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Laser heating of a transparent crystal via adsorbed atoms

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A coated surface of a crystal is irradiated by intense infrared light. The optically active atomic bonds absorb photons from the laser field, and the subsequent spontaneous decay goes together with emissions of phonons into the crystal. This photon-to-phonon conversion results in an energy flux into the crystal. An equation for this flux is derived from the master equation for the level populations of the dressed atomic states. The saturation limit is discussed, and the general theory is illustrated with two examples. Furthermore, it is outlined with qualitative arguments that the quantum yield of photodesorption is not sensitive to the laser power.

I. INTRODUCTION

The thermal desorption rate of atoms, which are bound to the surface of a crystal and occupy a series of vibrational states, can be very low. Irradiation with resonant infrared laser light can enhance the desorption considerably,[1-6] especially at low temperatures. Then the thermal relaxation (coupling to the phonon field of the crystal) will tend to confine the atoms to the low-lying nondesorptive vibrational levels, but the laser will sustain a continuous excitation of the system. The balance between the thermal decay and the coherent excitation determines the level populations. Since atoms in high-lying states can more easily desorb into a continuum state through a resonant one-phonon transition than atoms in low-lying states, the driving laser will increase the desorption rate. The effect will be most pronounced as the optical frequency ω_L is close to an atomic-bond transition. However, the desorption rate as a function of ω_L is not tantamount to the optical-absorption profile, due to the competing thermal relaxation. Indeed, an excited bond might decay to a lower state together with an emission of a phonon into the crystal. This process can be considered as a photon-to-phonon conversion, with a heat flow into the crystal as a net result.[7,8] Hence, the quantum yield of photodesorption will be diminished strongly by thermal relaxation. Experimental values acquire an order of magnitude of at most 10^{-2}, which implies that more than 99% of the absorbed energy ends up in the phonon field.[2] Conversely, for a crystal which is transparent at frequency ω_L, a dye coating on the surface can provide a medium for an efficient laser heating of the solid.

In this paper we derive a microscopic equation for the energy flux into the crystal. It contains the laser power and frequency, the temperature of the crystal, and the transition matrix elements of the atomic potential well as parameters. The results can be applied as the source terms for the macroscopic diffusion equation, which describes the temperature distribution in the crystal.[9,10] Our work extends earlier treatments[7,8] in that we allow the irradiance to be arbitrarily intense, which will enable us to study, for instance, saturation effects.

II. POPULATIONS OF DRESSED STATES

The vibrational eigenstates of the atomic bond will be denoted by $|k\rangle$, their populations by $n_k(t)$, and the energy eigenvalues by $\hbar\omega_k$. The strong incident radiation will be assumed to couple only resonantly a ground state $|g\rangle$ and an excited state $|e\rangle$, with $\omega_e-\omega_g=\omega_0>0$. We indicate the detuning with the driving field by $\Delta=\omega_L-\omega_0$, and the coupling strength is expressed in the Rabi frequency $\Omega=|\mathbf{E}_0\cdot\boldsymbol{\mu}|/\hbar$. Here, $\mathbf{E}_0$ is the amplitude of the electric component of the incident field, and $\boldsymbol{\mu}$ is the electric dipole moment of the transition. The parameter Ω^2 will be referred to as the laser intensity, since it is proportional to E_0^2. The diagonalization of the Hamiltonian of the driven atomic bond is easily accomplished, and it amounts to a transformation of the bare states $|e\rangle$, $|g\rangle$ (eigenstates for $\Omega^2=0$) into the dressed states $|+\rangle$, $|-\rangle$.[11] This is illustrated in Fig. 1. The eigenvalues are

$$\hat{\omega}_{\pm}=\tfrac{1}{2}(\omega_e+\omega_g+\omega_L)\mp\tfrac{1}{2}\,\mathrm{sgn}(\Delta)(\Omega^2+\Delta^2)^{1/2}\ , \tag{2.1}$$

with $\mathrm{sgn}(\Delta)$ representing the sign of Δ. We indicate by $\hbar\hat{\omega}_k$ an eigenvalue of the dressed state $|k\rangle$.

The interaction with the phonon field of the crystal can now be considered as a coupling between dressed states.[12] We suppose that the separations between adjacent levels are smaller than the Debye frequency ω_D, which implies that we can omit multiphonon processes. The coupling strengths are governed by the matrix elements $\langle k|S|l\rangle$ of the atomic operator $S=dV/dz$, which is the derivative of the potential well in the direction perpendicular to the surface. In a previous paper[11] we derived an equation for the populations of the dressed states, as they are determined by the single-phonon relaxation constants a_{kl}. With a_{kl} the inverse lifetime of the transition $|k\rangle\rightarrow|l\rangle$, this master equation reads

$$\frac{d}{dt}n_k(t)=\sum_l\,[n_l(t)a_{lk}-n_k(t)a_{kl}]\ . \tag{2.2}$$

Here the summation runs over the dressed states $|+\rangle, |-\rangle$ and the bare states $|k\rangle$, with $k\neq e,g$, since for $k\neq e,g$ a dressed state is identical to a bare state. In

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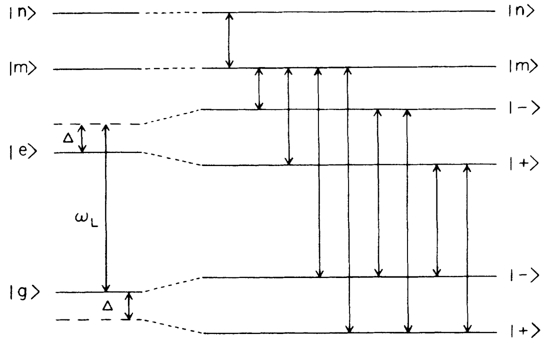

FIG. 1. The laser field couples the atomic levels $|e\rangle$ and $|g\rangle$. Bare-state transitions occur as radiationless or laser-assisted single-phonon excitations or decays. Diagonalization of the dipole interaction transforms the set $|e\rangle, |g\rangle$ into a ladder of dressed states $|+\rangle, |-\rangle$, where the doublets are separated by the photon energy $\hbar\omega_L$. The distance between $|+\rangle$ and $|-\rangle$ in a single doublet equals $(\Delta^2+\Omega^2)^{1/2}$, and the absolute position of the upper set of states is $\hat{\omega}_\pm$ from Eq. (2.1). The occurring single-phonon transitions are indicated. The state $|m\rangle$ couples in four ways with the ladder of dressed states, where each transition has a different phonon energy. There are four couplings between the two doublets, but $|+\rangle$ to $|-\rangle$ and $|-\rangle$ to $|+\rangle$ transitions in a single doublet are not present. The unperturbed states $|m\rangle$ and $|n\rangle$ couple only through a resonant one-phonon process. The transitions of $|n\rangle$ to the ladder of dressed states are suppressed in this picture.

the derivation of Eq. (2.2) we adopted the secular approximation, which asserts that the level separations, and especially $(\Omega^2+\Delta^2)^{1/2}$, are sufficiently larger than the damping constants. Hence our approach applies to situations where the detuning or the laser power Ω^2 is large. This case can be considered to be complementary to the weak-field limit of Refs. 7 and 8.

In the expressions for the relaxation constants a_{kl}, we can separate the dependence on the optical parameters Ω and Δ from the pure thermal part. It appears that Ω and Δ only enter the expressions for the lifetimes in the combination $g_\pm$, defined by

$$g_\pm=\tfrac{1}{2}[1\mp(1+\Omega^2/\Delta^2)^{-1/2}] \ . \tag{2.3}$$

Hence, the distribution of population over the dressed states is governed by the single dimensionless optical parameter Ω^2/Δ^2. In the strong-field limit $\Omega^2/\Delta^2\to\infty$, both g_+ and g_- tend to the finite asymptotic value of $\frac{1}{2}$, which indicates saturation.

The temperature-dependent part of the relaxation constants can be expressed in the field-free inverse lifetimes for transitions between bare states. In a simple Debye model the rate constants attain the form

$$a_{kl}=\frac{v'}{2\pi\hbar Mc^3}\,|\langle k\,|S\,|\,l\rangle|^2\frac{\omega}{1-\exp(-\hbar\omega/k_BT)} \times\Theta(\omega_D-|\omega|) \ , \tag{2.4}$$

where v' is the volume of a unit cell, M is the mass of a crystal atom, c is the speed of sound, k_B is Boltsmann's constant, T is the temperature of the solid, Θ is the Heaviside step function, and $\omega=\omega_k-\omega_l$ is the level separation whose absolute value equals the phonon energy in a transition. The genuine impact of Eq. (2.4) on the thermal redistribution of level populations originates from its dependence on the sign of ω. A positive value of ω implies $\omega_k>\omega_l$, and hence the transition $|k\rangle\to|l\rangle$ is a decay of the system, whereas $\omega<0$ reflects a thermal excitation of the same transition. For any two levels $|k\rangle, |l\rangle$, with $\omega_k>\omega_l$, both phonon absorption (excitation, a_{lk}) and phonon emission into the crystal (decay, a_{kl}) occurs, and it follows from Eq. (2.4) that $a_{kl}\gg a_{lk}$.

With these preliminary remarks, we can now write down the inverse lifetimes. If both levels $|k\rangle$ and $|l\rangle$ are each unequal to $|+\rangle$ or $|-\rangle$, the rate constant is simply a_{kl} from Eq. (2.4). For laser-assisted transitions we have[11]

$$a_{\pm k}=g_\mp a_{ek}+g_\pm a_{gk} \ , \tag{2.5}$$

$$a_{k\pm}=g_\mp a_{ke}+g_\pm a_{kg} \ , \tag{2.6}$$

for $|k\rangle\neq|+\rangle, |-\rangle$. The pure dressed-state transitions are governed by the four rate constants

$$a_{\pm\mp}=g_\pm^2 a_{ge}+g_\mp^2 a_{eg} \ , \tag{2.7}$$

$$a_{\pm\pm}=g_+g_-(a_{ge}+a_{eg}) \ . \tag{2.8}$$

A transition $|+\rangle\to|+\rangle$ or $|-\rangle\to|-\rangle$ obviously does not alter the population of a dressed state. In the master equation (2.2), the a_{kk} contributions vanish indeed, but we will see in the next section that the $|+\rangle\to|+\rangle$ and $|-\rangle\to|-\rangle$ transitions do contribute to the energy transportation, as can be anticipated from Fig. 1. Therefore, we cannot discard these transitions in general. Furthermore, we note that a rate constant gains a contribution from two distinct processes, whenever a $|+\rangle$ or $|-\rangle$ state is involved. This is again clear from Fig. 1.

With Eqs. (2.3)—(2.8) the explicit dependence of the coefficients a_{kl} on the laser parameters, the temperature, and the properties of the potential well is tracked down completely. For any configuration of states, the master equation (2.2), accompanied by the normalization

$$\sum_k n_k(t)=1 \ , \tag{2.9}$$

can be solved immediately.

III. ENERGY FLUX

From the master equation it follows that a transition $|k\rangle\to|l\rangle$ occurs at a rate $n_k(t)a_{kl}$ (number of transitions per unit of time). Every decay or excitation corresponds to an absorption or emission of a phonon by the crystal, with an energy equal to the level distance $\hbar(\hat{\omega}_k-\hat{\omega}_l)$. If we write $\hbar(\hat{\omega}_k-\hat{\omega}_l)$ for the gain of energy of the crystal in a single $|k\rangle\to|l\rangle$ transition, then the distinction between absorption and emission is included in the sign of $\hat{\omega}_k-\hat{\omega}_l$. Care should be exercized in the transitions to and from the dressed states $|+\rangle, |-\rangle$ since these transitions involve two diagrams with different phonon energy. Therefore, these rates should be divided accordingly, and for the gain of energy the contributions from the two doublets in Fig. 1 should be distinguished. It is immediately clear which part of the rate constant corresponds to a specific transition, since the argument $\omega_k - \omega_l$ in a_{kl} equals the phonon frequency. These notions yield the formal expression for the energy flux into the crystal (absorbed energy per unit of time)

$$\frac{dW}{dt} = \sum_{kl} \hbar(\hat{\omega}_k - \hat{\omega}_l) n_k(t) a_{kl} \ , \tag{3.1}$$

where the summation runs over all diagrams of Fig. 1, and $\hbar(\hat{\omega}_k - \hat{\omega}_l)$ is the appropriate phonon energy.

The double sum is easily evaluated after substitution of the explicit expressions (2.4)—(2.8) for the relaxation constants, Eq. (2.1) for the energies of the dressed states, and after application of the master equation. We obtain

$$\begin{aligned} \frac{dW}{dt} = &-\sum_{k} \hbar\hat{\omega}_k \frac{d}{dt} n_k(t) \\ &+\hbar\omega_L \sum_{k\neq\pm} \{a_{kg} n_k(t) - a_{gk}[g_+ n_+(t) + g_- n_-(t)]\} \\ &+\hbar\omega_L \{a_{eg}[g_- n_+(t) + g_+ n_-(t)] \\ &\qquad - a_{ge}[g_+ n_+(t) + g_- n_-(t)]\} \ . \end{aligned} \tag{3.2}$$

Here the summations run over the bare states $|k\rangle \neq |e\rangle, |g\rangle$, and over $|+\rangle, |-\rangle$, but no longer over diagrams. The right-hand side of Eq. (3.2) contains the bare-states inverse lifetimes a_{kl}, the optical parameters $g_\pm$, and the populations $n_k(t)$ of the dressed states. This implies that dW/dt is expressed entirely in known parameters and in the solution $n_k(t)$ of the master equation. The expressions in curly brackets are combinations of gain and loss terms pertaining to the same transition, which is reminiscent of the structure of the master equation.

IV. STEADY STATE

After a transient time of the order of a_{kl}^{-1}, the system will approach a steady state, due to the phonon relaxation. The populations tend to their long-time limit

$$\bar{n}_k = \lim_{t\to\infty} n_k(t) \ , \tag{4.1}$$

and the master equation reduces to

$$\sum_{l} \bar{n}_l a_{lk} = \sum_{l} \bar{n}_k a_{kl} \ . \tag{4.2}$$

In the energy equation (3.2), the first term on the right-hand side disappears, and the energy flux dW/dt acquires a time-independent value in this limit.

In order to reveal more clearly the structure of the steady-state energy flux, we transform Eq. (3.2) to its bare-state equivalent. Due to the fact that the coherences with respect to the dressed states vanish in the long-time limit, the populations of the excited state and the ground state can be expressed in $\bar{n}_+$ and $\bar{n}_-$ according to

$$\bar{n}_e = g_{--}\bar{n}_+ + g_+\bar{n}_- \ , \tag{4.3}$$

$$\bar{n}_g = g_+\bar{n}_+ + g_-\bar{n}_- \ . \tag{4.4}$$

Then Eq. (3.2) for $t \to \infty$ assumes the transparent form

$$\frac{dW}{dt} = \hbar\omega_L \sum_{k=(\text{bare states})} (\bar{n}_k a_{kg} - \bar{n}_g a_{gk}) \ . \tag{4.5}$$

Notice that the optical parameters $g_\pm$ have vanished completely in this representation. They only enter the energy flux through the populations $\bar{n}_k$ of the states, which are affected by the laser field. The summation in Eq. (4.5) is a gain-loss balance for the population of the ground state $|g\rangle$. The first term (gain) reflects that a photon-absorption rate is maintained by a permanent driving of the transition $|g\rangle \to |e\rangle$ by the laser. The subsequent thermal relaxation to the ground state is accompanied with phonon emissions into the crystal, which yields the net energy flux. Conversely, the second term (loss) corresponds to stimulated photon emissions in $|e\rangle \to |g\rangle$ transitions. Then the crystal should provide the energy for the subsequent thermal redistribution.

The summation over all bare states in Eq. (4.5) can be eliminated with the master equation (4.2) and the relations (4.3) and (4.4) between bare-state and dressed-state populations. Recall that Eq. (4.2) pertains to dressed states, whereas the summation in Eq. (4.5) runs over bare states. The result can be cast in the remarkably simple form

$$\frac{dW}{dt} = \hbar\omega_L \frac{\Omega^2}{4\Delta^2}(A_g + A_e)(\bar{n}_g - \bar{n}_e) \ . \tag{4.6}$$

The optical prefactor arises from the combination

$$\frac{g_- g_+}{(g_- - g_+)^2} = \frac{\Omega^2}{4\Delta^2} \ , \tag{4.7}$$

and the total inverse lifetime A_k of a state $|k\rangle$ is defined as

$$A_k = \sum_{l=(\text{bare states})} a_{kl} \ . \tag{4.8}$$

The photon-absorption (-emission) rate is proportional to $\bar{n}_g(\bar{n}_e)$, and it appears that just the difference $\bar{n}_g - \bar{n}_e$ enters the expression for dW/dt. This is reminiscent of the standard result for the low-intensity absorption profile, but the expression (4.6) holds for arbitrary intensity Ω^2.

V. SATURATION

It might appear from Eq. (4.6) that the energy flux is proportional to Ω^2, and therefore can increase unlimited with the laser intensity. Such is, however, not the case, since for Ω^2/Δ^2 large, the population inversion $\bar{n}_e - \bar{n}_g$ tends to zero. In this section we shall derive an upper limit for dW/dt.

To this end, we first write Eq. (4.5) in the form

$$\frac{dW}{dt} = \hbar\omega_L \left[-A_g \bar{n}_g + \sum_{k=(\text{bare states})} \bar{n}_k a_{kg} \right] \ . \tag{5.1}$$

From the master equation and Eqs. (4.3) and (4.4), it is easy to derive the identity

$$\sum_{k=\text{bare}} \bar{n}_k(a_{kg}+a_{ke})=A_g\bar{n}_g+A_e\bar{n}_e \ . \tag{5.2}$$

Expression (5.1) for dW/dt refers to transitions from and to the ground state, but with Eq. (5.2) we can convert the reference level to the excited state. This yields

$$\frac{dW}{dt}=\hbar\omega_L\left[A_e\bar{n}_e-\sum_{k=(\text{bare state})}\bar{n}_k a_{ke}\right] , \tag{5.3}$$

and we note the complementary nature of Eqs. (5.1) and (5.3). Since $\bar{n}_k a_{ke}\geq 0$, we obtain from Eq. (5.3) the upper limit to the energy flux

$$\frac{dW}{dt}\leq\hbar\omega_L A_e\bar{n}_e \ . \tag{5.4}$$

With $\bar{n}_e\leq 1$, this reduces to $dW/dt\leq\hbar\omega_L A_e$, where the right-hand side is independent of the optical parameters. Hence, the inequality (5.4) implies that for strong fields the e,g transition saturates, and thus the energy flux is bounded. The limit (5.4), however, is an upper bound and not the saturation limit in general. The behavior of dW/dt for $\Omega^2/\Delta^2\rightarrow\infty$ will depend on the phonon-relaxation parameters a_{kl} and the level configuration.

The inequality (5.4) with $\bar{n}_e=1$ expresses the upper bound in the loss coefficient A_e of level $|e\rangle$. The complementary relation follows from Eq. (5.1) and becomes

$$\frac{dW}{dt}\leq\hbar\omega_L\sum_k a_{kg} , \tag{5.5}$$

which pertains to the gain coefficient of the ground state.

VI. TWO LEVELS

Already the most simple case, the two-level system, exhibits an interesting feature. We discard the explicit transient solutions, since they only display the trivial exponential decay. The steady-state master equation (4.2) is readily solved for $\bar{n}_+$ and $\bar{n}_-$. Then $\bar{n}_e$ follows from Eq. (4.3), which gives

$$\bar{n}_e=\frac{(1-2g_+g_-)a_{ge}+g_+g_-(a_{eg}-a_{ge})}{(1-2g_+g_-)(a_{eg}+a_{ge})} \tag{6.1}$$

and $\bar{n}_g=1-\bar{n}_e$. With $A_e=a_{eg}$, $A_g=a_{ge}$, the energy flux becomes

$$\frac{dW}{dt}=\hbar\omega_L\frac{\Omega^2}{2\Omega^2+4\Delta^2}(a_{eg}-a_{ge}) , \tag{6.2}$$

where we used the expression (2.3) for $g_\pm$. From the definition of the rate constants a_{kl}, Eq. (2.4), we deduce the properties

$$a_{kl}(T)-a_{lk}(T)=a_{kl}(T=0) , \tag{6.3}$$

$$a_{lk}(T=0)=0 , \tag{6.4}$$

both for $\omega_k>\omega_l$. Combining everything yields the alternative formulation of Eq. (6.2) as

$$\frac{dW}{dt}=\hbar\omega_L\bar{n}_e(T=0)a_{eg}(T=0) \ . \tag{6.5}$$

This reveals that the energy flux is independent of the temperature of the crystal, which is rather remarkable. From Eq. (6.5) we find the saturation limit to be

$$\frac{dW}{dt}=\tfrac{1}{2}\hbar\omega_L a_{eg}(T=0) , \tag{6.6}$$

which is smaller than the upper-bound $\hbar\omega_L\bar{n}_e(T)a_{eg}(T)$ from Eq. (5.4). Furthermore, we notice that for $T=0$ ($a_{ge}=0$), the dependence of $\bar{n}_e$ on the damping constant a_{eg} vanishes, so that the steady-state level populations are completely determined by the optical parameters Ω and Δ. This peculiar feature is a consequence of the assumed secular limit $[(\Omega^2+\Delta^2)^{1/2}\gg a_{eg}]$.

VII. THREE LEVELS

Let us now consider the configuration with a third level $|\zeta\rangle$ present. We then find

$$\frac{dW}{dt}=\hbar\omega_L\frac{\Omega^2}{4\Delta^2}(A_e+A_g)[(a_{eg}-a_{ge})A_\zeta+a_{e\zeta}a_{\zeta g}-a_{g\zeta}a_{\zeta e}]$$
$$\times\left[a_{eg}A_\zeta+a_{g\zeta}A_e+a_{\zeta e}A_g+a_{e\zeta}a_{\zeta g}+a_{ge}a_{e\zeta}+a_{\zeta g}a_{ge}+\frac{\Omega^2}{4\Delta^2}(A_e+A_g)(a_{e\zeta}+a_{g\zeta}+2A_\zeta)\right]^{-1} , \tag{7.1}$$

which becomes in the saturation limit $\Omega^2/\Delta^2\rightarrow\infty$

$$\frac{dW}{dt}=\hbar\omega_L\frac{(a_{eg}-a_{ge})A_\zeta+a_{e\zeta}a_{\zeta g}-a_{g\zeta}a_{\zeta e}}{a_{e\zeta}+a_{g\zeta}+2A_\zeta} \ . \tag{7.2}$$

In the limit $A_\zeta^{-1}\rightarrow 0$, Eq. (7.1) reduces to the two-level result from the preceding section, as it should.

In the limit $T\rightarrow 0$, the rates for upward transitions vanish. This implies that we have to distinguish three cases. First, for $\omega_\zeta>\omega_e>\omega_g$ we find again the results for the two-level case, since the population of $|\zeta\rangle$ becomes zero. For the situation $\omega_e>\omega_g>\omega_\zeta$ we obtain $dW/dt=0$, as a result of the fact that all population resides in $|\zeta\rangle$. This prohibits any excitation by the laser field. The interesting case is $\omega_e>\omega_\zeta>\omega_g$, for which we obtain

$$\frac{dW}{dt}=\hbar\omega_L A_e\frac{\Omega^2}{4\Delta^2+\Omega^2(2+a_{e\zeta}/a_{\zeta g})} \ . \tag{7.3}$$

This exhibits clearly that a nonzero value of the ratio $a_{e\zeta}/a_{\zeta g}$ diminishes the energy transfer to the crystal. More generally, this idea can be inferred from Eq. (5.3). Any appearance of additional levels with a finite population tends to reduce the energy flux. The population of the excited state for $T=0$ and $\omega_e>\omega_\zeta>\omega_g$ is found to be

$$\bar{n}_e=\frac{\Omega^2}{4\Delta^2+\Omega^2(2+a_{e\zeta}/a_{\zeta g})} \ . \tag{7.4}$$

Comparison with Eq. (7.3) then yields

$$\frac{dW}{dt}=\hbar\omega_L A_e \bar{n}_e \ , \tag{7.5}$$

which is reminiscent of the result (6.5) for the two-level case and of the saturation constraint (5.4).

VIII. CONCLUSIONS

We have studied the surface-adbond mediated conversion of laser photons into phonons of a harmonic crystal. A net energy flux dW/dt into the crystal emerges from the different laser-assisted single-phonon transitions. We have derived a variety of expressions for dW/dt, which include the explicit dependence on the laser power, the detuning, the temperature, and the properties of the vibrational bond. This was achieved by a proper interpretation of the thermal transition rates, as they appear in the master equation with respect to the dressed states. Our approach applies to arbitrarily strong incident fields and to any configuration of atomic levels, but is restricted to one-phonon processes. We digressed on saturation effects to derive an upper limit for dW/dt. The general treatment was exemplified by an explicit evaluation of dW/dt for the cases of a two-level and a three-level system. We find that for the two-level system the energy flux is independent of the temperature of the crystal. For three levels and $T\rightarrow 0$, we find the relation $dW/dt=\hbar\omega_L A_e\bar{n}_e$, which can readily be understood. The only process which gives rise to energy transportation is an optical excitation $|g\rangle\rightarrow|e\rangle$ and a successive thermal decay $|e\rangle\rightarrow|g\rangle$ or $|e\rangle\rightarrow|\zeta\rangle\rightarrow|g\rangle$. The rate for this process equals $A_e\bar{n}_e$, and the energy gain per transition is $\hbar\omega_L$. The effect of the laser is reflected in $\bar{n}_e\neq 0$, since for $\Omega^2\rightarrow 0$ the system is bound to be in the ground state $|g\rangle$.

Another interesting feature can be deduced immediately from our results. If the laser is used for photodesorption of the atoms, then the desorption rate will roughly be proportional to the sum of the populations of the high-lying states. For the case of a three-level system with $\omega_e>\omega_\zeta>\omega_g$, the number of desorbed atoms per unit of time will be $\bar{n}_e a_{ec}$, where a_{ec} is the rate constant for a transition to the continuum. On the other hand, the number of absorbed photons per unit of time equals $(dW/dt)/\hbar\omega_L$. If we define the quantum yield as the ratio of these two numbers, then we find from Eq. (7.5) that it becomes a_{ec}/A_e for low temperatures and in the three-level case, and in general for a two-level system. This ratio is independent of Ω^2/Δ^2, so the efficiency of photodesorption cannot be enhanced by tuning the laser or increasing the power. The absolute rate is, however, proportional to $\bar{n}_e$, which depends on the intensity. For not too strong fields we have $\bar{n}_e\propto\Omega^2$, which is not surprising. Resonance effects appear if we tune ω_L into the line center of the absorption profile $(\sim\omega_0)$. Then $\bar{n}_e$ approaches its saturation limit $(\lesssim\frac{1}{2})$, which provides the maximum photodesorption yield.

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