

Diamond-II Proposal for flagship project Undulator source for B07

Science Group: Structures and Surfaces

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Outline proposal for a flagship beamline project Diamond-II

1. Summary/Impact statement

Catalysis and new functional materials have been highlighted as key research areas and of significant benefit to the chemical industry, as indicated in the Diamond-II science case. Common features of the latest generation of functional materials (e.g. zeolites, MOFs, electrochemical interfaces, liquid phase heterogeneous catalysis, bio-inspired materials) are that they are engineered at the molecular level and interact strongly with their environment. This requires new approaches for their study, which Diamond-II can uniquely offer. The nanoscale size and low concentration of active components demands a high-flux light source and photon energies that enable high interaction cross sections. This favours soft X-rays over hard X-rays for base metals and organic materials and adding variable polarization of the synchrotron source provides the capability to discriminate between different species. The interaction of such materials with their environment can only be studied in reactive atmospheres and/or liquid environments, also requiring high flux and appropriate photon energies in the soft/tender regime (up to 4 keV). A high coherence / high flux source would also open up new approaches to study conventional materials, which are currently not accessible with soft X-ray spectroscopy methods. For example, a sub-second time resolution would allow monitoring processes like rearrangements of surface atoms or changes in surface composition in real time; coherent soft X-ray scattering could reveal the nanometre-scale size and shape of objects and their correlation with chemical resolution. The current beamline has two branches, which can be operated simultaneously, one for near ambient pressure photoelectron spectroscopy (NAP-XPS, operational since 2017) and the other for high throughput XPS (HT-XPS) and near edge x-ray absorption fine structure (NEXAFS, operational in autumn 2020). These techniques uniquely provide very high resolution chemical state analysis of a wide range of samples under realistic conditions and provide unparalleled insights into understanding and developing catalysts and materials. The current beamline layout is based on using a single bending magnet to source the two branchlines. Diamond-II offers the opportunity to change the optical layout such that the two branches can maintain the same physical footprint but the NAP-XPS branch can be sourced by a mid-straight undulator with the HT-XPS/NEXAFS branch sourced by the bending magnet. The dark period is the ideal time to upgrade the beamline, as the layout requires a lead hutch to be installed and an additional (or enlarged) hole through the ratchet wall.

2. Scientific Case:

Catalysis has been highlighted as a key research area that could be revolutionised by Diamond II. *In-situ* and *operando* soft X-ray photoemission and absorption experiments (XPS or XAS) involving catalytic materials under ambient pressure conditions have been very successful in identifying the chemical state and in some cases reaction intermediates [Star13, Held20]. The advantage of soft X-rays is that the data are extremely surface sensitive (where most catalytic reactions occur) at an atomic-scale level. A side effect of this feature is, however, strong attenuation of both X-rays and electrons in the gas phase. This directly leads to the need for higher photon flux compared to vacuum experiments on the same materials. Below are some examples that link to the Diamond-II science case – relevant sections are highlighted in brackets.

Nanoscale Catalysis: (Chemistry: Experiments at the nano-scale, new paradigms at the nanoscale) The most successful and most widely used catalyst materials are metal or metal oxide nanoparticles, often supported by carbon or another oxide. These are used in key processes, such as exhaust purification or CO₂ activation, and often consist of precious metals. In addition to increasing their activity and selectivity, it is therefore one of the great challenges to replace some (or all) of the precious metal contents by more abundant materials. Approaches that are currently taken are, amongst others, bimetallic catalysts (alloys, core-shell, Janus-type), complex oxides with tuneable properties (e.g. perovskite, spinel, zeolites, making use of strong metal-support interactions), and single atom/small cluster catalysts in organic frameworks (MOFs, enzyme

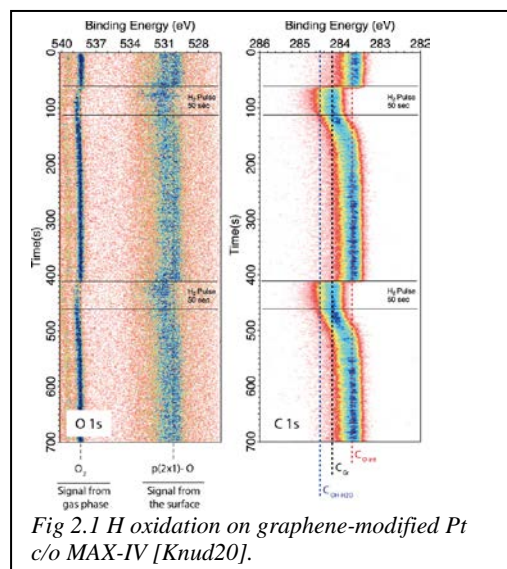
model systems, simple C, N ligands). By their very nature, nanoparticles are small and sparse. Typical metal loadings are 1-5 wt%, which often leads to an atom ratio of less than 1 : 100 of catalyst vs support material, and consequently the need of a high-flux light source to avoid long data acquisition times. The L electron levels of 3d base metals (290-1530eV) are ideal to probe their chemical states and surface composition in catalyst materials, either by XPS or XAS. Linear or circular polarisation from an undulator source can be used to characterise spin states and orbital orientation within these materials.

Active sites of Enzymes: (Chemistry: Sensitivity to ligands with spatial resolution) A particularly exciting new field in catalysis research is modelling the active sites of enzymes. As a first step, this requires a fundamental atomic-level understanding of reaction steps and electronic structure at the active site. One example is the active site of Nitrogenase [Bjor15, Lanc11] which has been studied extensively in the last decade, as it may lead the way to a much more energy-efficient process for synthesising ammonia than the current Haber process. The active site MoFeCS complex has been characterised crystallographically and spectroscopically, as far as the metals are concerned, but little is known about the role of the organic ligands. Soft X-ray spectroscopy under ambient conditions could make a significant contribution to this and many other enzyme-related and/or ligand-modified metal catalyst systems. The main constituents of organic ligands are H, C, N, and O; the latter three have K levels between 280 eV and 540 eV, the sulphur K level is around 2470 eV, which is also within the energy range of the proposed beamline. XAS with variable linear and circular polarization, not available currently due to the BM source, will be used to determine the orientation of bonds within organic frameworks and the local chirality of active sites.

Materials characterisation in the time domain: (Chemistry: Catalyst characterisation: combination of techniques and using external triggers, Biocatalysis, Probing kinetic correlations in space and time) There are still many unknowns with existing (catalyst) materials with respect to their dynamic behaviour in response to their environment (e.g. gas composition or temperature). Reactor experiments indicate response times between sub-seconds and several minutes. The current B07 beamline allows NAP-XPS experiments at a time scale of minutes, i.e. the upper end of this range, whereas a higher flux will enable detection rates at the (sub-)second scale and thus the study of many more catalyst responses in near real time. Figure 2.1 shows an example from MAX-IV where the reactant and product composition at the catalyst surface is recorded as a function of gas composition with a time resolution of a few seconds. Such experiments will enable real-time quantification of:

- changes in reactant/intermediate coverage under reaction conditions;
- restructuring of nano-particles (sintering, oxidation – reduction; core-shell – alloy transition);
- response of biological systems to external stimuli.

Exploring buried/internal surfaces and interfaces: (Chemistry: In situ experiments at the micro and nanoscales, Biocatalysis, Porous materials Energy: Battery Research) The study of electrochemical interfaces is a very fast expanding field in *operando* catalysis research, mostly triggered by the search for new energy materials, both in terms of (photo-)electrochemical hydrogen generation and batteries. The need to penetrate a layer of electrolyte between the detector and the interface demands higher photon energies than in normal XPS experiments. Analysis of cross sections and attenuation lengths shows that “tender X-rays” with photon energies around 4 keV are ideal for experiments with surfaces covered by



electrolyte layers in the nm range [Fava16]. Ground-breaking work has been done by the group in Berkeley, who devised graphene membrane cells and the so-called dip-and-pull method. Similar work is currently conducted by UK researchers in Manchester (A. Thomas & A. Walton) and Oxford (R. Weatherup). This type of approach will enable the same type and quality of information from solid-liquid interfaces as we currently have for solid-gas interfaces (chemical state, chemical composition, interface electronic and geometric structure). Such experiments would be applicable to other heterogeneous catalysts in the liquid phase and bio-inorganic interfaces under native (i.e. wet) conditions, which is largely unexplored. Extending the photon energy range to tender X-rays will also be of benefit for the study of porous materials, e.g. zeolites, MOFs, where chemically active sites are usually within the pores, i.e. up to several nm below the surface. The combination of soft and tender X-rays enables depth-profiling (by tuning the penetration depth of the emitted electrons) and thus allows discriminating between surface and pore-signals. In combination with time-resolved measurements, this would even allow studying the diffusion of reactants in and out of the pores.

Soft X-ray Scattering: (Chemistry: Experiments at the micro and nanoscales, Kinetic correlations in space and time; Biological Imaging) The high coherence of the Diamond-II synchrotron beam

offers new possibilities for resonant soft X-ray scattering (RSoXS) experiments, a technique which has been used to study polymers and magnetic materials very successfully [Coll12,Liu16] but is largely unexplored in the context of catalytic systems. The technique is similar to small angle X-ray scattering (SAXS) in terms of revealing meso-structures at the nm to μm length scale, however it has the great advantage that photon energies can be tuned into resonances and thus structural features can be linked to certain elements or even bonding features, such as C=O vs C=C bonds or oxidation states. The absorption K-edges of C, N, O and the L-edges of most 3d transition metals correspond to wave lengths between 1 nm and 5 nm, i.e. characteristic dimensions of nanoparticles and organic frameworks. Therefore this method can reveal structural information about correlation of active sites, organic ligands or even cell structures, in time and space, which is very difficult to extract otherwise.

3. Benefit to the Diamond research community

NAP-XPS is an emerging technique already with a strong user base in the catalysis community, where the opportunity to study systems under *operando* conditions has been recognised as an important step-forward in understanding and improving catalysts. It is, however, a technique that is applicable to many areas of science as outlined by the examples given in section 2. A key limitation of the current arrangement includes the limited penetration depth of the probe soft X-ray beam due to the flux from the bending magnet source. An increase in the flux by up to two order of magnitude enables either being able to carry out experiments under higher (and more realistic) gas pressures or to measure faster, to enable the study of dynamics in the systems. This brings the technique closer to the timescales and pressures used in industrial processes. The opportunity to bring tuneable polarisation to the community opens up other possibilities including improved studies of chiral systems and the orientation of bonds.

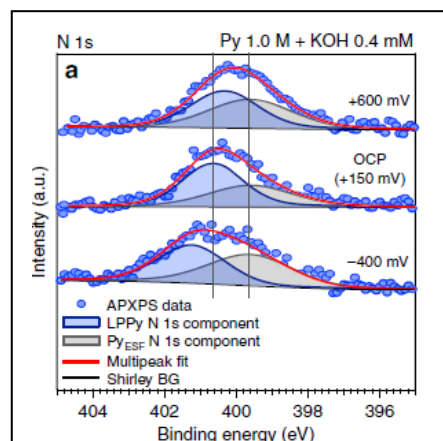


Fig 2.2: N1s XP spectra of pyrazine adsorbed on a Au electrode under 30 mM electrolyte [Fava16].

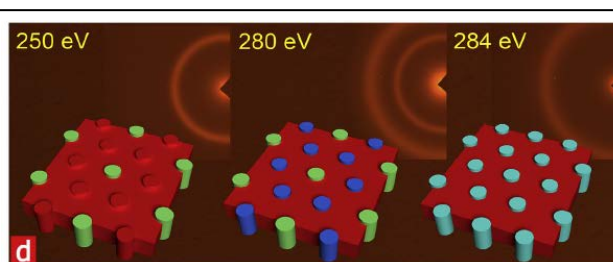


Fig. 2.3: Energy dependent RSoXS images of the the PI-b-PS-b-P2VP block copolymer, highlighting different structural correlations depending on the chemical species [Liu_16].

Many synchrotron sources have built NAP-XPS beamlines on undulator sources, an opportunity that was not possible at Diamond until the proposed Diamond-II lattice enabled the mid-straight sections to house insertion devices. The beamline is highly competitive and oversubscribed at present and will reach its most productive period close to the Diamond-II dark period. In order to maintain a world leading and competitive activity in this research field, it is essential that the flux on the sample is maximised through the addition of an undulator source. The upper energy range will be extended, thanks to the higher ring energy, enabling further improvements in the penetrating power that will be exploited in some of the most challenging experiments (e.g. *operando* electrochemical interfaces as found in batteries).

4. Outline Specification

The main requirements are:

- Energy range 170–4000 eV (or higher)
- Flux at sample $> 10^{13}$ ph s⁻¹ (up to at least 2000 eV)
- Resolution > 8000 over entire energy range.

Two options have been investigated:

1. **Use one of the 'DQ' gradient dipoles in the Diamond-II machine as source for both beamlines** in an analogous way to the current design. This would preserve the status quo of the beamline (Figure 4.1 shows the bending magnet performance at DLS, which is within 10% to that of a DQ at Diamond-II) with relatively little extra mechanical effort to re-start operation after the shutdown. Using the existing beamline optics, the energy range would remain the same (B: 50 – 2500 eV; C: 170 – 2800 eV). By the time Diamond-II comes back online, the performance of this beamline would be inferior to most of the AP-XPS beamlines at other synchrotrons, which will then have been upgraded to low-emittance undulator beamlines with significantly more flux and better energy resolution.
2. **Use a DQ for B07-B and an undulator source in the K07 mid straight section for B07-C.** The proposal is to shift the B07c branch outboard (away from B07b) and position a new M1c / PGM / M3c mirror arrangement in the Optics Cabin rather than in the Front End (see Fig. 4.2). This would also enable at least the incident angles on M1c and M3c to be reduced to increase efficiency at higher photon energies. With this option the performance of Branch B would be largely unchanged whereas flux and resolving power of Branch C would be significantly increased. Fig. 4.1 shows the photon flux (at the source) to be expected for the undulator. In the key energy range 250 – 2500 eV the flux would increase by a factor 120 (250 eV) – 20 (2500) eV, while doubling the resolving power for most of the range. Variable linear and circular

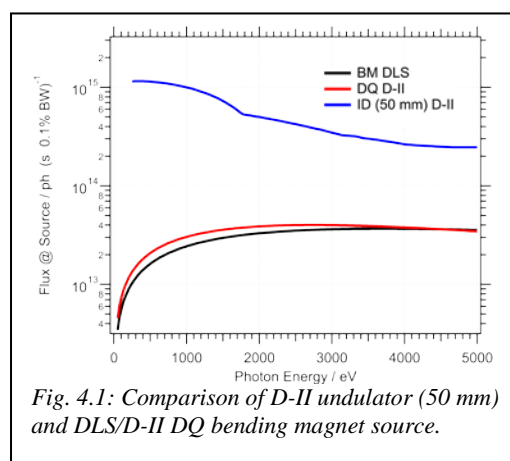


Fig. 4.1: Comparison of D-II undulator (50 mm) and DLS/D-II DQ bending magnet source.

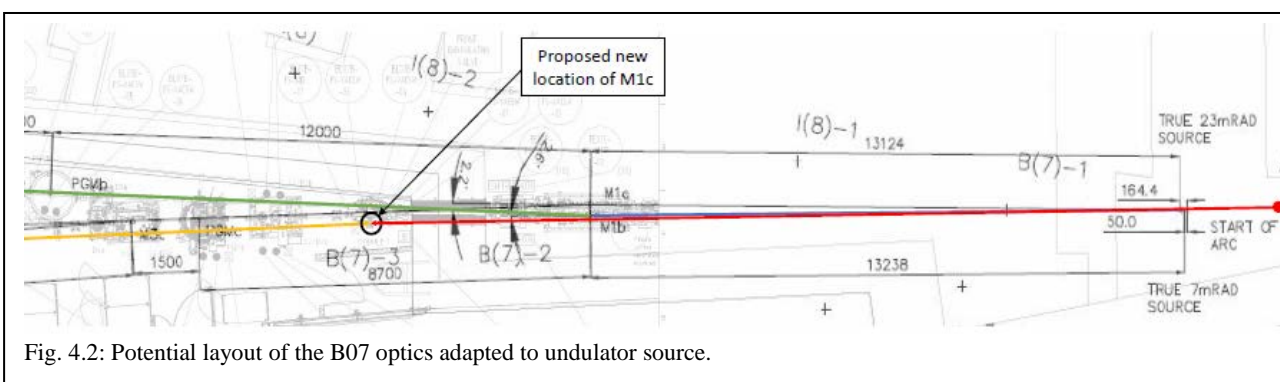


Fig. 4.2: Potential layout of the B07 optics adapted to undulator source.

polarization could be achieved up to 1500 eV, crucially including the K edges of the main constituents of organic materials (C, N, O) and the L edges of all 3-d metals. With a suitable optics design (this will most likely include a combination of PGM and DCM, as in the current design), the photon energy range of the source can be used up to > 4000 eV. In this scenario, most of branch C needs to be re-built and/or re-aligned and a lead hutch needs to be installed in the optics cabin to house the M1 and the monochromator.

5. State of the art benchmark

Synchrotron	AP-XPS beamline	undulator	Energy range / flux
<i>DLS</i>	B07		Current (BM): 170 eV – 2800 eV/10 ¹¹ ph s ⁻¹ Proposed (Undulator): 170 eV – 4000 eV/10 ¹³ ph s ⁻¹
<i>MAX-IV (4th gen)</i>	HIPPIE		250 eV – 2200 eV/10 ¹³ ph s ⁻¹
<i>ALS Berkeley</i>	11.0.2		160 eV – 2000 eV/
<i>BESSY II</i>	EMIL		Soft: 80 eV – 2300 eV/ Hard: 200 eV – 10000 eV/
<i>SOLEIL</i>	TEMPO		50 eV – 1500 eV/4x10 ¹³ ph s ⁻¹

The updated B07 beamline aims to increase the flux available on the sample by up to 100 times, making it comparable with other NAP-XPS beamlines sourced by undulators. The beamline will be designed with both a plane grating monochromator (PGM) and a double crystal monochromator (DCM) as in the current design, extending the energy range to 4keV, higher than most other beamlines. The end station on B07 is currently state-of-the art and will be transferable to the reoptimised beamline. Whilst the upgrade will be disruptive, it will maintain B07 as a world-leading NAP-XPS instrument over the next 15 years and use the opportunity to reconfigure the front end during the Diamond-II build. Such a development after Diamond-II becomes operational would be highly disruptive to the operations of the synchrotron.

6. Community engagement

Three key groups of users have been identified that will be critical in developing this proposal. The highly regarded and active UK catalysis community (UK catalysis hub based at the Research Complex at Harwell) are major current users, who see the opportunities provided by increased flux for photoelectron spectroscopy on B07. The development of nano-catalysts is a developing area for the UK community and we have identified Andy Beale (UCL), Paul Webb (St Andrews) and Edman Tsang (Oxford) as partners in helping with community engagement. We have strong links with Johnson Matthey, who we will talk to with as part of our industry engagement.

Similarly the possibilities opened up by time-resolved measurements will be developed in partnership with Stephan Hofmann (Cambridge) and Edman Tsang (Oxford). The increased opportunities in the study of electrochemical interfaces will be developed with Rob Weatherup (Oxford), Alex Walton (Manchester) and Geoff Thornton (UCL). We will also ensure that we consult the Faraday Institution, to make certain that the facilities will enable research into a range of battery technologies.

Whilst biological interfaces do not form a significant part of the B07 portfolio, we will use our links with the Rosalind Franklin Institute to identify opportunities to study bio-materials using soft-X-ray photoelectron spectroscopy.

7. References

[Held20] G. Held et al. Ambient-Pressure Endstation of the Versatile Soft X-ray (VerSoX) Beamline at Diamond Light Source, submitted to J. Synchrotron Radiation.

[Bjor15] R. Bjornsson et al., Molybdenum L-Edge XAS Spectra of MoFe Nitrogenase. *Z. anorg. allg. Chem.*, 641 (2015) 65-71. doi:10.1002/zaac.201400446

[Coll12] B.A. Collins et al., Polarized X-ray scattering reveals non-crystalline orientational ordering inorganicfilms, *Nat. Mater.* 135 (51) (2012) 19248–19259

[Fava16] M. Favaro, et al., Unravelling the electrochemical double layer by direct probing of the solid/liquid interface, *Nat. Commun.* 7:12695, 2016

[Knud20] J. Knudsen et al., private communication

[Lanc11] K. M. Lancaster et al., X-ray Emission Spectroscopy Evidences a Central Carbon in the Nitrogenase Iron-Molybdenum Cofactor, *Science* 2011, 334 (2011) 974–977.

[Liu_16] Feng Liu, Michael A. Brady, Resonant soft X-ray scattering for polymer materials, Cheng Wang *European Polymer Journal* 81 (2016) 555–568.

[Star13] D. E. Starr et al., Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy, *Chem. Soc. Rev.* 42 (2013) 5833