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INFRARED SYNCHROTRON RADIATION INSTRUMENTATION AND APPLICATIONS

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ABSTRACT

Infrared Synchrotron Radiation (IRSR) is a blossoming field which has three working beamlines, U4IR at the National Synchrotron Light Source, Brookhaven National Laboratory, USA, and two at the Institute of Molecular Sciences in Okasaki, Japan with extensive research projects. There are also several new beamlines in the planning and development stages, both in the United States and abroad.

IRSR offers a unique way to access the far infrared (30 μ to approx 1 mm) which is a notoriously difficult region to work in. In particular, experiments that demand high brightness are well suited to IRSR just as they are in the x-ray region. The central issue in all of the experiments to date has been good signal to noise, which has been the focus of the instrumentation improvements at the U4IR beamline. A commercial Fourier transform instrument was the chosen spectrometer. Then modifications were made in order to expand the usable region of the existing experiments, in both the far and near infrared.

As an example of the performance of this beamline, I will focus on the reflection absorption spectroscopy results for adsorbates on clean surfaces in ultra-high vacuum.

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MASTER

INTRODUCTION

In the three years since the U4IR beamline at the NSLS[1] has become operational, nine scientific programs have been developed, using various bandpasses of the broad wavelength region ($1\ \mu$ to approx $1\ \text{mm}$) provided by the infrared port. These programs and regions are shown in Fig. 1. In addition to these, there are two beamlines operating at UVSOR, Okasaki, Japan[2,3]. Due to the scientific impact of the projects, there has been increasing interest in building new infrared facilities at many synchrotrons. Thus, there are beamlines under construction at LURE, Orsay, France, SRS, Daresbury, England[4] and MAX, Lund, Sweden. There are also two additional beamlines being proposed at the NSLS, one for the near infrared (less than $10\ \mu$) region, and the other similar to U4IR. Finally, there are also 12 ports built into the design of the Advanced Light Source, Berkeley, USA.

IRSR is a unique source of infrared because of its emittance. While conventional IR sources, such as globars and mercury arc lamps, radiate into a 2π solid angle (approx. $1\ \text{sr.}$), the synchrotron emits into a 100×100 milliradian solid angle, ($.01\ \text{sr.}$). The source area is also at least a factor of 10 smaller. As a result, some experiments can gain large factors in detected intensity even though the total flux from the synchrotron is less than the total flux emitted from a typical globar (for wavelengths shorter than $100\ \mu$). This is illustrated in Fig. 2 in which the detected signal for various situations is shown to be at least 1000 times higher than that obtained using a conventional source.

Another unique aspect of the synchrotron is its pulsed structure, which is utilized for the pump-probe work that has just begun on high temperature superconductors and other systems and is described in an earlier paper in this volume[5]. The timing structure has also been utilized to study nanosecond time-scale infrared response of various materials as well[6].

INSTRUMENTATION

There are several instrumentation issues that have evolved in the development of the U4IR beamline. Initially it was shown that a large opening angle was necessary in order to extract infrared wavelengths. Thus, a modification of the VUV ring at Brookhaven was necessary, as can be seen from previous work[7].

Next, the instrumentation for analyzing the spectra from the ring had to be chosen. In contrast to grating spectrometers which are used in the soft x-ray region, Michelson interferometers are the spectrometers of choice for the infrared. The multiplex advantage is an important feature of such instruments, as all wavelengths are analyzed for all of the measuring time and fast Fourier transform methods can be used. In Fig. 3, a schematic of an interferometer is shown. The collimated input is separated at the beam splitter into two parts of equal amplitude. Half of the beam travels to the fixed mirror, and the other half to the moving mirror. The light is then reflected back to the beam splitter, recombined and finally exits the spectrometer to the experiment and detector. The signal at the detector is a function of path difference between the fixed and moving mirrors which results in an interference pattern called an interferogram. This can be Fourier analyzed to determine the output spectrum. In addition, rapid scanning techniques were developed[8] in 1954, which have the advantage of improving the signal to noise ratios, as described below.

Another spectrometer has been tested and further developed to collect the longer wavelength part of the spectrum more efficiently. Called a "wavefront dividing spectrometer"[9], this works using the same principle as described above but the wavefront rather than its amplitude is divided. This avoids the structure that an amplitude splitting beamsplitter could introduce into the spectrum by selectively absorbing or reflecting certain wavelengths. It has two parallel mirrors, one placed above the other, one of which moves. Once again the output is an interferogram and can be Fourier analyzed. This principle has also been incorporated into a new instrument, in which the

interferometer is combined with a grating spectrometer which limits the spectral bandwidth. This is described in detail in another article in these proceedings[10].

One final improvement was focused on choosing appropriate windows to expand the frequency range of the uhv experiment. As can be seen from Fig 2., the frequency range delivered by the IR port goes to 1 mm, but the longest wavelength achievable using alkali-halide uhv window materials is 50 μ (CsI). One candidate for a window with good transmission at longer wavelengths is diamond, the window used to separate the U4IR port from ring vacuum. This transmits 60 percent of the light over the spectral region of the beamline, but is very expensive and therefore not economically feasible due to the large (2 inch) diameter required. Another candidate material is silicon which was tested on the uhv chamber but yielded spectra which were plagued by irreproducibilities probably due to phonons, at the 0.1% level. As will be seen in the application section, this irreproducibility is unacceptable for the surface science experiments. Finally, a common window material for lower vacuum far infrared experiments, graded polyethelene with no plasticizer, was installed as a window/ contamination barrier[11]. These .7 mm thick windows transmit 80% from 10 cm^{-1} to 600 cm^{-1} . We successfully obtained a base pressure of 1×10^{-10} torr when 1×10^{-3} torr was maintained on the other side. As a result we expanded our usable range of frequencies down to 50 cm^{-1} for the surface science experiments. Below 50 cm^{-1} the signal to noise ratio, to be discussed in detail next, is dominated by other features of the experimental apparatus.

As mentioned above, reproducibility is an important characteristic that must be optimized. The interferometer was chosen over grating spectrometers because it appeared to offer the possibility for achieving adequate signal to noise ratios. Rapid-scanning[8] helps to realize these statistics by transforming the detected signal into the audio frequency range and hence above the common noise frequencies. For example, if the mirror of Fig. 3 scans at a velocity of 5mm/sec then the path difference changes by 1

cm/sec which transforms a $100\ \mu$ input into a 100 Hz signal at the detector. The synchrotron has large components of noise in the 1 to 100 Hz range, but is very stable above 100 Hz due to the vertical global feedback system[12]. In fact, if a 1 cm/sec scanning rate is used, the signal to noise ratio above $100\ \text{cm}^{-1}$ is approx .05 percent in 30 secs scanning time. This can be further improved by signal averaging.

We can easily demonstrate the utility of this by changing the mirror velocity, and the effect of doing this is shown in Fig. 4. Here it can be seen that each time the scanning rate is halved, the inherent noise from the source moves to double the frequency in the spectrum. Measurements of the intrinsic beam noise with a frequency analyzer also showed a correlation with these data. The future addition of horizontal feedback to the VUV ring should further improve the situation.

APPLICATION TO SURFACE VIBRATIONAL SPECTROSCOPY

Finally, one application of IRSR will be shown in detail. A cartoon summarizing the experiment is shown in the inset of Fig. 5. The p-polarized light is focused onto the sample at $88\pm 1^\circ$. This results in an $\vec{E}$ field that is predominantly normal to the surface that can couple to dynamic dipoles perpendicular to the surface. Data is obtained by collecting a reflection spectrum from a clean substrate, then dosing with an adsorbate, and collecting another spectrum. The two spectra are then subtracted, taking account of the beam current, and normalized to 100%, resulting in a difference spectrum.

A model system for demonstrating the capability of IRSR for surface vibrational spectroscopy is CO on Cu(100) at sub-monolayer coverages[13]. This was chosen because the morphology of the system is well-known - the CO stands perpendicular to the Cu surface, on atop sites, with the C sticking to the Cu. There are six normal modes of which two have dynamic dipoles normal to the surface, and are therefore IR-active. These modes are a C-O internal stretching mode, and a carbon-metal stretching

motion. The two other distinct modes, both doubly degenerate, contain motions that are predominantly parallel to the surface, a frustrated rotation and a frustrated translation. These should not be dipole active due to the fact that the $\vec{E}$ field is perpendicular to the substrate.

Several features of the data will now be described. First, notice that the peak under study changes the reflectivity by only 0.1% but the "noise" or reproducibility of the spectrum is .01%, or 100 parts per million. Thus the signal to noise even for such a weak feature is 10 to 1 rendering it easily visible. Next, the low frequency cutoff is 50 cm^{-1} , due to the polyethelene windows on the uhv chamber. Below 50 cm^{-1} we are limited by source noise as described above. The high frequency cutoff is due to a commercial gold scatter filter with a cut-on at 600 cm^{-1} [14]. At 335 cm^{-1} a dip can be seen which corresponds to the carbon-metal stretch[15]. The asymmetric feature at 285 cm^{-1} is assigned using isotopic shift measurements to the frustrated rotation which was not expected to be dipole active. Finally, the feature at 116 cm^{-1} could correspond to a phonon in Cu which has been seen in EELS[13]. It becomes active when the Brillouin zone is reduced due to the symmetry of the adsorbate plus substrate system.

CONCLUSION

In conclusion, IRSR has demonstrated its potential of producing spectra in the far infrared region for limited throughput systems which are far superior to any produced with conventional sources. Many promising results have been obtained which are stimulating the construction of many new facilities in the United States and abroad.

DISCLAIMER

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REFERENCES

- [1] G.P. Williams, Review of Scientific Instruments, to be published.
- [2] T. Nanba, Rev. Sci. Instrum. **60**, (1989) 1680.
- [3] T. Nanba, et al., Review of Scientific Instruments, to be published.
- [4] D. Slater, et al. Review of Scientific Instruments, to be published.
- [5] D.L. Ederer, J.E. Rubensson, D.R. Mueller, R. Shuker, W.L. O'Brien, J. Jai, Q.Y. Dong, T.A. Colcott, G.L. Carr, G.P. Williams, C.J. Hirschmugl, S. Etemad, A. Inam, D.B. Tanner, Review of Scientific Instruments, this volume.
- [6] G.L. Carr, M. Quijada, D.B. Tanner, C.J. Hirschmugl, G.P. Williams, S. Etemad, R. DeRosa, T. Venkatesan, B. Dutta, D. Hemmick, X. Xi, SPIE, **1292** (1990) 187.
- [7] G.P. Williams, Int. Journal Millimeter Waves **5**, (1984) 829.
- [8] R. Madden and J. Strong, J. Opt. Soc. Am. **44**, (1954) 352.

- [9] K.D. Moeller, D.P. Siddons, C.J. Hirschmugl, D. Scardino, P. Petrone, D. Carlson, G.P. Williams, *Applied Optics*, **30** (1991) 4297.
- [10] K.D. Moeller, G.P. Williams, C.J. Hirschmugl, *Review of Scientific Instruments*, this volume.
- [11] Nicolet Instruments, Verona Road, Madison, Wisconsin.
- [12] L.H. Yu, R. Biscardi, J. Bittner, E. Bozoki, J. Galayda, S. Krinsky, R. Nawrocky, O. Singh and G. Vignola, *Proceedings of 1989 Particle Accelerator Conference*, March 20-23, Chicago, IL. (1989) 1792-1794.
- [13] P. Uvdal, P. A. Karlsson, C. Nyberg, S. Andersson and N.V. Richardson, *Surf. Sci.* **292**, (1988) 197.
- [14] Infrared Laboratories, Inc., East 17th Street, Tucson, Arizona.
- [15] C. J. Hirschmugl, G. P. Williams, F. M. Hoffmann and Y. J. Chabal, *Physical Review Letters* **65** (1990) 408.

FIGURE CAPTIONS

Fig 1. The nine operating scientific programs at the U4IR beamline at the NSLS.

Fig 2. Illustration of the importance of optical matching applied to several experimental arrangements and source emittances. A comparison of the detected signals for a globar and NSLS sources is shown on the right.

Fig 3. Optical schematic of the Michelson interferometer.

Fig 4. Three spectra corresponding to different velocities of the scanning mirror are shown as a function of frequency. The data were obtained by collecting two similar spectra (collection time of 30 sec. each), and dividing and normalizing to 100 percent. A noise free spectrum would not deviate from a straight line at 100 percent.(a.) 5

mm/sec, (b.) 2.5 mm/sec and (c.) 1.25 mm/sec.

Fig 5. The data for CO on Cu(100) is shown here with a cartoon of the experiment in the inset. The feature at 335 cm^{-1} is the carbon-metal stretch, while the features at 285 cm^{-1} and 116 cm^{-1} are the frustrated translation and a Cu phonon, respectively.

Science In The Infra-Red

The 9 Major Programs At The NSLS U4IR Beamline

$10^{-3}-10^{-4} \text{ cm}^2 \text{ Sr}$
Synchrotron

$1 \text{ cm}^2 \text{ Sr}$
10mm x 1mm Globar

Diamond Anvil Cell
Cryostat
Small Crystal
 $10^{-4} \text{ cm}^2 \text{ Sr}$

Clean Surface
 $10^{-4} \text{ cm}^2 \text{ Sr}$

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