Role of coherences in the relaxation of adsorbates

Henk F. Arnoldus and Thomas F. George

Department of Physics and Astronomy and Department of Chemistry, State University of New York at Buffalo,
239 Fronczak Hall, Buffalo, New York 14260

Adsorbed species on a solid-state surface interact with the large number of substrate modes, which gives rise to thermal relaxation. Commonly, the temporal evolution of the quantum state of the adsorbate is described by a master equation for the level populations (vibrational bond, internal modes, etc). It is pointed out that this approach does not necessarily give a correct account of the coupling to the solid when the effective level widths become comparable to the level separations, or larger. It is shown that the evolution of the populations does not decouple any more from the time evolution of the coherences (off-diagonal matrix elements), which implies that a random-phase approximation cannot be justified, and that the density matrix of the adsorbate is not determined only by the golden-rule transition constants. Especially, the line profiles turn out to be very sensitive to the coherence-coherence couplings. Although the coherences vanish in thermal equilibrium, their time-regression operator, and hence their mutual couplings and their couplings to the populations, which determine the absorption profile, do not. This information is lost in a master-equation treatment of relaxation.

I. INTRODUCTION

Coupling of adsorbed atoms or molecules on a surface to the degrees of freedom of the substrate, amounts to effective thermal relaxation of the internal molecular modes, or the vibrational bond with the solid. For molecules like CO on a metal surface, the excitation of internal stretching modes (vibrational levels) corresponds to a charge displacement, which couples to the motion of the electrons in the conduction band of the metal. Interaction of the electron cloud of the single molecule with the large number of electrons in the substrate then provides that the small system (the admolecule) is driven towards thermal equilibrium with the heat bath (the metal).[1] This process is usually regarded as electron-hole pair formation in the metal.[2] Another example of relaxation of adsorbates pertains to the kinetic coupling of an adatom in a vibrational (electromagnetic) bond with a crystal to the thermal motion of the surface atoms, which support the bond. In this fashion the kinetic and potential energy of an atom in an excited bound state on the surface, can be transferred into kinetic and potential energy of the crystal atoms.[3] Usually, this process is viewed as a phonon exchange between the adatom and the substrate.[4] Finally, we mention the irreversible dipole coupling of dye molecules (coatings) on a dielectric to the surface-plasmon field.[5] This interaction is responsible for a dramatic change in the lifetime of the molecule,[6] which in turn yields the celebrated phenomenon of enhanced Raman scattering, and surface-induced (Raman) resonances.

Commonly, the above-mentioned mechanisms for molecular relaxation, due to coupling with the substrate, are incorporated in the rate equations for the level populations $n_i(t)$ (internal vibrational, kinetic, or electronic) of the adparticle as[7]

$$\frac{d}{dt} n_i(t) = -\sum_j [n_i(t)a_{ij} - n_j(t)a_{ji}] + \cdots , \qquad (1.1)$$

where the transition constants a_{ij} are determined by the golden rule. Level $|i\rangle$ decays to the other levels $|j\rangle$ at a rate $n_i a_{ij}$ (loss term), and gains population from transitions of levels $|j\rangle$ to $|i\rangle$ at a rate $n_j a_{ji}$. Balancing the contributions then gives the master equation (1.1), where the ellipsis denotes the remaining interactions with, for instance, a laser field.[8] In a more thorough approach, which yields exactly the same result for the coupling with a heat bath, one starts with the full Schrödinger equation for the density operator $\rho(t)$ of the solid, the adparticle, and the interaction. With standard reservoir theory,[9] projection techniques,[10] or a Langevin approach,[9] one then derives an equation of motion for the reduced density operator $\rho_0(t)$ of the adsorbate, defined as

$$\rho_0(t) = \text{Tr}_r \rho(t) , \qquad (1.2)$$

where Tr_r indicates the partial trace over the reservoir states. Taking the diagonal part of the equation then results in the master equation (1.1) for the populations

$$n_i(t) = \langle i | \rho_0(t) | i \rangle . \qquad (1.3)$$

If we consider the off-diagonal matrix elements (the coherences) of $\rho_0(t)$, we obtain

$$\frac{d}{dt}\langle i | \rho_0(t) | j \rangle = [-i(\omega_i - \omega_j) - \tfrac{1}{2}(A_i + A_j)]$$

$$\times \langle i | \rho_0(t) | j \rangle + \cdots , \qquad (1.4)$$

for $i \neq j$, where

$$A_i = \sum_j a_{ij} \qquad (1.5)$$

equals the inverse lifetime of level $|i\rangle$, due to transitions to every other level $|j\rangle$, and $\hbar\omega_i$ is the energy of $|i\rangle$. Hence any initial coherence $\langle i|\rho_0(0)|j\rangle$ vanishes exponentially on a timescale $(A_i+A_j)^{-1}$ in the evolution to thermal equilibrium (long-time limit $t\rightarrow\infty$, or steady state). In a random-phase approximation one omits the coherences from the beginning and considers only the time evolution of the populations. Since Eq. (1.4) for the coherences does not couple to the master equation (1.1) for the populations, this approach is justified by more elaborated theories.

However, this is not the whole story. First, the master equation does not embody the full dynamical behavior of the adparticle. It only provides information on the distribution of populations, the energy content of the molecule, and the energy transfer into the solid. [Equation (1.1) implies an equation for energy conservation, because a level at $\hbar\omega_i$, which is populated with $n_i(t)$, corresponds to an energy $n_i\hbar\omega_i$ of the molecule.] Spectral information, like the line profiles for the absorption of radiation and the temporal correlations between the populations, which appear for instance in the response to a pulsed laser, are governed by the time regression of the coherences, rather than by the master equation.[11] Therefore, in discarding Eq. (1.4) one looses valuable information on observable properties of the system.

Second, in the derivation of the master equation there is always the tacit assumption that the width of a specific transition $|i\rangle\rightarrow|j\rangle$, which equals a_{ij}, is much smaller than the level separation $|\omega_i-\omega_j|$. Then one drops fast-oscillating terms with the Bohr frequencies $\Delta_{ij}=\omega_i-\omega_j$, with the argument that they will approximately average out to zero. This is a correct procedure if $|\Delta_{ij}|\gg a_{ij}$. In general, however, it is not obvious that this condition is always satisfied. To be specific, for electron-hole pair formation, both a_{ij}^{-1} and Δ_{ij}^{-1} acquire values of the order of a picosecond, and for CO on copper, for instance, the inverse lifetime of the stretching modes exceeds the level separations. In the case of adsorption of atoms on a crystal, the timescales for relaxation typically range from nanoseconds to picoseconds. For weakly bounded atoms (shallow potentials) the levels become closely spaced, and their separations can easily assume the order of magnitude of the damping constants.

In this paper we shall retain the couplings, which are due to the overlap of levels, and point out their significance. Especially, the absorption profile for weak radiation appears to be sensitive to the coherence-coherence coupling, as will be illustrated by an example.

II. RELAXATION THEORY

In order to display clearly the various approximations and to set the notation, we summarize the basic elements of relaxation theory in this section.[12] With H_a the Hamiltonian of the adsorbate, which includes the binding energy to the surface (attractive force of electromagnetic origin), and H_r the substrate Hamiltonian, the equation of motion for the density operator $\rho(t)$ of the active system reads

$$i\hbar\frac{d}{dt}\rho(t)=[H_a+H_r+SR,\rho(t)]\ ,$$
$$\rho^\dagger(t)=\rho(t),\quad \mathrm{Tr}\rho(t)=1\ . \tag{2.1}$$

Here the interaction between the molecule and the substrate, which gives rise to the relaxation, is divided as SR, where $S=S^\dagger$ is a molecular operator (S denotes systems), and $R=R^\dagger$ (reservoir) is an operator in the subspace of the solid. For instance, for coupling by single-phonon transitions, the operator S equals the derivative of the binding potential well, perpendicular to the surface, and R is the amplitude operator of an atom in the crystal.[13] With a Taylor expansion it is always feasible to factorize the interaction as $\sum_i S_i R_i$, but in order to avoid many obfuscating subscripts, we only retain a single term. In the case of phonon coupling, the subscript i indicates the number of phonons which are involved in a one-step transition. By writing SR for the interaction, we only keep track of single-phonon transition. This is already very accurate if the transition frequencies Δ_{ij} are smaller than the Debye frequency of the crystal, since then every pair of levels is resonantly coupled by a single-phonon interaction.

The standard integral of Eq. (2.1), which is suitable for the development of relaxation theory, is most conveniently derived with the aid of the interaction picture. With the Liouvillians

$$L_a\cdots=\hbar^{-1}[H_a,\cdots],\quad L_r\cdots=\hbar^{-1}[H_r,\cdots]\ , \tag{2.2}$$

we define the transformed density operator as

$$\sigma(t)=\exp[i(L_a+L_r)t]\rho(t)\ , \tag{2.3}$$

which obeys the equation of motion

$$i\hbar\frac{d}{dt}\sigma(t)=[S(t)R(t),\sigma(t)]\ . \tag{2.4}$$

The free evolution of S and R is displayed in their time dependence, according to

$$S(t)=\exp(iL_a t)S,\quad R(t)=\exp(iL_r t)R\ . \tag{2.5}$$

Iterating Eq. (2.4) twice and differentiating the result with respect to time then yields the integral

$$i\frac{d}{dt}\sigma(t)=\hbar^{-1}[S(t)R(t),\sigma(0)]-i\hbar^{-2}\int_0^t dt'[S(t)R(t),[S(t')R(t'),\sigma(t')]]\ . \tag{2.6}$$

As the initial value we can choose arbitrarily $\sigma(0)=\sigma_0(0)\rho_{\mathrm{eq}}$, with $\sigma_0(0)=\mathrm{Tr}_r\sigma(0)$ the reduced density operator of the adsorbate and ρ_{eq} the thermal-equilibrium state of the solid. By definition, ρ_{eq} commutes with H_r, and we shall assume that

$$\mathrm{Tr}_r R\rho_{\mathrm{eq}} = 0 \ .$$ (2.7)

This means that the interaction does not give rise to a net energy content of the molecule, which is exact in most cases. Otherwise the restriction (2.7) can be enforced by a proper transformation, which shifts the interaction over its average. As a second step we write $\sigma(t') = \sigma_0(t')\rho_{\mathrm{eq}} +$correction, which can always be done. After taking the trace in Eq. (2.6) over the reservoir states, we then obtain

$$\frac{d}{dt}\sigma_0(t) = -\frac{1}{2\pi}\int_0^t d\tau [G(\tau)S(t)S(t-\tau)\sigma_0(t-\tau) + G^*(\tau)\sigma_0(t-\tau)S(t-\tau)S(t)$$

$$-G^*(\tau)S(t)\sigma_0(t-\tau)S(t-\tau) - G(\tau)S(t-\tau)\sigma_0(t-\tau)S(t)] +\text{correction} \ .$$ (2.8)

For later purposes we do not impose the condition $\sigma_0^\dagger = \sigma_0$, which would allow a contraction of terms. The interaction with the substrate is incorporated in the complex-valued reservoir correlation function

$$G(\tau) = 2\pi\hbar^{-2}\mathrm{Tr}_r R(\tau)R\rho_{\mathrm{eq}} \ ,$$ (2.9)

which can be evaluated immediately for any prescribed R and H_r. Among other features, this $G(\tau)$ encompasses the temperature dependence of the coupling. Equation (2.8) is the usual starting point for reservoir theory.

A particularly transparent representation of Eq. (2.8) emerges if we adopt a Liouville-operator notation for the couplings in the integrand. To this end, we substitute $S(t) = \exp(iL_a t)S$, transform back to the ρ picture, and define

$$L_s \cdots = [S, \cdots] \ .$$ (2.10)

Then Eq. (2.8) assumes the form

$$i\frac{d}{dt}\rho_0(t) = L_a\rho_0(t) - \frac{i}{2\pi}L_s\int_0^t d\tau\{G(\tau)e^{-iL_a\tau}[S\rho_0(t-\tau)] - G^*(\tau)e^{-iL_a\tau}[\rho_0(t-\tau)S]\} +\text{correction} \ .$$ (2.11)

Next we introduce the correlation operator

$$L_c(\tau)\cdots = S\cdots G(\tau) - G^*(\tau)\cdots S \ ,$$ (2.12)

which enables to rewrite Eq. (2.11) compactly as

$$i\frac{d}{dt}\rho_0(t) = L_a\rho_0(t) - \frac{i}{2\pi}L_s\int_0^t d\tau\, e^{-iL_a\tau}L_c(\tau)\rho_0(t-\tau) +\text{correction} \ .$$ (2.13)

As long as the correction terms are taken into consideration, and provided that condition (2.7) holds, this is still an exact integral of Eq. (2.1). Equation (2.13) clearly reveals the significance of $L_c(\tau)$. It accounts for the memory in the interaction.

III. RESEVOIR CONDITION

A solid has a broad, continuous spectrum of modes, which are coupled to the molecule by the SR interaction. This property assures that the correlation function $G(\tau)$ from Eq. (2.9) decays to zero very fast for increasing τ. Typically, the time width of $G(\tau)$ is of the order of the inverse cutoff frequency of the mode distribution, which is the Debye frequency for a harmonic crystal. Hence this time is much shorter than any timescale on which $\sigma_0(t)$ varies, due to its coupling with the same continuum. If we indicate the correlation time of the reservoir by τ_c, and the damping constant for the transition $|i\rangle \rightarrow |j\rangle$ by a_{ij}, as in Eq. (1.1), then the reservoir condition reads

$$a_{ij}\tau_c \ll 1$$ (3.1)

for every i,j. For rare-gas atoms on a crystal like KCl, typical values of the product $a_{ij}\tau_c$ range from 0.1 to 0.01. By definition, the value of the integral in Eq. (2.13) has an order of magnitude of a_{ij}, and it is easy to estimate[12] that the correction terms are of the order of $a_{ij}^2\tau_c$. Therefore

they can be discarded in comparison with a_{ij}. In the interaction picture, $\sigma_0(t-\tau)$ evolves on a timescale a_{ij}^{-1}, which implies that we can replace $\sigma_0(t-\tau)$ by $\sigma_0(t)$ in Eq. (2.8). In the ρ picture the density operator oscillates with the Bohr frequencies, and hence the corresponding approximation in Eq. (2.13) is[14]

$$\exp[iL_a(t-\tau)]\rho_0(t-\tau) \simeq \exp(iL_a t)\rho_0(t) \ .$$ (3.2)

Then we can take $\rho_0(t)$ outside the integral, and again with condition (3.1) we can replace the upper integration limit by $t = \infty$. Combining everything then leads to the concise form of the equation of motion

$$i\frac{d}{dt}\rho_0(t) = (L_a - i\Gamma)\rho_0(t) \ .$$ (3.3)

The Liouville operator Γ is defined by

$$\Gamma = \frac{1}{2\pi}L_s\int_0^\infty d\tau\, e^{-iL_a\tau}L_c(\tau)e^{iL_a\tau} \ ,$$ (3.4)

which accounts for the relaxation of the molecule, due to the coupling with the modes of the substrate. Recall that the only assumption in deriving Eq. (3.3) is the condition (3.1), which is fairly justified for adsorbates. Equations (3.3) and (3.4) constitute the full effect of the coupling to the substrate, including the time evolution of the coherences, coupling between coherences, level shifts, etc. The advantage of the Liouville approach, in contrast to a

master-equation treatment, which relates matrix elements, is that the dynamics of the interaction is completely disentangled from the structure of the equation of motion, Eq. (3.3).

IV. EVALUATION OF Γ

Equation (3.4) defines the relaxation operator Γ in terms of the Liouvillians L_a and $L_c(\tau)$. If we remember that

$$\exp(\pm iL_a\tau)\cdots = \exp(\pm iH_a\tau/\hbar)\cdots\exp(\mp iH_a\tau/\hbar) ,$$

$$(4.1)$$

and then insert the definition (2.12) of $L_c(\tau)$ into Eq. (3.4), we find that Γ can alternatively be represented by

$$\Gamma\cdots = L_s(Q\cdots - \cdots Q^\dagger) ,\qquad (4.2)$$

which involves the Hilbert-space operator

$$Q = \frac{1}{2\pi}\int_0^\infty d\tau\, G(\tau)e^{-iL_a\tau}S .\qquad (4.3)$$

Notice that Eq. (4.2) still contains four terms, because L_s is a commutator. This also immediately implies the properties

$$(\Gamma\sigma)^\dagger = \Gamma\sigma^\dagger ,\quad \text{Tr}_a(\Gamma\sigma) = 0 ,\qquad (4.4)$$

for any σ. These relations are necessary for the conservation of Hermiticity and trace in the time evolution of $\rho_0(t)$.

Since L_a appears in an exponent in the definition of Q, an expansion in matrix elements is most convenient on a basis where L_a is a diagonal, e.g., the adsorbate states $|i\rangle$. For simplicity we shall suppose that the states $|i\rangle$ are nondegenerate. This is no restriction at all, but it avoids cumbersome notations. In terms of the projectors

$$P_i = |i\rangle\langle i| ,\qquad (4.5)$$

the exponential in Eq. (4.3) can be expanded as

$$\exp(-iL_a\tau)\cdots = \sum_{i,j}\exp(-i\Delta_{ij}\tau)P_i\cdots P_j .\qquad (4.6)$$

Then Q assumes the simple form

$$Q = \tfrac{1}{2}\sum_{i,j} g_{ji}P_i S P_j ,\qquad (4.7)$$

where the reservoir parameters g_{ji} are defined by

$$g_{ji} = \frac{1}{\pi}\int_0^\infty d\tau \exp(-i\Delta_{ij}\tau)G(\tau) ,\qquad (4.8)$$

which is essentially the Laplace transform of $G(\tau)$. Substituting Q and its Hermitian conjugate into Eq. (4.2) gives

$$\Gamma\sigma = \tfrac{1}{2}\sum_{i,j} S_{ij}(g_{ji}S\,|i\rangle\langle j|\,\sigma - g_{ij}^* S\sigma\,|i\rangle\langle j|$$

$$-g_{ji}\,|i\rangle\langle j|\,\sigma S + g_{ij}^*\sigma\,|i\rangle\langle j|\,S) ,\qquad (4.9)$$

which defines the action of Γ or an arbitrary Liouville vector σ. Here $S_{ij} = \langle i\,|\,S\,|\,j\rangle$ is a matrix element of the molecular part of the interaction.

Equation (4.9) is a hybrid representation of Γ, since it contains matrix elements S_{ij}, as well as the operator S itself. With the closure relation

$$\sum_i P_i = 1 ,\qquad (4.10)$$

we can cast Eq. (4.9) in the form

$$\Gamma\sigma = \tfrac{1}{2}\sum_{i,j,k}(c_{kiij}\,|k\rangle\langle j|\,\sigma + c_{kiij}^*\sigma\,|j\rangle\langle k|)$$

$$-\tfrac{1}{2}\sum_{i,j,k,l}(c_{klij}\,|i\rangle\langle j|\,\sigma\,|k\rangle\langle l| + c_{klij}^*\,|l\rangle$$

$$\times\langle k|\,\sigma\,|j\rangle\langle i|) ,\qquad (4.11)$$

where we introduced the coefficients

$$c_{klmn} = S_{kl}S_{mn}g_{nm} .\qquad (4.12)$$

Hence the relaxation operator is determined by the reservoir parameters g_{ij} and the matrix elements S_{ij} between the wave functions $|i\rangle$ and $|j\rangle$ of the adsorbate. Both g_{ij} and S_{ij} can be evaluated directly, once the kind of substrate and the molecular wave functions (internal modes), or the binding potential (vibrational coupling to a crystal), are prescribed.[15]

The relaxation gives rise to an effective width of the levels (their inverse lifetimes). If we assume that the overlap between different resonances is negligible, then we only have to retain couplings between pairs of levels in Eq. (4.11), rather than between four levels simultaneously. If we further neglect the imaginary part of g_{ij} (the level shifts), then Eq. (4.11) attains the familiar form[16]

$$\Gamma\sigma = \tfrac{1}{2}\sum_{i,j} a_{ij}(P_i\sigma + \sigma P_i - 2P_j\langle i\,|\,\sigma\,|\,i\rangle) ,\qquad (4.13)$$

in terms of the rate constants a_{ij} for the transitions $|i\rangle \to |j\rangle$

$$a_{ij} = \text{Re}\,c_{kllk} = |S_{kl}|^2\text{Re}\,g_{kl} .\qquad (4.14)$$

It is easy to check that the simplified form (4.12) leads to the master equation (1.1).

V. EQUATION OF MOTION

Numerical solution of the equation of motion (3.3) requires an expansion in matrix elements. With Eq. (4.11) for the relaxation, and

$$L_a\rho_0 = \sum_i \omega_i(\,|i\rangle\langle i|\,\rho_0 - \rho_0\,|i\rangle\langle i|\,) ,\qquad (5.1)$$

for the free evolution, we obtain

$$\frac{d}{dt}\langle m\,|\rho_0|\,n\rangle = -i\Delta_{mn}\langle m\,|\rho_0|\,n\rangle - \tfrac{1}{2}\sum_{i,j}(c_{miij}\langle j\,|\rho_0|\,n\rangle + c_{niij}^*\langle m\,|\rho_0|\,j\rangle) + \tfrac{1}{2}\sum_{i,j}(c_{inmj}\langle j\,|\rho_0|\,i\rangle + c_{imnj}^*\langle i\,|\rho_0|\,j\rangle) .$$

$$(5.2)$$

If we subsequently set $m = n$ and use $\rho_0^\dagger = \rho_0$, we find

$$\frac{d}{dt}\langle m \mid \rho_0 \mid m \rangle = -\tfrac{1}{2} \sum_{i,j} (c_{miij}\langle j \mid \rho_0 \mid m \rangle$$
$$- c_{immj}\langle j \mid \rho_0 \mid i \rangle) + \text{H.c.} \quad (5.3)$$

for the time derivative of the population $\langle m \mid \rho_0 \mid m \rangle$. This result is by no means equivalent to the master equation (1.1). Even if we were to neglect the imaginary part of the coefficients, then the time evolution of the populations would still couple to the real part of the coherences $\langle j \mid \rho_0 \mid m \rangle$ $(j \neq m)$, due to overlapping resonances. Conversely, the time evolution of the coherences, as it follows from Eq. (5.2) with $m \neq n$, couples to the populations and to every other coherence, in contrast to the simple exponential decay [Eq. (1.4)] in the limit of nonoverlapping resonances. In conclusion, if the widths of transitions become comparable with the level separations, it is inevitable that the coherences be taken into consideration, which in turn prohibits the derivation of a genuine master equation. Stated otherwise, in this case a random-phase approximation cannot be justified.

VI. STEADY STATE

Of particular importance is the long-time solution $\bar{\rho}_0 = \rho_0(t \to \infty)$. This steady-state density operator obeys $d\bar{\rho}_0/dt = 0$, and its matrix elements follow from Eqs. (5.2) and (5.3) with the left-hand sides replaced by zero. The relaxation of the reduced density operator to a steady state is a result of the coupling to the substrate. Apart from extravagent situations, this $\bar{\rho}_0$ is unique. Therefore we can solve Eq. (5.3) by trial and error. If we assume that the coherences vanish in the steady state, e.g.,

$$\langle i \mid \bar{\rho}_0 \mid j \rangle = \delta_{ij}\langle i \mid \bar{\rho}_0 \mid i \rangle = \delta_{ij}\bar{n}_i , \quad (6.1)$$

then Eq. (5.3) reduces to

$$\sum_j (\bar{n}_i a_{ij} - \bar{n}_j a_{ji}) = 0, \quad \sum_i \bar{n}_i = 1 , \quad (6.2)$$

where the rate constants a_{ij} are defined in Eq. (4.14). This equation is exactly the same as Eq. (1.1) for $t \to \infty$, with the left-hand-side set equal to zero. Hence the long-time solution of the density matrix is diagonal, and determined by the golden-rule transition constants a_{ij}. Note that the imaginary parts of c_{kllk} do not contribute. In terms of the solution $\bar{n}_k$ of Eq. (6.2) and the projectors P_k, we can write $\bar{\rho}_0$ as

$$\bar{\rho}_0 = \sum_k \bar{n}_k P_k , \quad (6.3)$$

which will be used in the next section.

Only in the transient region the coherences affect the details of the time evolution of the populations $n_k(t)$. Therefore it might appear that the importance of the coupling to the coherences, and in particular the coupling between different coherences, is marginal. This is, however, not the case. Even in the steady state, where the coherences disappear identically, their time regression has a great significance for the calculation of observable quantities. It should be emphasized that, for instance, a level

population is not directly accessible to experimental observation in general.

VII. ABSORPTION PROFILE

A common method to observe resonances of adsorbates is by irradiation of the surface with a low-power monochromatic laser, and measuring the absorption as a function of the photon energy (frequency). Probing the system with a weak radiation field has the advantage that it does not disturb the molecule (excitation of internal modes), nor desorb the layer or heat the substrate. Furthermore, the intensity of the radiation (scattered or transmitted) can be detected with high accuracy, partly due to the fact that only a relative measurement is required, which relates the absorption at a particular frequency to a calibrated off-resonance background level. Care should be exercised, however, in the interpretation of the spectrum. It is not the free molecule which absorbs the radiation, but the joint system of molecule, substrate, and interaction. Conversely, this feature provides an interesting tool to investigate the molecule-surface interaction (binding potential, charge-exchange mechanism), or properties of the substrate (dispersion relations of phonons or polaritons). Especially for a transparent crystal, like for instance ir light on KCl, information about the crystal can be obtained by spectroscopic methods in this way, which is not feasible without the coating. The adbond-mediated absorption profile will reflect the details of the coupling mechanism of the molecule to the substrate, and the properties of the solid itself. We remark that even if both the adsorbate and the substrate are transparent for a particular frequency, the bond can be optically active. This is for instance the case for rare-gas atoms on an alkali chloride crystal. Then the absorption profile will reveal the properties of the wave function of the vibrational state, and as we show below, in great detail.

If we indicate by μ the dipole-moment operator of the molecule or the bond (or both), and by ϵ the polarization of the probe beam, then the absorption profile is determined by the time regression of the operator

$$d = \mu \cdot \epsilon . \quad (7.1)$$

With $d(t)$ the Heisenberg representation of d, the number of absorbed photons per unit of time from the incident field with frequency ω equals[17]

$$I(\omega) = I_p(\epsilon_0 \hbar^2 c)^{-1} \text{Re}\left[\int_0^\infty dt\, e^{i\omega t} \text{Tr}\bar{\rho}[d(t)^\dagger, d] \right] , \quad (7.2)$$

where I_p is the laser power (energy per unit of time through a unit area, perpendicular to the direction of propagation). Multiplication of $I(\omega)$ by $\hbar\omega$ gives the absorbed energy per unit of time. Here, $\bar{\rho}$ is the thermal-equilibrium state of the entire system, and the time regression of $d(t)$ is governed by the Hamiltonian $H_a + H_r + SR$ from Eq. (2.1).

After a transformation to the Schrödinger picture, we can eliminate the reservoir degrees of freedom from the integrand in Eq. (7.2) along exactly the same lines as we derived Eq. (3.3) for the reduced density operator $\rho_0(t)$. We obtain

$$\mathrm{Tr}\bar{\rho}[d(t)^{\dagger},d]=\mathrm{Tr}_a\left[d^{\dagger}e^{-i(L_a-i\Gamma)t}[d,\bar{\rho}_0]\right]\ ,\qquad(7.3)$$

where Tr_a runs over the adsorbate states only. Equation (7.3) can be regarded as a Liouville-operator representation of the quantum-regression theorem.[18] Then we insert Eq. (7.3) into Eq. (7.2) and perform the time integration, which yields the representation

$$I(\omega)=I_p(\epsilon_0\hbar^2 c)^{-1}\mathrm{Re}\,\mathrm{Tr}_a\left[d^{\dagger}\frac{i}{\omega-L_a+i\Gamma}[d,\bar{\rho}_0]\right]\qquad(7.4)$$

in terms of an operator inversion. The upper limit $t=\infty$ does not contribute, due to the identity

$$\lim_{t\to\infty}e^{-i(L_a-i\Gamma)t}[d,\bar{\rho}_0]=\bar{\rho}_0\mathrm{Tr}_a[d,\bar{\rho}_0]=0\ ,\qquad(7.5)$$

which in turn follows from the facts that $\bar{\rho}_0$ is the solution of

$$(L_a-i\Gamma)\bar{\rho}_0=0\qquad(7.6)$$

and that trace is conserved in a time regression with $\exp[-i(L_a-i\Gamma)t]$. We recall that the commutator $[d,\bar{\rho}_0]$ gives rise to the terms $d\bar{\rho}_0$ and $\bar{\rho}_0 d$, which correspond to stimulated absorption and emission in the laser mode, respectively. The profile $I(\omega)$ is the balance between these two processes.

Since we suppress the degeneracies of the levels, we can expand the operator d on the adsorbed states as

$$d=\sum_{i,j}d_{ij}\,|\,i\,\rangle\langle\,j\,|\ .\qquad(7.7)$$

With the representation (6.3) of the steady-state solution, we find

$$[d,\bar{\rho}_0]=\sum_{i,j}(\bar{n}_j-\bar{n}_i)d_{ij}\,|\,i\,\rangle\langle\,j\,|\ .\qquad(7.8)$$

Substitution into Eq. (7.4), expanding $d^{\dagger}$ as in Eq. (7.7), and taking the trace then gives

$$I(\omega)=I_p(\epsilon_0\hbar^2 c)^{-1}\sum_{i,j,k,l}(\bar{n}_j-\bar{n}_i)\mathrm{Re}\,d_{ij}d_{kl}^*\langle\,k\,|\left[\frac{i}{\omega-L_a+i\Gamma}\,|\,i\,\rangle\langle\,j\,|\right]|\,l\,\rangle\ .\qquad(7.9)$$

The matrix elements of $\omega-L_a+i\Gamma$ can be read off immediately from Eq. (5.2), and after inversion of this matrix, Eq. (7.9) yields the absorption profile. Hence for a system of N levels, the evaluation of $I(\omega)$ requires only the inversion of an $N^2\times N^2$ matrix.

From the explicit representation (7.9) it follows that $I(\omega)$ is determined by the time regression of the coherence $|\,i\,\rangle\langle\,j\,|$ ($i\neq j$). In the time domain, like in Eq. (7.1), we propagate $|\,i\,\rangle\langle\,j\,|$ with $\exp[-i(L_a-i\Gamma)t]$, and then take the coherence $\langle\,k\,|\cdots|\,l\,\rangle$ of the result at time t. A Fourier transform then gives the spectral profile. This elucidates the importance of the coherences in the observation of adsorbates with spectroscopic methods. It is their time regression which determines the spectral distribution, whereas the populations only appear as an overall factor $\bar{n}_j-\bar{n}_i$. Furthermore, the spectral resolution involves the complete operator $L_a-i\Gamma$, which represents the free evolution of the molecule, the damping, the level shifts, and all the couplings between coherences and populations.

In the secular approximation, Eq. (4.13), where only couplings between pairs of levels are taken into account, only the terms with $i=k$, $j=l$ survive in Eq. (7.9). We notice that for $i,j\neq k,l$ an overall factor $d_{ij}d_{kl}^*$ arises, rather than $|\,d_{ij}\,|^2$. This product of matrix elements carries information on the relative phases of the dipole-moment matrix elements d_{ij}, which is not the case in the secular limit, where only $|\,d_{ij}\,|^2$ appears. Therefore, for transitions which have a sufficient overlap, it should be feasible to extract their relative phase from an absorption measurement.

VIII. TWO-LEVEL SYSTEM

In order to display the significance of the various notions, we utilize the two-level system. For the case of a vibrational coupling of an atom to a crystal, this situation can occur if the potential well is shallow enough, so that it supports only two discrete levels. The steady-state populations are readily found from Eq. (6.2). We obtain

$$\bar{n}_1=\frac{a_{21}}{a_{21}+a_{12}},\quad\bar{n}_2=\frac{a_{12}}{a_{21}+a_{12}}\ .\qquad(8.1)$$

Next we neglect the self-coupling of a level, which means that we assume $S_{11}=S_{22}=0$. The equation for the coherence $\rho_{21}(t)$ follows from Eq. (5.2). Explicitly,

$$\frac{d}{dt}\rho_{21}(t)=-i\Delta_{21}\rho_{21}(t)-\tfrac{1}{2}(c_{2112}+c_{1221}^*)\rho_{21}(t)$$
$$+\tfrac{1}{2}(c_{2121}+c_{1212}^*)\rho_{12}(t)\ ,\qquad(8.2)$$

and the equation for $\rho_{12}(t)=\rho_{21}(t)^*$ follows after a complex conjugation. We shall write $\Delta_{21}=\omega_0$ for the resonance frequency of the adsorbate, before coupling to the reservoir, and we introduce the notations

$$\eta=\tfrac{1}{2}\,|\,S_{21}\,|^2(g_{21}+g_{12}^*)\ ,\qquad(8.3)$$

$$S_{21}=|\,S_{21}\,|\exp(i\phi)\ ,\qquad(8.4)$$

where the latter defines the phases ϕ of S_{21}. Then Eq. (8.2) attains the form

$$\frac{d}{dt}\rho_{21}(t) = -(i\omega_0 + \eta)\rho_{21}(t) + \eta^*\exp(2i\phi)\rho_{12}(t) , \quad (8.5)$$

which shows immediately that $\bar{\rho}_{21} = \bar{\rho}_{12} = 0$, in agreement with Eq. (6.1). The second term on the right-hand side represents a coupling between the coherences $\rho_{21}(t)$ and $\rho_{12}(t)$. This term would be discarded in a secular approximation.

Equation (8.5) together with its complex conjugate constitutes a closed set, which has the characteristic frequencies

$$\omega_\pm = \pm\{\omega_0[\omega_0 + i(\eta^* - \eta)] - \tfrac{1}{4}(a_{21} + a_{12})^2\}^{1/2}$$
$$- \tfrac{1}{2}i(a_{21} + a_{12}) , \quad (8.6)$$

where we used

$$\eta + \eta^* = a_{21} + a_{12} . \quad (8.7)$$

In the secular limit $\omega_0 \gg a_{21} + a_{12}$, they reduce to

$$\omega_\pm \simeq \pm\omega_0 - \tfrac{1}{2}i(a_{21} + a_{12}) ,$$

and hence the resonance is situated at ω_0 with a width equal to $\tfrac{1}{2}(a_{21} + a_{12})$. Conversely, for $a_{21} + a_{12} \gg \omega_0$ we find $\omega_+ \simeq 0$, $\omega_- \simeq -i(a_{21} + a_{12})$, which are both situated at $\omega = 0$.

The full absorption profile $I(\omega)$, Eq. (7.9), is determined by the Liouville operator $\omega - L_a + i\Gamma$. From Eq. (5.2) we can easily construct a matrix representation for $-i(L_a - i\Gamma)$, which in turn gives

$$\omega - L_a + i\Gamma = \begin{pmatrix} \omega + ia_{21} & -ia_{12} & 0 & 0 \\ -ia_{21} & \omega + ia_{12} & 0 & 0 \\ 0 & 0 & \omega - \omega_0 + i\eta & -i\eta^*\exp(2i\phi) \\ 0 & 0 & -i\eta\exp(-2i\phi) & \omega + \omega_0 + i\eta^* \end{pmatrix} , \quad (8.8)$$

on the basis $|2\rangle\langle 2|$, $|1\rangle\langle 1|$, $|2\rangle\langle 1|$, $|1\rangle\langle 2|$. Inversion of this matrix and substitution into Eq. (7.9) then readily yields

$$I(\omega) = BI_p \frac{a_{21} - a_{12}}{a_{21} + a_{12}} \frac{1}{\pi} \mathrm{Re} \left[\frac{2i\omega_0}{(\omega + \omega_0 + i\eta^*)(\omega - \omega_0 + i\eta) + \eta\eta^*} \right] , \quad (8.9)$$

where we introduced the Einstein B coefficient

$$B = \frac{\pi}{\epsilon_0 \hbar^2 c} |\mu_{21}\cdot\epsilon|^2 , \quad (8.10)$$

pertaining to stimulated transitions between $|1\rangle$ and $|2\rangle$. Notice that the phase ϕ of S_{21} disappears from $I(\omega)$, as could be anticipated. Only relative phase differences between wave functions of pairs of levels might have a significance, and hence the phase difference ϕ, related to the wave functions of a two-state system, should vanish in observable quantities. The resonances of $I(\omega)$ are situated at the real parts of the zero's $\omega_\pm$ of the denominator. Since $\mathrm{Re}\,\omega_+ = -\mathrm{Re}\,\omega_-$ there is only a single peak in $I(\omega)$ for positive frequencies ω.

In the secular limit we can omit the term $\eta\eta^*$ in the denominator (with respect to ω_0^2), and then the profile reduces to

$$I(\omega)_s = BI_p \frac{a_{21} - a_{12}}{a_{21} + a_{12}} \frac{1}{\pi} \mathrm{Re} \left[\frac{i}{\omega - \omega_0 + i\eta} \right] , \quad (8.11)$$

which is a Lorentzian around $\omega_0 + \mathrm{Im}\,\eta$, with a half width at half maximum equal to $\mathrm{Re}\,\eta = \tfrac{1}{2}(a_{21} + a_{12})$. In Figs. 1 and 2 we have plotted $I(\omega)$ and $I(\omega)_s$ for $\mathrm{Im}\,\eta = 0$ and for different values of $\mathrm{Re}\,\eta$. Note that $I(\omega)$ and $I(\omega)_s$ assume the same value at the transition frequency ω_0, if $\mathrm{Im}\,\eta = 0$. Increasing $\mathrm{Re}\,\eta$ shifts the peak in $I(\omega)$ towards lower frequencies, without a significant broadening.

On the other hand, an increase of $\mathrm{Re}\,\eta$ in $I(\omega)_s$ broadens the line, without shifting it. The qualitative different effects on $I(\omega)$, as compared to the approximation $I(\omega_s)$, arise purely due to the inclusion of the coherence-coherence coupling. The shift of the line in $I(\omega)$ should not be confused with the shift $\mathrm{Im}\,\eta$ (Lamb shift), which is always present but, in general, small. Shifts and widths of

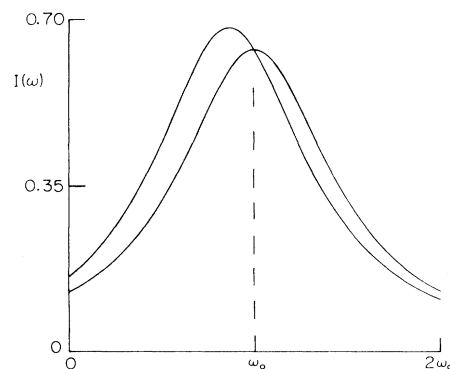FIG. 1. Absorption profile $I(\omega)$ from Eq. (8.9) as a function of ω. The overall factor $BI_p(a_{21} - a_{12})/(a_{21} + a_{12})$ is taken to be unity. Frequencies are in units of ω_0, and the relaxation constant equals $\eta = 0.5$. The profile which is symmetric around ω_0 is the secular approximation $I(\omega)_s$ from Eq. (8.11).
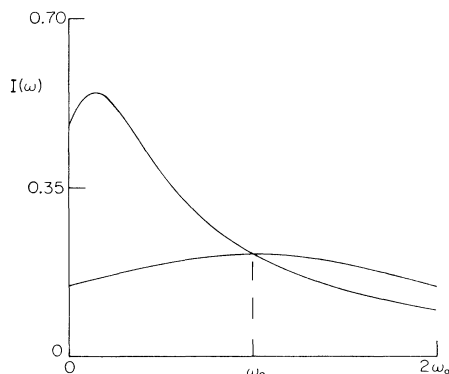
FIG. 2. Same as Fig. 1, but with $\eta = 1.5$. In this case the width of the transition is larger than the level separation, and it is seen that the resonance at ω_0 vanishes completely. The combined system of adsorbate and substrate gives rise to a resonance near $\omega = 0$, which is not found in the secular limit. There the peak at ω_0 is smeared out to form a continuous background. This exhibits clearly the significance of the nonsecular couplings if the levels have overlapping resonances.

absorption lines are directly amenable to experimental observation, and hence a verification of these predictions should be feasible.

IX. CONCLUSIONS

Coherences play a pronounced role in the relaxation of adsorbates if the widths of the transitions (relaxation constants) become comparable to or exceed the level separations. In the transient region the time evolution of the populations of the adsorbate states couples to the evolution of the coherences, which prohibits a description in terms of a master equation. For $t \rightarrow \infty$ (steady state, thermal equilibrium) the coherences vanish, and a time-independent master equation emerges, which contains the golden-rule transition constants as parameters. Measurable quantities which are determined by a two-time quantum expectation value, like correlation functions or spectrally-resolved properties, however, involve the time-evolution operator $L_a - i\Gamma$ for the density matrix $\rho_0(t)$. This includes all couplings between populations and coherences, and between coherences among each other. Even in the steady state, where the coherences disappear, their time-regression operator obviously does not. Therefore, a correct evaluation of steady-state properties requires that the coupling with coherences is retained. In other words, a random-phase or secular approximation is not exact in general.

We have applied a Liouville-operator formalism to derive a condensed form, Eq. (3.3), of the equation of motion for the reduced density operator $\rho_0(t)$ of the adsorbate. After some algebraic manipulations, and an expansion in matrix elements, we arrived at Eq. (5.2), which generalizes the master equation (1.1). It should be stressed that Eq. (5.2) contains the same parameters as Eq. (1.1), so that no additional information about the system is required. Only the coupling between the different matrix elements is more complicated. Discarding various nonsecular couplings yields again Eq. (1.1).

Subsequently we have considered the probe-absorption spectrum $I(\omega)$, which was expressed in the resolvent $(\omega - L_a + i\Gamma)^{-1}$ in Eq. (7.9). With a two-level example it has been illustrated how the formal expression can be evaluated and what the relevance of the coherence-coherence coupling can be for the spectral distribution. The results have been compared with the secular approximation, where $I(\omega)$ is a Lorentzian.

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