Enhancement of Scientific Facilities for Medium-Energy-Resolution Inelastic Scattering and Liquid Surface Scattering at Beamline 9-ID

The operation of the insertion device beamline 9-ID at the APS is focused primarily on two fields of scientific research: inelastic x-ray scattering (IXS) with medium-energy-resolution for the study of correlated electron systems, and scattering at liquid surfaces and interfaces for inorganic, biological and nano-materials applications. A number of very exciting, new scientific possibilities are appearing on the horizon in both fields, which can be realized in the near future if beamline and instrumental capabilities are enhanced substantially. Higher incident photon fluxes into smaller focal spots, smaller energy band passes, realization of diverse and extreme sample environments combined with improved instrumental precision and, most importantly, the ability to capture, time-resolve and analyze simultaneously large solid angles of scattered photons with modern linear- and area solid state detectors, are all imperative in the approach and successful treatment of these forefront scientific subjects.

Scientific Opportunities for Inelastic Scattering

Resonant Inelastic X-ray Scattering (RIXS)

The emergence of inelastic x-ray scattering as a main stream experimental technique has been one of the most significant development in x-ray instrumentation. RIXS is an application in which the incident photon energy is near an absorption edge. It thus combines the element specificity of resonant x-ray scattering and the spectroscopic capability of inelastic x-ray scattering to provide momentum-dependent information on electronic excitations in complex, correlated systems with many constituent atoms. Although resonantly enhanced, scattering cross sections are very small and only the advent of modern high-brightness undulator sources at 3rd generation synchrotron facilities have made these challenging experiments possible.

Of enormous scientific and technological importance are transition-metal oxides. The electronic structure in these novel materials gives rise to a variety of complex phenomena, such as high-Tc superconductivity and colossal magnetoresistance (CMR), which are recognized to result from the interplay and competition between the internal degrees of freedom of the strongly correlated electron system. IXS is a perfect probe for the investigation of such phenomena. A particular topic, intensely debated in the context of high-Tc superconductivity is the coupling of charge excitations to phonons and magnons. In this regard, studies at 9-ID have uncovered a previously unobserved mode in the excitation spectrum of $La_{2-x}Sr_xCuO_4$ and Nd_2CuO_4 [Hil], providing important new insights into the high-energy Hamiltonian of cuprate materials. Also, a detailed study of Cu *K*-edge RIXS of La_2CuO_4 [Lu] was recently successful in resolving a multiplet of charge-transfer excitations in this material, evidencing the need for a new, multi-band theoretical approach to the description of the charge dynamics of high-Tc cuprate superconductors. Similar studies envisioned in the future will need an improved energy resolution of < 50 meV.

Finding low cost alternative for silicon technologies such as flat displays, solar cells and sensors remains a significant scientific and technological challenge: Organic Semiconductors are widely believed to hold great promise and are presently the subject of intense study. Recent experiments at 9-ID have discovered strong directional dependence of electronic excitations [Kod], necessitating single crystal samples which, in organometallic compounds, are often very small. Improved focusing to beam sizes of ~10 μm is urgently needed to further study these important materials.

Non-Resonant Inelastic X-ray Scattering (NIXS)

RIXS measurements benefit greatly from the resonant enhancement of the scattering cross section, but relating these measurements to the dynamic structure factor is vastly more complicated than the simple relationship that exists for non-resonant measurements of core and valence electron excitations [Lar]. Thus, high-resolution NIXS is the next frontier in inelastic scattering, which is feasible only with a substantial enhancement of incident flux and scattered photon detection.

One exciting scientific opportunity aims at “truly” imaging an electronic excitation with atomic resolution spatially, and attosecond resolution temporally, by directly inverting the measured non-resonant structure factor. For real materials exhibiting spatial structure on an atomic scale, measurements would have to include a large number of inelastic scattering profiles recorded in the presence of simultaneously excited Bragg reflections. Direct inversion measurements have already been successful in the approximation of a homogeneous medium for some materials, such as water, LiF and Be. If “true” imaging could be accomplished, specific atoms would be visible together with electronic excitations propagating on an underlying lattice, which would have an extraordinary impact on fields concerned with imaging or ultra-fast phenomena [Abb].

A second novel opportunity involves the study of ground state configurations in strongly correlated transition-metal oxides, materials of great fundamental and technological importance, displaying a diverse spectrum of properties from colossal magnetoresistance to high-temperature superconductivity. Here the strong sensitivity of the angular dependence of non-resonant inelastic scattering profiles for local d-d transitions to the detailed nature of the ground state becomes a powerful tool to probe crystal field and orbital excitations in these important materials [vVe].

Another opportunity relates to the study of gases, such as N_2, with important implications to atmospheric, environmental and space sciences. Selected emissions of monatomic Oxygen and Nitrogen together with the Lyman-Birge-Hopfield (LBH) band emissions from N2 are the dominant emissions in the terrestrial UV airglow and aurora. Studying these emissions is the key to understanding the radiative energy balance in the upper atmosphere [Sei] It has been recently demonstrated, that NIXS can play a significant role in the solution of this important problem. For example, an improvement in energy resolution from the current 120 meV at 9-ID to better than 25 meV would enable the isolation of three low-lying resonances in the LBH band and complement our understanding of this atmospheric phenomenon in a way that cannot currently be attained by any other technique. First and foremost, all NIXS project need a dramatically increased incident photon flux, underscoring the need for an extended undulator source.

Scientific Opportunities: Liquid Surface Scattering

Synchrotron x-ray scattering is the most powerful probe of the structure at the liquid-gas, liquid-solid and liquid-liquid interfaces, which has led to many key discoveries including surface freezing in alkanes, surface layering and surface alloy formation in liquid metals, the structures of two-dimensional macromolecular and biomolecular films on aqueous and liquid metal surfaces, and tests of capillary wave theory at the liquid/vapor and liquid-liquid interfaces.

Synthetic biomolecular material such as α-helical bundle peptides can be designed to incorporate cofactors, which can impart specific functionalities to these peptides. Their relative positioning and environment within the core of the bundle can be used to control their functionality, while the exterior of the bundle can be tailored to control the vectorial association of the bundles with an liquid-gas, solid-gas, solid-liquid interface. As a result, the cofactor’s molecular functionality can be transformed into a macroscopic materials property of the interface. Amphiphilic 4-helix bundle peptides have recently been designed and characterized at 9-ID for the generation of light-induced electric charge separation across an interface between polar and non-polar media, utilizing biological cofactors. In addition, non-biological cofactors can be designed to impart exceptional non-linear optical properties to the interface. Detailed information concerning the intramolecular structures and packing of the vectorially-oriented bundles is obtained by grazing incidence x-ray diffraction and x-ray or neutron specular reflectivity, with non-resonant and resonant measurements yielding the electron density profile as well as the locations of the resonant atoms within the molecules [Str].

In molecular electronics the nature and pathways of charge transfer through single organic molecules is among the most intensely studied open questions. Experimental studies either employ single molecules or self-assembled monolayers (SAMs), suspended between two electrodes in such a way that they perform a prescribed electronic function. A detailed knowledge of the *in situ* molecular-level structure of the SAM after the molecules have been brought into contact with both electrodes is crucial for understanding the charge transport, and other molecular-electronics-oriented properties of any molecular-electronics device. Nevertheless, such Angstrom-resolution structural studies pose a formidable experimental challenge, as these deeply buried interfaces are inaccessible to scanning probe and high-resolution electron microscopy techniques. High-resolution x-ray scattering studies at higher energies (25-30 keV) using an enhanced liquid surface spectrometer at 9-ID are an ideal tool for addressing this problem [Lef].

The most definitive structural information on organic and bio-organic materials that can be obtained from elastic scattering of either x-rays or neutrons requires a determination of both the amplitude and the phase of the scattered radiation as a function of momentum transfer. In fact, for soft matter, the phase information is more important in determining the correct structure than the amplitude. The phase problem for x-ray & neutron reflectivity from liquid-gas, liquid-liquid and liquid-solid interfaces, and for thin films at these interfaces, can be solved via interferometry with a multilayer reference structure, precisely aligned parallel to the interface and brought into juxtaposition with the thin film at the interface at a separation of 10-100Å. Besides solving the phase problem, the interference between the relatively weak specular reflectivity from sample and the much stronger reflectivity from the multilayer reference structure, dramatically enhances the spatial resolution attainable in determining the structure of the sample [Bla].

Bacterial pathogens generate protein-toxins that work in fascinating ways to disrupt the normal processes of host cells. These bacterial toxins are key factors in determining the outcome of infections and are among the most potent poisons known to humans. Many bacterial toxins act by enzymatically modifying substrates in the cytosol of mammalian cells. The mechanism of these interactions is mostly unknown. X-ray and neutron specular reflectivity studies of model membranes at the air-liquid interface supply direct structural information for the entire toxin as it adsorbs to planar lipid monolayers and subsequently undergoes pH-dependent conformational changes to insert and translocate the enzyme. Future studies of supported lipid bilayers will examine inserted DT in a configuration more similar to that in cells. Grazing incidence x-ray diffraction which probes the in-plane structure of the adsorbed protein will be important to complement the reflectivity data and determine the overall oligomeric structure [Ken].

The liquid mercury–electrolyte interface is the most extensively studied electrochemical system, but despite its central importance, structural data on this deeply buried liquid-liquid interface is lacking. In-situ high-energy x-ray reflectivity measurements of Hg electrodes in simple salt solutions could clarify the interface structure along the surface normal as a function of applied electrical potential and reveal the effect of substantial excess surface charges on surface capillary waves and surface layering. These measurements are of greatest interest for the development of advanced theories of the electrochemical interface as well as for a more detailed understanding of the complex surface structure of liquid metals [Ock].

Proposed Technical Enhancements

In order to facilitate a successful and productive approach to these exciting, new scientific opportunities, technical enhancements to beamline 9-ID and its instruments are necessary. An upgrade is proposed and envisioned to proceed in 2 stages:

First Stage:

Enhancement of the undulator source and improvements of x-ray optics and instruments

X-ray Source

1) Expansion of the current single-undulator source to two, preferably three undulators A in an extended straight section of the accelerator. This will double or even triple the incident photon flux and will have an immediate benefit for both IXS and LSS experiments by increasing data throughput proportionally. est. price: **2.0 M$**

2) Replacement of the existing coarse focusing optics on 9-ID by micro-focusing bimorph mirrors. This will decrease the beam size at the experiment from typically 150 μm to the 10 μm needed est. price: **1.2 M$**

IXS instrumentation

3) Implementation of a versatile, vacuum-compatible, secondary monochromator for IXS. This will greatly improve the energy resolution and enable tailoring of the energy bandpass – throughput relation for specific materials and experiments. est. price: **0.4 M$**

4) Reconfiguration and expansion of the IXS spectrometer for vertical and horizontal scattering geometries with dual, independent, fully addressable detector arms and full polarization analysis. This will greatly broaden the spectrum of experiments that can be performed, including the true imaging project described above. est. price: **0.6 M$**

5) Implementation of expanded sample environments, including very high and very low temperatures (2 – 800 k) and pressures (10 GPa), micro positioning. est. price: **0.2 M$**

LSS instrumentation

6) Implementation of a new harmonic rejection mirror. This would enable LSS lower energy studies which currently suffer strongly from harmonic contamination. est. price: **0.2 M$**

7) Reconfiguration and expansion of the liquid surface spectrometer and auxiliary facilities to include SEXAFS, GISAXS at the liquid-gas interface with fluorescence detection, Brewster angle microscopy, improved mechanical precision to allow studies at higher energies, est. price: **0.8 M$**

8) Implementation of direct interferometric phasing of reflectivity for thin films at the liquid-gas interface without any perturbation of the film. est. price: **0.2 M$**

9) Addition of a multi-steering-crystal extension for rapid, fixed-sample reflectivity measurements

10) Acquisition of a linear detector system, such as the SLS Mythen, and area detector system, such as the SLS Pilatus. These modern detectors allow parallel processing of scattered photons in IXS and LSS experiments and thereby increase data throughput and productivity proportionally. They are also fast enough to enable time-resolved studies of biological membranes est. price: **0.5 M$**

11) Improved, user-friendly computer software for data acquisition, visualization and post-processing for both IXS and LSS experiments. est. price: **0.1 M$**

total est. price, first stage: **6.8 M$**

Second Stage:

Implementation of a secondary beamline, dedicated to liquid surface scattering

The implementation of a companion beamline to 9-ID is particularly simple, since the original sector layout was conceived with two ID beamlines in mind. Thus the first optics enclosure is both designed to accommodate two parallel beamlines at a separation of 1m and has space reserved for a horizontal monochromator to supply the secondary beamline with radiation from a source in line with the primary beamline. The experimental stations are structured to allow independent operation of two instruments (IXS and LSS) in 9-ID B and 9-ID C. A secondary undulator beamline at Sector 9, dedicated to the operation of the Liquid Surface spectrometer would more than double the capacity for users to conduct IXS and LSS experiments and accumulate scientific data in this sector. Both fields and their instruments are currently vastly oversubscribed and would benefit immediately from this substantial increase in capacity.

An implementation of the secondary beamline would include

1) Reconfiguration of the main (Kohzu) monochromator to diamond crystal to permit a transmitted beam as source for the secondary beamline

2) Development and implementation of a side-bounce horizontal monochromator, allowing a wide energy range between 4 keV and 30 keV

3) Implementation of auxiliary beamline optics, including photon shutter, beampipes, ion pumps and windows

4) Implementation of micro-focusing x-ray mirrors

Assuming that the extended straight section and undulators are in place, additional beamline optics and instrumentation will cost approx. total est. price, second stage: **2.0 M$**

total est. price, first + second stage: **8.8 M$**

The completion of the first stage will have immediate benefits for the operation and experimental and scientific throughput of the beamline, independent of the completion of the second stage.

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