BERRIES

(Bright Environment for x-ray Raman, Resonance Inelastic and Emission Spectroscopies)

Prepared for Diamond SAC/DISCo

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2. Executive Summary

This proposal sets out the case for developing internationally competitive photon-in/photon-out spectroscopy capabilities in the UK. The proposed beamline, BERRIES, will bring two new techniques to Diamond, pink-beam X-ray emission spectroscopy (pink-beam XES) and X-ray Raman scattering (XRS), whilst also enhancing the provision of high energy resolution fluorescence detection XAS (HERFD-XAS) and resonance XES (RXES). The faster data collection and relatively small focal spot of pink-beam XES will transform XES data collection, enabling *operando* and spatially resolved measurements even on weak valence to core emission lines. XRS is a bulk sensitive probe that provides access to low atomic number/low energy absorption edges and that can be used for performing experiments *in situ* and with a broad range of sample environments.

The scientific case demonstrates both the range and depth of the research areas that will be impacted by BERRIES and the existence of a vibrant academic and industrial user community with potential for further growth. The science case is presented in terms of 5 areas: *Chemistry and Catalysis; Energy; Earth, Environment and Planetary Sciences; Materials and Physics; and Biological Sciences*.

In short, BERRIES is an essential addition to the suite of beamlines at Diamond-II if the facility is to remain internationally competitive in modern X-ray spectroscopy.

3. Scientific case

3.1 Introduction

X-ray spectroscopy is widely used as an in-depth characterisation tool for chemically specific electronic and structural properties. BERRIES will provide access to two newly developed spectroscopy techniques: pink-beam X-ray emission spectroscopy (XES) and X-ray Raman Scattering (XRS), and will enable other types of complementary measurements such as High Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy (HERFD-XAS) and Resonant XES (RXES).

These specialised photon-in/photon-out spectroscopic techniques, operating in the hard X-ray region, tackle some of the shortcomings of conventional XAS. XRS enables the study of low atomic number/low energy absorption edges with bulk sensitivity and can be used for performing experiments *in situ* and with a broad range of sample environments, that are otherwise very challenging to implement when using soft X-rays. Furthermore, making use of the dependency of XRS with the scattering momentum transfer **q**, information about dipole forbidden electronic transitions can be obtained. At high **q** values, XRS becomes sensitive to higher order transitions, providing access to the entire unoccupied density of states[1]. XRS will thus enable direct measurement of the *s*-*d* and *s*-*f* transitions in 3d metals, rare-earths and actinides, which hold key information to understand the chemical and electronic properties of many materials. XES on the Valence-to-Core emission line (VtC-XES) overcomes one of the main limitations of XAS: the inability to distinguish ligands that are neighbouring in the periodic table, such as carbon, nitrogen and oxygen. At present, the main drawback of the traditional VtC-XES technique is the long acquisition times (typically several hours) needed to collect good data at these very weak emission lines of samples with realistic concentrations of active components. In contrast, pink-beam VtC-XES will open the door to perform these experiments in a time-resolved manner, significantly reducing the acquisition times to minutes. This will bring the experimental measuring conditions of new materials in a regime much closer to their expected operating conditions.

The current wave of upgrades at facilities around the world has brought the opportunity to build instruments dedicated and optimised for the exploitation of more advanced X-ray spectroscopy tools. The move to more demanding techniques at synchrotron sources has also been aided by the development of more efficient laboratory sources that enable routine XAS/XES more widely. There is little doubt that new and transformative science will be enabled by these new instruments and will be carried out over the next 10 to 20 years. From the perspective of the X-ray spectroscopy community in the UK, BERRIES is an essential development to offer competitive research tools to stay at the forefront of science areas such as catalysis, energy materials or nuclear materials.

The broad interests of the spectroscopy user community are represented in the science case presented below. The science undertaken on X-ray spectroscopy instruments is very dynamic and reflects and adapts quickly to the needs of new research areas. As such, we expect that BERRIES will have wide impact, and that it will open up many new opportunities to further grow the user community.

3.2 Science enabled by project

The capabilities that the proposed beamline will bring to Diamond will have an impact in many areas of science. In this proposal we will focus on the impact that BERRIES will have on Chemistry and Catalysis, Energy research, Environmental Sciences, Materials and Physics, and Biology.

3.2.1 Chemistry and Catalysis

X-ray spectroscopy techniques have, since their origin, been used to push boundaries in the area of Chemistry and Catalysis. The ability to study local atomic and electronic structure for solids, liquids or gases, in a range of sample environments, and under *operando* conditions has been key for this successful partnership. **BERRIES, through XRS and pink-beam XES, will provide newly developed and advanced spectroscopy techniques that will broaden the structural and electronic information that can be extracted**

from these systems, deepening our understanding of reaction mechanisms. Below we have chosen some examples that will help illustrate how BERRIES can make a difference in this field.

The use of pink-beam VtC-XES will enable time-resolved studies with resolution of minutes, pushing the frontier from steady state studies to critically important dynamic measurements. A system that is expected to benefit from this capability is the NH_3-mediated selective catalytic reduction of harmful nitrogen oxides (NH_3-SCR). This is a key process for the automotive sector, as any diesel car under the EU6 emission standard requires the SCR of NO_x gases[2]. Cu, as a catalyst, is showing considerable promise in this application[3–5], but a thorough understanding of the reaction mechanism at low temperatures is still needed. To this effect, the determination of the structure of the intermediates formed at different stages of the oxidation cycle is critical, but challenging due to the difficulty of discriminating between quasi iso-electronic elements ligated to the metallic centres (e.g. O, C, N). VtC-XES has been recently performed at I20-Scanning on static samples (Figure 1), and the potential of the technique to investigate NH_3-SCR shown[6]. The slow collection times currently limit the applicability of the method and it is not yet practical to perform the studies under real operating conditions but BERRIES would make them feasible.

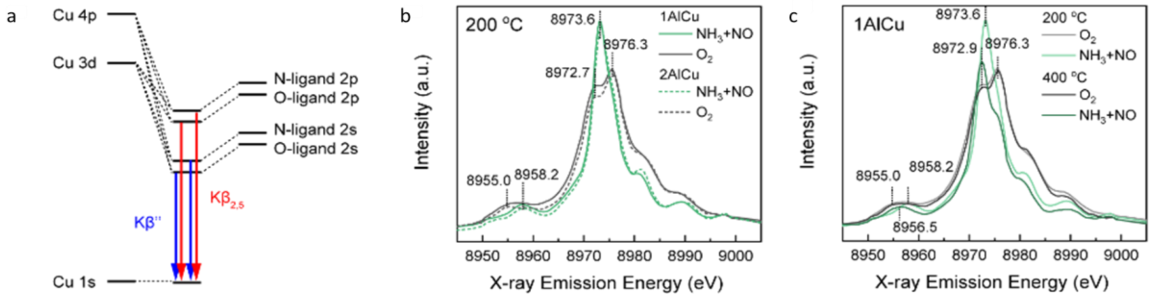


Figure 1. *a) Molecular orbitals for Cu-N and Cu-O bonds and electronic de-excitations, b, c) Cu VtC-XES for Cu-exchanged zeolites under different conditions: gas mixture, temperature, Al:Cu ratio (taken from ref. [6])*

XRS will offer new opportunities in the field of heterogenous catalysis. For example, during hydrogenation and oxidation reactions catalysed by Pd nanoparticle (NP) catalysts[7,8], interstitial hydride, carbide, and nitride phases have been observed, where they play a fundamental role. The structure around the Pd centres has been widely studied by XAS under *operando* conditions but understanding how carbidic and nitridic Pd structures are formed, and the stability of these structures under process conditions remains a challenge. XRS provides the opportunity to probe the C and N environments directly with bulk sensitivity and under the same environmental conditions, and this will aid us to learn how to harness these structures for new catalytic technologies.

XRS will also have a large impact on the study of boron chemistry, an area of increasing interest that permeates several fields of research, including hydrogen storage materials and frustrated Lewis pairs. XRS has already been used to study *in situ* the electronic properties of bulk lithium borohydride ($LiBH_4$)[9], that is used as an attractive option for hydrogen storage due to its relative stability, ease of handling, and relatively high content of H_2 by mass. The kinetics of H_2 absorption of this material, and its comparison with the kinetics of the compound when confined in porous carbon ($LiBH_4$/C) was determined by measuring the *K*-edges of C and B. On the other hand, the investigation of the structure of frustrated Lewis pairs (FLPs), sitting at the intersection between main group chemistry and catalysis[10], will also be aided by the use of XRS. FLPs are combinations of sterically hindered Lewis acids and Lewis bases capable of cooperative catalytic activity, leading to metal-free activation of H_2 and other small molecules[11]. Access to structural and electronic structure information in these compounds is not straightforward, and techniques such as soft X-ray absorption spectroscopy pose a real challenge due to the liquid and absorbing nature of the samples.

BERRIES will also provide new insight into electrocatalytic processes. Electrocatalytic transformations of small molecules provide a route to more distributed production of chemicals and fuels that will enable a more sustainable approach to their supply and a decreased reliance on fossil fuels. The four main areas of current interest are water electrolysis for hydrogen production (OER – oxygen evolution reaction), CO_2 reduction (CO_2RR) to produce carbon-based products, reduction of N_2 to produce ammonia (N_2RR), and methane partial oxidation (CH_4OR)[12]. In the case of ORR, there is increasing interest in non-PGM transition metal (TM) oxide catalysts (also of interest as bifunctional ORR/oxygen evolution catalysts for metal-air batteries). While static *operando* measurements at the metal centre K_β emission lines have enabled a detailed understanding of the potential dependence of the TM ions' oxidation states[13], pink-beam VtC-XES will enable time resolved studies of such materials, providing a deeper insight into the dynamics of the process. The current state-of-the-art CO_2RR electrocatalysts are either heterogenous, nanostructured, Cu, Au, or Pd[12], or homogenous TM complexes[14]. XRS measurements at BERRIES at the metal *L*-edges and VtC-XES measurements at the *K*-edges will enable the details of the metal oxidation state and ligand coordination to be understood. Electrocatalysis of the N_2RR is in its infancy and primarily driven by theoretical/DFT calculations. The mechanism of the N_2RR reaction is predicted to be strongly dependent on the catalyst, with the rate determining intermediate being the formation of (adsorbed *) $*NH_2$ for Sc, Y, Ti, and Zr, and $*N_2H$, $*NH_2$, or desorption of NH_3 for Mo, Rh, and Fe[15]. Pink-beam VtC-XES measurements will enable the study of the oxidation states and coordination of many of the TM.

3.2.2 Energy

Spectroscopy is fundamental in the investigation of new materials for energy applications, offering direct access to information about oxidation states. The detection of the degradation of materials during cycling can give information about the electronic and atomic structure in non-crystalline (including liquid) components. **BERRIES represents a new core-capability for this community, providing a bulk sensitive probe for light elements and the ability to explore the redox cycling of the non-metal component of battery electrode materials.**

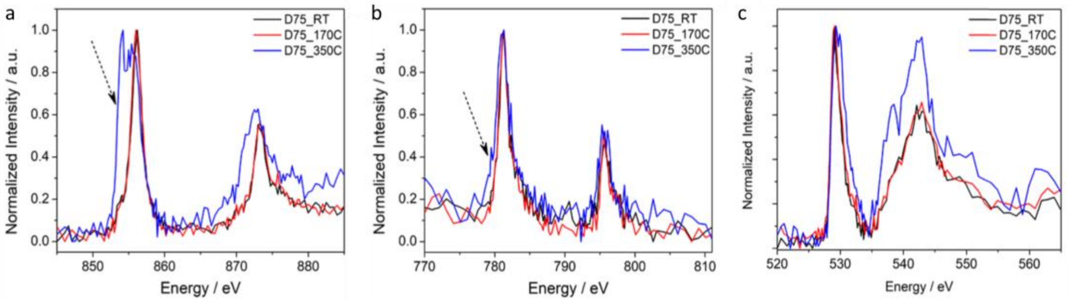


Figure 2. *X-ray Raman Scattering data showing (a) Ni L-edge, (b) Co L-edge, and (c) O K-edge for 75% de-lithiated* $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ *powders at room temperature and after heating to 170 or 350 °C (adapted from ref. [16])*

XRS offers the exciting prospect of a bulk-sensitive probe of the *K*-edges of highly relevant light elements (e.g. Li, C, O, F, Na) as well as transition metal L-edges (e.g. Mn, Fe, Co, Ni) that is not currently possible with any other approach. This will allow chemical changes occurring in the electrodes and electrolytes of batteries to be tracked, including the oxidation states of redox active species in the active electrode materials[16] (Figure 2) and the evolution of species in the electrolyte, including products of undesired side-reactions[17]. Results will inform the development of novel battery electrode materials, particularly high- capacity cathodes, where understanding the origin of redox activity is critical to optimising the material's chemistry. It will also reveal the degradation products resulting from electrolyte breakdown during repeated cycling, and due to dissolution from the active electrode materials, which will inform strategies to extend battery lifetime, and ultimately reduce device cost. XRS at BERRIES will enable studies of redox flow batteries to observe chemical changes in electroactive elements in both anolyte and catholyte, and, if the concentrations allow, even allow for probing ions adsorbed within porous electrodes in supercapacitors. The information obtained will be complementary with the surface sensitive TEY mode XAS available at other beamlines (e.g. B07, I09, I10), but without the limitations to the sample environments or cells imposed by working under high vacuum. This means that realistic sample environments can be realised much more straightforwardly (including standard coin cell and pouch cell battery electrodes and components).

Pink-beam XES further promises improved time-resolution that would make operando VtC-XES a reality, reducing the measurement time to minutes. This will be particularly valuable for probing anion redox processes in alkali-ion batteries, including TM-anion bond and anion oxidation state[18,19]. Pink-beam XES at BERRIES will allow the redox processes to be observed during charge and discharge at realistic rates (including for fast charging), fundamental for understanding the origins of reversible and irreversible capacities in novel electrode materials. It will also provide the opportunity to resolve intermediate states that are not detectable with current *ex situ* methods.

3.2.3 Earth, Environment and Planetary Sciences

Research in this area is very diverse, tackling questions ranging from understanding how our planet is formed, to strategies to clean contaminated water, the development of sustainable materials, improvements in recycling processes, and the decommissioning of radioactive sites. It is expected that the relevance of these topics will only grow in the coming years and decades, as many of these issues are becoming important drivers within the worldwide economy and environmental sustainability.

Research in actinide chemistry and electronic structure is a large area that not only poses interesting fundamental questions, but it is also critical to develop strategies for storage of radioactive materials and decommissioning of radioactive sites. **BERRIES will open exciting opportunities in this field, in line with the Government's Nuclear Industrial Strategy through the Nuclear National User Facility (NNUF).**

Established actinide X-ray spectroscopy at Diamond routinely takes advantage of L_3-edge XANES, but transition selection rules forbid direct access to the 5f valence shell. Ligand *K*-edge XANES provides access to both 5f and 6d frontier molecular orbitals, as shown in Figure 3a,[20] and has become an extremely powerful probe of actinide–ligand bonding, despite being mainly limited to ligands with high energy absorption thresholds (Cl, S etc). XRS has the capacity to revolutionise these measurements since it will permit access to elements that are the most commonly bonded to actinides, but currently are inaccessible due to their soft X-ray *K*-edge energies (C, N, O, etc.), enabling the direct interrogation of novel molecular complexes prepared to explore actinide bonding, and environmentally relevant species. Perhaps the most powerful aspect of XRS measurements is the ability to tune transition selection rules with X-ray momentum transfer (**q**). XRS at high-**q** makes it possible to access the characteristic 5f multipole transitions of $O_{4,5}$-edge. These transitions are sharp, with rich multiplet features characteristic of oxidation state and coordination symmetry, with sensitivity to 5f covalency[21], as shown in Figure 3b, where imaging of the sample with the direct tomography method[22] was crucial to separate the Np and Pu scattering signals from that of the Be encapsulation.

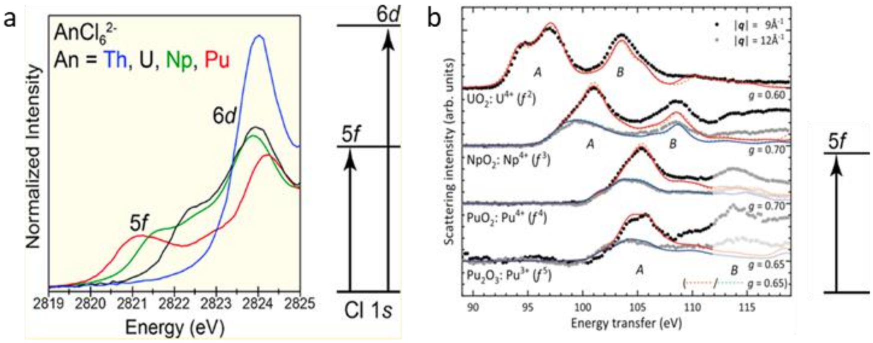


Figure 3. *a) Cl ligand K pre-edges revealing variations in actinide (An) 5f and 6d contributions to An-Cl bonding for* $[AnCl6]^{2-}$ *where An= Th, U, Np Pu (reproduced from ref.* [20]*) b) Actinide O-edge XRS for U, Np and Pu oxides quantified with atomic multiplet simulations (reproduced from ref.* [21]*).*

BERRIES will also impact on experiments performed to study the 6d ligand field splitting[23] and the 2p – 5f pre-edge features[24] using L_3-edge XES, HERFD-XAS and RXES. The small beam size and the high flux will enable the study of smaller samples, reducing the amount of radionuclide needed. The small beam will also expand the use of photon-in/photon-out spectroscopies to studies requiring the determination of spatial distribution of the radioactive element in a heterogeneous sample[25].

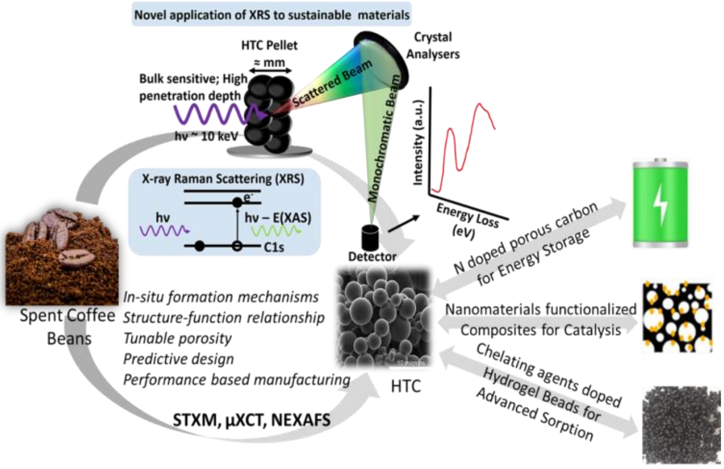


Figure 4. Diagram illustrating stages involved in the study of HTC synthesis and functionalised materials (B. Mishra).

The high flux and small beam sizes offered by BERRIES will also be essential for studies in Earth and planetary science, where high pressure vessels such as diamond anvil cells (DAC) are used to mimic the conditions of matter in the interior of the Earth and on other planets. XRS has been successfully used to study silicate glasses under the conditions of the Earth's mantle[26]. XES in the dispersive configuration can be used to investigate magnetic transitions under high pressure and temperature conditions, which have an effect on the compressional behaviour of materials[27,28].

An important aspect on environmental science is the search for sustainable materials. Hydrothermal carbon (HTC) embodies all the desirable principles: it is produced from biomass (such as agricultural waste residues) under moderate hydrothermal conditions using only water as a solvent, and is a multi-scale porous material with tuneable porosity and surface functionality. Doping heteroatoms in HTC improves the electrical conductivity, material stability, and catalytic performance owing to an increase in the number of active sites, making doped-HTC suitable for a range of applications including energy storage, catalyst supports and high value sorbents. In spite of significant progress, a fundamental understanding of the formation mechanisms governing HTC growth and structure (e.g. nucleation or pore formation) remains unknown due to technological limitations on element-specific *in-situ* measurements of low-Z elements. XRS is the first technique to enable such experiments. XRS, combined with STXM, µXCT and NEXAFS (Figure 4) can provide a transformational multi-scale *in situ* understanding of the physical and chemical processes involved in the production of this versatile material[29,30].

3.2.4 Materials and Physics

The development of new materials is a driving force for both fundamental and applied research and has particularly benefited from the techniques available at synchrotron sources and other large facilities. Spectroscopic measurements are very valuable because they can be applied to all the breath of systems that are investigated, from 3D single crystals to disordered systems, pure and doped.

It is expected that a generation of materials for new electronic and computational architectures will be developed in coming years. In particular, there is considerable interest in semiconductors which exhibit room temperature ferromagnetism and are compatible with standard CMOS technology. From a more fundamental point of view, they are also ideal systems for studying new physics such as quantum spintronics and spin solar cells. **Pink-beam VtC-XES will give valuable information on the nature of the interaction of the magnetic ions with different ligands**. This information is extremely difficult to obtain with other spectroscopic techniques. Having access to this type of data will open up the possibility of studying complex systems with multiple ligands such as $Zn_{1-x}Cr_xTe$ co-doped with N, where the low concentrations will require the high flux at BERRIES[31]. **In addition, the pink-beam will open the door for time resolved experiments at these weak emission lines**. In a recent study, Vanko *et al*. used a MHz laser to excite a low spin iron complex into the high spin state, and probed the transient high spin state using XES[32] by following the strong K_α emission lines (Figure 5). BERRIES will enable this kind of experiment to be performed on the magnetically sensitive but weaker K_β emission lines.

A second example is provided by the high temperature superconducting (HTS) cuprates, which have been studied intensively for over 30 years and proved to be very challenging materials. We are now on the brink of using them in real technological applications, such as the high field magnets for nuclear fusion reactors being developed and built by Tokamak Energy (a local SME based in Didcot) and there is a pressing need to understand the effect of neutron irradiation on their electronic properties. Irradiation lowers the transition temperature of HTS compounds and can suppress superconductivity before any structural changes can be observed by standard techniques other than XAS. Soft XAS to study 3d electrons is not ideal in this context, as the surfaces can be damaged (and hence not representative of the material) or buried under protective overlayers. However, XRS will enable the study of technological superconductors thanks to the higher penetration of the photons. It would even be possible to study activated samples (neutron irradiated) which need to be kept in shielded containers.

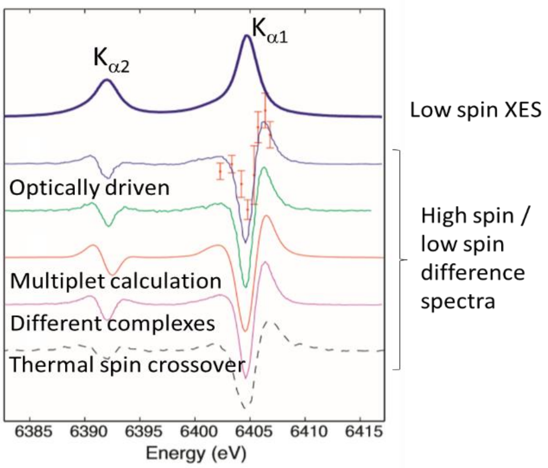


Figure 5. *Pump and probe experiment showing a measurement of transient low spin to high spin with XES. Adapted from ref.* [32].

XRS also offers the possibility of probing the 1s-3d quadrupole transitions in transition metals using high momentum transfer (**q**) vectors. A recent study by Yavas *et al.* has shown that XRS can directly measure the shape of 3d orbitals of transition metals in real space by rotating the sample to probe different **q** directions[33]. It is easy to imagine the impact that this type of work can have in future years for a wide range of materials (e.g. the many perovskites that are being explored for a wide range of applications).

BERRIES represents a step change for this area of science. Most research programs rely on the use of complex sample environments such as cryostats, magnets or high pressure cells, and this new instrument will enable O K-edge spectroscopy to be performed in the hard X-ray regime[34,35]. In addition, the relatively small spot size, the ability to accommodate complex sample environments, and the time-resolved capabilities enabled by pink-beam XES will also enable *operando* experiments on devices such as spin field effect transistors, which can use dilute magnetic semiconductors for spin injection and are controlled by modulation of a gate voltage. Complementary spin-selective K_β HERFD-XAS, also accessible at BERRIES, would also be a valuable tool for this type of work.

3.2.5 Biological Sciences

Biological X-ray spectroscopy is undergoing a worldwide resurgence, fuelled largely by development of synchrotron beamlines dedicated to photon-in/photon-out spectroscopies. Studies of bond activation carried out in nature by metal-containing enzymes and critical to understand processes such as N_2 activation, O_2 activation, and CO_2 capture, are one of the main applications of these advanced techniques. There is considerable interest in this chemistry, with applications in green energy technologies including, H_2 production, fuel cell catalysts, CO_2 sequestration, NH_3 production and water remediation[36–39].

Hard X-ray techniques such as pink-beam VtC-XES can provide information about the extent of activation (lengthening) of molecules bound to a metal centre by probing transitions from ligand-based σ/σ^* and π/π^* orbitals. A recent theoretical study of O_2 bond activation in bridged 'Cu_2O_2' complexes demonstrates the potential of VtC-XES to determine not only the presence or absence of a bond, but also to characterise progress along the reaction coordinate[40] (Figure 6a). The technique has also been used as a direct probe for ligand identity and protonation state[41] (Figure 6b) and to identify the presence of hydride ligands at metal centres[42] under static conditions. **The pink-beam available at BERRIES provides a marked**

uplift in capability over the current state of the art[43], enabling in situ studies of protonation state changes and proton (H^+) transfer, considered key steps in the mechanism and function of many catalytic processes (for biological, heterogeneous, and homogeneous catalysts).

In addition to the benefits of pink-beam XES, the enhanced energy resolution of BERRIES will offer opportunities to distinguish contributions from metal ions of different spin states in biological systems using K$_\beta$ HERFD-XES. This will be of particular use for deducing the electronic structure of iron-based catalytic centres in proteins, where a single low-spin iron site often needs to be distinguished against a background of high-spin sites in electron transfer chains.

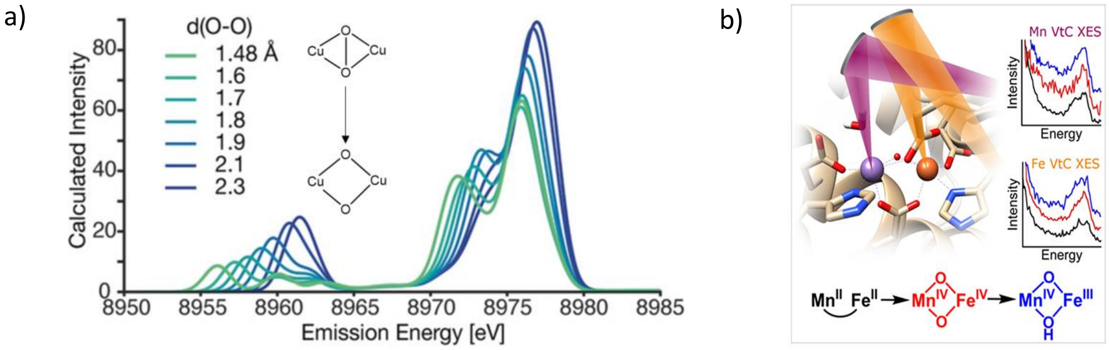


Figure 6. a) Effect of O-O bond length, calculated spectra for a 'Cu_2O_2' fragment between limits of μ-η^2:η^2-O_2 (green, 1.48 Å) and bis(μ-oxo) (blue, 2.3 Å). Adapted from ref. [40] b) VtC-XES from Mn (top) and Fe (bottom) used to probe intermediates in catalysis by a metal-containing ribonucleotide reductase, revealing unprecedented details of protonation states during catalysis. Reproduced from ref. [41].

In the context of biological research, it is important to mention that radiation damage is always of particular concern when the sample is exposed to a high brilliance beam. The experience from I20 (and other synchrotrons and XFEL sources), has already paved the way to sample cells and measuring strategies to counteract this difficulty[44].

3.3 Diamond-II portfolio

One of the drivers that emerged from the Diamond-II consultation with the spectroscopy user community was the need to increase the competitiveness of the Spectroscopy Group in advanced photon-in/photon-out spectroscopy. BERRIES will help to fulfil this objective by offering two techniques to the community currently not available in the UK: X-ray Raman Scattering (XRS) and pink-beam X-ray Emission Spectroscopy (XES). Both techniques complement those already on offer or planned on other instruments at Diamond, within the spectroscopy group and beyond. BERRIES will not only take advantage of the added capacity offered by Diamond-II, but the increased flux delivered will also be essential for these very photon hungry experiments.

XRS allows the spectroscopic investigation of light elements, from Li to Si in challenging environments, and will provide access to a part of the periodic table that is currently not accessible by any of the instruments of the spectroscopy group. The bulk sensitivity of this technique complements the surface sensitivity provided by soft XAS available at the VERSOX beamline, B07, and the electron energy loss spectroscopy (EELS) currently available at ePSIC. Consequently, the provision of XRS within the Diamond instrument suite will facilitate a more comprehensive understanding of many systems of interest. Direct tomography with XRS with micrometre resolution contrast[22] will also be extremely complementary to other imaging techniques currently available at Diamond, and in particular to the I08 Scanning Transmission X-ray Microscopy (STXM) instrument, but with the added benefit that bulk samples can be imaged. It is important to highlight that the availability of XRS, soft XAS, EELS and STXM capabilities will, within Europe, be unique to the instrument portfolio at Diamond, as no facility other than Spring-8 offers this variety of techniques for the study of spectroscopy in light elements.

Pink-beam XES will complement the XES capabilities already existing at I20, but its faster measurement speed will enable the study of processes under *operando* conditions. The smaller focal spot that can be achieved with the new instrument will also enable spatially resolved studies, as well as experiments under high pressure conditions. Spatially resolved studies in the hard X-ray regime accessible at BERRIES will complement the emission studies that will take place at I18 in the tender X-ray regime.

3.4 Academic user community and beneficiaries

Although the techniques offered by BERRIES are new to the UK user community and not widely extended worldwide, they will have an impact in many areas of science, as has been described in section 3.2. Research areas as diverse as chemistry and catalysis, energy, environmental sciences, hard condensed matter and biology will profit greatly from BERRIES. All these communities make already frequent use of the existent spectroscopy beamlines, as shown in Figure 7, and we expect that these research teams will rapidly become BERRIES users.

As shown in Figure 7, chemistry and catalysis is the largest community currently using the spectroscopy beamlines, and we expect BERRIES to have a large impact in this area as well. XES has already been proven as an important technique for the study of the evolution of the electronic structure of *in situ* catalytic reactions, and the possibility of performing XES with a broad energy band-pass that considerably decreases the time needed for data collection, opens the door to *operando* studies. On the other hand, some interesting studies are also starting to emerge in the study of crystallization using XRS. It is foreseen that the beamline will play a large role in meeting the research objectives of the UK Catalysis Hub, funded by EPSRC and recently renewed until 2023.

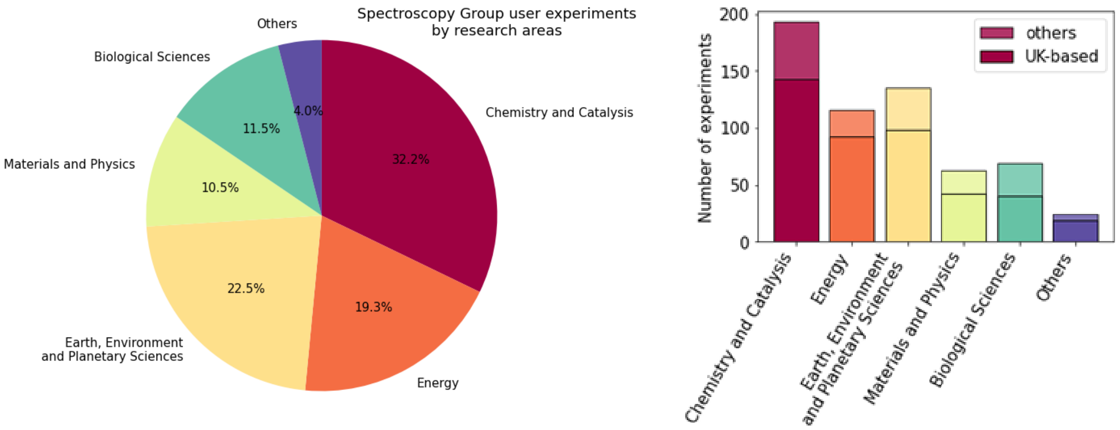


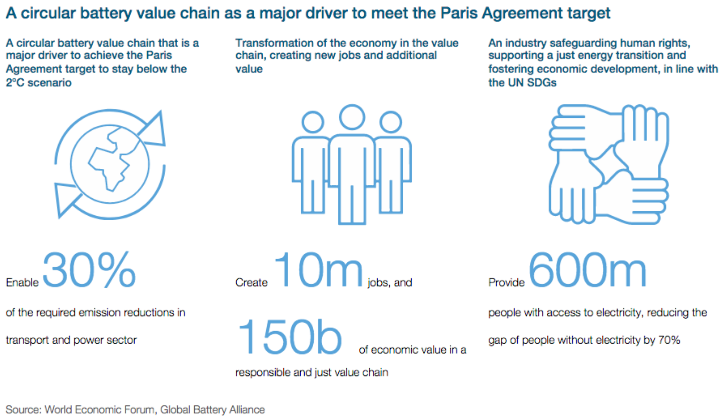
***Figure 7**. Left – Break-out of Spectroscopy Group user experiments (>600 in last five years) by research areas. Right- stacked bar chart of total number of experiments for each research community; the separator in each bar divides UK-based users from others.*

BERRIES will also contribute to the research undertaken in the area of energy materials in the UK. XRS is already having a significant impact in this area, allowing the study of the K and L absorption edges in the low energy regime with bulk sensitivity and in real devices, and this will grow further the more extended the technique becomes. Pink-beam XES will also be of great utility in this field, as fast battery cycling will then be possible. BERRIES will become an essential tool supporting key government initiatives such as the Faraday Institution.

To attract users to BERRIES, we will need to ensure that the potential of the beamline for the key areas of research is widely promoted. Besides current users of the spectroscopy beamlines, we will also target users of beamlines highly complementary to BERRIES (see section 3.3) so they are aware of the new possibilities that the beamline will open for their research. To achieve this, workshops to train users in XRS and pink-beam XES, including data analysis, will be organized, following the successful experience of the spectroscopy group in the area, through the organization of the yearly XAS Data Analysis Workshop.

3.5 Industrial user community and beneficiaries - impact on UK PLC

There are 12 industrial users that already collect spectroscopy data at Diamond on a regular basis with 54 beamtime sessions booked in the last 5 years. More than 80% of the beamtime has been dedicated to experiments in the areas of chemistry and catalysis (45 sessions, 8 companies), the remaining 20% being split almost equally between studies in the areas of environmental and nuclear (4 sessions, 2 companies) or healthcare and pharmaceutical (5 sessions, 2 companies). This community has a good understanding of the value of spectroscopy measurements for their work and the facility has experience supporting the particular needs of these types of experiment. Consequently, industrial users are well placed to make full use of the new tools BERRIES will provide for them. XRS will enable experiments in realistic environments for light elements, and pink-beam XES measurements will be possible under more realistic *operando* conditions. These techniques will be of great value for the industrial user community, as it will enable work at all TRL levels 1-9 (i.e. from fundamental research to the assessment and development of prototypes). Consequently, we anticipate that building BERRIES will result in an increase in demand (and use) of beamtime at Diamond by industrial users.



Source: World Economic Forum, Global Battery Alliance

Figure 8. *Key elements of the sustainable battery value chain as proposed in* [49].

BERRIES will bring new capabilities to industries like Infineum UK. Ltd, that already uses Diamond to develop future lubricant additives. This industry was worth 127 billion USD worldwide in 2019[45]. The chemical and pharmaceutical companies are the second largest UK industry, with revenues of the order of £60bn in2019[46]. Companies like JM, for example, will be able to use BERRIES for their extensive catalysis research program. For the pharmaceutical industry, the new beamline will be valuable for example, for investigating polymorphic transitions and physicochemical properties[47].

BERRIES will also support research in energy materials and green industries. Both areas are expected to see substantial growth over the next 10 years and the UK has invested heavily in them recently as part of the "Clean Growth" Grand Challenge, one of the 4 described in the latest Industrial Strategy White Paper published by the government[48]. A report by the World Economic Forum about the battery value chain anticipates that according to their development model, by 2030 it will be worth 150 billion USD (Figure 8)[49]. The last few years have seen the creation of a large number of industrial spin-outs and start-ups in the clean energy area, heavily underpinned by excellent research of a type that BERRIES will be able to support for in-depth characterisation of battery systems (rather than screening of new materials). Under the broad classification of green growth, we find several industries that will also benefit from access to BERRIES, such as waste management, green construction materials or hazard assessment of the environment.

3.6 Comparison to other synchrotron facilities, current and planned

The XRS and pink-beam XES techniques that are the focus of this proposal, have only recently become available at synchrotron sources and are showing great potential in several areas of science (see section 3.2). This makes the BERRIES proposal very timely, as many synchrotrons are in the process of upgrading their existing spectrometers so higher quality XRS measurements can be performed by capturing a large solid angle, or they are planning new instruments to perform pink-beam XES.

XRS spectrometers based on insertion device beamlines and equipped with multiple analyser crystals to increase their efficiency, are available at several synchrotron facilities around the world[50–54]. One of the most sophisticated XRS instruments that is currently available can be found at the ESRF[51], where 72 crystals are used to collect the scattered Raman photons at different **q** values using three (four) 1m undulators as the X-ray source, providing an incident flux at the sample of 2 × 10^{13} ph/s at 9.7 keV (Si311) in a 3 × 3 μm^2 (H × V) spot after the EBS upgrade[55]. Other spectrometers are currently being developed and/or optimized for XRS studies in other sources. For example, the APS is building a new XRS spectrometer equipped with over 100 crystals covering a large **q** range[56], while the GALAXIES beamline at Soleil is currently upgrading their instrument to 40 analyser crystals[53]. Both instruments are expected to deliver of the order of 10^{13} ph/s at the sample. The proposed XRS spectrometer at BERRIES will use the flux delivered by a long in-vacuum undulator coupled with a state-of-the-art bespoke multi-analyser spectrometer that will collect the scattered photon signal over a large solid angle around the sample. This configuration will make it internationally competitive (see specification details in section 4).

The use of pink-beam for XES is a recent development and only a handful of proof of principle experiments have been performed[57,58]. This year the technique has become available at the Super-XAS beamline at the SLS using a multilayer monochromator[59], in a similar manner as the instrument proposed as part of the APS upgrade[56]. BESSY II, on the other hand, is building a dedicated instrument optimized for pink-beam XES operating in the energy range from 2 to 10 keV, providing 10^{14} ph/s at 6 keV in a 20 x 500 μm^2 (VxH) spot[60]. The BERRIES pink-XES station will be competitive with these new instruments both in photon flux and beam size (see specification details in section 4).

With the development of this beamline Diamond can retain its international competitiveness in the rapidly evolving field of X-ray spectroscopy, whereas the facility risks falling behind if it cannot offer these new and promising techniques. The early results coming from these developing methods around the world, are already demonstrating significant impact in several scientific areas that are important UK research priorities.

3.7 Combined impact of project and added value in relation to activities on the Harwell Campus and beyond.

BERRIES will bring new opportunities for collaboration between Diamond and other facilities placed at the Harwell Campus, such as the ISIS Neutron and Muon Facility, and STFC's Scientific Computing Department (SCD). The complementarity between neutron diffraction's sensitivity to light elements and XRS can be used to provide a new structural perspective for advanced materials studies. These combined techniques allow the development of a coherent understanding of both local chemically specific and electronic-state behaviour, within the context of a material's longer-range structural order. The preparation of the XRS experiments, as well and the analysis of XRS and XES data, requires the use of advanced computational methods based on quantum mechanical calculations. This need will thus drive the development of closer collaborations between Diamond and the Theoretical and Computational Physics Group of the STFC's SCD.

The development of new sample environments and sample handling capabilities will benefit from collaboration with the Life Science XFEL Hub based at Diamond, as similar challenges dealing with high flux at the sample have to be met.

BERRIES will also strengthen Diamond's links with the Faraday Institution by providing insight into the local atomic scale structure and electronic states of light elements, such as O and Li, that are central to the properties and behaviour of many energy materials. The bulk sensitivity of the XRS technique advantageously makes it suitable for application to real devices and will thus enable studies that are expected to be critical for properly understanding and developing new energy materials and associated technology. In a similar manner, the availability of pink-beam XES will enhance the already strong collaborations between the UK Catalysis Hub and the Diamond Spectroscopy Group, by making available new capabilities to study catalytic materials under operating conditions in a spatially resolved manner. In addition, the potential impact of BERRIES in scientific areas such as bioscience and materials will be relevant for major research initiatives like the Sir Henry Royce Institute and the Rosalind Franklin Institute. The beamline will also complement the capabilities of the National Nuclear User Facility Active Materials Laboratory being built at Diamond with NNUF funds for the handling of nuclear materials.

4. Beamline performance specification and requirements

BERRIES will consist of two end-stations. The XES end-station, operating in the energy range from 4 to 20keV, will be optimized for performing XES experiments with pink-beam, characterised by a polychromatic beam with a band pass of ca. 2%. Monochromatic beam will also be available in this end-station, so RXES and HERFD-XAS experiments will also be possible. The second end-station will be optimised for XRS experiments, scanning the incident energy approximately 1000eV around two selected energies, 6.5keV and 9.7keV. All these photon-in/photon-out techniques are very photon hungry, so the combination of a bright source with state-of-the-art spectrometers is necessary to ensure that the beamline is competitive with respect to other facilities (see section 3.6). To maximize the flux delivered to the sample, we are proposing to build BERRIES on the available long straight section (Straight 17) so a long undulator can be fitted. A reduction of between four and three in flux is expected if the beamline is built in a mid-straight.

The main specifications for both end-stations are summarized in Table 1.

Table 1. *Outline specifications for the BERRIES end-stations.*

End Station	**XES**	**XRS**
Energy range (keV)	4 to 20	6.46 and 9.69
Flux (DCM Si(311)) (ph/s)	~ 5.0x10^{13}	~ 5.0x10^{13} at 6.46 keV ~ 3.0x10^{13} at 9.69 keV
Flux (ML) (ph/s)	~ 10^{16}	
Beam size (FWHM) (µm)	14 x 11 (HxV)	13 x 11 (HxV)
Energy resolution (eV)	~ 1*	0.3 at 6.46 keV* (using Si(311)) 0.6 at 9.69 keV* (using Si(311))

* The specific figure will depend on the energy and the crystal analysers used.

XES using monochromatic beam can currently be performed at I20, but the availability of pink-beam on BERRIES will enable measurements of more dilute samples, weaker emission lines, and will reduce the data acquisition time needed to reach analytically viable signal-to-noise levels. By using a large bandpass (2%) the flux will be more than a factor 1000 higher than with monochromatic beam, reducing the acquisition times proportionally. The increased flux will also reduce the concentration limit of the samples to study, opening the door to core-to-core XES measurements on sub mM concentration samples. In addition, the smaller beam size available at BERRIES (20 µm in BERRIES versus 400 µm in I20) will improve the overall energy resolution of the experiment by approximately 40% for the K_α and the K_β emission lines of the first transition row elements if a 1 m Rowland circle is used. The small beam will also open the possibility of recording XES in a spatially resolved manner.

XRS is a technique that is currently not available at Diamond. As described in the previous sections, XRS provides information about the electronic and geometric structure of light elements. Equivalent structural information is obtained when performing spectroscopy experiments using soft X-rays. However, by using hard X-rays, BERRIES will be able to probe the bulk of the material thanks to the higher penetration depth of the hard X-rays. For example, when studying the C K-edge the penetration depth will increase by approximately three order of magnitude when using 10 keV photons instead of 280eV photons (carbon absorption edge), taking the actively probed sample depth from a few microns to a few millimetres.

4.1 Additional developments required

BERRIES will require an increased level of theoretical support to ensure that spectroscopy data (XES, RXES, HERFD-XANES and XRS) is efficiently, and accurately interpreted. Crucially this will need to go beyond the traditional analysis techniques of multiple scattering theory within the limits of the muffin-tin (MT) potential. This is supported by the significant development in first principles techniques based upon high-level quantum chemistry calculations that have recently been developed. Examples include time-dependent density functional theory, configuration interaction, algebraic diagrammatic construction, coupled cluster and restricted active space methods. In addition, the development of machine learning methods used to both predict the spectra and speed up quantum chemistry calculations will increase the ability of these approaches to be applied to some of the challenging systems discussed above. This will be supported through interaction with the COllaborative NEtwork for X-ray Spectroscopy (CONEXS), an established UK community for X-ray spectroscopy whose primary focus is to nurture a strong synergy between experiment and theory ensuring maximum impact from the UK's research and investment in this area.

5. Schematic outline of beamline or project

We are proposing to build BERRIES on the available long straight section (straight 17) as the use of a long undulator is needed to deliver the required flux for the instrument. The layout of the beamline is shown in Figure 9. The beamline consists of an optics hutch (OH) that houses most of the optical components, a large component and instrumentation area (CIA) housing the electronic racks, and two experimental hutches. EH1 will operate in the energy range from 4 keV to 20 keV and will be optimized for performing pink-beam XES as well as HERFD-XAS and RXES, while EH2 will house an X-ray Raman Spectrometer operating at two energies, 6.46 keV and 9.69 keV. The XES end-station will be available for setting up experiments while the XRS end-station is used, and vice versa. A large control cabin will complete the layout of the beamline.

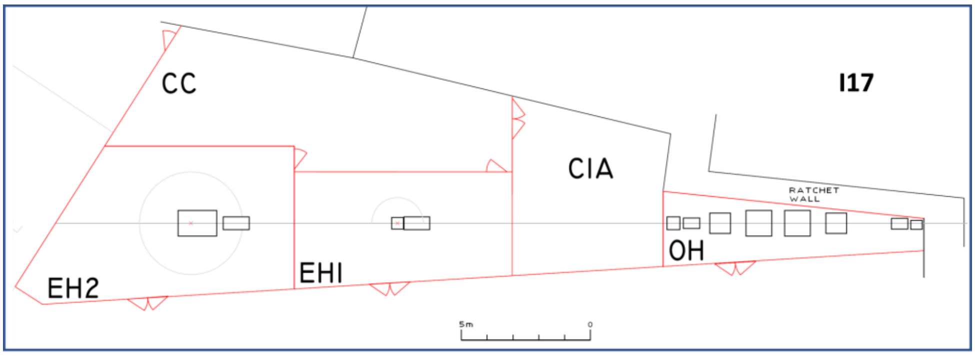


Figure 9. *Layout of the BERRIES beamline in straight 17*

5.1 Source

As mentioned above, both XRS and XES are photon hungry techniques that will benefit from a high brilliance source, so an undulator has been selected as the most appropriate type of source. This insertion device will also be the most suitable source for performing pink-beam XES, as the experiments can be performed by selecting a single harmonic which already delivers the appropriate energy bandwidth (~2%). The optimized device for BERRIES is thus a 19.2 mm period, 4.5 m cryocooled undulator placed on the available long straight section. This device will be able to deliver the desired flux at the sample position in a relatively small focal spot (10-20 µm). The selected undulator will also be able to cover the energy range of the beamline, allowing spectroscopy experiments to be performed by simultaneously scanning the gap of the device and the monochromator energy.

5.2 Optics

The BERRIES optical layout is show in Figure 10. The optics hutch houses the first optical element, an upward reflecting mirror. The mirror will be used to collimate the beam in the vertical direction. Downstream of the first mirror, at approximately 27.5 m from the source, several energy selection devices will be located. For XRS, RXES and HERFD-XAS, a double crystal monochromator (DCM) will be available with a choice of two different crystal cuts: Si111 for higher flux and Si311 for higher energy resolution. For those experiments that require the use of pink-beam, the beamline will also be equipped with a broad energy band pass device, either a multilayer monochromator or a transmission prism used to separate the undulator harmonics, such as the one developed by Inoue[61]. After the monochromator, a downward reflecting toroidal mirror will be placed at 30.5 m from the source. The mirror will focus the beam at a secondary source to a focal size of 33 µm x 56 µm FWHM (HxV).

The beam will be further focussed by a pair of Kirkpatrick-Baez mirrors placed in each of the experimental hutches. The working distance for the second mirror in both hutches is kept to 0.5 m, so enough space is available for sample environment. The XES end-station is placed at 43 m from the source, and the calculated focal size is 14 µm x 11 µm FWHM (HxV). The XRS end-station is placed at 51 m from the source, and the calculated focal size is 13 µm x 11 µm FWHM (HxV) (see Figure 11)

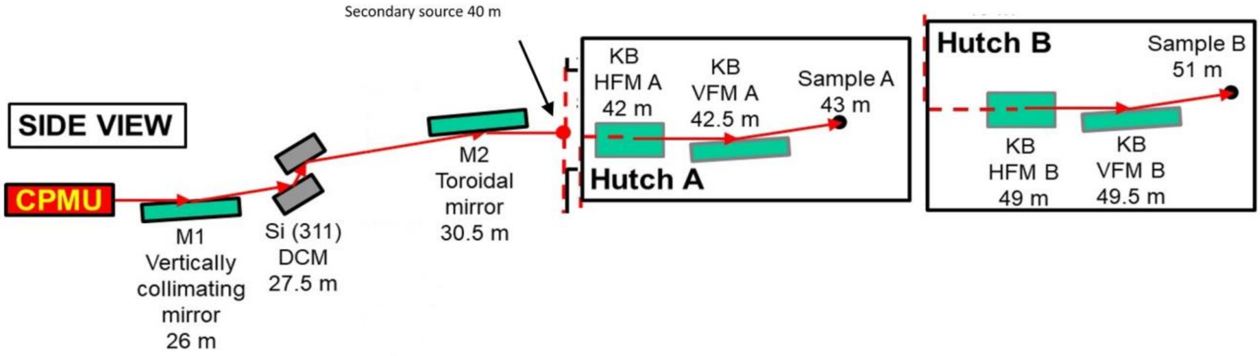


Figure 10. *Optical layout of the BERRIES beamline*

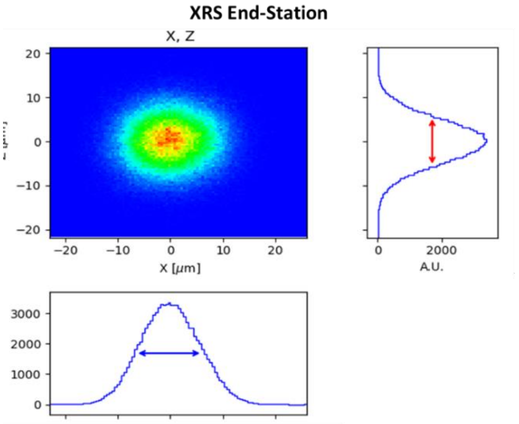


Figure 11. *Calculated beam size, horizontal and vertical profiles at the sample position after the KB focusing mirrors for the XRS end-station.*

5.3 End-station(s)

The beamline consists of two end-stations, one dedicated to X-ray Emission Spectroscopy with pink-beam, although resonant XES and HERFD-XAS will also be available, and the second optimized for X-ray Raman scattering experiments. While both end-stations will take beam from the same insertion device and will not run simultaneously, it will be possible to align the spectrometers and set up experiments off-line in one hutch while experiments are running in the other hutch. Both end stations will be equipped with a goniometer for the orientation of crystalline samples. This is necessary for **q**-dependent XRS[33] and polarization dependent XES studies.

XES end-station

We envisage the use of two different spectrometers in the XES end-station: a von Hamos dispersive spectrometer and a Johan point to point spectrometer.

The multi-crystal von Hamos spectrometer will be used when performing pink-beam XES experiments, as the full emission spectrum is collected in a single shot, which enables the acquisition of fast time-resolved XES measurements. A point-to-point Johan type spectrometer working in the vertical plane will be also available in the beamline. The collection efficiency of this spectrometer at each energy point is superior to the von Hamos, so it will be used when the sample concentration is low. The combination of the pink-beam and the Johan spectrometer will increase the detection limit. The Johan spectrometer will also be used for HERFD-XAS measurements.

Both spectrometers will be equipped with a pixel-area detector capable of imaging the focus achieved by each analyser crystal, optimised for the beamline energy range.

XRS end-station

The XRS spectrometer will consist of several groups of spherically bent analyser crystals in a nearbackscattering geometry, to maximize collection efficiency and energy resolution. The design will include a large module with multiple analyser crystals positioned at low scattering angle for dipole-limited type measurements, in a similar manner as the design pioneered by the ESRF and being adopted by Petra. In addition, several other modules will be available, and they will be positioned at different scattering angles for **q**-dependent studies, as it is done at the ESRF and it is planned for the APS upgrade of the instrument.

Each of the analyser modules will be equipped with a dedicated pixelated area detector. This will allow efficient separation of the desired signal from the sample and spurious scattering that can come from complicated sample environments. This will also enable direct tomography experiments with XRS.

5.4 Sample preparation facilities and sample environment

Our experience has shown that access to off-line sample preparation and characterization facilities are often key for the success of spectroscopy experiments, and we expect this to be the same for BERRIES. As described in the Science Case, BERRIES will attract experiments from many different research areas, from chemistry and catalysis to energy materials, biochemistry, quantum materials, etc… This diversity is not uncommon in the Spectroscopy Group, and as a consequence, access to different sample preparation facilities will be needed.

In situ and *operando* experiments in chemistry and catalysis and energy materials constitutes a large part of the BERRIES science case and access to a well-equipped chemistry laboratory will be essential to satisfy the needs of these communities. On the other hand, access to a materials characterisation laboratory will also be essential for the BERRIES user community interested in studying quantum materials, including the use of a Laue diffractometer and a magnetic characterization instrument. The relatively small focal spot delivered by BERRIES will also be used to perform experiments under HP conditions, so access to a HP laboratory will be necessary to prepare and load samples into Diamond Anvil Cells. In addition, the Active Material Laboratory that is currently being built at Diamond will provide state of the art facilities for the handling of radioactive materials, facilitating the experiments that will take place in BERRIES in this area of research.

The development of optimized sample environments will also be essential for the success of the beamline. Building on our experience of working with spectroscopy users, we will develop and integrate sample environments to perform *in situ* and *operando* studies in heterogenous and homogeneous catalysis and electrochemistry. Amongst the many anticipated environments, systems such as plug-flow reactors, gas delivery systems, flow cells, and electrochemical cells will be developed. Availability of furnaces and cryostats for temperature and Diamond Anvil Cells for HP experiments will also be included. In the case of XES experiments, attention will need to be paid to the limited spaced available around the sample, and we will ensure that the sample environments already developed for the I20 spectrometer will be compatible with BERRIES. In the case of XRS experiments, completely new sample environment will need to be developed so as to allow a large solid angle of data collection, especially for the **q**-dependent studies.

It is important to highlight that the development of novel sample environment and sample handling methodologies that allow us to mitigate the effect that the high intensity beam delivered by BERRIES will have on the studied samples will be a priority. Ensuring that the beam only sees undamaged material by moving a solid sample or by flowing a liquid is a strategy often used, as well as measuring at cryogenic temperatures. More recently electrochemistry has been used successfully to protect samples, and the advances made at various XFELs will help us to address this challenge.

5.5 Computing infrastructure and support

The large number of optical elements and the complexity of both end-stations means that BERRIES will need more than a hundred motion axes and vacuum components that need to be controlled. Taking I20 as an example, more than 10 racks will be needed to house all the necessary electronics. To accommodate all these electronics, a large CIA is being planned as part of the beamline layout (see Figure 9).

The BERRIES control and data acquisition software will need to be fit for purpose for the different type of experiments planned. For XES experiments, the control software and GDA software will be similar to what is already deployed at I20-Scanning in the case of the Johan spectrometer, and what will be developed at I18 for the von Hamos spectrometer. The capability of 2D mapping is also going to be essential if the planned experimental programme is going to be able to profit from the small focal spot delivered by BERRIES.

The requirements for the control software for the XRS end-station includes the need to be able to choose the position of the different groups of analyser crystals depending on the value of the momentum transfer of interest. The data acquisition will need to be able to sum up the contributions from the different analyser crystals at a given **q** value, as well as provide an effective methodology for accurate background removal that is necessary for the extraction of the XANES signal. The GDA will also need to be able to handle collected images and reconstruct 3D volumes from slices in order to take advantage of the XRS direct tomography capabilities

6. References

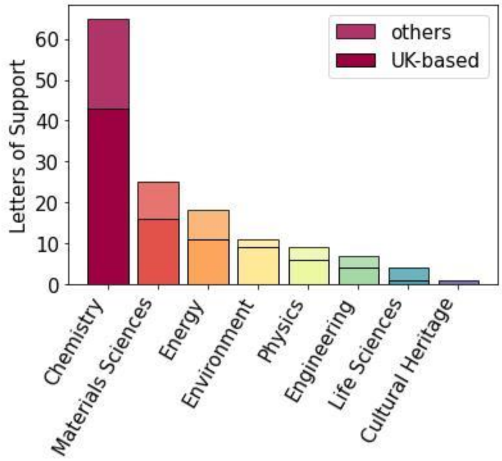
1. Inkinen, J. *et al.* Interplay between Temperature-Activated Vibrations and Nondipolar Effects in the Valence Excitations of the CO2 Molecule. *J. Phys. Chem. A* **118**, 3288–3294 (2014).
2. Beale, A. M., Gao, F., Lezcano-Gonzalez, I., Peden, C. H. F. & Szanyi, J. Recent advances in automotive catalysis for NOx emission control by small-pore microporous materials. *Chem Soc Rev* **44**, 7371–7405 (2015).
3. Paolucci, C. *et al.* Dynamic multinuclear sites formed by mobilized copper ions in NOx selective catalytic reduction. *Science* **357**, 898–903 (2017).
4. Sushkevich, V. L., Palagin, D., Ranocchiari, M. & van Bokhoven, J. A. Selective anaerobic oxidation of methane enables direct synthesis of methanol. *Science* **356**, 523–527 (2017).
5. Kang, L. *et al.* Adsorption and activation of molecular oxygen over atomic copper(I/II) site on ceria. *Nat Commun* **11**, 1–11 (2020).
6. Wang, F. R. *et al.* Paper in preparation.
7. Seriani, N., Mittendorfer, F. & Kresse, G. Carbon in palladium catalysts: A metastable carbide. *J Chem Phys* **132**, 024711 (2010).
8. Dann, E. K. *et al.* Structural selectivity of supported Pd nanoparticles for catalytic NH3 oxidation resolved using combined operando spectroscopy. *Nat Catal* **2**, 157–163 (2019).
9. Miedema, P. S. *et al.* In situ X-ray Raman spectroscopy of LiBH4. *Phys Chem Chem Phys* **14**, 5581–5587 (2012).
10. Welch, G. C., Juan, R. R. S., Masuda, J. D. & Stephan, D. W. Reversible, Metal-Free Hydrogen Activation. *Science* **314**, 1124–1126 (2006).
11. Stephan, D. W. & Erker, G. Frustrated Lewis pairs: metal-free hydrogen activation and more. *Angew Chem Int Ed Engl* **49**, 46–76 (2010).
12. Martín, A. J. & Pérez-Ramírez, J. Heading to Distributed Electrocatalytic Conversion of Small Abundant Molecules into Fuels, Chemicals, and Fertilizers. *Joule* **3**, 2602–2621 (2019).
13. Celorrio, V., Russel, A. E., *et al.* paper in preparation.
14. Jiang, C., Nichols, A. W. & Machan, C. W. A look at periodic trends in d-block molecular electrocatalysts for CO2 reduction. *Dalton Trans* **48**, 9454–9468 (2019).
15. Zeinalipour-Yazdi, C. D., Hargreaves, J. S. J. & Catlow, C. R. A. Nitrogen Activation in a Mars–van Krevelen Mechanism for Ammonia Synthesis on Co3Mo3N. *J. Phys. Chem. C* **119**, 28368–28376 (2015).
16. Tian, C. *et al.* Distinct Surface and Bulk Thermal Behaviors of LiNi0.6Mn0.2Co0.2O2 Cathode Materials as a Function of State of Charge. *ACS Appl Mater Interfaces* **12**, 11643–11656 (2020).
17. Ketenoglu, D. *et al.* X-ray Raman spectroscopy of lithium-ion battery electrolyte solutions in a flow cell. *J Synchrotron Radiat* **25**, 537–542 (2018).

18. House, R. A. *et al.* First-cycle voltage hysteresis in Li-rich 3d cathodes associated with molecular O2 trapped in the bulk. *Nat Energy* **5**, 777–785 (2020).
19. Pollock, C. J., Delgado-Jaime, M. U., Atanasov, M., Neese, F. & DeBeer, S. Kβ Mainline X-ray Emission Spectroscopy as an Experimental Probe of Metal–Ligand Covalency. *J Am Chem Soc* **136**, 9453–9463 (2014).
20. Su, J. *et al.* Energy-Degeneracy-Driven Covalency in Actinide Bonding. *J Am Chem Soc* **140**, 17977–17984 (2018).
21. Sundermann, M. *et al.* Transuranium compounds probed by nonresonant inelastic x-ray scattering. *Phys Rev B* **101**, 075103 (2020).
22. Huotari, S., Pylkkänen, T., Verbeni, R., Monaco, G. & Hämäläinen, K. Direct tomography with chemical-bond contrast. *Nat. Mater.* **10**, 489–493 (2011).
23. Bao, H. *et al.* Uranium-Induced Changes in Crystal-Field and Covalency Effects of Th4+ in Th1–xUxO2 Mixed Oxides Probed by High-Resolution X-ray Absorption Spectroscopy. *Inorg Chem* **57**, 11404–11413 (2018).
24. Kvashnina, K. O. & de Groot, F. M. F. Invisible structures in the X-ray absorption spectra of actinides. *J Electron Spectrosc Relat Phenom* **194**, 88–93 (2014).
25. Bots, P. *et al.* Neptunium(V) and Uranium(VI) Reactions at the Magnetite (111) Surface. *Geosciences* **9**, 81 (2019).
26. Lee, S. K. *et al.* Oxygen Quadclusters in SiO2 Glass above Megabar Pressures up to 160 GPa Revealed by X-Ray Raman Scattering. *Phys Rev Lett* **123**, 235701 (2019).
27. Lin, J.-F. *et al.* Spin transition of iron in magnesiowüstite in the Earth's lower mantle. *Nature* **436**, 377–380 (2005).
28. Spiekermann, G. *et al.* A portable on-axis laser-heating system for near-90° X-ray spectroscopy: application to ferropericlase and iron silicide. *J Synchrotron Radiat* **27**, 414–424 (2020).
29. Higgins, L. J. R., Sahle, C. J., Balasubramanian, M. & Mishra, B. X-ray Raman scattering for bulk chemical and structural insight into green carbon. *Phys Chem Chem Phys* **22**, 18435–18446 (2020).
30. Higgins, L. J. R. *et al.* Evidence for a core-shell structure of hydrothermal carbon. *Carbon* **161**, 423–431 (2020).
31. Rovezzi, M. & Glatzel, P. Hard x-ray emission spectroscopy: a powerful tool for the characterization of magnetic semiconductors. *Semicond Sci Technol* **29**, 023002 (2014).
32. Vankó, G. *et al.* Spin-state studies with XES and RIXS: From static to ultrafast. *J. Electron Spectrosc. Relat. Phenom.* **188**, 166–171 (2013).
33. Yavaş, H. *et al.* Direct imaging of orbitals in quantum materials. *Nat. Phys.* **15**, 559–562 (2019).
34. Frati, F., Hunault, M. O. J. Y. & de Groot, F. M. F. Oxygen K-edge X-ray Absorption Spectra. *Chem Rev* **120**, 4056–4110 (2020).
35. Fukui, H. *et al.* Electronic structure of dense solid oxygen from insulator to metal investigated with X-ray Raman scattering. *Proc Natl Acad Sci USA* **116**, 21385–21391 (2019).
36. Armstrong, F. A. & Hirst, J. Reversibility and efficiency in electrocatalytic energy conversion and lessons from enzymes. *Proc Natl Acad Sci USA* **108**, 14049–14054 (2011).
37. Woolerton, T. W., Sheard, S., Chaudhary, Y. S. & Armstrong, F. A. Enzymes and bio-inspired electrocatalysts in solar fuel devices. *Energy Env. Sci* **5**, 7470–7490 (2012).
38. Mazurenko, I., Wang, X., de Poulpiquet, A. & Lojou, E. H2/O2 enzymatic fuel cells: from proof-of-concept to powerful devices. *Sustain. Energy Fuels* **1**, 1475–1501 (2017).
39. Rapson, T. D. *et al.* Insights into Nitrogenase Bioelectrocatalysis for Green Ammonia Production. *ChemSusChem* **13**, 4856–4865 (2020).
40. Cutsail, G. E., Gagnon, N. L., Spaeth, A. D., Tolman, W. B. & DeBeer, S. Valence-to-Core X-ray Emission Spectroscopy as a Probe of O-O Bond Activation in Cu2O2 Complexes. *Angew Chem Int Ed* **58**, 9114–9119 (2019).

41. Martinie, R. J. *et al.* Two-Color Valence-to-Core X-ray Emission Spectroscopy Tracks Cofactor Protonation State in a Class I Ribonucleotide Reductase. *Angew Chem Int Ed* **57**, 12754–12758 (2018).
42. Hugenbruch, S. *et al.* In search of metal hydrides: an X-ray absorption and emission study of [NiFe] hydrogenase model complexes. *Phys Chem Chem Phys* **18**, 10688–10699 (2016).
43. Casadei, C. M. *et al.* Neutron cryo-crystallography captures the protonation state of ferryl heme in a peroxidase. *Science* **345**, 193–197 (2014).
44. Levin, N. *et al.* Ruthenium 4d-to-2p X-ray Emission Spectroscopy: A Simultaneous Probe of the Metal and the Bound Ligands. *Inorg Chem* **59**, 8272–8283 (2020).
45. *Lubricants Market Size, Share | Global Industry Report, 2020-2027*. (2020).
46. *Topic: Chemical industry in the UK*. *Statista* (2020).
47. Bhatia, A. *et al.* Polymorphism and its Implications in Pharmaceutical Product Development. in *Dosage Form Design Parameters* 31–65 (Academic Press, 2018). doi:10.1016/B978-0-12-814421-3.00002-6.
48. Department for Business, E. & I. S. Industrial Strategy: building a Britain fit for the future. *GOV* (2018).
49. *A Vision for a Sustainable Battery Value Chain in 2030*. *World Economic Forum* (2020).
50. Fister, T. T. *et al.* Multielement spectrometer for efficient measurement of the momentum transfer dependence of inelastic x-ray scattering. *Rev. Sci. Instrum.* **77**, 063901 (2006).
51. Huotari, S. *et al.* A large-solid-angle X-ray Raman scattering spectrometer at ID20 of the European Synchrotron Radiation Facility. *J. Synchrotron Radiat.* **24**, 521–530 (2017).
52. Sokaras, D. *et al.* A high resolution and large solid angle x-ray Raman spectroscopy end-station at the Stanford Synchrotron Radiation Lightsource. *Rev. Sci. Instrum.* **83**, 043112 (2012).
53. Ablett, J. M. *et al.* The GALAXIES inelastic hard X-ray scattering end-station at Synchrotron SOLEIL. *J. Synchrotron Radiat.* **26**, 263–271 (2019).
54. XRS Spectrometer at P01 Dynamics beamline at PETRA-III. https://photon-science.desy.de/facilities/petra_iii/beamlines/p01_dynamics/inelastic_x_ray_scattering_station/xrs_spectrometer/index_eng.html (2020).
55. Dimper, R. *et al.* ESRF UPGRADE PROGRAMME PHASE II (2015-2022) TECHNICAL DESIGN STUDY.
56. APS Upgrade | Advanced Photon Source. https://www.aps.anl.gov/APS-Upgrade.
57. Kvashnina, K. O., Rossberg, A., Exner, J. & Scheinost, A. C. Hard X-ray emission spectroscopy with pink beam. *Annu. Rep. 2016 Inst. Resour. Ecol.* (2016).
58. Tu, M.-F. *et al.* Micro-focused MHz pink beam for time-resolved X-ray emission spectroscopy. *J. Synchrotron Radiat.* **26**, 1956–1966 (2019).
59. Dikaya, O. *et al.* Operation of a bending magnet beamline in large energy bandwidth mode for non-resonant X-ray emission spectroscopy. *Results Phys.* **18**, 103212 (2020).
60. The PINK beamline at BESSY II. *HZB Website* https://www.helmholtz-berlin.de/projects/emil/instruments/analytics/pink_en.html.
61. Inoue, I. *et al.* An X-ray harmonic separator for next-generation synchrotron X-ray sources and X-ray free-electron lasers. *J. Synchrotron Radiat.* **25**, 346–353 (2018).

7. Expressions of interest & support from the community

BERRIES has attracted strong support from the user community, as evidenced by the 138 statements received from UK and international researchers, institutions and companies. The support has come from many different science areas, reflecting all the themes set out in the science case and demonstrating the high overall impact of this instrument to UK research. Chemistry is the largest supporting community, followed by Material Sciences and Energy[1]. BERRIES has attracted interest and institutional support from many of the most prominent national research centres and government initiatives in areas such as: i. chemistry and catalysis (the **UK Catalysis Hub**), ii. nuclear research and environmental sciences (the **National Nuclear Laboratory (NNL)**, the **Dalton Nuclear Institute** and the **Centre for Radiochemistry Research**), iii. materials science (the **Henry Royce Institute**), iv. energy research (**The Faraday Institution**, the **STFC Global Challenge Network in Batteries**, and the **UCL Electrochemical Innovation Laboratory**), v. cultural heritage and planetary sciences (the **Mary Rose Trust**, and the **Natural History Museum**) and vi. biological sciences (**The Rosalind Franklin Institute**).



From the industrial sector, **Infineum UK Ltd, PETRONAS, Shell, BP, Johnson Matthey, Seren Technologies Ltd., Finden Ltd., MOF Technologies Ltd,** and **Tokamak Energy Ltd.** have all submitted company wide support statements. Each of these highlights the impact that the capabilities of BERRIES will have in their research programmes. According to Shell, *“The capabilities offered by the BERRIES upgrade would create opportunities across several areas of interest to Shell”.* For BP, *“The implementation of BERRIES at Diamond will give a transformative capability that bp/industry will require for the development and understanding of chemical catalysis going forward”.*

Other illustrative statements drawn from the submissions received from the community are:

“I write as Vice Dean for Research for the Faculty of Science and Engineering at the University of Manchester to support the case for BERRIES. This beamline will help underpin research in 3 of our 5 beacon research areas, Advanced Materials, Energy and Industrial Biotechnology”. **Prof. Wendy Flavell, The University of Manchester.**

“The BERRIES beamline will be an excellent addition to Diamond and these new techniques will be important in battery research”. **Prof. Peter Bruce, University of Oxford.**

“The BERRIES flagship project offers some very interesting new possibilities that will enhance our research in the area of ionic liquids, with a focus on catalytic and energy storage applications”. **Dr John Slattery, The University of York.**

“The Faraday strongly support this proposal to make the techniques provided by BERRIES available to our communit”’. **Craig Chapling, on behalf of The Faraday Institution.**

“The capability BERRIES offers will be very valuable in characterising actinide species, particularly those of technological (fuels and wasteforms) and environmental (surface and solution species) relevance”. **Prof. Francis Livens, Director of the Dalton Nuclear Institute (DNI) (on behalf of DNI).**

“The BERRIES beamline will enable the UK to remain competitive with other countries such as the US, Germany and Japan in this respect. The availability of high-quality experimental data will drive forward developments in the computational simulation of these spectroscopies while also providing opportunities to further establish collaborations with experimental colleagues”. **Prof. Nicholas Besley, University of Nottingham.**

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[1] It is important to highlight that many of the supporting statements associated to Materials Science are also associated with energy related research, and similarly, there is significant overlap for submissions in chemistry and life sciences.

Statements of support summary

Total number of submissions: 138

Key for statements in Appendix A	Respondent's primary field of research	Percentage of respondents
🟦	Chemistry	47.1%
🟥	Materials Sciences	17.4%
🟦	Energy	13.0%
🟧	Earth Sciences & Environment	8.0%
🟦	Physics	6.5%
⬛	Engineering & Technology	4.3%
🟩	Life Sciences & Biotech	2.9%

Respondent location	Percentage of respondents
UK	69.6%
International	30.4%

Type of organisation supporting	Percentage of respondents
Academic	81.2%
Industry	8.0%
Government	5.1%
Charity	0.7%
Non-Governmental Organisation (NGO)	0.7%
Other	4.3%

Diamond user status	Percentage of respondents
Not currently a user at Diamond	18.1%
Currently a user at Diamond	81.9%

About 30% of the 138 statements of support received for BERRIES have been submitted on behalf of institutions, large research groups or industries. The remaining 70% represent individual support statements from researchers from academia, industry or government institutions.

The BERRIES Webinar was very well attended, and the discussions helped shape the science case, and ensure that the needs of the community were covered.

Engagement webinar summary

Date of webinar: Monday 14th October 2020

Number of attendees: 131

Attendee location	Percentage of attendees
UK	77.3%
International	22.7%