1 of 1

**LOW FREQUENCY DYNAMICS OF CO/Cu -
BREAKDOWN OF BORN-OPPENHEIMER APPROXIMATION.**

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ABSTRACT

Synchrotron infrared studies of adsorbates on surfaces offer the possibility of probing low frequency vibrational modes and dynamics at high resolution (1 cm^{-1} , $125\text{ }\mu\text{eV}$). Extensive experiments have been performed for ordered submonolayers of CO on low index Cu surfaces [$(\sqrt{3}\times\sqrt{3})R30^\circ$ CO/Cu(111), $c(2\times 2)$ CO/Cu(100) and (1×2) CO/Cu(110)], in the $100\text{--}2500\text{ cm}^{-1}$ ($\sim 12.5\text{--}312.5\text{ meV}$) range. These are the first IR experiments to directly probe the adsorbate-substrate vibrations for this system. In addition, however, several surprising features are observed including the dipole-forbidden hindered rotation and an unexpected broadband absorption. Two theories have been motivated by this work, and will be compared to our experimental results. The first theory is a cluster calculation by Head-Gordon and Tully, which takes into account the breakdown of the Born-Oppenheimer approximation and predicts lifetimes and frequencies of the vibrational modes for CO/Cu(100). Another Drude-based theory, proposed by Persson, considers the coupling of the conduction electron current to the vibrations of the adsorbates, accounting for the observation of both the broadband absorption and dipole-forbidden peak.

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INTRODUCTION

Vibrational dynamics of adsorbate-substrate modes of adsorbed atoms and molecules can yield direct information on the nature of the bonding with the surface and on the energy exchange between the adsorbate and the substrate. Such modes are found at frequencies below those normally studied by infrared spectroscopy but are accessible when a synchrotron is used. CO on Cu has proved to be an ideal system to study because it is a well understood, extensively studied system, and in particular there has been a lot of IR work published on the higher frequency intra-molecular C-O stretch¹, and EELS work including the low and high frequency modes². Atop sites are occupied first for all of the low index planes studied here, resulting in similar local geometries for the adsorbates at low coverages. Different degrees of degeneracy exist for the 6 normal modes of the 2 atom adsorbate depending on the surface symmetries. Three of these modes, namely the internal C-O stretch, the C-Cu stretch and the hindered rotation have been observed and reported previously for CO/Cu(100) and (111)^{3,4}. In the present work we report measurements taken at high resolution on electropolished samples. Here we see the same features, but they are sharper and of larger amplitude. Also, presented here for the first time is the data for CO/Cu(110), a lower symmetry surface, which breaks the previously doubly degenerate hindered rotation into two unique modes.

In previous papers^{3,4} we have demonstrated how infrared synchrotron radiation has been used to extend surface vibrational spectroscopy of metal surfaces to low frequencies. The 1000 fold increase in brightness⁵⁻⁷ over conventional black-body sources compensates for the poor signal to noise in the far-ir region particularly below 400 cm^{-1} . Thus, measurements can be made down to frequencies as low as 100 cm^{-1} , with reproducibilities in the 0.02% region and measuring times as low as 80 secs. even though the sample throughput is as low as 10^{-4} cm^2 steradians.

EXPERIMENTAL PROCEDURES

The experiments were performed at the National Synchrotron Light Source using beamline U4-IR⁵. The white beam was focused through a wedged CsI window, then collimated into a Nicolet 20F Michelson interferometer. This vacuum instrument is equipped with a silicon beamsplitter which allows us to collect data over the frequency range of 30 cm^{-1} to 2500 cm^{-1} without changing the optical setup. The lower frequency for the present experiments is limited to 180 cm^{-1} by the CsI windows on the

beamline and the UHV chamber. The beam emerging from the interferometer was refocused (f10) into a UHV chamber and reflected at grazing incidence ($\sim 87^\circ$) off a single crystal of dimensions 25 mm x 6mm x 3 mm. Finally, it was focused onto a boron doped silicon bolometer at 4.2K for low frequency measurements (180 - 500 cm^{-1}) or a copper doped germanium photoconductive detector at 4.2K for high frequency measurements (350 - 2500 cm^{-1}). This detector signal is strictly proportional to the current in the storage ring assuming a stable electron orbit, which has recently been improved by the installation of a global feedback system⁸.

The Cu(111) and (110) samples were first mechanically polished, ending with cerium oxide, and then electropolished in a 70% Phosphoric Acid, 30% distilled water solution with a constant current density of .07 A/ cm^2 applied for ~ 1 minute. Subsequent electron channeling patterns, acquired from a secondary electron microscope (JSM 6400) operated at 25KeV and 6° grazing incidence, revealed high quality Kikuchi bands indicating good crystal quality in the surface region. These samples also gave very sharp LEED patterns after the first sputter and anneal cycle. The Cu(100) sample was mechanically polished and then cycled through hundreds of sputter and anneal cycles. Subsequent SEM Kikuchi bands were visible but not as well defined as on the electropolished samples. Sputtering was done at 1×10^{-4} torr of Ne^+ , at 500 eV and 300K for 20 minutes, with the sample rotated to grazing incidence (both directions). The crystal was briefly annealed upto 850K. Auger spectra showed no sulfur, carbon or oxygen peaks, with an upper limit on the detection of $<2\%$ of the copper (105 eV) peak. The measurements were all made with a chamber base pressure of $\sim 1 \times 10^{-10}$ torr.

Details of the infrared experiments are as follows. Two spectra of the clean sample were collected and ratioed to determine the stability and reproducibility of the synchrotron beam. If the reproducibility was better than .02% over the region of interest in 100 seconds collection time per spectrum, then the sample would be dosed by backfilling the chamber with CO gas. The final spectrum was collected within 12 minutes of the first clean sample spectrum, ensuring minimal contamination of the sample. The results shown in the next section are the division of the co-added dosed spectra by the co-added clean copper spectra. For the data taken with the bolometer, several sets of these were added together to improve the signal to noise. For the data taken with the photoconductive detector absolute changes in reflectivity were determined by normalizing to the exponentially decaying beam current and was found to be reliable within $\pm 0.2\%$.

RESULTS

The synchrotron has three main advantages over a global source, which include the ability to measure below 350 cm^{-1} , the feasibility of measuring the absolute change, ΔR , in the high frequency range and the ability to measure quickly. To illustrate these advantages we show data over a broad frequency range in Fig. 1 for CO/Cu(111). The data show a broadband background change, a sharp absorption feature at around 2100 cm^{-1} , and two very weak features below 350 cm^{-1} (see Fig. 2 which focuses on this region). Notice that the strengths of these latter absorptions are two orders of magnitude smaller than that for the high frequency mode. On the figure we point out the usual limit of "conventional" surface vibrational spectroscopy at around 800 cm^{-1} and the absolute limit of non-synchrotron spectroscopy at around 350 cm^{-1} , the lowest frequency for excitation of carriers in photo-conductive detectors. The Silicon beam-splitter is optimized for the low frequency region, and the measurements for the high frequency region were collected quickly to determine the absolute magnitude of the broadband absorption, ΔR , which explains the increased noise above 400 cm^{-1} . The extension to the far-ir, quick measuring times and the absolute intensity measurements are the most important improvements afforded by using a synchrotron.

We now concentrate on the low frequency region. Fig 2 shows data for $(\sqrt{3}\times\sqrt{3})R30^\circ$ CO/Cu(111), $c(2\times2)$ CO/Cu(100) and (1×2) CO/Cu(110), where the solid lines are fits that will be described in detail later. The common features induced by the adsorbates are: 1.) The Lorentzian dips in the $330\text{--}350\text{ cm}^{-1}$ region, 2.) The Fano-type features at $\sim 275\text{ cm}^{-1}$, and 3.) The background slope. The first two features have been previously assigned to the C-metal stretch and dipole forbidden hindered rotation, respectively, by isotopic substitution. The C-metal modes have different widths and frequencies for the different substrates where the adsorption geometries are indicated in Fig. 2. Considerable differences are also observed in the Fano-type features.

In Fig. 3, the broadband spectra as a function of coverage for CO/Cu(100) and fits (solid lines) are presented. In the inset, the absolute change in reflectivity, (ΔR at 2300 cm^{-1}), as a function of coverage has been plotted with a linear least squares fit. Thermal desorption mass spectroscopy was used to calibrate the coverages by integrating under the desorption peak and assuming that the saturation coverage was $\Theta=0.57$.

DISCUSSION

One of the remarkable features of the data is the appearance of the dipole forbidden peaks. Note that the existence of these peaks cannot be accounted for by direct excitation via s-polarized light due to their strengths. In the discussion that follows we will discuss the data and fits in terms of two models^{10,11}. One describes the physics of the background change and how this leads to the concomitant appearance of the dipole forbidden mode¹⁰. The second is a cluster calculation¹¹, in which a breakdown of the Born-Oppenheimer approximation is taken into account, leading to a description of the complex interplay between the adsorbates and conduction electrons and predictions of the lifetimes of the vibrational modes.

Persson and Volokitin¹² have proposed a theory based on coupled equations of motion for adsorbates and conduction electrons for a Drude like substrate. The adsorbate motion parallel to the surface couples to the induced current parallel to and beneath the surface. There are two major consequences of this theory. The first is a broadband background absorption, due to the non-specular scattering of the conduction electrons when the adsorbates are present. The second is that all adsorbate modes parallel to the surface, the dipole forbidden modes, are observed as anti-absorption peaks. This is because there is no relative motion between the vibrating adsorbate and the collective motion of the electron gas.

The solid lines in Figs 1 and 3 are fits to the data using the high frequency limit of the following equation¹⁰:

$$R = 1 - \frac{4Mn_a}{mnc\tau} \frac{1}{\cos\theta} \frac{[\Omega^2 - \omega^2]}{[\Omega^2 - \omega^2]^2 + [\omega/\tau]^2} \frac{\omega^2}{\omega^2 + \frac{6}{5}b^2} \quad (1)$$

where the assumptions are that the light frequency $\omega \gg 1/\tau_b$ with τ_b the bulk relaxation time, and $\omega/\omega_p \gg v_F/c$ where ω_p is the plasma frequency. In Eq. 1, τ is the relaxation time, dominated by the lifetime of the hindered translation, n_a is the adsorbate density, θ is the angle of incidence, ω is the frequency of the incident radiation, Ω is the frequency of the hindered translation and b is equal to $\frac{v_F}{\delta}$ (v_F = Fermi velocity of the conduction electrons, and δ = skin depth). Since the hindered translation is well below 100 cm^{-1} ^{13,14}, the high frequency limit should be valid, and is as follows:

$$R = 1 - a \frac{\omega^2}{\omega^2 + \frac{6}{5}b^2} \quad (2)$$

where a is the high frequency asymptotic limit, The inset of Fig. 3 shows the change

in the high frequency asymptotic limit, a , of the broadband absorption as a function of coverage. As can be seen from Eqs. 1 and 2, one should expect a linear relationship between a and n_a , and this is indeed what is found experimentally. Finally, the observation of the anti-absorption peak is also taken account of in Eq. 1, where the second term on right hand side goes to zero when the vibration of the hindered translation is the same as the frequency of the incident electric field. This can be extended to describe the features due to any parallel normal modes of adsorbates on "Drude-like" substrates. Physically this means that the conduction electrons are moving in phase with the adsorbates. At the other frequencies there is additional scattering of the electrons off the adsorbates.

Turning now to calculations of the frequencies and lifetimes of the normal modes, the major conclusion from the cluster calculation by Head-Gordon and Tully for CO/Cu(100) is that the adsorbates dissipate their energy predominantly through the production of electron-hole pairs¹⁵.

In order to compare the measurements with these calculations we have fitted the data of Fig. 2, and show the fits as solid lines. In each case the background was fitted by a least squares method to a straight line over the limited frequency range 200-430 cm^{-1} . Then the hindered rotation mode was fitted to the formula for a Fano line shape, developed by Langreth¹⁶ for the line-shape of a vibrational mode arising from an electron-hole-pair decay process, thus:

$$L(\omega) = A \left[\frac{\omega_r}{\omega} \right] \left[\frac{\mu_1^2}{\gamma} \right] \frac{(1 - \omega\tau x^2)}{(1 + x^2)} \quad (1)$$

where $x = (\omega^2 - \omega_r^2)/\gamma\omega$. ω_r is the fully renormalized Born-Oppenheimer vibration frequency, ω the probing radiation frequency, μ_1 the real part of the net dynamic dipole moment, γ the width of the electronic damping and $\omega\tau$ the phase delay. In practice, γ is proportional to the width of the peak, and μ_1 to its amplitude. Finally the carbon-metal stretch was fitted to a Lorentzian. The modes are sufficiently well separated to allow convergence with very few iterations.

Table 1 includes the calculated frequencies (ω) and lifetimes (τ); the experimental frequencies and widths (γ) from the fits, and resulting experimental lifetimes. The experimental lifetimes are calculated assuming that an observed peak width of 5 cm^{-1} corresponds to a lower lifetime limit of 1 psec.

There appears to be good general agreement between the predictions and the experimental results. However, the calculations predict a lifetime of 82 psec for the carbon-metal mode which would imply a width of $.06 \text{ cm}^{-1}$ whereas the observed width is 5 cm^{-1} . This discrepancy can be explained by inhomogeneous broadening, since experiments performed with rougher surfaces showed a much greater sensitivity to amplitude and width of this and the Fano mode than to the internal stretch. The data shown for the Cu(111) surface, which had the best defined Kikuchi bands in the SEM diffraction experiment, showed widths of $\sim 1 \text{ cm}^{-1}$, corresponding to a lifetime of > 5 psecs. This trend agrees with the calculations, but the data are still believed to be limited by inhomogeneous broadening.

Finally there are some obvious differences for the hindered rotation as a function of surface symmetry as can be seen in Fig. 2. The largest difference occurs for CO/Cu(110) which is smaller in intensity and broader. The double degeneracy for this mode (on the (111) and (100) surfaces) is broken due to the two-fold symmetry of the (110) surface. If only one such mode is being observed it would have, at most, only half the amplitude of the hindered rotational modes on the other surfaces. It was calculated for CO/Ni¹⁸ that when the degeneracy for the hindered rotation is lifted, one mode would shift down by $\sim 100 \text{ cm}^{-1}$ and one up $\sim 100 \text{ cm}^{-1}$. This is clearly not the case here as at least one mode is not significantly shifted. It is possible that the frequencies for the two modes could be close and therefore not resolvable, since from the fits we find that Fano type modes have influence over a broad frequency range. Perhaps more significant is the fact that for CO/Cu(110), the molecules are adsorbed at atop positions, but on the second layer of Cu atoms¹⁹ and thus in troughs. A smaller and broader feature similar to this was also observed for the hindered rotation for NO/Cu(111), where the NO is at a higher coordination site (either bridge or three fold hollow)²⁰. Like this situation one can imagine the parallel vibration inhibited due to the molecule sitting deeper in the conduction electron environment.

In conclusion, infra-red reflectivity data for CO/Cu on several low index faces clearly reveal the vibrational modes for the systems, and broadband absorptions. The features associated with the vibrational modes appear to be sensitive to the differences in the symmetries. The lifetimes and frequencies for the modes for CO/Cu(100) are in good agreement with expected values from cluster calculations and the induced background change is well explained with a Drude type theory.

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Figure Captions

Fig. 1. Infrared reflectivity spectra from a Cu(111) surface for a submonolayer coverage of CO. The discrete vibrational modes are seen superimposed on a background which changes with coverage.

Fig 2. Far infrared spectra for $(\sqrt{3}\times\sqrt{3})R30^\circ$ CO/Cu(111), $c(2\times2)$ CO/Cu(100) and (1×2) CO/Cu(110) with fits (solid lines as discussed in the text. Schematics for each of these systems are also included. The peak at the left is the hindered rotational mode, while the dip is the carbon metal stretch mode.

Fig 3. Infrared reflectivity spectra from CO/Cu(100) as a function of coverage with fits (solid lines). The inset is the high frequency asymptotic change in reflectivity as a function of coverage and is discussed in the text.

	Theory		Experiment		
	$\omega(cm^{-1})$	$\tau(psecs)$	$\omega(cm^{-1})$	$\gamma(cm^{-1})$	$\tau(psecs)$
Carbon-Oxygen	2304	3.3	2078	6	$>.7(2^{\dagger})$
Carbon-Metal	247	82	344	5	>1
Hind. Rot.	288	2.3	287	4	>1

[†] Pump-probe experiment using Sum-Frequency Generation¹⁷.

Fig 1

CO/Cu ordered overlayers

Fig 2

Fig 3

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