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THE APPLICATION OF INFRARED SYNCHROTRON RADIATION TO THE STUDY OF INTERFACIAL VIBRATIONAL MODES

CAROL J. HIRSCHMUGL AND GWYN P. WILLIAMS
*National Synchrotron Light Source,
Brookhaven National Laboratory,
Upton, New York, 11973, USA*

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ABSTRACT. Synchrotron radiation provides an extremely bright broad-band source in the infrared which is ideally suited to the study of surface and interface vibrational modes in the range $50\text{-}3000\text{ cm}^{-1}$. Thus it covers the important range of molecule-substrate interactions, as well as overlapping with the more easily accessible near-ir region where molecular internal modes are found. Compared to standard broadband infrared sources such as globars, not only is it 1000 times brighter, but its emittance matches the phase-space of the electrochemical cell leading to full utilization of this brightness advantage. In addition, the source is more stable even than water-cooled globars in vacuum for both short-term and long-term fluctuations. Thus one can work at high resolution and use isotopic shifts to identify modes as well as study very weak modes.

We will summarize the properties of synchrotron radiation in the infrared, in particular pointing out the distinct differences between this and the x-ray region. We will use experimental data in discussing important issues of signal to noise and will address the unique problems and advantages of the synchrotron source. Thus we will emphasize the important considerations necessary for developing new facilities. This analysis will then lead to a discussion of phase-space matching to electrochemical cells, and to other surfaces in vacuum.

Finally we will show several examples of the application of infrared synchrotron radiation to surface vibrational spectroscopy. The examples will all be for metal crystal surfaces in ultrahigh vacuum and will include CO/Cu(100) and (111) and CO/K/Cu(100). The experiments will show how the stability of the synchrotron source allows subtle changes in the background to be observed in addition to the discrete vibrational modes. These changes are due to electronic states induced by the adsorbate. In some cases we have seen interferences between these and the discrete vibrational modes, leading to a breakdown of the dipole selection rules, and the observation of additional modes. These important experiments serve as sensitivity limit indicators and thus as a guide to future applications in the electrochemistry field.

1. Introduction

We have used infrared synchrotron radiation to study vibrational modes of adsorbates on metal surfaces in ultrahigh vacuum. The experiments can also be extended to interfaces in electrochemical cells as reported elsewhere in this conference[1]. Signal to noise is critical in the experiments that we report here, since some of the vibrational modes give a reflectivity change

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of less than 0.1%.

In this paper we report in some detail the critical components of the synchrotron radiation extraction and delivery system, pointing out differences between a beamline of this type and a more conventional x-ray one. We discuss in detail how instabilities in the electron beam position in the ring translate into noise in the data, and we show how these have been minimized at the NSLS facility.

Finally we present data for CO/Cu(111), and for O/K/Cu(100) as examples of the capability of the system as a probe of interfacial vibrational modes. Such studies yield data not only about the energetics of such modes, but about surface species and bonding geometries as well as the dynamics.

2. Infrared Synchrotron Radiation

2.1 BRIGHTNESS AND FLUX

Calculations of infrared synchrotron radiation for a dipole source can be relatively easily carried out on a PC using the algorithms of Kostroun[2] applied to the equations given in Hulbert and Weber[3]. The long wavelength approximations for the emitted flux presented in Duncan and Williams[4] are also useful as a guide, and the treatment of the source term is valuable for brightness calculations. One finds three important facts from such a calculation. 1. Synchrotron radiation is several orders of magnitude brighter than a conventional global source. 2. For wavelengths longer than 100 microns, (frequencies less than 100 cm^{-1}), synchrotron radiation also gives more photons per second, even into its limited angle-area product (emittance) of $\sim 10^{-2}\text{ mm}^2\text{ steradians}$ than a 10 mm^2 2000K global does into its $\sim 100\text{ mm}^2\text{ steradian}$ emittance. 3. Synchrotron radiation has very large natural opening angles in the infrared, which are at least 100 times larger than those found for x-rays from the same storage rings.

The situation is summarized in Fig. 1, in which we have also included the free electron lasers CLIO at LURE, Orsay, France and Santa Barbara, USA for comparison. In Fig. 1 we have deliberately restricted the 2000K, 10 mm^2 global to emission angles of 0.1×0.1 radians. This was chosen to closely match the acceptance of the systems that we will be studying.

As mentioned in the introduction, however, it is signal to noise which is more critical than flux or brightness. Due to fundamental detector noise limits the S/N ratio is improved if the delivered flux can be increased without introducing additional noise of its own. It is this last issue that we now concentrate on.

2.2 SYNCHROTRON RADIATION "NOISE".

Source fluctuations can have several origins, and for a thermal source the most notable is from temperature fluctuations. For a synchrotron source, the output is strictly proportional to the stored beam current which decays in a slow exponential fashion, and cannot fluctuate up and down. There are fluctuations, however, in signal detected from synchrotron radiation experiments. These arise from motions of the electron beam in the storage ring and consequent

changes in the collection efficiency. These beam motions are responsible for much of the noise observed in synchrotron radiation experiments of all kinds.

Fig. 1. Average flux as a function of wavelength for various infrared sources including a conventional globar, the National Synchrotron Light Source, and various IR free electron lasers at University of California at Santa Barbara, Los Alamos, Exxon Research, Annandale, NJ, USA and at LURE, Orsay, France (CLIO).

In the case of the NSLS, these movements of the beam turned out to be critical to our experiments, since we were trying to measure reflectivity changes of <0.1% in some cases. We also found that they varied with the time of day, being less pronounced at night and at weekends thus giving some confidence that they might be able to be dealt with. If signals from pick up electrodes (pue's) around the ring are recorded and frequency analyzed, then it is found that most of the beam motions are at frequencies below 100Hz, with a few distinct higher frequency ones, such as at 360 Hz. The abundance of low frequency peaks is a consequence of the fact that the aluminum vacuum chamber screens out and reduces the effects of unintentionally applied magnetic fields of higher frequencies. Nevertheless some higher frequency peaks, which were easily seen in our early data taken with the rapid-scan Michelson interferometer (see later), were found to be coming from dipole and quadrupole power supplies, and these were replaced.

When the pue's are recorded every 20 seconds or so, then we conclude that the beam movements are typically of the order of ± 5 microns in the vertical and ± 25 microns in the horizontal. In addition to this there is a horizontal drift of up to 0.5mm as the beam decays from 1000 mA to 200 mA. The beam size as seen by the infrared experiment is typically 1mm vertically $\times$ 3mm horizontally. These source motions give a reproducibility in the data or "noise" of around 1% as determined from the difference between 2 successive spectra, each averaged for 270 seconds. Due to other drifts, averaging for longer periods of time does not improve the situation.

To take care of the lower frequency fluctuations, a feedback system was built and installed on the ring[5]. Actually two independent systems take care of the vertical and horizontal. The effects of these feedback systems are shown in Fig. 2 in which we have plotted the beam position as a function of time in both the vertical and horizontal for an 8 hour time period. Several times during this period the feedback systems were turned on and off to demonstrate what would happen to the beam in the absence of any control. With the respective feedback on, the beam position is held close to position "zero". The horizontal and vertical systems are completely independent of each other and this can be seen in Fig. 2 when the horizontal feedback was turned off at $\sim 11:40$, and there was no effect on the vertical position. The vertical feedback system confines the vertical beam motion to ± 3 microns over several hours, while the horizontal motion is limited to ± 10 microns, also over several hours. All of the horizontal drift with beam current is removed, as are any sudden jumps in vertical position. For example the vertical jump between 11:30 and 12:00 was due to a 1° temperature change in the ring cooling water. Repeatability is also good from fill to fill.

Fig. 2. Effects of feedback on electron beam position in the NSLS 750 MeV electron storage ring. The feedback system was cycled on and off throughout the day. The beam position is held near zero with feedback on, but drifts considerably without feedback control.

Our surface science experiment is more sensitive to the vertical motions due to our particular experimental geometry. With the vertical feedback on, we reliably achieve a repeatability of 0.1%. With both feedback systems operating, we achieve a repeatability of much less than 0.1% even down to 100 cm^{-1} and in 270 seconds of scanning. However notice that the feedback systems play more of a role in controlling beam drift and jumps than rms beam movement. Thus they ensure that no sudden changes in signal occur, and they optimize the utilization of the beam.

2.3 THE MICHELSON RAPID-SCAN INTERFEROMETER

In order to fully understand how we have been able to achieve the signal to noise values which allow us a confidence in our spectra of $<0.1\%$ in spectra taken over a 3 minute scan period, we now describe the spectrometer in more detail. These issues have also been described in more detail by Hirschmugl[6].

Fig. 3. Schematic of a Michelson Interferometer with a rapidly scanning mirror. The effect is a modulation of the incoming beam at a frequency proportional to wavelength.

Our beamline uses an interferometer instead of a spectrometer, a schematic of which is shown in Fig. 3. It is of the conventional amplitude dividing Michelson type - in our case a modified commercial Nicolet model 20F. This instrument is of the rapid-scan type[7], in which the moving mirror moves at a speed of typically 5 mm/sec. Thus the path difference is changed by 1 cm/sec and the signals are modulated at the detector in the audio frequency range without the need for a chopper which would halve the signal available at the detector. Wavelengths of 100 microns are modulated at 100 Hz, of 10 microns at 1000 Hz and so on. Fourier analysis of the interferogram generated while the mirror scans the required distance can then be understood as a transform from time space to 1/time or frequency space. In practice we co-add up to 1000 such interferograms.

Thus it is easy to see that at this scanning velocity, any beam motion occurring at frequencies less than 100 Hz will appear in the spectrum at wavelengths less than 100 microns. The data is gathered on a time scale short compared with the beam noise and is thus largely eradicated automatically.

2.4 THE BEAM EXTRACTION SYSTEM

Fig. 4. Schematic of the infrared beam extraction system at the NSLS. This design allows light to be collected into an angle of almost 100×100 milliradians.

In order to deal with the very large opening angles for infrared synchrotron radiation discussed earlier, we modified the NSLS VUV storage ring as shown in Fig. 4. The extraction mirror, in this case SiC mounted in a water-cooled copper block, is placed in a special chamber immediately downstream of a dipole, and thus close to the electron beam itself. Special radio-frequency damping resistors beneath the mirror "spoil" the resonance of the cavity, so as to minimize the effect on the beam.

The arrangement shown allows $90 \text{ mrad} \times 90 \text{ mrad}$ to be collected from the source. A series of mirrors [8] delivers this to the interferometer as a 4 cm dia. collimated beam.

3. Surface Vibrational Spectroscopy

3.1 GENERAL

Fig. 5. Geometry of the surface vibrational spectroscopy experiment for metal surfaces in vacuum. Electric fields parallel to the surface undergo a phase change, giving a net field of zero immediately above the surface.

The general principle of the surface vibrational spectroscopy experiment is shown in Fig. 5. Light reflected at grazing angles from metal surfaces excites vibrational modes perpendicular to the surface - the so-called surface dipole selection rule [9, 10]. If we look at a specific system, namely CO adsorbed in atop positions on low index Cu surfaces, then Fig. 6 shows that there are 4 possible vibrational modes. Since only the carbon-metal and the internal C-O stretch modes are dipole allowed, then in a reflectivity experiment such as that shown schematically in Fig. 7, we would expect a transfer of energy from the incoming beam to these vibrational modes with a corresponding loss at certain frequencies in the reflected beam. In fact we will see that for this system there is a breakdown of the dipole selection rule at low frequencies and the spectrum obtained yields richer information.

Fig. 6. The four possible vibrational modes for a CO molecule adsorbed in an atop position on Cu. v_1 and v_2 are the only dipole active modes.

Fig. 7. Schematic of the reflectivity experiment, in which the discrete vibrational modes remove intensity from the reflected beam as shown.

The adsorbate-substrate modes are of particular interest as they can in principle yield information not only about the adsorbing species but also about the adsorption site symmetry, and more importantly about energy transfer mechanisms or dynamics. These adsorbate-substrate modes are all at low energies, or long wavelengths in the far infrared beyond 10 microns, and particularly benefit from the use of synchrotron radiation as can be seen from Fig. 1. The throughput of the sample matches the synchrotron emittance well. For electrochemical systems whose electrolytes are highly absorbing the synchrotron offers another advantage. In this case the additional light available from the synchrotron source boosts the detected signal levels well above detector noise thresholds. We should also point out that unfortunately there are many water vapor lines in this spectral region, necessitating the use of vacuum for the whole beamline and adding to the complexity of studying electrochemical systems since the windows have to provide an interface to vacuum.

One can in general determine 4 things from peaks observed in a surface vibrational spectroscopy experiment. From the **frequencies** one can learn about dipole-dipole interactions, self image shifts, chemical shifts, identification (atomic, molecular intermediate etc.) and molecular symmetry. The **peak widths** contain information about the dynamics, phonon or electron-hole coupling, vibrational phase relaxation and inhomogeneous broadening. The **shapes** yield information about possible adiabatic and other energy coupling mechanisms and the **intensity** gives the dynamic dipole moment. In many cases it is of interest to investigate the behavior of peaks as conditions change at the surface. Isotopic substitutions are helpful in identifying some of the modes and interactions.

3.2 RESULTS FOR CO, O+K ON Cu.

In Fig. 8 we show actual data for CO/Cu(111) in which the differences from the schematic of Fig. 7 are immediately apparent. We have plotted the ratio of the reflectivity of a CO covered surface to a clean surface for 2 coverages. If the adsorbate had no effect, then we would have a straight line at 100%. Two things are immediately clear - there is a broadband background change and a large peak at around 2100 cm^{-1} . Note that this spectrum was measured with the same Si beamsplitter in the Nicolet 20F. Two detectors were used - a Cu doped Ge detector above and a B doped Si bolometer below 600 cm^{-1} . The optical arrangement is actually optimized for the region below 500 cm^{-1} and in fact one can see that the noise in this region is considerably lower than elsewhere. In fact the variations in the background in the region from $500\text{--}1000\text{ cm}^{-1}$ are probably due to noise. On the figure we point out the usual limit of "conventional" surface vibrational spectroscopy at around 800 cm^{-1} . The absolute limit of non-synchrotron spectroscopy is shown at around 350 cm^{-1} , the lowest frequency for excitation of carriers in photo-conductive detectors of higher sensitivity but not necessarily better signal to noise.

If we zoom in on the region below 400 cm^{-1} we see the spectrum shown in Fig. 9. Here we see two features on the sloping background. The features, however, are extremely weak compared with the $>5\%$ of the 2100 cm^{-1} feature of the carbon-oxygen mode and are only visible due to the extremely low noise level of 0.01% . In Fig. 9 each spectrum was averaged for ~ 10 minutes for the background and the same time for the CO covered sample. We identify the peaks as the carbon-metal stretch at 346 cm^{-1} and the hindered (dipole-forbidden) rotation at 284 cm^{-1} . The latter appears as more of a peak than a dip. We attribute its

appearance to the background change and to an interference with electrons excited in the bulk[11]. The assignments are based on the isotopic shifts shown in the additional 2 spectra. Notice how the frequency of the hindered rotation mode is independent of oxygen mass - as expected for a bending mode if the molecule is adsorbed linearly atop with the carbon adjacent to the metal.

Fig. 8. Infrared reflectivity spectra from a Cu(111) surface for 2 coverages of CO. The discrete vibrational modes are seen superimposed on a background which changes with coverage.

We make one remark based on the above and on other work that we and others have carried out on surface vibrational spectroscopy. Most of the internal molecular modes for molecules lie well above 1000 cm^{-1} , while most of the metal-molecule modes lie below 400 cm^{-1} . Thus there are relatively few modes in the range $400\text{--}1000 \text{ cm}^{-1}$. Thus studies which extended conventional spectroscopy to lower frequencies were frequently abandoned with no new peaks seen. With the synchrotron, however, we see a whole new region full of adsorbate-substrate vibrations.

The spectra in Fig. 9 show the present limits of the technique in terms of signal to noise, and the ability to observe weak transitions. Not all of the vibrational modes are this weak, and in Fig. 10 (left) we show data taken as a function of time during the exposure to oxygen of a potassium multilayer on Cu(100)[12]. The potassium oxide vibration at 350 cm^{-1} has a magnitude of 9%. Annealing of this potassium superoxide layer yields the spectrum shown on the right in Fig. 10 in which we see the formation of cuprous oxide, Cu_2O .

Fig. 9. Far infrared reflection spectra for 3 isotopes of CO/Cu(111). The peak at the left is the hindered rotational mode, while the dip is the carbon metal stretch mode. This assignment is based on the observed shifts as discussed in the text.

Fig. 10. Far infrared reflection spectra from a Cu(100) surface covered with a K multilayer. On the left is a series of spectra taken as a function of exposure to oxygen. On the right is the effect of annealing to various temperatures and the formation of Cu₂O.

4. Conclusions.

We have attempted to show the capabilities of the new technique of low frequency surface vibrational spectroscopy using synchrotron radiation. In doing so we have discussed in detail the measures that are essential to the success of the experiments. To summarize, these are:

- A careful calculation of the source emittance and the provision of large enough extraction angles.
- Careful attention to the stability of the electron beam in the storage ring.
- Rapid scan interferometry with beam splitters covering as wide a range as possible.
- A vacuum light path for the complete optical system.
- Resolution of typically 1 cm^{-1} .

The U4IR beamline at the NSLS has demonstrated the capability of observing 10% of a monolayer of CO/Cu via the carbon-metal mode. We are undertaking an extensive program to study the low frequency modes of CO on Cu and Ni on the low index faces. These experiments have motivated cluster[13] and surface scattering theories[14] whose goal is to model the dynamics of these systems.

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