Australian Synchrotron Development Plan
Project Submission Form

Section A: Summary and Proponent Details

Project Title

High Accuracy XANES, XAFS, absorption and fluorescence at medium and higher X-ray energies: at 100 times better accuracy than the world standard, for new insight into structure, bonding, extreme chemistry and applications

Spokesperson

Name	Christopher Chantler, FAIP
Institution	School of Physics, University of Melbourne
Email	chantler@unimelb.edu.au
Phone	83445437

Executive Summary (approx. 100 words)

Structure, bonding, coordination, oxidation, phases, active sites, disorder and broadening are key scientific issues driving synchrotron research. Proposals for XAFS beamlines at low or high energies are complementary to this proposal. Proposals for ultra-fast techniques improve productivity. This proposal sets out to achieve an increase in quality and accuracy compared with other beam-lines worldwide. XAFS and XANES techniques have evolved to be standard research techniques, especially in biomedical, chemical and earth science applications. They offer, however, only a limited understanding of the science because of inherent problems with the experimental arrangement and the underlying theory. Techniques developed by Australians at overseas facilities offer accuracies of data, structure and insight into processes some 100 times better than the world standard. Key insight into active sites and disordered systems follows inevitably from this higher accuracy. With a purpose-built beam-line, productivity at this level of quality for the ~30% of the world-wide [XAFS/XANES] community can be attained. The beam-line can be operated in standard as well as non-standard modes at a relatively small cost. A very large Australian and international community exists, ready to take advantage of these improvements in accuracy in routine implementation.

Other proponents (add more rows if necessary)

Name	Institution	Email address
LIEF Signatories		
Joel Brugger	University of Adelaide	Joel.brugger@adelaide.edu.au
Prof AM Bond	Monash University	Alan.Bond@sci.monash.edu.au
A/Prof BK O'Neill	University of Adelaide	boneill@chemeng.adelaide.edu.au
Prof D McNaughton	Monash University	Don.McNaughton@sci.monash.edu.au
Prof AR Gerson	University of South Australia	Andrea.Gerson@unisa.edu.au
Dr CG Ryan	CSIRO - Exploration & Mining	Chris.Ryan@csiro.au
Dr W Liu	CSIRO - Exploration &	weihua.liu@csiro.au

	Mining	
Dr SP Best	University of Melbourne	spbest@unimelb.edu.au
Prof L Spiccia	Monash University	leone.spiccia@sci.monash.edu.au
Prof P Mulvaney	University of Melbourne	mulvaney@unimelb.edu.au
Prof RN Lamb	University of Melbourne	Robert.Lamb@synchrotron.org.au
Other XAFS grouping		
Prof Yves Joly	Neel Institute, CNRS	yves.joly@grenoble.cnrs.fr
Prof Dudley C Creagh	University of Canberra	dcreagh@bigpond.net.au
Assoc. Prof Martin C Feiters	Radboud University Nijmegen	m.feiters@science.ru.nl
Assoc. Prof. Zwi Barnea	University of Melbourne	barnea@physics.unimelb.edu.au
Other		
Dr C Q Tran	La Trobe University	CQ.Tran@latrobe.edu.au
Matias Daniel Rodriguez	ANU	matias.rodriguez@anu.edu.au
Wilfred Fullagar	Monash	Wilfred.Fullagar@sci.monash.edu.au
Bill Maher	Canberra	bill.maher@canberra.edu.au
Vera Grishina	UWA	vera@physics.uwa.edu.au
The Australian XAS Community	Multiple	List as in Enhanced capabilities for beamline 12-ID

Section B: Detailed Description
B1: Description of Proposed Beamline/Development Project
B1.1 Capabilities

The high-accuracy investigations for XAFS and XANES absorption and fluorescence provide the vehicle for completely novel research fields including for example those of accurate determination of bonding, orientation, phase and vibrational parameters and disordered systems[1]. In all these fields, accuracies of up to 100 times better than previous work can be achieved (further details and explanation can be found in the recent publication [2]). In particular systems this will yield more rigorous determinations of structure and dynamics[3], of active sites and enzymatic or catalytic activity. In other words, bonding structure can be more reliably determined[4], and in test cases can already equal the accuracy of lattice spacing determinations using crystallographic techniques[5]. A key issue might be in a complex organo-metallic, what are the arrangements of the first two coordination shells? By characterizing the offset energy, and the dynamical bond length to high accuracy, the thermal uncertainties and correlation uncertainties are minimized, and hence such secondary but critical insights can be tied down and yield greater insight. Much of this has been proven in existing publications and those in press. When reading a paper we are struck by quality when a superlative accuracy of an interesting or critical datum is obtained, or when a new idea, field or implementation of technology becomes possible. By being able to probe these effects separately and independently, a researcher will have a tool with which to investigate longitudinal or correlated bond distances versus transverse motion or mean square displacements from lattice sites[6]; and then to investigate the same parameters in disordered systems where crystallographic methods are not feasible. The proposed wide energy range will enable both standard XAFS and XANES measurement as well as advanced approaches, where the user will have to address relatively minimal sample preparation issues to access the higher level of accuracy in a routine manner. The energy range will also be complementary to other beam-lines and proposals and will therefore serve a large existing community.

B1.2 Diagnostics

[1] C. Q. Tran, C. T. Chantler, Z. Barnea, "X-Ray Mass Attenuation Coefficient of Silicon: Theory versus Experiment", Physical Review Letts 90 (2003) 257401

[2] C. T. Chantler, 'Development and Applications of Accurate Measurement of Absorption; The X-ray Extended Range Technique for high accuracy absolute XAFS by transmission and fluorescence,' European Physical Journal ST 169 (2009) 147-153

[3] J. L. Glover, C. T. Chantler, A. V. Soldatov, G. Smolentsev, M. C. Feiters, 'Theoretical XANES study of the activated Nickel (t-amylisocyanide) molecule,' 625-627, CP882, "X-ray Absorption Fine Structure – XAFS13", B. Hedman, P. Pianetta, eds (2007, AIP 978-0-7354-0384-0).

[4] J. L. Glover, C. T. Chantler, 'The Analysis of X-ray Absorption Fine Structure: Beam-line independent interpretation,' Meas. Sci. Tech. 18 (2007) 2916-2920

[5] J. L. Glover, C. T. Chantler, Z. Barnea, N. A. Rae, C. Q. Tran, Measurement of the X-ray mass-attenuation coefficients of gold and derived quantities between 14 keV and 21 keV submitted

[6] q.v. recent papers by Ridgway, Pettifer and others

The beam-line would be fitted with novel components and diagnostics to routinely determine harmonic content at any energy[7], to investigate scattering contributions to the absorption or fluorescence signals[8] and to calibrate the energy in an effective manner to below 0.1 eV as needed for example for XANES and for subtle Fermi level changes, phase changes and thermal studies. The group has used both powder[9] and single crystal methods for this purpose in the past: The recommended approach is a fast-scanning automated single-crystal technique implemented successfully in numerous experiments at different synchrotrons, but other approaches are possible. Further, the techniques can be used to determine the band-pass of the beam to high accuracy when required[10]. For example, techniques have determined the band-pass in one application to be 1.57 eV ± 0.03 eV. This sort of determination allows the possibility of the accurate characterization of beam-line parameters, which even now pose a threat to validity and interpretation of results at some beam-lines worldwide.

B1.3 Ability to coordinate with other proposals

Many of the details, diagnostics and routines can be implemented in part on some other beamline; however, it is important to incorporate these features in the design from the onset because retro-fitting normally involves less control, less routine sample manipulation and less flexible operation. *For example, this proposal could be combined with a particular (X-ray) energy range on another proposal, so long as this was coordinated at early stages. Standard applications have been made on proposals from 5 keV through approximately 60 keV.* In general, any beam-line investigating absorption (XAS) will require advanced diagnostics and characterization in order to reduce systematic errors near edges and in XANES or XAFS regions, especially as theoretical techniques are improving. Also, it is important to recognize a complementarity between techniques using either advanced or conventional set-ups, and to allocate time in an effective ratio for both these types of implementation on the one beam-line. We have intentionally been general about the specific beam-line optics in order to be flexible and to in principle coordinate details with other and perhaps complementary parties.

B1.4 Feasibility

Experiments using these techniques at ANBF and APS in particular have proven the potential accuracy for ideal systems, for determining the edge energy, the bond distances and other XAFS parameters to high accuracy. Also, the ability to investigate materials and beam properties exists. The Australian Synchrotron is a very good choice for locating such a beam-line, especially given the technical expertise in such measurements amongst beam-line staff, and the fact that these ideas and implementation originated with Australian researchers.

B1.5 Scattering

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[7] C. Q. Tran, et al., "Quantitative Determination of Major Systematics in Synchrotron X-Ray Experiments: Seeing Through Harmonic Components," X-ray Spectrometry 32 (2003) 69-74

[8] C. Q. Tran, M. D. de Jonge, Z. Barnea, C. T. Chantler, 'Absolute determination of the effect of scattering and fluorescence on x-ray attenuation measurements,' J. Phys. B37 (2004) 3163-3176

[9] C. T. Chantler et al., 'Precise measurement of the lattice spacing of LaB_6 standard powder by the x-ray extended range technique using synchrotron radiation', Phys. Rev. A69 (2004) 042101

[10] M. D. de Jonge, Z. Barnea, C. T. Chantler, "X-ray bandwidth: Determination by on-edge absorption and effect on various absorption experiments'', Phys. Rev. A 69 (2004) 022717

Scattering is monitored by daisy wheel aperture investigations, but the fluorescence detector signal will include elastic, inelastic and fluorescence components which are able to be distinguished from one another. It is not impossible that a scattering geometry might include the possibility of a RIXS analyzer for detailed studies.

B1.6 Roughness

We have shown that these studies can be designed to investigate the roughness of small and nanostructures[11], where roughness includes surface profile roughness, correlated top and bottom deviations and void or density variation. Suitable systems could be investigated to high accuracy, for example to consider the origin of roughness and whether the roughness arose from growth, manufacture or stochastic processes. This is a completely new application and opportunity arising from the accuracy of these investigations. Standard approaches cannot observe or measure these effects.

B1.7 Fluorescence and dilute systems

Conventional wisdom is that dilute systems must use fluorescence detection (because the background absorption dominates). While this fluorescence mode is valuable the loss of quality in statistics and in self-absorption is very significant. We have demonstrated the investigation of systems of modest dilution by absorption and fluorescence, and have shown high statistical precision in both cases. Hence one of the prime applications of these accurate methods may in fact be in the study of systems with disorder and/or possessing modest dilution. The limits of the technique are not yet known, but are certainly below 0.1%. The accuracy of the techniques in principle allows this to be of order 100 times less than previous limits.

B1.8 Complex phase studies

Similarly, some extreme chemistry studies are so complex with, for example, three or more simultaneous phases in disordered liquid varying with temperature and pressure[12]. Separating these components using conventional methods is fraught and leads to large uncertainties[13]. The potential of this beam-line proposal is to address directly these problems in a coordinated manner and because of the high statistical information and quality, extract accurate answers to almost impossible questions.

B1.9 Pure single crystals for XAFS!?!

Conventional wisdom is that XAFS is ideal for disordered systems or isolated clusters or molecules. And that the method is quite inappropriate for single crystals or perhaps any system with large domains. It is often asserted that (single-crystal) crystallography should be used in

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[11] J. L. Glover, C. T. Chantler, M. D. de Jonge, 'Nano-roughness in gold revealed from X-ray signature,' Phys. Lett. A373 (2009) 1177-1180

[12] Best, S. P.; Figgis, B. N.; Forsyth, J. B.; Reynolds, P. A.; Tregenna-Piggott, P. L. W., Spin Distribution and Bonding in $[Mo(OD_2)_6]^{3+}$, *Inorg. Chem.* **1995***, 34*, 4605-10; Bruce, M. I., Low, P. J., Costuas, K., Halet, J.-F., Best, S. P., Heath, G. A., *J. Amer. Chem. Soc.* **2000**, 122, 1949-1962; Cheah, M. H., Tard, C., Borg, S. J., Liu, X., Ibrahim, S. K., Picket, C. J. and Best, S. P. *J. Amer. Chem. Soc.*, **2007**, *129*, 11085-11092

[13] C.G. Ryan, W.L. Griffin and N. Pearson, 1996, *Garnet Geotherms: pressure-temperature data from Cr-pyrope garnet xenocrysts in volcanic rocks*, J. Geophysical Research B3, 5611-5625

such cases. However, it has been proven that single crystal XAFS of high quality can be determined and extracted, even for something as ideal as silicon crystal, despite the considerable problem (issue or systematic) of Bragg diffraction[14]. Rather than being limiting, this allows direct comparison of mean square relative displacements (i.e. dynamical bonding) versus mean square lattice displacement (i.e. lattice parameters), thermal anisotropy, temperature studies and the nature of thermal diffuse scattering, still poorly understood. A whole range of potential users and questions can arise if this technology were to be available. Research in this field has been led by Australian researchers.

B1.10 Beam-line characteristics

This proposal aims to use a bending magnet beam-line both for reasons of cost and availability. And because the existing XAS beam-line is a wiggler it has other capabilities. The monochromator would use different possible crystals for low or high energy ranges, but these would be de-tuned double crystal monochromators for ease of set-up and alignment, the construction of which is well understood. This proposal does not aim in particular to possess any microprobe or micro capabilities, already well-served by other beam-lines and beam-line proposals. Spot size would be of order 0.2 mm to a few mm in each direction, truncated as needed by collimating slits. The emphasis here is on simplicity and utility. Hence the robustness of the design using standard elements. Of course, the experiments would run faster if higher fluxes were available, so particularly at the higher energy range a superbend or energy-shifting system would yield improved performance.

B1.11 Cells and stages

A principle of high-accuracy techniques is the requirement to have multiple samples. It is not usually feasible to have multiple dilutions or cells (for high or low temperature) in the same experiment at the same time. This is a minor detail but worth addressing. The high-accuracy techniques use reference samples of high quality to benchmark beam-line, detector and scattering response functions, with multiple samples. Different dilutions (if applicable) can be investigated in a calibrated time sequence. Alternatively, for many systems a different dilution leads to different chemistry, phase or local ordering, so it is important to separate these two components of the experiments. In some cases a transfer standard will achieve this objective, and transfer standards have been investigated and demonstrated in recent work.

B1.12 Polarization Studies

Recent international attention has considered the polarization dependence of XAFS and XANES for oriented and usually nano- samples. This occurs because each of these modes is isolated by particular selection rules of the bound-bound or continuum transition probability and therefore reflects the multipole character of ground and excited or ionized states. Further: with relatively thin oriented samples it can defined the local or active site orientation. Bending magnet sources are not ideal for this purpose but this is at present an area of rapidly increasing interest worldwide. The concept of adjustable polarization including linear, positive and negative circular polarizations (switched via beam orientation, off-axis slit selection, or half-wave plates) is interesting but tends to focus on lower energy ranges. Interestingly, partial polarization in an

[14] C. T. Chantler, C. Q. Tran, Z. Barnea, 'X-ray Absorption Fine Structure for Single Crystals', sub. J. Appl. Cryst. (July 20 2009)

XAFS or XANES study invalidates some analyses because of these effects – however, quantification and use of both theory and experiment to gain information and insight from these make them more useful than before and without attendant loss of information.[15]

B1.13 Ultra-fast?

The high-accuracy techniques are not predicated upon high-throughput or ultrafast dynamic observation. With optimization, scans can be 'fast' i.e. of order minutes, although statistics will always favour longer times or higher fluxes. At some level, high fluxes (i.e. short times) argue for a superbend or perhaps wiggler / undulator, especially as discussed in the two recent international conferences ISRP-11 and SRI. Short times (counting periods below 1 sec or 0.1 second) require fast preamplifiers. While high-throughput is not necessarily a desirable goal of what the AS, (we want quality, and to attract overseas applications and visitors), the issue of the study of dynamical processes is important and interesting. These fast systems have been developed in Europe and elsewhere. Australia has no leadership in this area, but for example Best et al. and Brugger et al. look at transitions and catalytic reactions without requiring ultrafast methods, and there Australia does display leadership.

B2: Applications and Potential Outcomes to Australian Scientific Community
Applications and outcomes can be categorized by (i) ARC guidelines; (ii) new fields with new potential user groups; (iii) new problems which could then be solved.

(i) ARC Guidelines: Frontier Technologies for Building and Transforming Australian Industries:

Breakthrough Science: accurate bond information at active sites of small molecules and large organometallics including enzymes and catalysts; bond lengths, edge energies, dynamical bond lengths, longitudinal and transverse thermal parameters, comparisons of crystallographic site distances versus bonding, thermal and pressure phase transitions

Frontier technologies: diagnosis of harmonics, bandpass, roughness for beam-line independent interpretation of XAFS and XANES, quantification of scattering and scattering processes; calibration of fluorescence measurements

Advanced materials: roughness determination and distribution of nano-materials; characterization of dilute or complex systems using absorption; micro- and nano-layers

Safeguarding Australia:

Border Security: development of X-ray techniques for more sensitive diagnostic screening; development of systems for the discrimination of drug and explosive types (using small (10mM) samples)

Waste recovery and diagnosis: chemical leaching investigations using XAFS in contaminated soils; the study of heavy elements and their ionic state in the muscles of fishes

An Environmentally Sustainable Australia:

[15] Feiters, private communication

Transforming existing industries: mineral discovery; mineral processing recovery

Promoting and Maintaining Good Health:

A healthy start to life: Arsenic uptake in children; study of the ionic state of such elements as chromium and arsenic in the food which we eat

Preventative healthcare: active sites of enzymes, catalysts and bioactive organometallics

(ii) New fields and new potential user groups

The field of investigations of XAFS bonding parameters (dynamical bond lengths) versus crystallographic lattice spacings is just beginning. Australia is at the leading edge in quantifying this complex field, and it requires high accuracy, but applies to a wide range of chemical and biochemical investigations. The XAFS and XANES communities in Australia and across the world are very large. Interest in this has led to the proponent being appointed to the IUCr International Commission on XAFS, in part due to nominations from the Australian community.

Development of theoretical models for routine community use requires testing with data of known accuracy. In the past many theoretical predictions differ at the 1% level but experimental uncertainties were commensurate. With much higher experimental accuracy comes the potential for deeper insight in all theoretical inquiry, especially e.g. for FEFF and FDMNES (the best-known theoretical XAFS/XANES codes).

Determination of roughness in nano-samples is a high-profile area and this technique has originated (and requires) high accuracy. This is a community which might normally use AFM or STEM techniques but can now use synchrotron approaches.

Extension of XAFS-style techniques to single crystals to determine bond flexibility requires multiple techniques. Some of the conventional crystallographic community will be able to investigate difficult anomalies or ambiguities at the active sites of their target species, in order to relate structure to function.

Extension of absorption techniques to dilute systems. 1%? Easily. 0.1%? Certainly. 1 mM? The limits of this, and hence the range of applicability to particular systems, is currently unknown – this is an exciting new technology which does not exist anywhere. Whatever the limits, a range of users down to those limits will be attracted to establish greater insight in difficult samples.

Inelastic mean free paths of (photo-)electrons is historically investigated using electron microscopy and direct electron scattering techniques (EELS). However, high accuracy XAFS investigations permit measurement of IMFP's in areas inaccessible to other techniques. In other words this again creates a new field of inquiry for beam-line development.

Specific examples relate to all of the contributing groups either as realized in test experiments or as potential for Australia's research and technological future.

For example, the Brugger group investigates complex phase changes in disordered systems[16], where greater insight and accuracy in a routine but advanced approach is likely to clarify key

[16] J. Brugger, B. Etschmann, W. Liu, D. Testemale, J.-L. Hazemann, W. van Beek, W. and O. Proux, An XAS study of the chloride complexing of Cu(I) in brines. Geochim. Cosmochim. Acta, **71**, 4920-4941 (2007)

results and outcomes. The Best group is investigating active sites in catalysis and hence probing dynamic structure and function[17]. The Gerson group have particular interest in industrial and related bio-organometallic issues[18].

B3: Match to Selection Criteria
Criterion 1 – Meet the demands of an identified group of users

Group 1: Conventional XAFS users
Group 2: Conventional XANES users
Group 3: Conventional Absorption (XAS) or Fluorescence users

For these three groups, the demand is for clearly better data outcomes, for better defined quantitative assessment of bonding, structure and coordination, and for applications.

Group 4: Investigations of roughness across the nano-scale. This is a very strong group internationally, but here is the possibility of a new tool and hence user community within the synchrotron community.

Group 5: Investigations of inelastic mean free paths. This is another strong international community which has hitherto been unable to make use of synchrotron activity for their studies and research. Hence this is a new group of users.

Group 6: Complex phase evaluation under extreme conditions for earth science, mineralogy, mining and related applications. This is a strong group, strong in Australia and in a number of cases keen to make use of this new technology.

Group 7: Cold cell and catalytic / enzymatic investigations. A strong group in chemistry and biochemistry around the world, again strong links to industrial research. Showing the potential of such methods to such a potential and existing group will enable them to resolve new key questions.

Group 8: Single crystal crystallographers is a large and strong existing community in Australia and world-wide. Conventionally many of them would seek other methods to establish key conclusions for their research. This beam-line would open up a new opportunity for their investigations.

Criterion 2 – Take advantage of an existing third generation light source

XAFS and XANES in general essentially require advanced third generation facilities, especially insofar as beam flux, divergence and brightness are concerned. The discussed new areas and applications have advanced light source requirements.

[17] Cheah, M. H., Tard, C., Borg, S. J., Liu, X., Ibrahim, S. K., Picket, C. J. and Best, S. P. *J. Amer. Chem. Soc.*, **2007**, *129*, 11085-11092
[18] A.R. Gerson, 3D-microdiffraction: A facility for the Australian synchrotron, Current Applied Physics, **8**, 463-466 (2008)

Criterion 3 – Will position Australasian scientists at the leading edge of the field

This is clearly explained above. Consider for example 19,20,21,22. Importantly, it has the potential to establish not just the Australian proponents but general Australian and other local users with key applications at the leading edge of their fields in ways that a workhorse simply cannot. The quality of even a single result achieves this, and the potential to do high quality research of several types at the Australian Synchrotron and nowhere else will encourage these opportunities.

Criterion 4 – Can be demonstrated to be feasibly constructed in three years

As discussed above, design elements can be somewhat flexible but all can be designed and constructed within a brief timeframe – well within three years. Given the time-frame of this submission deadline we would only comment that this is obvious, and would refer to experimental set-ups which have been constructed on much shorter timescales in published literature.

B4: Potential Users

Does the project address a clearly identified need in the community? The need may be actual or potential.

The examples and areas outlined above prove the actual, existing and potential needs. We need to be able to determine longitudinal and transverse bonding and thermal parameters in local disordered systems to higher accuracy. We need to develop theoretical methods for the whole international community, by comparison to the results of high accuracy experiments. The potential needs of new fields and areas of inquiry opened up by these methods are significant and the potential growth in these fields is large.

[19] J. L. Glover, C. T .Chantler, Z. Barnea, N. A. Rae, C. Q. Tran, D. C. Creagh, D. Paterson, B. B. Dhal, 'High-accuracy measurements of the X-ray mass-attenuation coefficient and imaginary component of the form factor of copper,' Phys. Rev. A78 (2008) 052902

[20] M. D. de Jonge et al., 'Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic form-factor of tin over the energy range of 29 keV – 60 keV,' Phys. Rev. A75 (2007) 032702

[21] M. D. de Jonge et al., 'Measurement of the x-ray mass attenuation coefficient and determination of the imaginary component of the atomic form-factor of molybdenum over the energy range of 13.5 keV - 41.5 keV,' Phys. Rev. A 71, 032702 (2005)

[22] C. Q. Tran et al.,, "Measurement of the X-Ray Mass Attenuation Coefficient and the Imaginary Part of the Form Factor of Silicon Using Synchrotron Radiation," Physical Review A 67, 042716 (2003)