Thermal relaxation of adsorbed atoms in an intense laser field

Henk F. Arnoldus, Sander van Smaalen, 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
(Received 17 April 1986)

Adsorbed atoms on the surface of a harmonic lattice are immersed in a strong laser field. The optical Bloch equations are derived, which include the thermal relaxation and the coherent excitation of the adbond. This is accomplished by a transformation to dressed states, which diagonalizes the interaction with the laser. The single-phonon couplings are then understood as transitions between dressed states. The radiative contributions for arbitrarily strong fields are obtained in the master equation, and it is shown that the coherences with respect to the dressed states decay exponentially, due to the phonon relaxation. General properties of the competing phonon-induced redistribution and optical excitation of the level populations are presented, and exemplified by an explicit elaboration of a three-level system. The results are amenable to analytical evaluation once the interaction potential is prescribed, and extensions of the approach to include multiphonon processes are straightforward.

I. INTRODUCTION

Relaxation or desorption of an atom in a vibrational bond with a surface of a crystal with finite temperature is fairly described by a Pauli-type master equation and has been studied extensively.[1-6] The vibrational levels of the adbond are coupled by the phonon field of the crystal, and phonon-exchange reactions of the bond with the crystal, which acts as a thermal bath, cause the relaxation or desorption. The latter process can be either a result of successive single-phonon excitations up the ladder of vibrational states or, when the level separations are larger than the Debye frequency ω_D, as a one-step multiphonon process. Besides the academic interest in these processes, the thermal desorption of adatoms is the major technical method to obtain clean surfaces. However, when the distances between the lower levels are large in comparison with ω_D, the desorption rate might be very low, since the first excitations can only occur through multiphonon processes.

An obvious way to enhance the desorption is by irradiation of the surface with infrared laser light. The laser, with frequency ω_L, is tuned in resonance with a vibrational transition. In this fashion one can efficiently populate a high-lying state, such that the transition to the continuum can be established by a resonant one-phonon process.[7-11] There is obviously a competing effect, which diminishes the efficiency of this procedure. An optically excited bond can decay to a lower state under emission of a phonon into the crystal. This can be considered as a conversion of a photon into a phonon, and the net result is an energy flux into the crystal, without desorption of the atom. On a much larger time-scale, however, this process heats the crystal, and consequently the desorption is again enhanced.

The problem of irradiation of an adsorbed atom, in combination with thermal relaxation due to the coupling with the phonon reservoir, has been treated in the weak-field limit[12-18] with a perturbative approach and for special choices of the coupling potential (harmonic, Morse).[19] A systematic development of a concise theory for strong laser fields, which does not rely on a specific form of the potential, is apparently not available yet. In this paper, we investigate the interaction of an intense radiation field with the bounded atom. We interpret the results in terms of transition diagrams, and we identify the contributions of pure-phonon, phonon-photon exchange, and one-phonon—two-photon processes to the laser-assisted redistribution of the level populations and to the decay of the coherences. Common features are illustrated by an example.

II. EQUATION OF MOTION

We consider an atom with mass m, which is adsorbed on the surface of a harmonic-lattice crystal. The van der Waals forces are represented by the potential V between the adatom and its nearest surface atom, and by an effective surface potential ϕ. The lateral motion of the atom will be neglected, since it couples only weakly to the phonon field, and the direction perpendicular to the surface will be denoted by z. If we choose the origin of our coordinate system at the equilibrium position of the surface atom, with mass M, and indicate the position of m by $z\mathbf{e}_\perp$ and of M by $\mathbf{u}$, then V will only depend on the distance $|z\mathbf{e}_\perp-\mathbf{u}|$. Since $|\mathbf{u}|$ is much smaller than $|z|$, we can expand the potential as

$$V(|z\mathbf{e}_\perp-\mathbf{u}|)=V_0(z)-\mathbf{u}\cdot\mathbf{e}_\perp\frac{d}{dz}V_0(z)+\cdots, \quad (2.1)$$

where $V_0(z)$ is defined as the interaction for $\mathbf{u}=\mathbf{0}$. We will only retain these two terms, which implies that we neglect multiphonon processes. This will keep the formulation concise and the interpretation transparent. It is, however, straightforward to retain higher-order terms. The atomic part of the interaction is abbreviated as

$$S=\frac{d}{dz}V_0(z)\ , \tag{2.2}$$

and the amplitude of the phonon field for the surface atom M will be represented by[20]

$$\mathbf{u}=\sum_{\mathbf{k},s}\left[\frac{\hbar v'}{2Mv\omega(k)}\right]^{1/2}(a_{\mathbf{k}s}+a_{\mathbf{k}s}^{\dagger})\mathbf{e}_{\mathbf{k}s}\ . \tag{2.3}$$

Here v and v' are the volumes of the crystal and unit cell, respectively, $\mathbf{e}_{\mathbf{k}s}$ is the unit polarization vector of the phonon mode $\mathbf{k}s$, $a_{\mathbf{k}s}$ and $a_{\mathbf{k}s}^{\dagger}$ are the annihilation and creation operator for the mode $\mathbf{k}s$, and $\omega(k)$ is the dispersion relation. With this notation, the vibrational coupling of the adbond to the crystal is accounted for by the Hamiltonian $K+V_0+\phi+H_{\rm ph}-\mathbf{u}\cdot\mathbf{e}_{\perp}S$, with K the kinetic energy of m and $H_{\rm ph}$ the free-field phonon Hamiltonian,

$$H_{\rm ph}=\sum_{\mathbf{k},s}\hbar\omega(k)a_{\mathbf{k}s}^{\dagger}a_{\mathbf{k}s}\ . \tag{2.4}$$

The pure atomic part $K+V_0+\phi$ of the Hamiltonian will be termed the bare-atom Hamiltonian, since it describes the atomic bond with $\mathbf{u}=0$ and without a laser field. Its eigenvalues $\hbar\omega_i$ and eigenstates $|\,i\,\rangle$ are defined by

$$(K+V_0+\phi)\,|\,i\,\rangle=\hbar\omega_i\,|\,i\,\rangle\ , \tag{2.5}$$

and explicit representations in coordinate space can easily be found for a number of potentials.[21] A prime example here is the Morse potential, which provides a fair representation of the binding potential well, and for which analytical expressions for $\hbar\omega_i$ and $|\,i\,\rangle$ are known. With respect to its own eigenvectors, we can write the bare-atom Hamiltonian as

$$H_b=K+V_0+\phi=\sum_i\hbar\omega_iP_i\ , \tag{2.6}$$

with

$$P_i=|\,i\,\rangle\langle i\,|\ , \tag{2.7}$$

the projector onto the eigenstate $|\,i\,\rangle$. We shall assume that for the atomic part S of the interaction with the phonon field, the diagonal matrix elements $\langle i\,|\,S\,|\,i\,\rangle$ vanish. This is only an approximation in the presence of a laser field, since the $\langle i\,|\,S\,|\,i\,\rangle$ term will give rise to a small radiative contribution, but not to pure phonon transitions.

A continuous single-mode laser is tuned into resonance with a specific transition of the vibrational bond. The electric component of the electromagnetic field at the position of the bond is

$$\mathbf{E}(t)=E_0\mathrm{Re}[\boldsymbol{\varepsilon}\exp(-i\omega_Lt)]\ , \tag{2.8}$$

and the coupled levels will be denoted by $|\,e\,\rangle$ and $|\,g\,\rangle$. This excited state and ground state (which is not necessarily the lowest state) are separated by $\omega_e-\omega_g>0$, and the frequency mismatch with ω_L, the detuning, will be indicated by $\Delta=\omega_L-(\omega_e-\omega_g)$. The strength of the dipole coupling is expressed in terms of the Rabi frequency[22,23]

$$\Omega=\hbar^{-1}E_0\langle e\,|\,\boldsymbol{\mu}\cdot\boldsymbol{\varepsilon}\,|\,g\,\rangle\ , \tag{2.9}$$

which contains the dipole-moment operator $\boldsymbol{\mu}$ of the vibrational bond. The interaction Hamiltonian is then $-\boldsymbol{\mu}\cdot\mathbf{E}(t)$.

The full equation of motion can now be summarized as

$$i\hbar\frac{d\rho}{dt}=[H,\rho],\quad \rho^{\dagger}=\rho,\quad \mathrm{Tr}\rho=1\ , \tag{2.10}$$

where $\rho(t)$ is the density operator of the atomic bond and the phonon field. The Hamiltonian is given explicitly by

$$H=H_b+H_{\rm ph}-\sum_{\mathbf{k},s}\beta_{\mathbf{k}s}(a_{\mathbf{k}s}+a_{\mathbf{k}s}^{\dagger})S -\tfrac{1}{2}\hbar\Omega(\,|\,e\,\rangle\langle g\,|\,e^{-i\omega_Lt}+e^{i\omega_Lt}\,|\,g\,\rangle\langle e\,|\,)\ , \tag{2.11}$$

with the free evolution of the adbond H_b and the phonon field $H_{\rm ph}$ given by Eqs. (2.6) and (2.4), respectively. The coupling parameter with the phonon mode $\mathbf{k}s$ is given by

$$\beta_{\mathbf{k}s}=\left[\frac{\hbar v'}{2Mv\omega(k)}\right]^{1/2}\mathbf{e}_{\mathbf{k}s}\cdot\mathbf{e}_{\perp}\ . \tag{2.12}$$

III. DRESSED STATES

The interaction between the bare states and the laser mode can be diagonalized directly. To this end we introduce the transformed density operator $\sigma(t)$ by[24]

$$\sigma(t)=e^{-i\omega_Lt\mathcal{P}_g}\rho(t)e^{i\omega_Lt\mathcal{P}_g}\ , \tag{3.1}$$

with $\mathcal{P}_g$ the projector onto the ground state. This transformation eliminates the oscillatory factors in the interaction term $-\boldsymbol{\mu}\cdot\mathbf{E}(t)$, but at the expense of the appearance of a time-dependent coupling with the phonon field. The equation of motion for $\sigma(t)$ reads

$$i\hbar\frac{d\sigma}{dt}=[H_d+H_{\rm ph},\sigma] -\sum_{\mathbf{k},s}\beta_{\mathbf{k}s}[(a_{\mathbf{k}s}+a_{\mathbf{k}s}^{\dagger})q(t),\sigma]\ , \tag{3.2}$$

with

$$q(t)=e^{-i\omega_Lt\mathcal{P}_g}Se^{i\omega_Lt\mathcal{P}_g}\ . \tag{3.3}$$

The dressed-atom Hamiltonian H_d is defined as

$$H_d=\sum_{i\neq e,g}\hbar\omega_iP_i+\tfrac{1}{2}\hbar(\omega_L+\omega_e+\omega_g)(P_e+P_g) -\tfrac{1}{2}\hbar\Delta(P_e-P_g)-\tfrac{1}{2}\hbar\Omega(\,|\,e\,\rangle\langle g\,|+|\,g\,\rangle\langle e\,|\,)\ , \tag{3.4}$$

which has the interpretation of the bare atom H_b dressed with the photons of the laser field, including the interaction.[25]

Similarly to Eq. (2.6), we now write

$$H_d=\sum_i\hbar\hat{\omega}_i\hat{P}_i\ , \tag{3.5}$$

with $\hbar\hat{\omega}_i$ the eigenvalues of H_d, and $\hat{P}_i$ the projectors onto the eigenstates $|\,i\,\rangle$ of H_d. The eigenvalue equations of H_d are readily derived from Eq. (3.4). We obtain

$$H_d \mid i \rangle = \hbar\omega_i \mid i \rangle, \quad i = \text{bare}, \quad i \neq e,g \tag{3.6}$$

$$H_d \mid \pm \rangle = \hbar\hat{\omega}_\pm \mid \pm \rangle \ , \tag{3.7}$$

with

$$\hat{\omega}_\pm = \tfrac{1}{2}(\omega_L + \omega_e + \omega_g) \mp \tfrac{1}{2}\Omega' \ , \tag{3.8}$$

where

$$\Omega' = \Delta(1+\Omega^2/\Delta^2)^{1/2} \ . \tag{3.9}$$

Hence the dressed states are identical to the bare states, provided that $i \neq e,g$. The states $\mid e \rangle$ and $\mid g \rangle$ are coupled to form $\mid + \rangle$ and $\mid - \rangle$ according to

$$\mid + \rangle = \mid e \rangle \cos(\theta/2) + \mid g \rangle \sin(\theta/2) \ , \tag{3.10}$$

$$\mid - \rangle = \mid g \rangle \cos(\theta/2) - \mid e \rangle \sin(\theta/2) \ , \tag{3.11}$$

which is a parametrization in terms of the angle $\theta/2$, where θ is defined by[26]

$$\theta = \arctan(\Omega/\Delta) \ . \tag{3.12}$$

For weak driving fields ($\Omega \to 0$) we have $\mid + \rangle \simeq \mid e \rangle$ and $\mid - \rangle \simeq \mid g \rangle$, but for strong fields we find $\mid \pm \rangle \simeq (\mid g \rangle \pm \mid e \rangle)/\sqrt{2}$. The summation in Eq. (3.5) runs over the bare states $i \neq e,g$, and over $i = \pm$, where $\hat{P}_\pm = \mid \pm \rangle\langle \pm \mid$. This diagonalizes the laser interaction. The relation between the eigenvalues of H_b and H_d is illustrated in Fig. 1.[27,28]

The coupling to the phonon field is now regarded as an interaction between the dressed bond and the free phonons. The time dependence of this interaction is embodied in $q(t)$ from Eq. (3.3). With the idempotent property $P_g^2 = P_g$, we can expand the exponentials as

$$e^{\pm i\omega_L t P_g} = 1 - P_g + e^{\pm i\omega_L t} P_g \ , \tag{3.13}$$

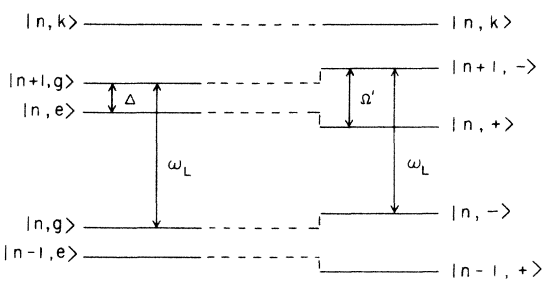

FIG. 1. Energy levels of the bare system plus the free laser field are represented by the diagram on the left-hand side. The detuning Δ is taken positive. The number of photons in the laser mode is indicated by n. If the dipole coupling $-\boldsymbol{\mu}\cdot\mathbf{E}$ is included, a new diagonalization yields the dressed energy-level system on the right-hand side. The level separations Δ and ω_L in the bare system now become Ω' and ω_L, where Ω' is always larger than Δ due to $\Omega^2 \neq 0$. This is the ac-Stark shift (Ref. 27). The state $\mid k \rangle$, which is not coupled to another level by the laser, remains unaltered. In general, we suppress the quantum number n and represent the dressed atom as an infinite ladder of states $\mid \pm \rangle$, which is the famous Jaynes-Cummings model for the interaction of a two-level system with a strong radiation field (Ref. 28).

which allows us to write

$$q(t) = \bar{S} + e^{-i\omega_L t} P_g S + e^{i\omega_L t} S P_g \ . \tag{3.14}$$

Here we used that $\langle g \mid S \mid g \rangle = 0$, and we introduced the time-independent part of the interaction by

$$\bar{S} = S - P_g S - S P_g \ . \tag{3.15}$$

The identification of the contributions to the interaction of the three frequencies in Eq. (3.14) will facilitate the following computations considerably.

IV. INTERACTION PICTURE

In contrast to the photon field, where only the laser mode is occupied, the phonon field consists of many modes **ks**, which all contribute to the interaction. This prohibits an immediate diagonalization, so other methods have to be applied. In this section we set up the notation and write down the basic equation. To this end, we introduce the density operator in the interaction picture by

$$\tilde{\sigma}(t) = e^{i\hbar^{-1}(H_d + H_{\rm ph})t} \sigma(t) e^{-i\hbar^{-1}(H_d + H_{\rm ph})t} \ . \tag{4.1}$$

When there is no coupling between the dressed system and the phonon field, we have $\tilde{\sigma}(t) = \sigma(0) = \tilde{\sigma}(0)$. The equation of motion for $\tilde{\sigma}(t)$ follows from Eq. (3.2), and we obtain

$$i\hbar \frac{d}{dt} \tilde{\sigma}(t) = [W(t), \tilde{\sigma}(t)] \ . \tag{4.2}$$

The interaction Hamiltonian $W(t)$ is then

$$W(t) = -\sum_{\mathbf{k},s} \beta_{\mathbf{ks}} (a_{\mathbf{ks}} e^{-i\omega(k)t} + a_{\mathbf{ks}}^\dagger e^{i\omega(k)t}) \tilde{q}(t) \ , \tag{4.3}$$

with the transformed atomic part given by

$$\tilde{q}(t) = e^{i\hbar^{-1}H_d t} q(t) e^{-i\hbar^{-1}H_d t} \ . \tag{4.4}$$

If we expand the exponentials in the projectors on the dressed states and use the expression (3.14) for $q(t)$, we obtain

$$\tilde{q}(t) = \sum_{k,l} e^{i\hat{\Delta}_{kl} t} \hat{P}_k \{ \bar{S} + e^{-i\omega_L t} P_g S + e^{i\omega_L t} S P_g \} \hat{P}_l \ , \tag{4.5}$$

where

$$\hat{\Delta}_{kl} = \hat{\omega}_k - \hat{\omega}_l \tag{4.6}$$

is the level separation between the dressed states $\mid k \rangle$ and $\mid l \rangle$. Besides the usual time dependence $\exp(i\hat{\Delta}_{kl}t)$ in the interaction picture, we now also find $\exp[i(\hat{\Delta}_{kl} \pm \omega_L)t]$.

Since the system of interest is the adbond, we define the reduced density operator of the dressed atom by

$$\sigma_0(t) = \mathrm{Tr}_{\rm ph}\sigma(t) \ , \tag{4.7}$$

and similarly for $\tilde{\sigma}_0(t)$. Taking the trace over the phonon field in Eq. (4.1) yields

$$\sigma_0(t) = e^{-i\hbar^{-1}H_d t} \tilde{\sigma}_0(t) e^{i\hbar^{-1}H_d t} \ , \tag{4.8}$$

and therefore it is sufficient to derive an equation for $\tilde{\sigma}_0(t)$. If we iterate the first integral of Eq. (4.2) twice, dif-

ferentiate the result with respect to time, and take the trace over the phonon field, we obtain

$$\frac{d}{dt}\tilde{\sigma}_0(t)=-\frac{1}{\hbar^2}\mathrm{Tr}_{\mathrm{ph}}\left[\int_0^t dt'[W(t),[W(t'),\tilde{\sigma}(t')]]\right] . \tag{4.9}$$

The right-hand side of this equation accounts for the phonon interaction in the evolution of $\sigma_0(t)$.

V. PHONON RESERVOIR

The phonon field will be considered as a large reservoir,[29–31] or heat bath, with a short recovery time. Then the integral in Eq. (4.9) can be evaluated by standard techniques,[29–33] so here we merely state the result. Care should be exercised, however, since the atomic part of the interaction, $\tilde{q}(t)$, contains three frequencies for a single kl matrix element. This gives rise to a number of cross terms, which do not appear without a laser field.

The average number of phonons in mode ω for the crystal in thermal equilibrium at temperature T is

$$n(\omega)=[\exp(\hbar\omega/k_BT)-1]^{-1} . \tag{5.1}$$

We extend the definition of $n(\omega)$ to negative values of ω, which enables us to write

$$n(\omega)+1=-n(-\omega) . \tag{5.2}$$

This will simplify the notation considerably. Next we introduce another function of ω by

$$f(\omega)=\zeta\frac{1}{\omega}\left|\frac{dk(|\omega|)}{d|\omega|}\right|k^2(|\omega|)[n(\omega)+1] , \tag{5.3}$$

with

$$\zeta=\frac{v'}{2\pi\hbar M} , \tag{5.4}$$

in terms of the dispersion relation $k=k(\omega)$, which is the inverse of $\omega=\omega(k)$. This $f(\omega)$ enters because of the summation over all modes $\mathbf{k}s$ of the reservoir.

After these preliminary definitions, we can evaluate the integral in Eq. (4.9). We obtain the simple result

$$\begin{aligned}\frac{d}{dt}\tilde{\sigma}_0(t)=&-\tfrac{1}{2}\sum_{k,l}|\bar{S}_{kl}|^2 f(\hat{\Delta}_{kl})[\hat{P}_k\tilde{\sigma}_0(t)+\tilde{\sigma}_0(t)\hat{P}_k-2\hat{P}_l\langle k|\tilde{\sigma}_0(t)|k\rangle]\\&-\tfrac{1}{2}\sum_{\pm,l}g_\pm|S_{gl}|^2 f(\hat{\Delta}_{\pm l}-\omega_L)[\hat{P}_\pm\tilde{\sigma}_0(t)+\tilde{\sigma}_0(t)\hat{P}_\pm-2\hat{P}_l\langle\pm|\tilde{\sigma}_0(t)|\pm\rangle]\\&-\tfrac{1}{2}\sum_{k,\pm}g_\pm|S_{gk}|^2 f(\hat{\Delta}_{k\pm}+\omega_L)[\hat{P}_k\tilde{\sigma}_0(t)+\tilde{\sigma}_0(t)\hat{P}_k-2\hat{P}_\pm\langle k|\tilde{\sigma}_0(t)|k\rangle]\\&-g_+g_-|S_{eg}|^2[f(\omega_L)+f(-\omega_L)]\sum_\pm\hat{P}_\pm\tilde{\sigma}_0(t)\hat{\mathbf{P}}_\mp .\end{aligned} \tag{5.5}$$

The first term comes from the time-independent part $\bar{S}$ of the interaction, and is proportional to $|\bar{S}_{kl}|^2=|\langle k|\bar{S}|l\rangle|^2$. Here the summation runs over all dressed states k,l. The second and the third terms only connect the dressed states $\pm$ with all other states. In the first term, the overall factor contains $f(\hat{\Delta}_{kl})$, which depends only on the level distance $\hat{\omega}_k-\hat{\omega}_l$, but in the other two terms, this frequency is shifted by the optical frequency ω_L. Furthermore, they involve the geometrical factors

$$g_\pm=\langle\pm|P_g|\pm\rangle , \tag{5.6}$$

e.g., the matrix elements of the projector on the ground state with respect to the dressed states. This factor is only nonvanishing for the states $|+\rangle$ and $|-\rangle$, which explains the limited summations in the last two terms. For later purposes we note that $g_\pm$ can be expressed in terms of the optical parameters Ω' and Δ according to

$$g_\pm=\frac{\Omega'\mp\Delta}{2\Omega'} , \tag{5.7}$$

as can be found from the definitions (3.10) and (3.11) of the dressed states.

Notice that the operator equation (5.5) for $\tilde{\sigma}_0(t)$ involves only well-defined quantities. The projectors inside the square brackets select a specific matrix element of $\tilde{\sigma}_0(t)$ with respect to the dressed states, and the prefactors contain $f(\omega)$, a given function of ω and the temperature, and the matrix elements of $S=dV_0/dz$. Besides that, the optical parameters $g_\pm$ appear, which are known functions of Ω^2 and the detuning Δ. In view of Eq. (2.9), the parameter Ω^2 is proportional to the laser intensity and to the square of the transition-dipole moment. It is this combination that determines whether a laser field can be treated as a weak field (perturbation), or not. We address this item in more detail in Sec. VII. The temperature enters parametrically through $f(\omega)$ from Eq. (5.3). If the laser heating of the crystal is considerable, the temperature will depend on time, and hence an additional macroscopic heat-transport equation has to be supplied. However, if the direct heating is dominant, the details of the atomic evolution and the radiative excitation of the adbond have no importance. Therefore, we assume an "adiabatic following" with temperature in this paper.

VI. BLOCH EQUATIONS

For a given transition $|k\rangle\rightarrow|l\rangle$ there might be a contribution from more than one term in Eq. (5.5) if $k=\pm$ or $l=\pm$. In order to distinguish between the various contri-

butions in every transition, we rearrange the terms. Furthermore, we will express all matrix elements of S and $\bar{S}$ in terms of bare-state matrix elements. This implies that the optical parameters will appear in the overall factors, and hence the effect of the laser is tracked down explicitly in every transition.

From the definition of $\bar{S}$, Eq. (3.15), it follows immediately that

$$\langle k|\bar{S}|l\rangle=\langle k|S|l\rangle, \quad \text{if } k\neq\pm, \quad l\neq\pm \tag{6.1}$$

so that for states $|k\rangle$, $|l\rangle$, which are not directly coupled by the laser, we can replace $\bar{S}$ by S. If one of these states equals $|+\rangle$, or $|-\rangle$, we obtain

$$|\bar{S}_{\pm k}|^2=g_{\mp}|S_{ek}|^2, \quad \text{if } k\neq\pm \tag{6.2}$$

and again $g_{\mp}$ accounts for the optical effects. We note that these matrix elements connect the excited state $|e\rangle$ with $|k\rangle$. Finally, we find

$$\langle k|\bar{S}|l\rangle=0 \tag{6.3}$$

if both $|k\rangle$ and $|l\rangle$ are one of the states $|+\rangle$ or $|-\rangle$. For the matrix elements of S itself, as they appear in the second and the third terms of Eq. (5.5), we find

$$|S_{g\pm}|^2=g_{\mp}|S_{eg}|^2. \tag{6.4}$$

A transition $|k\rangle\rightarrow|l\rangle$ might gain contributions from more than one term in Eq. (5.5), but for the time evolution of $\tilde{\sigma}_0(t)$ these terms add up. Hence, we can define the effective rate constants a_{kl} for every specific transition $|k\rangle\rightarrow|l\rangle$. The radiationless coupling between two bare states is governed by

$$a_{kl}=f(\hat{\Delta}_{kl})|S_{kl}|^2, \quad k\neq\pm, \quad l\neq\pm. \tag{6.5}$$

For $k=l$ this rate constant is zero, because we assumed $S_{kk}=0$. If one of the states equals $|+\rangle$ or $|-\rangle$, we obtain

$$a_{\pm l}=g_{\mp}f(\hat{\Delta}_{\pm l})|S_{el}|^2+g_{\pm}f(\hat{\Delta}_{\pm l}-\omega_L)|S_{gl}|^2, \tag{6.6}$$

$$a_{k\pm}=g_{\mp}f(\hat{\Delta}_{k\pm})|S_{ek}|^2+g_{\pm}f(\hat{\Delta}_{k\pm}+\omega_L)|S_{gk}|^2, \tag{6.7}$$

for $l\neq\pm$, $k\neq\pm$. The transition rates between the two $|\pm\rangle$ doublets are determined by

$$a_{++}=a_{--}=g_+g_-[f(-\omega_L)+f(\omega_L)]|S_{eg}|^2, \tag{6.8}$$

$$a_{+-}=[g_+^2f(-\Omega'-\omega_L)+g_-^2f(-\Omega'+\omega_L)]|S_{eg}|^2, \tag{6.9}$$

$$a_{-+}=[g_-^2f(\Omega'-\omega_L)+g_+^2f(\Omega'+\omega_L)]|S_{eg}|^2. \tag{6.10}$$

We note that $a_{kk}\neq0$ if $k=+$ or $k=-$.

With these identifications of the various contributions, Eq. (5.5) can be summarized as

$$\frac{d}{dt}\tilde{\sigma}_0(t)=-\tfrac{1}{2}\sum_{k,l}a_{kl}[\hat{P}_k\tilde{\sigma}_0(t)+\tilde{\sigma}_0(t)\hat{P}_k-2\hat{P}_l\langle k|\tilde{\sigma}_0(t)|k\rangle]-a_{++}\sum_{\pm}\hat{P}_{\pm}\tilde{\sigma}_0(t)\hat{P}_{\mp} \tag{6.11}$$

for the atomic density operator in the interaction picture. Transforming back with Eq. (4.8) then yields the optical Bloch equations for this system. We find

$$\begin{aligned} &i\hbar\frac{d}{dt}\sigma_0(t)=[H_d,\sigma_0(t)]-i\hbar\Gamma\sigma_0(t), \\ &\sigma_0(t)^{\dagger}=\sigma_0(t), \quad \mathrm{Tr}\sigma_0(t)=1, \end{aligned} \tag{6.12}$$

where the Liouville operator Γ is defined by its action on an arbitrary operator ρ according to

$$\begin{aligned} \Gamma\rho=&\tfrac{1}{2}\sum_{k,l}a_{kl}(\hat{P}_k\rho+\rho\hat{P}_k-2\hat{P}_l\langle k|\rho|k\rangle) \\ &+a_{++}\sum_{\pm}\hat{P}_{\pm}\rho\hat{P}_{\mp}. \end{aligned} \tag{6.13}$$

Here the summation runs over all dressed states. This Γ represents the relaxation of the adbond due to single-phonon transitions, and it incorporates the combined phonon-photon processes, as will be explained in Sec. VII.

VII. DIAGRAMS

The structure of the relaxation operator Γ is quite transparent. Every kl combination assumes the form

$$\tfrac{1}{2}(\hat{P}_k\sigma_0+\sigma_0\hat{P}_k-2\hat{P}_l\langle k|\sigma_0|k\rangle)$$

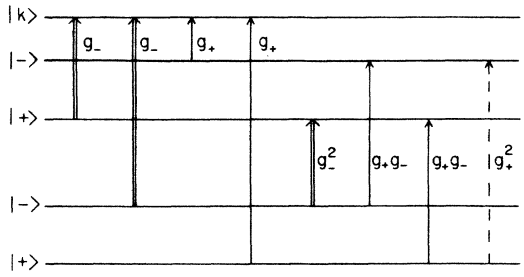

FIG. 2. Illustration of the single-phonon transitions, whenever a $|+\rangle$ or $|-\rangle$ state is involved. The parameters near the arrows are the optical parts of the prefactors as they occur in the transition rates. Without a driving laser, the g_+ vanishes, and hence only the double-arrowed transitions survive. For weak incident fields, the single arrows appear, and only for sufficiently strong fields will the dashed transition $|+\rangle\rightarrow|-\rangle$ be present. We note that there are no transitions in a single doublet. Furthermore, the corresponding downward transitions have the same optical factor but a different $f(\omega)$, e.g., a different temperature dependence. Besides these transitions, we have single-phonon processes between any two bare states $|k\rangle$ and $|l\rangle$, which are obviously independent of the laser parameters.

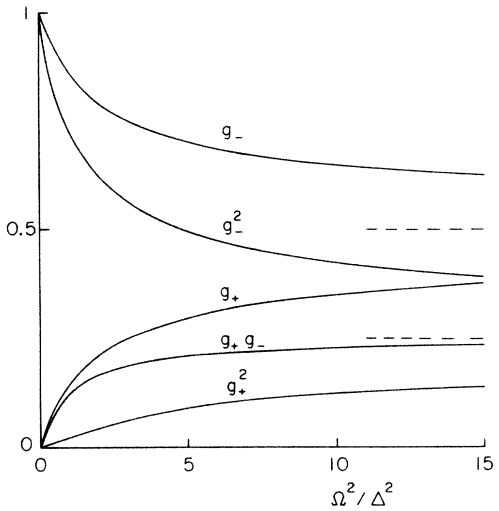

FIG. 3. Optical factors in the transition rates as a function of Ω^2/Δ^2. For strong fields or small detunings, both g_+ and g_- tend to their asymptotic value of $\frac{1}{2}$, which is the upper dotted line, and g_+^2, g_-^2, and g_+g_- will approach $\frac{1}{4}$ in this limit. For weak fields or large detunings, we have $g_-=g_-^2=1$ and $g_+=g_+^2=g_+g_-=0$. For increasing field strengths, the g_-^2 transition will diminish very strongly, in favor of the other three processes between the $|\pm\rangle$ doublets.

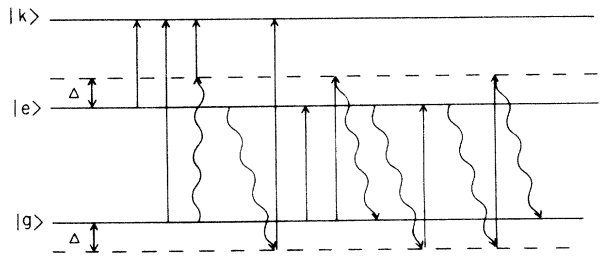

FIG. 4. Single-phonon excitations in the low-intensity limit. For Ω^2 small, we can consider the transitions between the dressed states, as given in Fig. 2, as photon-assisted transitions between the bare states. The diagrams in this picture have the same order as the transitions in Fig. 2. Here every diagram connects two of the three bare states $|k\rangle$, $|e\rangle$, or $|g\rangle$, since we cannot populate a virtual level (dotted lines). A straight line indicates a phonon, and a wiggly arrow is a photon with frequency ω_L. The three double-arrow transitions in Fig. 2 are the three radiationless transitions, so they persist even if we switch off the laser field. The single arrows from Fig. 2 appear to correspond to one-phonon transitions in this diagram, so they arise already for low intensities. The diagram on the right-hand side is a two-photon process, which consequently appears for relatively strong fields only. It is the dashed g_+^2 transition from $|+\rangle$ to $|-\rangle$ in Fig. 2. The phonon-decay processes correspond to the inverse diagrams (reverse the direction of all arrows). In this figure we only draw the phonon excitations, which correspond to the absorption of a phonon by the adbond from the crystal. The third diagram represents the absorption of a photon from the laser field, but all other diagrams give rise to stimulated emissions of photons.

times a constant a_{kl}, and in Sec. VIII it will become clear that this action on σ_0 corresponds to a transition $|k\rangle\rightarrow|l\rangle$ at a rate of a_{kl} times the population of level $|k\rangle$. Therefore, a_{kl} is termed the rate constant or the inverse lifetime of the transition. On the other hand, we actually know which term corresponds to which transition, because every term reflects a single-phonon excitation or decay. The particular transition can then be inferred from the definition (6.5)—(6.10) of the rate constants, since any appearance of a factor $f(\omega)$ displays the occurrence of a single-phonon transition with phonon frequency $|\omega|$. Here a positive argument ω pertains to a downward transition, and $\omega<0$ corresponds to an excitation. Both $f(\omega)$ and $f(-\omega)$ appear for every transition, and the inverse lifetime for a decay is always larger than for an excitation. For zero temperature we have $n(\omega)=0$, so that the upward transitions disappear identically, and we are left with a pure decaying system. The occurring transitions between dressed states with their optical part of the rate constants are pictorially represented in Fig. 2, and in Fig. 3 we plot the explicit dependence on the optical parameters Ω and Δ.

At this stage it is elucidating to consider the limit of a weak driving field. The laser intensity is proportional to Ω^2. For $\Omega^2\approx 0$ we find from Eq. (5.7)

$$g_-\simeq 1,\quad g_+\simeq\frac{\Omega^2}{4\Delta^2} \tag{7.1}$$

for the parameters which determine the transition rates. Furthermore, the dressed states of Fig. 1 approach the bare states, since $\Omega'\simeq\Delta$. If we inspect the transitions of Fig. 2, we can now also consider them as bare-state transitions, where every appearance of a factor g_+ corresponds to one photon. This is illustrated in Fig. 4 for single-phonon excitations. We obtain three diagrams without photons, and five radiation-assisted transitions, which disappear for a zero intensity.

VIII. MATRIX ELEMENTS

Equation (6.12) contains all information about the state of the bounded atom, including its interaction with the phonon field and the radiation. It is a condensed operator equation, but in order to solve it, we have to rewrite it in matrix form. This is easily accomplished if we use the explicit form (6.13) of the damping operator. The equation of motion for the klth matrix element of $\sigma_0(t)$ attains the form

$$\frac{d}{dt}\langle k|\sigma_0(t)|l\rangle=-i(\hat{\omega}_k-\hat{\omega}_l)\langle k|\sigma_0(t)|l\rangle-\tfrac{1}{2}\langle k|\sigma_0(t)|l\rangle\sum_n(a_{kn}+a_{ln})$$
$$+\delta_{kl}\sum_n a_{nk}\langle n|\sigma_0(t)|n\rangle-a_{++}\langle k|\sigma_0(t)|l\rangle\sum_{\pm}\delta_{k\pm}\delta_{l\mp}\,. \tag{8.1}$$

Now we can distinguish two cases. First, for $k \neq l$ and k and l not both equal to $+$ or $-$ we find

$$\frac{d}{dt}\langle k \mid \sigma_0(t) \mid l \rangle = [-i(\hat{\omega}_k - \hat{\omega}_l) - \tfrac{1}{2}(A_k + A_l)] \times \langle k \mid \sigma_0(t) \mid l \rangle , \tag{8.2}$$

where we introduced the abbreviation

$$A_k = \sum_n a_{kn} . \tag{8.3}$$

Equation (8.2) is an equation for a single coherence of $\sigma_0(t)$, and we note that its time evolution decouples from the evolution of the other matrix elements. The solution is

$$\langle k \mid \sigma_0(t) \mid l \rangle = e^{-i(\hat{\omega}_k - \hat{\omega}_l)t} e^{-(A_k + A_l)t/2} \times \langle k \mid \sigma_0(0) \mid l \rangle \tag{8.4}$$

for a given initial state $\sigma_0(0)$. For $t \gg (A_k + A_l)^{-1}$ we find $\langle k \mid \sigma_0(t) \mid l \rangle = 0$ for any initial state $\sigma_0(0)$. This justifies the random-phase approximation with respect to dressed states and in the long-time limit. Since the coherences between dressed states vanish, they do not disappear with respect to the bare states, as is commonly assumed in a random-phase approximation.

For $k = l$ we obtain the master equation

$$\frac{d}{dt} n_k(t) = -A_k n_k(t) + \sum_l a_{lk} n_l(t) , \tag{8.5}$$

where we have denoted the population of the kth level by

$$n_k(t) = \langle k \mid \sigma_0(t) \mid k \rangle . \tag{8.6}$$

Equation (8.5) involves the populations of all levels, but it does not couple with the coherences. This shows that a master-equation approach is only correct with respect to the dressed states, since transformation of Eq. (8.5) to bare states involves coherences. In the bare-state basis we have to include all matrix elements simultaneously, which is a cumbersome procedure.

Equation (8.5) for the populations is a simple set of linear first-order differential equations with time-independent coefficients, and it can be solved easily for any configuration of states $\mid k \rangle$. The set (8.5) has to be accompanied by the normalization

$$\sum_k n_k(t) = \mathrm{Tr}\sigma_0(t) = 1 . \tag{8.7}$$

The structure of Eq. (8.5) is obvious. The population of $\mid k \rangle$ decays exponentially with an inverse lifetime A_k due to decay and/or excitation to all other levels, and it is modified by the gain term $a_{lk} n_l(t)$ from every other level $\mid l \rangle$. This shows that a $\mid k \rangle \rightarrow \mid l \rangle$ transition occurs at a rate $a_{kl} n_k(t)$, as already mentioned in Sec. VII. Furthermore, level $\mid k \rangle$ decays with a total rate $A_k n_k(t)$, and the coherence between $\mid k \rangle$ and $\mid l \rangle$ decays with $\frac{1}{2}(A_k + A_l)$. This also clarifies, at that stage, the arbitrary factor $\frac{1}{2}$, which was separated from the overall factors in Eq. (5.5).

IX. DECAY OF DRESSED STATES

The rate constants a_{kl} for every transition $\mid k \rangle \rightarrow \mid l \rangle$ between dressed states are defined in Eqs. (6.5)–(6.10). They are also defined for k or l equal to e or g in Eq. (6.5). We now make a slight approximation in the level-distance dependence of the constants by assuming that $f(\omega)$ does not vary significantly over one $\mid \pm \rangle$ doublet. This is exact for weak fields and perfect resonance. Then we can express the rate constants entirely in the bare-atom transition constants (6.5) and the laser parameters $g_\pm$. We obtain

$$a_{\pm l} = g_\mp a_{el} + g_\pm a_{gl}, \quad l \neq \pm \tag{9.1}$$

$$a_{k\pm} = g_\mp a_{ke} + g_\pm a_{kg}, \quad k \neq \pm \tag{9.2}$$

$$a_{++} = a_{--} = g_+ g_- (a_{eg} + a_{ge}) , \tag{9.3}$$

$$a_{+-} = g_+^2 a_{ge} + g_-^2 a_{eg} , \tag{9.4}$$

$$a_{-+} = g_-^2 a_{ge} + g_+^2 a_{eg} . \tag{9.5}$$

In analogy with the definition (8.3) for the total decay constant A_k of a dressed state, we now define

$$A_k = \sum_{n=\text{bare}} a_{kn}, \quad k = \text{bare} \tag{9.6}$$

which would be the relaxation constant for the bare state $\mid k \rangle$ if the laser field were not present. Now it can be proven immediately from Eqs. (9.1)–(9.5) that the definition (9.6) is identical to

$$A_k = \sum_{n=\text{dressed}} a_{kn}, \quad k = \text{bare} \tag{9.7}$$

provided that we define $a_{g\pm}$ and $a_{e\pm}$ as in Eq. (9.2). This remarkable result states that the decay constant for the bare state $\mid k \rangle$, including $k = e$ and $k = g$, is unaffected by the presence of the laser.

The decay of the dressed states $\mid \pm \rangle$ can now easily be expressed in terms of the rate constants of the bare levels $\mid e \rangle$ and $\mid g \rangle$. The result is

$$A_\pm = g_\mp A_e + g_\pm A_g . \tag{9.8}$$

Here A_e and A_g are defined by Eq. (9.6), and they are independent of optical parameters. The $g_\pm$ factors enter into Eq. (9.8), so that the decay of the dressed states does depend on Ω and Δ. From $g_+ + g_- = 1$ it follows that

$$A_+ + A_- = A_e + A_g , \tag{9.9}$$

which is not so obvious, since $A_+ + A_-$ or $A_e + A_g$ has no direct physical interpretation. Recall that the loss rate from the doublet $\mid \pm \rangle$ equals $A_+ n_+(t) + A_- n_-(t)$.

X. STEADY STATE

The master equation (8.5) can be solved immediately for any initial set of populations $n_k(0)$. The transient behavior of the solution is however trivial, since we have a pure exponentially decaying system. Furthermore, it is experimentally not feasible to prepare the system in a well-defined initial state. Due to the relaxation, however, every $\sigma_0(0)$ will evolve to a steady state $\bar{\sigma}$, defined as

$$\bar{\sigma}=\lim_{t\to\infty}\sigma_0(t)\ , \tag{10.1}$$

which is not necessarily unique. Similarly, we denote $n_k(\infty)$ by $\bar{n}_k$. In this limit, the master equation reduces to

$$A_k\bar{n}_k=\sum_{l=\text{dressed}}a_{lk}\bar{n}_l\ , \tag{10.2}$$

or equivalently

$$\sum_{l=\text{dressed}}(\bar{n}_l a_{lk}-\bar{n}_k a_{kl})=0\ . \tag{10.3}$$

We will now derive some salient features of the steady-state solution. We recall that the coherences vanish with respect to the dressed states, so that $\bar{\sigma}$ is given by

$$\bar{\sigma}=\sum_{k=\text{dressed}}\bar{n}_k\hat{P}_k\ , \tag{10.4}$$

in terms of the solution of Eq. (10.3) and the projectors $\hat{P}_k$ on the dressed states. With the definition of the $|\pm\rangle$ states in Eqs. (3.10) and (3.11), we can transform the density matrix $\bar{\sigma}$ to the bare-state representation, which yields

$$\bar{\sigma}=\sum_{k=\text{bare}}\bar{n}_k P_k+\frac{\Omega}{2\Omega'}(\bar{n}_+-\bar{n}_-)(|e\rangle\langle g|+|g\rangle\langle e|)\ . \tag{10.5}$$

Here $\bar{n}_k$ is the same as $\bar{n}_k$ in Eq. (10.4) for $k\neq e,g$, and the relation between the populations $\bar{n}_e$, $\bar{n}_g$, and $\bar{n}_\pm$ is explicitly

$$\bar{n}_e=g_-\bar{n}_++g_+\bar{n}_-\ , \tag{10.6}$$

$$\bar{n}_g=g_+\bar{n}_++g_-\bar{n}_-\ . \tag{10.7}$$

Equation (10.5) shows that a nonvanishing coherence $\langle e|\bar{\sigma}|g\rangle$ appears in the bare-state representation. With the aid of Eqs. (10.6) and (10.7), we find the relation

$$\bar{n}_+-\bar{n}_-=\frac{\bar{n}_g-\bar{n}_e}{g_+-g_-}\ , \tag{10.8}$$

and with the expression (5.7) for $g_\pm$, we obtain for the coherence

$$\langle e|\bar{\sigma}|g\rangle=\frac{\Omega}{2\Delta}(\bar{n}_e-\bar{n}_g)\ . \tag{10.9}$$

In the absence of a laser we have $\Omega=0$, and $\langle e|\bar{\sigma}|g\rangle$ vanishes.

Relations (10.6) and (10.7) can be inverted to express $\bar{n}_\pm$ in terms of $\bar{n}_e$ and $\bar{n}_g$. If we subsequently use Eq. (9.8) for the relation between the rate constants, we find

$$A_+\bar{n}_++A_-\bar{n}_-=A_e\bar{n}_e+A_g\bar{n}_g\ . \tag{10.10}$$

This identity expresses that the total loss rate of $|\pm\rangle$ equals the sum of the loss rates of $|e\rangle$ and $|g\rangle$, as could be expected.

An advantage of the application of dressed states is that the master equation (10.3) has a simple form. With the relations of Sec. IX, we can transform Eq. (10.3) to its bare-state equivalent. We find

$$\sum_{l=\text{bare}}\bar{n}_l a_{lk}=\begin{cases}A_k\bar{n}_k, & k\neq e,g\\ A_g\bar{n}_g+\dfrac{\Omega^2}{4\Delta^2}(A_e+A_g)(\bar{n}_g-\bar{n}_e), & k=g\\ A_e\bar{n}_e-\dfrac{\Omega^2}{4\Delta^2}(A_e+A_g)(\bar{n}_g-\bar{n}_e), & k=e\end{cases} \tag{10.11}$$

where all quantities pertain to bare-state properties. This result is remarkably simple also. The laser only modifies the master equation for $k=g$ and $k=e$ in the form of an additional term, and the optical parameters only appear in the combination Ω^2/Δ^2. The set (10.11) couples, however, between all k values, and therefore the extra terms affect all populations $\bar{n}_k$. We notice that the right-hand side of the master equation for $k=e$ and $k=g$ contains the same radiative contribution. If we add the two equations, we are left with

$$\sum_{k=\text{bare}}\bar{n}_k(a_{kg}+a_{ke})=A_g\bar{n}_g+A_e\bar{n}_e\ , \tag{10.12}$$

and the laser has disappeared completely in this combination.

Let us now consider a specific situation. Suppose that the ground state $|g\rangle$ is the lowest state and that its separation from every other level is larger than the Debye frequency. Then the single-phonon transition rates from and to $|g\rangle$ can be neglected in comparison with the radiative coupling to $|e\rangle$. From Eq. (10.11) for $k=g$, it then follows that

$$\bar{n}_g=\bar{n}_e\ , \tag{10.13}$$

and the master equation reduces to

$$\sum_{l=\text{bare}}\bar{n}_l a_{lk}=A_k\bar{n}_k\ , \tag{10.14}$$

for every bare state $|k\rangle$. This is, however, the master equation in the absence of the laser, and it might seem that the laser has no effect at all. Such is not the case. The master equation always provides one superfluous equation, which allows us to impose the normalization (8.7) on the solution. Now we have the restriction $\bar{n}_e=\bar{n}_g$, so Eq. (8.7) should be replaced by the constraint

$$2\bar{n}_e+\sum_{k\neq e,g}\bar{n}_k=1\ . \tag{10.15}$$

This proves that for this specific configuration the distribution of population over the states is purely thermal for $k\neq g$, e.g., independent of the laser intensity. The normalization (10.15) indicates that we can ignore the ground state completely, provided that we take into account that there is a population equal to $\bar{n}_e$ missing. The desorption rate is determined by the populations of the upper levels, which implies that the presence of the laser enhances the desorption. Indeed, population which would be trapped in the ground state is now continuously pumped upwards to the desorptive states.

XI. SIMPLE THREE-LEVEL EXAMPLE

In order to demonstrate the applicability of our approach, we elaborate an example. Suppose that we have, beside the levels $|e\rangle$ and $|g\rangle$, one other level $|\eta\rangle$. Three independent rate equations are then

$$\bar{n}_e a_{eg} + \bar{n}_\eta a_{\eta g} = A_g \bar{n}_g + \frac{\Omega^2}{4\Delta^2}(A_e + A_g)(\bar{n}_g - \bar{n}_e) , \tag{11.1}$$

$$\bar{n}_e a_{e\eta} + \bar{n}_g a_{g\eta} = A_\eta \bar{n}_\eta , \tag{11.2}$$

$$\bar{n}_e + \bar{n}_g + \bar{n}_\eta = 1 , \tag{11.3}$$

which are Eq. (10.11) for $k=g$, $k=\eta$ and the normalization. If we add Eq. (11.1) to Eq. (10.11) for $k=e$, we obtain Eq. (11.2). The solution of the set (11.1)—(11.3) is easily found. For $\bar{n}_\eta$ we obtain

$$\bar{n}_\eta = \left[a_{eg}a_{g\eta} + a_{ge}a_{e\eta} + a_{g\eta}a_{e\eta} + \frac{\Omega^2}{4\Delta^2}(A_e + A_g)(a_{e\eta} + a_{g\eta}) \right] \times \left[a_{eg}A_\eta + a_{g\eta}A_e + a_{\eta e}A_g + a_{e\eta}a_{\eta g} + a_{ge}a_{e\eta} + a_{\eta g}a_{ge} + \frac{\Omega^2}{4\Delta^2}(A_e + A_g)(a_{e\eta} + a_{g\eta} + 2A_\eta) \right]^{-1} , \tag{11.4}$$

and similar expressions hold for $\bar{n}_e$ and $\bar{n}_g$. This result displays explicitly the dependence on the optical parameter Ω^2/Δ^2 and the laser-independent inverse lifetimes.

If we now set $\omega_\eta - \omega_g > \omega_D$ and $\omega_e - \omega_g > \omega_D$, Eq. (11.4) reduces to

$$\bar{n}_\eta = \frac{a_{e\eta}}{a_{e\eta} + 2a_{\eta e}} , \tag{11.5}$$

and the populations $\bar{n}_e$ and $\bar{n}_g$ are

$$\bar{n}_e = \bar{n}_g = \frac{a_{\eta e}}{a_{e\eta} + 2a_{\eta e}} . \tag{11.6}$$

This shows that in this limit the dependence on the laser intensity indeed vanishes, as stated in general in Sec. X. Without a laser, the stationary state for this limit becomes

$$\bar{n}_\eta = \bar{n}_e = 0, \quad \bar{n}_g = 1 . \tag{11.7}$$

Hence the laser sustains a finite population of the states $|e\rangle$ and $|\eta\rangle$, which have a finite desorption rate.

XII. CONCLUSIONS

We have studied the interaction of a physisorbed atom with strong coherent radiation. The mechanisms of spontaneous phonon transitions of the vibrational atomic bond and the photon absorptions and stimulated emissions all give rise to a redistribution of the level populations. The thermal relaxation, due to phonon-exchange reactions, drives the system towards equilibrium with the phonon reservoir, but the irradiance tends to maintain a temperature gradient between the adbond and the phonon field. This can be understood from the underlying photon-phonon exchange reactions via the adbond, as pictorially displayed in Fig. 4. Since the absorption rate does not necessarily equal the rate of stimulated emission, a net photon absorption rate will remain. For strong fields this simple picture does not apply anymore, and we have to consider multiphoton processes as well. This was accomplished by the introduction of the dressed states, which are schematically presented in Fig. 1. The Hamiltonian of the atom plus the laser, including the interaction, is diagonal with respect to these dressed states. The interaction with the phonon field was restricted to single-phonon transitions, which were assumed to be dominant. For situations where this is not the case, higher-order processes can easily be included. In practical situations only two, not necessarily adjacent, levels will be coupled resonantly by the laser. The generic idea is to drive a $|g\rangle \rightarrow |e\rangle$ transition, with $|g\rangle$ as one of the low-lying states and $|e\rangle$ as close as possible to the continuum. This configuration prohibits resonant coupling of other transitions and gives a maximum enhancement of the desorption. Besides that, the optical frequency will be larger than ω_D, and consequently the direct crystal-heating is absent. Hence, our two-level and adiabatic approach can be regarded as quite general.

The dressed states appear to be a convenient basis set for the derivation of the optical Bloch equations for this configuration. The master equation was obtained by taking the matrix elements of the full operator equation, and it was shown that the populations obey the Pauli equation. The coefficients involve, however, the optical parameters Ω and Δ, and hence the lifetimes of the transitions depend on the properties of the driving field. Furthermore, it was shown that the coherences with respect to the dressed states decay exponentially to zero. The master equation in the bare-state representation and in the steady state was obtained by applying the relation between dressed states and the bare states. We found that the master equation greatly resembles the radiationless equations, and that the presence of the laser could be incorporated entirely by the addition of a few terms.

The general theory was exemplified by the simple case of a three-level system. We achieved the explicit steady-state solution for the bare-state populations, and it was pointed out that the system can be desorptive due to the continuous optical excitation, whereas the bond would be completely in its lower, nondesorbing state in the absence of the irradiance.

ACKNOWLEDGMENTS

This research was supported by the Air Force Office of Scientific Research (AFOSC), United States Department of the Air Force, under Contract No. F49620-86-C-0009, by the Office of Naval Research (ONR), United States Department of the Navy, and by the National Science Foundation, under Grant No. CHE-85-19053.

[1]B. J. Garrison, D. J. Diestler, and S. A. Adelman, J. Chem. Phys. **67**, 4317 (1977).
[2]G. S. De, U. Landman, and M. Rasolt, Phys. Rev. B **21**, 3256 (1980).
[3]S. Efrima, K. F. Freed, C. Jedrzejek, and H. Metiu, Chem. Phys. Lett. **74**, 43 (1980).
[4]C. Jedrzejek, K. F. Freed, S. Efrima, and H. Metiu, Chem. Phys. Lett. **79**, 227 (1981).
[5]C. Jedrzejek, K. F. Freed, S. Efrima, and H. Metiu, Surf. Sci. **109**, 191 (1980).
[6]S. Efrima, C. Jedrzejek, K. F. Freed, E. Hood, and H. Metiu, J. Chem. Phys. **79**, 2436 (1983).
[7]M. S. Slutsky and T. F. George, Chem. Phys. Lett. **57**, 474 (1978).
[8]J. Lin, X. Y. Huang, and T. F. George, Z. Phys. B **48**, 355 (1982).
[9]Z. W. Gortel, H. J. Kreuzer, P. Piercy, and R. Teshima, Phys. Rev. B **27**, 5066 (1983).
[10]J. Lin, X. Y. Huang, and T. F. George, J. Vac. Sci. Technol. B **3**, 1525 (1985).
[11]Z. W. Gortel, P. Piercy, R. Teshima, and H. J. Kreuzer, Surf. Sci. **165**, L12 (1986).
[12]J. Lin and T. F. George, Surf. Sci. **100**, 381 (1980).
[13]J. Lin and T. F. George, J. Phys. Chem. **84**, 2957 (1980).
[14]G. Korzeniewski, E. Hood, and H. Metiu, J. Vac. Sci. Technol. **20**, 594 (1982).
[15]A. C. Beri and T. F. George, J. Chem. Phys. **78**, 4288 (1983).
[16]A. C. Beri and T. F. George, Z. Phys. B **60**, 73 (1985).
[17]A. C. Beri and T. F. George, J. Vac. Sci. Technol. B **3**, 1529 (1985).
[18]X. Y. Huang, T. F. George, and J. M. Yuan, J. Opt. Soc. Am. B **2**, 985 (1985).
[19]A. C. Beri and T. F. George, J. Chem. Phys. **83**, 2482 (1985).
[20]A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Theory of Lattice Dynamics in the Harmonic Approximation*, Suppl. 3 of *Solid State Physics* (Academic, New York, 1971).
[21]J. A. Beswick and J. Jortner, J. Chem. Phys. **68**, 2277 (1978).
[22]L. Allen and J. H. Eberly, *Optical Resonance and Two-Level Atoms* (Wiley, New York, 1975).
[23]S. Stenholm, *Foundations of Laser Spectroscopy* (Wiley, New York, 1984).
[24]H. F. Arnoldus and G. Nienhuis, J. Phys. B **16**, 2325 (1983).
[25]C. Cohen-Tannoudji, in *Frontiers in Laser Spectroscopy*, Proceedings of the 27th Les Houches Summer School, edited by R. Balian, S. Haroche, and S. Liberman (North-Holland, Amsterdam, 1977).
[26]G. Nienhuis, Acta Phys. Pol. A **61**, 235 (1982).
[27]H. J. Carmichael and D. F. Walls, J. Phys. B **9**, 1199 (1976).
[28]E. T. Jaynes and F. W. Cummings, Proc. IEEE **51**, 89 (1963).
[29]W. H. Louisell, *Quantum Statistical Properties of Radiation* (Wiley, New York, 1973).
[30]J. Dalibard, J. Dupont-Roc, and C. Cohen-Tannoudji, J. Phys. (Paris) **43**, 1617 (1982).
[31]J. Dalibard, J. Dupont-Roc, and C. Cohen-Tannoudji, J. Phys. (Paris) **45**, 637 (1984).
[32]R. W. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).
[33]R. W. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Britten, B. Downs, and J. Downs (Interscience, New York, 1961), Vol. III, p. 106ff.