The Science Case

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The Science Case for 4GLS

A World Leading Facility for UK Science

Presented by

The UK Scientific Community

December 2001

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Executive Summary

This document is presented by over 200 members of the UK Scientific Community and contains the scientific case for the establishment of the 4th Generation Light Source (4GLS) at CLRC Daresbury Laboratory. It forms a part of the proposal to establish a National Centre for Accelerator Science Imaging and Medicine (CASIM) at the laboratory which was first submitted to the North West Science Review Committee in 2000.

The proposal for 4GLS will be assessed through the 'Gateway Process', with peer review organised by EPSRC on behalf of OST. The mechanism of this process is described in Appendix I. In line with the stages of this process, the purpose of this document is to present the *outline science case only* for peer review. The full business case with a complete analysis of costs and risks will be presented at the appropriate stage of the process, following a design study.

The UK has had an established and documented need for a low energy SR source for at least 15 years and the initial drive to establish such a source was borne out of the need to provide scientists both in the UK and internationally[1] with access to a world class source of high quality UV – XUV radiation. However, developments in accelerator technology during this period have now allowed us to propose a facility that will realise long-awaited scientific goals in the field of dynamics and nanoscience that far surpass our original expectations. This in turn brings together two previously rather independent communities, the 'low energy SR' community and the 'laser' community, and allows the synergies between SR and laser sources to be exploited to the full, for the first time, in cutting-edge experiments.

This document is a proposal to establish the world's leading low energy source. 4GLS is a suite of accelerator-based light sources designed to complement the ESRF and *diamond* by providing state-of-the-art radiation in the low energy photon regime – from the far-infrared (IR) to the extreme ultraviolet (XUV). At its heart is a low energy ring based on a superconducting energy recovery linac (ERL) which will provide optimised synchrotron radiation from a variety of free electron lasers (IR to XUV), undulators and bending magnets.

The 4GLS undulators will be *optimised* to generate spontaneous high flux, high brightness radiation, of variable polarisation, over the photon energy range 3-100 eV. However, they will also generate usable radiation in the higher harmonics up to around 500 eV. The intensity and extremely broad tunability of this undulator radiation are two of its main attractions to synchrotron radiation users. The ERL technology of 4GLS will allow much shorter bunches and higher peak photon fluxes than is possible on conventional storage ring sources. It will also give users the added bonuses of pulse structure flexibility and an effectively infinite beam lifetime; benefits unavailable to storage ring users.

In addition, three free electron laser (FEL) sources will operate in the IR (3 – 75 μm, variable polarisation), VUV (visible – 10 eV, variable polarisation) and XUV (5 – 100 eV). The FELs will be used to generate short pulses of radiation that are broadly tunable and more than a million times more intense than the equivalent spontaneous undulator radiation. The FEL sources are designed to operate effectively in regimes where they offer considerable advantages over table top sources, *i.e.* in both the far IR (THz) regimes, and at all frequencies higher than deep UV. The extraordinary flexibility of the ERL design of 4GLS means that

[1] D P Woodruff and A M Bradshaw, *Physics World*, 11 (1998) 17-18

these outstanding sources may be used individually, in combination with undulator radiation or other FEL radiation or together with table-top IR or visible/UV laser sources. No other laboratory in the world has IR-, VUV- and XUV-free electron lasers in close proximity both to each other and to state-of-the-art low energy synchrotron radiation.

This makes possible an entirely new generation of experiments in the VUV based on 'pump-probe' techniques, where dynamic processes and transient species of all types may be probed on timescales into the fs regime. We will be able to study transient species that do not occur naturally on earth, such as those present in the interstellar medium, with profound implications for models of the origin of the universe and the homochirality of life. Studies of reaction intermediates will revolutionise our understanding of all types of catalysis, electrochemistry and photochemistry. Fast energy transfer processes may be studied in unprecedented detail, providing the foundation for improved models of processes such as DNA damage and repair. 4GLS will also allow truly real-time conformational dynamics measurements of biomolecules, even in dilute solutions, thus improving our understanding of the links between protein structure, dynamics and function.

The high brightness of the sources making up 4GLS will allow individual nanoclusters of material to be studied both on surfaces and in flight, allowing us to develop an understanding of the transition between molecular and condensed phases and to exploit it in the development of new materials. Key nanoimaging techniques will be developed. For example, the intensity available from the IR-FEL is essential for achieving resolutions substantially beyond the diffraction limit in near field imaging and the powers available from the VUV and XUV-FELs will allow non-linear sum-frequency and second harmonic imaging to be performed. The tunability of the sources allows these imaging tools to be targeted to specific dynamical processes, leading to step advances in functional imaging. The brightness of these sources, particularly the XUV-FEL, will lead us into a new regime of high field physics where non-linear processes may eventually be exploited, for example in the development of coherent control of reactions.

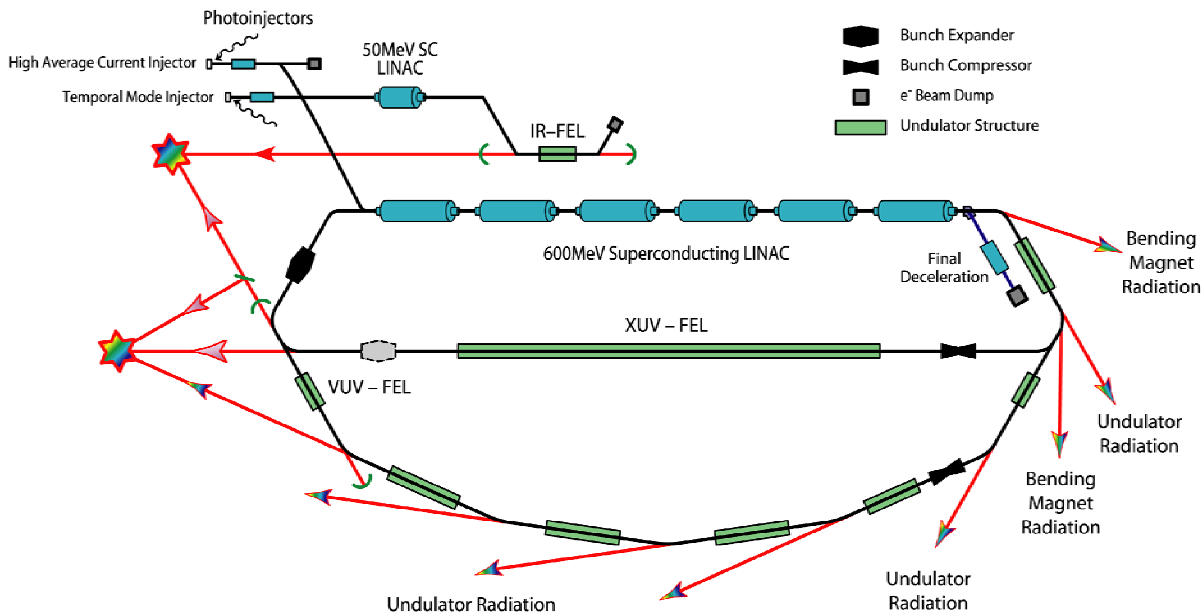
4GLS is entirely complementary in its provision to the planned *diamond* source, both in terms of its photon energy coverage and its capacity for dynamic measurements. This issue is addressed explicitly in the report by Professor D P Woodruff recently commissioned by the UK SR Forum (Appendix VI). It is also complementary to planned European sources, such as the TESLA XFEL facility and will seed the symbiotic development of a new generation of world sources through European collaborations, for example with DESY Laboratory, and collaborations with other leading international laboratories, notably Jefferson Laboratory and SSRL. 4GLS will foster development of a crucial expertise base in technologies relevant for the UK's involvement in other world projects. It will provide the impetus for the development of the UK's accelerator science capability through the internationally renowned work of the accelerator physicists at Daresbury Laboratory and place the UK at the forefront of accelerator design and development.

Contents

1 THE 4GLS VISION

Our vision for 4GLS is to create the world's leading low energy light source in order to carry out internationally outstanding science that cannot be conducted elsewhere.

The fourth generation light source is a uniquely flexible source of ultra-high brightness continuous and pulsed radiation covering the IR to XUV parts of the spectrum. It is the first light source in the world that is planned from the outset to be a multi-user, multi-source facility combining ERL (energy recovery linac) and FEL (free electron laser) technology. As such, it will place UK accelerator science at the forefront of world developments. ERL technology provides high quality, very high brightness radiation, which vastly surpasses that provided by conventional storage ring technology. It also provides easily tailored pulse characteristics, leading to a high level of experimental flexibility. It is widely regarded by the international community as the technology on which future advances in synchrotron radiation science will be based. FEL technology provides the opportunity to complement this with pulses of very short duration and ultra-high brightness from IR-, VUV- and XUV-FELs which are themselves individually world class. The use of locked laser photoinjectors and superconducting technology throughout confers high stability and allows the different parts of the facility to be brought together in a unified whole, and in particular to be used in combination, with the pulses from one source matched and synchronised with those from another. The ERL technology lends itself to easy upgrade paths which are described later in this document. This is a source that will not become rapidly outdated but will provide the UK with a world leading facility for many years after its construction.



The outstanding properties of 4GLS will enable a paradigm shift in scientific research using low energy photons. The high brightness of the source will lead to step advances in research aimed at exploiting and manipulating the novel properties of systems with dimensions reduced below 10 nm. Indeed, the brightness of the radiation from the new source is so high that *single* nanoscale objects can be studied, for example the distribution of electron spins in single nanoclusters of magnetic material may be determined for the first time. The high brightness also enables the development of a number of imaging techniques, for example the use of the huge brightness of the IR-FEL to develop near-field functional imaging on truly sub-cellular (30 nm) dimensions. The short pulse lengths provided by the source allow us to access the dynamics or kinetics of processes previously inaccessible, for example studies of real-time protein folding, molecular conformational changes and chemical reactions on timescales down to tens of fs. The flexibility and ease with which photon sources may be combined will allow unparalleled opportunities for the development of 'pump-probe' experiments. Of particular importance here are those using the VUV- and XUV-FEL sources, which allow, for example, the creation of transient, short-lived species (such as those created in the upper atmosphere or in interstellar dust clouds) and their subsequent study using continuous radiation. The brightness of these sources, particularly the XUV-FEL lead us into a new regime of high field physics where non-linear processes may be exploited, for example in the development of coherent photon scissors and related tools.

The potential for technological exploitation of the results of this research can scarcely be overestimated particularly when one realises that the small distances and fast timescales that will be probed are precisely those governing many 21st century technologies. For example, semiconductor device structures based on Si are set to become so small that they will operate normally in a non-equilibrium regime which makes dynamic carrier distribution measurements of the type described in this document essential for their further exploitation. The development of spintronic memories will require the nanoscale characterisation of electron spin distributions of magnetic clusters of the type 4GLS is ideally suited to provide. The capacity of 4GLS for dynamic measurements of protein folding in realistic solutions on fast timescales will provide complementary information to the 'static' structure information provided by protein crystallography to the post-genomics world. The ability to manipulate molecules in high fields will lead to opportunities for exploitation of the coherent control of reactions, while the ability to study reaction intermediates will lead to a fundamentally improved understanding of all types of catalysis.

The demand for this facility comes from the UK and the international research community, more than 200 of whom have contributed to this document. For over 15 years it has been recognised that UK researchers requiring low energy synchrotron radiation are being severely disadvantaged by the lack of access to high brightness VUV photons. Indeed, enhanced provision of VUV radiation was an explicit recommendation of both the Blundell and Woolfson reviews on synchrotron radiation science which were presented in 1986 and 1993 respectively[2]. None of the current European 3rd generation sources offers optimised radiation below 100 eV. The 4GLS ERL technology provides high brightness undulator radiation in a multi-user facility, giving this 'low energy' community a source quality surpassing any other world low energy source. In addition, 4GLS provides individual, internationally leading FEL sources meeting a number of the needs of the 'laser' community, in particular access to intense deep UV and XUV sources. The facility thus brings together two previously rather independent communities and allows the synergies between SR and laser sources to be exploited to the full for the first time in cutting-edge experiments.

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[2] Blundell report on Scientific Requirements for Synchrotron Radiation Research in the UK, 1986; Woolfson Report on Synchrotron Radiation, 1993.

In summary the design concept of 4GLS is unmatched anywhere in the world. It will enable completely new research using low energy photons, which will allow the UK scientific community to lead the field, and will place the UK at the forefront of accelerator design, development and exploitation for many years to come.

2 THE CASIM CONTEXT: THE FOURTH GENERATION LIGHT SOURCE COMPONENT OF THE CASIM PROJECT

The proposal to establish a National Centre for Accelerator Science Imaging and Medicine (CASIM) at the Daresbury Laboratory was first submitted in the summer of 2000 to the North West Science Review (NWSR) established by Lord Sainsbury. The proposal received the enthusiastic support of the NWSR and of the North West and Daresbury Development Group established by the Secretary of State for Trade and Industry, Stephen Byers.

In order to facilitate an assessment of the CASIM proposal a more detailed case for the fourth generation light source (4GLS) and Radioactive Ion Beam facility (SIRIUS) components of CASIM was submitted to the UK Research Councils by the CLRC Daresbury Laboratory in February 2001. At a meeting at the Daresbury Laboratory in March 2001 the Secretary of State for Trade and Industry promised Government support for CASIM subject to a satisfactory response to issues raised in the report on the peer review process prepared by the Engineering and Physical Sciences Research Council (EPSRC).

This document is presented by more than 200 scientists, on behalf of the UK science community, and with the approval of the UK SR Forum. It provides the scientific justification for the 4GLS component of CASIM, together with a description of the main characteristics of the facility in comparison with other planned UK and world facilities. We present a full response to issues raised by the EPSRC report on the 4GLS component of the case submitted by CLRC in February 2001. In the case of the SIRIUS component the response to the review panel has gone forward as a separate document following acceptance of the basic science case. The current proposal for 4GLS will be assessed through the 'Gateway Process', with peer review organised by EPSRC on behalf of OST. The mechanism of this process is described in Appendix I. In line with the stages of this process, the purpose of this document is to present the *outline science case only* for peer review. The full business case with a complete analysis of costs and risks will be presented at the appropriate stage of the process, following a design study.

The vision behind the CASIM proposal is based on a recognition that advances in science, engineering and medicine are becoming increasingly dependent on accelerators. CASIM at Daresbury will provide the UK with a focus to maintain and develop its world-leading expertise in accelerator science, to train accelerator scientists and to exploit the potential of accelerators in a wide range of fields.

In assessing the cost effectiveness of CASIM it is important to consider the overall synergies of the project. The synergies between 4GLS and SIRIUS are apparent, for example, in the fields of imaging, radiobiology, and in the spectroscopy of radioactive and neutron rich ions important to our understanding of stellar evolution. These and other synergies will be easily lost if the project is considered as separate components which are evaluated in isolation. In particular we draw attention to the traditional separation between funding of the science base and the health service in the UK. CASIM offers a unique opportunity to break down barriers between these activities.

3 4GLS SCIENCE CASE

3.1 Introduction

In world terms, 4GLS is a unique source that will enable completely new experiments. The extraordinary flexibility of the ERL design means that the FEL sources may be used individually, in combination with undulator radiation or other FEL radiation or together with table-top laser sources. This makes possible an entirely new generation of experiments in the VUV based on ‘pump-probe’ techniques, where dynamic processes and transient species of all types may be probed on timescales into the femtosecond (fs) regime. Thus 4GLS will be used to probe the relationship between structure and reactivity in all types of matter with unprecedented precision. The first parts of the science case describe the new science that will be carried out using the pump-probe approach, in areas as diverse as conformational dynamics of biomolecules, spin and electron dynamics, and the study of short-lived transients of importance in pollution control.

The brightness of the 4GLS sources make possible many new experiments on small clusters of material and indeed it will be possible to study individual nanoclusters. It will also be essential for flux hungry experiments where the material under study is present only in very small amounts or where the detection technique is intrinsically inefficient. Key nanoimaging techniques will be developed. For example, the intensity available from the IR-FEL is essential for achieving resolutions substantially beyond the diffraction limit in near field imaging, and the powers available from the VUV and XUV-FELs will allow nonlinear sum-frequency and second harmonic imaging to be performed. The tunability of the sources allows these imaging tools to be targeted to specific dynamical processes. The second main part of the science case describes the contribution of the source to nanoscience, ranging from measurements of the spin polarised electronic structure of individual magnetic clusters to the development of new biomaterials.

Finally, the brightness of these sources, particularly the XUV-FEL will lead us into a new regime of high field physics where short-wavelength non-linear processes will be accessible. 4GLS will have a ground-breaking role to play here in contributing to the interplay between theory and experiment and improving our understanding of the behaviour of molecules in intense XUV fields. This work is summarised in the final section of the science case.

3.2 Time-Resolved Pump Probe Studies

Understanding the relation between structure and reactivity is one of the most important challenges in chemical physics research. A key role in this research is played by time-resolved pump-probe experiments which provide a real-time observation of the nuclear motions of atoms and molecules in the process of undergoing chemical change. In 1999 Prof Ahmed Zewail was awarded the Nobel Prize in Chemistry for his pioneering work in this area[3].

The radiation pulses used in pump-probe experiments need to satisfy a number of requirements. The pulse duration has to be short compared to the dynamics under investigation, which typically implies pulses in the picosecond or femtosecond domain. Indirect photoionisation, rotation and intramolecular vibrational relaxation can be studied on a

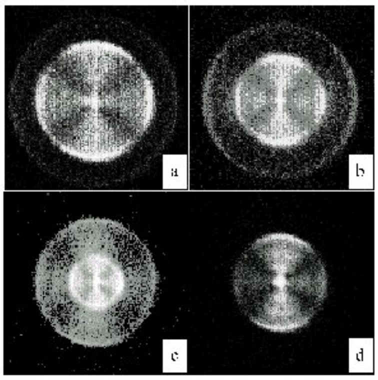
[3] Femtochemistry, A H Zewail, World Scientific Press, Singapore 1994

picosecond (ps) timescale whilst direct photoionisation, vibrational motion and chemical exchange can be probed in the femtosecond time domain. In addition, the intensity of the pulses must be sufficient to achieve finite excitation probabilities during the short interaction. 4GLS, with its combination of VUV- and XUV-FELs, together with its undulator radiation, offers unique opportunities for these and other types of studies. Furthermore, the high average power of the VUV-FEL and the possibility of synchronising the FEL radiation with conventional pulsed laser sources will enable sophisticated pump-probe experiments to be performed. Alternatively, non-perturbative experiments can be undertaken using only the high intensity VUV-FEL.

At present, pump-probe experiments are limited to specific targets that can be excited by one laser and probed by a second laser, both of which are limited in their photon range. Hence it is impossible to study photolysis products over a wide range of irradiation wavelengths. 4GLS will allow not only the photodissociative products to be probed (including for the first time those from super-excited states) but will also enable the subsequent chemical reactions of such fragments with neighbouring species (*e.g.* on surfaces) to be probed. Detailed studies of this kind will allow the dynamics and mechanisms of heterogeneous chemistry to be studied directly and unprecedented information obtained.

To demonstrate the potential of 4GLS for pump-probe studies, consider the following example of picosecond dynamics using a conventional laser[4]. In this experiment, Xe atoms were photoionised in the presence of a DC electric field, and the resulting electrons detected using velocity map imaging techniques. The experiment revealed both direct and indirect contributions to the photoionisation process, depending on the ejection angle of the electron with respect to the electric field axis.

However, the time difference between the direct and indirect processes could not be resolved in this experiment. By using the VUV-FEL on 4GLS, in combination with a streak camera, the two processes could, for the first time, be separated. The implementation of streak camera techniques with the FEL will allow measurements of time-resolved photoionisation on picosecond timescales. This is currently a very active research area in both atoms and complex molecules/clusters that holds great future promise when 4GLS is operational.



Photoelectron images recorded for 2-photon excitation of Xe(6s[3/2]$_2$) in a 170 V/cm DC field with the laser polarisation parallel to the plane of the imaging detector, as a function of the wavelength of the excitation laser: a) 650.14 nm; b) 650.40 nm; c) 650.78 nm; d) 651.12 nm. The images show an inner and an outer contribution corresponding to indirect and direct photoionisation, respectively. With the VUV-FEL these two contributions could be studied in the time-domain.

The pump-probe technique can be extended to experiments on time-resolved molecular dynamics in which photodissociation can be induced by a photon obtained from the VUV-FEL and then probed by a conventional laser. Experiments can also be performed where the

[4] C Nicole, I Sluimer, F Rosca, M Warntjes, F Texier, F Robicheaux, C Bordas and M J J Vrakking, *Phys Rev Let*, 85 (2000) 4024

dissociation is induced by a conventional laser, and a photon from the VUV-FEL used to monitor the time evolution of the parent molecule (time-resolved photoelectron spectroscopy). The appearance of fragments in these experiments can be monitored using time-resolved photofragment imaging.

All these experiments will benefit greatly from recent developments in two-dimensional ion/electron imaging techniques, that make it possible to study the photodissociation simultaneously in both the time- and energy-domains.

3.2.1 Molecular Dynamics

3.2.1.1 Photodissociation of neutral molecules

If a molecule is excited at an energy above the threshold for breaking two (or more) bonds, then it is predicted that the dissociation will be dominated by many-body processes. Although such fragmentations appear rare so far, this is more a reflection of the shortage of sufficiently intense light sources in the appropriate VUV energy range. 4GLS will offer a huge step forward in this regard; its combination of spectral brightness, short pulse duration and high repetition rate will open the way to coincidence studies for determining the fragmentation pathways of neutral molecules.

The photodissociation dynamics of neutral hydrogen-containing molecules can be studied using H Rydberg atom time-of-flight spectroscopy[5]. In this technique, the first (photolysis) photon, from the VUV-FEL, will photodissociate the reactant molecule to form H (n=1) and a neutral fragment. A second photon from a table-top laser will then excite the H-atom from n=1 to n=2. Finally, the H-atom will be tagged through the absorption of a third photon from a second table-top laser that excites it into a high Rydberg state. The recoil velocities of the tagged atoms will be measured using a time-of-flight spectrometer and field ionisation. Such studies allow the dissociation product branching ratios, and the electronic, vibrational and rotational populations in the fragments to be determined. Information about the potential energy surfaces involved in the transitions is also obtained. Furthermore, the character and lifetime of the prepared excited state can be deduced by determining the H-atom angular intensity distribution with respect to the polarisation vector of the photolysis radiation. So far this technique has been limited to the low photon energies provided by conventional lasers. The higher energy radiation available from the VUV-FEL will enable the dissociation dynamics of higher-lying excited states to be studied. This experiment will take full advantage of the intensity, tunability and timing properties of the VUV-FEL.

3.2.1.2 Polarisation and symmetry studies

Electron-molecule (or electron-ion) interactions and the angular momentum transfer between the excited or ejected electron and the remaining molecular core can be probed via photoionisation. Such studies are of great value for understanding electronic structure in the asymptotic region and the coupling of electron-nuclear motions. A particularly powerful method for studying these phenomena is to use electron-ion recoil vector correlation techniques[6]. These permit fragment angular distributions (electrons and ions) to be recorded in

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[5] P A Cook, S R Langford, R N Dixon and M N R Ashfold, *J Chem Phys*, 114 (2001) 1672

[6] A Lafosse, M Lebech, J C Brenot, P M Guyon, O Jagutzki, L Spielberger, M Vervloet, J C Houver and D Dowek, *Phys Rev Lett*, 84 (2000) 5987

the molecular coordinate frame[7]. In essence, measuring such photoelectron distributions establishes in great detail the scattering amplitudes and phases of electron angular momentum which are sensitive probes of the potential and dynamics of the photoexcited species. 4GLS will contribute to these experiments which address vibronic-coupling in ionised systems giving new insights into non-adiabatic reaction paths and such topics as symmetry breaking in symmetric molecules. Such photoionisation phenomena are also a model and stimulus for the wider consideration of electron-molecule scattering processes and have far-reaching ramifications.

4GLS will significantly advance photoelectron-photoion correlation studies by providing radiation with selectable polarisation and with a pulse-to-pulse time structure suited to time-of-flight detection techniques. The ability to control the polarisation is important because it has been shown that a symmetry selection of the normally degenerate ionisation continua can be made by combining linearly polarised radiation with oriented molecules[8]. Many of the innovative techniques developed at synchrotron radiation facilities use time-of-flight methods for the high transmission detection of electrons and ions. Coincidence measurements require a gap of up to 10 microseconds between light pulses. This is impossible on any 3rd generation source but is ideally matched to the flexible time structure offered by 4GLS.

3.2.1.3 Molecular chirality and the homochirality of life

4GLS will allow experiments aimed at the investigation of the origins of homochirality of natural biological molecules. It is well established that terrestrial life utilises almost exclusively L-amino acids and D-sugars. Indeed homochirality may be a prerequisite for the origin of life, but its own origin remains unsettled. Abiotic theories assume that the homochirality and stereospecific molecular interactions characteristic of the current biosphere could not have originated without some initial asymmetric bias.[9] A persuasive postulate is that the initial asymmetry is found in the partial circular polarisation of incident radiation, perhaps atmospherically scattered sunlight, driving some form of selective photochemistry. In particular, the finding of an excess of L-amino acids in the Murchison meteorite[10,11] has led to the suggestion of an extra-terrestrial asymmetric bias.[12] There is thus strong speculation that the circularly polarised radiation found from neutron stars[13] or reflection nebula[14] may lead to enantiomeric excess in pre-biotic molecules in the interstellar medium, either in gas clouds or frozen on grain surfaces, which are subsequently transported to earth.

4GLS is ideal for studies simulating such environments, such as the protoplanetary disc which surrounded the forming Sun, because of the variable elliptical polarisation of its sources and their wide wavelength coverage, from the far IR to the XUV. These features allow investigation not just of enantiomer selection by photodissociation using UV radiation, but also the biasing of molecular energy level populations by lower energy photons, which may lead to enantiomer-selective chemistry.[15] These exo-biology investigations target not just

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[7] J H D Eland, M Takahashi and Y Hikosaka, *J Chem Soc Faraday Trans*, 115 (2000) 119
[8] P Downie and I Powis, *J Chem Phys*, 111 (1999) 4535
[9] W A Bonner, *Top Stereochem*., 18 (1988) 1
[10] M.H. Engel, *Nature*, 248 (1990) 47
[11] J R Cronin, *Science*, 275 (1997) 951
[12] W A Bonner, *Orig Life*, 21 (1991) 59
[13] E Rubinstein, *Nature*, 306 (1983) 118
[14] J Bailey *et al*., *Science*, 281 (1998) 672
[15] J M Greenberg *et al*., *J Biol Phys*, 20 (1994) 61

understanding of the observed bias to the left-handed enantiomers of life on Earth and life's origins but also the possibilities of life existing on other planets.

Novel forms of chiral discrimination are also emerging in studies of photoionization by circularly polarised light[16,17] and in the (formally related) area of polarised electron scattering (which is also dependent on circularly polarised photoionization sources).[18] A recent prediction, by workers at the University of Nottingham, of a pronounced (*ca.* 10%) circular dichroism in the angular distributions of photoelectrons (CDAD) emitted from randomly oriented, gas phase enantiomers of pre-biotic molecules[19] has been confirmed by preliminary results obtained for both valence[9,20] and core level ionization.[21] 4GLS provides high intensity CP light for furthering and extending these studies. For example, the IR-FEL may be used to prepare specific molecular vibrational levels, allowing more precise probing of the predicted structural sensitivity and of putative vibronic effects of the CDAD phenomenon. These experiments have very exacting requirements in terms of purity of polarisation, photon flux and pulse structure; only 4GLS will be able to satisfy all these experimental requirements simultaneously.

The magnitude of chiral molecule CDAD will, in general, be even further enhanced by any prior alignment or orientation of the molecules. 4GLS provides unique opportunities for the development of two-colour pump-probe CDAD experiments to exploit optical alignment effects in the gas phase, but which may also provide the selectivity and sensitivity required for chirally selective detection and analysis, for example in breath testing applications of interest in clinical and food sciences.[22] Orientation, and the consequent CDAD enhancement likely, may also result at interfaces, suggesting that chirally selective photoemission probes of both solid and liquid surfaces may be developed, the latter employing liquid microjet technology.[23] A range of applications for such interface probes can be ultimately envisaged, ranging from the identification of surface structure in chiral catalysts to chirally selective HPLC detection techniques.

3.2.1.4 Ion-molecule reactions

Charge transfer processes represent an important class of reactions in ion chemistry and, when such processes are exothermic, they usually constitute the dominant product channel following an ion-molecule interaction. The goal is to perform state-to-state ion-molecule reaction studies, wherein the reactant and product ion states are fully defined and translational energies are specified. No experimental measurement has yet approached this ultimate aim. The primary difficulty concerns the production of an intense source of state selected reactant ions. This will be overcome, in one of two ways, using the intense and tunable radiation provided by 4GLS. The state selected reactant ions can be produced either by using monochromatic synchrotron radiation to photoionise a parent molecule followed by energy analysis of the photoelectron, or, alternatively, through a resonant two-photon ionisation process via a Rydberg state[24]. As

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[16] J Paul and K Siegmann, *Chem Phys Lett*, 304 (1999) 23
[17] N Bowering *et al.*, *Phys Rev Lett*, 86 (2001) 1187
[18] M Musigmann *et al.*, *J Phys B*, 32 (1999) 4117
[19] I Powis, *J Phys Chem A*, 104 (2000) 878; I Powis, *J Chem Phys,* 112 (2000) 301
[20] L Nahon, I Powis *et al., Paper presented at* Soleil Workshop, LURE, Oct 2001
[21] E Rennie, I Powis, U Hergenhahn *et al.*, *Poster presented at* BESSY User Meeting, Dec 2001
[22] A J Taylor, *Crit Rev in Food Science and Nutrition*, 36 (1996) 765; H S Winter, *Paediatrics,* 16 (1987) 259
[23] M Faubel *et al.*, *J Chem Phys*, 106 (1997) 9013
[24] S L Anderson, *Adv Chem Phys*, 82 (1992) 177

the geometry of the Rydberg state is similar to that of the ion, the ions so produced have a very high degree of vibrational purity. Furthermore, the intense radiation available from the VUV-FEL will enable state selected ions to be produced from a precursor radical (*e.g.* CH^+ from CH). This will open up the possibility of studying reactions, such as $CH^+ + H_2 \rightarrow CH_2^+ + H$, which are important in astrochemistry. The product ion state will be determined by probing the ion with radiation from a conventional laser and using either laser induced dissociation or laser induced fluorescence. These experiments will examine the roles played by the various forms of reactant ion energy (electronic, vibrational or translational) on the reaction cross sections.

The Aurora Borealis over Alaska, an example of complex interactions between photons, electrons, ions and molecules

Such ion-molecule reaction data are essential for a proper modelling of atmospheric phenomena, and in the understanding of processes occurring in plasma etching which is vital to the semiconductor industry. Therefore, reactions involving nitrogen, oxygen, silicon or halogen atoms, either as the ion or the neutral, will constitute an important part of the studies carried out on 4GLS. The UK already has an established community[25] performing ion-molecule reaction experiments, and so is well placed to exploit the new opportunities offered in this area by 4GLS.

3.2.1.5 Multiply charged molecular ions

Molecular double and multiple ionisation is a largely unexplored field. Experiments carried out using either laboratory or synchrotron light sources have, hitherto, provided only a very limited view of highly ionised species[26]. This is because the loss of two or more electrons causes large changes in molecular structure, with the result that the most important stable molecular ion configurations lie far outside the accessible Franck-Condon zones.

It has been realised for some time that one viable route to the new species is a two-step process, where, for example, stable, state selected singly charged molecules are photoionised and the energy and angle of the ejected electron are analysed. In order to achieve this, however, the selected ions in a focussed beam must be photoionised using a light source many orders of magnitude brighter than those available at present. Furthermore, the most efficient use must be made of the available light and target density, and this is best done by electron

[25] P Calandra, C S S O'Connor and S D Price, *J Chem Phys,* 112 (2000) 10821;C Atterbury, R A Kennedy, C A Mayhew and R P Tuckett, *Phys Chem Chem Phys,* 3 (2001) 1949; S R Mackenzie and T P Softley, *J Chem Phys*, 101 (1994) 10609

[26] D B Thompson, G Dawber, N Gulley, M A MacDonald and G C King, *J Phys B,* 30 (1997) L147; B O Fisher, M K Thomas, P A Hatherly, K Codling, M Stankiewicz, A Karawajczyk and M Roper, *J Phys B* 32 (1999) 4437

time-of-flight techniques, which can be fully multiplexed in energy and angle and can achieve near 100% collection efficiency. The effective use of time-of-flight analysis requires a light source with short pulse length and long interpulse period. These are exactly the characteristics that are offered by the 4GLS source.

An example of one such experiment would be to compare the molecular fragmentation pattern due to the absorption of a single, high energy, photon with that resulting from a two photon (two colour) process, where the sum of the photon energies in the latter process equals that of the single photon. In the two colour process, one of the photons would be obtained from the VUV- or the XUV-FEL, and the other from an undulator. Studies of this kind would provide information on double excitation/ionisation phenomena and on the dissociation mechanisms, thus complementing investigations involving one-photon direct double ionisation, core ionisation leading to double ionisation *via* the Auger effect, and multiphoton ionisation using intense visible/IR lasers.

Chiral studies are also an important aspect of double ionisation; circular dichroism in double ionisation and molecular fragmentation is a sensitive probe of ionisation mechanisms[27]. In the case of simple targets, *e.g.* helium and molecular hydrogen, the chirality of the photon is transferred to the escaping particles. Preliminary experiments on 3rd generation sources are just beginning to demonstrate this, though they are limited by the synchrotron light pulse width. The high intensity of 4GLS and its ability to operate in "temporal" mode, combined with new kinds of particle detection methods that can detect over 4π steradians[28] (and can therefore be calibrated to give an absolute cross section) will provide a much more exacting test of developing theoretical methods. For more complex molecules, it will be essential also to vary the state of polarisation of the incident radiation, as will be possible on 4GLS. With the current state of fast timing electronics, with deadtimes of <50 ps, and further improvements expected, coincidence methods (which involve the detection of two correlated particles) will be ideally matched to the timing structure of 4GLS.

3.2.1.6 Detection of low molecular densities

Resonance-enhanced multiphoton ionisation (REMPI) techniques have proven to be highly sensitive for the detection of chemical reaction products in single collision experiments (10^6 molecules per quantum state per cm^3 typically). Unfortunately these techniques are highly restricted to molecules with a convenient intermediate state for the resonant enhancement. In some cases (*e.g.* OH, CN, H_2O, NH_3) only a 2+1 or a higher-order process is possible, which results in a much lower sensitivity and the need to focus lasers to produce sufficient intensity. (In general the ionisation step is saturated and therefore the transition probability is proportional to I^N for an N+1 photon process.) In cases where REMPI has proved to be particularly sensitive, *e.g.* NO, it is where there exists a convenient 1+1 process below 5 eV.

As virtually all neutral molecules have accessible Rydberg states in the 7-10 eV range and have ionisation energies below 20 eV, the VUV-FEL will allow highly sensitive, selective and universal detection of a very wide range of molecules without the complications (*e.g.*, dissociative ionisation or Stark broadening) that arise through the need to focus the laser in

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[27] C Dawson, S Cvejanovic, D P Seccombe, T J Reddish, F Maulbetsch, A Huetz, J Mazeau and A S Kheifets, *J Phys B,* 34 (2001) L525

[28] J Ullrich, R Moshammer, R Dorner, O Jagutzki, V Mergel, H Schmidt-Bocking and L Spielberger, *J Phys B*, 30 (1997) 2917

higher-order processes. The very high sensitivity achieved (approximately 10^3 molecules per cm^3) should be particularly valuable for product detection in reaction dynamics experiments, trace gas analysis or the detection of vibrationally excited molecules.

3.2.1.7 Inner-shell ionisation by multiphoton excitation

The ionisation of inner-shell electrons by multiphoton excitation is a novel possibility with an intense VUV source. In principle the excitation should be highly localised in large molecules and the subsequent fragmentation dynamics will be of considerable interest. An important physical question to explore will be how the localisation of the excitation is affected by intermediate resonance effects in the multiphoton process, compared to single photon excitation. In the sub-picosecond range the multiphoton ionisation of inner shell electrons should be ideally suited for studying the dynamical motion of individual atoms; there should be a "chemical shift" of the inner-shell electron ionisation potential that varies with nuclear geometry, and is directly measurable by multiphoton photoelectron spectroscopy.

3.2.1.8 Photon induced reactions in biomolecules

Photon induced reactions in biomolecules (*e.g.* DNA, proteins or carbohydrates) underpin all radiation chemistry. However, there is currently almost no mechanistic information on these effects. Given the low density of these biomolecular samples in the gas phase, and the limited lifetime of the sample, a high intensity VUV source will be required to examine the break-up of biological molecules upon irradiation. Very high resolution time-of-flight mass spectrometry is one technique that is being applied successfully to the study of such large molecules within a matrix[29]. Furthermore, recent progress has lead to the discovery of an organic matrix, from which the sample biomolecule can be ionised efficiently without extensive fragmentation. Thus, biomolecules can be studied using these time-of-flight techniques with the intense radiation provided by the VUV-FEL. Biomolecular sequencing for input to databases for bioinformatics is just one example of the type of work which will be performed.

3.2.1.9 *Radiation damage and repair*

Damage to the DNA of organisms, including humans, is a frequent and important fact of life. Such damage occurs many thousands of times a day as a result of radiation, pollutants and the oxidative products of metabolism. However, cells have evolved a variety of mechanisms to counter the damage caused by these agents. The most common of the repair mechanisms is nucleotide excision repair in which damaged segments of DNA are ‘cut out’ and replaced by repair replication. The repair processes work extremely well but occasionally replication errors occur and these can lead to the formation of aberrant proteins that can disrupt normal cell function leading to a variety of diseases including cancer. Paradoxically, DNA damage is also at the heart of radiation- and chemo- therapeutic methods to counter cancer.

The molecular damage induced by high-energy ionising radiation, with energies typically of the order of millions of eV is actually a result of a multitude of low energy events, in the range provided by the tunable 4GLS. It has recently been reported that one mechanism of DNA damage results from a resonant electron attachment state centred at about 11 eV[30]. Careful

[29] U Bahr, M Karas and F Hillenkamp, *J Anal Chem*, 348 (1994) 783
[30] Boudaffa *et al.*, *Science* 287 (2000) 1603; Prise *et al.*, *Int J Radiat Biol*, 76 (2000) 881

measurement of dose dependance confirms that double strand break generation occurs via a single absorbed photon event, and not by the proximity of two single strand breaks occurring on opposite strands. The tunability of the 4GLS in the UV range will allow action spectra of such damage to be measured, and kinetic experiments using short pulses will enable detection of intermediates, previously technically impossible. Such experiments will allow a more robust model of DNA damage to be proposed.

Exploitation of the VUV-FEL and XUV-FEL would enable micro volumes of radiation to be targetted on to individual living cells and cell nuclei across any required photon energy range with previously selected polarisation, combined with a time structure which should enable complete characterisation of the individual cells under study. These investigations will allow imaging techniques to be employed to follow biochemical processes within the cell. This approach will provide a better model to investigate *in vivo* radiation damage[31].

It is now becoming feasible to follow the molecular dynamics of protein interactions with DNA damage, their localisation within cells and the consequences of radiation damage. Using micro-focussed beams, it is possible to explore the dependence on photon energy of the movement of proteins in response to the radiation in terms of foci formation at damaged sites or the recruitment of proteins to form protein complexes based on FRET detection[32]. This approach will allow exploration of the cell signalling processes governing cell damage and repair, and inter cell interactions.

3.2.2 Conformational Dynamics in Biomolecules

3.2.2.1 *Structure and dynamics of proteins and biomacromolecules: fast processes of protein folding*

The question of how proteins fold to their unique and highly organised functional three-dimensional structure is one of the most challenging topics currently investigated in biological research; it has become even more important in the post-genomic era as many of the several hundred thousand proteins to be characterized will not be suitable for the standard techniques of x-ray crystallography and multi-dimensional NMR.

The exceptional sources on 4GLS will not only allow study of the three-dimensional structure of the final protein, but - even more significantly - they are extremely well suited for studying in detail *all* of the dynamic processes that occur on the way from the random conformation of the unfolded polypeptide to the final protein structure.

Generally, it is assumed that the initial rapid phase of protein folding, the collapse from the fully unfolded polypeptide to a more compact form, involves the formation of secondary structural elements like α-helices, β-sheets or β-turns, thus significantly narrowing the conformational space the protein has to explore in the search for the lowest free-energy state, the so-called “folding funnel” shown overleaf. Regions with secondary structure may even act as nucleation sites for further collapse to the final native state. Formation of secondary structural elements and other folding processes often occur within milliseconds, or faster, of the initiation of protein folding and though there are methods available to follow these fast

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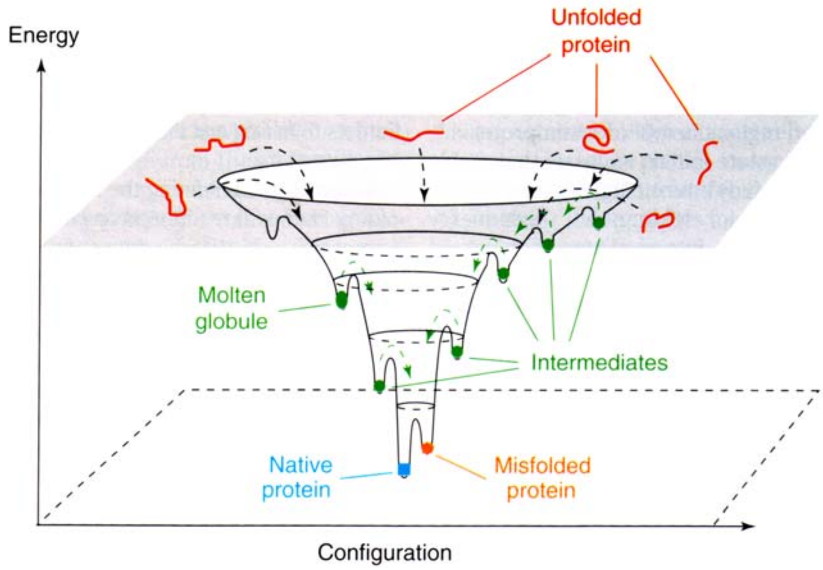
[31] *e.g.* Nelms *et al. Science*, 280 (1998) 590
[32] Llanos *et al. Nature Cell Biol*, 3 (2001) 445

processes[33] the information content of the measurements diminishes rapidly with the reduction in time scale. Specialised techniques have been developed for initiating and observing these fast processes of protein folding and secondary structure formation, and some first observations have been made[34]. From these investigations it was concluded that secondary structural changes can occur on the nanosecond time scale, thus showing the need to investigate protein folding on such short time scales.



The greatest handicap for extending standard protein folding experiments to these time scales is the requirement of starting the folding reaction on the time scale of interest. Several experimental approaches have been developed for this purpose[35]. Some of these trigger protein folding with a short light pulse, that is designed either to interact directly with the protein or to modify abruptly solvent conditions such as temperature or pH[36]. The ensuing protein folding process is then probed with optical techniques[37]. 4GLS with its capability of simultaneously providing well-synchronised powerful light pulses over a wide range of wavelengths will offer unique opportunities for performing such studies.

The UK currently enjoys a world-leading position in UV CD, through exploitation of the relatively high UV flux of the existing SRS. Although UV CD (220 nm) and resonance Raman (205 nm) measurements have been used for the determination of protein and peptide secondary structures and these have been extended to the sub-millisecond time-scale[38], the restricted wavelengths accessible mean that the observed spectral changes can rarely be related to changes in specific secondary structural components. This is because intensities at different wavelengths are biased by the different percentages of secondary structures and the individual amide absorption bands vary in sensitivity to a particular structural element. The high

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[33] S E Radford, *TIBS* 25 Dec., (2000) 611

[34] W A Eaton, P A Thompson, C K Chan, S J Hagen, J Hofrichter, *Structure* 4 (1996) 1133; R H Callender, R B Dyer, R Gilmanshin, W H Woodruff, *Annu Rev Phys Chem,* 49 (1998) 173; M Gruebele, *Ann Rev Phys Chem,* 50 (1999) 485

[35] D J Brockwell, D A Smith and S E Radford, *Current Opinion in Structural Biology,* 10 (2000) 16

[36] M Volk, *Eur J Org Chem,* (2001) 2605

[37] N Ferguson, C M Johnson, M Macias, H Oschkinat and A Fersht, *PNAS, 98* (2001) 13002; T J T Pinheiro, H Cheng, S H Seeholzer and H Roder, *J Mol Biol,* 303 (2000) 617

[38] S Akiyama, S Takahashi, K. Ishimori and I Morishima, *Nature Struct Biol,* 7 (2000) 514; I K Lednev, A S Karnoup, M C Sparrow and S A Asher, *J Am Chem Soc,* 121 (1999) 8074

brightness of the 4GLS UV sources will for the first time provide the opportunity to extend the accessible wavelength and time range of the standard UV CD technique to give full spectra at timescales pertinent to the dynamic process under investigation. Indeed, the flux from the 4GLS VUV-FEL is so high that in favourable cases 'one shot' CD experiments, where the experiment is accomplished using a single pulse (or a few pulses) of radiation may become possible.

4GLS will allow extension of the range of probing techniques available for the observation of fast processes of protein folding. The secondary structural content of a protein sample (and its variation with time) can be determined by a range of UV- or IR-spectroscopic techniques. IR spectroscopy is a particularly important technique for studying protein structure. The amide I band, in particular, is an established indicator of secondary structure because of its sensitivity to hydrogen bonding, dipole-dipole interactions, and the geometry of the peptide backbone. Seminal work on fast time-resolved infrared (TRIR) spectroscopic studies of protein folding from National Laboratories and elsewhere in the United States have demonstrated the enormous power of such experiments[39]. The application of TR^3 (time resolved resonance Raman spectroscopy) has been much more limited. Resonance Raman is complementary to IR, and the main features in the Raman spectra of proteins are the amide II and III bands. Recent work by Asher and co-workers has shown the potential of using a combination of temperature jump and UV-TR^3 to probe the kinetics of protein folding[40]. However, this work is hampered by factors such as the low beam intensity of benchtop UV lasers, and thus these experiments necessitate the use of high sample concentrations, which can be prohibitive for precious biological samples. The availability of tunable very high intensity ultraviolet laser beams with well-defined polarisation would alleviate this difficulty and facilitate many new Raman experiments, for example ultraviolet resonance versions of the chiral form of Raman spectroscopy (Raman optical activity, ROA)[41] and ultraviolet resonance Raman experiments. Selective probing of the structure and dynamics of the protein and nucleic acid components of intact viruses could be especially important. 4GLS will thus provide the opportunity to perform in parallel complementary UV-CD and IR- and Raman measurements. In the case of IR measurements, the high photon flux in the near-IR could be used to effect an efficient T-jump, and ultra-sensitive detection, such as the PIRATE system (see Appendix V), could be used to elucidate the spectral changes produced. This is a unique combination as the PIRATE system can easily monitor spectral changes in the ps – ms regime, thus monitoring the complete protein folding reaction. The battery of techniques that would be enabled by 4GLS raises the promise of major advances on the protein folding problem.

The intensity profile of the new sources will not only improve resolution in the time domain, but also will allow measurements to be made well into the deep-UV. Theoretical work on the electronic structure of amides and proteins suggests that there is a wealth of information to be gleaned from this higher-energy region of the spectrum[42]. Work on aqueous samples is always difficult because of the absorption of water in the region of 160 nm, but the high brilliance of 4GLS presents the best opportunity to overcome pathlength problems.

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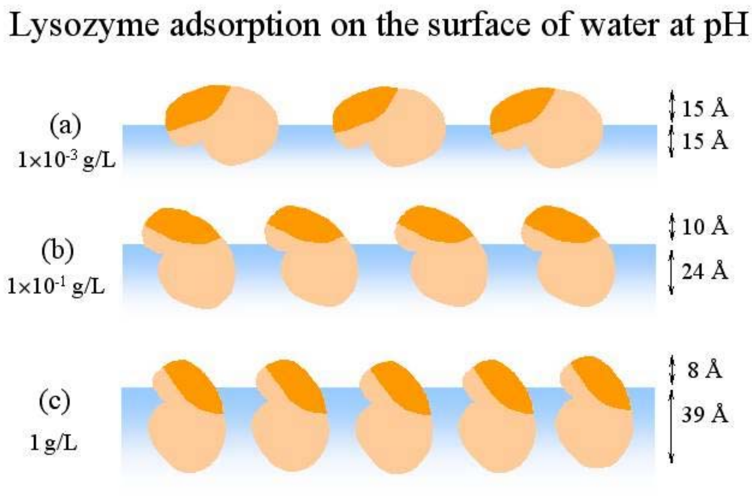
[39] R B Dyer, F Gai, W H Woodruff, R Gilmanshin and R H Callender, *Acc Chem Res,* 31 (1998) 709; and other articles in the same issue.

[40] I K Lednev, A S Karnoup, M C Sparrow and A A Asher, *J Am Chem Soc*, 121 (1999) 4076

[41] L Barron, Glasgow University, personal communication.

[42] N A Besley and J D Hirst, *J Phys Chem A,* 102 (1998) 10791; N A Besley and J D Hirst, *J Am Chem Soc,* 121 (1999) 9636

Considerable effort[43] has been focussed on developing the theoretical framework needed to interpret such experiments fully and on improving calculations of the circular dichroism and infrared spectra of proteins from first principles in order to understand the subtle relationship between conformation and spectra. In addition, work is underway to couple such calculations to all-atom simulations of protein dynamics and folding. Molecular dynamics simulations on proteins now routinely reach the multi-nanosecond to microsecond timescales[44] - precisely the timescales that could be accessed by experiments utilising 4GLS technology.



There are a number of possibilities for extension of spectroscopic studies of proteins and other biomolecules into new regimes with 4GLS. One example is Fourier-Transform Sum-Frequency Generation (SFG), an objective of which would be the characterisation of membrane-bound proteins in supported lipid bilayers and more generally, the study of biomolecular behaviour at interfaces, as exemplified by the lysozyme/water system[45] above. Different secondary structures will have characteristic vibrational signatures and the polarisation dependence of the spectra will contain information on the orientation of the vibrational chromophore. With 4GLS, it may even be possible to detect individual amino acids in small proteins and to determine their environment and orientation. This difficult objective would be assisted by doubly resonant SFG utilising the tunability of the UV-FEL.

3.2.3 *Electron Dynamics*

3.2.3.1 *Fast electron and energy transfer in biosystems*

The interaction of light with living organisms associated with biological energy conversion has been a rapidly moving field of research. The very high efficiency of these systems suggests that their study will provide a model for future commercial developments. During the last five years, the molecular stuctures of some of the most important photosynthetic pigment-protein

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[43] J D Hirst, Nottingham University, personal communication.
[44] Y Duan and P A Kollman, *Science*, 282 (1998) 740
[45] *J Chem Soc, Faraday Trans,* 94 (1998) 3279

complexes have been determined; photosystem 1[46], photosystem 2[47], higher plant light harvesting complexes[48] and the bacterial light harvesting complexes[49]. The first photosynthetic reaction centre structural determination was that of photosynthetic bacteria, in 1984[50]. The structural information provided a springboard for the interpretation of kinetic data and stimulated extensive fast kinetic experiments. It is therefore extremely timely to propose similar experiments on the higher plant pigment-protein complexes. The proposed pulse length options and tunability of 4GLS will render it an ideal facility to probe energy transfer and fast electron transfer in these complexes. For example, energy equilibration in the light harvesting pigments of photosystem 1 is complete in 4 ps, and the primary electron transfer occurs in 2 ps. Knowledge of the structure of the pigment-protein complexes will allow site-directed mutagenesis experiments to explore the function of the protein in relation to the efficiency of energy and electron transfer. Time-resolved infrared and Raman spectroscopy has been widely used to probe electron transfer and isomerisation in biological processes. Of particular interest with 4GLS will be the opportunity to exploit ultrafast infrared excitation to probe low energy bands in reaction centre complexes. In light harvesting complexes, the priority is to uncover the mechanism by which the dynamics of carotenoid-chlorophyll associations are able to control the partitioning of energy absorbed in the light harvesting complexes between transfer to the photosynthetic reaction centres and dissipation of energy as heat.

Carotenoids are not only of importance in photosynthesis, but are essential for vision and a significant pigment component in human diet. There is some contradictory evidence[51] on the beneficial and deleterious effects of carotenoids within the diet which may relate to interactions with different cellular components. The excited states of carotenoids are extremely short lived in organic solvents, but no information is available in near *in vivo* environments. Using the sub picosecond double pulse facility of 4GLS the complex photochemistry of the carotenoids in unilamellar liposomes, cell cultures and skin samples could be investigated.

4GLS will enable the extension of investigations on intact cell systems pioneered using other techniques. For example, recent inelastic incoherent neutron scattering (IINS) measurements at <20 K coupled with IR measurements at room temperature have identified a population of water molecules interacting with biomolecules and biomembranes, with characteristic changes in the vibrational (70-100 meV) and O-H stretch (400-450 meV) regions[52]. The IR-FEL facility would be used to study these regions utilising the very high intensity to probe complex samples (cells and tissues) not usually amenable to conventional IR spectrometers. Combined with molecular dynamics simulations and the IINS measurements, the data should lead to valuable insights on the structure and dynamics of interfacial water in cells. It is estimated that this takes up a large fraction of the volume of the cellular water, and thus has implications for transport through membranes and enzyme mechanisms.

The opportunity to image intact cells will enable protein complexes already characterised to be measured *in vivo*. Such measurements include, for example the photosynthetic pigment protein complexes described above, which can be measured in intact leaves still attached to the

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[46] Schubert *et al., Nature Struct Biol*, 3 (1997) 965
[47] Zouri *et al., Nature*, 409 (2001) 739
[48] Karasch *et al., EMBO* 14 (1995) 631
[49] McDermott *et al.*, *Nature* 374 (1995) 517
[50] Deisenhofer *et al.*, *Nature* 318 (1985) 618; Deisenhofer *et al., J Mol Biol*, 246 (1995) 429
[51] Lowe *et al.*, *Free Rad Res* 30 (1999) 141
[52] S V Ruffle *et al., J Amer Chem Soc*, in press.

plant[53]. This enables the effects of various environmental parameters to be measured *in vivo.* The intensity, tunability and time resolution of 4GLS would allow more than one parameter to be measured in such systems simultaneously. Thus studies on photomorphogenesis would be facilitated by the ability to excite phytochrome and cryptochrome and their intermediates, as well as chlorophyll in intact cells.

3.2.3.2 Pump-probe measurements of electron-hole pair dynamics in microdevices

The feature size on VLSI chips has reduced logarithmically over the past three decades, to the extent where the decreased size and increased speed of microdevices now pose challenges to our fundamental understanding of the dynamics of electron transport. The process of miniaturisation is set to continue and the current ASTM "Road-Map" for technology development leads us now into a regime where the whole device structure can be thinner than the typical semiconductor space charge layer. Thus such devices are typically operating in a transient, nonequilibrium regime. Fast time-resolved studies of electron-hole pair dynamics in semiconductor junctions are therefore now of critical importance to the semiconductor industry.

The 4GLS VUV-FEL in combination with undulator or other radiation offers unparalleled opportunities for 'pump-probe' experiments, where electron-hole pairs are created by a FEL pulse, and the result (*e.g.* on the surface photovoltage measured in photoemission) is measured using a naturally synchronised pulse from an undulator. Such experiments were pioneered at the Super-ACO FEL in 1997[54], and attracted widespread international attention. In experiments on Si and Si/SiO_2 interfaces, these experiments provided a *direct* measure of band bending variations related to surface carrier dynamics in the transient regime. This was achieved by measuring the surface photovoltage effect in Si 2p photoemission, using undulator pulses synchronised with the FEL radiation. In many cases, the results obtained were contrary to those expected on the basis of the 'static regime' analysis – for example the observation that in the case of n-type Si coated with a thin (approx 12 Å) layer of SiO_2, electrons accumulate at the surface of the outer oxide layer on a very fast (sub – 0.2 ns) timescale. The huge importance of these experiments to semiconductor technology becomes apparent when we realise that the leakage current through a Si/SiO_2 gate oxide changes by as much as 6-7 orders of magnitude as the thickness of the oxide layer changes from 10 Å to 18 Å[55], precisely the range probed in these experiments, and that these thicknesses also represent the current technological limit for these gates.

This work demonstrated the feasibility of these challenging pump-probe experiments, and also their power when applied to semiconductor heterostructures. The experiments were, however, limited to wavelengths below 350 nm (energies below 3.5 eV; this is for example less than the valence band offset in Si/SiO_2), and used a pulse length from the FEL of 60 ps and from the undulator of 500 ps. The accessible time window, determined by the width of the undulator pulse, and the separation between the storage ring pulses, was around 0.2 ns – 120 ns. The 4GLS VUV-FEL will open up completely new vistas for these experiments, both in terms of

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[53] Kshirsager *et al.*, *New Phytologist*, 151 (2001) 451
[54] M Marsi, M E Couprie, L Nahon, D Garzella, T Hara, R Bakker, M Billardon, A Deloulbe, G Indlekofer and A Taleb-Ibrahimi, *Appl Phys Lett*, 70 (1997) 895; M Marsi, M E Couprie, L Nahon, D Garzella, T Hara, R Bakker, M Billardon, A Deloulbe, G Indlekofer and A Taleb-Ibrahimi, *J Electron Spectrosc Relat Phenom*, 94 (1998) 149; M Marsi, R Belkhou, C Grupp, G Panaccione, A Taleb-Ibrahimi, L Nahon, D Garzella, D Nutarelli, E Renault, R Roux, M E Couprie and M Billardon, *Phys Rev B,* 61 (2000) R5070
[55] D A Muller, *et al., Nature*, 399 (1999) 758

time resolution and energy range. The VUV-FEL (visible - 10 eV) allows us to access wavelengths sufficiently short to study all semiconductors (including GaN and other large band gap semiconductors used as photodetectors), and indeed insulators – of particular importance here are nanocrystalline oxides such as anatase TiO_2, used as part of the pn junction in dye-sensitised photovoltaic cells and photocatalysts. In combination with the IR-FEL, it will allow the selective filling of states within the bandgap of all semiconductors of technological interest, and spectroscopy of the photoexcited states, enabling us to understand the role of individual electronic levels in the recombination processes and charge carrier dynamics. The much shorter pulses from both the 4GLS FEL and the ERL undulators, both around 0.5 ps, allow access to time domains in the sub-ps regime. Many interesting effects occur in semiconductor interfaces and devices on these timescales – for example the surface accumulation on SiO_2 referred to above could not be probed directly because it occurred on a timescale faster than the 0.2 ns resolution of the Super-ACO experiment.

In addition to the tunability of the pump radiation, allowing resonant excitation, the availability of undulator radiation optimised up to 100 eV and its harmonics will allow us to resonantly probe specific components of complicated device structures. Examples might be the pn junctions in oxide photovoltaic cells, where low-lying resonances of the n-type oxide (TiO_2, Ti 3p), the sensitising dye (Ru-bipyridyl, Ru 4p) or the p-type electrode (CuI, Cu 3p) may be accessed, photovoltaics based on nanocrystalline (Si 2p), where the variation in exciton lifetime may be measured as a function of nanoparticle size (band gap) and passivation, or 'core-shell' semiconductor quantum dots, such as those based on CdSe/CdS (Se 3d, S 2p). The resonant pump-probe approach would be particularly powerful in combination with scanning PEEM (photoelectron emission microscopy)[56], opening up opportunities for the study of pulsed laser treatment and etching of semiconductor interfaces/devices in a highly spatially and laterally resolved way, or for the creation and study of the role of defects such as F-centres (induced by the VUV-FEL) in oxide surfaces, and their influence on catalytic reactivity.

4GLS thus offers unique opportunities to study the role of individual electronic levels on non-equilibrium electron-hole pair dynamics in technologically important device structures.

3.2.3.3 *Spin dynamics of excitons in semiconductors*

The tunable, intense, infrared radiation from the 4GLS IR-FEL particularly in the THz regime will enable measurements aimed at probing and manipulating the quantum states of electrons in semiconductor heterostructures and quantum dots. These experiments will exploit the complementarity between the 4GLS and table-top sources in combined pump-probe experiments[57].

Recently the rich variety of phenomena revealed when atoms are subjected to extremely intense THz electric fields has excited considerable interest. The strength of such effects is usually expressed by the ratio of the ponderomotive potential due to the AC field and its frequency, *i.e.* proportional to intensity times the cube of the wavelength[58]. The IR-FEL with its extremely high peak powers (around 10^6 x conventional sources) at very long wavelengths thus provides a unique opportunity to study the effects of these fields on excitons in semiconductor quantum wells. The simplest experiment is the observation of NIR (near

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[56] A J Nelson, M Danailov, L Gregoratti, M Marsi and M Kiskinova, *J Appl Phys*, 87 (2000) 3520; R J Phaneuf, H-C Kan, M Marsi, L Gregoratti, S Günther and M Kiskinova, *J Appl Phys*, 88 (2000) 863
[57] B N Murdin *et al., Phys Rev B,* 62 (2000) R7755; B N Murdin *et al., Phys Rev B* 55 (1997) 5171
[58] K B Nordstrom *et al., Phys Rev Lett,* 81 (1998) 457

infrared) sidebands and FIR (far infrared) harmonics in the response of excitons created in such a field[59]. The reflected NIR at, and in the vicinity of, the exciton shows modulations in its spectrum which are strongly dependent on the intensity and wavelength and which are characteristic of the dynamical Franz-Keldysh effect (DFKE). These effects are strongest if the excitons may be created with a fs pulse from a Ti:sapphire laser, which is simply dispersed with a monochromator after reflection from the sample. Furthermore, harmonics up to ~10 of the driving field are expected to be observed in emission (and may be distinguished from harmonics from the FEL because of their enhancement when the NIR is on). The dynamic nature of these effects may be observed by measurement as a function of the phase of the FIR at the time when the fs pulse arrives. The variable elliptical polarisation of the radiation from the IR-FEL will allow the effect of the circular/linear polarisation state of the light to be explored, as the expected behaviour is very polarisation dependent. In the case of circular polarisation the electron and hole spiral away from each other after excitation and do not give rise to optical polarisation again. When a magnetic field is applied, the DFKE with circular polarisation may be recovered and even resonantly enhanced. The results will yield new insight into the driven motion of charges on very short timescales.

There has been considerable interest recently in spin relaxation in quantum wells, control of which may lead to so called "spintronic" memories and switches. Most experiments have used interband excitations[60], but a circularly polarised FIR FEL will allow direct study of the systems of interest technologically, namely doped (monopolar) systems. Pump-probe methods will be used to measure spin lifetimes[61]: a circularly polarised, resonant spin-flip pump pulse creates spin polarised electrons, and a linearly polarised probe, delayed in time, experiences a rotation or birefringence which depends upon the strength of the polarisation remaining. The experiments will be conducted in a variety of doped and un-doped, bulk and quantum well structures, and will give very important parameters required for the development of memory devices.

3.2.3.4 Coherent manipulation of Qubits in THz fields

The strong THz field of the IR-FEL also offers opportunities for the coherent manipulation of semiconductor-based quantum bits (Qubits). Qubits are the fundamental building blocks of quantum information processors, such as quantum computers. Several research groups worldwide are investigating the possibility of coherent manipulation of localised semiconductor electronic states such as impurity or quantum dot states using THz radiation. The aim is to induce Rabi oscillations between two states coupled by an intense THz field (*e.g.* by the use of microcavities). The Qubit can then arbitrarily be set to any desired superposition of its two states. The high THz intensity and wide tuning range of the IR-FEL are ideal for the study of this effect. An initial demonstration has been reported this year from the UCSB FEL[62].

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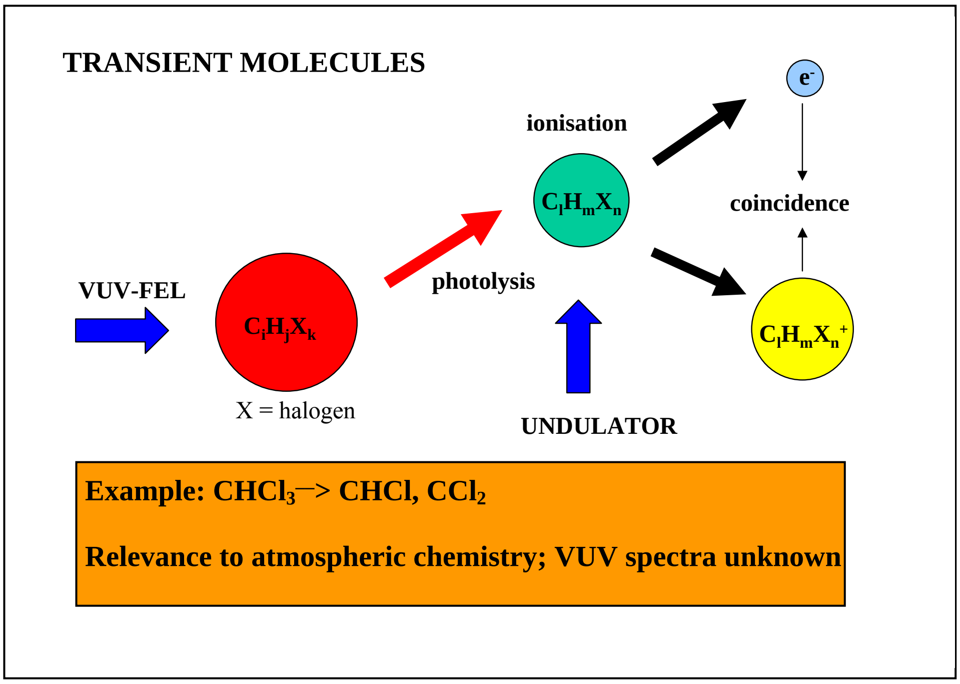
[59] S Hughes and D S Citrin, *Phys Rev Lett,* 84 (2000) 4228; J. Kono *et al. Phys Rev Lett,* 79 (1997) 1758
[60] D D Kikkawa *et al. Science,* 277 (1997) 1284
[61] B N Murdin *et al., Phys Rev B,* 59 (1999) R7817
[62] M Sherwin *et al.*, *Nature*, 410 (2001) 60

3.2.4 *Transients, Short-lived Species and Excited States*

3.2.4.1 Spectroscopy of free radicals and ions found in the Earth's atmosphere

Short-lived, or transient, molecules (such as electronically excited O_2 $a^1\Delta_g$, O_3, and ClO) are important constituents of the Earth's atmosphere and, along with unsaturated hydrocarbons, play an important role in both the generation and removal of pollutants. These transient molecules are all highly reactive. However, despite the importance of these molecules, little is known of their photoionisation spectra. The bulk of the measurements have been taken using single wavelength laboratory light sources[63], with synchrotron radiation recently beginning to make a contribution[64]. Such transient molecules are usually made by either RF discharge or chemical reaction. The result, in either case, is a mixture of species, all of which contribute to the photoelectron spectrum.



The relative photoionisation cross section is usually obtained by using an electron spectrometer in Constant Ionic State (CIS) mode where the analysis energy is set to a particular vibrational level of the molecule and then scanned synchronously with the incoming photon energy. This method is viable only if the vibrational band of the molecule of interest is well separated from those of the other molecules present.

The availability of intense radiation from the VUV-FEL synchronised with VUV undulator radiation from 4GLS will transform this situation. The experiment is shown in outline in the figure above.

A generic example of a chlorohydrocarbon is shown, from which a transient molecule (for example CHCl, $CHCl_2$) is produced by using the VUV-FEL, tuned to the energy of a specific transition in the parent molecule. The transient species is then probed using VUV radiation

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[63] J M Dyke, A Morris and N Jonathan *Int Rev Phys Chem*, 2 (1982) 3
[64] J B West, J M Dyke, A Morris, T G Wright and S D Gamblin, *J Phys B: At Mol Opt Phys*, 32 (1999) 2763

from an undulator, using electron spectroscopy to make CIS measurements. Coincidence experiments will be able to make use of the fact that the VUV radiation from the undulator is also pulsed, on a time scale of ps or shorter, lending itself to the use of highly efficient time-of-flight methods to detect ions and electrons.

Since both the VUV-FEL and the undulator are easily synchronised to one another it will be straightforward to vary the interval between the photolysis and probe pulses on at least a picosecond timescale, giving further selectivity in the analysis. It should also be possible to determine the evolution of the fragmentation process, in effect by means of time resolved electron and mass spectrometry.

3.2.4.2 Interaction of free radicals with proteins and membranes

Time-resolved resonance Raman spectroscopy (TR^3) using bench top lasers has proved highly suitable in the investigation of transient free radicals and their effect on proteins and membranes[65]. The technique gives detailed information on structure and bonding and is particularly well-suited for studies in aqueous environments. The picosecond time resolution of the proposed VUV-FEL of 4GLS will allow pump-probe investigations of excited states and free radicals using TR^3 spectroscopy. The availability of deep UV/VUV excitation brings into scope structural studies of hitherto unattainable species, such as aliphatic free radicals, which do not absorb significantly in the region more generally accessible by femtosecond lasers, whilst simultaneously having the general advantages of reduced contamination by molecular fluorescence and the more intense Raman scattering of short wavelength photons. The picosecond UV/VUV technique could also be used for structural and kinetic studies of excited states of photosensing pigments, of small organic and inorganic free radicals and of intermediate states in protein-radical enzymes. Of particular interest are studies of free radicals related to health and disease, including antioxidants, drugs and unstable species participating in enzymic and signalling pathways. There are also current applications of the technique to studies of electron conduction in polymers and charge separation in molecular donor-acceptor systems.

3.2.4.3 Spectroscopy of radioactive species

The proton cyclotron, which is part of the CASIM project intended for the study of exotic nuclei, will also be a source of species which, to date, have not been available for photoionisation studies. The high intensity of the VUV-FEL radiation, compensating for the very low density of the nuclei, will enable spectroscopic measurements on radioactive species and non-naturally occurring isotopes generated by the proton cyclotron. One important area for study at SIRIUS is the hot CNO cycles thought to occur at the surfaces of white dwarf stars. Almost all of the reactions constituting these cycles remain to be measured, since they involve short-lived radioactive species. A typical example is the $^{14}O(\alpha,p)^{17}F$ reaction, which plays an important role in determining the astrophysical conditions necessary for breakout from the hot CNO cycles into the rapid proton process. Such species may be produced at SIRIUS, and the reaction products identified by spectroscopic measurements using the VUV-FEL on 4GLS.

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[65] A W Parker and R H Bisby, *J Chem Soc, Faraday Trans,* 89 (1993) 2873; R H Bisby, S A Johnson, A W Parker and S M Tavender, *J Chem Soc, Faraday Trans*, 94 (1998) 2069; R H Bisby, S A Johnson and A W Parker, *J Phys Chem*, 104 (2000) 5832

3.2.4.4 Spectroscopy of highly charged ions

Plasmas are an intriguing state of matter; fundamental questions of how they are formed and remain stable have yet to be answered and hence the experimental study of the interaction of ions with photons is of great importance. From a more fundamental perspective, data pertaining to isoelectronic or isonuclear sequences are valuable for determining trends along such sequences, and for testing the understanding of the basic atomic physics of the photoionisation process. To date experimental studies in this area have been severely constrained due to the difficulties associated with producing sufficient quantities of ions.

An excellent opportunity to overcome this limitation arises by using the 10 MeV electrons which have been decelerated through the superconducting energy-recovery linac of 4GLS. With a beam current in the range of 5 - 100 mA these electrons could be used in an electron beam ion trap (EBIT)[66]. The characteristics seem ideal, since the beam cross section is small (30 μm x 30 μm) and a set of superconducting Helmholtz coils between the linac and the collector could provide an impressive EBIT with two orders of magnitude greater energy than any existing device.

The EBIT could be used to make highly charged ions, which would be available for independent studies or for use with photons with 4GLS. The addition of an EBIT to 4GLS would open up the possibility for additional scientific possibilities. For example, the ionisation cross sections of highly stripped ions, such as U^{91+}, could be determined in order to test quantum electrodynamics and quantum chromodynamics.

3.2.4.5 Fundamental measurements in astrophysics

Absorption processes in the intergalactic medium

Spectroscopy has played and will continue to play the key role in our understanding of the universe. Until the 1970s, observations at UV and x-ray wavelengths, which require platforms above the atmosphere, were non-existent. In recent years, a number of space missions, with significant spectroscopic capabilities, have been launched. These include SOHO, used to probe the solar corona, and XMM-Newton and Chandra, which study x-ray emission from a variety of environments.

These missions are revolutionising our view of the universe, particularly through the study of ionised gas in regions as diverse as stellar coronae, massive star evolution, planetary nebulae, cooling flows in galaxies, active galactic nuclei, and the accretion disks around black holes. These new observational results need to be interpreted with theoretical models which incorporate the most accurate data in order to determine important astrophysical parameters such as elemental abundances, excitation conditions, ionisation fraction, dynamics, and so on. Although collisional ionisation can be important, most ionisation is driven by photons, so that there is a need for photoionisation cross sections. The UK has world-leading research groups in solar and x-ray astronomy who will benefit greatly from the spectroscopic capabilities of 4GLS.

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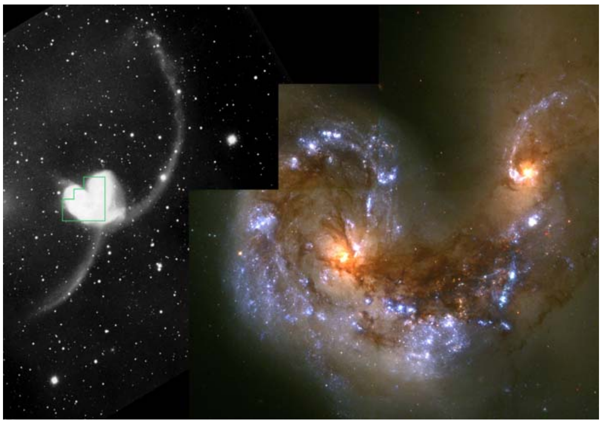
[66] M A Levine, R E Marrs, J N Bardsley, P Beiersdorfer, C L Bennett, M H Chen, T Cowan, D Dietrich, J R Henderson, D A Knapp, B M Penetrante, M B Schneider, and J H Scofield, *Nucl Instrum and Methods* B43, (1989) 347; R E Marrs, P Beiersdorfer and D Schneider, *Physics Today*, (October 1994) 27; http://www.fi.uib.no/Fysisk/Teori/KURS/EBIT/



Left panel: A ground-based telescopic view of 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: An Hubble Space Telescope image of the 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.

This natural-color image is a composite of four separately filtered images taken with the Wide Field Planetary Camera 2 (WFPC2), on January 20, 1996. Resolution is 15 light-years per pixel (picture element). Credit: Brad Whitmore (STScI), and NASA

There is currently a considerable amount of experimental information on the spectroscopy of atoms and ions, but very few data exist on their photoionisation cross sections, and none at all for charge states above doubly charged. Such data are crucial to accurate modelling of stellar atmospheres, where multiple absorption and emission takes place, and to account for absorption processes which take place over the huge distances of the intergalactic medium. For this reason major computational projects such as the solar OPACITY project[67] and the IRON project[68] have been undertaken to calculate both structure and ionisation cross sections.

The first measurements of the photoelectron cross sections of singly charged ions were made by Peart, Dolder and their colleagues[69] at the Daresbury SRS over 15 years ago using the merged beam method. With the advent of 3rd generation sources this field has become very active worldwide[70]. However, absolute measurements for multiply charged ions are at the limit of the capabilities of even the present day 3rd generation sources, primarily because of the low ion beam densities. Yet these are precisely the measurements that are required for astrophysical purposes, and where the very high photon flux from a fourth generation light source will be needed. The photon energy range covered by a 4GLS undulator is ideally suited because it is in this region that strong inter-electron correlation effects occur for the lighter ions of astrophysical interest, and it is in this region that theoretical calculations fail most often. A typical example is the 2p ionisation spectrum of Mg^+, where strong configuration interactions exist between the 2p - ns and 2p - nd series and several theoretical calculations have been made to account for them. Only with the help of absolute measurements[71], where it was possible to provide reliable relative intensities and oscillator strengths, has it been possible to identify the structure unambiguously and develop an appropriate theoretical description. The long term aim is to make absolute measurements on isoelectronic sequences (*e.g.* Na and Ar), thereby following the evolution of the structure and determining the distribution of oscillator strength, in order to test current calculations and provide guidance for future theoretical development. 4GLS will be needed for any further progress in this respect.

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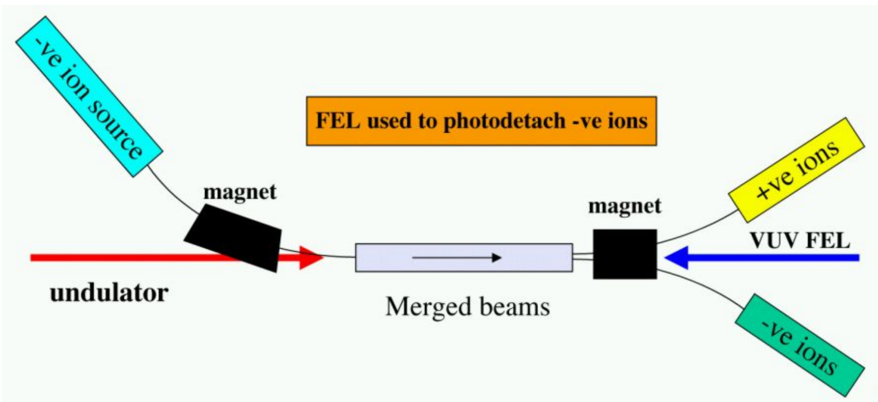
[67] M J Seaton, *J Phys B, At Mol Phys,* 20 (1987) 6409
[68] S N Nahar and A K Pradhan, *Phys Rev* A, 49 (1994) 1816
[69] I C Lyon, B Peart, J B West and K Dolder *J Phys B: At Mol Phys* 19 (1986) 4137
[70] J B West *J Phys B: At Mol Opt Phys* 34 (2001) R45
[71] H Kjeldsen, J B West, F Folkmann, H Knudsen, and T Andersen *J Phys B: At Mol Opt Phys*, 33 (2000) 1403

Negative ions and neutral species

There is considerable theoretical interest in negative ions, but due to the low intensity of ion sources, the experimental problems are severe even with present day synchrotron radiation sources. The majority of the existing data comes from the use of lasers in photodetachment experiments, where the energies required are low. The high intensity of the 4GLS source provides a means to measure and probe these negative ions and will allow a major advancement in this area. In addition the negative ions can also be used in the novel application outlined below.

In the universe, the vast majority of matter is in ionic or atomic form. However, apart from the rare gases and a few easily vapourisable metal atoms, there are almost no data on the photoelectron cross sections of neutral atoms. Such data are urgently required both for astrophysical purposes and as the fundamental basis for comparison with theoretical calculations. Furthermore, such experiments are an integral part of the study of isoelectronic sequences. 4GLS has the potential to contribute results in this field in a unique way. Neutral species could be prepared by utilising the VUV-FEL to photodetach electrons from a negative ion beam, leaving a beam of neutral atoms available for a merged beam experiment. This beam would be combined with undulator radiation and neutral atom cross sections measured. A possible experimental layout is shown below

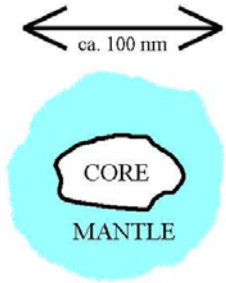


In this setup, the beam density is measured using the negative ion detector, then the VUV-FEL radiation is used to photodetach the outer electron, ensuring that the photon energy is low enough to avoid doubly ionising the ion. The photons from the undulator would then be used to ionise the atoms. The timing between the laser and undulator pulses would be adjusted to optimise the overlap between the atoms and the undulator light pulse.

Photon-induced chemistry and physics of ultracold ices

The interaction of molecules with ultracold solid surfaces plays a crucial role in controlling the chemistry of the interstellar medium and even in stellar evolution. Little, however, is known in detail of the physics and chemistry that occurs under such conditions. 4GLS will provide new and fundamental data on surface processes that occur on dust grains in the interstellar medium and on planetary surfaces. These data are essential if we are to develop our understanding of the fundamental astrophysics of star formation. Additionally, the data will provide insight into the fundamental astrochemistry that leads to molecular synthesis in the interstellar medium and which characterises the surface composition and structure of many of the planetary bodies in our own solar system.

In denser regions of interstellar medium (ISM), the timescale for thermal gas/dust interactions becomes comparable to other important timescales (those of dynamics, chemistry, ambipolar diffusion, *etc.*). Hence it is increasingly accepted that such interactions play a crucial role in the formation of the complex molecular systems that are observed in the ISM. However, detailed laboratory studies of gas-grain interactions have only commenced in recent years. These experiments have, to date, focussed on relatively simple processes involving neutral atomic and molecular species[72], such as the interaction of CO with water, ammonia and methanol ices. However, cationic species (which may be created by photon irradiation) are known to play a key role in the chemistry of the interstellar medium and so it is inevitable that they too will interact with grains. Such ion-surface interactions are themselves likely to be equally as important in the chemistry of the interstellar medium as their gas phase analogues. Such ion-surface interactions have also recently been implicated in molecular synthesis (including the formation of ozone) on the surface of the ice-covered moons of Jupiter, where ionic bombardment of their icy surfaces may result from their orbits entering the magnetosphere of Jupiter. This in turn may lead to observable changes in the planetary albedo. This hypothesis is yet to be experimentally tested.



A schematic diagram of a dust grain in the interstellar medium. The core of the particle is surrounded by an icy mantle.

The synergistic combination of light sources of appropriate wavelength coverage and intensity that will be offered at 4GLS provides a unique environment at which to pursue the investigation of these crucial ion-surface interactions. Such measurements will be new, and inherently of fundamental importance to our understanding of the chemical evolution of the interstellar medium and planetary surfaces. The questions to be addressed are numerous. What are the physical and chemical processes that occur on and in ultracold molecular ices during photon irradiation in the sub-300 nm region? How important are such processes in generating new chemical species in the solid and gas phase? What are these species? The experiments proposed will focus on a range of processes relevant to understanding the interaction of low energy (< 20 eV) ions commonly found in the interstellar medium (H^+, He^+, OH^+, CO^+, CH_3^+) with the surfaces of (a) interstellar grain mimics at low temperatures (around 10 K) and (b) mimics of planetary surfaces at their appropriate temperature (10 to 100 K). Two types of experiment may be envisaged using the 4GLS facility.

In the first class of experiments, the 4GLS sources will used as a probe of processes involving ions incident on a mimic surface from the gas phase. These will use a simple source of low energy ions incident on the surfaces, with the results monitored by temperature-programmed

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[72] H J Fraser, M P Collings, M R S McCoustra and D A Williams, *Mon Notes Roy Astron Soc*, 327 (2001) 1165

desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). The 4GLS light sources have several characteristics that make them ideal tools for use in these studies. The bending magnets can easily be optimised to provide a bright source of IR for RAIRS for investigation of the adsorbed species (charged or otherwise) and the intense VUV/XUV radiation available from an undulator is ideal for photoionisation detection of scattered neutral molecules in the gas phase by time-of-flight mass spectrometry (TOFMS).

In the second class of experiments, the 4GLS sources will be used to produce ions in well-defined environments on and in mimic materials, and their subsequent physical and chemical interactions with their surroundings will be probed. While the gas phase is naturally a source of ions in the interstellar medium, ion production on and in grains by interaction with UV radiation and cosmic rays is also possible. Such ionisation events in and on grains may well be responsible for their charging and hence crucial to understanding the magnetic support of clouds. These events may, in addition, be accompanied by other physical and chemical processes associated with the relaxation of the perturbed mimic matrix, *e.g.* desorption and reaction. Intense radiation in the region up to 10 eV (*ca.* 120 nm) from the VUV-FEL will be utilised to produce the ions and will permit measurements of net ion yield by TOF electron spectroscopy as a function of photon energy across this key energy regime. The chemical nature of the surface and bulk photoions themselves and their subsequent chemical interactions will be investigated by RAIRS. The polarisation properties of the radiation from the VUV-FEL will then permit us to investigate the effect of circular polarisation on the yield of specific surface reaction products. This is crucial to understanding the asymmetry found in biological systems, *i.e.* D-sugars and L-amino acids. Neutral photoablation will undoubtedly compete with photoionisation following photon absorption in this regime and so must also be considered. TOFMS techniques, using pulsed VUV-FEL radiation for excitation, and undulator radiation for ionisation of the gaseous desorbates will allow the competition between these channels on astrophysical surfaces to be investigated.

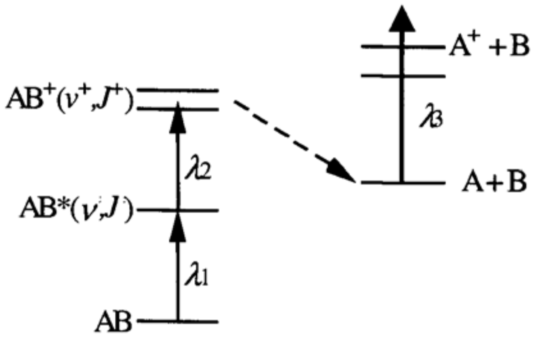
3.2.4.6 Rydberg Wavepacket Spectroscopy

Electronic and molecular dynamics of small molecules in the gas phase can be studied using Rydberg wavepacket spectroscopy. A significant achievement to date has been the first observation of Rydberg wavepacket dynamics in a molecule[73]. Such systems are exceptionally challenging since the electronic motion is strongly coupled to the rotational motion of the ion core and the Born-Oppenheimer approximation breaks down. In the new area of coherent control[74] the application of carefully phased or shaped pulses of light can be used to manipulate the electronic and molecular dynamics. Three examples of experiments that can be envisaged for 4GLS are (a) the employment of picosecond pump-probe methods to monitor the predissociation dynamics of Rydberg electron wavepackets in NO by single-photon ionisation of the product $N(^1D)$, (b) the generation of phase-locked pulse sequences and feedback-optimised pulses to create exotic electron wavepackets whose predissociation/autoionisation ratios may be manipulated, and (c) the observation of the effect of intense (10^{14} W cm^{-2}) ultrashort laser pulses on the ionisation and dissociation dynamics of Rydberg states.

A great advance in current research, which utilises existing laser systems, will be realised by using synchronised VUV and XUV short pulses from the FELs to directly study dissociation

[73] V G Stavros , J A Ramswell, R A L Smith, J R R Verlet J Lei and H H Fielding, *Phys Rev Lett,* 83 (1999) 2552; R A L Smith, J R R Verlet, E D Boleat, V G Stavos and H H Fielding, *Faraday Disc,* 115 (2000) 63
[74] D J Tannor and S A Rice, *Adv Chem Phys,* 70 (1988) 441

processes. Multiphoton excitation of small molecules in a pulsed expansion, with the output of a table-top tunable narrow bandwidth nanosecond laser, will allow specific rotation-vibration levels of an electronically excited state of the neutral molecule to be excited. From this intermediate, specific electronic orbital angular momentum and core rotational angular momentum states will be excited coherently using a broad bandwidth picosecond pump pulse from the VUV-FEL. In order to follow the dynamics of a wavepacket created from predissociating Rydberg states, the production of one of the products will be monitored by ionising it with a delayed picosecond pulse from the XUV-FEL, followed by detection using time-of-flight mass-spectrometry. The general excitation scheme is illustrated in the figure below.



In this multiphoton scheme, λ_1 is a narrow bandwidth nanosecond pulse used to excite specific angular momentum states of an excited intermediate of molecule AB, λ_2 is a VUV (~4 eV) picosecond pump pulse for Rydberg wavepacket studies and λ_3 is a delayed XUV (>14 eV) picosecond probe pulse for direct monitoring of the dissociation process.

Such pump-probe experiments will significantly advance the time-resolved studies of wavepacket dynamics currently being performed using the optical Ramsey method[75]. Currently, this work is restricted to the detection of ions formed through autoionisation. The intense, high energy, photons provided by the XUV-FEL will add the capability of monitoring the products of neutral predissociation in an optical Ramsey experiment. This will enable a detailed investigation of the competing autoionisation/predissociation decay routes. Exotic wavepacket states generated using phase-locked pulse sequences and pulse-shaping methods will also be investigated. Studying highly excited Rydberg states in intense laser fields beyond the perturbative regime will improve our understanding of the coupling of molecular electronic potentials with the intense electric field of the laser pulse. There is already a significant UK and international interest in this area[76].

Short XUV pulses can also be used as a probe of molecular dynamics; molecular alignment by interaction with an intense femtosecond laser has attracted a lot of interest in recent years[77]. Experiments have shown that molecules have a tendency to align their internuclear axis along the polarisation axis of an intense laser before dissociative ionisation takes place. In a recent experiment[78] an intense picosecond laser has been used to prepare a rotational wavepacket in the ground electronic state of the I_2 molecule. The angular distribution of the molecule evolves in time and leads to a field-free alignment of the molecule along the laser polarisation axis at well defined time delays following the laser-molecule interaction. The use of femtosecond or

[75] Q Hong, J A Ramswell, V G Stavros, C J Barnett and H H Fielding, *Meas Sci Technol,* 9 (1998) 378
[76] J R R Verlet and H H Fielding, *Int Rev Phys Chem*, 20 (2001) 283
[77] J J Larsen, K Hald, N Bjerre, H Stapelfeldt and T Seideman, *Phys Rev Lett,* 85 (2000) 2470
[78] F Rosca-Pruna and M J J Vrakking *Phys Rev Lett,* 87 (2002) 153902-1

picosecond pulses from the XUV-FEL on 4GLS would allow important dynamical studies, such as photoionisation and/or photodissociation, to be carried out with aligned molecules, and would amount to studying the dynamics in the molecular rather than the laboratory frame[79].

3.2.4.7 Time–resolved studies of excited states in solids via 2-colour 2-photon photoemission (2-PPE)

Information about empty states in solids and surfaces may be obtained in pump-probe experiments through 2-colour 2-photon photoemission via the conduction band. The dynamics of electrons in excited states is particularly interesting from the point of view of understanding relaxation processes and the role of electron-electron interactions - this is a topic of great current interest with many real technological applications.

An example is the molecular organolanthanide complexes, under development by the Oxford spin-out company Opsys Ltd, as narrow bandwidth multicolour light emitting phosphor materials for use in thin film organic light emitting diode (OLED) display devices. The organolanthanides offer much better colour purity than the alternative organic polymer phosphors owing to the sharp atomic-like nature of the lanthanide emission. A typical molecular OLED device consists of a transparent conducting anode, a hole transport material, the light emitting phosphor, an electron transport material such as aluminium quinolate and a metal cathode, usually calcium or aluminium. Many issues surrounding these materials and their application in OLED devices demand the use of state of the art low energy photemission techniques. These include charge injection across barriers within the OLEDs and issues of band edge alignment, the generation and decay of excited states within phosphor and charge transport layers, and the influence of adsorbates and defects in quenching excitations. These phenomena would be best explored using time resolved excited state photoemission, which in turn demands the ability to generate excitonic states and then to excite photoemission from them.

Further examples include the study of metallic and semiconductor nanowires - a fundamental component in future device nanofabrication. Measurement of 2-PPE spectra with selected polarisation of incident light using 4GLS will enable the study of the fundamental properties of individual wires, such as how the exciton or plasmon life-time may vary within a size distribution. Excitonic transitions in organic semiconductor multilayers can have significantly larger energy and longer lifetime than in corresponding optically-active inorganic semiconductors, and the time-resolved capability of the new facility would allow these to be probed for the first time. The pulse structure will also enable the electronic structure of short-lived chemical bonds to be studied, and this will lead to new insights into the processes of catalysis and surface chemical reactions.

3.2.5 ***Reaction Dynamics at Surfaces and Interfaces***

3.2.5.1 New prospects for dynamic studies of adsorbates and interfaces from new techniques in vibrational and optical spectroscopy

Vibrational spectroscopy has made crucial contributions to the study of surfaces and interfaces over the past 25 years. The identification of adsorbed species and surface reaction intermediates by electron energy loss spectroscopy (EELS) and reflection absorption infrared

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[79] S C Althorpe and T Seideman, *J Chem Phys,* 110 (1999) 147

spectroscopy (RAIRS) has improved our understanding of mechanisms in catalysis, chemical vapour deposition of semiconductor surfaces, molecular self assembly and in the action of thin film molecular electronic devices. Synchrotron radiation enhanced the capability of the RAIRS technique in the 100-500 cm^{-1} region where vibrations involving the molecule-surface bond are found, thus providing direct information on bonding mechanism and on frictional processes at surfaces.

The brilliance, time structure and wide photon energy coverage of 4GLS, particularly from the IR and VUV-FELs opens up entirely new prospects for the development and wide exploitation of an armoury of IR and optical spectroscopies, including Sum Frequency Generation (SFG), Resonance Raman and Reflection Anisotropy Spectroscopy (RAS). To date, these techniques have been applied largely to problems of the identity, structure and conformation of adsorbates and surface phases. Much of the excitement in future will lie in the investigation of fast surface reaction kinetics (sub-ms) and ultra-fast dynamics (ps and sub-ps) of surface processes, using both linear and non-linear spectroscopies in 'pump-probe' experiments. The 4GLS facility will provide a focus for UK and European activity in this field providing unique access to laser wavelengths in the deep UV and far-infrared in combination with wide band IR synchrotron radiation.

3.2.5.2 Intramolecular vibrational energy redistribution (IVR) in the surface-adsorbate complex

An understanding of IVR in the surface-adsorbate complex is essential to improving our understanding of the adsorption, reaction and desorption of chemical species at any catalyst surface. The essence of the experiment is to use IR-FEL radiation, tuned to a specific vibrational mode of an adsorbed molecule, to pump that mode and to use synchronised IR synchrotron radiation to probe the entire mid–IR range down to 200 cm^{-1} at time intervals in the ps range. The intensity variation of all the observed bands will be used to determine the mechanism of energy transfer, although it is anticipated that the low frequency surface-adsorbate modes will be important. The experiment will require spatial as well as temporal overlap of the laser and synchrotron radiation beams on the surface. The synchrotron radiation beam in a conventional storage ring RAIRS experiment usually covers tens of mm^2 of the surface; this experiment will require the development of a RAIRS microscope attachment coupled to a UHV chamber to reduce that coverage to about $1mm^2$. The flexibility inherent in the ERL design will allow the electron beam shape at the bending magnet to be optimised for this application, while the temporal synchronisation is one of the essential features of the 4GLS design. In fact, 4GLS will have particular beam characteristics that are highly desirable for these types of experiment. In particular, the high brightness and stability will improve signal to noise characteristics, and hence reduce acquisition times, while the available beam area multiplied by the angular divergence, the etendue as it is known, will be particularly small - a condition which ideally suits both RAIRS and IR microscopy type experiments.

A number of types of adsorbate /substrate combinations are envisaged for study initially. A model system such as CO on a copper crystal surface will provide the greatest challenge in terms of time resolution since homogeneous broadening studies suggest T_1 to be of the order of a few ps for the C-O stretch, however this is an appropriate target to aim for. Larger molecules, such as long chain alkoxy species on copper, would provide a target for which the surface chemistry is well understood and where timescales might be longer and easier to manage, if the initial pumping is into a methyl or methylene stretch or deformation. Similarly semiconductor substrates will provide systems which are less challenging in terms of time-scale but equally fascinating. For example, a current research programme (at the University of

Nottingham) is investigating the chemisorption of substituted fullerenes on silicon crystal surfaces with scanning probe techniques and IR spectroscopy. Methyl substituted C_{60} adsorbed on silicon surfaces could be excited in a methyl stretching or deformation mode and vibrational energy transfer observed through the C_{60} cage to the crystal, by measuring time resolved synchrotron IR spectra in Brewster angle transmission mode.

Dynamic measurements of CVD growth on technologically important oxide surfaces

Pump-probe experiments will provide a unique insight into processes of film growth – an important example is the surface chemistry of CVD processes such as the growth of metal oxides on glass (including tin oxide glass for energy efficient and smart glass applications). In these experiments, the surface-adsorbate complexes produced in the experiments will be pumped with low energy IR pulses designed to excite substrate phonons in order to simulate the effects of rapid surface heating upon the adsorbed CVD precursors. These experiments will enable RAIRS to be used to monitor the effects of surface phonon excitation upon the structure of the adsorbed CVD precursors. In addition, under favourable conditions, it will be possible to monitor the molecular relaxation that results from the absorption of the pump photon by the substrate in dynamic RAIRS.

Surface photochemistry and photophysics

The ability to look at a surface spectroscopically (by IR absorption, SFG, or Raman) in concert with photolysis from a widely tunable VUV-FEL (visible – 10 eV) source will enable new experiments probing the lifetimes and intermediates in photoassisted processes to be performed. For example, it will become possible to look directly at excited states on surfaces using the pump-probe type approach with synchronised UV and IR pulses, and this will enable the dynamics of surface processes to be followed in unprecedented detail. These types of experiment are not currently feasible at any existing light source. Studies of UV-induced surface photochemistry on metal surfaces will extend from monitoring the evolution of transition states on the ps time scale, to monitoring the evolution of surface intermediates and products on the ns time scale. The ability to monitor metal-adsorbate modes will again be a significant advantage given their sensitivity to the nature of the metal-molecule bond. There is also much interest in the heterogeneous photochemistry of the troposphere and stratosphere (which may be modelled using alkali halides, oxides including TiO_2, and with surfaces covered with acidic adsorbed layers), and in CVD-grown TiO_2 photocatalysts. While TiO_2 photocatalysts have been known for some time, the nature of the mechanisms by which they catalytically oxidise adsorbed organics is considerably less well understood. RAIRS data may be recorded while exciting various forms of CVD-grown TiO_2 deposits with UV photons of energy greater than the bandgap of the TiO_2, in order to study the photocatalytic process as it occurs, on the molecular level.

3.2.5.3 New Horizons for Sum Frequency Generation

Non-linear spectroscopies such as Sum Frequency Generation (SFG) have made a considerable impact, particularly in analysing conformation in large admolecules. The dependence on a lack of centrosymmetry enables this technique to be applied to solid-liquid and liquid-liquid interfaces, where both phases may be infrared transparent. However, as the technique relies on the detection of the nonlinear 'sum' frequency of an IR photon with a UV photon, the full potential of this technique has not been realised to date. Its application is severely limited by lack of highly intense, tunable deep-UV sources, giving high sensitivity from only a few surfaces (*e.g.* Au) where the SFG response may be resonantly enhanced by available table-top

UV/visible lasers. In addition, inadequate coverage in the IR, particularly to low wavenumber, can limit the types of vibration that can be probed. Due to the lack of suitable and sufficiently tunable IR laser sources, currently performed laboratory based SFG experiments are restricted to the measurement of vibrational sub-spectra in the C-H and O-H stretching regions. In contrast, the wide spectral range now available at the 4GLS IR-FEL would allow for the first time the recording of complete SFG spectra permitting a full vibrational characterisation of active surface species. Although there have been attempts in the past to exploit FEL radiation for IR+visible SFG on surfaces (notably at CLIO and FELIX), they have been hampered by poor beam stability and “ease of tuning”, as well as problems in pulse synchronisation. 4GLS will help in a number of areas, notably the high intensity compared to other sources and the tunable range. In particular the range and tunability of the 4GLS VUV-FEL offers the opportunity to further enhance sensitivity of SFG by utilising resonance features at these higher photon energies, enormously widening the number of systems that can be studied. This contrasts markedly with most current SFG studies where the fixed “visible” wavelength is restricted to a single near-IR or visible wavelength.

4GLS will thus enable SFG to be exploited to the full, in experiments from a range of surfaces (including insulators) never previously amenable to study in this way. These include mimics of heterogeneous catalysts (oxide surfaces and supported metal particles on oxide surfaces), condensed acid hydrates and their salts (of environmental relevance), functionalised organic surfaces (immobilised monolayers of nanoparticles and potential single molecule magnetic clusters) and the adsorption of surfactants such as partially fluorinated hydrocarbons from supercritical fluids onto a variety of surfaces. The technique will be particularly powerful in studies of biological interfaces, such as functionalised self-assembled monolayers of peptides and proteins, at the solid-fluid interface. Such measurements in the mid IR region, require access to FEL light sources because of the need for tunability of the light source and also because of intense adsorption from atmospheric water. The advantages of 4GLS over conventional table-top sources (OPO/OPAs) in the low wavenumber region between 1000 and 100 cm^{-1}, where for example external vibrational modes of adsorbate/substrate complexes occur, will be fully exploited.

An example – SFG studies of the surfactant-nanoparticle interaction

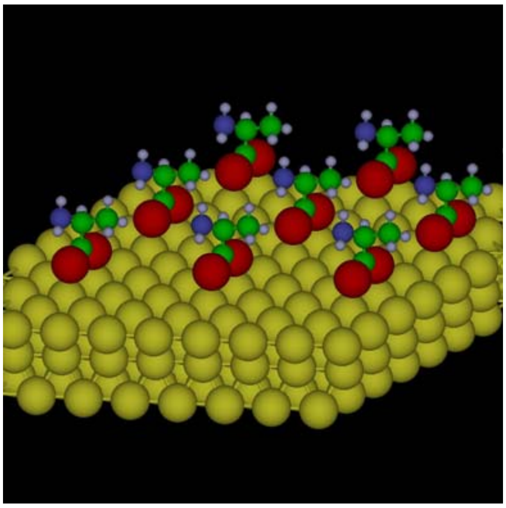
A good illustration of the way in which the range of the VUV-FEL facilitates the SFG experiment is given by work underway at the University of Cambridge aimed at understanding the adsorption of surfactants on metallic and semiconductor nanoparticles. In a novel proof of principle experiment the group have recently shown that it is possible to detect surfactants adsorbed on nanoparticles using sum frequency spectroscopy. Preliminary experiments were performed using 15 nm citrate–stabilised gold nanoparticles and the dichain cationic surfactant DODAC. The SF spectrum of the DODAC/nanoparticle film was significantly different from those of DODAC recorded on planar gold or dielectric surfaces, due to the influence of the surface plasmon resonance of the nanoparticles. The surface plasmon resonance of isolated 15 nm Au nanoparticles is near the wavelength of the visible laser used in the experiments (532 nm). However, the formation of films from Au nanoparticles leads to a shift in the λ_{max} of the plasma resonance due to a degree of two dimensional aggregation. The efficiency of SF generation is thereby lowered significantly. An immediate benefit of conducting these experiments on 4GLS would be the capacity to tune the UV/visible laser light to the peak of the plasmon resonance yielding much higher SF signals. Furthermore the much greater sensitivity of a ps versus ns spectrometer would permit spectra to be recorded for other polarisation combinations in addition to ppp (namely, ssp, sps and pss). A comparison of the spectra on the nanoparticle in these polarisations with those on planar metal (Au) will be highly informative for understanding the surface fields on the nanoparticle and the orientation and conformation of the surfactant. Additionally the tunability of the VUV-FEL will permit SF spectra of different multilayer thicknesses of nanoparticle films to be investigated. A variety of other nanoparticles will now be amenable to study, including silver and semi-conductor nanoparticles, such as InP nanoparticles which are usually stabilised with the surfactant trioctylphosphine oxide (TOPO). This surfactant may be readily exchanged for a wide range of other surfactants such as amines and other phosphines. Hence the wide IR tunability of the 4GLS IR-FEL will be essential for detecting a wider range of functional groups than the present nanosecond instruments, which mainly record spectra of C-H and C-D resonances. Complementary UV/visible spectroscopy of the semiconductor nanoparticle films will permit the correlation of band gap effects and hence optoelectronic properties with the surfactant type, conformation and packing.

Adsorbate dynamics via SFG

The ability to conduct SFG on fast (ps and sub-ps) timescales using 4GLS naturally means that experiments in the time domain become feasible. Recently time resolved Sum Frequency Generation (TR-SFG) has been used to follow the dynamics of changes to a CO adsorbate, induced by a sub-ps visible pulse. It has been shown that this approach may ultimately be used to investigate the dynamics of surface transition states. It should also be possible to use TR-SFG to follow IVR in the surface–adsorbate complex (described above), and this might be particularly productive once the interesting regions of the IR spectrum have been identified by the broad band synchrotron IR approach. There is clearly also significant potential in the study of surface reactions or phase changes, for example surface polymerisation reactions. It order to match the timescale of the polymerisation kinetics (~ 1-2 hours) a ps spectrometer such as that proposed here would be ideally suitable, as ns instruments require times of the order of hours rather than minutes to acquire usable spectra. Additionally, the facility for rapidly changing IR wavelengths will enable different functional resonances to be monitored almost simultaneously.

Studies of Chiral Adsorbates via Sum Frequency Optical Activity (SFOA)

The development of chiral heterogeneous catalysts through modification of metal surfaces by chiral molecular monolayers is of major importance to the fine chemicals industry. An understanding of the chemical bonding of chiral molecules to surfaces and its influence on the structure of the monolayer is crucial to the design of chiral catalysts. Perfect chirality can be bestowed on achiral metal single crystal surfaces by the adsorption of amino acid and bicarboxylate molecules. These surfaces possess extended chirality rather than limited chiral domains and are observed only at certain points on the adsorption phase diagram, where rigid bonding between the molecules occurs and the resulting supramolecular assemblies impose a particular growth direction on the whole monolayer. The extended chirality of the surface may be switched by the adsorption of the opposite enantiomer of the molecule.



A plane wave DFT-GGA calculation by DL Computational Science and Engineering Department showing the adsorption sites of chiral alanine molecules on a Cu (100) surface.

The variable elliptical polarisation possible using both IR and VUV-FELs on 4GLS lends itself to enantiomerically specific studies of adsorbate-substrate bonding and conformation in chiral systems, for example using SF techniques. Sum Frequency Optical Activity (SFOA) is a new vibrational spectroscopic technique which combines common sum frequency generation (SFG) from suitable (gas/liquid, liquid/liquid, liquid/solid, gas/solid, *etc*.) interfaces with the simultaneous detection of optical activity (OA) in vibrational transitions from appropriate chiral surface molecules. It can consequently be regarded as an optically active variant of conventional (surface) SFG. SFOA involves the simultaneous use of circularly polarised IR and linearly polarised visible laser pulses. Since circularly polarised radiation interacts differently with (chiral) molecules of a particular handedness (enantiomers), SFOA directly probes the chiral environment of molecular vibrations thereby displaying a much better sensitivity to local molecular conformations than the parent SFG technique. However, apart from one isolated claim of interface SFOA detection a few years ago (which still needs to be confirmed experimentally), SFOA from chiral surface species has not been observed yet. Therefore the 4GLS IR-FEL facility will provide a unique opportunity to conduct the first successful interface SFOA measurements. Because of its inherent sensitivity to sub-monolayer detection and molecular chirality SFOA offers great potential to evolve into a major spectroscopic probe of both significant practical and fundamental theoretical interest for novel surface science studies.

3.2.5.4 Ultra-high sensitivity in deep UV Resonance Raman Spectroscopy

Resonance Raman Spectroscopy has found important applications in structural biology and in the analysis of samples at rough surfaces through its contribution to the surface enhanced Raman spectroscopy (SERS) effect. Both of these areas will be revolutionised by the ability to shift the wavelength of the scattered light from the visible into the deep UV, offered by the 4GLS VUV-FEL (visible – 10 eV). The information content in both static and dynamic structural biology will be greatly enhanced by tuning into resonance with the amide groups of proteins, which means operating at wavelengths down to 120 nm (10 eV photon energy). In the case of molecules bound to surfaces there are generally electronic excited states in the 5-10 eV range which may also be accessed with the VUV-FEL allowing for resonant enhancement of Raman scattering without the need for roughened, ill-defined surfaces. This will open up possibilities for resonance Raman spectroscopy to analyse sub-monolayers on single crystal surfaces of metals, semiconductors and insulators, both in static and time-resolved experiments.

Experiments planned over the next twelve months at the Rutherford Central Laser Facility (CLF) are aimed at developing UVRR spectroscopy as a sub-monolayer sensitive, surface analytical tool. The development of FTIR for monolayer and thin film analysis has had a major impact on surface science and on wider areas such as thin polymer film and self-assembled monolayer research. Resonance Raman spectroscopy will complement and enhance the IR techniques in surface science particularly for vibrational modes in the 100-1000 cm^{-1} region. The wide tuning range of the 4GLS VUV-FEL will allow a proper systematic investigation of the resonance profiles associated with the Raman bands of molecule-surface complexes. This will widen the applicability of the technique to metal, semiconductor and insulator surfaces and *virtually any adsorbate*, as suitable electronic excitations should be generally exist in the visible – 10 eV range.

Experiments on the origins of the SERS phenomenon have established that the contribution from the resonance Raman effect is considerable and is related to charge-transfer absorption bands associated with the metal-adsorbate complex, which for pyridine on Ag(111) extend into the visible range only in the presence of Ag adatoms[80]. More recent reports from Campion[81] have established a direct relationship between electronic excitation bands measured by EELS and Resonance Raman excitation profiles in the visible range for the "large" molecular adsorbate pyromellitic dianhydride. UV resonance Raman spectroscopy has been demonstrated on monolayers by Sakamoto[82], using a pulsed source and in other analytical applications by Klenerman[83] using a quasi-continuous laser source, and by Asher using a CW source[84]. Stair has also carried out UV Raman studies of catalyst surfaces[85]. In current work, UV Raman spectroscopy is being carried out using a CW frequency doubled argon ion laser at the CLF operating at UV wavelengths of 244 and 257 nm (around 5 eV) to access the charge transfer bands known to exist for adsorbed molecules and atoms[86] on 'flat' single crystal metal surfaces. The 4GLS VUV-FEL will offer a much wider range of useful wavelengths, especially below 200 nm (around 6 eV) where table-top lasers are unlikely to be useful. This will allow optimum resonance wavelengths to be identified for combinations of surface and adsorbed species relevant to virtually any application. The FEL can be operated as a quasi-continuous source at 20 MHz repetition rate or as a pulsed source for time resolved studies at 1-10 kHz repetition rate.

An example: Reaction dynamics on single crystal electrodes

In situ vibrational spectroscopy at the electrode/solution interface was a major advance brought about by the development of SERS. However, the need for a roughened metal electrode for SERS precludes its use in the study of adsorption and electrode reactions on single crystal electrodes, where the important effects of electrode surface structure may be investigated. IR spectroscopy has been successful in this context but it is limited by strong water absorptions, particularly in the 100-500 cm^{-1} range, and its sensitivity is limited on non-metal electrodes.

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Resonance Raman spectroscopy using the VUV-FEL can be tuned to focus on particular adsorbed species, such as the intermediates in methanol fuel cell reactions on platinum electrodes. The technique will be particularly sensitive to metal-surface bonding and surface reaction kinetics can be followed on the sub-ns time scale under working electrode conditions.

3.2.5.5 Reflection Anisotropy Spectroscopy using the 4GLS VUV-FEL

The high intensity of the linearly polarised photon flux made available in the visible to 10 eV range by the cavity VUV-FEL will revolutionise the exploitation of the emerging optical technique of reflection anisotropy spectroscopy (RAS)[87]. The RAS technique is important because as an optical probe with very high surface sensitivity it is applicable to the study of surfaces in a wide range of environments and has considerable potential for exploitation in a number of fields of research. RAS was developed by Aspnes in the 1980s as a probe of semiconductor surfaces and as a monitor of semiconductor growth[88]. Its range of application has expanded rapidly in recent years[89].

Currently, the spectral range and speed of response of RAS instruments is limited by the lack of a tunable source of intense linearly polarised radiation in the deep UV. RAS has similarities with the Circular Dichroism (CD) technique used to investigate protein folding. Both techniques employ a photoelastic modulator (PEM) but while CD operates in transmission and measures the difference in absorption of left and right circularly polarised light, RAS measures the difference in reflection of linearly polarised light from a surface. Like CD the speed of response of the RAS apparatus is limited by the need to allow time to achieve a signal to noise sufficient to allow an accurate extraction of the signal using Fourier analysis techniques. This limitation will be removed by the 4GLS FEL, allowing the technique to be fully exploited in the study of dynamic processes for the first time.

Measurement of the kinetics of surface phase transitions and molecular assembly at metal-liquid interfaces

While RAS offers opportunities to study the electronic structure of surfaces in a range of conditions and monitor chemical changes and molecular assembly on surfaces it is arguable that its main strength lies in its potential to measure kinetic effects on a fast timescale. This was the reasoning behind the development of a Rapid RAS instrument in 2000 by the University of Liverpool. This instrument has been completed and in studies of the deposition of Cu on Au in an electrochemical cell it has been shown to be capable of measuring an RAS spectrum over the range 1.4 to 3.2 eV in 0.1 s[90]. While this instrument offers a major advance in measuring kinetic effects of molecular assembly at metal/liquid interfaces it is not fast enough to follow changes in the RAS spectrum which are associated with surface phase

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transitions, such as the (1x2) to (1x1) phase transition of the Au(110) surface in an electrolyte as the electrode potential changes, or the change in orientation of molecules adsorbed on metal/liquid interfaces during molecular assembly.

The intense flux of the VUV-FEL will make it possible to improve the performance of RAS instruments of the traditional design by a factor of at least 10^3. This will make it possible to monitor surface phase transitions and molecular assembly on a timescale of ~ 20 μsec which is the limitation imposed on the speed of response of traditional instruments by the use of a PEM. The time structure of the intense pulses (10^{25} photons/sec peak flux) supplied by the VUV-FEL, pulse width of a few hundred fs and MHz pulse frequencies, will make it possible to omit the PEM and develop an instrument capable of a faster response. It will also be possible to exploit the high flux of the VUV-FEL to obtain a spatially dispersed response similar to the reflection anisotropy microscope (RAM) developed by Ertle and co-workers[91]. The RAM studies have made it possible to study oscillatory chemical reactions on surfaces and have shown that the progress of chemical reactions on surfaces in UHV and ambient conditions can be very different. The tunability of the VUV-FEL and its intense flux will make it possible to follow the progress of chemical reactions in the far UV where many large molecules have a strong optical anisotropy. This opens up the possibility of determining the optimum conditions for the production of particular chemical species, if necessary by the addition of functional groups with a strong optical anisotropy to act as orientational "tags".

3.2.5.6 The surface science of liquid surfaces

Laboratory studies of solid surfaces probing atomic and molecular structure under clean, reproducible and well-defined conditions have benefited over the past 40 years through the extensive application of high and ultrahigh vacuum technology. In contrast, our understanding of the liquid-gas interface with such definition is rather more limited. Some experimental techniques can yield a detailed atomistic picture of the structure of the liquid-gas interface (*e.g.* neutron reflection techniques and non-linear optical methods). However, attempts to carry out equivalent "surface science" style studies on liquid surfaces to those carried out on solid surfaces have proved difficult, because of the high evaporation rate of the liquid, and the resultant load on the pumping system. The development of a liquid microjet by Toennies and co-workers[92] in the early 1990's, however, now offers the surface science community the ideal tool with which to investigate liquid surfaces with the same rigour as has been applied to the solid surface in vacuum. The liquid microjet source offers an ideal means of introducing unperturbed liquid phase material into a high vacuum system for mass spectroscopic analysis utilising laser desorption in the infrared or ultraviolet[93]. A number of novel scientific programmes will make use of the unique combination of light sources in 4GLS and a liquid microjet source for studies of the liquid-gas interface. The microscopic dimensions of the introduced microjet droplets (< 20 μm in diameter) necessitate the use of intense photon sources such as the 4GLS FELs.

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Dynamics of photodesorption and photodissociation in the liquid selvedge

The photodissociation of small molecules in the gas phase is well understood following many years of detailed investigation. Likewise, we have a growing understanding of the more complex behaviour that accompanies photoexcitation at solid surfaces, especially metals and semiconductors. Our understanding of such processes at the surface of liquids, in contrast, is severely limited. It is proposed to use a liquid microjet source in combination with the FEL sources of 4GLS to probe the dynamics of photodesorption and photodissociation in this more complex regime.

In single laser experiments utilising either the IR-FEL or the VUV-FEL as an excitation source, the disposal of energy into the translation of photogenerated atomic and molecular fragments will be investigated by electron impact ionisation TOFMS. By systematically changing the wavelength of the radiation, it will be possible to investigate the correlation between the energy of the incident photons and the desorbate kinetic energy, while reducing the pulse width and increasing the radiation fluence on the liquid surface will allow the investigation of the competition between relaxation channels in the selvedge and dissociation/desorption. More complex experiments will seek to probe the internal energy distributions of the desorbates using high resolution laser-based spectroscopies, but will clearly involve synchronising the 4GLS sources to an external laser system.

Photoelectron spectroscopy of chiral molecules at liquid surfaces

As discussed earlier, it has been shown both theoretically, and in preliminary experimental results, that the angular distributions of photoelectrons ejected by photoexcitation by circularly polarised light are a sensitive probe of chirality in molecules in the gas phase. This effect will be even more pronounced in the ordered regime of a liquid-gas interface. It has been demonstrated that it is possible to measure photoemission spectra from liquid surfaces and a natural progression of this work is to conduct measurements of circular dichroism in photoemission from such surfaces when they contain chiral molecules. These experiments would exploit the variable elliptical polarisation of the 4GLS undulator radiation, or (for states close to the Fermi energy), the VUV-FEL.

Liquid surface analysis by post-desorption ionisation TOFMS

The combination of the liquid microjet with table top laser systems is a powerful analytical tool for the analysis of liquid surfaces. Equally powerful will be the technique of secondary ion mass spectrometry (SIMS). Central to this technology is use of a polyatomic ion source to enhance the yield of large secondary molecular ions and fragments compared to atomic ion sources[94]. Such sources have only recently been commercialised (Ionoptica Ltd) using C_{60}^{+} ions and crucially offer high ion currents in spot dimensions ideally matched to those of the liquid microjet. Equally important is the combination of quadrupolar ion trapping for accumulation, thermalisation and localisation of the desorbed ions prior to mass analysis in a reflection TOFMS. The apparatus will offer a practical mass range of up to 10 kDa. In addition, our proposed mass spectrometer configuration will offer MS-MS capabilities that will enhance the utility of the apparatus in identifying species.

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[94] E R Fuoco *et al.*, *J Phys Chem B*, 105 (2001) 3950

These techniques suffer from the limitation that they fail to probe the significant number of neutral species that accompany the ion desorption. Indeed, it is known in SIMS, that the predominant species present in the desorption plume are in fact neutral and that the ions are the minor product. By coupling tunable laser desorption in the infrared with VUV-FEL ionisation in the source of our quadrupole ion trap/time-of-flight mass spectrometer, it should be possible to enhance the sensitivity of this new surface analytical tool by several orders of magnitude. The tunable nature of the IR-FEL source will allow the excitation wavelength to be carefully tuned to select excitation either on solvent absorptions or solute absorptions. This will be particularly important in studying labile biological molecules and complexes in aqueous solution. Likewise, single photon ionisation in the VUV offers many advantages over multiphoton ionisation (higher efficiency, less fragmentation) for such systems. The combination of the IR-FEL with the VUV-FEL and or undulator radiation represents the most flexible approach to deploying this novel analytical tool.

3.3 Nanoscience

3.3.1 The Nanotechnology Revolution

There is no doubt that the sources of intense collimated and coherent radiation provided by 4GLS will make an important contribution to the study and understanding of nanoscale structures and materials. Nanoscience and nanotechnology are probably the fastest growing areas of science and technology for two reasons. Firstly, it has become apparent that systems with dimensions reduced to the nanoscale have properties quite unlike those of bulk material. Secondly there is a worldwide expansion of the technology which utilizes these structures and materials. Thus it is apparent that one can make step changes in several areas, including catalysis, magnetic storage media, photovoltaic devices and fuel cells, by exploitation and manipulation of the novel properties of systems with dimensions reduced below 10 nm. It is difficult to overemphasise the importance of 4GLS in this context. The brightness of the radiation from the new source is so high that *single* nanoscale objects or clusters can be studied. We can also, for the first time, contemplate the study of the details of the excited electronic states of clusters using pump-probe techniques.

3.3.2 Free Radicals and Clusters

The output of the VUV-FEL will be excellent for studies of free radical and cluster beams. There are many methods now available to generate intense molecular beams of chemically-reactive free radicals. By measuring the fluorescence excitation spectra and the dispersed fluorescence (as a function of excitation energy in the range 0 - 10 eV), information on the low-lying electronic states of the radicals and on the energy disposal and dynamics of their photodissociation decay channels will be gained. By photoexciting cluster beams that contain aggregates of several species (*e.g.* molecules embedded in rare gas clusters), a chromophore in one component of the cluster can be excited and the transfer of electronic energy to the other species in the cluster monitored. These beams of radical and cluster species are very dilute compared with conventional gas phase sources of stable species. However, the high intensity and pulsed nature of the radiation from the VUV-FEL will allow the techniques used in conventional laser-induced fluorescence spectroscopy to be used on these dilute systems, over a much broader energy range than is available from conventional lasers.

3.3.3 Clusters as Probes of Liquid-Solid Transition Properties

Clusters represent a state of matter that is intermediate between the gaseous and condensed phases. By doping a molecule in a cluster and monitoring its properties as a function of cluster size, it is possible to study the effect that this transition has on the molecule. In this way, the process of solvation can be observed if the cluster is liquid-like or adsorption if the cluster approaches the solid state. Innovative and novel experiments could be performed with the IR-FEL that would offer unique opportunities presently not available to conventional laser-based experiments. For example, detailed information can be obtained about the molecules during the solvation or adsorption processes by measuring the infrared absorption spectrum. Because the molecule is very weakly bound to the cluster, when it absorbs an infrared photon it will dissociate (vibrational predissociation), and the cluster fragments will scatter out of the beam. A mass spectrometer, located on the beam axis, can be used to measure the infrared absorption spectrum by observing the dip in the beam signal as a function of excitation wavelength (Infrared Depletion Spectroscopy). This technique has been employed successfully by Buck and Huisken at Göttingen[95], using tunable infrared lasers, but is limited in its extent and range of applicability by the available infrared lasers.

3.3.4 Electronic Structure of Single Clusters

Mass-selected nanoscale clusters in the size range 1 - 5 nm mark the boundary between molecular and solid state systems and have properties distinct from both. They offer the unique opportunity to study the evolution of the properties of matter as it is built atom by atom from the monomer. They are also a means to carry out experiments on systems whose size marks the threshold of overtly quantum behaviour facilitating a sophisticated understanding of the subtleties of quantum mechanics including macroscopic quantum effects.

The intense interest in clusters that has developed globally in the last decade is due not only to fundamental scientific curiosity arising from the issues above but also to an awareness of their enormous potential in the creation of new materials with 'engineered' properties. In the short term using clusters as building blocks will enable the production of very high performance materials and in the longer term they will be central to emerging technologies such as spintronics, single electron devices and quantum computing.

Up to now work has focussed on the electronic and magnetic properties of exposed clusters supported on surfaces in UHV and also particles embedded in matrices of other materials. Thus a sufficient density of clusters can be accumulated for experiments using second and third generation light sources. The building of a fourth generation light source will enable the long-awaited goal of flexible photoemission measurements using a wide band of VUV and XUV radiation on free clusters in flight before they have landed. This has been done with laboratory based near-UV lasers in the past but the 4GLS will open up a range of new experimental opportunities. Some examples are given below.

3.3.4.1 Photoelectron spectroscopy from free mass-selected nanoclusters using the combined output from the VUV and XUV-FELs

Undoubtedly the most powerful probe of electronic structure is photoemission, especially if shallow core levels can be excited. The beam from the VUV-FEL (~0.2 mJ/pulse) focussed to

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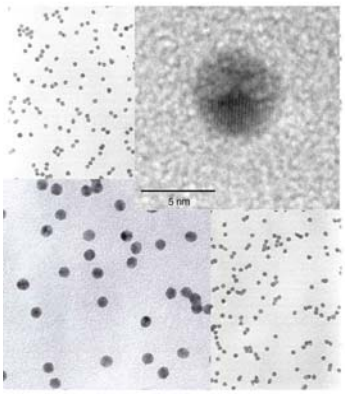
[95] U Buck and F Huisken, *Chem Rev*, 100 (2000) 3863

a spot of 50 µm or less will provide sufficient intensity to produce nanoclusters by laser ablation in conjunction with rare-gas (carrier gas) pulses at the same frequency. The peak flux of this type of source is exceptionally high and each dense bunch of clusters can be made to enter a target chamber in coincidence with the pulses from the XUV-FEL. Thus the two beams with a common timing structure are able to combine a very high intensity cluster beam and an ultra-high intensity light source. The pulsed production of photoelectrons from the cluster bunch allows the use of a time-of-flight technique to measure the photoelectron spectrum producing a massive enhancement in collection efficiency relative to conventional spectrometers. Moreover, if the ablated nanoclusters are focussed and fed into a drift tube before entering the target chamber, during flight the higher mass clusters will accumulate at the trailing edge and the lighter clusters will gather at the leading edge as a result of differential velocity slip during the free jet expansion. The important result is that simply changing the time between electron bunches enables the XUV beam to probe a specific section of the cluster sausage that contains clusters of a specific size. Thus mass-selection can be achieved with 100% efficiency.

The combination of these factors will enable, for the first time, flexible photoemission measurements to be carried out on free clusters in flight. This is an enormous step forward as there is an entire family of powerful photoemission-based techniques that can probe the electronic and atomic structures of clusters.

The cluster bunches can also be illuminated by the IR-FEL and this may be used for example to determine the size-dependent specific heat and melting temperature of the clusters by observing the photofragmentation spectra as a function of cluster temperature. The technique has been demonstrated recently using a laboratory based laser but the availability of tunable radiation with a time structure phased to the cluster production will enormously improve the sensitivity of the technique.

The free cluster results can be compared to those from particles after they have landed on a substrate. Determining precisely how the electronic and magnetic properties of a free particle change when it is bonded to a substrate is one of the most important goals in nanoparticle research and is important for the industrial application of cluster assemblies. The measurements of the supported clusters will benefit from the very high brilliance of the 4GLS undulator that, in conjunction with a photoelectron microscope, will enable the study of *individual* nanoscale clusters. This will remove averaging inherent in wide beam experiments and reveal how properties depend on the bonding site.



Electron micrograph of mass-selected Au nanoclusters from the Daresbury Cluster Source

Many further developments in experiments where a dense cluster beam interacts with high brilliance 4GLS photon beams may be envisaged – for example with a cluster beam source capable of producing clusters of bulk superconducting metals with very low thermal energy (such as the Daresbury Cluster Source[96]), the onset of Bose condensation in free clusters may be explored, using either the IR spectrum or the high resolution photoemission spectrum as a probe.

3.3.4.2 XMCD studies of free clusters

Using the higher harmonics from the undulators in high flux mode, it will be possible to measure the dichroism in the L absorption edges of clusters of the magnetic transition metals. These will be produced by a continuous-beam cluster source and passing the undulator radiation along the cluster beam will produce a high columnar density and enhance the absorption. The experiment will separately measure the orbital and spin contributions to the magnetic moment of the clusters after they have been magnetised by a gradient field. Measurements of the total magnetic moment in free Fe, Co and Ni clusters show a strong enhancement relative to the bulk but it is not known which component of magnetism is responsible for this. The spin and orbital moments are important quantities needed to understand the onset of ferromagnetic behaviour in systems containing only a few thousand atoms. These measurements will give important new information when compared with data from clusters supported on a substrate, where again the high brilliance of the source may be exploited to carry out the experiment with nanoscale imaging capability. For example in the case of Co nanocrystals, it will be possible to determine at what size cobalt assumes a uniaxial structure (hcp) with sufficiently large magnetocrystalline anisotropy to make its use in magnetic memories a practical possibility at room temperature.

3.3.5 Spin Physics of Clusters and Magnetic Materials

Photoelectron spectroscopy of single clusters is a leading example of the way in which new horizons for photoemission will be opened up by the brightness of the 4GLS source. More generally, the source opens up opportunities for both ultra-high energy resolution and high lateral resolution photoemission (PEEM), for time-resolved experiments, and for a new generation of spin-resolved measurements. These are outlined below.

One of the most significant benefits of 4GLS in this field will undoubtedly be in the measurement of spin-resolved densities of states, where the detection of the spin polarisation is inherently inefficient. Spin resolved electronic structure studies of magnetic materials have burgeoned over the last five years as a result of powerful undulator sources of radiation at third generation storage ring sources and important fundamental contributions have been reported in fields as diverse as half metallic ferromagnets[97] and high temperature superconductors. However, this progress has not been matched in more demanding experimental situations such as the study of free molecular species and the study of competing decay processes.

Free chiral molecules are of particular interest as the availabilty of spin resolved information would complement and extend more traditional methods of probing electron-molecule interactions by combining the sensitivity of spin-dependent experiments with the "handle" of chiral symmetry breaking. More speculatively, such studies hold the promise of shedding light

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[96] P M Denby and D A Eastham, *Appl Phys Lett*, 79 (2001) 2477
[97] J-H Park, E Vescovo, H-J Kim, C Kwon, R Ramesh and T Venkaatesan, *Nature*, 392 (1998) 794

on the intriguing problem of the origins of biological homochirality. A limited foundation for this work is being built at present at third generation sources but, ultimately, it is essential to study chiral spin resolved photoemission dynamics using gaseous, unoriented targets, so that the complicating factors associated with multiple scattering processes and purely orientational effects, which have the effect of swamping the effects under study, are eliminated. This demands access to peak photon fluxes deliverable on the XUV-FEL of 4GLS.

Determination of the spin resolved electronic structure of mass selected clusters in the size regime of tens to hundreds of atoms is a challenge that is now being met theoretically but not experimentally. Using the output from the XUV-FEL will transform this endeavour. For the first time there is the realistic prospect of information on a wide range of cluster types.

Probing dynamical changes induced by chemistry at the surface of a magnetic material is crucial to an understanding of the details of its performance, especially as the length scale of technologically important devices reduces. Spin-resolved high resolution information close to E_F will be of particular importance in this context. The intensity of the VUV-FEL is sufficiently large to enable this information to be obtained from clusters of magnetic material.

Spin polarimetry is inherently inefficient but current polarimeter technology, especially when combined with time-of-flight energy analysis, is well suited to the pulsed output from the short wavelength FELs. The UK holds a commanding position in these developments.

3.3.6 New Horizons for Ultra-High Resolution Photoemission from Correlated Materials, Surfaces and Clusters

Many important electronic transitions in functional materials occur on meV energy scales. Examples are spin transitions in GMR materials and superconductivity in cuprate oxides, and indeed it is the latter case which during the 1990's provided the impetus to improve the best resolution attainable in photoemission from 10's or 100's of meV to a few meV; the result was that high resolution photoemission has provided the most important direct evidence to date for the nature of the pairing mechanism (so-called d-wave pairing) in superconducting oxides. The current experimental impetus is to improve resolution still further, in order to be able to investigate the superconducting gap in conventional (low temperature) superconducting oxides, requiring a further resolution improvement to around 1 meV. So far, the best achieved is around 1.4 meV at 10 K, from Nb and Pb using a conventional lab-based line source[98]. There remains an urgent need for high quality photoemission data from both conventional and oxide superconducting materials for comparison with calculations such as the bipolaron model of HTc materials. These measurements would be of fundamental importance in examining the validity of competing theories of high-temperature superconductivity, but require a routinely attainable experimental resolution of only a few meV.

The high brightness of 4GLS, combined with the quality of the ERL beam, will mean that it will now be possible to achieve this resolution from a tunable undulator source. This is a crucial development, as it allows for the resonant excitation of different chemical species, including species of the same element with signals chemically shifted by only a few meV. This might be used, for example to enable ultra-high resolution angle-resolved photoemission

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[98] Kiss *et al., J Electron Spectrosc Relat Phenom,* 114-116 (2001) 635

studies of quantum well states in ultra-thin metallic films[99]. A key aspect of this work is the need to be able to vary the photon energy over a wide energy range to explore some rather striking phenomena in resonant photoemission and surface/interface interference phenomena, *combined* with high lateral momentum (analyser opening angle or angular) resolution and high energy resolution. Both are important in studying the spectral line-shapes and temperature dependence of these line-shapes, in order to determine the electron-phonon coupling strength (a parameter which is of great relevance in conventional superconductivity). These experiments require access to a true low-energy fourth-generation synchrotron radiation source, such as 4GLS. The only planned competitive source will be MAX III at Lund in Sweden, and even this, being based on an conventional low energy storage ring, will be significantly inferior in potential to the 4GLS ERL design.

Similarly, 4GLS will revolutionise the use of ultra-high resolution shallow core level photoemission to study simple surface reactions and to fingerprint coadsorbed species on surfaces. Here photon energies required are perhaps 50-200 eV. This general approach has been used at the SRS[100], but the resolution achievable falls far short of the current state-of-the-art, and is simply no longer competitive. Very recent work in this area using the third-generation MAX II facility has highlighted a whole new layer of information on adsorbate vibrations and surface phonons which can be obtained by working at the highest spectral resolution[101]. Here, too, 4GLS will prove crucial for the UK community.

In our earlier discussion of 2-PPE, we saw that time resolution down to the ps regime may be obtained through the synchronization of the FEL pump pulse and the undulator/FEL pulse exciting photoemission. 4GLS will also have an impact where direct 'real-time' measurement of surface phenomena is required. Recent developments in multi-channel detection for low energy electron spectrometers should reduce data collection in electron spectroscopic techniques from minutes to seconds using conventional radiation sources, and this could be reduced to the ms regime by coupling to a bright radiation source such as 4GLS. This unique combination offers a method for probing, in real-time, processes such as thin film growth and temperature-dependent phenomena such as phase transitions, chemical reaction and desorption. Small area probing in real time also becomes feasible.

Imaging using photoelectron spectroscopy (PEEM) is a technique which benefits greatly from the use of a brilliant monochromatic light such as can be obtained from a synchrotron or a FEL. PEEM microscopes have already been installed on synchrotron beamlines at ELETTRA, ALS, BESSY2 and UVSOR. By making available both undulator UV from the ERL and monochromatic light from a FEL, 4GLS will provide the ideal combination of excitation sources for this technique. With the addition of a spin selective detector, the technique will be particularly powerful in the characterisation of magnetic clusters.

3.3.7 Nanoimaging Capabilities of 4GLS

The high brightness of the sources making up 4GLS will enable the development and full exploitation of a wide range of nanoimaging techniques, such as PEEM, of generic benefit to

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[99] P Pervan, M Milun and D P Woodruff., *Phys Rev Lett,* 81 (1998) 4995; M Milun, P Pervan, B Gumhalter and D P Woodruff, *Phys Rev, B* 59 (1999) 5170; M Kralj, A Siber, P Pervan, M Milun, T Valla, P D Johnson and D P Woodruff *Phys Rev B,* 64 (2001) 085411 (1-9)

[100] M S Kariapper, G F Grom, G J Jackson, C F McConville and D P Woodruff, *J Phys:Condens Matter,* 10 (1998) 8661

[101] J Andersen *et al., Phys Rev Lett,* 86 (2001) 4398

the whole scientific community. A number of high resolution imaging techniques, such as near field IR microscopy, require high photon fluxes to achieve further enhancements in spatial resolution, and 4GLS will enable these advances to be made – for example in this case it will be possible to image sub-cellular structures on lengthscales of a few tens of nm for the first time.

An astonishing number and range of imaging techniques will be developed at 4GLS. For this reason, we describe these techniques, and their potential applications in Appendix II. Some of the major benefits to specific areas of science are highlighted below.

3.3.8 Magnetic Imaging Using Spectroscopic Second Harmonic Magneto-optics

Currently, second harmonic generated magneto-optics (SHGMO) is finding increasing importance as a tool for probing interface and surface magnetism. The reason for this is that many magnetic materials of commercial importance have a crystal symmetry that is centro-symmetric. As a consequence, second harmonic optical and magneto-optical effects originate at surfaces or interfaces where the crystal symmetry is broken. As new devices are developed, that utilise spin-dependent electron scattering, the magnetisation and physical and electronic structure of surfaces become extremely important. Second harmonic magneto-optics, with its particular surface-sensitivity is a unique, non-destructive, tool for probing the physics of interfaces.

SHGMO techniques have been used for the observation of sub-domain structures in garnets, study of quantum-well states in mesoscopic metallic structures, layered magnetic structures, particularly magnetic tunnel junctions, and the determination of the influence of the band structure and surface/interface contributions on magneto-optical properties[102]. Being spin sensitive on the atomic scale, SHG provides a tool that can be used to perform femtosecond spectroscopy of spin dynamics in ferromagnetic systems which is needed for the development of ultra-fast switching devices. The ability of the magnetic second-harmonic generation technique for visualisation of surface magnetic properties has been demonstrated by near-field imaging of the domain structure of magnetic materials[103].

At present, a great deal of effort is being put into the exploitation of SHGMO, although the number of laboratories working in the area is limited due to the need for expensive, very fast, (femtosecond) intense laser sources. In the UK only Queen's Belfast has such facilities and also has the necessary expertise in magneto-optics. However, like most laboratories the work is confined to a very narrow range of wavelengths of the probing radiation. Since SHGMO is an optical phenomenon, albeit a nonlinear one, the dispersion of the effects with photon energy is crucially important for a full understanding of the electronic origins of the effect. This is, of course, also the case in linear optics. However, because of the particular requirements on the light source needed to make SHG observations, the technical problems of doing SHGMO over a wide photon energy range are presently beyond even the most well-equipped modern laboratory.

With the 4GLS, however, there is the prospect of very fast pulsed, intense optical beams and tunability over a wide spectral range (3—75 μm with IR-FEL and visible—10 eV with VUV-

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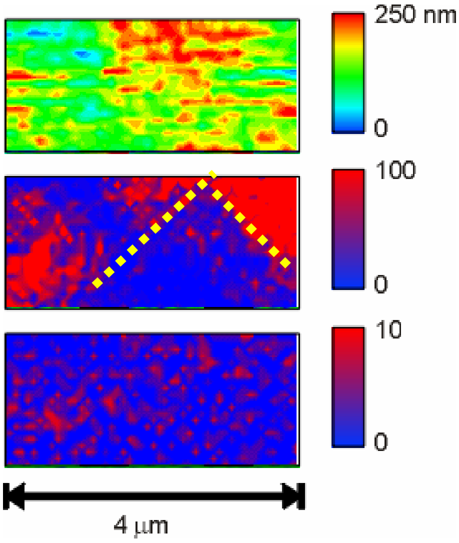
[102] Th Rasing, in *Notions and Perspectives of Nonlinear Optics*, O Keller, Ed., World Scientific Publ., Singapore, 1996, p. 339; S E Russek, T M Crawford, T J Silva, *J Appl Phys*, 85 (1999) 5273
[103] I I Smolyaninov, A V Zayats, C C Davis, *Opt Lett*, 22 (1997) 1592

FEL). Such sources would provide unique opportunities to explore the fundamental aspects of SHGMO in the broad spectral range and evaluate its potential as an analytical tool for the study of interface science. Already there are serious theoretical studies of the origins of SHGMO effects with *ab initio* calculations providing the basis for future experimental studies[104].



Topography (top) and near-field second-harmonic images of a single crystal Ni surface[105]: (middle) before and (bottom) after magnetisation. Magnetic domains are marked with dotted lines.

The reduction of thickness and lateral dimensions of magnetic structures often results in new behaviour, *e.g.,* the change of magnetisation direction from normal to in-plane for thin ferromagnetic films, enhanced or reduced magnetic moments at surfaces, oscillating exchange coupling through nonmagnetic layers in multilayered structures, quantum size effects. Second-harmonic generation spectroscopy will enable us to characterise the micromagnetic and magneto-optical properties of these materials and adopt a bottom-up approach in the search for new materials with improved characteristics.

The long term goal is to make use of the high sensitivity of nonlinear magneto-optical effects for non-invasive and non-contact investigations of advanced magnetic structures in the broad spectral range provided by 4GLS. This will give the possibility for studying mesoscopic (and/or) structured magnetic films and devices particularly their domain structure and dynamics. It will provide information on basic electronic, magnetic, and optical properties related to domain structure such as exchange anisotropy, re-magnetisation mechanisms as well as the influence of local structural inhomogeneities. From this work we will gain valuable experience and knowledge about phenomena that play important roles in the physics and engineering of thin magnetic films and mesoscopic nanostructured devices.

3.3.9 Functional Imaging

Visualisation of living cells and tissues is a key target that will be supported by the developments of 4GLS. Specimens are structurally and chemically complex and highly heterogeneous. The physiochemical and optical similarity of the material results in poor contrast giving poor signal-to-noise, therefore, unresolved spatial and temporal information. Furthermore, physiologically active systems may become disfunctional on attempting to improve spatial resolution by decreasing the wavelength of illuminating light beyond *ca.* 140 nm, the boundary between ionising and non-ionising radiation. The prime requirements are

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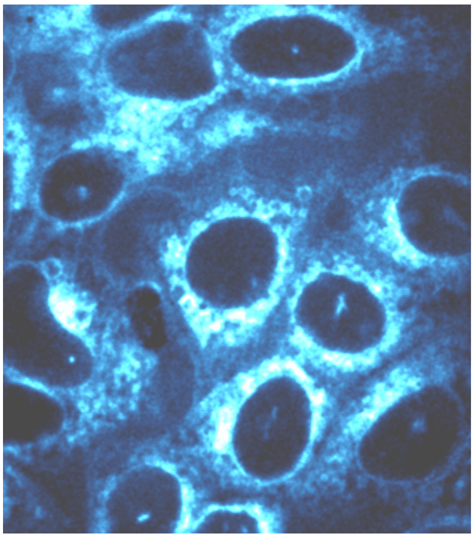
[104] N F Kubrakov, R. Atkinson, *IEEE Trans Magn*, 37 (2001) 2420
[105] I I Smolyaninov, A. V. Zayats, C. C. Davis, *Opt Lett*, 22 (1997) 1592

methods of interrogating physiological processes in live cells and tissues, with high signal-to-noise allowing spatial resolution to the size of the organelle generating the signal and to the time domain of the process to be followed.



UV fluorescence confocal imaging of the plant-derived oestrogen *coumestrol.*

Fluorescence microscopy, in one form or another, is by far the dominant bioimaging technique and fluorescence probes include those that are naturally occurring, such as chlorophyll, and those that are artificially induced, for example by cloning a fluorescent protein moiety onto a target protein. Optical methods exist for studying the dynamics of a detected single fluorescent molecule[106] and these have been extended to the sub-second time domain[107], albeit at resolutions limited by diffraction or the depth of the evanescent wave. Other developments can circumvent the diffraction limit of non-ionising radiation, for example, stimulated emission microscopy[108] which uses two co-incident laser beams to "engineer" the optical point spread function, by ground state depletion, thus providing improved resolutions (~50 nm). The enormous increase in the numerical aperture of 4pi-theta confocal imaging[109] also gives marked improvements in spatial resolution (100 nm). Scanning nearfield microscopy[110] shows great promise as a method for examining cell membrane phenomena with resolutions of 80 nm being demonstrated, although 50 nm should, in principle, be achievable if higher fluxes were available.

Many of the advances possible with 4GLS are expected to arise from the combination of high resolution imaging (enabled by the brightness and tunability of the 4GLS sources) together with the advances in detection and high speed readout techniques. The resulting high speed, high resolution time resolved fluorescence imaging has applications in many areas including:

- Single molecule spectroscopy of receptor molecules on cell membranes. By combining the high data acquisition rates that will become possible through advances in readout electronics with high contrast imaging methods such as total internal reflection microscopy

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[106] D W Pierce, N Hom-Booher and R D Vale, *Nature*, 388 (1997) 338; Sako *et al., Nat Cell Biol*, 2 (2000) 168
[107] Moerner *et al., Cytometry*, 36 (1999) 232
[108] T A Klar, M Dyba and S W Hell, *Appl Phys Lett*, 78 (2001) 393
[109] M Schrader, S W Hell and H T M v.d. Voort 84 (1998) 4033
[110] Subramaniam *et al., Cell Mol Biol*, 44 (1998) 689

(which have already been demonstrated to be capable of *imaging* single molecules[111], it will become possible to *spectroscopically* monitor these binding events in individual receptor molecules

- Virus entry into live cell systems - studying single virus particles.

- High throughput screening - The efficiency of for example novel DNA primers can be screened based on the efficiency of incorporation of tagged bases. It may become possible to examine this on the basis of single DNA molecules.

- Localisation and interaction of naturally occurring oestrogen like molecules. High spatial resolution would improve the determination of possible organelle localisation, and time resolved imaging will provide information on receptor binding.

- Physical interactions of plants and fungi, where fungal structures and metabolites penetrate plant cells. This phenomenon has substantial environmental consequences for forest maintenance.

Probeless functional imaging is best served by utilising internal localised structure and/or chemistry. Infrared and NMR would be obvious candidates, but while they may have adequate time resolution they are very limited in spatial resolution (~5 µm). Only by using shorter wavelengths will the desired resolutions be achieved. Therefore circular dichroism and resonance Raman microscopies at wavelengths over the non-ionising range of 140 to 220 nm are the best candidates for real-time functional imaging at high spatial and time resolutions. This region is immensely rich in information. For example, the amide bands yield direct structural detail on proteins. The conformation of carbohydrate and nucleic acids may also be derived from the spectromicroscopy in this wavelength range. Time-resolved resonance Raman microscopy will provide a specific method of interrogating the chemistry of sub-cellular domains in real–time and this will be very powerful. 4GLS together with even conventional confocal optics, will provide enough flux to achieve sub-100 nm spatial and sub-microsecond time resolved functional imaging. Sub-micron CD microscopy has been demonstrated in Japan using a variable polarisation undulator[112], but the huge advantage in flux, polarisation, band-width and coherence of the beams from 4GLS will provide a UK platform to take a clear lead in real-time functional imaging.

IR imaging using broadband radiation from 4GLS bending magnets could be coupled to IR microscope mapping systems with either Fourier transform interferometer scanning systems, or with newly developed dispersive array detection systems. The method of "imaging" would be to use sample scanning with collection of a complete IR spectrum at each sample point. This is the method employed by currently available point scanning FTIR microscopes now implemented on many synchrotron IR beamlines world-wide. Spatial resolution is limited by diffraction, to around 4 µm, but the intensity of IR radiation from 4GLS and the low noise of the IR source would make such IR imaging beamlines more attractive than storage ring beamlines. The potential of dispersive detection, using a multielement IR detector, is currently under investigation, but it could provide an alternative high speed method of data collection.

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[111] D W Pierce, N Hom-Booher and R D Vale, *Nature*, 388 (1997) 338
[112] Yamada *et al., Jpn J Appl Phys*, 39 (2000) 310

3.3.10 Opportunities for SFS Imaging

4GLS also offers sufficient intensity from the FELs to allow spatially resolved SFG/SFS experiments. Recently two groups have independently shown (in proof of principle type experiments[113]) that it is possible to perform an SFG experiment (using a combination of UV/-visible and IR lasers) which rather than detecting the far field SFG signal uses the near-field SFG signal, extracted by means of a Scanning Near-field Optical Microscopy (SNOM) probe. Although extremely difficult and at present yielding signal to noise ratios in single figures, the advantage of this method is that inherently surface sensitive vibrational spectra at very high spatial resolution (significantly below the diffraction limit) may be obtained. This is a technique in the very early stages of development, but one in which it is nevertheless clear that the high brilliance of the 4GLS VUV and IR-FELs offer substantial gains in signal, together with the ability to access the important low wavelength region below 10 μm inaccessible with table-top lasers. A Scanning Near-field SFG system on 4GLS would, for example, undoubtedly permit localised imaging of sub-cellular structures and studies of the spatial distribution of protein attachment on surfaces, with functional group specific imaging at resolutions approaching 30 nm.

3.3.11 Receptor-mediated Signalling Systems in Membrane Rafts: High Spatial Resolution Vibrational Spectroscopy

The 4GLS facility thus offers the capability of applying laser probes from the deep UV to the far IR to problems in biochemistry and biomedicine. One of the most exciting prospects and challenges is to use a variety of linear and non-linear spectroscopies to probe molecular structure in living cells at a spatial resolution of better than 100 nm; tools that will be brought to bear include

- Near Field IR spectroscopy (apertured and apertureless[114])
- Sum Frequency Spectroscopy (conventional and near-field[115])
- UV Resonance Raman Spectroscopy.

The scannable IR and UV free electron lasers will provide flexibility to tune into resonances in the deep UV for both Sum Frequency and Resonance Raman applications and to access down to low frequency torsions in IR absorption and Sum Frequency Spectroscopy. These will not be simple experiments as problems of power dissipation will need to be overcome, but the rewards will be great and our competitors are well aware of the possibilities[116]. A spatial resolution of ≤ 100 nm is achievable using all three of the above approaches. We illustrate the importance of spectroscopic probing on this dimensional scale by the potential application of vibrational spectroscopy to the investigation of the molecular structure of microdomains within membranes known as "rafts"[117] It has become apparent relatively recently that many inter-cellular signalling processes take place through receptor-systems located within such

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[113] R D Schaller and R J Saykally, *Langmuir,* 17 (2001) *2055*
[114] B Knoll and F Keilmann, *Nature*, 399 (1999) 48
[115] R D Schaller and R J Saykally, *Langmuir*, 17 (2001) 2055
[116] Scientific Frontiers with Accelerator-based Lasers, Report of a Meeting sponsored by Brookhaven Science Associates, the Southeastern Universities Research Association and the US Department of Energy, October 2000, Washington DC.
[117] T Asawakarn, J Cladera and P O'Shea, *J Biol Chem*, 276 (2001) 38457

microdomains within membranes. The virtue of this phenomenon is that it seems the behaviour of the receptor systems becomes altered (in a controlled manner) once localised within the raft structures. It has become imperative, therefore, to develop technologies that may interrogate the properties of these membrane structures. Since the work outlined above little technological development has taken place. It is clear, however, that the identification of specific biochemical events localised about the cell[118] will underlie much of 21st century experimental cell biology. Such studies will necessitate the involvement and close collaboration of physical scientists with life scientists and will be facilitated by the novel and versatile light sources at 4GLS.

3.3.12 2-D Vibrational Imaging

Exciting prospects for future developments at 4GLS arise from techniques that are presently at an embryonic stage. These include 2-D IR and 2-D Raman spectroscopy in conjunction with femtosecond laser technology and near-field vibrational imaging. Present 2-D NMR techniques are routinely employed for spectroscopic analysis of the dynamics of large molecules. Such information is more difficult to obtain from vibrational spectroscopy, but recent advances in femtosecond laser technology have allowed the initial development of both IR and Raman 2-D vibrational spectroscopy[119] With future development at 4GLS, there is potential for this technique to permit the unravelling of complex spectra. The goal will be to detect particular analytes in complex mixtures and to understand the dynamics of biomolecules. The key to the 2-D IR measurement is to be able to use a tunable narrow-band pump to selectively excite specific modes while monitoring the entire vibrational spectrum. The 4GLS IR-FEL, coupled to the PIRATE detection system will be very effective in this application and will be powerful in the study of structural changes on timescales faster than those accessible to NMR.

3.3.13 Development of New Biomaterials: Nanoscale Surface – Environment Interactions

There is a recognised need for biomaterials with improved or highly specific properties and the field has been highlighted by both the Technology Foresight Programme[120] and the EPSRC as being important to both the national economy and quality of life. “Biomaterials” range from natural materials, such as teeth and bones, to synthetic materials with a range of applications. For example, surgical implant devices are required for both permanent and temporary applications; dental materials include fillings and crowns and must be stable, well fitting and non-toxic; catheters and stents ideally require materials which inhibit surface fouling and drug delivery systems are required for controlled localised release of therapeutic agents. There is also a general awareness that simple tissue replacement materials, while undoubtedly important, are likely to be superceded in the future by materials which stimulate tissue regeneration[121]. These “tissue engineering” scaffolds have potential for encouraging both *in-* and *ex-situ* tissue growth.

In all of these areas, the nature of direct interactions between the biomaterial surface and the biological environment plays a critical role in determining the subsequent response of the system. For example, encouraging cell attachment to a surface may directly impact tissue regeneration or implant device integration, while limiting bacterial adhesion and colonisation

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[118] *e.g.* J Cladera, I Martin and P O'Shea, *EMBO Journal* 20 (2001) 19-26
[119] *e.g.* M C Asplund, M T Zanni and R M Hochstrasser, *Proc Nat Acad Sci USA*, 97 (2000) 8219
[120] “Tomorrow’s Materials”. Office of Science and Technology, Department of Trade and Industry
[121] J R Jones, L L Hench, *Mater Sci Technol*, 17 (2001) 891

will have major implications in reducing infection. As a result, the study of biomaterials is increasingly moving towards investigation of the material-biological matrix interface. This is a complex biophysical environment which, whilst difficult to describe as an intact, complete natural system, has numerous important sub-components that can be investigated, modelled and understood[122]. The investigation of the interactions that occur at highly controlled and well characterised biomaterials surfaces is emerging as a rapidly expanding research field, which is currently dominated by researchers in the USA.

Over the next few decades, research aimed at exploring fundamental molecular interactions with biomaterials surfaces will increase significantly. Synchrotron radiation-based techniques including infrared spectroscopy and photoelectron spectroscopy are already being used to explore interactions between simple biomolecules and model surfaces[123], allowing assessment of molecular binding, orientation and conformation. 4GLS will facilitate the natural extension of these and similar techniques to more complex systems. In addition to such "conventional" surface science tools, the major flux and spatial resolution advantages over existing light sources in the low photon energy range will enable 4GLS to lead the way in development of high resolution infrared and photoelectron microscopies and the extension of techniques such as circular dichroism to studying processes at surfaces.

Themes of particular importance will include the identification of biomolecule binding sites, examination of molecular conformation and orientation, and measurement of strengths of interactions and rates of adsorption, denaturing and replacement. 4GLS will allow the investigation of such processes over very short time scales. Polymeric biomaterials, for example, often exhibit high mobility of polymer chains. Surface reorganisation may be studied by "conventional" surface analytical techniques such as photoelectron spectroscopy[124], where low energy photons provide ionisation cross section advantages, or by application of non-linear optical techniques such as sum frequency generation[125] which utilise two photon beams. The latter is ideal for studying the solid-liquid interface, since it depends on a selection rule which ensures that only the structure of the interface is probed.

4GLS will also provide scope for examining the influence of surfaces on the behaviour of entire cells. Surface chemistry is known to affect cellular attachment and proliferation. High spatial resolution infrared and confocal microscopies will allow the structural and chemical process of cell adhesion and proliferation on surfaces to be probed in intimate detail. Nanostructures may prove to be as important in the field of biomaterials as they are elsewhere, since it is well known that cell response to a surface can be considerably modified by changes in topography. The specific response induced, however, appears to have some degree of cell-type dependence, suggesting that molecular bonding and signalling may be important. "Contact guidance" can significantly alter cellular morphology, even for nanometer-scale surface features, although the mechanism is not fully understood[126]. "Natural nanostructuring", such as crystallite nucleation, may also be important in influencing cellular response. In addition, there is some evidence that "template" molecules may influence the size and shape of apatite crystals during bone formation[127], while other molecules may play important roles in

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[122] F H Jones**,** *Surf Sci Rep,* 42 (2001) 79-205
[123] R Raval, J Williams, A J Roberts, T S Nunney, M Surman, *Nuovo Cimento D,* 20 (1998) 553; E Soria, I Colera, E Roman, E M Williams, J L de Segovia, *Surf Sci*, 451 (2000) 188
[124] G Beamson, B.T. Pickup, W. Li and S.M. Mai, *J Phys Chem B,* 104 (2000) 2656
[125] D H Gracias, Z Chen, Y R Shen and G A Somorjai, *Acc Chem Res,* 32 (1999) 930
[126] P Clark, P Connolly, A S G Curtis, J A T Dow and C D W Wilkinson, *J Biomed Mater Res,* 99 (1991) 73
[127] S I Stupp, P V Braun, *Science*, 277 (5330) (1997) 1242

inhibiting nucleation of pathological mineralisation. The study of biomolecule adsorption at individual, deliberately fabricated nanostructures and microstructures may help unravel the processes involved.

4GLS has considerable potential for dynamic experiments allowing real-time assessment of changes in molecular conformation on binding (protein folding and denaturing) and replacement reactions (*e.g.* water displacement, protein exchange). An important area is the folding dynamics of natural connective tissue macromolecules, and of their interactions with low molecular weight solutes, which may diffuse, intercalate and bind. These interactions influence bioactivity and mass transport to a degree not fully evaluated to date, and are completely "reprogrammed" at the material interface. The use of non-damaging radiation would also permit examination of (unlabelled) macro and micro molecules, with minimum distortion and enable speciation of short lifetime molecules, *e.g.* free radicals, with spatial resolution in the tissue inflammatory environment in the very thin layer of reactive tissue at the surface of a biomaterial. It would also prove valuable to integrate short timescale intra-molecular energetic change at macromolecules with inter- and supra-molecular interactions. This will enable better mechanistic understanding of how both the macromolecular milieu meshes around an implant system and how specific, very early interactions with surfaces are translated as information to surface interactive bio-species.

With 4GLS there is a unique opportunity to go beyond the current phase of rather static interactive studies that have been the mainstay of research into biomaterials hitherto.

3.4 Nonlinear Processes

3.4.1 High Field and Multiphoton Processes in Multielectron Atoms, Molecules, and Ions

Strong nonlinear effects arise at field intensities above some threshold value which, in the case of light atoms, is ~10^{13} W/cm^2. At low intensity, the AC Stark effect produces a shift in the energy of the atomic energy levels and a lifetime for ionisation which follow the predictions of perturbation theory. If the ponderomotive energy (the cycle-averaged energy of a free electron in the field) approaches or exceeds half the photon energy, then perturbation theory becomes inapplicable. In the nonlinear regime, tunnelling or field ionisation may occur and multiphoton ionisation may dominate. A range of new phenomena occur including Above Threshold Ionisation, Harmonic Generation, Light Induced Continuum Structure, Channel Closing, and Light Induced Degenerate States[128]. Experimental work with high power lasers has stimulated the development of theoretical work in the high field regime. Wavepacket methods for solving the time-dependent Schrödinger equation have been developed at Belfast[129], and time-dependent R-matrix theory is being developed at Daresbury[130] to solve the full time-dependent Schrödinger equation for multielectron systems in strong electric fields. The theories developed to treat multiphoton processes in strong laser fields predict the existence of stabilisation where the ionisation rate decreases as the field intensity increases. The power required scales with frequency, which means that in the VUV an increase of two orders of magnitude is required before the nonlinear effects outlined above can be observed. The XUV-FEL is estimated to provide 10^{15} W/cm^2, opening up an entirely new domain in the high frequency regime.

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[128] Atoms in Intense Laser Fields, ed M Gavrila, Advances in Atomic and Molecular Physics, Academic Press, New York 1992

[129] J S Parker, L R Moore, K J Meharg, D Dundas and K T Taylor, *J Phys B*, 34 (2001) L69

[130] P G Burke and V M Burke, *J Phys B*, 30 (1997) L383

At the higher frequencies provided by an XUV-FEL the photon field couples strongly to both the valence and outer core shells of atoms. Therefore the study of single and multiphoton ionisation in multielectron atoms can be extended to cases in which electrons are ionised from outer core levels leaving the atom or molecule in a highly excited state. The decay of 'hollow' atoms is already an important topic in the field-free domain, where a range of new Auger processes arise in the high-frequency domain. Theoretical calculations predict strong resonant effects for multiphoton processes involving multielectron atoms and ions. The tunability of the FEL source will allow these resonant processes to be located and studied.

Research on the single- and multi-photon dynamics of atoms, ions and molecules will open up a completely new area of research on multiphoton physics at high frequency and intensity. Amongst many areas of interest, multiphoton ionisation of inner shells is expected to be an important process, in particular the giant 3p-3d and 4d-4f resonances of the 3d metal series, the rare earths and the heavier elements in the periodic table. Multiphoton ionisation of aligned or oriented atoms, such as transition metal atoms embedded in solids, is also an exciting prospect as well as being of considerable practical importance.

3.4.2 Molecular Dynamics in Intense XUV Fields : 'Photon Scissors'

In the low-intensity, high-frequency regime, radiation couples predominantly to the inner shell electrons, whilst in the high-intensity, low-frequency regime, the radiation couples predominantly to the outer shell electrons. An interesting fundamental question is "What is the coupling mode of the intense, high-frequency XUV radiation?". 4GLS is expected to deliver 1 mJ, 1 ps pulses in the XUV region of the spectrum. After focusing to intensities above 10^{14} W/cm^2, these pulses create a new physical regime of light interacting with matter. The most relevant theoretical treatment of this problem has been published for the hydrogen atom; the results imply that different physical mechanisms take place under various frequency and intensity regimes[131].

Molecules such as N_2, O_2 or CO, whose fragmentation patterns are well known in both the single photon, low-intensity[132] and multiphoton, high-intensity[133] regimes, are prime candidates for studies in which they are exposed to intense XUV pulses. It may be possible to infer the ratio of inner to outer shell coupling from their ion fragment spectra. If an intensity dependence of this ratio is found, it can be used as a handle to optimise selective breaking of a chemical bond in polyatomic molecules and could thus lead to improved "photon scissors", in which a well-defined pulse of light is used to 'snip' or break a specific bond in a molecule to yield two fragments.

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[131] L J Frasinski, M Stankiewicz, K J Randall, P A Hatherly and K Codling *J Phys B: At Mol Phys,* 19 (1986) L819

[132] L J Frasinski, K Codling and P A Hatherly *Phys Letters* A, 142 (1989) 499–503; P A Hatherly, L J Frasinski, K Codling, A J Langley and W Shaikh *J Phys B: At Mol Phys,* 23 (1990) L291

[133] Bauer, L Plucinski, B Piraux, R Potvliege, M Gajda and J Krzywinski*, J Phys B: At Mol Opt Phys,* 34 (2001) 2245; L J Frasinski, K J Randall and K Codling *J Phys B: At Mol Phys,* 18 (1985) L129

4 WIDER EXPLOITATION

4.1 Medical Exploitation of 4GLS

The 4GLS suite of facilities has considerable potential for exploitation in the bio-medical field in the long term and a few of the possibilities are presented here. These applications are attracting interest world wide but are at very early stages of development.

4.1.1 The Diseased State

Progress in genomic research is providing the opportunity for early identification of individuals with susceptibility to specific diseases. This will provide an unprecedented view of the early progression of diseases which previously were only identified at a late symptomatic stage. This has two benefits, firstly it will be possible to study the initial molecular causative changes and secondly therapy will become more effective as diseases will be detected earlier. At present therapy for many diseases is ineffective because it is started too late. A notable example is osteoarthritis, in which there is a known genetic predisposition, but the connection between this and the advanced disease is poorly understood. Other progressive diseases which would benefit from early-stage studies include motor neurone disease, multiple sclerosis, and a collection of autoimmune conditions such as Type I diabetes, psoriasis and rheumatoid arthritis. There is increasing evidence that antigen receptors, which are membrane proteins, are deeply linked to the pathogenesis of many autoimmune conditions and structural studies of membrane receptors, their conformation, distribution in tissues, and activity would be possible on 4GLS in both single-cell and imaging modes, allowing both an understanding of the disease and the development or screening of new therapies.

This knowledge of the early stage of disease onset has resulted in a paradigm shift in which there is an enormous demand for molecular biophysical studies of the disease rather than clinical studies. This has resulted in the need to elucidate the structural biochemistry of many novel protein systems and image their distribution and activity in tissues and cells. Functional and chemical imaging within the cell will become an essential part of the study of disease. 4GLS will be invaluable for many such studies as it would enable detailed measurement of the conformation and interaction of normal and abnormal proteins, not only using tissue imaging techniques such as CD imaging or resonance Raman imaging, but also in single-cell or even single- molecule studies.

The ability to probe the molecular origins of diseases will also be invaluable in the study of many other conditions which are poorly understood. Examples include the structure and progression of prion-based diseases such as CJD and BSE. Alzheimer's disease is an example of a condition which has already been considerably clarified by the application of leading-edge biophysical techniques[134] which will eventually lead to improved therapy.

The application of functional imaging techniques will be particularly valuable in the study of structural tissues such as cartilage and bone. There is currently considerable interest in the early stages of osteoporosis in which calcium loss weakens bone in postmenopausal women.

[134] C Goldsbury, J Kistler, U Aebi, T Arvinte and G J S Cooper, *J Mol Biol,* 285 (1999) 33

The molecular connection between hormone status and bone formation is beginning to be understood and a collection of tumour necrosis factor (TNF) family proteins appear to be involved in other age-related conditions such as prostate cancer, atherosclerosis and cardiovascular disease and would be an attractive target for functional imaging studies in tissue samples.

4.1.2 Novel Therapies

The past 20 years have seen a major change of emphasis in the development of medicines from small molecule to macromolecules such as peptides, proteins, and most recently DNA. The potential of 4GLS in the study of fundamental chemistry of these materials such as protein folding and peptide-membrane interaction has already been mentioned in this proposal. These studies will inevitably have consequences for the development of drugs based on these materials. Particular areas of activity include peptide conformation, in which the use of CD has been critical in understanding the variation in potency of different calcitonin analogues[135] and DNA conformation. This latter is of particular interest due to the development of transcription-blocking agents such as antisense oligonucleotides[136] which bind to specific base sequences. The detailed effect of these agents on DNA conformation and their intracellular tracking and fate is poorly understood as most present studies simply focus on final gene expression. Studies of binding to DNA, and its conformational changes, are also of interest in understanding the carcinogenesis of cationic materials such as rhodamine or sudan dyes, many of which are DNA binding agents.

4.1.3 Drug Delivery Systems

The drug delivery community has always been among the first to exploit the potential of novel biophysical techniques to illucidate the molecular interaction between drug, delivery system, and physiology. Leading-edge techniques such as neutron scattering[137], probe microscopies[138] and surface analysis[139] have led to an improved ability to design complex drug delivery systems. The introduction of macromolecular therapeutic agents has led to an increased demand for detailed molecular structural information of this type.

A notable example of current interest is the delivery of DNA as a therapeutic agent. DNA is not taken up into cells in the free state and must be condensed into small (100-200 nm) particles with a polyelectrolyte before it can be absorbed[140]. A central problem with the devleopment of DNA delivery systems is the sequential nature of the biological barriers that must be crossed in order to achieve gene expression. The system, in this case a submicron DNA polymer complex, has to cross the cell membrane, enter the cytosol and cross the nuclear membrane before expression is possible. In addition the DNA must detach from the complexing polymer at an appropriate, currently unexplored, point. The development of techniques to control these sequential steps is impossible if only the final gene expression is

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[135] T Arvinte, A Cudd and A F Drake, *J Biol Chem* 268 (1993) 6415

[136] S Akhtar, M D Hughes, A Khan, M Bibby, M Hussain, Q Nawaz, J Double and P Sayyed, *Advanced Drug Delivery Reviews,* 44 (2000) 3

[137] C Washington, S M King and R K Heenan, *J Phys Chem,* 100 (1996) 7603

[138] S Clarke, M C Davies, C J Roberts, S J B Tendler, P M Williams, A L Lewis and V O'Byrne, *Macromolecules* 34 (2001) 4166

[139] A M Belu, M C Davies, J M Newton and N Patel, *Anal Chem* 72 (2000) 5625

[140] B J Rackshaw, A L Martin, S Stolnik, C J Roberts, M C Garnett, M C Davies and S J B Tendler, *Langmuir* 17 (2001) 3185

measured, since a change to the design of the DNA polymer system may simultaneously affect the efficiency of several of these steps and it becomes impossible to study or optimise any particular point in the chain. As a result it is essential to develop methods to study the intracellular behaviour of the DNA polymer complex in a time-resolved manner. The use of CD techniques to study the change of DNA conformation would be particularly valuable here. To do this within individual cells, to separate the conformation and dynamics of DNA at various stages of trafficking would only be feasible with a high-intensity source such as the 4GLS.

A further example of the application of 4GLS to drug delivery is the understanding of protein-surface interactions which have already been highlighted in the discussion of biomaterials. The use of colloidal particles, polymer microspheres, liposomes, *etc.*, for drug delivery and targeting is a well established field of research. The most significant problem in their use is to prevent the particles being scavenged by fixed and itinerant macrophages. The most successful approach to date is to coat or graft an outer layer of hydrophilic polymer, such as polyethylene oxide, to the particle surface, which hinders protein adsorption and subsequent recognition. However, this then also reduces the uptake of the drug-loaded particles by the target tissue *e.g.* tumour.

It is evident that what is needed is a more sophisticated knowledge of the way particles interact with cells, both in tissues and within individual cells. It is important to know:

(a) The extent of protein adsorption on surfaces, orientation, conformational change on adsorption and how this depends on the nature of the particle surface. Techniques such as time-resolved CD would be invaluable for this type of study. It is possible to envisage elegant experiments using laser tweezers in which individual cells are moved into contact with surfaces or particles and the intervening region probed by CD or resonance Raman spectroscopy to study the interstitial accumulation of proteins in a time-resolved manner.

(b) The influence of particle interfacial composition and surface molecule conformation of particle-cell interactions. This would be particularly interesting for the case of phospholipid-coated particles or emulsion droplets in which the phosphate group could be used as a spectroscopic probe to study the cell membrane-surface interactions.

(c) The behaviour of the particles inside the cell. It is increasingly necessary to deliver the drug load to a particular organelle, notably in the case of DNA delivery, to the nucleus. The ability to track the particle in the cell, and to obtain a probe of its location (membrane, endosome, cytosol, *etc.*) would allow us to understand how the particle structure influences the intracellular behaviour. This is a particular problem with DNA delivery.

4GLS is important for this type of work as the high intensities and stability enables the study of single particles interacting with single cells, thus providing information on the heterogeneity of response. This is a particular problem with biological systems, where, for example, the success of cancer chemotherapy is usually limited by the fraction of cells that are resistant to the therapeutic agent.

4.2 Industrial Exploitation of 4GLS

The capabilities of the 4GLS suite of sources will make a major contribution to fundamental work in the UK and this will lead to advances in technology in the long term. Truly industrial applications of 4GLS are relatively uncertain, but there is no doubt that the facility will catalyse innovative basic research which will in turn underpin more applied applications relevant to industry. Nevertheless we can identify fields, many of which cross disciplinary and academic-industrial boundaries, in which 4GLS is expected to foster technological advances on a shorter timescale. These opportunities are described in some detail in the letters of support for the project which we have received from groups and individuals with a direct interest in the contribution that 4GLS will make to advances in technology. At other international FEL facilities such as the Thomas Jefferson National Laboratory in the USA and FELI in Osaka a significant industrial programme has evolved simply because of the high technological capability of the laboratory including its FEL facilities. Here we draw attention to specific industrial applications where 4GLS will make a significant contribution; others will emerge but not be fully realised until the source is operational.

4.2.1 Semiconductor Technology and Electronics

The unique capabilities of 4GLS will be important to a large number of UK groups working on the development of electronic devices. The high energy resolution, high intensity and surface sensitivity of photoelectron spectroscopy made possible with 4GLS will yield major advances in the measurement of barrier heights between quantum wells and interface band offsets in semiconductor devices fabricated from both traditional, group IV, III-V, II-VI and nitrides and from organic materials. The coupling of these source characteristics with the high spatial resolution of 4GLS will become increasingly important as semiconductor device technology moves to the nanoscale. The ultra-short pulses available using the VUV and XUV photon sources are expected to give extreme improvements in spatial resolution and site selectivity during real-time etching of semiconductor surfaces. Quantum wire devices will be central to the design of the next generation of semiconducting materials where laser ablation using the 4GLS FEL technology will be important. The power of the FELs can be used to maximise overall production rates while frequency tuning can be used to optimise the ablation as well as for diagnostics. 4GLS will play a unique role in the synthesis of complex 2D nanostructures from Si, Ge, GaAs, CN, BCN and WS_2.

The flexible pulse structure of 4GLS will yield unprecedented accuracy in measurements of the timescale of electron and hole transport in these complex multicomponent and nanostructured materials. Fundamental studies such as these are critical for the optimisation of semiconductor devices such as “Quantum Cascade Lasers” which are complex devices potentially very useful for applications such as pollution monitoring. The two-colour experiments feasible using 4GLS will allow the measurement of the exact transition rates for these devices. Without these experiments, transition rates between lasing states (which are both excited states) are very difficult to measure because of different types of scattering competing with the useful optical transition.

4.2.2 Manufacturing Process Improvement

The drive to improve manufacturing processes to either reduce costs or to develop higher quality products is well established within competitive industries. Lead technologies such as 4GLS will provide industry with competitive advantage in these areas. Indeed, at the Jefferson Laboratory, a Laser Processing Consortium involving major companies, DuPont, 3M, IBM, Xerox, Armco and Northrop Grumman, has been established to exploit the UV and IR-FELs to do just this. It is anticipated that industry will use 4GLS for three major purposes in this area:

i) Development of high performance materials - to conduct research which will exploit the high brightness, tuneability and narrow beam collimation to optimise specific processes and macroscopic performance of materials through phase domain and layer analyses of polymers and composites. These are typically low étendue, energy limited, near and far-field infrared studies which require high signal-to-noise, high spectral contrast spectra at high lateral spatial resolution over a wide wavelength range to be recorded from throughput limited sample domains. The infrared offers superior spatial resolution for studying the structure and function of polymeric materials using micro-spectroscopy, being of technological importance in applications as diverse as upholstery foam and electroluminescent displays. There is a myriad of opportunities with polymer blends. For example, to gain the full advantage of organic electronics patterning technologies being developed for cheap, disposable displays, IR microspectroscopy will facilitate full working chemical understanding. A rapidly expanding market in composite materials is the use of polymer blends for targeted drug release. Uptake and release studies rely on measurement of active species in solution. It is becoming increasingly important to examine the composite itself and in particular its surface structure and the nature of binding of the active species. Non-linear techniques such as sum frequency generation will become an increasingly important surface analysis technique for complex systems such as these.

ii) Chemical engineering enhancements – chemical engineering is undergoing a tremendous upheaval, with the traditional emphasis on large scale processing involving powders, complex distillations and separations, as in the petrochemicals industries, being extended to include smaller scale batch processing of soft solids and complex fluids. The global drive to shorten development times for new processes and formulations requires a molecular-based understanding of the systems involved. This can only be obtained from a combination of detailed measurements (a wide variety, preferably on-line), computer modelling (over a range of length scales) and thermodynamics, which relate macroscopic behaviour to chemical (molecular) structure. The 4GLS facility represents a world leading facility that will provide measurement abilities including IR and THz imaging, with stations which will be utilised in conjunction with the recently funded JIF Pilot Plant at UMIST. The Pilot Plant is aimed at providing a modern facility for the manufacture of a wide range of multi-phase materials where details of structure, flow and mixing kinetics can be studied on and off-line by numerous techniques (spectroscopic and thermodynamic). Applications include:

- Imaging of flow in pipes of multi-phase products, including complex geometries and extensional flow
- Mixing processes (including dissolution and drying) in complex non-Newtonian fluids such as surfactant liquid crystals
- Structure development in multi-phase soft solids (surfactant/polymer/dye-drug mesophases)

- Powder flow processes, granulation and compaction into tablets in the presence of liquids and liquid crystals – formation of meta-stable phases, dissolution/dispersion kinetics.

The M^2C initiative at UMIST (the North West Centre for Molecular Materials Chemistry and Processing) aims to work with the Chemical industry to enable the world-class skills in materials and colloid science of North West Universities to be employed in product formulation and processing of Industry. At least 15 Companies are already interested including Unilever, ICI, Syngenta, Avecia and other multi-nationals as well as many SME's. The range of products to be studied include pharmaceuticals, agrochemicals, catalysts, speciality chemicals, coatings, household cleaners and personal care products.

iii) Production line FEL processing (R&D) - the high peak power, tuneability and pulse structure of the FEL output will enable its use in the modification of surfaces by ablation or selective recrystallisation. For example, in the area of polymer processing, when tuned to 5.85 μm for PET (polyethylene terapthalate) and 6.11 μm for Nylon, the carbonyl absorption band, the FEL output may be used to impart ordered surface structure on a dimensional scale of 5 to 10 μm. This technique is being used by Dupont to treat nylon film so as to make it resistant to bacteria and to micro-roughen polyester fibres to impart natural fibre characteristics. The consortium at Jefferson Laboratory are evaluating FEL technologies for long-term installation on production lines. Use of FELs will boost production of modified polymer products by a factor of 10 over conventional laser systems. The polymer sector is only one industrial community evaluating the impact of FEL technology on manufacturing process improvements. Other examples include metals processing by companies to develop wear and corrosion resistant materials and those companies developing novel lithography techniques for nanodevice fabrication.

4.2.3 Display Technology

Optimisation of organic light emitting diodes (OLED) for display devices will be achieved using state of the art low energy photoemission techniques, time resolved excited state photoemission and pump probe experiments of various sorts that will be available on 4GLS, as described in Section 3.2.4.7. Opsys Ltd., a spin-out company of Oxford University, has shown significant interest in 4GLS for applications in this area.

4GLS will also facilitate the development work on phosphor materials which convert infrared radiation into visible light *via* multiphoton absorption steps which is taking place at the Centre for Phosphor Research in Greenwich. The efficiency of the non-linear processes on which the properties of these phosphors depend is highly dependent on the incident light power so the combination of the intense source provided by the infrared FEL together with the pump-probe capabilities of 4GLS is an ideal combination for studying them.

4.2.4 Study of Growth Processes

The 4GLS project is strongly supported by the EPSRC funded Network on CVD growth which is a collaboration between twenty academic groups and six industrial concerns (Pilkington, Epichem/Inorgtech, Thomas Swan, QinetiQ, Optical Reference Systems and Agilent). The Network is concerned with the development of growth technology for use in the fabrication of a range of materials including semiconductors, complex oxides, organic films and diamond.

Applications in this field will benefit considerably from the use of the Free Electron Lasers of 4GLS in pump-probe studies of surface-adsorbate species important in growth. For example using RAIRS to study the effects of surface phonon excitation on the structure of CVD precursors. The combination of a reflection anisotropy microscope and spectrometer on 4GLS will make a major contribution to the studies of companies such as De Beers Industrial Diamonds which is continually searching for improved methods of monitoring and controlling the CVD growth of diamond surfaces.

4.2.5 Nanomaterials and engineering

The primary thrust of nanomaterials research has been to develop, characterise and understand the physics and chemistry of these novel systems. The progress in the manufacture of new nanodevices is pushing the limit of knowledge about the optical properties of materials in the UV and VUV. Fabrication devices are being planned for using 190 nm and 120 nm radiation with instruments planned for 12 nm lithographic devices. The US Department of Commerce has proactively funded this area of research. In the short term using clusters as building blocks will enable the production of very high performance materials and in the longer term they will be central to emerging technologies such as spintronics, single electron devices and quantum computing. In contrast to conventional laser sources, with relatively long pulse lengths, 4GLS will enable real-time high throughput nanofabrication and growth characterisation which is of great interest to QinetiQ. For example, using two-photon photoemission spectra to characterise individual metallic and semiconductor nanowires.

4.2.6 High Throughput Screening (HTS) of Bio-assays

As the human genome sequence nears completion and gene identification and annotation efforts provide researchers with overwhelming quantities of genomic information, DNA microarrays are emerging as an important tool for parallel analysis of gene expression and gene variation. These same devices are revolutionising proteomics and screening for potential drug candidates. Traditional 2D gel electrophoresis followed by time of flight mass spectrometry is rapidly becoming the bottle-neck in the identification process and is poor for isolation of membrane proteins and quantitative analysis. Microarrays coupled with robotics and CCD array detection are improving throughput dramatically and moving towards bio arrays for single molecule detection using near field methods. A consortium comprising UMIST, Liverpool, Manchester and CLRC has recently been successful in obtaining £2.4M of funding to design, fabricate and model prototype microsystems for pharmaceutical drug target identification. Although this technology is state-of-the-art, it is still relient on the use of fluorescent labels for probing binding sites and potential drug targets. As technology pushes towards even more rapid throughtput, more sensitive detectors capable of measuring very low light levels will be required. The high intensity of the VUV-FEL in 4GLS will have a role to play here. The ultimate vision for HTS in the long term is to move from fluorescent probes, to techniques which are “tagless” *i.e.* rely only on the signals derived intrinsically from the proteins and drugs themselves. Circular dichroism on 4GLS may be a key technique for identifying protein-drug binding interactions without the need for fluorescent markers. It is ideally suited to high throughput methods and array detectors, robotics and databasing methods are currently under development for use on the SRS. Several letters of support (Medichem, Manchester Innovations Ltd., Farfield Sensors and CLS Inc.) have identified CD as an important method for future HTS developments for industrial research.

4.2.7 Instrumentation Development Outreach

The high photon fluxes and pulsed nature of the 4GLS sources will require significant developments in associated accelerator, detector and data handling capability. New imaging detectors able to handle high count rates and multiple data streams arising from pump-probe experiments will be essential. These systems will be built in collaboration with CLRC Centre for Instrumentation and industrial partners such as QinetiQ who have substantial IPR in related fields. Furthermore, a confidential Memorandum of Understanding has been signed with Manchester Innovations Ltd to develop its novel detection technology on the VUV and IR-FELs. This will revolutionise fluorescence lifetime imaging capabilities of 4GLS and commercial markets have already been identified. Dstl Porton Down has shown significant interest in the detection capabilities of 4GLS for bio-particle characterisation. The ultimate aim will be the development of "in-field" detection devices for use by UK MOD. Other infrastructural technologies such as the GRID, e-science, high performance computing, visualisation and robotics are all planned developments at Daresbury and will be integrated into the 4GLS strategy. Commercial opportunities are already being negotiated with companies in several of these areas.

4.2.8 Wider Exploitation Avenues and Networks

The vision for Daresbury Laboratory is one which has a vibrant international science activity centred around the CASIM large scale facilities and very strong integration with the universities in the NW region. Beyond this, it is the intention of CLRC and the NWRDA to establish a joint venture company which will identify IPR within the organisation and incubate start-up companies in a science park under development at Daresbury. Equity realised from these companies will be reinvested in the facilities on-site for the benefit of the academic community. In this sense, 4GLS will exist as a state-of-the-art research facility in symbiosis with a strong commercial environment. This model has been adopted at the Jefferson Laboratory in the USA where local universities, industry and the FEL facility are successfully working together. The Jefferson Laboratory has officially recognised the 4GLS project by agreeing to donate an undulator FEL to initiate the R&D programme for the machine. Other international facilities have seen the industrial potential of 4GLS once it is operational. A tripartite Memorandum of Understanding is currently being negotiated between Canadian Light Source Inc., Medichem (APS) and DARTS (SRS) for seamless industrial access to the three synchrotrons. This agreement also identifies 4GLS as a facility which will extend the technique portfolios of each of the participants.

5 FACILITY DESCRIPTION

5.1 Concept

The exploitation of synchrotron radiation has evolved over several decades into the present situation, commencing with small scale parasitic usage but followed by construction of a large number of dedicated electron storage rings: the very first such low energy source was at a university in the USA but the UK became the world leader with its operation of the SRS in 1980. This and other such rings were therefore second generation light sources that relied heavily on radiation from their bending magnets. The next major development was the design of a new (third) generation of sources that instead utilised specialised magnetic insertion devices (IDs) called undulators located in extended spaces within a complex arrangement of ring focussing elements: the ESRF at Grenoble is an advanced example of this, as is the new UK source *diamond*[141].The principal characteristic of these sources is their extremely high average brightness output.

In parallel with these developments has been a related programme to demonstrate the potential of another, related source: the free electron laser (FEL). Such sources extend the interaction between the electrons and the undulators into a regime where huge brightness increase can be obtained, generating laser-like output. So far a number of infrared user facilities, based on low energy electron linacs, have been established (*e.g.* FELIX[142] in the Netherlands, with EPSRC supported UK users, and CLIO in France) and there have also been a limited number of attempts to transfer the technology onto storage rings at higher electron energy: in Europe two such devices are in operation at the national light sources Super-ACO (France) and ELETTRA (Italy)[143]. These FELs all use mirrors to trap the emitted radiation in optical cavities, with consequent restrictions from falling reflectivity at higher energies. Recently, however, there has been great excitement at the demonstration of higher energy photon output from an alternative accelerator, the high brightness electron linac developed at DESY (Germany) as a prototype for a future particle physics collider (TESLA); in this case a regime (known as SASE) of such high gain is employed that mirrors can be avoided[144].

Synchrotron light sources based on storage rings are a successful but highly mature discipline with limited scope for further improvements. Enhancing their output brightness is hampered by the very emission process for which they are created, since the associated electron recoils shake up the beam: their source cross section can only be reduced by building ever larger rings, such as the 'ultimate' third generation source of 2 km circumference proposed as a successor to the ESRF. The duration of radiation pulses from a storage ring is also similarly restricted and cannot be less than some tens of picoseconds. Furthermore even if much brighter beams could be established there is another major problem: the high electron density leads to increased beam losses and resultant lifetime collapse of the stored beam; this effect is particularly severe in electron rings of relatively low energy (*i.e.* less than about 1 GeV). A final third generation source problem is the inability to exploit IDs with very small magnet gaps (*i.e.* a few mm) since again the stored beam lifetime is seriously compromised. The solution to these serious

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[141] M W Poole *et al.*, *Proc Part Accel Conf*, Chicago, 2001

[142] G von Helden, I Holleman, M Putter and G Meijer, *Nucl Instrum & Methods Phys Res*, 144 (1998) 211; see also http://ns2.rijnh.nl/n4/n3/f1234.htm

[143] R P Walker *et al.*, *Nucl Inst Meth A,* 429 (1999) 179

[144] A M Kondratenko and E L Saldin, *Part. Accel.* 10 (1980) 207; T Orzechowski *et al.*, *Phys Rev Lett*, 54 (1985) 889; K-J Kim, *Phys Rev Lett*, 57 (1986) 1871

weaknesses is to consider the adoption of alternative accelerator technology, in particular the use of electron linacs that have already demonstrated great success in existing FEL experiments.

Exploiting the latest linac technology advances and combining the positive features of a traditional light source (high average power and brightness) with those of advanced FELs (high peak power and brightness), enables a step change in capability to produce a true fourth generation source as is now proposed: the 4GLS project.

5.2 Facility Overview

5.2.1 Energy recovery linac concept

The selection of a high brightness linac as the chosen accelerator of an advanced radiation source has been made feasible by the recent milestones achieved utilising this technology. Obtaining extremely high brightness electron beams has been the development goal of two very separate world activities: linear colliders for particle physics, and x-ray SASE FELs. Recent progress on colliders has included the operation of the TESLA Test Facility (TTF) at DESY and the release this year of the comprehensive Design Study for the full TESLA facility. Furthermore a major R&D programme is underway in the USA to extend operation of SASE-based FELs to very short wavelengths, with a series of experimental successes already demonstrated[145]; the TTF-FEL is a parallel and significant existing development[146] and an x-ray FEL version is now an integral part of the major DESY TESLA proposals.

Despite their high peak brightness capabilities linacs have not traditionally been a challenge to storage rings in the case of average power. A beam of electrons in a storage ring can efficiently reach high average current levels (several 100s mA) due to frequent re-passage of its circulating particles: the electron beam itself has relatively low intrinsic power. In contrast the single transit linac beam has huge equivalent power at the same mean current level (*e.g.* a 100 mA current at 500 MeV represents 50 MW!); as a result linacs usually have had a very low duty cycle. The solution is to restore efficient operation by returning the linac output beam into the accelerator after it has been used, but on this second passage to decelerate it in order to recover its energy.

The energy recovery linac (ERL) principle is an old one, perhaps originating at Cornell[147]: it was first demonstrated during early FEL studies both at Stanford[148] and Los Alamos[149] laboratories about fifteen years ago. It has also been proposed by the Russian team at Novosibirsk. However it is only very recently that it has received wide attention with the successes of two advanced projects at the Jefferson Laboratory in Virginia. The first of these is a multi-GeV nuclear physics facility (CEBAF) and the second is an infrared FEL that has exceeded 2 kW output power. Their ERL for the IR radiation source has so far reached an average current of 5 mA at 50 MeV, but a 20 mA upgrade project is underway; even higher currents are being pursued in several R&D programmes in the USA (a 100 mA proposal has been made[150]). The Jefferson team has already demonstrated recovery of in excess of 99.98 %

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[145] G R Neil *et al.*, *Phys Rev Lett,* 84 (2000) 662; S V Milton *et al.*, *Proc. EPAC 2000*, Vienna, p755
[146] J Andruszkow *et al.*, *Phys Rev Lett*, 85 (2000) 3825
[147] M Tigner, *Nuovo Cimento,* 37 (1965) 1228
[148] T I Smith *et al.*, *Nucl Instr Meth A* ,259 (1987) 1
[149] D W Feldman *et al.*, *Nucl Instr Meth A,* 259 (1987) 26
[150] S M Gruner and M Tigner, *CHESS Tech Memo* 01-003, Jul 2001

of the beam energy (ie less than 1 μA lost). The above results give confidence in proposing a 4GLS facility based on the same principles, and this is illustrated conceptually in Fig. 1.

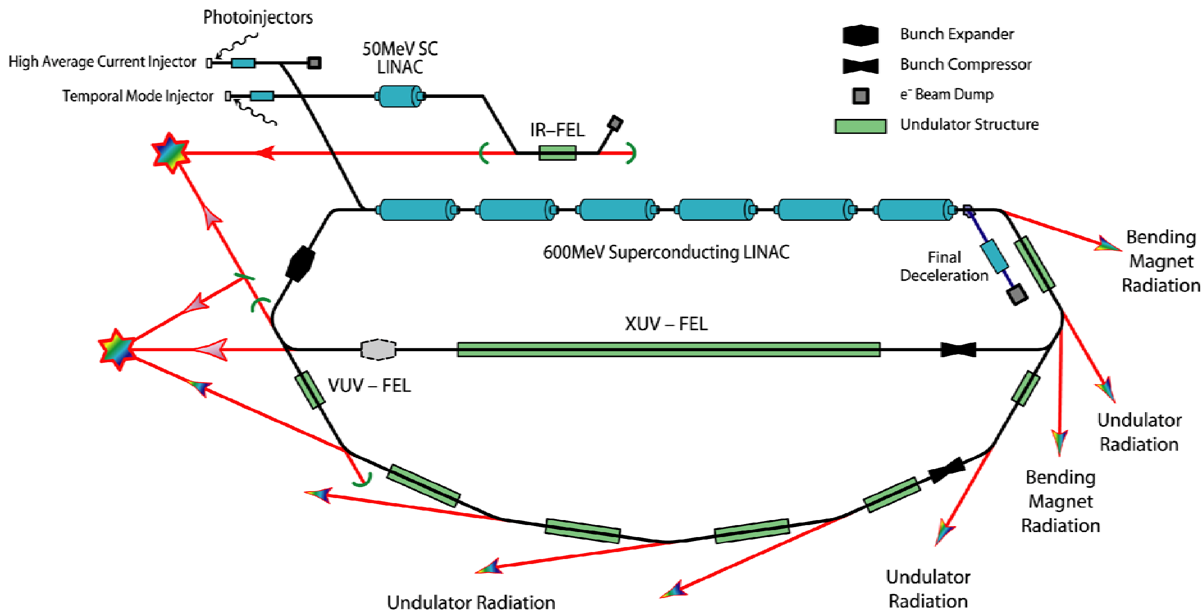

Figure 1 Concept schematic diagram for 4GLS

An electron beam of high brightness but low energy (5-10 MeV) originates in one of the two injectors and is transported into the superconducting linac structure which boosts it to 600 MeV. The extracted beam passes through a series of bending and focussing magnets, interspersed with spaces for IDs in a layout analagous to that of a storage ring but with much greater flexibility in its local characteristics: undulators with a wide variety of lengths, gaps and field strengths can be employed and the electron beam itself can have both its transverse dimensions and its bunch length tailored to the demands of each beam line. Inclusion of three independent FEL facilities is also shown in the figure: an infrared one utilising a lower energy electron beam extracted part way along the accelerator; a VUV one in the same path as the synchrotron light source beam transport line; and an XUV one in its own separate, parallel path. Finally the beam returns to the linac entrance, is decelerated back to its injection energy and eventually deposited in a beam dump. The whole accelerator system is driven by phase-locked radio-frequency (RF) generators that allow synchronisation of its many radiation sources for pump-probe experimentation.

The following sections examine each major aspect of this revolutionary source concept in more detail.

5.2.2 Beam dynamics

A high brightness beam is initially generated in the injector, probably from a photo-cathode illuminated by a mode-locked laser[151]. Electrons must be accelerated to relativistic energies as soon as possible in order to overcome intense space charge effects and this will be done in a closely coupled, small RF accelerator structure delivering 5-10 MeV output. An emittance compensation scheme will be included to maximise beam brightness. At this stage the RF-modulated electron beam will comprise a train of bunches each of length about 10 ps. A short beam transport line must preserve good beam properties up to the linac entrance.

A superconducting linac structure is essential to support the high average powers that are planned. It must transmit simultaneously both accelerating and decelerating beams (separated by π in phase) and this doubles the current and the associated beam loading effects. Superconducting RF structures have high impedance and this can induce the well known phenomenon of beam breakup (BBU) at high beam current levels, caused by wake fields induced by passage of electrons and a positive feedback effect. Threshold predictions depend on exact parameters but the process can be suppressed with careful selection of focussing parameters (including contributions both from the linac RF fields and the supplementary effect of external magnets distributed along the linac) and also by use of feedback systems. The double beam effect mentioned above does complicate the energy dependent dynamics[152] and may in principle restrict the ratio of input to output beam energies, but a factor of about 100 is almost certainly still achievable. Finally damping of higher order modes (HOMs) in the structure will be essential to minimise both instabilities and unwanted power losses.

The 600 MeV beam emerging from the linac will need to be carefully controlled in the subsequent transport line. The overall path length must be exactly matched for the reinjection to the linac and the beam at each of the defined IDs must also be well optimised. The major system components are the two 180 degree arcs and these will comprise achromatic and isochronous sections of a type familiar to accelerator ring designers, including highly accurate steering control systems. Another topic of potential importance is positive ion trapping in the intense electron beam, a process familiar in electron storage rings; however this has proven relatively unimportant in the Jefferson experiments. The most challenging feature of the transport line will however be its compressor sections, designed to vary the bunch length over a range from several ps to 100 fs or less. The principle has been well developed at linear collider laboratories and involves a chicane of four bending magnets to exploit energy correlated variations along the bunch length (*cf.* chirped pulse control in lasers). The beam dynamics is greatly complicated by radiation emission in these bends in the case of sub-ps bunches, in particular the phenomenon of coherent synchrotron radiation (CSR); however this process will probably only be important at bunch lengths well below 1 ps, when it could induce both significant energy loss and emittance growth. The ultimate short bunch limit that can be achieved for experiments will probably be set by this limitation and will require extensive design optimisation, with full pulse compression not applied to beams as they traverse the main arcs in order to minimise these effects. It may prove necessary to decompress the bunch length before its reinjection to the linac to avoid wake field effects in the accelerating structures.

Transport to the infrared FEL will not pose particular problems as the beam of about 50 MeV will have bunches of a few ps duration and emittance control is in any event much less critical

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[151] C Hovater and M Poelker, *Nucl Instr Meth A* , 418 (1998) 280
[152] L Merminga *et al.*, *Nucl Instr Meth A* , 429 (1999) 58

for diffraction limited radiation at these long wavelengths. The average current associated with this will be too low to necessitate energy recovery and the structure, its power feed and its cooling are all far simpler than the main linac systems. Electron beam properties required for the VUV-FEL will be no more demanding than for many of the other (spontaneous) radiation sources distributed around the transport loop, with one exception: it will be important to achieve suitably high charge in a single electron bunch since this optimises the FEL interaction that occurs at this local level. This may imply an extension of the pulse sharing mode, at least for optimisation of the shortest output wavelengths. An alternative is to impose substantial bunch compression before the interaction region.

For the XUV-FEL a major change in beam properties is essential, with extremely high charge in a bunch requiring a separate photo-injector source, operating with a much lower duty cycle; it may be possible to pulse share between the two injectors but this will have to be confirmed at a more detailed design stage. The XUV-FEL demands extremely high peak bunch currents (ca 1 kA) and this will necessitate upstream bunch compression approaching 100 fs (see above comments, including CSR effects). These high peak currents are vulnerable to disruption by associated strong wake fields in nearby metallic chamber walls and this effect will need to be modelled and minimised. A particular issue is the dynamics within the interaction undulator itself, with probable small magnet gaps and complex distributed focussing and correction systems. Such dynamics optimisations are already undertaken for all existing SASE FEL projects.

5.2.3 Injectors

The beam current delivered by a photo-cathode is proportional both to the input laser power (P_L) and to the quantum efficiency (QE) of its cathode material. To achieve 100 mA average current implies a (P_L.QE) product of 20-50 W-%: the optimum choice is a high QE semiconductor (*ca*. 10 %) that limits the laser average power to a few watts and has the added advantage of requiring visible wavelengths if a negative electron affinity material is chosen. A possible solution is a cesiated GaAs cathode driven by a mode locked Ti-sapphire laser at a 260 MHz fundamental frequency, delivering a train of 20 ps pulses containing up to 100 pC of charge and allowing phase locking to the 1.3 GHz accelerator via a gain switched diode laser. The cathode will be best embedded in a DC gun that can be operated at 500 kV, probably the maximum voltage that can avoid breakdown in this mode; the alternative RF gun structures adopted by some teams can run at higher voltages but tend to have poorer vacuum performance and this is critical for achieved cathode lifetimes with this material, where ion back bombardment sets the performance limit. The ultimate solution for desirable high energy guns may be a complete superconducting one, possibly with the cathode itself formed from a niobium button: experiments on this have commenced both in USA and Germany, although QE values are very low with metallic cathodes.

Although the partially relativistic 500 keV electron bunches are very vulnerable to space charge forces lowering their brightness it is possible to compensate this to a large extent with a solenoidal emittance compensation scheme, as has been demonstrated on the Jefferson project and elsewhere. The room temperature gun is then integrated with a cryogenic post-accelerator to boost the energy to a few MeV and ease the quality control problems.

For the alternative operating mode of the XUV-FEL a different gun solution is required. In this case a low duty cycle is acceptable so that average power limitations no longer apply. Advantage can be taken of the technology developed for linear colliders and already applied to earlier FEL experiments. Metallic cathodes can deliver the required beams and be conveniently buried in an RF gun structure. Charges of several nanoCoulomb per bunch have already been demonstrated and the 4GLS XUV-FEL project would not need to achieve a quality as high as the projected x-ray ones. A copper or magnesium cathode is a proposed solution at present, coupled with a UV drive laser probably running at 0.1 % duty cycle; however alternatives such as Cs_2Te will be considered.

Both proposed guns are clearly feasible, and indeed there is already commercial interest in their supply. However the record mean current in any such gun so far is 32 mA by Boeing[153], albeit run at 25 % duty cycle (*i.e.* 128 mA pulsed current). A more similar gun is the Jefferson one and an R&D phase is clearly needed to discover the optimum solution for the 4GLS target of 100 mA (or more in the longer term). The XUV-FEL gun will also benefit from an R&D programme to optimise performance. This whole topic is ideal for Daresbury and Rutherford Laboratory involvement through the ASTeC accelerator centre, the Central Laser Facility and the surface science expertise within the Synchrotron Radiation Department.

5.2.4 Linear accelerator

Superconducting RF structures have been used in accelerators for more than 20 years, including the world's first FEL experiment at Stanford in 1977. However it is only recently that they have attracted widespread interest. Large scale systems have been pioneered both at Jefferson Laboratory and at CERN. The technology has now been adopted for *diamond* and for its French equivalent, SOLEIL. It is also the selected system for the DESY linear collider linac TESLA and there has been extensive prototype manufacture for the Tesla Test Facility (TTF): this has achieved accelerating gradients of 20-25 MeV/m at the 1.3 GHz operating frequency, and for the present time can be taken as a baseline design for 4GLS, indicating minimum realistic operating performance.

The TTF standing wave structure comprises a stack of nine cells forming a single cavity 1 m in length, with eight such cavities contained in a cryo-module operating at 2K. The modules contain full instrumentation, including beam diagnostics. Since they have only been tested up to 1 % duty cycle a conservative gradient of 15 MeV/m will be assumed, implying a total of five such modules to deliver 600 MeV beams and a total length of at least 40 m; this will probably allow useful longer term energy upgrades. The associated RF power source driving these modules will be 1.5 MW, probably a set of klystrons feeding individual modules. A large cryogenic plant will also be necessary; although each module has static losses of less than 4 W at 2K and 13 W at 4.5K, the dynamic losses are much larger: even at 15 MeV/m probably in excess of 100 W per module. Overall optimisation of structure, power feed and cooling will be a significant design study task.

As already discussed, there is a potentially major issue of HOM losses. The existing DESY design has two HOM output couplers per cavity but these are probably inadequate for CW operation and will need redesign. Predicted CW HOM losses could be greater than 100 W per cavity so that it will be essential to couple out almost all of this HOM power in a modified design. The problem could be reduced further if more effective HOM damping were to be introduced too.

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[153] D H Dowell *et al.*, *Appl Phys Lett,* 63 (1993) 2035

In conclusion, a feasible route exists to upgrade the TTF modules for 4GLS application. However this area will benefit from an extensive R&D programme to examine superior alternatives and to optimise cost factors.

5.2.5 Undulators

The 4GLS project is able to take advantage of the many dramatic developments in undulator technology that are ongoing, both in synchrotron light sources and FELs. Narrow gap, short period undulators are already under investigation for *diamond*, as are variable polarisation devices based on planar permanent magnet solutions. Similar magnets are required for the infrared and VUV-FELs, and the latter can double up as a 'standard' light source beam line when the mirrors are removed.

The XUV-FEL undulator does however present extraordinary challenges. It is likely to be 30-50 m in length, although constructed from shorter modules, and it will certainly incorporate advanced beam focussing and steering. Nevertheless it is not as demanding as an x-ray version as planned at DESY and SLAC in future facilities.

Application of anticipated undulators to 4GLS output is explained in more detail later in this report.

5.2.6 Other technical features

Comprehensive diagnostic systems will form a crucial part of such a facility, with precise beam control being a high priority necessitating advanced feedback systems. Measuring such high brightness beam dimensions will require specialised developments, especially in the fs time regime. It will be equally important to ensure very precise control of equipment parameters if optimum performance is to be guaranteed. A major feature will be the synchronisation of systems at the sub-ps level, implying suppression of jitter at a similar range.

Although overall high cleanliness is essential and low pressures in the regions of high voltage acceleration fields are necessary, the 4GLS complex does not have the exacting standards of a storage ring and in general pressures of several nanotorr are more than adequate in most areas. The exceptions are the photo-cathodes that must be protected from deterioration and the superconducting RF structures that must be carefully conditioned and preserved.

Protection of both personnel and equipment will be based on extensive interlock protection schemes, as is normal in such accelerator based facilities. In the case of an ERL it will be essential to detect and protect against even low beam losses in either the accelerator or transport lines. The beam dump at the linac output will also need careful specification: power levels up to 1 MW may have to be handled and this is probably best dealt with by incorporating a further RF deceleration scheme to dissipate such high power into an RF field rather than a target material.

The *diamond* project will adopt the EPICS toolkit as its main controls system and it seems likely that 4GLS should follow this lead and exploit the growing UK knowledge base. Integration of radiation beam lines with the source control system is essential for efficient operation of such an advanced source with its complex operating modes. The degree that this can be extended to the user equipment, data acquisition and on-line analysis will need to be considered carefully, but great benefits will follow from a wholly integrated approach.

6 THE PHOTON SOURCES

The unique feature of 4GLS is the facility to provide state-of-the-art VUV and IR light sources which can be used either singly or in synchronism, opening up an entirely new range of high intensity and pump-probe experiments, This section gives the details of the radiation sources contained in 4GLS, which will permit the experiments described in the scientific case to be carried out.

The facility is based, as described in an earlier section, on a superconducting energy recovery linac. The photoinjector cathode electron guns provide a very flexible pulse-pulse structure and pulse lengths as short as 50 fs will be achievable. The radiation will be generated in free electron lasers, undulators and bending magnets.

6.1 Stimulated SR from Free Electron Lasers

As indicated in Figure 1 (see Section 5.2.1) three free electron laser sources are envisaged for 4GLS. Between them these sources will provide tunable, extremely intense and fully transversely coherent radiation from the far infrared, through the visible to the extreme ultraviolet/soft x-ray region of the spectrum. Although the lasers proposed for 4GLS have not been designed in detail, using the considerable amount of information on such sources either currently working or proposed elsewhere, is possible to convey their anticipated performance with a reasonable degree of confidence.

6.1.1 The IR-FEL

The IR-FEL will cover the far-IR region and will generate sub-picosecond laser pulses in the range 3 to 75 μm (0.4 – 0.017 eV) though it will be optimised for wavelengths longer than 5 μm; its main characteristics, under illustrative operating conditions, are given in Table 1 below. The use of advanced photoinjectors together with superconducting linac technology means that the 4GLS IR-FEL will deliver shorter pulses, with better energy stability and higher average power than possible at the few existing European IR-FEL sources. The 4GLS IR-FEL will be based on a multi-pass optical cavity and its output will be diffraction and transform limited over its operating range. It will have the facility to operate either independently or in conjunction with the other 4GLS sources. The electron beam for the IR-FEL will have an energy of up to 50 MeV.

Table 1 Illustrative output characteristics for the IR-FEL in 4GLS

Infrared FEL undulator		**Photon output**	
Period	40	Average photon flux	2×10^{23}
Length	2 – 5 m	Peak photon flux	4×10^{28}
Electron beam		Number of photons per pulse	2×10^{16}
Charge per bunch	80 pC	Energy per pulse	70 μJ
Pulse length	0.2-1 ps	Average power	900 W
Repetition rate	10 MHz	Peak power, W	$\sim 10^{8}$

6.1.2 The VUV-FEL

It is proposed that the VUV-FEL be based on an optical klystron arrangement. Such systems have been successfully implemented in several storage ring facilities. For example, EUFELE on ELETTRA which has lased at wavelengths from 356 nm to 190 nm and the free electron laser on Super-ACO which has operated from 350 nm to visible wavelengths.

The success of existing storage ring cavity FELs has depended heavily on the development of very high reflectivity multilayer mirrors, with reflectivities of 95% or better[154], and this has limited the short wavelength performance of current devices to ~190 nm. Mirror technology is still advancing, and it is confidently expected that, by the use of pure Al mirrors, the limit will be extended to 120 nm in the near future, the radiation being extracted through a small aperture in the mirror[155]. 4GLS has a particular advantage over storage ring devices, in that the higher bunch charge combined with shorter bunch lengths and a long undulator results in improved gain (by a factor of *ca.* 5) and hence the mirror performance is not so critical. Nevertheless, the greatest technological challenge associated with a VUV-FEL is the development of high quality, normal incidence, cavity mirrors that can simultaneously withstand the high power load of the photon beam and yet reflect efficiently at wavelengths below 190 nm, and this is a prime target of the current, EU funded project on EUFELE.

As an illustrative example, estimates for the performance of the VUV-FEL in high average photon flux mode, (assuming a bunch charge of 200 pC and a repetition rate of ~6 MHz) are given in Table 2. Even though the average current is only about 1 mA, the figures in Table 2 show that the average flux and brightness for the VUV- FEL should be 3 orders of magnitude higher than the spontaneous output from storage ring undulators. The table also reveals that the VUV-FEL has the capability to deliver as many photons in a single, sub-picosecond, pulse as present, 3rd generation, SR experiments receive per second.

Table 2 Illustrative output characteristics for the VUV-FEL in 4GLS

Example VUV-FEL undulator		**Photon output (at 5 eV, 248 nm, based on 100W average power, 0.5 ps pulse)**	
Period	50 mm	Average photon flux	~10^{20} ph/s
Length	7 m	Peak photon flux	~10^{25} ph/s
Tuning range	vis-10 eV	Number of photons per pulse	~10^{13}
Electron beam		Energy per pulse	~16 μJ
Charge per bunch	200 pC	Average brightness	~10^{21} ph/(s mm^2 $mrad^2$ laser bandwidth)
Average current	1.25 mA	Peak brightness	~10^{26} ph/(s mm^2 $mrad^2$ laser bandwidth)
Peak current	80 A	Line width, FWHM	~ 5 x 10^{-4}
Pulse length	0.2-1 ps	Peak power	12 MW
Repetition rate	6.25 MHz		

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[154] K Yamada, N Sei, H Ohgaki, T Mikado, S Sugiyama and T Yamazaki, *Nucl Inst Meth A*, 445 (2000) 173

[155] M Marsi, R P Walker, L Giannessi, G Dattoli, A Gatto, N Kaiser, S Günster, D Ristau, M E Couprie, D Garzella, J A Clarke, M W Poole, submitted to *Applied Physics Letters*

In summary, the VUV-FEL has the potential to generate sub-picosecond, VUV laser pulses in the range visible – 10 eV with broad tunability. Output at selected energies higher than this may also be possible, depending on the availability of sufficiently robust multilayer mirrors with high reflectivity. With a peak brightness of around 10^{26} ph/(s mm^2 mrad^2 laser bandwidth) the output of the VUV-FEL will be 5-6 *orders of magnitude* more intense than the spontaneous VUV radiation from undulators on third generation sources.

6.1.3 The XUV-FEL

Without the constraints of a cavity and its associated mirrors the XUV-FEL can potentially generate photons well into the extreme ultraviolet/ultra soft x-ray region of the spectrum. Intense, short duration electron bunches are fed into a long undulator and interaction of the spontaneously emitted radiation with the electrons within the bunch leads to stimulated emission – so called SASE (Self Amplified Spontaneous Emission). The intensity and coherence of the emitted light builds gradually to saturation down the undulator. In addition to being very demanding in terms of the required electron beam characteristics, good electron beam diagnostics and a long, high-precision, undulator are also necessities (for example, a 15 m undulator is used at TTF). The SASE principle was first demonstrated at the University of California Los Angeles at a wavelength of 16 μm, and recently the TTF has achieved saturation at 98 nm.

The electron bunch characteristics required for the XUV-FEL are so different from demanded by high average current operation that two photoinjectors are proposed for 4GLS.

The XUV-FEL intended for 4GLS is technologically far less demanding than that required for x-ray free electron laser projects such as the LCLS (Linac Coherent Light Source) and the XFEL project at DESY, since it will not be required to provide hard x-rays. Even so, it will be a state-of-the-art device, and its detailed design will be undertaken as an integral part of the 4GLS design study. Illustrative XUV-FEL properties are given in Table 3.

Table 3 Illustrative output characteristics for an XUV-FEL in 4GLS

XUV-FEL undulator		**Photon output at 100 eV**	
Period, mm	24	Average photon flux	$3x10^{18}$
Length	~30 m	Peak photon flux	$3x10^{26}$
Electron beam		Number of photons per pulse	10^{14}
Charge per bunch	1000 pC	Energy per pulse	2 mJ
Average current	0.04 mA	Average brightness	~ 10^{22}
Peak current A	400 A	Peak brightness	~ 10^{29}
Pulse length	0.2-1 ps	Resolving power	10^3 - 10^4
Micro bunch Repetition rate	65 MHz	Photon pulse length	~100 fs
Pulse per macro bunch	650	Peak power	4 GW
Macro bunch repetition rate	60 Hz		

6.1.4 Seeding

The natural photon pulse shape from a SASE FEL is not smooth like a cavity FEL output but is intrinsically spiky, both in energy and time. It will be essential for many experiments, particularly those seeking to exploit the possibilities for multiphoton ionisation in the XUV, to improve the temporal coherence of the source. Considerable time and effort has already been expended on this issue by teams involved with the TESLA FEL and the BESSY FEL projects[156]. The result will be a much shorter pulse length - ~100 fs - with ideally a bandpass which is Fourier transform limited, ~20 meV at 100 eV. Two promising schemes for making this improvement are the Regenerative Amplifier, which under the name of RAFEL is already under test at the TTF[157], and the double undulator[158]. In the first scheme, part of the output from the FEL is monochromatised and fed back into the FEL, in co-incidence with a subsequent electron pulse. Photon amplification to saturation then occurs on the second pass through the FEL. In the double undulator scheme the first undulator is used to generate stimulated emission but not at saturation. This output is then passed through a monochromator before entering a second undulator in coincidence with the demodulated electron pulse, where amplification to saturation occurs. This is shown schematically below.

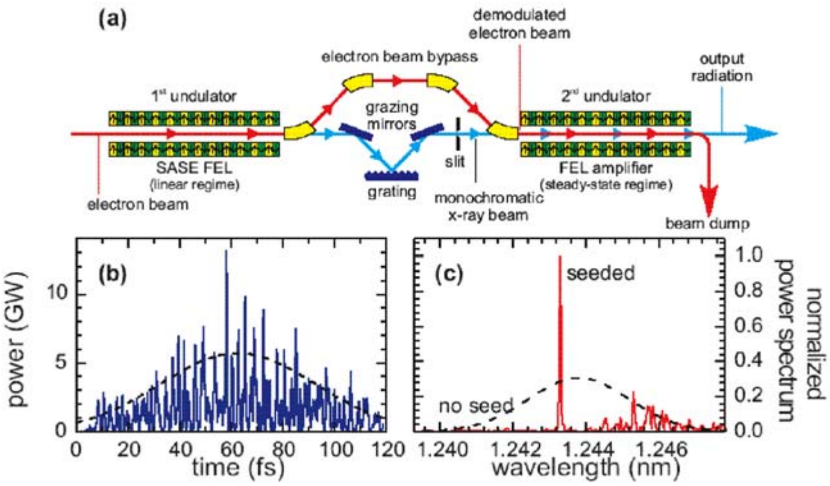

Figure 2

(a) Basic scheme of a two stage FEL, providing full longitudinal and transverse coherent light; (b,c) a simulation of the two-stage FEL employing a 3 kW seed in the second undulator with seeding. (R. Bakker, Approaches and Prospects for VUV and Soft x-ray Free-Electron Lasers, The BESSY FEL Project http://www.bessy.de/FEL/fel_seminars/)

A FEL optics design team will be established and will collaborate with the teams already working on these issues in order to produce appropriate schemes for 4GLS.

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[156] TESLA-Technical Design Report, DESY 2001-011, ECFA 2001-209; Part V 'The X-ray Free Electron Laser'
[157] J Goldstein, D Nguyen and R Sheffield, *Nucl Inst Meth A*, 393 (1997) 137
[158] J Feldhaus, E L Saldin, J R Schneider, E A Schneidmiller and M V Yurkov, *Optics Communications,* 140 (1997) 341

6.2 Spontaneous emission

Two sources of spontaneous synchrotron radiation will be available:

- **Undulators** – the 600 MeV electron energy results in optimal performance from 3 to 100 eV with a tenth of the total optics power load of storage rings operating in the 2 – 3 GeV range. The undulator length is not constrained by lattice symmetry considerations and lengths between 5 and 15 m are envisaged, undulator lengths up to 30m would be possible.

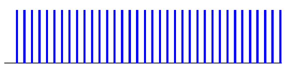
- **Bending magnets** – the bending magnet output will range from the far infrared to over 1000 eV. The lack of hard x-ray emission reduces considerably the heat load on high aperture optics and the field strength or bending radius can be tuned to a particular experimental requirement.

For maximum flux and brightness from the spontaneous emission, an injection source optimised specifically for high average currents will be used. Such sources are currently under development as indicated in Section 5. Operating in this mode is similar to the multi-bunch mode on current storage rings; the pulse structure is not exploited and the source is viewed as providing continuous flux. This mode is ideal for steady-state measurements.

Other modes of operation similar to, but more flexible than, single bunch operation on the SRS and the ESRF hybrid modes are also possible. As the electron beam in 4GLS is not stored, users will not be constrained to a maximum bunch separation and repetition rate. In storage rings these quantities are determined by the circumference of the ring and the RF frequency, and in practice are limited to 1 μs or less.

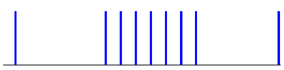
6.2.1 Pulse structure

In addition to pulse repetion rate flexibility, it will be possible to control the pulse intensity and duration of the photon pulses to suit user requirements. Consultation with the potential user community has already revealed that there is interest in control of pulse duration over the range of a few ps, through a few hundreds of fs, to tens of fs. In addition, whilst some experiments demand the most intense pulses possible others are disadvantaged by this. The two injectors envisioned for 4GLS will give some considerable control over these parameters. However, it must be stressed that not every parameter can be controlled independently. Some examples of possible time structures are shown below:



Uniform multi-bunch mode with minimal separation between the bunches.

The equivalent of single bunch mode with longer, uniform bunch separation.



A possible hybrid filling pattern.

6.2.2 *Source matching*

Due to the lifting of storage ring symmetry restrictions, a symmetrical photon spot can be provided at the experiment as opposed to the letterbox shape of existing storage rings. This leads to much greater flexibility in the design of optical systems where the source shape at the sample is critical - for example, imaging systems or systems that require measurements around the axis of the photon beam.

6.2.3 *Lifetime*

A particular benefit of 4GLS to the low energy community is the effectively infinite beam lifetime. A major drawback of high brightness low energy storage rings is the short beam lifetime, which can be limited by electron-electron scattering (Touschek effect) to a few hours or even less. The ERL technology adopted for 4GLS has removed this limitation.

6.2.4 *4GLS undulator spontaneous emission*

The vacuum ultraviolet (VUV) and extreme ultraviolet (XUV) to soft x-ray (SXR) photon energy ranges, typically defined as from a few eV to a few hundred eV in photon energy, underpin a substantial amount of current synchrotron radiation science mainly in photoemission, photoionisation and photoabsorption studies. Controlof linear and circular polarisation would be used to good effect in all areas - gas-phase, solid surfaces, bulk solid state and biological molecules.

The 4GLS undulators will be optimised to generate spontaneous high flux, high brightness radiation, of variable polarisation, over the photon energy range 4-100 eV. However, they will also generate usable radiation (in the higher harmonics) up to around 500 eV. The intensity and extremely broad tunability of the radiation that these undulators will produce are two of their main attractions to synchrotron radiation users.

6.2.5 *Illustrative Examples of Undulator Output*

Preliminary studies have been undertaken to calculate the output for some illustrative undulators on 4GLS. The results for two examples are shown in Figure 3. U48 is a 48 mm period undulator, with an 8 mm gap, optimised for 4 - 30 eV radiation. Two lengths 5 m and 15 m have been chosen. The former length is typical of 3rd generation storage rings such as ALS or ELETTRA; the latter is an example of one of the possibilities for long undulators on 4GLS. U28 is a 28 mm period undulator optimised for higher photon energies 10 - 100 eV. The output is shown for both 5 and 15 m lengths, assuming an electron current of 100 mA. These undulators will generate fluxes of 1 x 10^{16} ph/(s 0.1% bp 100 mA) and brightnesses up to 1 x 10^{19} ph/(s 0.1%bp mm^2 mrad^2).

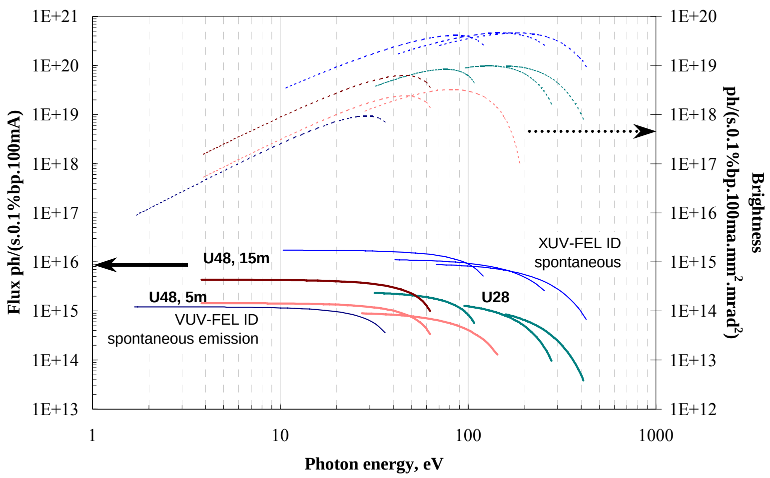


Figure 3 Average flux and brightness for illustrative 4GLS undulators. Also shown is the average flux and brightness for the spontaneous emission from the VUV-FEL and XUV-FEL undulators.

The 4GLS undulators will be superior to existing third generation sources in the 10 – 100 eV range. Whilst optimised for radiation up to 100 eV they clearly produce high intensity synchrotron radiation up to 500 eV in the higher harmonics.

6.2.6 4GLS bending magnet sources

Bending magnets on 4GLS will provide photons from the far infrared to over 1 keV, with two major advantages in comparison to higher energy rings:

- it will be straightforward to obtain large vertical and horizontal apertures (tens of milliradians) due to the smaller physical size of the ring;
- distortion and radiation damage of the optics will be far less severe as a result of the low energy of the electrons.

This will be of particular advantage to users who need high intensity continuous flux, for example the IR community. The bending magnet sources will also produce coherent radiation in the IR and because the electron bunch lengths on 4GLS will be of the order of the wavelength of the emitted light for energies below 0.02 eV (160 cm^{-1}) considerable flux enhancement due to multi-particle coherent emission occurs. This increases the flux output by N_e where N_e=number of electrons in the bunch. For high average current mode the enhancement is ~10^8 times. This enhancement has recently been demonstrated at Jefferson Laboratory where measured outputs of 1 W cm^{-2} total average power are in agreement with theoretical predictions[159]. Thus, for energies below 0.02 eV, the very short bunch lengths possible on 4GLS will result in unparalleled flux and brightness compared to the output of conventional bending magnet synchrotron sources. Brightness calculations of the various sources on 4GLS, including the coherent emission in the IR, are shown in Figure 4 below.

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[159] G P Williams, *Rev Sci Inst,* in press.

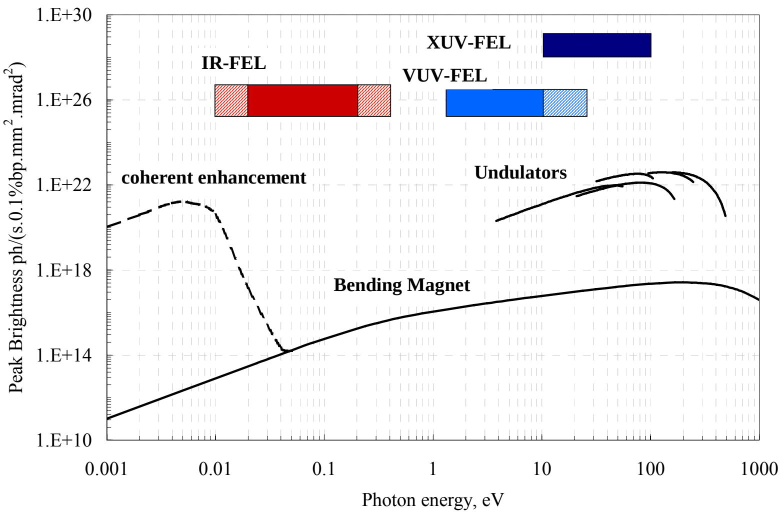

Figure 4 Peak output fluxes, including the predicted output for coherent synchrotron emission. In the case of the FELs the optimal output is shown as solid bars.

6.3 Modes of use of 4GLS

4GLS is a new concept in the provision of VUV radiation, and the aim is to have its sources running together and in synchronisation. The achievement of this will require some development work, and this will be given priority at the early stages of the project. Optimum performance for the three FELs and the spontaneous sources will require different pulse properties:

- the XUV-FEL requires very high charge per bunch (~1000 pC), which is possible only with a low duty cycle from a high charge injection system;

- in the case of the VUV- and IR-FELs, lasing is stimulated by the interaction of the electron bunch with the radiation field trapped in an optical cavity. These require moderately high charge per bunch (100-200 pC) with a repetition rate that ensures the electron bunches overlap with a high radiation field in the cavity and therefore have a minimum repetition rate limit;

- the spontaneous sources will emit light for any electron bunch density and repetition rate; the only limit is the usability of the total flux as it is directly proportional to average current.

A possible operational mode for providing all sources simultaneously is bunch sharing. High charge, low repetiton rate bunches for the XUV-FEL, moderate charge moderate repetition rate bunches for the VUV-FEL, moderate charge moderate repetition rate bunches for the IR-FEL all interleaved with lower charge high repetition rate bunches for the undulators and bending magnets.

In this mode, all the sources will be synchronised as they share the same injection system and RF pattern. In addition, synchronisation with external sources such as table-top lasers can be achieved by using the master oscillator of the RF system as the reference signal for the laser trigger. The synchronisation is then limited by jitter in the injection system, the RF system and pulse-to-pulse variation in the XUV-FEL output. Synchronisation is a priority development area for major SR/laser facilities world-wide.

The optimum synchronisation arises from using the same electron bunch in a series of photon sources, but this will require compromise in the electron bunch properties. For example, the VUV-FEL, the undulators, the bending magnets (including coherent emission) could all emit light with a 200 pC charge, 0.2 ps electron bunch at a repetition rate of 6.25 MHz. The VUV-FEL flux will be as in Table 2, but the undulator and bending magnet flux will be scaled to the average current. The bending magnet coherent emission will scale with the increased number of electrons per bunch and the repetition rate. The synchronisation in this case will be limited by jitter in the electron and photon beam transport systems.

7 DETECTORS

The present generation of detectors will find immediate use on 4GLS. However, the source capabilities of 4GLS and in particular those of the FELs will provide a similar stimulus to detector development in the UK as that generated by the construction of FELs in other countries. As a result the UK will continue to have a strong interest in international collaboration in detector development.

As an illustration of the challenge to detector development, the XUV-FEL will have an instantaneous photon flux, in ~100 fs, equal to the typical flux obtained from an undulator in one second. In other words the instantaneous intensity is many orders of magnitude higher. The ideal detector will have the following attributes:

- the ability to maintain linearity at very high instantaneous count rates (GHz);
- the ability to separate events on a sub-picosecond timescale;
- stability in the presence of very high EM pulsed fields.

We consider these attributes in order. Although there are predictions that the response of phosphors and scintillators will be non-linear at the high count rates expected from the FELs, there are no experimental data to quantify this. It is already known that particle detectors such as channel plates are presently limited to ~ 10 MHz count rates, and this limitation will need to be addressed for experiments where integrating the signal is not an option.

Currently time resolution of detectors has reached the sub-picosecond region, but very few technologies have the ability to resolve time scales of less than 50 fs. Photoconducting detectors and streak cameras are the best in this respect, but are still an order of magnitude too slow. Given the short electron bunch lengths in the ERL, and the intention to provide pulses of less than 100 fs duration, significant advances in detectors will be needed to exploit this time structure. Fortunately this problem is of particular interest to the telecommunications industry and collaboration with industry in this field should be mutually beneficial. Time-of-flight spectroscopy would particularly benefit from such developments, where increased time resolution is immediately reflected in particle energy/mass resolution.

Of the topics above, the last is particularly challenging and is already being addressed at other facilities; careful shielding methods are being developed to prevent EM disturbance of the signal.

For some experiments, primarily those on 4GLS undulators on dilute samples, present detector technology and the future developments envisaged for it will suffice. Area detectors are already in use for recording both particle energy and spatial distribution information, (*e.g.* COLTRIMS, toroidal imaging analysers) and coincidence techniques are used in combination with this to provide multiple particle detection. As a general rule, however, the use of particle detectors will be limited in practice to count rates below 10 MHz.

For high count rates, therefore, it will be necessary to make full use of integrating imaging detectors, with the additional requirement that high detection efficiency will be needed for "one-shot" experiments. This is relevant for biological and similar samples which cannot withstand repeated irradiation at the high intensities provided particularly by the XUV-FEL. CCD based systems will be appropriate for this as will integrating detectors using storage phosphor systems. Such systems are already in use for x-ray diffraction experiments, and the sensors, interconnections, mechanical design and much of the electronics can remain the same, with future developments such as an in-pixel analogue-digital converters being highly desirable. Pixel size is not anticipated to be a major factor, because optical systems can be used to match the image to the size of the detector.

It is clear that major developments are necessary to address the issues raised above, building on current detector development programmes. A highly sensitive IR detection system for time-resolved IR measurements, which will be essential for many of the experiments utilising the IR-FEL, is already under development at RAL. The PIRATE (Picosecond InfraRed Absorption Transient Excitation) facility represents a world lead in the area of time-resolved IR detection systems and presently is able to monitor minute transients with $\Delta OD < 5 \times 10^{-5}$ in < 1 minute using conventional laser technology. Since this technology is over 5 years old, it is timely now to exploit the existing expertise at RAL by the commissioning of a new IR laser and detection system. This should lead to the development of the next generation transient IR detection system offering 1 to 2 orders of magnitude improvement in sensitivity. Full details of PIRATE are contained in Appendix V.

There is also rapid progress with the development of fast UV detectors. Current development is being driven by military applications and solid state detectors based on GaN, SiC and diamond are replacing the limited spatial resolution of photomultiplier tubes. Such science areas as energy dispersive circular dichroism with wavelength response shorter than 190 nm could be significantly advanced by the combination of an intense source, dispersive optics and linear or area detectors. Again in this area the science for 4GLS can borrow heavily from the astronomy community for the detector technology and combine this with the high speed electronics developed for particle physics. UV detector and readout technology is being developed by the Centre for Instrumentation (CLRC) for the CD beamline currently being commissioned on the SRS. A continuation of this programme for 4GLS would be a natural extension.

Spin detection schemes utilising time-of-flight techniques are ideally suited to the intense pulsed output of the free electron lasers. Currently, commercial TDC electronics limitations restrict timing resolutions to around 60ps but this is set to improve to less than 10 ps over the next few years. Advances in this area are being incorporated into the TOF-spin polarimeter systems developed at Daresbury Laboratory.

Detector development will have to be built into the budget for the facility, as it is for similar facilities worldwide. It is anticipated that significant cost savings can be achieved by collaboration with other laboratories with similar interests such as the DESY Laboratory. In view of the widespread interest in this area, and its relevance to several other facilities as well as industry, this could form the basis of a European project.

8 COMPLEMENTARY FACILITIES

The superconducting linac, which is at the heart of 4GLS, will be an excellent source of high energy electrons with a well defined pulse structure. Instead of simply dumping the electrons once they have been around the ring they could be exploited further. Three potential uses are outlined below.

8.1 The Electron Beam Ion Trap (EBIT)

In high current mode the 10 MeV beam which has been decelerated through the linac could be used very effectively in an EBIT source. Currently such sources are limited to electron energies of ~100keV which imposes a significant limitation on the highest charge state accessible in the heavier elements. The high instantaneous current density available from the 4GLS linac would considerably increase the range of current traps. A brief outline of some scientific objectives is given in the scientific case. In addition the ions generated, when extracted from the source, could be used in a wide variety of experiments in plasma- and surface physics.

8.2 Free Radical Research

The Free Radical Research Facility at Daresbury Laboratory has recently been established as a centre for European scientists to undertake pulse radiolysis and laser flash photolysis experiments. Currently the 12 MeV electron beam of the SRS linac is used for pulse radiolysis. The decelerated electron beam at the end of the 4GLS superconducting linac would, in view of its higher intensity, be much better for this purpose.

The ionising radiations generated by 4GLS could be used for radiolysis and the creation of transient radical species. This would allow time-resolved investigations using probe wavelengths from the whole range provided by 4GLS and utilising the shortest timescales available. Detection of intermediates would require tunable probe wavelengths in transient absorption spectroscopy or time-resolved resonance Raman spectroscopy. The latter technique gives detailed information on structure and bonding and is particularly well-suited for studies in aqueous environments. The use of 4GLS to generate tunable deep UV wavelengths would be particularly advantageous compared with table-top laser sources and would yield the absorption spectra of many radical species whose study has so far been inaccessible.

8.3 Inverse Compton scattering

It has long been recognised that the combination of an intense laser with high energy electrons provide monoenergetic x-rays through the inverse Compton scattering process. Indeed, a beamline has been set up for this purpose at the ESRF, and preliminary experiments have been carried out at the ALS[160] where femtosecond x-ray pulses have been generated from the electrons in a bending magnet. However in these experiments the radiation is very weak, primarily because of the low electron bunch density. 4GLS has a number of inherent advantages over these sources which could lead to a very bright source of monoenergetic x-rays. First, the 4GLS linac contains much higher current densities. Secondly the laser used for scattering can be synchronised with the laser used for the photoinjector cathode thereby

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[160] R W Schoenlein *et al., Science,* 287 (2000) 2237

ensuring maximum overlap between the two sources. This source of monoenergetic x-rays would have applications in materials research and medical imaging[161].

[161] http://www.vanderbilt.edu/fel/Xray/default.html

9 ALTERNATIVE WAYS OF MEETING THE NEED

In establishing the case for 4GLS, it is important that consideration be given to alternative ways of enabling the science described in Section 3. The main alternatives that might be considered are:

- to carry out the work on other existing or planned sources outside the UK;
- to carry out the work at the UK's planned 3rd generation source, *diamond*;
- to carry out the programme by using existing or anticipated table-top laser sources.

These three alternatives are assessed in the following three sections. Our overall conclusions are:

- both in terms of capacity and capability, this science programme cannot be carried out at any other existing or planned source outside the UK. This is of course to some extent axiomatic as 4GLS is clearly world-leading;
- 4GLS is highly complementary in its provision both to *diamond* and to available table-top laser sources (see Figure 5, Section 9.3). 4GLS will allow the synergies between laser sources (both table-top and FEL) and SR to be exploited fully for the first time.

9.1 Comparisons with Other Advanced Radiation Sources

Third generation light sources based on storage rings have reached a stage of maturity that allows their performance to be predicted with good accuracy. The highest energy examples are the three very large trans-national facilities; the European Synchrotron Radiation Facility (ESRF), the Advanced Photon Source (APS) and SPring-8. These operate at electron energies of 6-8 GeV and deliver optimised photon output above 10 keV. Such facilities are approximately 1 km in circumference and have a capital cost of in excess of £500M.

There are a considerable number of smaller operating facilities that are in effect scaled down versions of the above. In Europe these are represented by the Swiss Light Source (SLS) in Villigen, ELETTRA in Trieste, BESSY-2 in Berlin and MAX II in Lund. The latest versions are the SOLEIL (France) and *diamond* (UK) projects that will come on line in about five years. All of these rings operate at well above 1 GeV, mostly around 2-3 GeV, and mostly the science associated with them focusses on utilisation of output radiation in the range 100 eV to 10 keV. There are also other lower specification (2nd generation or 2nd/3rd generation user facilities such as Super-ACO in Paris, ASTRID at Aarhus, DORIS at Hamburg, ANKA at Karlsruhe and the SRS at Daresbury.

The only new European synchrotron radiation facility that is designed to provide high intensity undulator and bending magnet radiation below 100 eV is MAX III at Lund in Sweden[162]. This is a storage ring facility that is due to come on-line in 2002. The proposed 4GLS will surpass the predicted performance of MAX III in a number of respects. No storage ring source will

[162] G Leblanc *et al.*, *Proc EPAC 2000*, Vienna Austria, p643

produce electron pulses less than about 10 ps in length, nor are usable emittances less than about 1 nm-rad likely to be achieved: achieving such ultra-high source brightness (transverse and longitudinal) meets fundamental limitations. Beam dynamics aspects pose additional threats to any performance enhancements as at maximum brightness the non-linear behaviour becomes dominant and stored beam losses increase. Furthermore, the residual gas scattering, even in a UHV system, limits minimum acceptable undulator magnet apertures to about 5-7 mm and places a corresponding severe limit on the output radiation properties that can be achieved. None of the above limitations will apply in a linac driven ERL source as embodied in 4GLS. It is for this reason that there is now great international interest in development of very high energy ERLs that might eventually replace the largest x-ray rings; Cornell has completed an assessment of a 6 GeV version but proposes first to build a high current (100-200 mA) prototype at 100 MeV[163].

In parallel with the development of storage ring light sources the FEL community has in the last 10-20 years moved from R&D facilities to established user facilities, although, thus far, mostly in the infrared region. FELIX and CLIO run for several thousand hours annually with scheduled user group access, but they operate in a pulsed mode (*ca.* 10 Hz) because they utilise conventional linac technology. Of several similar USA facilities mention should be made of that at Stanford, since this employs a superconducting linac with corresponding excellent beam quality and reliability; there is a mature research programme involving sophisticated time resolved (ps) work. In Virginia the Jefferson infrared FEL facility has smashed all known power performance records in the last two years, recently achieving in excess of 2 kW average power at 3-6 μm and there are plans to increase this yet further. This latter facility's use of superconducting ERL technology gives great confidence in the proposed 4GLS solutions, which will be able to exploit the same technology and therefore to match its performance (although such high average power *per se* is not a prime objective, well in excess of 100 W should be readily achievable on the 4GLS version).

Storage ring FELs have developed more slowly, not least due to extremely restricted ring access. The Super-ACO FEL in Orsay is now highly developed and has an active user programme, but is restricted to the range 300-350 nm. The EU-funded Trieste (with UK participation) project (EUFELE) now holds the world record for shortest wavelength at 190 nm and is starting to assess a user programme through a series of demonstration experiments; its aim is also to extend to 155 nm in the next two years and it has new EU funds to support this. There is a proposal to incorporate a FEL on SOLEIL but, as in the case of the other rings, this implies a special operating mode including a reduction of electron beam energy that will be unwelcome to many of its wider user community; a final decision on this project has yet to be made. There is no proposal for any similar facility on *diamond*. However despite these issues such storage ring FELs have attracted considerable interest and much development effort: the broadly tunable, high brightness output also has attractive features of natural synchronisation with the spontaneous emission radiation from other beam lines. A final point is that the Trieste project has demonstrated that such an FEL can easily share its undulator with a more standard light source beam line, so that the incremental cost of the FEL is modest. The 4GLS version of a cavity VUV-FEL can utilise all of these lessons but it will also exploit the electron beam properties of an ERL, especially high peak current, short bunch length and selectively variable pulse structure – to result in a source with superior performance.

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[163] Phase I Energy Recovery Linac (ERL) Synchrotron Light Source at Cornell Univerisity, Ed. S M Gruner and M Tigner, *CHESS Technical Memo* 01-003, JLAB-ACT-01-04, July 2001

SASE-based FELs are now receiving enormous world-wide attention. The principles were first demonstrated experimentally at Lawrence Livermore National Laboratory in 1985, but in the microwave and far infrared regions. The last three years have seen major advances with a series of shorter wavelength demonstrations of amplifier operation, culminating in operation down at 80 nm on the TTF FEL at DESY[164]. In the USA similar experiments at Argonne (LEUTL)[165] and a parallel programme at Brookhaven (VISA) have also demonstrated major steps forward in the technology. All of these experiments require high performance photo-guns and undulators, together with advanced diagnostics, but only the TTF at DESY utilises a superconducting linac. SASE FELs therefore already operate in the VUV but the goal of many laboratories, unlike 4GLS, is to reach hard x-ray output (*e.g.* 0.1 nm) and such aims will demand greater advances than are necessary for the XUV target of 4GLS. Nevertheless, there are many overlapping aspects that will be of great benefit, such as simulation code development, high brightness guns, fs bunch control, undulators and diagnostics. There is also at least one other European proposal for a SASE FEL, at the BESSY laboratory, albeit assuming a higher energy (GeV) linac and targetted at x-ray production.

In conclusion, 4GLS will be a unique combination of advanced sources without direct comparison elsewhere, especially in its merging of high peak and average power devices. Its high current ERL basis will be common technology with a small number of international laboratories, mainly in the USA. Its high brightness photoinjectors will be examples of state-of-art world developments being pursued in Europe, USA and Japan. Each of its FELs will be internationally competitive in its own right, and probably world leaders in the VUV/XUV regions. No other centre, existing or proposed, can match the synergies and potential of 4GLS.

9.2 4GLS/*diamond*

The third generation, medium-energy (3 GeV), electron storage ring, *diamond*, will be built at the Rutherford Appleton Laboratory in Oxfordshire. Its primary radiation sources will be undulators and wigglers which will be *optimised* to produce x-rays with energies from 100 eV to 30 keV although much higher energies will also be available. Radiation covering a broad range of wavelengths from infrared to hard x-rays will be produced at the bending magnets of *diamond*.

The relative capabilities and merits of *diamond* and 4GLS for synchrotron radiation production in the soft x-ray to far infrared regime is an important issue that has been addressed by a working party established by the Synchrotron Radiation Forum. The panel, which was chaired by Professor D.P. Woodruff of the University of Warwick, had the explicit remit:

> "To consider the relative roles of 4GLS and DIAMOND in the provision of low energy radiation for the UK community."

The working party delivered a unanimous report to the Forum in September 2001; this can be found, in full, in Appendix VI. Although the report concentrates on the core question of the complementarity of *diamond* and 4GLS as radiation sources for the UK community, it also touches on some of the scientific opportunities that are emerging for 4GLS.

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[164] J Andruszkow *et al*., *Phys Rev Lett*, 85 (2000) 3825
[165] S V Milton *et al., Science*, 292 (2001) 2037

In summarising its report the working party concluded that, "It is clear that 4GLS will provide radiation sources which are entirely complementary to, rather than in competition with, those of *diamond*, and that the two sources together provide the suite of UK national facilities envisaged by the Woolfson and Blundell Committees".

In full, the conclusions of the report are:

i. For mainstream applications of undulator radiation 4GLS and *diamond* are complementary. 4GLS is substantially superior for photon energies in the 5-100 eV energy range, *diamond* is superior for all photon energies above 200 eV. An intermediate overlapping range should be provided at both facilities to aid researchers working at the boundaries.

ii. The two VUV-FEL devices proposed for 4GLS, covering the 3-100 eV photon energy range, will offer unique facilities in terms of both flux and time structure for new and demanding experiments which cannot be matched at *diamond* or elsewhere.

iii. Current plans for UV/VUV biological CD spectral measurements can be met equally well in terms of flux provision by bending magnet sources on either *diamond* or 4GLS. *diamond* probably has significant advantages in terms of infrastructure support for protein and nucleic acid studies, 4GLS may have some slight technical advantages in optical design. In the longer term, however, insertion devices on 4GLS offer the potential for a new generation of CD experiments, especially in the time domain.

iv. The output flux of IR radiation from bending magnets is essentially identical on *diamond* and 4GLS, and for the mid-IR in particular, and spectromicroscopy experiments, either source could be used. In the far IR, especially relevant to some spectroscopic experiments such as the investigation of surfaces, the need for a very large aperture of acceptance probably favours 4GLS. The IR-FEL of 4GLS provides a unique facility in the UK which, especially in conjunction with broad-band radiation from the ERL devices, may open up wholly new areas of science.

There are two *diamond* reports covering aspects of low energy photon provision on the storage ring (DM-WG-TN-002 and DM-WG-TN-003). These are summarised in a third document (DM-WG-TN-001) and all three are available on the *diamond* web site (http://www.diamond.ac.uk). These reports were produced in February 2001 when free electron lasers and a low energy storage ring was the option for 4GLS. Since that time the ERL approach has been adopted and developed and the 4GLS concept has matured considerably. Whilst conclusions regarding the utility of free electron lasers are still valid for other comparisons the conclusions of the Woodruff report supercede them.

9.3 4GLS and Laser Light Sources – A Comparison

This section addresses a crucial question; is the anticipated photon provision of 4GLS already covered by tabletop laser sources or developments in these that are likely over the next few years?

In order to answer this question, it is necessary to consider the state-of the-art in both facility-based small-scale laser systems (*i.e.* excluding those high-energy laser facilities, such as the

Vulcan laser at the CLF, developed for fusion research) and tabletop laser systems. We should also include consideration of likely improvements in the performance of these sources, and then contrast this information with the expected performance of the sources proposed for 4GLS. To this end, the performance characteristics of relevant table-top systems is presented in some detail in Appendix VII. For comparison, the equivalent characteristics of the 4GLS sources are detailed in Section 6. Evaluation of the relative merits of these sources is complicated, as might be expected, as there are several parameters upon which comparisons should be made. Primarily we need to consider the wavelength coverage and output powers (average and peak) of these sources. But equally important are the pulse duration and repetition rates, achievable optical linewidths in spectroscopic applications and polarisation behaviour of the sources.

The first and most obvious comparison to make is in **wavelength coverage**. Figure 5 summarises the wavelength coverage offered by 4GLS in comparison with a number of established UK (PIRATE[166] and ASTRA[167] at the CLF, TOPS[168] at Strathclyde University) and EU (LENS[169] at the University of Florence) laser facilities and table-top systems typical of those that might be utilised in a university (or other) laser laboratory.

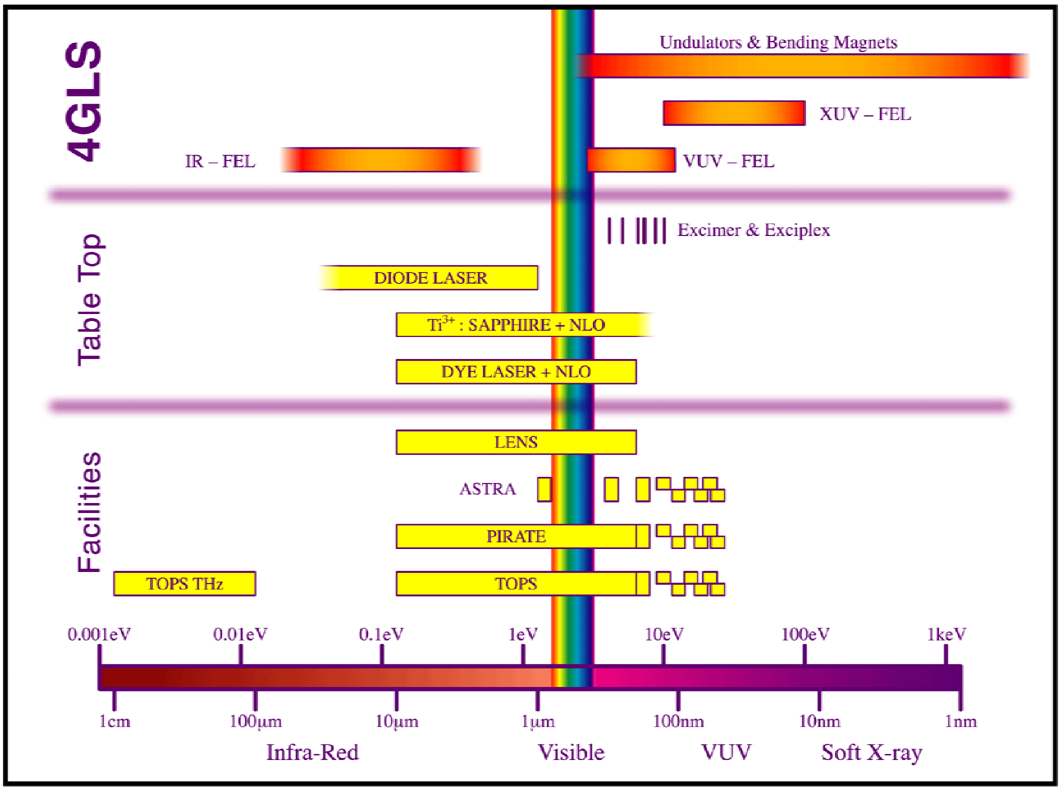


Figure 5 Comparison of the wavelength coverage of advanced light sources

[166] M Towrie, R Barton, P Matousek, A W Parker, A Stanley, M W George and D C Grills, "Development of the PIRATE Facility" in CLF RAL Annual Report (CLRC CLF, Chilton, Didcot, 1999-2000) pp204-206
[167] A J Langley, E J Divall, C H Hooker, M H R Hutchinson, A J –M Lecot, D Marshall, M E Payne and P F Taday, "Development of a Multi-terawatt Femtosecond Laser Facility – Astra" in CLF RAL Annual Report (CLRC CLF, Chilton, Didcot, 1999-2000) pp.196-200
[168] http://dutch.phys.strath.ac.uk/TOPS/
[169] http://www.unifi.it/lens

As described in more detail in Appendix VII, to wavelengths shorter than 400 nm, excimer and the exciplex lasers provide discrete lines, while tunable visible lasers (dye lasers and latterly Ti^{3+}:Sapphire systems) combined with non-linear optical methods in inorganic crystals (SHG and SFG) and high harmonic generation in gases (HHG) can be used to provide coverage over discrete ranges to 100 nm and below. In contrast, 4GLS will provide continuous coverage (with instrumental changes) over the entire region from ca. 400 nm to below 1 nm. For most purposes, radiation from undulators and bending magnets will provide users with the wavelength coverage they require at moderate fluxes. However, for applications requiring substantially higher fluxes but perhaps more limited wavelength performance, the unique design of 4GLS permits the ready incorporation and simultaneous operation of free electron lasers (FEL) within the light source. In this short wavelength region, two devices are planned. The 4GLS cavity VUV-FEL will be optimised for operation in the wavelength range 413 to 124 nm, although it will possible to operate it up to wavelengths *ca.* 1.2 μm. While, a cavity-free XUV-FEL will provide coverage at shorter wavelengths from around 124 to 12.4 nm in the fundamental and down to *ca.* 4 nm in the third harmonic.

Looking toward the long wavelength region, existing continuously tunable mid-infrared laser systems (diode lasers, DFG lasers, mid-infrared OPO/OPA systems) perform poorly beyond *ca.* 20 μm, but provide excellent coverage of the shorter 1 to 20 μm region. Beyond 100 μm, and out to 1 cm, the so-called terahertz (THz) region, traditional tabletop sources (mid-IR pumped molecular gas lasers and microwave sideband generation on diodes) are limited and difficult to operate. However, the ready availability of intense, short (<100 fs) pulsed visible lasers has seen a surge in interest in this region and is reflected in the excellent coverage provided by facilities such as TOPS. In terms of 4GLS, as in the short wavelength region, the bending magnet and undulator sources will provide the broad coverage of the region that will be essential for many of the proposed experiments. More crucially, it should be noted that THz radiation is available from the bending magnets of 4GLS and that this will be many orders of magnitude more intense than available from commercial THz systems[170]. However, the key component of 4GLS at long wavelengths, as at shorter wavelengths, is a free electron laser. In terms of spectral coverage, the IR-FEL will provide readily tunable radiation from *ca.* 3 μm to around 75 μm, in the first instance. Extension beyond 75 μm, to close the gap in the infrared that can be seen in Figure 5, may follow.

Across the visible and into the near- and mid-IR (400 nm to *ca.* 20 μm), the current generation of laser technologies provides near continuous tunability in user friendly tabletop packages that 4GLS does not seek to surpass. However, across the entire spectral region covered in Figure 5, it is clear that *the broad wavelength coverage offered by the combination of sources comprising 4GLS and the relative ease with which they may be tuned and scanned far surpasses those of any current laser sources operating across this wide region and is likely to do so for the foreseeable future.*

The next comparison to make is in **output power** (both average and pulsed) and **power stability**. From comparison of the average output power of a variety of laser and non-laser sources with the VUV- and XUV-FEL components of 4GLS, it is clear that at certain specific wavelengths some individual laser systems (*e.g.* CO_2, Nd^{3+}:glass, excimer and exciplex lasers) exceed the performance of one or more components of the 4GLS package. However, these cannot be considered as useful *general* tools. Rather they find specific applications *e.g.* as

[170] G P Williams, *Rev Sci Inst*, to be published

cutting or machining tools, light sources for photochemical studies or pump lasers for tunable laser systems. Nor should we seek to compare such non-tunable lasers with tunable sources. Rather we should firstly compare the performance of the bending magnet and undulator sources across their broad operating spectral region with traditional light sources and other synchrotron sources operating in the same region. This has been presented previously in Section 6. Secondly, we should compare the performance of the IR-, VUV- and XUV-FELs with current laser systems operating in these spectral regions. For the most part this comparison tells us that *the output powers, both average and peak, available from the FEL components of 4GLS are comparable to, or significantly exceed, those available from the current generation of laser sources.* However, it should be noted that although there are rapid developments in new mid-IR laser sources (*e.g.* quantum cascade lasers), novel non-linear optical materials (*e.g.* silver chalcogenides and periodically poled materials) and techniques (*e.g.* intracavity pumping of OPOs) these are not matched by comparable progress in the far-IR.

The issue of power stability is also crucial to consider as it is fluctuations in power that often determine the measurement times required to achieve a specific signal-to-noise in an experiment. With typical nanosecond (ns) tabletop lasers, the workhorses of laser-based spectroscopy in university laboratories, shot-to-shot stability is of the order of ±10% within the fundamental region of laser output. Applying SHG, SFG and HHG methods to these lasers for the generation of short wavelength radiation is possible, but is reliant for efficient conversion on the occurrence of random intensity spikes on the sub-ns timescale. This can mean that shot-to-shot stability will be significantly decreased in moving to shorter wavelengths such that intensity fluctuations of nearly ±100% are possible. In contrast, with the types of short pulse lasers now commonly used for ultrafast spectroscopy, where the current generation of systems operate with better than ±5% and improvements to less than ±2% are in the pipeline, this decreasing stability with increasing complexity of the applied non-linear generation scheme is much less important. Once again, *the performance expected from the various components of 4GLS, at around ±2%, is comparable to the current generation of laser technologies and will continue to be so.*

Moving on, it is now worth considering the issue of **pulse durations and repetition rates**. As the basic laser technology driving the 4GLS photoinjectors is in fact identical to many laboratory-based ultrafast laser systems, this issue is perhaps less relevant. However, *it should be remembered that it is this technology that allows the unprecedented flexibility of pulse structures that will be offered by 4GLS in comparison to other synchrotron light sources* (see Section 6).

The next issue to consider is that of **linewidth**. There is little doubt that for the ultimate in narrow linewidth performance continuous wave (CW) lasers are unsurpassed. From a variety of CW sources across the mid-IR, visible and near-UV, linewidths of as little as a few kHz are possible. Such linewidths are, of course, impossible to achieve using bending magnet and undulator sources.

With pulsed sources, the issue to consider is the transform-limited linewidth. For a pulse of width τ, the relationship

$$\tau = \frac{0.441}{\Delta\nu} = \frac{0.441}{c\Delta\overline{\nu}}$$

allows us to determine this factor. For the typical 10 ns pulsed laser, a transform-limited linewidth of *ca.* 0.0015 cm^{-1} is obtained. Most ns lasers, however, operate far from the transform-limit with linewidths of *ca.* 0.1 cm^{-1} and larger. Moving to shorter pulsewidths, where transform-limited performance is the norm for modern short pulse lasers, broadens the linewidth, thus in principle limiting spectral resolution. For example, pulses of 1 ps width have a transform-limited linewidth of *ca.* 15 cm^{-1}. How does this compare with the FEL performance? In principle the FELs in 4GLS can reach transform-limited linewidths on a range of pulse profiles and so the performance of 4GLS is on the fs and ps timescales comparable to that of table-top laser systems.

The final issue to address is that of **control of the polarisation** of the radiation. Here again the two types of source are broadly comparable. Most lasers and their associated non-linear optical extension systems produce radiation that is well linearly polarised. While there is no internal control of the polarisation available from these laser systems, external optical components, (*e.g.* photoeleastic modulators, Fresnel rhombs, waveplates) are readily available for control, modulation and modification of laser source polarisation. This is equally true with the sources available within the 4GLS package. Here external control *etc.* is possible, but there is the additional flexibility offered by utilising the variable polarisation generated directly by the undulators. Potentially, this will give 4GLS the edge over table-top laser systems in the production of circularly and elliptically polarised radiation.

It is clear from the discussion above and elsewhere in this document that it is the synergy of sources within the 4GLS package that is important. The coexistence of all the elements of 4GLS will greatly enhance the value of any individual source within it by virtue of the wide range of possible combination of source possibilities (bending, undulator, IR-FEL, VUV-FEL and XUV-FEL). The ability to operate at multiple wavelengths in pump-probe configurations with a high degree of synchronisation between light pulses of different wavelengths is crucial to the development of this light source and to much of modern biology, chemistry and physics. It can be argued that many of the laser facilities currently in existence offer this ability. But they do so over a relatively limited range of wavelengths covering the mid-IR, through the visible and into the near-UV. However, they can offer pulse synchronisation to better than 10 fs in some cases. The synchronisation offered by the photoinjector technology driving the 4GLS sources means that there is ‘natural’ synchronisation of subsets of the sources (*e.g.* undulator/VUV-FEL and bending magnet/VUV-FEL) as there is with laser-based experiments. However, the SCRF technology also offers the potential to electronically synchronise, with jitters of less than 1 ps, the remaining source combinations with an external SR source or laser system(s) for excitation or detection at any of the 4GLS sources.

The range of experiments that will be feasible at 4GLS will be much wider than is possible with any other specific source currently in existence in the UK, by virtue of both the performance of the light source itself and of the setting. CLRC is rich in skills appropriate to this program. Daresbury Laboratory brings to this project a wealth of experience in accelerator physics, vacuum science and technology, while the Central Laser Facility at the Rutherford-Appleton Laboratory is equally rich in experience in laser technologies. This unprecedented combination of experience and abilities will be essential for the success of 4GLS as a facility and is probably unsurpassed in the UK. Only within this combination will 4GLS be able to open the many new avenues of low energy photon science discussed elsewhere in this document.

10 BENEFICIARIES

The science case we have presented for 4GLS is strongly interdisciplinary, encompassing fields from bioscience and biomedicine to theoretical nuclear astrophysics. All these communities will benefit from the paradigm shifts which 4GLS will enable in nanoscience and imaging, studies of dynamics and transient species and in the study of non-linear effects. In this section we summarise some of the main benefits to each community from the photon sources making up 4GLS.

10.1 Biosciences

4GLS will provide dynamic measurements of protein folding and other conformational changes in biomolecules in realistic solutions and on fast timescales, through techniques such as time-resolved CD supplemented by Raman optical activity and SFG. The extraordinary brightness of 4GLS (particularly the VUV-FEL) will thus allow the potential of CD in secondary structure determination to be fully exploited and will ensure the continued development of the technique in the UK, into regimes where timescales in the μs – ns range may be probed routinely. This will provide information complementary to, and just as important as, the 'static' structure information provided by protein crystallography using higher energy SR sources to the post-genomics world. As it is now quite clear that secondary structural changes can occur on timescales as fast as ns, the importance of 4GLS in this work can hardly be overstated.

The short pulse lengths and tunability of the sources making up 4GLS mean that it is also well-suited to studies of fast electron and energy transfer mechanisms in biosystems. It will give important information on photosynthetic pigment-protein complexes, such as the mechanisms by which carotenoid-chlorophyll associations control the partitioning of absorbed energy between transfer to photosynthetic reactions centres and dissipation as heat. The tunability of 4GLS in the UV range means it is an important source for studies of radiation damage and repair, both of DNA and of whole cell damage. The ability to carry out these studies in a fast time-resolved way using pump-probe techniques will fundamentally improve our understanding of the mechanisms of energy transfer within biomolecules following absorption of radiation.

4GLS offers enormous generic benefits in many areas of biological science through the development and full exploitation of an armoury of functional imaging techniques which will aid the visualisation of living cells and tissues. Prime among these is the development of fluorescence microscopy, utilising the high brightness and tunability of 4GLS, to the level where, for example, it will become possible to monitor *spectroscopically* the binding events in individual receptor molecules on cell membranes. Time-resolved resonance Raman microscopy will provide a specific method of interrogating the chemistry of sub-cellular domains in real–time, while 4GLS together with even conventional confocal optics, will provide enough flux to achieve sub-100 nm spatial and sub-microsecond time resolved functional imaging. The use of the IR-FEL in combination with near field optical techniques will allow the chemical mapping of sub-cellular structures on length scales of around 30 nm.

10.2 Biomaterials

4GLS will contribute enormously to developing our understanding of the nature of direct interactions between biomaterial surfaces and the biological environment. These play a crucial role in determining the subsequent response of the system. For example, encouraging cell attachment to a surface impacts directly on tissue regeneration or implant device integration, while limiting bacterial adhesion and colonisation has major implications in reducing infection. Areas where 4GLS will yield major benefits for the community include the identification of biomolecule binding sites, examination of molecular conformation and orientation, and measurement of strengths of interactions and rates of adsorption, denaturing and replacement. 4GLS will allow the investigation of such processes over very short time scales in the vicinity of the solid state, which may itself be governed by short time scale surface fluctuations. The development on 4GLS of high resolution IR spectroscopies, PEEM, SFG and surface CD are all of importance to this work. 4GLS will also provide an important tool for examining the influence of surfaces on the behaviour of entire cells. High spatial resolution infrared and confocal microscopies will allow the structural and chemical process of cell adhesion and proliferation on surfaces to be probed in intimate detail.

10.3 Biomedical and Pharmaceutical

4GLS will offer unprecedented opportunities to improve our understanding of the early progression of diseases such as motor neurone disease and multiple sclerosis, through the development of molecular biophysical techniques. These will enable detailed measurement of the conformation and interaction of normal and abnormal proteins, not only in tissue imaging techniques such as CD imaging or resonance Raman imaging, but also in single-cell or even single-molecule studies. Studies of membrane receptors, their conformation, distribution in tissues, and activity will improve our understanding of the pathogenesis of many autoimmune conditions such as Type 1 diabetes, psoriasis and rheumatoid arthritis, allowing the development or screening of new therapies. The outstanding capability of 4GLS in functional imaging will be particularly valuable in understanding the early stages of osteoporosis.

The high intensity and stability of the sources making up 4GLS offer enormous potential in the development of new drug delivery systems, for example through the ability to study single colloidal particles (such as polymer microspheres) interacting with single cells. In the design of DNA delivery systems, the ability to study the intracellular behaviour of the DNA:polymer complex in a time-resolved manner, for example by CD of individual cells will be of enormous benefit.

The VUV-FEL also offers potential benefit to the biomedical and pharmaceutical industries in the development of new high throughput screening techniques. The high intensity of the VUV-FEL will improve the sensitivity of detection of fluorescent labels for probing binding sites and potential drug targets, but a more important potential benefit will be the contribution of 4GLS to the development of techniques which are “tagless” *i.e.* which rely only on the intrinsic signals derived from the proteins and drugs themselves. Circular dichroism on 4GLS will be a key technique for identifying protein-drug binding interactions without the need for fluorescent markers.

The extraordinary intensity of 4GLS in the THz part of the spectrum compared with table-top sources offers realistic prospects for the full exploitation of ‘T-ray’ in medical imaging applications. The potential of THz radiation in this field is already being actively researched by a number of multinational companies, including Toshiba, as well as by several UK and international university spin-off companies. The high output power of 4GLS removes a fundamental limitation to its use in imaging of hard and soft tissues for clinical diagnosis, conformational dynamics in proteins and novel non-invasive diagnostic procedures, such as the identification of pharmaceuticals in minute traces in blood.

10.4 Surface Science

4GLS will enable the development and full exploitation of a new generation of surface probes, including time-resolved SFG, deep UV Raman and RAS, with wide ranging benefit to a broad community of surface scientists interested in surface dynamics. 4GLS will clearly enable a step advance in the study of surface processes in real time such as thin film growth and temperature-dependent phenomena including phase transitions, chemical reaction and desorption.

A similar generic benefit will be gained by the surface science community from the development on 4GLS of a wide range of nanoimaging techniques including PEEM, and a range of near-field imaging techniques.

The exploitation of the variable elliptical polarisation and high intensity of the sources will benefit the rapidly expanding surface science community working on the properties of chiral surfaces and chiral adsorbates. This area offers substantial potential for the development of asymmetric heterogeneous catalysts.

10.5 Catalysis

4GLS lends itself to the study of reaction processes, as the pulse lengths available are well-tuned to the timescales of bond-making and bond-breaking. The resulting ability to study reaction intermediates in real time using pump-probe techniques will lead to a fundamentally improved understanding of both homogeneous and heterogeneous catalysis, of benefit both to the academic and industrial communities. The potential benefits to the pharmaceutical industry from a better understanding of asymmetric synthesis through exploitation of circularly polarised light are substantial, as discussed above.

10.6 Photochemistry and Photophysics

The ability to study a surface spectroscopically (by either RAIRS, SFG, Raman or UPS) in concert with photolysis from the tunable VUV-FEL source will enable new experiments probing the lifetimes and intermediates in photoassisted processes to be performed. It will be possible to follow the dynamics of surface processes in unprecedented detail. These types of experiment are not currently feasible at any existing light source, and will revolutionise our understanding of photochemical processes, such as the action of TiO_2- and $InTaO_4$-based photocatalysts and photovoltaics. These experiments will have a major impact in the drive to harness the power of sunlight to split water producing hydrogen fuel, an area where direct splitting of water by an oxide photocatalyst under visible light irradiation has very recently been demonstrated[171].

10.7 Electrochemistry

Electrochemistry has been a target area of several EPSRC initiatives as well as being named as an important area in the Foresight exercises. Advances in electrochemical technologies influence areas as diverse as clean synthesis, sensors and energy technologies. Common to all of these fields/applications is the heterogeneous nature of the electrochemical interface. Access to the 4GLS facility will provide unique opportunities to further our understanding of this interface. Surface sensitive and surface specific techniques such as second harmonic and sum

[171] Z Zou, J Ye, K Sayama and H Arakawa, *Nature*, 414 (2001) 625

frequency generation as well as scanning near field microscopy will enable characterisation of the surface of electrodes in the working environment. The 4GLS source will also enable such measurements to be conducted with time resolution, to probe the dynamics of this complex interface. For example, deep UV Raman using the VUV-FEL can be tuned to focus on particular adsorbed species, such as the intermediates in methanol fuel cell reactions on platinum electrodes. The technique will yield measurements of surface reaction kinetics on the sub-nanosecond time scale under working electrode conditions. The dynamic electrode interface is an area of considerable current research effort and will be the topic of a Faraday Discussion in early 2002.

10.8 Earth and Environmental Sciences

The benefit of 4GLS to environmental concerns is substantial, particularly in the areas of atmospheric chemistry and atmospheric pollution control and in the development of a number of clean technologies and renewables. An example, referred to above, is the drive to develop a clean and renewable source for hydrogen fuel from harnessing the photocatalytic splitting of water into hydrogen and oxygen using solar energy. A similar 'pump-probe' approach will be of importance to research into the effects of atmospheric and fungal toxins on photosynthetic systems, using fluorescence lifetime experiments, and the development of metal oxide-based environmental sensors.

The understanding of our environment, and especially man's impact on it, requires an understanding of reactions and processes in the biosphere, which in turn requires the ability to study biological materials at a molecular scale. This has been realised by both the geology and the biology communities, who are already beginning to make extensive use of world facilities for IR microspectroscopy. For example, 'geology' accounts for around 20 % of the current use of IR-FEL facilities such as CLIO at LURE, with 'biology' accounting for a further 40 %. The benefit of a source which provides outstanding facilities for IR microspectroscopy, *together* with high brilliance radiation from undulators at the carbon K-edge (and in the water window between the O and C K-edges) is therefore substantial. This allows the development of element-specific and morphological imaging techniques which may be used, for example, in the imaging of biological samples (algae, bacteria) under real environmental conditions and in the study of mineral/bacterial interactions. This will improve our understanding of the effectiveness of bacteria in land remediation and bio-attenuation of toxic plumes and the role of biofilms in element mobility. The high flux at the C K-edge will be invaluable in XANES mapping of organic species in biogenic and abiogenic 'fossil' materials and of organic species adsorbed on inorganic minerals, important to our understanding of the origins of life. 4GLS will also yield an improved understanding of the molecular scale interaction between organic species and mineral surfaces, crucial to mineral separation processes. *In situ* analysis of these systems will provide a much greater understanding that can be used to improve plant efficiency, thus reducing environmental damage and extending mineral resources.

The VUV molecular spectroscopy programme at 4GLS on greenhouse and other gases in the earth's atmosphere has far-reaching environmental implications. The high quality spectroscopic data which will be obtained from short-lived or transient molecules, such as electronically excited O_2 ($^1\Delta_g$), O_3, and ClO will transform our understanding of the role of these species in the generation and removal of pollutants in the Earth's atmosphere. Work on photon-induced reactions in biomolecules described above will contribute significantly to our understanding of UV-irradiation damage of living matter.

10.9 Atomic and Molecular Spectroscopy

The benefit of 4GLS to the atomic and molecular spectroscopy community can scarcely be overestimated, indeed, this community has consistently placed the development of a low energy synchrotron source at the top of its list of priorities for many years. The source will yield vastly improved spectroscopic data (for example measurements of absolute cross sections) for comparison with theoretical models, which in turn are crucial to the accurate modelling of both stellar atmospheres (described below), and the earth's atmosphere (described above). It will lead to a fundamentally improved understanding of energy transfer processes in molecules, and of the way in which photons interact with molecules, which in turn is of importance in the understanding of radiation damage of biomolecules.

However, perhaps of even greater significance to this community is the very high intensity of the FEL sources, in particular the XUV-FEL, which produce field intensities strong enough to give significant non-linear effects. Research on the single- and multi-photon dynamics of atoms, ions and molecules will open up a completely new area of research on multiphoton physics at high frequency and intensity. A new understanding of the way in which these high frequency, high intensity fields couple to molecules will be obtained, which may lead to optimisation of the selective breaking of a chemical bond in polyatomic molecules, and hence to improved 'photon scissors'. The ability to manipulate molecules in high fields in this way will lead to opportunities for exploitation of the coherent control of reactions.

10.10 Astrophysics

The benefits of this source to the astrophysics, astrochemistry and astrobiology communities will be immense, primarily through the provision of spectroscopic data from species which are not known on earth, but which occur in interstellar space. The facility will provide accurate photoionisation cross sections for a wide range of species, including measurements of cross sections from neutral species, allowing a full comparison with theoretical calculations (*e.g.* the OPACITY project), and informing theoretical models for stellar evolution. Recent space missions, such as SOHO, with significant UV and XUV spectroscopic capability, have revolutionised our understanding of the universe, particularly through the study of ionised gas in regions as diverse as stellar coronae, massive star evolution, planetary nebulae, cooling flows in galaxies, active galactic nuclei, and the accretion disks around black holes. These new observational results need to be interpreted with theoretical models which incorporate the most accurate data in order to determine important astrophysical parameters such as elemental abundances, excitation conditions, ionisation fraction, dynamics, and so on.

4GLS will provide new fundamental data on surface processes occurring on dust grains in the interstellar medium and on planetary surfaces. These data are essential to our understanding of the fundamental astrophysics of star formation and of the fundamental astrochemistry that leads to molecular synthesis in the interstellar medium. This will include the study of ion-surface interactions that have recently been implicated in molecular synthesis (including the formation of ozone) on the surface of the ice-covered moons of Jupiter. Ions incident from the gas phase or produced on and in the surface mantle matrix undoubtedly undergo chemical reactions with surrounding molecules. 4GLS will radically improve our understanding of these processes. This is important, as they are believed to be the major source of complex pre-biotic molecules in the interstellar medium.

The availability of high quality circularly polarised radiation from the sources making up 4GLS will allow experiments aimed at the investigation of the origins of homochirality of biological precursor molecules, such as amino acids, in an environment which simulates conditions in the protoplanetary disc which surrounded the forming Sun. This will be of major benefit to the new discipline of Astrobiology, in improving our understanding of the conditions necessary for life to begin.

The Radioactive Beams Facility (SIRIUS) component of CASIM, in conjunction with 4GLS offers substantial benefit to the nuclear astrophysics community. Explosive stellar events are highly non-equilibrated and occur over short timescales in conditions of extreme temperature and density. As a result the pathway of nucleosynthesis becomes controlled by nuclear reactions involving radioactive nuclei. One important area for study is the hot CNO cycles thought to occur at the surfaces of white dwarf stars. Almost all of the reactions constituting these cycles remain to be measured, since they involve short-lived radioactive species. Such species may be produced at SIRIUS, and their spectroscopy studied using 4GLS, giving the basic spectroscopic information needed for the interpretation of astronomical observations. This is of enormous importance to those working at the interface between observational astronomy and terrestrial nuclear astrophysics, and will revolutionise our understanding of the origins of the universe.

10.11 New nanomaterials and polymers

Generic advantages to the whole materials community arise from the development on 4GLS of a range of powerful imaging techniques, particularly high resolution (few μm) near field IR microspectroscopy and THz imaging, where 4GLS has a 10^6 intensity advantage over conventional lasers. In the development of polymer materials IR microspectroscopy is a key tool in understanding the microstructure and function of new materials in applications as diverse as upholstery foam and electroluminescent displays. For example, full chemical mapping of working displays will be possible, allowing the development of organic electronics patterning technologies being developed for cheap, disposable displays. The flexibility of the source offers unique opportunities for 'total characterisation' of nanoscale objects, where chemistry, structure and the electronic structure of ground and excited states are probed in the same experiment using a variety of probes and detection techniques (*e.g.* XAFS, photoemission, photoluminescence, *etc*.)

Similarly, the ability to carry out real time studies of molecular conformational changes will allow studies of the morphology and dynamics of polymeric materials, using UV light for example for time-resolved fluorescence, phosphorescence and anisotropy measurements. This will lead to a fundamentally improved understanding of the self-association of amphiphilic molecules as well as of resonant energy transfer between macromolecules in solution.

10.12 Functional materials

4GLS will yield very high quality ultra-high resolution and spin-resolved measurements of the electronic structure of a range of materials which are of fundamental interest, but which are also of great importance as functional materials. This includes all highly correlated oxides, including superconductors, CMR and GMR perovskites and transition metal catalysts, heavy Fermion materials, conventional superconductors, magnetic layers and alloys and many others. These measurements will be of fundamental importance to the academic community in examining the validity of competing models for electronic and magnetic structure, and to the functional materials community in enabling the full exploitation of their properties.

10.13 New magnetic materials

4GLS will enable a paradigm shift in research on new magnetic materials, as it offers the possibility for step changes in a number of fields of importance, including spin-polarised photoemission and magnetic imaging techniques. The development of spintronic memories will require nanoscale characterisation of electron spin distributions in magnetic clusters of the type 4GLS is ideally suited to provide. The ability to image magnetic materials using the non-linear magneto-optic Kerr effect (NOMOKE) is of crucial importance to the study of interface magnetism in magnetic multilayers and thus to the characterisation of new materials for magneto-optic recording and permanent magnets.

10.14 Semiconductor and semiconductor thin film technology

The ability to measure the non-equilibrium characteristics of device structures in pump-probe measurements using the VUV-FEL will be invaluable. Semiconductor device structures based on Si are set to become so small that they will operate normally in a non-equilibrium regime which makes these dynamic carrier distribution measurements essential for their further exploitation. Related experiments will also yield an understanding of the transport processes in a range of nanocrystalline materials, including photovoltaic cells based on nanocrystalline oxides.

4GLS will give a unique insight into the dynamic processes of thin film growth, surface processing and plasma etching. A particularly important example here is time-resolved studies of CVD thin film growth of semiconducting materials. This will include studies of precursor breakdown, and studies of the surface chemistry and photochemistry of TiO_2-based photocatalysts. Both of these topics have been cited as areas of great interest by the members of the UK EPSRC CVD Network. This group, which consists of over 20 academic groups and *ca.* 6 industrial concerns, has given its full and unequivocal support to the 4GLS proposal simply on the basis of the potential insight into CVD processes coupled with the possible technological developments in terms of materials growth that could result from the proposed experiments.

In the THz regime, 4GLS offers enormous intensity advantages over conventional laser sources, and these will be of direct benefit to the semiconductor community, for example in work aimed at the coherent manipulation of localised semiconductor electronic states (Qubits) such as impurity or quantum dot states using THz radiation, and in the development of spintronic memories through studies of spin relaxation in quantum wells.

10.15 Theoretical Studies

4GLS will enable world-leading experimental work and provide very high quality data which will inform theorists, and enable the development of current models in a number of areas of crucial importance to modern physics. These include accurate modelling of stellar atmospheres, leading models for the origin of the universe, and modelling of the electronic structure of highly correlated metal oxides, leading to differentiation between alternative models for phenomena such as high temperature superconductivity and GMR behaviour. In some cases, initial experimental work is required in order to develop an appropriate model; one such example is work on the behaviour of molecules in intense XUV fields, where 4GLS will contribute ground-breaking data.

10.16 Accelerator technology

4GLS will place the UK (and hence CCLRC/ASTeC) at the forefront of world development of both ERL *and* FEL technology for many years to come. It has been clear for some time that there is no scope for the further worldwide development of storage ring technology beyond SLS, SOLEIL and *diamond*. However, there is considerable enthusiasm in the international community for ERL, FEL and XFEL development. ERL technology in particular allows the flexibility and easy upgrade paths that will be essential to carrying out 21st century experiments in a cost-effective way. Through the development work needed in superconducting accelerator systems and high brightness electron sources, the UK will gain an international lead in these technologies, and will be able to exploit this to support other accelerator projects, such as the superconducting ion linac of SIRIUS and the next linear collider. 4GLS thus will provide a platform from which ASTeC will be centrally involved in supporting accelerator projects for light sources and high energy physics worldwide, including beam delivery systems, particle sources, damping rings and high power RF systems.

10.17 Detector Development

The construction of all new SR sources lends a natural impetus to the development of associated detector technology of all types, as the scientific community exploits the source to the full. In the case of 4GLS, the very high brightness of the sources will make them natural homes for the development of new photon and electron detectors. In particular, development of detectors for use with the high intensity FEL sources will pose tremendous challenges and opportunities. The development of new types of detector with the ability to resolve timescales shorter than 50 fs, such as photoconducting detectors, will be required for full exploitation of the timestructure of 4GLS, and this will be of immediate benefit to the telecommunications industry. 4GLS is an ideal source on which to develop the next generation of fast IR detectors of the PIRATE type. Other areas where significant improvements are likely are 2D imaging detector technology including CCD-based systems, ultra-high count rate MCP detection, the development of electron spin detectors using time-of-flight approaches, UV detector and readout technology for CD and fluorescence detection.

10.18 Industrial

The capabilities of the 4GLS suite of sources will make a major contribution to fundamental work in the UK and this will lead to technological exploitation in the long term. The likely areas for initial industrial exploitation have been described in Section 4.2 on Industrial Exploitation. The beneficiaries highlighted include the semiconductor and electronics industries, including companies developing display technology, nanotechnology, high throughput screening and the instrumentation industry. There will also be generic benefits to industry from manufacturing process improvements in areas including the chemical engineering industry and the production of high performance materials.

11 COMMUNITY

The user community will develop from two groups of scientists who presently work separately, those who have been using the SRS and 3rd generation SR sources abroad, and the conventional laser community whose experiments are very much concerned with pump-probe techniques and experiments in very high EM fields. 4GLS provides an ideal opportunity to bring these two communities together for novel experiments combining the advantages of both kinds of source.

A substantial fraction of the user base will derive from those who wish to make use of the undulators in 4GLS which provides them with a factor of 10^3 increase in brightness in the low energy photon region from 10 – 100 eV. This performance is not available from any source either available now or currently under construction worldwide. In addition, the bending magnets are competitive sources of broadband infrared radiation.

The VUV-FEL will certainly be of interest to the above community, particularly in those cases where the sample is dilute or available in only small quantities. It is however the opportunities to carry out pump-probe experiments, and experiments on excited or transient species, with both photons in the VUV, that has kindled the interest of those who use conventional lasers and who are currently limited by intensity and duty cycle restrictions to photon energies below 5 eV. Many of these are interested in synchronising their conventional laser systems to the VUV-FEL, which gives them access to much higher excited or ionised states than is currently possible with laboratory laser sources. There is also interest in using the VUV-FEL for resonant two-photon ionisation in the VUV, an entirely novel area of investigation.

The XUV-FEL is primarily of interest to those who carry out experiments in very high fields, *e.g.* power densities > 10^{15} watts/cm^2. Though this figure is certainly available with high power conventional lasers, access to such power using high energy photons avoids many of the complications which arise in the analysis of the experiment when using multiple low energy photons, where the large number of alternative pathways in the excitation/ionisation process is difficult to handle theoretically. There are also those who wish to use the FELs to study the behaviour of high Rydberg states in very high EM fields. Such experiments will be state-of-the-art and completely unique to 4GLS.

The IR-FEL user base is at present the community that utilises European IR-FEL sources and has started to use the IR-FEL at Jefferson Laboratory in the USA, but there are unique opportunities for pump-probe experiments using both IR and VUV-FELs, and also using IR radiation from a 4GLS bending magnet and the VUV-FEL. The synchronisation between these two sources is a particular advantage. This will bring together both the current community which uses the IR facilities at the SRS and those using FELIX. At Super-ACO the availability of IR radiation and FEL radiation is already beginning to be exploited in experiments where the UV laser is being used as the pump and the IR radiation as the probe, giving ro-vibronic information for example on excited species and molecular fragments. A large expansion in this area of research, extending to industrial use of 4GLS, is envisaged. There are clear applications in materials science, for example as a probe of photocarrier density in large band gap semiconductors and investigations of time resolved modifications of thin films and surfaces under VUV irradiation

In summary we estimate that **150 UK groups** will be users of the insertion devices and bending magnets on 4GLS.

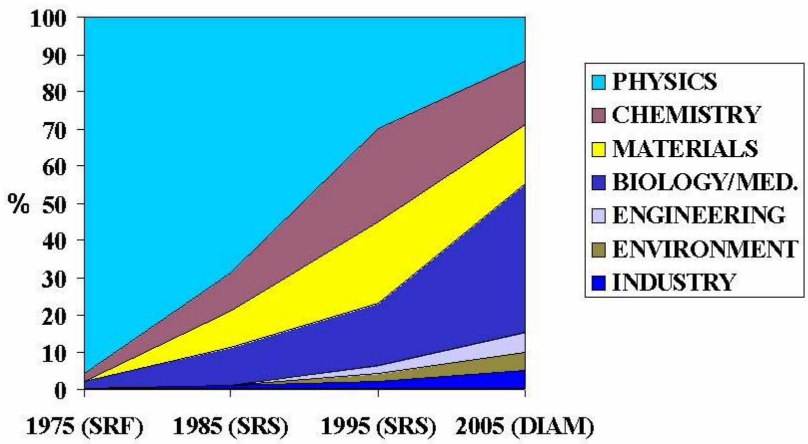
In the case of the XUV-FEL, those groups presently interested in the non-linear effects of high radiation fields in molecular ionisation foresee exciting opportunities using this source. It is however a novel device and it is difficult to quantify how many groups will be interested initially. Once it is operating its potential will be realised and the user community correspondingly is likely to expand rapidly. We estimate a minimum user community of ~**40 UK groups**.

At present the facilities at FELIX are regularly oversubscribed by a core of UK semiconductor physics users (some 10 or so groups). A large expansion in this community and that interested in using the VUV-FEL alone or combined with broad band IR for materials science and biological applications is expected, perhaps to ~**70 UK groups**.

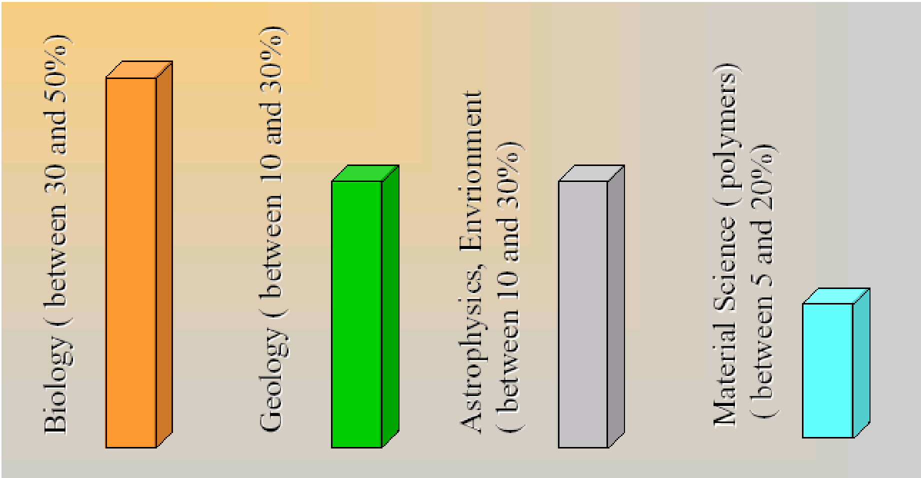
Nowhere are SR, VUV, XUV and IR-FEL experimentation integrated to such an advanced level as planned for 4GLS. The UK low energy photon community is thereby likely to expand significantly and the facility will become a major attractor of world class investigators from both Europe and further afield. The user base of 4GLS when fully developed is likely to be some **920 scientists**.

The section on wider exploitation indicates significant industrial interest in the 4GLS facility. The future size of this community is difficult to quantify, but a significant number of expressions of support have already been obtained, and are included in the 'Letters of Support' section.

Some indication of the balance of the user community between disciplines can be gained from comparisons with the usage patterns for established facilities. The diagram below shows the variation in the proportions of users from different disciplines using the existing SRS since its construction.



It clearly indicates a strong increase in use by the biomedical and bioscience community in the 25 years of operation of the SRS, a pattern repeated at other sources around the world. The science case we have presented indicates that there is already a substantial demand for this source from the biological sciences, and we expect that once the source is established, this will grow further. In the case of the IR-FEL, this expectation is confirmed by already established patterns of use. The distribution of users for the CLIO facility at LURE is shown below, and indicates a very even spread across a range of physical sciences and biology.



11.1 Consultation

As many avenues as possible have been taken to engage with synchrotron radiation users, with laser users and with accelerator physicists both in the UK and abroad. This has taken several forms, *e.g.* one day meetings, formal oral presentations (sometimes combined with poster presentations), 4GLS web pages *etc.* A list of Presentations and Meetings is given in Appendix III. In total five one-day consultation meetings (total attendance 300) have been held. More than 15 UK and international presentations have been made to over 2000 scientists. In addition, detailed discussions have taken place with experts from various overseas laboratories. In this way it has been possible to identify the new opportunities that 4GLS offers for both high brightness VUV radiation from its insertion devices, the unique opportunities presented by its laser sources and the combination experiments that can be carried out using both kinds of source. The response, particularly from the laser community whose scientific interests in the past have focussed on high instantaneous intensities and very high resolution, has been very encouraging, and this is reflected in the scientific case to which they have made major contributions. Around 160 letters of support from *ca.* 170 signatories are attached to this proposal. These span fields including chemistry, physics, life sciences, earth sciences, materials science and industry. They indicate support from universities, government laboratories, other world facilities and the NHS.

The consultation process will continue, particularly as the potential for exploitation of 4GLS becomes better understood, together with the opportunities it presents for novel experiments.

12 COLLABORATIONS

12.1 Research

Internationally, 4GLS has already provided the stimulus for increased collaboration with several major synchrotron laboratories, in particular Jefferson Laboratory, Brookhaven National Laboratory, DESY (Hamburg) and BESSY (Berlin). Involvement and participation in two European FEL projects is already under way.

The unique potential of 4GLS has attracted considerable interest and support for the new facility, as is evident from the letters of support. There are three overseas groups in particular who envisage collaborative research programmes:

MAX-Lab, Lund University, Sweden

At present MAX III, a low energy storage ring of 700 MeV nearing completion, is one of only two genuine low energy sources in Europe. Experimental groups there are already involved in experiments using either SR or laser sources in the VUV, although they are not at present planning a combination of the two. They are eager to particpate in the development of pump-probe experiments at 4GLS (contact: Svante Svensson), and are also interested in contributing to the design of 4GLS. They already work with UK scientists on experiments in Atomic and Molecular physics using MAX II.

LURE, Orsay, France

With the near certainty that SOLEIL will now run routinely at 2.75 GeV, the low energy community at LURE is being increasingly isolated. This is particularly unfortunate in view of the fact that that community has pioneered several areas of research using low energy photons, and in particular in the development of cavity FELs and pump-probe experiments using the Super-ACO FEL with SR. There is strong support for the 4GLS project from that community, and it is expected that they will wish to be involved in both the design and implementation stages. (contact: Laurent Nahon)

Storage Ring Facility ASTRID, Aarhus, Denmark

A Memorandum of Understanding (MoU) already exists between Daresbury Laboratory and ASTRID, primarily for collaboration in machine physics, although there has been considerable involvement of Daresbury scientists in both beam line design and the experimental programmes on ASTRID. This machine is the other low energy source in Europe, but unfortunately funds could not be found for further development of the facility from within Denmark, and the ASTRID II project has been shelved. As a result the 4GLS project is of considerable interest to scientists currently working at ASTRID, and collaboration within the MoU is expected to expand. (contact: Søren Pape Møller).

12.2 Technology

4GLS is a world leading project that will exploit the latest advances in accelerator science and technology to the full. It will necessitate both a major design study phase and also a significant R&D programme in order to deliver its planned performance levels. However there are a significant number of potential collaborators who will have a mutual interest in joint development of a considerable number of these solutions. Contact has already been made with major international centres and in every case these have expressed a willingness to enter into collaborative agreements. CLRC, through Daresbury Laboratory, has recently been negotiating a wide ranging Memorandum of Understanding with the DESY Laboratory in Hamburg; this will allow strong links to develop with the TTF and TESLA design team there, covering both accelerator and FEL technology. In particular there is mutual interest in photoinjectors, superconducting linacs and detectors. A similar cooperation agreement with the Stanford Linear Accelerator Centre (SLAC) on a broad range of light source topics will give the 4GLS team access to the second major world project that is focussed on developing the most demanding FEL technological solutions for x-ray production.

The world leader in ERL development is undoubtedly the Jefferson Laboratory. Fortunately the 4GLS team already has extremely strong links there and has been helped greatly in preparing this proposal. In a dramatic gesture of collaboration the Jefferson group has offered one of their advanced undulator magnets for use in the 4GLS R&D programme in the UK. Jefferson also has very close links with the Cornell team and together they are proposing an ERL programme with many similar challenges to those apparent for 4GLS: close links between this programme and 4GLS will be a priority. Discussions have also already been held between 4GLS and Brookhaven Laboratory senior staff, especially concerning high performance electron sources, and collaboration will again be pursued.

Another x-ray ERL programme is developing at the Advanced Light Source, Berkeley and contact with the team developing this is already strong. Finally, there is a wider community in the USA that is pursuing an integrated programme of SASE FEL development, including for example the Argonne Photon Source Laboratory with which existing UK links are already strong through its existing third generation light source activities.

In Europe collaboration with the 4GLS team has already been actively sought by the team developing a SASE FEL proposal at BESSY, Berlin. It is expected that the collaboration will be on all aspects from beam dynamics through to high technology equipment.

Daresbury accelerator physicists and engineers are major partners on the free electron laser project, EUFELE, on ELETTRA which has received substantial EU support and which currently holds the world record for the highest photon energy in a storage ring FEL. Recently, additional funding was approved and this collaboration has been expanded to include development of the science programme for this free electron laser source.

Strong links already exist with the two major IR-FEL user centres in Europe, FELIX in Nieuwegein and CLIO in Orsay, and these will allow valuable collaboration on this aspect of the 4GLS design.

In the UK collaborations will of necessity be at a different level, in the absence of major accelerator-based projects outside the CLRC laboratories. However one centre with which major collaboration has already started is the Department of Physics and Applied Physics at Strathclyde University. A contractual agreement with ASTeC at Daresbury will support theoretical work on advanced SASE FEL processes. ASTeC is also a collaborator on high brightness photoinjectors and associated diagnostics incorporated into the TOPS (Terahertz to Optical Pulse Source) facility at Strathclyde. Discussions on collaboration on ultra-fast diagnostics with the photonics centre at Abertay-Dundee University have also been initiated. A long standing collaboration on RF systems between Daresbury and the Electrical Engineering Department at Lancaster will also be fully exploited in addressing related problems on the ERL complex; it is likely that there will be a role too for the new High RF Power Faraday Partnership that will include industrial links.

In conclusion a very substantial network of collaborations, both within Europe and the USA, is already in place. Subsequent design studies on 4GLS will therefore not be undertaken in isolation but within a dynamic and emerging world community with overlapping interests. Through staff exchanges, visits and workshops 4GLS concepts will be further developed. Exposure of 4GLS to constant *international* peer review will ultimately ensure the robustness of the solutions adopted for the project.