Nuclear Resonance Spectroscopy at the APS in 5 years

1. Past and present

Nuclear Resonance Spectroscopy (NRS) has been practiced at the APS from the very beginning in 1997, mainly at Sector 3-ID beamline, and since 2002 at Sector 16. NRS consists of two separate but related methods: Nuclear Forward Scattering (NFS) and Nuclear Resonant Inelastic X-Ray Scattering (NRIXS). The first method is also known as Synchrotron Mössbauer Spectroscopy (SMS) and latter as Nuclear Resonant Vibrational Spectroscopy (NRVS).

NFS or SMS is the time domain equivalent of traditional Mössbauer spectroscopy. NRIXS or NRVS is a new type of phonon spectroscopy and it is related to inelastic x-ray or neutron scattering, as well as to Brillouin and Raman Spectroscopy in terms of its information content, with some unique and distinct advantages in terms of momentum transfer range covering entire Brillouin zone, isotopic and element selectivity, selection rules that do not require dipole moment formation, and sensitivity both in terms amount of material (nanograms to pico-grams, monolayers), and form (transparent or opaque glass, crystal, nano-cluster…).

Both of these techniques require a specific bunch structure, which is easily achievable at the APS with a large circumference of 1108 m. Currently, NRS technique at the APS is limited to five isotopes, namely ^{83}Kr, ^{57}Fe, ^{151}Eu, ^{119}Sn, and ^{161}Dy. We can project that it can be extended to include yet another six isotopes, namely Ta, Tm, Sm, I, Sb and Ni, in the next five years, provided that more beamlines become interested in practicing this method. There is no special beamline configuration for this method, and therefore, any beamline equipped with high-resolution monochromators can use a limited set of nuclear resonances given above.

In order to project the future, one has to look at the successes and shortcomings of the last decade, and appraise the progress relative to the other major research centers. Currently, there are six operating beamlines worldwide (2 ESRF, 2 APS, and 2 Spring-8) and there are plans to build a very competitive beamline at PETRA III. The major scientific accomplishment has been the introduction and further development of a new vibrational spectroscopy to physics, chemistry, geology and biology. This application has been so successful that it dwarfed all other areas, generating over 170 proposals in the last 5 years, resulting in a beamtime request over three times the capacity, reaching over seven times the available beamtime in 2008-3 cycle. The rich information content of the phonon measurements includes the phonon density of states, Debye sound velocity, vibrational entropy, mode-specific Grüneisen constant, direct access to amplitude of vibrations of all the atoms involved in the molecule or solid with the help of modeling, Debye temperature and its temperature dependence, and finally actual temperature of the sample under extreme conditions of pressure. Furthermore, coupled with modern microfocusing optics, the method has found a unique niche in geophysics and mineral physics by engaging in high-pressure applications. APS-developed data analysis software, PHOENIX, has become the standard method of data analysis, further establishing our leadership in this field.

In biological applications, NRVS has now become a method of choice when it comes to protein and enzyme vibrational studies. The unusually selective nature of NRVS has led to a renewal of interest in the evaluation of the dynamics of model compounds of porhyrins, and cubanes through the help of modern DFT calculations.

Finally, in materials science, NFS and NRIXS has found a wide range of applications in terms of determination of valence and spin transitions in magnetism of thin films, oxides, sulfides, phosphates, silicates, carbides, nitrates and borides of iron. Again the data analysis software package CONUSS has evolved to become the recognized standard in data analysis of NFS spectra, uniquely able to handle thickness and field distributions frequently encountered in real situations, and applicable to all isotopes.

So what are the shortcomings? Clearly, the need to utilize all of the isotopes in one beamline where the energy ranges from 6-70 keV is a fundamental limitation. Undulators can be optimized over a limited range, and we had chosen 7-15 keV in the first harmonics, to facilitate 9.4 keV Kr, 14.4 keV Fe, 21.4 keV Eu, 23.3 keV Sn and 25.7 keV Dy, plus the 21.6 keV non-resonant IXS spectrometer for the non-timing mode application at 3-ID. This should change, and the following scenario is very realistic:

Move Sn, and Dy program to Sector 30-ID, and use the existing cryo-cooled mono infrastructure and add a second energy choice, which the IXS program also benefits. Move the MERIX program to Sector 9 for full time MERIX beamline. This is consisten with the high energy IXS spectrometer which is designed to work at 1 meV at 25.7 keV, which is not feasible now because the compromised undulator period. If the undulator period is chosen such that 21-26 keV region is in the first harmonics, the flux can be boosted by a factor of 5, and that will then provide an extremely competitive beamline for physics, mineralogy, and materials science.

There are equally important, but less obvious side to the success of the NRS program, and that is mainly in the instrumentation development. Before nuclear resonance studies begun at synchrotron radiation sources, there were no good methods of diagnostics for the perfection of silicon and other crystals, which are used in high-energy resolution crystal monochromators (HRM) at the level of 10^7 or better. With the availability of a nuclear resonant probe, whose energy width is in the range of nano-eV, we have pushed and broke many world records in the last decade, and APS has become the undisputed world-leader in terms of development of science, methodology and instrumentation aspects of high-resolution optics. Starting from 1991, we have developed 4 generations of HRM, starting with nested, channel-cut monochromators. We have developed and patented the weak-link rotary and translational stage technology, and built first “in-line, no-offset” HRM. After this, in an attempt to further improve the efficiency, we have developed the first cryogenically cooled HRM, and extended this into user programs at Sectors 3 and 30.

2. Future

Full realization of the potential of NRS method is limited by the number of beamlines it is practiced, lack of specialized or custom-made undulators and array APD detectors, and inability to develop methodology because of large demand from user programs.

2.1. Beamlines
2.2 Undulator sources
2.3 Methodology development
2.4 Detector development
2.5 Training and software for data analysis

2.1 Beamline

2.1.1 Expand the current NRS activities to Sector 30 for Eu, Sn and Dy, and develop Sm and Iodine there.
2.1.1 Enlarge Sector 3-ID-B station so that 2 new permanent experimental tables can be added, and cryogenic experiments can be perfomed, which is not possible now due to lack of space.
2.1.2 Target 0.1 meV resolution nuclear resonance spectroscopy for Fe as primary activity of this beamline,
2.1.3 Upgrade the 2 meV resolution IXS instrument from horizontal to vertical geometry with 30 analyzers and new detectors.
2.1.4 Add new specialized environmental chambers like "in-situ" deposition system for catalysis and nano-science applications, and a second-laser heatings system for liquids under high pressure at IXS instrument in 3-ID-C. There is demonstrated demand for both activities.

2.2 Undulator source

We propose to switch from the current planar permanent magnet technology to cryogenically-cooled in-vacuum undulator technology, to reduce the undulator magnetic period from the current 2.7 cm to 1.8 cm, and the current undulator gap from 10.5 mm to 7 mm. This itself will provide a factor of 7 gain in flux, with no extension of the current straight section. When coupled with possible increased stored current, extended straight section, we can foresee a gain of 30-50 in the next five years.

2.3 Methodology development

Currently we are involved in developing the cryogenically cooled weak-link technology to further reduce the energy resolution to 0.1 meV level. This current R&D works will have a significant impact on how we configure the beamline, and its scientific priorities.

We have learned how to work lasers, and with high-pressure equipment using DAC technology. We plan to extend the method to study liquids under pressure and this will require to work with multi-anvil apparatus, and external heating.

We would like to extend our work on determining melting point of alloys and compounds of iron, by incorporating more stable fiber-lasers, and in-situ pressure-measurements via a Raman system. Also, we would like to move to dynamicDAC as well as membrane cells for in-situ pressure adjustments. All of this will require subject-matter experts at the beamline.

2.4 Detectors

The detector of choice for NRS is Avalanche Photodiode Detectors. Currently we use single element detectors. However, we would like to have A desired set of specifications could be as follows:

Time resolution:	1 nsec
Area:	10 x 10 mm^2
pixel size:	0.3 x 0.3 mm^2
Thickness:	0.1-0.2 mm Si
Bump bonded ASIC,	
Integrated electronics (amplifier + threshold + time discriminator)	
Count rate:	10^7 Hz
Fast frame readout	< 10 ns

It turns out that such detectors are also needed for intensity fluctuation spectroscopy, thus we see a common ground with them. Similar detectors are being developed as European/Japanese collaboration, and either we take place in such development projects, or we end buying some version of the commercial detectors a few years later. We prefer that our detector group at the APS spearheads an effort and obtain/participate/develop APD based detectors.

2.4 Training and software

Our experience shows that the best way to increase productivity is to have the best personnel at the beamline during the measurement time. This includes beamline personnel as well as users. We believe that training users periodically as well as each time they visit the beamline will increase the productivity, but this will require one additional staff whose focus is getting users up to speed every week, and provide data analysis support during the experiment.