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Enhanced creation of dispersive monolayer phonons in Xe/Pt(111) by inelastic helium atom scattering at low energies

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Conditions likely to lead to enhanced inelastic atomic scattering that creates shear horizontal (SH) and longitudinal acoustic (LA) monolayer phonons are identified, specifically examining the inelastic scattering of $^4$He atoms by a monolayer solid of Xe/Pt(111) at incident energies of 2–25 meV. There is strong inelastic scattering for both dispersive phonon branches (SH and LA) of the monolayer at incident energies below 8 meV. Several improvements enable more complete wave packet calculations of the inelastic scattering than in previous work. Long propagation times are made feasible by adding an absorbing potential at large distance. The times now extend to beyond 100 ps and enable a clarification of processes involving transient trapping of the He atoms. The wave packet is made more monochromatic by significantly increasing the spatial width of the initial Gaussian shape. The narrower energy distribution in the incident beam then enables a demonstration of strong energy dependence of the scattering over a scale of less than 0.3 meV. © 2007 American Institute of Physics. [DOI: 10.1063/1.2786990]

I. INTRODUCTION

Inelastic scattering from a nearly harmonic lattice and its low-temperature thermodynamics are expressed in terms of the properties of the excitation quanta, the phonons, of the normal modes of vibration. Thus, determining the phonon dispersion relations is basic to a fundamental characterization of the response of the lattice. It is now feasible to do such measurements on single monolayer solid domains using low energy inelastic helium atom scattering (HAS). An unanticipated result of the experiments was that all branches of the dispersion relations were accessed for wave vectors near high-symmetry azimuths in the first Brillouin zone. In a previous paper, denoted as Paper I, we demonstrated that the anomalous excitation of shear horizontal (SH) phonon modes by HAS from a physically adsorbed monolayer can be understood using a strong coupling inelastic scattering theory and known atomic interactions. The basic calculation was to generate the time-dependent solution for wave packet scattering, with the inelastic processes treated in the one-phonon creation approximation. The apparent violation of basic polarization selection rules can be an intrinsic effect arising from a small misalignment, $1^\circ$–$2^\circ$, of the scattering plane relative to high-symmetry axes of the monolayer solid lattice. Such small misalignments are common in experiments on physisorbed monolayers, but they had been assumed to have no serious consequences.

The present paper, we attempt to provide some guidance for future experiments by identifying conditions that enhance the strength of the inelastic scattering for creating dispersive phonons, especially by treating lower incident energies. Also we determine the time scales for transient trapping of the incident atom that has been noted in previous calculations and which extends over times of 20–80 ps in several cases. Our results are for the scattering of $^4$He by a Xe/Pt(111) monolayer at incident energies of 2–25 meV and the parameter space has been reduced by specifying that the geometry is such that the incident angle leads to an inelastic outgoing wave at an angle corresponding to the scan curve geometry of the principal experiments. (Fig. 1). The strong inelastic scattering and the long transients in the elastic scattering both are associated with strong coupling effects in low energy scattering, but they do not coincide with resonance conditions, e.g., they do not seem to be directly associated with selective adsorption resonances. Quantum reflection is a phenomenon at far lower energy than treated here.

We find that the inelastic scattering generally is enhanced as the incident wave packet energy $E_i$ decreases from 8 to 4 meV, i.e., still about 2 meV above the threshold for most of the cases treated here. We also calculate the response as a function of energy $E_f$ near 8 meV, with energy increments of 0.15 meV, and demonstrate that there are large variations in the scattered strengths for energy variations of order 0.3 meV. Together these results suggest that a fruitful line for experiments will be to explore scattering energies in the range 4–8 meV with a resolution of better than 0.3 meV.

There are several improvements in the methodology relative to Paper I. (1) The calculations are extended to much longer propagation times to ensure that the scattering event is completed. The packet propagates on a bounded space grid, so some of the packet reaches the far boundary while some is still near the monolayer. Therefore, an absorbing potential is added at large perpendicular distance from the monolayer.
II. THEORY

A. Notation and definitions

The mass of an atom in the incident beam ($^4$He in this paper) is denoted $m$ and of an atom in the target monolayer [Xe/Pl(111)] is denoted $M$. The monolayer is a regular planar triangular lattice incommensurate with the substrate and with one atom per unit cell and nearest-neighbor spacing $L_{nn}$. Then, a monolayer of $N$ atoms has $N$ wave vectors in the first Brillouin zone. The reciprocal lattice is spanned by primitive vectors $g_1$ and $g_2$ of length $g_0=4\pi/(L_{nn}\sqrt{3})$ and at an angle 120° to each other.

There are three branches to the dispersion relation, denoted S for the polarization primarily perpendicular ($\hat{z}$) to the monolayer plane and SH (shear horizontal) and LA (longitudinal acoustic) for the branches primarily in the plane and which have the pure designated polarizations for wave vectors along high-symmetry azimuths of the monolayer. $\omega(q,\lambda)$ is the frequency of the normal mode with wave vector $q$ in the branch $\lambda$ and $\hat{e}(q,\lambda)$ is the normalized polarization vector. Vibrations perpendicular to the monolayer plane (S mode) decouple from those in the plane and are nearly dispersionless.

Let the incident probe atom ($^4$He) wave vector $k_i=(k_{i||},k_{i\perp})$ and energy $\epsilon_i=h^2k_i^2/2m$. The final energy is $\epsilon_f=\epsilon_i-\hbar\omega(q,\lambda)$ for inelastic scattering creating a $(q,\lambda)$ phonon. The channels are labeled by the parallel wave vectors $k_j=(k_{j||},k_{j\perp})$, where $g=i g_1+j g_2$ with $i$ and $j$ integers. The corresponding free-atom kinetic energy is $\epsilon_j=h^2k_j^2/2m$ and channels are defined to be closed or open according to whether the sign of $\Delta=\epsilon_f-\epsilon_j$ is positive or negative. For diffraction (elastic scattering), the $q=0$ case of these definitions is used. The $g=0$ channel is termed the specular channel.

Depending on the parameters, a channel with a given $g$ can be open or closed for one or both elastic and inelastic scattering. As a scale for discussing the closed channels, we use the bound state energy levels $\epsilon_g$ of the atom in the laterally averaged potential $V_0(z)$ from the monolayer. Table I gives the properties of these states. For $q=0$, the condition $\Delta=|\epsilon_g|$ is an approximation to selective adsorption resonances which neglects band structure effects.

Throughout the paper, energies are given in meV and $K$, lengths in Å, and wave numbers in Å$^{-1}$.

### Table I

<table>
<thead>
<tr>
<th>State</th>
<th>Energy (meV)</th>
<th>$\langle z \rangle$ (Å)</th>
<th>$\sigma_z$ (Å)</th>
<th>Classical turning points (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Inner</td>
</tr>
<tr>
<td>1</td>
<td>$-5.434$</td>
<td>3.79</td>
<td>0.38</td>
<td>3.19</td>
</tr>
<tr>
<td>2</td>
<td>$-2.365$</td>
<td>4.57</td>
<td>0.79</td>
<td>3.07</td>
</tr>
<tr>
<td>3</td>
<td>$-0.863$</td>
<td>5.92</td>
<td>1.20</td>
<td>3.03</td>
</tr>
<tr>
<td>4</td>
<td>$-0.259$</td>
<td>8.37</td>
<td>1.93</td>
<td>3.02</td>
</tr>
<tr>
<td>5</td>
<td>$-0.059$</td>
<td>13.19</td>
<td>3.36</td>
<td>3.01</td>
</tr>
</tbody>
</table>

The inner and outer classical turning points are determined by the requirement that an atom of mass $m$ cannot pass through the layer. They are given in Å.

\[\Theta_z = \Theta_{SD} = 95.8°\] in one set of experiments (Ref. 6) and the present calculations. The magnitude $k_f$ is set by energy conservation and $\Theta_f$ is chosen to make $k_f-k_i=\mathbf{q}$, corresponding to the specular channel ($g=0$). The plane of incidence is specified by $\mathbf{k}_i$ and $\hat{z}$.
parallel to the surface and a Gaussian for the spatial distribution
wave is rather monochromatic; i.e., the spread in the
ponent
II C–II E.
full description of the theory but repeat a few central parts
in the
uct of a plane wave function for the lateral motion
of the incident atom is a wave packet formed from the prod-

The potential energy of interaction $V_s(r, z)$ of the probe
atom with the static monolayer is decomposed with the
Steele series
\begin{equation}
V_s(r, z) = V_0(z) + \sum_g V(g, z) \exp(ig \cdot r),
\end{equation}
where $g$ are the monolayer reciprocal lattice vectors.

The Schrödinger equation for the channel amplitudes in
the elastically scattered (diffracted) wave function $\Psi_0$ is
\begin{equation}
\frac{i\hbar}{2m} \frac{\partial \psi_i(z, t)}{\partial t} = \frac{\hbar^2}{2m} \left[ (\mathbf{g} + \mathbf{k}_i)^2 - \frac{\partial^2}{\partial z^2} \right] \psi_i(z, t) + \sum_{g'} V(\mathbf{g} - \mathbf{g}', z) \psi_{g'}(z, t).
\end{equation}
The final term on the right-hand side of the equation couples
the channels with potential energy coefficients $V(\mathbf{g} - \mathbf{g}', z)$.

The Schrödinger equation for the channel amplitudes in
the one-phonon inelastic wave function $\Psi_1$ is

\begin{table*}[h]
\centering
\caption{Phonon energies in meV as a function of wave number $q$ in Å$^{-1}$ along an azimuth at 2.6$^\circ$ to the $\Gamma M$ azimuth of a xenon monolayer with $L_{\text{w}}=4.33$ Å, calculated for the HFD-B2 potential with McLachlan substrate-mediated interactions as in Paper I. The S-mode energy is $\hbar \omega_s=3.5$ meV.}
\begin{tabular}{cccc}
\hline

$q$ (Å$^{-1}$) & $\hbar \omega(q)$ (meV) \\
\hline
0.125 & 0.636 & 1.12 \\
0.250 & 1.24 & 2.18 \\
0.500 & 2.21 & 3.91 \\
\hline
\end{tabular}
\end{table*}

\begin{table*}[h]
\centering
\caption{Summary of angles of incidence $\Theta_i$ and asymptotic decay times $\tau$ for the elastic (diffracted) wave function $\Psi_0$. The plane of incidence is at 2.6$^\circ$ to the $\Gamma M$ axis of the Xe/Pt(111) monolayer and the phonon wave vectors $\mathbf{q}$ are along this azimuth, as in Paper I. For each case, $\Theta_i$ is given as a second line below the $\tau_1$ and the columns are ordered to make a monotonic variation of $\Theta_i$ as one goes across a row. Calculations of $\Theta_i$ are for scan curve conditions at $\Theta_{35}=95.8^\circ$ and the specified inelastic scattering mode and wave vector. Energies $E_i$ are in meV, wave numbers $q$ in Å$^{-1}$, and times $\tau$ in ps. The … denote cases where a second decay time $\tau_2$ could not be determined.}
\begin{tabular}{cccccccc}

\multicolumn{4}{c}{$\tau_1$ (ps)} & \multicolumn{4}{c}{$\tau_2$ (ps)} \\
\hline

$q$ (Å$^{-1}$) & $-0.125$ & $-0.125$ & $-0.25$ & $-0.25$ & $-0.125$ & $-0.125$ & $-0.25$ & $-0.25$ \\
$E_i$ (meV) & SH & LA & SH & LA & SH & LA & SH & LA \\
\hline

2.0 & 2.7 & 5.2 & 34.0 & 58.5 \\
& 38.98$^\circ$ & 59.93$^\circ$ & 13.7$^\circ$ & 35.1$^\circ$ & 10 & … & 130 \\
2.5 & 5.9 & 8.9 & 12.0 & 21.3 & 20.5 & 33.5 & 82.3 \\
& 43.20$^\circ$ & 40.68$^\circ$ & 37.85$^\circ$ & 31.28$^\circ$ & 35.09$^\circ$ & 35.1$^\circ$ & 66.8 & 33.5 & 82.3 \\
5.0 & 1.9 & 4.3 & 14.8 & 11.3 & 21.7 & 66.8 & … \\
& 54.00$^\circ$ & 42.10$^\circ$ & 39.71$^\circ$ & 35.09$^\circ$ & 35.1$^\circ$ & 35.1$^\circ$ & 35.1$^\circ$ & 35.1$^\circ$ & 35.1$^\circ$ \\
6.0 & 2.4 & 3.0 & 18.9 & 5.5 & 10.9 & 14.5 & … & 29.1 \\
& 44.54$^\circ$ & 43.01$^\circ$ & 40.92$^\circ$ & 37.36$^\circ$ & 37.36$^\circ$ & 37.36$^\circ$ & 37.36$^\circ$ & 37.36$^\circ$ & 37.36$^\circ$ \\
8.2 & 2.9 & 4.0 & 5.4 & 8.5 & 17.2 & 20.3 & … & 29.1 \\
& 45.25$^\circ$ & 44.20$^\circ$ & 42.50$^\circ$ & 40.15$^\circ$ & 40.15$^\circ$ & 40.15$^\circ$ & 40.15$^\circ$ & 40.15$^\circ$ & 40.15$^\circ$ \\
16.6 & 2.1 & 4.4 & 12.3 & 2.0 & 13.6 & 14.4 & … & 14.9 \\
& 46.34$^\circ$ & 45.84$^\circ$ & 44.74$^\circ$ & 43.72$^\circ$ & 43.72$^\circ$ & 43.72$^\circ$ & 43.72$^\circ$ & 43.72$^\circ$ & 43.72$^\circ$ \\
26.5 & 1.9 & 2.1 & 3.6 & 3.2 & 6.5 & 7.3 & … & 9.5 \\
& 46.77$^\circ$ & 46.47$^\circ$ & 45.63$^\circ$ & 45.02$^\circ$ & 45.02$^\circ$ & 45.02$^\circ$ & 45.02$^\circ$ & 45.02$^\circ$ & 45.02$^\circ$ \\
\hline
\end{tabular}
\end{table*}
C. Absorbing potential

In order to allow for the time evolution of an atom transiently trapped in a bound state of $V_0(z)$, it is necessary to propagate the system for long times, usually to at least 50 ps and even longer for low incident atom energy. Then, artifacts might arise from components of the outgoing wave functions that reflect from the far end of the spatial grid at $z_{\max}$. To eliminate the reflection, we add an absorbing potential $-iU$ of a form treated by Vibók and Balint-Kurti.\(^\text{16}\) In the notation of Appendix A, the function $U$ is

$$U(z) = A \exp[-2L/(z-z_U)], \quad z_U < z < z_U + L,$$

and is zero otherwise. Ordinarily, we take $z_U = z_{\max} - L$, so $U$ only acts near the far end of the grid. The values of $A$ and $L$ depend on the incident energy and, based on the optimization study of Vibók and Balint-Kurti,\(^\text{16}\) we use $L = 8\pi/|k_{\parallel}|$ and $A = 24.24\, (h^2 k_{\parallel}^2 / 2m)$. These are set to give very small total reflected and transmitted (i.e., nonabsorbed) intensities for the specular elastic channel and, in our experience, these intensities are very small in other channels too.

The time propagation scheme for the calculations which include $U$ is modified\(^\text{27}\) as described in Appendix A.

D. Debye-Waller factor

We make ad hoc estimates of the effect of thermally excited monolayer vibrations on scattered strengths using the harmonic approximation to the Debye-Waller factor $F_{DW}$. The effect of the complex platinum surface dynamics\(^\text{28}\) on the incommensurate monolayer is omitted; some model calculations\(^\text{29}\) for dynamically coupled higher-order commensurate xenon-platinum systems had found only small shifts in the xenon density of states (mean-square displacements were not evaluated, though).

The structure factor $S(\Delta k)$ for scattering with wave vector transfer $\Delta k$ from a lattice with average positions $s_j$ and fluctuations $u_j$ about those positions is

$$S(\Delta k) = \left\langle \exp\left[i\Delta k \cdot (s_j + u_j)\right] \right\rangle = \sum_j \exp\left[i\Delta k \cdot (s_j + u_j - u_0)\right].$$

(6)

Thermal effects greatly reduce $S(\Delta k)$ at large $|\Delta k|$. For diffraction by a two dimensional (2D) (planar) Bravais lattice ($\hat{z}$ denotes a unit vector perpendicular to that plane), where the parallel wave vector transfer is a monolayer reciprocal lattice vector $g$, $\Delta k = \Delta k_{\parallel} \hat{z} + g$, the structure factor becomes

$$S(\Delta k) = \sum_j \exp\left[i\Delta k \cdot (u_j - u_0)\right].$$

(7)

The harmonic approximation has been used in the second equality. With neglect of substrate corrugation, the perpendicular and parallel normal modes of vibration decouple,
The whisker tensor vectors in the first Brillouin zone. The dominant contribution where
diagonal and is expressed in terms of the longitudinal and transverse speeds of sound by

\[ \langle [\Delta \mathbf{k} \cdot (\mathbf{u}_j - \mathbf{u}_0)]^2 \rangle = \Delta k_z^2 \langle (u_{jz} - u_{0z})^2 \rangle + \langle [\mathbf{g} \cdot (\mathbf{u}_j - \mathbf{u}_0)]^2 \rangle. \]  (8)

The \( z \) average simplifies because the S-mode frequency \( \omega_z \) has negligible \( q \) dependence:

\[ \frac{1}{2} \langle (u_{jz} - u_{0z})^2 \rangle = \langle u_{jz}^2 \rangle = \frac{\hbar}{2M \omega_z} \coth(\beta \hbar \omega_z/2). \]  (9)

The last term in Eq. (8) reduces to a tensor average over the normal modes:

\[ \frac{1}{2} \langle [\mathbf{g} \cdot (\mathbf{u}_j - \mathbf{u}_0)]^2 \rangle = \mathbf{g} \cdot \mathbf{M}_j \cdot \mathbf{g}, \]  (10)

where

\[ \mathbf{M}_j = \left( \frac{\hbar}{2NM} \right) \sum_{q,\nu} (1 - \cos \mathbf{q} \cdot \mathbf{s}_j) \times \coth(\beta \hbar \omega_{q,\nu}/2) \hat{e}_{q,\nu} \hat{e}_{q,\nu}^* / \omega_{q,\nu}. \]  (11)

In Eq. (11), the sum goes over two polarizations \( \nu \) (nominally SH and LA) with unit vectors \( \hat{e}_{q,\nu} \) and over the \( N \) wave vectors in the first Brillouin zone. The dominant contribution to the tensor \( \mathbf{M}_j \) arises from small wave numbers because of the factors \( 1/\omega_{q,\nu} \). For the assumed experimental conditions (xenon monolayer with \( T \approx 50 \) K), the mode populations are given by the equipartition theorem. Then, the tensor is nearly diagonal and is expressed in terms of the longitudinal and transverse speeds of sound by

\[ \mathbf{M}_j \approx \mathbf{I}(k_B T/2M)[(1/e_s^2)] + \langle \mathbf{g} \cdot (\mathbf{u}_j - \mathbf{u}_0) \rangle + \gamma. \]  (12)

The sum in Eq. (12) varies logarithmically with \( |s_j| \) at large \( |s_j| \), a well-known anomaly of the 2D harmonic lattice, and we evaluate the sum over neighbors in Eq. (6) for a patch containing 250 000 atoms, roughly the number of atoms on the terraces for the finest Pt(111) crystals.

At low energies, \( E_i \) is comparable to the depth of the atom-monolayer potential energy [e.g., \( E_i \approx 4–6 \) meV and \( V_{\text{diff}}(\text{min}) = -8 \) meV for He/Xe/Pt(111)]. The effect on the Debye-Waller factor is estimated using the Beeby correction, although its reliability at such low energies \( E_i \) has not been established. The magnitudes of the perpendicular components of the wave vector in \( \Delta k_z = |k_{z1}| + |k_{z2}| \) are modified to reflect the inner potential:

\[ |k_{zj}| \rightarrow \sqrt{k_{zj}^2 + 2mD_0 \hbar^2}, \]  (13)

where \( D_0 \) is the magnitude of the ground state energy of \( V_{\text{diff}}(z) \) and \( D_0 = 5.43 \) meV from Table I. The final form of the Debye-Waller factor is then

\[ F_{\text{DW}} = \sum_j \exp[\Delta k_z^2 (u_{jz}^2) - \mathbf{g} \cdot \mathbf{M}_j \cdot \mathbf{g}]. \]  (14)

The Debye-Waller factor for the phonon creation strengths is estimated by using \( \mathbf{g} - \mathbf{g} - \mathbf{q} \) in Eq. (14).
TABLE V. Diffracted strengths for the cases in Table IV from a thermally excited monolayer. These data are formed from the data of Table IV by multiplying by the Debye-Waller factor at 50 K, including the Beeby correction.

<table>
<thead>
<tr>
<th>(E_i) (meV)</th>
<th>(I(g=0))</th>
<th>(\bar{T})</th>
<th>(\sigma(t))</th>
<th>(I(g)_{\text{max}})</th>
<th>(S/\ln(N_{\text{spec}}))</th>
<th>(N_{\text{spec}})</th>
<th>(N_{&gt;})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2⁺</td>
<td>0.108</td>
<td>0.087</td>
<td>0.031</td>
<td>0.123</td>
<td>0.953</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>4⁺</td>
<td>0.117</td>
<td>0.041</td>
<td>0.042</td>
<td>0.121</td>
<td>0.795</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>5⁺</td>
<td>0.124</td>
<td>0.024</td>
<td>0.031</td>
<td>0.124</td>
<td>0.791</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>6⁺</td>
<td>0.098</td>
<td>0.020</td>
<td>0.024</td>
<td>0.0986</td>
<td>0.819</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>8.2⁺</td>
<td>0.079</td>
<td>0.015</td>
<td>0.016</td>
<td>0.0792</td>
<td>0.800</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>16.6⁺</td>
<td>0.029</td>
<td>0.003</td>
<td>0.005</td>
<td>0.0298</td>
<td>0.747</td>
<td>41</td>
<td>0</td>
</tr>
<tr>
<td>26.5⁺</td>
<td>0.008</td>
<td>0.001</td>
<td>0.002</td>
<td>0.0129</td>
<td>0.695</td>
<td>65</td>
<td>2</td>
</tr>
<tr>
<td>7.75⁺</td>
<td>0.043</td>
<td>0.013</td>
<td>0.016</td>
<td>0.0518</td>
<td>0.802</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>7.90⁺</td>
<td>0.086</td>
<td>0.013</td>
<td>0.020</td>
<td>0.0861</td>
<td>0.756</td>
<td>19</td>
<td>0</td>
</tr>
<tr>
<td>8.05⁺</td>
<td>0.123</td>
<td>0.012</td>
<td>0.026</td>
<td>0.123</td>
<td>0.660</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>8.2⁺</td>
<td>0.120</td>
<td>0.012</td>
<td>0.024</td>
<td>0.120</td>
<td>0.688</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>8.35⁺</td>
<td>0.099</td>
<td>0.011</td>
<td>0.020</td>
<td>0.0996</td>
<td>0.723</td>
<td>21</td>
<td>0</td>
</tr>
<tr>
<td>8.50⁺</td>
<td>0.099</td>
<td>0.012</td>
<td>0.021</td>
<td>0.0996</td>
<td>0.726</td>
<td>22</td>
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</tr>
<tr>
<td>8.65⁺</td>
<td>0.122</td>
<td>0.012</td>
<td>0.024</td>
<td>0.122</td>
<td>0.692</td>
<td>22</td>
<td>0</td>
</tr>
</tbody>
</table>

\(\text{FWI}=100, N_{\text{ZO}}=375.\)  
\(\text{FWI}=600, N_{\text{ZO}}=1960.\)

E. Scattering rates

The solutions to Eq. (3) are used to form inelastic channel norms on the grid,

\[N_{q,t}(g,t) = \int |S_{q,t}(g,z)|^2 dz,\]

and the corresponding averages of \(z\). Similarly, the diffraction channel norm on the grid is defined by

\[N_{\text{diff}}(g,t) = \int |\psi_{q,t}(z)|^2 dz.\]

The absorbed intensities calculated with Eq. (A4) are added to these to form the net channel norms \(N_{q,t}(g,t)\) and \(N_{\text{diff}}(g,t)\). The final values are determined at a large enough time \(t_f\) (\(t_f \approx 40\) ps for \(E_i \approx 8\) meV) that most of the wave packet has propagated to distances more than 100 Å from the monolayer and much of the scattered intensity has been absorbed by the potential \(V_{\text{diff}}\).

The final calculated inelastic and elastic strengths incorporate additional factors and are \(I_{\text{inel}}(q,t) = (k_f/k_i)N_{q,t}(g,t)F_{DW}\) and \(I_{\text{el}}(g)=N_{\text{diff}}(g,t)F_{DW}\), respectively. The Debye-Waller factor \(F_{DW}\) is given in Eq. (14). \(I_{\text{inel}}\) also has a factor \(k_f/k_i\), where \(k_f\) and \(k_i\) are the final wave number and perpendicular component of the initial wave vector,\(^{31}\) and a factor arising from thermally excited phonons in the target monolayer: \(^{20}\)

\[f_{q,t}(T) = 1 + \tilde{h}[\omega(q,t)] = 1/[1 - \exp(-\tilde{h} \omega(q,t)/k_B T)].\]

F. Interactions and scattering conditions

We use parameters and interactions for Xe/Pt(111), as given in Paper I, as representative of those for a physically adsorbed incommensurate monolayer. The normal modes of the monolayer solid are evaluated using the HFD-B2 Xe–Xe potential\(^{32}\) supplemented by the McLachlan substrate-mediated dispersion energy. Some of the calculated phonon energies are listed in Table II. The pair potential between the probe atom and monolayer atoms is \(^{33}\) the HFD-B2 for He–Xe and \(V_{q}(z)\) includes the probe atom-substrate van der Waals energy \(-C_{\text{vdW}}/z^3\).

The monolayer temperature is \(T=50\) K and the scan angle between the incident wave vector and the \(g=0\) outgoing beam is \(\Theta_{\text{SD}}=95.8°\). See also Fig. 1. The misalignment of the scattering plane relative to the \(\Gamma M\) azimuth of the monolayer is \(\alpha=2.6°\), the Novaco-McTague orientational alignment angle at \(T_{\text{min}}=4.33\) Å determined in the Xe/Plt(111) experiments.\(^{8}\) This value is not crucial because a misalignment \(\alpha=0.5°\) also gives strong symmetry-breaking SH-mode excitation.\(^{9}\) Mostly, the phonon wave vectors are directed antiparallel to \(k_q\) because of the experimental experience\(^{8}\) that this led to better resolved SH-mode excitation.

III. SCATTERING RESULTS

The wave packet scattering is evaluated for a basic set of 24 cases formed from two polarizations (SH and LA), two wave numbers \((-0.125\) and \(-0.25\) Å\(^{-1}\)), and six incident energies \(E_i\) in the range \(4\)–26.5 meV. These are augmented by two series of cases for the SH mode at \(E_i=8\) meV: one is a scan with \(\Delta E_i=0.15\) meV at \(-0.125\) Å\(^{-1}\) and the other is a scan over \(q\) at \(E_i=8.2\) meV. There are a few cases for \(E_i\) near the threshold for creating the phonons. From Table II, the SH mode has energy up to 2.2 meV and the LA mode up to 4 meV for the \(q\)'s in our calculations.

We begin with some general remarks on the relative strengths in the specular and nonspecular channels. The full discussion for relatively narrow wave packets is given for diffraction in Sec. III A, for inelastic scattering in Sec. III B, and for broader packets with higher energy resolution in Sec. III C.
The Xe monolayer is a very corrugated target and the scattering is the result of strong coupling of the $^4$He to the monolayer. Thus, it was expected that there would be much diffracted strength in nonspecular $\mathbf{g} \neq 0$ channels. This is fulfilled in all the cases we studied, although the strength in the specular channel $I_{\text{spec}}(\mathbf{g} = 0)$ generally is higher than the average $I_{\text{el}}$. For $E_i < 8$ meV, the specular channel in $\Psi_{0}$ is almost always the strongest one. Near 8 meV, the specular intensity has significant nonmonotonic variations over increments $\Delta E_i = 0.15$ meV.

It was also expected that there would be significant probability for exciting the SH mode in $\mathbf{g} \neq 0$ channels, as that is how the polarization selection rules are overcome in the weak coupling theory of inelastic neutron scattering. However, HAS does excite the SH mode in the first Brillouin zone near symmetry azimuths, which was not anticipated before the experiments were performed. A remarkable result of the strong coupling calculations is that the strength $N_{\text{SH}}(\mathbf{g} = 0)$ in the specular channel frequently is largest or nearly the largest for $E_i < 10$ meV. Further, the $\mathbf{g} = 0$ inelastic strengths and the total (over all open channels) inelastic strengths $I_{\text{inel}}(\text{tot})$ generally are larger for the SH excitations than for the LA excitations at given $E_i$ and $\mathbf{q}$. This too is an effect of the strong coupling and is markedly different from that expected for weak coupling, as in neutron scattering.

**A. Diffraction**

The diffraction calculation ($\Psi_{0}$) is linked to the inelastic scattering calculation because the angle of incidence $\Theta_i$ is set by the scan curve condition. Thus, for many of the incident energies $E_i$, we have several calculations of the distribution of diffracted strengths. The angles $\Theta_i$ are presented in Table III.

Except at energies $E_i < 5$ meV, overall trends for the diffraction are insensitive to the changes in $\Theta_i$ that arise in satisfying the scan curve constraints for excitations with different $\mathbf{q}$ and polarization. This is shown for $I(E_i)$ [the average of $I_{\text{inel}}(\mathbf{g})$ over open channels as a function of incident energy] in Fig. 2. The error bars in Fig. 2 and subsequent figures represent the standard deviation in an average over channels; the strength in a given channel is calculated with a precision better than 1%. Although the strength in a given channel is the result of a complicated pattern of couplings between all channels in $\Psi_{0}$, $I(E_i)$ clearly decreases with increasing $E_i$. For the $N_{\text{diff}}$, there is a conservation law and $\tilde{I} = 1/N_{\text{open}}$, where $N_{\text{open}}$ is the (energy-dependent) number of open diffraction channels. As $E_i$ increases, $N_{\text{open}}$ increases linearly with $E_i$, as shown in Table IV, and the $\tilde{I}$ in Table IV varies as $1/E_i$. The effect of the Debye-Waller factor is to
reduce markedly the contributions from many of the open channels, and the net variation of $\bar{I}$ in Table V and Fig. 2 is close to $1/E_i^2$.

Tables IV and V give a rather full characterization of the distribution of diffracted energies over open channels for a series of incident energies with $\Theta_i$ set by the scan curve condition for the SH mode at $q=-0.125$ Å$^{-1}$, the first being based on $N_{\text{diff}}$ [Eq. (16)] and the second on $I_{\text{el}}(q)$ [including the Debye-Waller factor]. The first column is the incident energy and the second is the strength of the $g=0$ peak. The remaining columns give a sense of the statistical nature of the distributions as formulated in Appendix B, presenting the average over open channels, its standard deviation (defined to be the square root of the variance for these non-Gaussian distributions), the maximum channel strength, the fractional entropy, and the numbers of open channels and of those with strengths greater than the $g=0$ strength. Comparing the tables shows the marked changes in the distributions that arise by including the Debye-Waller factor for thermal attenuation. Figure 3 graphically shows these changes for another case with $E_i=8.2$ meV.

The relatively large ratios $\sigma/\bar{I}$ and $S/\ln(N_{\text{open}})$ in Tables IV and V demonstrate the statistical nature of the distributions arising from the “deterministic” wave packet propagation in a strong coupling regime. The Debye-Waller factor decreases the strength for channels with large $\Delta q$, Table V, so that the distribution is concentrated in fewer channels and the fractional entropy tends to be smaller at the larger values of $E_i$. A significant part of the statistical character arises from the energy width of the wave packet, which was demonstrated by comparing the fractional entropies for packets with NWI=100 and 600 (e.g., compare the two sets of entries for $E_i=8.2$ meV in these tables). The NWI parameter regulates the width of the initial wave packet as defined in Appendix C. The fractional entropies usually were smaller for larger values of NWI, consistent with more order in a more monochromatic scattering event.

### B. Inelastic strengths

Figure 4 and Tables VI and VII give an overview of the energy dependence of the strengths of SH and LA excitations created by inelastic atomic scattering. It is very clear that the SH branch is much stronger than the LA branch at energies below 10 meV and that this feature is not restricted to special choices of $E_i$. Tables VIII and IX are fuller characterizations

#### TABLE VI. Summary of the specular inelastic strengths $I_{\text{el}}(q,g=0, \lambda)$ at $T=50$ K as a function of incident energy $E_i$ (in meV) for $\lambda=$ SH and LA. Wave numbers $q$ are given in Å$^{-1}$; the plane of incidence and the orientation of the wave vectors are as specified in the caption of Table III. Except as noted, the initial wave packet has NWI=100 and NZ0=375.

<table>
<thead>
<tr>
<th>$q$</th>
<th>$E_i$</th>
<th>SH</th>
<th>LA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>0.615</td>
<td>0.179</td>
<td>0.0417</td>
</tr>
<tr>
<td>2.5</td>
<td>0.418</td>
<td>0.0184</td>
<td>0.0482</td>
</tr>
<tr>
<td>4.0</td>
<td>0.323</td>
<td>0.0182</td>
<td>0.0153</td>
</tr>
<tr>
<td>5.0</td>
<td>0.263</td>
<td>0.1014</td>
<td>0.0665</td>
</tr>
<tr>
<td>6.0</td>
<td>0.0654</td>
<td>0.0209</td>
<td>0.0160</td>
</tr>
<tr>
<td>8.2</td>
<td>0.0243</td>
<td>0.0013</td>
<td>0.0044</td>
</tr>
<tr>
<td>16.6</td>
<td>0.0050</td>
<td>0.0018</td>
<td>0.0020</td>
</tr>
</tbody>
</table>

*NWI=600, NZ0=1960.  
*The SH entries for $q=0.125, 0.25$, and 0.5 are 0.0575, 0.0269, and 0.0109, respectively.  
*The S-mode values for $q=−0.25, −0.125, 0.125, 0.25$, and 0.5 are 0.026, 0.031, 0.035, 0.043, and 0.043, respectively.

#### TABLE VII. Summary of the total inelastic strengths $I_{\text{el}}(q,\lambda)$ at 50 K as a function of incident energy $E_i$ (in meV) for $\lambda=$ SH and LA for the same cases as in Table VI. Wave numbers $q$ are given in Å$^{-1}$. Initial wave packets are as specified in Table VI.

<table>
<thead>
<tr>
<th>$q$</th>
<th>$E_i$</th>
<th>SH</th>
<th>LA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>2.58</td>
<td>0.261</td>
<td>0.18</td>
</tr>
<tr>
<td>2.5</td>
<td>2.03</td>
<td>0.212</td>
<td>0.46</td>
</tr>
<tr>
<td>4.0</td>
<td>1.10</td>
<td>0.248</td>
<td>0.07</td>
</tr>
<tr>
<td>5.0</td>
<td>0.98</td>
<td>0.211</td>
<td>0.34</td>
</tr>
<tr>
<td>6.0</td>
<td>0.62</td>
<td>0.303</td>
<td>0.095</td>
</tr>
<tr>
<td>8.2</td>
<td>0.35</td>
<td>0.114</td>
<td>0.08</td>
</tr>
<tr>
<td>16.6</td>
<td>0.21</td>
<td>0.080</td>
<td>0.04</td>
</tr>
</tbody>
</table>

*The SH entries for $q=0.125, 0.25$, and 0.5 are 0.46, 0.14, and 0.068, respectively.  
*The S-mode values at 16.6 meV for $q=−0.25, −0.125, 0.125, 0.25$, and 0.5 are 0.136, 0.167, 0.182, 0.180, and 0.177, respectively.
of the inelastic scattering for the SH mode with $q = -0.125 \text{ Å}^{-1}$ (generally the strongest of the excitation processes). The role of the Debye-Waller factor in modifying the distribution of strengths over channels is illustrated in Fig. 5 for the LA mode at $q = -0.125 \text{ Å}^{-1}$ and 8.2 meV; in this rather extreme case, including the Debye-Waller factor decreases the value of $N_>$ from 10 to 1.

To assure convergence of the calculations for the inelastic scattering, the wave packet must be propagated for a longer time than would be decided from an analysis of $\Psi_0$ alone. For a given scattering event, the norm of $\Psi_1$ grows rapidly with time after the turning point (i.e., the time $t_i$ when the average $\langle \varepsilon \rangle$ is a minimum) as the elastic wave ($\Psi_q$) recedes from the monolayer. The division of strength among the open channels evolves for rather long times, especially at smaller $E_i$ where there is more transient strength in closed channels. At the higher energies, $E_i = 16.6$ and 26.5 meV, there are many open channels ($= 40 – 60$) for both the elastic and inelastic scattering, and the strengths in individual channels become smaller. Time scales are shorter, in

<table>
<thead>
<tr>
<th>$E_i$ (meV)</th>
<th>$I(g=0)$</th>
<th>$\bar{I}$</th>
<th>$\sigma(f)$</th>
<th>$I(g)_{\max}$</th>
<th>$S/\ln(N_{\text{open}})$</th>
<th>$N_{\text{open}}$</th>
<th>$N_&gt;$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2$^b$</td>
<td>0.140</td>
<td>0.166</td>
<td>0.0379</td>
<td>0.220</td>
<td>0.981</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>4$^b$</td>
<td>0.068</td>
<td>0.0799</td>
<td>0.0165</td>
<td>0.105</td>
<td>0.989</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>5$^a$</td>
<td>0.0675</td>
<td>0.0309</td>
<td>0.0166</td>
<td>0.0675</td>
<td>0.949</td>
<td>11</td>
<td>0</td>
</tr>
<tr>
<td>6$^a$</td>
<td>0.0561</td>
<td>0.0239</td>
<td>0.0151</td>
<td>0.0561</td>
<td>0.929</td>
<td>14</td>
<td>0</td>
</tr>
<tr>
<td>8.2$^b$</td>
<td>0.0168</td>
<td>0.0175</td>
<td>0.0986</td>
<td>0.0426</td>
<td>0.946</td>
<td>19</td>
<td>9</td>
</tr>
<tr>
<td>16.6$^b$</td>
<td>0.00744</td>
<td>0.00705</td>
<td>0.00633</td>
<td>0.0266</td>
<td>0.913</td>
<td>40</td>
<td>7</td>
</tr>
<tr>
<td>26.5$^a$</td>
<td>0.00226</td>
<td>0.00518</td>
<td>0.00631</td>
<td>0.0259</td>
<td>0.856</td>
<td>63</td>
<td>35</td>
</tr>
<tr>
<td>7.75$^b$</td>
<td>0.0635</td>
<td>0.0289</td>
<td>0.0252</td>
<td>0.0945</td>
<td>0.870</td>
<td>17</td>
<td>1</td>
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<tr>
<td>7.90$^b$</td>
<td>0.0313</td>
<td>0.0226</td>
<td>0.0189</td>
<td>0.0655</td>
<td>0.884</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>8.05$^b$</td>
<td>0.0242</td>
<td>0.0187</td>
<td>0.0131</td>
<td>0.0551</td>
<td>0.914</td>
<td>18</td>
<td>5</td>
</tr>
<tr>
<td>8.2$^b$</td>
<td>0.0148</td>
<td>0.0153</td>
<td>0.00962</td>
<td>0.0355</td>
<td>0.925</td>
<td>19</td>
<td>9</td>
</tr>
<tr>
<td>8.35$^b$</td>
<td>0.00427</td>
<td>0.0123</td>
<td>0.00766</td>
<td>0.0259</td>
<td>0.928</td>
<td>19</td>
<td>15</td>
</tr>
<tr>
<td>8.50$^b$</td>
<td>0.0080</td>
<td>0.0103</td>
<td>0.00979</td>
<td>0.0339</td>
<td>0.853</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>8.65$^b$</td>
<td>0.00488</td>
<td>0.00968</td>
<td>0.00907</td>
<td>0.0329</td>
<td>0.871</td>
<td>19</td>
<td>12</td>
</tr>
</tbody>
</table>

$^a$NW1 = 100, NZ0 = 375. $^b$NW1 = 600, NZ0 = 1960.

TABLE IX. Strengths of excitation of the shear horizontal (SH) mode by a beam of helium atoms from a thermally excited monolayer as function of incident energy at wave vector transfer $q = -0.125 \text{ Å}^{-1}$ for the same cases as in Table VIII. These strengths are the final $I_{\text{inel}}(q, g, \text{SH})$ of Sec. II E obtained from the data of Table VIII by correcting for flux factors and thermal excitation effects at 50 K.

<table>
<thead>
<tr>
<th>$E_i$ (meV)</th>
<th>$I(g)=I_{\text{inel}}(q, g, \text{SH})$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I(g=0)$</td>
</tr>
<tr>
<td>2$^a$</td>
<td>0.615</td>
</tr>
<tr>
<td>4$^a$</td>
<td>0.418</td>
</tr>
<tr>
<td>5$^a$</td>
<td>0.323</td>
</tr>
<tr>
<td>6$^a$</td>
<td>0.263</td>
</tr>
<tr>
<td>8.2$^a$</td>
<td>0.0741</td>
</tr>
<tr>
<td>16.6$^b$</td>
<td>0.00502</td>
</tr>
<tr>
<td>26.6$^a$</td>
<td>0.284</td>
</tr>
<tr>
<td>7.75$^b$</td>
<td>0.139</td>
</tr>
<tr>
<td>7.90$^b$</td>
<td>0.107</td>
</tr>
<tr>
<td>8.05$^b$</td>
<td>0.0654</td>
</tr>
<tr>
<td>8.35$^b$</td>
<td>0.0188</td>
</tr>
<tr>
<td>8.50$^b$</td>
<td>0.0035</td>
</tr>
<tr>
<td>8.65$^b$</td>
<td>0.0213</td>
</tr>
</tbody>
</table>

$^a$NW1 = 100, NZ0 = 375. $^b$NW1 = 600, NZ0 = 1960.
part because the speed of the probe atom is greater for given energy loss $\hbar \omega(q, \lambda)$. There is a rather fast development of the inelastic beams, as measured by the difference between the time at which the norm of $\Psi_1$ reaches 75% of its final value and the turning point time $t_i$ for $\Psi_0$.

We can identify some general trends in the results for $I_{\text{inel}}(q, g, \lambda)$, $\lambda = \text{SH}$ and LA. Except for the lowest values of $E_i$ used in these calculations (2 and 2.5 meV), the total inelastic strength $I_{\text{inel}}(q, \lambda)$ decreases as $E_i$ increases. The number of open inelastic channels increases from 7 at 4 meV to about 60 at 26.5 meV. The strength in a given open channel tends to be larger for smaller $E_i$, i.e., the excitation of the dispersive long wavelength phonons is stronger at low, but above-threshold, incident energy. $I_{\text{inel}}(g=0)$ is greater than $I_{\text{inel}}$ in most of the cases for both the SH and LA branches. Also, even with the Debye-Waller attenuation of the non-spectral channels, the distribution of inelastic strength over channels remains quite statistical with ratios $\sigma/I$ of order 1 in most cases. For given $q$ and polarization $\lambda$, the fractional entropy $S/\ln(N_{\text{open}})$ tends to decrease as $E_i$ increases from 4 to 25 meV.

However, there are special conditions where the specular channel strength is much larger than anticipated from statistical considerations. For example, the SH phonon of $q=-0.25 \text{ Å}^{-1}$ at $E_i=6$ meV has $I_{\text{inel}}(g=0)/I_{\text{inel}} = 6$, while the ratio is 0.7 and 1.2 at $E_i=5$ and 8.2 meV, respectively. The occasional very strong inelastic peaks found in the experiments $^6, ^{10}$ are also indications of such sensitivity. There are optimal energies in the calculations, depending on the wave number and the polarization, for phonon excitation both in an individual channel and for the total inelastic strength, Tables VI and VII. The total inelastic strength for these SH phonons has a maximum at $E_i$ in the range 2–5 meV.

The inelastic strength $I_{\text{inel}}(g=0)$ for $q=-0.125 \text{ Å}^{-1}$ is higher than for $q=-0.25 \text{ Å}^{-1}$ for the SH and the LA series. In several cases, though, the margin in the comparison comes from the factor $1+\bar{n}$, Eq. (17), rather than the intrinsic strengths $N_{q\lambda}$.

The calculations give inelastic strengths for the non-spectral $g \neq 0$ channels which were not measured in most of the HAS experiments. As already noted, one surprise for the SH branch is that the specular channel is the strongest one at 4–6 meV for $q=-0.125 \text{ Å}^{-1}$. For $q=-0.25 \text{ Å}^{-1}$, the strongest SH scattering was in nonspectral channels for five of
the seven values of $E_i$ that were studied. Although the excitation of the LA branch in the first Brillouin zone does not depend crucially on the small misalignment of the scattering plane (i.e., no selection rule to be broken), the occurrence of strong nonspecular inelastic peaks for the LA cases has much similarity to the SH cases.

The excitation of the SH mode has been calculated as a function of $q$ from $-0.5 \text{ Å}^{-1}$ to the Brillouin zone boundary value, at a $2.6^\circ$ misalignment with the $\Gamma M$ direction and constant $E_i=8.2 \text{ meV}$. Some of the results are given in Table VII. The trends for the channel norms $N_{q,\text{SH}}$ and the final calculated strength $I_{\text{inel}}(q, g=\text{SH})$ are markedly different because the thermal factor $1+\bar{n}$, Eq. (17), strongly enhances the small $|q|$ strength, both for the specular channel and the total $I_{\text{tot}}(q, \text{SH})$. The asymmetry between the $\pm q$ cases arises from the differences in initial conditions ($k_i$) to satisfy the scan curve constraints. The total inelastic strengths are $30\%$ to $100\%$ larger for the negative $q$ cases.

The decreases of $I_{\text{inel}}(q, g=0, \text{SH})$ with increasing $|q|$ occurs also at $E_i=5 \text{ meV}$ and the trend is also present in the results for the LA mode. A decrease with increasing $|q|$ near the Brillouin zone center that results from the intrinsic scattering (form factors) has been known for some time but these calculations show the very important role of the thermal factor $1+\bar{n}$ for dispersive branches.

Our calculations for the S mode are much less extensive and consist mainly of a scan of the wave vector dependence of the excitation at $E_i=16.6 \text{ meV}$, the energy used in a recent measurement. In contrast to the other branches, the strongest inelastic channel is the specular one for $q=-0.25$ to $0.5 \text{ Å}^{-1}$ at $2.6^\circ$ to the $\Gamma M$ axis. The dependence of $I_{\text{inel}}(q, g=0, S)$ on $|q|$ is much smaller for the S mode with its nearly dispersionless frequency $\omega_i=3.5 \text{ meV}$; some values at $E_i=16.6 \text{ meV}$ are included in Tables VI and VII.

### C. Higher energy resolution

There are suggestions of significant energy dependence for channel strengths in the data presented thus far. To explore this more thoroughly, we made a series of calculations with packets that have narrower energy spreads, using a spatial width NWI=600. An overview of the results is given in Fig. 6, which shows the strengths $I_{\text{tot}}(g=0)$ and $I_{\text{inel}}(q=-0.125, g=0, \text{SH})$ on a grid with $\Delta E_i=0.15 \text{ meV}$. There clearly is a strong energy dependence to the inelastic scattering and also a marked variation of the specular elastic strength. The channel strengths vary strongly with incident energy $E_i$ in a nonmonotone way. Calculations, and experiments, with broader energy distribution in the incident beam result in scattering strengths that are averaged over fine details in the spectrum. The fuller statistical analyses are presented in Tables IV, V, VIII, and IX.

The sensitivity to the spatial width is present in other examples too. For instance, at $E_i=6 \text{ meV}$, $I_{\text{inel}}(q=-0.25 \text{ Å}^{-1}, g=0, \text{SH})$ is 0.018 for NWI=600 and is 0.026 for NWI=100.

![Fig. 7. The bound norm $N_b$ as a function of time (in ps) at six incident energies $E_i$ for the elastic wave $\Psi_0$ that arises in simulating the inelastic excitation of SH phonons of $q=-0.25 \text{ Å}^{-1}$. The plane of incidence and wave vector are as specified in the caption of Fig. 2. The initial wave packets have NWI=600 and are centered at $z_0=119$ Å. For reference, the times (in ps) at the turning point are $t_i=35.4, 32.2, 29.4, 26.3, 18.6$, and $14.9$ for $E_i=4, 5, 6, 8.2, 16.6$, and $26.5 \text{ meV}$.](image)

#### IV. ANALYSIS OF TRANSIENT TRAPPING

##### A. Transient trapping in elastic scattering

Many closed channels are populated during the elastic scattering, but at sufficiently large times, those norms eventually decay to zero via couplings to the open channels and all of the norm is in outgoing channels because there is no mechanism in Eq. (2) for the formation of permanently trapped probe atoms. We calculate the transiently bound ("trapped") norm $N_b(t)$ by projecting the channel amplitudes $\psi_k(z,t)$ onto the bound eigenstates of $V_0$ for all channels, whether nominally closed or open. The evolution of the total bound intensity $N_b(t)$ is shown for several energies $E_i$ in Fig. 7; in this series, the initial wave packet is centered at $z_0=119$ Å and has a turning point near 20 Å at a time $t_i=35–15$ ps for $E_i=4–26.5 \text{ meV}$. For other polarization and wave vector combinations, the $\Theta$ are different and there are changes in the detailed time evolution. For instance, in some series the maximum of $N_b$ decreases monotonically as $E_i$ increases although that is not the behavior in Fig. 7. Because the construction of $N_b$ does not allow for the 2D band structure of the selective adsorption states, there is a small error which becomes significant at large times and limits our analysis to time ranges where $N_b$ is greater than 0.001.

The norm $N_b$ initially increases to a maximum at a few picoseconds after the wave packet turns. Beyond the maximum, we fit the time dependence of $N_b$ to one or two exponential decay terms:
\[ N_0(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2). \]  

(18)

Results for the decay times \( \tau \) are given in Table III for initial conditions on \( \Psi_0 \) set by the scan curve constraints for the SH and LA modes at two wave vectors \( q \). (The amplitudes \( A_j \) are not given here.) In several cases, statistically significant fits were only obtained using one term and there is no entry for \( \tau_2 \). In most of the low energy cases \( (E_i \leq 5 \text{ meV}) \), there was a long decay time \( \tau_2 \) and much of the data range for those cases was dominated by that term. One of the 16.6 meV cases \( (\text{SH}, q = -0.25 \text{ Å}^{-1}) \) has an unusual evolution of \( N_{0t} \), which persists at values near its maximum for more than 20 ps as shown in Fig. 7. That case has large transient population in two channels closed by \( \Delta < 0.2 \text{ meV} \), but does not seem to be correlated to strong inelastic scattering. There are competing processes that create a closed channel with a wave function \( \psi \) localized near the monolayer that has a long-lived norm in the scattering event. Channels with small energy deficit \( |\Delta| \) are all coupled to at least one open channel by a term \( V(g, z) \), which nominally is strong. However, the \( \psi \) of such channels mostly overlaps shallow bound states of \( V_0 \) with probability concentrated far enough from the surface that \( V(g, z) \) is small. That slows the desorption process. For the channels with larger \( |\Delta| \), the desorption may also be slow because the coupling to open channels either goes by a larger wave vector transfer or by first mixing with channels of small \( |\Delta| \). An analysis using the “density” of closed states in narrow ranges of \( \Delta \), which can be done without the scattering solution, helps to identify initial conditions likely to lead to strong transient trapping. Concentrations (or degeneracies) in the number of channels in energy ranges overlapping the bound states of \( V_0 \) correlate rather well with the strongest trapping cases.

In summary, the decay times \( \tau \) in Table III demonstrate that there are many cases with long times for completion of the elastic scattering.\(^{13}\) It takes some tens of picoseconds after the turning point of the scattering to reach a time when more than 95% of the norm of \( \Psi_0 \) is in outgoing channels. This effect is particularly marked at \( E_i < 8 \text{ meV} \).

**B. Permanently trapped probe atoms**

Probe atoms with very long trapping times may be produced in a low energy inelastic scattering event if sufficient energy is transferred to the target monolayer. In the one-phonon loss approximation used here, there is no mechanism for the probe atom to recover enough energy to escape again. We have demonstrated the trapping for the LA mode at \( q = -0.25 \text{ Å}^{-1} \) and \( E_i = 2.5 \text{ meV} \) with two simulations which differ slightly in the angle of incidence \( \Theta_i \). In a case with \( \Theta_i = 13.9^\circ \) there is no open final channel in \( \Psi_1 \), while for \( \Theta_i = 13.7^\circ \) there is one open channel in \( \Psi_1 \). For both cases there are six open channels in \( \Psi_0 \).

The decay of the transiently bound norm \( N_{0t}(t) \) for \( \Psi_0 \) in very slow and the simulations were continued beyond 280 ps to reach times where \( N_{0t} < 0.002 \). The results of a fit to two exponentials are given in Table III. The decay times are very different, one at about 10 ps and a much longer one of about 100 ps. The decay apparently is a little slower in the case with one open \( \Psi_1 \) channel, probably because this has more closed \( \Psi_0 \) channels of very small \( |\Delta| \).

The distribution of inelastic strength over channels did not tend to a limit in either case, even for times beyond 400 ps. We have generally used the large time behavior of the specular channel norm \( N_{q,t}(g = 0, t) \), Eq. (15), as the diagnostic for completion of the scattering event. However, for these cases at \( E_i = 2.5 \text{ meV} \), this channel norm continued to oscillate and did not converge to a limit at \( t = 400 \text{ ps} \). Other cases could be propagated to such large times that most of the total inelastic strength became absorbed by the potential \(-iU\). For these two cases, only a small part of the inelastic strength was absorbed and most of the inelastic strength remained on the spatial grid. Thus, the probe atom has been trapped by the monolayer and the oscillation of the inelastic strength in the specular channel arises from an exchange of strength between a few channels with wave functions \( S_{q,t}^{\text{LA}}(g, z, t) \) that are localized near the surface.

**V. CONCLUSIONS**

Our results confirm that the excitation of the SH branch for scattering planes at small misalignment to symmetry azimuths of the monolayer lattice is a robust phenomenon and show that it is enhanced at low incident energy. Remarkably, both the specular inelastic strength and the total inelastic strength increase steadily as the energy decreases below \( E_i = 6 \text{ meV} \). The SH branch can be readily excited in HAS experiments at low incident energies without invoking effects of defects or of second layer gas above the monolayer solid. The excitation of the LA phonons is also enhanced by using low incident energies, below 10 meV or so.

At given \( E_i \), the final calculated inelastic strengths \( I_{\text{inel}}(q, g = 0, \lambda) \) decrease as \( |q| \) increases for both the SH and LA modes. This is shown explicitly at \( E_i = 5 \) and 8.2 meV in Table VI. In many of the cases, the enhancement by thermally excited phonons, Eq. (17), is an important contribution to making the inelastic strength for SH greater than for LA excitations at the same \( q \). Thus, thermal effects play an important role in determining the strength distributions for both the elastic and inelastic atomic scattering. These include an enhancement of the low-\( q \) strengths by thermally excited phonons and the Debye-Waller-factor attenuation of scatterings with large reciprocal lattice vector transfers. This arises because in the HAS experiments thus far, a common working temperature has been 40–50 K, which leads to an appreciable thermal excitation of the target.

The sensitivity of the calculations to \( \Theta_i \) and the specifics of the scan curve construction limit the transferability of the detailed results to other experimental configurations. For instance, the \( \Theta_i \) for the SH \( q = -0.125 \text{ Å}^{-1} \) mode at 8.2 meV changes from 45.2° to 42.5° when \( \Theta_0 \) changes from 95.8° to 90°. The qualitative features we have identified do survive. To derive full information from low energy inelastic atomic scattering experiments, the work will have to be accompanied by scattering calculations such as those presented here.
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APPENDIX A: TIME PROPAGATION WITH AN ABSORBING POTENTIAL

The general form of the time-dependent Schrödinger equation for the wave function of the scattered (4He) atom is

\[ i\hbar \partial \psi / \partial t = (K + V - iU)\psi, \]  

(A1)

where \( K \) denotes the kinetic energy operator, \( V \) is the atom-monolayer potential energy, and \(-iU\) is an absorbing potential that is introduced to eliminate reflections of the outgoing atom from the large-\( z \) boundary. For \( U=0 \), we found \( d \) that the time development was given very stably by a simple second-order stepping procedure, using a fast Fourier transform to evaluate the effect of \( K \):

\[ \Psi(t + dt) = \Psi(t - dt) - 2dt(i/\hbar)(K + V)\Psi(t). \]  

(A2)

With the absorbing potential \((U > 0 \text{ leads to a loss of probability})\), we adopt

\[ \Psi(t + dt) = \left[ 1 - \frac{U}{\hbar} 2dt \right] \Psi(t - dt) - 2dt(i/\hbar)(K + V)\Psi(t). \]  

(A3)

This propagation is stable according to the formal analysis of Koonin \(27\) and also in our experience with the numerical implementation.

The totals \( \int |\Psi|^2 \, d\mathbf{r} (j=0,1) \) decrease at large times as components of the outgoing wave packet are absorbed. As a check on the stability of the calculation, we monitored the current in each channel, \( I_j(\mathbf{g}) = (\hbar/2mi)[\chi_0^* \partial \chi_0^*/\partial z - \chi_0 \partial \chi_0^*/\partial z] \), just before \( z_U \) [Eq. (5)], and calculated the total absorbed current as

\[ I_{abs}(\mathbf{g}, t) = \int_0^t I_j(\mathbf{g}, t') \, dt', \]  

(A4)

where \( \chi \) is \( \psi_\mathbf{g} \) or \( S_{\mathbf{g}, \lambda} \) [Eq. (2) or (3)] for the diffractive and inelastic scattering, respectively. The total of the \( \Psi_0 \) norm on the spatial \( (z) \) grid and its accumulated current into the absorber remained constant over the total propagation time to a few parts in \( 10^4 \).

APPENDIX B: ENTROPY ANALYSIS OF STRENGTH DISTRIBUTIONS

The scattering calculations give so much information that we have used some statistical measures to get an overview of the data. These are the average, square root of the variance, and information theory entropy for the channel strengths of either the elastic or the inelastic scattering.

Let the strengths in the \( \eta \) open channels be denoted by \( s_j \). The average (mean) and mean-square strengths are then defined by

\[ \bar{s} = \eta \sum_{j=1}^\eta s_j / \eta, \quad \bar{s}^2 = \sum_{j=1}^\eta s_j^2 / \eta, \]  

(B1)

and the standard deviation (square root of variance) is \( \sigma = \sqrt{\bar{s}^2 - \bar{s}^2} \).

For the entropy \( S \), define the normalized weights constructed from the \( s_j \),

\[ p_j = s_j / \sum_{j=1}^\eta s_j = s_j / \eta \bar{s}, \]  

(B2)

and then form \( 23 \)

\[ S = - \sum_{j=1}^\eta p_j \ln p_j. \]  

(B3)

Convexity relations \(22 \) give general upper and lower bounds on the entropy. For a function \( f \) with positive second derivative, the convexity bound on the average is \((f(x)) \geq f(x)\) and the sense reverses for negative second derivative. A lower bound is obtained using \( x = p_j \) and \( f(x) = \ln x \) and an upper bound with \( x = 1/p_j \) and \( f(x) = -\ln x \):

\[ \ln \eta - \ln(\bar{s}^2/\bar{s}) \leq S \leq \ln \eta. \]  

(B4)

The fractional entropy \( S/\ln \eta \) is used to follow trends for these non-Gaussian distributions; it is 1 for a uniform (random) distribution.

APPENDIX C: IMPLEMENTATION OF THE WAVE PACKET CALCULATION

The initial wave packet has the following form:

\[ \Psi_i(\mathbf{r}, z) = (2\pi/\eta)^{1/4} \times \exp[i(k_0(z - z_0) + \mathbf{k}_0 \cdot \mathbf{r})] \exp(-A[z - z_0]^2), \]  

(C1)

with width \( \sigma_z = 1/2\sqrt{A} \) and energy expectation value \( E_i = \hbar^2(k_0^2 + \mathbf{k}_0^2 + A)/2m \). The value of the width parameter \( A \) is expressed in terms of the spatial grid \( \Delta z (= 0.06 \, \text{Å}) \) as

\[ A = 1/2[(2\text{NWI} \times \Delta z)^2]. \]  

(C2)

The initial center of the packet (in angstroms) is set by the condition \( z_0 = 1.5 + \text{NZZ} \times \Delta z \). NWI and NZZ are both integers. The range of \( z \) was 1.5–124.32 Å in Paper I (NWI = 100), but now for larger values of NWI, it is taken as 1.5–247.2 Å so that the packet can be started far enough from the monolayer that its center is at least 4 Å from it. For NWI = 600, this led to a choice \( z_0 = 119 \, \text{Å} \) (NZZ = 1960).

The square root of the variance of the energy is

\[ \sigma_E \approx (\hbar^2|k_0|/m)^{1/2}. \]  

(C3)

For \( |k_0| \approx 3.0 \, \text{Å}^{-1} \) (a typical value in our examples) and NWI = 100, this gives \( \sigma_E \approx 0.4 \, \text{meV} \), comparable to the overall energy resolution of 0.3 meV in recent HAS experiments.
The number of $g$ shells in the Fourier decomposition of the probe-monolayer potential $V_r$, Eq. (1), is NVG = 6. Increasing this parameter to 9 and to 12 had negligible effect. However, decreasing it to 1, in some tests of the coupling schemes, led to pathological behavior (loss of norm) because there are “holes” in the potential energy surface at small $z$, i.e., the potential energy surface is very corrugated and is poorly represented at small $z$ by the leading Fourier component.

The number of channels is set by including all terms $g$ coupled to the incident channel and satisfying $(k_i^2 + g^2) \leq (2m/\hbar^2)(E_i - E_{cut})$. In paper I, we used $E_{cut} = -170$, $-250$, $-430$ K for $E_i = 8.2$, 16.6, 26.5 meV. For the present work, we have made tests to see that the specular channel strengths and total inelastic strengths have converged to better than 10% and found that $E_{cut} = -250$ K sufficed for energies of $2$–$26.5$ meV. This surprised us because our reading of the literature was that it was expected that we would have to increase $|E_{cut}|$ as the energy $E_i$ increased. The cutoffs for the SH series at $q = -0.125$ and $-0.25$ Å$^{-1}$ in this paper are $E_{cut} = -250$ K for $E_i \leq 16.6$ meV and $E_{cut} = -430$ K for $E_i = 26.5$ meV, for the other cases, $E_{cut} = -170$ K is used for $E_i \leq 10$ meV.

For the numerical implementation, a parallel formulation of the computer code was used. Details of that are given in another paper.\(^{35}\)

13. It has been suggested that for such corrugated targets, the spectra will be complex and not easy to interpret: H. Jönsson and J. H. Weare, Faraday Discuss. Chem. Soc. 80, 29 (1985).
19. Because of the energy spread of the initial wave packet, a part of the norm in channels with small positive $\Delta$ may be in true outgoing waves. To quantify this effect for $\Psi_0$, the projections of the corresponding $\hat{g}$ on the bound state wave functions of $V_0$ are formed and the corresponding total norm is taken to be the bound component.
22. S. E. Koonin, Computational Physics (Benjamin Cummings, Menlo Park, 1986), Sec. II D.