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Time-dependent optical transitions in vibronic systems

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We show that the resonant interaction between a field mode and a pair of vibronic levels is influenced by dynamical coupling to nonresonant states. The dependence of the occupation probability of vibronic states on dipole coupling, displacement, and resonance condition is discussed.

I. INTRODUCTION

Field-induced transitions are usually described in quantum optics as transitions between electronic states. Due to the resonant character of the interaction with the electromagnetic field, and to the limitations introduced by selection rules, the number of relevant levels can be reduced to only two. This natural approximation has a broad field of application, ranging from laser theory to coherent pulse propagation and transient effects such as superfluorescence.[1] In this paper we study the question of whether a two-level description is correct when a different type of transition, namely, the transition between vibronic states, is considered. As is well known, vibronic models are used to describe the optical properties of molecules or of impurities in crystals. The solid-state laser is an example where the vibronic model is useful, the usual two-level model being oversimplified to cope with the complexity of the coupled transitions giving rise to its characteristic broad emission spectrum,[2] which is the key to the tunability of this laser. The intrinsic multilevel structure of the vibronic system makes a description of its dynamical properties in terms of a two-level model questionable, and a more complete multilevel description is needed. We discuss here the full dynamical consequences of resonant and nonresonant level coupling in a vibronic system. Besides its intrinsic interest, our dynamical analysis of a vibronic model allows us to discuss the limits of validity of a two-level description of such a system. Furthermore, in spite of the different physical characteristics of atomic and vibronic transitions, our results can give a good indication of the importance of nonresonant transitions and level coupling in a more general multilevel system.

In the following we consider a vibronic system coupled to one optical field mode in the rotating-wave approximation (RWA). The vibronic system, characterized by a strong electron-vibration interaction, considers a pair of electronic levels coupled to vibrations in the harmonic approximation. The vibronic levels correspond then to the energy levels of two displaced oscillators, the displacement being related to the strength of the electron-vibration coupling. Transition probabilities between vibronic levels are related to the dipole moment for the underlying electronic transition as well as to the Franck-Condon overlap integrals[3] between the vibrational parts of the wave function. This model has been recently discussed in the framework of a perturbation calculation;[4,5] its full dynamical study is presented here as an illustration of the importance of nonresonant effects on resonant transitions.

II. MODEL AND HAMILTONIAN

The description of a two-electronic-level system interacting with a vibrational field is well known, and has already been discussed in the literature. For more details, the reader is referred to previous work.[6] Here, we briefly recall the form of the vibronic Hamiltonian, which in its simplest form (and for one vibrational mode only) is given in the rotating-wave approximation by

$$H = H_{\text{el-phon}} + H_{\text{el-phot}} , \tag{1}$$

with

$$H_{\text{el-phon}} = \hbar\Omega b^\dagger b + \lambda\sigma_z(b+b^\dagger) + \hbar\varepsilon\sigma_z ,$$

$$H_{\text{el-phot}} = \hbar\omega a^\dagger a + g(\sigma^+ a + \sigma^- a^\dagger) .$$

Here λ is the electron-vibration coupling constant and g is the dipole coupling between the optical field and electronic states. Ω, ε, and ω are the frequencies of the vibration, the electronic transition, and the optical field, respectively. $b^\dagger, b$ and $a^\dagger, a$ are creation and annihilation operators for the vibration mode and for the optical modes, respectively. The field is treated as a classical complex variable. σ_z, σ^+, and σ^- are pseudospin operators which describe the two-level system. No dissipation is included, thus allowing us to consider coherent effects only. Using a standard technique, we transform the Hamiltonian (1) to a form which is diagonal in the eigenstates of the electron-phonon interaction. Following Ref. 6, we obtain our final form of the Hamiltonian:

$$H = \hbar\Omega b^\dagger b + \hbar\omega a^\dagger a + \hbar\varepsilon\sigma_z + g\sum_{m,n}(af_{mn}S^\dagger_{mn} + \text{H.c.}) , \tag{2}$$

where $f_{mn} = \langle m|\exp[\pm\lambda/\Omega(b-b^\dagger)]|n\rangle$ are the

Franck-Condon factors,[7] $S_{mn}^{+}=|m\uparrow\rangle\langle\downarrow n|, S_{mn}^{-}$ being their Hermitian conjugate. The states $|m\uparrow\rangle, |n\downarrow\rangle$ are eigenstates of $\hbar\Omega b^{\dagger}b+\hbar\varepsilon\sigma_z$, where we have labeled the upper vibronic states by $\uparrow m$ and the lower ones by $\downarrow n$. The operators S_{mn} describe transitions between vibronic states belonging to different electronic states, i.e., to different harmonic potentials. The algebra for S_{mn} involves new operators $T_{mm'}=|m\uparrow\rangle\langle\uparrow m'|$ that correspond to transitions between states belonging to the same harmonic potential. The quantities S_{mn} and $T_{mm'}$ are dynamically coupled because all transitions are coupled in the medium. Each transition between a pair of vibronic levels $m\uparrow$ and $n\downarrow$ has a definite strength, which is determined by the dipole coupling constant g (which is the same for all pairs of states) and by the Franck-Condon factor f_{mn}, which is specific for each pair of vibronic levels. This factor oscillates as a function of the difference $(m-n)$ of the indices and strongly depends on the displacement λ/Ω. The distribution of the values f_{mn} remarkably changes from $m=0$ to $m\neq 0$, i.e., the transition scheme from $\uparrow m\neq 0$ may be quite different from that for $\uparrow m=0$. The Schrödinger equations for the transition amplitudes between vibronic levels, interacting with one field mode, become in the RWA

$$\begin{aligned}\frac{d}{dt}\langle\uparrow m|\psi\rangle&=-i\frac{\varepsilon}{2}\langle\uparrow m|\psi\rangle-im\Omega\langle\uparrow m|\psi\rangle\\&\quad-ig\langle a\rangle\sum_{l}f_{lm}^{+}\langle\downarrow l|\psi\rangle\ ,\\\frac{d}{dt}\langle\downarrow n|\psi\rangle&=i\frac{\varepsilon}{2}\langle\downarrow n|\psi\rangle-in\Omega\langle\downarrow n|\psi\rangle\\&\quad-ig\langle a^{\dagger}\rangle\sum_{l}f_{ln}^{-}\langle\uparrow l|\psi\rangle\ .\end{aligned}\tag{3}$$

To complete our model, we assume that the field mode is described by a time-dependent amplitude, determined consistently from Maxwell's equations. The polarization term is constructed from the wave functions of the vibronic system. This yields the following mode equations:

$$\begin{aligned}\frac{d}{dt}\langle a\rangle&=-i\omega\langle a\rangle-ig\sum_{m,n}f_{mn}^{+}\langle\uparrow m|\psi\rangle\langle\psi|n\downarrow\rangle\ ,\\\frac{d}{dt}\langle a^{\dagger}\rangle&=i\omega\langle a^{\dagger}\rangle+ig\sum_{m,n}f_{nm}^{-}\langle\downarrow n|\psi\rangle\langle\psi|m\uparrow\rangle\ .\end{aligned}\tag{4}$$

The coupled nonlinear equations (3) and (4) cannot be solved analytically in a general case.

III. NUMERICAL EXAMPLES AND DISCUSSION

We present here a few examples of numerical solutions of this system of equations and discuss on the basis of their characteristics the relevance of the multilevel description. For simplicity we reduce ourselves to a system where only six vibronic levels are considered in each harmonic potential. We illustrate the effects of multilevel coupling through the time dependence of the occupation probability of the different vibronic levels for a "one-particle" vibronic system (no cooperative effects are considered). We choose the field mode frequency ω at resonance with the electronic frequency ε and normalize equations (3) and (4) with the vibration frequency Ω. Finally we fix the normalized dipole coupling g/Ω to an arbitrary value. The initial conditions for Eqs. (3) and (4) are the following: all states but $m=0,\uparrow$ are empty, and the real part of the field amplitude is different from zero. Only the normalized displacement λ/Ω is left as free parameter.

In a first example, we choose $\lambda/\Omega=0.2$. The time-dependent level occupations are presented in Fig. 1. Here, as well as in Figs. 2 and 3, only the occupations of the states in the lower harmonic potential are shown, the behavior of the population in the upper states being similar. We notice that although the main contribution comes from the $\uparrow m=0\rightarrow n=0\downarrow$ transition, there is a non-negligible occupation probability for the levels $\uparrow m=1$ and $\downarrow n=1$. Furthermore, the oscillation pattern of the resonant level occupation is more complex than that found in a two-level model. This is a consequence of level mixing through coupling to the field, which is important in spite of the small occupation of the nonresonant levels. An increase of the displacement to $\lambda/\Omega=1$ induces dramatic changes. As it is obvious in Fig. 2, the transition $\uparrow m=0\rightarrow\downarrow n=0$ is not the only important transition any more. Three pairs of levels from both harmonic potentials contribute to the dynamics in a non-negligible way. This is shown both by the values of the maximal occupation of the nonresonant states and by the oscillation pattern.

The quantitative characteristics of the time dependence displayed in Figs. 1 and 2 are understood as follows. Three main processes contribute to the dynamics of the vibronic system. On one side, the dynamics is determined by the transitions $S_{mn}^{\pm}, m\neq n$ and the magnitude of the corresponding Franck-Condon factors, which indicates how many levels are involved in the emission and the relative weight of each transition. On the other side, as soon as the states in the lower potential become populated, two more processes come into play: field-induced

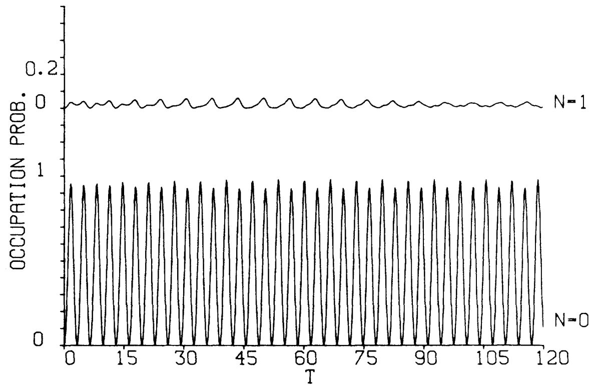

FIG. 1. Occupation probabilities of the lower vibronic levels for the parameter choice: displacement $\lambda/\Omega=0.2$, dipole coupling $g/\Omega=0.8$, $\omega=\varepsilon$. The initial field $\mathrm{Re}(\langle a\rangle)=1$ and the excited state $\uparrow m=0$. $T=\Omega t$ is the normalized time. In this figure, as well as in Figs. 2 and 3, only the occupation of the states in the lower harmonic potential are shown, the behavior of the population in the upper states being similar.

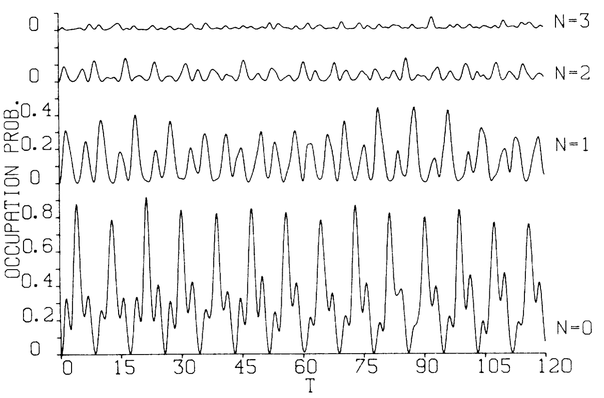

FIG. 2. Same as Fig. 1 with $\lambda/\Omega=1$.

transitions between levels in the same potential and transitions to levels in the upper potential, $m=n$, which are degenerate in energy with the $\uparrow m=0\rightarrow\downarrow n=0$ transition. Schematically when starting from $\uparrow m=0$, transitions happen to lower vibronic states which are dynamically coupled together. From these states, the field induces transitions to upper levels, where the same dynamical coupling causes a redistribution of occupation. This influences the next emission steps, and so on. The relative weight of these three interplaying processes is manifest in Fig. 3. Here we compare the occupation of the n lower vibronic levels, for two different systems: one consisting of a single vibronic level in the upper harmonic potential, the other being the full six-level system. As a result of dynamical coupling and excitation to the upper levels, a higher occupation is obtained on the resonant levels for the full system, with a different oscillation pattern. These examples show very clearly that even if the mode is resonant with the purely electronic transition, which in the examples considered here corresponds to the strongest transition, a reduction to two levels only does not account for the distribution of population in the system.

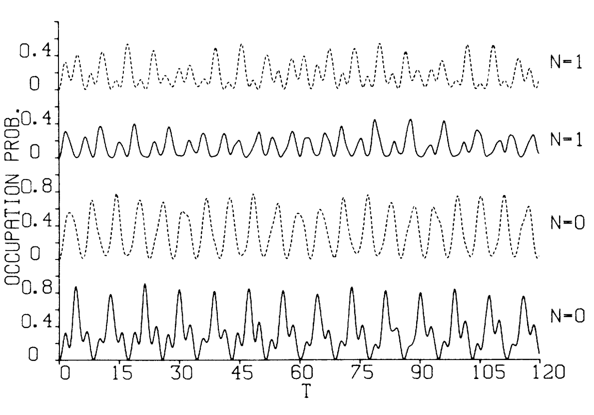

FIG. 3. Occupation probabilities for the lower levels of the six-upper-level scheme (solid line), and one upper level only (dashed line). Only the levels $\downarrow n=0,1$ are displayed.

So far, all the parameters other than the displacement have been kept constant. To complete our discussion, we quote some results which are found when parameters other than the displacement are changed. The dependence on the dipole coupling g/Ω of multilevel effects is quite involved. From Eq. (3), it is evident that g/Ω influences the dynamics through the products $g/\Omega\langle a\rangle, g/\Omega\langle a^{\dagger}\rangle$, i.e., that the effects of its variation mix up with those of the field oscillations. As a consequence we notice an increase of multilevel effects when g/Ω is increased between 0 and 1, as well as a strong variation in the oscillation frequency. However, the relevance of these effects strongly depends on λ/Ω, too, and its understanding requires a thorough discussion of the dynamics which lies beyond the scope of this paper.

The importance of the Franck-Condon factors f_{mn} is evident when the resonance condition and the initial excitation state are changed. For example, when we choose $\omega=\varepsilon-\Omega$ and fix $\lambda/\Omega=0.2$, the occupation probability of the upper and lower states decreases with respect to the $\omega=\varepsilon$ case. This is not surprising because, for $\lambda/\Omega=0.2$, the ratio f_{00} to f_{01} is about 5 and the f_{00} nonresonant transition dominates. However, when λ/Ω is increased, f_{00} and f_{01} become of comparable magnitude and a shift in the occupation maximum from the transition $\uparrow m=0\rightarrow\downarrow n=0$ to $\uparrow m=0\rightarrow\downarrow n=1$ is observed.

A change in the initial condition for the excitation has drastic effects too. For the less favorable value $\lambda/\Omega=0.2$ of the displacement we choose $m=3$ as the initial state. The time-dependent occupation probabilities of the upper vibronic states are shown for this case in Fig. 4. There is a remarkable amount of transfer from $\uparrow m=3$ to $\uparrow m=2,4$ and influence of the dynamical coupling is present in $\uparrow m=5$ and $\uparrow m=4$ as well (not shown in the figure). On the contrary, the state $\uparrow m=0$ remains empty. Here the Franck-Condon factors f_{33}, f_{34}, and f_{32} are not very different from each other, thus allowing a better redistribution of population between adjacent states. It is interesting to know that the mixing is a lot more efficient in this case than in the example of Fig. 1, where the role of the neighboring vibronic states is small. This effect is

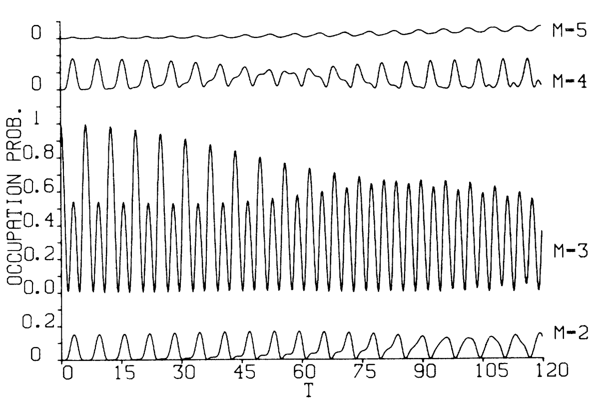

FIG. 4. Occupation probabilities of the upper vibronic levels for the same parameters as in Fig. 1, and initial excited state $\uparrow m=3$.

related to the broader distribution of the values f_{3n} ($n = 0,1,2$) with respect to f_{0n}, which are strongly concentrated around f_{00}.

IV. CONCLUSION

We summarize the results of our analysis as follows. In a first approximation, resonant optical interaction are assumed to influence the dynamics of the two resonant levels only. As far as coherent processes are involved, the accuracy of this two-level transition scheme is related to the energy distribution of all levels and to the transition coupling factors between them. In a vibronic system in the harmonic approximation, these quantities are fixed by the energy difference between displaced oscillator levels and by the Franck-Condon factors. Already for small values of the displacement, the nonresonant states have a definite influence on the resonant transition. Off-resonant levels become more and more important once the displacement between oscillators and hence the Franck-Condon factors are increased. In particular, they contribute in a non-negligible way to the population dynamics, and therefore influence the response of the system to resonant excitation. These results lead to a criterion for the limit of validity of the two-level approximation for the vibronic system: this approximation is only valid if the displacement λ/Ω is very small. In this case, the vibronic level structure only slightly modifies the underlying electronic structure. One should notice that other multilevel systems, in which the electronic transitions play a major role, will not exhibit the peculiar dependence of the coupling on the Franck-Condon factors and different selection rules. However, the main features of our result, namely, the influence of nonresonant levels in function of the strength of the coupling, should hold for other multilevel models too.

We have restricted our discussion to the simple case of one field mode in order to stress the importance of nonresonant effects, in complex systems similar to vibronic systems. As has been discussed in laser theory[5] and nonlinear optics,[8] we expect more substantial effects on the optical response to appear when more modes are considered. We plan to discuss this and related problems in a future publication.

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