Prepared for SRI89 - Lawrence Berkeley Laboratory, Aug. 7-11 1989.

THE INITIAL SCIENTIFIC PROGRAM AT THE NSLS INFRARED BEAMLINE

BNL--43345

DE90 002299

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Unique extraction optics (90 x 90 mrad) at the NSLS U4IR line offer high brightness beams at up to mm wavelengths with a ~1ns pulse structure. Radiation from this port has now been carefully characterized and agrees well with calculations, making it 100-1000 times brighter than conventional sources in the middle and far infrared regions. Using rapid scan Michelson interferometers with liquid He cooled bolometer detectors we have been able for the first time to measure molecule substrate vibrations in surface science. We have also made the first measurements of the transmission of a film of the high T_c material YBaCuO in the BCS gap region. These initial experiments have demonstrated the advantages of the superior signal to noise available from this infrared beamline.

[†]Research at Brookhaven National Laboratory is performed under the auspices of the U.S. Department of Energy under contract DE-ACO2-76CH00016. In addition some of this work was sponsored by the NSLS/HFBR Faculty Support Program.

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Introduction

As a general introduction, we show in Fig. 1 the spectral output from the NSLS VUV ring divided into the three main regions. It can be seen immediately that the infrared (IR) region covers four decades of photon energy and thus poses many challenges instrumentally. Synchrotron radiation (SR) from high current dedicated storage rings is, then, continuously tunable, is between 100 and 1000 times brighter than that from any other source over the entire IR spectrum and is sharply pulsed^{1,2}. In the far IR region beyond 100 μ SR also has more power than any other source. IR synchrotron radiation measurements have been reported at Tantalus^{3,4}, LURE^{5,6}, BESSY⁷ and Daresbury^{8,9} but there are currently only 2 operational IR beamlines in the world, one operated by T. Namba at UVSOR, Okasaki, Japan^{10,11} and one at the NSLS, Brookhaven National Laboratory¹²⁻¹⁴. Both these beamlines operate full scientific programs in solid-state physics utilizing the high brightness for experiments using pressure cells, cryostats and surface science chambers.

Details of the NSLS U4IR beamline have been presented elsewhere and are only summarized here. 90 x 90 mradian (f10) of beam are extracted by a retractable water cooled SiC plane mirror¹⁵ whose maximum power loading is 500 *Watts/cm*² but whose total power is ~150 *Watts*. A 1:1 image of the source is produced at a 9 mm clear aperture 0.25 mm thick diamond window bonded to molybdenum which is clamped into a conflat flange using a lead wire seal. Machine vacuum is maintained only up to this window. A rotatable and retractable plane mirror allows beam to be taken in turn by one of three end stations. For station A, the beam is collimated before entering a Nicolet 20F rapid scan vacuum Michelson interferometer with a Si beamsplitter. Station B provides direct beam and station C is equipped with a step and repeat scanning lamellar grating interferometer.

Prior to the scientific program, we conducted a series of measurements of beamline performance and characteristics. Due to the lack of absolute standards in the infra-red we chose to compare the NSLS output with that of a standard black body (globar) source. The power and brightness of such a source can be calculated accurately, the only uncertainty being the emissivity as a function of wavelength. For all the calculations, we took this quantity to be unity. In the measurements of both sources, all the same optics, including beamsplitters, filters etc. were used and both sources were well matched into the optical system.

In Fig. 2, we show curves for the total infra-red power into a 0.1% bandwidth of the NSLS (1 ampere stored beam) and a 2000K, 10mm $\times$ 1mm globar source. Excellent agreement was obtained in our experiments between theory and experiment¹⁶. The curves show that the NSLS is superior at wavelengths $> 100\mu\text{m}$.

If we now compare the brightness of the two sources, we obtain the curves shown in Fig. 3. These data were confirmed by measuring the flux through pinholes of various sizes in a sample cell whose input angle was also defined - simulating a sample in a pressure cell or cryostat. Thus at all wavelengths a brightness advantage of 100-1000 times is available.

A key issue for new scientific opportunities in the IR is, however, signal to noise (S/N) and thus in addition to brightness and its concomitant advantage we have also considered this question and in particular we have focused on source and detector noise. The source noise at the NSLS, after several months of power supply work and installation of a global orbital feedback system, is currently slightly less than that of our temperature stabilized globar source in vacuum for frequencies $< 100\text{Hz}$. Frequencies lower than this are eliminated in our rapid scan instrument or by signal averaging. Detector noise increases with area and solid angle and thus it is reasonable to imagine

detector noise plotted on a brightness curve such as Fig. 2. Doing this illustrates two things. (1) Very high S/N ratios can be obtained compared with globar sources across the entire IR spectrum for brightness limited experiments for the same measuring time. Note also that to obtain the same signal to noise with a conventional source would require scanning for a period of time 10000 to 1000000 times longer, which is not always possible. (2) High quality transmission spectra can be taken on highly absorbing (0.1% transmitting) samples. Examples of measurements exploiting both of these advantages will be discussed.

In the far infra-red, beyond 100 μ the NSLS delivers more power than a globar and advantages are available for all types of measurements and not exclusively for those in which the sample etendue is small.

Surface Molecular Vibrational Spectroscopy

This experiment takes advantage of the superior signal to noise which SR offers to study extremely small absorption coefficients. The samples are highly reflecting but must be illuminated at very grazing angles of incidence, thus requiring a high brightness source. We are interested in adsorbed molecules on metal and semiconductor surfaces and in particular in the vibrational modes with the substrate which lie at energies corresponding to the mid IR. Adsorbate-substrate mode energies are critical to understanding bonding geometries and mechanisms and in fact several have been determined by high resolution electron energy loss spectroscopy (EELS). The only adsorbate-substrate mode to have been measured by IR spectroscopy, however, has been that of hydrogen on tungsten¹⁷. This is a light molecule with a mode in the near IR at $\sim 10\mu$. IR spectroscopy has three advantages over EELS, one being the possibility of taking

measurements at higher pressures closer to those found in real corrosive or catalytic environments, one being the ability to measure at lower energies and the major one being the much higher resolution. In an EELS experiment the incoming beam has a energy width of several *meV* whereas our high resolution spectrometer has a resolution of 0.1 cm^{-1} , which is $12\mu\text{eV}$ at 12 meV ($100\text{cm}^{-1}, 100\mu\text{m}$).

Critical to measuring molecule substrate vibrational modes is signal/noise. Typical absorption coefficients for the submonolayer coverages typical of initial absorption states are 0.1% which make them 100 times weaker than, for example, CO molecular stretch modes. For reactive surfaces it is desirable then to measure spectra from both the clean surface and the adsorbate covered surface in a time period of the order of 10 mins and with a reproducibility of 0.01% so that the ratios reveal the adsorbate modes. This has now been accomplished at U4IR for several systems. As an example, we show the results for a roughly half-monolayer coverage of CO on Cu(111) in Fig. 4. As a check of the peaks being associated with adsorbate modes we measured the isotopic shifts by repeating the experiment on $\text{C}^{13}\text{O}^{18}$. The top curve in the figure shows that the reproducibility is $\sim 0.0006\%$ plus a small drift. The two lower curves show two modes in the frequency range shown. In the lower curve, for $\text{C}^{12}\text{O}^{16}$, the dip at 341 cm^{-1} (42meV , $30\mu\text{m}$) is interpreted as the carbon-metal stretch. The structure at $\sim 290\text{ cm}^{-1}$ (36meV , $34\mu\text{m}$) appears at this time to be a Fano resonance involving another mode of the molecule such as a frustrated rotation or translation which is degenerate with a substrate phonon. These first spectra demonstrate the great potential of this technique for studying surface vibrations. They are superior to EELS spectra which in this region suffer severe background effects due to the elastic tail and diffuse scattering.

High T_c Superconductors

An example of the application of the higher signal/noise for measurements of strongly attenuating samples is found in the high T_c absorption experiments. These are the first such transmission experiments on these materials and transmission coefficients as low as 0.1% were measured down to frequencies of 20 cm^{-1} (2.5meV, 500 μm) with a S/N of 1%. Thus it was possible not only to measure these materials in the region of the BCS energy gap but to extrapolate conductivities successfully to the DC limit. This should enable, for example, the conductivity of metallic hydrogen or xenon¹⁸ to be measured in low temperature diamond anvil pressure cells. For the present experiment a 1 μm thick film of YBaCuO on MgO was measured from 10K to 300K. Superconducting behavior is clearly apparent with decreasing temperature as shown in the inset to Fig. 5. Here we plot ratios of superconducting to normal behavior and see the development of the bell shaped curve¹⁹ with decreasing temperature. Without the onset of superconductivity these "curves" would be unity. Instead the gap forces the transmission to zero at zero frequency as supercurrent screening increases the reflectivity to 100%. At higher frequencies the transmission falls as transitions occur across the gap. Although this film was highly oriented with the c-axis perpendicular to the substrate, we nevertheless observed some c-axis phonons from misoriented parts of the film, so the data will average out gap anisotropies if they exist. We also measured the conventional superconductor Nb₃Ge and show the similarity between the two in Fig. 5. The solid curves are theoretical fits using BCS theory with gaps of 3.5KT and with the phonons removed. The curve for the high T_c material, $T_c=78\text{K}$, is shifted roughly three times up in energy from that for the Nb₃Ge film for which $T_c=21\text{K}$.

Spatial Coherence, Pulsed Structure

For wavelengths longer than $100\mu\text{m}$, the wavelength is longer than the vertical source height and a fully spatially coherent wavefront is obtained. This has been verified using a specially constructed interferometer which divided the wave-front in two, varying the path length of one beam and then recombining the two. The resulting interferogram yielded good water vapor rotational spectra, and is the basis for a new instrument in which phase and amplitude changes will be measured in solid-state and gaseous samples placed in the interferometer in the so-called asymmetric mode. These measurements permit both real and imaginary parts of the dielectric function to be measured simultaneously.

Preliminary experiments to utilize the unique pulsed structure of the IR SR beam have also begun. The IR radiation is delivered in pulses which are less than 1 nanosecond long and which repeat either every 20 nanoseconds or every 180 nanoseconds depending on user selectable machine running conditions. These should provide unique capabilities in two areas. First, for studies of fast electronic response and relaxation times particularly in semiconductors, and second for related studies having to do with the use of these and/or other materials such as the high T_c superconductors as fast infrared detectors.

Acknowledgements

I am extremely grateful to my Participating Research Team colleagues and to the staff of the NSLS for making this beamline and research program possible. I would particularly like to thank Carol Hirschmugl, Yves Chabal, Fritz Hoffmann, Dieter Moeller,

Larry Carr, Sid Perkowitz, Eric Kneedler, Mark Shleifer and Dennis Carlson for the untiring efforts which were required in the implementation of this project.

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Figure Captions

Figure 1. Output spectrum of the NSLS VUV ring operating at 0.75 GeV and showing the three main spectral regions.

Figure 2. Comparison between the power output of the NSLS VUV ring into 90mradians at 1 Ampere stored beam, and a 2000K black body of dimensions 10mm $\times$ 1mm and with an emissivity of unity.

Figure 3. Comparison between the brightness of the NSLS VUV ring and a 10mm $\times$ 1mm 2000K global source.

Figure 4. Ratios of the reflected IR beam from a clean and $\sqrt{3}\times\sqrt{3}$ CO overlayer (~ 0.5 monolayers) covered Cu(111) crystal showing absorption lines associated with the Carbon-Metal stretch vibrations shown in the inset. Note how these lines shift with the

isotope. Note also that the change on reflectance is only of the order of 0.1%. The change in slope is associated with induced changes in the dielectric function. The lower energy structure has a Fano line shape due to interactions with substrate phonons.

Figure 5. Ratios of the transmission at 8K, 50K and 70K over the transmission above T_c at 90K for a thin film of YBaCuO on MgO, showing the evolution of the characteristic bell shaped curve (see Ref.19).

Figure 6. Transmission ratios of films of Nb₃Ge and YBaCuO above and below the superconducting transition temperatures. The characteristic bell shaped curve, whose evolution is shown in the inset, is caused at low frequencies by reflectivity increases due to supercurrent screening and at high frequencies by absorption to states above the gap. The solid lines represent BCS theory, the gap frequencies are marked.

Carbon Metal Stretch for $\sqrt{3} \times \sqrt{3}$ CO on Cu(111)

I-R DIRECT GAP OBSERVATION Y-Ba-Cu-O