

Memory-Induced Extra Resonances of Adsorbates

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The optical absorption profile of an atom-surface vibrational bond is studied. From Markovian relaxation theory it follows that the line shape is a Lorentzian around the adsorbate resonance frequency ω_0 . Dispersion relations for crystals have a fairly small cutoff frequency ω_D , which prohibits the use of such a simple theory. We calculated the spectral profile with finite-memory-time reservoir theory, and we found that the modified Lorentzian vanishes above ω_D . Also a new spectral line at $\omega_0 + \omega_D$ is predicted, which disappears in the Markovian limit. The physical origin of the new line is explained.

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Adsorbed atoms on the surface of a crystal can absorb photons from an incident infrared laser beam. Coupling between the van der Waals bond and the radiation is brought about by the motion-induced dipole moment μ (the atom itself is assumed to be neutral for ir light), and the atom-crystal interaction is governed by the single-phonon coupling Hamiltonian¹

$$H_i = -(\mathbf{u} \cdot \mathbf{e}_z) dV/dz, \quad (1)$$

in terms of the derivative of the binding potential well $V(z)$. Here z denotes the normal direction to the surface (we neglect lateral motion) and \mathbf{u} is the phonon-field amplitude operator,² evaluated at the position of the surface atom which is closest to the adsorbate. Relaxation of the atomic bond due to phonon exchange with the crystal is most conveniently described with reservoir theory, where the crystal is regarded as a thermal bath.³

$$I(\omega) = \omega_0(n_1 - n_2) \text{Re}\{i[\omega - \omega_0 + ia[g(\hat{\omega}_0) + g^*(-\hat{\omega}_0)]]\}. \quad (2)$$

This profile is a Lorentzian with its peak value at $\omega = \omega_0 + a \text{Im}[g(\hat{\omega}_0) + g^*(-\hat{\omega}_0)]$, and a half width at half-maximum equal to $a \text{Re}[g(\hat{\omega}_0) + g^*(-\hat{\omega}_0)]$. The notation is $\hat{\omega} = \omega/\omega_D$, ω_0 = unperturbed adsorbate resonance, and n_i = population of the i th level ($n_1 > n_2$). The temperature dependence is incorporated in $g(z)$, and the phonon-coupling strength is measured by

$$a = (3\pi/2\hbar M\omega_D^2) \langle 2 | dV/dz | 1 \rangle^2. \quad (4)$$

Most crucial for the derivation of the line profile (3) is the conjecture that the phonon-amplitude correlation function $\langle [\mathbf{u}(\tau) \cdot \mathbf{e}_z][\mathbf{u} \cdot \mathbf{e}_z] \rangle$ decays to zero very fast for $\tau > 0$, which would justify the Markov approximation. It is an essential feature of a crystal, however, that its dispersion relation has a finite cutoff frequency ω_D , which sets the lower limit of $1/\omega_D$ on the decay time. In fact, the structure of the amplitude operator \mathbf{u} is such that the correlation function decays only as $1/\tau$ for $\tau \rightarrow \infty$, rather than exponentially, which makes a Markov approximation (zero memory time) at least doubtful.

Then an equation of motion for the reduced adsorbate density operator can be derived, in which the properties of the heat bath only enter parametrically, and can be expressed in terms of the Fourier-Laplace transform of the reservoir correlation function

$$g(\omega/\omega_D) = \frac{2M\omega_D^2}{3\pi\hbar} \int_0^\infty d\tau e^{i\omega\tau} \langle [\mathbf{u}(\tau) \cdot \mathbf{e}_z][\mathbf{u} \cdot \mathbf{e}_z] \rangle. \quad (2)$$

Equation (2) defines the dimensionless function $g(z)$ in terms of the mass M of a bulk atom and the Debye frequency ω_D . Then it can be shown that $g(z)$ depends only on the dimensionless temperature $\gamma = \hbar\omega_D/k_B T$, with k_B Boltzmann's constant. An explicit expression for $g(z)$ can be found elsewhere.⁴

In the most simple theory of relaxation⁵ one adopts the Markov and secular approximations, which yields for the low-intensity absorption line shape as a function of the laser frequency ω

$$(3)$$

In order to investigate this problem quantitatively, we have developed a finite-memory-time relaxation theory,⁶ with no restriction on the time scales. Subsequently, we have applied this theory to the evaluation of the absorption line shape, with the formal result⁷

$$I(\omega) = \omega\mu_{21}^{-2} \text{Re Tr} L_X \frac{i}{\omega - L_a + i\Gamma(\omega)} [L_Y - iY(\omega)] \bar{\rho}. \quad (5)$$

This expression holds for any configuration of adsorbate levels and includes multiphonon transitions as well. In Eq. (5), $\bar{\rho}$ equals the adsorbate density operator in thermal equilibrium, and the Liouvillians L_X and L_Y are defined by $L_X\sigma = \mu\sigma$, $L_Y\sigma = [\mu, \sigma]$ in terms of their action of an arbitrary adsorbate density operator σ . The relaxation operator $\Gamma(\omega)$ is frequency dependent, which reflects the memory in the time regression of two-time quantum correlation functions. In the time domain this would be a memory kernel,⁸ and in the Markov approxi-

mation $\Gamma(\omega)$ assumes an ω -independent value. Furthermore, a Liouville operator $Y(\omega)$ appears, which accounts for the fact that the density operator of the entire system does not factorize as $\rho_{\text{adsorbate}} \times \rho_{\text{crystal}}$ in thermal equilibrium if the memory time is finite. We call this term the initial correlation contribution to the line shape, in contrast to the term L_Y , which is referred to as the regression part. In a zero-memory-time approximation the operator $Y(\omega)$ vanishes identically, since then a factorization of the density operator can be justified. Both $\Gamma(\omega)$ and $Y(\omega)$ are complicated operators. Elsewhere⁷ we have studied the modifications of the Lorentzian profile (3) due to the memory effects, and we have derived an explicit expression for $I(\omega)$, pertaining to the situation where ω_0 is smaller than ω_D .

In this Letter we report a peculiar feature of the ab-

sorption profile (5) which arises as a consequence of the memory in the interaction. Since Eq. (5) applies to any configuration, we can consider the case where the vibrational resonance ω_0 is larger than ω_D . Then we scan the laser over this resonance, implying that also $\omega > \omega_D$. For frequencies larger than ω_D a Markov approximation can never be justified, and it is imperative to include the memory in the time evolution. At this stage we neglect the small contribution of multiphonon processes, in order to emphasize the significance of the predicted effects. Then it can be shown⁹ that the regression part ($\sim L_Y$), which would lead to the Lorentzian in the Markov approximation, is identically zero for $\omega > \omega_D$. Hence, any absorption is due to the initial-correlation term $Y(\omega)$, and therefore a mere consequence of the finiteness of the memory time. We obtain for the absorption spectrum

$$I(\omega) = a \left[\frac{\mu_{22} - \mu_{11}}{\mu_{21}} \right]^2 \text{Re} \frac{g(\hat{\omega} - \hat{\omega}_0)}{\omega + ia[g(\hat{\omega} - \hat{\omega}_0) + g^*(\hat{\omega}_0 - \hat{\omega})]}, \quad (6)$$

for $\omega > \omega_D$. Here we used the fact that the population of the upper state must be zero for $\omega_0 > \omega_D$ (so that $n_1 = 1$), and the general property $\text{Reg}(z) = 0$ for $|z| > 1$ of the reservoir correlation function. A characteristic example of $I(\omega)$ is plotted in Fig. 1.

We observe that $I(\omega)$ has a spectral line for $\omega > \omega_D$. Recalling that our result (6) only includes single-phonon transitions,¹⁰ this might appear to be a contradiction.

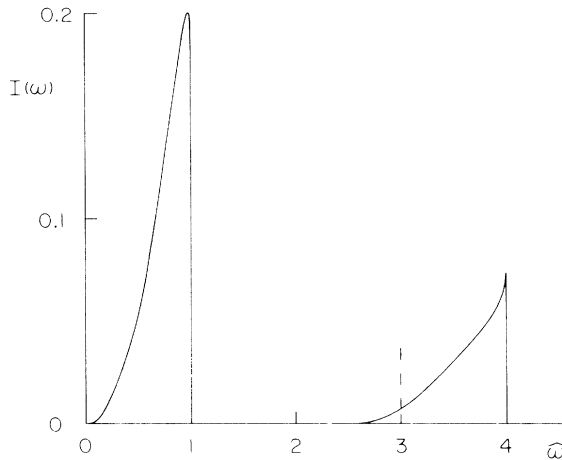


FIG. 1. Absorption profile $I(\omega)$ from Eq. (5) as a function of $\hat{\omega} = \omega/\omega_D$, and for $\omega_0 = 3\omega_D$ (dashed line), $a = 0.4 \times \omega_D$, $\gamma = 10$ (low temperature), and $(\mu_{22} - \mu_{11})^2 = 0.5 \times \mu_{21}^2$. The left peak at $\omega < \omega_D$ is the far red wing of the regression part of the line, which is brought about by transitions with $\omega = \omega_{\text{phonon}}$ [diagram (a) of Fig. 2], and governed by the transition dipole moment μ_{21} . The peak on the right-hand side is the memory-time-induced extra resonance, with $|\omega - \omega_0| = \omega_{\text{phonon}}$. Processes represented by the diagrams (b) and (c) of Fig. 2 give rise to this line, and its line shape is given by Eq. (6). In a zero memory-time approximation this line vanishes.

We see, however, that the line is not brought about by the transition dipole moment μ_{21} , as usual, but by the permanent dipole moments μ_{22} and μ_{11} of the two levels. From the diagrams of Fig. 2 we then anticipate that it could be possible to absorb a photon with $\omega > \omega_D$, and in such a way that energy conservation can be met with a single-phonon process. The mismatch between ω and ω_0 is simply the phonon frequency. Although level $|2\rangle$ cannot be populated because of $\omega_0 > \omega_D$, it can nevertheless be reached via a photon-phonon process. This mechanism gives rise to the line at $\omega > \omega_D$.

Figure 2 suggests that the processes responsible for

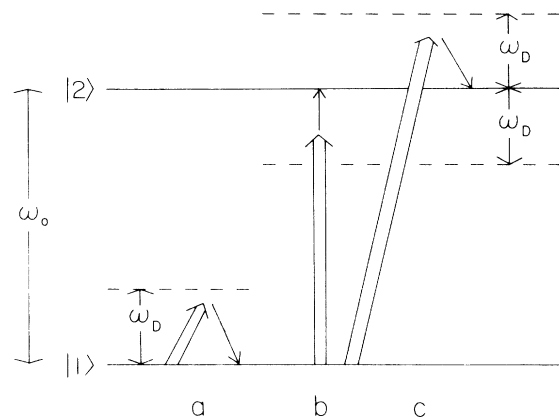


FIG. 2. Energy-conserving diagrams which contribute to the absorption spectrum $I(\omega)$. Double arrows indicate a photon and single arrows a phonon. Diagram (a) and its reverse are responsible for the profile at $\omega < \omega_D$, whereas diagrams (b) and (c) represent processes which yield the line at $\omega > \omega_D$. Since level $|2\rangle$ is not populated, the reverse processes (stimulated emission) of diagrams (b) and (c) do not occur.

this line [(b) and (c)] can only occur for $|\omega - \omega_0| < \omega_D$, since otherwise the the phonon frequency would become larger than ω_D . This can be shown explicitly from Eq. (6). If we work out the real part and use $\text{Reg}(z) = 0$ for $|z| > 1$, we find

$$I(\omega) = 0 \text{ for } |\omega - \omega_0| > \omega_D. \quad (7)$$

Furthermore, from Eq. (6) it follows that the line must be situated at the zero of the real part of the denominator, e.g., at the solution of $\bar{\omega} \approx a \text{Im}[g(\bar{\omega} - \hat{\omega}_0) + g^*(\hat{\omega}_0 - \bar{\omega})]$. We know that $g(z)$ attains its extreme at $z = \pm 1$ [for a Debye model we have $g(\pm 1) = \pm \infty$] and that $\omega > \omega_D \gg a$, which gives for the position of the line $\bar{\omega} \approx \omega_0 + \omega_D$. Together with Eq. (7), this explains the sharp edge of the line at the blue side. In conclusion, the finite memory time in the atom-crystal interaction prohibits the factorization of the density operator in thermal equilibrium, which in turn gives rise to a new spectral line at $\omega_0 + \omega_D$, provided that the system has a permanent dipole moment. Its profile is given by Eq. (6).

As a last remark we mention that the detailed shape of the line at $\omega_0 + \omega_D$ depends crucially on the adopted model for the phonon dispersion relation. The sharp peak at $\omega = \omega_0 + \omega_D$ is a consequence of the cutoff of the dispersion relation at ω_D . In a more realistic model, where the detailed structure of the first Brillouin zone for a specific crystal is taken into consideration, this peak will smooth out. Expression (6) for the line shape remains valid, but the function $g(z)$ will behave more realistically. The infinities in $z = \pm 1$ will turn into finite van Hove singularities.¹¹

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¹⁰A low-intensity laser can only cause transitions between two states $|n\rangle$ and $|m\rangle$ for which $\langle n|H_i|m\rangle \neq 0$, according to the Fermi "golden rule." The Hamiltonian H_i from Eq. (1) connects only states which differ by one phonon. See, for instance, S. W. Lovesey, *Condensed Matter Physics, Dynamic Correlations* (Benjamin, London, 1980), p. 3.

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