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Atom scattering from surface Einstein modes

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We consider the scattering of thermal-energy atoms by a surface with a dilute coverage of adsorbates having a dispersionless Einstein vibrational mode. We show that the diffuse elastic scattered intensity has a Debye-Waller-type thermal attenuation only at low temperatures, and at large temperatures the attenuation saturates to a much weaker form. Similar thermal attenuation behavior occurs for the diffuse inelastic intensities. For an ordered adsorbate layer there is also a diffuse elastic intensity which increases with temperature at small temperatures.

I. INTRODUCTION

Experiments using thermal-energy atom scattering have demonstrated several surface adsorbate systems which exhibit dispersionless Einstein phonon modes. These occur in physisorbed systems[1-3] involving rare gases, in chemisorbed systems,[4] and even certain clean surfaces exhibit modes which are nearly dispersionless.[5,6] The typical experimental configuration is to direct a nearly monoenergetic beam towards the surface and then to carry out a time-of-flight energy analysis on the scattered intensity at an angle well away from the specular direction. The time-of-flight spectrum often reveals a single quantum peak as well as multiple quantum peaks for both annihilation and creation of the Einstein modes.

In this paper we develop the theory for the large-angle scattering of light atoms by a dilute coverage of adsorbates on the surface. We find that for scattering angles sufficiently far from specular and in the absence of multiple scattering between different adsorbate atoms, the scattered intensity can be written as the product of a form factor and a structure factor, similar to many other types of particle scattering from solids. The major difference is that the form factor for scattering from individual adsorbates must take into account multiple scattering and reflection from the substrate surface. For the case of adsorbates having a dispersionless phonon band (an Einstein mode), an examination of the structure factor reveals interesting behavior for the Debye-Waller factor (or thermal attenuation). For temperatures small compared to the mode energy the Debye-Waller factor appears in standard form for atom-surface scattering but for higher temperatures the rate of thermal attenuation strongly decreases. The reason for this decrease is multiple exchange of real quanta, as opposed to virtual quanta. It is virtual multiphonon events which produce the Debye-Waller factor, but in the special case of an Einstein mode, real multiple phonon exchange can make a non-negligible contribution to either the elastic or any of the inelastic intensity peaks. The net effect of all real multiquantum exchanges is in opposition to the virtual multiphonon exchanges appearing in the Debye-Waller factor. Such an effect is absent if the phonon frequency distribution function is dispersive.

In the next section we present the theory for the scattering of a collection of adsorbates on a flat surface substrate. In Sec. III we evaluate the scattered intensity for the situation in which the adsorbates vibrate with a dispersionless phonon frequency, exhibiting in the process the Debye-Waller factor and the corrections due to real multiphonon exchange. Section IV is a discussion of the contributions which arise from the vibrational motion of the surface substrate. In Sec. V we consider some interesting effects which arise if the adsorbates form an ordered or partially ordered layer. Section VI gives a few concluding remarks.

II. SCATTERING FROM A DILUTE LAYER OF SURFACE ADSORBATES

The starting point for our treatment of scattering by a dilute layer of adsorbates on the surface is the transition rate between the initial-state i and final-state f of the entire system;

$$w_{fi}=\frac{2\pi}{\hbar}\,|\,T_{fi}\,|^2\delta(E_f-E_i) \tag{1}$$

where T_{fi} is the transition matrix and the Hamiltonian is written as

$$H=H_0+H^c+V\ , \tag{2}$$

where H_0 is the unperturbed particle Hamiltonian, H^c is the Hamiltonian of the unperturbed crystal, and V is the interaction. The measurable quantity is the transition rate between final and initial particle states, which is the sum of Eq. (1) over all final crystal states $\{n_f\}$ and the average over initial crystal states

$$w(\mathbf{k}_f,\mathbf{k}_i)=\left\langle \sum_{\{n_f\}} w_{fi}\right\rangle\ , \tag{3}$$

where $\langle\ \rangle$ signifies the initial-state average. If we write the δ function Eq. (1) as a Fourier transform, and upon defining time-dependent operators in the interaction picture as

$$T(t)=e^{iH^ct/\hbar}Te^{-iH^ct/\hbar}\ , \tag{4}$$

the sum over final crystal states becomes trivial and we have

$$w(\mathbf{k}_f\mathbf{k}_i)=\frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt\, e^{-i(\varepsilon_f-\varepsilon_i)t/\hbar}\langle T_{if}(0)T_{fi}(t)\rangle \ , \qquad (5)$$

where ε_f and ε_i are the final and initial particle energies, respectively.

At this point we introduce the approximation that the adsorbates are dilute, implying that there is negligible multiple scattering between adsorbates. Furthermore, we will be interested in scattering at sufficiently large angles away from specular that the potential of a single adsorbate can be regarded as a rigid hard-core repulsion. This appears to be a reasonable approximation in the case of elastic scattering for sufficiently large momentum exchange, i.e., for the intensity scattered outside of the small range about the specular direction where the van der Waals attractive force scatters its large total cross section.[7] If all the adsorbates are identical, the T-matrix elements taken with respect to initial $|\mathbf{k}_i\rangle$ and final $|\mathbf{k}_f\rangle$ particle states are

$$\langle \mathbf{k}_f \mid T(t) \mid \mathbf{k}_i\rangle=\tau(\mathbf{k}_f,\mathbf{k}_i)\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l(t)} \ , \qquad (6)$$

where the summation runs over all adsorbed particles, and the adsorbate position can be written as

$$\mathbf{R}_l(t)=\mathbf{R}_l+\mathbf{u}_l(t) \ , \qquad (7)$$

where $\mathbf{R}_l$ is the time-independent equilibrium position and $\mathbf{u}_l(t)$ is the displacement from equilibrium. The vector $\mathbf{k}=\mathbf{k}_f-\mathbf{k}_i$. Although we have assumed that multiple scattering between different adsorbates is unimportant, we cannot neglect multiple scattering between the adsorbate and the surface. Thus the single adsorbate transition matrix amplitude $\tau(\mathbf{k}_f,\mathbf{k}_i)$ must be calculated in a manner which includes the interaction with the surface substrate.

Inserting (6) and (7) into (5) leads to

$$w(\mathbf{k}_f,\mathbf{k}_i)=\frac{1}{\hbar^2}\int_{-\infty}^{\infty} dte^{-i(\varepsilon_f-\varepsilon_i)t/\hbar}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2\sum_{l,j}\langle\langle e^{ik\cdot(\mathbf{R}_l-\mathbf{R}_j)}\langle e^{i\mathbf{k}\cdot\mathbf{u}_l(0)-ik\cdot\mathbf{u}_j(t)}\rangle\rangle\rangle \ , \qquad (8)$$

where the symbols for averaging have changed meanings somewhat; a single bracket $\langle\ \rangle$ denotes the average over vibrational motion, while the double bracket $\langle\langle\ \rangle\rangle$ denotes the average over defect positions. Thus we see that under the assumed conditions the transition rate can be written as the product of a form factor $|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2$ and the Fourier transform of a structure factor $S(\mathbf{k},\omega)$,[8] where the dynamical structure factor is

$$S(\mathbf{k},t)=\sum_{l,j}\langle\langle e^{i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_j)}\langle e^{i\mathbf{k}\cdot\mathbf{u}_l(0)}e^{-i\mathbf{k}\cdot\mathbf{u}_j(t)}\rangle\rangle\rangle \ . \qquad (9)$$

All of the dynamical information involving energy exchange is contained in this structure factor. We extract the Debye-Waller factor and the thermal attenuation in the next section.

The form factor is the square modulus of the transition amplitude for scattering from the particle state $\mathbf{k}_i$ to the state $\mathbf{k}_f$, taking into account the gain or loss of energy due to phonon exchange with the adsorbate. For a repulsive hard-core bump on a flat hard surface it can be calculated by considering a linear combination of atomiclike wave functions, the direct term corresponding to a beam incident from above the surface and the image problem of a beam coming from below the surface. This is the standard method used for elastic scattering.[7,9,10] One can also obtain somewhat more approximate results using modifications of the eikonal approximation, but care must be taken to include multiple reflections between the hard-core adsorbate and the surface.

We note that it is the differential reflection coefficient that is usually measured rather than the transition rate. This is obtained from $w(\mathbf{k}_f,\mathbf{k}_i)$ upon dividing by the incident flux $j_i=\hbar k_{iz}/m$ and multiplying by the density of states for a final scattered particle $N_f=m\,|\mathbf{k}_f|/\hbar^2(2\pi)^3$.

III. THERMAL ATTENUATION

In order to develop the transition rate of Eq. (8) further we must examine the structure factor (9). As long as we remain within the harmonic approximation the vibrational average involving the defect displacements can be handled by standard methods.[11] We have

$$\langle e^{i\mathbf{k}\cdot\mathbf{u}_l(0)}e^{-ik\cdot u_j(t)}\rangle=e^{-(1/2)\langle[\mathbf{k}\cdot\mathbf{u}_l(0)]^2\rangle}e^{-(1/2)\langle[\mathbf{k}\cdot u_j(t)]^2\rangle}e^{\langle\mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle} \ . \qquad (10)$$

Since all adsorbates are the same and located at similar sites, the first two factors on the right of Eq. (10) are independent of position and are the Debye-Waller factors:

$$e^{-(1/2)\langle[\mathbf{k}\cdot\mathbf{u}_j(t)]^2\rangle}=e^{-(1/2)\langle(\mathbf{k}\cdot\mathbf{u})^2\rangle}=e^{-W(\mathbf{k})} \ . \qquad (11)$$

An important simplification occurs in the displacement correlation function in the case of Einstein modes. The meaning of a dispersionless adsorbate mode is that each adsorbate vibrates at a single frequency and the vibrations between neighbors are uncorrelated:

$$\langle\mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle=\langle\mathbf{k}\cdot\mathbf{u}(0)\mathbf{k}\cdot\mathbf{u}(t)\rangle\delta_{lj} \ . \qquad (12)$$

Furthermore, if there is only one vibrational frequency, this will be associated with motion in a particular direction. If we let the momentum exchange in that direction be Q then the correlation function becomes

$$\langle \mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle = Q^2\langle u(0)u(t)\rangle\delta_{lj}\;. \tag{13}$$

In the case of physisorbed noble gases, the direction of the vibrational motion is normal to the surface.[1-3] For CO chemisorbed on a Pt(111) surface the Einstein frequency is identified with a wagging mode[4] and the displacement is parallel to the surface. However, even in this latter case we need consider only a single direction of momentum transfer since in most experiments the incident beam and detector are in the same plane with the normal to the surface. The displacement correlation function of the single mode can be written in terms of the frequency distribution function $\rho(\omega)$ as

$$\langle u(0)u(t)\rangle = \frac{\hbar}{2M}\int_0^{\omega_D}\frac{d\omega}{\omega}\rho(\omega) \times\{n(\omega)e^{i\omega t}+[n(\omega)+1]e^{-i\omega t}\}\;, \tag{14}$$

where ω_D is the cutoff frequency, $n(\omega)$ is the Bose-Einstein function, and M is the mass of the adsorbate. For an Einstein mode of frequency Ω the spectral density is a δ function,

$$\rho(\omega)=\delta(\omega-\Omega) \tag{15}$$

and we have

$$\langle u(0)u(t)\rangle = \frac{\hbar}{2M\Omega}\{n(\Omega)e^{i\Omega t}+[n(\Omega)+1]e^{-i\Omega t}\}\;. \tag{16}$$

We now return to the question of the scattering transition rate. This can be developed in terms of a series in numbers of quanta exchanged by developing the exponential of the displacement correlation function in Eq. (10):

$$e^{\langle \mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle} = 1+\langle \mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle +\tfrac{1}{2}\langle \mathbf{k}\cdot\mathbf{u}_l(0)\mathbf{k}\cdot\mathbf{u}_j(t)\rangle^2+\cdots\;. \tag{17}$$

Keeping only the zeroth-order term in Eq. (8) leads to

$$w(\mathbf{k}_f,\mathbf{k}_i)=\frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\, e^{-i(\varepsilon_f-\varepsilon_i)t/\hbar}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 \times e^{-2W(Q)}\sum_{l,j}\langle\langle e^{i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_j)}\rangle\rangle\;. \tag{18}$$

If the adsorbates are randomly distributed on the surface the double summation is equal to η where η is the number of adsorbates, giving

$$w(\mathbf{k}_f\mathbf{k}_i)=\frac{2\pi\eta}{\hbar}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2e^{-2W(Q)}\delta(\varepsilon_f-\varepsilon_i)\;. \tag{19}$$

There are, however, other contributions to the elastic scattering. For example, the second-order term of the development in Eq. (17) contributes to double quantum annihilation, double quantum creation, and to terms involving the creation of one quantum and the annihilation of another at different times. These latter processes give no net energy exchange, but they are real quantum exchange processes as opposed to the virtual processes which contribute to the Debye-Waller factor of Eq. (11). The total real double quantum contribution to the transition rate is

$$\begin{aligned} w^{(2)}(\mathbf{k}_f,\mathbf{k}_i)=\frac{2\pi Q^4\eta}{\hbar M^2\Omega^2}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2e^{-2W(Q)} &\times\{\delta(\varepsilon_f-\varepsilon_i-2\hbar\Omega)n^2(\Omega)\\ &+\delta(\varepsilon_f-\varepsilon_i+2\hbar\Omega)[n(\Omega)+1]^2\\ &+2\delta(\varepsilon_f-\varepsilon_i)n(\Omega)[n(\Omega)+1]\}\;. \end{aligned} \tag{20}$$

The double summation over adsorbate sites again produces the factor η because of the δ_{lj} appearing in the displacement correlation function (13). In the brackets, the first and second terms give the double quantum annihilation and creation, respectively, while the third term is the elastic contribution. Clearly, all terms involving the exchange of an even number of quanta will give a positive contribution to the elastic intensity. It is a straightforward matter to sum all such terms and the result for the total elastic transition rate is

$$w^{(0)}(\mathbf{k}_f,\mathbf{k}_i)=\frac{2\pi\eta}{\hbar}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2e^{-2W(Q)} \times I_0\left[\frac{Q^2\hbar}{m\Omega}\sqrt{n(\Omega)[n(\Omega)+1]}\right]\delta(\varepsilon_f-\varepsilon_i)\;, \tag{21}$$

where $I_0(z)$ is the Bessel function of imaginary argument. We note here that Eq. (21) describes diffuse or incoherent elastic scattering although energy is conserved, $|\mathbf{k}_f|=|\mathbf{k}_i|$. The particles are scattered in all directions according to the distribution dictated by the form factor $|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2$. At low temperatures $k_BT \ll \hbar\Omega$ we have $n(\Omega)\to 0$ and the Bessel function approaches unity leaving the ordinary Debye-Waller behavior of Eq. (19). On the other hand, at high temperatures, $k_BT>\hbar\Omega$ where $n(\Omega)\to k_BT/\hbar\Omega$. The higher-order quantum transfers make an important correction to the thermal attenuation. From Eqs. (11) and (16) we have for the Debye-Waller exponent

$$W(Q)=\tfrac{1}{2}Q^2\langle u^2(0)\rangle=\frac{\hbar Q^2}{2M\Omega}[n(\Omega)+\tfrac{1}{2}]\;. \tag{22}$$

The large-argument form for the Bessel function is

$$I_0(z)\xrightarrow[z\to\infty]{} e^z/\sqrt{2\pi z}\;. \tag{23}$$

Thus at large temperatures the decreasing exponential of the Debye-Waller factor is canceled by the exponential part of the Bessel function, leaving

$$\begin{aligned} w^{(0)}(\mathbf{k}_f,\mathbf{k}_i)&\approx\frac{2\pi\eta}{\hbar}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2\frac{1}{(2\pi Q^2\hbar n(\Omega)/M\Omega)^{1/2}}\\ &\approx\frac{2\pi\eta}{\hbar}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2\frac{\sqrt{M}\,\Omega}{(2\pi Q^2k_BT)^{1/2}}\;. \end{aligned} \tag{24}$$

These results show that the diffuse elastic scattering from a collection of Einstein oscillators exhibits a quite different thermal attenuation behavior from the coherent or diffractive scattering, and this difference becomes very apparent at high temperatures where the thermal attenuation varies according to $1/\sqrt{T}$.

Although until this point we have examined the elastic scattering, such corrections due to higher-order quantum exchange also appear in all of the inelastic intensities. For example, the contribution to the intensity from the exchange of three real quanta has terms involving both annihilation and creation which lead to a net exchange of only a single quantum. All of these inelastic exchange processes can be summed and expressed as

$$w(\mathbf{k}_f,\mathbf{k}_i)=\frac{2\pi}{\hbar}\eta\sum_{\alpha=1}^{\infty}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 e^{-2W(Q)} I_\alpha\left[\frac{Q^2\hbar}{m\Omega}\sqrt{n(\Omega)[n(\Omega)+1]}\right]$$
$$\times(\delta(\varepsilon_f-\varepsilon_i-\alpha\hbar\Omega)\{n(\Omega)/[n(\Omega)+1]\}^{\alpha/2}+\delta(\varepsilon_f-\varepsilon_i+\alpha\hbar\Omega)\{[n(\Omega)+1]/n(\Omega)\}^{\alpha/2}) . \quad (25)$$

Again, as in Eq. (24) above, at high temperatures the Debye-Waller factor is canceled by the exponential part of the Bessel function, leaving a thermal attenuation which falls off as $1/\sqrt{T}$. At very low temperatures as $n(\Omega)\rightarrow 0$, the transition rate for multiple quantum exchange is the well-known Poisson distribution

$$w(\mathbf{k}_f,\mathbf{k}_i)\xrightarrow[k_BT\ll\hbar\Omega]{}\frac{2\pi}{\hbar}\eta\sum_{\alpha=0}^{\infty}|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2$$
$$\times e^{-\hbar Q^2/2M\Omega}\left[\frac{\hbar Q^2}{2M\Omega}\right]^{\alpha}\frac{1}{\alpha!}$$
$$\times\delta(\varepsilon_f-\varepsilon_i+\alpha\hbar\Omega) . \quad (26)$$

Figure 1 is a plot of the temperature dependence of the thermal attenuation of the diffuse elastic peak as given by Eq. (21). On the vertical axis is the product of the Debye-Waller factor and the Bessel function

$$I=e^{-2W(Q)}I_0\left[\frac{Q^2\hbar}{M\Omega}\sqrt{n(\Omega)[n(\Omega)+1]}\right] \quad (27)$$

plotted as a function of the dimensionless temperature $x=Q^2k_BT/M\Omega^2$. The parameters are chosen for the case of CO adsorbates on Pt(111) in which $\hbar\Omega\sim 6$ meV and we take a typical value for Q of 4 Å^{-1}. Also plotted on the same figure is the Debye-Waller factor $\exp[-2W(Q)]$. At temperatures low compared to the Einstein frequency the thermal attenuation looks very much like the Debye-Waller factor, but at higher temperatures the saturation effect due to the multiquantum contributions becomes dominant. Note that the temperature at which the transition occurs $T\sim M\Omega^2/Q^2k_B$ depends strongly on the momentum transfer Q, with the saturation to the high-temperature region occurring much sooner at large Q (or large scattering angles away from specular).

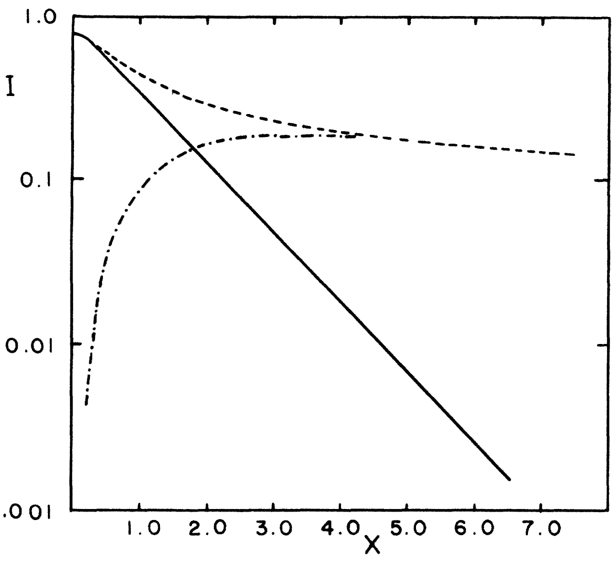

FIG. 1. The temperature dependence of the diffuse elastic intensity plotted as a function of the variable $x=Q^2k_BT/M\Omega^2$. The momentum exchange is $Q=4$ Å^{-1} and $\hbar\Omega=6$ meV, corresponding to CO adsorbed on Pt(111). —— is the Debye-Waller factor, $\exp[-2W(Q)]$; — — — is the temperature dependence of Eq. (27), $\exp[-2W(Q)]I_0$; and —·—·— is the temperature-dependent part of Eq. (37) for an ordered surface, $\exp[-2W(Q)](I_0-1)$.

IV. A VIBRATING SURFACE SUBSTRATE

Up to this point we have considered a collection of vibrating adsorbates on a flat, rigid surface substrate. In any real situation, the substrate will also be vibrating and this certainly has important consequences for the thermal attenuation of the diffuse scattering. To a good approximation, we can write the displacement of the jth adsorbate as the sum of two terms,

$$\mathbf{u}_j(t)=\mathbf{u}_j^s(t)+\mathbf{u}_j^a(t) , \quad (28)$$

where $\mathbf{u}_j^a(t)$ is the displacement due to the Einstein mode vibrations [written simply as $u_j(t)$ up to this point] and $u_j^s(t)$ is the additional contribution due to the substrate vibrations. It is a good assumption that the substrate modes and the Einstein mode are independent, which can be expressed as

$$\langle\mathbf{k}\cdot\mathbf{u}_j^s(t)\mathbf{k}\cdot\mathbf{u}_l^a(0)\rangle=0 , \quad (29)$$

where $\mathbf{k}$ can be a vector in any direction.

Now we need to reconsider the phonon average appearing in a structure factor of the transition rate in Eq. (8). Again, in the harmonic approximation we arrive at an expression identical with Eq. (10) except that the displacements are given by Eq. (28). We first consider the terms which produce the Debye-Waller factor

$$\begin{aligned}\langle[\mathbf{k}\cdot\mathbf{u}_j(t)]^2\rangle &= \langle\{\mathbf{k}\cdot[\mathbf{u}_j^s(t)+\mathbf{u}_j^a(t)]\}^2\rangle \\ &= \langle[\mathbf{k}\cdot\mathbf{u}_j^s(t)]^2\rangle+\langle[\mathbf{k}\cdot\mathbf{u}_j^a(t)]^2\rangle \\ &\quad +\langle\mathbf{k}\cdot\mathbf{u}_j^s(t)\mathbf{k}\cdot\mathbf{u}_j^a(t)\rangle+\langle\mathbf{k}\cdot\mathbf{u}_j^a(t)\mathbf{k}\cdot\mathbf{u}_j^s(t)\rangle \;.\end{aligned} \tag{30}$$

The last two terms on the right vanish because of Eq. (29) and we are left with a Debye-Waller exponent which is the sum of two contributions,

$$\tfrac{1}{2}\langle[\mathbf{k}\cdot\mathbf{u}_j(t)]^2\rangle = W^s(\mathbf{k})+W^a(\mathbf{k}) \;, \tag{31}$$

where $W^s(\mathbf{k})$ is the contribution due to the substrate vibrations and $W^a(\mathbf{k})$ is the contribution from the Einstein modes which we have simply called $W(\mathbf{k})$ up to this point. Because of Eq. (29) the time-dependent correlation function also separates into substrate and adsorbate contributions

$$\begin{aligned}\langle\mathbf{k}\cdot\mathbf{u}_j(0)\mathbf{k}\cdot\mathbf{u}_l(t)\rangle &= \langle\mathbf{k}\cdot\mathbf{u}_j^s(0)\mathbf{k}\cdot\mathbf{u}_l^s(t)\rangle \\ &\quad +\langle\mathbf{k}\cdot\mathbf{u}^a(0)\mathbf{k}\cdot\mathbf{u}^a(t)\rangle\delta_{jl} \;.\end{aligned} \tag{32}$$

Thus the transaction rate (8) takes the form

$$w(\mathbf{k}_f,\mathbf{k}_i) = \frac{1}{\hbar^2}\int_{-\infty}^{\infty} dt\, e^{-i(\varepsilon_f-\varepsilon_i)t/\hbar}\,|\tau(\mathbf{k}_f\mathbf{k}_i)|^2 e^{-2W^s} e^{-2W^a} \sum_{j,l}\langle\langle e^{i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_j)} e^{\langle\mathbf{k}\cdot\mathbf{u}_j^s(0)\mathbf{k}\cdot\mathbf{u}_l^s(t)\rangle} e^{\langle\mathbf{k}\cdot\mathbf{u}^a(0)\mathbf{k}\cdot\mathbf{u}^a(t)\rangle\delta_{jl}}\rangle\rangle \tag{33}$$

The major changes in comparison with our previous expression of Eq. (8) are the addition of the substrate Debye-Waller factor, and the possibility of exchange of substrate phonons provided by the presence of the substrate displacement correlation function in the exponential.

Starting from Eq. (33) we now consider the elastic scattering contributions to the transition rate. Again the first-order contribution comes from replacing the displacement correlation function exponentials by unity. The double summation over adsorbate sites gives a factor η for a random distribution and we recover an expression similar to (19) except that it is multiplied by the substrate Debye-Waller factor. Correlation terms coming from multiquantum exchange of the adsorbate Einstein modes lead to the same correction that we obtain in the previous section, and we have

$$\begin{aligned}w(\mathbf{k}_f,\mathbf{k}_i) &= \frac{2\pi}{\hbar}\eta\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 e^{-2W^2(\mathbf{k})} e^{-2W^a(Q)} \\ &\quad\times I_0\left[\frac{Q^2\hbar}{M\Omega}\sqrt{n(\Omega)[n(\Omega)+1]}\right]\delta(\varepsilon_f-\varepsilon_i) \;.\end{aligned} \tag{34}$$

Corrections to the thermal attenuation coming from the multiple exchange of real substrate phonons are negligible. This is due to the fact that the frequency distribution function $\rho^s(\omega)$ for the substrate modes is a continuous function of ω. This is most easily demonstrated by replacing $\exp[\langle\mathbf{k}\cdot\mathbf{u}_j^s(0)\mathbf{k}\cdot\mathbf{u}_l^s(t)\rangle]$ in Eq. (33) by its second-order expansion in order to examine the two-phonon contribution. If $\rho^s(\omega)$ is a smoothly varying function the two-phonon contribution will be an inelastic background without a δ-function contribution at the elastic condition $\varepsilon_f=\varepsilon_i$. Thus the major contribution of substrate vibrations is simply to multiply the elastic diffuse scattered intensity by an additional Debye-Waller factor.

V. ORDERED OVERLAYERS

Experimental observations of adsorbate Einstein modes are often carried out at coverages approaching a monolayer. At such coverages the overlayer must take on a certain amount of two-dimensional ordering. For the case of CO on Pt(111) observations were made under conditions of ordered phases where diffraction peaks were detected. The Einstein mode was always visible, although it was shifted up in energy somewhat.[4]

It is interesting to examine both the coherent and diffuse elastic contributions in the situation in which there is an ordered overlayer. For such an overlayer, at very low surface temperatures all of the elastic intensity will be scattered into the coherent diffraction peaks and there will be no diffuse elastic contribution. As the temperature increases, multiple quantum exchange gives rise to contributions with no net energy exchange, and such contributions appear as a diffuse elastic background. Thus, as opposed to the case of random surface adsorbates, an ordered overlayer has a diffuse elastic contribution which initially increases with temperature and rises to a maximum before exhibiting the decrease due to thermal attenuation.

For simplicity we will again consider the adsorbates to be on a rigid substrate. As in Sec. III above, the elastic transition rate is given by Eq. (18). In the case of an ordered overlayer the summation over adsorbate sites becomes

$$\sum_{l,j}\langle\langle e^{i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_j)}\rangle\rangle = \eta^2\sum_{\mathbf{G}}\delta_{\mathbf{k},\mathbf{G}} \;, \tag{35}$$

where $\mathbf{G}$ is a surface reciprocal lattice vector of the ordered array of defects and η is again the number of defects. Thus the zeroth-order elastic scattering becomes

$$\begin{aligned}w(\mathbf{k}_f,\mathbf{k}_i) &= \frac{2\pi\eta^2}{\hbar}\sum_{\mathbf{G}}\delta_{\mathbf{k},\mathbf{G}}\delta(\varepsilon_f-\varepsilon_i)\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 \\ &\quad\times\exp[-W^a(Q)] \;.\end{aligned} \tag{36}$$

This is clearly a coherent contribution because it appears only at the diffraction peak positions and is proportional to η^2 as opposed to the diffuse or incoherent contribution which is proportional to η. There is no correction to this term due to exchange of real multiple Einstein quanta. For example, the two-quantum contribution is the same as Eq. (20). It is proportional to η and not η^2 as is Eq. (36) and is consequently a diffuse or incoherent contribution. The reason for this again lies in the independence of the vibrational motion of Einstein oscillators as expressed in Eq. (12). Thus Eq. (36) shows that the thermal attenuation of the coherent diffraction intensities is given by the classic Debye-Waller behavior. If we allow the substrate to vibrate also it would contribute an additional factor of $\exp[-2W^s(\mathbf{k})]$, as in the preceding section.

Moving on to a discussion of the diffuse or incoherent elastic contribution, all of it comes from the exchange of even numbers of multiple real quanta. We have already seen that the lowest-order contribution is the double quantum elastic term of Eq. (20). It is a straightforward matter to sum all of the higher-order corrections, which produces the following:

$$w^{(0)}(\mathbf{k}_f,\mathbf{k}_i)=\frac{2\pi\eta}{\hbar}\,|\tau(\mathbf{k}_f,\mathbf{k}_i)|^2 e^{-2W^a(Q)} \times\left[I_0\left[\frac{\hbar Q^2}{M\Omega}\sqrt{n(\Omega)[n(\Omega)+1]}\right]-1\right] \times\delta(\varepsilon_f-\varepsilon_i)\ . \tag{37}$$

This vanishes at low temperatures $k_B T \ll \hbar\Omega$, and increases with temperature initially as $\exp(-\hbar\Omega/k_B T)$. After rising to a maximum it decays at very large temperatures according to the $1/\sqrt{T}$ form discussed in Sec. III. The temperature-dependent part of Eq. (37), namely $\exp[-2W^a(Q)](I_0-1)$, is compared to that for a random distribution of adsorbates in Fig. 1, again for the conditions appropriate to CO adsorbed on Pt(111).

We mention in passing that the inelastic scattering intensity due to the ordered layer of Einstein oscillators is also diffuse and of exactly the same form as Eq. (25) for randomly distributed oscillators. Once again, it is constrained to be a diffuse or incoherent contribution because of the independence of different vibrators. This explains why the inelastic signal from the Einstein modes is clearly observed regardless of whether the adsorbate layer is ordered or disordered.

As a final note in this section we discuss briefly the question of partial ordering of the adsorbate layer. In particular, the surface substrate will in general have preferred sites, and even under conditions of dilute coverage the adsorbates will tend to locate in these preferred sites. Since the preferred sites form a lattice reflecting the periodicity of the surface, such a dilute layer of adsorbates will be a two-dimensional lattice gas. For elastic scattering, this distinction can be illustrated by considering the double summation over occupied lattice sites of Eq. (18). As usual for a lattice gas, this can be broken down into two terms,

$$\sum_{l,j}\langle\langle e^{i\mathbf{k}\cdot(\mathbf{R}_l-\mathbf{R}_j)}\rangle\rangle=\eta^2\sum\delta_{\mathbf{k},\mathbf{G}}+\eta\ , \tag{38}$$

where η is now the number of occupied sites instead of the total number of surface lattice cells as in the first part of this section.[12] The first term of (38) is proportional to η^2 and gives the coherent contribution, while the second term is the diffuse or incoherent part and is proportional to η. It is now easy to show that the coherent elastic part will have an intensity given by the same expression as Eq. (36), while the incoherent part is identical with the expression for random adsorbates appearing in Eq. (21). The inelastic intensity is also diffuse and has the same form as Eq. (25). These results are valid only for dilute coverages. As the coverage becomes more dense the overlayer will deviate from a random lattice-gas distribution due to the lateral forces between adsorbates. However, this discussion gives a general idea of the expected scattered intensity.

VI. CONCLUSIONS

We have considered here some aspects of the scattering of a beam of thermal-energy atoms by a dilute surface layer of adsorbates exhibiting a dispersionless Einstein mode. We see that the coherent elastic part, which exists if the adlayer is ordered or partially ordered, has a thermal attenuation behavior which is well described by a Debye-Waller factor. The diffuse elastic signal, on the other hand, has a thermal attenuation which can be regarded as coming from two sources, the vibrations of the substrate and the vibrations of the Einstein mode. The contribution from substrate vibrations is again given by a Debye-Waller factor. However, the contribution coming from the adsorbate vibrations, assumed to be a dispersionless Einstein mode, shows quite different behavior. At very low temperatures and for small momentum exchange the thermal attenuation looks very much like the Debye-Waller form, but at higher temperatures there is a saturation to a much weaker decay. The origin of this behavior is real multiquantum transfers which result in a net exchange of zero energy and hence add to the elastic intensity. These processes act in opposition to the virtual-phonon exchanges which are the origin of the Debye-Waller factor.

We also discuss the inelastic scattering by the Einstein modes and we find that this inelastic signal is always diffuse, even in the case in which the adsorbate layer is ordered or partially ordered. The inelastic intensity for an energy exchange corresponding to a given number of quanta also has strong corrections coming from higher-order quantum number interactions. These higher-order corrections give each inelastic peak a type of thermal attenuation behavior which is very similar to the elastic case. At low temperatures and momentum exchange the attenuation is essentially a Debye-Waller behavior, but at high temperatures the thermal attenuation saturates to a $1/\sqrt{T}$ behavior.

Since at least one system, that of CO on Pt(111), exhibits an Einstein mode even when the coverage is sufficiently high to form an ordered overlayer it is of interest to examine such a situation. The diffuse elastic signal for such a system should exhibit an interesting behavior. At low temperatures, all elastic intensity of an ordered system should appear in the diffraction peaks. At higher temperatures, when there can be both annihilation as well as creation of the Einstein quanta, the even numbered multiquantum processes will always have terms involving equal numbers of creative and annihilation events, and this leads to a diffuse signal at zero energy exchange. This diffuse elastic signal will increase with temperature and rise to a maximum before it finally decreases due to the thermal attenuation.

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