Double losses and overtones in electron-energy-loss studies of surface vibrations: The role of lateral interactions

J. C. Ariyasu and D. L. Mills

Department of Physics, University of California, Irvine, California 92717

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Within a simple model of an ordered overlayer of adsorbed molecules on a crystal surface, we develop a theory of two-phonon losses in the regime of small-angle scattering, where dipole losses dominate. Two features which correspond to a double loss and excitation of an overtone are identified in the model, and we study the role of lateral interactions on each of these. We find that the lateral interactions shift the overtone relative to the double loss; the overtone loss band may also have both its width and shape influenced significantly. The implications of these results are discussed, most particularly as they relate to estimates of dissociation energies by the Birge-Sponer extrapolation procedure.

I. INTRODUCTION

Electron-energy-loss spectroscopy has proved a powerful means of studying the vibrational normal modes of molecules adsorbed on the crystal surface.[1] Most experimental studies explore only inelastically scattered electrons which emerge very close to the specular direction. In this regime where the angular deflection of the electron from the specular trajectory is small, the primary mechanism which couples the electron to the vibration is its interaction with the fluctuating electric field produced by the time varying component of the electric dipole moment of the molecule in the vacuum above the crystal. In this dipole scattering regime, a selection rule[2] states that one observes only normal modes with oscillating dipole moments normal to the surface.

In recent experiments, multiquantum vibrational losses have been observed.[3,4] For example, if one has an adsorbed species with a vibrational normal mode of frequency ω_0, then two types of double losses may be observed. The electron can interact with one molecule, to excite it by the amount $\hbar\omega_0$, then excite a second distinctly different one by the same amount, to lose the energy $2\hbar\omega_0$ before it exits from the surface. We assume for the moment that the molecules are independent and noninteracting. On the other hand, the electron may excite a single molecule from its ground to second excited level to produce a loss at $2\hbar(\omega_0-\Delta)$, where Δ is an anharmonic shift. If 2Δ is greater than the linewidth, one sees two loss peaks, so the value of the anharmonic shift may be inferred from the data. The results reported by Schmeisser et al.[4] are particularly spectacular since, by using impact energies which coincide with negative-ion resonances of physisorbed species, they observe not only double losses such as those just described, but multiquantum losses near $n\hbar\omega_0$, with n as large as 8. The information obtained from such spectra is valuable because through use of an extrapolation procedure known as the Birge-Sponer rule,[5] the dissociation energy of the bond activated in the vibrational loss may be inferred.

The preceding comments assume the adsorbed molecules are noninteracting, as remarked earlier. In fact, many measurements are performed on dense overlayers,

where lateral interactions may produce shifts in the spectra comparable to the relatively small anharmonic shift. The purpose of this paper is to explore the role of lateral interactions on both processes described above in the two-quantum loss regime. We do this in a simple model of small-angle deflections appropriate to electric dipole dominated scattering. We conclude this section with a brief outline of our principal conclusions.
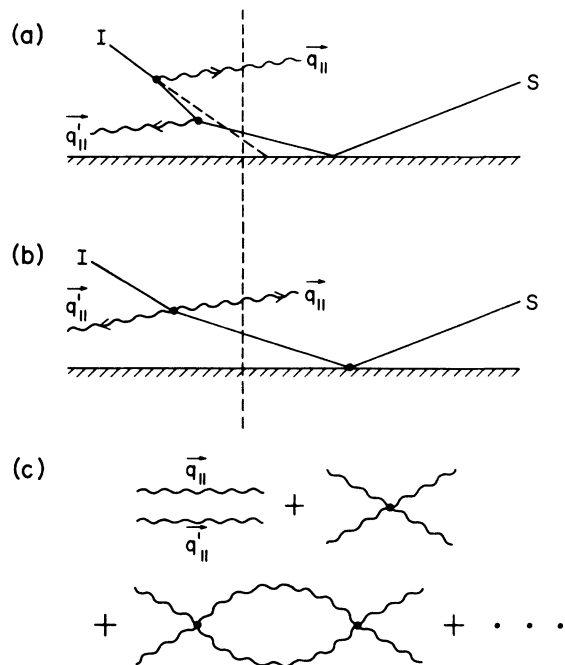

FIG. 1. (a) Schematic illustration of one process which contributes to the double loss. Here two phonons are created in a two-step process, with one phonon created at each vertex. (b) The double loss, where a pair of phonons is created in one event. (c) After the pair of phonons is created in the scattering event depicted in either (a) or (b), they may interact via the anharmonic terms in the surface-phonon Hamiltonian. Here we illustrate scatterings induced by the quartic terms in the normal coordinate.

Within this paper we view the two basic processes within the language of phonon theory, where anharmonicity is treated as a perturbation imposed upon the basic two-dimensional phonons of the adsorbate layer, which are described by a dispersion curve $\omega_s(\vec{q}_\parallel)$ in the presence of lateral interactions. Here $\vec{q}_\parallel$ is the wave vector of the surface phonon, which lies within the appropriate two-dimensional Brillouin zone. Then the processes we examine are those in which an electron emits two phonons as it reflects off the crystal surface. This may be done in one of two ways, as illustrated in Figs. 1(a) and 1(b). As the electron approaches the surface, it may emit two phonons in two distinctly different scattering events in which a single phonon is emitted each time. We show such a scattering process in Fig. 1(a). (Of course, the electron can also emit one or both phonons as it exits the crystal. We show only one process here.) This is the double loss, viewed in the phonon language.[6] The electron may also emit a pair of phonons in a single scattering event; we shall see that with anharmonicity incorporated this becomes the double loss, in the limit that lateral interactions are ignored. As implied, inclusion of anharmonicity is crucial, and in the phonon theory a key element is the fact that the two phonons emitted may interact via anharmonicity, as illustrated in Fig. 1(c). The outline of this paper is as follows: Section II discusses the description of the scattering process, and leads us to a certain two-phonon Green's function which must be studied; Sec. III explores the Green's function, within a certain decoupling scheme; Sec. IV presents the results of numerical studies and our conclusions.

II. DESCRIPTION OF TWO-PHONON SCATTERING PROCESSES

This section develops a theoretical description of near-specular inelastic electron scattering, under the assumption that it is the fluctuating electric dipole moment of the adsorbed species that is responsible for coupling the electron to the interactions. We shall consider the simplest case of an adsorbate with a single normal mode of frequency ω_0 (in the harmonic approximation), and with an associated normal coordinate u. In a more complex and realistic system, in addition to the two-phonon losses considered here, all of which occur near the frequency $2\omega_0$, one may have combination bands near $\omega_a + \omega_b$, with ω_a and ω_b as the frequencies of distinct normal modes. While we confine our attention to the simple case outlined above, very similar considerations surely apply to such combination bands.

The Hamiltonian we consider consists of three terms,

$$H = H_{\rm ph} + H_e + V , \qquad (2.1)$$

where $H_{\rm ph}$ describes the normal modes of the vibrating adsorbate layer, with lateral interactions and anharmonicity included. We shall not need the explicit form of $H_{\rm ph}$ here, though in our discussion we shall invoke certain assumptions about its form. The second term H_e describes the electron in the vacuum above the crystal and its interaction with the (static) lattice. Again, we need say little about this term also. Finally, V describes the coupling of the electron to the vibrating adsorbate. As in earlier work,[2] we suppose the dominant contribution to V comes

from interaction between the electron and the fluctuating electric field in the vacuum produced by the vibrating molecules. We invoke the dipole selection rule[2] and suppose that only the component of the electric dipole moment normal to the surface $P_\perp$ is responsible for this field. Then if $P_\perp^{(i)}$ is the dynamic dipole moment of the ith adsorbate, V has the form[2]

$$V = \frac{4\pi e e}{A(1+\epsilon)} \sum_{\vec{Q}_\parallel} \sum_i P_\perp^{(i)} e^{i\vec{Q}_\parallel \cdot (\vec{x}_\parallel - \vec{R}_\parallel^{(i)})} e^{-Q_\parallel z} . \qquad (2.2)$$

Here e is the electron charge, ϵ is the dielectric of the substrate ($\epsilon \to \infty$ for a metal), A is the area of the surface, $\vec{R}_\parallel^{(i)}$ is the location of the ith adsorbate in the layer parallel to the surface, and the position of the electron in the vacuum above the crystal is $\vec{x} = \vec{x}_\parallel + \hat{z}z$, with the vacuum in the half-space $z > 0$.

The dynamic dipole moment $P_\perp$ is a function of the normal coordinate u of the dipole-active vibrational mode. One has the Taylor-series expansion

$$P_\perp^{(i)} = e^* u^{(i)} + e^* \gamma (u^{(i)})^2 + \cdots , \qquad (2.3)$$

where e^* is the dynamic effective charge [the influence of the image charge is incorporated in the prefactor of Eq. (2.2)] and γ is a parameter with dimensions of inverse length which enters the quadratic term. Earlier theories of dipole scattering incorporate only the linear term in their treatment of scattering by one-phonon events[1,2] and in the discussion of multiphonon scattering.[6] In the present treatment the quadratic term will play a crucial role, in that it allows the incoming electron to excite a particular adsorbate directly from the ground to the second vibrational level. (This is the overtone feature in the loss spectrum, if the molecules are regarded as uncoupled and independent.) Excitation of one particular molecule from the ground to the second vibrational level may be achieved by treating the linear term in second order, but the probability that such a "double excitation" of one adsorbate, via this process, occurs is very small. The reason is, as discussed elsewhere,[1] that the electron excites the molecular vibration via the dipole mechanism when it is 50–100 Å above the crystal surface, under typical experimental conditions. If it excites molecule i via the linear term in $P_\perp^{(i)}$ when it is that far above the surface, it is overwhelmingly probable that a second interaction will involve excitation of a distinctly different adsorbate $j \neq i$. Thus in the limit of independent adsorbates, we have the double loss as the dominant feature produced by this process.

When Eq. (2.3) is inserted into Eq. (2.2), we have

$$V = V_1 + V_2 , \qquad (2.4)$$

with V_1 and V_2 linear and quadratic in $u^{(i)}$, respectively. We shall treat V_1 in the second order of perturbation theory and V_2 in the first order, realizing that in the presence of lateral interactions the adsorbates are not independent entities, so V_2 in first order and V_1 taken to second order couple to the same final state of the system. Thus we must calculate the two matrix elements and add them together before calculating the total scattering cross section. We begin by sketching the calculation of the contribution to the scattered wave second order in V_1, then we

add on the first-order term from V_2. The wave function $|\psi_s^{(2)}\rangle$ second order in V_1 may be written, in operator notation similar to that used elsewhere,[7]

$$|\psi_s^{(2)}\rangle = \frac{1}{(H_{\rm ph}+H_e-E_0)}V_1\frac{1}{(H_{\rm ph}+H_e-E_0)}V_1|\psi_0\rangle ,$$

(2.5)

where E_0 is the energy of the initial state. We have $|\psi_0\rangle = |\psi_I^{(e)}\rangle|N\rangle$, where $|\psi_I^{(e)}\rangle$ describes the incident electron wave, including its interaction with the rigid crystal, and $|N\rangle$ is the vibrational eigenstate encountered by the electron. Also $E_0 = \epsilon_I + E_N$, with ϵ_I as the incident electron kinetic energy, and E_N that of the vibrational eigenstate. One may insert in various places in Eq. (2.5) the identity operator

$$\hat{I} = \sum_{N'}\int d^3r\,|N'\rangle\,|\vec{r}\rangle\langle\vec{r}|\langle N'| ,$$

(2.6)

and note that

$$\langle N\,|\langle\vec{r}'\,|\,V_1\,|\,\vec{r}\rangle\,|\,M\rangle = \delta(\vec{r}'-\vec{r})\langle N\,|\,V_1(\vec{r})\,|\,M\rangle$$

(2.7)

to obtain the following form for the quantity $\langle M\,|\langle\vec{r}\,|\,\psi_s^{(2)}\rangle$, which is the probability amplitude for finding the electron at the position $\vec{r}$ with the crystal in the vibrational eigenstate $|M\rangle$:

$$\langle M\,|\langle\vec{r}\,|\,\psi_s^{(0)}\rangle = \sum_{N'}\int d^3r\,G(\vec{r},\vec{r}';\epsilon_s)$$

$$\times\langle N\,|\,V_1(\vec{r}')\,|\,N'\rangle G(\vec{r}'\vec{r};\epsilon_n)$$

$$\times\langle N'\,|\,V_1(\vec{r})\,|\,N\rangle\psi_I^{(e)}(\vec{r}) .\quad(2.8)$$

Here $G(\vec{r},\vec{r}';\epsilon)$ is the Green's function of the electron, as it moves in the vicinity of the rigid crystal,

$$G(\vec{r},\vec{r}';\epsilon) = \langle\vec{r}\,|\,(H_e-\epsilon)^{-1}\,|\,\vec{r}'\rangle ,$$

$$\epsilon_n = \epsilon_I + (E_N - E_{N'}) ,$$

$$\epsilon_s = \epsilon_I + (E_N - E_M)$$

is the energy of the scattered electron, and $\psi_I^{(e)}(\vec{r})$ is the wave function of the incoming electron. As in earlier work, we suppose for simplicity that the crystal surface is a perfectly smooth plane (the results obtained below are, in fact, independent of this assumption). Then the Green's function has the form

$$G(\vec{r},\vec{r}';\epsilon) = \int\frac{d^2k_\parallel}{(2\pi)^2}e^{i\vec{k}_\parallel\cdot(\vec{r}_\parallel-\vec{r}'_\parallel)}g(z,z';\vec{k}_\parallel,\epsilon) ,$$

(2.9)

and it will be convenient to write V_1 in the form

$$V_1 = \frac{1}{A^{1/2}}\sum_{\vec{q}_\parallel}\Gamma(\vec{q}_\parallel)e^{-\vec{q}_\parallel\cdot\vec{x}_\parallel}e^{-q_\parallel z}(a^\dagger_{\vec{q}_\parallel}+a_{-\vec{q}_\parallel}) .$$

(2.10)

We retain only the terms which describe the emission of two vibration quanta. Finally, one has

$$\psi_I^{(e)}(\vec{r}) = \exp(i\vec{k}_\parallel^{(I)}\cdot\vec{r}_\parallel)\phi_I(z) ,$$

and after some algebra, one finds that

$$\langle M\,|\langle\vec{r}\,|\,\psi_s^{(2)}\rangle = \frac{1}{A}\sum_{\vec{q}'_\parallel}\sum_{\vec{q}''_\parallel}\Gamma(\vec{q}'_\parallel)\Gamma(\vec{q}''_\parallel)\langle M\,|\,a^\dagger_{\vec{q}'_\parallel}\,|\,N'\rangle\langle N'\,|\,a^\dagger_{q''_\parallel}\,|\,N\rangle e^{i\vec{k}_\parallel^{(s)}\cdot\vec{r}_\parallel}$$

$$\times\int_0^\infty dz'\int_0^\infty dz''g(z,z';\vec{k}_\parallel^{(s)},\epsilon_s)e^{-q'_\parallel z'}g(z',z'';\vec{k}_\parallel^{(n)},\epsilon_n)e^{-q''_\parallel z''}\phi_I(z'') ,$$

(2.11)

where

$$\vec{k}_\parallel^{(n)} = \vec{k}_\parallel^{(I)} - \vec{q}''_\parallel$$

(2.12a)

and

$$\vec{k}_\parallel^{(s)} = \vec{k}_\parallel^{(I)} - \vec{q}'_\parallel - \vec{q}''_\parallel .$$

(2.12b)

The explicit form of $g(z,z';\vec{k}_\parallel\epsilon)$ has been presented some time ago.[2] We only require its form for z and z' in the vacuum above the crystal, in the present work. If $k_\perp$ is the magnitude of the component normal to the surface of the wave vector of an electron of energy ϵ, then for z and $z'>0$ one has

$$g(z,z';\vec{k}_\parallel\epsilon) = i\frac{m}{k_\perp}[\psi^+(\epsilon,z)\psi^-(\epsilon,z')\Theta(z-z')$$

$$+\psi^-(\epsilon,z)\psi^+(\epsilon,z')\Theta(z'-z)] ,$$

(2.13)

where for $z>0$, $\psi^+(z) = \exp(ik_\perp z)$ and

$$\psi^-(z) = \exp(-ik_\perp z) + R(\epsilon)\exp(ik_\perp z) ,$$

where $R(\epsilon)$ is the amplitude of the reflected wave of an electron which strikes the surface with energy E and wave vector $\vec{k}_\parallel$.

The next task is to perform the integrals on z' and z'' which appear in Eq. (2.11). This is a tedious matter and, in fact, in an early paper[6] which ignored both the role of lateral intractions and anharmonicity, a detailed discussion is given of this step and the physical meaning of the various terms that enter the final expression. Thus we shall only quote the final result. As before, we assume the dominant contribution to the cross section comes from those events in which the electron is scattered in the near forward direction off of the vibrational modes; then elastic back reflection off the surface allows it to emerge near the specular direction. As earlier, we neglect the energy and

angle variation of the amplitude for backscattering off the surface, so $R(\epsilon)$ is replaced by $R(\epsilon_I)$ everywhere. If $\vec{v}^{(I)}=\vec{v}_{||}^{(I)}+\hat{z}v_\perp^{(I)}$ is the velocity of the incoming electron, two quantities which enter the final expression are

$$\alpha_{\vec{q}\,''_{||}} \equiv v_\perp^{(I)} q\,''_{||} + i[(E_N - E_{N'}) - \vec{v}_{||}^{(I)}\cdot\vec{q}\,''_{||}] \qquad (2.14a)$$

and

$$\alpha_{\vec{q}\,'_{||}} \equiv v_\perp^{(I)} q\,'_{||} + i[(E_{N'} - E_M) - \vec{v}_{||}^{(I)}\cdot\vec{q}\,'_{||}] . \qquad (2.14b)$$

Here E_N, $E_{N'}$, and E_M are the energies of the various vibrational eigenstates which enter Eq. (2.11). Then Eq. (2.11) gives

$$\langle M \mid \langle \vec{r} \mid \psi_s^{(2)} \rangle = -\frac{R(\epsilon_I)}{A}\sum_{N'}\sum_{\vec{q}\,'_{||}}\sum_{\vec{q}\,''_{||}}\Gamma(\vec{q}\,'_{||})\Gamma(\vec{q}\,''_{||})\langle M \mid a^\dagger_{\vec{q}\,'_{||}} \mid N'\rangle\langle N' \mid a^\dagger_{\vec{q}\,''_{||}} \mid N\rangle e^{i\vec{k}_{||}^{(s)}\cdot\vec{r}_{||}}$$

$$\times e^{ik_\perp^{(s)}z}\left[\frac{1}{\alpha_{\vec{q}\,''_{||}}(\alpha_{\vec{q}\,''_{||}}+\alpha_{\vec{q}\,'_{||}})}+\frac{1}{\alpha_{\vec{q}\,''_{||}}\alpha^*_{\vec{q}\,'_{||}}}+\frac{1}{\alpha^*_{\vec{q}\,'_{||}}(\alpha^*_{\vec{q}\,'_{||}}+\alpha^*_{\vec{q}\,''_{||}})}\right] . \qquad (2.15)$$

We now make one approximation. So far, we have said little about the nature of the vibrations of the adsorbate layer. We envision, for simplicity, a system such as adsorbed CO, where the vibrational frequency ω_0 of the isolated species is very large compared to any shift provided by lateral interactions, or that provided by anharmonicity. In this limit, it is reasonable to replace the energy differences $E_N - E_{N'}$ and $E_{N'} - E_M$ by simply ω_0, a good approximation to energy difference between these states (we use units with $\hbar = 1$). This allows one to perform the sum over intermediate states N' which appear in Eq. (2.15), and after some algebra the result may be shown in the form

$$\langle M \mid \langle \vec{r} \mid \psi_s^{(2)} \rangle = -\frac{2R(\epsilon_I)}{A}\sum_{\vec{q}\,'_{||}}\sum_{\vec{q}\,''_{||}}\frac{(v_\perp^{(I)})^2 q\,'_{||}q\,''_{||}\Gamma(\vec{q}\,'_{||})\Gamma(\vec{q}\,''_{||})\langle M \mid a^\dagger_{\vec{q}\,'_{||}}a^\dagger_{\vec{q}\,''_{||}} \mid N\rangle}{(\omega_0 - \vec{v}_{||}^{(I)}\cdot\vec{q}\,'_{||})^2+(v_\perp^{(I)}q\,'_{||})^2}\frac{\exp(i\vec{k}_{||}^{(s)}\cdot\vec{r}_{||}+ik_\perp^{(s)}z)}{(\omega_0 - \vec{v}_{||}^{(I)}\cdot\vec{q}\,''_{||})^2+(v_\perp^{(I)}q\,''_{||})^2} .$$

$$(2.16)$$

For this expression it is a straightforward matter to derive the final scattering cross section for the two-phonon excitation. However, as shown earlier, the term V_2 in Eq. (2.4) scatters the electron from the same initial to the same final state. We thus must include this contribution to the scattering amplitude before we proceed. The derivation proceeds along very similar lines, so once again we shall only quote the result. It is convenient to let $\vec{Q}_{||}=\vec{q}\,'_{||}+\vec{q}\,''_{||}$, so that the wave vector of the scattered electron becomes $\vec{k}_{||}^{(s)}=\vec{k}_{||}^{(I)}-\vec{Q}_{||}$, when projected onto a plane parallel to the surface. If we call $\mid \psi_s^{(T)}\rangle$ the total scattered wave function, with both contributions included, then we have

$$\langle M \mid \langle \vec{r} \mid \psi_s^{(T)} \rangle = -\frac{2v_\perp^{(I)}R(\epsilon_I)}{A}\sum_{\vec{Q}_{||}}e^{i\vec{k}_{||}^{(s)}\cdot\vec{r}_{||}}e^{ik_\perp^{(s)}z}$$

$$\times\sum_{\vec{q}_{||}}\left[\frac{v_\perp^{(I)}q_{||}\mid\vec{Q}_{||}-\vec{q}_{||}\mid}{[(v_\perp^{(I)}q_{||}^2+(\omega_0-\vec{v}_{||}^{(I)}\cdot\vec{q}_{||})^2][(v_\perp^{(I)}\mid\vec{Q}_{||}-\vec{q}_{||}\mid)^2+(\omega_0-\vec{v}_{||}^{(I)}\cdot\vec{Q}_{||}+\vec{v}_{||}^{(I)}\cdot\vec{q}_{||})^2]}\right.$$

$$\left.-ir\frac{Q_{||}}{\omega_0[(v_\perp^{(I)}Q_{||}^2+(2\omega_0-\vec{v}_{||}^{(I)}\cdot\vec{Q}_{||})^2]}\right]\Gamma(\vec{q})\Gamma(\vec{Q}_{||}-\vec{q}_{||})\langle M \mid a^\dagger_{\vec{q}_{||}}a^\dagger_{\vec{Q}_{||}-\vec{q}_{||}} \mid N\rangle .$$

$$(2.17)$$

We have introduced (including $\hbar$) the dimensionless parameter

$$r=\frac{(1+\epsilon)\gamma\hbar\omega_0}{4\pi n_s\epsilon ee^*} . \qquad (2.18)$$

The final step is to use the wave function above to calculate the scattering cross section. Upon converting the sum on $\vec{Q}_{||}$ to an integration, Eq. (2.17) may be written

$$\langle M \mid \langle \vec{r} \mid \psi_s^{(T)} \rangle = -\frac{AR(\epsilon_I)}{(2\pi)^2}\int d^2Q_{||}M_{MN}(\vec{Q}_{||})e^{i\vec{k}_{||}^{(s)}\cdot\vec{r}_{||}}e^{ik_\perp z} , \qquad (2.19)$$

where this statement provides a definition $M_{MN}(\vec{Q}_{||})$, which we shall write in the form

$$M_{MN}(\vec{Q}_{||})=\frac{1}{A}\sum_{\vec{q}_{||}}m(\vec{q}_{||},\vec{Q}_{||})\langle M \mid a^\dagger_{\vec{q}_{||}}a^\dagger_{\vec{Q}_{||}-\vec{q}_{||}} \mid N\rangle . \qquad (2.20)$$

Using techniques described elsewhere,[7] one may now form an expression for the total scattering efficiency S_{MN}, which is the fraction of electrons that scatter off the surface after encountering it in the initial vibrational state $|N\rangle$, and leaving it in $|M\rangle$ after exiting. If θ_I is the angle between the wave vector of the incoming electron and the normal to the surface, and m is the mass of the electron, then

$$S_{MN} = \frac{A\,|R(\epsilon_I)|^2 m^2 (v^{(I)})^2 \cos\theta_I}{(2\pi)^2} \int d\Omega(\hat{k}_s)\,|M_{MN}(\vec{Q}_{||})|^2 , \tag{2.21}$$

where it is understood that $\vec{Q}_{||}$ is given by $\vec{k}_{||}^{(s)} - \vec{k}_{||}^{(I)}$, and $d\Omega(\hat{k}_s)$ is an element of the solid angle for the scattered electron.

We now require an average over the initial vibrational state $|N\rangle$ and we also wish to sum over the final state $|M\rangle$, to ultimately obtain an expression for the scattering efficiency per unit solid angle. If P_N is the probability of finding the initial state $|N\rangle$ in the statistical ensemble, use of Eq. (2.20) then gives

$$\bar{S} = \sum_N \sum_M P_N S_{MN} = \frac{|R(\epsilon_I)|^2 m^2 (v^{(I)})^2 \cos\theta_I}{(2\pi)^2 A} \sum_{M,N} \sum_{\vec{q}_{||}\vec{q}\,'_{||}} \int d\Omega(\hat{k}_s)\,m^*(\vec{q}\,'_{||},\vec{Q}_{||})$$

$$\times m(\vec{q}_{||},\vec{Q}_{||}) P_N \langle N | a_{\vec{Q}_{||}-\vec{q}\,'_{||}} a_{\vec{q}\,'_{||}} | M\rangle\langle M | a^{\dagger}_{\vec{q}_{||}} a^{\dagger}_{\vec{Q}_{||}-\vec{q}_{||}} | N\rangle . \tag{2.22}$$

Upon noting that $\int d\omega\,\delta(\omega - E_M + E_N) = 1$, then using the Fourier representation of the δ function, Eq. (2.22) may be given in the following form:

$$\bar{S} = \frac{|R(\epsilon_I)|^2 m^2 (v^{(I)})^2 \cos\theta_I}{(2\pi)^3 A}$$

$$\times \sum_{\vec{q}_{||}\vec{q}\,'_{||}} \int d\Omega(\hat{k}_s) \int_{-\infty}^{+\infty} d\omega \int_{-\infty}^{+\infty} dt\, m^*(\vec{q}\,'_{||},\vec{Q}_{||})$$

$$\times m(\vec{q}_{||},\vec{Q}_{||}) \langle a_{\vec{Q}_{||}-\vec{q}\,'_{||}}(0) a_{\vec{q}\,'_{||}}(0) a^{\dagger}_{\vec{q}_{||}}(t) a^{\dagger}_{\vec{Q}_{||}-\vec{q}_{||}}(t)\rangle e^{-i\omega t} , \tag{2.23}$$

which can be decomposed to give the scattering efficiency per unit solid angle, per unit frequency range $d\omega$, $d^2\bar{S}/d\Omega(\hat{k}_s)d\omega$, where $\hbar\omega$ is the energy lost by the electron (i.e., when $\omega > 0$, the energy of the scattered electron is less than that of the incident electron). One finds

$$\frac{d^2\bar{S}}{d\omega\,d\Omega(k_s)} = \frac{|R(\epsilon_I)|^2 m^2 (v^{(I)})^2 \cos\theta_I}{(2\pi)^3 A} \sum_{\vec{q}_{||}\vec{q}\,'_{||}} m^*(\vec{q}\,'_{||},\vec{Q}_{||}) m(\vec{q}_{||},\vec{Q}_{||})$$

$$\times \int_{-\infty}^{+\infty} dt\, e^{-i\omega t} \langle a_{\vec{Q}_{||}-\vec{q}\,'_{||}}(0) a_{\vec{q}\,'_{||}}(0) a^{\dagger}_{\vec{q}_{||}}(t) a^{\dagger}_{\vec{Q}_{||}-\vec{q}_{||}}(t)\rangle . \tag{2.24}$$

In an earlier treatment of electron scattering by multiphonon processes, which contained an explicit discussion of two-phonon scattering, Evans and Mills[6] ignored direct coupling to the two-phonon manifold provided by the term V_2 in Eq. (2.4). Thus to recover their results, one begins by setting $\gamma = 0$. Evans and Mills also ignored both anharmonicity and lateral interactions, so to reproduce their results, one also takes $a^{\dagger}_{\vec{q}_{||}}(t) = \exp(i\omega_0 t) a^{\dagger}_{\vec{q}_{||}}$ with ω_0 independent of $\vec{q}_{||}$. Then one recovers the earlier results from Eq. (2.24); note the original derivation contains an error in the form of an overall factor of 2.[8]

While our derivation allows for interference between the two contributions to the cross section, in fact examination of the definition of $m(\vec{q}_{||},\vec{Q}_{||})$ shows one contribution to be purely imaginary and one to be real. See Eq. (2.17) and note the factor of i in front of the quantity r. Thus we write

$$\frac{d^2S}{d\Omega(\hat{k}_s)d\omega} = \frac{d^2S^{(a)}}{d\Omega(k_s)d\omega} + \frac{d^2S^{(b)}}{d\Omega(k_s)d\omega} . \tag{2.25}$$

One has

$$\Gamma(\vec{q}_{||}) = [4\pi\epsilon ee^*/(1+\epsilon)](n_s/2M\omega_0)^{1/2} ,$$

with n_s as the number of adsorbate molecules per unit area, and M as an effective mass of the vibrating molecule. We define

$$D(q_{||},\omega)=(v_{\perp}^{(I)}q_{||})^2+(\omega-\vec{v}_{||}^{(I)}\cdot\vec{q}_{||})^2\ ,$$

and the two contributions to the cross section can be written as

$$\frac{d^2S^{(a)}}{d\Omega(k_s)d\omega}=\frac{2\pi\,|\,R\,(\epsilon_I)\,|^2n_s^2m^2(v^{(I)})^6\cos^5\theta_I}{AM^2\omega_0^2}\left[\frac{2ee^*\epsilon}{1+\epsilon}\right]^4$$

$$\times\sum_{\vec{q}_{||},\vec{q}_{||}'}\frac{q_{||}q_{||}'\,|\,\vec{Q}_{||}-\vec{q}_{||}\,|\,|\,\vec{Q}_{||}-\vec{q}_{||}'\,|}{D(\vec{q}_{||},\omega_0)D(\vec{q}_{||}',\omega_0)D(\vec{Q}_{||}-\vec{q}_{||},\omega_0)D(\vec{Q}_{||}-\vec{q}_{||}',\omega_0)}$$

$$\times\int_{-\infty}^{+\infty}dt\,e^{-i\omega t}\langle a_{\vec{Q}_{||}-\vec{q}_{||}'}(0)a_{\vec{q}_{||}'}(0)a_{q_{||}}^{\dagger}(t)a_{\vec{Q}_{||}-\vec{q}_{||}}^{\dagger}(t)\rangle\ , \tag{2.26}$$

$$\frac{d^2S^{(b)}}{d\Omega(k_s)d\omega}=\frac{2\pi\,|\,R\,(\epsilon_I)\,|^2n_s^2r^2m^2(v^{(I)})^4\cos^2\theta_I}{AM^2\omega_0^4}\left[\frac{2ee^*\epsilon}{1+\epsilon}\right]^4$$

$$\times\frac{Q_{||}^2}{[D(Q_{||},2\omega_0)]^2}\sum_{\vec{q}_{||},\vec{q}_{||}'}\int_{-\infty}^{+\infty}dt\,e^{-i\omega t}\langle a_{\vec{Q}_{||}-\vec{q}_{||}'}(0)a_{\vec{q}_{||}'}(0)a_{\vec{q}_{||}}^{\dagger}(t)a_{\vec{Q}_{||}-\vec{q}_{||}}^{\dagger}(t)\rangle\ . \tag{2.27}$$

The results in Eqs. (2.26) and (2.27) are the principal results of the present section. Our next task is to obtain an expression for the correlation functions that appear on the right-hand side of these equations. The result in Eq. (2.26) will emerge as the cross section for the double loss, in the appropriate limit, while that in Eq. (2.27) will describe overtone excitation. The full expressions for the correlation functions are required before the dependence of each contribution on n_s, the adsorbate density, becomes clear.

III. LATTICE DYNAMICS OF AN ARRAY OF ANHARMONIC MOLECULES

In this section we turn our attention to the calculation of the response functions which appear on the right-hand side of Eqs. (2.26) and (2.27). We do this for a model of an ordered overlayer of molecules, each of which is anharmonic, which are then linked by lateral interactions. The model Hamiltonian is thus written

$$H=H_1+H_2\ , \tag{3.1}$$

where H_2 is the lateral interactions, and H_1 describes the lattice of anharmonic molecules,

$$H_1=\frac{1}{2M}\sum_l P_l^2+\sum_l V(u_l)\ . \tag{3.2}$$

We shall turn to H_2 shortly, but first we will concentrate on H_1.

A convenient choice of the potential $V(u)$ is the Morse potential which, if u is the normal coordinate of the molecule, has the form

$$V(u)=D[1-\exp(-au)]^2\ , \tag{3.3}$$

where D is the dissociation energy of the molecule and a is a parameter which may be determined, in principle, from the vibrational spectrum. For example, the normal-mode frequency ω_0 calculated in the harmonic approximation is $\omega_0=a(2D/M)^{1/2}$. The vibrational energy levels of the Morse potential may be found in closed form. If Ω_n is the frequency of the nth vibrational level, then

$$\hbar\Omega_n=\hbar\omega_0(n+\tfrac{1}{2})-\hbar\omega_0x_e(n+\tfrac{1}{2})^2\ , \tag{3.4}$$

where $x_e=\hbar\omega_0/4D$, and we have bound levels for all integers $n<n_M$, where $n_M+\tfrac{1}{2}=2D/\hbar\omega_0$.

Before we proceed with the analysis, we pause to discuss the primary issue that motivates this analysis. In this model, with neglect of lateral interactions, the frequency of the fundamental vibration is $\Omega_1-\Omega_0=(1-2x_e)\omega_0$, shifted from ω_0 by the anharmonicity represented by x_e. Of course, from $\Omega_1-\Omega_0$ one cannot deduce values for each of these two parameters. Now the double loss occurs at the frequency $2(\Omega_1-\Omega_0)$, and the overtone frequency is $\Omega_2-\Omega_0$, so if these two features appear as distinct in an electron-energy-loss spectrum, then we have

$$2(\Omega_1-\Omega_0)-\Omega_2-\Omega_0=2x_e\omega_0\ .$$

The splitting between the features, combined with knowledge of the fundamental vibration frequency, allows one to infer the value of x_e, and hence the dissociation energy D. It is of considerable interest to compare dissociation energies of chemical bonds in the gas phase and in adsorbed species. We have just described a primitive version of a procedure known as the Birge-Sponer extrapolation[5] that has been used in gas-phase studies of molecules. In surface studies, in the absence of negative-ion resonance (present for physisorbed species[4]), and in electron-energy-loss spectra, one frequently sees only the double loss and simple overtones at best, so only the two-phonon manifold is accessible to study.

The principal point of this paper is now the following. The above discussion assumes that the molecules are independent; it is surely a correct assumption in this limit, though one may raise questions about quantitative applicability of the Morse potential in the analysis. If transverse interactions are present, then there is no longer a clear meaning to the notion of the double loss and the overtone excitation; excitation of one molecule, e.g., molecule A, excites the entire system, so if the electron later excites molecule B in the double-loss mechanism, this entity has already been excited to some degree by the first scattering of molecule A. Similarly, when a particular adsorbate is excited from $n=0$ to $n=2$ in the overtone processes, necessarily the excitation will extend to its neighbors if lateral interactions are present. In typical systems

where our model applies (adsorbed CO may be an example), shifts produced by lateral interactions are quite small, typically a few tens of wave numbers.[9] If $\Delta\omega$ is such a frequency shift, then $\Delta\omega/\omega_0 \sim 10^{-2}$, and in this sense the lateral interactions are very weak. We shall soon appreciate, however, that the dimensionless parameter which describes their role is not $\Delta\omega/\omega_0$, but rather the ratio $x_e\omega_0/\Delta\omega$, the ratio of a typical anharmonic shift to the strength of the lateral interactions. Both parameters are small, in fact, and the ratio is often of order unity. We now turn to the remaining details of our analysis.

Rather than employ the full Morse potential displayed in Eq. (3.3), it will be more convenient mathematically to replace the anharmonic part of $V(u)$ by the sum of a term cubic in u, and one quartic. Thus instead of Eq. (3.3), we shall employ the form

$$V(u) = \frac{M\omega_0^2 u^2}{2}\left[1 - x_e^{1/2}\left[\frac{u}{u_0}\right] + \frac{7}{12}\alpha x_e\left[\frac{u}{u_0}\right]^2\right].$$

$$(3.5)$$

In Eq. (3.5), the parameter $u_0 = (2M\omega_0)^{-1/2}$ is the rms displacement of the oscillator in its ground state, calculated in the harmonic approximation, and the parameters x_e and α are both dimensionless measures of the strength of the anharmonicity. With $\alpha = 1$, Eq. (3.5) agrees with the Morse potential expanded through quartic terms. If

$x_e \ll 1$, as will be usual in the situations of interest here, the level shift produced by the anharmonic terms in Eq. (3.5) agrees precisely with that in Eq. (3.4) for $\alpha = 1$, if the calculation is carried through only to first order in x_e.[10] Thus for small x_e, Eq. (3.5) reproduces the Morse-potential results, and by allowing α to differ from unity, we have a potential of more flexible form.

For the form of the lateral interaction between molecules, we take

$$H_2 = \frac{1}{2}M\sum_l \sum_{\delta \neq 0} \omega_2^2(\delta)(u_l - u_{l+\delta})^2, \qquad (3.6)$$

where $\omega_2^2(\delta)$ is a measure of the strength of the coupling between a molecule at l and a molecule at $l+\delta$. If one wishes to model dipole-dipole interactions between adsorbates, then this mathematical form is not appropriate. In the end, only minor technical modifications of the formulas derived here are required if one wishes to model the dipole-dipole interactions. We shall give an explicit prescription for this at the end of this section.

The correlation functions which appear in Eqs. (2.26) and (2.27) are calculated as follows. Let $u(l)$, the displacement of molecule l, be expanded in boson annihilation and creation operators, in the standard fashion:

$$u(l) = \frac{1}{(2M\omega_0)^{1/2}}(a_l + a_l^{\dagger}), \qquad (3.7)$$

and consider the Green s function

$$D(l_4, l_3; l_2, l_1; t) = -i\Theta(t)\langle[a_{l_4}(0)a_{l_3}(0), a_{l_2}^{\dagger}(t)a_{l_1}^{\dagger}(t)]\rangle. \qquad (3.8a)$$

Here $\Theta(t)$ is unity for $t > 0$; it vanishes when $t < 0$. From knowledge of this function, the required correlation functions may be constructed. To do this, first let

$$a_{\vec{q}_{\parallel}} = \frac{1}{(N_s)^{1/2}}\sum_l a_l e^{-i\vec{q}_{\parallel}\cdot\vec{l}}, \qquad (3.8b)$$

$$a_{\vec{q}_{\parallel}}^{\dagger} = \frac{1}{(N_s)^{1/2}}\sum_l a_l^{\dagger} e^{i\vec{q}_{\parallel}\cdot\vec{l}}, \qquad (3.8c)$$

and introduce the function

$$F_{\vec{Q}_{\parallel}}(\vec{q}_{\parallel}, \vec{q}_{\parallel}'; t) = -i\Theta(t)\langle[a_{\vec{Q}_{\parallel} - \vec{q}_{\parallel}'}(0)a_{\vec{q}_{\parallel}'}(0), a_{\vec{q}_{\parallel}}^{\dagger}(t)a_{\vec{Q}_{\parallel} - \vec{q}_{\parallel}}^{\dagger}(t)]\rangle, \qquad (3.9a)$$

which is related to Eq. (3.8) via a Fourier-transform procedure:

$$F_{\vec{Q}_{\parallel}}(\vec{q}_{\parallel}, \vec{q}_{\parallel}'; t) = \frac{1}{N_s^2}\sum_{\vec{l}_1, \vec{l}_2, \vec{l}_3, \vec{l}_4} \exp[i\vec{Q}_{\parallel}\cdot(\vec{l}_1 - \vec{l}_4)]\exp[i\vec{q}_{\parallel}'\cdot(\vec{l}_4 - \vec{l}_3)]\exp[-i\vec{q}_{\parallel}\cdot(\vec{l}_1 - \vec{l}_2)]D(\vec{l}_4, \vec{l}_3; \vec{l}_2, \vec{l}_1; t).$$

$$(3.9b)$$

If $F_{\vec{Q}_{\parallel}}(\vec{q}_{\parallel}, \vec{q}_{\parallel}'; t)$ is Fourier transformed with respect to time in the standard fashion,

$$F_{\vec{Q}_{\parallel}}(\vec{q}_{\parallel}, \vec{q}_{\parallel}'; t) = \int_{-\infty}^{+\infty} \frac{d\Omega}{2\pi} F_{\vec{Q}_{\parallel}}(\vec{q}_{\parallel}, \vec{q}_{\parallel}'; \Omega)e^{-i\Omega t}, \qquad (3.10)$$

then one may establish the relationship

$$\int_{-\infty}^{+\infty} dt\, e^{-i\omega t}\langle a_{\vec{Q}_{\parallel} - \vec{q}_{\parallel}'}(0)a_{\vec{q}_{\parallel}'}(0)a_{\vec{q}_{\parallel}}^{\dagger}(t)a_{\vec{Q}_{\parallel} - \vec{q}_{\parallel}}^{\dagger}(t)\rangle = i[1 + \bar{n}(\omega)][F_{\vec{Q}_{\parallel}}(\vec{q}_{\parallel}, \vec{q}_{\parallel}'; -\omega + i\eta) - F_{\vec{Q}_{\parallel}}(\vec{q}_{\parallel}, \vec{q}_{\parallel}'; -\omega - i\eta)].$$

$$(3.11)$$

To determine $D(l_4, l_3; l_2, l_1; t)$, we use an equation-of-motion method, with anharmonic terms treated by means of a decoupling scheme that yields the correct form of this function (in a sense described below), in the limit of vanishing la-

teral interactions. Throughout the analysis, in the interest of simplicity, we shall assume ω_0 is large compared to both $x_e\omega_0$ and the strength of the lateral interactions, as measured by the value of $\omega_2(\delta)$. Thus when Eq. (3.7) is inserted into Eq. (3.6), one may ignore the influence of the terms which involve $a_l a_{l+\delta}$ and $a_l^\dagger a_{l+\delta}^\dagger$, compared to those from $a_l a_{l+\delta}^\dagger$ and $a_l^\dagger a_{l+\delta}$.

The equation of motion for $D(l_4, l_3; l_2 l_1; t)$ then has the general form

$$\left[i\frac{\partial}{\partial t} + 2\omega_0 + 2\sum_\delta \Delta\omega(\delta) \right] D(l_4, l_3; l_2, l_1; t) - \sum_\delta \Delta\omega(\delta)[D(l_4, l_3; l_2 + \delta, l_1; t) + D(l_4, l_3; l_2, l_1 + \delta; t)]$$

$$= \delta(t)(\delta_{l_2 l_3}\langle a_{l_4}a_{l_1}^\dagger \rangle + \delta_{l_2 l_4}\langle a_{l_3}a_{l_1}^\dagger \rangle + \delta_{l_1 l_3}\langle a_{l_2}^\dagger a_{l_4} \rangle + \delta_{l_1 l_4}\langle a_{l_2}^\dagger a_{l_3} \rangle) - i\Theta(t)\langle [a_{l_4}(0)a_{l_3}(0), [a_{l_2}^\dagger(t)a_{l_1}^\dagger(t), V_A]]\rangle \ ,$$

$$(3.12)$$

where

$$\Delta\omega(\delta) \equiv \frac{[\omega_2(\delta)]^2}{\omega_0} \ ,$$

$$(3.13)$$

and V_A contains the anharmonic terms, as described by Eq. (3.5) in combination with Eq. (3.2).

We shall need to introduce a decoupling scheme and various approximations to treat the terms on the right-hand side of Eq. (3.12). In the limit $\hbar\omega_0 \gg k_B T$, relevant to the internal modes of simple molecules on a surface at or near room temperature, the averages $\langle a_{l_2}^\dagger a_{l_2} \rangle$ may be set to zero, and in the limit $\omega_0 \gg \Delta\omega_2(\delta)$, one may approximate $\langle a_{l_4}a_{l_1}^\dagger \rangle$ and $\langle a_{l_3}a_{l_1}^\dagger \rangle$ by $\delta_{l_1 l_4}$ and $\delta_{l_3 l_1}$, respectively, so we have

$$\left[i\frac{\partial}{\partial t} + 2\omega_0 + 2\sum_\delta \Delta\omega(\delta) \right] D(l_4, l_3; l_2, l_1; t) - \sum_\delta \Delta\omega(\delta)[D(l_4, l_3; l_2 + \delta, l_1; t) + D(l_4, l_3; l_2, l_1 + \delta; t)]$$

$$= \delta(t)(\delta_{l_2 l_3}\delta_{l_1 l_4} + \delta_{l_2 l_4}\delta_{l_1 l_3}) - i\Theta(t)\langle [a_{l_4}(0)a_{l_3}(0), [a_{l_2}^\dagger(t)a_{l_1}^\dagger(t), V_A]]\rangle \ . \quad (3.14)$$

To discuss the treatment of the anharmonic terms, we must separate V_A into cubic and quartic terms, and consider each separately. If we consider the quartic terms first, and denote their contribution to V_A by $V_A^{(4)}$, then

$$[a_{l_2}^\dagger a_{l_1}^\dagger, V_A^{(4)}] = -\alpha x_e\omega_0 \frac{7(M\omega_0^2)^{1/2}}{6\sqrt{2}u_0^2}$$

$$\times [a_{l_2}^\dagger u^3(l_1) + u^3(l_2)a_{l_1}^\dagger] \ . \quad (3.15)$$

We may introduce a decoupling approximation on this term directly, after it is inserted into Eq. (3.14). One does this by using Eq. (3.7), assuming $\hbar\omega_0 \gg k_B T$, then examining the action of each term as it operates on the ground state of the harmonic oscillator array. The case where $l_1 \neq l_2$ must be considered separately from the case where $l_1 = l_2$. As an example, one term encountered is proportional to $a_{l_2}^\dagger a_{l_2}^\dagger a_{l_1} a_{l_1}^\dagger$. For $l_1 \neq l_2$, after the ground-state wave function is acted upon by $a_{l_1}^\dagger$, the oscillator at site l_2 remains in its ground state, so $a_{l_2}^\dagger a_{l_2}$ operating on the resulting wave function gives zero. On the other hand, with $l_2 = l_1$, this operator now becomes $a_{l_1}^\dagger a_{l_1}$ and this operates on the first excited state of the oscillator, so the operator is replaced by unity. Thus the combination $a_{l_2}^\dagger a_{l_2}^\dagger a_{l_2} a_{l_1}^\dagger$ is replaced by $\delta_{l_1 l_2}a_{l_2}^\dagger a_{l_1}^\dagger$, and the remaining terms are treated

in a similar fashion. This procedure does assume $\Delta\omega(\delta) \ll \omega_0$ (weak lateral interactions) so when the oscillator at l_1 is excited by the operator $a_{l_1}^\dagger$, to a good approximation the oscillator at $l_2 \neq l_1$ remains unexcited. But the procedure makes no assumption about the relative magnitude of $x_e\omega_0$ and $\Delta\omega(\delta)$. When a similar approximation is introduced for each term in Eq. (3.15), we find a result which may be written

$$[a_{l_2}^\dagger a_{l_1}^\dagger, V_A^{(4)}] \cong \tfrac{7}{2}\alpha x_e\omega_0(1 + \tfrac{1}{2}\delta_{l_1 l_2})a_{l_1}^\dagger a_{l_2}^\dagger \ . \quad (3.16)$$

We next turn to the cubic terms. The treatment of these is a bit more involved, and again our approach will be aimed at producing relatively simple final results suitable for our particular purpose. One finds

$$[a_{l_2}^\dagger a_{l_1}^\dagger, V_A^{(3)}] = \tfrac{3}{2}M\omega_0^2 x_e^{1/2}[a_{l_2}^\dagger u^2(l_1) + u^2(l_2)a_{l_1}^\dagger] \ . \quad (3.17)$$

Since each term in Eq. (3.17) involves an *odd* number of boson operators, the decoupling scheme described above is not suitable. What we shall do is insert the full form of Eq. (3.17) into Eq. (3.14), and note that we then encounter a new set of Green's functions. We find the equation of motion for each member of this set, and decouple at this stage. We shall show how this is done for one example. Consider

$$G(l_4, l_3; l_2, l_1; t) = -i\Theta(t)\langle [a_{l_4}(0)a_{l_3}(0), a_{l_2}^\dagger(t)a_{l_1}^\dagger(t)a_{l_1}^\dagger(t)]\rangle \ , \quad (3.18)$$

and calculate the equation of motion of this function; for this moment we ignore the influence of both lateral interactions and the quartic anharmonic terms. The reasons for this will be clear shortly. One finds

$$\left[3\omega_0 + i\frac{\partial}{\partial t}\right]G(l_4,l_3;l_2,l_1;t) = -i\Theta(t)\tfrac{3}{2}M\omega_0^2 x_e^{1/2}\{\,\langle[a_{l_4}(0)a_{l_3}(0),a_{l_2}^\dagger(t)a_{l_1}^\dagger(t)u^2(l_1,t)]\rangle$$

$$+\langle[a_{l_4}(0)a_{l_3}(0),a_{l_2}^\dagger(t)u^2(l_1,t)a_{l_1}^\dagger(t)]\rangle$$

$$+\langle[a_{l_4}(0)a_{l_3}(0),u^2(l_2,t)a_{l_1}^\dagger(t)a_{l_1}^\dagger(t)]\rangle\,\}\,.\tag{3.19}$$

The right-hand side may be decoupled in precisely the same way as the terms in Eq. (3.17) introduced by the quartic contributions to the anharmonic terms. After this is done, we have

$$\left[3\omega_0 + i\frac{\partial}{\partial t}\right]G(l_4,l_3;l_2,l_1;t) = x_e^{1/2}\omega_0(3+\tfrac{15}{4}\delta_{l_1 l_2})D(l_4,l_3;l_2,l_1;t)\,.\tag{3.20}$$

One now Fourier transforms both sides of Eq. (3.20) with respect to time, and notes from Sec. III that in the limit of small anharmonicity, all features of interest will lead us to evaluate the Fourier transform near $\Omega = -2\omega_0$. Thus we simply replace Ω by $-2\omega_0$ to obtain

$$G(l_4,l_3;l_2,l_1;\Omega) \cong x_e^{1/2}(3+\tfrac{15}{4}\delta_{l_1 l_2})D(l_4,l_3;l_2,l_1;\Omega)\,.\tag{3.21}$$

The point is that the denominator $3\omega_0 + \Omega$ is never evaluated near its zero at $\Omega = -3\omega_0$, so this simple approximation suffices. Inclusion of lateral interactions in the equation of $G(l_4,l_3;l_2,l_1;t)$ will lead to, in essence, a small correction to this denominator, and thus may be ignored to good approximation. Inclusion of the quartic anharmonicity will lead to corrections to the right-hand side of Eq. (3.21) smaller than the term retained by the factor of x_e, when one examines the structure of the decoupling scheme.

When the results of the above decoupling procedure are completed, we find the following equation of motion for the Green's function of interest:

$$\left[2(1-\lambda)\omega_0 + 2\sum_\delta \Delta\omega(\delta)+\Omega\right]D(l_4,l_3;l_2,l_1;\Omega) - \sum_\delta \Delta\omega(\delta)[D(l_4,l_3;l_2+\delta,l_1;\Omega)+D(l_4,l_3;l_2,l_1+\delta;\Omega)]$$

$$= \delta_{l_2 l_3}\delta_{l_1 l_4}+\delta_{l_2 l_4}\delta_{l_1 l_3}+\lambda\omega_0\delta_{l_1 l_2}D(l_4,l_3;l_2,l_1;\Omega)\,,\tag{3.22}$$

where

$$\lambda = \tfrac{15}{4}x_e(1-\tfrac{7}{15}\alpha)\,.\tag{3.23}$$

It is a straightforward matter to solve Eq. (3.22) in closed form. First note that in the absence of lateral interactions, one has

$$D(l_4,l_3;l_2,l_1;\Omega) = \frac{\delta_{l_2 l_3}\delta_{l_1 l_4}+\delta_{l_2 l_4}\delta_{l_1 l_3}}{2(1-\lambda)\omega_0 - \lambda\omega_0\delta_{l_1 l_2}+\Omega}\,.\tag{3.24}$$

If $l_1 \neq l_2$, this has a pole at $\Omega = -2\omega_0(1-\lambda)$; for $\alpha=1$, one has $\lambda=2x_e$, so this describes a loss at the frequency $2(\Omega_1-\Omega_0)$, in our earlier notation. This is the double loss, as illustrated in Fig. 1(a), where the electron excites two different, now decoupled, molecules. For $l_1=l_2$, the pole shifts to $2(1-\tfrac{3}{2}\lambda)\omega_0$, and with $\lambda=2x_e$ this equals $\Omega_2-\Omega_0$, the frequency of the overtone of one isolated molecule. Clearly, our decoupling procedure reproduces the exact results in the limit of vanishing lateral interactions.

When the lateral interactions are nonzero, one may proceed by writing

$$D(l_4,l_3;l_2,l_1;\Omega) = \frac{1}{N_s^2}\sum_{\vec{Q}_{||},\vec{Q}\,'_{||}}\sum_{\vec{q}_{||},\vec{q}\,'_{||}} \exp[i\vec{Q}\,'_{||}\cdot(\vec{l}_3+\vec{l}_4) - i\vec{Q}_{||}\cdot(\vec{l}_1+\vec{l}_2)]$$

$$\times \exp[i\vec{q}\,'_{||}\cdot(\vec{l}_3-\vec{l}_4) - i\vec{q}_{||}\cdot(\vec{l}_1-\vec{l}_2)]D_{\vec{Q}_{||}\vec{Q}\,'_{||}}(\vec{q}_{||},\vec{q}\,'_{||};\Omega)\,.\tag{3.25}$$

Then from Eq. (3.22), one finds

$$D_{\vec{Q}_{||}\vec{Q}\,'_{||}}(\vec{q}_{||},\vec{q}\,'_{||};\Omega) = \delta_{\vec{Q}_{||}\vec{Q}\,'_{||}}\Lambda_{\vec{Q}_{||}}(\vec{q}_{||},\vec{q}\,'_{||};\Omega)\,,\tag{3.26}$$

where

$$\Lambda_{\vec{Q}_{||}}(\vec{q}_{||},\vec{q}\,'_{||};\Omega) = (\delta_{\vec{q}_{||},\vec{q}\,'_{||}}+\delta_{\vec{q}_{||},\vec{Q}_{||}-\vec{q}\,'_{||}})s_{\vec{Q}_{||}}(\vec{q}_{||},\Omega) + \frac{2\lambda\omega_0}{N_s}s_{\vec{Q}_{||}}(\vec{q}_{||},\Omega)s_{\vec{Q}_{||}}(\vec{q}\,'_{||},\Omega)[1-\lambda\omega_0 S(\vec{Q}_{||},\Omega)]^{-1}\,.\tag{3.27}$$

Here one has

$$s_{\vec{Q}_{||}}(\vec{q}_{||},\Omega) = \frac{1}{\tilde{\omega}(\vec{Q}_{||}+\vec{q}_{||})+\tilde{\omega}(\vec{Q}_{||}-\vec{q}_{||})+\Omega} \ , \quad (3.28)$$

$$S(\vec{Q}_{||},\Omega) = \frac{1}{N_s}\sum_{\vec{q}_{||}} s_{\vec{Q}_{||}}(\vec{q}_{||},\Omega) \ , \quad (3.29)$$

and finally $\tilde{\omega}(\vec{q})$ is a renormalized phonon frequency, which in our model is given by

$$\tilde{\omega}(\vec{q}_{||}) = \omega_0(1-\lambda) + \sum_{\vec{\delta}}\Delta\omega(\delta)[1-\cos(\vec{q}_{||}\cdot\vec{\delta})] \ . \quad (3.30)$$

The expressions summarized in Eq. (3.26) are the principal results of this section, and they may be used in conjunction with the results of Sec. II to explore the role of lateral interactions on the two contributions to the loss cross section. We shall summarize the results of our study in Sec. IV.

The particular model of lateral interactions employed here is not the only form that may be appropriate; indeed, in the situations where the influence of lateral interactions on adsorbate vibrations have been delineated in a quantitative fashion, it is the dipole-dipole interaction between adsorbates which dominates.[9] The formulas above are readily modified to apply to this case; one simply uses a slightly different form for the renormalized phonon frequency $\tilde{\omega}(\vec{q}_{||})$ in Eq. (3.30). Since the dipole-dipole interaction is geometry dependent, we need an explicit example to see how this is done. Consider a lattice of diatomic molecules such as CO, and suppose the molecules rest with the internuclear axis vertical to the plane of the surface. The dipole-dipole interaction may then be written in the form for a model analogous to that in Sec. II, where the dipole and its image interact with its neighbors,

$$H_z^{(\mathrm{dip})} = \frac{1}{2}\left|\frac{2e^*\epsilon}{1+\epsilon}\right|^2 \sum_{\vec{l}}\sum_{\vec{\delta}\neq 0}\frac{1}{|\vec{\delta}|^3}u(\vec{l})u(\vec{l}+\vec{\delta}) \ . \quad (3.31)$$

Then in place of Eq. (3.30), we have

$$\tilde{\omega}(\vec{q}_{||}) = \omega_0(1-\lambda) + \frac{1}{M\omega_0}\left|\frac{2e^*\epsilon}{1+\epsilon}\right|^2 \sum_{\vec{\delta}\neq 0}\frac{1}{|\vec{\delta}|^3}\cos(\vec{q}_{||}\cdot\vec{\delta}) \ . \quad (3.32)$$

A principal difference between Eqs. (3.32) and (3.30) is that for $\vec{q}_{||}\cong 0$, $\tilde{\omega}(\vec{q}_{||})$ is upshifted from $\omega_0(1-\lambda)$ by the dipole-dipole interactions, an effect evident in both electron-energy-loss and infrared studies of adsorbed CO. We note it is possible to transform the slowly converging dipole sum into Eq. (3.32) into an alternative form which converges very rapidly.[11]

IV. RESULTS AND DISCUSSIONS

The purpose of this section is to discuss implications of the results of Secs. II and III. A full study of the energy- and angle-dependent cross section is a formidable task, but, in fact, certain simplifications may be introduced which allow essential features to be isolated. We consider first the overtone contribution to the cross section, then we turn to the double loss.

The time integral on the right-hand side of Eq. (2.27), in combination with the sums on $\vec{q}_{||}$ and $\vec{q}'_{||}$ and the factor of $1/A$, may be expressed simply in terms of the function $S(\vec{Q}_{||},\Omega)$ defined in Eq. (3.29). If we call this combination $\mathscr{S}(\vec{Q}_{||},\omega)$, then

$$\mathscr{S}(\vec{Q}_{||},\omega) = \frac{4n_s}{\lambda\omega_0}[1+\bar{n}(\omega)]\mathrm{Im}\left|\frac{1}{1-\lambda\omega_0 S(\vec{Q}_{||},-\omega+i\eta)}\right| \ . \quad (4.1)$$

Upon noting that the factor r in Eq. (2.27) is inversely proportional to n_s, the prefactor in Eq. (2.27) then scales linearly with the coverage n_s.

As in earlier discussions of dipole scattering, the denominator $[D(\vec{Q}_{||},2\omega_0)]^2$ in Eq. (2.27) causes the cross section to be peaked strongly around the specular direction, with values of momentum transfer $|\vec{Q}_{||}|\cong 2\omega_0/v^{(I)}$ as the most important. For typical experimental conditions, $|\vec{Q}_{||}|\cong 10^6$ cm^{-1}, and since the function $\mathscr{S}(\vec{Q}_{||},\omega)$ varies slowly with $\vec{Q}_{||}$ this close to the center of the Brillouin zone, we may replace $\mathscr{S}(\vec{Q}_{||},\omega)$ by its value at $\vec{Q}_{||}=0$. Once this is done, if desired, one may integrate the scattering efficiency over the solid angle, exactly as in earlier studies,[2] to obtain an expression for $dS^{(b)}/d\omega$, the scattering efficiency per unit frequency. Except for the multiplicative prefactor, which is an expression of the different coupling mechanism, the energy variation of the cross section and its dependence on the angle of incidence is identical to earlier results obtained in the study of one-phonon processes. [See Eq. (42) of Ref. 2. When one calculates ψ_E, one should replace ω_0 by $2\omega_0$.]

The calculations presented shortly will be based on a numerical evaluation of the right-hand side of Eq. (4.1), for a model described below. This will be done at $\vec{Q}_{||}=0$. Note from the preceding paragraphs that the energy variation of $dS^{(b)}/d\omega$ is virtually identical to that expected for a one-phonon loss process, provided ω_0 is replaced by $2\omega_0$.

We now turn to the double loss, as described by Eq. (2.26). We note from Eqs. (3.9), (3.25), and (3.26) that

$$F_{\vec{Q}_{||}}(\vec{q}_{||},\vec{q}'_{||};\Omega) = \Lambda_{\vec{Q}_{||}/2}(\tfrac{1}{2}\vec{Q}_{||}-\vec{q}_{||},-\tfrac{1}{2}\vec{Q}_{||}+\vec{q}'_{||};\Omega) \ , \quad (4.2)$$

and the right-hand side, through the use of Eq. (3.27), consists of two terms. The first, proportional to the factor $\delta_{\vec{q}_{||},\vec{q}'_{||}}+\delta_{\vec{Q}_{||}-\vec{q}_{||},-\vec{q}'_{||}}$, describes a scattering in which two phonons are created in sequence, and each one propagates off without interacting with the other member of the pair. Of course, as one sees from Eq. (3.30), each has its frequency renormalized by the anharmonicity. The second term describes contributions in which the two phonons, after being created, interact with each other via anharmonicity (final-state interaction). From the expressions given in Sec. III, taken in the limit of small lateral interactions, the ratio of the second contribution to the first contribution to the cross section can be shown to be the order of $\lambda^2(a_0\omega_0/v^{(I)})^2$, where λ is the anharmonic coupling parameter defined in Eq. (3.23), and a_0 is a mean distance between molecules, defined by writing $\pi a_0^2 = n_s^{-1}$, with n_s the density of molecules per unit area. The ratio is very small, less than 10^{-6}, and final-state interactions contri-

bute negligibly to the cross section.

The physical reason for this is the following. In the dipole scattering regime, the electron is a distance the order of $d \simeq v^{(I)}/\omega_0$ above the surface when it scatters off a molecule, exciting a vibration in the process.[1] It thus "sees" all molecules which lie below it, within a circle whose radius is the order of d. Since two phonons can interact only when they are on the same site, e.g., the probability

that the two phonons created in this fashion will scatter off each other is proportional to $(a_0/d)^2$, the factor which enters the above estimate. Note that when large-angle deflections are studied, as in the work of Demuth and co-workers,[4] final-state interactions may enter the double-loss contribution to the cross section importantly.

With final-state interactions ignored, the double-loss contribution becomes

$$\frac{d^2 S^{(a)}}{d\Omega(\hat{k}_s) d\omega} = \frac{4\pi \, | R \, (\epsilon_I) |^2 n_s^2 m^2 (v^{(I)})^6 \cos^5 \theta_I}{M^2 \omega_0^2} \left[\frac{2ee^* \epsilon}{1-\epsilon} \right]^4 [1 + \bar{n}(\omega)]$$

$$\times \frac{1}{A} \sum_{\vec{q}_{||}} \frac{q_{||}^2 \, | \vec{Q}_{||} - \vec{q}_{||} |^2}{D^2(\vec{q}_{||}, \omega_0) D^2(\vec{Q}_{||} - \vec{q}_{||}, \omega_0)} \mathrm{Im} \left[\frac{1}{\tilde{\omega}(\vec{Q}_{||} - \vec{q}_{||}) + \tilde{\omega}(\vec{q}_{||}) - \omega - i\eta} \right] . \tag{4.3}$$

When the dipole excitation form factor in Eq. (4.3) is considered as a function of $\vec{q}_{||}$, for $\vec{Q}_{||}$ fixed, then for $q_{||} \gg \omega_0/v^{(I)}$, it falls off as $q_{||}^{-4}$. We may thus evaluate the remainder of the integrand at $\vec{q}_{||} = 0$ and, in fact, we may set $\vec{Q}_{||} \cong 0$ also, since here we are interested only in near specular scattering. Then if we replace $i\eta$ by $i\Gamma$, with Γ finite to simulate damping of the molecular vibrations, one finds

$$\frac{d^2 S^{(a)}}{d\Omega(\hat{k}_s) d\omega} = \frac{| R \, (\epsilon_I) |^2 n_s^2 m^2 (v^{(I)})^2 \cos^5(\theta_I)}{\pi M^2 \omega_0^2} \left[\frac{2ee^* \epsilon}{1+\epsilon} \right]^2 [1 + \bar{n}(\omega)]$$

$$\times \left[\int d^2 q_{||} \frac{q_{||}^2 \, | \vec{Q}_{||} - \vec{q}_{||} |^2}{D^2(q_{||}, \omega_0) D^2(\vec{Q}_{||} - \vec{q}_{||}, \omega_0)} \right] \frac{\Gamma}{[2\omega_0(1-\lambda) - \omega]^2 + \Gamma^2} . \tag{4.4}$$

Note that the prefactor in Eq. (4.4) is proportional to the square of the coverage n_s^2 as expected.

If one integrates both sides of Eq. (4.4) over the solid angle $d\Omega(\hat{k}_s)$, then as described elsewhere[2] one may convert this to an integral on $d^2 Q_{||}$. The prefactor of the Lorentzian-loss feature then separates into the product of two factors, each of which describes the probability that a single vibrational quantum is excited. Once again, this is expected once one appreciates that final-state interactions may be ignored. Note, then, that the energy variation of the overtone and double-loss contributions to the cross section are thus very different. We have seen that the former is the same as that for exciting a single vibrational quantum, and the latter is essentially the square of the overtone contribution. Since dipole excitation cross sections vary strongly with energy, to fall off with increasing energy when $\psi_E < \psi_c$, with $\psi_E = \hbar \omega_0 / 2E^{(I)}$ and ψ_c the spectrometer cutoff angle, these different energy variations may allow unambiguous identification of the two contributions to the cross section. We shall appreciate shortly that in the presence of lateral interactions, this may prove difficult to do, with data taken at only a single impact energy.

At least for the case of normal incidence, it is possible to perform the integration over $\vec{q}_{||}$ in Eq. (4.4) to find an explicit expression for the angular variation of the cross section for the double loss. One has

$$\frac{d^2 S^{(a)}}{d\Omega(\hat{k}_s) d\omega} = \frac{| R \, (\epsilon_I) |^2 n_s^2 m^2}{M^2 (v^{(I)})^6 \omega_0^2} \left[\frac{2ee^* \epsilon}{1+\epsilon} \right]^2 [1 + \bar{n}(\omega)]$$

$$\times \frac{1}{Q_{||}^2} \left\{ \left[1 + 8 \left[\frac{\omega_0}{v^{(I)} Q_{||}} \right]^4 + 10 \left[\frac{\omega_0}{v^{(I)} Q_{||}} \right]^4 \right] \ln \left[1 + \left[\frac{v^{(I)} Q_{||}}{\omega_0} \right]^2 \right] - 3 - 10 \left[\frac{\omega_0}{v^{(I)} Q_{||}} \right]^2 \right\} . \tag{4.5}$$

where at normal incidence, $Q_{||} = k^{(I)} \Delta\theta$, with $k^{(I)}$ the wave vector of the incident electron and $\Delta\theta$ the angular deflection, assumed to be small. As $\vec{Q}_{||} \to 0$, the scattering efficiency remains finite, since the quantity in large curly brackets in Eq. (4.5) vanishes.

We now turn to our study of the influence of lateral interactions on the two-phonon loss spectra. At least in the dipole regime, and for our model of the lateral interactions [Eq. (3.6)], the double loss is simply a Lorentzian structure centered about the renormalized frequency $2\omega_0(1 - \lambda)$, and this is uninfluenced by the lateral interactions. If we in-

clude lateral interactions of dipolar form, the double loss remains centered around the $2\tilde{\omega}(\vec{q}_{||} = 0)$, but there will be a coverage-dependent shift of this frequency, as discussed elsewhere.[1,9] Our principal interest here will then be in the study of the overtone contribution to the spectrum, as displayed in Eq. (4.1) with $\vec{Q}_{||} = 0$.

In Figs. 2 and 3 we display a series of numerical calculations which illustrate the basic trends produced by the presence of anharmonicity. These calculations have been carried out for a square lattice of adsorbates, with nearest-neighbor coupling. Then the phonon bandwidth
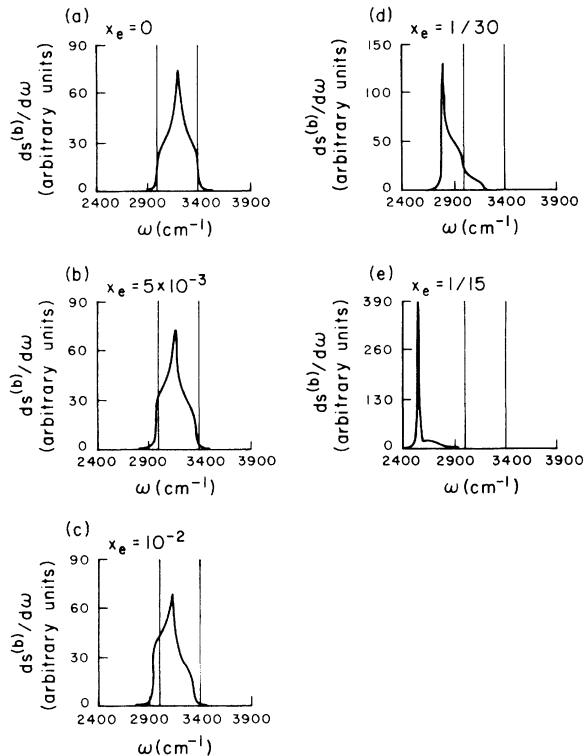
FIG. 2. Numerical calculations of the overtone contribution to the scattering cross section. For these calculations we have taken $\omega_0 = 1500$ cm^{-1}, $W = 200$ cm^{-1}, and $\Gamma = 10$ cm^{-1}. Note in (a) that when $x_e \equiv 0$, the overtone spectrum mirrors the two-phonon density of states. Note also that as x_e increases, the overtone peak shifts down in energy. As the overtone peak shifts down below the onset of the two-phonon continuum, it becomes sharper, reflecting the production of a two-phonon bound state.

W is given by $W = 8\Delta\omega$, with $\Delta\omega$ defined in Eq. (3.13). The calculations in Fig. 2 take $\omega_0 = 1500$ and $W = 200$ cm^{-1}, and the effect of lifetime broadening has been introduced phenomenologically by replacing the infinitesimal η in $S(\vec{Q}_{||}, \Omega + i\eta)$ by a finite number Γ. The calculations in Fig. 2 take $\Gamma = 10$ cm^{-1}. From the figure one may appreciate the structure and asymmetries introduced into the line shape by the combination of lateral interactions and anharmonicity.

When $x_e \equiv 0$, the process in Fig. 1(b) leads to the creation of a pair of noninteracting phonons, and the spectrum is then simply a mirror of the two-phonon density of states. For our model this has a prominent peak (a lifetime-broadened Van Hove singularity) in the middle of the phonon band. Thus when $x_e = 0$, the peak in the overtone spectrum is at 3200 cm^{-1}, which is 200 cm^{-1} *above* the double loss which, in the model, occurs at 3000 cm^{-1}. We shall see that the effect of lateral interactions will always be to shift the peak in the overtone spectrum upward, relative to the double loss, though the two need not always be inverted as in this extreme example. The dimensionless parameter of the problem can be seen to be $\lambda\omega_0/W$, and whenever the lateral interactions are large enough for this parameter to be comparable to or smaller

than unity, the shift of the overtone peak relative to the double loss will be appreciable.

As λ is increased in value, the overtome peak is downshifted; when λ is sufficiently large, it lies *below* $2\omega_0$, the onset of the two-phonon continuum. This is illustrated in Figs. 2(d) and 2(e). In the language of solid-state physics, the anharmonicity is sufficiently strong to produce a two-phonon bound state, with excitation energy less than $2\omega_0$. This two-phonon bound state dominates the scattering cross section for all the examples we have explored. As the lateral interaction parameter W vanishes, of course, we are left with the noninteracting molecule picture discussed in Sec. I. Formally, the $N(N-1)$ excited states which involve excitation of two distinctly different molecules from their $n = 0$ to their $n = 1$ level correspond to the two-phonon continuum, while the N excited states with one molecule excited from $n = 0$ to $n = 2$ constitute a band of two-phonon bound states, with zero bandwidth. As $W \to 0$, our decoupling scheme reproduces this behavior exactly, as one sees from Eq. (3.24).

Figure 3 shows a sequence of calculations identical to those given in Fig. 2, but Γ has been increased to 50 cm^{-1}. The trends are very similar to those in Fig. 2, but the various structures evident in Fig. 2 are smoothed out by the influence of lifetime broadening.

Figure 4 shows a plot of the splitting between the peak in the overtone spectrum and the double loss, for the case where $W = 40$ cm^{-1}, a realistic value for an adsorbed species at monolayer coverage. The trend is similar to those displayed in Figs. 2 and 3, with very appreciable shifts away from the noninteracting molecule limit ($\lambda = \infty$
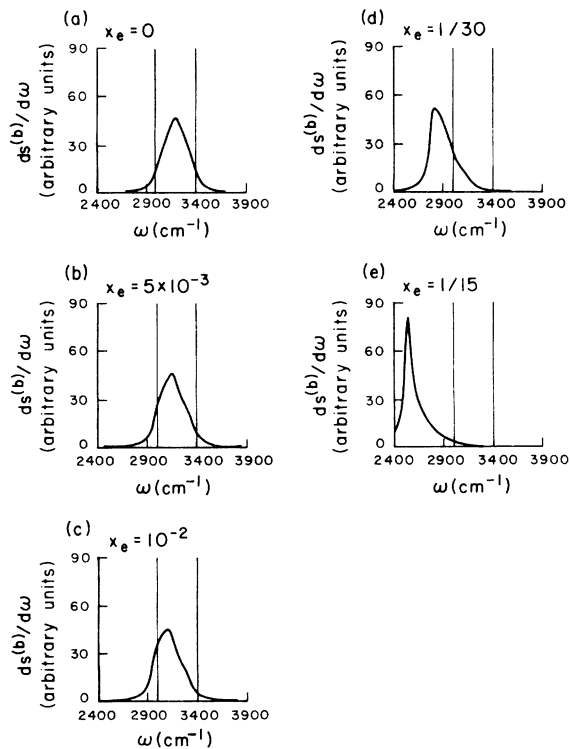

FIG. 3. More numerical calculations of the overtone contribution to the scattering cross section. These calculations are for $\omega_0 = 1500$ cm^{-1} and $W = 200$ cm^{-1}, as in Fig. 2, but here we have a more realistic value for Γ, viz., $\Gamma = 50$ cm^{-1}.
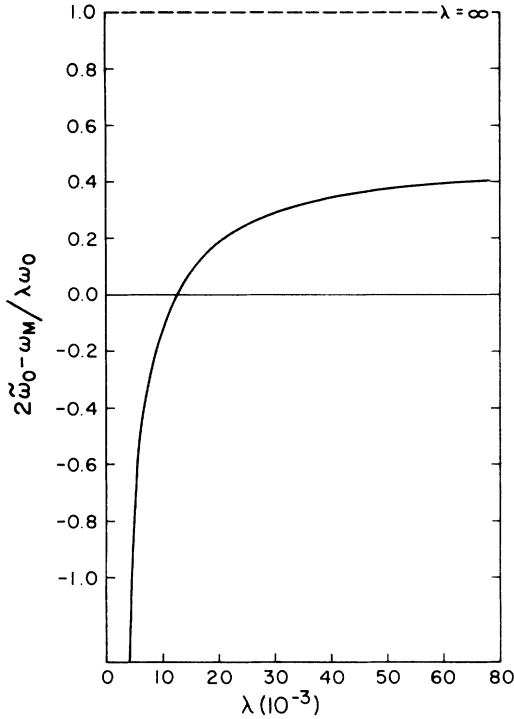
FIG. 4. Plot of the splitting between the overtone and double-loss spectrum peaks as a function of λ. As $\lambda \rightarrow \infty$, the splitting approaches the value $\lambda \omega_0$ as predicted by the Birge-Sponer extrapolation.

limit in the figure) for physically realistic values of λ. Table I summarizes a series of calculations carried out for a wider range of parameters. Note that as the strength of the lateral interactions increases, the overtone feature always progressively broadens.

While we have presented a series of calculations based on a particular model of the adsorbate lattice and lateral interactions between adsorbates, the trends illustrated in the calculations can be seen to be insensitive to these details. With dipolar coupling between adsorbates, the frequency of the double-loss feature exhibits a coverage-dependent shift, but lateral interactions will influence the *relative* position of the overtone and double-loss features in a manner very similar to the calculations displayed here. If W is the phonon bandwidth, once again the key parameter is $\lambda \omega_0 / W$, and this must be substantially larger than unity for the noninteracting model to apply. We conclude with a discussion of the implications of these results.

In our view these calculations call into question the use of the Birge-Sponer extrapolation as a means of estimating dissociation energies of bonds in adsorbed species, unless the data are obtained in the submonolayer regime, when lateral interactions can be expected to play a minor role. We predict that as coverage increases, and the strength of lateral interactions does also, then the width of the overtone feature should increase, while the width of the double loss does not if the damping factor Γ is dominated by interaction of the adsorbate with the substrate and is thus not coverage dependent. We note that broadening with increased coverage is evident in the overtone regime of the electron-energy-loss spectrum of ethylene on Ni(111).[12] It is likely that lateral interactions are responsible for this

TABLE I. Summary of the results of numerical calculations of the overtone spectrum for several realistic values of $\Delta \omega$ and x_e. For all of the entries in this table, $\omega_0 = 1500$ cm^{-1} and $\Gamma = 50$ cm^{-1}. Note that the overtone and double-loss peaks switch positions (so that the overtone peak lies at higher energy than the double loss) when $\lambda \omega_0 / W \sim 1$. This table also shows that as $\lambda \omega_0 / W$ decreases, the width of the overtone peak increases.

W (cm^{-1})	x_e	$\dfrac{\lambda \omega_0}{W}$	$\lambda \omega_0 (1-\lambda)$ (cm^{-1})	ω_M (cm^{-1})	Full width at half maximum (cm^{-1})	$2\omega_0(1-\lambda-\omega_M)$ (cm^{-1})
10	5×10^{-3}	1.50	2970	2965	102	5
10	7.6×10^{-3}	2.28	2954	2941	101	13
10	10×10^{-3}	3.00	2940	2920	101	20
20	5×10^{-3}	0.75	2970	2974	110	-4
20	7.6×10^{-3}	1.14	2954	2950	107	4
20	10×10^{-3}	1.50	2940	2929	105	11
40	5×10^{-3}	0.38	2970	2992	121	-22
40	7.6×10^{-3}	0.57	2954	2967	118	-13
40	10×10^{-3}	0.75	2940	2945	117	-5
64	5×10^{-3}	0.23	2970	3014	144	-44
64	7.6×10^{-3}	0.36	2954	2988	143	-34
64	10×10^{-3}	0.47	2940	2964	137	-24
80	5×10^{-3}	0.19	2970	3030	165	-60
80	7.6×10^{-3}	0.29	2954	3003	162	-49
80	10×10^{-3}	0.38	2940	2978	159	-38
96	5×10^{-3}	0.16	2970	3046	185	-76
96	7.6×10^{-3}	0.24	2954	3019	182	-65
96	10×10^{-3}	0.31	2940	2993	177	-53
120	5×10^{-3}	0.13	2970	3072	215	-102
120	7.6×10^{-3}	0.19	2954	3045	213	-91
120	10×10^{-3}	0.25	2940	3019	210	-79

broadening, through the mechanism explored here.

Schmeisser *et al.*[4] have studied vibrations of physisorbed N_2 and O_2 on polycrystalline Ag and Cu films by means of electron-energy-loss spectroscopy. The experiments are carried out in the impact scattering regime where the angular deflection of the electron beam is large, not the near-specular dipole-dominated regime explored explicitly here. Negative-ion resonances are found for these species, and with beam energy tuned to resonance, multiquantum losses (up to $\sim 8\hbar\omega_0$) are observed in the study. In this paper, in the multiquantum regime, two distinct loss features are observed near $n\hbar\omega_0$, and the authors identify the low-frequency feature as an overtone, and the high-frequency one as the multiple loss. Since the high-frequency member of the doublet is, in fact, substantially broader than the low-frequency member, in our view one should not rule out the possibility that it is, in fact, the overtone, upshifted and broadened by lateral interactions, as in our theoretical studies of two-phonon losses. Whether or not this is the case could be determined by studying both the relative position and the width of these features as a function of coverage.

Ibach[13] has pointed out that it would be of considerable interest to compare electron-energy-loss and infrared spectra in the two-phonon loss regime, since there is no analog of the double loss in infrared study. Such a comparison may be possible in the near future if infrared techniques continue to evolve rapidly.

ACKNOWLEDGMENTS

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[5]See the discussion which begins on p. 310 of Ref. 1.

[6]Such multiquantum losses were considered some years ago in E. Evans and D. L. Mills, Phys. Rev. B 7, 853 (1973), but without attention to the role of lateral interactions and anharmonicity.

[7]P. Mazur and D. L. Mills, Phys. Rev. B 26, 5175 (1982).

[8]See the footnote on p. 93 of Ref. 1.

[9]S. Andersson and B. N. J. Persson, Phys. Rev. Lett. 45, 1421 (1980).

[10]The level shift to first order in x_e is calculated by treating the quartic term in Eq. (3.5) in first-order perturbation theory, and the cubic term to second order.

[11]H. Benson and D. L. Mills, Phys. Rev. 188, 849 (1969).

[12]See the feature in the 5600-cm^{-1} spectral region in Fig. (6.21) of Ref. 1. We would like to thank H. Ibach for pointing out this example.

[13]H. Ibach (private communication).