

Selective multiple-photon absorption by an anharmonic molecule

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We discuss a model of selective absorption of infrared radiation by an anharmonic molecular vibrational mode. The effects of the rotational sublevels and of the energy dissipation mechanisms are described phenomenologically. We show that in the context of our model the absorption process is described by coupled nonlinear equations for the complex vibrational amplitude and for the average excitation quantum number. Two distinct dynamic regimes (coherent and adiabatic limit) can be identified depending on the relative magnitude of the rotational relaxation time and of the laser pulse duration.

I. INTRODUCTION

The rapid advances in laser photochemistry and isotope separation¹ have generated considerable interest in the selective absorption of radiation leading to either molecular dissociation or chemical reactivity. The chemical end of the problem² is still beset with formidable difficulties. The selective absorption part of the process, on the other hand, is fairly well understood qualitatively, and has been considered in several theoretical models.³⁻⁶ A popular approach views the vibrational degrees of freedom as harmonic oscillators^{3,7-9} coupled to relaxation mechanisms that induce energy exchanges between the accessible internal and external degrees of freedom.

It has been recognized, however, that the anharmonic contribution can hardly be ignored in most molecules of interest.¹⁰⁻¹³ In fact, the increasing loss of resonance between the driving electromagnetic field and the higher anharmonic transitions causes a natural saturation of the absorption process which, in turn, limits the amount of energy that can be transferred to a molecule. Since, on the other hand, there is evidence that highly excited vibrational states can be created under high-power irradiation conditions,¹⁴⁻¹⁷ it is of interest to examine in detail the dynamics of multiple-photon absorption in an anharmonic system.

Our objective here is to formulate a description of the selective absorption of infrared laser radiation in certain polyatomic molecules in a fashion which takes vibrational anharmonicity and rotational effects into account with reasonable accuracy while retaining computational tractability. To this end, we begin with the Hamiltonian for an oscillator which has quadratic, cubic, and quartic terms in its potential energy and which is coupled to an external electric field through its dipole moment. This Hamiltonian is then unitarily transformed, using a perturbative method formulated

elsewhere¹⁸ in connection with the study of electromagnetic "dressing" effects but employed here only to simplify the calculation and interpretation of results. To incorporate rotational and other relaxational effects, the dynamical evolution of the absorption process is then described in the framework of the master-equation formulation.

The effect of the rotational sublevels of the molecule on the absorption process¹⁹⁻²¹ is incorporated into the master equation after consideration of the various time scales of the main energy relaxation pathways which are available to an excited molecular mode in the presence of collisions. In general, many rotational levels are excited by the applied pump field. However, for many molecular species the cross section for collision-induced rotational transitions is larger than that for vibrational energy transfer, so that the rotational equilibrium distribution is established in a time that is short compared to the relaxation time to vibrational equilibrium. In fact, under usual conditions²¹ one finds that rotational equilibrium is established first, followed by vibrational equilibrium in a given mode. Next, equilibrium between different vibrational modes takes place. Finally, equilibrium between vibrational and translational degrees of freedom is reached.

These facts suggest that each vibrational level may be approximately characterized by a linewidth contribution due to the energy relaxation between different vibrational levels, and by an intrinsic linewidth resulting from rotational relaxation within each vibrational level.²² Since the latter process is assumed to conserve the average population of a given vibrational level, it is modeled here as producing a decay of the complex vibrational amplitude while maintaining the average level population constant. (This model is adapted from some early work by Bonifacio and Haake²³ on the relaxation of an oscillator in contact with a reservoir.) The remaining relaxation processes, which do not affect the average population of a

given vibrational level, are mathematically represented as producing decay of the vibrational-state occupation operator itself.

As a result of our model, the dynamical evolution of the excitation process is described in terms of a system of three coupled equations for the oscillator average occupation number and for its complex amplitude. Under pulsed excitation conditions and for moderately large incident field strengths, we find it possible to solve adiabatically for the oscillator amplitude. In this case the average excitation energy satisfies a single nonlinear differential equation, which has been solved numerically under a variety of physical conditions.

In Sec. II we describe the details of the theoretical model and derive the basic equations of motion. The physical predictions of our model and the numerical solutions of the equations of motion are discussed in Sec. III.

II. THEORETICAL MODEL

Of the several infrared-active vibrational modes of a molecule, we focus on the one that is resonant, or nearly resonant, with the applied laser field. At low applied field strengths, the resonant mode will be selectively excited with all the non-resonant modes remaining virtually in their ground state. At higher pump levels, the anharmonic contribution to the vibrational potential energy will cause mode mixing and subsequent energy transfer from the excited to the unexcited modes. In order that we may concentrate on the essential features of the absorption process, we have, as mentioned in the previous section, chosen to model all the energy relaxation mechanisms out of the excited mode in terms of an effective reservoir whose main effect is to induce vibrational relaxation at a specified rate.

The reversible interaction between the resonant mode and the applied field is described by the unperturbed anharmonic oscillator Hamiltonian

$$H_0 = \hbar\omega a^\dagger a + \beta(a^\dagger + a)^3 + \gamma(a^\dagger + a)^4, \quad (1)$$

and by the molecule-field interaction Hamiltonian

$$H_1 = \mu\epsilon(t)(a^\dagger e^{-i\Omega t} + a e^{i\Omega t}). \quad (2)$$

In Eq. (1) we have limited the anharmonic contributions to cubic and quartic potential-energy terms; the operators a^\dagger and a are the usual harmonic-oscillator-type ladder operators, μ is the dipole moment associated with the molecular normal coordinate of interest, $\epsilon(t)$ is the envelope of the applied electric field, and Ω is its carrier frequency. In Eq. (2) we have written the interaction Hamiltonian in the usual rotating-wave approxima-

tion.

The main difficulty with the total Hamiltonian in Eqs. (1) and (2) is the presence of excitation conserving and nonconserving terms. The latter ones (i.e., operators of the type $a^{\dagger m} a^n$ with $m \neq n$) cause the equations of motion of the relevant observables to be inconveniently complicated. Thus, the Heisenberg equations of motion for the amplitude and number operators, a and $a^\dagger a$, are members of an infinite hierarchy. Since in this representation a^\dagger is not an excitation operator for the anharmonic vibrational states, it is not clear how to truncate this infinite set of coupled equations or to select contributions which are consistent with an assumed order of approximation in the anharmonic parameters.

A scheme of calculation¹⁸ developed in connection with the electromagnetic dressing of a quantum system can eliminate the difficulties just described. The basic idea of the method is to carry out a certain unitary transformation of a Hamiltonian composed of "unperturbed" and "interacting" parts so that the unperturbed part is invariant and the transformed interaction Hamiltonian commutes with this unperturbed part. The technique is applied here to the Hamiltonian H_0 given in Eq. (1), with the harmonic oscillator term $\hbar\omega a^\dagger a$ treated as the unperturbed part and the cubic and quartic potential terms as the perturbation. The determination of the unitary transformation is based on a lengthy but simple perturbation procedure that requires only algebraic manipulations. An outline of the calculation is given in Appendix A. Here we merely state that by direct application of the procedure the transformed oscillator Hamiltonian, to second order in β and first order in γ ,²⁴ takes the form

$$H'_0 = \hbar\omega a^\dagger a - \hbar\epsilon a^\dagger a(a^\dagger a + 1), \quad (3)$$

where the anharmonic correction is defined by

$$\hbar\epsilon = 30\beta^2/\hbar\omega - 6\gamma.$$

The parameter ϵ is usually a positive quantity.

One of the useful features of the method is that in the new unitary frame the eigenstates of the total Hamiltonian are linear combinations of degenerate eigenstates of the old *unperturbed* Hamiltonian. Since in the present case the old unperturbed Hamiltonian is nondegenerate, the new molecular Hamiltonian (3) is already diagonal in the states generated by a^\dagger and has eigenvalues²⁵

$$E_n = \hbar\omega n - \hbar\epsilon n(n+1), \quad n = 0, 1, 2, \dots \quad (4)$$

Upon appropriate adjustment of the parameters ω and ϵ the lower-lying vibrational states of a typical anharmonic spectrum can be approximated. The contributions of order γ^2 can also be included in

the Hamiltonian (3), but the price one has to pay is the presence of a cubic term in the number operator.

When the Hamiltonian (2) which couples the anharmonic oscillator to the electric field is subjected to the same unitary transformation, it is found that to the same order of approximation in the anharmonic parameters used in deriving Eq. (3), this part of the Hamiltonian retains the form given by Eq. (2). A survey of the lengthy transformation and a discussion of the various terms that have been discarded is given in Appendix B.

In the new unitary frame the density operator W of the anharmonic oscillator satisfies the usual reversible Liouville equation

$$\begin{aligned} \frac{dW}{dt} = & -i(\omega - \epsilon - \Omega)[a^\dagger a, W] + i\epsilon[(a^\dagger a)^2, W] \\ & -i\omega_R(t)[a^\dagger + a, W], \end{aligned} \quad (5)$$

where $\omega_R(t)$ is the Rabi frequency $\mu\epsilon(t)/\hbar$.

We observe that the energy separation between the ground and first excited vibrational states is $\hbar\omega_0 \equiv \hbar(\omega - 2\epsilon)$. It should also be noticed that the new unperturbed Hamiltonian of the system is unbounded below. This, of course, would cause serious problems if we attempted to apply Eq. (5) to describe the interaction of the molecule with excessively large fields. Practically speaking, difficulties will not arise as long as the average vibrational excitation remains well below the turning point of the unperturbed energy spectrum, i.e., as long as $\langle a^\dagger a \rangle \ll \hbar\omega/2\hbar\epsilon$. Since the anharmonic contribution $\hbar\epsilon$ is usually a small fraction of the fundamental transition energy $\hbar\omega_0$, mathematical difficulties are not anticipated for most realistic cases of interest.

To describe the incoherent energy relaxation (ER) to other molecular degrees of freedom, we add to the master Eq. (5) the relaxation terms²⁶

$$\begin{aligned} \left(\frac{\partial W}{\partial t}\right)_{\text{ER}} = & \frac{\bar{n}}{\tau} ([a^\dagger, W a] + [a^\dagger W, a]) \\ & + \frac{\bar{n} + 1}{\tau} ([a, W a^\dagger] + [a W, a^\dagger]), \end{aligned} \quad (6)$$

where \bar{n} measures the average thermal excitation of all the molecular degrees of freedom that act as a reservoir for the anharmonic mode of interest and τ^{-1} is the sum of the intermolecular and collisional energy dissipation rates. Strictly speaking, the irreversible contribution (6) describes the relaxation of a *harmonic* oscillator in the Born and Markoff approximations. We have verified, however, that in the Born and Markoff approximation, the deviations from Eq. (6) due to the anharmonic potential-energy terms are unimportant if the reservoir density of states is

reasonably uniform in the neighborhood of the fundamental transition frequency.

In addition, as indicated in the Introduction, the mathematical model describing the effect of rotational relaxation is required to account for energy redistribution among the rotational sublevels, while maintaining a constant average occupation-number distribution in the vibrational manifold. This suggests that the complex amplitude of the vibrational normal-mode coordinate will be damped by the collision-induced rotational relaxation, while the average occupation number of the vibrational level will remain constant. The phase relaxation model²³ for a harmonic oscillator justifies these requirements, and just as for the energy relaxation terms (6) we assume that the rotational relaxation (RR) for the anharmonic oscillator also can be described by the irreversible contribution to the oscillator master equation

$$\left(\frac{\partial W}{\partial t}\right)_{\text{RR}} = \eta([a^\dagger a, W a^\dagger a] + [a^\dagger a W, a^\dagger a]), \quad (7)$$

where η is a measure of the rotational width of the vibrational levels. That the effect of the irreversible process described by Eq. (7) on the amplitude and number operators is the desired one can be easily verified, since the expectation values $\langle a(t) \rangle$ and $\langle a^\dagger a(t) \rangle$ predicted on the basis of Eq. (7) are given by

$$\frac{d}{dt} \langle a(t) \rangle = -\eta \langle a(t) \rangle, \quad (8a)$$

$$\frac{d}{dt} \langle a^\dagger a(t) \rangle = 0. \quad (8b)$$

We therefore combine all these effects and assume that the irreversible evolution of the active vibrational mode is described by the total master equation

$$\begin{aligned} \frac{dW}{dt} = & -i(\omega - \epsilon - \Omega)[a^\dagger a, W] + i\epsilon[(a^\dagger a)^2, W] \\ & -i\omega_R(t)[a^\dagger + a, W] + \left(\frac{\partial W}{\partial t}\right)_{\text{RR}} + \left(\frac{\partial W}{\partial t}\right)_{\text{ER}}, \end{aligned} \quad (9)$$

where the relaxation terms are given by Eqs. (7) and (6), respectively.

We are especially interested in the time evolution of the observables a , a^\dagger , and $a^\dagger a$. As expected the equation of motion for the expectation values $\langle a(t) \rangle$, $\langle a^\dagger(t) \rangle$, and $\langle a^\dagger a(t) \rangle$ do not form a closed system due to the presence of the anharmonic term. We ignore the difficult but probably not very important problem of quantum correlations, and assume the factorization ansatz $\langle a^\dagger a a \rangle \approx \langle a^\dagger a \rangle \langle a \rangle$ and $\langle a^\dagger a^\dagger a \rangle \approx \langle a^\dagger \rangle \langle a^\dagger a \rangle$. (Note that this factorization could not have been justified before the unitary transformation, since in the original representa-

tion, a and a^\dagger were not the amplitude and occupation-number operators for the anharmonic oscillator). Upon identification of $\langle a \rangle$ with $A(t)$ and $\langle a^\dagger a \rangle$ with $N(t)$, we arrive at the following closed set of equations of motion:

$$\begin{aligned} \frac{dA}{dt} &= -i(\omega_0 - \Omega)A - \left(\eta + \frac{1}{\tau}\right)A + 2i\epsilon NA - i\omega_R(t), \\ \frac{dA^*}{dt} &= i(\omega_0 - \Omega)A^* - \left(\eta + \frac{1}{\tau}\right)A^* \\ &\quad - 2i\epsilon NA^* + i\omega_R(t), \\ \frac{dN}{dt} &= -i\omega_R(t)(A^* - A) - \frac{2}{\tau}(N - \bar{n}). \end{aligned} \quad (10)$$

Under usual pulsed excitation conditions (pulse duration $\tau_p \approx 100$ – 200 nsec) one expects the relaxation time $(\eta + 1/\tau)^{-1}$ to be much shorter than τ_p . Thus the amplitude $A(t)$ is expected to follow the time evolution of the Rabi frequency adiabatically, always remaining in equilibrium with the rotational relaxation mechanisms. Mathematically, this amounts to assuming $|dA/dt| \ll (\eta + 1/\tau)|A|$. In the adiabatic approximation, the anharmonic motion can be described by the time-dependent average excitation $N(t)$, which is the solution of the nonlinear differential equation

$$\frac{dN}{dt} = \frac{2(\eta + 1/\tau)\omega_R^2(t)}{(\eta + 1/\tau)^2 + (\omega_0 - \Omega - 2\epsilon N)^2} - \frac{2}{\tau}(N - \bar{n}). \quad (11)$$

III. RESULTS AND DISCUSSION

It has been recognized that, as a result of the anharmonic nature of the vibrational spectrum, the largest molecular excitation for a fixed driving field amplitude occurs when the driving frequency is smaller than the fundamental vibrational frequency.²⁷ This effect, called the red shift, is described by Eq. (11), and can be understood qualitatively as follows: Consider for simplicity a fixed value of the Rabi frequency, and ignore the energy relaxation term: if the driving frequency is such that $\omega_0 - \Omega < 0$, the largest rate of increase of the vibrational excitation occurs for $N \approx 0$. As the average excitation increases, its rate of growth declines steadily until the irradiation process is completed. If, on the other hand, the driving frequency Ω is such that $\omega_0 - \Omega > 0$, a rapid increase of the average excitation is observed whenever $N(t)$ becomes as large as $(\omega_0 - \Omega)/2\epsilon$. This, of course, may not happen if the detuning $\omega_0 - \Omega$ is too large, or the Rabi frequency is too small or the pulse duration too short. This argument suggests the existence of an optimum detuning range,¹⁰ a fact that is borne out by our numerical solutions of the equations of motion. If the pulse duration is comparable to the relaxation time $(\eta + 1/\tau)^{-1}$, the adiabatic ap-

proximation breaks down and a "coherent" regime is established that can be described only by the full set of equations (10).

We have analyzed the behavior of the average excitation quantum number $N(t)$ under a variety of conditions both in the adiabatic and coherent regimes. For definiteness, our numerical computations have been performed assuming $\bar{n} = 0$ (i.e., a cold reservoir). Furthermore, the incident field envelope has been assigned the functional form

$$\omega_R(t) = \omega_R^0 \sin^2(\pi t/\tau_p), \quad 0 \leq t \leq \tau_p. \quad (12)$$

A typical set of solutions corresponding to a long pulse irradiation ($\tau_p = 200$ nsec) is shown in Fig. 1. (Table I gives a summary of the parameters used in the figures). The figure displays a set of time-dependent average excitations $N(t)$ for different values of the detuning parameter $\delta = \omega_0 - \Omega$. As anticipated by previous qualitative arguments, the maximum excitation for a given value of the Rabi frequency ω_R^0 occurs when the incident frequency Ω is red shifted with respect to the fundamental vibrational transition by an amount which is a function of the field strength, of the relaxation parameters, and of the anharmonic correction. In particular, the solutions in Fig. 1 show the rapid growth of the excitation $N(t)$ resulting when the approximate threshold condition $N(t) \sim (\omega_0 - \Omega)/2\epsilon$ is met. For sufficiently large values of the detuning parameter, a rapid decrease in the resulting vibrational excitation is observed, a fact that is directly analogous to the behavior of

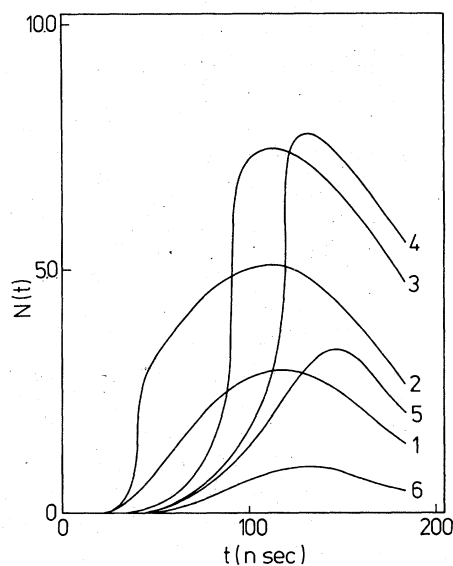


FIG. 1. Average vibrational excitation under long pulse irradiation. Each curve corresponds to a different detuning parameter δ : (1) $\delta = -5$ cm^{-1} , (2) $\delta = 5$ cm^{-1} , (3) $\delta = 15$ cm^{-1} , (4) $\delta = 17$ cm^{-1} , (5) $\delta = 19$ cm^{-1} , (6) $\delta = 25$ cm^{-1} .

TABLE I. List of parameters used in the figures. The anharmonicity factor ϵ was chosen to be 1.65 cm^{-1} (corresponding to the ν_3 mode of BCl_3) in all the figures.

Figure number	τ_p (nsec)	τ (nsec)	ω_R^0 (cm^{-1})	η (cm^{-1})
1	200	100	0.5	1.0
2	200	100	0.5	5.0
3	1.0	100	1.0	0.5
4	1.0	100	1.0	5.0

a classical forced anharmonic oscillator.¹⁰ The effect of the rotational relaxation is to introduce a natural width to the vibrational levels, thus reducing the detuning effects of the anharmonicity.

The red-shift effect is displayed in Fig. 2 where the maximum excitation for a given value of $\omega_0 - \Omega$ is plotted as a function of the detuning parameter $\omega_0 - \Omega$ itself. As indicated above, the optimum energy transfer from the applied field to the oscillator corresponds to a positive value of the detuning. For values of $\omega_0 - \Omega$ larger than a certain critical value, one observes a rapid decrease of the available vibrational excitation. When the incident pulse duration becomes comparable to or shorter than the rotational relaxation time, the average excitation $N(t)$ can break into oscillations which relax at a rate $\eta + 1/\tau$. This situation is illustrated in Fig. 3, where an incident pulse of duration 1 nsec and Rabi frequency 1 cm^{-1} is assumed to be interacting with the absorbing oscillator for different values of the de-

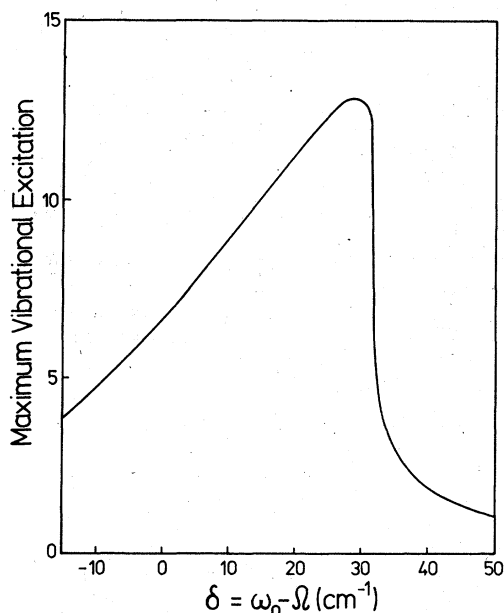


FIG. 2. Behavior of the maximum average vibrational excitation as a function of the detuning parameter δ .

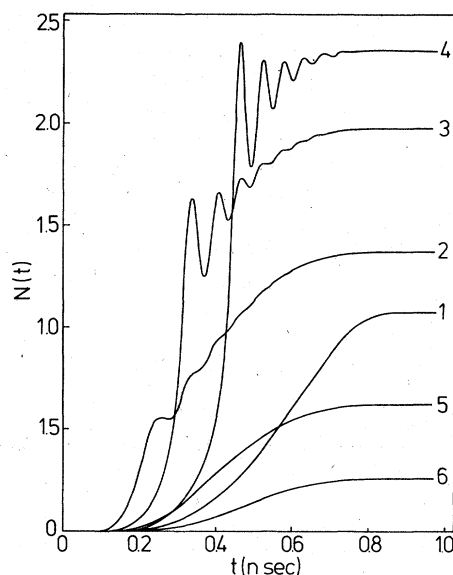


FIG. 3. Average vibrational excitation under short pulse irradiation. Each curve corresponds to a different detuning parameter δ : (1) $\delta = -3 \text{ cm}^{-1}$, (2) $\delta = 0.0 \text{ cm}^{-1}$, (3) $\delta = 2 \text{ cm}^{-1}$, (4) $\delta = 3.5 \text{ cm}^{-1}$, (5) $\delta = 5 \text{ cm}^{-1}$, (6) $\delta = 7 \text{ cm}^{-1}$.

tuning parameter. We observe again the existence of an optimum detuning range beyond which there follows a rapid drop-off of the excitation and the disappearance of the coherent oscillation.

A situation similar to that of Fig. 3 is shown in Fig. 4 (pulse duration 1 nsec). This time, however, the rotational width is large enough to

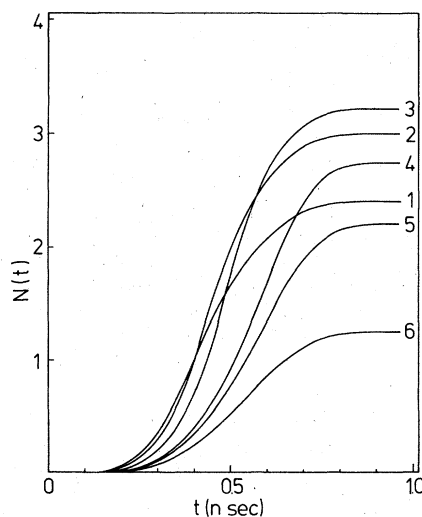


FIG. 4. Average vibrational excitation under short pulse irradiation. Each curve corresponds to a different detuning parameter δ . (1) $\delta = 0.0 \text{ cm}^{-1}$, (2) $\delta = 3 \text{ cm}^{-1}$, (3) $\delta = 5 \text{ cm}^{-1}$, (4) $\delta = 7.5 \text{ cm}^{-1}$, (5) $\delta = 8.25 \text{ cm}^{-1}$, (6) $\delta = 10 \text{ cm}^{-1}$.

quench the coherent oscillation of the excitation $N(t)$. It is to be observed that the largest energy transfer between a given applied field and the molecule occurs in the long pulse configuration. Thus, the pulse energy rather than its peak power seems to be the important physical quantity that determines the maximum accessible vibrational excitation.

A question of importance for both isotope separation and laser-induced chemical reactions is the probability distribution of the vibrational occupation number. In principle, the answer follows from the master equation (9) upon calculation of the diagonal elements $\langle n|W(t)|n\rangle$ of the density operator. In practice, the calculation appears to be nontrivial and will be the subject of further work.

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APPENDIX A: DERIVATION OF EQUATION (3)

The key technical step in the transformation of Ref. 18 is the construction of a unitary operator such that the transformed Hamiltonian $H' = UH_0U^{-1}$ in the new unitary basis is diagonalized by the eigenstates of the old unperturbed Hamiltonian. Specifically, if

$$H = H_0 + \lambda H_1 \quad (\text{A1})$$

is the original Hamiltonian of a system, we look for a unitary operator $U(\lambda)$ such that

$$H' = U(H_0 + \lambda U_1)U^{-1} \equiv H_0 + D(\lambda), \quad (\text{A2})$$

where $D(\lambda)$ commutes with H_0 . As shown in Ref. 18, the operators U and D can be expressed as power series in the coupling parameter λ as

$$U(\lambda) = \exp \left[i \left(\sum_{n=1}^{\infty} \lambda^n K_n \right) \right] = e^{iK(\lambda)}, \quad (\text{A3})$$

$$D(\lambda) = \sum_{n=1}^{\infty} \lambda^n D_n.$$

The operators D_1, D_2, \dots and K_1, K_2, \dots satisfy an infinite hierarchy of algebraic operator equations, the first two having the form

$$D_1 = i[K_1, H_0] + H_1, \quad (\text{A4})$$

$$D_2 = i[K_2, H_0] + (i^2/2)[K_1, [K_1, H_0]] + i[K_1, H_1] \\ = i[K_2, H_0] + \frac{1}{2}i[K_1, D_1 + H_1]. \quad (\text{A5})$$

The n th equation in the hierarchy contains two

operators D_n and K_n not contained in previous equations in the set; these operators must be simultaneously determined from this equation. To see how this determination is made, consider Eq. (A4). The sum of the two terms on the right-hand side of this equation must commute with H_0 ; and since an operator of the form $[K_1, H_0]$ cannot have a part which commutes with H_0 , one must require

$$D_1 = H_1^c \quad (\text{A6})$$

and

$$i[K_1, H_0] + H_1^{nc} = 0, \quad (\text{A7})$$

where H_1^c and H_1^{nc} are the parts of H_1 which commute and fail to commute with H_0 , respectively. The operator K_1 is determined by Eq. (A7) up to an additive part which commutes with H_0 ; so a requirement of "simplicity" is added to make its definition unique: K_1 is composed only of terms which do not commute with H_0 . Next, D_2 is chosen such that

$$D_2 = \frac{1}{2}i[K_1, D_1 + H_1]^c, \quad (\text{A8})$$

where the superscript c indicates the contribution of the commutation which commutes with H_0 . If the transformed Hamiltonian (A2) is required to be unitarily equivalent to H [Eq. (A1)] only up to second order in λ , explicit knowledge of K_2 is not required. However, for reasons to be discussed in Appendix B, the operator K_2 will be needed. It is calculated so as to satisfy the algebraic relation

$$i[K_2, H_0] = -\left[\frac{1}{2}i[K_1, D_1 + H_1] - D_2 \right] \\ \equiv -\frac{1}{2}i[K_1, D_1 + H_1]^{nc}, \quad (\text{A9})$$

and, again, K_2 is the simplest operator satisfying this equation, etc. Adapting the foregoing considerations to our needs with appropriate changes of notation for the various Hamiltonians, we choose the simple harmonic oscillator as the unperturbed system, and the anharmonic corrections as the perturbation. We are interested in constructing

$$H'_0 = U(\lambda)(H_{\text{harm}} + \lambda H_{\text{anharm}})U^{-1} \\ = H_{\text{harm}} + D(\lambda), \quad (\text{A10})$$

where

$$H_{\text{harm}} = \hbar \omega a^\dagger a, \quad (\text{A11})$$

$$\lambda H_{\text{anharm}} = \beta(a^\dagger + a)^3 + \gamma(a^\dagger + a)^4, \quad (\text{A12})$$

and where the parameter λ plays the role of an expansion variable to be set equal to unity at the end of the calculation. Usually $\beta \gg \gamma$; hence, we wish to construct an expansion of Eq. (A9) that

contains terms of order β^2 and γ in the anharmonic constants. The calculation of D_1 is trivial. The only terms in Eq. (A11) which commute with H_{harm} are

$$D_1 = 6\gamma\{(a^\dagger a)^2 + a^\dagger a + \frac{1}{2}\}. \quad (\text{A13})$$

K_1 must be constructed from the equation

$$0 = i[K_1, H_{\text{harm}}] + \lambda H_{\text{anharm}}^{\text{nc}}. \quad (\text{A14})$$

This may be done by inserting an appropriate energy denominator in each term of $\lambda H_{\text{anharm}}^{\text{nc}}$ and multiplying the resulting operator by i . The result of the calculation is

$$\begin{aligned} K_1 = & -(i\beta/\hbar\omega)(\frac{1}{3}a^{\dagger 3} + 3a^{\dagger 2}a - 3a^\dagger a^2 + 3a^\dagger - 3a - \frac{1}{3}a^3) \\ & - (i\gamma/\hbar\omega)(\frac{1}{2}a^{\dagger 4} - \frac{1}{4}a^4 + 2a^{\dagger 3}a - 2a^\dagger a^3 + 3a^{\dagger 2} - 3a^2). \end{aligned} \quad (\text{A15})$$

The simple but lengthy construction of D_2 requires the calculation of the commutator $\frac{1}{2}i[K_1, D_1 + H_1]$ and the selection of all the terms that commute with H_{harm} . Upon including terms up to the required order of approximation, the operator D_2 is found to be

$$D_2 = -30(\beta^2/\hbar\omega)\{(a^\dagger a)^2 + (a^\dagger a) + \frac{11}{30}\}. \quad (\text{A16})$$

The transformed Hamiltonian $H'_0 = H_{\text{harm}} + D_1 + D_2$ has the form given by Eq. (3) (with c -number terms dropped).

APPENDIX B: INTERACTION HAMILTONIAN IN THE NEW UNITARY FRAME

The interaction between the anharmonic oscillator and the applied field is given by Eq. (2) in the

$$\begin{aligned} H'_1 \equiv U(\lambda)H_1U(\lambda)^{-1} = & \hbar\omega_R a^\dagger e^{-i\Omega t} + \hbar\omega_R \left(\frac{\beta}{\hbar\omega}\right) e^{-i\Omega t} (3a^{\dagger 2} - 6a^\dagger a - 3 - a^2) \\ & + \hbar\omega_R \left(\frac{\gamma}{\hbar\omega}\right) e^{-i\Omega t} (-a^3 + 2a^{\dagger 3} - 6a^\dagger a^2 - 6a) + \hbar\omega_R \frac{\beta^2}{(\hbar\omega)^2} e^{-i\Omega t} (6a^{\dagger 3} - 8a^{\dagger 2}a + 30a^\dagger a^2 - 8a^\dagger + 30a - 3a^3) \\ & + \hbar\omega_R \frac{\beta\gamma}{(\hbar\omega)^2} e^{-i\Omega t} (124 - 309a^{\dagger 2} + 10a^{\dagger 4} + 648a^\dagger a - 198a^{\dagger 3}a + 75a^2 + 312a^{\dagger 2}a^2 + 50a^\dagger a^3 - 6a^4) \\ & + \text{H.a.} + O(\gamma^2). \end{aligned} \quad (\text{B4})$$

We observe that both $a^\dagger e^{-i\Omega t}$ and its Hermitian adjoint (H.a.) undergo secular variation, i.e., variations over a time scale which is much longer than the optical period. Next, we notice that the terms of order $(\beta/\hbar\omega)^0$ in Eq. (B4) are all secular terms, while the terms of order $\beta/\hbar\omega$, $\gamma/\hbar\omega$, and $\beta\gamma/(\hbar\omega)^2$ are all rapidly varying terms. The terms of order $(\beta/\hbar\omega)^2$ are in part secular ($-8a^{\dagger 2}a - 8a^\dagger + \text{H.a.}$) and in part rapidly varying. The secular terms, however, are ω_R/ω times smaller than

original reference system. After application of the unitary transformation induced by $U(\lambda)$, the Hamiltonian (2) describing the interaction of the anharmonic oscillator with the electric field becomes

$$H'_1(\lambda) = U(\lambda)H_1U(\lambda)^{-1}. \quad (\text{B1})$$

It is required to expand $H_1(\lambda)$ to the same order of approximation in the anharmonic parameters that was used in the construction of H'_0 [Eq. (3)]. An elementary calculation shows that the expansion of Eq. (B1) to order λ^2 takes the form

$$H'_1 = H_1 + i[K_1, H_1] + i[K_2, H_1] - \frac{1}{2}[K_1, [K_1, H_1]]. \quad (\text{B2})$$

In Eq. (B2) we have set the expansion parameter λ equal to unity. Our objective is to analyze each term on the right-hand side of Eq. (B2) and retain only the contributions of orders β^2 and $\beta\gamma$ in the anharmonic parameters. For this purpose we need to calculate K_2 from Eq. (A8), and to evaluate all the commutators on the right-hand side of Eq. (B2). A simple but lengthy calculation leads to

$$\begin{aligned} K_2 = & i \frac{\beta^2}{(\hbar\omega)^2} (9a^{\dagger 2} + 6a^{\dagger 3}a - \frac{3}{4}a^{\dagger 4}) \\ & + i \frac{\beta\gamma}{(\hbar\omega)^2} (122a^\dagger + \frac{621}{2}a^{\dagger 2}a + 16a^{\dagger 3} + \frac{199}{2}a^{\dagger 3}a^2 \\ & + 8a^{\dagger 4}a - \frac{11}{10}a^{\dagger 5}) + \text{H.a.} + O(\gamma^2). \end{aligned} \quad (\text{B3})$$

It remains now to evaluate the commutators on the right-hand side of Eq. (B2) using Eq. (A15) for K_1 and Eq. (2) for H_1 . The result is

the second-order contributions of the unperturbed Hamiltonian H'_0 and $(\beta/\hbar\omega)^2$ times smaller than the main secular contribution to H'_1 . Thus to an excellent approximation we can take

$$H'_1 = H_1 + (\text{rapidly varying terms}). \quad (\text{B5})$$

The effect of the rapid variation, of course, averages out to zero over times which are longer than the optical period.

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