Laser-linewidth effects on the photon–phonon conversion rate at a gas–solid interface

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An atom, bounded to the surface of a crystal, absorbs photons from a strong incident laser field and subsequently emits phonons into the solid. In this paper we study the influence of the laser linewidth on this photon–phonon conversion process. The appearance of coherences obscures the interpretation of the equation of motion in terms of transition rates and prohibits the derivation of a master equation in the transient region. The absorbed energy from the driving field, which is assumed to be resonant with a set of two levels only, results from the work done by the external field on the transition dipole. In the steady state, the energy absorption from the radiation field equals the energy emission in the phonon field. It is shown that in this long-time limit the coherences can be expressed in terms of the populations, and hence the system is again described by a masterlike equation. Specific aspects of the finite laser bandwidth are pointed out.

1. INTRODUCTION

Irradiation of dye-coated surfaces or adsorbed atoms on a crystal with strong infrared laser light amounts to photon–phonon conversion reactions. The internal vibrational modes of the molecule or the atom-surface bond absorbs photons from the radiation field (stimulated excitation), and the subsequent spontaneous decay (coupling to the phonon field of the crystal) is accompanied by a phonon emission into the solid. Additional processes such as thermal or radiative desorption and spontaneous emission of radiation are negligible in comparison with the thermal transitions in the adbond. In this fashion the resonant coupling of vibrational modes of adsorbed species with the incident electromagnetic field provides an effective method for heating a crystal, which itself might be transparent for the impinging light. In this paper, we study the effect of the laser linewidth on the adbond-mediated energy transport from a laser field into the phonon field.

The interaction of an adsorbed atom in a vibrational bond with a harmonic crystal is commonly described by a Pauli-type master equation.[1–6] The distribution of the population over the vibrational levels is determined by the phonon absorption and emission processes, which occur at a rate $n_k(t)a_{kl}$ for a transition from the initial state $|k\rangle$ to the final state $|l\rangle$. Here the rate constants a_{kl} depend on the temperature of the crystal and the shape of the potential well in which the atom is bounded (apart from an overall k, l-independent constant). The a_{kl}'s gain in general contributions from single-phonon and multiphonon processes. The population $n_k(t)$ of level $|k\rangle$ follows from the master equation and the initial state at $t = 0$, whereas thermal relaxation to a unique steady state is inherent in the structure of the master equation.

Incorporation of the presence of a weak driving laser field is easily done in a perturbative way.[7–12] Stimulated absorption and emission rates are included in the master equation

as additional transitions between optically coupled levels. The energy-absorption rate from the radiation field is then simply the difference between the number of absorptions and emissions per unit time multiplied by the photon energy $\hbar\omega_L$. This approach does not apply any longer for an intense laser field, since the appearance of multiphoton processes prohibits such a simple interpretation of radiative transitions.[13–15] In two previous papers,[16,17] we showed that transparent mechanisms can be recovered, provided that we diagonalize the laser-atom interaction first. This was accomplished by a transformation to the famous dressed-states representation.[18] With respect to these joint atomic and laser states, including the interaction, the phonon relaxation processes were understood as transitions between dressed states; then every transition $|k\rangle \rightarrow |l\rangle$, which occurs at a rate $n_k(t)a_{kl}$ (the subscripts k and l now refer to dressed states), corresponds to a phonon absorption from or emission into the crystal, where the phonon energy equals the level separation of the states $|k\rangle$ and $|l\rangle$. Summation over all transitions then yields the net energy flux into the crystal.

The derivation of these energy-transport equations hinges on the existence of a master equation for the level populations, both in the low-intensity limit and in the dressed-state picture. This enables us to identify the occurring transitions, the rate constants, and the energies of the involved phonons and photons. A simple balance then gives the expression for the energy transport from the laser into the atomic bond and finally into the crystal. It is not so obvious that this procedure can be employed in general, because the equations for the populations might couple to the time evolution of the coherences, which obscures any direct interpretation. We shall show that this problem already emerges when a finite laser linewidth is taken into account. A more sophisticated approach to the energy-transport problem, an approach that does not rely on a specific structure of the equation of motion, will be used to tackle this apparent complication.

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2. DRIVEN ADBOND

An atom is bound to the surface of a harmonic-lattice crystal by attractive electromagnetic forces. If we denote the non-degenerate vibrational eigenstates by $|k\rangle$, we can write the Hamiltonian of the adbond as

$$H_a = \sum_k \hbar\omega_k P_k \tag{2.1}$$

in terms of the energy eigenvalues $\hbar\omega_k$ and the projectors $P_k = |k\rangle\langle k|$ onto the eigenstates. This system is irradiated by a laser field, with an electric component

$$\mathbf{E}(t) = E_0 \mathrm{Re}\, \boldsymbol{\varepsilon}_L \exp\{-i[\omega_L t + \phi(t)]\} \tag{2.2}$$

at the position of the atom. Here E_0 is the real amplitude, $\boldsymbol{\varepsilon}_L$ is the normalized polarization vector ($\boldsymbol{\varepsilon}_L{}^* \cdot \boldsymbol{\varepsilon}_L = 1$), and $\phi(t)$ is a stochastically fluctuating phase, which broadens the laser line around its central frequency ω_L. The coupling to the atomic bond is established by a dipole interaction $H_{ar}(t) = -\boldsymbol{\mu} \cdot \mathbf{E}(t)$, with $\boldsymbol{\mu}$ the transition dipole-moment operator between the eigenstates $|k\rangle$. Phonon absorption/emission is considered a relaxation process, and hence it is most conveniently accounted for by a Liouville operator Γ, which acts on the density operator ρ of the adbond according to[19]

$$\Gamma\rho = \tfrac{1}{2}\sum_{kl} a_{kl}(P_k\rho + \rho P_k - 2P_l\langle k|\rho|k\rangle). \tag{2.3}$$

Every term k, l pertains to a transition $|k\rangle \rightarrow |l\rangle$, and a_{kl} is the inverse lifetime of level $|k\rangle$ because of its spontaneous decay ($\omega_k > \omega_l$) or excitation ($\omega_k < \omega_l$) to level $|l\rangle$. The laser-driven and thermally damped atomic bond is then represented by the density operator $\rho(t)$, whose time evolution is governed by the full equation of motion

$$i\hbar\frac{d\rho}{dt} = [H_a, \rho] + [H_{ar}(t), \rho] - i\hbar\Gamma\rho, \qquad \rho^\dagger = \rho, \qquad \mathrm{Tr}\,\rho = 1. \tag{2.4}$$

The laser field $\mathbf{E}(t)$ is a stochastic process because of its randomly fluctuating phase, and this turns Eq. (2.4) into a stochastic differential equation for $\rho(t)$.

We will assume that only two levels $|e\rangle$ (excited) and $|g\rangle$ (ground) of the bond are significantly coupled by the incident radiation. The detuning between the optical frequency ω_L and the level separation $\omega_0 = \omega_e - \omega_g > 0$ of the driven transition will be indicated by

$$\Delta = \omega_L - \omega_0, \tag{2.5}$$

and the coupling strength is expressed in the Rabi frequency

$$\Omega = E_0 |\langle e|\boldsymbol{\mu} \cdot \boldsymbol{\varepsilon}_L|g\rangle|/\hbar. \tag{2.6}$$

The interaction Hamiltonian with the radiation field then attains the form

$$H_{ar}(t) = -\tfrac{1}{2}\hbar\Omega|e\rangle\langle g|\exp\{-i[\omega_L t + \phi(t)]\}$$

$$+ \text{Hermitian conjugate.} \tag{2.7}$$

3. TRANSFORMATION AND AVERAGE

The interaction Hamiltonian $H_{ar}(t)$ oscillates with frequency ω_L and is stochastic through the phase $\phi(t)$. With a stochastic transformation to the rotating frame, we can elim-

inate the $\exp(\pm i\omega_L t)$ dependence and facilitate the appearance of $\phi(t)$.[20,21] We define the density operator $\sigma(t)$ as

$$\sigma(t) = \exp\{-i[\omega_L t + \phi(t)]P_g\}\rho(t)\exp\{i[\omega_L t + \phi(t)]P_g\}, \tag{3.1}$$

which has the equation of motion

$$i\frac{d\sigma}{dt} = \hbar^{-1}[H_d, \sigma] + \dot\phi(t)[P_g, \sigma] - i\Gamma\sigma, \tag{3.2}$$

where the time-independent dressed-atom Hamiltonian is explicitly

$$H_d = \sum_{i \neq e,g} \hbar\omega_i P_i + \tfrac{1}{2}\hbar(\omega_e + \omega_g + \omega_L)(P_e + P_g)$$

$$- \tfrac{1}{2}\hbar\Delta(P_e - P_g) - \tfrac{1}{2}\hbar\Omega(|e\rangle\langle g| + |g\rangle\langle e|). \tag{3.3}$$

Now the time derivative $\dot\phi(t)$ of the phase enters the equation, and in a multiplicative way [e.g., as $\dot\phi(t)\sigma(t)$]. Notice that no information is lost in the transformation, since Eq. (3.1) can be inverted.

The solution of the equation of motion [Eq. (3.2)] for $\sigma(t)$ refers to a single realization of the process $\phi(t)$, but only the average over the stochastics of the phase have a significance. In general, this average would depend on the details of the stochastics of $\phi(t)$, but it can be shown[22] that for Eq. (3.2) the average is quite insensitive to the precise specification of the process as long as the phase fluctuations represent the broadening of a single-mode laser line. For any Markoffian diffusion process $\phi(t)$ and for the uniform random-jump process, the average of Eq. (3.2) acquires the simple form

$$i\frac{d\Pi}{dt} = \hbar^{-1}[H_d, \Pi] - iW\Pi - i\Gamma\Pi, \tag{3.4}$$

where we have introduced the abbreviation

$$\Pi(t) = \nleftrightarrow\sigma(t)\nleftrightarrow, \tag{3.5}$$

with the slashed angle brackets denoting a stochastic average (in order to distinguish from a quantum-mechanical average $\langle \ldots \rangle$). The operator W, which accounts for the laser linewidth, equals

$$W\Pi = \lambda[P_g, [P_g, \Pi]], \tag{3.6}$$

where λ is the half-width at half-maximum of the Lorentzian laser line. Alternatively, we can write W as

$$W\Pi = \lambda(P_g\Pi + \Pi P_g - 2P_g\langle g|\Pi|g\rangle), \tag{3.7}$$

which is reminiscent of the structure of the phonon-relaxation operator Γ from Eq. (2.3). Just as a_{kl} can be considered a contribution to the width of level $|k\rangle$, we can interpret 2λ as the additional width of the ground state, which is due to phase fluctuations. This can also be inferred from Eq. (2.2) if we rewrite it as

$$\mathbf{E}(t) = E_0 \mathrm{Re}\, \boldsymbol{\varepsilon}_L \exp\left\{-i\int_0^t ds[\omega_L + \dot\phi(s)]\right\}. \tag{3.8}$$

The laser frequency ω_L can be regarded to be shifted instantaneously by the amount $\dot\phi(t)$, which diminishes or increases the detuning $\Delta = \omega_L - \omega_0$ by $\dot\phi(t)$. Effectively, this gives rise to a width 2λ.

4. MATRIX ELEMENTS

Equation (3.4) is an operator equation for the density matrix $\Pi(t)$ of the driven adbond. This determines the populations, abbreviated as

$$\Pi_k(t) = \langle k|\Pi(t)|k\rangle, \tag{4.1}$$

and the coherences $\langle k|\Pi(t)|l\rangle$, $k \neq l$, with respect to the eigenstates $|k\rangle$ of the unperturbed bond. After taking the diagonal part of Eq. (3.4), we find for the time evolution of the populations

$$\frac{d}{dt}\Pi_l = -A_l\Pi_l + \sum_k \Pi_k a_{kl}, \qquad l \neq e, g, \tag{4.2}$$

$$\frac{d}{dt}\Pi_e = \Omega \, \mathrm{Im}\langle e|\Pi|g\rangle - A_e\Pi_e + \sum_k \Pi_k a_{ke}, \tag{4.3}$$

$$\frac{d}{dt}\Pi_g = -\Omega \, \mathrm{Im}\langle e|\Pi|g\rangle - A_g\Pi_g + \sum_k \Pi_k a_{kg}, \tag{4.4}$$

where we have introduced the total-decay constant of level $|k\rangle$ as

$$A_k = \sum_l a_{kl}, \tag{4.5}$$

and we have used the Hermiticity of $\Pi(t)$. The set [Eqs. (4.2)–(4.4)] resembles a master equation, but it contains the inhomogeneous term $\Omega \, \mathrm{Im}\langle e|\Pi|g\rangle$, and hence it is not a closed set. The equation for the coherence between the excited state and the ground state is readily found to be

$$i\frac{d}{dt}\langle e|\Pi|g\rangle = \tfrac{1}{2}\Omega(\Pi_e - \Pi_g)$$
$$- [\Delta + \tfrac{1}{2}i(A_e + A_g + 2\lambda)]\langle e|\Pi|g\rangle. \tag{4.6}$$

Equations (4.2)–(4.4) and (4.6), accompanied by the normalization

$$\sum_k \Pi_k(t) = 1, \tag{4.7}$$

which is Tr $\Pi(t) = 1$, determine the populations $\Pi_k(t)$ and the coherence $\langle e|\Pi(t)|g\rangle$. This generalizes the master equation for the case of an arbitrarily strong incident field with a finite bandwidth. These are simple linear first-order differential equations, and they can be solved immediately for any configuration of levels. Notice that the laser linewidth λ enters only in the last term on the right-hand side of Eq. (4.6) and that the coupling of Eq. (4.6) with the set [Eqs. (4.2)–(4.4)] is brought about by the inversion $\Pi_e - \Pi_g$ rather than by the separate populations.

5. ABSORPTION RATE

Since the coherence $\langle e|\Pi|g\rangle$ enters the equations for the populations Π_k, it is not so obvious which transitions occur and at which rates. Therefore we have to start from more elementary principles. The absorbed energy by the atomic bond from the external field equals the work that is done on the dipole by the field. Hence we can write for the absorption rate (energy per unit time)[23]

$$\frac{dZ}{dt} = \mathbf{E}(t) \cdot \frac{d}{dt}\langle \boldsymbol{\mu}(t)\rangle, \tag{5.1}$$

where $\boldsymbol{\mu}(t)$ is the dipole moment of the system in the Heisenberg picture. This expression accounts for absorptions and stimulated emissions of photons from and into the field, and the balance between these gain and loss terms is the net energy absorption rate dZ/dt from the radiation field into the adbond. In the steady state, there can be no accumulation of energy in the bond, so then dZ/dt equals the balance between the emission and absorption rates of phonon energy into the crystal. Effectively, this is a conversion of radiation energy into the thermal energy, or a photon-phonon conversion reaction, mediated by the optically active atomic bond.

Transformation of Eq. (5.1) to the Schrödinger picture gives

$$\frac{dZ}{dt} = \mathrm{Tr}[\mathbf{E}(t) \cdot \boldsymbol{\mu}] \frac{d\rho}{dt}, \tag{5.2}$$

and with the equation of motion (2.4) for $\rho(t)$, the stochastic transformation (3.1) to the σ representation and with $\sigma^\dagger = \sigma$, we obtain

$$\frac{dZ}{dt} = \hbar\Omega \frac{d}{dt}\mathrm{Re}\langle e|\sigma(t)|g\rangle + \hbar\Omega[\omega_L + \dot{\phi}(t)]\mathrm{Im}\langle e|\sigma(t)|g\rangle. \tag{5.3}$$

This relation reveals that the absorption rate is basically determined by the coherence $\langle e|\sigma|g\rangle$ rather than by the populations of the levels. From a slightly different point of view, we can interpret this as the fact that the occurrence of coherent transitions between states is reflected in the presence of off-diagonal matrix elements. This is in contrast to the incoherent thermal decay, which is governed by a master equation for the populations only.

The appearance of $\dot{\phi}(t)$ in the second term on the right-hand side of Eq. (5.3) is not very convenient. With the aid of the equation of motion [Eq. (3.2)] for $\sigma(t)$, we can eliminate the $\dot{\phi}(t)$ term and the time derivative in the first term simultaneously. We find

$$\frac{dZ}{dt} = -\tfrac{1}{2}\hbar\Omega(A_e + A_g)\mathrm{Re}\langle e|\sigma|g\rangle + \hbar\Omega\omega_0\mathrm{Im}\langle e|\sigma|g\rangle. \tag{5.4}$$

Comparison with Eq. (5.3) shows that the time differentiation of the real part of the coherence is replaced by $-\tfrac{1}{2}(A_e + A_g)$, and the instantaneous laser frequency $\omega_L + \dot{\phi}(t)$, which multiplies the imaginary part, is altered into the atomic resonance frequency ω_0. This indicates that the contribution to dZ/dt from the real part originates from the cooperation of thermal decay and coherent excitation, whereas the imaginary part is pure optical, since it persists even in the absence of the crystal. The stochastic average of dZ/dt is now easily found. We simply replace $\sigma(t)$ by $\Pi(t)$ in Eq. (5.4).

6. STEADY STATE

Because of the thermal relaxation, the density matrix $\Pi(t)$ will reach a steady state after a time of the order of a_{kl}^{-1}, elapsed from the instant of preparation (for instance, the

switching on of the laser). The long-time solution will be indicated by

$$\bar{\Pi} = \lim_{t \to \infty} \Pi(t). \qquad (6.1)$$

This $\bar{\Pi}$ then obeys the set of Eqs. (4.2)–(4.4) and (4.6) with the left-hand sides set equal to zero. By taking the imaginary part of Eq. (4.6), we obtain

$$\mathrm{Re}\langle e|\bar{\Pi}|g\rangle = \frac{-\Delta}{\tfrac{1}{2}(A_e + A_g) + \lambda} \mathrm{Im}\langle e|\bar{\Pi}|\lambda\rangle. \qquad (6.2)$$

This relation between the real and imaginary parts of the coherence holds only in the steady state. Subsequently, we consider the real part of Eq. (4.6). Application of Eq. (6.2) then yields

$$\mathrm{Im}\langle e|\bar{\Pi}|g\rangle = \tfrac{1}{2} \Omega \frac{\tfrac{1}{2}(A_e + A_g) + \lambda}{[\tfrac{1}{2}(A_e + A_g) + \lambda]^2 + \Delta^2} (\bar{\Pi}_g - \bar{\Pi}_e). \qquad (6.3)$$

The results [Eqs. (6.2) and (6.3)] show that the coherence can be expressed entirely in terms of the population inversion $\bar{\Pi}_e - \bar{\Pi}_g$ in this limit.

With Eqs. (6.2) and (6.3) we can rewrite Eqs. (4.2)–(4.4) in the steady state as

$$\sum_k \bar{\Pi}_k a_{kl} = A_l \bar{\Pi}_l, \qquad l \neq e, g, \qquad (6.4)$$

$$\sum_k \bar{\Pi}_k (a_{ke} + a_{kg}) = A_e \bar{\Pi}_e + A_g \bar{\Pi}_g, \qquad (6.5)$$

$$\sum_k \bar{\Pi}_k (a_{ke} - a_{kg}) = A_e \bar{\Pi}_e - A_g \bar{\Pi}_g - \Omega^2$$
$$\times \frac{\tfrac{1}{2}(A_e + A_g) + \lambda}{[\tfrac{1}{2}(A_e + A_g) + \lambda]^2 + \Delta^2} (\bar{\Pi}_g - \bar{\Pi}_e), \qquad (6.6)$$

where the coherence $\langle e|\bar{\Pi}|g\rangle$ has disappeared. This set of equations contains only populations, and it can be regarded as a masterlike equation for a coherently driven system. Notice that the optical parameter Ω enters only as Ω^2, which is proportional to the laser intensity. The coherence [Eqs. (6.2) and (6.3)], however, also depends on the field amplitude Ω.

With the use of Eq. (6.2), the stochastic average of the absorption rate, Eq. (5.4), can be written as

$$\ast \frac{dZ}{dt} \ast = \hbar \left(\omega_L - \Delta \frac{2\lambda}{A_e + A_g + 2\lambda} \right) \Omega \, \mathrm{Im}\langle e|\bar{\Pi}|g\rangle. \qquad (6.7)$$

If the laser linewidth λ is small in comparison with the relaxation constant $A_e + A_g$, the second term in parentheses vanishes, and the absorption rate reduces to the $\hbar\omega_L\Omega \, \mathrm{Im}\langle e|\bar{\Pi}|g\rangle$. Since $\hbar\omega_L$ is the energy of a laser photon, this implies that $\Omega \, \mathrm{Im}\langle e|\bar{\Pi}|g\rangle$ equals the number of photons per unit time, which is converted into thermal energy. For $\lambda \gg A_e + A_g$, the term in parentheses becomes $\omega_L - \Delta = \omega_0$. This is consistent with the fact that for a large bandwidth the energy of a photon is no longer well defined. Now the

radiation excites the system from $|g\rangle$ to $|e\rangle$, and subsequent thermal decay corresponds to an effective gain of phonon energy $\hbar\omega_0$. This process occurs again at a rate $\Omega \, \mathrm{Im}\langle e|\bar{\Pi}|g\rangle$.

Substitution of Eq. (6.3) into Eq. (6.7) finally yields

$$\ast \frac{dZ}{dt} \ast = \hbar \left(\omega_L - \Delta \frac{2\lambda}{A_e + A_g + 2\lambda} \right)$$
$$\times \tfrac{1}{2} \Omega^2 \frac{\tfrac{1}{2}(A_e + A_g) + \lambda}{[\tfrac{1}{2}(A_e + A_g) + \lambda]^2 + \Delta^2} (\bar{\Pi}_g - \bar{\Pi}_e). \qquad (6.8)$$

The masterlike set of equations [Eqs. (6.4)–(6.6)], together with the normalization [Eq. (4.7)], constitutes a simple set of linear algebraic equations that are easily solved for a particular case. This determines $\bar{\Pi}_g - \bar{\Pi}_e$ and, thereby, the energy-absorption rate [Eq. (6.8)].

For $\lambda \ll A_e + A_g$, the laser linewidth has no significance at all, since it disappears from Eqs. (6.4)–(6.6) and Eq. (6.8). If we then take $|\Delta| \gg A_e + A_g$, we recover our previous results.[16,17] In the situation $\lambda \gg A_e + A_g$, the energy-absorption rate reduces to

$$\ast \frac{dZ}{dt} \ast = \hbar\omega_0 \cdot \tfrac{1}{2} \Omega^2 \frac{\lambda}{\lambda^2 + \Delta^2} (\bar{\Pi}_g - \bar{\Pi}_e). \qquad (6.9)$$

If the system is driven close to resonance ($\Delta \simeq 0$), the prefactor is proportional to ω_0/λ, and hence the absorption is diminished by an increasing linewidth. This can be understood from the representation [Eq. (3.8)] of the laser field. The probability for a photon absorption is the largest if $\omega_L \simeq \omega_0$, but because of $\dot{\phi}(t) \neq 0$, the optical frequency is temporarily shifted out of resonance. This reduces the absorption. Conversely, for $|\Delta|$ large, the phase fluctuations can shift ω_L into resonance and thereby enhance the absorption. From Eq. (6.9) we see that this is indeed the case, since $\ast dZ/dt \ast$ becomes proportional to $\omega_0\lambda/\Delta^2$.

7. CONCLUSIONS

We have considered the irradiation of an atom, bound to a crystal, by intense nonmonochromatic laser light. The single-mode laser line is broadened by stochastic phase fluctuations, which turns the equation of motion for the density operator $\sigma(t)$ of the atomic bond into a stochastic differential equation. The average over the stochastics of $\phi(t)$ was performed in a rotating-frame representation, yielding the equation of motion [Eq. (3.4)] for $\Pi(t) = \ast\sigma(t)\ast$. It appears that the laser linewidth gives rise to an additional width 2λ of the ground state. This is a consequence of the specific form of our transformation [Eq. (3.1)] to the rotating frame. We remark that other kinds of transformation[24] that also eliminate the $\exp(\pm i\omega_L t)$ time dependence in the interaction Hamiltonian would result in effective widths of both $|e\rangle$ and $|g\rangle$.

The combination of laser-linewidth damping and thermal relaxation with coherent excitation by an arbitrarily strong radiation field prohibits the derivation of a master equation for the populations of the vibrational levels. It becomes necessary to take the coherences between the optically coupled states into consideration. This gives the set of Eqs. (4.2)–(4.4) and (4.6), which can be regarded as a generalized

master equation.   Only in the long-time limit can we express the coherence $\langle e|\bar{\Pi}\|g\rangle$ in the population difference $\bar{\Pi}_g - \bar{\Pi}_e$, which implies the emergence of a genuine master equation.

The energy absorption from the laser field by the adbond is evaluated by calculating the work done on the dipole moment of the bond.   In general, the absorption rate is determined by the coherence $\langle e|\Pi(t)|g\rangle$ [Eq. (5.4)], and in the steady state it can be expressed in the inversion $\bar{\Pi}_e - \bar{\Pi}_g$, which follows from the solution of the master equation.   The transport of energy from the bond to the phonon field is brought about by thermal relaxation.   This can be inferred directly from Eqs. (6.6) and (6.8).   For $a_{kl} = 0$ for all k, l, we find $\bar{\Pi}_e = \bar{\Pi}_g$ in the steady state, and hence $\langle dZ/dt\rangle = 0$. We have shown how the overall factor changes from $\hbar\omega_L$ to $\hbar\omega_0$ with increasing linewidth, and we see that a finite λ enhances (diminishes) the energy flux if the detuning is large (small).

ACKNOWLEDGMENTS

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Laser Surface Physics

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Henk F. Arnoldus was born in 1955 in 's Hertogenbosch, The Netherlands. He obtained his master's degree in physical engineering in 1981 from Eindhoven University of Technology, concentrating on theoretical nuclear physics. His graduate studies on stochastic processes, collisional redistribution, and quantum optics were performed at Utrecht State University under the supervision of G. Nienhuis. After receiving the Ph.D. in 1985, he joined the research group of Thomas F. George at the State University of New York at Buffalo, where he is currently working on spectroscopy of adsorbed molecules on surfaces.

Thomas F. George

Thomas F. George was born in 1947 in Philadelphia, Pennsylvania. After receiving the Ph.D. degree in chemistry from Yale University in 1970, he spent successive years as a research associate at MIT and the University of California at Berkeley. He joined the faculty of the University of Rochester in 1972 as assistant professor of chemistry and was promoted to associate professor in 1974 and to professor in 1977. In 1985 he moved to the State University of New York at Buffalo as dean of natural sciences and mathematics/professor of chemistry and physics. His awards and honors include the following: Dreyfus Teacher-Scholar, 1975–1985; Sloan Fellow, 1976–1980; Marlow Medal and Prize from the Royal Society of Chemistry, 1979; New York Academy of Sciences Fellow, 1981–; Guggenheim Fellow, 1983–1984; American Physical Society Fellow, 1984–. He has served on the advisory/editorial boards of *Chemical Physics Letters*, *Journal of Physical Chemistry*, and *Molecular Physics*. He was chairman of the Gordon Research Conference on Molecular Energy Transfer in 1981. He has served on the executive committee of the Physical Division of the American Chemical Society and is chairman-elect for 1986–1987. In 1986 he was named to the board of managers of the Buffalo Museum of Science. His research interests include molecular energy transfer, reaction dynamics, and the interaction of laser radiation with molecular rate processes in the gas phase and at a gas–solid interface. His attention has been focused recently on the development of theoretical techniques and computer codes to describe a variety of surface processes, such as desorption, migration, chemical vapor deposition, grating growth of metal films on semiconductor substrates, charge transfer in ion-surface scattering, resonance fluorescence, surface-state excitation, and electron–hole pair formation by molecule–semiconductor collisions. He has a special interest in microstructures and cluster phenomena. His research activities have led to 250 publications and a total of 150 invited conference lectures, seminars, and colloquia.