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Coherent two-photon processes: Transient and steady-state cases

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A class of molecular two-photon processes, occurring under transient or steady-state conditions, is analyzed exactly for certain cases using a density-matrix formalism. Our results are relevant to the recently observed phenomena of transient coherent Raman beats and steady-state two-photon absorption of oppositely directed laser beams. Lowest-order perturbation theories have shown that these processes are insensitive to the Doppler effect, and consequently the linewidth is unaffected by Doppler broadening and by elastic collisions that change molecular velocity. The solutions presented here are of the same form for the Raman and two-photon problems and reveal significant power-dependent frequency shifts and line broadening that correct the ideal Doppler-free solutions. For the transient case, we assume a molecular three-level quantum structure that can be switched in or out of optical resonance with cw laser radiation by means of a pulsed dc Stark field, but the solutions also apply when resonant optical pulses are introduced. During the resonant condition when the Stark pulse is on, the three levels are prepared in coherent superposition, and during the nonresonant condition following the Stark pulse, the laser field(s) stimulates the coherently prepared sample in a transient two-photon process. One of these processes, the Raman-beat effect, has been observed in forward scattering, but the second one, transient two-photon emission, should be observable in backward scattering. Bloch-like equations are derived for this three-level problem that facilitate an exact pulse solution for state preparation. Following the pulse, transient decay is well-approximated by a perturbation calculation. For the steady-state case, an exact solution is also obtained and is of interest for continuous-wave spectroscopy or for transient experiments requiring an initial preparation of quantum states, prior to Stark switching. These solutions exhibit a power-dependent line broadening and a frequency shift of magnitude $\sim\Delta(\alpha^2-\beta^2)/(\Delta^2+1/T_2^2)$, in agreement with our earlier estimate, where α and β are the Rabi flopping frequencies for the two intermediate transitions and Δ is the off-resonance tuning behavior for one of them.

I. INTRODUCTION

This article discusses a class of coherent two-photon[1] processes that can occur in a three-level quantum system under transient or steady-state conditions. The problem arises also in nuclear magnetic and quadrupole resonance[2] and has emerged recently at optical frequencies, as in the phenomena of coherent Raman beats,[3,4] two-photon absorption with oppositely directed beams,[5,6] and self-induced transparency.[7]

In the case of Raman beats, observed recently by Shoemaker and Brewer,[3] three molecular levels are prepared initially in superposition by means of continuous laser radiation. Two of the levels are degenerate and connect optically with a third level during a resonant steady-state preparative phase [see Fig. 1(a)]. Upon application of a dc Stark field, the molecular-level degeneracy is removed and coherent forward Raman scattering then occurs in the presence of the same laser field during the nonresonant condition. The two beams, laser and Raman light, strike a photodetector where they produce a coherent beat at a frequency that corresponds to the level splitting between initial and final states in this two-photon process. The Raman-beat effect has been analyzed[4] in terms of a three-level density-matrix perturbation treatment, both during the *steady-state preparation* and the subsequent transient Raman scattering which follows.

In this article, we treat the Raman-beat effect and also the related problem of two-photon absorption of oppositely directed beams for the case of *pulse preparation*, and we find, in contrast to previous attempts, that an exact pulse solution is attainable for certain experimentally interesting situations. An exact solution is necessary because the relevant density-matrix elements swing through large excursions in time and perturbation techniques become invalid. We will show that Bloch-like equations of motion for the three-level problem can be derived to yield a solution quite analogous to the standard two-level case. The transient regime which follows the pulse preparation is still well approximated by a perturbation calculation.

Exact steady-state solutions for the Raman effect and two-photon absorption are also included, applicable to continuous-wave spectroscopy or for transient experiments requiring an initial preparation of quantum states. In general, the form of the solutions is the same for the Raman and two-photon absorption problems in either transient or steady-state conditions.

II. RAMAN BEATS

A. Pulse preparation: Basic equations

We consider the Raman-beat case first using the molecular-level configuration of Fig. 1. The two-photon absorption problem is fundamentally the same and will be handled later. The molecular-gas sample is subject to a laser field

$$E_x(z,t)=\tfrac{1}{2}E_0(e^{i(\Omega t-kz)}+\text{c.c.}), \tag{1}$$

of frequency Ω and amplitude E_0, polarized along the x axis and propagating in the z direction. Normally levels 1 and 2 are split by a frequency ω_{12} due to a dc Stark bias field ϵ applied along the y axis. However, when a Stark pulse of amplitude $-\epsilon$ appears, levels 1 and 2 become degenerate and the laser field excites the transitions 1-3 and 2-3, placing all three levels in superposition [Fig. 1(a)]. Insofar as the Raman-beat effect is concerned, the preparation of states is contained in the off-diagonal density-matrix element ρ_{12} which persists after the pulse is removed and gives rise to the coherent transient Raman scattering that follows [Fig. 1(b)].

Our objective, therefore, is to obtain a closed-form solution for $\rho_{12}(t_w)$ as a result of a Stark pulse of arbitrary duration t_w. This exact solution constitutes the initial condition for transient Raman scattering for times $t>t_w$. For this latter period, a perturbation treatment developed in Ref. 4 suffices and will be referred to again.

The time-dependent behavior of the density matrix ρ is given by

$$i\hbar\dot{\rho}=[H,\rho], \tag{2}$$

where we neglect damping terms, assuming the pulse to be sufficiently short compared to actual molecular decay times. Molecules interact with the laser field, Eq. (1), through the dipole interaction part

$$H_I=-\vec{\mu}\cdot\vec{E}(z,t) \tag{3}$$

of the total Hamiltonian H.

The electric dipole matrix elements are given by

$$\begin{aligned}&\langle 1|\mu|3\rangle\equiv\mu_{13}\neq 0,\\ &\langle 2|\mu|3\rangle\equiv\mu_{23}\neq 0,\\ &\langle 1|\mu|2\rangle=0.\end{aligned} \tag{4}$$

The time dependence arising from molecular motion along the z direction is introduced by defining the molecular position coordinate

$$z=z_0+v_zt,$$

where $\vec{v}_z$ is the molecular velocity and z_0 is a fixed reference point in the moving frame. Such a transformation applied to (1) results in

$$\begin{aligned}&E_x(z_0,t)=\tfrac{1}{2}E_0e^{i(\omega t-kz_0)}+\text{c.c.},\\ &\omega=\Omega-kv_z,\end{aligned} \tag{5}$$

where the Doppler shift is expressed by kv_z.

We remove the rapidly oscillating factors of the off-diagonal elements by using

$$\rho_{13}=\tilde{\rho}_{13}e^{i(\omega t-kz_0)}, \tag{6a}$$

$$\rho_{23}=\tilde{\rho}_{23}e^{i(\omega t-kz_0)}, \tag{6b}$$

and adopt the definitions

$$\begin{aligned}&\omega_{ij}=(E_i-E_j)/\hbar,\\ &\alpha=\mu_{13}E_0/2\hbar,\quad \beta=\mu_{23}E_0/2\hbar,\\ &\Delta=\omega-\omega_{31}=\omega-\omega_{32}.\end{aligned}$$

The equations of motion in the rotating-wave approximation then become

$$\dot{\tilde{\rho}}_{13}+i\Delta\tilde{\rho}_{13}=i\alpha(\rho_{33}-\rho_{11})-i\beta\rho_{12}, \tag{7a}$$

$$\dot{\tilde{\rho}}_{23}+i\Delta\tilde{\rho}_{23}=i\beta(\rho_{33}-\rho_{22})-i\alpha\rho_{21}, \tag{7b}$$

$$\dot{\rho}_{12}+i\omega_{12}\rho_{12}=i\alpha\tilde{\rho}_{32}-i\beta\tilde{\rho}_{13}, \tag{7c}$$

$$\dot{\rho}_{11}=i\alpha(\tilde{\rho}_{31}-\tilde{\rho}_{13}), \tag{7d}$$

$$\dot{\rho}_{22}=i\beta(\tilde{\rho}_{32}-\tilde{\rho}_{23}), \tag{7e}$$

$$\dot{\rho}_{33}=i\alpha(\tilde{\rho}_{13}-\tilde{\rho}_{31})+i\beta(\tilde{\rho}_{23}-\tilde{\rho}_{32}). \tag{7f}$$

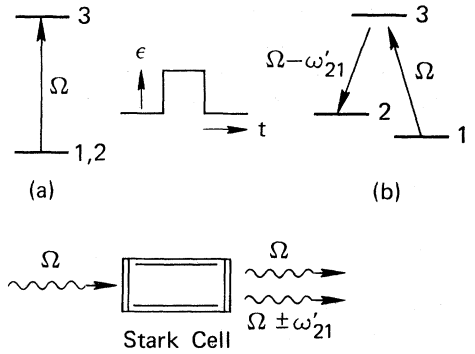

FIG. 1. Molecular energy-level diagrams illustrate (a) coherent preparation of a three-level quantum system during a Stark pulse when the levels 1 and 2 are degenerate ($\omega_{21}=0$); and (b) transient forward scattering following the pulse because of the coherent Raman-beat effect. A second frequency component $\Omega+\omega'_{21}$, not shown in (b), is also emitted.

An exact solution of Eqs. (7) is easily obtained for the Raman-pulse preparation case when $\omega_{12}=0$, a condition that has been easily satisfied in previous experiments.[3]

B. Three-level Bloch equations

Pairs of equations in (7) may be combined to give Bloch-like functions u, v, and w where the matrix elements are

$$u_{ij}=\tilde{\rho}_{ij}+\tilde{\rho}_{ji}\,, \tag{8a}$$

$$iv_{ij}=\tilde{\rho}_{ij}-\tilde{\rho}_{ji}\,, \tag{8b}$$

$$w_{ij}=\tilde{\rho}_{ii}-\tilde{\rho}_{jj}\,. \tag{8c}$$

The condition $\omega_{12}=0$ is imposed for the Raman problem and we obtain the following set of equations:

$$\dot{u}_{13}-v_{13}\Delta-\beta v_{12}=0\,, \tag{9a}$$

$$\dot{u}_{23}-v_{23}\Delta+\alpha v_{12}=0\,, \tag{9b}$$

$$\dot{v}_{13}+u_{13}\Delta+2\alpha w_{13}+\beta u_{12}=0\,, \tag{9c}$$

$$\dot{v}_{23}+u_{23}\Delta+2\beta w_{23}+\alpha u_{12}=0\,, \tag{9d}$$

$$\dot{w}_{13}-2\alpha v_{13}-\beta v_{23}=0\,, \tag{9e}$$

$$\dot{w}_{23}-2\beta v_{23}-\alpha v_{13}=0\,, \tag{9f}$$

$$\dot{u}_{12}-\alpha v_{23}-\beta v_{13}=0\,, \tag{9g}$$

$$\dot{v}_{12}-\alpha u_{23}+\beta u_{13}=0\,, \tag{9h}$$

$$\dot{w}_{12}-\alpha v_{13}+\beta v_{23}=0\,. \tag{9i}$$

Equations (9) can now be symmetrized in the following way. First, (9a) and (9b) are multiplied respectively by the dimensionless quantities $\alpha_1=\alpha/\epsilon$ and $\beta_1=\beta/\epsilon$, and then added together. The parameter

$$\epsilon=2(\alpha^2+\beta^2)^{1/2}$$

evolves from the treatment below. Similarly, (9c) is multiplied by α_1 and (9d) by β_1 and the two equations added. In the resulting equations we identify terms of the form

$$U=\alpha_1 u_{13}+\beta_1 u_{23}\,, \tag{10a}$$

$$V=\alpha_1 v_{13}+\beta_1 v_{23}\,, \tag{10b}$$

$$W=(\alpha_1^2 w_{13}+\beta_1^2 w_{23}+\alpha_1\beta_1 u_{12})/(\alpha_1^2+\beta_1^2)^{1/2}\,. \tag{10c}$$

After substitution of expressions for $\dot{w}_{13}$, $\dot{w}_{23}$, and $\dot{u}_{12}$ from Eqs. (9) into $\dot{W}$, the particular identity $\dot{W}=\epsilon V$ results. (This ϵ is not to be confused with the dc Stark field.) A set of reduced Bloch equations may now be written as

$$\begin{aligned}&\dot{U}-\Delta V=0\,,\\ &\dot{V}+\Delta U+\epsilon W=0\,,\\ &\dot{W}-\epsilon V=0\,.\end{aligned} \tag{11}$$

For constant ϵ, the well-known solutions[8] to Eq. (11) are given by

$$U(t)=K\Delta[\cos(\gamma t)-1]\,, \tag{12a}$$

$$V(t)=-K\gamma\sin\gamma t\,, \tag{12b}$$

$$W(t)=W(0)+K\epsilon[\cos(\gamma t)-1]\,, \tag{12c}$$

with

$$\gamma=(\Delta^2+\epsilon^2)^{1/2},\quad K=\epsilon\,W(0)/(\Delta^2+\epsilon^2)\,.$$

When the Stark pulse is applied at $t=0$, the initial conditions are $W(t=0)=W(0)$ and $U(0)=V(0)=0$.

Note that the quantity γ is an effective precession frequency in the frame of reference rotating at frequency Ω, and γt is the angle through which the Bloch vector turns in a time t.

C. Pulse solution of ρ_{12}

The next step is to derive solutions for $u_{12}(t)$ and $v_{12}(t)$ using Eqs. (9)–(12) since the desired quantity over the pulse interval $0\leq t\leq t_w$ is

$$\rho_{12}(t)=\tfrac{1}{2}[u_{12}(t)+iv_{12}(t)]\,. \tag{13}$$

These equations ultimately reduce to

$$\frac{d^4v_{12}}{dt^4}+[\Delta^2+2(\alpha^2+\beta^2)]\frac{d^2v_{12}}{dt^2}+(\alpha^2+\beta^2)^2v_{12}=0\,. \tag{14}$$

With the initial conditions

$$v_{12}(0)=\dot{v}_{12}(0)=\frac{d^2v_{12}(0)}{dt^2}=0\,,$$

$$\frac{d^3v_{12}(0)}{dt^3}=2\Delta\alpha\beta w_{12}(0)\,,$$

we find from (14) that

$$v_{12}(t)=\frac{\alpha\beta w_{12}(0)}{\delta}\left(\frac{\sin(\delta-\Delta/2)t}{\delta-\Delta/2}-\frac{\sin(\delta+\Delta/2)t}{\delta+\Delta/2}\right)\,,$$

$$\delta=(\alpha^2+\beta^2+\Delta^2/4)^{1/2}\,. \tag{15}$$

Note that $w_{12}(0)=\rho_{11}(0)-\rho_{22}(0)$ is the occupation probability difference at time $t=0$ preceding the pulse. The quantity

$$u_{12}(t)=\frac{8\alpha\beta K}{\epsilon}(\cos\gamma t-1)-\left(\frac{\alpha\beta}{\delta}\right)\frac{(\alpha^2-\beta^2)}{(\alpha^2+\beta^2)}\,w_{12}(0)\times\left(\frac{\cos(\delta-\Delta/2)t-1}{\delta-\Delta/2}+\frac{\cos(\delta+\Delta/2)t-1}{\delta+\Delta/2}\right) \tag{16}$$

derives from (9g) where $v_{23}=\epsilon(V-\alpha_1 v_{13})/\beta$, V is given by (12b), and

$$v_{13}=\frac{-\alpha\beta^2 w_{12}(0)}{\delta(\alpha^2+\beta^2)}[\sin(\delta-\Delta/2)t+\sin(\delta+\Delta/2)t]-\frac{\alpha K\gamma\epsilon}{(\alpha^2+\beta^2)}\sin\gamma t\,. \tag{17}$$

Equation (17) follows by taking the time derivative of (9h), and then inserting into it expressions for $\dot{u}_{23}$ and $\dot{u}_{13}$ from (9b) and (9a) and for v_{23} from (10b).

Equations (15) and (16) combine finally to give $\rho_{12}(t_w)$ of Eq. (13), evaluated at $t=t_w$ at the end of a pulse of duration t_w.

D. Steady-state preparation

An exact expression for ρ_{12} under steady-state conditions can be derived also and is given by Eq. (34c) in Sec. III C. It reduces to the perturbation result[4]

$$\rho_{12}(\text{s.s.})=\frac{2(\tau_2/T_2)\alpha\beta(\rho_{33}^0-\rho_{22}^0)}{(\omega-\omega_0)^2+1/T_2^2}, \tag{18}$$

when the levels 1 and 2 are degenerate during preparation. For this case, $\omega_0=\omega_{31}=\omega_{32}$ and the thermal difference in state occupation probability is $\rho_{33}^0-\rho_{22}^0=\rho_{33}^0-\rho_{11}^0$ in the absence of an external field. Equation (18) is included here to allow an easy comparison of the steady-state case with that of pulse preparation, Eqs. (13), (15), and (16).

E. Transient decay

Previously, a perturbation solution was derived for the heterodyne beat signal following preparation under steady-state conditions.[4] The result is given in Eq. (35) of Ref. 4. In the steady-state situation described by Eq. (18), ρ_{12} is real, but in the present pulse solution for $\rho_{12}(t_w)$, real and imaginary parts of (13) contribute to the beat signal so that a slight generalization of our earlier treatment is required (see Sec. III B for additional details).

We find for the period $t\geq t_w$ following the pulse that the velocity-averaged beat amplitude of the optical flux in terms of $\rho_{12}(t_w)$ is

$$\begin{aligned}(E_TE_T^*)^b=&-4\pi NL(\hbar\Omega/c)\alpha\beta e^{-t/\tau_2}\\&\times\langle[v_{12}(t_w)\cos\omega_{12}'t+u_{12}(t_w)\sin\omega_{12}'t]\\&\times[(1/\Delta_{13}')-(1/\Delta_{23}')]\rangle_{\text{vel}}.\end{aligned} \tag{19}$$

E_T is the total optical field and levels 1 and 2 are no longer degenerate due to the Stark bias field, so that $\omega_{31}'=\omega_{31}+\Delta\omega_{31}$ and $\omega_{32}'=\omega_{32}+\Delta w_{32}$, and

$$\omega_{12}'\neq 0,\quad \Delta_{13}'=\Omega-kv_z-\omega_{31}',\quad \Delta_{23}'=\Omega-kv_z-\omega_{32}'.$$

The quantity N is the molecular density, L is the sample length, and τ_2 is the (Raman) dephasing time associated with ρ_{12}.

For steady-state preparation, we see that Eq. (19) reduces to Eq. (35) of Ref. 4,

$$\begin{aligned}(E_TE_T^*)_{\text{s.s.}}^b=&-8\pi NL(\hbar\Omega/c)\alpha\beta e^{-t/\tau_2}\\&\times\langle\rho_{12}(\text{s.s.})\sin\omega_{12}'t[(1/\Delta_{13}')-(1/\Delta_{23}')]\rangle_{\text{vel}},\end{aligned} \tag{20}$$

because $\rho_{12}(\text{s.s.})=\frac{1}{2}u_{12}(\text{s.s.})$ is real and $v_{12}(\text{s.s.})=0$ according to (18). [Equation (20) corrects the error in the sign of the Δ_{23}' term in Ref. 4.]

For pulse preparation, considerable simplification of (19) results when there is a zero difference in occupation probability $w_{12}(0)\sim 0$. This condition corresponds to the experiments of Shoemaker and Brewer[3] so that (15) and (16) become

$$\begin{aligned}&v_{12}(t_w)\sim 0,\\&u_{12}(t_w)\sim\frac{8\alpha\beta W(0)}{\Delta^2+4(\alpha^2+\beta^2)}(\cos\gamma t_w-1).\end{aligned} \tag{21}$$

Note that

$$W(0)=\frac{\alpha_1^2w_{13}(0)+\beta_1^2w_{23}(0)}{(\alpha_1^2+\beta_1^2)^{1/2}}$$

is large compared to $w_{12}(0)$. The effect of a Stark pulse is now easily visualized as causing a precession of an effective Bloch vector through the angle γt_w during the pulse interval t_w. The maximum beat amplitude in (19) will occur for a $\frac{1}{2}\pi$ pulse for the resonance case, i.e.,

$$\gamma t_w=2(\alpha^2+\beta^2)^{1/2}t_w=\tfrac{1}{2}\pi. \tag{22}$$

If the level structure has more than three levels so that different three-level combinations are possible, each corresponding to a different $(\alpha^2+\beta^2)$ term in (21), then varying the pulse width t_w will give a series of maxima as the various $\frac{1}{2}\pi$ conditions are achieved. Since (19) is velocity dependent through the terms Δ_{13}, Δ_{13}', Δ_{23}, and Δ_{23}', it must be Doppler-averaged numerically over the molecular velocity v_z, care being taken to avoid the divergence in (19) for small Δ_{13}' and Δ_{23}'.

III. TWO-PHOTON ABSORPTION AND EMISSION

A. Pulse preparation

We will show that the exact solutions obtained for pulse preparation of Raman beats, Sec. II, also apply to pulsed two-photon absorption when the two light beams propagate collinearly in opposite directions. The transient two-photon emission which follows the pulse is treated in a manner analogous to the Raman problem. In addition, exact steady-state solutions for two-photon absorption (preparation) are presented in Sec. III C in connection with recent experiments.[6] The appropriate molecular-level structure is shown in Fig. 2 where the sample is excited by two cw collinear optical beams,

$$E_x(z,t)=E_1\cos(\Omega_1t-kz)+E_2\cos(\Omega_2t+kz), \tag{23}$$

polarized in the x direction and propagating along the z axis in opposite directions. The frequency Ω_1 is assumed to be in near resonance with the

3-1 transition and Ω_2 is in near resonance with the 2-3 transition. The two frequencies are sufficiently different that each beam excites only one transition rather than both transitions simultaneously. Yet it can be assumed that $\Omega_1 - \Omega_2$ is sufficiently small, say in the microwave region, that we can neglect in (23) the difference in propagation vectors $k_i = \Omega_i/c$ $(i=1,2)$. We also retain the optical selection rules expressed by Eq. (4). The effect of a Stark pulse, directed along the y axis, is to shift the molecular levels into resonance for a two-photon transition where the frequency condition $\Omega_1 + \Omega_2 = \omega_{21}$ is satisfied [Fig. 2(a)]. This process places the three levels in coherent superposition and constitutes the preparative stage over the pulse duration. As in the Raman-beat effect, memory of the preparation is contained in the off-diagonal element ρ_{12} and gives rise to a transient two-photon emission following the pulse [Fig. 2(b)]. Two light beams are emitted in *opposite directions* along the z axis where each beam exhibits a *beat,* due to the Stark shift, that is analogous to the Raman beat.

The appropriate density-matrix equations are of the form

$$\dot{\tilde{\rho}}_{13} + i\tilde{\rho}_{13}(\Delta - i/T_2) = i\alpha(\rho_{33} - \rho_{11}) - i\beta\tilde{\rho}_{12}\,, \quad (24a)$$

$$\dot{\tilde{\rho}}_{23} - i\tilde{\rho}_{23}(\Delta' + i/T_2) = i\beta(\rho_{33} - \rho_{22}) - i\alpha\tilde{\rho}_{21}\,, \quad (24b)$$

$$\dot{\tilde{\rho}}_{12} + i\tilde{\rho}_{12}(\Delta + \Delta' - i/\tau_2) = i\alpha\tilde{\rho}_{32} - i\beta\tilde{\rho}_{13}\,, \quad (24c)$$

$$\dot{\rho}_{11} = i\alpha(\tilde{\rho}_{31} - \tilde{\rho}_{13}) - (\rho_{11} - \rho_{11}^0)/T_1\,, \quad (24d)$$

$$\dot{\rho}_{22} = i\beta(\tilde{\rho}_{32} - \tilde{\rho}_{23}) - (\rho_{22} - \rho_{22}^0)/T_1\,, \quad (24e)$$

$$\dot{\rho}_{33} = i\alpha(\tilde{\rho}_{13} - \tilde{\rho}_{31}) + i\beta(\tilde{\rho}_{23} - \tilde{\rho}_{32}) - (\rho_{33} - \rho_{33}^0)/T_1\,, \quad (24f)$$

where now

$$\Delta = \Omega_1 - kv_z - \omega_{31}\,, \quad (24g)$$

$$\Delta' = \Omega_2 + kv_z - \omega_{23}\,, \quad (24h)$$

rapidly oscillating terms are removed with the definitions

$$\rho_{13} = \tilde{\rho}_{13}e^{i(\Omega_1 t - kz)}\,, \quad (25a)$$

$$\rho_{23} = \tilde{\rho}_{23}e^{-i(\Omega_2 t + kz)}\,, \quad (25b)$$

$$\rho_{12} = \tilde{\rho}_{12}e^{i(\Omega_1 + \Omega_2)t}\,, \quad (25c)$$

and antiresonant terms have been dropped. The quantity ρ_{ii}^0 represents the thermal equilibrium population of level i. The decay time T_1 is assumed to be the same for all diagonal elements, and T_2 is taken to be the same for ρ_{13} and ρ_{23}, but we designate a different decay time τ_2 for ρ_{12}. The form of the source terms ρ_{ii}^0/T_1 assumes that relaxation between levels 1, 2, and 3 is slow compared to decay from these states to other nearby levels. For stark pulses shorter than the decay times T_1 and T_2, the relaxation and source terms in

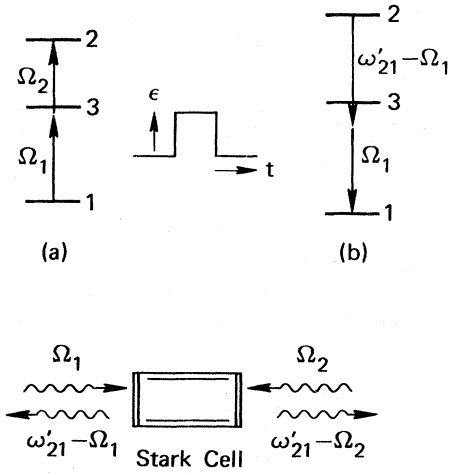

FIG. 2. Molecular energy-level diagrams illustrate (a) coherent preparation of a three-level quantum system by two oppositely directed beams (Ω_1 and Ω_2); a Stark pulse shifts the levels so that the condition $\Omega_1 + \Omega_2 = \omega_{21}$ is satisfied; and (b) transient two-photon emission (backward scattering) following the pulse. A second frequency component $\omega'_{21} - \Omega_2$, not shown in (b), is also emitted.

(24) can be neglected, but they will be of importance in the steady-state calculation of Sec. III C. We notice that if the two-photon resonance condition

$$\Delta + \Delta' = \Omega_1 + \Omega_2 - \omega_{21} = 0 \quad (26)$$

is satisfied, Eqs. (24a)–(24f) are identical to Eqs. (7) for the pulse Raman case when

$$\omega_{12} = 0\,. \quad (27)$$

In this situation, the pulse Raman solutions for ρ_{12} (Raman) [Eqs. (13), (15), and (16)] will be valid also for the $\tilde{\rho}_{12}$ (two-photon) case.

The condition (26) is seen to be no more restrictive than that of (27). For Eq. (27) to be satisfied, the dc Stark field must be zero during the pulse and this condition is easily achieved in practice. On the other hand, for (26) to be valid it is only necessary that ω_{21} match the sum of the two laser frequencies and this can also be accomplished with a Stark pulse of appropriate magnitude.

B. Transient decay

For the period following pulse excitation, $t > t_w$, transient two-photon emission will occur. In addition to the two fields of Eq. (23) which are always present, two new fields will be generated. These are seen in the linearized form of Maxwell's equations

$$\frac{\partial E_{23}(z,t)}{\partial z} = -2\pi i k_2 N\mu_{23}\langle\tilde{\rho}_{23}(z,t)\rangle_{\rm el}\,, \quad (28a)$$

$$\frac{\partial E_{13}(z,t)}{\partial z} = -2\pi i k_1 N\mu_{13}\langle\tilde{\rho}_{13}(z,t)\rangle_{\rm el}\,, \quad (28b)$$

where $\langle\rangle_{\rm vel}$ denotes a velocity summation over the Doppler distribution. The total field then becomes

$$E_T = (E_{13} + E_1/2)e^{i(\Omega_1 t - kz)} + (E_{23} + E_2/2)e^{-i(\Omega_2 t + kz)} + \text{c.c.} \tag{29}$$

The matrix elements $\tilde{\rho}_{13}$ and $\tilde{\rho}_{23}$ are obtained from Eqs. (24a)–(24c) in a perturbation treatment following Ref. 4. This assumes that the right-hand side of (24c) can be neglected, giving

$$\tilde{\rho}_{12}(t) = \tilde{\rho}_{12}(t_w)\exp[-i(\Omega_1 + \Omega_2 + \omega'_{12})t - t/\tau_2] \ , \tag{30}$$

where ω'_{12} is the level splitting for times $t > t_w$.

Considering only the two-photon (beat) terms of (24a) and (24b), it follows that

$$\tilde{\rho}^b_{23}(t) = -\frac{\alpha\tilde{\rho}_{21}(t_w)\exp[i(\Omega_1 + \Omega_2 + \omega'_{12})t - t/\tau_2]}{\Omega_1 - kv_z + \omega'_{13}} \ , \tag{31a}$$

$$\tilde{\rho}^b_{13}(t) = -\frac{\beta\tilde{\rho}_{12}(t_w)\exp[-i(\Omega_1 + \Omega_2 + \omega'_{12})t - t/\tau_2]}{-\Omega_2 - kv_z + \omega'_{23}} \ . \tag{31b}$$

Note that the pulse preparation is contained in $\rho_{12}(t_w)$ as given by Eqs. (13), (15), and (16).

The absolute square of (29) yields beat terms in the intensity

$$\begin{aligned}(E_T E_T^*)^b &= -4\pi i NL\langle\alpha(\hbar\Omega_1/c)(\tilde{\rho}^b_{13} - \tilde{\rho}^b_{31}) + \beta(\hbar\Omega_2/c)(\tilde{\rho}^b_{23} - \tilde{\rho}^b_{32})\rangle_{\rm vel} \\ &= -4\pi NL\alpha\beta e^{-t/\tau_2} \\ &\times \left\langle[-v_{12}(t_w)\cos(\Omega_1 + \Omega_2 + \omega'_{12})t + u_{12}(t_w)\sin(\Omega_1 + \Omega_2 + \omega'_{12})t]\left(\frac{\hbar\Omega_2/c}{\Omega_1 - kv_z + \omega'_{13}} + \frac{\hbar\Omega_1/c}{\Omega_2 + kv_z - \omega'_{23}}\right)\right\rangle_{\rm vel} \ ,\end{aligned} \tag{32}$$

where the in and out of phase components oscillate at a beat frequency $\Omega_1 + \Omega_2 + \omega'_{12}$. Since $\Omega_1 + \Omega_2 + \omega_{12} = 0$ during the Stark pulse, we see that after the pulse, the beat $\Omega_1 + \Omega_2 + \omega'_{12} = \omega'_{12} - \omega_{12}$ is simply the Stark shift. As in the Raman case, Eq. (19), the Doppler average must be handled numerically.

Examination of the frequency content of (29), using (28) and (31), shows that there are two possibilities for two-photon emission (as there are in Raman emission). In the first case, a photon of frequency $\omega'_{21} - \Omega_1$ is emitted in the $-z$ direction and one of frequency Ω_1 in the $+z$ direction, the direction of emission being contained in the $\vec{k}$ vectors of (29). In the second case, a photon of frequency Ω_2 is emitted in the $-z$ direction and one of frequency $\omega'_{21} - \Omega_2$ in the $+z$ direction. Therefore, a photodetector that samples either the $+z$ or the $-z$ propagating beams will detect both two-photon processes simultaneously. The relative contributions of each process are weighted by the off-resonant tuning behavior expressed in the last two terms of (32). Speaking classically, we may say that the coherently prepared sample modulates the Ω_1 beam at a frequency ω'_{21} to produce an oppositely directed sideband at $\omega'_{21} - \Omega_1$; similarly, the sample also modulates the Ω_2 beam to generate an oppositely directed sideband at $\omega'_{21} - \Omega_2$.

It is interesting to speculate on whether or not the beat signal (32) would be observed if the two fields E_1 and E_2 of (23) prepared the sample but only one of them, say E_1, was allowed to probe the sample afterwards. In such a situation, the total field becomes

$$E_T = (E_{13} + E_1/2)e^{i(\Omega_1 t - kz)} + E_{23}e^{-i(\Omega_2 t + kz)} + \text{c.c.} \ , \tag{33a}$$

instead of (29), and the intensity associated with the beat signal is

$$(E_T E_T^*)^b = E_1(E_{13} + E^*_{13}) \ , \tag{33b}$$

where $E_1 = E_1^*$. The beat term $E_1(E_{13} + E^*_{13})$, which appears in (32) through the term containing $(\Omega_2 + kv_z - \omega'_{23})$, represents one of the two possible two-photon processes, while the second process contained in the term $(\Omega_1 - kv_z + \omega'_{13})$ of (32) is absent. We see, therefore, that the two fields E_1 and E_2 are not only needed in the preparation stage but in the detection process as well.

Note that $u_{12}(t_w)$ and $v_{12}(t_w)$ in (32) do not simplify as in (21) for the Raman case because $w_{12}(0) \neq 0$. Nevertheless, most of the features discussed here for two-photon emission apply to the Raman-beat problem. A comparison of the Raman-beat expression Eq. (19) with the two-photon expression (32) shows indeed that they are of the same form. A unique feature of transient two-photon emission, due to the nature of the preparation, is that the two waves are emitted collinearly in opposite directions. If, on the other hand, the beams of frequency Ω_1 and Ω_2 propagated in the same direction, the two photons would also be emitted in the same

direction, but then the Doppler shifts would not cancel and the decay times would be severely shortened because of the Doppler dephasing effect. In the case of coherent Raman beats, only forward scattering is possible where Doppler dephasing does not appear and the incident beam is modulated at frequency ω_{21}' corresponding to the $1 \rightarrow 2$ and $2 \rightarrow 1$ transitions.

We might add that when the E_1 and E_2 fields travel in the same direction, Doppler dephasing could be eliminated in a two-pulse photon-echo experiment, in a manner analogous to the two-level photon-echo problem.

Another property of Eq. (19) and (32) is that the two-photon emission and Raman-beat effects decay as e^{-t/T_2}, independent of molecular velocity. This result is expected in lowest-order perturbation theory because the first-order Doppler shift vanishes for these collinear two-photon processes. All of the velocity packets prepared contribute to the beat signal. It follows that elastic collisions should have no effect on the decay time for either two-photon emission of oppositely directed beams or for Raman beats because the superposition of states remains unaffected. Raman-beat experiments[9] verify this conclusion for molecular vibration-rotation transitions. Whether or not two-photon electronic transitions behave differently because of the influence of phase-interrupting elastic collisions on state superposition is not known at present. However, power-dependent frequency shifts can occur in higher-order solutions as discussed in Sec. III C, and then these two-photon processes are no longer velocity-independent.

C. Steady-state preparation

Several experiments[6] have been reported recently involving steady-state two-photon absorption of two oppositely propagating beams, following the results of an earlier perturbation calculation.[5] We include here an exact treatment of this problem which reveals a significant power-dependent line broadening and frequency shift that is not evident in the perturbation treatment of Vasilenko *et al.*[5] However, the exact calculation given in this section does verify our previous estimate[4] of the power-dependent shift and broadening for the Raman-beat effect. In fact, the steady-state two-photon and Raman solutions are again of the same form, as in the transient case.

We consider the two-photon absorption problem first and then the Raman case, and continue to use the optical arrangement and level structure of Fig. 2 where laser radiation of frequency Ω_1 is in near resonance with the 1-3 transition while Ω_2 is in near resonance with the 2-3 transiton but $\Omega_1 \neq \Omega_2$. The nine equations, given by the off-diagonal elements Eqs. (24a)–(24c) and their complex conjugates and by the diagonal elements Eq. (24d)–(24f), can then be solved simultaneously in a straightforward manner by setting the time derivatives equal to zero.

The solutions are

$$w_{23} = \frac{Dw_{23}^0 - Pw_{12}^0}{T_1(MP - DQ)}, \tag{34a}$$

$$w_{12} = \frac{Qw_{12}^0 - Mw_{23}^0}{T_1(MP - DQ)}, \tag{34b}$$

$$\tilde{\rho}_{12} = a\left(\frac{w_{23}}{\Delta' - i/T_2} + \frac{w_{12} + w_{23}}{\Delta - i/T_2}\right), \tag{34c}$$

$$\tilde{\rho}_{23} = \frac{\alpha\tilde{\rho}_{21} + \beta w_{23}}{\Delta' + i/T_2}, \tag{34d}$$

$$\tilde{\rho}_{13} = \frac{-\beta\tilde{\rho}_{12} - \alpha(w_{12} + w_{23})}{\Delta - i/T_2}, \tag{34e}$$

where $w_{ij}^0 \equiv \rho_{ii}^0 - \rho_{jj}^0$ is the occupation probability difference of levels i and j in the absence of an external field, and we have defined the following quantities

$$a = \alpha\beta \Big/ \left((\Delta + \Delta' - i/T_2) - \frac{\alpha^2}{\Delta' - i/T_2} - \frac{\beta^2}{\Delta - i/T_2}\right), \tag{35a}$$

$$M = a^*b^*e + abe^* - \frac{2\alpha^2/T_2}{\Delta^2 + 1/T_2^2} + \frac{2\beta^2/T_2}{\Delta'^2 + 1/T_2^2}, \tag{35b}$$

$$Q = a^*b^*j + abj^* - \left(\frac{2\alpha^2/T_2}{\Delta^2 + 1/T_2^2} + \frac{4\beta^2/T_2}{\Delta'^2 + 1/T_2^2} + 1/T_1\right), \tag{35c}$$

$$e = i\alpha\beta\left(\frac{-1}{\Delta + i/T_2} + \frac{1}{\Delta' + i/T_2}\right), \tag{35d}$$

$$b = \frac{1}{\Delta - i/T_2} + \frac{1}{\Delta' - i/T_2}, \tag{35e}$$

$$D = -\left(\frac{2\alpha^2/T_2}{\Delta^2 + 1/T_2^2} + 1/T_1\right) + \frac{a^*e}{\Delta + i/T_2} + \frac{ae^*}{\Delta - i/T_2}, \tag{35f}$$

$$j = -i\alpha\beta\left(\frac{2}{\Delta' + i/T_2} + \frac{1}{\Delta + i/T_2}\right), \tag{35g}$$

$$P = -\frac{2\alpha^2/T_2}{\Delta^2 + 1/T_2^2} + \frac{a^*j}{\Delta + i/T_2} + \frac{aj^*}{\Delta - i/T_2}. \tag{35h}$$

It will be seen that Eqs. (34) simplify considerably for the level configuration of Fig. 2 because the thermal occupation probability $w_{23}^0 \approx 0$ whereas $w_{12}^0 \neq 0$.

The set of solutions (34) also apply to the corresponding steady-state Raman process of Fig. 1 when the off-resonance tuning terms are defined

as

$$\Delta = \Omega - kv_z - \omega_{31}\ , \quad -\Delta' = \Omega - kv_z - \omega_{32}\ ,$$

in place of Eqs. (24g) and (24h). However, now $w_{23}^0 \neq 0$, $w_{12}^0 \approx 0$ and the Raman tuning behavior is given by $\Delta + \Delta' = \omega_{12}$ in contrast to the two-photon case, Eq. (26), $\Delta + \Delta' = \Omega_1 + \Omega_2 - \omega_{21}$.

To be specific, we return to the two-photon absorption solution which reduces to the expected two-level solution when we set one of the two external fields equal to zero. For example, when $\beta = 0$, Eq. (34e) becomes

$$\tilde{\rho}_{13} = -\frac{\alpha w_{13}^0}{\Delta - i/T_2}\left(1 - \frac{4\alpha^2 T_1/T_2}{\Delta^2 + 1/T_2^2 + 4\alpha^2 T_1/T_2}\right)\ , \tag{36}$$

which is the result anticipated.

Equation (34d) also reduces to the first order two-photon perturbation solution[5,10]

$$\tilde{\rho}_{23}^{(1)} = \frac{\alpha^2 \beta w_{13}^0}{\Delta' + i/T_2}\,\frac{1}{\Delta + i/T_2}\left(\frac{1}{\Delta + \Delta' + i/\tau_2} - \frac{2T_1/T_2}{\Delta - i/T_2}\right) \tag{37}$$

when one of the external fields is much weaker than the other, corresponding to the condition $\beta \ll \alpha$. The velocity average of (37)

$$\langle \tilde{\rho}_{23}^{(1)} \rangle_{\text{vel}} = \frac{1}{\sqrt{\pi}\,u}\int_{-\infty}^{\infty} e^{-v_z^2/u^2}\,\tilde{\rho}_{23}^{(1)}\,dv_z$$

$$\cong \frac{2\sqrt{\pi}}{ku}\,\alpha^2 \beta w_{13}^0 e^{-v_1^2/u^2}\,\frac{\tau_2}{\Delta + \Delta' + i/\tau_2}\ , \tag{38}$$

can be carried out by contour integration assuming that the velocity group v_1 excited has a much narrower frequency bandwidth kv_1 than the Doppler width ku so that the Gaussian may be factored from the integral. For simplicity, we have also assumed that $T_1 = T_2 = \tau_2$. The polarization associated with (38) generates a field E_{23} according to (28a) that propagates in the same direction as the E_2 laser beam, as in the transient case. A detector viewing this light monitors a cross term in the total intensity E_T of Eq. (29),

$$|(E_T E_I^*)^b| = 16\pi^{3/2} NL\alpha^2\beta^2\,\frac{e^{-v_1^2/u^2}}{ku}\left(\frac{\hbar\Omega_2}{c}\right) w_{13}^0 \times \frac{1}{(\Delta + \Delta')^2 + 1/\tau_2^2}\ , \tag{39}$$

which displays the expected two-photon resonance tuning behavior having a Doppler-free linewidth $1/\tau_2$ that is independent of the intermediate level and elastic collisions. A second detector viewing light from the opposite direction would show essentially the same behavior as (39) due to the $\langle \tilde{\rho}_{13}^{(1)} \rangle$ source term.

When the exact forms of $\tilde{\rho}_{23}$ and $\tilde{\rho}_{13}$ in Eq. (34) are to be used in obtaining $(E_T E_I^*)^b$ from (28) and (29), a numerical evaluation is required as the Doppler average cannot be performed analytically. However, it is still possible to investigate the two-photon resonance denominator or tuning behavior through (35a), namely,

$$a = \alpha\beta \Big/ \left((\Delta + \Delta' - i/\tau_2) - \frac{\alpha^2}{\Delta' - i/T_2} - \frac{\beta^2}{\Delta - i/T_2}\right)$$

$$= \alpha\beta \Big/ \left\{ \Delta\left(1 - \frac{\beta^2}{\Delta^2 + 1/T_2^2}\right) + \Delta'\left(1 - \frac{\alpha^2}{\Delta'^2 + 1/T_2^2}\right) - i\left[\frac{1}{\tau_2} + \frac{1}{T_2}\left(\frac{\beta^2}{\Delta^2 + 1/T_2^2} + \frac{\alpha^2}{\Delta'^2 + 1/T_2^2}\right)\right]\right\}\ .$$

This exhibits an effective linewidth

$$\frac{1}{T_2(\text{eff})} = \frac{1}{\tau_2} + \frac{1}{T_2}\left(\frac{\alpha^2}{\Delta'^2 + 1/T_2^2} + \frac{\beta^2}{\Delta^2 + 1/T_2^2}\right)\ , \tag{40}$$

and a frequency shift

$$\nu = -\left(\frac{\beta^2\Delta}{\Delta^2 + 1/T_2^2} + \frac{\alpha^2\Delta'}{\Delta'^2 + 1/T_2^2}\right) \tag{41}$$

that are power-dependent and thus corrects the perturbation result (39). Furthermore, we see that the two-photon resonance condition is no longer independent of velocity and elastic collisions. It is interesting that the exact expressions (40) and (41) agree with an earlier estimate[4] of the power-dependent line broadening and frequency shift in the case of Raman beats.

When the frequency shift (41) is not excessively large so that $\Delta + \Delta' \sim 0$, its magnitude

$$\nu \sim \frac{\Delta(\alpha^2 - \beta^2)}{\Delta^2 + 1/T_2^2} \tag{42}$$

can be readily estimated. For instance, in the case $\alpha = \beta$, the frequency shift vanishes. More typically, the condition $\alpha \gg \beta$ (or $\beta \gg \alpha$) prevails, and then the shift

$$\nu \sim \frac{\Delta\alpha^2}{\Delta^2 + 1/T_2^2} \tag{43}$$

can be quite large where the direction of the shift is determined by the sign of Δ. For example, when $\Delta \gg 1/T_2$, $\nu \sim \alpha^2/\Delta$ which may be orders of magnitude larger the homogeneous linewidth $1/T_2$. Large power-dependent shifts of this kind have

been observed in recent two-photon absorption measurements.[11]

IV. SUMMARY

We have shown that the coherent Raman-beat effect with a single beam[3,4] and two-photon absorption of oppositely directed laser beams[5,6] contain identical mechanisms for yielding Doppler-free spectra. The difference between the two cases is only one of level spacing. In the Raman problem, two of the levels are nearly degenerate and connect optically with a third level. In the two-photon problem, the third level is intermediate in eigenenergy with respect to the other two where the selection rules are the same as in the Raman case. Thus far, the Raman-beat effect has been seen only in the transient regime with Stark switching[3] whereas two-photon absorption has been observed only under steady-state conditions.[6] However, our solutions apply to both transient and steady-state cases for these two problems. We predict that transient two-photon emission should be observable in backward scattering and will exhibit a beat oscillation that is analogous to the Raman beat seen in forward scattering. Exact steady-state solutions for the Raman and two-photon problems reveal power-dependent frequency shifts and line broadening that must be considered in precision spectroscopy.

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