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Dispersion of surface phonons in xenon overlayers physisorbed on the Ag(111) surface

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Computer simulation and lattice dynamics have been used to investigate phonons propagating in monolayers, bilayers, and trilayers of xenon physisorbed on a Ag(111) surface. Agreement with the experimentally determined dispersion of the surface phonons has been achieved by the use of a realistic interatomic potential for the Xe adatoms and a new surface-adatom potential.

The inelastic scattering of helium atoms has proved to be a powerful method of studying surface phonons.[1] The extension of this technique to physisorbed overlayers[2] now offers an important complement to neutron scattering[3] as a means of probing the dynamics of such systems. Surface phonon dispersion curves have recently been measured for monolayer, bilayer, trilayer, and bulk xenon supported on a Ag(111) surface.[4] A dispersionless surface phonon branch for the monolayer was observed to evolve with increasing coverage to a Rayleigh wave behavior for the bulk Xe(111) surface.[4]

Previous experimental[5] and theoretical work[6] on such overlayers lead to a characterization of the relevant adatom-surface and adatom-adatom interactions. We have used a model based on this earlier work to calculate phonon dispersion curves which are compared with the He-beam data. Anticipating our results, we find that the existing surface-adatom potential[6] cannot account for the measured surface phonon dispersion curves. We are therefore led to propose a new softer adatom-surface potential which has enhanced dispersion interactions in the region of the potential minimum.[7] The revised model, coupled with a realistic Xe-Xe potential[8] which includes substrate mediation effects,[9,10] now gives a good account of the He-beam data.

We begin with a review of the salient facts. Experimental data indicate that a xenon monolayer is not in registry with a Ag(1$\underset{\circ}{1}$1) surface. At 20 K the monolayer Xe-Xe spacing (4.42 Å) is slightly larger than that of the bulk solid,[5] whereas the bilayer and trilayer have essentially the bulk value 4.33 Å.[4] At low temperatures the mean height of the monolayer above the Ag ion cores is 3.55 ± 0.10 Å.[11] The depth of the surface-adatom holding potential (172 meV) has been estimated[6] from the latent heat of adsorption of a monolayer (225 meV) by allowing for substrate mediated lateral interactions (65 meV) as well as the contribution from adsorption dipoles (6 meV), three-body forces (1.5 meV), and the zero-point energy (2.6 meV). At larger adatom-surface separations z the holding potential is known to have the form $-C_3/(z-d)^3$, where d is the height of the image plane above the Ag ion cores.[7] The original Debye-Waller factor measurements yield a value of 480 meV/Å^2 for the curvature at the minimum of the holding potential,[6] whereas a later determination[5] implies a curvature of 300 ± 60 meV/Å^2. We have used this information to parametrize surface-adatom potentials of the form $V(z) = A/z^m - C_3/(z-d)^3$, which, together with a realistic[8] substrate mediated Xe-Xe potential,[10] completes the characterization of the relevant interactions.

We have studied phonon vibrations in Xe overlayers physisorbed on a rigid Ag substrate using both conventional lattice dynamics[12] and molecular dynamics (MD) calculations.[13] In the latter case the Xe atoms were initially arranged (12×12) on triangular lattices with lattice constant $a = 4.33$ Å, periodic boundary conditions being used to simulate infinite layers. For the trilayer an hcp stacking sequence was adopted. The equations of motion were integrated using standard methods, the lateral potentials being truncated at 15 Å. An initial equilibration period was used to scale the temperature to the desired value (usually 20 K), and to relax the overlayer spacings normal to the surface. Phase-space trajectories were then collected for longer periods, typically 100 ps, in order to study the phonons.[14]

In the lattice dynamics calculations the required dynamical matrix was evaluated from the derivatives of the surface-adatom and adatom-adatom potential in standard fashion, with an option to optimize both the vertical and lateral lattice spacings if desired. If we neglect the dilation due to adsorption dipoles,[6] the zero-point energy, and three-body forces, the optimized monolayer spacing is 4.378 Å, which differs by only 1% from the experimental value.[5] We have ignored the contribution of these three effects to the phonon frequencies.

The modes propagating in the overlayers can be characterized by a two-dimensional wave vector $\bar{k} = (k_x, k_y)$, which is perpendicular to the surface normal $\bar{n}$; the plane defined by $\bar{k}$ and $\bar{n}$ is called the sagittal plane.[12] For a given $\bar{k}$ the modes are conveniently labeled by their dominant polarization characteristic: SH (shear horizontal) when the displacements are normal to the sagittal plane, $SP_\perp$ and $SP_\parallel$ when the displacements are in the sagittal plane, perpendicular and parallel to $\bar{k}$. With this classification in mind the appropriate correlation functions for probing the phonons via molecular dynamics have the form

$$F(\bar{k},t) = \langle f(\bar{k},t) f(-\bar{k},0) \rangle ,$$

with

$$f(\bar{k},t) = \sum_i W_i(t) \exp(i\bar{k}\cdot\bar{R}_i) ,$$

where $W(SP_\parallel) = (\bar{k}\cdot\bar{u}_i)$, $W(SP_\perp) = (\bar{n}\cdot\bar{u}_i)$, and $W(SH)$

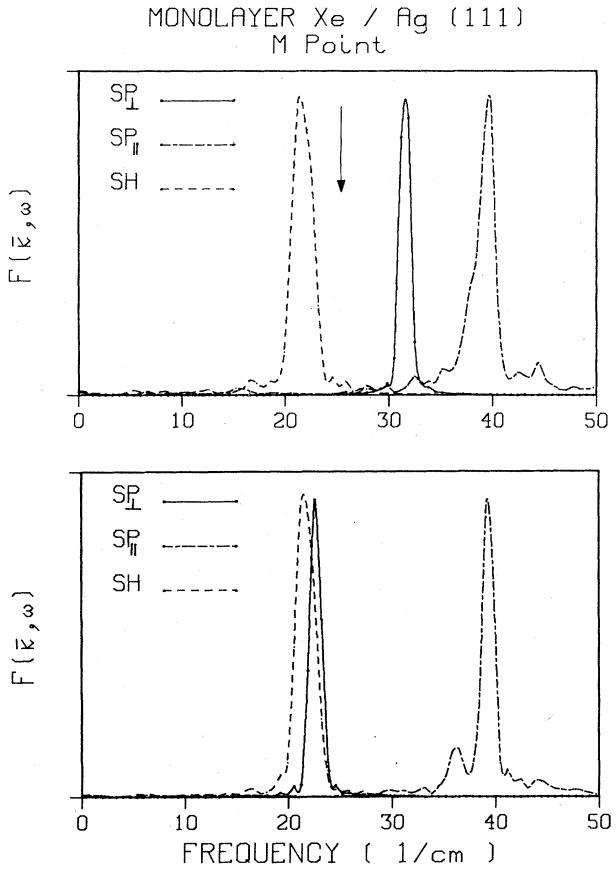

FIG. 1. Phonon response functions $F(\bar{k},\omega)$ in arbitrary units for the Brillouin zone M point calculated for a Xe monolayer on Ag(111) using molecular dynamics at 20 K. The measured $SP_\perp$ phonon frequency is 22.6 cm^{-1} (Ref. 4). The upper curves employ a surface-adatom potential fitted to the original Debye-Waller factor data (Ref. 6). The arrow indicates the $SPj_\perp$ peak position based upon revised Debye-Waller data (Ref. 5). The lower curves are based on a surface-adatom potential fitted to the experimental $SP_\perp$ frequency.

$=(\bar{n}\cdot\bar{k})\cdot\bar{u}_i$. The summation index i runs over all the atoms in a given layer and $\bar{u}_i$ is the time-dependent displacement from the mean positions $\bar{R}_i$. The phonon frequencies are determined from the peaks in the response function $F(\bar{k},\omega)$ which has been evaluated using a direct method[14]

$$F(\bar{k},\omega)=\lim_{\tau\to\infty}|f(\bar{k},\omega)|^2/\tau \ ,$$

where

$$f(\bar{k},\omega)=\int_0^\tau \exp(i\omega t)f(\bar{k},\tau)\,d\tau \ .$$

In lattice dynamics the $\bar{k}$ vectors can be chosen at will but in MD our system size limits us to six distinct points on the branch $\Gamma\to M$, two for $M\to K$, and four for $K\to\Gamma$. Figure 1 shows $F(\bar{k},\omega)$ for the monolayer M-point phonons calculated using potentials of the type described above. A model fitted to the original Debye-Waller factor data, the adatom-surface separation,[11] and the holding potential (172 meV) has a $SP_\perp$ peak at 32 cm^{-1}, in poor agreement with

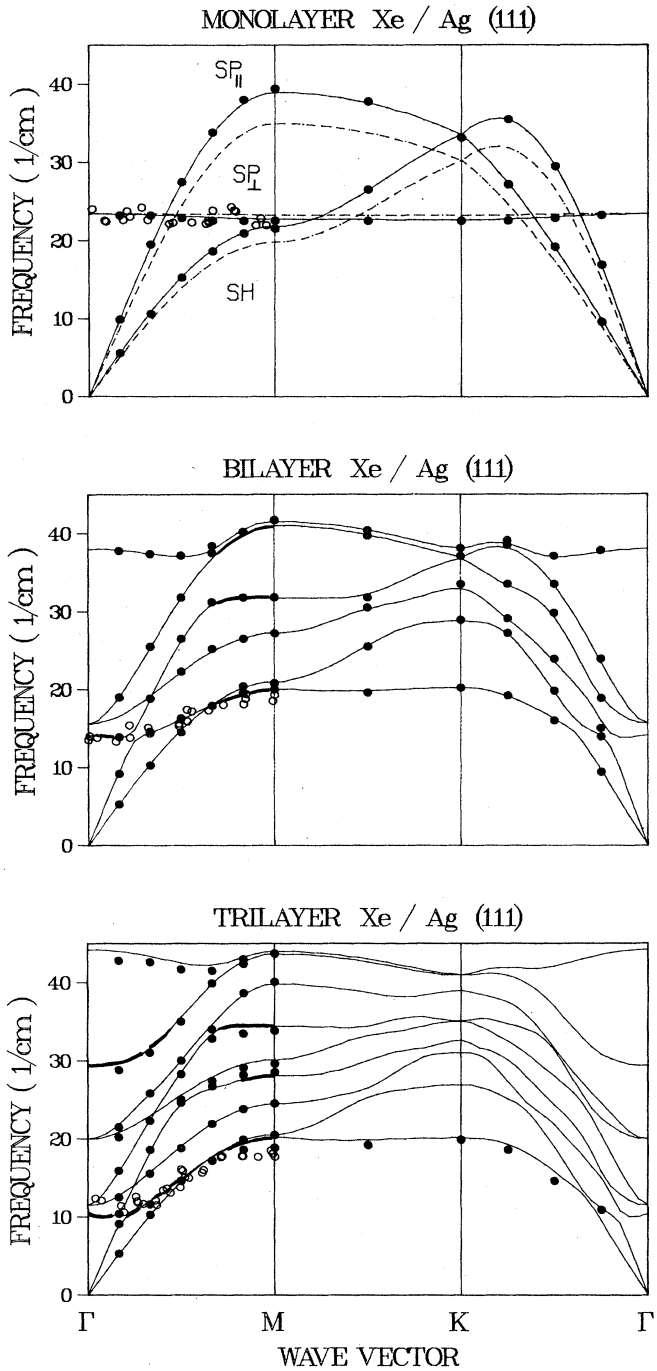

FIG. 2. Phonon dispersion curves for a monolayer, bilayer, and trilayer of Xe on Ag(111) based on a revised surface-adatom potential. The bold portions of the dispersion curves indicate that upper layer atoms have dominant motions with $SP_\perp$ polarization and are thus, in principle, probed by the atomic beam. The full circles indicate peaks in $F(\bar{k},\omega)$ derived from MD calculations at 20 K. The solid curves are lattice dynamics results with the same lateral spacing of 4.33 Å, whereas the dashed monolayer curves use a spacing of 4.378 Å. The bilayer curves were evaluated using the vertical spacings determined in the MD calculations, whereas for the monolayer and trilayer, statically optimized spacings were used. The softening of the trilayer M-point $SP_\perp$ phonon due to the vertical thermal expansion should be noted. The He atomic beam data of Ref. 4 are shown as open circles.

the experimental value[4] of 22.6 cm^{-1}. Use of the revised Debye-Waller factor data[5] yields a $SP_\perp$ peak at 25 ± 3 cm^{-1}, which is consistent with the beam data. However, in view of the relatively large uncertainty in the revised Debye-Waller factor data[5] we prefer to constrain the surface-adatom potential to also fit the observed monlayer M-point frequency, rather than the Debye-Waller factor. The resulting potential ($m=8$, $d=1.80$ Å, $A=12350$ eV Å,[8] $C_3=3.524$ eV Å^3) gave the dispersion curves for the monolayer, bilayer, and trilayer that are compared in Fig. 2 with the MD calculations and the beam data.[4] The monolayer lattice dynamics results show that lateral thermal expansion predominantly affects the SH and $SP_\parallel$ modes, whereas the $SP_\perp$ branch that is probed by the He-beam data is relatively insensitive to this effect.

The bilayer results shown in Fig. 2 indicate that provided the same interatomic spacings are used there is excellent agreement between the two independent methods of calculating the phonon dispersion curves. This fact plus the sharp response functions (Fig. 1) suggest that explicit anharmonic effects are small, at least at 20 K. It should be noted that in the trilayer case there is an important softening of the $SP_\perp$ branches due to thermal expansion normal to the surface. The agreement between the theory and the measurements (Fig. 2) was achieved via an enhanced surface-adatom attractive interaction, i.e., we employed $d=1.80$ Å, rather than the recommended value[7] $d=1.42$ Å. The need for additional attractive interactions accords well with theoretical expectation, since the term $-C_3/(z-d)^3$ is only the leading contribution of an asymptotic series.[15,16] Indeed, we have confirmed that a surface-adatom potential of the form $A\exp(-az)-C_3/(z-d)^3-C_5/(z-d)^5$, with d fixed at the theoretical value[7] 1.42 Å and both C_3 and C_5 taken from theory,[15] fits the beam data equally well.

In summary, it appears that inelastic scattering of the atoms from overlayers is a powerful means of characterizing adatom-surface interactions in systems where the heavy mass of the physisorbed atoms makes direct atom-surface scattering[1] very difficult.

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