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Inelastic Electron Scattering by a Collective Vibrational Mode of Adsorbed CO

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The C-O stretching vibrational mode of the Cu(100) + $c(2\times 2)$CO system has been examined by angle-dependent inelastic electron scattering. The mode is collective and its dispersion is found to be dominated by dipole-dipole interactions among the adsorbed molecules. The vibrational excitation cross section is satisfactorily described by dipole scattering theory.

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One important feature of high-resolution electron-energy-loss spectroscopy (EELS) as a tool to study surface vibrations is the potential ability to measure normal-mode dispersion relations for ordered structures of atomic and molecular adsorbates. In this Letter we will explore this ability in order to investigate the collective behavior of vibrationally excited CO molecules in the $c(2\times 2)$CO structure on Cu(100). Infrared spectroscopy studies of isotopic mixtures of adsorbed CO have revealed a composition-induced "coupling shift"[1-4] of about 40 cm^{-1} (~ 5 meV) for the C-O stretching vibrational mode. Dipole-dipole interaction between the vibrating molecules has been considered as a possible cause of this frequency shift.[1,2,4-6] In principle the strength as well as the nature of the interaction should be revealed in a straight-forward manner by measuring the phonon dispersion relation in an inelastic-electron-scattering experiment. In practice this is still a quite difficult experiment since the frequency shifts are small and the experiments have to be performed at optimum resolution of present instruments (~ 4 meV).

The spectroscopic measurements reported here were carried out with use of a new high-resolution electron spectrometer consisting of a monochromator and an analyzer, both of cylindrical-mirror design. The analyzer and the specimen can be rotated such that the polar angles of collection θ (measured with respect to the specularly scattered electron beam, positive towards the surface normal) and incidence α (measured with respect to the surface normal) can be varied independently. The experimental data (shown in Figs. 1–3) were obtained for an energy $E_0 = 3$ eV (relative to the vacuum level) and angle $\alpha = 65°$ of the incident electron beam. The spectrometer was operated at an energy resolution of 4.5 meV which is only slightly poorer than the designed resolution 4 meV at the employed pass energy 0.4 eV. The angular acceptance of the analyzer was a cone of half angle 1.0°. The scattering plane containing the incident and the scattered beams was defined by the surface normal and the [100] crystal direction in the surface plane.

Figure 1 shows an EEL spectrum for the Cu(100) + $c(2\times 2)$CO system measured in the specular direction, i.e., $\theta = 0°$, at 80 K specimen temperature. The experimental procedure concerning the specimen cleaning and the CO adsorption has been described previously.[7] The two loss peaks at 42.5 and 259 meV correspond to the excitation of the fundamental Cu-CO and C-O stretching vibrations of CO adsorbed in the on-top position.[7] The low-energy loss peak at 14.5 meV is interpreted to be due to the excitation of a surface phonon at the M point of the substrate surface Brillouin zone.[8] The inset in Fig. 1 shows the C-O loss peak at three different values of the wave vector $\vec{q}_\parallel$ along the [100] direction in the surface plane, where

$$q_\parallel = [|\vec{k}'|\sin\alpha - |\vec{k}|\sin(\alpha-\theta)]a/\pi,$$

$\vec{k}$ and $\vec{k}'$ are the wave vectors of the incident and scattered electrons, respectively, and $a = 3.61$ Å is the $c(2\times 2)$CO unit mesh edge.

We have previously found[9] that the interaction between the low-energy electron and the C-O vibrational mode shows the characteristic features of dipole excitation. The inelastic scattering cross section was then calculated assuming that the vibrational state was a localized excitation. Here we will treat the vibrating molecules as interacting.

Let us denote the stationary states of this collective vibrational system by $|a\rangle$, $|b\rangle, \ldots$, where $|a\rangle$ is the ground state and $|b\rangle$ is an excited state. The stationary states of the electrons in the absence of adsorbed molecules are denoted by $\psi_{\vec{k}}$. The transition rate w for an electron to be scattered from $\psi_{\vec{k}}$ to $\psi_{\vec{k}'}$ may then be found from the golden-rule formula

$$w = (2\pi/\hbar^2)\textstyle\sum_b|\langle b,\psi_{\vec{k}'}|H'|a,\psi_{\vec{k}}\rangle|^2\delta(\omega_{ba}-\omega), \tag{1}$$

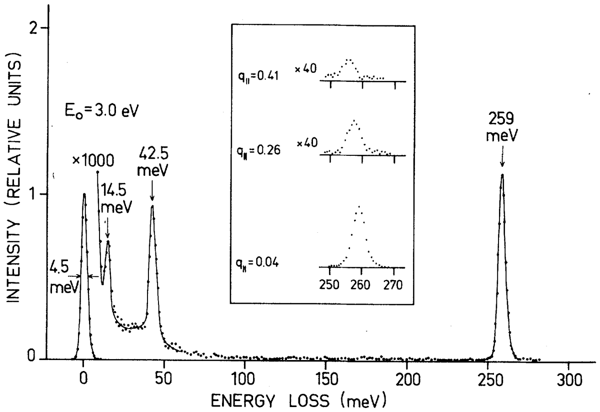

FIG. 1. Electron energy-loss spectrum from Cu(100)-$c(2\times 2)$CO measured in the specular direction at 80 K specimen temperature and for an energy 3 eV and angle 65° of the incident electron beam. The inset shows the C-O loss spectra at three values of the momentum $q_\parallel$ (units of π/a) along the [100] direction in the surface plane.

where $\hbar\omega_{ba} = E_b - E_a$ is the energy needed to excite the system from $|a\rangle$ to $|b\rangle$ and must equal the energy loss $\hbar\omega = E_{\vec{k}} - E_{\vec{k}'}$. H' is the interaction energy between the incident electron and the adsorbed molecules, $H' = -\sum_i \vec{\mu}_i\cdot\vec{E}(\vec{x}_i)$ where $\vec{\mu}_i$ is the dipole moment operator of molecule i and $\vec{E}(\vec{x}_i)$ is the electric field at molecule i from the incident electron and its image. Equation (1) can be rewritten as

$$w = \frac{2\pi}{\hbar^2}\sum_b\Big|\sum_j\langle b|\mu_j|a\rangle\exp i\vec{q}_\parallel\cdot\vec{x}_j\Big|^2|\langle\psi_{\vec{k}'}|\vec{E}(0)|\psi_{\vec{k}}\rangle|^2\delta(\omega_{ba}-\omega). \tag{2}$$

This expression can be connected to the polarizability $\alpha(\vec{q}_\parallel,\omega)$ of the monolayer (consisting of N molecules)

$$\mathrm{Im}\,\alpha(\vec{q}_\parallel,\omega) = (1/N)(\pi/\hbar)\textstyle\sum_b|\sum_j\langle b|\mu_j|a\rangle\exp i\vec{q}_\parallel\cdot\vec{x}_j|^2\delta(\omega_{ba}-\omega) \tag{3}$$

thus,

$$w = (2N/\hbar)|\langle\psi_{\vec{k}'}|\vec{E}(0)|\psi_{\vec{k}}\rangle|^2\,\mathrm{Im}\,\alpha(\vec{q}_\parallel,\omega). \tag{4}$$

To proceed, we will assume that the adsorbed molecules interact with each other through their dipole fields. It can be shown from Mahan and Lucas' treatment of such a system[5] that

$$\alpha(\vec{q}_\parallel,\omega) = \alpha_0/[1+\alpha_0 U(\vec{q}_\parallel)], \tag{5}$$

where $U(\vec{q}_\parallel)$ is the spatial Fourier transform of the dipole field. The polarizability α_0 of one single adsorbed molecule may be expressed in terms of α_e and α_v, the electronic and vibrational polarizabilities, respectively, as

$$\alpha_0 = \alpha_e + \alpha_v[1-(\omega/\omega_0)(\omega/\omega_0+i\delta)]^{-1}, \tag{6}$$

where δ is a small number determined by the finite lifetime of the vibrationally excited molecule. Combining (5) and (6) and assuming that δ is infinitesimal, we obtain

$$\mathrm{Im}\,\alpha(\vec{q}_\parallel,\omega) = \frac{\pi\alpha_v\omega_0^2}{2\omega(\vec{q}_\parallel)|1+\alpha_e U(\vec{q}_\parallel)|^2}\,\delta(\omega(\vec{q}_\parallel)-\omega), \tag{7}$$

$$[\omega(\vec{q}_\parallel)/\omega_0]^2 = 1+\alpha_v U(\vec{q}_\parallel)/[1+\alpha_e U(\vec{q}_\parallel)]. \tag{8}$$

Equation (8) gives the normal-mode dispersion relation $\omega(\vec{q}_\parallel)$ for the dipole-dipole interacting system.[5] Since the transition rate w is proportional to $\mathrm{Im}\,\alpha(\vec{q}_\parallel,\omega)$, we notice that the screening due to the electronic polarizability of the adsorbed molecules will reduce w by a factor $|1+\alpha_e U(\vec{q}_{\parallel})|^{-2}$. This turns out to be an appreciable correction for the $c(2\times 2)$CO system since typically[10] α_e is a few Å^3.

The inelastic differential scattering cross section $d\sigma/d\Omega$ can now be derived from Eqs. (4) and (7)[11]

$$\frac{d\sigma}{d\Omega}=N\frac{8m^2e^2\omega_0^{\,2}}{\hbar^3\omega(\vec{q}_{\parallel})}\left|\frac{\vec{k}'}{\vec{k}}\right|\frac{1}{\cos\alpha}\frac{\alpha_v}{|1+\alpha_e U(\vec{q}_{\parallel})|^2}|\langle\psi_{\vec{k}'}|\vec{E}(0)|\psi_{\vec{k}}\rangle|^2. \tag{9}$$

The matrix element $|\langle\psi_{\vec{k}'}|\vec{E}(0)|\psi_{\vec{k}}\rangle|$ is evaluated in accordance with a previous treatment[11] which accounts for the Coulomb interaction between the incident electron and the charge density it induces in the surface region of the metal.

The experimental C-O loss-peak intensity as a function of collection angle θ is shown in Fig. 2. The intensity has been normalized to the elastic intensity in the specular direction. The peak in the elastic angular distribution defines the specular condition. The solid curve represents a dipole scattering calculation of the relative loss intensity σ/A as obtained by integrating $d\sigma/d\Omega$ over the solid angle of collection and dividing by the area A occupied by the N molecules. $U(\vec{q}_{\parallel})$ was obtained for[4] a nearest-neighbor adsorbate distance of 3.61 Å placing the molecular dipole 0.8 Å above the "image plane" as defined in the jellium model.[12] This gives, e.g., $U(0)=0.30$ Å^{-3}. The value of $\alpha_e=2.5$ Å^3 was found by adjusting the shape of the calculated curve to the experimental data and $\alpha_v=0.16$ Å^3 was then found from the magnitude of the experimental loss intensity around the specular direction. The scatter in the experimental intensities and hence in α_v is about 30% and is mainly due to inaccuracies in the specimen alignment and the electron optical adjustment of the spectrometer. The general agreement between experiment and theory as demonstrated by the results in Fig. 2 shows that dipole scattering dominates the inelastic scattering process.

In Fig. 3 we show the experimental C-O loss energies plotted versus $\vec{q}_{\parallel}$. The range of $\vec{q}_{\parallel}$ is limited to about half the Brillouin zone primarily because of the demand to work at sufficiently good energy resolution. The error bars derive from the scatter in the experimental data. The energy 259.0 ± 0.5 meV at $\vec{q}_{\parallel}\sim 0$ agrees well with the infrared spectroscopic result 2088 cm^{-1} $=258.9$ meV.[4,13] The possibility that the measured loss energies could suffer from any substantial systematic error when the analyzer was ro-

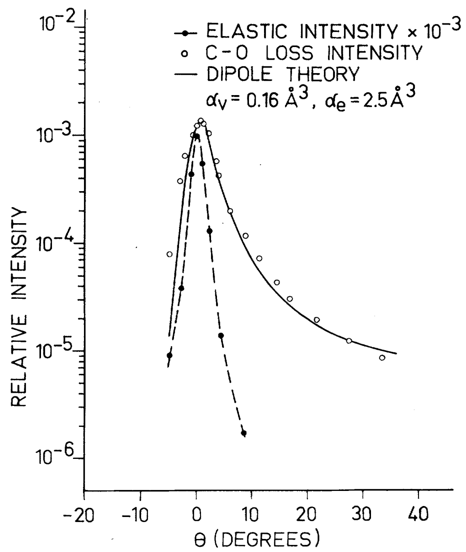

FIG. 2. Experimental elastic peak intensity (solid circles) and C-O loss peak intensity (open circles) vs collection angle θ. Conditions as in Fig. 1. The solid curve is a dipole theory calculation.

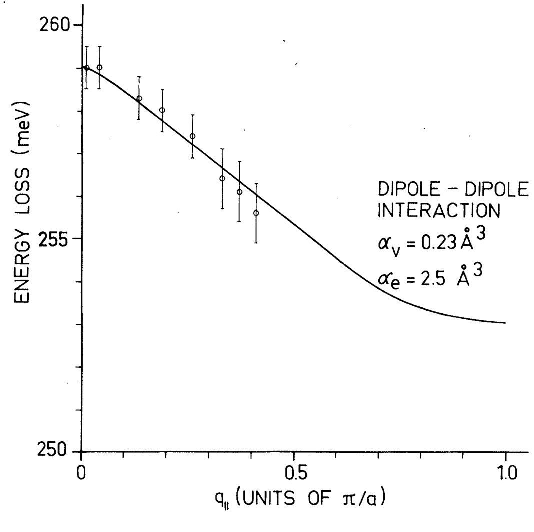

FIG. 3. Experimental C-O loss energy (open circles) vs momentum $\vec{q}_{\parallel}$ along the [100] direction in the surface plane. Conditions as in Fig. 1. The solid curve is a calculated C-O mode dispersion relation assuming dipole-dipole interactions among the adsorbed molecules.

tated has been tested for a dilute disordered CO layer [about $\frac{1}{4}$ of the $c(2\times 2)$ coverage]. The C-O loss energy was found to remain almost constant over the range of $\vec{q}_\parallel$ explored; 258.0 meV at $\vec{q}_\parallel = 0.04$ and 257.5 meV at $\vec{q}_\parallel = 0.33$.

The solid curve in Fig. 3 is a dispersion relation calculated according to Eq. (8). $U(\vec{q}_\parallel)$ was obtained as described above. In order to make a direct comparison with the polarizabilities derived from the cross section data we used $\alpha_e = 2.5$ Å^3 which gave $\alpha_v = 0.23$ Å^3 when the theory was fitted to the experimental data. This figure is compatible with $\alpha_v = 0.16$ Å^3 found above and we conclude that the C-O mode dispersion is dominated by dipole-dipole interactions among the adsorbed molecules.

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Ordering and Phase Transitions in Antiferromagnetic Potts Models

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Monte Carlo simulations and ϵ expansion techniques are used to analyze the behavior of antiferromagnetic Potts models and the Ashkin-Teller model. The Monte Carlo data show that the three- and four-state antiferromagnetic Potts models have an ordered low-temperature phase in three dimensions. Evidence is presented for the existence of a novel low-temperature, metastable, glassy "plastic crystal" phase in the four-state antiferromagnetic Potts model in three dimensions.

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There has been considerable recent work on the phase transition of the Potts model.[1] It is now believed that the ferromagnetic q-state Potts models with $q \geq 3$ exhibit first-order transitions in three dimensions.[2] The situation with antiferromagnetic (AF) Potts models is not as clear. Such systems have a highly degenerate ground state for $q \geq 3$. Studies of the Ashkin-Teller model,[3] in three dimensions, in the neighborhood of the four-state AF Potts point have also shown rich and unexpected behavior.[4] More recently, Berker and Kadanoff[5] have applied one-parameter-rescaling arguments to such systems and have suggested that they can exhibit a distinctive low-temperature phase in which correlations decay algebraically with distance.

In this Letter, we present results of Monte Carlo and ϵ-expansion analyses of the AF Potts models and the Ashkin-Teller model. Our Monte Carlo computations indicate that the AF Potts