High Resolution Helium Scattering Studies of Inelastic Interference Structures of the Frustrated Translational Mode of CO on Cu(001)

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The angular distributions of multiquantum excitations of the lowest energy, frustrated translational vibrations of a low coverage of CO chemisorbed on Cu(001) have been investigated by high resolution helium scattering time-of-flight measurements. The elastic and the one-phonon creation and annihilation cross sections show several interference undulations as a function of parallel momentum transfer, and up to four multiquantum overtones. All the experimental observations are in reasonable agreement with a multiquantum scattering theory, which also provides information on the height and width of the adsorbed CO molecules.

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Important information on the structure and dynamics of adsorbates on surfaces comes primarily from spectroscopic studies of the frequencies of the vibrational modes, whereas information on energy exchange and deexcitation comes from the linewidths [1,2]. The higher vibrational frequencies of chemisorbed molecules are usually measured by infrared absorption [1,2] or by electron energy loss spectroscopy (EELS) [3] whereas for the low frequency vibrations helium atom scattering (HAS) has established itself as an ideal experimental probe [4–6].

Carbon monoxide adsorbed on ordered crystal surfaces has probably been studied more than any other adsorbate system [7]. At the on-top position it exhibits two high frequency modes for the molecule-surface stretch (ν_2 mode) and the C-O stretch (ν_1 mode) with energies of several 100 meV, an intermediate frequency mode attributed to the frustrated rotational motion (ν_3) with an energy less than 100 meV, and a very low frequency mode associated with frustrated translational motion (ν_4, designated ν_T in the present paper) of the molecule with an energy often less than 10 meV. This lowest frequency mode, which has been measured with both HAS [4–6] and recently EELS [8,9] on a variety of surfaces, is important for a number of reasons. Because of its small energy it is the major contributor to the mean square vibrational amplitude of the CO molecule and the vibrational entropy [10]. Moreover, it is an important source of information on the lateral CO-surface potential [11], and because of its low frequency provides an efficient energy transfer pathway for the deexcitation of the internal C-O stretch and CO-surface stretch modes to the phonons of the substrate [12]. The phonon dispersion curves of the clean Cu(001) surface have recently been intensively studied by HAS [13] and preliminary HAS results for the frustrated translation mode for CO on Cu(001) were also recently published [14].

In the present study we report on a detailed HAS investigation of the excitation of the frustrated translational mode as a function of parallel momentum transfer in the very low coverage regime where the CO adsorbate molecules are isolated on on-top sites with the C atom closest to the surface. At small parallel momentum transfer $\hbar\mathbf{Q}$ (close to specular scattering conditions) the HAS time-of-flight (TOF) spectra exhibit only single-phonon clearly resolved vibrational peaks with a width of 1.0 meV (FWHM) and an energy of 4.1 meV (33.2 cm^{-1}). At angles far from specular the TOF spectra show up to eight or more multiple quantum (overtone) excitations which are nearly equally divided between energy gain and energy loss. The stronger inelastic coupling at large parallel momentum transfers indicates a predominant coupling to the parallel momentum and not to the perpendicular momentum. The diffuse elastic and first order gain and loss peak intensities exhibit an undulatory interference behavior with parallel momentum transfer. The undulations in the annihilation, elastic, and creation intensities are shifted with respect to each other as expected for the phase shift of the inelastically backward reflected amplitude with respect to the forward amplitude involving a second reflection from the nearby surface. A new multiquantum scattering theory explains both the number of peaks and their intensities and oscillations with parallel momentum transfer and makes it possible to determine the effective size of the adsorbate molecule.

In the apparatus [15], the helium beam is formed by a supersonic nozzle expansion with an energy of 42 meV (de Broglie wavelength 0.7 Å) and energy resolution of 2%. Time-of-flight spectra of the scattered helium atoms were measured at a fixed angle of 95.8° to the incident beam for different polar angles to the crystal surface normal. The Cu(001) crystal was oriented to better than 0.25° and then prepared by cycles of sputtering with

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800 eV Ar^+ ions and annealing at 850 K under UHV conditions. No impurities above the 0.5% of a monolayer Auger detection limit could be detected. For the CO measurements, the exposure was below 1.5×10^{-6} mbar s corresponding to about 15% of the $c(2 \times 2)$ ordered phase (coverage $\theta = 0.5$). The temperature of the crystal was maintained at 111 K which is about 2.5 times the energy of the 4 meV excitation energy of the frustrated translation mode, consequently this mode is thermally occupied.

A series of representative time-of-flight spectra, converted to energy transfer, are exhibited in Fig. 1 for different incident angles. An intense diffuse elastic peak at zero energy exchange, as well as distinct energy loss and gain peaks are observed in all spectra. The elastic peak which at large angles is up to a factor of 5 greater than for the clean surface arises not only from purely elastic scattering, but also has important contributions from multiple quantum exchange with the adsorbate mode, since all even order multiquantum transfers provide a partial contribution to zero energy transfer [16]. As seen in Figs. 1(a)–1(c) at angles near the specular ($\theta_i = 47.9°$), the frustrated translational (T) peak is weak, and the inelastic parts of the spectra are dominated by a combination of substrate phonon features coming from the very closely spaced Rayleigh mode (R) and longitudinal resonance (L) near the Cu surface Brillouin zone center. At angles farther from the specular corresponding to larger parallel momentum transfer there are multiple adsorbate mode peaks on both the creation and annihilation side, and as on the clean surface the substrate features become less prominent [13]. There is a slight systematic broadening of the multiquantum overtones which increases from the energy loss side to the energy gain side which can be fully accounted for by the experimental resolution which decreases nearly linearly with increasing scattered He energy.

Figure 2 shows the experimental data for the scattered intensity as a function of Q for the elastic and the two first-order inelastic adsorbate mode peaks at $\Delta E =$ ± 4 meV. In the elastic peak the large increase due to the Fraunhofer contribution at smaller Q and the oscillations at larger Q are clearly visible, as was seen earlier for the *total* (without TOF resolution) scattering of He from CO adsorbed on Pt(111) [17]. Even more pronounced oscillations are observed in the much weaker intensities of the inelastic annihilation and creation peaks. It is interesting to observe a definite phase relation between the oscillations of the three different sets of data, with the troughs of the $\Delta E = -4$ meV angular distribution at nearly the same Q values as the peaks of the $\Delta E = +4$ meV data (i.e., a phase difference of ~180°). The elastic oscillations fall midway between, making a phase difference of ~90° with each of the inelastic peaks.

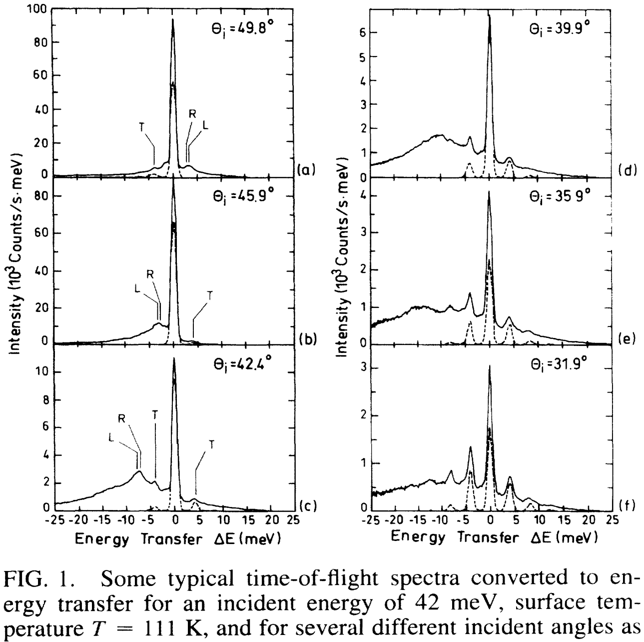

FIG. 1. Some typical time-of-flight spectra converted to energy transfer for an incident energy of 42 meV, surface temperature $T = 111$ K, and for several different incident angles as marked. The dashed line under the experimental data in each group is the theoretical prediction of Eq. (3). The locations of the frustrated translation mode, the longitudinal resonance, and the Rayleigh mode of the clean surface are indicated by T, L, and R, respectively.

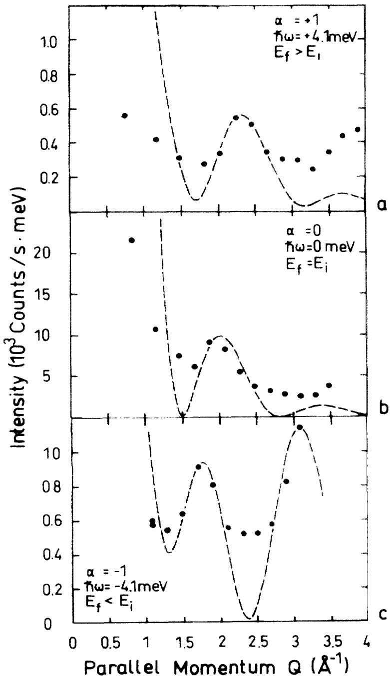

FIG. 2. Measured scattered intensity of (a) the single quantum creation peak, (b) the elastic peak, and (c) the single quantum annihilation peak as a function of parallel momentum transfer. The points are the data and the solid line is the theoretical prediction using the form factor calculated from Eq. (4). Incident energy and temperature are the same as for Fig. 1.

A convenient starting point for the theoretical description is the generalized golden rule for the transition rate from an initial projectile state of momentum $\hbar \mathbf{k}_i$ to final projectile state $\hbar \mathbf{k}_f$ [16]

$$w(\mathbf{k}_f, \mathbf{k}_i) = \frac{2\pi}{\hbar} \left\langle\!\left\langle \sum_{n_f} |T_{fi}|^2 \delta(\mathcal{E}_f - \mathcal{E}_i) \right\rangle\!\right\rangle, \qquad (1)$$

where $\mathcal{E}_f$ and $\mathcal{E}_i$ are the final and initial energies of the total system consisting of the He probe plus crystal, the sum is over final crystal states and the average is over initial crystal states as well as an average over the distribution of adsorbates. To obtain tractable solutions to Eq. (1) we make the quick collision assumption in which the matrix elements of the transition operator taken with respect to particle states are given by [16]

$$T_{\mathbf{k}_f,\mathbf{k}_i} = (\mathbf{k}_f|\hat{T}|\mathbf{k}_i) = \sum_{l,\kappa} e^{-i\mathbf{k}\cdot[\mathbf{r}_l + \mathbf{r}_\kappa + \mathbf{u}_{l,\kappa}]} \tau^{\kappa}_{\mathbf{k}_f,\mathbf{k}_i}, \qquad (2)$$

where $\mathbf{r}_l$ denotes the position of a surface unit cell, $\mathbf{r}_\kappa$ denotes elements within the unit cell (including the position of an adsorbate), $\mathbf{k} = \mathbf{k}_f - \mathbf{k}_i$, and $\mathbf{u}_{l,\kappa}$ is the displacement from equilibrium. In this approximation the scattering amplitude $\tau^{\kappa}_{\mathbf{k}_f,\mathbf{k}_i}$ is assumed to be independent of $\mathbf{u}_{l,\kappa}$, so that the only dependence on displacement is in the phase factor of (2). This assumption is valid since the collision time is indeed shorter than the 10^{-12} s period of the vibrations.

When the transition matrix of Eq. (2) is used in (1) all averages and sums can be carried out. Considering the CO adsorbates to be isolated Einstein oscillators of mass M on a flat substrate, the final result is expressed in the form of the measured differential reflection coefficient as [18]

$$\begin{aligned}\frac{d^3R}{d\Omega_f\, dE_f} = {} & \frac{\rho}{(2\pi)^2 \hbar^4} \frac{m^2 k_f}{|k_{iz}|} \sum_{\alpha=-\infty}^{+\infty} |\tau_{\mathbf{k}_f,\mathbf{k}_i}|^2 e^{-2W^s(\mathbf{k}_f,\mathbf{k}_i)} e^{-2W(Q)} \\ & \times I_{|\alpha|}\left(\frac{\hbar Q^2}{M\omega}\sqrt{n(\omega)[n(\omega)+1]}\right) \\ & \times \left[\frac{n(\omega)}{n(\omega)+1}\right]^{\alpha/2} \delta(E_f - E_i - \alpha\hbar\omega),\end{aligned} \qquad (3)$$

where m is the He mass, k_{iz} is the perpendicular component of the incident wave vector, ω is the frequency of the mode, $n(\omega)$ is the Bose occupation function, ρ is the surface density of adsorbates, and $I_n(z)$ is the modified Bessel function of integral order n. The function $\exp(-2W^s)$ is the Debye-Waller factor arising from the substrate, while the Debye-Waller factor of the CO mode is $2W(Q) = \hbar Q^2[n(\omega) + 1/2]/M\omega$.

A more complete derivation of the scattering intensity of Eq. (3) identifies the scattering amplitude $\tau_{\mathbf{k}_f,\mathbf{k}_i}$ [whose squared modulus is the form factor in (3)] as being the off-energy-shell transition matrix element for scattering by an isolated adsorbate [18]. Thus Eq. (3) through $\tau_{\mathbf{k}_f,\mathbf{k}_i}$ includes multiple scattering collisions of the He with the isolated adsorbate plus surface system, as well as all multiple creation and annihilation quantum transfers with the phonon mode.

The calculated time-of-flight spectra in Fig. 1 are based on the hard wall potential implying a constant form factor $|\tau_{\mathbf{k}_f,\mathbf{k}_i}|^2$ in which the adsorbates scatter uniformly in all directions. We are justified in neglecting the soft, long range van der Waals part of the potential because it is weak and contributes only to near specular scattering. Consequently, only the strongly repulsive hard core interactions can scatter He out to the larger values of $\mathbf{Q}$ relevant to this experiment. The result of the calculation in the eikonal approximation is [19]

$$\tau_{\mathbf{k}_f,\mathbf{k}_i} = -\frac{\hbar^2|k_{fz}|}{m} \int d\mathbf{R}\, e^{-i\mathbf{K}\cdot\mathbf{R}}\left(e^{-iq\xi(\mathbf{R})} - e^{-iq'\xi(\mathbf{R})} - 1\right), \qquad (4)$$

where $q = |k_{fz}| + |k_{iz}|$ and $q' = -|k_{fz}| + |k_{iz}|$ and $\xi(\mathbf{R})$ is the corrugation function of the adsorbate core profile. The integral in (4) is over the surface subtended by the defect core. After convolution with a Gaussian distribution the number and relative intensity of the CO peaks in Fig. 1 are well described. The experimental diffuse elastic peak has a somewhat greater intensity than the calculated value, as expected for the additional elastic incoherent contributions from other defects which are always present even on a clean well ordered surface. The solid curves in Fig. 2 are the results of best fit calculations with Eq. (3) using the scattering amplitude of (4) for a cosine corrugation profile of the single CO molecule given by $\xi(\mathbf{R}) = A\cos(\pi b R/2A)$ with $A = 2.3$ Å and $b = 1.2$. The calculations shown in Fig. 2 are sensitive to the form of the corrugation function $\xi(\mathbf{R})$, for example, an ellipsoid does not work as well, and they are quite sensitive to the values of A and b as reasonable agreement can be obtained only within a narrow range of these parameters. The agreement with the data is quite good, considering the approximate semiclassical nature of the calculated form factor.

To understand the observed oscillations we recall that there are two semiclassical paths which scatter from the illuminated face of the core into the same final direction [17]. One is due to the direct scattering from the core and the second path which depends on the profile of the core involves an additional backwards reflection from the smooth substrate which acts as a mirror. In addition, there is a Fraunhofer or shadow term coming from the region of the mirror surface which is covered by the adsorbate core. These three contributions correspond, respectively, to the three terms inside the parentheses on the right hand side of Eq. (4). The Fraunhofer contribution to the scattering intensity falls off rather rapidly with $\mathbf{Q}$ according to the envelope function $1/Q^3$, but the two illuminated face contributions typically scatter over a large range of angles and they interfere with each other leading to an oscillatory behavior in the scattering intensity at larger **Q**. These oscillations are a type of supernumerary rainbow behavior and have been called reflection symmetry oscillations [19,20]. The peaks and troughs of the oscillations fall at the same points as those of the experiment. The relative changes in phase as a function of energy transfer evident in Fig. 2 are correctly predicted. This clearly indicates that this effect is due to the change in wave vector of the scattered particles as they lose or gain energy upon collision with the adsorbate. The predicted oscillations being stronger than observed is not surprising in view of the assumption of a hard core, and a more sophisticated potential with a soft repulsive part is expected to produce weaker oscillations. It is gratifying to find that the shape of the adsorbed CO on Cu(001) turns out to be quite similar to the shape of CO on Pt(111), determined previously but without TOF resolution [17]. On Pt the CO molecules could be modeled well by a hard hemisphere with a radius of 2.5 Å. The smaller radius of 1.92 Å obtained here for Cu can be explained by the increase in the density of electrons on the CO molecule upon adsorption [21], which is expected to be larger on Pt due to the stronger bonding (binding energy of 1.4 eV compared with 0.58 eV for Cu). It is very interesting to note that the height of $A = 2.3$ Å is nearly identical to the value 2.2 Å for the height of CO islands above the bare Cu surface jellium edge as measured by He scattering [22].

In summary, with helium atom scattering we have observed a novel inelastic interference effect in energy resolved measurements in the annihilation, elastic, and creation peaks for excitation of the frustrated translation mode. A theoretical model was developed to explain the physical nature of the dependence of the multiquantum He scattering peaks as a function of parallel momentum. With the model we extract important information about the size and shape of the adsorbate and the polarization of its lowest frequency vibrations. With the sensitivity and high resolution of He scattering we have demonstrated that characterization and detailed information on these modes can be obtained readily and directly.

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