Non-Markovian Line Shapes of Physisorbed Atoms on a Crystal

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# Non-Markovian Line Shapes of Physisorbed Atoms on a Crystal

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NON-MARKOVIAN LINE SHAPES OF PHYSISORBED ATOMS ON A CRYSTAL

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ABSTRACT

An atom adsorbed on the surface of a harmonic crystal is considered. The binding potential well supports many vibrational bound-states, and the coupling of the motion of the atom with the substrate gives rise to phonon-exchange reactions, which subsequently amount to atomic transitions between the bound states. This process of thermal relaxation of the adatom density operator is commonly described with reservoir theory, in which the crystal is regarded as a thermal bath with an extremely short correlation time. The latter property then justifies the neglect of any memory in the interaction, which is usually referred to as the Markov approximation. It is shown, however, that the reservoir correlation time is not necessarily small in comparison with the inverse (relaxation) frequencies of the system, which implies a breakdown of this approach. The equation of motion for the adatom density-operator is then solved without the Markov approximation, and the result is used for the evaluation of the spectrum and line profile for absorption of infrared radiation. Essentially different results are obtained than with the approximate theory, but it turns out that the solutions can be expressed in terms of the same parameters.

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I. INTRODUCTION

A very sensitive method for studying atomic or molecular systems and the interaction with their environment (for instance collisions) is by observation of the absorption line shapes. A low-intensity laser with power $I_L$ (energy per unit of time through a unit area, perpendicular to the direction of propagation), frequency $\omega_L$, and polarization $\varepsilon_L$ is scanned over the resonances of the molecule. Dipole coupling between the system and the laser field then amounts to absorption of radiation at a rate (energy per unit of time)$^1$

$$I(\omega_L) = \frac{I_L \omega_L}{\varepsilon_0 \hbar c} \text{Re} \int_0^{\infty} dt \ e^{-i \omega_L t} \text{Tr}[\hat{\mu}(t) \cdot \varepsilon_L^* \cdot \varepsilon_L] ,$$ (1.1)

with $\hat{\mu}(t)$ the dipole-moment operator in the Heisenberg picture. The thermal-equilibrium density operator $\hat{\rho}$ represents the state of the entire system of the molecule, environment and interaction, but not the laser. The advantage of weak-field absorption is that the incident field does not disturb the system, but only probes it. Then the absorption profile can be obtained from the Golden Rule which leads to Eq. (1.1), where reference to the laser field in the dynamical variables $\hat{\rho}$ and $\hat{\mu}(t)$ has disappeared.

We consider adsorbed atoms on the surface of a crystal. Electromagnetic (van der Waals) interaction between an adsorbate and the atoms of the substrate is accounted for by a potential well, which supports many bound states. The motion of the atom will be restricted mainly to the direction perpendicular to the surface, which will be denoted by the unit vector $\varepsilon_z$. Transition frequencies between vibrational states are in the infrared, and the motion of the atom induces an optical activity in this region of the spectrum. This implies that the bond has non-vanishing dipole-moment matrix elements between the various states, whereas both the atom and the crystal are assumed to be transparent for infrared light. Since we neglect lateral motion, the dipole-moment operator
takes the form \( \mu = \mu e_z \), with \( \mu \) a scalar operator in the Hilbert space, which is spanned by the adatom states. Then we can write

\[
\mu(t) = e_z \exp(iLt)\mu ,
\]  
(1.2)

for the time evolution of \( \mu \), where \( L \) is the Liouvillian, which is related to the Hamiltonian according to

\[
L\rho = H^{-1}[H,\rho] ,
\]  
(1.3)

for an arbitrary Hilbert-space operator \( \rho \). Here, \( H \) represents the entire system of atom, crystal and interaction. Subsequently we use the identity

\[
\text{Tr}\rho[\mu(t),\mu] = \text{Tr}\mu\exp(-iLt)[\mu,\rho] ,
\]  
(1.4)

which allows to cast the absorption profile in the form

\[
I(\omega_L) = I\omega_L \frac{|e_z \cdot \xi_L|^2}{\varepsilon_0 \hbar c} \text{Re} \text{ Tr} \mu \int_0^\infty \text{d}\tau e^{i(\omega_L-L)\tau} [\mu,\rho] .
\]  
(1.5)

This representation clearly shows that the peaks of the spectrum are located at the resonances of the complete system, which equal the eigenvalues of \( L \) rather than the adatom transition frequencies. Moreover, the frequency dependence of \( I(\omega_L) \) reveals the details of the dynamics. From Eq. (1.5) it follows that the shape of a spectral line is germane to the time evolution of the density operator, which explains the significance of the study of absorption spectra.

II. EQUATION OF MOTION

The atom with mass \( m \) is bounded to the crystal by a potential \( V(z) \), where \( z \) is the atom-surface normal distance, and hence the adband Hamiltonian takes the explicit form
\[ H_{a} = \frac{-\hbar^2}{2m} \frac{d^2}{dz^2} + V(z) \quad (2.1) \]

We shall not specify \( V(z) \) any further, but only remark that the common choice is a Morse potential.\(^{2-7}\) A general representation for the Hamiltonian of a harmonic crystal reads\(^{8}\)

\[ H_{p} = \sum_{k_s} \hbar \omega_{s}(k)a_{k_s}^\dagger a_{k_s} \quad (2.2) \]

in terms of the phonon creation (\( a_{k_s}^\dagger \)) and annihilation (\( a_{k_s} \)) operators, which obey boson commutation relations. The summation runs over the modes \( k_s \), with \( k \) the wave vector and \( s \) the polarization, and \( \omega_{s}(k) \) is the dispersion relation. Coupling between the adatom bond and the phonon field is assumed to be brought about by single-phonon transitions, which is accurate, as long as the level separations of \( H_{a} \) do not exceed the cut-off frequency of the dispersion relation. Then the complete Hamiltonian can be written as

\[ H = H_{a} + H_{p} - RS \quad (2.3) \]

with the atomic part of the coupling given by\(^{3}\)

\[ S = \frac{dV}{dz} \quad (2.4) \]

in terms of the prescribed potential \( V(z) \). The operator \( R \) equals the \( z \)-component of the displacement field for the crystal atoms evaluated in the vicinity of the adsorbate. Explicitly this becomes

\[ R = \sum_{k_s} \sqrt{\frac{\hbar}{2M\omega_{s}(k)}} (a_{k_s}^\dagger + a_{-k_s})(e_{k_{s}z}^\dagger e_{z}) \quad (2.5) \]

which involves the mass \( M \) of a crystal atom, the volumes \( V \) and \( v \) of the crystal
and a unit cell, respectively, and the unit polarization vectors $e_{ks}$.

The equation of motion for the density operator $\rho(t)$ is

$$i\hbar \frac{d}{dt} \rho(t) = [H, \rho(t)], \quad (2.6)$$

which has the solution

$$\rho(t) = \exp(-iLt)\rho(0) \quad (2.7)$$

in terms of a given initial state $\rho(0)$. Comparison with expression (1.5) then shows that the time evolution of $\rho(t)$ is governed by the same exponential which determines the spectral distribution of the absorption. Furthermore, Eq. (1.5) contains the thermal-equilibrium state $\overline{\rho}$, which equals the long-time solution

$$\overline{\rho} = \lim_{t \to \infty} \rho(t) \quad (2.8)$$

III. RESERVOIR INTEGRAL

It will be obvious that an exact evaluation of $\exp(-iLt)$ is not feasible. Fortunately, this is not necessary. It will turn out to be sufficient for the calculation of observable quantities, like $I(\omega_L)$, to obtain an equation for the reduced adatom density-operator, defined by

$$\rho_o(t) = \text{Tr}_p \rho(t), \quad (3.1)$$

where the trace runs over the states of the phonon field. The large crystal with its many, closely-spaced, degrees of freedom (phonon modes) merely acts as a thermal bath, and its thermal-equilibrium density operator $\overline{\rho}_p$ is not affected by the presence of the single atom.

Now it is a standard procedure in reservoir theory to derive an integral of the equation of motion (2.6), which only involves the adatom density operator $\rho_o(t)$. In particular, the product-form RS for the interaction allows a concise
formulation, and the result is \( \rho_o(t) = L_a \rho_o(t) - \frac{i}{2\pi} L_S \int_0^t \exp(-iL_a\tau)L_c(\tau)\rho_o(t-\tau) \), \( (3.2) \)

where we have introduced the Liouvillians

\[
L_a \rho = \mathbb{H}^{-1}[H_a,\rho] \quad (3.3)
\]

\[
L_S \rho = [S,\rho] \quad (3.4)
\]

pertaining to the free evolution of the adatom \( L_a \) and the atomic part of the interaction \( S \). The Liouvillian \( L_c(\tau) \) is defined as

\[
L_c(\tau)\rho = G(\tau)S\rho - G(\tau)^*\rho S \quad (3.5)
\]

which contains the reservoir correlation function

\[
G(\tau) = 2\pi \mathbb{H}^{-2}_p \text{Tr}_p \rho \rho \exp(iL_p\tau)R \quad (3.6)
\]

with \( L_p \rho = \mathbb{H}^{-1}_p[H_p,\rho] \). Properties of the substrate only enter the equation \( (3.2) \) through the function \( G(\tau) \), which equals the correlation function of the displacement of the surface, due to thermal motion of the crystal atoms. In Section VIII we shall evaluate \( G(\tau) \) explicitly for a simple model.

In deriving Eq. \( (3.2) \) from Eq. \( (2.6) \) we have taken for the initial state the factorized form

\[
\rho(0) = \rho_o(0)\rho_p \quad (3.7)
\]

which can be done arbitrarily, since \( \rho(0) \) is not prescribed by the equation of motion. The only approximation which had to be made to arrive at Eq. \( (3.2) \) was a factorization \( \rho(t-\tau) = \rho_o(t-\tau)\rho_p \) in the integrand. Of course, this is not exact, but it is much better than the usual Markov approximation (Section VI), which can
be argued as follows. The first term on the right-hand side of Eq. (3.2), 
$L_a \rho_o(t)$, would account for the evolution of the adatom if there were not crystal 
at all ($RS \equiv 0$), and the second term represents the coupling to the heat bath. 
This interaction gives rise to phonon transition between levels $|k\rangle$ and $|t\rangle$, 
which can be regarded as stimulated absorptions of phonons from the crystal 
(excitation of the atomic bond), and emissions of phonons into the crystal (decay 
of the adsorbate). A transition $|k\rangle \rightarrow |t\rangle$ then occurs at a rate $n_k a_{kt}$, with $n_k$ 
the population of level $|k\rangle$ and $a_{kt}$ the rate constant for this particular 
transition. If we look at the relaxation integral in Eq. (3.2) as an operator 
acting on $\rho_o(t-\tau)$, then $a_{kt}$ equals a matrix element of this operator. The 
factorization $\rho(t-\tau) = \rho_o(t-\tau)\tilde{\rho}_p$ in the integrand then introduces a small error 
in $a_{kt}$, but the correct time dependence is retained. Because it is the time 
evolution of the density operator which determines the spectral distribution of 
the absorption, rather than the density operator itself, only a small error is 
made by the factorization.

IV. SOLUTION

In this section we solve Eq. (3.2). To this end, we first introduce the 
Fourier-Laplace transform of $G(\tau)$ by

$$\tilde{G}(\omega) = \pi^{-1} \int_0^\infty dt \exp(i\omega t)G(\tau) \quad (4.1)$$

which has the inverse integral

$$G(\tau) = \frac{1}{i} \int_{-\infty}^{\tau} d\omega \exp(-i\omega t)\tilde{G}(\omega) \quad , \quad \tau > 0 \quad (4.2)$$

and in the same way we define the Fourier-Laplace transform of any other time-
dependent quantity. Substitution of the inverse integral of $L_c(\tau)$ into the 
equation of motion (3.2) then yields
\[
\frac{d}{dt} \rho_o(t) = L_a \rho_o(t) - \frac{i}{4\pi} L_s \int_0^t d\tau \int_{-\infty}^{\infty} d\omega \exp(-i(\omega+L_a)\tau) L_c(\omega) \rho_o(t-\tau) .
\] (4.3)

With Eq. (3.5) we can express \( L_c(\omega) \) in \( C(\omega) \) as
\[
L_c(\omega) \rho = C(\omega) S \rho - C(-\omega)^* S \rho .
\] (4.4)

The Fourier-Laplace transform of Eq. (4.3) is now easily found to be
\[
\tilde{\rho}_o(\omega) = \frac{1/\pi}{w-L_a+i\Gamma(\omega)} \rho_o(0)
\] (4.5)

in terms of an operator inversion. Here, the frequency-dependent relaxation operator \( \Gamma(\omega) \) is defined as
\[
\Gamma(\omega) = \frac{1}{4\pi} L_s \int_{-\infty}^{\infty} d\omega' \frac{1}{w-\omega' - L_a} L_c(\omega') .
\] (4.6)

Equation (4.5) relates the (transformed) adatom density operator for \( t \geq 0 \) to the given initial value \( \rho_o(0) \), which is the desired solution.

Although Eq. (4.5) is an explicit solution, the combination of the operator inversion, with the definition of \( \Gamma(\omega) \) as an integral over a product of an inverse operator with \( L_c(\omega) \), might seem awkward. We shall show, however, that the evaluation of the absorption profile has exactly the same degree of complexity as in the usual Markov approximation.

V. EVALUATION OF \( \Gamma(\omega) \)

A matrix representation of \( \Gamma(\omega) \) is easily derived. First we rewrite Eq. (4.6) in the form
\[
\Gamma(\omega) = \frac{1}{4\pi} L_s \int_{-\infty}^{\infty} d\omega' \int_0^t d\tau \ e^{i(\omega-\omega'-L_a)\tau} L_c(\omega') .
\] (5.1)

Then we insert the inverse integral for \( L_c(\omega') \) and perform the \( \omega' \) integration, which yields the alternative expression for \( \Gamma(\omega) \)
\[ \Gamma(\omega) = \frac{1}{2\pi} \mathcal{L}_S \int_{0}^{\infty} dt \, e^{-i\omega \mathcal{L}_S} \mathcal{L}_C(t). \]  

(5.2)

Atomic-bond states are by definition the eigenstates of \( \mathcal{H}_a \) from Eq. (2.1). The eigenvalue equation reads

\[ \mathcal{H}_a |k\rangle = \hbar \omega_k |k\rangle, \]

which defines the states \( |k\rangle \) and the eigenvalues \( \hbar \omega_k \). In turn, \( \mathcal{H}_a \) can be represented with respect to its own eigenstates as

\[ \mathcal{H}_a = \sum_k \hbar \omega_k P_k, \]

(5.4)

where \( P_k = |k\rangle \langle k| \) is the projector onto \( |k\rangle \). Then we can express \( \mathcal{L}_a \), Eq. (3.3), in terms of projectors and calculate the exponential \( \exp(-i\mathcal{L}_a \tau) \). Finally we obtain

\[ \exp(-i\mathcal{L}_a \tau) \rho = \sum_{kl} \exp(-i\Delta_{kl} \tau) P_k \rho P_l \]

(5.5)

in terms of the transition frequencies

\[ \Delta_{kl} = \omega_k - \omega_l. \]

(5.6)

Next we substitute the definition (3.5) of \( \mathcal{L}_C(\tau) \) into Eq. (5.2) and apply the expansion (5.5), which gives

\[ \Gamma(\omega) \rho = \frac{i}{\hbar} \sum_{kl} \mathcal{L}_S (P_k \rho S P_l \mathcal{G}(\Delta_{kl} + \omega) - P_k \rho S P_l \mathcal{G}(\Delta_{kl} - \omega)^*) \].

(5.7)

This result shows that \( \Gamma(\omega) \) can be expressed entirely in the adatom operator \( S \) and the Fourier-Laplace transform of the reservoir correlation function \( G(\tau) \). In order to find the matrix representation of \( \Gamma(\omega) \), we expand \( \mathcal{L}_S \) as a commutator and then insert the closure relation.
\[ \sum_k P_k = 1 \quad (5.8) \]

in various places in Eq. (5.7). In terms of the matrix elements

\[ S_{kl} = \langle k | S | l \rangle = S_{lk}^* \quad (5.9) \]

we then find

\[ \langle a | (\Gamma(\omega)\rho) | b \rangle = \frac{1}{2} \sum_{kl} \{ S_{ak} S_{kl} \tilde{c}(\Delta_{bk} + \omega) < l | \rho | l \rangle \\
+ S_{bk}^* S_{kl}^* \tilde{c}(\Delta_{ak} - \omega)^* < a | \rho | l \rangle \}
- \frac{1}{2} \sum_{kl} \{ S_{ak} S_{kb} \tilde{c}(\Delta_{ka} + \omega)^* \\
+ S_{bk}^* S_{ka} \tilde{c}(\Delta_{kb} - \omega)^* \} < k | \rho | l \rangle \quad , \quad (5.10) \]

which relates the matrix elements of \( \Gamma(\omega)\rho \) to the matrix elements of \( \rho \). We notice that the frequency dependence of \( \Gamma(\omega) \) only enters as a shift of the resonances \( \Delta_{kl} \) in the arguments of the correlation function.

From Eq. (5.4) we immediately find

\[ \langle a | ((\omega - \Delta_L)\rho) | b \rangle = (\omega - \Delta_{ab}) \langle a | \rho | b \rangle \quad (5.11) \]

for the matrix representation of \( \omega - \Delta_L \). Combination with Eq. (5.10) then gives the expansion of \( \omega - \Delta_L + i\Gamma \), which is the matrix to be inverted for evaluation of \( \tilde{\rho}_\alpha(\omega) \) from Eq. (4.5) and, as we shall see in due course, for the evaluation of the absorption profile.

VI. MARKOV APPROXIMATION

In order to illuminate the physical significance of a frequency-dependent relaxation operator, and to establish the relation to earlier approaches, we
summarize the commonly-applied Markov approximation. The phonon field has a broad spectrum of closely-spaced modes and a relatively high cut-off frequency which equals the Debye frequency $\omega_D$ for a crystal. These features guarantee that the reservoir correlation function $G(\tau)$ decays to zero quite rapidly for increasing $\tau$, and typically on a time scale $\omega_D^{-1}$. Besides $\omega_D^{-1}$, the other two typical time scales in the problem are the inverse of a level separation $\Delta_{kl}$ and the inverse of a relaxation constant $a_{kl}$, which is a matrix element of $\Gamma(\omega)$.

One then asserts that

$$a_{kl} \ll \omega_D,$$

for all $kl$, which implies that $L_c(\tau)$ in the integrand of Eq. (3.2) only deviates from zero for $\tau \leq \omega_D^{-1}$. Since this is small in comparison with the relaxation time, by virtue of Eq. (6.1), we can replace the time evolution of $\rho_o(t-\tau)$ over this small time interval by its free evolution. Hence we approximate $\rho_o(t-\tau)$ in Eq. (3.2) as

$$\rho_o(t-\tau) = \exp(iL_{a_\tau})\rho_o(t),$$

(6.2)

and subsequently we can take $\rho_o(t)$ outside the integral. Then we assume that we are not interested in the time evolution of $\rho_o(t)$ in a time interval of the order of $\omega_D^{-1}$ after the preparation of the initial state $\rho_o(0)$, which implies that we can replace the upper integration limit $t$ by infinity. In spectral terms the restriction (6.1) means that the width of a line is much smaller than the Debye frequency, and the second approximation states that we do not consider the details of the line in the far wings, where "far" means of the order of $\omega_D$ from the line center. Combining everything then yields the equation of motion in the Markov approximation

$$\frac{d}{dt} \rho_o(t) = (L_a - i\Gamma_M)\rho_o(t),$$

(6.3)
where the relaxation operator is now defined as

$$\Gamma = \frac{1}{2\pi} L_S \int_0^\infty d\tau e^{-iL_a \tau} L_c(\tau)e^{iL_a \tau}. \quad (6.4)$$

The solution of Eq. (6.3) reads

$$\rho_o(t) = \exp(-i(L_a - i\Gamma_M)t)\rho_o(0), \quad (6.5)$$

which has the Fourier-Laplace transform

$$\tilde{\rho}_o(\omega) = \frac{i/\pi}{\omega - L_a + i\Gamma_M} \rho_o(0). \quad (6.6)$$

Comparison with our result (4.5) shows that the frequency dependence of the relaxation operator has vanished, and that the Markov approximation effectively amounts to the substitution $\Gamma(\omega) \rightarrow \Gamma_M$. Conversely, it then follows from the discussion in the first paragraph of this section that the frequency dependence of $\Gamma(\omega)$ reflects a time resolution on a time scale of the order of $\omega_D^{-1}$. This, in turn, gives the process a memory time of the order of $\omega_D^{-1}$. In the frequency domain this has the implication that now also the line wings are properly described, rather than only the line center.

VII. RELATIONS BETWEEN $\Gamma(\omega)$ AND $\Gamma_M$

From the representation (5.2) of $\Gamma(\omega)$ we directly deduce

$$\int_{-\infty}^\infty d\omega \exp(-i\omega \tau)\Gamma(\omega) = L_S \exp(-iL_a \tau)L_c(\tau), \quad \tau > 0, \quad (7.1)$$

which reveals that the Fourier-Laplace inverse of $\Gamma(\omega)$ is proportional to $L_c(\tau)$, and therefore it decays to zero as a function of $\tau$ on a time scale $\omega_D^{-1}$. Then $\Gamma(\omega)$ must have a frequency width of the order of $\omega_D$. The right-hand side of Eq. (7.1) also appears in the definition (6.4) of $\Gamma_M$, which gives rise to the relation
\[ \Gamma_M = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \int_0^\infty d\tau \Gamma(\omega) \exp(-i(\omega - L_a)\tau) \]  

(7.2)

between \( \Gamma_M \) and \( \Gamma(\omega) \). Carrying out the time integral gives alternatively

\[ \Gamma_M = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \Gamma(\omega) \frac{i}{L_a - \omega} \]  

(7.3)

showing that \( \Gamma_M \) does not equal \( \Gamma(0) \).

From Eq. (5.11) we observe that \( L_a - \omega \) is diagonal with respect to the tetradic adatom states \( |a><b| \). Therefore, expansion of the inverse of \( L_a - \omega \) in terms of projectors reads

\[ \frac{1}{L_a - \omega} \rho = \sum_{k\ell} \frac{1}{\Delta_{k\ell} - \omega} P_k \rho P_{\ell} \]  

(7.4)

in terms of its action on an arbitrary \( \rho \). With the general relation for Fourier-Laplace transforms

\[ \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \frac{1}{\omega' - \omega} \tilde{\rho}(\omega') = \tilde{\rho}(\omega) \]  

(7.5)

we can evaluate the integral in Eq. (7.3), which gives

\[ \Gamma_M \rho = \sum_{k\ell} \Gamma(\Delta_{k\ell})(P_k \rho P_{\ell}) \]  

(7.6)

This simple relation between \( \Gamma_M \) and \( \Gamma(\omega) \) displays that the relaxation operator in the Markov approximation is determined by \( \Gamma(\omega) \), where \( \omega \) only attains values which are equal to the level separations \( \Delta_{k\ell} \).

With Eq. (5.10) we can calculate the action of \( \Gamma(\Delta_{k\ell}) \) on \( P_k \rho P_{\ell} \). We replace \( \rho \) in Eq. (5.10) by \( P_k \rho P_{\ell} \) and use the orthonormality relation \( <a|b> = \delta_{ab} \) for any two states \( |a> \) and \( |b> \). Then we sum over \( k \) and \( \ell \) and recall that \( \Delta_{ab} + \Delta_{bc} = \Delta_{ac} \) for every \( a, b, c \), which gives the expansion of \( \Gamma_M \) in matrix elements. We obtain
\begin{equation}
\langle a | (\Gamma_{\rho}) | b \rangle = \frac{1}{4} \sum_{kl} \left\{ S_{ak} S_{lt} \bar{C}(\Delta_{tk}) \langle \bar{\xi} | \rho | \bar{\xi} \rangle 
+ S_{bk} S_{kt} \bar{C}(\Delta_{tk}) \langle a | \rho | b \rangle 
- \frac{1}{4} \sum_{kl} (S_{ak} S_{tb} \bar{C}(\Delta_{ka}) 
+ S_{bk} S_{ta} \bar{C}(\Delta_{tb}) \langle k | \rho | t \rangle) \right\}
\end{equation}

which is the usual result. Comparison with the expansion (5.10) of $\Gamma(\omega)$ shows that the different matrix elements of $\rho$ are connected by the same matrix elements of $S$ in both cases. The only distinction is that the correlation function $\bar{C}$ appears with a different argument in the corresponding matrix elements of $\Gamma_{H}$ and $\Gamma(\omega)$. Since knowledge of the function $\bar{C}(\omega)$ is already required in the Markov approximation, no additional information about the crystal or the atomic states is necessary in order to go beyond the Markov approximation.

VIII. RESERVOIR CORRELATION FUNCTION

Whether a Markov approximation can be justified or not depends on the behavior of the reservoir correlation function $G(\tau)$ from Eq. (3.6). In order to study this issue quantitatively, we adopt a Debye model for the distribution of phonon modes in the crystal. Then the dispersion relation reads

\begin{equation}
\omega_s(k) = c' k H(\omega_D - c' k),
\end{equation}

with $c'$ the speed of sound and $H$ the unit step function. For the thermal-equilibrium density operator of the crystal at temperature $T$ we take

\begin{equation}
\tilde{\rho}_{\rho} = \left\{ \text{Tr}_p \exp(-H_p/k_B T) \right\}^{-1} \exp(-H_p/k_B T),
\end{equation}

where $k_B$ is Boltzmann's constant. With the explicit form of the reservoir operator $R$, Eq. (2.5), we then immediately find

\begin{equation}
\end{equation}
\[ G(\tau) = \zeta \int_0^{\omega_D} dw \omega \left( (n(\omega)+1)\exp(-i\omega\tau) + n(\omega)\exp(i\omega\tau) \right), \quad (8.3) \]

where \( n(\omega) \) equals the average number of phonons in a mode with frequency \( \omega \), which is
\[ n(\omega) = \frac{\exp(\hbar\omega/k_B T) - 1}{\hbar\omega^2} . \quad (8.4) \]

The parameter \( \zeta \) is found to be
\[ \zeta = \frac{3\pi}{\hbar\omega_D^3} , \quad (8.5) \]

which depends only on the mass of a substrate atom and the cut-off frequency \( \omega_D \) of the dispersion relation.

It is advantageous to subdivide \( G(\tau) \) into a spontaneous and a stimulated part according to
\[ G(\tau) = G(\tau)_{sp} + G(\tau)_{st} , \quad (8.6) \]

with \( G(\tau)_{sp} \) by definition the correlation function for \( T = 0 \). Since \( n(\omega) = 0 \) for \( T = 0 \), we find with Eq. (8.3)
\[ G(\tau)_{sp} = \zeta^2 \omega_D^2 \frac{(1+i\omega_D\tau)\exp(-i\omega_D\tau)-1}{(\omega_D\tau)^2} , \quad (8.7) \]
\[ G(\tau)_{st} = 2\zeta \int_0^{\omega_D} dw n(\omega)\omega \cos(\omega\tau) , \quad (8.8) \]

showing that the stimulated part is real, whereas the spontaneous contribution acquires an imaginary component. In Figs. 1 and 2 the correlation functions \( G(\tau)_{sp} \) and \( G(\tau)_{st} \) are plotted, and it appears that they indeed decay to zero on a time scale of the order of \( \omega_D^{-1} \). However, the spontaneous part only disappears as \( 1/(\omega_D\tau) \), which is very slow. This implies that in integrals like in Eq.
(3.2), there is a relatively large contribution from the tail of $G(\tau)$, which makes a Markov approximation at least doubtful when the Debye frequency becomes of the order of other frequencies in the problem.

Matrix elements of the relaxation operator $\Gamma(\omega)$ are determined by the Fourier-Laplace transform of $G(\tau)$, which we split up in the same way. From Eq. (8.7) and Eq. (8.8) we derive

$$\bar{G}(\omega)_{sp} = \zeta \omega H(\omega_D - \omega) - i\pi^{-1} \zeta (\omega_D + \omega \log |1 - \omega_D/\omega|) \ , \quad (8.9)$$

$$\bar{G}(\omega)_{st} = \zeta |\omega| n(|\omega|) H(\omega_D - |\omega|)$$

$$- i\pi^{-1} \zeta \int_0^{\omega_D} d\omega' \frac{2\omega' \omega}{\omega'^2 - \omega^2} \ , \quad (8.10)$$

where $P$ stands for principal value. The real part of $\bar{G}(\omega)_{sp}$ is only nonvanishing for positive frequencies, which has the significance that the spontaneous part of the relaxation only amounts to a decay, whereas from the relation

$$\bar{G}(-\omega)_{st} = \bar{G}(\omega)_{st}^* \ , \quad (8.11)$$

it follows that the rate constants for stimulated excitation and decay of the adatom are equal. In taking the limit $\omega \to 0$ in Eqs. (8.9) and (8.10) we obtain

$$\int_0^\tau d\tau G(\tau)_{sp} = - i\zeta \omega_D \ , \quad (8.12)$$

$$\int_0^\tau d\tau G(\tau)_{st} = \pi \zeta k_B T/\hbar \ , \quad (8.13)$$

which can be regarded as a measure of the relative contribution of the spontaneous and stimulated component to the reservoir correlation function. The functions $\bar{G}(\omega)_{sp}$ and $\bar{G}(\omega)_{st}$ are drawn in Figs. 3 and 4, respectively.
IX. ABSORPTION SPECTRUM

Evaluation of the absorption spectrum \( I(\omega_L) \) from Eq. (1.5) is now straightforward. First we introduce the correlation operator

\[
D(\tau) = e^{-iLT}[\mu, \bar{\rho}] , \tag{9.1}
\]

which is an operator in the Hilbert space of the adatom and the crystal. Its reduced atomic part is denoted by \( D_0(\tau) \), and the Fourier-Laplace transform \( \tilde{D}_0(\omega) \) is defined by Eq. (4.1). Then Eq. (1.5) is equivalent to

\[
I(\omega_L) = I_L \omega_L \frac{\pi}{\epsilon_0 \hbar c} \left| \frac{\text{Tr} \cdot \epsilon_L}{\epsilon_0 \hbar c} \right|^2 \text{Re} \text{Tr} \cdot \omega_L \tilde{D}_0(\omega_L) . \tag{9.2}
\]

Next we notice that \( D(\tau) \) obeys the equation of motion

\[
i \frac{d}{dt} D(\tau) = LD(\tau) , \tag{9.3}
\]

which is identical to Eq. (2.6) for the complete density operator \( \rho(t) \). Hence we can solve Eq. (9.3) for the reduced correlation operator along exactly the same lines that led to Eq. (4.5). This gives

\[
\tilde{D}_0(\omega) = \frac{i/\pi}{\omega - L_a + i\Gamma(\omega)} D_0(0) , \tag{9.4}
\]

and the initial value equals

\[
D_0(0) = \text{Tr} \cdot [\mu, \bar{\rho}] = [\mu, \bar{\rho}_0] . \tag{9.5}
\]

in terms of the long-time solution \( \bar{\rho}_0 \) of Eq. (4.5). Combining everything then yields

\[
I(\omega_L) = I_L \omega_L \frac{\left| \frac{\text{Tr} \cdot \epsilon_L}{\epsilon_0 \hbar c} \right|^2}{\omega_L - L_a + i\Gamma(\omega_L)} \text{Re} \text{Tr} \cdot \mu \frac{1}{\omega_L - L_a + i\Gamma(\omega_L)} [\mu, \bar{\rho}_0] . \tag{9.6}
\]
as a formal expression for the absorption spectrum. With the matrix representation of $\Gamma(\omega)$ from Section V, we can perform the operator inversion and subsequently evaluate $I(\omega_L)$ for any configuration of bound states. We notice that the relaxation operator $\Gamma$ in the denominator has the incident frequency $\omega_L$ as its argument. This reflects that the $\omega_L$-dependence of the absorption will reveal the (non-Markovian) frequency dependence of the relaxation operator.

Expression (9.6) for $I(\omega_L)$ involves the steady-state solution $\rho_0$ of the adatom density operator. From the general identity

$$\lim_{t \to \infty} \rho_0(t) = \rho_0 = \lim_{\omega \to 0} -i\omega \rho_0(\omega), \quad (9.7)$$

and Eq. (4.5), it follows that $\rho_0$ is the solution of

$$(A_\omega - i\Gamma(\omega))\rho_0 = 0. \quad (9.8)$$

Therefore, it is not necessary to calculate the Fourier-Laplace inverse of Eq. (4.5) and then take the limit $t \to \infty$, which would be a cumbersome procedure. We remark that $\rho_0$ is completely determined by the relaxation operator at the single frequency $\omega = 0$, in contrast to $\rho_0(t)$ for $t < \infty$, which involves $\Gamma(\omega)$ at all frequencies $\omega$.

X. **LINE SHAPE**

An adsorbate potential $V(z)$ will in general have many bound states (- 25), and every transition frequency $\Delta_{k\ell}$ gives rise to a spectral line around $\omega_L = \Delta_{k\ell}$. In order to disentangle the contributions from the various resonances to the absorption spectrum $I(\omega_L)$, we now consider the situation of two levels $|2\rangle$ and $|1\rangle$ which are separated by $\omega_2 - \omega_1 = \omega_0 > 0$. The resulting profile $I(\omega_L)$ is then called a spectral line.
Diagonal matrix elements of the derivative of any potential vanish identically if the wave functions are eigenfunctions of a Hamiltonian of the form (2.1). This implies $S_{11} = S_{22} = 0$, and it follows from Eq. (5.10) that the relaxation operator $\Gamma(\omega)$ does not couple between populations and coherences. Since for two levels the phase of a wave function can have no significance, we can take the matrix elements $\mu_{12}$ and $S_{12}$ to be real. Then Eq. (9.6) can be rewritten as

$$I(\omega_L) = I_L \hbar \omega_L B(\bar{n}_1 - \bar{n}_2) \frac{1}{\pi} \Re \sum_{k\ell} \langle k | \{ \frac{1}{\omega_L - \omega_0 + i\Gamma(\omega_L)} (|2><1| - |1><2|) \} | \ell \rangle ,$$

(10.1)

where $\bar{n}_k = \langle k | \bar{\rho}_0 | k \rangle$ is the steady-state population of level $|k\rangle$, and $B$ is the Einstein coefficient for stimulated transition, defined as

$$B = \pi (\hbar c)^2 \frac{1}{\pi} |\mu_{12} - \epsilon_L|^2.$$

(10.2)

The summation in Eq. (10.1) runs over $(k, \ell) = (1, 2)$ and $(2, 1)$ only.

Solving Eq. (9.8) for $\bar{\rho}_0$ in the case of two levels is trivial. We only mention that the population difference $\bar{n}_1 - \bar{n}_2$, which occurs in $I(\omega_L)$, becomes

$$\bar{n}_1 - \bar{n}_2 = \frac{\Re \tilde{G}(\omega_0)_{sp}}{\Re(\tilde{G}(\omega_0)_{sp} + 2\tilde{G}(\omega_0)_{st})} .$$

(10.3)

We note that this quantity is independent of the interaction matrix element $S_{12}$ and completely determined by the reservoir correlation function $\tilde{G}(\omega_0)$. Obviously, this is an artifact of a two-level system.

With the basis $|2><1|$ and $|1><2|$ we find

$$\omega_L - \omega_0 + i\epsilon(\omega_L) = \left( \begin{array}{cc} \omega_L - \omega_0 + i\epsilon(\omega_L) & -i\epsilon(\omega_L) \\ -i\epsilon(\omega_L) & \omega_L + \omega_0 + i\epsilon(\omega_L) \end{array} \right) ,$$

(10.4)
for the relevant part of this matrix. Here the parameter function \( \eta(\omega_L) \) is defined by

\[
\eta(\omega_L) = \frac{1}{3} \Delta^2 \left( \delta(\omega_L) + \delta(-\omega_L) \right),
\]

(10.5) which represents the operator \( \Gamma(\omega_L) \) in Eq. (10.4). Then the absorption line shape is readily found to be

\[
I(\omega_L) = I_L \frac{4\omega L_{\text{Re}\,\eta(\omega_L)}}{(\omega_0^2 - \omega_L^2 + 2\omega L \text{Im}\eta(\omega_L))^2 + 4\omega_L^2 (\text{Re}\eta(\omega_L))^2}.
\]

(10.6) In the Markov approximation \( \eta(\omega_L) \) assumes the constant value \( \eta(\omega_0) \), independent of \( \omega_L \). Then \( \eta(\omega_0) \) is merely a parameter, which can be adjusted to fit a line shape. It appears that in our more thorough approach, the function \( \eta(\omega) \) should be evaluated at the frequency \( \omega_L \) of the probe field. Especially the property

\[
\text{Re}\,\eta(\omega_L) = 0, \quad \omega_L > \omega_D,
\]

(10.7) for a Debye model shows that the absorption is identically zero for \( \omega_L > \omega_D \), whereas in the Markov approximation the absorption is finite in this case. That \( I(\omega_L) \) should vanish for \( \omega_L > \omega_D \), follows from energy conservation. An absorbed photon must eventually end up as an excitation of the phonon field, but for \( \omega_L > \omega_D \) there are no phonon modes which can accommodate the quantum. Different features of the line shape are illustrated in Figs. 5 and 6.
XI. CONCLUSIONS

Vibrational relaxation of physisorbed atoms on a harmonic crystal is studied, without the usual Markov approximation. It has been shown that the Markov approximation can be poor if the Debye frequency has an order of magnitude which is comparable to the widths and positions of the spectral lines, or in general where the line wings are concerned. We have derived a frequency-dependent relaxation operator $\Gamma(\omega)$, and from Eq. (7.1) it follows that $\Gamma(\omega)$ deviates from a constant value due to the finite correlation time of the reservoir. This in turn gives rise to a memory in the time evolution of $\rho_o(t)$, which is expressed by the fact that $\rho_o(t)$ obeys an integro-differential equation (Eq. (3.2)) rather than a first-order differential equation. The memory is brought about by the finite time-width of the operator $L_c(t)$ in the integrand.

We have solved the equation of motion with a Fourier-Laplace transform and applied the same technique to evaluate the absorption spectrum. Significant differences between the present theory and its Markovian equivalent are found in the spectral line profile.

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APPENDIX. DERIVATION OF EQ. (3.2) FROM EQ. (2.6)

In this Appendix we derive Eq. (3.2) from the general equation of motion (2.6). As an abbreviation we introduce the interaction Liouvillian $L_1$ as

$$L_1\rho = -\mathcal{H}^{-1}[RS,\rho] . \quad (A1)$$

Then Eq. (2.6) reads

$$i\frac{d}{dt}\rho(t) = (L_a + L_p + L_1)\rho(t) , \quad (A2)$$

which has to be transformed into an appropriate equation for $\rho_0(t)$. Integration of Eq. (A2) gives

$$\rho(t) = e^{-i(L_a+L_p)t}\rho(0)$$

$$-i\int_0^t e^{-i(L_a+L_p)(t-t')}L_1\rho(t') . \quad (A3)$$

Next we replace $t$ by $t'$ and substitute the right-hand side of Eq. (A3) for $\rho(t')$ in the integrand. Differentiating the result with respect to time and changing the integration variable then yields

$$i\frac{d}{dt}\rho(t) = (L_a + L_p)\rho(t) + L_1e^{-i(L_a+L_p)t}\rho(0)$$

$$-iL_1\int_0^t d\tau e^{-i(L_a+L_p)\tau}L_1\rho(t-\tau) \quad (A4)$$

as an exact integral of Eq. (A2).
As initial state $\rho(0)$ we take $\rho(0) = \rho_0(0)\tilde{\rho}_p$, Eq. (3.7), and subsequently we factorize $\rho(t-\tau)$ in the integrand, as argued to be reasonable in section III. Then we take the trace over the phonon states and insert definition (A1) for $L_1$. The second term on the right-hand side vanishes identically as follows from

$$\text{Tr}_p (R(e^{-\frac{i}{\hbar} H t\tilde{\rho}})) = \text{Tr}_p R\tilde{\rho} = 0,$$

where the right-most equality relies on the explicity form (2.5) of $R$. The appearance of two factors $L_1$ in the last term of Eq. (A4) gives rise to four terms, since $L_1$ is a commutator. Because $R$ and $S$ commute, as do $L_a$ and $L_p$, we can rearrange every term in such a way that all phonon operators are to the right, and all adatom factors are to the left. As a last step we use $R^+ = R$, the cyclic invariance for operators under a trace, and

$$e^{-iLt\rho} = e^{-\frac{i}{\hbar} H t\rho} e^{\frac{i}{\hbar} H t\rho}$$

for any $L$ and $\rho$. Comparison with the definition (3.5) of $L_c(\tau)$ then shows that Eq. (A4) can be cast in the form (3.2).
FIGURE CAPTIONS

**Fig. 1.** Real (a) and imaginary (b) part of the spontaneous component of the reservoir correlation function as a function of $\omega_D \tau$ and divided by $\zeta \omega_D^2$.

**Fig. 2.** Stimulated part of the reservoir correlation function, which is real, as a function of $\omega_D \tau$ and divided by $\zeta \omega_D^2$. Curve (a) corresponds to $\hbar \omega_D = k_B T$. In curve (b) ($\hbar \omega_D = 2k_B T$) the plot is truncated at $\omega_D \tau = 10$.

**Fig. 3.** Real (a) and imaginary (b) part of $\tilde{G}(\omega)_{sp}$ as a function of $\omega/\omega_D$ and divided by $\zeta \omega_D$. For $\omega < 0$ and $\omega > \omega_D$ the real part vanishes identically. The singularity of the imaginary part at $\omega = \omega_D$ is a result of the sharp cut-off $\omega_D$ of the dispersion relation. For any smooth but still arbitrarily steep decay at $\omega = \omega_D$, the value of Im$\tilde{G}(\omega)_{sp}$ would remain finite.

**Fig. 4.** Plot of the real (a) and imaginary (b) part of $\tilde{G}(\omega)_{st}/\zeta \omega_D$ as a function of $\omega/\omega_D$, and for $\hbar \omega_D = 2k_B T$. For $|\omega| > \omega_D$ the real part disappears.

**Fig. 5.** Line profile $I(\omega_L)$ as a function of $\omega_L/\omega_0$ and divided by $I_L \hbar^{-1} B(\bar{n}_1 - \bar{n}_2)$. The parameters are $\zeta \omega_D^2 S_{12}^2 = 0.4$, $\omega_D = 3\omega_0$ and $k_B T = \hbar \omega_D$. Curve (b) is calculated with Eq. (10.6) and curve (a) is the Markov approximation. The line shapes are not Lorentzians, as follows from their asymmetry around the dotted line at $\omega_L = \omega_0$. For $\omega_L = \omega_0$ the exact value and the Markov approximation always yield the same value for the absorption.

**Fig. 6.** Same as Fig. 5 but with $\hbar \omega_D = 0.3k_B T$. In this case of relatively large temperature the Markov approximation (curve (a)) deviates considerably from the exact value in the blue wing ($\omega_L > \omega_0$) of the line. Especially for $\omega_L > \omega_D$ the Markov approximation predicts a finite absorption, which cannot be correct.
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