Collective Motion and Structural Order in Adsorbate Vibrational Dynamics

M. V. Pykhtin,[1] Steven P. Lewis,[2,*] E. J. Mele,[1] and Andrew M. Rappe[2]
[1]*Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104*
[2]*Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104*

(Received 10 August 1998)

A simple, broadly applicable theory is developed to describe resonant vibrational coupling between adsorbates and a substrate lattice. This is one of the principal mechanisms governing the relaxation of adsorbate vibrations. This theory can be applied to widely varying surface coverages and arbitrary overlayer structures, and it correctly incorporates collective adsorbate motion, which has been shown to have a critical impact on the relaxation dynamics. Vibrational lifetimes predicted by this theory are in excellent quantitative agreement with experiments on adsorbate systems ranging from a diffuse, disordered overlayer to a dense, periodic overlayer. [S0031-9007(98)08012-0]

PACS numbers: 82.20.Rp, 68.35.Ja, 68.45.Kg, 82.65.My

A key factor in many surface chemical phenomena is the existence of low-energy molecular vibrations associated with fluctuations about the adsorption bond. These modes involve relative motion between the adsorbate molecule and substrate, and thus act as vibrational precursors to surface reactions, diffusion, and desorption [1]. Indeed, the systematic study of these modes through inelastic spectroscopic techniques has become the chief tool for characterizing the potential energy surface encountered by atoms and molecules in heterogeneous catalysis, epitaxial growth, and other complex surface phenomena [2].

These low-energy excitations of the adlayer are not isolated from their surroundings; they can exchange energy and momentum with various propagating substrate excitations. At the surface of a metal, for example, the relevant bulk modes include propagating elastic waves, electron-hole pair excitations, and various collective modes arising from electron-electron and electron-phonon interactions. These bulk excitations provide decay channels which govern the lifetimes of the adsorbate vibrational modes and, thus, play a critical role in determining the surface dynamics and reactivity [3,4].

In this Letter, we develop a general theory for the relaxation dynamics of low-frequency adsorbate vibrations due to resonant coupling to substrate elastic waves [5–9]. This theory applies to adsorbate modes with frequencies in the acoustic range of the substrate phonon spectrum, and is relevant, for example, to the in-plane frustrated translation (FT) of adsorbates on metal surfaces. Two recent experiments examined the FT relaxation dynamics of carbon monoxide molecules on the Cu(100) surface under very different conditions of coverage. One considered an ordered half monolayer and measured a lifetime of 2.3 ± 0.4 ps [10], whereas the other considered a disordered adlayer at 3% coverage and found an 8 ± 1 ps lifetime [11]. Our theory shows conclusively that the vibrational relaxation is governed by bulk elastic coupling, even for these widely varying adlayer conditions.

This conclusion contrasts with the results of an earlier theory due to Persson and Ryberg (PR) [6]. They also considered relaxation via phonon emission, but focused on the case of an isolated adsorbate. Since direct adsorbate-adsorbate interactions are weak for all but the densest coverages, this case was presumed applicable for most experimental conditions. Their model gives a damping-rate law that varies with the vibrational frequency as ω^4. However, when applied to various experimental systems [e.g., the CO on Cu(100) systems described above], the PR model predicts damping rates that are much smaller than the measured values. Furthermore, the PR model has no explicit coverage dependence; coverage enters the damping-rate law only implicitly through its effect on the resonance frequency. However, the two experimental coverages of CO on Cu(100) exhibit the *same* FT resonance frequency but have *different* FT lifetimes.

Our theory is developed for a completely arbitrary overlayer structure and, thus, incorporates the effects of lateral coherent motion within the adlayer. These collective effects arise from *indirect* adsorbate-adsorbate interactions mediated by the substrate phonons. Since the adsorbate modes of interest oscillate at the long-wavelength end of the substrate phonon spectrum, the range of the indirect, phonon-mediated interaction is quite large, and thus collective adsorbate motion is important even for rather dilute overlayers.

The theory presented here is a generalization of our recent work [12] on ordered overlayers. We found that the FT vibrational relaxation for the ordered half monolayer of CO on Cu(100) is accurately described by resonant elastic coupling only when the collective effects are properly included. For long-wavelength surface excitations (relevant to the experiments), collective motion of the adsorbate lattice plays a crucial role in the adsorbate dynamics, changing both the accessible phase space of the substrate decay channels and the strength of the coupling. This effect was also described in the context of

© 1998 The American Physical Society

noble-gas atoms physisorbed on silver [7] and graphite [9] surfaces. Our previous work also demonstrated how the results cross over to the dilute (i.e., isolated-adsorbate) limit as coverage is decreased. We found that, for a hypothetical series of ordered CO/Cu overlayer structures with varying coverage, only coverages *well below* a critical value ($\theta \ll \theta_c \approx 1\%$) are properly described by the PR theory of an isolated adsorbate. For all higher coverages, collective effects dominate the dynamics.

In this paper, we extend our previous theory to a form which describes an *arbitrary* adlayer structure, to include the possibilities of disorder, vacancies, coadsorption, etc. We then apply this theory to three structural models: an isolated adsorbate, an ordered overlayer (at coverage above θ_c), and an uncorrelated, disordered overlayer. The first model shows that our theory includes the PR result as a special case. The latter two models are appropriate for making comparisons to the experimental work on CO on Cu(100), Refs. [10] and [11], respectively. These models provide remarkably simple expressions for the decay rate that predict lifetimes in excellent agreement with the experiments. Thus, one theory provides a unified, simple, and accurate description of the low-frequency vibrational dynamics for a wide range of adsorbate configurations.

We consider a semi-infinite, classical, anisotropic elastic medium with elastic modulus tensor C_{ijkl} and density ρ. Although previous theories [6,12] considered the case of an isotropic substrate medium, we find that anisotropic effects can be quantitatively important. The medium occupies the half space $z < 0$, terminated on the xy plane, and is described by a displacement field $\boldsymbol{u}(\boldsymbol{x}, t)$. (We denote three-dimensional vectors in boldface and two-dimensional vectors in the xy plane by arrows.) The adlayer consists of a collection of point masses m coupled to the elastic surface at sites $\{\vec{R}_a\}$ by harmonic springs of frequency ω_0. This model is an appropriate description for a low-frequency adsorbate mode, such as the FT, where ω_0 lies within the acoustic part of the substrate phonon spectrum.

We now suppose that an x-polarized external force, $f(\vec{R}_a, \omega)e^{i\omega t}$, drives the adsorbate overlayer at frequency ω. This leads to x-polarized adsorbate motion, represented here by the instantaneous displacement pattern $s(\vec{R}_a, t)$. The coupled equations of motion for the elastic substrate [13] and the adlayer are given in the frequency domain by

$$\left[-\omega^2\delta_{ik} - \frac{C_{ijkl}}{\rho}\,\partial_j\partial_l\right]u_k(\omega,\boldsymbol{x}) = \frac{m}{\rho}\,\omega_0^2\delta_{ix}\delta(z)\sum_a[s(\vec{R}_a,\omega) - u_x(\omega,\boldsymbol{x})]\delta^{(2)}(\vec{r} - \vec{R}_a)\,, \tag{1}$$

$$-\omega^2 s(\vec{R}_a,\omega) + \omega_0^2[s(\vec{R}_a,\omega) - u_x(\omega,\vec{r} = \vec{R}_a, z = 0)] = \frac{f(\vec{R}_a,\omega)}{m}\,, \tag{2}$$

with stress-free boundary conditions $[\delta_{jz}C_{ijkl}\partial_l \times u_k(\omega,\boldsymbol{x})]_{z=0} = 0$, where summation over repeated Cartesian indices is assumed, and the symbol ∂_i denotes the partial derivative with respect to the ith Cartesian coordinate. Equation (1) describes the motion of the elastic substrate, driven by the x-polarized oscillations of the adsorbates; Eq. (2) describes the motion of the adsorbates, coupled to the substrate and driven by the external force. The theory consists of integrating out the dynamics of $\boldsymbol{u}(\boldsymbol{x}, t)$ from Eqs. (1) and (2) to obtain an effective theory for the adsorbate dynamics. The result is expressed [14] as an adsorbate response function, $\chi(\vec{R}_a, \vec{R}_b; \omega) = s(\vec{R}_a, \omega)/f(\vec{R}_b, \omega)$, given in reciprocal space by

$$\chi(\vec{q},\omega) = \frac{1}{m}\left[-\omega^2 + \omega_0^2 - \omega_0^2\,\frac{T(\vec{q},\omega)}{1 + T(\vec{q},\omega)}\right]^{-1}, \tag{3}$$

where

$$T(\vec{q},\omega) = \frac{m}{\rho}\,\omega_0^2\int\frac{d^2k}{(2\pi)^2}\,D_{xx}(\vec{k},\omega)S(\vec{k} - \vec{q})\,. \tag{4}$$

$D_{ij}(\vec{k}, \omega)$ is the Fourier transform in the variables $\vec{r} - \vec{r}'$ and $t - t'$ of the substrate Green's function [15,16] evaluated at $z = z' = 0$, and $S(\vec{k})$ is the static structure factor defined as

$$S(\vec{k}) = \frac{1}{N}\left\langle\sum_{a,b}\exp[-i\vec{k}\cdot(\vec{R}_a - \vec{R}_b)]\right\rangle, \tag{5}$$

where N is the total number of adsorbates and $\langle\cdots\rangle$ denotes the ensemble average for disordered structures. $\operatorname{Im}\chi(\vec{q}, \omega)$ gives the measured absorption spectrum. When the damping rate is small, we can evaluate $T(\vec{q}, \omega) = R(\vec{q}, \omega) + iI(\vec{q}, \omega)$ at $\omega = \omega_0$, which gives a shifted frequency $\bar{\omega}_0$ and damping rate γ:

$$\begin{aligned}\bar{\omega}_0^2 &= \omega_0^2\,\frac{1 + R(\vec{q},\omega_0)}{[1 + R(\vec{q},\omega_0)]^2 + I^2(\vec{q},\omega_0)}\\ &\approx \frac{\omega_0^2}{1 + R(\vec{q},\omega_0)}\,,\end{aligned} \tag{6}$$

$$\gamma = \frac{\omega_0 I(\vec{q},\omega_0)}{[1 + R(\vec{q},\omega_0)]^2 + I^2(\vec{q},\omega_0)} \approx \frac{\omega_0 I(\vec{q},\omega_0)}{[1 + R(\vec{q},\omega_0)]^2}\,. \tag{7}$$

Equations (3)–(7) provide a general theory for the low-frequency vibrational dynamics for an adsorbed overlayer of arbitrary structure described by the structure factor $S(\vec{k})$. We now explicitly evaluate these expressions to study γ for three specific structural models of the adsorbate overlayer: (a) An isolated adsorbate, (b) a periodic adlayer, and (c) a disordered adlayer. These three systems are illustrated in Fig. 1, along with schematic representations of their corresponding structure factors.

(a) Isolated adsorbate.—Here $S(\vec{k}) = 1$, and the integral on the right-hand side of Eq. (4) sums over *all* the modes of the substrate (and is independent of the adsorbate). This reduces to the theory of PR, who showed that the imaginary part of the integral is proportional to ω. For an anisotropic substrate, the integral is $\alpha + i\beta\omega$, where α and β depend on the elastic constants and must be determined numerically. [We find, using experimental values for the density and elastic moduli, that $\alpha = 3.1 \times 10^{-4}$ s^2/cm^3 and $\beta = 2.85 \times 10^{-13}$ s^3/cm^3 for the Cu(100) surface.] The decay rate in Eq. (7) thus becomes

$$\gamma = \frac{m}{\rho}\,\beta\bar{\omega}_0^4 . \tag{8}$$

which generalizes the result of PR [6] to an anisotropic elastic medium.

(b) Periodic adlayer.—For a periodic array of adsorbates, the area of the surface unit cell is $A_c = A_0/\theta$, where A_0 is the area of the substrate unit cell and θ is the coverage. Here, the structure factor consists of a series of δ functions on the grid of overlayer reciprocal lattice vectors $\{\vec{G}\}$. This shows that the adsorbate lattice can couple only to a discrete set of the possible substrate modes, and thus the integral in Eq. (4) becomes a discrete sum. For $\omega_0 < c_R|\vec{G}_1|$ ($\vec{G}_1$ is the smallest nonzero reciprocal lattice vector, and c_R is the speed of the corresponding Rayleigh wave), one finds that only the $\vec{G} = 0$ reciprocal lattice vector can contribute to the imaginary (i.e., damping) part of $T(\vec{q}, \omega_0)$, giving, for $\vec{q} = 0$,

$$\gamma = \frac{m\bar{\omega}_0^2\theta}{\rho A_0 c_{xz}(1 + m\bar{\omega}_0^2\alpha/\rho)} , \tag{9}$$

where c_{xz} is the speed of an x-polarized acoustic wave propagating in the z direction. Equation (9) generalizes our previous result [12] to an anisotropic medium. The inequality $\omega_0 < c_R|\vec{G}_1|$, which defines the regime in which Eq. (9) applies, can be recast in terms of coverage as $\theta > \theta_c$. [The exact form of θ_c depends on the overlayer lattice type, and for a square lattice is given by $\theta_c = A_0\omega_0^2/(2\pi c_R)^2$.] One should not expect that the damping rate in Eq. (9) approach the isolated case [Eq. (8)] in the limit of vanishing coverage, since additional reciprocal lattice vectors begin to contribute below θ_c.

To test the validity of Eq. (9), we apply our model to the experimental system of Ref. [10]: an ordered half monolayer of carbon monoxide on the Cu(100) surface. In this experiment, the metal substrate is pumped by a visible or ultraviolet picosecond laser pulse. Frustrated translations are excited indirectly via coupling to the heated substrate. If this process is dominated by resonant vibrational coupling, then only FT modes near $\vec{q} = 0$ are excited, since the FT band lies below the bulk phonon continuum at larger wave vectors [7]. From the published phonon dispersion relations for bulk copper [17] and the FT mode of half monolayer CO on Cu(100) [18], we estimate that the FT band overlaps the bulk continuum only in a small region around $\vec{q} = 0$ covering less than 10% of the Cu(100) surface Brillouin zone. Within this region, the FT bandwidth is only about 10% of the zone-center FT frequency. Based on this analysis, it is reasonable to compute the FT lifetime setting $\vec{q} = 0$.

Using experimental parameter values, we find $\theta_c = 1\%$ for this system. Since adsorbates only order at coverages much larger than this value, Eq. (9) will be valid for all periodic overlayers. Equation (9) predicts the lifetime ($\tau = 1/\gamma$) of the in-plane FT for this system to be 2.1 ps, where experimental values of the various parameters (e.g., $\hbar\bar{\omega}_0 = 4$ meV [18]) have been used. This theoretical lifetime is in excellent quantitative agreement with the experimental value of 2.3 ± 0.4 ps. By contrast, Eq. (8) predicts $\tau = 13.4$ ps, which is much longer than the experimental lifetime.

(c) Disordered adlayer.—For a random array of adsorbates, we write the structure factor $S(\vec{k})$ in terms of the pair correlation function $g(\vec{r})$ [14]:

$$S(\vec{k}) = 1 + \frac{\theta}{A_0}\int d^2r\,\exp(i\vec{k}\cdot\vec{r})g(\vec{r}) , \tag{10}$$

For $g(\vec{r})$, we assume an uncorrelated lattice gas: $g(\vec{r}) = A_0\sum_R \delta(\vec{r} - \vec{R})$, where $\{\vec{R}\}$ are the lattice sites of the bare surface. This is a reasonable model for low density coverage. Inserting this model for $S(\vec{k})$ into Eq. (4) gives

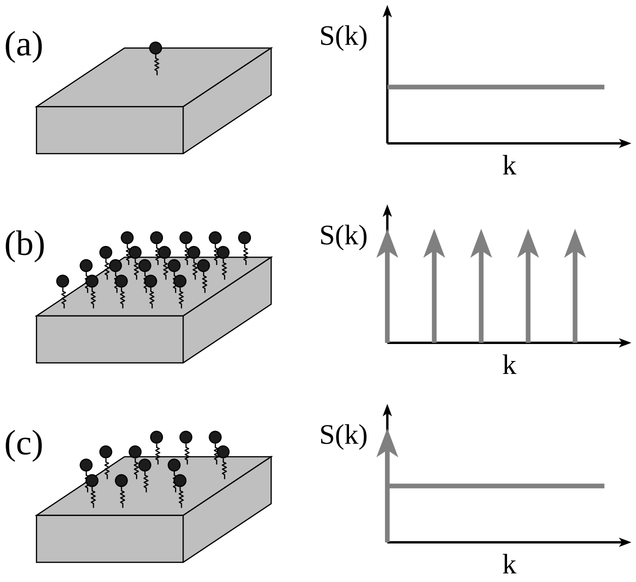

FIG. 1. Illustrations of the three adlayer structural models to which we have applied our theory of low-frequency vibrational damping. Included with each illustration is a schematic representation of the corresponding static structure factor $S(\vec{k})$: (a) Isolated adsorbate; (b) periodic overlayer; (c) disordered overlayer.

a simple damping-rate formula:

$$\gamma = \gamma_{\mathrm{isolated}} + \gamma_{\mathrm{ordered}} = \frac{m}{\rho}\,\beta\bar{\omega}_0^4 + \frac{m\bar{\omega}_0^2\theta}{\rho A_0 c_{zx}(1 + m\bar{\omega}_0^2\alpha/\rho)}\,. \tag{11}$$

The first term in Eq. (11) is the damping rate for an isolated adsorbate, and gives the full damping rate in the limit $\theta \to 0$. The second term is proportional to the coverage, and depends on the lateral phase coherence of the adsorbate motion. This term has the same algebraic form as the damping-rate law of Eq. (9) for an ordered overlayer.

We can test the validity of Eq. (11) for describing a random distribution of adsorbates by revisiting the system of CO on Cu(100). A recent He-atom scattering experiment by Graham *et al.* [11] on a $\theta = 3\%$ disordered overlayer of CO on Cu(100) measured an 8 ± 1 ps lifetime for the in-plane FT mode. Our model in Eq. (11) predicts the FT lifetime for this system to be 9.7 ps, in very good agreement with the experiment, especially considering the rather simple model of disorder.

It is interesting to note that FT vibrations in an *ordered* overlayer at the same coverage would have a lifetime of 34.6 ps—about 3.5 times longer than in a disordered layer, even though the damping mechanism is the same in both cases. This dramatically illustrates the strong influence of adlayer structural order on the vibrational dynamics. The reason for this behavior is that the symmetry of an ordered overlayer provides additional selection rules restricting the phase space of substrate modes available for coupling. This disparity between ordered and disordered overlayers is more prominent for dilute overlayers than dense overlayers.

The above results for CO on Cu(100) at two very different coverages clearly imply that FT vibrational damping for this system is dominated by resonant coupling to substrate phonons. However, because metals also have low-lying *electronic* excitations, it is important to consider this decay channel for FT vibrations, as well. Several previous experimental and theoretical investigations concluded that FT vibrations are (comparatively) weakly coupled to substrate electronic excitations for CO on Cu(100) [19–21], with estimated lifetimes due to this mechanism in the range 40–110 ps. Germer *et al.*, on the other hand, find that their pump-probe measurements on the half monolayer system are consistent with a phenomenological two-heat-bath diffusion model in which the FT lifetime due to electronic coupling is about 5 ps [10]. However, this value is obtained rather indirectly.

We have presented a unified theory for the vibrational relaxation dynamics due to indirect coupling of adsorbate motions through their coupling to an anisotropic elastic medium. We find that the theory for an isolated adsorbate does not correctly describe the vibrational dynamics and that the correlated collective motion in the adlayer must be included to properly describe the vibrational relaxation. Including these effects, the predicted vibrational lifetimes are in good quantitative agreement with experiment regardless of the nature of the overlayer structure, thereby demonstrating the validity of the theory and showing that elastic coupling inevitably dominates the low-frequency dynamics of an adlayer for situations of experimental interest.

Financial support for this research was provided by the Laboratory for Research on the Structure of Matter, by the National Science Foundation under Grants No. DMR 97-02514 and No. DMR 93-13047, by the Petroleum Research Fund of the American Chemical Society under Grant No. 32007-G5, and by the U.S. Department of Energy under Grant No. 91ER45118. In addition, A. M. R. acknowledges the Alfred P. Sloan Foundation.

---

*Present address: Department of Physics and Astronomy, University of Georgia, Athens, GA 30602-2451.

[1] B. N. J. Persson, Chem. Phys. Lett. **149**, 278 (1988).
[2] F. Hofmann and J. P. Toennies, Chem. Rev. **96**, 1307 (1996).
[3] S. Holloway, Surf. Sci. **299/300**, 656 (1994).
[4] C. T. Rettner, D. J. Auerbach, J. C. Tully, and A. W. Kleyn, J. Phys. Chem. **100**, 13 021 (1996).
[5] G. Wahnström, Surf. Sci. **159**, 311 (1985).
[6] B. N. J. Persson and R. Ryberg, Phys. Rev. B **32**, 3586 (1985).
[7] B. Hall, D. L. Mills, and J. E. Black, Phys. Rev. B **32**, 4932 (1985).
[8] J. A. Leiro and M. Persson, Surf. Sci. **207**, 473 (1989).
[9] L. W. Bruch and F. Y. Hansen, Phys. Rev. B **55**, 1782 (1997).
[10] T. A. Germer, J. C. Stephenson, E. J. Heilweil, and R. R. Cavanagh, Phys. Rev. Lett. **71**, 3327 (1993); J. Chem. Phys. **101**, 1704 (1994).
[11] A. Graham, F. Hofmann, and J. P. Toennies, J. Chem. Phys. **104**, 5311 (1996).
[12] S. P. Lewis, M. V. Pykhtin, E. J. Mele, and A. M. Rappe, J. Chem. Phys. **108**, 1157 (1998).
[13] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon, New York, 1986), 3rd ed.
[14] For a discussion of linear response functions and structure factors, see, for example, P. M. Chaikin and T. C. Lubensky, *Principles of Condensed Matter Physics* (Cambridge University Press, Cambridge, England, 1995).
[15] A. A. Maradudin and D. L. Mills, Ann. Phys. (N.Y.) **100**, 262 (1976).
[16] M. G. Cottam and A. A. Maradudin, *Surface Excitations*, edited by V. M. Agranovich and R. Loudon (Elsevier, New York, 1984).
[17] R. M. Nicklow, G. Gilat, H. G. Smith, L. J. Raubenheimer, and M. K. Wilkinson, Phys. Rev. **164**, 922 (1967).
[18] J. Ellis, J. P. Toennies, and G. Witte, J. Chem. Phys. **102**, 5059 (1995).
[19] B. N. J. Persson, Phys. Rev. B **44**, 3277 (1991).
[20] M. Head-Gordon and J. C. Tully, Phys. Rev. B **46**, 1853 (1992).
[21] A. I. Volokitin and B. N. J. Persson, J. Exp. Theor. Phys. **81**, 545 (1995).