Sector 25 at the APS-U: Two new beamlines for advanced spectroscopy

Steve Heald, Jonathan Knopp, Tim Graber, and Dale Brewe
Advanced Photon Source, Argonne National Laboratory, Argonne, IL, USA
heald@anl.gov

As part of the Advanced Photon Source (APS) Multibend Achromat lattice upgrade two new beamlines for spectroscopy will be constructed on a canted undulator source at Sector 25. The programs at the 20-ID beamline at the APS need to move to sector 25 to make room for a planned long beamline. These will be combined with some other APS spectroscopy programs at sector 25 to use two new beamlines on a canted undulator. These two beamlines will service existing and upgraded endstations covering a variety of spectroscopy applications. There will be a microprobe branch that will provide sub-micron beams for fluorescence imaging, and micro-XAFS. These can be combined with confocal optics for micron level depth sensitivity. This branch will also have a station for XAFS experiments requiring a high-brilliance high-flux beam such as doped thin films or ultra-dilute samples. The second Advanced Spectroscopy branch will provide beam to two inline hutches. The first will have stations for both an enhanced LERIX spectrometer for non-resonant inelastic scattering (x-ray Raman), and spectrometers for high resolution emission spectroscopy. The second hutch will provide space for experiments requiring extensive setup, such as time-resolved pump-probe experiments. Both hutches will have a variety of focusing options providing beam sizes down to a few microns. To provide greater beam separation, both lines will have side deflecting mirrors for harmonic rejection, and focusing/collimation. The planned energy ranges are 4-32 keV for the microprobe branch, and 4-40 keV for the Advanced Spectroscopy branch. The horizontal deflection mirrors allow use of small offset monochromators equipped with liquid nitrogen cooled Si (111) crystals for monochromatic beam, and wide-bandpass multilayers providing higher flux for experiments that do not need high resolution such as imaging and non-resonant emission spectroscopy. The Advanced Spectroscopy branch will also have a secondary monochromator for experiments needing better resolution than provided by Si (111).

This research used resources of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357.

X-ray Raman Scattering in Extreme Conditions and Extreme X-ray Raman Scattering

Gerald T. Seidler[1]
[1] University of Washington, Seattle WA, United States (seidler@uw.edu)

X-ray spectroscopies, broadly defined, will gain exciting new opportunities as a consequence of the APS-U project and the new MBA lattice. These include especially: (1) the new science that can be achieved with XAFS, XES, or RIXS as a consequence of higher flux with small focal spots, and (2) the emergence of resonant- or MCD-enhanced ptychography that comes from the higher coherent flux on small spots. In the context of x-ray Raman scattering (XRS), the key issues surround not only applications requiring the finer focusing capability but also the new technical and organizational opportunities for novel or upgraded endstation equipment. Other speakers in the workshop will address the science case for the highest profile small-spot XRS application: studies at Mbar pressures. Here, I will address other extreme environments, such as electrochemical cells and molten salts, and also new directions in endstation instrumentation. My discussion of the latter topic will include an overview of the conceptual design proposed LERIX-2 endstation for the new 25-ID beamline in addition to possible new instrumentation directions to extended routine XRS to much higher energies and, when needed, correspondingly higher momentum transfers. In the latter effort, we aim to both increase penetration capacity in special environments and also open the possibility of more aggressively shaping the *q*-dependent atomic backgrounds so as to greatly enhance the quality of extended XRS to obtain structural information around light elements.

Recent Developments in X-ray Spectroscopy of Matter under Extreme Conditions

Georg Spiekermann[1]

[1]University of Potsdam, 14476 Potsdam, Germany, geospiek@uni-potsdam.de

The importance of X-ray spectroscopy techniques for the investigation of matter under extreme conditions will continue to grow in the future, due to their mostly element-specific insight into structure and properties.
In the last years, photon-hungry techniques like valence-to-core X-ray emission spectroscopy (vtc-XES) and X-ray Raman scattering (XRS) have become more common in application to diamond anvil cell (DAC) high pressure experiments. We will present important cornerstones on this way, including own scientific cases and technical developments [1,2,3].
Due to the high acquisition times and other experimental difficulties, there is still a general gap between X-ray spectroscopy techniques and laser-heated DACs, which enable measurements at both extreme pressure *and* extreme temperature, like they prevail in the Earth's mantle. This gap has been bridged only at few end stations around the world, despite the big potential of X-ray spectroscopy at mantle conditions. Small and optimized laser-heating systems, portable to X-ray spectroscopy beam lines, are a promising way to further close the gap [4]. Eventually, with such systems at high-flux spectroscopy beam lines, the next big step can be explored: Probing directly melts in the DAC at extreme temperatures.

[1] Spiekermann, G., Harder, M., Gilmore, K., Zalden, P., Sahle, C. J., Petitgirard, S., Wilke, M., Biedermann, N., Weis, C., Morgenroth, W., Tse, J. S., Kulik, E., Nishiyama, N., Yavas, H., Sternemann, C. (2019) Persistent octahedral coordination in amorphous GeO2 up to 100 GPa revealed by Kbeta" X-ray emission spectroscopy. Physical Review X. DOI: 10.1103/PhysRevX.9.011025

[2] Petitgirard, S., Sahle, C., Weis, C., Gilmore, K., Spiekermann, G., Tse, J. S., Cavallari, C., Cerantola, V., Sternemann, C. (2019) Magma properties at Earth's lower mantle conditions inferred from electronic structure and coordination of silica. Geochemical Perspectives Letters. DOI: 10.7185/geochemlet.1902

[3] Petitgirard S., Spiekermann G., Weis C., Sahle C., Sternemann C., Wilke M. (2017) Miniature diamond anvils for X-ray Raman scattering spectroscopy experiments at high pressure. Journal of Synchrotron Radiation. DOI: 0.1107/S1600577516017112

[4] Spiekermann, G., Kupenko, I., Petitgirard, S., Harder, M., Nyrow, A., Weis, C., Albers, C., Biedermann, N., Libon, L., Sahle, C. J., Cerantola, V., Glazyrin, K., Konopkova, Z., Sinmyo, R., Morgenroth, W., Sergueev, I., Yavas, Y., Dubrovinsky, L., Tolan, M., Sternemann, C., Wilke, M. (2020) A portable on-axis laser heating system for near-90° X-ray spectroscopy: Application to ferropericlase and iron silicide. Journal of Synchrotron Radiation. DOI: 10.1107/S1600577519017041

An outlook from applications and instrumentation perspective

Hasan Yavas, SLAC National Accelerator Laboratory, Menlo Park, California

Inelastic X-ray scattering (IXS), as a photon-in/photon-out spectroscopy technique, has been a prolific method for materials research for more than two decades. The penetrating power of high-energy X-ray photons is particularly advantageous for investigating samples under extreme conditions, where it is difficult or impossible for other probes to reach. As an exceptional variety of IXS, X-ray Raman Scattering (XRS) holds an uncontested supremacy when shallow atomic edges need to be examined under extreme conditions like samples in a pressure cell. In this talk, I will attempt to venture potentially rewarding applications of IXS/XRS that could benefit from the unique properties of the MBA lattice upgrade.

Pressure tuning of magnetism in Eu-based magnetic superconductors

Wenli Bi
University of Alabama at Birmingham

Divalent Eu-based intermetallic compounds exhibit rich magnetic properties due to the strong local magnetic moment. In Eu-based pnictide superconductors, peculiar coexistence of two collective phenomena, magnetic order from Eu ions and bulk superconductivity from Fe-As layers, makes these systems ideal platform to investigate the competition of magnetism and superconductivity. We have studied the magnetic behavior in selected Eu-based pnictides at hydrostatic pressures using synchrotron Mössbauer spectroscopy in ^{151}Eu. Results on evolution of magnetism and valence state in Eu ions will be discussed in this talk.

Nuclear resonant inelastic x-ray scattering at pressure and temperature

Brent Fultz, Applied Physics and Materials Science, California Institute of Technology

Nuclear resonant inelastic x-ray scattering (NRIXS) is now established as an important probe of phonon spectra of materials. Sometimes with guidance from ab initio computation, NRIXS spectra have proved reliable for obtaining the vibrational entropy of materials, and vibrations are usually the dominant source of entropy. An advantage of NRIXS over inelastic neutron scattering is that the volume under study is sufficiently small to permit measurements on materials in diamond anvil cells. While the effects of pressure on phonon spectra can be calculated today with some reliability, reliable phonon calculations with simultaneous pressure and temperature are still emerging. NRIXS measurements with good control over temperature and pressure can provide a large part of the free energy, G(P,T), revealing cross-terms that scale with the product PT.

The APS upgrade should improve the capabilities of NRIXS by increasing the flux on small samples by a factor of about four, from both the increased current and from improved monochromator operation. Very small sample sizes will be possible, allowing for measurements at higher pressures. Challenges remain for simultaneous temperature and pressure, but some planning today could expedite new science soon after the upgrade.

Direct Probing of Bonding Transitions in Amorphous Oxides through x-ray Raman Scattering and *ab initio* Calculations

Sung Keun Lee[1*]

[1]School of Earth and Environmental Sciences, Seoul National University, Seoul, 08826 Korea

E-mail: sungklee@snu.ac.kr http://hosting03.snu.ac.kr/~sungklee

A full understanding of the densification of amorphous oxides above megabar pressures (100 Gigapascal or 1 million atm) remains challenging due to their inherent structural disorder and the lack of suitable experimental probes at high pressures. Recent experimental breakthroughs in element-specific X-ray Raman scattering (XRS), along with *ab initio* calculations have revealed the unprecedented details of bonding changes in glass and melts under compression. Here, we provide an overview of the earlier and mainly recent progress and insights by XRS into structures of amorphous under extreme compression above megabar pressures [1-4]. Because of the intrinsic inefficiency of the technique, most earlier achievements with XRS is limited to ~50-60 GPa, revealing the pressure-induced boron coordination transformation and formation of oxygen tricluster. Advances in a post-sample collimation allow an efficient collection the XRS signal with a reduced background signal beyond megabar pressures. When compressed above ~120 GPa, amorphous oxides undergo structural transitions into densely packed networks around compressed oxygen that are not observed at low pressures and substantially differ from those in the crystalline silicates. Particularly, the densification in is accompanied with the prevalence of quadruply coordinated oxygens above megabar pressures. The extreme densification paths with compressed oxygens account for anomalous negative buoyance of the complex partial melts in the deeper part of the mantle and those in the super-Earth bodies. Finally, we discuss the further direction of XRS to further delve into the structures of non-crystalline materials.

[1] Lee, S. K., Kim, Y.-H., Yi, Y. S., Chow, P., Xiao, Y., Ji, C., and Shen, G., Oxygen quadclusters in SiO_2 glass above megabar pressures up to 160 GPa revealed by x-ray Raman scattering, *Physical Review Letters*, 123 235701 (2019)

[2] Lee, S. K., Kim, Y.-H., Chow, P., Xiao, Y., Ji, C., and Shen, G., Amorphous boron oxide at megabar pressures via inelastic x-ray scattering, *Proceedings of the National Academy of Sciences*, 115(23) 5855-5860 (2018)

[3] Lee, S. K., Eng, P. and Mao, H.K., Probing of pressure-induced bonding transitions in crystalline and amorphous Earth materials: Insights from X-ray Raman scattering at high pressure, *Reviews in Mineralogy and Geochemistry,* 78 139-174 (2014)

[4] Lee, S.K., Eng, P., Mao, H.K., Meng, Y. Newville, M., Hu, M.Y & Shu, J., Direct probing of bonding changes in borate glasses at high pressure. *Nature Materials* 4 851 (2005)

High Pressure Inelastic X-ray Scattering at HPCAT

Yuming Xiao and Paul Chow

HPCAT, X-ray Science Division, Argonne National Laboratory, Argonne, IL, 60439

The structural, electronic and magnetic properties of materials under high pressure are of fundamental interest in physics, chemistry, materials science, and earth sciences. The 16 ID-D beamline of the High Pressure Collaborative Access Team (HPCAT) at the Advanced Photon Source (APS) is dedicated to high-pressure research using X-ray spectroscopy techniques typically integrated with diamond anvil cells. The beamline provides X-rays of 4.5-37 keV, and current available techniques include X-ray emission spectroscopy, inelastic X-ray scattering and nuclear resonant scattering. [1,2] In this presentation, we will mainly cover high pressure inelastic X-ray scattering program at HPCAT.

Firstly, we discuss on the particular requirements and instrumentation for inelastic X-ray scattering under high pressure. We then present several examples to illustrate the recent progress in high-pressure IXS studies at HPCAT including development of XRS spectrometer with a polycapillary full lens. [3] An outlook toward future development in high-pressure inelastic X-ray scattering with new diffraction-limited storage rings (APS-U etc.) is also discussed.

[1] Xiao, Y., P. Chow, G. Boman, L. G. Bai, E. Rod, A. Bommannavar C. Kenney-Benson, S. Sinogeikin, and G. Y. Shen. (2015) *Rev. Sci. Instrum.* 86, 072206

[2] Xiao, Y.; P. Chow, G.Y. Shen. (2016) *High Press. Res.,* Vol. 36, 3, 315-331

[3] Chow, P., Y. Xiao., E. Rod, L. G. Bai, G. Y. Shen, S. Sinogeikin, N. Gao, Y.Ding., and H.-K. Mao. (2015) *Rev. Sci. Instrum.* 86, 072203

Properties and electronic structures in high pressure glasses using a combination of X-ray Raman spectroscopy, total X-ray scattering and Molecular Dynamic calculations.

Sylvain Petitgirard [1*], Georg Spiekermann [2], Christoph Sahle [3], Christopher Weis [4], Keith Gilmore [3], John S. Tse [5], Max Wilke [2] and Christian Sternemann [4]

[1] Department of Earth Sciences, ETH Zürich, Zürich 8025, Switzerland
[2] Institut für Geowissenschaften, Universität Potsdam, Potsdam, Germany
[3] European Synchrotron Radiation Facility, 71 Avenue des Martyrs, Grenoble 38000, France
[4] Fakultät Physik / DELTA, Technische Universität Dortmund, D-44221 Dortmund, Germany
[5] Department of Physics and Engineering Physics, University of Saskatchewan, Saskatoon, Saskatchewan S7N 5E2, Canada

* Corresponding author (email: **sylvain.petitgirard@erdw.ethz.ch**)

Melt properties at high pressure are crucial to model the evolution of the deep part of the Earth formation and evolution. Knowledge of the short-range atomic and electronic structure in melts measured via spectroscopic techniques bring important constraints about their compressibility and viscosity at depth. A primary step toward studying melt at extreme conditions consist in probing glasses with relevant compositions for the Earth interior. In the past five years, there has been a blossoming amount of studies looking at properties of glasses under extreme pressures using spectroscopic method, such as X-ray ram spectroscopy (XRS) or X-ray total scattering, pushing the limits of such measurements. However, in many cases it has also brought other problems, in particular concerning the resolution either in pressure steps or in energy resolution or Q-range for pair distribution analysis.

Our approach has consisted in the development of unique tools to improve spectroscopic measurements under pressure that also prove to be useful for X-ray total scattering. In particular, we have concentrated our effort on the canonical model SiO2, and measured the O K-edge and the Si $L_{2,3}$-edge in silica up to 110 GPa using X-ray Raman scattering spectroscopy with unprecedented energy resolution and pressure steps for both edges. We found a striking match to calculated spectra of the quenched high-pressure melt based on structures from molecular dynamics simulations [1], but also with our X-ray total scattering analysis. The combination of MD simulation, XRS and total scattering measurements together with density measurement using the X-ray absorption method [2] are keys to understand more complex systems relevant for plenary interiors.

In this presentation, I will review recent works on silicate glasses under pressure and discuss the limitations of the different approaches and the imperious need to combine methods in order to comprehend the properties of glasses and melts at high pressure.

References

[1] - S. Petitgirard *et al.* Magma properties at deep Earth's conditions from electronic structure of silica. *Geochem. Persp. Let.* **9**, 32-37. (2019)

[2] - S. Petitgirard *et al.*, SiO_2 glass density to lower-mantle pressures. *Phys. Rev. Lett.* **119**, 215701 (2017).

A statistical view on core-level spectra of liquids

J. Niskanen*, Ch.J. Sahle, M. Fondell, S. Eckert, R.M. Jay, K. Gilmore, F. Uhlig, J. Smiatek, A. Pietzsch, M. Dantz, X. Lu, D.E. McNally, T. Schmitt, V. Vaz da Cruz, V. Kimberg, F. Gel'mukhanov, and A. Föhlisch

*Department of Physics and Astronomy, University of Turku, FI-20014 Turun yliopisto, Finland;johannes.niskanen@utu.fi

Rather than a single geometry, the atomistic structure of liquid systems is described by a collection of possible configurations, each assigned with a probabilistic weight for occurrance [1]. This fact means that properties derived from atomistic configurations are averages over the corresponding statistical ensemble. Most notably for spectroscopists, X-ray spectra from liquids are not an exception to this principle.

In this contribution we will discuss the consequences of this idea, using our recently established line of thought [2-3] as an example. We start with the fundamental difference between a gas-phase and a liquid system, and then proceed with the idea of ensemble averages as the obtained experimental result. What follows is a method of analyzing statistical simulations for structural interpretation of the core-level spectra. The protocol [2] relies on a a-posteriori analysis of a simulation for the ensemble averaged core-level spectrum to establish a statistical link between structural information and spectral regions of interest. Here, the role of core-level spectroscopy is fundamental: as the 1s orbital is local, each individual transition event occurs locally, which allows for connecting the behavior of averaged spectra to atomistically local structural parameters.

Last, we will consider analysis of experimental data from hard X-ray Raman scattering spectroscopy and other core-level spectroscopic techniques.

References

[1] M.P. Allen and D.J. Tildesley, "Computer Simulation of Liquids" Oxford University Press, Oxford (1987).
[2] J. Niskanen, Ch.J. Sahle, K. Gilmore, F. Uhlig, J. Smiatek, and A. Föhlisch, "Disentangling structural information from core-level excitation spectra", Physical Review E 96, 013319 (2017).
[3] J. Niskanen, M. Fondell, Ch.J. Sahle, S. Eckert, R.M. Jay, K. Gilmore, A. Pietzsch, M. Dantz, X. Lu, D.E. McNally, T. Schmitt, V. Vaz da Cruz, V. Kimberg, F. Gel'mukhanov, and A. Föhlisch, "Compatibility of quantitative X-ray spectroscopy with continuous distribution models of water at ambient conditions", PNAS 116, 4058--4063 (2019).

Marriage of X-ray Raman Scattering with Soft X-ray Techniques for Securing a Sustainable Future for Carbon Materials

Bhoopesh Mishra
School of Chemical and Process Engineering, University of Leeds, UK

Need for developing sustainable advanced carbon materials of the future is both important and timely. Currently available alternatives such as graphene and nanotubes (CNTs) require environmentally problematic syntheses conditions including toxic chemicals for their production. Hydrothermal carbon (HTC), produced under moderate temperature-pressure conditions, embodies all the characteristics of a sustainable functional carbon. HTC has been shown to have wide-ranging applications from energy storage to catalysts and adsorbents to composites. Nonetheless, a fundamental understanding of the formation mechanisms governing HTC growth and structure (e.g., nucleation, pore formation etc), essential to underpin new or boost existing applications, are not well understood. We have integrated soft (e.g., STXM) and hard X-ray (e.g., XRS) techniques for understanding the complex network of reaction mechanisms, intermediates, and pathways governing hydrothermal carbonization processes. These fundamental insights will be used to identify performance bottlenecks and tailor the design of HTC for energy storage, catalysts, and advanced sorbents.