Observation of a Zone-Center Gap in the Longitudinal Mode of an Adsorbate Overlayer: Xenon on Cu(111)

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Using inelastic scattering of thermal energy He atoms we have determined the phonon dispersion curves in commensurate $(\sqrt{3} \times \sqrt{3})R30°$ Xe monolayers adsorbed on Cu(111). In addition to the well known transverse acoustic mode the dispersion curve of the longitudinally polarized phonon branch could be measured. Since this is the first case where a finite zone-center phonon gap (here 0.4 ± 0.15 meV) has been seen for a Q-resolved phonon branch, a normal mode analysis and theoretical calculations on the phonon excitation probabilities have been carried out to confirm the assignment. From the gap magnitude important information on the corrugation of the Xe-atom–substrate potential is derived. [S0031-9007(97)04932-6]

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Recently the properties of monolayers of noble gas atoms, in particular Xe, adsorbed on solid substrates have attracted interest in connection with fundamental experiments on the microscopic origin of friction carried out by Krim and co-workers [1]. Up to now, however, no consensus has been achieved concerning the proper theoretical modeling of these layers. Two recent attempts to theoretically analyze the results of the friction experiments [1] using molecular dynamics have obtained rather different results [2,3]. These discrepancies may in part be due to uncertainties concerning the proper model potentials describing the corrugation of the metal substrate as seen by the Xe atoms. These uncertainties result from the lack of direct experimental information on the potential energy surface governing the lateral motion of Xe atoms on the substrate. So far it has only been possible to extract indirect information from, e.g., detailed analyses of thermodynamical properties and thermal desorption spectroscopy [4].

In the present Letter we will describe the outcome of experiments where high resolution scattering of thermal energy He atoms (HAS) has been successfully used to determine the dispersion of the longitudinal phonon in the commensurate $(\sqrt{3} \times \sqrt{3})R30°$ Xe overlayer on Cu(111). A detailed analysis of this mode provides two important pieces of information: (1) At the zone center of the surface Brillouin zone [cf. Fig. 1(a)] this mode corresponds to a lateral displacement of the whole Xe layer, and the corresponding frequency thus directly measures the curvature of the potential energy surface describing the interaction of the individual Xe atoms with the substrate. (2) From the slope of the longitudinal phonon dispersion curve (or the velocity of sound) the force-constant coupling between adjacent Xe atoms can be obtained. As to (1) a Q-resolved phonon branch with a finite zone-center phonon gap has not yet been seen experimentally, although in previous neutron scattering studies this quantity has been extracted from the total density of states [5]. With regard to (2) one may expect the force-constant coupling of the adsorbed Xe atoms to be very similar to that predicted from accurate gas-phase potentials [6] or from the analysis of bulk phonon data [7], but recent work has revealed a huge, unexpected softening for the Xe-Xe interaction in adlayers of monatomic thickness [8].

The experiments to be described here were performed in a HAS apparatus with a fixed angle between the incoming and outgoing beam of 90.5° (base pressure 8×10^{-11} torr) described in detail elsewhere [9]. The structural properties of the Xe monolayer [10] were characterized by He-atom diffraction. The width of the adlayer-induced $\frac{1}{3}$ and $\frac{2}{3}$ diffraction peaks in the scan along the $[1\bar{1}0]$ direction

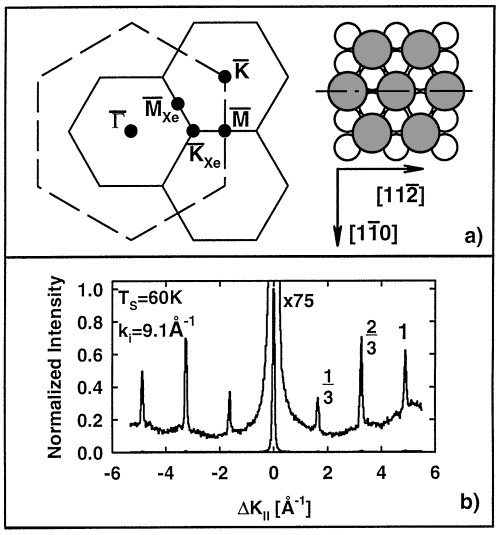

FIG. 1. (a) Diagram of the surface Brillouin zones of the bare Cu(111) surface (dashed line) and the $(\sqrt{3} \times \sqrt{3})R30°$ structure (solid line). The inset shows a hard sphere model of the $(\sqrt{3} \times \sqrt{3})R30°$ Xe/Cu(111) surface. (b) Angular distribution of the $(\sqrt{3} \times \sqrt{3})R30°$ structure recorded along the $[1\bar{1}0]$ direction.

[Fig. 1(b)] reveals the presence of a well-ordered Xe overlayer with $(\sqrt{3} \times \sqrt{3})R30°$ structure [Fig. 1(a)].

Figure 2 shows a series of time-of-flight (TOF) spectra recorded for the same adlayer along the $[11\bar{2}]$ direction. The spectra are dominated by a peak at 2.6 meV (labeled "FT_Z") exhibiting only very little variation with incident angle. This feature can be assigned to a Xe vibration with a polarization vector normal to the surface, which has been seen previously for several noble gas atoms adsorbed on a number of other metal surfaces [11,12]. We note that the measured frequency is similar to that of Xe adsorbed on Cu(100) ($\hbar\omega_Z = 2.7$ meV [8]) and Cu(110) ($\hbar\omega_Z = 2.5$ meV [13]). In addition to this strong peak, the spectra shown in Fig. 2 reveal the presence of a weak feature (labeled "L"), the energy of which is found to strongly disperse with angle of incidence Θ_i (denoted in Fig. 2). Inspection of Fig. 3, where the experimental data are shown together with the results of the lattice-dynamical analysis, which will be discussed later, reveals that this mode is located significantly below the lower bulk band edge of Cu [14] (dotted line in Fig. 3) and must therefore be due to a Xe-induced mode. The intensity of this mode was found to strongly decrease with transferred wave vector so that data points could be obtained only for the first third of the Brillouin zone.

In order to aid the assignment of this mode the dynamical properties of a Cu(111) surface covered by a $(\sqrt{3} \times \sqrt{3})R30°$ monolayer of Xe were determined by carrying out a lattice-dynamical calculation (for details on the computational approach see Ref. [15]). The interaction between nearest-neighbor Cu atoms was accounted for by a single radial force constant $\beta_R^{\mathrm{Cu}} = 28.0$ N/m as obtained from a fit of the bulk phonon dispersion curves [16]. The coupling of Xe atoms (which were placed in on-top sites) to nearest Cu substrate atoms was described by a radial force constant β_R^{Xe} and a tangential force constant β_T^{Xe}, which were treated as parameters, as well as the radial force constant $\beta_R^{\mathrm{Xe,Xe}}$ coupling nearest-neighbor Xe atoms. The results of the calculations are shown in Fig. 3. The agreement with the experimental data is very satisfying, and the calculations thus are consistent with an assignment of the L mode to the longitudinally polarized phonon in the Xe adlayer.

A rather disturbing consequence of this assignment, however, is the fact that the radial Xe-Xe force constant resulting from this fitting procedure, $\beta_R^{\mathrm{Xe,Xe}} = 0.5$ N/m, is significantly smaller than the value predicted from the highly precise HFD-B2 gas-phase potential [6], namely, $\beta_R^{\mathrm{HFD}} = \frac{\partial^2}{\partial^2 r} V(r) = 1.67\ \mathrm{N\,m^{-1}}$.

This large discrepancy, which has recently also been observed for Xe monolayers on Cu(100) [8], is rather surprising considering that previously the gas phase potentials were believed to provide a good approximation for describing the Xe-Xe atoms on the surface of a metal like Cu [4]. In a recent comment on the Xe/Cu(111) results Bruch has suggested a different assignment of the L mode, namely, to a mode of shear horizontal character [17]. In the present case, however, the measurements were recorded along a high symmetry direction with a mirror plane [inset of Fig. 1(a), dash-dotted line], in contrast to the measurements for Xe on Cu(100). The presence of a symmetry plane results in a strict partitioning into two orthogonal classes of vibrational modes [18]: the

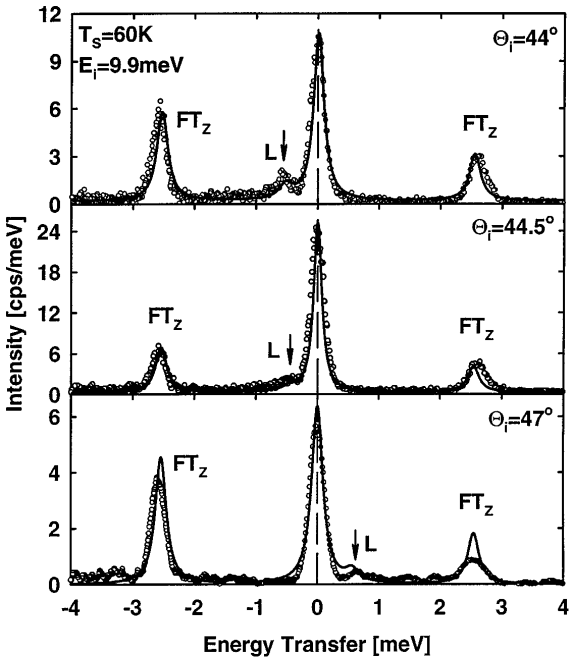

FIG. 2. Series of measured (open circles) and calculated (solid lines) TOF spectra of 1 monolayer (ML) Xe/Cu(111) along the $[11\bar{2}]$ direction. The peaks corresponding to the observed longitudinal mode of the monolayer are denoted by L and marked by an arrow. The vertically polarized mode of the monolayer is denoted by FT_Z.

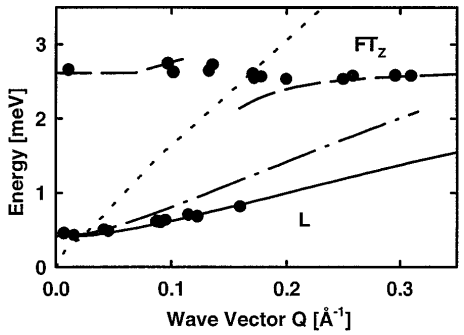

FIG. 3. Experimentally determined and calculated phonon dispersion curves along the $[11\bar{2}]$ azimuth for 1 ML Xe/Cu(111). Besides the best fit achieved for the longitudinal mode of the Xe layer (solid line) also the longitudinal polarized mode calculated using the force constants derived from the gas-phase Xe-Xe pair potential (dash-dotted line) and the projected bulk-phonon edge of the copper substrate (dotted line) are shown. The fitted force constants (see text) were $\beta_R^{\mathrm{Cu}} = 28$ N/m, $\beta_R^{\mathrm{Xe}} = 3.7$ N/m, $\beta_R^{\mathrm{Xe,Xe}} = 0.5$ N/m, and $\beta_T^{\mathrm{Xe}} = 0.086$ N/m.

first class is polarized in the sagittal plane (formed by the phonon wave vector and the surface normal), and the second class consists of purely shear horizontal modes with odd symmetry as regards a reflection at the mirror plane. Since the He atoms cannot couple to such odd modes [19] an assignment to the transversely polarized phonon mode can unambiguously be ruled out.

Considering the above-mentioned controversy on the mode assignment it seems worthwhile, however, not only to exclude the assignment of the L mode as a transversely polarized phonon but to corroborate its assignment to a longitudinal adsorbate phonon by accurately computing the phonon excitation probabilities. Despite the success in the pioneering work of Bortolani *et al.* [20] in describing the excitation probabilities in the scattering of He atoms from surface phonons on clean metal surfaces, this method has so far not been applied to scattering from vibrations in adlayers. In the following we will briefly describe the results of calculations using a novel approach [21] which has already proved successful in reproducing multiphonon excitation probabilities for Xe monolayers on Cu(100) and Cu(111) substrates [22,23]. A detailed description of the calculations will be presented in a forthcoming paper [24].

The probability density that a transfer of energy ΔE and lateral momentum $\Delta\mathbf{K}$ occurs upon collision of a projectile (here the He atom) with a solid substrate is given by the energy and lateral momentum resolved scattering spectrum $N(\Delta E, \Delta\mathbf{K})$ [25]. In the regime of HAS it is very well approximated by the so-called exponentiated distorted wave Born approximation (EBA) expression [21,23]:

$$N^{\mathrm{EBA}}_{\mathbf{k}_i,T_s}(\Delta E, \Delta\mathbf{K}) = \int_{-\infty}^{\infty} \frac{d\tau\, d^2\mathbf{R}}{(2\pi\hbar)^3}\, e^{(i/\hbar)[(\Delta E)\tau - \hbar(\Delta\mathbf{K})\cdot\mathbf{R}]} \exp[2W^{\mathrm{EBA}}(\mathbf{R},\tau) - 2W^{\mathrm{EBA}}(0,0)], \quad (1)$$

with the scattering function

$$2W^{\mathrm{EBA}}(\mathbf{R},\tau) = \sum_{\mathbf{Q},j,k_z} [|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q},j}_{k_z,k_{zi}}(+)|^2[\bar{n}(\hbar\omega_{\mathbf{Q},j}) + 1]e^{-i(\omega_{\mathbf{Q},j}\tau - \mathbf{Q}\cdot\mathbf{R})} + |\mathcal{V}^{\mathbf{K}_i,\mathbf{Q},j}_{k_z,k_{zi}}(-)|^2\bar{n}(\hbar\omega_{\mathbf{Q},j})e^{i(\omega_{\mathbf{Q},j}\tau - \mathbf{Q}\cdot\mathbf{R})}]. \quad (2)$$

Here $\bar{n}(\omega_{\mathbf{Q},j})$ is the Bose-Einstein distribution at temperature T_s and the symbols $|\mathcal{V}^{\mathbf{K}_i,\mathbf{Q},j}_{k_z,k_{zi}}(\pm)|^2$ denote the one phonon emission $(+)$ and absorption $(-)$ probabilities of inelastic He atom-surface scattering [21]. Their explicit form depends on the choice of the total He atom–Xe overlayer interaction.

Previous calculations of the multiphonon spectra for the same collision system at higher incident energies and their comparison with experiment have indicated that the total potential describing the He-Xe adlayer interaction is not obtainable from a straightforward pairwise summation of the gas-phase potentials. It has been found necessary to renormalize the position of its minimum and the softness of the repulsive part ("metallization" of the overlayer) so as to produce the correct ratio of the intensities of multiply excited FT_Z modes [23]. The static part of this renormalized potential was modeled by the Morse potential with the parameters: well depth $D = 4.5$ meV, position of the minimum relative to the Xe atom centers $z_0 = 4.84$ Å, and the range $d = 1.8$ Å. From this the dynamic part of the potential was obtained following the procedure outlined in Ref. [26] with $Q_c = 0.57$ Å^{-1}.

Using the dispersion relations and polarization vectors obtained from the lattice dynamical analysis described above we have calculated the scattering function (2) and thereby the scattering spectrum for the collision conditions typical of the TOF spectra described above. Figure 2 shows comparisons of the experimental and theoretical results for three different angles of incidence. As expected the longitudinal mode, although exhibiting also partial (weak) vertical polarization in this range of Q values, couples significantly weaker to the He atoms. The good agreement of the relative excitation probabilities for the transverse and longitudinal phonon gives additional credibility to the experimental assignment of the experimentally observed L mode to the longitudinally polarized phonon branch.

As mentioned in the introduction one feature of this longitudinal mode is of particular interest, namely, the zone-center gap. The analysis of our data yields a value of 0.4 ± 0.15 meV. In the previous measurements of a Xe monolayer adsorbed on Cu(100) the zone-center phonon gap was found to be zero (within experimental error). This result was expected, since in an incommensurate structure the overlayer is translationally invariant with respect to lateral displacements, the longitudinal vibration ceases to exist at the zone boundary, and a new phonon mode ("Goldstone mode") with zero frequency at the zone center emerges [27].

The energy of the zone-center phonon gap of 0.4 meV seen here can be directly used to estimate the corrugation of the Xe-substrate potential. For this purpose the potential describing the interaction between Xe atom and surface is approximated by [28]

$$V(\mathbf{r}) = E_B[\exp^{-2\alpha(z-z_0)} - 2\exp^{-\alpha(z-z_0)}] + U_0[2 - \cos(kx) - \cos(ky)]\exp^{-\alpha'(z-z_0)}, \quad (3)$$

with E_B the Xe-Cu(111) binding energy, $2U_0$ the approximate activation barrier for diffusion [28], and $k = 2\pi/a$. The parameter α can be obtained from the FT_Z energy via [28] $\alpha = [M\omega_Z^2/(2E_B)]^{-1/2}$, and U_0 can be estimated from the zone-center phonon gap energy $\omega_L(0)$ via $U_0 = M\omega_L(0)^2/k^2$, yielding a total corrugation of $2U_0 = 1.9$ meV.

This corrugation is twice as large as that used by Cieplak *et al.* [2] in their molecular dynamics simulation of the friction in Xe adlayers on Ag(111). Since no dramatic differences are expected between Cu(111) and Ag(111) (He-atom diffraction intensities do not indicate a significant difference in noble gas atom-surface corrugation [29]) the present results suggest that the previous molecular dynamics (MD) simulations [2] should be repeated with improved potentials.

In conclusion, we have determined the major part of an adlayer phonon dispersion curve with a zone-center phonon gap of 0.4 meV. Results from a lattice dynamical analysis and excitation probabilities computed using a recently developed theoretical approach allow for an unambiguous identification of the L mode as dominantly longitudinally polarized phonon, thus virtually eliminating recent concerns on the correctness of this assignment [17]. The present results suggest that potentials used previously to describe the Xe-Xe as well as the Xe substrate interaction do not provide a good description of Xe monolayers.

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