Probing Surface Short Range Order and Inter-Adsorbate Interactions through IR Vibrational Spectroscopy: CO on Cu(100)[†]

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It is demonstrated that surface vibrational spectroscopy can be used to probe local ordering of adsorbates and the nature of inter-adsorbate interactions through dynamical dipole coupling among neighboring adsorbates. Our studies show that for CO adsorbed on Cu(100), first and second nearest neighbor interactions are repulsive. This repulsion prevents the formation of long range ordered structures at low and medium coverages and can be best understood as an adsorbate induced modification in the local electron density, i.e., Friedel oscillation.

How molecules interact with each other and how these interactions lead to the formation of the various phases of matter have long been a central concern in physics and chemistry. On two-dimensional systems such as crystalline surfaces where the number of adsorbed molecules is small (10^{14} molecules per cm^2 or smaller), it is experimentally challenging to probe the nature of intermolecular interactions and their influence on structure and dynamics.

Understanding how adsorbate−substrate and inter-adsorbate interactions affect two-dimensional ordering and phase transitions requires experimental measurements of *local* ordering of adsorbates. Several techniques, such as low energy electron diffraction (LEED), X-ray diffraction, and He atom scattering, have been widely used to study long range order on surfaces. These coherent scattering techniques are sensitive to structures that are ordered on distances comparable to the coherence length of the probe. For probing short-range order in two-dimensional systems, recent diffuse-LEED, core electron spectroscopic and photoemission holographic investigations have reported sensitivity to local order and coordination of substrate atoms. Also, the use of scanning probe microscopies for characterizing local order of medium/large organic molecules on surfaces has been explored.[1] In this Letter, we report that local ordering and inter-adsorbate interactions, particularly those of small molecular adsorbate, can be characterized by surface infrared (IR) spectroscopy. This is demonstrated for the first time in the study of CO adsorbed on a stepped Cu(100) surface.

IR spectroscopy is a versatile tool for probing surfaces.[2] It is sensitive to small quantities of adsorbates and can provide information on the vibrational modes of the adsorbate−substrate system, allowing elucidation of the chemical nature and structure, including adsorption sites,[2,3] of adsorbates. As a noninvasive, nondestructive optical probe in surface diagnosis, it is capable of operating in a range of pressures and environments and with time resolution.[2−5]

There have been IR spectroscopic studies of ordering on surfaces, primarily through examining inhomogeneous broadening in spectral line width. Evidence in IR spectroscopy has been found indicating ordered structure,[6] island formation,[7,8] or unique distribution of terraces.[9] In addition to line width broadening, another unique mechanism, namely, the dynamical dipole coupling, which may affect IR spectral intensity, frequency, and line shape, can also be used to deduce the ordering of adsorbates.

It has been established that dynamical dipole coupling can adversely affect the IR absorption intensity and frequency of the surface species.[10−12] When the coupling is strong, it induces frequency shifts as well as intensity sharing between different species, complicating the interpretation of the IR spectra. However, it has been shown that this coupling effect can be quantitatively characterized for accurate deduction of the concentration and chemical nature of the absorbing species from the IR spectra.[11] In treating dynamical dipole coupling among adsorbates, one recognizes that the extent of the coupling depends intimately on the arrangement of and the distances between molecules in the overlayer. This constitutes the basis for using IR spectroscopy to deduce local ordering of adsorbate molecules even in cases where LEED patterns are not obtainable.

The adsorption of CO on Cu(100) has been characterized by a variety of surface science techniques.[11,13,14] CO weakly chemisorbs on top of the Cu atom in a straight up configuration. No LEED patterns, indicative of long range order, appear with coverage below 0.45. A c(2×2) structure appears only for the compression phase of coverage higher than 0.5.[13]

We have obtained IR absorption spectra near the CO stretching region (2000−2120 cm^{-1}) as a function of CO coverage from zero to saturation coverage ($\theta = 0.57$) on a stepped Cu(100) surface.[11] The surface IR spectra were acquired using a Transient Diode Laser IR Reflection Absorption Spectroscopy technique capable of IR-detector-limited time resolution and 10^{-3} monolayer sensitivity.[5] The density of steps of this particular surface was determined to be about 6% of the total number of surface atoms using X-ray Laue diffraction. CO adsorption on the two different sites, the steps and terraces, has been quantitatively established by Thermal Desorption Spectroscopy (TDS).[5,11] Selected IR absorption spectra at submonolayer coverages are shown in Figure 1. Combined TDS and IR studies indicate that the high-frequency spectral feature is associated with CO adsorbed at step sites and the low-frequency feature with CO at terrace sites.[11]

As a result of dynamic dipole coupling, the IR spectra are characterized by shifting frequencies as well as disproportionate

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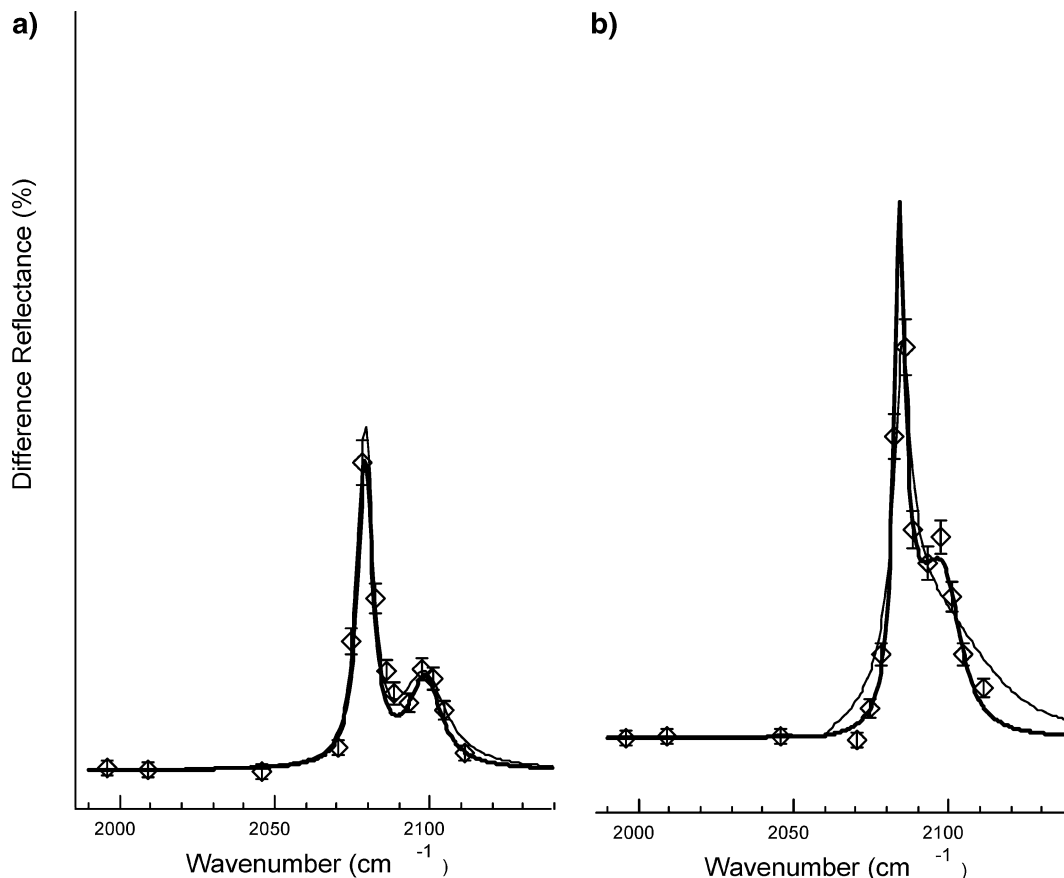
Figure 1. IR absorption spectra of CO on a stepped Cu(100) surface (open diamonds) at (a) $\theta = 0.01$ and (b) $\theta = 0.3$. The solid line is a nonlinear least-squares fit using the dynamic dipole coupling model with correlated repulsive adsorption pattern ($n = {}^3/_2$). The dashed line is a fit with random adsorption ($n = 1$).

intensity behavior throughout the submonolayer coverage range ($\theta \sim 0{-}0.5$). The integrated IR intensity of each spectral feature is not proportional to the concentration of the adsorbate species assigned to that spectral feature. This is clearly indicated by the spectrum for $\theta = 0.3$ ML in Figure 1. Here, the broader, higher frequency fearture with two-thirds of the total intensity, determined by a conventional Gaussian-shape spectral fitting,[11] is nomially assigned to the step CO which has about only a tenth of the total population at this coverage. The majority terrace CO, comprising 90% of the population, accounts for only one-third of the intensity (the narrower, low-frequency feature).

We have shown that the spectra of CO/Cu(100) can be quantitatively simulated at all coverages as illustrated in Figure 1.[11] Spectral simulation was done on the basis of the Persson–Ryberg model which was originally constructed for treating dynamic dipole coupling among CO isotopes at a fixed coverage.[10] The IR absorption at the frequency ν is proportional to the imaginary part of the overlayer polarizability at ν. The latter is affected by the potential through which the transition dipoles interact. The evaluation of the interaction potential requires a direct sum over all the occupied sites on the two-dimensional lattice. This lattice sum depends on the arrangement of molecules in the overlayer as well as the distance between the interacting species.

There are an infinite number of possible arrangements that adsorbates can assume on a two-dimensional lattice. We consider three limiting cases. When intermolecular forces are negligible the adsorbates distribute in a random fashion (random adsorption). On the other hand, if repulsive intermolecular forces are present the adsorbates distribute as far apart from each other
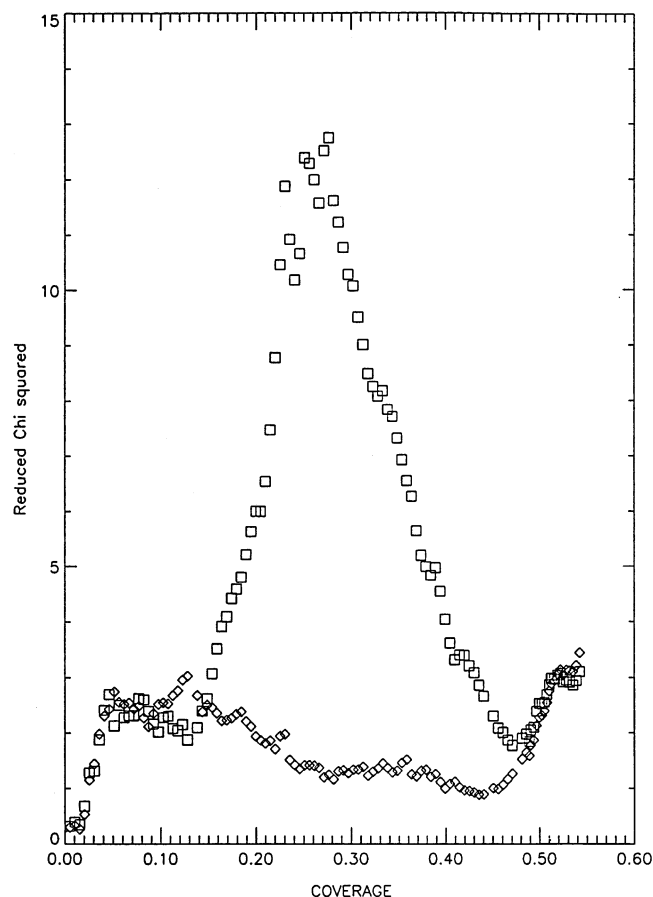
as is necessary to minimize the interaction (repulsively correlated adsorption). Yet when attractive forces between adsorbates dominate, they tend to form islands. The lattice sum then depends on the size distribution of the islands. Initially, as islands begin to form the lattice sum increases, because the total number of molecules contributing increases. As the islands grow larger than the convergence length of the lattice sum, additional molecules do not modify the lattice sum.

The lattice sum, $U_o(\theta)$, evaluated at the center of the Brillouin zone ($q = 0$) can be calculated by summing over each occupied site for any specific lattice configuration. The effect of image dipoles at the metal surface must be included. Once this is done for a reference coverage θ_m, the dependence of U_o on θ can be related to $U_o(\theta_m)$ as

$$U_o(\theta) = (\theta/\theta_m)^n U_o(\theta_m) \tag{1}$$

where n, the order parameter, has been determined for the cases of random ($n = 1$),[15] and correlated-repulsive ($n = {}^3/_2$)[16] adsorption.

With eq 1 depicting the dynamic dipole coupling potential used in combination with the formalism of Persson and Ryberg,[10] the IR spectra can be simulated at all coverage. Details of this simulation can be found in ref 11. Briefly, each of the two types of oscillators (step and terrace CO) is described by a molecular polarizability that is susceptible to the field due to other oscillators and their images. The molecular polarizability is composed of a nonresonant and a resonant part, whose frequencies and widths are distinct for each CO species. In agreement with experimental observations, the CO at steps are described by a frequency higher than that of CO adsorbed at

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Figure 2. Reduced χ^2 from the simulations of individual spectra, for the entire submonolayer coverage range, in the limits of random (squares) and repulsively correlated (diamonds) adsorption.

Figure 3. Total integrated IR absorption intensity of CO on the stepped Cu(100) surface as a function of coverage. The lines are from dynamic dipole coupling model calculations in the limits of random (- - -) and repulsively correlated (—) adsorption.

the majority terrace sites and a wider width reflecting the broader distribution of possible sites (kinks, high and low coordination step sites, defects) at the steps. The magnitudes of polarizabilities are set to be otherwise identical. The total polarizability of the overlayer is evaluated using the Coherent Potential Approximation[17] in conjunction with eq 1.

The adsorbate molecular vibrational and electronic polarizabilities, which are independent of coverage, are determined from the total integrated IR absorption intensity. The total coverage θ is determined from TDS experiments. The other parameters in the model calculation of the spectra, including the concentrations of the two CO species, their pre-coupling adsorbate frequencies and line widths, were determined from a nonlinear least-squares fit of each individual spectrum spanning the coverage range $\theta = 0.005-0.55$, in steps of 0.005. These simulations were carried out in the limits of random and repulsively correlated adsorption, as the observed spectral behavior was not consistent with island formation due to attractive interactions. In the latter case the lattice sum would show no coverage dependence, except at very low coverage, resulting in a linear dependence of overall IR absorption intensity on coverages, contrary to the experimental observations (see below and ref 11).

The two cases of repulsively correlated vs random adsorption can be distinguished by examining the quality of the simulated spectra, indicated by the reduced-chi-squares (χ_r^2) of the fit, using one or the other model. The χ_r^2 for the 110 spectra covering the entire submonolayer coverage range is shown in Figure 2. The two adsorption models show markedly different behavior. Overall, the repulsively correlated adsorption model
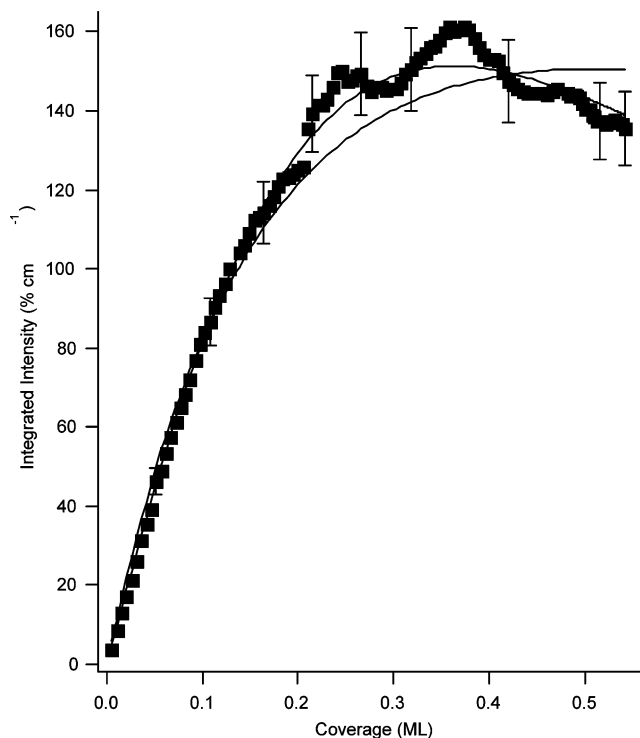
with $n = {}^3/_2$ provides a much better description of the spectra with χ_r^2 of less than 3.5 for all coverage. In addition, the step-CO concentration determined from the fitting saturates at 7% of the total number of available sites, in agreement with the TDS/LAUE determination. For random adsorption ($n = 1$), the χ_r^2 varies significantly with coverage and is over an order of magnitude greater than that of repulsively correlated adsorption. Furthermore, the step-CO concentration obtained in the calculation exceeds 20% of the total number of surface sites, in stark contradiction of the experimentally determined step-site density of this particular surface.

Other evidence supporting correlated adsorption of CO on Cu comes from the dependence of overall integrated intensity on coverage. The total integrated intensity, also affected by dynamic dipole coupling,[10,11] increases initially with coverage followed by a decrease reaching saturation. Figure 3 clearly shows that only the correlated adsorption model with $n = {}^3/_2$ reproduces the observed behavior.

For coverage below 0.17 ML, both random and correlated adsorption models give almost identical χ_r^2. This is understandable as at low coverage the average inter-adsorbate distance is large and the likelihood of two molecules being in adjacent sites is low. Thus IR spectra are much less affected by dynamic dipole coupling. Beyond $\theta = 0.17$, the χ_r^2 for the two models diverge. At the higher coverage, nearest neighbor sites constitute a larger fraction of the available sites and adsorption pattern now makes a definitive influence on the spectral shape (see Figure 1). Finally, at coverage greater than 0.5 there is very little difference between the two models because there is little choice of adsorption site.

The point of divergence between the χ_r^2 for the two models enables the range of the repulsive interaction between molecules to be deduced. At $\theta = 0.17$ the area per molecule is estimated as 38 Å^2 from $1/(0.17 \times 1.54 \times 10^{15})$ cm^2, giving an average inter-adsorbate distance of 6.2 Å. At this distance the force

correlating adsorption becomes significant. Considering the CO/Cu(100) c(2×2) overlayer structure determined for $\theta = 0.5$, the second nearest distance is 5.1 Å and the third 7.2 Å. The 6.2 Å range of repulsive interaction renders occupation of first and second nearest neighbor sites improbable at low and intermediate coverage, preventing LEED patterns until $\theta \sim 0.5$.

A study of isothermal desorption of CO molecules from Cu(100) has suggested repulsive first and second neighbor interactions.[14] The repulsive interaction between adsorbates also explains the observed coverage dependence of the step-CO population.[11] Even though CO binds more strongly at step sites than at terrace sites, the IR spectroscopic study has shown that the step sites do not saturate until significant terrace coverage is achieved.[11] In this repulsively correlated adsorption model, a fraction of the stronger binding sites stay vacant because of adsorption on neighboring sites. Whereas in the "random" adsorption model that does not include any inter-adsorbate interaction, the stronger binding sites (steps) should all be filled first. Finally, theoretical simulations[18,19] have shown that repulsive interactions lead to an absence of long range ordering on fcc(100) surfaces, consistent with our results and the absence of overlayer LEED patterns till close to saturation.

One question now arises: what is the origin of the repulsive interaction between the adsorbed CO molecules on Cu? Direct repulsive interaction due to overlap of molecular orbitals is not significant given the large average intermolecular separations, i.e., ~ 6 Å, at which distance repulsive forces become apparent. Direct overlap occurs at a range <3 Å. Other possibilities related to Coulombic forces such as parallel static dipole interaction must be considered. Although the dipole moment of CO in the gas phase is small (0.1 D), it may vary considerably upon adsorption due to charge transfer between the adsorbate and the substrate. The static dipole of CO on Cu(100) has been estimated to be 0.23 D from the change in work function upon CO adsorption.[13,20] The repulsive potential due to this dipolar interaction including image dipoles is calculated to be only 6 meV at the first nearest neighboring site distance of 3.6 Å. This is much too small in comparison with the 0.6 eV binding energy[14] to have a discernible effect in CO adsorption patterns. Another Coulombic interaction arises from the dispersion force. However, at the distance of 3.6 Å, this weak interaction should be attractive, not repulsive. Thus, it appears that mechanisms based on Coulombic forces cannot account for the repulsive inter-adsorbate interaction at medium distances.

Indirect, substrate-mediated interactions between adsorbates on metal have been suggested more than two decades ago.[21,22] The basis for these interactions is screening of static charges in a conductor. Recent scanning tunneling microscopy studies[23–26] have shown that electrons at metal surfaces can be scattered by localized potentials such as those produced by defects or adsorbates. This scattering leads to Friedel oscillations in the local density of states (LDOS). Thus the region around the adsorbate is alternately electron rich or deficient, leading to decreased or enhanced bonding, respectively, for electron donating species. Oscillations of 15 Å periods have been observed in the vicinity of electron donating impurities, such as sulfur or antimony, on Cu surfaces.[23] The result is an increase in LDOS in the immediate vicinity of the adsorbate, with a first valley at 7.5 Å. In the case of CO on Cu, where bonding has been shown to involve electron donation from the adsorbate to the metal,[11] the likelihood of another CO adsorbing is reduced in the region of increased LDOS. This is consistent with the repulsive first (3.6 Å) and second (5.2 Å) nearest neighbor interactions we determined for CO on this Cu surface.

In conclusion, we have shown that although dynamical dipole coupling may be a nuisance for accurate interpretation of surface vibrational spectroscopy, it can be used to probe local ordering as well as the nature of inter-adsorbate interactions. In this first demonstration, it has revealed repulsive first- and second-nearest neighbor interactions for CO on Cu(100). This repulsion prevents the formation of long range ordered structures at low coverage, explaining why no overlayer LEED patterns have been observed for coverage less than 0.5. These long-range repulsive forces are consistent with adsorbate induced modifications of the LDOS reported in recent STM studies, providing strong evidence for substrate mediated inter-adsorbate interactions.

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