PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

Vibrational spectra of coupled adsorbed molecules

Richard S. Sorbello
Department of Physics and Laboratory for Surface Studies, University of Wisconsin—Milwaukee, Milwaukee, Wisconsin 53201

(Received 19 June 1985)

The general theory of coupled molecular dipoles is applied to the vibrational spectra of interacting molecules on surfaces. Both classical and quantum-mechanical analyses are presented for the infrared-absorption spectrum. Asymmetric (Fano-effect) line shapes are derived for coupled molecules that interact with electron-hole pairs or optical phonons in the substrate. A very general intensity sum rule is derived which may be useful in constructing theoretical models to explain experimental data. The sum rule may aid in assessing the relative importance to electrodynamic coupling effects, chemical effects, and electromagnetic-field-enhancement effects.

I. INTRODUCTION

Experimental studies of the vibrational spectra of adsorbed molecules can yield important information on the bonding of molecules to surfaces and on dynamical processes occurring between molecules and surfaces.[1,2] This information is usually obtained by fitting theoretical models[3–19] to the experimental data. Depending upon the number of effects the theoretical models incorporate, one may be faced with an uncomfortably large number of fitting parameters. It may then become difficult to assess the validity of the theoretical models. Consequently, it seems appropriate to examine critically the most general theoretical models, with an eye toward establishing how model dependent the resulting vibrational spectrum is and whether there are any universal relations, or sum rules, that are insensitive to the details of the theoretical model.

The need for such critical studies is particularly strong when one is investigating adsorbates at partial coverages. In such cases, one can expect adsorbate island structures or adsorbate clustering around structural defects such as steps and kinks on imperfect surfaces or edges and corners on small particles.[20] The corresponding modes of vibration of the coupled adsorbate molecules become more complicated[9,20,21] and field-enhancement effects[21,22] may need to be considered. It would obviously be useful here to make some general model-independent statements that would aid in sorting out the various physical processes which give rise to the vibrational spectrum. This is one of the goals of our paper.

The shape of the vibrational spectrum may appear asymmetrical because of the excitation of different adsorbate modes having similar natural frequencies. This can occur for a single island[9,21] or for an ensemble of different adsorbate groups. The resulting vibrational spectrum would be composed of a sum of pure Lorentzian line shapes of various center frequencies and linewidths. However, there is another, more interesting kind of line shape that can occur even for a single adsorbate mode of vibration. This line shape, having the same form as the Fano line shape of atomic physics,[23] is caused by the excitation and interference of adsorbate modes with the continuum of excited states of the substrate. Recently, Langreth[19] demonstrated that a Fano line shape occurs when an adsorbed molecule interacts with the electron-hole pairs of a metal substrate. Langreth's theory is couched in terms of generalized susceptibilities and response functions. The analysis we shall present is more closely related to the standard Fano analysis.[23,24] We also treat the case of substrate excitations other than electron-hole pairs. In addition, it is shown that there is a very general intensity sum rule which remains valid even in the presence of Fano line shapes.

In Sec. II we present the classical analysis of coupled molecular vibrations in some depth. A good portion of the classical analysis is a review, but it does provide the framework for a precise discussion of the parameters which enter the quantum-mechanical analysis, as well as the classical analysis. The new results in the classical analysis are, as far as we are aware, the intensity sum rule, our identical-oscillator results in the electrodynamic coupling model, and our simple model for asymmetric line shapes. The quantum-mechanical analysis of Sec. III corroborates the classical results, except for an important feature concerning asymmetric line shapes. The practical significance of our results in interpreting experimental data is discussed in Sec. IV.

II. CLASSICAL CALCULATION

A. Normal modes and absorption spectrum

Our analysis is based on the coupled-dipole theory introduced by Decius[25] for molecular crystals, and first applied to an overlayer of adsorbed molecules by Hammaker, Francis, and Eischens.[3] Subsequent refinements, mostly concerning the form of the dipole-dipole coupling, were made by Moskovits and Hulse,[4] Mahan and Lucas,[5] Scheffler,[6] and Persson and Liebsch.[10] In these coupled-dipole theories, a single adsorbed molecule, or more precisely, a given vibrational transition of a single adsorbed molecule, is described in terms of an oscillating dipole. In a system of molecules, the individual dipoles couple to each other, giving rise to normal modes. An incident electromagnetic wave may then excite an individual normal mode if the frequency of the radiation coincides with a normal-mode frequency.

The ith adsorbed molecule is described by a reduced mass m_i, a natural frequency ω_{0i}, and an effective charge e_i. Following Persson and Liebsch,[10] we regard these to be renormalized quantities which include chemical effects and self-image effects due to the substrate. In the presence of an applied radiation field whose component along the vibrational-dipole axis of the ith molecule is $E_i(t)$, the (linearized) equations of motion for a system of N-coupled molecules are

$$\frac{m_i d^2\xi_i(t)}{dt^2}+m_i\omega_{0i}^2\xi_i(t)+\sum_j K_{ij}\xi_j(t)=e_iE_i(t) \ , \qquad (1)$$

where $\xi_i(t)$ is the coordinate of the ith oscillator at time t and K_{ij} is the coupling coefficient between molecules i and j. (The K matrix is a real symmetric matrix.) The sum over j is over all N molecules. The dipole moment of the ith molecule is

$$p_i(t)=e_i\xi_i(t) \ . \qquad (2)$$

It is convenient to define a new coordinate $u_i(t)$ by

$$\xi_i(t)=u_i(t)/m_i^{1/2} \ . \qquad (3)$$

Substitution of expression (3) into Eq. (1), yields

$$\frac{d^2u_i(t)}{dt^2}+\omega_{0i}^2u_i(t)+\sum_j C_{ij}u_j(t)=\left[\frac{e_i}{m_i^{1/2}}\right]E_i(t) \ , \qquad (4)$$

where $C_{ij}=(m_im_j)^{-1/2}K_{ij}$.

We now look for solutions of Eq. (4) in which all quantities oscillate harmonically at frequency ω. Writing

$$E_i(t)=\mathrm{Re}(E_ie^{-i\omega t}) \qquad (5a)$$

and

$$u_i(t)=\mathrm{Re}(u_ie^{-i\omega t}) \ , \qquad (5b)$$

where Re stands for the real part, we obtain, from Eq. (4),

$$\sum_j L_{ij}(\omega)u_j=F_i \ , \qquad (6)$$

where

$$L_{ij}(\omega)=(\omega_{0i}^2-\omega^2)\delta_{ij}+C_{ij} \qquad (7)$$

and

$$F_i=e_iE_i/m_i^{1/2} \ . \qquad (8)$$

The normal modes of oscillation are the solutions in the absence of the applied field. If we set $E_i=0$ for all i, Eq. (6) becomes an eigenvalue equation for the N normal modes. Denoting the normal modes with the label ν, the normal-mode eigenvalues ω_ν^2 and eigenvectors u^ν satisfy

$$\sum_j A_{ij}u_j^\nu=\omega_\nu^2u_i^\nu \ , \qquad (9)$$

where

$$A_{ij}=\omega_{0i}^2\delta_{ij}+C_{ij} \ . \qquad (10)$$

The eigenvectors of the real symmetric matrix A satisfy the usual relations of orthonormality

$$\sum_i u_i^\nu(u_i^{\nu'})^*=\delta_{\nu\nu'} \qquad (11a)$$

and completeness

$$\sum_\nu u_i^\nu(u_j^\nu)^*=\delta_{ij} \ . \qquad (11b)$$

The complex conjugates in Eqs. (11a) and (11b) allow for the choice of complex eigenvectors when there is mode degeneracy.

The solutions to the driven-oscillator equation (6) can be written in terms of the normal modes. Noting that

$$L=A-\omega^2\mathbb{1} \ , \qquad (12)$$

where $\mathbb{1}$ is the unit matrix, the solution of Eq. (6) is, in matrix notation,

$$u=(A-\omega^2\mathbb{1})^{-1}F \ . \qquad (13)$$

Insertion of the completeness relation (11b) just before F in Eq. (13) leads to

$$u_i=\sum_\nu\frac{u_i^\nu}{\omega_\nu^2-\omega^2}\sum_j(u_j^\nu)^*F_j \ . \qquad (14)$$

The absorption intensity, or the time-averaged power absorbed at frequency ω, is the time average of the force $e_iE_i(t)$ times the velocity $d\xi_i/dt$ summed over all the molecules. This leads to the intensity expression

$$I(\omega)=-\frac{\omega}{2}\mathrm{Im}\left[\sum_i F_iu_i^*\right] \ , \qquad (15)$$

where Im denotes the imaginary part.

It is easily seen that substitution of expression (14) into Eq. (15) gives zero. The problem is that the oscillators were originally assumed to be perfectly lossless. To remedy this unphysical assumption, one usually adds damping into the equations of motion. If we add a damping term $\gamma du_i/dt$ to the left-hand side of Eq. (4), it is apparent that the only effect of this is to replace ω^2 by $\omega^2+i\omega\gamma$ in Eqs. (7), (12), (13), and (14). Combining Eq. (15) and the modified form of Eq. (14), we finally obtain

$$I(\omega)=\sum_\nu I_\nu(\omega) \ , \qquad (16)$$

where

$$I_\nu(\omega)=\frac{1}{2}\,\frac{\omega^2\gamma}{(\omega^2-\omega_\nu^2)^2+\omega^2\gamma^2}\left|\sum_j u_j^\nu F_j^*\right|^2 \qquad (17)$$

is the intensity contribution from mode ν.

We remark that, to be more general, one may assume a different damping rate γ_ν for each normal mode. The only effect is to replace γ by γ_ν in Eq. (17). Note that each normal mode gives rise to a Lorentzian function of width γ_ν centered at ω_ν. (It is assumed that $\gamma_\nu \ll \omega_\nu$.)

The integrated intensity for each mode is readily determined. Denoting this quantity by P_ν, and denoting the total integrated intensity by P_T, we write

$$P_\nu=\int_0^\infty I_\nu(\omega)d\omega \qquad (18)$$

and

$$P_T = \int_0^\infty I(\omega)d\omega \ . \tag{19}$$

Calculation of P_ν from Eqs. (17) and (18) yields

$$P_\nu = \frac{\pi}{4}\left| \sum_i u_i^\nu F_i^* \right|^2 , \tag{20}$$

and summation of this expression over ν yields

$$P_T = \frac{\pi}{4}\sum_i \frac{e_i^2 |E_i|^2}{m_i} , \tag{21}$$

where we have made use of Eqs. (8) and (11b). Expression (21) is our intensity sum rule. Note that it is independent of the assumed damping constants γ_ν of the normal modes.

B. Local-field effects

In general, $E_i(t)$ is not the radiation field that would be experienced by a solitary molecule (with no other molecules present). Rather, $E_i(t)$ is the total time-dependent field at the ith molecule when we imagine that all oscillators are fixed at their equilibrium positions (all $u_j=0$) so that no vibrational dipole coupling is included. (The latter coupling is already included in the C_{ij}.) Thus,

$$E_i(t) = E_i^{\rm ext}(t) + E_i'(t) , \tag{22}$$

where the external field $E_i^{\rm ext}(t)$ is the radiation field on a solitary adsorbed molecule at site i and $E_i'(t)$ is the field due to the electronic polarizability of other adsorbed molecules. Obviously, $E_i(t)$ implicitly depends upon the location of the other adsorbates. Similarly, C_{ij} implicitly depends upon the complete adsorbate configuration, and is not simply a function of the positions of the ith and jth molecules. None of these complications affects the validity of the equations given thus far.

In the remainder of this section we consider the most common model for dipole-dipole coupling[5-12] In this model, the vibrational dipoles are assumed to be point dipoles which interact by quasistatic electrodynamic coupling through space and through the substrate via included image potentials. The electronic polarizability causes electronic dipoles to be created, and these are assumed to give rise to quasistatic electric fields just as a vibrational dipole would (i.e., through space and through image potentials). For simplicity, we assume that the electronic dipole of molecule is oriented along the same direction as the vibrational dipole, so that tensor polarizabilities can be avoided. The electronic polarizability of the ith molecule is denoted by $\alpha_i^{\rm el}$, and the electrodynamic coupling between dipoles is described by a matrix D_{ij}.

We can easily determine the matrix C and the vector F in Eqs. (7) and (8) in terms of $\alpha^{\rm el}$ and D. To do this, we consider the equation of motion for the complex amplitude u_i. In place of Eq. (6), we write

$$(\omega_{0i}^2 - \omega^2)u_i = F_i^{\rm eff} , \tag{23}$$

where $F_i^{\rm eff} = e_i E_i^{\rm eff}/m_i^{1/2}$ and $E_i^{\rm eff}$ is the amplitude of the effective electric field. $E_i^{\rm eff}$ is the sum of $E_i^{\rm ext}$ and the total electric field amplitude at the ith molecule due to all other electron *and* vibrational dipoles. $F_i^{\rm eff}$ satisfies the self-consistency relation

$$F_i^{\rm eff} = F_i^{\rm ext} - \sum_j D_{ij}\left[u_j + \frac{m_j \alpha_j^{\rm el}}{e_j^2} F_j^{\rm eff} \right] , \tag{24}$$

where $F_i^{\rm ext} = e_i E_i^{\rm ext}/m_i^{1/2}$ and $D_{ii} \equiv 0$. The form of Eq. (24) when $F_i^{\rm ext}$ and $\alpha_j^{\rm el}$ are set equal to zero defines the coupling matrix D. [It follows that the through-space part of D_{ij} equals $e_i e_j / r^3 (m_i m_j)^{1/2}$ for point dipoles separated by a distance r on a flat surface and oriented perpendicular to it.] The term with $\alpha_j^{\rm el}$ in Eq. (24) follows from the equivalence of an electronic dipole moment $\alpha_j^{\rm el} E_j^{\rm eff}$ and a vibrational dipole $p_j = e_j u_j / m_j^{1/2}$ having the same amplitude.

The solution of Eq. (24) is, in matrix notation,

$$F^{\rm eff} = (\mathbb{1} + DB)^{-1}(F^{\rm ext} - Du) , \tag{25}$$

where

$$B_{ij} = (m_j \alpha_j^{\rm el}/e_j^2)\delta_{ij} \ . \tag{26}$$

We now see that Eq. (23) is equivalent to Eqs. (6)–(8) provided that we make the identifications

$$C = (\mathbb{1} + DB)^{-1}D \tag{27}$$

and

$$F = (\mathbb{1} + DB)^{-1}F^{\rm ext} \ . \tag{28}$$

In the special case of identical oscillators, characterized by parameters ω_0, m, e, and $\alpha^{\rm el}$, we note that $B = (m\alpha^{\rm el}/e^2)\mathbb{1}$. It then follows from Eqs. (9), (10), and (27) that there is a simple relation between the normal-mode frequencies with and without electronic polarizability. Denoting these frequencies by ω_ν and ω_ν^0, respectively, we find

$$\left[\frac{\omega_\nu}{\omega_0}\right]^2 = 1 + \frac{X}{1+\beta X} , \tag{29}$$

where $X = (\omega_\nu^0/\omega_0)^2 - 1$ and $\beta = \alpha^{\rm el} m \omega_0^2 / e^2$, which is the ratio of electronic to vibrational polarizability for an adsorbate molecule. Similarly, we find that the integrated intensity for mode ν is

$$P_\nu = \frac{P_\nu^0}{(1+\beta X)^2} , \tag{30}$$

where P_ν^0 pertains to the case of vanishing electronic polarizability.

We emphasize that Eqs. (29) and (30) remain valid for identical oscillators no matter how complicated are the molecular configurations, the coupling coefficients D_{ij}, the normal mode patterns, or the local variation of the radiation field $E_i^{\rm ext}$. However, there is a further simplification if the system happens to support a uniform mode (u_j^ν the same for all j). For such a mode it is easy to show from Eq. (9) that

$$X = \frac{1}{N\omega_0^2}\sum_{ij} D_{ij} \quad \text{(uniform mode)} , \tag{31}$$

which reproduces the well-known results[1,2,11] for ω_ν and

P_ν in the uniform mode of an ordered overlayer. We remark that the use of expression (31) in Eq. (29) is also likely to be a good approximation for the in-phase (nodeless) mode of a finite structure (such as an island) of identical oscillators, even though such a structure does not strictly support a uniform mode. The point is that using Eq. (31) in Eq. (29) is equivalent to obtaining a variational solution for the eigenvalue of Eq. (9) using the trial function $u_j = 1/\sqrt{N}$. The insensitivity of eigenvalue to choice of variational trial function implies that the resulting ω_ν should be a good approximation for the in-phase mode. We have numerically verified that in the case of one-dimensional islands, expression (31) leads to in-phase-mode frequency shifts that are accurate to within a few percent.

C. Asymmetric line shapes

In the classical model thus far described, each mode gives a Lorentzian contribution to the intensity, as seen from Eq. (17). The true line shape for a single mode may in fact be asymmetrical. One way to obtain an asymmetric line shape is to couple the mode to a system that has a broad-band (continuum) spectrum that overlaps the single mode. If the applied radiation field can directly excite the single mode and the broad-band system as well, one can expect something analogous to the Fano effect[23] of atomic physics to occur. Fano line shapes have been theoretically obtained by Langreth[19] for an adsorbed molecule coupled to electron-hole pairs at the surface of a metal. A quantum-mechanical calculation such as that performed by Langreth, appears to be necessary for a quantitative description of Fano line shapes of adsorbed molecules. Nonetheless, it is helpful to consider classical models that highlight some of the physics of the Fano line shape. The quantum-mechanical theory is presented in Sec. III.

In a particularly simple classical model, one may couple a normal mode ν to a lossy broad-band system, such as an overdamped oscillator or a viscous bath that can be described by one degree of freedom.[26] The equations of motion for the normal mode amplitude U^ν and the bath degree-of-freedom amplitude U^B are taken to be

$$(\omega_\nu^2 - \omega^2)U^\nu + cU^B = F^\nu \tag{32}$$

and

$$Z(\omega)U^B + cU^\nu = F^B , \tag{33}$$

where c is a coupling coefficient and $Z(\omega)$ is a complex response function characterizing the bath. $Z(\omega)$ is assumed to be nearly independent of ω in the region of interest close to ω_ν. (For a purely viscous bath, $Z(\omega) = -i\omega/\tau$, where τ is an effective relaxation time.) F^ν and F^B are the amplitudes of the driving forces on the oscillator and the bath, respectively. (The ratio F^ν/F^B is a parameter that depends only on the type of excitation field, not on its strength.) Note that if we take $Z(\omega) = \omega_B^2 - \omega^2 - i\omega\gamma_B$, Eqs. (32) and (33) would formally describe two coupled-dipole oscillators, with one oscillator (the bath) having frictional damping parameter γ_B and resonance frequency ω_B.

In the absence of direct excitation of the bath ($F^B = 0$), and assuming weak coupling between oscillator and bath, the absorption spectrum obtained from Eqs. (32) and (33) is a Lorentzian centered at $\omega_\nu + \Delta\omega_\nu$ with linewidth γ, where

$$\Delta\omega_\nu = -\frac{c^2}{2\omega_\nu}\mathrm{Re}\frac{1}{Z(\omega_\nu)} \tag{34}$$

and

$$\gamma = \frac{c^2}{\omega_\nu}\mathrm{Im}\frac{1}{Z(\omega_\nu)} . \tag{35}$$

The occurrence of a Lorentzian line shape in the absence of direct excitation of the bath is a key aspect of the Fano effect which is contained in this model.

The absorption spectrum when both F^ν and F^B are nonvanishing is calculated to be

$$I(\omega) = \mathrm{Im}\left[i + \frac{k_1 + ik_2}{(\omega_\nu + \Delta\omega_\nu)^2 - \omega^2 - i\omega\gamma} \right] I^0(\omega) , \tag{36}$$

where k_1 and k_2 are real constants depending on the model parameters and

$$I^0(\omega) = (\omega/2)\,|F_B|^2 \mathrm{Im}[Z^{-1}(\omega)]$$

is the background intensity due to direct excitation of the bath. The ik_2 term is responsible for non-Lorentzian line shapes.

The true Fano line shape is[23]

$$I(\omega) = [(q+\epsilon)^2/(1+\epsilon^2)]I^0(\omega) \tag{37}$$

where $\epsilon = 2(\omega - \omega_\nu - \Delta\omega_\nu)/\gamma$ and q is a parameter governing the line-shape asymmetry. If we set $k_2/k_1 = 2q/(q^2-1)$, we find that expressions (36) and (37) give the same result (in the vicinity of resonance) for the difference spectrum $I(\omega) - I^0(\omega)$, except for a multiplicative constant. Thus the simple classical model gives the same *shape* for $I(\omega) - I^0(\omega)$ as does the Fano expression, but it does not, in general, give the same strength or integrated intensity. For agreement on integrated intensity, we need to consider a bath that contains infinitely many degrees of freedom, rather than a bath modeled by a single degree of freedom subject to frictional damping. The bath is appropriately modeled as a continuum in the quantum-mechanical calculation described in the next section.

III. QUANTUM-MECHANICAL CALCULATION

In our quantum-mechanical analysis of coupled molecular vibrations on surfaces, we invoke the viewpoint commonly taken in the theory of lattice vibrations.[27] That is, the adsorbate normal modes of vibration are assumed to be calculated classically from an adiabatic potential energy derived within the Born-Oppenheimer approximation. These modes are then quantized, resulting in what we shall call "phonons." The phonons can then be coupled to an external field. Nonadiabatic effects are included by means of a coupling between the phonons and other excitations, e.g., electron-hole pairs. Note that adiabatic interactions between the adsorbate molecules and the substrate are implicitly included in the phonons.

The normal modes are obtained from the classical equations of motion (9). The displacement operator $\hat{\xi}_j$ for the jth molecule is written in terms of the adsorbate phonon operators b_ν and $b_\nu^\dagger$ in the usual way,[27] viz.,

$$\hat{\xi}_j=\sum_\nu \left[\frac{\hbar}{2\omega_\nu m_j}\right]^{1/2} [b_\nu u_j^\nu + b_\nu^\dagger (u_j^\nu)^*] \ , \tag{38}$$

where $b_\nu^\dagger$ creates (and b_ν annihilates) a phonon in mode ν.

The rate $W(\omega)$ at which the system absorbs photons of frequency ω is given by the golden rule

$$W(\omega)=\frac{2\pi}{\hbar}\sum_f |\langle f|M|i\rangle|^2\delta(\hbar\omega-\epsilon_f+\epsilon_i) \ , \tag{39}$$

where $|i\rangle$ is the initial state of the system, $|f\rangle$ is one of the possible final states, and ϵ_i,ϵ_f denote the energies of the initial and final states, respectively. The sum is over all possible final states. M is the interaction Hamiltonian between the system and the radiation field, and may be written in the form

$$M=M^0+M' \ , \tag{40}$$

where M^0 is the interaction with the phonons and M' is the interaction with all other excitations. The explicit form of M^0 for coupling to molecular dipoles is

$$M^0=\tfrac{1}{2}\sum_j e_j\hat{\xi}_j E_j \ , \tag{41}$$

where we have used Eq. (2) for the dipole moment of an adsorbate. M', like M^0, is linear in the (classical) radiation field. By definition, $|i\rangle$ and $|f\rangle$ are the system states in the absence of the radiation field. We shall assume that the system is initially in the ground state (no phonons or other excitations present).

The adsorption intensity is related to the transition rate by

$$I(\omega)=\hbar\omega W(\omega) \ . \tag{42}$$

The frequencies of interest are generally confined to a frequency range $\Delta\omega$ about the normal mode frequencies ω_ν, such that $\Delta\omega \ll \omega_\nu$. Consequently, the $\hbar\omega$ factor in Eq. (42) may be taken as a constant, to an excellent approximation.

The interesting Fano-effect line-shape asymmetries are due to interferences brought about by the presence of M', which describes the coupling between the radiation field and the continuum system of excitations (recall Sec. II C). For the moment, however, we ignore these excitations completely. The states of the system in the absence of radiation are then the adsorbate phonon states, which we denote in the occupation-number representation by $|\{\mathcal{N}_\nu\}\rangle$. Noting that $|i\rangle=|\{0_\nu\}\rangle$, and using Eq. (41) for M in expression (39), we easily obtain $I(\omega)=\sum_\nu I_\nu(\omega)$, where

$$I_\nu(\omega)=\frac{\pi}{4}\left|\sum_j \frac{e_j u_j^\nu E_j^*}{m_j^{1/2}}\right|^2 \delta(\omega-\omega_\nu) \ . \tag{43}$$

This agrees with the classical expression (17) in the limit that $\gamma\to 0$. Consequently, the classical expressions (20) and (21) for the integrated intensities are also valid in the quantum-mechanical analysis.

We now wish to allow coupling to the continuum of excitations. This will introduce a finite linewidth and, possibly, a line-shape asymmetry. Before deriving an expression for the line shape, we show that the total integrated intensity measured with respect to the continuum background absorption satisfies the intensity sum rule (21). To do this, consider the quantity $\Delta W(\omega)$, which is the total transition rate minus the transition rate due to excitation of the continuum background alone. By definition,

$$\Delta W(\omega)=\frac{2\pi}{\hbar}\sum_f (|\langle f|M|i\rangle|^2-|\langle f|M'|i\rangle|^2) \times\delta(\hbar\omega-\epsilon_f+\epsilon_i) \ . \tag{44}$$

Integration of ΔW over all frequencies yields

$$\int_0^\infty \Delta W(\omega)d\omega=\frac{2\pi}{\hbar}\langle i|(M^0)^2|i\rangle \ , \tag{45}$$

where we have used the completeness relation $\sum_f |f\rangle\langle f|=1$, and noted that M^0 acts only on the phonons, while M' acts only on the excitations. The right-hand side of Eq. (45) is precisely the result that obtains in the absence of coupling between phonons and the excitations. It follows from Eq. (42) that to an excellent approximation the difference spectrum satisfies the intensity sum rule

$$\int_0^\infty [I(\omega)-I^0(\omega)]d\omega=\frac{\pi}{4}\sum_j \frac{e_j^2|E_j|^2}{m_j} \ , \tag{46}$$

where $I^0(\omega)$ is the background intensity due to absorption by the continuum, i.e., the intensity calculated from Eq. (39) with $M=M'$. The right-hand side of Eq. (46) is the total integrated intensity in the limit of vanishing coupling between the phonons and the excitations.

The intensity line shape is readily determined by a straightforward extension of the Fano analysis.[23] For convenience, we shall use the form of the Fano analysis that was introduced by Shibatani and Toyozawa.[24] The Hamiltonian of the system in the absence of the radiation field is written as

$$H=H_0+H' \ , \tag{47}$$

where H_0 is the Hamiltonian for the system of adsorbate phonons and continuum excitations in the absence of coupling, and H' is the coupling term. We now specialize to the case of electron-hole pair excitations and write

$$H'=\sum_{kk'} g_{kk'}^\nu c_k^\dagger c_{k'} b_\nu + \text{H.c.} \ , \tag{48}$$

where the electron states are labeled by k and k', with $c_k^\dagger$ and $c_{k'}$ being the electron creation and annihilation operators. $g_{kk'}^\nu$ is the electron-phonon coupling constant for phonon mode ν. (We are ignoring intermode conversion via the coupling, so we consider each mode ν independently.)

The coupling of the electronic system to the radiation field has the form

$$M'=\sum_{k,k'} m_{k'k}' c_{k'}^\dagger c_k \ , \tag{49}$$

where the $m'_{k'k}$ are coupling coefficients.

Following Shibatani and Toyozawa,[24] we rewrite expression (39) in terms of the Green's function $G=(\hbar\omega - is - H)^{-1}$, where s is a positive infinitesimal. The result is

$$W(\omega)=\frac{2}{\hbar}\mathrm{Im}\langle i\,|MGM\,|\,i\rangle \; . \tag{50}$$

To determine G, we use the Dyson equation

$$G=G_0+G_0H'G \; , \tag{51}$$

where $G_0=(\hbar\omega - is - H_0)^{-1}$. The matrix elements of Eq. (51) are evaluated in the representation in which H_0 is diagonal, i.e., the $|\{\mathcal{N}_\nu\};\{n_k\}\rangle$ basis. These matrix elements of G are then used in expression (50). After some algebra which is formally identical to the algebra performed by Shibatani and Toyozawa,[28] we obtain precisely the Fano line shape (37), with the parameter q given by

$$q=\frac{1}{\pi}\left[\frac{m^{0}_{\nu\nu}+\mathrm{P}\sum\limits_{k,k'}\dfrac{[g^{\nu}_{kk'}m'_{k'k}f_{k'}(1-f_k)]}{(\hbar\omega-\epsilon_k+\epsilon_{k'})}}{\sum\limits_{k,k'}g^{\nu}_{kk'}m'_{k'k}f_{k'}(1-f_k)\delta(\hbar\omega-\epsilon_k+\epsilon_{k'})}\right] , \tag{52}$$

where $m^{0}_{\nu\nu}=\langle 0_\nu;\{n^0_k\}\,|M^0|\,1_\nu;\{n^0_k\}\rangle$, and $\{n^0_k\}$ is the set of occupation numbers for the electrons in the ground state, P denotes principal value, and f_k, the Fermi function, equals unity if the electron energy ϵ_k is below the Fermi energy, and equals zero otherwise. In obtaining Eq. (52) we have taken the initial state $|i\rangle$ to be the state $|0_\nu;\{n^0_k\}\rangle$ in which there are no phonons or electron-hole excitations. The Fano line-shape asymmetries arise from the mixing (due to H') of phonons and excitations in the final states $|f\rangle$ in Eq. (39), and from the coupling to these states via M^0 and M'. If $M'\rightarrow 0$, then $q\rightarrow\infty$ and the difference spectrum $I(\omega)-I^0(\omega)$ approaches a Lorentzian whose width is equal to the natural linewidth parameter γ, which is given by the usual golden rule expression

$$\gamma=\frac{2\pi}{\hbar}\sum_{k,k'}|g^{\nu}_{kk'}|^2 f_{k'}(1-f_k)\delta(\hbar\omega-\epsilon_k+\epsilon_{k'}) \; . \tag{53}$$

A similar calculation can be performed for substrate excitations other than electron-hole pairs. For example, if the substrate excitations are optical phonons (i.e., infrared-active vibrations), we can write

$$H'=\sum_{Q} r^{\nu}_{Q}(a_Q+a^{\dagger}_{Q})b_\nu+\mathrm{H.c.} \; , \tag{54}$$

where $a_Q,a^{\dagger}_Q$ are substrate-phonon operators and r^{ν}_Q is a coupling constant. In this model, the radiation couples to the substrate phonons through an interaction of the form

$$M'=\sum_{Q} m'_Q(a_Q+a^{\dagger}_Q) \; . \tag{55}$$

The calculation proceeds as before; the q parameter of the resulting Fano line shape turns out to be

$$q=\frac{1}{\pi}\left[\frac{m^{0}_{\nu\nu}+\mathrm{P}\sum\limits_{Q}(r^{\nu}_{Q}m'_{Q})/[\hbar(\omega-\omega_Q)]}{\sum\limits_{Q} r^{\nu}_{Q}m'_{Q}\delta(\hbar\omega-\hbar\omega_Q)}\right] , \tag{56}$$

and the natural linewidth parameter is

$$\gamma=\frac{2\pi}{\hbar}\sum_{Q}|r^{\nu}_{Q}|^2\delta(\hbar\omega-\hbar\omega_Q) \; . \tag{57}$$

In a typical experiment, there may be other independent sources of the background absorption spectrum besides the excitations. Denoting this extra absorption as $I'(\omega)$, we should add this quantity to the Fano line shape (37). The intensity sum rule (46) is still valid for the true difference spectrum, i.e., $I-I^0-I'$ rather than $I-I^0$. Thus, the true difference spectrum satisfies the relations

$$\int_0^\infty [I(\omega)-I^0(\omega)-I'(\omega)]d\omega=2\gamma(q^2-1)I^0(\omega_\nu) \tag{58}$$

$$=\frac{\pi}{4}\sum_j\frac{e_j^2\,|E_j\,|^2}{m_j} \; . \tag{59}$$

The first line would allow the experimental determination of the absorption I^0 due to the excitations alone, which is a quantity not ordinarily accessible by experiment. The second line is the intensity sum rule. We emphasize that these expressions are not obtained in the simple classical model of Sec. II C, despite the fact that the shape of the difference spectrum in that model has the same form as in the Fano theory.[29]

It should be pointed out that if the radiation couples to two or more adsorbate phonon modes which involve the same molecules and which would produce strongly overlapping Fano line shapes, then the spectrum is not a simple sum of the individual Fano line shapes. Instead, a more complicated spectrum is expected because of indirect coupling of the modes via the continuum.[23] However, the intensity sum rule [Eqs. (46) or (59)] remains valid since its derivation does not assume noninteracting phonon modes.

IV. DISCUSSION

We have presented very general classical and quantum-mechanical descriptions of the vibrational spectra of coupled adsorbates. Classical and quantum-mechanical calculations are in essential agreement, except for the case of asymmetric line shapes (Fano effect) where a simple classical model[29] misses an important feature of the quantum-mechanical calculation, namely, the intensity sum rule (59). This sum rule has been shown to be valid under the most general conditions, including the presence of chemical shifts (contained in the ω_{0i} and in the coupling coefficients C_{ij}), local-field enhancements, image effects, and arbitrary coupling between molecules.

Our quantum-mechanical analysis of asymmetric line shapes complements the recent work of Langreth,[19] which is more detailed in its modeling of the adsorbate-substrate interaction. The analysis presented here is couched in rather different terms, and makes closer contact with the original Fano analysis. In the case of indirect coupling of adsorbate modes via the Fano effect, the simple Fano (or

Langreth) line shape does not, in general, apply. Nonetheless, the total integrated intensity (over the background level) does satisfy the intensity sum rule (21). This property may be useful in interpreting asymmetric line shapes, should they be unequivocally seen in future experiments. The observation of Fano asymmetries requires that the magnitude of q not be too large, say, $|q| \lesssim 10$. Equation (52) implies that relatively small $|q|$ is expected for large adsorbate substrate coupling $g^{\nu}_{kk'}$ and large background absorption $m'_{k'k}$. Langreth's estimate is that an Anderson-Newns-type resonant-level model[14] for adsorbates would lead to relatively small q values for CO on Cu(100).[30] It appears that ordinary electrodynamic dipole-coupling of an adsorbate to a metal surface may be too weak to give appreciable linewidth asymmetry. This is consistent with the results of a classical model (Ref. 26), and with Langreth's usage of a resonant-level model to achieve appreciable asymmetry.

We now turn to the question of how the intensity sum rule and the identical oscillator expressions (29) and (30) might be put to practical use. From a theoretical point of view, these expressions can, at the very least, provide a useful check of numerical computations for spectra arising from general molecular configurations. In the case of the electrodynamic dipole-dipole coupling model for a system of identical oscillators, expressions (29) and (30) also show that it is unnecessary to solve the complete coupled-dipole problem with assumed values of the electronic polarizability α^{el}. Rather, one can use the results of the calculation in which α^{el} is set equal to zero, and then scale these results in a simple way. Such a procedure can be a significant simplification when the value of α^{el} is not known *a priori* and one is trying to fit experimental data to determine α^{el}.

The general effect of α^{el} on ω_ν and P_ν for identical oscillators is apparent from Eqs. (29) and (30). For example, consider the in-phase modes (for dipoles normal to the surface), whose frequencies in the $\alpha^{\mathrm{el}}=0$ case are expected to increase with coverage Θ because of the increase in the number of dipole-dipole coupling terms D_{ij} with N (or Θ) in Eq. (31). It follows from Eq. (29) that for such modes, as Θ increases, ω_ν vs Θ should bend increasingly downward with respect to the linear slope of ω_ν vs Θ at small Θ. Concomittantly, Eq. (30) implies an even more marked downward bending in P_ν vs Θ, which may in fact have a negative slope at sufficiently high coverage. This behavior has been noticed in some experiments, and has been understood in such terms only for the inphase, uniform coverage mode.[1,2,11] We point out that it is also true for more complex structures, where a uniform mode does not strictly exist. Note also that for other modes (i.e., out-of-phase modes) for which ω_ν^0 vs Θ may slope downward, we can expect that the P_ν vs Θ curve will be concave upward.

The intensity sum rule (21) yields its most powerful implications for adsorbates with negligible electronic polarizability. In that case, the electric field in Eq. (21) is simply E_i^{ext}, which is completely independent of the intermolecular coupling. In that case, it follows that in the absence of field enhancement effects ($E_i^{\mathrm{ext}}=\mathrm{const}$) or adsorbates of different reduced masses, P_T will be proportional to Θ, unless e_i is changing with Θ due to chemical effects arising from the intermolecular interactions or a change in bonding sites. In the more general case, we expect that a sudden drop in P_T vs Θ, as in some experiments,[20,31] is signaling a rearrangement of some atoms from sites of higher $e_i|E_i|$ to sites of lower $e_i|E_i|$. This idea has been used[21] in interpreting experimental data[20] for stepped crystals. The great generality of the intensity sum rule makes it a useful tool in developing theoretical models to fit experimental data.

We conclude that greater experimental effort should be focused on obtaining accurate integrated intensities and line shapes of vibrational spectra. Theoretical modeling should take into account the intensity sum rule.

ACKNOWLEDGMENTS

I would like to thank Professor Robert Greenler for many stimulating discussions. I have also benefited from useful conversations with Professor D. R. Snider, Professor A. Zangwill, and Mr. F. Leibsle.

---

[1] F. M. Hoffmann, Surf. Sci. Rep. **3**, 107 (1983).

[2] H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982).

[3] R. M. Hammaker, S. A. Francis, and R. P. Eischens, Spectrochim. Acta **21**, 1295 (1965).

[4] M. Moskovits and J. E. Hulse, Surf. Sci. **78**, 397 (1978).

[5] G. D. Mahan and A. A. Lucas, J. Chem. Phys. **68**, 1334 (1978).

[6] M. Scheffler, Surf. Sci. **81**, 562 (1979).

[7] S. Efrima and H. Metiu, Surf. Sci. **92**, 433 (1980); **108**, 329 (1981).

[8] S. Efrima, Surf. Sci. **110**, 56 (1981).

[9] P. Hollins, Surf. Sci. **107**, 75 (1981).

[10] B. N. J. Persson and A. Liebsch, Surf. Sci. **110**, 356 (1981).

[11] B. N. J. Persson and R. Ryberg, Phys. Rev. B **24**, 6954 (1981).

[12] P. R. Antoniewicz and B. I. Dunlap, Surf. Sci. **144**, 272 (1982).

[13] G. W. Ford and W. H. Weber, Surf. Sci. **129**, 123 (1983).

[14] B. N. J. Persson and M. Persson, Solid State Commun. **36**, 175 (1980).

[15] B. N. J. Persson, Surf. Sci. **116**, 585 (1982).

[16] Theoretical models for the linewidth of vibrational spectra are given by B. N. J. Persson and W. L. Schaich, J Phys C **14**, 5583 (1981); M. Persson and B. Hellsing, Phys. Rev. Lett. **49**, 662 (1982); B. N. J. Persson and N. D. Lang, Phys. Rev. B **26**, 5409 (1982); P. Apell, Solid State Commun. **47**, 615 (1983); B. N. J. Persson and S. Anderson, Phys. Rev. B **29**, 4382 (1984); A. G. Eguiluz, *ibid.* **30**, 4366 (1984); see also Refs. 17–19.

[17] B. Hellsing and M. Persson, Phys. Scr. **29**, 360 (1984).

[18] J. W. Gadzuk and A. C. Luntz, Surf. Sci. **114**, 429 (1984).

[19] D. C. Langreth, Phys. Rev. Lett. **54**, 126 (1985).

[20] B. E. Hayden, K. Kretzchmar, A. M. Bradshaw, and R. G. Greenler, Surf. Sci. **149**, 394 (1985).

[21] R. G. Greenler, F. Leibsle, and R. S. Sorbello (unpublished).

[22] R. G. Greenler, J. A. Dudek, and D. E. Beck, Surf. Sci. **145**,

L453 (1984).

[23] U. Fano, Phys. Rev. **124**, 1866 (1961).

[24] A. Shibatani and Y. Toyozawa, J. Phys. Soc. Jpn. **25**, 335 (1968).

[25] J. C. Decius, J. Chem. Phys. **22**, 1941 (1954); **22**, 1946 (1954); **23**, 1290 (1955); **49**, 1387 (1968).

[26] An interesting physical model that approximates this situation is realized for a uniform adsorbate overlayer on a small, spherical metal particle. The model would consist of a dielectric coating on a conducting sphere. The dielectric constant of the coating would depend on frequency and have the resonance form appropriate to an adsorbate layer. The lossy metal sphere is the bath system. The two coupled degrees of freedom would be the polarizations of the dielectric shell and the metal sphere. In this case, the coupled problem is readily solved as a standard boundary value problem [see, e.g., H. C. van de Hulst, *Light Scattering by Small Particles* (Dover, New York, 1957), p. 74]. The resulting absorption spectrum turns out to have a Fano-like asymmetry similar to that of Eq. (36). Unfortunately, the dielectric constant of a metal in the infrared is so large that the asymmetry turns out to be negligible for this model.

[27] See, e.g., J. Callaway, *Quantum Theory of the Solid State* (Academic, New York, 1974).

[28] The analysis of Ref. 24 carries over essentially unchanged when the states $|g\rangle$, $|\alpha\rangle$, and $|k\rangle$ used in Ref. 24 are replaced by $|0_\nu;\{n_k^0\}\rangle$, $|1_\nu;\{n_k^0\}\rangle$, and $|0_\nu;\{n_k\}\rangle$, respectively. As in Ref. 24, the matrix elements of H' and M' are taken to be real.

[29] A much more sophisticated classical model should produce the correct Fano line shape in the case where the substrate excitations are optical phonons. In that case, the appropriate classical model would be an adsorbate vibrational mode linearly coupled to a *continuum* of substrate vibrational modes. Since classical and quantum-mechanical calculations for the spectra of coupled harmonic oscillators give equivalent results, we conjecture that the classical model should reproduce the Fano line shape, with the q parameter given by Eq. (56).

[30] In the vicinity of resonance [$\omega \approx \omega_r$ in Langreth's (Ref. 19) notation], the Langreth line-shape function is of the Fano form (37) with $q=-(\omega_r\tau)^{-1}$. Langreth's estimate is $\omega_r\tau=0.13$ for CO on Cu(100). [To obtain the Fano line shape from Langreth's, replace ω by ω_r everywhere in Langreth's expression except where ω^2-ω_r^2 appears. For the latter, substitute $2\omega_r(\omega-\omega_r)$.]

[31] B. E. Hayden and A. M. Bradshaw, Surf. Sci. **125**, 787 (1983).