two molecular wavepackets in real time in an excited state of the I_2 molecule [22]. The evolution of this interference in real time is shown to be dependent on the relative phases of the locked pulses.

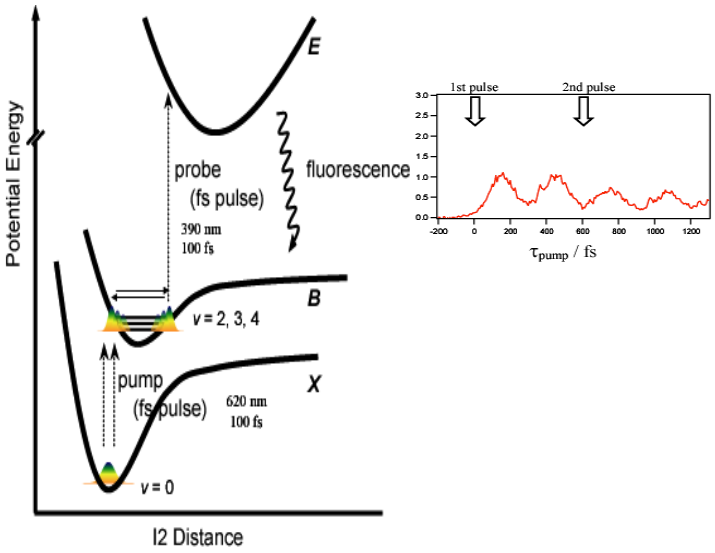

Figure 2-14: Pump-control-probe scheme for real-time measurement of wavepacket interference using fs pulses in the B-state of the I_2 molecule. The quantum interference is detected as oscillations in the fluorescence signal as a function of the time delay between the pump and probe pulses, τ_{probe} (inset, right). Reproduced with permission of Kiyoshi Ueda.

Experiments such as these begin to allow access to the phase and amplitude information contained in a wavepacket, and open up possibilities for coherent control of a variety of quantum systems – with the long-term goal of using shaped light pulses to control the direction of a chemical reaction. These experiments are possible using tabletop lasers because of the attosecond control of the relative phase of an IR fs pulse that may be achieved using nonlinear optical materials. A lack of suitable materials above around 6 eV remains a challenge to achieving the necessary pulse-shaping for quantum chemical control with VUV and XUV FEL sources. Possible approaches such as the use of phase-coherent double-pulse sequences using a VUV interferometer have been proposed, for example in the science programme envisaged in section B-2.

Many of the important reactions that the 4GLS scientific community would like to understand occur at very close to room temperature – an example is proton transfer in enzyme catalysis – and the question that then arises is can we really use a low energy IR FEL pulse to promote a specific reaction? Surely all the energy in the pulse will immediately be dissipated by internal vibrational relaxation (IVR), and we will just see a non-specific warming effect? One of the first indications that this is not the case came in 2006 from experiments by Norman Tolk (collaborator in section B-11) and his co-workers using the Vanderbilt FEL in the US [23].

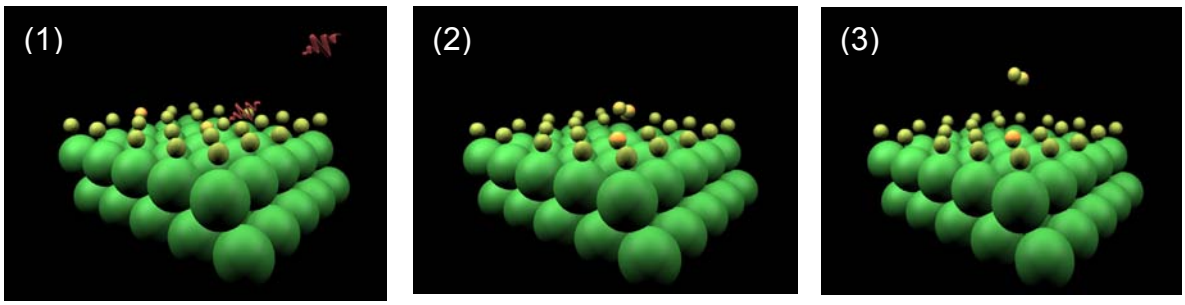

Figure 2-15: FEL-induced hydrogen desorption from a Si (111) surface. Si atoms are shown in green, and H in yellow. FEL photons come in and one photon excites one hydrogen adatom (1). Two excited neighbouring hydrogen adatoms pair up and as a result of "energy pooling" desorb associatively at room temperature (2) & (3). Reproduced with permission of N H Tolk.

These workers took a silicon (111) surface covered in hydrogen atoms, and gradually tuned the IR FEL to the frequency of the Si-H stretching vibration at around 4.8 μm. They saw a large rise in the desorption of hydrogen molecules as they hit this threshold. When they substituted deuterium for some of the hydrogen and measured the amounts of H_2, D_2 and HD emerging they discovered that the proportions were very far from what they would expect if the IR FEL energy was being dissipated throughout the system, and the reaction was occurring via the normal 'thermal' pathway. Their conclusion is that desorption of hydrogen only occurs when two adjacent Si-H bonds are simultaneously excited, and the two H atoms associate and are desorbed through 'energy pooling' (figure 2-15). These experiments are exciting as they suggest that site-selective chemistry can be carried out at room temperature with an IR FEL – perhaps leading to new methods of hydrogen storage or to room temperature refining of hydrocarbons.

Studies such as these lend credence to the idea of using THz or IR pulses to initiate or promote specific dynamic processes. An example where such studies may have immediate applicability is in experimental studies of quantum-mechanical tunnelling in proton transfers in enzyme reactions. This is one of a number of areas in molecular biology where *ab initio* calculation is ahead of experiment. Molecular dynamics simulations of quinoproteins suggest that the fast proton transfers observed in oxidative deamination occur through proton transfers mediated by a 'promoting vibration' [5] that acts to narrow the activation barrier to reaction and thus enhance tunnelling. The nature of the promoting vibration (whether short or long-range) is controversial. The relevant frequencies lie in the far-IR/THz, so the highly intense broadband THz radiation provided by energy recovery linac (ERL) sources such as that at JLab, US [13], or ERLP should provide the ideal source for a new generation of non-damaging macromolecular dynamics experiments. Indeed a programme of exploratory THz spectroscopy of biomolecules at Daresbury and JLab, has already been funded by EPSRC Lifesciences Initiative. This is headed by Nigel Scrutton (author of flagship programme B-7), with collaborators Peter Gardner (University of Manchester), Gwyn Williams (JLab) and Mark Surman (STFC Daresbury Laboratory). This has already yielded the world's best THz spectra of a small biomolecule (uric acid) at 0.5 cm^{-1} resolution from the SRS, and in May 2007, the first experiments at JLab commenced – with the key observation that the intense THz radiation from the energy recovery source could penetrate aqueous samples to depths of at least several hundred microns.

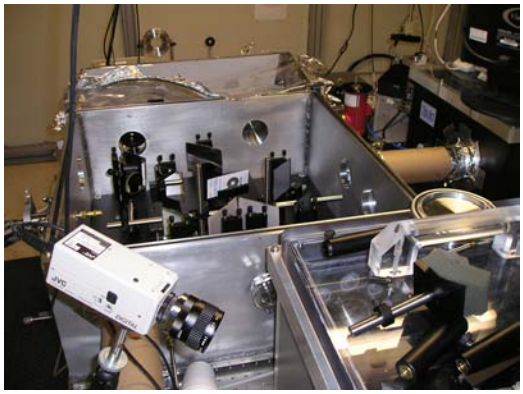

Figure 2-16: The JLab high power THz spectrometer, being used by the UK community to penetrate water to probe and promote low frequency modes of enzymes in their active environment.

The 4GLS prototype, ERLP will also have a valuable role in allowing the UK community to carry out some precursor experiments. ERLP has pulsed sources of light in three frequency ranges; terahertz, mid infrared and X-rays. In the THz range, ERLP will be the most intense broadband source in Europe. In order to enable some early science demonstrations of the potential of an ERL source, the 4GLS team have obtained a £2.9 M award from the Northwest Science Fund. This has three inter-related components:

i) combining a TW laser beam with the relativistic electron beam of ERLP to generate short pulses of X-rays;
ii) a pump-probe activity utilising combined fs laser/SRS and laser/ERLP sources; and
iii) studies of the effect of THz radiation on live cells.

Under the NWSF award, this radiation will be transported from the accelerator to a tissue culture laboratory for experiments (with medical diagnostic potential) aimed at understanding how THz radiation affects live cells, and at establishing the safe limits of human exposure to THz radiation. Dynamics studies will be undertaken with the THz radiation, mid infrared light (which is generated in a cavity-based FEL) and with the fast pulsed X-rays. Electro-optics electron beam diagnostics activities in collaboration with the FLASH facility are also being carried out.

Complementing this, a number of applications to research councils have been made by the UK Community. Some of these are currently under review, and some have already been funded. For example, The University of Manchester together with Imperial College London has been awarded £1.1 M over 4 years from April 2007, from EPSRC Materials for Energy Supply Initiative, to develop and build a new high efficiency hybrid solar cell for roof-top microgeneration. Pump-probe measurements using the NWSF ultrafast laser to create an exciton and ERLP THz absorption spectroscopy to measure its time evolution provides the ideal route to measuring the charge transport and recombination routes in these prototype cells. Ultimately, work of this generic type will require 4GLS, but activities such as this lay the groundwork for the 'functional materials' pump-probe programme on 4GLS, exemplified by the proposals in section B-11 and B-12.

ERLP is essentially a very low energy demonstration machine with a research programme that is necessarily very much narrower than that of 4GLS. It is also qualitatively inferior to that of 4GLS and it is clear that while the scientific potential of the ERLP is valuable and important it is very limited in comparison with the breadth, depth and versatility of the scientific programme of 4GLS.

2.9 Breadth of the science base; the size and nature of the user community

The user base of 4GLS when fully developed is estimated to be some 920 scientists [11]. The proposal brings together two previously rather independent communities, the 'SR' community and the 'laser' community, and allows the synergies between SR and laser sources to be exploited to the full in dynamics experiments. The scientific ferment that results gives rise to ground-breaking science; but in pure 'volume' terms, it can threaten to eclipse the fact that the 4GLS facility may also be run as a CW source of very high

quality low energy synchrotron radiation, serving multiple users. A schedule of alternating periods of pulsed and CW operation is envisaged to cater fully for the needs of the community.

The 4GLS Science Case [11] was prepared by over 200 scientists from 85 institutions in 15 different countries. Around 35% of contributors were from outside the UK, and it is envisaged that the international usage of the 4GLS source will be at least 25%. Throughout its genesis, the 4GLS proposal has enjoyed support from a wide community of UK and international scientists – for example the three annual 4GLS User Consultation Meetings have been attended by 135 – 190 participants. Numerous more specialist user consultations have been held; details may be found at the 4GLS website.

The distribution of the 200+ letters of support for the Science Case in 2001 suggested that the initial user community will be broadly made up of one-third from life sciences and medicine, and two-thirds from engineering and physical science. This is reaffirmed by the distribution of interests represented at the annual 4GLS Consultation Meetings. However, recent specialist bioscience meetings indicate very clearly that interest from this community is increasing. Historically although research in biological and medical science has been a major beneficiary of the development of light source facilities, members of these scientific communities have rarely been at the forefront in proposing that they be constructed. However this is not the case for 4GLS and a significant number of scientists working in biological and medical fields have recognised very early the potential of 4GLS to facilitate for major advances. This has lead to several Flagship Proposals, described in Part B.

The 4GLS team has identified the areas where significant knowledge exchange with industry can be anticipated. These are:

- lifelong healthcare (e.g. in wound healing and early diagnosis of disease)
- energy (e.g. in design of photovoltaics, reaction pathways of radioactive intermediates, combustion chemistry)
- catalysis and fine chemicals (e.g. in understanding reaction pathways, asymmetric synthesis, multi-technique approaches)
- semiconductors, electronics and nanotechnology (e.g. in design of next generation optoelectronic nanomaterials and high *k*-dielectrics, materials for spintronics)
- security (e.g. in THz imaging and spectroscopy of drugs and explosives, wide-gap fluorescent markers)
- synchrotron technology (in collaborative accelerator and detector developments, e.g. inductive output tubes, pulse diagnostics etc.)

An industrial advisory board representing theses sectors has been formed and two industry consultations (each attended by over 100 delegates) have been held. Again, full details are available at the 4GLS website. Industrial proposals for use of ERLP are being developed.

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Part B:

Summaries of the current flagship programmes for 4GLS

July 2007

1. ELECTRON DYNAMICS OF THE CHEMICAL BOND

Leszek Frasinski (University of Reading), Jon Marangos (Imperial College London), Gareth Roberts (University of Newcastle), Ken Taylor (The Queen's University of Belfast), Jonathan Underwood (University College London)

1.1. The need to understand electron dynamics

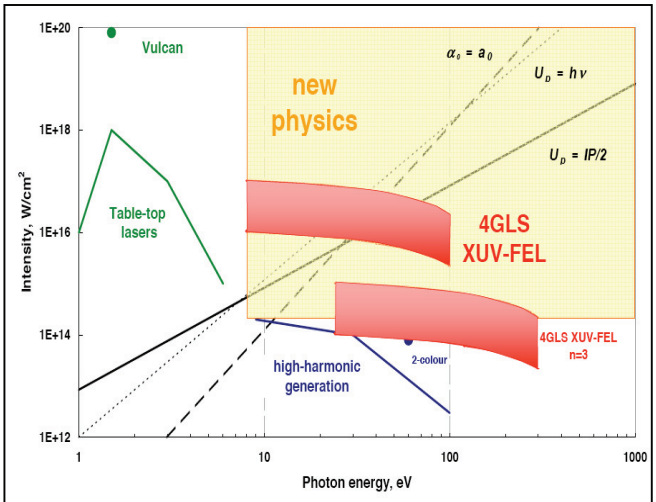

Figure 1.1 4GLS XUV FEL will allow us to study new regimes of electromagnetic interaction with matter. The black lines denote boundaries of these regimes when the amplitude of electron quiver motion, α_0, and the ponderomotive potential, U_p, associated with this motion become comparable with the Bohr radius, a_0, the photon energy, $h\nu$, or the ionization potential, IP.

Electron dynamics is at the heart of much of atomic physics and of all chemistry and biology. Intense radiation of the free electron laser (FEL) in the extreme ultraviolet region (XUV) of the spectrum will allow us to probe the motion of electrons in atoms and molecules, and to monitor the forming and breaking of the chemical bond. The experimental evidence gathered will be used to test theoretical models of the quantum micro-world and is likely to lead to important applications. Indeed, intense laser-matter interaction is the crucial first step in high energy density plasma formation, with applications in laboratory astrophysics, energy production and defence. We can expect to gain valuable insights into electron dynamics as 4GLS probes new physics (see figure 1.1).

1.1.1 Molecular dynamics

In the 1980's experimental studies of molecular dynamics received a boost from the invention of femtosecond lasers. It became possible not only to resolve *nuclear* motion but also to perform coherent control of chemical reactions. Despite its spectacular successes, this new field of science, femtochemistry[1] is still too slow to follow the primary cause of chemical reactions, the *electron* dynamics. Only very recently the advent of attophysics[2] promises to provide sufficient temporal resolution of electron motion by coherent manipulation of VUV and XUV radiation.

1.1.2 Electron correlations

To probe electron correlations we need the radiation field to interact with more than one electron at a time. Unfortunately, electrons in molecular orbitals screen each other from the field. As a result, at infrared (IR) and visible frequencies only one electron responds to the field – the rest are screened.[3] It is only when the frequency of light is increased to the VUV region that the first electron cannot follow the oscillations of the field and other electrons become "visible". This approach opens up a new area of science where electron correlations are prominent. Intense-field multielectron interactions cannot be explained through perturbative approximations to quantum mechanics but require new theoretical models and improved computational techniques. In addition to the fundamental interest, understanding electron correlations is vital to modern technology. Superconductors, quantum computers and novel nanomaterials are based on the unusual properties of electron correlations. As the effects of electron correlations are often counter-intuitive, we expect to discover new phenomena in this research.

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1.2. Scientific programme and methodology

4GLS will allow several aspects of molecular dynamics to be probed.

1.2.1 Tunnel ionization

The availability of intense, table-top lasers based on Ti:sapphire technology has driven much interest in the dynamics of single-electron ionization of atoms and simple molecules in the last fifteen years[4]. The availability of an XUV FEL opens up a unique parameter regime for studies of the intense field-atom/molecule interactions which cannot be accessed with Ti:sapphire fs lasers. A comparison of the ionization potentials of target atoms with the electron ponderomotive energy, quantitatively expressed via the Keldysh parameter[5], indicates that when the two are approximately equal (see the solid black line in Figure 1), ionization of an atom proceeds by electron tunnelling through a barrier formed from the atomic potential distorted by the applied *E*-field.

At the near infrared wavelengths of Ti:sapphire lasers, the strong-field regime ($U_p = IP/2$) is achieved for simple atomic gases at a ponderomotive energy (mean KE of the free electron in the field) higher than the photon energy, i.e. at intensities on the order of 10^{14} W cm^{-2}. With the XUV FEL at 30 eV photon energy, the strong-field regime can be reached under conditions where the ponderomotive energy is less than the photon energy. Important consequences of this are that single-electron removal proceeds under the simpler condition of single-photon impact, while multi-electron removal from an atom can occur in the absence of sequential scattering events involving additional photons or electrons. Initial exploration of tunnel ionization at photon energies in the range of 10–100 eV would adopt noble gas targets to establish the characteristics of single-electron removal promoted by a single photon.

1.2.2 Multiphoton ionization

Because the ponderomotive energy scales in direct proportion to the applied intensity and square of the wavelength of the applied *E*-field, the expected photon outputs from the XUV FEL at other photon energies indicate that for many atomic targets, the light-atom interaction will be dominated by multiphoton absorption. In addition to adopting the *ac* Stark effect for characterisation of FEL *E*-fields (see below), its role as a transient resonant facilitator of multiphoton absorption[6] could be elucidated from measurements of the rate of ionization induced by the FEL as a function of intensity and wavelength, coupled with spectrally-resolved photoelectron spectroscopy; these would give information of how different numbers of photons couple to the atomic structure. Pump-probe techniques incorporating a FEL pulse and another, time-delayed, optical pulse would directly access the transient population dynamics of different atomic levels. Optimal targets for these experiments would be argon and nitric oxide.

1.2.3 Coherent imaging of electron correlations

To probe electron correlation, a high temporal resolution is required. Several techniques that can reach down to the attosecond timescale have been developed recently[7]. The approach these methods have in common is to take the experimental data in the spectral (energy) domain and perform a Fourier transform to recover the temporal information. This requires recording both the spectral amplitudes and phases. Whilst the former is easily obtained from the photoelectron spectrum, the latter requires some sort of interferometric measurement. To implement this technique on the XUV FEL, IR laser pulses can be used to generate high harmonics in a noble gas with one of the generated high harmonics then used to seed the FEL. A delayed part of the IR pulse is required to accompany the XUV pulse with interferometric stability, as shown in figure 1.2. The XUV photoelectron spectra modulated by the IR field is recorded as a function of the IR-XUV phase.

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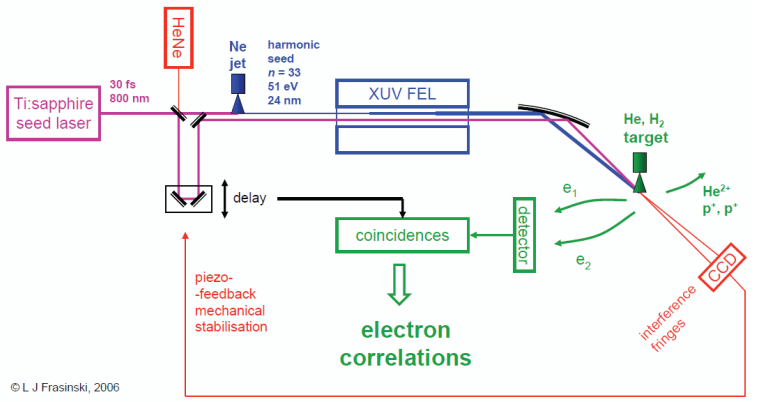

Figure 1.2. Coherent XUV-IR pump-probe experiment to study electron correlations. To ensure interferometric stability the XUV and IR optical paths need to be actively controlled within 10 nm.

Two-electron systems – He and H_2 – are of primary interest here. The Belfast group has world-class theoretical expertise in the modelling of such systems exposed to strong fields[8]. It is anticipated that detecting the signature of electron correlations will require electron-electron or even electron-electron-ion correlated measurements. These techniques of triple coincidences and covariance mapping have been pioneered by the Reading group[9].

1.2.4 Molecular alignment and orientation studies

The use of a non-resonant strong infrared laser field to align the axes of a molecule in the laboratory frame is now established[10]. A linearly polarized strong non-resonant laser field induces a dipole moment in the molecule along its most polarizable axis, and this dipole moment will tend to align to the polarization direction of the laser field. Molecular axis alignment can bring the molecular frame, where molecular processes occur, into the laboratory frame where measurements are made. This benefits emerging molecular dynamics techniques, where orientational averaging over all the molecular frame orientations leads to considerable loss of information. Examples include time-resolved photoelectron spectroscopy[11], time-resolved x-ray[12] and electron diffraction[13], timed Coulomb explosion[14], and most recently high-order harmonic generation[15].

However, in order to probe native structure and dynamics, the measurements must be made field free, i.e. in the absence of the alignment field that would otherwise strongly perturb the system. Furthermore, polyatomic molecules have a three dimensional structure, requiring alignment of all three molecular axes. The first of these requirements suggests the use of laser pulses which are short compared to the period of molecular rotation to impulsively (non-adiabatically) “kick" the molecules towards alignment, such that maximal alignment occurs after the laser pulse. The second requirement suggests the use of either elliptically polarized laser pulses, or sequences of laser pulses with different polarization states[16].

Currently these techniques have been successfully applied to molecules as large as substituted benzenes. Scaling to larger molecules may require moving to longer wavelengths than is routinely available from table-top laser systems in order to avoid multiphoton electronic transitions (including ionization). The IR FEL proposed as part of the 4GLS project will address this issue, by extending the range of wavelengths of aligning radiation. Crucially, however, such experiments will require

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control over the polarization state of the pulses from the FEL, and also the ability to generate two or more time delayed pulses. Synchronization of the IR FEL with the other beamlines of the 4GLS would then allow experiments to be conducted on aligned molecules. Furthermore, the high intensity THz radiation available from 4GLS will allow novel techniques for creating molecular axis orientation (where there is a preference for 'up' vs 'down') to be investigated.

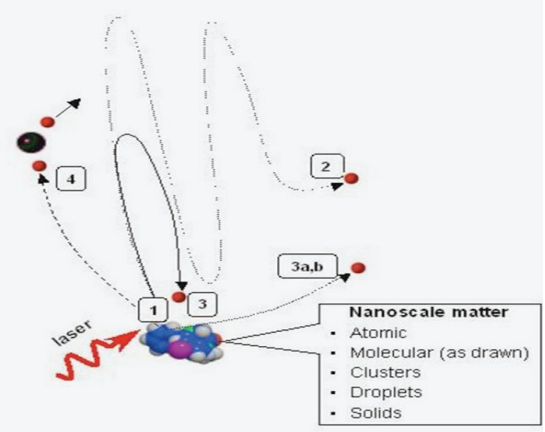

Figure 1.3. Recollision-induced processes in a molecular sample. Following ionization (1) the electron may be driven away (2) or recollide (3) with the molecule depending on the field phase at the instant of ionization. If recollision occurs the electron can (a) recombine – with the emission of a higher energy photon, (b) scatter elastically or inelastically from the molecule. In a dense sample the outgoing electron may collide with neighbouring atoms or molecules (4).

1.2.5 Recollision physics

Laser driven recollision is a new field that combines laser physics and collision physics (see figure 1.3). The resulting advantage is that the ultra-fast temporal duration and synchronization of the laser driven electron beam permits electron collisions to be used as a femtosecond timescale probe of processes in atoms and molecules. It has been shown using 800 nm and near-IR fields that by virtue of (a) the high recollision current, (b) the high energy/short de Broglie wavelength of the returning electrons, and (c) the sub-cycle duration of the process, that this can be used as an ultra-fast probe of molecular structure[17]. The availability of a high intensity XUV FEL allows unique opportunities in extending the scope of these techniques.

The energy of the recollision is scaled by the ponderomotive energy U_p, where $U_p = e^2E^2 / 4m\omega^2$, with a maximum possible energy at recollision of $3U_p$. Thus the energy scales as $I\lambda^2$, where I is the laser intensity and λ the wavelength. High energy electrons have, of course, short de Broglie wavelengths, permitting diffraction imaging[18] of molecules in the recollision event. The interaction of the recolliding electron can be observed either through elastic/inelastic electron scattering or from high order harmonic generation (HHG upon recombination. These experiments will therefore require an angle-resolved electron spectrometer and an XUV grazing incidence spectrometer.

Using the XUV FEL, it will be possible to explore how, as shorter wavelengths are approached, recollision behaves. Although for 10 eV photons, intensities > 10^{16} Wcm^{-2} will be required to see strong recollisions, the advantage is that the cycle time is much faster. Therefore less electron wavepacket spreading will occur and more intense electron currents can be achieved. These high current density, short duration pulses, provide a very fast (sub-100 attosecond) probe of electron dynamics. An immediate comparison can be made of the efficiency of HHG in the VUV with the output from IR-driven HHG from the same atoms. It is anticipated that because of the reduced wavepacket spreading, the conversion efficiency may be increased by several orders of magnitude.

1.2.6 Tomography of molecular orbitals

Tomographic imaging of molecular orbitals is a recent technique[19] that utilises molecular alignment, tunnel ionisation and recollision. In IR laser studies the recolliding electron (process 3 in figure 1.3) encodes information about the orbital in the HHG photons. Recording HHG spectral phases and amplitudes as a function of the molecular alignment angle makes the tomographic reconstruction of the orbital possible. An intense and coherent source of VUV or XUV photons can

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enhance this technique. The idea is to replace the recolliding electron with XUV photons[20] – a kind of pseudo-photon electron impact studies of transition amplitudes in reverse. At the time of writing, this is only a theoretical proposal and the details of the phase recovery are still being discussed.

1.2.7 Metrology

Characterization of short pulses is a challenging subject. Autocorrelation of femtosecond pulses is widely used in the IR, visible and near-UV regions of the spectrum. Unfortunately, this technique is generally unsuitable for shorter wavelengths due to lack of beam splitters and limited choice of nonlinear media. Cross-correlation of XUV FEL pulses with IR femtosecond laser pulses is more promising and the technology is developing quickly in this field.

Recently, two such techniques have been demonstrated[21,22] in separate experiments at the FLASH facility in Hamburg. Both rely on XUV photoionisation and sideband generation on the photoelectron spectrum by an intense IR field. With a collinear XUV-IR geometry[21] the sidebands are resolved in an electron spectrometer and in the orthogonal geometry[22] the production of the high-energy sidebands in the interaction region is imaged with a retarding electron lens. With modest improvements, both techniques are suitable for single-shot operation. We would like to propose an alternative method tailored for 4GLS.

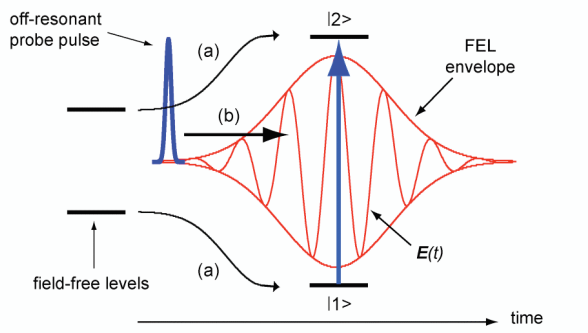

Figure 1.4. Schematic illustration of the use of an ultrashort laser pulse to determine the envelope shape and ***E***-vector of a FEL pulse through measurements of atomic level shifts. The FEL pulse brings about an ac Stark shift of a pair of atomic levels as a function of the local intensity $\langle \boldsymbol{E}^2(t) \rangle$ (a). The short probe pulse (with a duration less than half the period of the FEL) is scanned in time (b) relative to the FEL pulse to map out the level shift by monitoring the probability of photon absorption (blue arrow) between the dressed states |1> and |2> derived from the interaction of FEL light with the atomic target.

Rather than modify the energy of photoelectrons, we propose to influence the energy of the *bound* electrons. When an atom or molecule is irradiated by light, its eigenstate spectrum is shifted by an amount determined by the polarizability of its electron cloud and the intensity and frequency of the electric field of the light. The ac (dynamic) Stark shift of atomic levels, which may be as large as several electronvolts, can be exploited to make high-order correlation measurements of the pulse shape and, under suitable conditions, the amplitude and phase of the on-target ***E***-field, thereby facilitating complete characterization of the FEL pulses used directly in experiments in optics and high-field atomic physics[23]. Figure 1.4 illustrates this approach.

Measurements of XUV and VUV FEL pulse durations will take advantage of ionization[24] or fluorescence[23] spectra of eigenstate shifts at different, interferometrically controlled, time-delays between a FEL pulse and an optical pulse to map out the shape of the envelope profile. The 4GLS XUV and VUV pulses will typically contain hundreds of ***E***-field oscillations. Because of the relatively high number of oscillations, it is anticipated that measurements of the phase of the ***E***-field will not be required for most experiments which use these pulses. The use of a short correlating pulse in combination with an atomic target which exhibits large level shifts on the

[20] R Santra "Imaging molecular orbitals using photoionization", *Chem Phys* **329** 357–364 (2006)
[21] P Radcliffe *et al* "Single-shot characterization of independent femtosecond extreme ultraviolet free electron and infrared laser pulses" *Appl Phys Lett* **90** 131108 (2007)
[22] S Cunivic *et al* "Time-to-space mapping in a gas medium for the temporal characterization of vacuum-ultraviolet pulses" *Appl Phys Lett* **90** 121112 (2007)
[23] T W Schmidt, T Feurer, R B Lopez-Martens and G Roberts, *J Opt Soc Am B* **19** 1930 (2002); T W Schmidt and G Roberts, *J Phys B* **35** 2357 (2002)
[24] H G Muller, *Appl Phys B* **74** S17 (2002)

order of U_p (figure 1.1) will enable determination of the phase of the ***E***-field at the longest VUV wavelengths. For experiments which mandate access to the field (as opposed to the envelope) at shorter wavelengths in the VUV and XUV ranges, we can implement protocols based on photoelectron or X-ray interference using the techniques developed for attosecond technology. In the case of the IR FEL, the amplitude and phase of the ***E***-field can be determined directly by Fourier analysis[23] of the cross-correlation signal with short laser pulses.
Key advantages of the dynamic Stark effect as a nonlinear element for interferometry of light are its applicability at all wavelengths, that there is no maximum pulse width, that it is background-free and that it can be monitored to high-order such that the interferogram itself mimics the pulse shape.

1.3. The need for 4GLS

Besides the 4GLS several other X-ray/XUV FEL projects are planned in the world, and the FLASH facility is in operation. In the case of the XFELs, self-amplified spontaneous emission (SASE) is sufficient for diffraction and seeding of the XFELs is regarded as an unnecessary complication. Femtosecond lasers will be available at experimental areas but they will be rather poorly synchronised – because pump-probe experiments are not the priority. The repetition rate and pulse structure is often suitable for diffraction experiments but poor for time-of-flight spectroscopy.
4GLS will be ideal for the experiments proposed here. Compared to other planned 4th generation sources, many of which aspire to operate at frequencies too high for the most interesting strong field effects to be encountered, 4GLS has exactly the right combination of intensity and photon energy to make a world-leading contribution in this field (Figure 1.1). In contrast with FLASH, the XUV FEL will be seeded, and repeatable and well-characterised pulses will remove uncertainties from result interpretation. The 1 kHz 'day-one' repetition rate (with plans to reach 100 kHz) of single pulses contrasts with 10 Hz at FLASH, and the low repetition rates planned for non-superconducting devices. This is an excellent match for pump-probe and time-of-flight experiments. Moreover, if a stable reference pulse is split from the seed laser to the experiments, 4GLS has a clear advantage in laser synchronisation. Flexibility in combining beams from various sources is a clear strength of 4GLS, and key to this programme.

1.4. Wider collaboration

Figure 1.5: LaserLab Europe is the consortium of large laser laboratories that provides the infrastructure for the strong-field research community within the EU.

This project builds on the existing strong UK research on the dynamics of the molecular bond, encapsulated for example in the UK Attosecond Consortium. At high intensities this research currently relies on fs lasers usually operating at long, IR wavelengths. It is complemented by short wavelength pulses but of modest intensity produced by the HHG process. As the latter also relies on fs lasers, it is natural that most collaboration is expected with the short-pulse, strong-field laser community. In Europe there is an existing close collaboration within the LaserLab consortium (see figure 1.4) and the XTRA network[25]. The 4GLS facility will substantially strengthen this activity. Worldwide collaboration is anticipated with Canada (Steacie Institute in Ottawa, Université de Sherbrooke and Laval University in Quebec City), USA (Kansas State University, University of Maryland and Louisiana State University), India (Tata Institute in Mumbai) and Japan (Tokyo University, RIKEN Institutes and JAEA laboratories).

[25] http://xtra.dei.unipd.it/

2. QUANTUM CHEMICAL CONTROL

Ivan Powis (University of Nottingham), Helen Fielding (University College London), David Holland (STFC Daresbury Laboratory), George King (University of Manchester), Katharine Reid (University of Nottingham), Tim Softley (University of Oxford), Jonathan Underwood (University College London), Ben Whitaker (Leeds University).

2.1. Motivation; achieving chemical control

A long-standing goal for chemists, as old as the discipline itself, is to be able to exert some influence on the nature, direction, and rate of chemical processes. Developments made in the late 20th century, in both theory and experiment, have advanced this topic fully into the quantum realm so that now chemical reaction (and by implication the various "non-reactive" process which precede or compete with reaction itself) can be understood at the level of individual quantum states. How these quantum states evolve is, then, a central theme for the new century. Creating a broadly encompassing understanding of quantum molecular interactions with light and the localised environment, and of the subsequent evolution of such systems, will provide the bedrock on which the expected technical outcomes of selectively controllable molecular based processes operating at the micro, nano and macroscopic levels can be delivered.

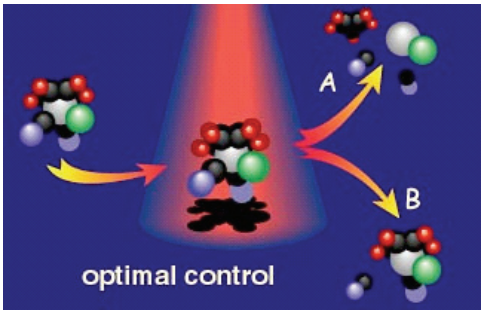

Figure 2.1: Influencing chemical reactions: shaped light pulses may be used to direct the course of a chemical reaction by quantum chemical control. (Reproduced with permission of Gustav Gerber, University of Würzburg)

The growth in this field over the course of the last two decades is best exemplified by the 1999 Chemistry Nobel Prize awarded to Zewail for his pioneering work in femtochemistry. Zewail was able to exploit developments in laser technology directly to allow the observation of molecular processes in the timeframe ($\sim 10^{-15}$ s) in which they naturally take place. Femtochemistry allows the experimentalist to prepare wave packets (coherent superpositions of quantum states) which then evolve in a manner which is fundamentally quantum mechanical in nature but which can offer some intuitive classical insight. It is now recognised that creation of such coherent state populations permits the resulting quantum interference effects to be exploited to allow outcomes such as the reaction pathway to be pre-selected and steered by the researcher — so-called Coherent Control — in a manner which may be far from intuitive but nevertheless can furnish understanding of more purely macroscopic chemical phenomena.

Photons provide the principal and most flexible toolkit for these efforts. They can allow selective deposition of energy *and* momentum into a target molecule in such a way as to prepare specific, spatially aligned quantum states. Light, through spectroscopy, also provides the means to probe the evolution of the prepared system. Short light pulses can follow events down to the timescale set by a single molecular vibration, and even to a single orbit of an electron within that molecule.

2.2. The Need for 4GLS

4GLS offers many advantages for researchers in this field. Extension of wavelength coverage to either side of the visible/UV region, simultaneously with more than one light beam, is the most significant of these. The selection of systems to be investigated by current state-of-the-art experiments is very much constrained by the limitation of current laser sources around these regions. Investigation of electron-mediated processes generally, however, requires vacuum ultraviolet/soft X-ray, while fully tunable, intense infrared radiation extending beyond the mid-IR also provides many new possibilities for initiation, probing and control of the molecular dynamics. Other 4GLS

characteristics, such as polarization, coherence, pulse lengths and repetition rates, flux and intensity can all be explicitly exploited in the future development of this field.

2.3. Scientific Programme and Methodology

The global objectives are:

• exploitation of phase, amplitudes and polarization to control competing reactive and non-reactive relaxation channels in molecular systems;

• monitoring, in real time, the evolution of prepared and aligned quantum states to better understand competition and interference processes;

• development of understanding of the electron dynamics and electron-nuclear couplings that influence observed chemical outcomes;

• exploration of quantum selectivity as the complexity of the molecular environment is progressively extended (e.g. size selected clusters, cold nano-droplets, aerosols, liquid jets) to better understand the primary and secondary molecular interactions with surrounding media.

2.3.1 Probing Molecular Dynamics

Time-resolved photoelectron spectroscopy has recently emerged as a powerful technique for probing dynamical processes in isolated molecules, ions and clusters enabling fundamental questions to be addressed. An emitted photoelectron carries with it the signature of its interaction with the other electrons in the system and so probes a multi-electron system as it is perturbed by excitation impulse from a photon. The energies and angular distribution of the electrons that are ejected give information about the changes in geometry of the molecule and the electronic wavefunction.

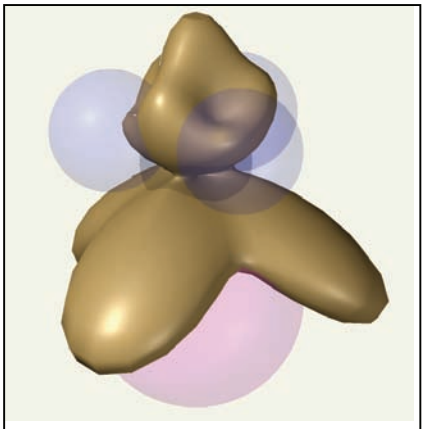

Figure 2.2: The computed molecule- frame photoelectron angular distribution function in CF_3I (I Powis, with permission.)

The electron-electron interactions respond to electron-nuclear couplings and so the photoelectron probes nuclear motion and rearrangements that occur under the influence of a dynamic electron potential. Questions of *why* and *how* chemically relevant processes occur can be directly addressed. Time-resolved techniques can reveal *where* the nuclei have moved under such electron mediated influences. The angle-resolved scattering of photoelectrons can be likened to diffraction of an *in situ* generated electron and — particularly when the initial orbital is highly localised and the molecular orientation is fixed — can provide structural detail. Among the more conventional array of diffraction techniques, gas phase electron diffraction using short intense electron beam pulses is particularly suited for development at 4GLS, while with very intense light pulses, Coulomb explosion techniques provide another alternative for inferring time-resolved structural details.

The increasing capabilities of tunable wavelength, polarization selectable, high intensity synchrotron radiation sources now truly allow the photoionization *per se* to be studied, and 4GLS will further enhance the state of the art for such core activities by permitting prior optical alignment and quantum state-selection of the target species to be introduced. The VUV region provides access to the chemically important valence shells of molecules, while at somewhat higher photon energies inner valence shell excitations, resonant Auger excitation etc. allow important electron correlation effects to be examined.

The available information can be made more explicit by the use of coincidence techniques to observe simultaneously the photoelectron and atomic or molecular fragments, photons, or secondary electrons emitted from the prepared system. Quantum state selection can be extended by coincidence techniques, which also open up the study of additional vector correlations — that is the relative disposition and magnitude of recoil velocities, light polarization, rotational and electronic

angular momenta. These correlations can, for example, enable studies to be conducted in the molecular reference frame whilst using free or isolated species. The availability of fully variable linear-circular polarization gives the experimentalist the ability to explore more completely the quantum interference between degenerate photoionization channels. By using isolated "fixed in space" target molecules that have been oriented either by coincidence methods or optical laser techniques a vastly expanded amount of quantum phase information can be extracted. Coincidence techniques typically require pulsed light sources to operate at high repetition rates for efficient data collection to be possible, and this can be identified as a significant advantage offered by 4GLS.

An example of a state-of-the-art experiment, but one where wavelength limitations of today's ultrafast laser systems very much constrain the choice of system for study, is the fs time-resolved multidimensional imaging of the NO dimer photodissociation reported by Stolow and co-workers[1]. Following a 'pump' laser pulse to create a quantum-mechanical wavepacket, an ionizing probe pulse was used to characterize the motion of the constituent atoms as a function of time. Coincidence techniques allowed the recoil vector correlations in the ionization step to be established from which anistotropic, time-varying molecular frame photoelectron angular distributions were obtained.

2.3.2 Molecular Preparation

2.3.2.1 Alignment and Orientation

Observations and measurements made with aligned or oriented molecular species are in general very much more informative (and rare) than the corresponding data obtained from randomly oriented sample. The methods described above allow molecular orientation to be inferred after the event. More proactive ways to induce alignment/orientation exist. A promising general approach that does not require a permanent dipole moment is to use strong (non-perturbative) non-resonant laser fields to produce molecular axis alignment through interaction with the molecular polarisability. However, while full three-dimensional molecular axis alignment has been demonstrated in the presence of a strong elliptically polarised laser field, this laser field strongly perturbs the system, distorting the electronic and vibrational structure of the molecule. Field-free alignment created with laser pulses shorter than the rotational timescales of the molecules under study is now well established[2] for alignment of a single molecular axis. This approach has recently been extended to the creation of field-free three dimensional axis alignment of a small molecular system.[3, 4]

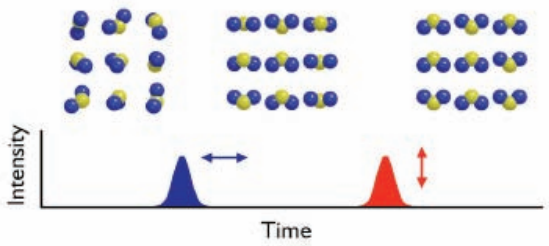

Figure 2.3: Field-free molecular alignment of SO_2 molecules using two time-separated fs laser pulses of perpendicular polarisation – the first produces 1D alignment of the most polarisable axis of the molecule, at which point the second produces a torque about this axis that brings the seond most polarisable axis of the molecule into alignment with the field of the second laser pulse. Adapted from Lee et al., Phys Rev Lett**, 97**, 173001 (2006), reproduced with permission of J Underwood

Currently these techniques have been applied successfully to molecules as large as substituted benzenes[5], using lasers of wavelengths of either 800 or 1064 nm. Scaling to larger molecules requires moving to longer wavelengths to avoid low order multiphoton transitions and ionisation, as well as to longer pulse widths as the rotational timescale of the molecules increases. The 4GLS IR-FEL will allow this issue to be addressed directly as it provides ps duration pulses with an intensity sufficient to produce significant alignment in larger molecules with increased polarisabilities compared to the smaller molecular systems previously studied.

2.3.2.2. Double Resonance Techniques - Biomolecules

In recent years there has been a vast growth in the number, and detail, of studies of biomolecules in the gas phase. While, of course, biology takes place in condensed media, detailed spectroscopic and structural investigations can be impeded in such environments; as Weinkauf *et al* [6] note " …

important properties of the bare molecules are buried under the inhomogeneous broadening [in such natural environments] and it is difficult to distinguish which properties are intrinsically intramolecular as opposed to being imposed by the environment …" Gas phase studies lift these restrictions to some degree, and moreover are frequently able to be performed in conjunction with some cooling that further removes spectral congestion.

These studies permit a better understanding of the role of solvent by making clear the intrinsic properties of the bare molecule. Investigations of small peptides have revealed preferred secondary structure motifs that change in the absence of solvent, thus revealing intrinsic folding properties of the peptide chain that are modified by solvation[7-9]. Cluster preparation techniques allow the influence of progressive solvation to be observed. Striking recent results on protonated tryptophan[10] demonstrate a dramatic change in electronic relaxation after solvation with just 2 water molecules[11].

Key issues are the way in which biomolecular conformation is controlled by the energetics of intramolecular forces associated with the bare species, how it responds to solvation effects and how this may convert to secondary structural forms when assembled into larger entities. These factors play a major role in protein folding and the molecular recognition that is central to biological function. Experimental techniques that combine the use of photons of two or more different colours can provide a means to unravel some of this complexity. In particular, the use of IR pumping can be used in a conformationally selective way. In this two colour scheme, the absorption of the first photon excites only a specific conformer into an intermediate state, and the second photon is used to probe this excited conformer. Alternatively, IR hole-burning and ion dip methods have been utilised in a number of structural investigations of amino acids[12, 13], small peptides[7-9, 14, 15] and similar species[16, 17]. In such cases an IR pump provides a conformer-specific excitation step, which depopulates a certain conformer; the spectrum then appears as depletion in the total ion or fluorescence signal. The 4GLS IR-FEL, synchronised to other photon sources for probing, offers some major advantages for hole-burning experiments. Its extended wavelength coverage opens up all possible excitation routes including those associated to intramolecular H-bond stabilised molecular configurations. The high average photon flux available from the IR-FEL pulse trains is very well adapted to efficient multi-photon dissociation, thereby ensuring efficient depletion of selected populations and the short pulse characteristics can be used for time-resolved experiments probing the relaxation dynamics of energetically excited conformations.

2.3.2.3 Extending the Molecular Environment

The function of many molecules is only fully revealed when they interact with their environment. The use of cluster techniques to simulate increasing solvation states well exemplifies this. Many novel sample environments that can be created experimentally are inherently dilute. An advantage of 4GLS sources will be high photon fluxes permitting investigation of dilute media. Studies of the properties of systems embedded in liquid helium nanodroplets[18] can be expected to benefit greatly. Heavily solvated species at liquid interfaces can also now be investigated using some of the techniques outlined above[19]. This is particularly relevant to the study of biomolecules, since their most important functions are usually encountered in solvated environments and at interfaces. Studies can also be on single aerosol particles of atmospheric and industrial importance.

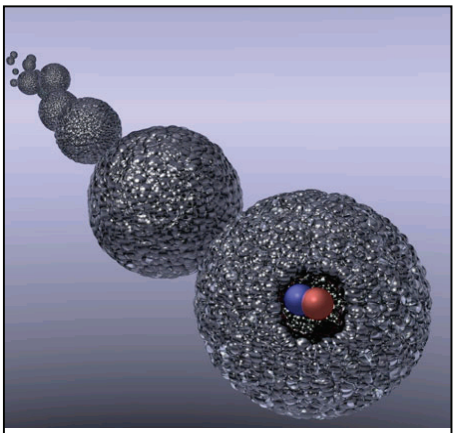

Figure 2.4 :Ultracold superfluid on-interacting He nanodroplets may be used to isolate novel species for study.

2.3.3 Exerting Control

Ever since the first lasers were built over 40 years ago, chemists have been trying to exploit laser light as a tool for controlling the outcome of chemical reactions. The idea of selective energy

deposition at sites chosen to promote specific reactive outcomes — mode-selective chemistry — was an early focus. More recently the ideas of coherent control have attracted much attention. The interaction of ultraviolet light with molecules can induce chemical changes that may lead to more than one set of products. It is anticipated that by exploiting the coherent properties of laser light to produce coherent wavepackets whose intrinsic quantum interferences can be controlled, it should prove possible to increase the selectivity in favour of the desired set of products. It is only during the last few years that real progress has been made in this direction using waveform-shaped fs laser pulses to control which chemical bonds can be made and broken.

Why is this of such intense interest? Realistically, apart possibly from a few niche processes that have been proposed (e.g. coherently controlled chiral "distillation"), coherent control by laser is unlikely to find applications in mass manufacturing processes. However, by understanding how to shift control in favour of certain defined outcomes, one can better understand the underlying processes; ultimately this understanding can be built into chemical process systems, so that an element of "control" can be designed in at the outset.

The most successful demonstrations of such postulated control have been involved adaptive control strategies, where the phase of fs laser pulses is automatically varied using genetic learning algorithms to optimise specific outcomes (e.g. a particular dissociation channel)[20]. Empirically developed experimental capabilities in this field are currently more advanced than our understanding of how such shaped light pulses actually achieve their selectivity. However, analysis of the optimised shapes indicates that these often display a relatively simple double pulse structure, at least when operating in a perturbative regime.[21] It is possible to envisage control as arising from the sequential optical manipulation of a prepared wavepacket, guiding it through the multidimensional electronic structure of the system towards a final outcome.

2.3.3.1 Coherent Control

Full coherent control via optical pulse shaping is seen as a long-term goal for 4GLS, and the expected near transform limited FEL outputs assist this. Simple transfer of techniques used for visible pulse shaping is not, however, possible due to the lack of comparable optical devices for operation in the VUV. Nevertheless adaptive pulse shaping has been very recently demonstrated in the soft X-ray region by using high harmonic generation from shaped visible laser pulses[22], and similar strategies may eventually be developed in conjunction with shaping of the seed laser pulses for the XUV-FEL. In the interim, preparation of phase coherent double pulses is feasible using adjustable interferometer/delay lines, as currently being developed at BESSY II. The potential of such intuitive double pulse schemes for exerting control has been well demonstrated in the manipulation of Rydberg electron wavepackets[23] in small molecules[24, 25].

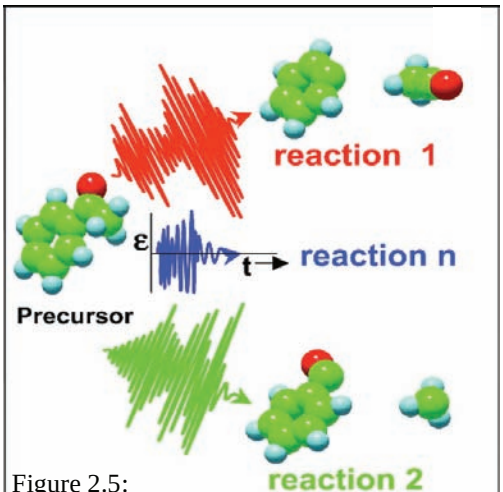

Figure 2.5: Selective product formation using optimally tailored strong field fs laser pulses. Adapted from Levis *et al.*,*Science*,**292,** 709 (2001).

2.3.3.2 Dynamic Stark Control

Many relaxation processes of electronically excited molecules involve complex non-adiabatic interactions between different electronic states. These create a series of potential barriers to be crossed by a prepared wavepacket as it evolves. The use of non-perturbative, non-resonant dynamic Stark shifts induced by an IR laser field to modify the barriers[26, 27] has recently been demonstrated[28]. A precisely-timed intense IR pulse at some delay after an initial wavepacket excitation pulse modulates the non-adiabatic interaction between two potential surfaces just as the wavepacket has propagated to this point, and can switch the transition on or off, with a consequent influence on the final outcomes. While this concept has been experimentally demonstrated[28] for the photodissociation

of IBr using a 1.7 μm control pulse, its wider applicability rests on the ability to generate synchronised non-resonant IR pulses, tunable further into the IR to match non-resonant windows in a given system, of appropriate duration and with some spatially uniform intensity below the ionization threshold — a demand 4GLS is ideally placed to meet.

2.3.3.3 Polarization Phase Control

Photoexcitation of aligned molecules into unbound continuum states also provides some control opportunities. Varying the relative polarization (spatial anisotropy) of photon source and molecular axes will in general allow the selection rules governing excitation of different symmetry continuum states to be exploited. Two such continua, coherently excited, will have a phase fixed by the molecule itself and can display interference effects and can lead to varying dissociation branching ratios[29]. Combining the fully variable polarization characteristics of the 4GLS sources with the enhanced opportunities discussed above for creation of aligned molecular samples will open up new possibilities for the exploration of such effects.

2.4. Wider collaboration

Major international supporters of this programme include Kiyohsi Ueda (Tohoku University, Japan) and Bernd Winter (MBI, Berlin).

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3. ORIGINS

A PROGRAMME OF LABORATORY CHEMISTRY AND PHYSICS IN SUPPORT OF ASTRONOMY AND ASTROPHYSICS

David Williams (University College London), Martin McCoustra (Heriot-Watt University), Wendy Brown (University College London), Robert Donovan (University of Edinburgh), Andrew Horn (University of Manchester), June McCombie (University of Nottingham), Nigel Mason (The Open University), Stephen Price (University College London), Ian Sims (University of Rennes 1)

3.1. Scientific Justification

Images of the heavens have for generations inspired man to create great works of art, music and literature. These beautiful images also inspire us to ask questions as to our origin and place in the scheme of things. How was the Universe formed and how does it work? How do stars form and work? How do they evolve and die? Where do planets come from? How did life originate? These are not purely philosophical questions, but issues that can be addressed by modern science.

Matter in the Universe participates in a cosmic cycle taking it from low density (*diffuse*) regions through regions of increasing density and chemical richness (*dense molecular clouds*) and into stars, their planetary systems and, perhaps, life. Star death closes the loop by recycling matter back into the diffuse interstellar medium. To understand this cycle is to understand how the Universe works.

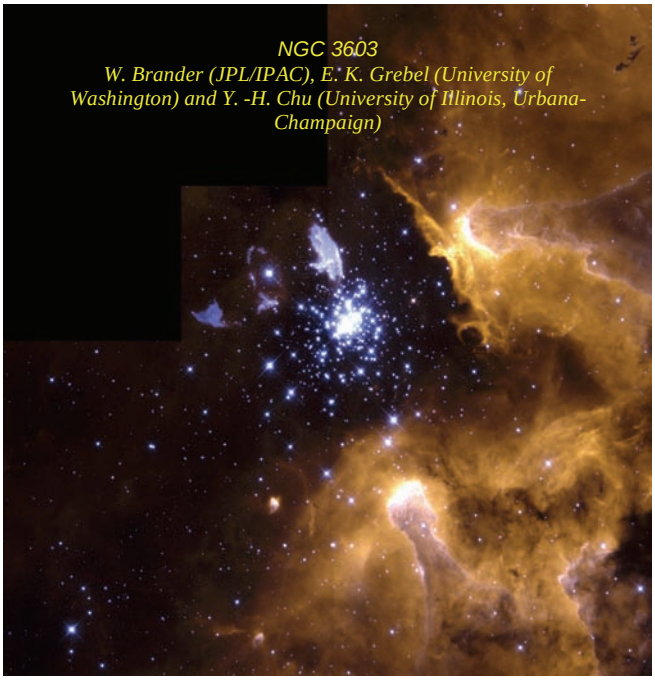

Figure 3.1: The region of space represented by NGC 3603 contains objects at every stage of the matter cycle in the Universe.

Numerous physical and chemical processes are known to participate in and may even control the fundamental matter cycle of the Universe. Astronomy is our window on to these processes and spectroscopy is a key tool in modern astronomy, revealing the Universe at a multitude of wavelengths across the electromagnetic spectrum. To understand what we see, we must complement our observations with laboratory studies. Laboratory physics and chemistry can help us to understand these processes and so provide essential support for our astrophysical understanding. The unique combination of light sources in 4GLS will permit us unrivalled access across the spectrum for such laboratory studies. The Origins programme on 4GLS, in providing a focus for laboratory studies, will present exciting new science that will help to unravel the workings of the Universe. It is made up of five keynote science projects, described below.

3.2. Spectroscopy of Transient Atoms, Molecules and Ions

June McCombie, University of Nottingham, Mats Larsson, University of Stockholm, John West, STFC Daresbury Laboratory, Wolf Geppert, University of Stockholm, Andrew Ellis, University of Leicester, Malcolm Gray, University of Manchester.

Our lack of knowledge in an astrophysical context is due in part to the limited availability of laboratory spectra for comparison with observational data. The combination of light sources within 4GLS, a combination of high intensity laser sources in the IR, VUV and XUV, together with

insertion device radiation, will give unrivalled access across the spectrum for laboratory studies that can fill in gaps in our knowledge. In addition, 4GLS will provide a unique environment in which to investigate the spectroscopy of both transient and (highly) charged species.

In order to remove the reliance on purely computed parameters, there is a need for accurate measurements of absolute cross sections of spectroscopic transitions in both stable and transient (free radical) species in order to achieve accurate modelling of the chemistry[1] and of a wide range of physical parameters, including density, temperature, elemental abundances, and the freeze out of molecules on to dust grains in both stellar and interstellar mediums.

The study of the interaction of ions with photons also forms an important part of any experimental probing as whilst collisional ionisation can play a role the emphasis is on the need for information on photon-dominated systems as opposed to collision-dominated systems given the very low number densities in the observational environment. The molecular syntheses occurring within interstellar clouds are dominated by ion chemistry; primary loss mechanisms for molecular ions in interstellar clouds are ion-neutral interactions and dissociative recombination. Considerable efforts have been expended to determine the rate constants and branching ratios of these processes in order to explain the relative abundances of species present in addition to providing data on the low energy ionising radiation present in interstellar space[2]. Standard gas–phase techniques such as direct absorption or standard Fourier transform spectroscopy are not applicable to probing such (possibly highly) charged species due to the very low number density that one can obtain as a consequence of space charge limitations.

The advent of 4GLS in conjunction with the widely tunable FELs proposed will allow studies such as -

a) The probing of short lived chemical intermediates produced by radiolysis using photon beam pulses from the FELs in pump-probe experiments[3]. By using the VUV FEL to generate transient species in a target beam, and then probe the result with radiation from a VUV undulator, it should be possible to follow the evolution and decay of transients as they proceed along a reaction pathway. The timing aspects of 4GLS will be ideal for this, since the interval between pump and probe can be varied at will, certainly at the 100 fs level and probably at the 10 fs level.

b) The dissociation of trapped ions[4] over a fingerprint infrared region probed using a widely tunable FEL in order to obtain true emission spectra analogous to observed interstellar emission region[5]. One class of molecules of interest are polyaromatic hydrocarbons (PAHs) and a number of studies, limited in accessible frequency range have been carried out on both neutral and cationic PAHs using laboratory infrared spectroscopy[5].

c) The utilization of the VUV-FEL to photo-detach electrons from a negative ion beam providing photoelectron cross section of neutral atoms[6] and the use of XUV-FEL in the absolute determination of photoionisation cross sections of atomic ions.

3.2.1 Potential National and International User Community

These include Christine Joblin, CESR, Toulouse, G. Meijer, Fritz-Haber-Institut der MPG, Berlin, Tom Millar, Queen's University Belfast, Eric Herbst, Ohio State Columbus, Ian Sims, Universite de Rennes, Yuri Aikawa, Kobe University, Japan.

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[1] See for example: H. Nomura and T. J. Millar, *Astron. Astrophys.*, 2005, **438 (3)**: 923-U97.

[2] B. J. McCall, *Nature*, 2006, **440** (9 March), 157-158.

[3] M. Larsson, *Ann. Rev. Phys. Chem*., 1997, **48**: 151-179; A. A. Viggiano, A. Ehlerding, S. T. Arnold and M. Larsson, *J. Phys. Conf. Ser*., 2005, **4**, 191-197

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[6] H. Wabnitz *et al.*, *Nature*, 2002, **420**, 482-485.

3.3. An electron beam ion trap for 4GLS

Fred Currell, Queen's University, Belfast, Dr. Ken Dunn, Queen's University, Belfast, Dr. Jose Crespo, Max Plank Institute, Heidelberg, Dr. Hywel Owen, STFC Daresbury Laboratory

Our understanding of the properties of the multiply-charged ionic species known to be present, for example in the interstellar medium, is very poor. The Electron Beam Ion Trap (EBIT)[7] is recognised as the table-top instrument of choice for the creation and study of highly charged ions, providing both spectroscopic access and acting as a source of highly charged ions. Having the trapped ions in an EBIT available as a target for the VUV and XUV FELs will provide new opportunities to perform fundamental table-top atomic physics and to provide important diagnostic information for astrophysics, underpinning observations from the Hubble Space Telescope, the Extreme Ultraviolet Explorer and the Hopkins Ultraviolet Telescope. The optimum configuration would be a machine like the Heidelberg EBIT[8] with the photon beam counter-propagating the electron beam as shown in **Figure 3.2**. The Heidelberg team have recently commissioned a new EBIT to work in exactly this fashion at FLASH and will collaborate with the Belfast EBIT group in the development of this complementary facility. Ions will be created and sometimes excited using the electron beam. Selected transitions will be excited using the FEL with the fluorescence photons being detected at 90^0.

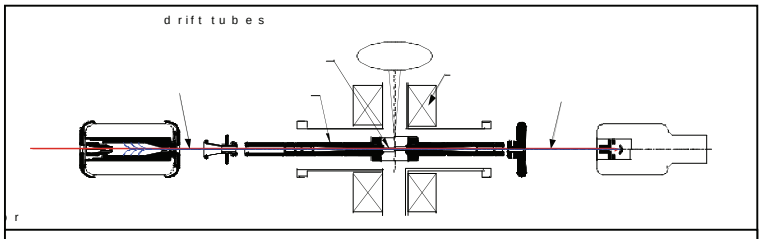

Figure 3.2: Schematic figure of the EBIT configuration with the electron beam (blue) propagating a distance of about 1m right to left from the electron gun to the collector. Counter-propagating, the FEL beam passes thorough the variable length interaction region to strike the cathode where it provides negligible extra heat loading. Fluorescence photons passing through the gap between the superconducting magnets can be detected using a spectrometer.

An example of the fundamental physics possible through the combination of an EBIT and 4GLS is the determination of the n=2 Lamb Shift of hydrogen-like ions: resonant excitation out of the population in the 2s state into either the $2p_{1/2}$ or $2p_{3/2}$ level will be followed by emission of an x-ray photon as the 2p-1s transition occurs. Scanning the wavelength to find the maximum increase in the yield of this transition will then give a spectroscopic value from which the n=2 Lamb shift can be derived. The energy range of photons available at the XUV FEL allows access to one of these transitions for a large range of nuclei, providing new and exacting tests of high-field Quantum Electrodynamics.

EBITs can also trap and create more complex ions. It is possible to create a Maxwellian plasma[9] or a non-Maxwellian plasma as required or simply excite the ions with a monoenergetic electron beam. Hence the EBIT will be able to create a wide range of plasmas of relevance to astrophysics in a controlled fashion. The VUV and XUV FELs can then be used to stimulate transitions of the ions in these plasmas with the resultant fluorescence signal giving useful diagnostic information about line strengths, transition energies and lifetimes. As one example of the comprehensiveness such a facility could provide, the VUV and XUV FELs can probe diagnostic transitions for charge states of Fe from 10^+ upwards[10]. Furthermore, the fluorescence signal can be measured as a function of distance along the trap using imaging optics, which in combination with the capability to vary the length of the plasma column can test models of line ratio enhancement towards the diagnosis of plasma geometry in distant astrophysical objects[11]. In this way the facility offers a unique underpinning of a new astronomical observation technique providing information below the resolution limit of the observing instruments.

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[7] *Phys. Scr.*, 1988, **T22**, 157
[8] *Phys. Scr.*, 2001, **T92**, 110
[9] *Rev. Sci. Instrum.*, 2000, **71**, 3362
[10] *Space Sci. Rev.*, 1996, **75**, 537
[11] *Astrophys. J.*, 2005, **629**, 1091

Exciting new opportunities occur when the relatively low energy electron beam of the EBIT is replaced by the high energy electron beam from 4GLS itself. Situating the central trap region shown in Figure 3.2 either just after the high average current injector or just before the final deceleration of the electron beam prior to dumping will result in an EBIT for study of electron-ion interactions in an unprecedented regime. A beam energy of 20 MeV can be achieved, two orders of magnitude higher than energies accessed previously with machines of this type, resulting in new fundamental physical tests of QED phenomena. Ions extracted from the EBIT can also be used as an alternative pump in a range of pump-probe experiments using the various 4GLS photon lines.

3.1 Potential National and International User Community

These include Francis Keenan, Queen's University, Belfast, Shunsuke Ohtani, University of ElectroCommunications, Tokyo, Nobuyuki Nakamura, University of ElectroCommunications, Tokyo, Yaming Zhou, Fudan University, Shanghai, John Gillaspy, NIST, Gaithersburg, Jaochim Ullrich, Heidelberg University, Germany

3.4. Ultracold Chemistry

N Mason, The Open University, S. Bergamini, The Open University, J. Hutson, University of Durham, I. Hughes, University of Durham, T Softley, University of Durham, D Jaksh, University of Oxford, A Murray, University of Manchester, F Renzoni, University College London, M Wiedermuller, Fribourg University, Germany, L D Noordam, FOM, Amsterdam, M D Havey, Old Dominion University, USA.

To date most chemistry has been performed under terrestrial conditions of standard temperature and pressure or under conditions pertaining to industry (*e.g.* high temperature combustion). In contrast chemistry at low temperatures, for example the chemical reactions leading to ozone depletion in the stratosphere ($200 < T / K < 270$) or the reaction dynamics at temperatures below 50 K necessary to understand molecular formation processes in interstellar space have only been developed in the last two decades. The development of laser cooling of atoms leading to the creation of Bose-Einstein condensation (BEC) in an atomic gas in 1995 has led to the creation of a new state of cold matter which in turn opens the possibility of opening an entirely new type of *'ultracold chemistry'* (below 1 K) where many room temperature reaction channels are closed and any chemical reactions are fully quantum mechanical in their nature often being governed by *tunnelling*. Such chemical reactions therefore have closer analogues to atomic scattering than the statistical ensembles of traditional chemistry - for example the formation of a complex between the reactants prior to the reaction product formation being similar to resonance formation in quantum scattering (*e.g.* the formation of transient negative ions in low energy electron scattering). Such 'ultracold chemistry' offers many new opportunities that are likely to form the basis of several future technologies ranging from high-precision measurement to the development of quantum computing and quantum information.

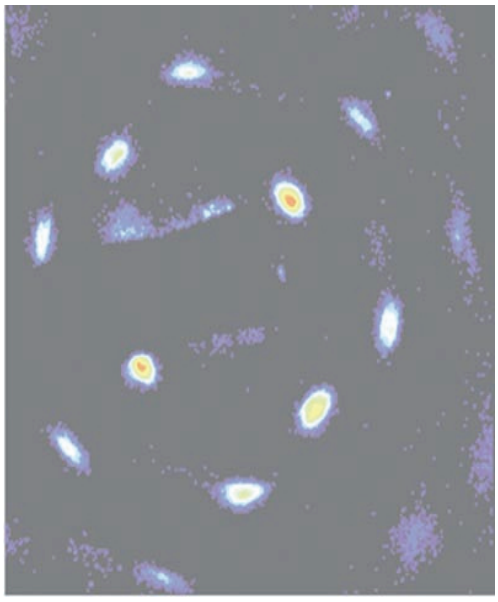

Figure 3.3: This image shows Bragg scattering in a strongly coupled one-component plasma of singly ionized beryllium, as obtained by David Wineland's group at NIST. The nearest-neighbour electrical energy in the plasma is much greater than the kinetic energy of the ions in the plasma ($T >> 1$). The ions try to move away from each other to minimize their electrical potential energy. However, because the ions are confined, they settle into an ion-lattice arrangement that behaves like a solid. It remains to be seen whether or not a two-component neutral plasma can evolve into this state. New experiments using calcium and strontium are ideally suited to addressing this problem. From the *Physics World* article by S. Bergeson and T. Killian on *Ultracold Plasmas and Rydberg Gases* published in February 2003.

4GLS will provide the opportunity to couple the latest technology in optical physics with research into and applications of quantum matter. One of the most obvious roles for 4GLS is to utilise the FELs to trap atoms and molecules. Conventional Lasers (*e.g.* CO_2) are used to create "Far-Off-Resonance-Trap" (FORT) traps. FELS have the advantage of wavelength tunability that makes them able to trap different atomic species and their high average power provides the ability to construct both deeper and larger traps than with conventional laser sources such that they may also provide a method for trapping molecular systems. Trial experiments are currently being developed on the JLab Free Electron Laser. Two main programmes are envisaged:

- *Creation and Tuning of Ultracold Plasmas and Rydberg Gases.* A new type of ultracold plasma in which the ion has T < 1 K and the electrons have temperatures of a few meV may be formed by pulsed laser photoionisation of atoms in a magneto-optical trap[12]. Ultracold plasma may be formed through excitation of Rydberg states. Cold atoms in a magneto-optical trap excited to Rydberg states of principal quantum number n > 30 evolve spontaneously to plasma on a time scale of *ca.*1 μs[13]. Ultracold plasma may spontaneously transform into an ultracold Rydberg gas. Such ultracold Rydberg gases have been suggested as an ideal tool for quantum computing since they may be formed in optical 'lattices' and due to their large 'size' interact with one another in a way that may be exploited to develop quantum 'qubits'. High resolution laser excitation of Rydberg atoms can also lead to photoassociation of Rydberg molecules, with the formation of the so-called trilobite or butterfly states. 4GLS provides an ideal light source for the formation and study of ultracold plasmas and Rydberg gases. Since it is both 'bright' and tuneable the VUV FEL can be used to photoionise any cold atom species and therefore form ultracold plasmas in any trapped system. The development of 4GLS as a terahertz radiation source is particularly timely since the first experiments investigating interaction of such radiation with Rydberg atoms are being developed following theoretical predictions by Hu and Collins[14] and this is a field that is expected to develop rapidly in the next few years.
- *Chemistry of Ultracold Molecules.* Developing a controlled ultracold chemistry is a major longterm goal. Just as we are now seeing phenomena in the ultracold atom field not dreamt about twenty years ago when BEC research was launched, we suspect that new and exciting molecular phenomena we cannot now imagine will emerge ten to twenty years hence. Obtaining full quantum control of the external and internal degrees of freedom will open up a variety of new research directions such as the production of molecular lasers. The most common method for the formation of cold molecules is from cold atoms is *via* photoassociation and subsequent radiative stabilisation. New prospects for photoassociation have appeared on the horizon through quantum control methods with tailored fs pulses. The initial work on these was theoretical, but several experimental projects have now started in Europe with pump-dump experiments with shaped vibrational wavepackets appearing quite promising to achieve coherent control of photoassociation and stabilisation. Shaped laser pulses can also offer the possibility for cooling of pre-cooled molecules. 4GLS provides an ideal tailored light source for such research with the VUV and XUV FELs being particularly useful photoassociation sources.

3.4.1 Potential National and International User Community

A major new five-year European programme funded by National governments through the ESF 'Eurocore programme' commencing in late 2006[15] has been funded in this field.

[12] T. C. Killian, S. Kulin, S. D. Bergeson, L. A. Orozco, C. Orzel, and S. L. Rolston, *Phys. Rev. Lett.*, 1999, **83**, 4776
[13] M. P. Robinson, B. Laburthe Tolra, Michael W. Noel, T. F. Gallagher, and P. Pillet, *Phys. Rev. Lett.*, 2000, **85**, 4466
[14] S. X. Hu and L. A. Collins, *Phys. Rev. A*, 2004, **89**, 041402
[15] http://www.esf.org/esf_activity_home.php?language=0&activity=7

3.5. Gas-Grain Chemistry: The Surface Science Approach

Martin McCoustra, Heriot-Watt University, Nigel Mason, Open University, Steve Price, University College London, Wendy Brown, University College, London, Wolf Geppert, Stockholm University, Malcolm Kadodwala, Glasgow University.

Chemistry plays a key role in the cycle of matter through the Universe[16]. Indeed, it can be argued that chemistry plays a fundamental role in controlling the formation of small, long-lived stars such as our own, for molecules have a controlling influence on this process. Understanding the formation of molecules in the interstellar medium is therefore a key question facing the astronomy and astrophysics communities. In the gas phase, the pathways from atoms and atomic ions to molecules and molecular ions are reasonably well mapped out[17,18]. They are known with sufficient certainty that simulations of the chemical evolution of a range of astronomical environments can be undertaken. However, these simulations highlight a limitation of such gas phase only models in that they fail to predict accurately the observed concentrations of many simple gaseous chemical species, including molecular hydrogen (H_2). Astronomers are now convinced that the contribution from gas phase chemistry must be complemented by chemistry occurring on the surfaces of the dust grains that make up around 1% of the mass of a typical dense cloud[19,20]. Since the 1990's surface science has contributed significantly to our understanding of the gas-grain interaction[21]. Experiments around the world have probed the formation of molecules such as H_2, the desorption of icy grain mantles by heating and other energy sources, and the processing of icy mantles into pre-biotic materials. UK groups have played a prominent role in this work. Two key areas remain to be visited. The combination of light sources offered by 4GLS and the associated potential for international collaboration paves the way for broaching these final frontiers.

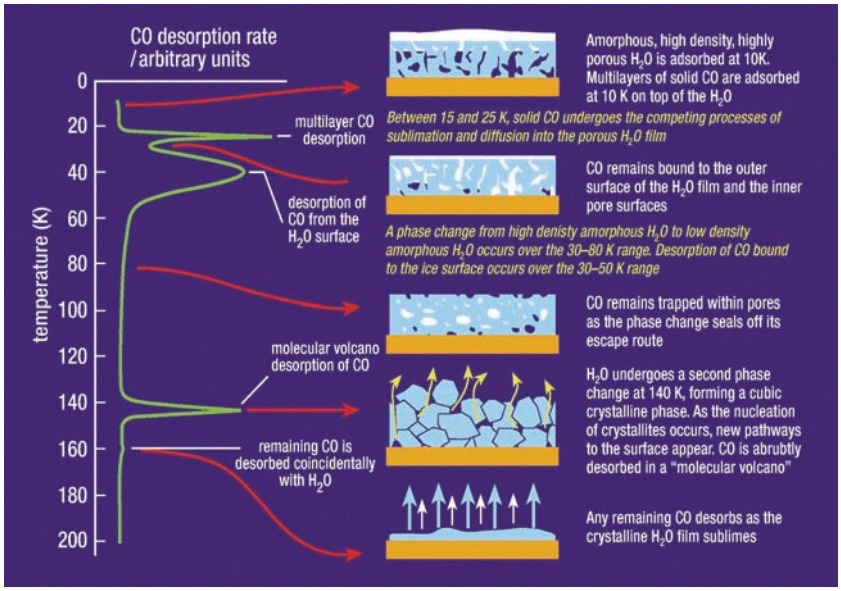

Figure 3.4: The adsorption, diffusion and desorption behaviour of CO on H_2O ice under laboratory pseudo-interstellar conditions. Adapted from ref 22. Cyan indicates H_2O, white CO and purple empty space.

Ion-molecule reactions represent the predominant fraction of gas phase chemical reactivity in the interstellar medium. Ion-grain interactions are believed to mediate the charge balance in dense star-forming clouds. The experimental investigation of this is far from straightforward. The primary difficulty will be in producing thermal (<1 eV) energy ion beams of such key interstellar

[16] W. W. Duley and D. A. Williams, *Interstellar Chemistry*, (Academic Press, 1984); T. W. Hartquist and D. A. Williams, *The Chemically Controlled Cosmos*, (Cambridge University Press, 1995).

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[20] D. A. Williams, in *Dust and Gas in Astronomy*, T. J. Millar and D. A. Williams (eds), (Oxford University Press, 1993), Chapter 7; D. A. Williams, *Faraday Discuss.*, 1998, **109**, 1.

[21] J. M. Greenberg, *Surf. Sci.*, 2002, **500**, 793; D. A. Williams and E. Herbst, *Surf. Sci.*, 2002, **500**, 823; T. E. Madey, R. E. Johnson and T. M. Orlando, *Surf. Sci.*, 2001, **500**, 838.

species as H^+, H_2^+, H_3^+, N_2H^+, HCO^+, some of the simple CH_x^+ ions and their deuterated isotopomers. Traditional electron impact sources produce hot ions with a broad range of energies. A photoionisation-based source, utilising VUV FEL output, may overcome this. Coupled with a simple cumulative ion trap for mass filtering and ion thermalisation, pulses of low energy ions could then be directed against model surfaces (graphite, model silicate materials and ices).

What happens to the surface as it is irradiated with ions? Here, the combination of reflection-absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TPD) used by McCoustra and others[22] will be deployed to probe both physical and chemical changes in the surface. One of the key advantages offered by 4GLS is the potential for constructing an optimised bending magnet IR source operating widely across the mid- and far-IR (say from 4 to 4000 cm^{-1}). This overlaps with the observationally increasingly important region in the far-IR where ices and grains are being probed by the likes of the Spitzer Space Observatory.

The second issue that the unique combination of facilities at 4GLS will permit us to address is the origin of the primary asymmetry in biological molecules. All biological relevant amino acids are left handed while the sugars that form the energy source and constructional material in many biological systems are right handed. Already numerous experiments are showing us that photon- and low energy electron-induced processes in simple ice mixtures can result in the formation of pre-biotic molecules. But this chemistry is achiral – it does not introduce a handedness into the reaction products. A range of mechanisms have been suggested that could result in the necessary enantiomeric excess that include photodestruction of specific enantiomers by CP VUV/XUV in the gas phase or in the icy mantle. Here again the optimised bending magnet IR source would be essential for the measurements focussing on destruction in the icy mantles on grains. Of course, some of these experiments would use CP VUV/XUV/soft X-rays from an insertion device. Others will investigate enantiospecific desorption with CP IR/Vis/UV from FEL and table-top laser sources. The additional enantiospecificity brought to the latter by enantiospecific gas phase photolysis could enhance the effectiveness of this latter mechanism for producing the primary asymmetry.

3.5.1 Potential National and International User Community

These include D. Chakarov, Chalmers University, Gothenburg, Sweden, H. J. Fraser, Strathclyde University, L. Hornaeker, Aarhus University, Denmark, C. Jager, Max Planck Institute for Astrophysics, Heidelberg and Jena, Germany, J. L. Lemaire, Paris Observatory, France, H. Linnartz, Leiden University Observatory, Netherlands, R. McCullough, Queen's University Belfast, M. E. Palumbo, Catania Observatory, Italy, H. Zacharias, University of Munster, Germany.

3.6. Gas-Grain Chemistry: Single Nanoparticle Surface Science

Andrew Horn, University of Manchester, Robert Donovan, University of Edinburgh, Nigel Mason, The Open University, Martin McCoustra, Heriot-Watt University, Stephan Schlemmer, University of Cologne, Wolf Geppert, University of Stockholm.

The gas-grain interaction in the interstellar medium is probably the most active area of research in laboratory astrochemistry and astrophysics at present. The majority of such studies, however, rely on studies of extended surfaces using relatively traditional surface science tools. The validity of such approaches has often been questioned as the real interactions involve nanoscale particles. Modern electrodynamic trapping methods allow us to isolate a single charged nanoparticle in a simple quadrupolar trap with the opportunity then of investigating the surface science of that single particle[23,24].

[22] M. P. Collings, H. J. Fraser, J. W. Dever, M. R. S. McCoustra and D. A. Williams, *Astrophys. J.*, 2003, **583**, 1058; M. P. Collings, J. W. Dever, H. J. Fraser and M. R. S. McCoustra, *Astrophys. Space Sci.*, 2003, **285**, 633.
[23] S. Schlemmer, J. Illemann, S. Wellert, and D. Gerlich, *J. Appl. Phys*., 2001, **90**, 5410.
[24] M. Grimm, B. Langer, S. Schlemmer, T. Lischke, W. Widdra, D. Gerlich, U. Becker and E. Rühl, *AIP Conf. Proc.*, 2004, **705**, 1062.

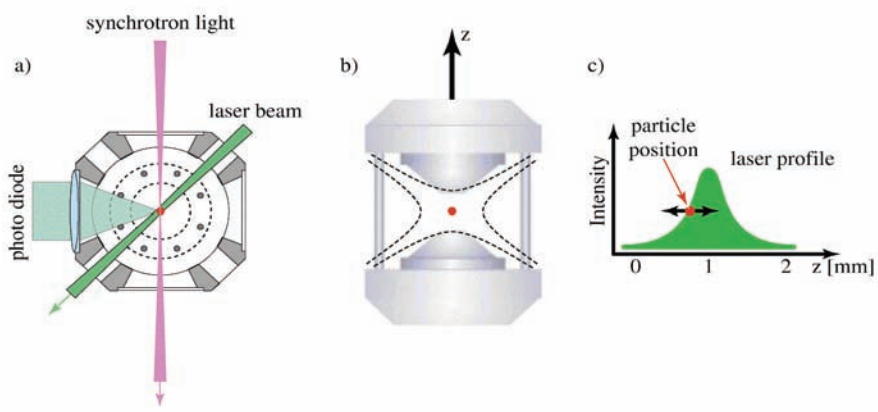

Figure 3.5: (a) Top view of a typical electrodynamic trap, where a single nanoparticle is stored in the centre; (b) z-plane view of the trap; (c) Schematic drawing of the Q/M measurement using secular motion of the particle through the gaussian laser beam profile. After reference 24.

Primarily this trapping technique allows us to directly determine the charge-to-mass ratio of the particle (Q/M) by monitoring the in-plane and out-of-plane eigenfrequencies of the particle oscillation in the centre of the trap using laser light scattering methods. Interaction of the particle with an electron beam is then used to change the charge state of the ion from which it is then possible to determine Q/M[23,24]. Alternatively as Schlemmer and co-workers have demonstrated high energy photons from a synchrotron can be combined with trapping to investigate the detailed charging process of such trapped nanoparticles[25]. However, such a trap in combination with the unique light sources available within 4GLS offers much more. Of course, direct mass measurements will be possible on such a trapped nanoparticle as we interact it with atoms, molecules, ions and electrons[26]. If we then couple electrodynamic trapping with IR FEL irradiation in appropriate lattice modes (*e.g. ca.* 10 m for silicate nanoparticles) as a heat source, we can reproduce TPD, the most basic of surface science methods. Moreover, Leisner and co-workers have demonstrated the potential of the infrared microspectroscopy in probing trapped particles[27]. This too can be applied to a trapping experiment on 4GLS.

3.6.1 Potential National and International User Community

These include D. Chakarov, Chalmers University, Gothenburg, Sweden, H. J. Fraser, Strathclyde University, L. Hornaeker, Aarhus University, Denmark, C. Jager, Max Planck Institute for Astrophysics, Heidelberg and Jena, Germany, J. L. Lemaire, Paris Observatory, France, H. Linnartz, Leiden University Observatory, Netherlands, R. McCullough, Queen's University Belfast, M. E. Palumbo, Catania Observatory, Italy, H. Zacharias, University of Munster, Germany.

3.7. Relationship to Existing National and International Activities

McCoustra, Brown and Mason with Serena Viti (UCL, Physics and Astronomy) and George Darling (Liverpool, Chemistry) have established an EPSRC-funded network with the purpose of encouraging and co-ordinating activity in surface science linked to astronomy. Details of the network can be found at http://www.chem.ucl.ac.uk/astrosurf/home.html. The success of AstroSurf has prompted the European community in this area to ask McCoustra to co-ordinate a FP7 Integrate Training Network Proposal. This proposal, LASSIE (Laboratory Astrochemical Surface Science in Europe), was submitted for preliminary consideration in May 2007 (http://www.chem.ucl.ac.uk/astrosurf/lassie.html). The network, if funded, will unite activities across a number of European centres and will form a focus group around which the Origins Gas-Grain Chemistry Projects will evolve. A visit in late 2004 by McCoustra and Mason to the atomic, molecular and chemical physics communities in India offered a number of opportunities to publicise 4GLS and the Origins programme. A number of other international presentations of the Origins programe have been made, including at IAU symposia.

[25] M. Grimm, B. Langer, S. Schlemmer, T. Lischke, W. Widdra, D. Gerlich, U. Becker and E. Rühl, *Phys. Rev. Lett.*, 2006, **96**, 066801.
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[27] T. Leisner, A. Simon, F. Weritz and L. Wöste, *Environ. Sci. & Pollut. Res.*, 2002, **Spec. Iss. 4**, 92.

4. PROBING THE LOW-ENERGY PHOTORESPONSE OF ATOMIC NUCLEI

Rolf-Dietmar Herzberg, Peter Butler (University of Liverpool), John Simpson (STFC), Norbert Pietralla (TU Darmstadt, Germany), Andreas Zilges (Universität zu Köln, Germany)

4.1. Aims of the Research Programme.

This programme will provide unique insight into long standing problems in nuclear physics:-

(i) The origin and distribution of the chemical elements and their isotopes.
(ii) The mechanism of core collapse in supernovas.
(iii) New form of nuclear excitations in neutron rich nuclei.
(iv) The role of the weak interaction in the nucleus.

The answer to these questions has far reaching consequences in nuclear structure physics as well as for our astrophysical understanding of the interplay of nucleosynthesis processes in explosive stellar scenarios.

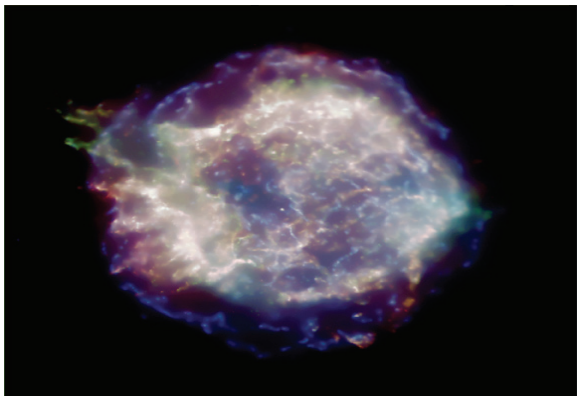

Figure 4.1: Cassiopeia A. A remnant of a supernova that reached temperatures up to $3x10^9$ K ~ 200 keV

4.2. Essence of the Science

Nuclear survival rates in the thermal photon baths of supernova explosions and other hot stellar scenarios are crucial for our understanding of the nucleosynthesis processes that are ultimately responsible for the creation of all heavy elements beyond iron in the universe. This survival rate is very sensitive to the photon induced particle evaporation cross sections. It is therefore crucial to understand the nuclear response to photons between 3 and 10 MeV as single resonances can dominate the cross section and thus vary the resultant elemental abundances significantly.

Circularly polarised MeV photons provide a uniquely selective probe into the role the weak interaction plays in the nuclear structure via the parity violating components of the nuclear wave functions. This in turn allows indirect measurements of the neutrino-nucleus reaction cross sections which play a vital role in core collapse in supernova explosions. Moreover, resonant photon scattering is a powerful tool to study exotic collective nuclear excitations such as the pygmy resonances in neutron rich systems that probe the detailed spatial distribution of protons and neutrons in the nucleus. All such studies depend crucially on the availability of a highly intense, nearly monochromatic, tuneable and polarised photon source with energies between 1 and 20 MeV. Such a source can be realised on 4GLS.

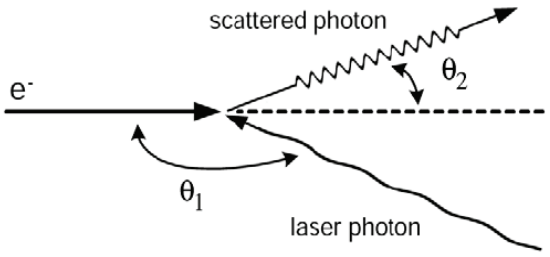

Figure 4.2:
The mechanism of Compton back scattering

4.2.1 Electric Dipole Strength distribution: The bulk of the electric dipole strength is located in purely isovector excitations such as the Giant Dipole Resonance (GDR). However, two main competing mechanisms exist which lead to an independent, natural electric dipole moment at lower energy and are thus available for study with NRF techniques: Octopole vibrations and Pygmy resonances. Both static and dynamic octopole deformation creates an electric dipole moment via the concentration of protons near the tip of the shape. This allows the study of octopole collectivity using the NRF method, including systematic studies of single and (hitherto elusive) double octopole phonons as well as mixed quadrupole-octopole two phonon excitations. Pygmy resonances occur in nuclei with neutron excess. As the neutron excess grows, the nucleus develops distinct neutron skins and halos surrounding a "normal" nucleus with a proton-neutron ratio closer to that required for stability against beta decay. In such a scenario the core can oscillate against the skin and the weak restoring forces lead to a low energy "miniature giant resonance" or pygmy resonance. The detailed fine structure of the pygmy resonance provides very sensitive tests for nuclear models and gives valuable reference points if these models are used to extrapolate the properties of exotic, very neutron rich nuclei available for study at modern radioactive beam facilities.

4.2.2. Magnetic Strength Distribution: Amongst the most intriguing nuclear excitations are those in which the nucleus forms low-lying isovector excitations, such as the "scissors mode". Recently this class of states has been extended to find mixed symmetry 2+ excitations in weakly deformed vibrational nuclei. As the mixed symmetry states occur in the same energy range as octopole excitations it is of prime importance to be able to determine the electromagnetic character and therefore parity unambiguously. Magnetic spin-flip excitations also provide an experimental handle on the size of the proton spin-orbit interaction, which ultimately determines the location of the "Island of stability" of shell stabilised super heavy nuclei with atomic numbers between 114 and 126.

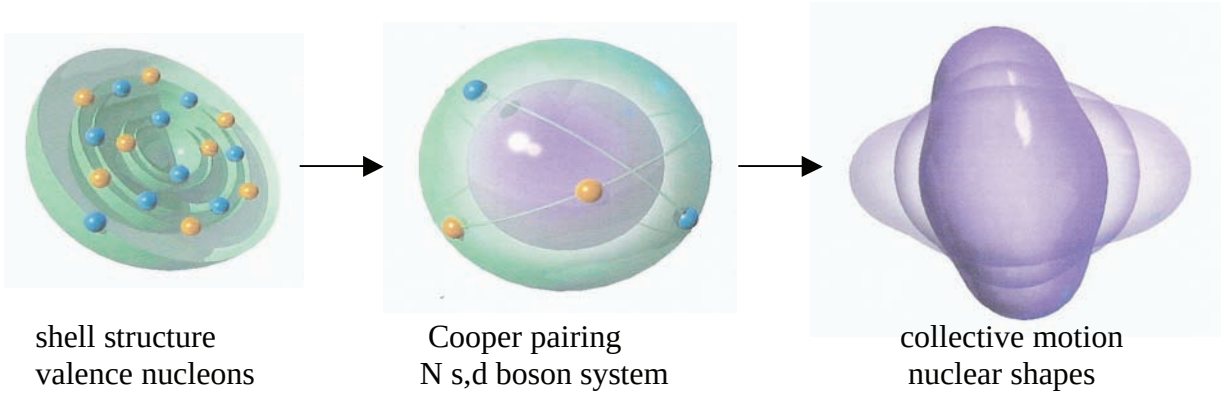

Figure 4.3: Structure and motion of the nucleus

4.2.3 Weak Interaction Studies: The use of CBS photons allows direct access to the weak interaction in nuclei via two different methods. One is the study of spin-flip M1 transitions. The mechanism is directly sensitive to the Gamov-Teller strength distribution and thus gives a handle on the weak interaction. It therefore becomes possible to connect the magnetic dipole response of the nucleus to the cross sections of neutrino induced reactions, which have direct bearing on the nucleosynthesis of rare stable isotopes such as ^{138}La and ^{180}Ta and many aspects of supernova dynamics. The other approach sensitive to the weak interaction is to use circularly polarised photons and use the parity breaking properties of the weak interaction to produce a forward-backward asymmetry in the scattering cross section that gives a direct handle on the parity violating components of the wave function. Favourable cases to study parity violation in nuclei exist where dipole excitations of opposite parity lie close in energy, e.g. in ^{20}Ne.

4.2.4 Astrophysical Consequences: A key question in nuclear astrophysics is that of the nucleosynthesis processes that lead to the observed abundances of chemical elements in the universe. In extreme stellar scenarios it is important to take into account the destructive (γ,n), (γ,p), and (γ,α) reactions in the intense photon baths whose Maxwellian temperature distributions extends up to several MeV. Here a detailed knowledge of the photo response in stable nuclei is a crucial ingredient in the nuclear models used to extrapolate to the nuclei on these nucleosythesis paths, which (apart from the s-process) all proceed very far from stability. The CBS setup at 4GLS will be of pivotal importance in the mapping of this response.

4.3. The need for 4GLS: the ideal photon source

The achievable photon flux on a CBS facility on 4GLS is at least an order of magnitude larger than achievable on any other machine worldwide and peerlessly brilliant photon flux will allow research on the electromagnetic dipole response in nuclei to progress far beyond present capabilities. We estimate an average of $N\gamma = 8.1 \times 10^8$ total γ rays per second, with $N\gamma = 1.8 \times 10^7$ γ rays per second in a collimated 3% energy spread if each photon has a single opportunity to interact with the electron bunch. This conservatively estimated intensity will be increased by a factor 10-1000 if the Compton backscattering process is done in a cavity as each laser photon can be used multiple times.

4.4. The Research Team

Rolf-Dietmar Herzberg is a former EPSRC Advanced Research Fellow and currently leads a research programme into superheavy nuclei. He has worked in Photonuclear Physics for nearly 10 years before joining the Liverpool group. He has published over 100 refereed papers and presented over 30 invited talks at conferences. Peter Butler has led research investigating superheavy nuclei and octupole phenomena and has made significant discoveries in this field. He was recently on leave of absence as Head of the Physics Group at ISOLDE (CERN) until 9/2005. He has over 170 refereed papers and presented over 50 invited talks to international conferences. John Simpson is a world-leading γ-ray spectroscopist with expertise in array design. He leads the γ-ray group at Daresbury and has over 210 refereed papers. He has made several leading contributions to the high spin world, including high spin shape changes, multiple band terminations, unpaired rotational bands and the study of shape coexistence in extremely neutron deficient heavy nuclei. Norbert Pietralla is an expert in mixed symmetry states and Compton Backscattering with over 150 refereed papers and numerous talks at international conferences. Andreas Zilges is an expert in Photon scattering and nuclear astrophysics with over 110 refereed papers and numerous conference talks.

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5. REACTION PATHWAYS IN CATALYTIC CHEMICAL PROCESSES

Richard Catlow FRS, Gopinathan Sankar, Geoff Thornton (University College London), Graham Hutchings, Albert Carley (University of Cardiff), Robbie Burch, Christopher H. Hardacre (The Queen's University of Belfast), John Evans (University of Southampton), Mike McDonald, Mark Surman, Steve G. Fiddy (STFC) Daresbury Laboratory, Sven L.M. Schroeder (The University of Manchester)

5.1. The Importance of Catalysis for Modern Societies

Catalytic processes are the backbone of the chemical industry, the products of which enhance the quality of our life and will sustain our economies for the foreseeable future. New catalytic processes will be the key technologies for a shift from fossil feedstocks towards sustainable resources. Catalysts will also remain essential for agricultural production, through their role in the manufacture of fertilisers, pesticides and fungicides. The textile industry will continue to depend on polymerisation catalysts for the synthesis of fibres, while energy production will increasingly use new catalytic technologies for the generation of clean power, for example through fuel cells, hydrogen generation and carbon-neutral catalytic combustion systems. Processed foods and chemical household products are generated using catalytic processes, while the production of commodity chemicals for the generation of high-performance materials almost always relies on a catalytic process. The global economic importance of catalysis is enormous. Catalytic processes are estimated to underpin approximately 30% of GDP in the UK. The UK's Office of National Statistics Annual Business Inquiry reports that the Chemicals, Pharmaceuticals and Biotechnology industries in the UK have a turnover in excess of £65.7 billion. Clean energy production, where the UK is a major player, both in the development of fuel cells and in the associated fuel processing technologies, represents a new market that is predicted to be worth £20 billion by 2010. The predicted shift to renewable feedstocks has resulted in a global drive to replace the rather mature traditional processes through technological approaches with a much greater level of sophistication and with higher complexity. The emphasis is on chemical intensification; designing one catalyst to achieve several tasks simultaneously. This we need to target new catalysts through better control of their molecular structure and composition, with a knowledge of their reaction pathways.

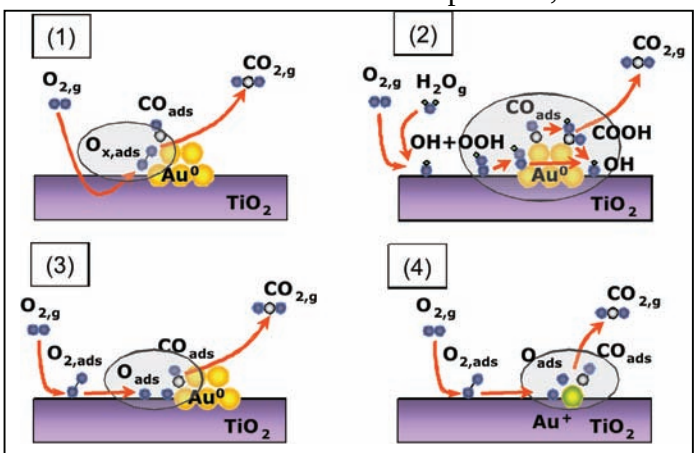

Figure 5.1: (1) Current mechanistic understanding of the reaction sequence leading from molecular O_2 to its dissociation and/or reaction with CO to CO_2 over supported Au. Note that the nature of the reactive oxygen species remains unspecified as $O_{x,ads}$ (2) Thermodynamically plausible, but experimentally unverified, sequence of elementary reactions leading from the adsorption of O_2 to CO_2 in the presence of moisture. (3) Langmuir-Hinshelwood type reaction of O_2 with CO. Experimentally not verified. (4) Alternative reaction scheme to (3) but involving a cationic Au species as the active site. Experimentally not verified. Reproduced with the permission of Sven Schroeder.

5.2. The Need to Improve Our Understanding of the Molecular Basis of Catalytic Processes

To design new processes and develop new catalysts, we need to determine the atomic-level architectures and reaction pathways that are responsible for effective performance. In general, through advanced characterisation techniques (including synchrotron radiation), we now have an emerging knowledge of active site structures for a limited number of systems. However, understanding of catalytic reaction mechanisms remains almost completely absent, and this is where 4GLS is uniquely suited to contribute.

Catalytic processes can be heterogeneous, involving chemical reactions at the interfaces between two phases, or homogeneous, with reactions proceeding in a single phase. Elucidating molecular

transformations in heterogeneous reactions is more difficult because the effective reaction networks are restricted to a thin interfacial layer with thicknesses of often only a single molecular layer.

5.2.1 Heterogeneous Catalysts Through the development of surface-sensitive laboratory spectroscopies, synchrotron radiation probes, laser sources and tremendous improvements in computational methodologies, our insight into the molecular basis for catalytic processes has advanced substantially, yet we are still very far from truly unravelling the networks of molecular transformations that determine catalytic action. We still cannot routinely design heterogeneous catalysts for a given task, and a scientific consensus about the molecular origin of catalytic activity remains elusive for many technologically important classes of catalyst materials. The catalytically effective reactions paths often appear to involve minority surface species and/or intermediates that are very difficult to detect against the background of generally unreactive majority species. To home in on the relevant species and distinguish them from the spectators we require more incisive and chemically more selective time-resolved surface probes.

5.2.2 Homogeneous Catalysis This form of catalysis is achieves the ideal combination of high reactivity and selectivity due to the high degree of control that is achievable for the environment of catalytically active metal centres. Single site catalysts can be designed from a view of the elementary steps of a reaction. A key illustration of this is the design of alkene metathesis reactions. In this reaction two carbon-carbon double bonds react to form two new carbon-carbon double bonds. The reaction takes place under mild conditions and is so general that it is widely applicable. Catalysts have been devised that enable a degree of control to be realised in high enantiomeric excesses of optically active (chiral) compounds vital to flavours, fragrances and pharmaceuticals.[1] However, most discoveries are refinements of serendipitous leads. Gaining a deeper understanding of the elementary steps in these chemical reactions will both ease this optimisation but would also help define the metal enviroments necessary to attain important chemical transformations such as C-C single bond metathesis, "green" oxidations and hydroammination of alkenes (to create amino acids) with high activity and selectivity. Primary steps have been identified by laser UV/Visible photoexcitation as a pump and UV/Visible[2] or IR[3] as the probe. This photolysis creates hot unsaturated transient species and then thermal reactions (rearrangements or associations) occur on timescales of ~ 10 ps or longer. A greater array or probes sensitive to the structural and electronic properties of these transients is required together with more specific excitations to allow study of the energy transfer during these chemical reactions.

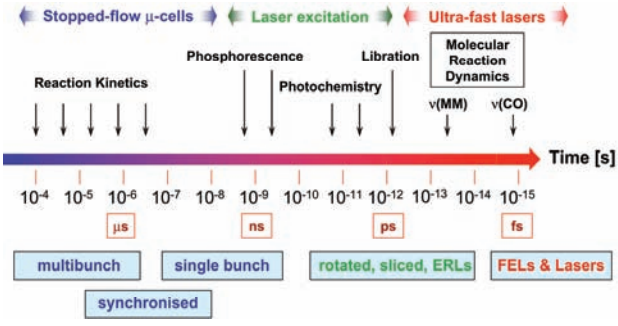

Figure 5.2 Timescales of physical processes and associated laser and synchrotron radiation techniques.

5.3. Watching molecules dance: 4GLS as the ultimate searchlight for unravelling molecular transformations in catalytic reactions

Over the last two decades laser and synchrotron X-ray techniques, in combination with computational methods, have been the most definitive in determining atomic architectures under catalytic reaction conditions. Although these techniques have enabled much scientific progress they also have limitations, in particular in achieving time-resolution in the ps - fs range – that is the timescales required for fully resolving the dynamic molecular structure changes *during* a reaction

[1] R H Grubbs, Nobel Lecture, *Angew. Chem, Int. Ed.*, **45**, 3760, (2006) and R R Shrock, *ibid*, 3748, (2006).
[2] V Montiel-Palma, D I Pattison, R N Perutz and C Turner, *Organometallics*, **23**, 4034, (2004)
[3] G E Ball, C M Brookes, A J Cowan, T A Darwish, M W George, H K Kawanami, P Portius and J P Rourke, *Proc NAS Amer*, **104**, 6927, (2007).

(fig. 5.2). As a result, current X-ray methodologies invariably provide an averaged picture of a multitude of molecular processes. Based on such data it is currently, with the exception of a very few sufficiently slow reactions, impossible to identify the crucial molecular transition states. 4GLS will for the first time provide an analytical tool with (i) the energy range, (ii) time resolution and (iii) power to resolve the required structural information on the timescale of catalytic reaction dynamics. It is already the case for some reactions that high quality simulations of the behaviour of the system over fs – ps timescales are available, but no experimental data exist to verify the predictions of reaction intermediates. 4GLS will provide these data, and its development is made doubly powerful by the synergy that will be achieved with the development of petascale computing that will occur over the same timescales. Using pump-probe dual beam techniques (figure 5.3) we will be able to identify and selectively detect the electronic and geometric structure of individual molecular species, including molecular complexes in the transition state. The unique structural incisiveness of the 4th generation source will enable us for the first time to 'see' molecules in a catalytic reaction progressing *via* the state transition state to reaction products. The proposed 4GLS source is ideal to achieve this dream of studying 'working catalyst' from beginning to the end. For example, THz radiation in sub-cycle pulses used in an impulsive mode may act as the pump for the reaction and synchronised soft X-ray and IR sources will provide the tool for local chemical and structural characterisation during the reaction through X-ray absorption and IR spectroscopy.

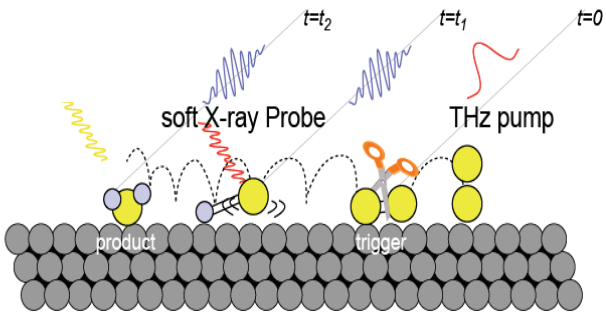

Figure 5.3: A pump-probe measurement at a surface. A very low energy half-cycle terahertz (THz) pulse causes initial dissociation of a molecule (yellow) at a surface at time t_0. The reaction is followed at times t_1 and t_2 using synchronised soft X-ray photons (blue) that monitor the reaction of the dissociated atoms with new species to form the product. (Adapted from original figure by Anders Nilsson and colleagues at SLAC, with permission).

Many of the important reactions that we would like to understand occur at very close to room temperature and the question that then arises is can we really use a low energy IR FEL or THz pulse to promote a specific reaction? Surely all the energy in the pulse will immediately be dissipated by internal vibrational relaxation (IVR), and we will just see a non-specific warming effect? One of the first indications that this is not the case came in 2006 from experiments by Norman Tolk and his co-workers using the Vanderbilt FEL in the US, that showed chemically selective bond dissociation of Si-H bonds at a silicon surface by resonant excitation at the Si-H stretching frequency[4].

5.4. Scientific Methodology

The reactions studied will concentrate on four key areas where catalysis makes key contributions: **energy, organic transformations, clean environment and *in situ* production of hazardous intermediates.** The experiments proposed, involving real-time reaction monitoring via ultrafast pump-probe approaches are complex and demanding. There is a need to make a relatively simple initial choice of system for study. Systems based on gold (nanoparticulate, anionic or cationic) are chosen; gold catalysis is an exciting field, and one where the chosen system catalyses a key reaction of global concern in each of the four areas listed (as shown in figure 5.4). The catalysts may also be tailored to both heterogeneous and homogeneous environments.

[4] Zhiheng Liu, L C Feldman, N H Tolk, Zhenyu Zhang, P I Cohen, Science, 312, 1024, (2006).

5.4.1Heterogeneous Catalysis

Supported Au catalysts have shown a remarkable activity in a variety of low-temperature oxidation reactions, such as the oxidation of CO[5]. Despite extensive investigations of powder and model catalysts the mechanism by which molecular oxygen is activated in these reactions is not understood. Gold single crystals are inactive towards oxygen unless energy is provided to break the O-O double bond. Activation of O_2 on the gold particles has been observed for TiO_2 and Al_2O_3. On the other hand, for reducible supports (such as TiO_2) it has been suggested that this step proceeds on the support, which then provides active oxygen to the gold cluster. This view is supported by the low reactivity of bulk gold towards O_2. DFT calculations predict two oxygen activation pathways for gold supported on oxides: (i) an activation on the gold cluster and (ii) activation on the support oxide. However, experimental data elucidating O_2 activation over these catalysts is scarce. Pump-probe spectroscopy with combined XAS and IR probes will allow the reaction mechanism to be established, distinguishing between the alternative proposed schemes illustrated in Figure 5.1.

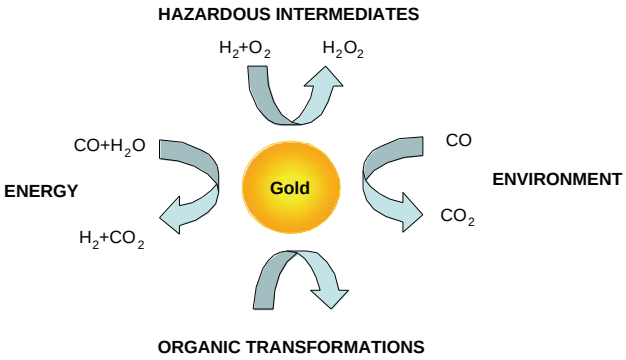

Figure 5.4: Important reactions of contemporary interest catalysed by gold. Clockwise from top: generation of hydrogen peroxide; oxidation of carbon monoxide; selective organic transformations important for renewable feedstocks; generation of hydrogen.

5.4.2 Homogeneous & Immobilised Catalysis: Enantioselectivity and Chiral Amplification

The ability to synthesise pure enantiomers is of crucial importance for the preparation of modern pharmaceuticals and agrochemicals. Most early progress has been focused on the design of molecular catalysts operating as homogeneous catalysts, work which culminated in the award of the Nobel Prize for Chemistry in 2001 to Noyori, Sharpless and Knowles[6]. However, industry has been slow to take up these synthetic methodologies since separation of the catalyst from the reaction mixture can be difficult and hence catalyst recycle and reuse can be very difficult. For this reason, attention has recently focussed on the design of immobilised catalysts which can overcome these problems[7]. Unfortunately, almost invariably, poorer enantioselection is achieved with the immobilised complex compared to the comparable homogeneous catalysts[8]. However, there are a number of studies indicating that improved enantioselectivity can be achieved by immobilisation. In 2000 Raynor *et al.*[9] showed that a carefully planned immobilisation strategy could result in enhanced enantioselection being observed with the immobilised catalyst when it is constrained within the ordered mesopores of a zeotype, MCM-41. The improved effect of immobilisation is considered to be due to a containment effect[10].

An alternative immobilisation strategy uses catalytically active cations that are electrostatically immobilised within microporous and mesoporous materials by ion exchange and they are subsequently modified by chiral ligands[7]. This immobilisation strategy has been used to synthesise stable reusable catalysts for enantioselective hydrogenation[11]. Asymmetric

[5] N. Weiher, A.M. Beesley, N. Tsapatsaris, L. Delannoy, C. Louis, J.A. van Bokhoven & S.L.M. Schroeder, Journal of the American Chemical Society 129 (2007) 2240-2241.
[6] Nobel lectures, *Angew. Chem., Int. Ed.*, 2002, **41**, 998.
[7] P. McMorn and G. J. Hutchings, *Chem. Soc. Rev.*, 2004, **33**, 108; L.-X. Dai, *Angew. Chem., Int. Ed.*, 2004, **43**, 5726.
[8] J. S. Johnson and D. A. Evans, *Acc. Chem. Res.*, 2000, **33**, 325.
[9] S. A. Raynor, J. M. Thomas, R. Raja, B. F. G. Johnson, R. G. Bell and M. D. Mantle, *Chem. Commun.*, 2000, 1925.
[10] J. M. Thomas, T.Maschmeyer, B. F. G. Johnson and D. S. Shephard, *J. Mol. Catal. A*, 1999, **141**, 139.
[11] W. Hems, P. McMorn, S. Riddel, s. Watson, F.E. Hancock and G.J. Hutchings, Org. Biomol Chem., 2005, 3, 1547

hydrogenation reactions continue to demand attention using a whole library of chiral phosphine ligands, however, in many cases the enantioselectivity achieved with the immobilised complex can be significantly lower than those observed for the non-immobilised catalyst. Progress can only be considered to be made if the enantioselection or overall turnover numbers achieved with the stabilised or immobilised catalyst is comparable to the homogeneous catalyst, and to date there are very few examples of such improvement[12].

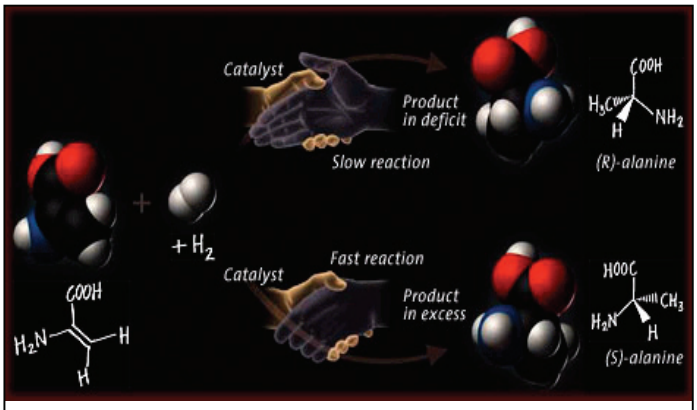

Figure 5.5: The mechanisms of asymmetric hydrogenation are not understood. Courtesy William Hems, Johnson Matthey Catalysts -Chiral Technologies

The enhancement in enantioselection and activity is considered to be associated with the confinement of the chiral complex, but very little mechanistic information is available on these working catalysts. The aim of the pump-probe studies will be to carry out detailed investigation of the interaction of the chiral catalysts and substrates and products to determine the origin of this fascinating effect. It is anticipated that in addition to XAS and IR probes, this work would make use of the flexible polarization of the 4GLS sources, for example in UV time-resolved CD or time-resolved optical rotatory dispersion, using the VUV FEL, where flux levels are expected to be sufficient to allow single-shot experiments. The use of IR CD will also be explored. These approaches will be extended to studies of so-called 'chiral amplification' such as the Soai autocatalytic reaction,[13] where symmetry breaking in an asymmetric reaction leads to high enantiomeric excess.

5.5. Wider collaboration

Wider collaborators include Lynn Gladden FRS (chemical reactor dynamics) and Phil Woodruff FRS (surface science). Existing collaborations are in place with the FHI, Berlin (Freund, Schlögl), BESSY, DESY, SSRL and Jefferson Laboratory and are expected to develop further through this work.

[12] e.g. N. A. Caplan, F. E.Hancock, P.C. Bulman-Page and G. J. Hutchings, *Angew. Chem., Int. Ed*., 2004, **43**, 1685.
[13] K Soai, T Shibata, H Morioka, and K Choji, *Nature*, **378**, 767 (1995).

6. RESRAD: REACTION DYNAMICS OF EXCITED STATES AND FREE RADICALS IN CHEMISTRY AND BIOLOGY

Ultrafast time-resolved pump-probe spectroscopy using pulsed electron and photon beams

Roger H Bisby (Biomedical Sciences Research Institute, University of Salford), Simon M Pimblott (Dalton Nuclear Institute, University of Manchester), Julia A Weinstein (Department of Chemistry, University of Sheffield), Hugh Burrows (University of Coimbra), Tony Parker (STFC RAL)

6.1. Motivation; the importance of free radical chemistry

Free radicals are of key importance in chemistry and biology – for example in intramolecular electron transfer in DNA and proteins (including photoactivation of metalloenzymes and thus biological energy conversion), and in charge transfer processes in molecular electronics. The materials area of organic electronics is now of major importance, with indications that the global market is likely to grow from its present level of about $1-2 bn/year to around $100 bn/year by 2020.[1] Conjugated polymers and other organic electroactive materials will play a major role in this area through applications in light emitting diodes, thin film transistors, photovoltaic systems for solar energy conversion, sensors, etc[2] Associated with this is the rapid development in nanotechnology; the importance of understanding charge-transfer processes at this level in the development of the next generation of advanced architectures for device applications has been highlighted through DOE and other international workshops. What is needed now is a detailed understanding of the dynamics and energetics of the various processes involved.

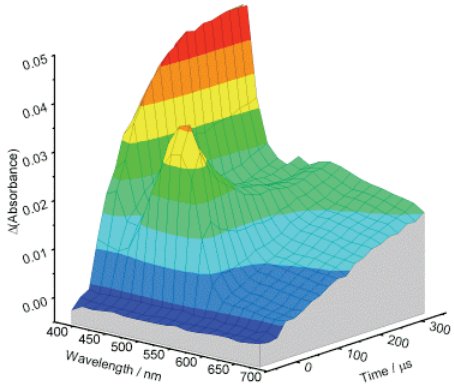

Figure 6.1: transient absorption data from a pulse radiolysis study of a-melanocyte stimulating hormone (MSH). One radical species absorbing at about 520 nm is created immediately upon excitation; as this decays another absorption grows in at shortest wavelengths sampled, about 400 nm. These absorption changes correspond to the radical transformation Trp$^{\bullet}$ -> TyrO$^{\bullet}$ (http://www.frrf.dl.ac.uk/)

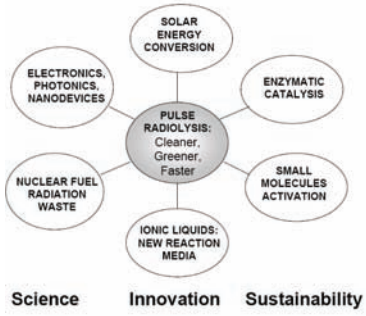

Figure 6.2: RESRAD; from fundamentals to practice.

Pulse radiolysis (using an electron beam) is an effective way of creating free radicals for study. It allows unique studies of DNA base damage and repair, the effects of radiotherapy and the development of drugs for photodynamic therapy. Irradiation effects in molecular liquids are important at various points in the nuclear cycle, and in the study of 'green' solvents. Here we propose to use the 4GLS electron beam to produce free radicals combined with fast time-resolved spectroscopies provided by the 4GLS photon sources to measure the ps dynamics of charge transport in radical systems in biology and electroactive materials. The proposal stems from an established platform of radiation chemical methods developed at the University of Notre Dame (USA, Pimblott – now at the Dalton Nuclear Institute, University of Manchester[3]) and the Free Radical Research Facility at Daresbury Laboratory[4] (Bisby, Weinstein and Burrows).

6.2. The need for 4GLS

The science programme requires a pulsed electron beam source with synchronised photon pulses across the infra-red – visible- UV- X-ray region for pump-probe studies of fundamental reactions in the ps to ns regimes. A laser-driven accelerator system provides the opportunity for ps synchronisation of electron and photon beams, for example by employing a laser-driven cathode in a

linac and coupling the same laser oscillator to optical parametric amplifiers covering a wide spectral region. Examples of such dedicated linac-based apparatus have recently been described[5-7] as has a laser-wakefield based setup[8]. Some of the ideal characteristics of the beam (for example beam stability, charge per pulse of a few nC and energies of around 5 MeV) will be provided by the beam dump for 4GLS; others (repetition rates of ≤ 100 Hz) will require assessment in the Technical Design Report for the source.

The full potential of the short pulse electron beam can only be realised by employing as wide as possible range of appropriate detection techniques with sufficient time resolution to study the transient species. Within the 4GLS context the following can be naturally implemented:

- Transient absorption (TA) spectroscopy: this is the most wide used detection methods used in ns and s pulse radiolysis. At ps times the solvated electron has strong absorption in the near infrared red (700 – 1200 nm) and has been characterised in a number of systems[5-8].
- Time-resolved vibrational spectroscopy. Both time-resolved infra red (TRIR) and time-resolved resonance Raman (TR^3) have the power to discriminate and identify molecular species down to ps timescales. Both methods have been extensively proved using two-colour laser pump-probe spectroscopy. The only example of these techniques being intensively applied to the study of radiation-induced transients is at the University of Notre Dame (USA). However preliminary results on a ms timescale have been obtained at Daresbury using the linac pulsed electron beam in combination with a ns pulsed Nd:YAG laser. Results showing the TR^3 spectrum of the triplet state of a prototype molecular wire[9] are shown in Figure 3 (Beeby, Parker and Bisby, unpublished).
- X-ray absorption. New work has recently demonstrated the use of time-resolved XAFS in the nanosecond regime as a probe for structure of small molecules ($Br_2^{-\cdot}$) in solution[10]. In this case a frequency-quadrupled Ti-sapphire laser was locked to the pulse structure of a synchrotron source, indicating the potential for exploration of species such as metal ions within inorganic, organometallic and biochemical systems.

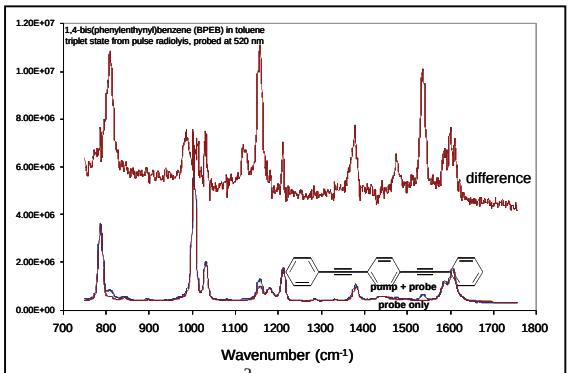

Figure 6.3: The TR^3 spectrum of a the triplet state of a prototype molecular wire, BPEB, in toluene using 520 nm excitation (R Bisby *et al.*,, with permission)

Within the UK, workers at CLF, STFC led by Parker have made enormous contributions to developing optical detection (TA, TRIR, TR^3) methods and novel instrumentation. This group is ideally placed to make a major contribution to detector technology for this proposal.

6.3. Scientific Methodology

Radiation chemistry provides the opportunity to form both one-electron oxidised and reduced species under well-understood conditions and the technique is applicable to an extremely wide range of topics in chemical, biological, medical and materials sciences[11]. However these methods have been used in the main to study diffusion-controlled reactions, thereby placing a fundamental limit on the time resolution that is attainable. At room temperature in liquid water a typical diffusion-controlled second order rate constant is ~10^{10} dm^3 mol^{-1} s^{-1}. In a solution containing solute at 1 mol dm^{-3}, the radical species of interest will formed within 100 ps. Some systems are available for study at these concentrations (carbohydrates, some amino acids) and offer a very valuable increase in time resolution by up to a factor of 10^2. Even in the systems without this advantage, the unique combination of sub-ns electron pulse and synchronised spectroscopies will open new areas for study. The diffusional limitation discussed above does not apply in several of the systems proposed for study here. These include radiation effects at surfaces and in molecular liquids. Molecular liquids include common solvents used in the nuclear industry, some novel “green” solvents which have

already been studied for their potential in the same area, and other systems which may act as prototypes for components in biological systems such as unsaturated lipids.

6.3.1 Biological Systems

6.3.1.1. Radical migration in DNA The formation of free radical induced strand breaks and base damage in cellular DNA are the major contributors to radiation induced cell death[11]. A full understanding of these processes is vital to our knowledge of the effects of low level environmental radiation[12] and in the radiotherapy of cancer[13]. Radical migration in DNA is responsible for generation of lethal double strand breaks. It is known to occur at two levels – within the ribose phosphates hydrogen atom transfer occurs too rapidly to be measured by ns measurements[14], and the additional time resolution of a ps apparatus will be vital in allowing such processes to be characterised. Migration of electron/hole sites along the double stranded DNA molecule is slower, occurring in the ns to ms regime[15]. However here the observations are hampered by a lack of spectral resolution in the UV-visible optical spectra that characterise radical sites on the different DNA bases. TR^3 or TRIR[16] using 4GLS sources will allow more precise identification of the radical species and enable kinetic measurements of molecular processes leading to lethal DNA damage. Preliminary work to link TR^3 to pulse radiolysis at Daresbury has already been carried out.

6.3.1.2. Oxidation of organic molecules and antioxidants – studies of molecular liquids The one-electron oxidation of certain organic molecules is of fundamental interest from a biochemical viewpoint. In particular organic free radicals are cofactors of several important enzymes including those utilising B_{12}. In these enzymes, cobalamin generates a free radical of the organic substrate which undergoes a re-arrangement[17]. Similarly the one-electron oxidation of polyunsaturated fatty acyl groups in lipids of membranes and lipoproteins potentially generates different unsaturated radicals, the relative stability having recently been calculated[18]. Reactions of these radicals with oxygen leads to the chain reaction of lipid peroxidation and is the biochemical basis for heart disease[19]. In order to circumvent the diffusion problem, these species will be studied in molecular liquids. For example, the one-electron oxidised species of the fatty acid will be formed by direct ionisation of methyl linoleate, a compound used in classical studies of oxygen uptake and peroxidisability by Ingold and co-workers[20]. The organic free radicals formed in such molecular liquids are ideally studied using TRIR. The organic peroxyl radicals expected to be formed in such systems are those species responsible for propagation of oxidative damage in biological systems. Free radical chain-breaking antioxidants prevent such damage, and their effectiveness depends on stereo-electronic properties that are conveniently studied by TR^3.[21,22]

6.3.1.3 Controlling light-induced charge-separation – photochemical energy conversion

Solar energy is one of the key sources of sustainable energy. A charge-separated excited state is the key intermediate, which is formed as a result of photo-induced electron transfer (PET) in an essential donor-spacer-acceptor component. In artificial systems, the [D$^+$-sp-A$^-$]* state is often too short-lived to be chemically useful due to facile back electron transfer. Stabilization of such charge-separated intermediate states is thus pivotal to the development of efficient artificial systems. We propose a new solution – molecular reorganization to form a transient sulfur-sulfur bond within the intermediate that acts

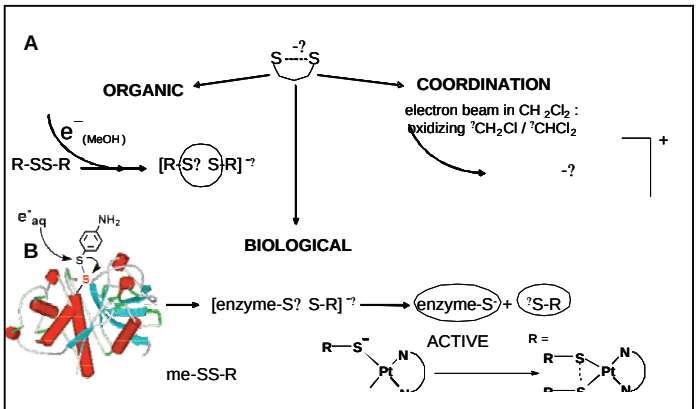

Figure 6.4: Reaction schemes for model Pt diimine-dithiolate systems that allow transient -SS- bond formation.
A: a reaction scheme for controlling light-induced charge separation in photochemical energy conversion;
B: a reaction scheme for active enzyme production via cleavage of the -SS- bond
(J Weinstein, reproduced with permission)

as a reservoir for the absorbed light quanta and creating an activation barrier for back electron transfer. In model Pt diimine-dithiolate systems (Figure 6.4A), thiolate → diimine PET forms a system with a thiolate anion and thiyl radical, which can interact with each other via the metal centre to give a [S∴S] 'hemibond', decreasing the S–S distance in the excited state and providing a barrier to back electron transfer[23]. The electronic properties of the RS ligand are used to control photoreactivity by tuning the energy of the S∴S bond. Raman spectroscopy is the only direct way of probing the the S∴S interaction as ν(SS) is strongly Raman active and will be signalled unambiguously by the appearance of an intense ν(SS) band. Pulse radiolysis[24] in combination with TR[3] capabilities will allow the identification of the vibrational signature of the S∴S bond. The lifetimes of radical cations as a function of electronic structure will be correlated with the stability of the S∴S bond. *A combination of pulse radiolysis with transient absorption and vibrational spectroscopies using the 4GLS sources will secure the vital step forward for the development of our novel concept of energy storage.*

6.3.1.4 Switching an enzyme on by pulse radiolytic cleavage of –SS-protecting group

A method is being developed for the caging of proteins depending on disulfide formation of protein thiol groups. Uncaging will then be achieved by reductive cleavage of the dilsufide bond. We have covalently labelled the single thiol of the cysteine at the active site of the protease papain by an aromatic thiol group, creating an –S-S-Ar bond which completely inactivated the enzyme. Heteroleptic –S-S- cleavage will be achieved by pulse radiolysis[25] under reductive conditions to generate [enzyme-S∴S-Ar]-radical anions, which can dissociate producing active enzyme-S^- (Fig. 6.4B). Preliminary measurements using pulse radiolysis, flash photolysis and steady-state spectrophotometric biological assays to concomitantly monitor release of thiyl radical and enzymatic activity have demonstrated the reactions in Fig 6.4B and recorded significant increases in enzyme activity. *This process will enable, for the first time, the use of pulse radiolysis as a non-invasive and chemical-free way of reactivating caged enzymes, which also allows for time-resolved investigation of enzyme dynamics using the 4GLS sources.*

6.3.2 Electroactive materials research

Pulse radiolysis has proved to be a major technique in elucidating many charge-transfer mechanisms in electroactive materials, and the development of this technique with ps time resolution within the 4GLS proposal is likely to lead to results with very high impact. The technique involves irradiating samples with an intense, short-lived burst of high energy radiation (typically tens of MeV) and following the return of the system to the same or a new equilibrium. Using microwave detection, ultrafast electronic conduction (approximating to molecular wire behaviour) has been observed in conjugated organic polymers,[26,27] while ultrarapid electron transfer has also been seen in other organic systems, including discotic liquid crystals.[27,28] High energy radiation selectively induces events in the species present in highest amount. For solutions this is the solvent, and using the technique it has proved possible to selectively generate excited states, free radicals or charged species. This technique has been used at Daresbury to obtain some of the first detailed information on the triplet states of conjugated organic polymers[29] or other electroactive materials, such as Alq_3,[30] and has demonstrated that their electronic properties should be treated within a molecular exciton model. The technique has shown other interesting phenomena, such as formation of multiple excitations on a single chain, leading to delayed fluorescence,[31] which provides important information for optimising efficiencies in devices using these materials. The industrial relevance of this work is clearly seen by the interest of major electronic and photonic industries in supplying materials to be studied by this technique. However, the studies till now have been limited by both the lifetime of high energy radiation pulses (typically > ns) and by detection systems. In this proposal ps pulses will be generated that approximate to lifetimes of initially produced excited and charge separated species. The viability of pulse radiolysis studies on this timescale has been demonstrated at Brookhaven National Laboratory by the LEAF facility.[3,28] Detection techniques such as TR[3] and

acoustic calorimetry provides the intriguing possibility of making measurements directly on thin film devices, allowing electro-optic processes to be followed *in situ* (i.e. in devices), and aiding the development of new device architectures.

A further related and as yet undeveloped area involves the study of the direct interaction of high energy radiation with organic electroactive materials, which may have implications in areas ranging from sensors to doping of solid organic and polymeric matrices. For example, preliminary (unpublished) studies using the photochromic system 2,4-dinitrobenzylpyridine have shown that upon high energy irradiation, colour changes are produced that can be used as cheap, personal high energy radiation sensors. Current awareness of international security problems indicates this is an area with major potential impact. To optimise this, it is important to follow the initial stages (ps timescale) of the photochromic processes.

6.4. Collaborations and wider community

The wider community supporting this development are based at Cardiff (Rozanowska), Durham (Beeby, Monkman), Keele (Land, McGarvey, Ramsden, Truscott), Leeds (Beddard, Parsons, Reid), London (Riley), Liverpool (Ismail), Manchester (Allen), Newcastle (Benniston, Harriman), NEWI (English), Nottingham (George), Oxford (O'Neill), Sheffield (Hunter, Wells) and STFC (Edge, Navaratnam). International collaborations are established or anticipated with the Czech Republic (Borovansky), France (Aukaulo, Bensasson, Leech, Leibl, Seta, Sinay, Saraka, Tanielian, Zhang), Germany (Boehm, Distel, Schussler), Greece (Hiska), Netherlands (Alia, Pavel, Smit), Italy (D'Inschia, Lanzalunga, Bietti, Napolitano), Norway (Kristensen, Tonnesen, Razi-Naqvi), Poland (Sarna, Sionkowska), Portugal (Burrows, de Melo, Mogado), Spain (Bosca, Canle-Lopez, Miranda) and Sweden (Back). The wider research programme will include free radical rearrangements in protein-radical enzymes, photoactivation of metalloenzymes, redox activated anticancer drugs, drugs for photodynamic therapy, Pt-DNA complexes, melanogenesis, dynamics of drug-target interactions, dynamical processes of eye pigments and proteins, and their oxidation related to disease, and time-resolved imaging of tissues over wide spectral ranges.

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7. BIOCATALYSIS, PHOTSYNTHESIS AND MEMBRANE PROTEINS

Nigel Scrutton (University of Manchester), Peter Henderson (University of Leeds), Miroslav Papiz (STFC)

7.1. Aims of the Research Programme

The aim is to produce a step change in the fundamental understanding of enzyme catalysis, photosynthesis and the action of membrane proteins.

The unique capabilities of 4GLS will be used to address the major controversy concerning the role of protein motions in enzyme catalysis and provide insight into the design of enzymes and proteins for biotechnological exploitation.

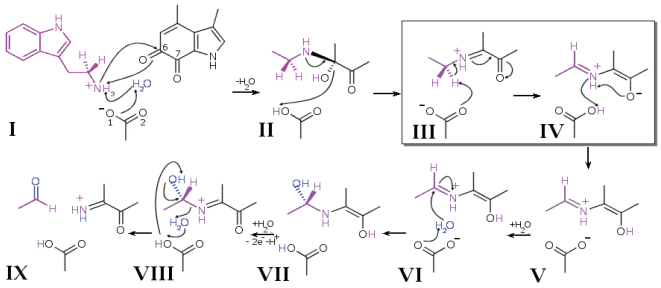


Figure 7.1: Schematic overview of the reductive half-reaction of AADH with tryptamine analysed by time resolved X-ray crystallography. Detailed chemical understanding is derived from this type of analysis, but quantitative understanding is lacking. AADH is one of the model proteins we wish to use in this flagship project to access sub picosecond motions that couple to the reaction coordinate and facilitate the chemical reaction mechanism.

A full appreciation of photosynthesis will advance the development of artificial solar cells and methods for manufacturing cheap clean bio-fuels. It will provide insight into how organisms adapt to changes in heat and light and into the management of environmental CO_2. New methods will be developed for studying the membrane proteins that comprise up to 30% of cell proteins but which cannot be crystallised and studied by protein crystallography. These proteins are important in targeting of cell receptors/transporters in therapeutic intervention.

7.2. Essence of the Science

This programme is concerned with the reaction dynamics of soluble and membrane bound systems, fields in which the UK has major strengths and which are the focus of intense debate on the mechanisms that control fundamental reactive processes in biology. The programme has three related sub-fields that will benefit from the unique experimental capabilities of 4GLS that will facilitate the development of radically new spectroscopic techniques.

7.2.1. Fast protein motions accompanying biological catalysis and electron/hydrogen transfer in soluble enzymes: Biological electron transfers and enzyme catalysed transformations are key reactive processes. However the physical basis of biocatalytic power remains contentious despite sustained and intensive research efforts. Our knowledge of enzyme catalysis is predominantly descriptive, gained from traditional protein

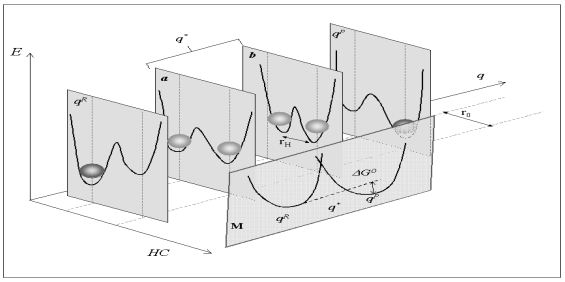


Figure 7.2. A model for the hydrogen transfer reaction used to interpret our experimental data. The three axes are: *E*, energy; *q*, environmental coordinate; *HC*, hydrogen coordinate. The four vertical panels show the potential energy curve as function of H coordinate for three values of the environmental coordinate: q^R is for the reactant, q^* is for the transition state and q^P is for the product. The grey spheres represent the groundstate vibrational wavefunction of the H nucleus. The panel labeled ***M*** shows a Marcus-like view of the free energy curves as functions of this environmental coordinate. The motions of the environment modulate the symmetry of the double well, thus allowing the system to reach a configuration with (nearly) degenerate quantum states (q=q^*), from which the hydrogen is able to tunnel. The difference between panels ***a*** and ***b*** is a gating motion that reduces the distance between the two wells along the *HC* axis (r_H) away from its equilibrium value (r_0).

crystallography and solution studies. The ultimate aim is develop a complete and quantitative picture of dynamic catalytic processes in enzyme systems and biological redox proteins.

7.2.2. Photosynthetic Dynamics and Pathways in Membrane Charge-transfer Systems:

Photosynthesis is the biological process of converting solar energy into ATP. Detailed information on photosynthetic macromolecules has been obtained from X-ray crystallography studies and fast dynamic studies of their chromophores and cofactors. While AFM imaging has revealed the organisation of native photosynthetic membranes. Protein dynamics play key roles in mechanisms of energy, electron, proton and chemical transport, but are difficult to study. The timescales of pigment energy relaxation is of the order of 100 fs, while energy transfer between complexes is 5–40 ps. The second step is dominated by perturbing protein vibrations that induce spectral overlap making the process very efficient (>95%). It is known that pigments are weakly coupled to the high energy vibrational states and strongly coupled to low frequency modes. These modes are of interest for effecting global change in pigment spacing and energy interaction and in so doing providing a conduit for energy flow. However they have been difficult to access experimentally.

7.2.3. Membrane Transporters and Channels: This sub-programme will make a major contribution to the world-wide initiative to establish the structures and functions of membrane proteins (MP) some 600 of which have been selected as targets by the UK and Europe MPSI and E-MeP projects. The targets have been chosen for their fundamental interest and importance to the pharmaceutical industry. It is estimated that it will be possible to determine the structures of at most 5% of these targets by conventional techniques whereas ~ 30% will be expressed and purified to a stage suitable for functional research using the new technologies of 4GLS. This will make it possible to investigate the function of MP's at the molecular level and investigate membrane protein function beyond a simple kinetic assay approach thus yielding an understanding of membrane/protein dynamics which can explain the observed specificities and kinetic rates.

7.3. The need for 4GLS

That protein motions promote catalysis is currently the major controversy in biological catalysis. We will address this directly by using the high power THz sources of 4GLS to excite the promoting vibration(s) and see if this promotes catalysis. The difference between results from normal and deuterated specimens will provide important insights into the role of protein motions.

THz spectroscopy: THz spectra will be obtained of key 'tunnelling' enzymes with very high spectral resolution and signal-to-noise ratio. The spectra will be interpreted by comparison with the molecular dynamics calculations used to identify promoting vibrations and by the changes induced by stable isotope substitutions of key enzyme-analogue complexes. Accurate measurements of line width and any asymmetry will provide information on the lifetime of promoting vibrations and yield insight into energy transfer processes. Additionally light activated catalysts will be used to initiate H-transfer providing direct access to the chemical step in pump-probe experiments.

THz initiation of reaction: Most biological reactions are initiated by rapid mixing. We will explore the use of THz initiation of reactions by perturbing systems at equilibrium to study internal electron and hydrogen transfer with complex redox systems. The potentially fast timescales achieved will provide unprecedented access to fast chemical changes (infrared, UV) and allow analysis of short-lived intermediates not possible with existing technologies. THz induced conformational changes will be monitored using reflection anisotropy spectroscopy.

4GLS will provide insight into a number of steps in photosynthesis. While the first light driven step is particularly suited to experiments with light sources we will also investigate the electron/proton and chemical transfer steps in the process. The questions to answer are :-

(i) Are low frequency dynamic modes responsible for exciton energy transfer?

(ii) Are these modes the consequence of excitation by a photosynthetic photon or are they pre-existing natural modes?

(iii) Are these modes evolved to optimise quantum mechanical mechanisms?
(iv) How is photosynthesis changed by novel or modified complexes?
(v) How are these transfers influenced by the organisation of supra-complexes in vesicles and lamella?
(vi) How are ubiquinone molecules reduced, escape the core complex and transported through the membrane to cytochrome bc1 complex?
(vii) What are the combined kinetics of a complete photosynthetic system including F0F1 ATP synthase.

Pump-probe experiments: Near infrared pump probe experiments will monitor the rate of relaxation and localisation of energy within pigments and between complexes. The rate change can then be measured in the presence of pre-pumping or post probing THz radiation. Low temperatures will be used to obtain defined THz spectral features and pulse shaping will be investigated as a means to drive and optimise mode enhanced energy transfer. Time resolved EXAFS of the Mg^{2+} K-edge can be used to correlate structural changes of chlorophyll pigments and their environments with near-IR/THz data. Structural modelling of simulated dynamics will provide a theoretical framework for linking the various time resolved spectral data. These pump-probe experiments will be extended to investigate larger supra-clusters of complexes and inter-complex energy transfer.

Transport of energy within membranes: Membrane structures can be isolated containing supra-complex arrays. The most promising of these are vesicles isolated from Rps sphaeroides containing 60-100 complexes and including 1 or 2 cytochrome bc1 and F0F1 ATP synthase molecules. The transfer of electrons and protons, across and through the membrane can be followed, on μs to ms timescales, by monitoring the evolution of oxidised ubiquinine (UQ) cofactors in the visible and the appearance of the reduced quinone (QH2) signatures in the infra-red with time-resolved spectroscopy. Ubiquinone is the co-factor that mediates the pumping of electrons and protons across the membrane. As the process is relatively slow it maybe possible to use the high repetition rates of 4GLS to probe transfer kinetics within a single vesicle using optical tweezers to isolate a vesicle and polarised light to measure the anisotropy of chemical transfer.

New spectroscopies: 4GLS will facilitate the development of new experimental techniques and extend the range of existing ones providing a suit of complementary multi-spectral measurements on different groups and timescales. Non-linear spectroscopies such as Sum Frequency Generation (SFG) at surfaces and 2D spectroscopy can measure the correlated dynamics of specific bands involved in energy transfer. 4GLS will facilitate a unique extension of 2D spectroscopy into the UV where correlated motions of large secondary structure elements maybe observed thus extending dynamic study of secondary structure into the tertiary. UV circular dichroism (CD) has been very useful in this field. 4GLS will make it possible to extend CD into the Raman and THz regions on fast timescales.

Dynamic Mechanisms: Although membrane channels and transporters are observed with relatively slow turnover rates (msec–sec), this represents the sum of a number of steps dominated by the slowest step. It is likely that the slowest step is the frequency of finding the transported molecule at the mouth of a channel and the most interesting steps are likely to occur on a faster timescale within the membrane. X-ray diffraction structures have been determined and used to model mechanisms by molecular dynamic techniques. These calculations indicate hinges or pores opening and closing at much faster frequencies (ps – ns) and, on the molecular level, are represented by either large domain motions or by side chain torsion changes modulating the pore cavity volume. These motions would be expected to occur in the THz/ far-IR region between 3–200 cm^{-1} with the lower part of thus range of frequencies responsible for conformational substate changes. These substates can occur quickly in tens of ps but can persist for μs or ms. This constitutes a wide time range that must be followed and will be a challenge for unravelling mechanisms.

Transport Dynamics: Specific modes will be stimulated by pulse shaping of THz radiation on the ps-ns timescale to produce enhanced kinetics. A pulse length/duration will have to be established that promotes persistent changes in a specific conformational states. FTIR probes will be used on the μs-ms timescale to follow changes of specific groups. A comparison of wild-type and mutant proteins, using difference FTIR spectroscopy, will establish amino acid assignments in spectra as well as determining the time evolution of these groups. The overall reaction can be followed during the course of the transport with specific fluorescence probes, by following tryptophan and tyrosine residue fluorescence or by changes in UV CD or Raman optical activity. These probes originate from different processes and provide information on a broad range of timescales, and will make it possible to establish, within molecular dynamics models, changes in atomic groups as stimulated by THz radiation, and the observed enhancement or otherwise of the transport turnover rate. The most powerful advantage of 4GLS is that these experiments can be performed at the same facility and correlated within the same experiment providing a great deal of complementary information.

Fast Macromolecular Dynamics: It is important to establish conformational fluidity of specific groups across membranes on a fast timescale (ps-ns). These times are relevant to the periodicity of correlated macromolecular vibrations and will anchor molecular dynamics calculations providing a basis for verifying simulations and giving an experimental overview. This can also stimulate further improvements in modelling algorithms. Non linear 2D-spectrosocopy and SFG can probe the dynamics of specific markers through deuteration or isotope labelling. In 2D-spectroscopy off-diagonal peaks provide information about changes in conformation of correlated groups while line broadening provides information of lifetime dynamics and mobility of groups. Site directed mutations can provide additional information on the roles and interactions of specific groups that facilitate transport. For those symporters utilising H^+ fast pH jumps by UV eradiation of caged compounds can be used to control the course of the reaction. Other forms of control can be introduced by rapid light driven lysis of solute containing vesicles.

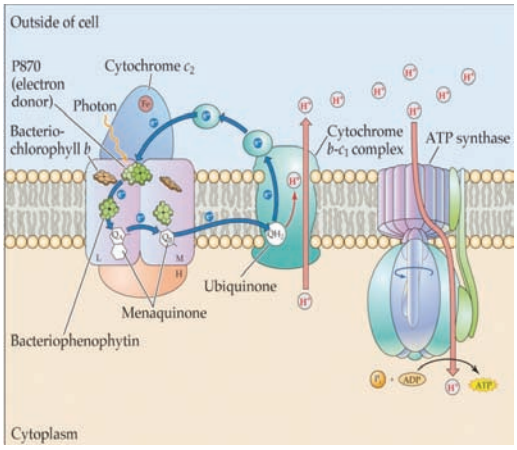


Figure 7.3: The membrane-bound photosynthetic apparatus and its relationship to the cytochrome bc1 complex and F0F1 ATP synthase.

7.4. The Research Team

This proposal brings together three communities with overlapping interests high levels of UK and international funding and strong national and international collaborations. ***Biocatalysis:*** Collaborators include the strong UK community Prof Allemann, (University of Cardiff), Profs Scrutton, Munro and Sutcliffe and Dr's Gardiner and Heyes, (University of Manchester), Profs van Grondelle and Groot (Vrie University, Holland), Profs D. Truhlar, J. Gao (University of Minnesota, USA), Prof G. Williams (Jefferson National Laboratory, USA) and Prof Kohen (Iowa State University). ***Photosynthesis:*** Collaborators include Prof. C.N. Hunter (University of Sheffield), Prof. R. Cogdell FRS (University of Glasgow), Prof. J Barber FRS, (Imperial College), Prof. R van Grondelle (Vrie University, Holland), Prof. T Aartsma, (Leiden, Holland) and Prof. G Fleming (UC Berkeley USA). ***Membrane proteins:*** Collaborators include the members of a large consortium (MPSI), comprising 8 UK laboratories (Leeds, Glasgow, Manchester, Darebury, Oxford, Birkbeck, Imperial, Sheffield) funded by the BBSRC to work on elucidating the structures of membrane transporters and ion-channels. The PI's of these groups are interested in exploring functional research techniques to complement the structural work. Prof. P. Henderson is a member of the consortium and a member of a European E-MeP group working on membrane proteins and

has many links with international groups. ***E-MeP partners:*** R Bill (Aston University), S Iwata, Naomi Chayen (Imperial College), J Walker (MRC, Cambridge), F Pattus, (CNRS, France), C Cambillau, (Univ. Mediterranee, France), K Lundstrom, (Bio-Xtal, France), H. Michel (Max-Planck-Institur für Biophysik, Germany), R Cogdell (Glasgow University), R Neutze, (Chalmers University, Sweden), P Booth (Bristol University), N le Novère (EMBL-EBI UK/Germany), H Vogel (Ecole Polytechnique Fédérale de Lausanne, Switzerland), R Rudolph (Martin-Luther-Universität Halle-Wittenberg, Germany), W de Grip (University Medical Centre Nijmegen, Holland), L-O Essen (Philipps-Universität Marburg, Germany).

8. THE RELATIONSHIP BETWEEN PROTEIN STUCTURE, PROTEIN DYNAMICS AND PROTEIN FUNCTION

David Klug, Mauricio Barahona, Ian Gould, Jasper van Thor, Sophia Yaliraki (Imperial College), Paula Booth (University of Bristol), Peter Rich (University College London), Keith Willison (Institute for Cancer Research, London)

8.1. Aims of the Research Programme

The unique capabilities of 4GLS will be employed to revolutionise the study of the relationship between the structure, dynamics and function of proteins. This will lead to a better understanding of the processes of small molecule recognition by proteins, protein-protein recognition and binding and drug binding/interference in these processes. It also has the potential for biomarker discovery. This will enable the UK to exploit its strong position in genomics by the development of internationally competitive post-genomic science and help to underpin the future of the UK pharmaceutical industry.

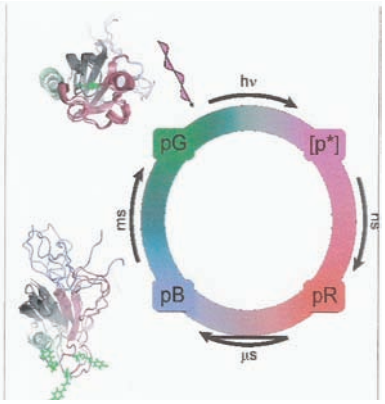


Figure 8.1: Certain photoreceptors undergo large-amplitude light induced conformational changes. This example shows the solution structure of the ground state and photocycle intermediate of the photoactive yellow protein that has a ms lifetime. The dramatic shape changes result in alterations of low frequency vibrations that lead to changes in optical linewidths. Pump-probe visible and mid-infrared spectroscopy shows a number of kinetic transformations from fs to ps to s timescales.

8.2. Essence of the Science

A protein structure encodes for many things including its ability to fold and change shape, to recognise and be recognised by other proteins, drugs or biological structures and to be activated by post-translational modifications. The relationship between the structure and function of a protein are its mobility, dynamics and thermodynamics. Biological function is deeply linked to the dynamics of large biomolecules, such as proteins and nucleic acids. For instance, proteins are key elements in biological processes such as enzymatic catalysis, signalling, genetic regulation, and molecular recognition, which are defined by sensitive, specific and robust chemical binding. Proteins are also involved in cellular transport, aggregation, membrane interactions and self-assembly, where less localised physico-chemical binding plays a central role. This activity is truly dynamical, involving conformational changes at different time and length scales, as molecules interact in space and time. Understanding and predicting these structural rearrangements and the pathways that link them in an uncertain environment is thus crucial and is the focus of this proposal.

There are very few methods of studying the conformational changes and dynamics of proteins with both structural and dynamical resolution. Two-dimensional NMR revolutionised the power of NMR and made it possible to solve large structures including those of proteins. Complementary information on dynamical properties can in principle be obtained from the optical analogues of 2D NMR, including 2D-Infrared spectroscopy (2DIR), that measure vibration-vibration coupling. This project focuses on the use of 2DIR techniques to measure coupled vibrations and low frequency protein motions. This is a route by which the protein dynamics that underpins the operation of the majority of the protein machinery of a living cell may be better understood. However current laboratory techniques are limited in their range of application. In this programme the wide spectral range of intense light sources available on 4GLS will be employed to revolutionise 2DIR techniques.

8.3. The Need for 4GLS

In terms of the accessible spectral range 4GLS will open up an area of investigative space some ten times greater than that currently explored with 2DIR. That means that nine tenths of the structural-dynamical elements comprising a protein will remain hidden without the development of 2DIR and its associated linear spectroscopic techniques on 4GLS.

In order to exploit the potential of 4GLS the team will develop a coordinated strategy based on spectroscopy measurements in the wider spectral regions opened up by 4GLS using linear techniques, the development of 2DIR instrumentation and underpinning theoretical work.

8.3.1. Linear spectroscopy in the far IR and THz: Due to the weakness of laboratory sources of THz radiation: the "THz gap", there is very little information on the spectral characteristics of molecules in this long wavelength region and almost no information on the lifetime of modes or on the coupling between modes that is the key to understanding molecular function. Indications in the literature include the observation of an unexpectedly long lifetime of 500 ps for the vibrationally excited state in thin films of bacteriorhodopsin from pump-probe experiments at 87 μm (115 cm^{-1}). This contrasts with lifetimes for modes in the mid-infrared region that are typically 2ps such as the amide I vibrations. Measurements have shown that relaxation and transfer processes of collective modes in the far-infrared region have much slower dynamics than more local modes, raising key issues with regard to pathways for the creation of productive conformations and dynamics in biomolecules. These coherence transfer processes can be measured using 2DIR on 4GLS but the analysis of the results obtained by extending the range of 2DIR techniques will require a good understanding of the basic features of protein spectra in these long wavelength regions. Consequently a linear spectrometer taking advantage of the high brightness and short pulses of 4GLS will be developed for this purpose. This will be used in combination with an externally synchronised ps laser in pump-probe THz spectroscopy experiments. The repetition rate will be dropped to 1 kHz as required for most light sensitive biological materials and this will require the use of a disperse photoconductive array detector. Non-linear experiments will naturally follow from the program on linear spectroscopy, typically by time-domain spectroscopy techniques, that focuses on the fundamental questions regarding cross-sections, linewidths and distribution of collective modes in this region in model compounds and biomolecules. Computational approaches will address the far-infrared mode density to aid in the non-linear and linear spectroscopy.

8.3.2. Development of 2DIR (DOVE-FWM) on 4GLS: Of the dozen or so groups in the world working in 2DIR only the Imperial College group are able to measure and interpret detailed data from whole functional enzymes and to study enzymatic intermediates. They have developed a particular version of 2DIR, DOVE-FWM, for this purpose, which has significant advantages for the study of certain areas of protein science:-

(i) The ability to tune into an enzyme active site containing a chromophore and measure the chemical dynamics of the site separately from the rest of the protein.
(ii) The ability to measure couplings between vibrations of very different frequencies no matter how far apart.
(iii) The ability to transfer this approach to the system of FELs proposed for 4GLS.

No other form of 2DIR can be used for the fingerprinting of proteins or the determination of catalytic site dynamics. This group built the UK's first 2DIR spectrometer funded by EPSRC and are constructing a second instrument funded by EPSRC and BBSRC for protein fingerprinting. These instruments can access the spectral range from the high combination band region (~8000 cm^{-1}) to the upper reaches of larger collective modes (~800cm^{-1}). However current tabletop laser technology cannot go much below this and is unable to produce sufficient powers for nonlinear

methods in spectral regions important to collective motions such as α-helical stretches, β-sheet movements and more global and longer range structural motions.

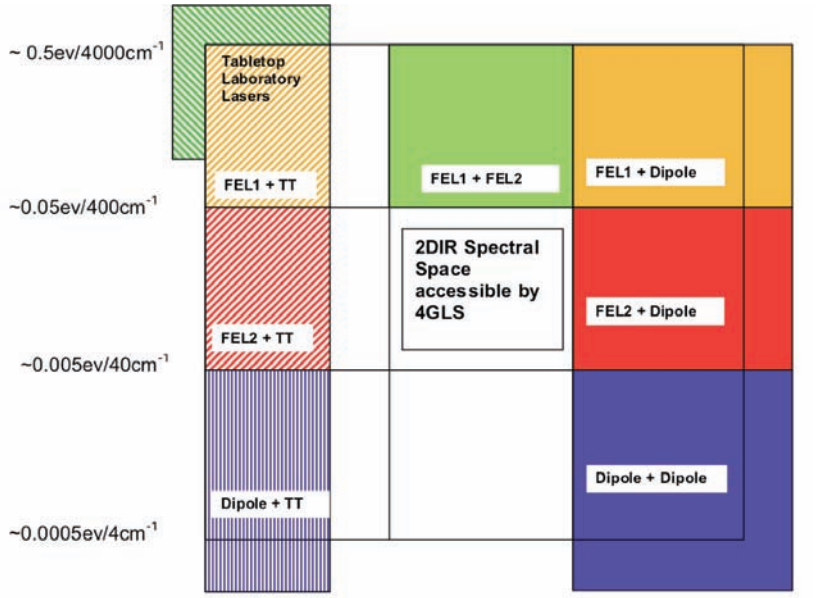


Figure 8.2: Illustration of the "spectral space" accessible with table top lasers and 4GLS. Nine tenths of the structural dynamic elements comprising a protein will remain hidden without the development of 4GLS for two dimensional spectroscopy

These long range structural motions are not only implicated in affecting enzymatic catalysis but also control key biological phenomena such as allostery. The development of this instrumentation on 4GLS will radically increase the spectral range available for these studies and is a key element of this proposal. 4GLS will open a completely new window for the study of these key biological processes. It is the combination of wavelengths that makes the potential of 4GLS particularly powerful for coherent two-dimensional methods allowing THz-THz mode couplings, THz-mid IR couplings and trebly resonant (vibration-vibration-electron) couplings to be studied. It is the ability to generate complex permutations of multiple wavelength high energy pulse sequences that is the key and unique strength of 4GLS. This proposal plays directly to those strengths.

8.3.3. Potential for fast throughput: The huge power of the 4GLS FELs will yield signals many orders of magnitude greater than can be achieved from a tabletop laser system, including spectral ranges that currently cannot be accessed at all. ie. below ~600-800 cm^{-1}. This allows for an intriguing mode of operation of 4GLS as a high throughput analytical tool that would be remarkably cost effective. 4GLS will allow a throughput of samples for omic or chemical analysis which is ~10^4 times greater than that possible with table top technology. Assuming that the facility can be multiplexed, so that all the flux can be used effectively without damaging the samples, and that methods of feeding a high throughput analysis pipeline can be developed, then 4GLS could screen the complete proteome of a cell line in a few minutes and monitor the interaction of 10^6 potential drug molecules against 10^3 proteins in six weeks. The technology is non trivial but if even a fraction of this level of work can be done by 4GLS then the facility would be remarkably cost effective when compared to the cost (£ 5 billion) of carrying out such a programme with table top systems each costing ~ £0.5 million.

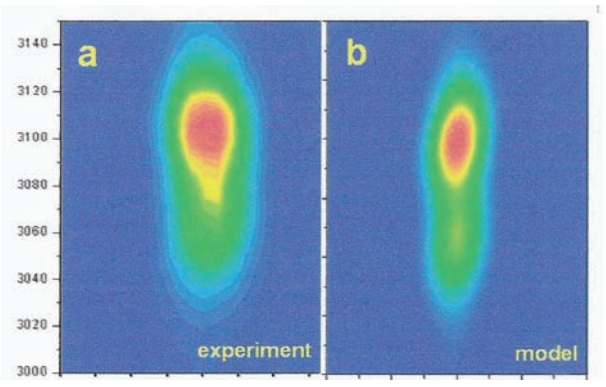


Figure 8.3: Quantum calculations of 2DIR features of benzene. This demonstrates that both the coupled modes and their line shapes can be identified and understood.

8.3.4. Theoretical programme: There are three broad areas where a strong theory programme is required to complement the experimental activity :-

(i) Calculations of normal mode frequencies
(ii) Calculations of couplings between low frequency modes with each other and with higher frequency modes
(iii) Multiscale modeling relating structure, dynamics and function

All three areas are currently underway in the applicants research groups and this provides an essential element to the programme as a whole. We have made significant progress in calculating signal sizes using density functional and non-linear optical theory, and such calculations should be possible for the much lower frequency regions accessed by 4GLS. Taking literature values for the dipole moments of characteristic vibrations in the THz region and making certain other extrapolations from the known molecular physics in the mid-IR leads to estimates that in the THz region the strength of the 2DIR signals from 4GLS will be approximately the same size as those in the mid-IR from the laboratory table-top system. That is to say, sufficient for taking spectra reasonably rapidly. More precise calculations will have to be part of the bridging research programme to determine whether it is possible to combine a tabletop system with either a FEL or the dipole to perform low sensitivity measurements in these new spectral regions.

8.4. The Research Team

The team have a track-record of research across the physical/life sciences interface. This includes a range of technical expertise including IR difference spectroscopy, time resolved IR spectroscopy, time resolved x-ray crystallography, biochemistry and cell biology, atomistic calculations, coarse-grained dynamical theories. The Klug group have lead the development of the DOVE-FWM technique as a biological research tool, and this is the key to this proposal. Van Thor will lead the development of the linear THz programme The team also bring strong theoretical support for the research including calculations of normal mode frequencies (Van Thor), of couplings between low frequency modes and of coupling between low and higher frequency modes (Ian Gold). The ultimate aim of understanding the relationship between protein structure dynamics and function requires the significant theoretical input of Yaliraki and Barahona who are experts in multiscale modeling and in particular multiscale modeling of biological systems. The three ‘biological’ groups are also expert in various areas of molecular biophysics. Rich is the UK’s leading exponent of IR spectroscopy of proteins. Booth is a world expert in membrane protein folding and Willison works on protein-protein interactions using a range of biophysical approaches including time resolved and single molecule spectroscopy as well as structural analysis. This is important as it means that the team comprises groups that are multidisciplinary in their own right. In similar vein Klug and van Thor also have expertise in particular biological systems; light activated and photosynthetic proteins in particular. The collaborators include Michael Johnston (Oxford) who uses TDS for measurements of THz absorption properties of reaction intermediates in the photo-accumulated state.

Collaborators: Jim Bowie (UCLA USA), Oscar Ces, (Imperial College), Harold Craighead, (Cornell University, USA), Andrew De Mello, (Imperial College), Les Dutton, (University of Pennsylvania USA), Paul French (Imperial College), Ali Jadbabaie, (University of Pennsylvania), Michael Johnston (Oxford University), Mark Neil (Imperial College), Peter Parker (London Research Institute of Cancer Research and Kings College London), J. Timothy Sage (Northeaster University, USA), Gebhard Schertler (LMB), Richard Templer, (Imperial College), Jonathan Widom, (Northwestern University), Marten Wikstrom (University of Helsinki, Finland), Dek Woolfson University of Bristol).

9. MOLECULAR ASSEMBLIES IN THE EXTRACELLULAR MATRIX AND CELL SIGNALLING

David Fernig, Edwin Yates (University of Liverpool), Andrew Almond (University of Manchester), Miroslav Papiz (STFC)

9.1. Aims of the Research Programme

This research programme will open a new window in the understanding of a wide range factors important in the human response to disease including: arthritis, cancer (eg. angiogenesis mediated by fibroblast growth factors and vascular endothelial growth factor carcinomas), neurodegeneration in Alzheimer's (eg. amyloid precursor protein cleaving enzyme (BACE1/β-secretase), prion protein in Creutzfeldt-Jakob disease, inflammation (eg. cytokines in rheumatoid arthritis and asthma), congenital disorders (eg. craniosynotoses, dwarfism, hereditary multiple exostoses), Simpson-Golabi-Behmel (SGB), pathogens eg. HIV, herpes, malaria and chlamydia.

The beneficiaries of this research include :-

(i) The pharmaceutical and biotechnology industries: glycosaminoglycans are by weight are the largest medical biotechnology product
(ii) The NHS: more effective and efficient diagnosis, avoidance and treatments
(iii) Patients: improved disease outcome/management

9.2. Essence of the Science

This programme will exploit the unique capabilities of 4GLS to provide insight into the extracellular matrix, which is a dense assembly of proteins and sugar chains that regulates most key cell functions. Attention will be focussed on the glycosaminoglycans that have a key role in deciding the structure of the matrix and the regulation of cells. These molecules and their functions are currently very poorly understood. Their detailed structure dictates their properties, interactions and functions at the molecular level, which in turn, determines the behaviour and interactions of cells, organs and ultimately organisms. These events are relevant to almost all human diseases and pathologies and are therefore potentially of immense medical, pharmaceutical and social importance.

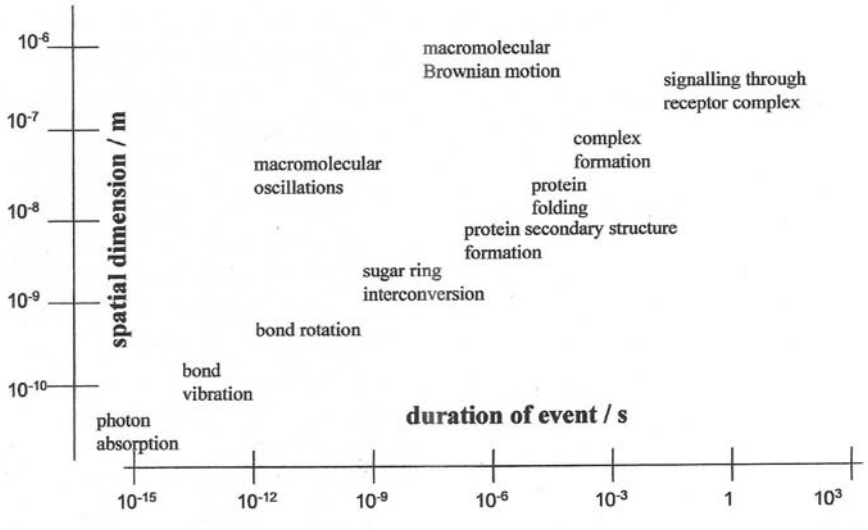


Figure 9.1: Molecular events in glycosaminoglycans encompass wide spatial and temporal dimensions. These events range from photon absorbtion by chromophores (fs) to signalling through receptor functions (s to h). By virtue of the structure of glycosaminoglycans dictating their functions, molecular events across the full spatial and temporal scales are linked.

The focus is on the glycosaminoglycans, since their varied size and conformational diversity precludes the structural biology approaches commonly applied to proteins. The challenge is to

understand how their structure determines their properties and drives their functional interactions with other extracellular matrix molecules and molecules on the surface of the cell.

9.3. The need for 4GLS

This programme will employ the unique high intensity, multiple-frequency and time-resolved capabilities of 4GLS to provide unique answers to structural questions by exploiting:-

(*i*) *Very high light intensity:* allowing experiments on very low concentrations, making it possible to study the behaviour of proteins in the presence of glycosaminoglycans at a concentration of μg/ml, similar to that which occurs in natural systems and which is inaccessible with conventional laboratory equipment.

(ii) Time-resolved spectroscopic measurements: allowing biological phenomena to be understood in terms of dynamic molecular processes; in most cases, for the first time.

(iii) Use of coherence and non-linear correlated spectroscopy: simplifying spectra and facilitating band assignment in complex biological molecules and assemblies.

(iv) Simultaneous experiments with several spectroscopic techniques*:* insight into molecular processes through multi-dimensional correlated spectroscopy.

(*v*) *The high polarisation:* facilitating selective observation of proteins, carbohydrates and DNA against a background of non-chiral molecules, such as water. This can be achieved by UVCD, VCD, Raman optical activity and THz spectroscopy.

The study of extracellular matrix model systems composed of multi-component molecular assemblies will yield a detailed understanding of:-

(i) The changes in secondary and tertiary structure during sub-unit interactions and complex assembly. This will include investigating the effect of structural modification of the carbohydrate components and protein glycosylation on extracellular matrix molecular assembly, structure and dynamics.

(ii) The detection and characterisation of long-range order in extracellular matrix molecular assemblies of proteins and carbohydrates. This will include measuring the stoichiometry, dynamics and order of complex assembly. The spatial arrangement and orientation of sub-units and their motional properties will also be investigated, eg. the mobility of protein components bound to carbohydrate extracellular matrix components.

(iii) The role of molecular assemblies in determining the localised physical environment in the extracellular matrix. For example, molecular diffusion of molecules (particularly small molecules) will be measured in the presence of other extracellular matrix molecules.

(iv) The role of molecular water in forming and disrupting molecular assemblies,
eg., by measuring dielectric properties of solvent water in and around complexes.

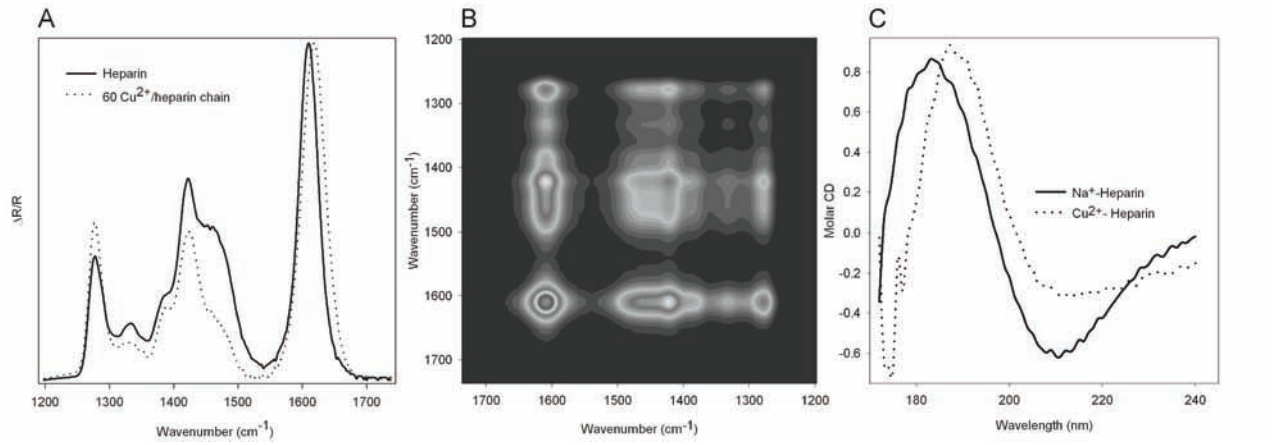


Figure 9.2: Infrared absorption and UV synchrotron radiation circular dichroism spectrum of two forms of the GAG heparin. GAGs such as heparin possess IR and chiral UV chromophores which enable the conformation of the sugar rings and the inter sugar glycosidic linkages to be probed. Co-ordination of the metal cation copper has a dramatic effect on the structure of the sugar rings and glycosidic linkages of heparin, which in turn alters the cellular activities of the polysaccharide. The infrared adsorption (A) and 2D-COS (B) spectra of heparin and heparin complexed with 60 copper cations per chain. Panel C shows the SRCD spectra of sodium-heparin and copper-heparin.

Extracellular matrix model systems will be investigated at three structural levels

(i) Structural macromolecular assemblies involving hyaluronan. Hyaluronan is ubiquitous in the extracellular matrix and will be studied to investigate the microscopic state of hyaluronic acid at both low and high concentration and in molecular complexes with assemblies of proteins.

(ii) Signalling macromolecular assemblies involving heparan sulphate and heparan sulphate proteoglycans. Currently structural probes such as X-ray crystallography and NMR, are either inappropriate, unfeasible or provide only a limited physical view of these large and complex structures in solution.

(ii) Macromolecular assemblies on membranes: It is essential to probe the structure of these assemblies in the context of a membrane surface. Artificial membranes, self-assembled on surfaces and containing receptors to which increasingly complex assemblies of molecules are bound can readily be produced. These can be probed using an array of spectroscopic techniques including transmission methods and surface-specific techniques. The small amount of material generally available, however, means that weak bench top sources currently limit the spectral information that can be acquired.

The unique capabilities of 4GLS to conduct multiple spectroscopic investigations and to pump molecular systems with electromagnetic radiation will allow molecular processes at a local level to be related to global molecular and macromolecular rearrangements and vice versa, permitting a detailed picture to be assembled of how structure determines function.

4GLS will provide information in four categories:

(i) Investigations of global conformational change: The radius of gyration, overall shape, folding and subunit rearrangement during molecular interactions and complex formation will be monitored by time-resolved scattering experiments.

(ii) Investigations of local structural motions and dynamic distances: The interaction kinetics, distance and orientation between components of the extracellular matrix and signalling complex model systems will be monitored using visible and UV fluorescence energy transfer (FRET) by specific excitation of naturally occurring amino acids and by site-specific incorporation of fluorescent probes into both protein and polysaccharide components.

Fluorescent polarisation and FRET ligand binding, experiments will yield details of the kinetics, distance and orientation of interacting species while environmental and structural probes will

provide polarity and rigidity information. Protein secondary structure and carbohydrate ring conformation and conformational populations will be investigated with time-resolved electronic (UV) and vibrational circular dichroism (IR), Raman (IR) optical activity and time-resolved THz and Far-IR spectroscopy.

(iii) Investigations of domain interactions and reorientations: Molecular vibrations in both the free and associated states will provide details of binding surfaces. The tertiary structure of molecular assemblies and the nature of transition states during binding phenomena will be investigated with time-resolved and 2D absorbance and UV, visible and IR Raman spectroscopies. Tertiary structural vibrations on the ps time scale and conformational changes involving groups of atoms or domains will be explored using high-power THz spectroscopy.

(iv) Investigations of conformation and interactions in membrane environments: The brightness of 4GLS means that macromolecular assemblies on a membrane can be probed using the transmission spectroscopy. In addition, a number of surface specific second order spectroscopic techniques, such as sum frequency generation (SFG) and coherent antiStokes Raman scattering (CARS), will allow the acquisition of new information on the dynamics of the structure of such assemblies as they go through their work cycles of assembly-disassembly. These include scanning near field optical microscopy (SNOM) to validate the assembly of particular complexes on the membrane and RAIRS/PMIRRAS to probe structural features of the assemblies, including membrane organisation and protein secondary structural features.

9.4. The Research Team

The UK is unique in having a vibrant glycosaminoglycan research community that is home to the highest concentration of scientists in this field anywhere in the world and their achievements are well respected by the international community. They are largely based in the NW of England (19 research groups in Liverpool, Manchester, Salford and Lancaster) as well as Edinburgh, London/SE and Cardiff. The core team have the support of the national and international communities to exploit 4GLS to elucidate structure-function relationships of glycosaminoglycans and their partners in the extracellular matrix. In the national context, formal support for this enterprise has been given by Proteoglycans North West (the forum for the 19 NW research groups) and the UK Glycoscience Forum, which brings together all UK glycobiologists.

UK Collaborators: Martyn Chamberlain (University of Durham), Anne Dell (Imperial College), John Gallagher (Christie Hospital, University of Manchester), Edwin Jesudason, (Pediatric Surgery, Alder Hey Children's Hospital, Liverpool), Gerry Ronan (Farfield Scientific Ltd.), Axel Zeitler, (University of Cambridge).

International collaborators: Fabrice Allain, (Université des Sciences et Technologies de Lille, France), William Birch (A-Star Institute of Material Research and Engineering, Singapore), Jose Courty (University Paris XII, France), Paul DeAngeli (University of Oklahoma, USA), Marco Guerrini (Ronzoni Institute of Chemistry and Biochemistry, Milan, Italy), Christian Heegaard (University of Aarhus, Denmark), Hubert Hondermarck (Université des Sciences et Technologies de Lille, France), Milos Hricovini (Slovak Academy of Sciences, Bratislava, Slovakia), René Marc Mege, (Institut national de la Santé et de la Recherche Médicale, France), Dina Ron (Technion, Israel).

The strength of the international collaborations is illustrated by the award of a grant of $1 million from the Human Frontier Science Programme: PI Fernig, CI's Brahim Lounis (Physics, Bordeaux) and Kazuyuki Sugahara (Frontier Life Sciences, Hokkaido) to explore the structural basis of the interactions of heparan sulfate with proteins such as fibroblast growth factors.

10. CELL IMAGING AND SPECTROSCOPY

Paul O'Shea, Mike Somekh (University of Nottingham), Angus Bain (University College London)

10.1. Aims of the Research Programme

The high performance imaging and spectroscopy capabilities of 4GLS will be used :-

(i) to obtain insight into the mechanisms by which viruses enter cells
(ii) to determine the safe limits of human exposure to THz radiation
(iii) to explore novel therapies based on the use of THz to modifying cell behaviour
(iv) to develop a new method of protein separation and analysis based on non-destructive ablation using high power THz radiation.
(v) to develop sub-cellular imaging of live cells.

10.2. Essence of the Science

4GLS will be used to interrogate biological structures and their interactions in the THz and infrared regions of the spectrum with unprecedented levels of sensitivity. In addition to revealing the sub cellular response of live cells to changes in their environment induced by the effects of disease or pharmaceuticals it is anticipated that exposure to this radiation will reveal hitherto unrecognised behavioural characteristics of living cells with a view to illuminating and possibly controlling biological function.

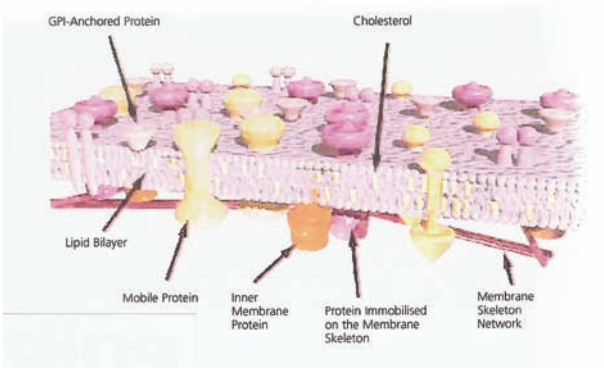


Figure 10.1: Cell membranes are complex assemblies of lipid bilayers and proteins that play a crucial role in regulating the activities of cells and the interactions between them.

A new technique will be developed for protein separation and analysis based on non-destructive ablation using high power THz radiation.

It may be possible to use high intensity THz radiation to alter biological function such as cell receptor interactions that are presently managed by drug therapy. This presents the exciting prospect that some treatments currently requiring pharmaceuticals and involving a large range of conditions from various cognitive disorders to narcotic dependencies eg. those presently treated by serotonin which targets G-protein-coupled receptors related systems may in the future simply require irradiation with EM radiation of certain frequencies and intensities. This could potentially revolutionise pharmaceutical practice, aspects of lifelong healthcare concerned with health monitoring and allow the UK to develop a technological lead in this field.

A comprehensive study will be undertaken to determine the safe limits of human exposure to THz radiation.

10.4. The need for 4GLS

The capability offered by 4GLS of synchronising high power levels of long wavelength radiation with optical sources will be used to develop imaging and spectroscopy techniques for probing biomolecular dynamics and the study of live cells with a precision that is significantly beyond current capabilities. This will include the development of a novel near field THz imaging instrument, of THz mediated second harmonic imaging and the use of 4GLS to transform the

emerging technique of time-resolved stimulated emission depletion (STED). We believe that combining the power of the 4GLS source with these instrumental improvements will yield routine resolution at least comparable with the best optical microscopes.

10.4.1. Probing biological structures: Conventional approaches to probing biomolecular dynamics have involved time-resolved transient absorption and fluorescence measurements. Due to the constraints inherent in single-photon selection rules the information provided by such measurements is restricted to the second-order dipole correlation function of the probe giving information on a limited range of the orientational space explored by a molecular probe. It has recently been demonstrated by the core team that this limitation can be overcome by using STED to prepare a virtual crystalline array of probe and host orientations, using a pump pulse, and to engineer these arrays by optical hole burning via a time delayed dump pulse. 'Hidden' probe dynamics can then be monitored via time resolved emission or a third probe pulse. The high quality pulsed THz of 4GLS and its synchronisation with laser systems designed for processes such as STED will dramatically improve the study of the dynamics of biomolecules.

10.4.2. New developments in near field microscopy: Recent work shows that it is possible to obtain lateral resolution close to 150 nm at THz frequencies by using a contrast mechanism involving an effective change in the impedance of the tip sample system. We will greatly improve the existing instrumentation by developing a different approach based on the use of the probe tip as a waveguide to direct the THz radiation. Local changes in sample properties will be monitored by the perturbation of the reflection as the sample probe separation is altered. Sensitivity will be further improved by introducing resonant structures on the probe so that the effective 'Q' and thus the sensitivity to the impedance of the termination may be enhanced. This waveguide approach also makes it possible to access the phase information reflected from the waveguide to give enhanced contrast on some samples.

10.4.3. THz radiation and biological function: dangers and opportunities: The increasing use of THz radiation in security applications makes it imperative to establish the safe limits of human exposure to radiation in this frequency range. Preliminary experiments to monitor the effects of exposure of live human tissue to THz are already planned using the prototype ERL and this will be taken to a more sophisticated level aimed at identify which frequencies are 'safe' and which affect strongly the receptor systems in living cells.

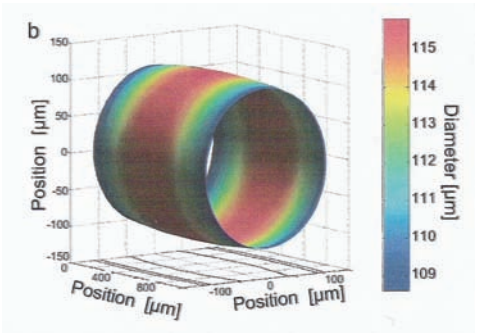


Figure 10.2: The axon layer surrounding nerve cells is typically ~ 2 μm thick. The diagram shows a three dimensional reconstruction of an axon from a live cell obtained from an assembly of near field THz images. The response of the axon to changes in the ionic concentration of the surrounding medium, the temperature and the introduction of toxins has been monitored. J.B. Masson et al PNAS **103** 4808 (2006)

Near field THz microscopy has recently been applied to monitor axonal water fluxes; this has allowed direct visualisation of neuron swelling induced by insult such as toxins or temperature change. The essential mechanism for the observed contrast is the far stronger absorption by potassium ions compared to sodium ions. The fact that THz radiation is sensitive to ionic contrast opens the way for label free examination of calcium channels etc., and thus to a vast array of biological imaging applications. This work is strongly suggestive that THz imaging can be used for label free functional imaging of the cell. The limiting factor for these techniques is the signal to noise ratio of the near field microscope used. The new microscope described above should allow high resolution imaging of neural function together with the capability of monitoring neuronal

images while irradiating with THz radiation to see how behaviour is modified under irradiation. THz mediated second harmonic imaging will allow us to visualise the time evolution of local structural changes in, for instance, cell membranes when the samples are subject terahertz illumination.

10.4.4. Altering and modulating behaviour: A fascinating area of speculative research opened up by the capabilities of 4GLS is the possibility of altering and modulating the behaviours of cells by exposure to intense selective wavelengths of THz radiation. For some conditions this may become an alternative therapy to the use of pharmaceuticals avoiding specific side effects.

10.4.5. Cell membrane studies: One route to a clear biomolecular question that may be affected by THz irradiation or perhaps be accessible to THz interrogation for function resides in studies with biological membranes.

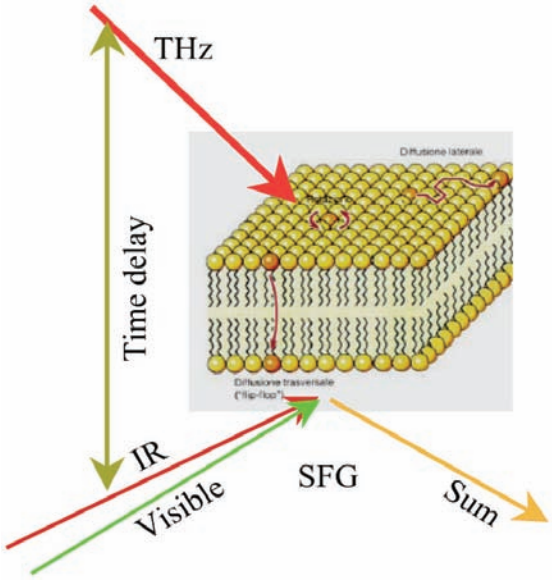


Figure 10.3: The principle of an experiment that would use the characteristics of 4GLS to study the transport of ions across cell membranes and the influence on this process of the coupling of between the vibrational excitations of the membrane and bound water.

It has been shown recently by the core team that membrane rafts possess particular dipolar properties to which bound water contributes. It has also been shown that modulation of these dipolar properties leads to changes in the activity of membrane proteins involved in receptor-mediated signalling processes. The latter appears to be a physiological process associated with the function of structures know as membrane rafts. Thus modulation of bound-water by THz absorption could well lead also to changes of membrane raft-associated signalling systems. Clearly this may represent a major problem in terms of chronic or intense irradiation of THz radiation of living systems and must be resolved. Moreover, it seems likely that the absorption bands for THz in water may be radically altered by hydration of biological macromolecules and macromolecular assemblies, ie proteins, nucleic acids (perhaps as chromosomes) and membranes (protein and lipids). This is borne out by the large changes observed for ionic species referred to above.

More intense irradiation of selected THz frequencies (ie. perhaps based on particular absorption bands) may also then be explored in order to address the question of whether such irradiation can change any macromolecular properties. The latter can then be correlated with any toxicological effects that irradiation of living cell cultures (etc) may lead to. The latter, therefore, would be the basis of identifying any potential toxic effects of THz irradiation of human beings or at least define limits of safe exposure and inform the burgeoning security-scanning industry.

10.4.6. Non destructive protein separation: Proteomics suffers from a lack of knowledge of the identity, population and structure of the proteins that are the basic units of the functional activity in biological systems. This lack of information is due in part to the difficulty of separating proteins from cells and membranes. A common technique (MALDI) used to isolate and identifying proteins is to eject them from surfaces into the gas phase using Laser ablation and then to identify the molecular fragments using mass spectrometry. However this technique results in considerable damage to the molecules causing them to break up and making it difficult to uniquely identify the primary structure of the protein from a knowledge of the fragments.

Recent research using the THz FEL at the Budker Institute has indicated a way of overcoming this problem of protein fragmentation, thus opening the way to more direct methods of analysis. It has been shown that the deposition of energy into the long range modes of vibration of large molecules causes them to desorb from surfaces into the gas phase without breaking up. It has even been possible to demonstrate that a biological molecule has retained its functional activity after being desorbed into the gas phase and subsequently deposited onto a surface. This approach will be developed on 4GLS.

10.4.7. Summary: The above outlines key instrumental developments and experiments that can only be done using 4GLS. There is a great deal of fundamental work to be done, but there is now growing evidence that THz radiation offers a powerful mechanism to monitor cellular processes. There are also strong *ab initio* reasons to study the effects of THz radiation on biological processes. We need to investigate the former with a view to developing a vital new tool in the biologists' armoury, and needless to say, we neglect the latter at our peril as THz becomes more pervasive.

10.4. The Research Team

Paul O'Shea and Mike Somekh apply physical principles to the understanding of biological systems. This also includes the development of spectroscopic and imaging technologies to the study of cellular systems. This is particularly concerned with non-covalent interactions and complexity. They have recently been developing multi-parametric chips (molecular arrays) for pattern recognition of diseases that do not exhibit singular molecular markers. The chips are interrogated using label-free technologies. Angus Bain recently developed stimulated emission depletion (STED) from two-photon excited states. This novel technique circumvents single photon electric dipole selection rules allowing the measurement of previously 'hidden' molecular properties. He is currently developing STED as a means of control of the single molecule fluorescence cycle. The interest of both the UK and International community in imaging studies of membranes, membrane-based targets of pharmaceuticals and spectroscopy of biomolecules is immense. These topics underlie much of the basic fabric of the endeavours of the pharmaceutical companies. Thus there is enormous interest in new technologies for both the study and treatment paradigms of human disease. ***Collaborators:*** Mischa Bonn (FOM Institute and University of Amsterdam), Martyn Chamberlain (University of Durham), Richard Clothier (University of Nottingham), Antonio Cricenti, (University of Rome II, Italy), Paul Dumas (Synchrotron SOLEIL), Boris Knaysev, (Budker Institute, Novosibirsk, Russia), David Martin (University of Liverpool), Jean-Michel Ortega (CLIO, University Paris-Sud), Hugh Rees (University of Liverpool), Norman Tolk (Vanderbilt University, USA), Peter Weightman (University of Liverpool), Gywn Williams (Jefferson Laboratory, USA).

11. SPIN@4GLS

Sarah Thompson (University of York), Elaine Seddon (STFC Daresbury Laboratory), Ben Murdin (University of Surrey), Chris McConville and Gavin Bell (University of Warwick), Chris Marrows (University of Leeds), Norman Tolk (Vanderbilt),Yongbing Xu (University of York)

1.1. *Motivation; integrating magnetism and semiconductor technology*

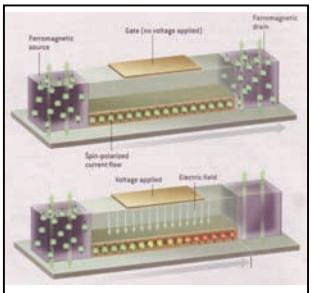


Figure 11.1: A proposed spin-FET. Reproduced from ref 3.

The magnetic and electronics industries are vast, ubiquitous and crucial to our highly technological society, for example, high performance computing, high capacity data storage and the development of magnetic materials underpin major advances in for example, medical imaging, weather forecasting, financial systems and climate research. The global data storage industry is a $20 billion industry with magnetic data storage representing approximately $7 billion. There continues to be a dramatic growth in the demand for stored digital data, driven in part by the internet and the storage of reconnaissance, surveillance and climate data. There is an urgent need to find a solution to the fast-approaching 'Moore's Law brick wall', i.e. to find new technologies for compact data storage.

Spintronics aims to integrate magnetic and semiconductor technologies and embed spin right at the heart of future electronics. Exploiting electron spin as well as charge will lead ultimately to magnetically controllable fast, multifunctional devices such as spin transistors, spin light emitting diodes and spin lasers[1,2]. '*Microelectronics devices that function by using the spin of electrons are a nascent multibillion dollar industry - and may lead to quantum microchips'* [3].

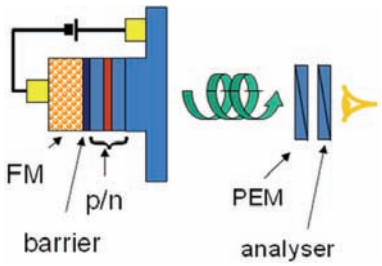


Figure 11.2: A narrow gap spintronic LED. B Murdin, reproduced with permission

To achieve true integration and new functionality presents both scientific and technological challenges that arise from materials development, nanoscience and the complexities that arise in hybrid devices that combine all these aspects. The field is in the emergent phase and in need of fundamental science to progress[4]: '*Right now we're focused on fundamental materials science. Integration is obviously a goal, but at the moment it's not on the near term horizon'*.

Looking further into the future, the forecast revolution in computing promised by quantum computing turns to atomic scale magnetic quantum bits as one of the contenders for realising this new technology. Improved understanding of magnetic materials on the nanoscale will also enable the development of nanoscale magnetic clusters in their own right – materials that have great potential as sensors for use in a wide variety of industry, most notably in medicine in targeted drug delivery and localised cell destruction.

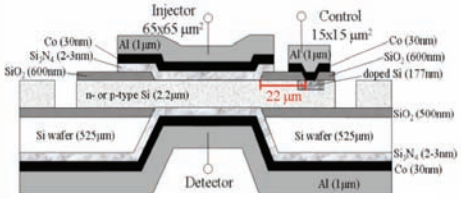


Figure 11.3: a Si spin transistor[2]

[1] G. A. Prinz, Science 250(23) 1092, 1995, J.F. Gregg et. al. J. Phys. D 35 R121 (2002); I. Zutic et. al. Reviews of Modern Physics 76 (2) 323 (2004); G. Schmidt J. Phys. D: Appl. Phys. 38 R107 (2005)

[2] C.L. Dennis et. al. Proc.-Circuits Devices Syst., 152 (4) 340 (2005); S. Datta & B. Das. Appl. Phys. Lett. 56(7) 665, 1990; Ohno et al. Nature 402 p790 (1999)

[3] D D Awschalom *et al., Scientific American*, **286**, 53, (2002)

[4] Scientific American in May 2007

11.3. Scientific Methodology

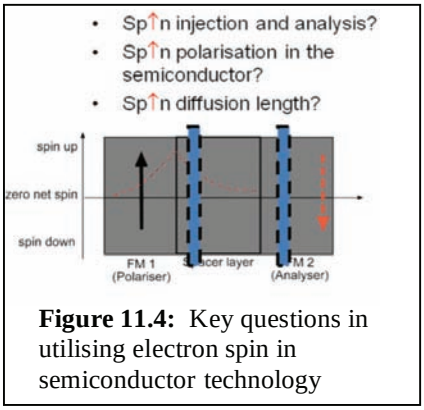


Figure 11.4: Key questions in utilising electron spin in semiconductor technology

The three key functionalities in a spintronic device are: spin injection from a magnetic material into a semiconductor, spin transport through the semiconductor and spin detection.[5] Essential requirements in the development of new magnetic materials for use as electron spin polarisers and injectors are understanding – and controlling - the behaviour of spin polarised electrons in semiconductor materials, in particular their dynamic spin coherence; the understanding of spin transport across interfaces and its correlation with atomic scale structure and impurities; and the understanding of the consequences of reduced dimensions in nanoscale devices.

11.3.1. The need for 4GLS

To address these scientific challenges and thus enable this spin revolution of technology, the *superior coherence, high flux, tunability* and *combination* of light sources of 4GLS will be used to unravel spin dependent electronic structure, study spin dynamics and spin dependent transport – often with spin, temporal and spatial resolution. Better spatial resolution is possible at 4GLS due to the *superior coherence* enabling tight focussing. The development of new magnetic materials requires knowledge of their spin dependent electronic structure which will be probed by techniques such as spin-polarised photoemission and soft x-ray magnetic circular dichroism (XMCD); magnetic switching in patterned structures will be observed using photoemission electron microscopy (PEEM), all of which will benefit from the *high flux* available at 4GLS. The behaviour of spin polarised electrons in semiconductor materials – in particular their dynamic spin coherence – will be studied using pump-probe techniques – in particular 2-colour pump-probe spectroscopy where the optical pumping is achieved using circularly polarised light. It is in these experiments that the unique possibility to *combine* different sources at different wavelengths (particularly in the UV, IR and THz) at 4GLS is exploited. Spin-dependent transport will be directly measured using magnetic field dependent IR spectroscopy and IR near field microscopy, for which the *intensity* and *tunability* of 4GLS is required – achieving spatial and temporal resolution not otherwise achievable.

11.3.2. Spin injection and coherence in semiconductors

The behaviour of spin polarised conduction electrons in semiconductor materials – in particular their dynamic spin coherence is crucial to the development of spintronics[6]. Most critical are the spin lifetimes of electronic excitations in a variety of semiconductor materials – about which there is currently very little knowledge. Factors influencing the spin lifetimes include the spin-orbit coupling and the structure of the material. 4GLS will allow the study of successful injection of a spin polarised charge carrier population into a semiconductor from a ferromagnetic material. The spin lifetimes, dynamics and coherence will be probed by 4GLS primarily using multi-colour pump-probe techniques. Typically the pump will be circularly polarised and in the Far-IR (1-60 meV) with the higher energy probe ranging from 0.2-3 eV, and ideally circularly polarised. It is also important that the MHz pump is synchronous with the probe. Attempts made to undertake similar, precursor, experiments at FELIX have served to highlight the difficulties currently faced[7].

[5] R. P. Borges et. al. J. Phys. D: Appl. Phys. 35 186 (2002)
[6] J.M. Kikkawa & D.A. Awschalom, Nature 397, 139 (1999)
[7] Murdin et al Phys. Rev. Lett 96, 96603 (2006); Arimoto et al Phys Rev B 67, 155319 (2003); Murdin et al, Phys Rev B 59, R7817 (1999)

The experiments were severely compromised by the jitter between adjacent macropulses, the extremely low duty cycle and the wavelength available. The high repetition rate of the superconducting 4GLS IR FEL and the ability to match sources in the MHz regime at 4GLS will enable the following experiments to be undertaken.

- In many semiconducting materials with very long spin lifetimes, far-IR excitation of doped structures by polarised pulses enables information relevant to all-electrical devices to be obtained. In silicon, far-IR excitation is required to probe its indirect band-gap. In wide, direct gap materials, intraband spin-pumping where holes are not generated is essential. The long-timescale relaxations require long periods between pulses of order milliseconds. In addition, intraband experiments demand high intensity since the spin-selectivity of non-resonant intraband excitations can be very low and direct resonant magnetic dipole allowed spin-flip transitions are also very weak. A second colour (1-3 eV) is required for the probe pulse for optical detection of far-IR spin resonance.
- Heterostructures of wide band-gap GaN-based materials: these anisotropic materials, with the würtzite structure, have strong internal piezo-electric fields and significant disorder. These properties have important consequences for spintronics - the wide band gap and the disorder should provide long spin dephasing lifetime, and the anisotropic strong internal electric fields should provide strong Rashba effects. The probe here would also be 1-3 eV.
- Spin-relaxation lifetimes in narrow gap materials with high spin-orbit coupling and/or low symmetry e.g. InSb and PbTe: these properties should produce a strong Rashba effect and with it the ability to manipulate spins with an electric field. There is therefore a need to perform far-IR intraband pumping experiments with a second colour (0.2–0.5 eV) for the probe. The lifetimes are expected to vary from sub-picosecond to 100's of picoseconds.
- Study of spin lifetimes as a function of applied magnetic field: semiconductor spintronic devices for external magnetic field sensing or in which there are internal magnetic fields due to incorporated ferromagnetic materials have different spin lifetimes from semiconductors in zero magnetic field. There are reports using very high pulsed magnetic fields that spin lifetimes might be many microseconds, whereas spin lifetimes in the similar structures at zero field have been shown to be 6 orders of magnitude smaller. It is therefore important to be able to perform spin lifetime measurements on semiconductor materials in controlled magnetic field conditions. Because magnetic dipole induced spin-flip transitions are very weak, high intensity pulses in the far-infrared (1-20 meV) will be necessary, with the probe varying from 0.2–3 eV.
- Electrically biasing a ferromagnetic/semiconductor interface to stimulate spin injection and then studying the spin-resolved band structure using as a function of distance from the interface would enable studies of both spin injection and resulting spin coherence in prototype spintronic heterostructures.

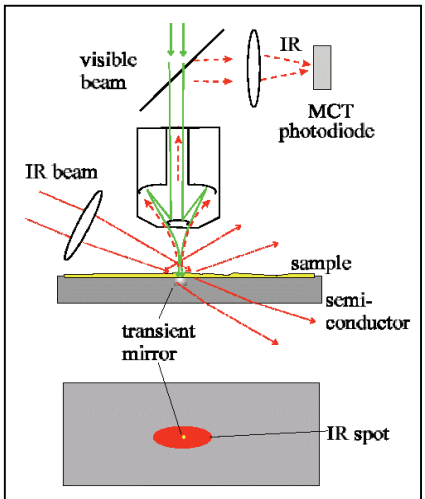


Figure 11.5 Near-field imaging with a photoinduced transient mirror at the SNIPER project (taken from ref. 9)

11.3.3. Spin-dependent transport

The reflection and transmission of near field IR allows electrical conductivity to be probed directly and using spectroscopy, linked to the band structure of the material. This has been successful exploited to study spin dependent transport by studying the dependence of reflection, transmission and emission of infra-red light on magnetic field – uniquely enabling spin dependent

transport information to be obtained with spatial resolution[8]. However, conventionally, the resolution is limited by the wavelength of the radiation, in this case 2-20 microns, which is very large in comparison to lateral dimensions of nanoscale spintronic devices. The intensity of 4GLS in the far infrared opens up the opportunity for near field measurements and the tantalising prospect of obtaining spin dependent transport information on the nanoscale. Further, the tunability of 4GLS would enable near-field spectroscopy leading the way to spatially and energy resolved quantitative information about spin dependent transport. Possible methods would include using 4GLS to flood a sample with IR radiation and a localised probe to detect the radiation such as a thermal atomic force microscope or photo-induced transient mirrors, as implemented at Stanford[9].

11.3.4. Materials development for magnetic technologies

11.3.4.1. Ferromagnetic materials for spin injection

In aiming to combine magnetic materials with conventional semiconductor technology, a key goal is to find a ferromagnet/semiconductor couple across which effective spin injection into a semiconductor can take place[10]. This requires not only a ferromagnetic material to act as an electron spin polariser, but a useful spin accumulation to be created across the ferromagnetic/semiconductor interface. This requires detailed knowledge of the spin-dependent electronic structure, and the measurement of spin-dependent transport across the interface. It is therefore critical to measure the variation of spin polarisation across a magnetic/semiconductor interface in cross-section. Electrically biasing or optically pumping a ferromagnetic/semiconductor interface to stimulate spin injection and then studying the spin-resolved band structure as a function of distance from the interface will enable studies of both spin injection and resulting spin coherence in prototype spintronic heterostructures. The capability of 4GLS for flux-hungry experiments such as spin-polarised photoemission (where Daresbury staff have pioneered the development of a time-of-flight detector for SP two-photon photoemission[11]), MXCD and PEEM means that magnetic, chemical and structural information will be available with spatial and temporal resolution. Additional magnetic characterisation is possible by combining with the Kerr and Faraday effect using visible light lasers and if interface sensitivity is required, non-linear second harmonic generation experiments.

11.3.4.2. nanoscale magnetic clusters

The magnetic properties of nanoparticles are dramatically different from those of the bulk material and include enhanced magnetic moments and surface anisotropies. The interest in these materials derives from their applications in medicine and magnetic data storage both of which require an understanding of their fundamental magnetic properties. The intensity of the 4GLS XUV FEL is such that it may be possible (using the time-of-flight detector) to measure the spin-resolved electronic structure of a nanoscale magnetic cluster. Measurements of isolated and deposited mass-selected clusters will give important information about magnetic couplings between clusters and between the cluster and the substrate.

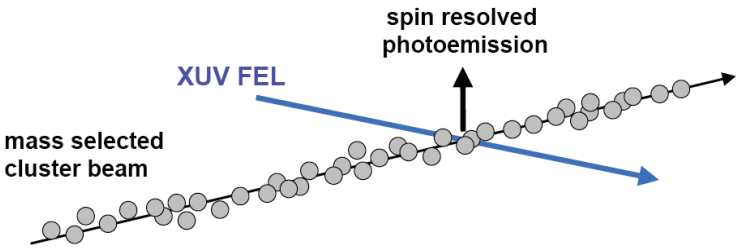


Figure 11.6: The 4GLS XUV FEL and time-of-flight spin detector offered unique opportunities for probing mass-selected magnetic nanoclusters

[8] M. Vopsaroiu et. al. Phys. Rev. B. 70 (21): art. no. 214423 (2004); S.M. Stirk et. al. Appl. Phys. Lett. 86 art: 102505 (2005)
[9] www.stanford.edu/group/FEL/palanker/SNIPER
[10] A. Fert & H. Jaffs, Phys. Rev. B 64, 184420, 2001
[11] SRD Annual Report 2005-6, CCLRC Daresbury Laboratory 2006.

11.3.4.3. Materials for quantum computing

There is an extremely active international challenge in searching for and characterising quantum qubit candidates such as hydrogenic impurity states in silicon and other semiconductors. These materials are difficult to make and demanding to characterise. The lifetimes of the spin excitations (about which very little is known) determine the capacity for coherent manipulation and entanglement between pairs of impurities. Two-colour pump-probe experiments will be used to measure lifetimes of hydrogenic impurity spin excitations in silicon and other semiconductors. Typically the pump will be in the far-IR (5-60 meV) and the probe tunable from 60-250 meV. The experiment will make use of the high intensity of the source in order to saturate the sample (typically 10-100 nJ/cm^2 to saturate a transition of cross-section 10^{-14} cm^2 in the far-infrared). A second colour is also needed to aim for full understanding of the relaxation processes as there are many states and pathways. Some pathways expected to be ~1 ps (e.g. at high temperature, or resonant with phonons), and some expected to be ~ 1 s (e.g. at very low temperature in magnetic field). With the 4GLS polarised source, it might be possible for the first time to demonstrate high intensity π-pulses for coherent manipulation. It may even be possible to demonstrate entanglement of pairs of impurities with high throughput scanning of the sample to find lucky impurity pairs implanted at random.

11.4. Wider collaboration and community

Spintronics and quantum computing are well represented and growing in the UK. There is a strong community working on both metal and semiconductor spintronics (e.g. Bath, Bristol, Cambridge, Durham, Exeter, Glasgow, Imperial, Leeds, Liverpool, Oxford, Nottingham, Salford, Southampton, Surrey, Warwick and York) and on spin dynamics in wide and narrow gap materials (e.g. Imperial, Herriot-Watt, Southampton and Surrey). The 1st World University Network conference on Spintronics will be held in York in 2007, involving 23 different countries. The international spintronics community is very diverse, deriving from the many mainstream magnetic and semiconductor research groups. Our interactions with the community have stimulated considerable interest; this was typified by the 4GLS ' Spintronics' Satellite meeting in 2004, which some 50 PIs attended. Significant future international collaborations are envisaged involving groups lead by, for example: David Awschalom (UCSB), Mike Coey (Dublin), Paul Kelly (Holland), Patrick Bruno (Halle), Markus Donath (Munster), Peter Dowben (Nebraska) and Antonio Cricenti (Rome II).

The potential impact of spintronics economically is recognised by major research and technology funding bodies. In the USA, this stimulated early DARPA programmes in spintronics: (SPins IN Semiconductors (SPINS)[12] and Spin Transport Electronics (Spintronics)[13]). A UK delegation from EPSRC visited China in October 2005 with the aim of establishing new collaborative research links between UK and Chinese academics. In 2006, the EPSRC, the British Embassy in Paris and the UK's DTI Global Watch Services sponsored the first Franco-British Spintronex seminar in Paris, with the aim of stimulating collaborations between French and UK based industrial and academic researchers. In the UK, EPSRC have identified spintronics as a strategic priority area[14], and recognise that there is a potential billion $ per annum global market[15]. EPSRC now spend £5 M p.a. on multidisciplinary spintronics related research.

[12] http://www.darpa.mil/dso/trans/spins.htm
[13] http://www.darpa.mil/dso/trans/spintron.htm
[14] http://www.epsrc.ac.uk/ResearchFunding/Programmes/Materials/RemitAndOrganisation/Spintronics.htm
[15] http://www.sciam.com

12. ATOM SCALE CORRELATION OF CHEMICAL AND ELECTRONIC STRUCTURE IN SOLIDS

Bruce Hamilton, Wendy Flavell (University of Manchester), Andrew Evans (Aberystwyth University), Peter Dobson (Oxford University), Lidiya Siller (University of Newcastle), Andreas Lang (University of Liverpool), Graeme Hirst (STFC)

12.1. Science and technology drive

Electronics and photonics technologies have provided the engine for world economic growth since the second half of the last century and it is clear that this trend will continue. These technologies currently account for 60% of the world's economy and this figure is increasing at a rate that suggests that electronics will be by far the dominant commodity base by the year 2020. Electronics based systems will underpin a huge range of consumer needs and be brought to bear on all of the key societal issues. Communications, healthcare, transport, energy harvesting and conversion will increasingly depend on new electronic and photonic systems.

The fundamental nature of emerging electronic and photonic devices is undergoing radical change. The demands on such systems are being stretched enormously: higher complexity circuits in the nm size regime, ultra high-speed (e.g. THz) functionality and enormous data storage are all pre-requisites for 21st century IT. On the other hand new and versatile materials are urgently needed to produce large area solar energy conversion systems and feed the growing need for cheap societal electronics such as displays, personal medical diagnostic systems etc. These new materials are spatially, chemically, energetically and structurally complex.

All electronic and photonic devices work by either active or passive control of energy and particle transfer: these are the processes must be measured and understood to advance fundamental science in this field. In turn, the ordering and arrangement of chemical composition on the nm or molecular scale achieve this control. The unique spectral and temporal properties of 4GLS, ranging from THz through to soft x-rays in the picosecond time domain, open up new avenues for experimental science in the field of functional materials.

12.2. *New photon-based measurements for complex solids*

Many emerging materials are chemically inhomogeneous on the nm scale and hence exhibit electronic structure variation on the same scale. In this quantum size effect regime the electronic structure is also sensitive to shape. Ideally then there is a need to measure these properties in some ultra high resolution-imaging mode and to have the ability to measure in the picosecond range in order to understand local dynamics (particularly carrier dynamics). Recent work[1,2] has shown that scanning probe microscopes can be tuned to detect UV and x-ray interactions with solids on a nm scale and hence to provide a direct correlation between chemistry and topology in nanostructures. In optically active, wide gap materials, two-photon x-ray-laser spectroscopy

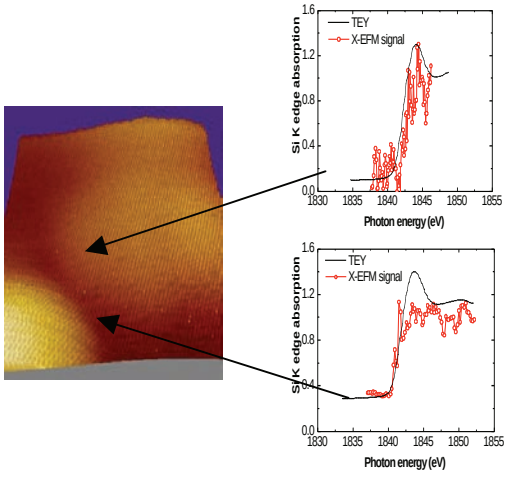


Figure 12.1: Local variations in Si K-edge XANES in 2 nm thick Hf silicate (a high *k*-dielectric), probed using an SPM tip in recent experiments at the APS. Locations separated by 4 nm (B Hamilton, with permission).

[1] Masashi Ishii and B Hamilton, Applied Physics Letters **85**, (30) (2004)
[2] B Hamilton *et al.* Applied Physics Letters, **90,** 063168 (2007)

has been shown to link electronic and chemical structure[3]. Meanwhile, 2 colour pump-probe measurements using SR and FEL radiation have given access to carrier dynamics with chemical specificity[4]. These are ***precursor experiments*** for the proposed programme, which will seek to advance experimental science and demonstrate that new levels of information can be obtained from new and complex materials.

12.2.1 SPM tip imaging and spectroscopy of photon interactions

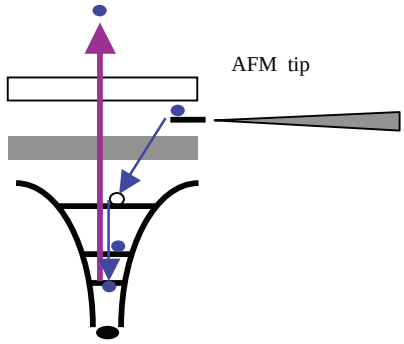


Figure 12.2: An AFM non-contact tip is a sensitive probe of a net hole charge in the bound system remaining after initial X-ray absorption and core hole decay. The tip effectively senses Coulomb force. (B Hamilton, with permission)

Non-contact mode AFM configured to measure Coulomb force interactions can sense charge that temporarily dwells in or on a nanostructure following x-ray or UV photon interaction, and has been demonstrated for dangling bond states in SiO_2 nano-oxides (figure 12.2). The charge sensed by the SPM may have lifetime of ms to s and so can be extensively averaged: the SPM senses, in a slow time domain, the "reaction product" of ultra fast energy transfer in a localised atomic system. This class of experiment breaks new ground in the sense that it spatially resolves x-ray interactions and correlates them with electronic properties of the solid. To achieve similar spatial resolution for chemical information requires detection of an x-ray absorption *spectrum* with SPM tip. Recent experiments at the APS5 have shown (in the case of Hf silicate) that it is possible to obtain the X-ray absorption near edge (XANES) spectrum with the SPM tip, and to use this to detect variations in oxygen stoichiometry associated with growth faults, thus correlating chemistry, electronic and defect structure.

12.2.2 Laser-XUV pump probe imaging and spectroscopy

Laser sources (typically in the 1 to 4 eV) and solids have provided a major spectroscopic tool, photoluminescence spectroscopy and excitation spectroscopy, for several decades. Primarily these photon sources couple into the electronic densities of states in the bands of the solid, and also interrogate defect states. Two-photon experiments, which measure the interaction between the dynamic mechanisms for light emission pumped by an x-ray source (via X-ray excited optical luminescence, XEOL) and a laser source (PL), have the potential to spatially discriminate chemically driven changes in electronic properties for photonic materials[6]. This has been demonstrated, for example, in studies of defect separation in feldspars[3] (which suggest that laser interaction probes both radiative and non-radiative electron transfer), and in the correlation between defect chemistry and electronic structure obtained in BN[6] (figure 12.3). These experiments demonstrated that large data sets, which contain chemical and electronic information in the time domain, may be obtained. The extension to the imaging mode has also been demonstrated, with spatial resolution of 0.5 microns.

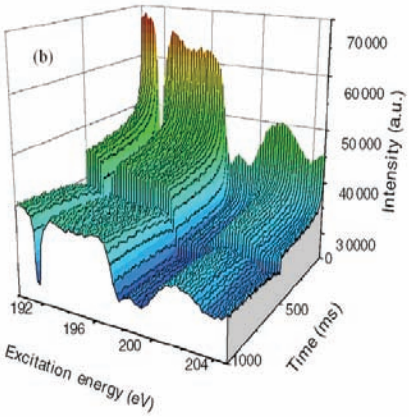


Figure 12.3: XAS measured via defect luminescence in hexagonal BN, allowing structurally distinct regions to be discriminated (B Hamilton, with permission)

[3] e.g. N R J Poolton, B M Towlson, B Hamilton, J Wallinga and A Lang, *J. Phys. D: Appl. Phys.* **40** (2007) 3557

[4] e.g. M Marsi, R Belkhou, C Grupp, G Panaccione, A Taleb-Ibrahimi, L Nahon, D Garzella, D Nutarelli, E Renault, R Roux, M E Couprie nad M Billardon, *Phys Rev B*, **61**, R5070 (2000).

[5] S Bernardini, M Ishii, E Whittaker, B Hamilton, J W Freeland and S De Gent, (in press, Microelectronics Engineering, August, 2007)

[6] e.g. N.R.J.Poolton, B.M.Towlson, D.A.Evans, B.Hamilton, New J. Phys. **8**, 76 (2006).

12.3. Some emerging materials systems and the need for 4GLS

Some important trends are clear which have clear connectivity with the source capability of 4GLS, viz.: **nanocomposites, 3rd generation dielectric and high energy gap UV semiconductors.**

There is an increasing awareness of the potential of wide energy gap nanoparticle based materials for both passive and active optical (especially solar) technologies. A number of large markets have developed for such **wide gap nanocomposites** and nanoparticles; these include nanocrystalline anatase-phase TiO_2 (used in dye-sensitised solar cells, as a sun screen, as a photocatalyst and as an inhibitor of polymer degradation), CeO_2 (used for example as a 'smart' fuel additive to reduce CO_2 production) and rare-earth oxides used as fluorescent security tags. Simultaneously, the market in organic and plastic-based systems for both displays and light harvesting has burgeoned.

Another very clear trend concerns the failure of the Si/SiO_2 system as a gate dielectric for the ubiquitous Si CMOS technology. This has led to the rapid development of higher dielectric constant insulators which are typically chemically more complex than SiO_2 e.g. hafnium silicate. Worldwide research into wide gap insulators is set to expand rapidly in the key area of data storage using flash memory. New oxide materials, which can be grown onto silicon with atomic precision, will be needed for this and wide gap oxides, which are transition metal based quaternary alloys, are strong contenders. These are truly novel oxides, **dubbed 3rd generation oxides**, and there is essentially zero knowledge at present concerning their complex chemical and electronic properties.

Wide gap semiconductors have applications in high temperature electronics, with SiC, BN and diamond the subject of much research. However, the development of 4GLS coincides with the start of a much more ambitious research goal: the quest for an efficient UV light emitting diode/laser. This is driven by the amazing success of GaN based visible emitters. The ability to push this technology towards AlGaN wide gap UV (210 nm) emission would have a huge societal impact. This technology, harnessed to solid state phosphor coated white light sources, would lead to a huge reduction in the energy cost of lighting our cities and urban areas; in the UK alone this demands the full power output of four major coal burning power stations. Worldwide, the reduction in CO_2 emission from such a development would be of major significance. In addition, **UV LEDs** would form the basis of cheap, low energy water purification systems fulfilling a urgent need for the developing world.

To address the challenges above requires the ability to:

- measure the electronic structure of both filled and empty states with high resolution;
- create particle excitations in high band gap materials, and to observe their relaxation and transport via a variety of methods on timescales down to fs;
- discriminate particle and energy transfer processes between bands and defect state and between chemically distinct regions of a solid;
- spatially resolve or image large data sets on the sub-nm scale, using photon pumped scanning probe methods which require high flux levels and wide energy tunability.

Given the large band gaps of many emerging materials to be studied, and their dilute nature, this requires pump-probe measurements in which the pump is a FEL that can access energies up to around 9 eV, synchronised with the probe - high quality short pulse SR of various wavelengths (from THz to soft X-ray). Previous FEL-SR pump-probe experiments of this type (at LURE and ELETTRA) have been limited at short wavelengths by the FEL used, and have been limited to 0.2 ns time resolution by the pulse length of the SR probe pulse (from a storage ring)[4]. Many excitonic charge-transfer processes occur on much

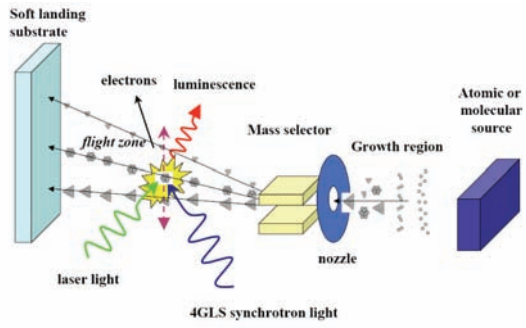


Figure 12.4: The ultimate goal of pump-probe measurements using mass-selected wide band-gap nanoparticles using 4GLS (Nigel Poolton, reproduced with permission.)

faster timescales. 4GLS will offer both a VUV FEL reaching energies up to 10 eV, and an SR pulse length of around 0.5 ps. The laser-XUV work achieved to date within the UK consortium is limited in its application by low XUV flux levels and lack of tunability of the laser source. Both these limitations are overcome by the 4GLS capability. This will allow full time domain spectroscopy of chemical and electronic structure including excited state spectroscopy, which holds key information for ultra small solids. Similarly, the scanning probe experiments described above would be radically extended to provide valence state and Fermi-edge related charge transfer onto isolated nanostructures using 4GLS.

12.4. Scientific methodology; the experimental palette

The combination of sources allows a palette of experiments to be designed to yield time- and spatially-resolved measurements of chemistry, transport, defect and electronic structure and topology. The experiments to be carried out include:

- measurement of ground and excited state electronic structure using high resolution photoemission and XANES using XUV SR;
- Pump-probe experiments, using 4GLS VUV FEL (resonant) excitation synchronised with
  - use of undulator SR to measure the ps evolution of surface photovoltage (via shifts in soft core level photoemission in the XUV);
  - high resolution photoemission of conduction band and defect/adsorbate states (2-photon photoemission, or 2PPE – typically using probe SR energies in the VUV;
  - measurement of total electron yield (TEY) as a function of temperature, giving information on transport;
  - simultaneous measurement and imaging of luminescence and XANES spectra and as f(pump-probe delay);
  - use of THz (ERL or FEL) radiation for THz absorption spectroscopy to probe exciton decay times through changes in sample dielectric function on ps timescales[7];
  - scanning probe tip probe detection of spectra and correlation with topology.

In addition, combination of some of the above with imaging capability (as in PEEM) may allow experiments on single nanoparticles to be performed; the image contrast in PEEM has been shown to be sensitive to variations in surface photovoltage[8]. Ultimately, these experiments may be carried out using mass-selected clusters either soft-landed or probed in flight, as shown in figure 12.4.

12.5. The UK Community and wider collaboration

The synchronisation of laser and SR pulses is quite a new experimental technology and this capability will need to be developed in the UK community before the work described here can be successful. To that end, as part of a £2.9 M award from the Northwest Science Fund (NWSF), funds have been obtained to purchase a high power fs laser system, tunable from the IR to UV energies of around 6 eV. The laser will be used in laser-SR pump-probe experiments, initially involving the SRS (which will limit the temporal resolution) and later with a THz probe from the 4GLS prototype, ERLP. This work is designed to lay the groundwork for the 4GLS programme described here, albeit with limited energy range (from the tabletop laser) and temporal resolution (from the SRS). In March 2007, the first synchronised

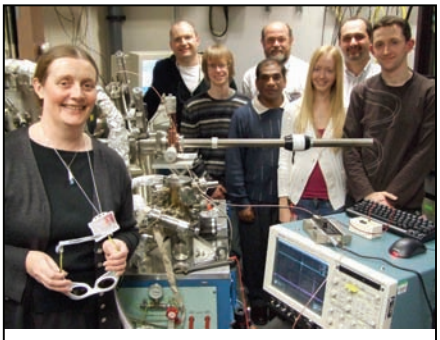


Figure 12.5: Initial steps towards fast laser-SR pump-probe spectroscopy of solids at Daresbury. A fs high power laser is synchronised to the SRS by 4GLS team members in March 2007

[7] R A Kaindl, M A Carnahan, D Hägele, R Lövenich and R S Chemla, *Nature*, **423**, 734 (2003)
[8] R J Phaneuf, H-C Kan, M Marsi, L Gregoratti, S Günther and M Kisinova, J Appl. Phys., **88**, 863 (2000)

laser-SR benchmarking experiments were carried out at the SRS, measuring the variation in surface photovoltage in p-type Si (111) as a function of pump-probe delay (figure 12.5). Part of the science programme for the laser system involves precursor pump-probe experiments probing electron-hole pair dynamics in nanoparticulate and thin film oxides; indeed funding for work in hybrid solar cell design has already been obtained from EPSRC 'Materials for Energy Supply' Initiative. A group of around 30 UK PI's supporting this work has nucleated around this facility. They include Russell Egdell (University of Oxford), Philip Moriarty and John O'Shea (University of Nottingham), David Binks, Rob Lindsay, Andrew Horn and Andrew Thomas (University of Manchester), Michael Hunt (University of Durham), Ronan McGrath (Liverpool University) Peter Dunsten (University of Wales, Swansea) and Chris Binns (University of Leicester). Collaborations may also be anticipated with Richard Friend FRS and Colin Humphries (University of Cambridge) and Paul O'Brien (University of Manchester), who have all expressed general support.

The international community interested in this area is large; these experiments formed a part of the 2001 4GLS Science Case, and related experiments form a part of the science cases of several planned 4th generation facilities (including the BESSY FEL). Of the facilities currently likely to be constructed, 4GLS is best equipped to carry them out. Key leading lights in the field are Laurent Nahon and Marino Marsi (SOLEIL); both wrote in support of these experiments in the 4GLS 2001 Science Case. Stefan Carlson (MaxLab), John Freeland (APS) and Masashi Ishii (SPring8 and RIKEN) are involved with the Manchester/STFC work on novel experimental technique development. Stefan DeGent (IMEC) has expressed strong interest collaborating and supplying nanodielectric material systems. Other key figures who have expressed support for this programme are Norman Tolk (Vanderbilt University, US), Fulvio Parmigiani (ELETTRA) and Andrzej Wojtowicz (N Copernicus).

13. MANY-BODY PROPERTIES OF SOLIDS STUDIED BY TIME-OF-FLIGHT ANGLE-RESOLVED PHOTOEMISSION SPECTROSCOPY AT 4GLS

Mark S. Golden (University of Amsterdam), Jörg Fink (Leibniz Institute for Solid State and Materials Research, Dresden), D Phil Woodruff FRS (University of Warwick)

13. 1. Motivation

The resistivity of metals and semiconductors is determined by scattering processes of the charge carriers. Part of these scattering processes is caused by excitations of phonons, electron-hole excitations, plasmons, magnons etc. These excitations are often called many-body effects because many degrees of freedom of the solid are contributing to these processes. These effects not only determine the resistivity but many other transport properties of solids, e.g. the magneto-resistivity, the thermopower, or the heat conduction. Ultimately, these many-body effects also determine such important material properties such as magnetism and superconductivity.

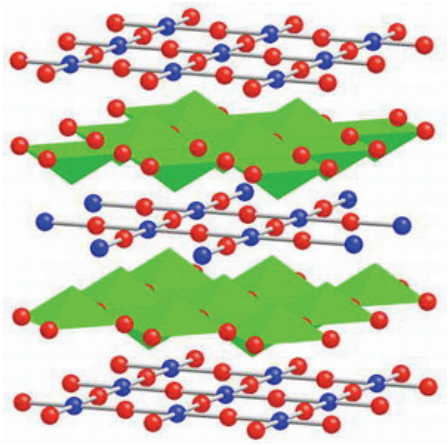


Figure 13.1: Typical T' structure of cuprate superconductors, consisting of CuO_2 sheets separated by thin sheets of rare-earth oxide (Argonne National Laboratory)

In a microscopic picture of these many-body properties, the polarization of the solid by the electrons and the scattering of the charge carriers are described by the real and the imaginary part of the self-energy, respectively. Angle-resolved photoemission started life as a method for the determination of the band structure of solids. With the advent of high-resolution spectrometers utilising two-dimensional detection (parallel in E and **k**) and third generation synchrotron facilities, it has now become possible to determine directly the self-energy of the charge carriers in a solid and thus opening the door to a complete microscopic understanding of the charge dynamics in metals, semiconductors and insulators. We are therefore at a juncture in which direct experimental probes of quasiparticle dynamics - such as high resolution ARPES - have become a cornerstone of an intensive international effort to image, and understand the many-body behaviour seen in many different materials Consequently, using angle-resolved photoemission as k-space microscopy to directly image the electronic states of novel electronic systems has become a flagship activity at all third generation light sources worldwide.

With an eye on the performance jump achievable using a dedicated low energy source such as 4GLS, we would place investigations of a growing number of electronic systems collectively describable as unconventional quantum electron matter at the forefront of this experimental effort. These sorts of systems include unconventional superconductors (cuprates, heavy Fermions), transition metal compounds exhibiting colossal magnetoresistance, and other low dimensional correlated systems. Understanding (and ultimately harnessing) their exotic many-body behaviour represents a dual challenge to both experiment and theory. In this field new concepts including those of quantum criticality and the associated non-Fermi liquid behaviour are of great interest, whereby the great complexity of the materials involved (both in terms of their solid state chemistry as well as the near degeneracy of many energy scales in the problem such as band-widths, electron-phonon interactions magnon/exchange energies, charge and orbital ordering energies) may well lie at the source of their spectacular properties, as an expression of the concept of *emergence*.

13.2. Scientific methodology

As an example of the present state-of-the-art, Fig. 13.2a shows an (E,**k**)-image of the electronic states in the high-T_c superconductor $Bi_2Sr_2CaCu_2O_8$, indicating not only the presence of the superconducting gap, but also a strong coupling of the charge carriers to a bosonic degree of freedom, which probably is a magnetic excitation that is also detected in inelastic neutron scattering studies. Fig. 13.2b illustrates that a similar maturity of data has also been reached in the colossal magnetoresistant manganites: in this case, of course, no superconducting gap exists, but again there are clear indications of strong structure in the self energy due to coupling to bosonic degrees of freedom.

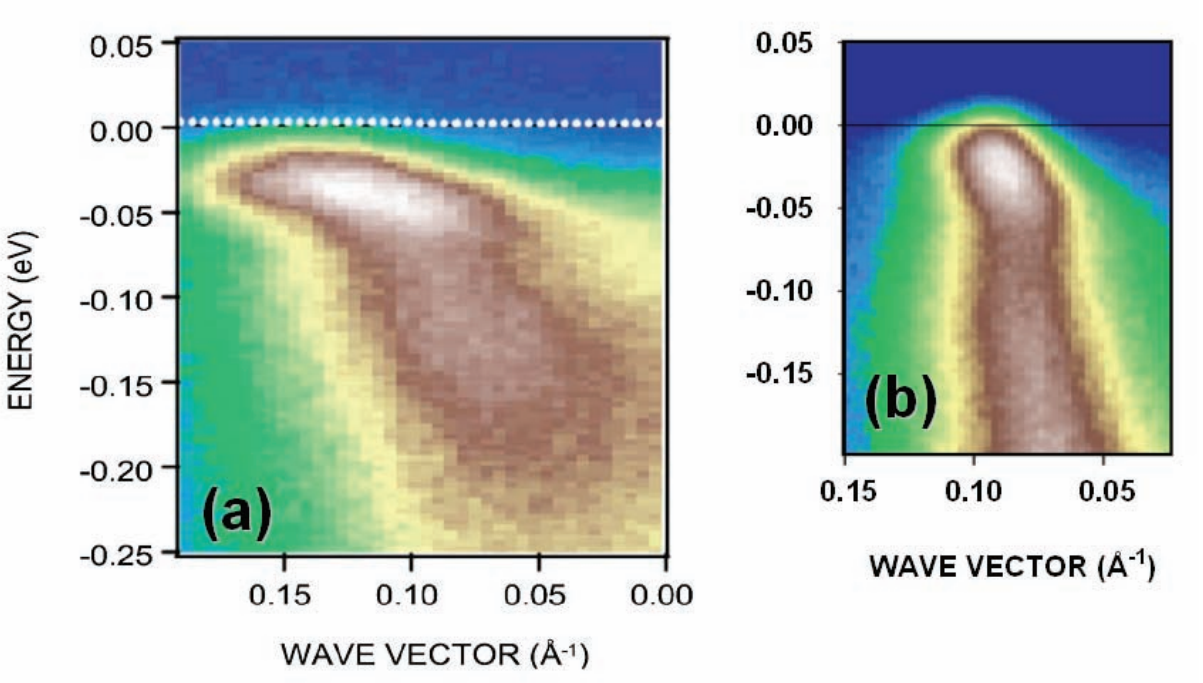


Figure 13.2. ARPES (E,**k**) images of (a) the high-Tc superconductor $Bi_2Sr_2CaCu_2O_8$ showing a superconducting gap of 30 meV and at 70 meV a huge coupling to a bosonic excitation mode and (b) the colossal magnetoresistant manganite $La_{1.36}Sr_{1.64}Mn_2O_7$, showing a clear quasiparticle feature at E_F followed by the strong band renormalisation at 70-100 meV.

The present status of ARPES at third generation synchrotron facilities is based upon a recording of the spectral function as a function of binding energy and wave vectors, $\mathbf{k}_x$ and $\mathbf{k}_y$. By using a two-dimensional detector at the output of a hemispherical electrostatic energy analyser, the binding energy and one wave vector direction (e.g. $\mathbf{k}_x$) can be detected simultaneously. By successive rotation of the sample, the whole wave vector space can be mapped. This is a tedious task which very often takes days or weeks, and also involves altering the incident angle of the polarised synchrotron radiation with respect to the sample crystal (thus affecting the matrix elements governing the photoemission intensity). Energy resolutions of the order of 10 meV are now routinely achieved at the best beamline/endstation combinations. In some ARPES spectrometers resolutions below 1 meV are aimed for.

13.3. The need for 4GLS

A new development in this field is the use of time-of-flight (TOF) electron spectrometers which require the use of pulsed photon sources. A TOF spectrometer will be soon be offered as a commercially available product by the leading ARPES company, VG-Scienta. Such a system

potentially possesses the huge advantage that energy and *two* momentum directions can be recorded simultaneously, thus reducing considerably the recording time required for achieving high quality data. Considering the most interesting materials are often complex (and sometimes have quite reactive cleavage surfaces), this win in time translates immediately to an improvement of 'regular' energy resolution to down below 1 meV and the possibility for control of new experimental parameters such as spin. The ideal light source for such a new generation of advanced ARPES spectrometers will be short-pulsed SR from an ERL, or FELs. The slightly longer pulse length of the former (around 1 ps) is in fact preferable for the highest energy resolution spectroscopy, as the bandwidth of the pulses is small enough to retain an overall spectral resolution on the meV scale. This is a key advantage of 4GLS. In addition, for solid state photoemission, the pulsed light source needs to have a high repetition rate (as is the case at 4GLS), in order to avoid otherwise crippling space-charge induced distortions of the angular distribution of the photoelectrons. Thus, the combination of 4GLS in combination with new time-of-flight ARPES spectrometers would open a whole new regime previously inaccessible using ARPES experiments at third generation sources.

In the following we illustrate possible applications of a time-of-flight spectrometer at 4GLS:

- high-resolution ARPES experiments could clarify the dressing of the charge carriers (e.g. phonons or magnetic excitations) which could lead to a definitive explanation of the mechanism of high-T_c superconductivity
- in addition, the unique appearance of a pseudogap in the underdoped region of high-Tc superconductors could be clarified
- determination of the symmetry of the superconducting order parameter and the mechanism of pairing via high resolution ARPES for a whole class of unconventional superconductors
- crucial new insight could be gained into novel magnetic materials, such as the elucidation of the nature of the colossal magnetoresistant transition in doped manganese oxides. In particular, explicit spin resolution of the scattering rates in ferromagnetic materials (manganites and other spintronic materials) is a dream that could approach fulfilment using 4GLS as a light source
- the superior energy resolution coupled to the fast acquiring times would open new doors in the investigation of the highly reactive surfaces of rare earth and actinide systems. Here fascinating synergies (and probably also differences) can be expected as regards the effects of quantum criticality in these 4f and 5f systems and the high T_c superconductors, and important fundamental inroads can be made into the uncharted territory of physics for metals far beyond the Landau Fermi liquid/quasiparticle paradigm
- the combination of multiple pulsed sources on offer at the 4GLS will also enable pulse-probe experiments, enabling selective 'tickling' of degrees of freedom such as lattice vibrations and (also spin-dependent) interband excitations into the unoccupied states with subsequent analysis of the newly populated states using the TOF-ARPES system.

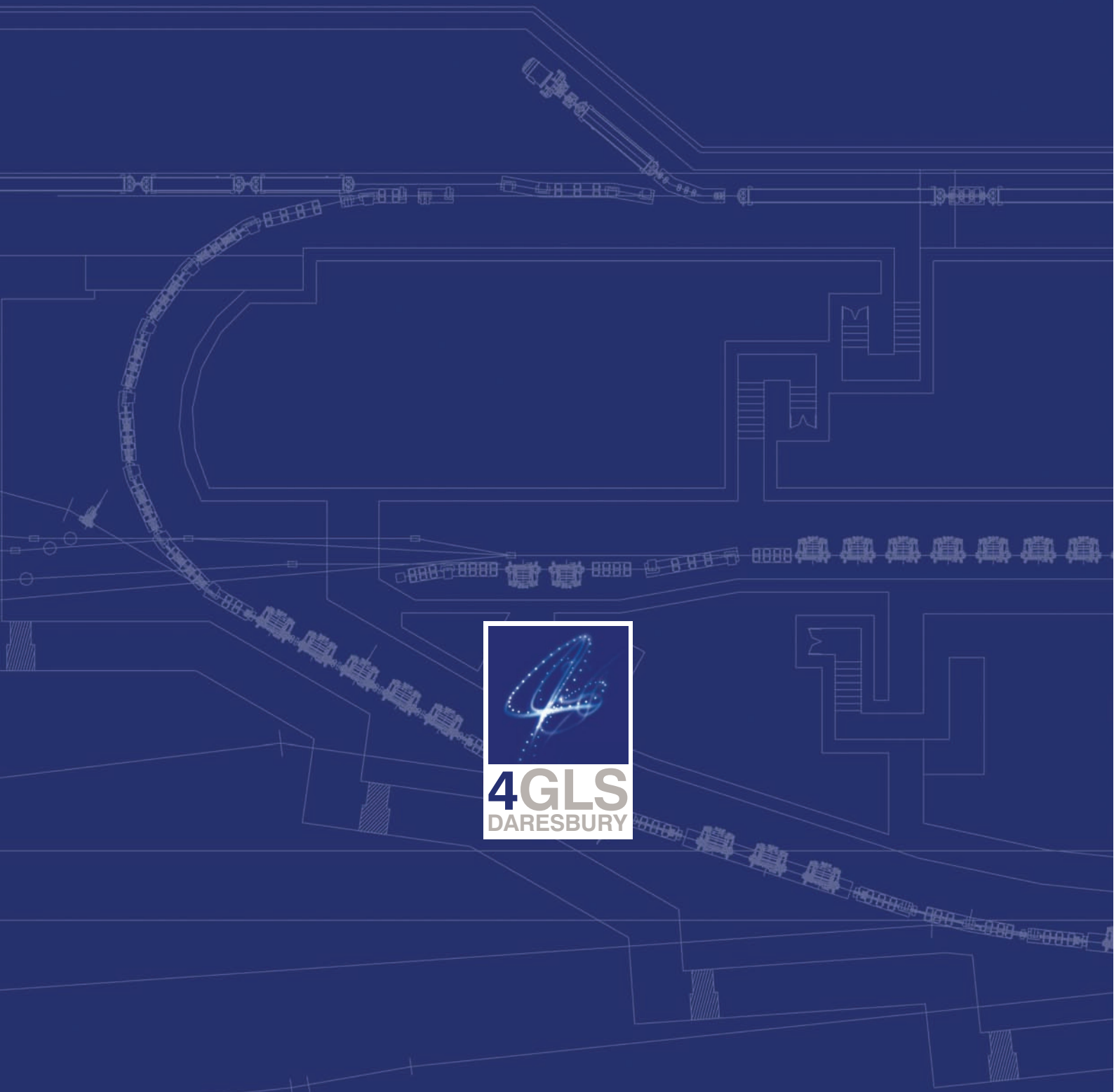
The use of the 4GLS XUV FEL for photoemission would make possible single-shot photoemission experiments, which may be particularly valuable for increasingly fragile samples that are prone to damage by the incident radiation. For many traditional inorganic semiconductors and metals, very high flux densities of XUV photons seem to have little adverse effect, but the range of materials for which this is a constraining influence is growing. This is a consequence of two trends. One is the wish to study systems that are intrinsically more fragile, particularly organic materials including semiconductors and molecular reactants at surfaces. The other is the problem that one increasingly needs a highly-focussed beam of incident radiation, in some cases to study very small single crystal samples or specific regions of inhomogeneous systems. While the number of photons needed to be incident on the sample to collect a satisfactory photoemission spectrum is fixed, the amount of sample degradation that these photons cause depends on the illuminated area; if the illuminated area is reduced, the fraction of damaged material increases, and with it the integrity of

the resulting data. In principle the solution to this problem is to collect the complete photoemission spectrum in a timescale shorter than that in which the photon-induced damage occurs. In such an experiment the sample is damaged by the experiment, but the collected data correspond to the undamaged state. This damage is induced by electronic excitations that take place on sub-femtosecond timescales, but the resulting movements of atoms within or out of the solid, that constitute the damage, occur on significantly longer timescales - longer than, but more comparable to, typical vibrational periods of hundreds of femtoseconds. Thus, if one can collect a complete photoemission spectrum using a single pulse of photons with a duration of ~100 fs, one can overcome this problem. The required number of photons to be delivered in a single 100 fs pulse to make this feasible is $\geq 10^{11}$. This the 4GLS XUV FEL will achieve; the expected number of photons per pulse is up to 10^{14}. Initial experiments at FLASH have already shown that single-shot photoemission is viable with these flux levels; the higher repetition rate of the 4GLS XUV FEL would make these experiments possible without the space-charge effects that are hampering the FLASH work.

In the last 15 years, high resolution ARPES has emerged as one of the leading experimental tools involved in pushing back the frontiers of solid state and materials research, and has become an important benchmark for many theoretical innovations in the field of unconventional quantum matter. Consequently, a new generation ARPES capability located at Daresbury, coupling TOF energy and 2D-($\mathbf{k}_x$,$\mathbf{k}_y$) analysis of photoelectrons to the pulsed excitation sources of 4GLS would enable wholly new experiments, just as (practically speaking) unthinkable today as today's state-of-the-art experiments were prior to the introduction of the 2D-(E,**k**) detection in the early days after the discovery of high T_c superconductivity.

13.4 Wider Community

International activity in this field is strong, with programmes at all world 3rd generation sources; of particular note are the programmes at BESSY, SSRL and the ALS. Collaborators, or anticipated collaborators in this work in the UK include Russell Egdell (University of Oxford), Philip Moriarty (University of Nottingham), Wendy Flavell (University of Manchester), Andrew Evans and David Langstaff (Aberystwyth University), Sasha Alexandrov (University of Loughborough) and Michael Hunt (University of Durham).



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