Theory of coherent three-level beats*

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We present a theoretical treatment of the coherent three-level beat signals occurring in the transient response of a Doppler-broadened molecular system with coupled closely spaced levels resonating with an intense monochromatic cw laser field. When the degenerate levels of the molecular system are suddenly split by means of an external Stark or Zeeman field, the transmitted laser radiation exhibits decaying beats at frequencies related to the level splitting or Raman frequency. This effect has been the subject of earlier theoretical analyses, but some relevant aspects such as the velocity integration, were not taken into account. A perturbation treatment, complete to third order in laser field strength, is used to calculate the velocity-integrated induced polarization and the corresponding reradiated field. The calculation takes into account both Raman-type processes, which lead to transient oscillations at the Raman frequency ω_{21}, and population-saturation effects. In particular, population-induced transient oscillations at half the Raman frequency, $\omega_{21}/2$, are predicted. The relative importance of the various oscillations is analyzed as a function of the laser detuning and other parameters, including velocity-changing collisions. The relationship between the three-level beat signals and the well-known quantum-beat effect studied in fluorescence is explored.

I. INTRODUCTION

Recently a variety of transient phenomena have been observed in the optical-infrared region. These include optical nutation,[1] free-induction decay,[2] photon echo,[1,3] quantum beats,[4] and Dicke superradiance.[5] Several of these are optical analogs of effects first explored in the microwave region.[6] Their extension into the optical range of the electromagnetic spectrum has created the possibility of measuring radiative and collisional relaxation processes in atomic and molecular systems in the time domain. The new techniques complement the laser saturation techniques, which have been used to measure relaxation processes in the frequency domain.[7,8]

The present paper presents a theoretical treatment of an effect[9] developed by Brewer and his collaborators in which the transient behavior of a Doppler-broadened resonance with level degeneracy interacting with an intense monochromatic laser field is studied after a small Stark or Zeeman field has been applied to break the degeneracy of the levels (Fig. 1). The sensitivity of the experiments is enhanced by studying the heterodyne beat between the applied laser field and the transient radiation signal. The coherent three-level beat then manifests itself as an exponentially decaying signal modulated at the Raman frequency ω_{21}, corresponding to the splitting between the closely spaced sublevels produced by the Stark or Zeeman field (Fig. 2). The effect has been called two-photon superradiance and coherent Raman beats, but in this paper we shall use the more general term coherent three-level beats to include beat phenomena occurring at other frequencies related to ω_{21}.

Theoretical interpretations of this effect have been presented in earlier papers[10,11] which showed that three-level beats are caused by Raman-type processes,[12] as manifested in the transient response of ρ_{12}, the density matrix element coupling the closely spaced levels ("Zeeman coherence"), after the applied static field is switched on and ρ_{12} approaches its new equilibrium value. However, in these analyses the details of the transient response are not fully taken into account, and important contributions such as those arising from velocity dephasing have been neglected. For example, after velocity integration, terms which contained velocity-dependent time factors cancel with velocity-independent terms, showing that the amplitude of the beat signal is not independent of

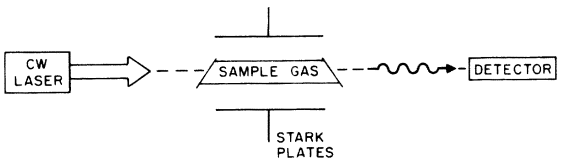

FIG. 1. Experimental setup for observing coherent beat signals. The Stark field is applied at time $t=0$.

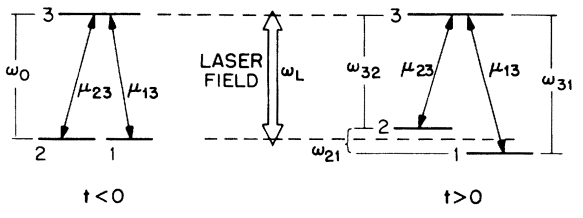

FIG. 2. Three-level system considered in the theoretical analysis.

Doppler dephasing. This velocity integration, which has not been performed in the earlier studies,[10,11] must be carried out in order to assess the relative importance of the different contributions to the three-level beat signal.

Other processes not of the Raman type also contribute to the transient beat signal. In addition to the well-known effects of free-induction decay and optical nutation present in a two-level system, the present calculation predicts a transient oscillation at frequency $\frac{1}{2}\omega_{21}$. Such an effect is partly due to the ρ_{12} coherence and partly to population-saturation interactions between the coupled transitions. The latter contribution would follow from an ordinary rate-equation treatment, which ignores Raman-type processes.

The present paper gives a complete third-order analysis of the coherent three-level beat effect. It is divided into five sections. Section II presents the equations of motion both for the electromagnetic (em) wave and the molecular medium. The solution to the density matrix equations of motion are given in Sec. III, along with a physical interpretation of the results. The velocity integration is discussed in Sec. IV, where the various contributions and cancellations are analyzed. The final expression for the reradiated field is discussed in Sec. V and compared with expressions obtained in earlier studies. The relationship of three-level beats to the quantum-beat effect[4] is also explored. Some details concerning the velocity integration are given in the Appendix.

II. EQUATIONS OF MOTION

We now proceed to calculate the transient polarization and the corresponding reradiated signal induced by an intense cw laser beam resonating with a three-level molecular system with degenerate levels which are suddenly split.[13] The levels are numbered $j=1,2,3$, with E_j the energy eigenvalue of level j (Fig. 2). Level 3, the common level, is coupled to levels 1 and 2 by electric dipole matrix elements μ_{13} and μ_{23}, respectively. From parity considerations $\mu_{12}=0$. The 3-1 and 3-2 transitions are centered at frequencies $\omega_{31}=(E_3-E_1)/\hbar$ and $\omega_{32}=(E_3-E_2)/\hbar$. Initially, levels 1 and 2 are degenerate, so that the center frequencies of both transitions coincide at ω_0. At $t=0$ this degeneracy is lifted and ω_{31} and ω_{32} are split by an amount $\omega_{21}=(E_2-E_1)/\hbar$, which is not necessarily small compared to the Doppler width.

The theoretical problem is to calculate the transient component of the em field produced when the initially degenerate levels are split. The problem may be solved conveniently using the ensemble-averaged density matrix equations and the wave equation. In this approach one uses the density matrix to calculate the macroscopic polarization induced by the applied field on a group of molecules moving with a given velocity component. The net macroscopic polarization is then obtained by integrating over the entire velocity distribution. This polarization acts as a source term in the wave equation for the transient em field.

A. Wave equation

The three-level system under consideration is shown in Fig. 2. The incident cw laser field is of the form

$$E_0(z,t)=\mathrm{Re}(\mathcal{E}_0 e^{-i(\omega t-kz)}), \tag{1}$$

where $\mathcal{E}_0$, the amplitude of the incident field, is a constant quantity which may be taken to be real. Within the gaseous medium, the E field can be written in the form

$$E(z,t)=E_0(z,t)+\mathrm{Re}[\mathcal{E}(z,t)e^{-i(\omega t-kz)}], \tag{2}$$

where $\mathcal{E}(z,t)$, the envelope of the reradiated em field, is assumed in the following discussions to be slowly varying, i.e.,

$$\frac{\partial\mathcal{E}}{\partial t}\ll\omega\mathcal{E} \quad \text{and} \quad \frac{\partial\mathcal{E}}{\partial z}\ll k\mathcal{E},$$

conditions which are well satisfied in the experiments. The macroscopic polarization induced in the medium will then be of the form

$$P(z,t)=\mathrm{Re}[\mathcal{P}(z,t)e^{-i(\omega t-kz)}], \tag{3}$$

where the envelope $\mathcal{P}(z,t)$ is also slowly varying.

In the slowly-varying-envelope approximation the equation for an em wave propagating in the $+z$ direction is given by[14]

$$\left(\frac{\partial}{\partial z}+\frac{1}{c}\frac{\partial}{\partial t}\right)\mathcal{E}(z,t)=+\frac{2\pi i\omega}{c}\mathcal{P}(z,t). \tag{4}$$

According to Eq. (2), at $z=0$ we have $\mathcal{E}(0,t)=0$, so Eq. (4) can be expressed in integral form as

$$\mathcal{E}(z,t)=+\frac{2\pi i\omega}{c}\int_0^z \mathcal{P}(z',t+(z'-z)/c)\,dz'. \tag{5}$$

Since $\mathcal{P}$ also depends on $\mathcal{E}$ via the density matrix equations to be introduced below, the most general solution for $\mathcal{E}$ and $\mathcal{P}$ must be obtained in a self-consistent manner. However, in an optically thin sample, another condition well satisfied in the experiments, the fraction of incident power absorbed is very small; thus the reradiated field will be much smaller than the applied field ($|\mathcal{E}|\ll\mathcal{E}_0$).[15] Therefore in determining the total field $E(z,t)$ may be approximated by $E_0(z,t)$. Then, since $\mathcal{E}_0$ is a constant, the envelope of the induced polarization obtained from the density

matrix will be uniform along the cell, that is, $\mathcal{P}(z,t)$ is z independent.

In integrating Eq. (5) over z', the time dependence of $\mathcal{P}(t)$ gives rise to a phase-matching condition for the reradiated field. However, in the case of a short cell of length L, another condition which is satisfied in the experiments, the phase mismatch of the various waves propagating through the cell is negligible [$(\omega'-\omega)L/c \ll 1$ and $\gamma L/c \ll 1$, where ω' is the frequency of a component of the reradiated field and γ is a characteristic decay rate of the transient polarization]. With this approximation the factor z'/c appearing in the time argument of $\mathcal{P}$ in Eq. (5) may be neglected and $\mathcal{P}$ can be removed from the integrand. Therefore after the cell $\mathcal{E}(z,t)$ is given by

$$\mathcal{E}(z,t) = +(2\pi i\omega L/c)\mathcal{P}(t-z/c). \tag{6}$$

The corresponding output intensity is given by

$$\begin{aligned} I &= (c/4\pi)\langle E^2(z,t)\rangle_t \\ &= (c/8\pi)(\mathcal{E}_0^2 + 2\mathcal{E}_0 \mathrm{Re}\,\mathcal{E} + |\mathcal{E}|^2), \end{aligned} \tag{7}$$

where $\langle\ \rangle_t$ denotes time average over an optical period. The first term on the right-hand side of Eq. (7) is I_0, the intensity of the applied field. The intensity of the heterodyne beat signal, I_b, is given by the second term. Note that since $\mathcal{P}$ is of the order of the optical susceptibility times $\mathcal{E}_0$,

$$\frac{I_b}{I_0} = \frac{4\pi\omega L}{c}\,\mathrm{Im}\left(\frac{\mathcal{P}}{\mathcal{E}_0}\right) \simeq gL \ll 1,$$

where g is the linear absorption coefficient per unit length. Consequently, the third term on the right-hand side of Eq. (7) can be neglected, since it is smaller than I_b by another factor gL.

B. Molecular medium equation

In order to obtain the macroscopic polarization envelope $\mathcal{P}(z,t)$ needed in Eq. (6), we consider the interaction of the electromagnetic field with molecules having a velocity component along the propagation direction of the laser field in a narrow interval between v and $v+dv$. For convenience we use the formalism of the ensemble-averaged density matrix. The equation of motion for the ρ_{ij} element $(i,j=1,2,3)$ is given by[16]

$$\begin{aligned} &\left(\frac{\partial}{\partial t} + v\frac{\partial}{\partial z} + i\omega_{ij} + \gamma_{ij}\right)\rho_{ij}(v,z,t) \\ &\quad = \frac{iE(z,t)}{\hbar}\sum_k (\mu_{ik}\rho_{kj} - \mu_{jk}^*\rho_{ki}^*) + \gamma_{ij}\rho_{ij}^0\delta_{ij}, \end{aligned} \tag{8}$$

where $\rho_{ij} = \rho_{ji}^*$, and where γ_{ij} is the decay rate of ρ_{ij}. The diagonal elements of ρ describe the level population densities per velocity interval for a particular velocity group v. In the absence of the applied field the population density for level j is $\rho_{jj}^0(v)$, and we may write

$$\rho_{jj}^0(v) = N_j G(v), \tag{9}$$

where N_j is the total population density of level j and $G(v)$ is the normalized velocity distribution (see the Appendix):

$$\int_{-\infty}^{+\infty} G(v)\,dv = 1. \tag{10}$$

The near-diagonal density matrix element ρ_{12} describes the phase coherence between levels 1 and 2. The off-diagonal elements of ρ are related to the induced polarization due to molecules moving with axial velocity in the interval between v and $v+dv$ by

$$P(v,z,t)\,dv = 2\,\mathrm{Re}(\mu_{31}\rho_{13} + \mu_{32}\rho_{23})\,dv. \tag{11a}$$

The total macroscopic polarization is obtained by considering contributions from all velocities:

$$P(z,t) = \int_{-\infty}^{+\infty} P(v,z,t)\,dv. \tag{11b}$$

The above $P(z,t)$ is the polarization, whose slowly varying envelope $\mathcal{P}(z,t)$ we insert into Eq. (6) to obtain the transient field. Except for small antiresonant contributions the solution of Eq. (8) is of the form[17]

$$\begin{aligned} &\rho_{ii} = \sigma_{ii}, \quad \rho_{12} = \sigma_{12}, \\ &\rho_{13} = \sigma_{13}e^{i(\omega t - kz)}, \quad \rho_{23} = \sigma_{23}e^{i(\omega t - kz)}, \end{aligned} \tag{12}$$

where the σ_{ij}'s are envelope functions which are slowly varying in space and time. Inserting Eqs. (12) in Eq. (8), taking the space and time derivatives as indicated in Eq. (8), equating the slowly varying envelopes of terms having like exponential space-time factors, and neglecting the small terms on the right-hand sides with rapid space-time variations, we obtain a set of coupled linear equations for the slowly-varying-envelope functions[18]:

$$\frac{\partial}{\partial t}\sigma_{11} + \gamma_1(\sigma_{11} - \sigma_{11}^0) = -i\alpha(\sigma_{13} - \sigma_{13}^*), \tag{13}$$

$$\frac{\partial}{\partial t}\sigma_{22} + \gamma_2(\sigma_{22} - \sigma_{22}^0) = -i\beta(\sigma_{23} - \sigma_{23}^*), \tag{14}$$

$$\frac{\partial}{\partial t}\sigma_{33} + \gamma_3(\sigma_{33} - \sigma_{33}^0) = i\alpha(\sigma_{13} - \sigma_{13}^*) + i\beta(\sigma_{23} - \sigma_{23}^*), \tag{15}$$

$$\left(\frac{\partial}{\partial t} - i(kv + \omega_{31} - \omega) + \gamma_{13}\right)\sigma_{13} = i\alpha(\sigma_{33} - \sigma_{11}) - i\beta\sigma_{12}, \tag{16}$$

$$\left(\frac{\partial}{\partial t} - i(kv + \omega_{32} - \omega) + \gamma_{23}\right)\sigma_{23} = i\beta(\sigma_{33} - \sigma_{22}) - i\alpha\sigma_{12}^*, \tag{17}$$

$$\left(\frac{\partial}{\partial t} - i\omega_{21} + \gamma_{12}\right)\sigma_{12} = i\alpha\sigma_{23}^* - i\beta\sigma_{13}, \tag{18}$$

with

$$\sigma_{ij} = \sigma_{ji}^*, \tag{19}$$

where

$$\alpha = \mu_{13}\mathcal{E}_0/2\hbar, \quad \beta = \mu_{23}\mathcal{E}_0/2\hbar.$$

The phases of states 1 and 2 may be conveniently chosen to make α and β real. Note that the thin-sample approximation mentioned in Sec. II A was made by neglecting $\mathcal{E}(z,t)$ as compared to $\mathcal{E}_0$ in the right-hand sides of Eqs. (13)–(18).

In these equations the diagonal elements σ_{jj} represent the level populations. The off-diagonal elements σ_{13} and σ_{23} describe the coherence between optically connected sublevels. The near-diagonal element σ_{12} describes the coherence between nearby sublevels, sometimes called "Zeeman coherence." This term is responsible for Raman-type coupling between the 1-3 and 2-3 transitions. In Eqs. (13)–(18) γ_{ij} is the decay constant of σ_{ij}, and for convenience we have set $\gamma_{ii} = \gamma_i$. For radiative decay and for hard collisions

$$\gamma_{ij} = \tfrac{1}{2}(\gamma_i + \gamma_j).$$

However, in the case where those collisions which destroy the nondiagonal elements of σ but leave the level populations unaffected are important, we will have

$$\gamma_{ij} > \tfrac{1}{2}(\gamma_i + \gamma_j).$$

Note that in going over from the ρ representation to the σ's, the rapid space-time variations have been removed ("rotating frame") and the σ_{ij}'s are all slowly varying functions of space and time.

The expression for the reradiated field follows directly from the velocity-integrated solution of Eqs. (13)–(18). Equations (3), (6), (11), and (12) give

$$\mathcal{E}(z,t) = +\frac{4\pi i\omega L}{c}\int_{-\infty}^{\infty}(\mu_{13}\sigma_{13}^* + \mu_{23}\sigma_{23}^*)\,dv. \tag{20}$$

III. SOLUTION OF THE EQUATIONS FOR MOLECULES IN A NARROW VELOCITY BAND

We seek a solution to the system of Eqs. (13)–(18) for $t > 0$, after the molecular levels have been split. An approximate solution can be obtained using a perturbation expansion of σ in powers of α/γ and β/γ, the saturation parameters for the two transitions:

$$\sigma_{ij} = \sum_{n=0}^{\infty}\sigma_{ij}^{(n)}, \tag{21}$$

where $\sigma_{ij}^{(n)}$ is a homogeneous polynomial of order n in α, β. It is easy to see that the expansion for the populations σ_{ii} and the near-diagonal element σ_{12} contain only even orders of n, whereas the off-diagonal elements σ_{13} and σ_{23} contain only odd orders. The solution of Eqs. (13)–(18) to third order in α, β is expected to describe the main physical features of the three-level beat signals.

A. Initial conditions

In order to solve the equations in the transient regime ($t > 0$) we have to specify the initial conditions at $t = 0$, when the Stark field is applied. For $t < 0$, when the levels are degenerate, we may assume that the system has reached a steady state, so that the σ_{ij} are all constant ($\partial\sigma/\partial t = 0$). The components of σ may be determined in successive orders of α, β by means of an iterative scheme. The zeroth-order (unperturbed) solutions are $\sigma_{ii}^{(0)} = \sigma_{ii}^0$, the background populations, and $\sigma_{12}^{(0)} = 0$. The first-order coefficients are obtained by replacing the σ_{ii} on the right-hand sides of Eqs. (16) and (17) by their unperturbed values. The steady-state solutions to Eqs. (16) and (17) then give the first-order optical-polarization envelopes $\sigma_{13}^{(1)}$ and $\sigma_{23}^{(1)}$. In the same manner, inserting the first-order coefficients on the right-hand sides of Eqs. (13)–(15) and (18), we then obtain the second-order corrections to the level populations $\sigma_{ii}^{(2)}$ and the near-diagonal element $\sigma_{12}^{(2)}$. These values may then be inserted in the right-hand sides of Eqs. (16) and (17) to give the third-order coefficients $\sigma_{13}^{(3)}$ and $\sigma_{23}^{(3)}$.

Assuming that in the absence of the laser field the populations of levels 1 and 2 are equal, we define the population inversion density between levels 3 and 1, and 3 and 2, by

$$\Delta\sigma_0 = \sigma_{33}^0 - \sigma_{11}^0 = \sigma_{33}^0 - \sigma_{22}^0 = N_0 G(v), \tag{22}$$

where $G(v)$ is the normalized velocity distribution and N_0 is the total inversion density. Introducing

$$L_j^0 = \gamma_{j3} - i(\omega_0 + kv - \omega), \quad j = 1, 2, \tag{23}$$

we have for the initial conditions

$$\sigma_{11} = \sigma_{11}^0 + \Delta\sigma_0(\alpha^2/\gamma_1)2\,\mathrm{Re}(1/L_1^0), \tag{24}$$

$$\sigma_{33} = \sigma_{33}^0 - 2\frac{\Delta\sigma_0}{\gamma_3}\mathrm{Re}\left(\frac{\alpha^2}{L_1^0} + \frac{\beta^2}{L_2^0}\right), \tag{25}$$

$$\sigma_{12} = \Delta\sigma_0\frac{\alpha\beta}{\gamma_{12}}\left(\frac{1}{L_1^0} + \frac{1}{L_2^{0*}}\right), \tag{26}$$

$$\sigma_{13} = \frac{i\alpha\Delta\sigma_0}{L_1^0}\left\{1 - \alpha^2\left(\frac{1}{\gamma_1} + \frac{1}{\gamma_3}\right)2\,\mathrm{Re}\left(\frac{1}{L_1^0}\right) - \beta^2\left[\frac{2}{\gamma_3}\mathrm{Re}\left(\frac{1}{L_2^0}\right) + \frac{1}{\gamma_{12}}\left(\frac{1}{L_1^0} + \frac{1}{L_2^{0*}}\right)\right]\right\}. \tag{27}$$

The corresponding solutions for σ_{22} and σ_{23} are obtained by interchanging α with β and 1 with 2 in σ_{11} and σ_{13}, respectively. The order to each term in the solution is evident by inspecting its power in α, β.

B. Solution

Once the initial conditions have been found, the solution of Eqs. (13)–(18) for $t>0$ can be obtained using the same iterative procedure described above. This time, in each order to perturbation we look for the general solution (inhomogeneous plus homogeneous) which matches the previously determined boundary conditions at $t=0$. The density matrix equation for the nth-order contribution to σ_{ij} is of the form

$$\left(\frac{\partial}{\partial t}+\lambda\right)\sigma_{ij}^{(n)}=\sum_{\lambda'}B'e^{-\lambda' t}, \tag{28}$$

where the driving terms on the right-hand side with complex frequency λ' are obtained from the solution of the equations of the next lower order, $n-1$. [The summation in Eq. (28) is over the primed quantities.] As can be seen from Eqs. (13)–(18), for the off-diagonal elements $\lambda=-i(\omega_{3j}-\omega+kv)+\gamma_{3j}$, whereas for the diagonal and near-diagonal elements, $\lambda=\gamma_i$ and $i\omega_{21}+\gamma_{21}$, respectively. Also note that B' and λ' may be functions of velocity. The general solution of this equation is

$$\sigma_{ij}^{(n)}(v,t)=\sigma_{ij}^{(n)}(v,0)e^{-\lambda t}+\sum_{\lambda'}B'\,\frac{e^{-\lambda' t}-e^{-\lambda t}}{\lambda-\lambda'}, \tag{29}$$

where the initial condition $\sigma_{ij}^{(n)}(v,0)$ is obtained from the steady-state solution ($t<0$). Let us examine the structure of Eq. (29):

(a) The first term on the right-hand side describes the free decay of $\sigma_{ij}^{(n)}$ from its initial value. This term is associated with the transient response of the molecular system, which occurs at the (complex) "natural" frequency of the system and not at the laser frequency.

(b) The remaining terms of Eq. (29) describe the response of the system to the excitation at complex frequency λ', and may be classified as optical nutation terms. The excitation gives rise to contribution at the driving frequency λ' ("inhomogeneous" term). However, the buildup of each term is determined by the natural response of the molecule, and so is accompanied by a transient contribution which decays at the natural frequency of the system.

The solutions for the $\sigma_{ij}^{(n)}$, $t>0$, can be directly obtained using Eq. (29) and the initial conditions given by Eqs. (24)–(27). To write the solutions we introduce the notation

$$L_j=\gamma_{j3}-i(\omega_{3j}+kv-\omega), \tag{30}$$

$$L_R=\gamma_{12}-i\omega_{21}. \tag{31}$$

For the zeroth-order solution of Eqs. (13), (15), and (18) we have

$$\sigma_{11}^{(0)}(t)=\sigma_{11}^{0},\quad \sigma_{33}^{(0)}(t)=\sigma_{33}^{0},\quad \sigma_{12}^{(0)}(t)=0. \tag{32}$$

The population densities are given by their background values, and there is no coherence between levels 1 and 2. The first-order polarization envelopes $\sigma_{13}^{(1)}$ and $\sigma_{23}^{(1)}$ are given by

$$\sigma_{13}^{(1)}(v,t)=i\alpha\Delta\sigma_0\left(\frac{e^{-L_1 t}}{L_1^0}+\frac{1-e^{-L_1 t}}{L_1}\right), \tag{33a}$$

$$\sigma_{23}^{(1)}(v,t)=i\beta\Delta\sigma_0\left(\frac{e^{-L_2 t}}{L_2^0}+\frac{1-e^{-L_2 t}}{L_2}\right). \tag{33b}$$

In the first-order response the system behaves as two independent two-level systems. The first terms of Eqs. (33) correspond to the free-induction decay of the initial polarization $[\sigma_{13}^{(1)}(v,0)]$. The second term describes the buildup of the steady state, the exponential term being the first-order contribution to the optical nutation signal.

For the second-order contributions we obtain

$$\sigma_{11}^{(2)}(v,t)=2\Delta\sigma_0\alpha^2\,\mathrm{Re}\left[\frac{e^{-\gamma_1 t}}{\gamma_1 L_1^0}+\frac{1-e^{-\gamma_1 t}}{\gamma_1 L_1}+\frac{e^{-L_1 t}-e^{-\gamma_1 t}}{\gamma_1-L_1}\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)\right], \tag{34a}$$

$$\sigma_{22}^{(2)}(v,t)=2\Delta\sigma_0\beta^2\,\mathrm{Re}\left[\frac{e^{-\gamma_2 t}}{\gamma_2 L_2^0}+\frac{1-e^{-\gamma_2 t}}{\gamma_2 L_2}+\frac{e^{-L_2 t}-e^{-\gamma_2 t}}{\gamma_2-L_2}\left(\frac{1}{L_2^0}-\frac{1}{L_2}\right)\right], \tag{34b}$$

$$\begin{aligned}\sigma_{33}^{(2)}(v,t)=-2\Delta\sigma_0\,\mathrm{Re}\Bigg\{&\alpha^2\left[\frac{e^{-\gamma_3 t}}{\gamma_3 L_1^0}+\frac{1-e^{-\gamma_3 t}}{\gamma_3 L_1}+\frac{e^{-L_1 t}-e^{-\gamma_3 t}}{\gamma_3-L_1}\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)\right]\\&+\beta^2\left[\frac{e^{-\gamma_3 t}}{\gamma_3 L_2^0}+\frac{1-e^{-\gamma_3 t}}{\gamma_3 L_2}+\frac{e^{-L_2 t}-e^{-\gamma_3 t}}{\gamma_3-L_2}\left(\frac{1}{L_2^0}-\frac{1}{L_2}\right)\right]\Bigg\},\end{aligned} \tag{34c}$$

$$\sigma_{12}^{(2)}(v,t)=\Delta\sigma_0\alpha\beta\left[\frac{e^{-L_R t}}{\gamma_{12}}\left(\frac{1}{L_1^0}+\frac{1}{L_2^{0*}}\right)+\frac{1-e^{-L_R t}}{L_R}\left(\frac{1}{L_1}+\frac{1}{L_2^*}\right)\right.$$
$$\left.+\frac{e^{-L_1 t}-e^{-L_R t}}{L_R-L_1}\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)+\frac{e^{-L_2^* t}-e^{-L_R t}}{L_R-L_2^*}\left(\frac{1}{L_2^{0*}}-\frac{1}{L_2^*}\right)\right]. \tag{35}$$

The first term in Eq. (34a) describes the free decay of $\sigma_{11}^{(2)}(v,0)$. The second and third terms are nutation (driven transient) contributions, leading to the steady state. Note that the free decay of the first-order element $\sigma_{13}^{(1)}$ gives rise to a nutation of the second-order element $\sigma_{11}^{(2)}$ (L_1^0 contribution in the last term). This type of contribution is a cross term not present in ordinary optical nutation, where initially ($t<0$) there is no em field present. In what follows we shall refer to all driven transients as nutations, in contrast to the free-decay transients, keeping in mind that for a coupled three-level system and our type of initial conditions there will be many more contributions to the nutation signal than in the usual case of a two-level system with no field present until $t=0$.[19]

It should also be noted that, being a perturbation calculation the resulting optical nutation contributions will exhibit only exponential behavior and not the ringing characteristic of optical nutation in a strong field.

For $\sigma_{33}^{(2)}$ [Eq. (34c)] there are also free-decaying, nutating, and steady-state contributions. However, since level 3 is the common level, both transitions can influence its population, the 1-3 transition giving rise to the α^2 terms and the 2-3 transition to the β^2 terms. The $\sigma_{12}^{(2)}$ term [Eq. (35)] is a coherent contribution due to the simultaneous interaction of the laser field with both transitions, and is therefore proportional to $\alpha\beta$.

For the third-order terms we get

$$\sigma_{13}^{(3)}(v,t)=-i\alpha\Delta\sigma_0\left(\left\{2\alpha^2\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_3}\right)\mathrm{Re}\left(\frac{1}{L_1^0}\right)+\beta^2\left[\frac{2}{\gamma_3}\mathrm{Re}\left(\frac{1}{L_2^0}\right)+\frac{1}{\gamma_{12}}\left(\frac{1}{L_1^0}+\frac{1}{L_2^{0*}}\right)\right]\right\}\frac{e^{-L_1 t}}{L_1^0}\right.$$
$$+\left\{2\alpha^2\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_3}\right)\mathrm{Re}\left(\frac{1}{L_1}\right)+\beta^2\left[\frac{2}{\gamma_3}\mathrm{Re}\left(\frac{1}{L_2}\right)+\frac{1}{L_R}\left(\frac{1}{L_1}+\frac{1}{L_2^*}\right)\right]\right\}\frac{1-e^{-L_1 t}}{L_1}$$
$$+2\alpha^2\mathrm{Re}\left[\left(\frac{1}{\gamma_1}-\frac{1}{\gamma_1-L_1}\right)\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)\right]\frac{e^{-\gamma_1 t}-e^{-L_1 t}}{L_1-\gamma_1}$$
$$+2\,\mathrm{Re}\left[\alpha^2\left(\frac{1}{\gamma_3}-\frac{1}{\gamma_3-L_1}\right)\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)+\beta^2\left(\frac{1}{\gamma_3}-\frac{1}{\gamma_3-L_2}\right)\left(\frac{1}{L_2^0}-\frac{1}{L_2}\right)\right]\frac{e^{-\gamma_3 t}-e^{-L_1 t}}{L_1-\gamma_3}$$
$$+\left[\alpha^2\left(\frac{1}{\gamma_1-L_1}+\frac{1}{\gamma_3-L_1}\right)+\frac{\beta^2}{L_R-L_1}\right]\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)te^{-L_1 t}$$
$$+\alpha^2\left(\frac{1}{\gamma_1-L_1^*}+\frac{1}{\gamma_3-L_1^*}\right)\left(\frac{1}{L_1^{0*}}-\frac{1}{L_1^*}\right)\frac{e^{-L_1^* t}-e^{-L_1 t}}{L_1-L_1^*}$$
$$+\frac{\beta^2}{\gamma_3-L_2}\left(\frac{1}{L_2^0}-\frac{1}{L_2}\right)\frac{e^{-L_2 t}-e^{-L_1 t}}{L_1-L_2}+\beta^2\left(\frac{1}{\gamma_3-L_2^*}+\frac{1}{L_R-L_2^*}\right)\left(\frac{1}{L_2^{0*}}-\frac{1}{L_2^*}\right)\frac{e^{-L_2^* t}-e^{-L_1 t}}{L_1-L_2^*}$$
$$+\beta^2\left[\frac{1}{\gamma_{12}}\left(\frac{1}{L_1^0}+\frac{1}{L_2^{0*}}\right)-\frac{1}{L_R}\left(\frac{1}{L_1}+\frac{1}{L_2^*}\right)-\frac{1}{L_R-L_1}\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)\right.$$
$$\left.\left.-\frac{1}{L_R-L_2^*}\left(\frac{1}{L_2^{0*}}-\frac{1}{L_2^*}\right)\right]\frac{e^{-L_R t}-e^{-L_1 t}}{L_1-L_R}\right), \tag{36a}$$

$$\sigma_{23}^{(3)}=-i\beta\Delta\sigma_0\{\alpha\longleftrightarrow\beta,1\longleftrightarrow2\}, \tag{36b}$$

i.e., the same as $\sigma_{13}^{(3)}$, but with α replaced by β (β by α) and 1 by 2. (Note that $\omega_{21}=-\omega_{12}$.) The first term of Eq. (36a) in curly brackets corresponds to the free-induction decay of $\sigma_{13}^{(3)}(v,0)$ from its initial value. The second-term contains the steady-state ($t\to\infty$) value and part of the optical nutation contribution leading to that state. The other terms are transients driven by second-order contributions to the level populations and the near-diagonal matrix element. The latter contribution is respon-

sible for the appearance of the beat signal at ω_{21}, the Raman frequency.

C. Discussion: Emission frequencies from molecules in a narrow velocity band

Let us now examine the solution obtained in this section in more detail. The rotating-wave approximation of Eq. (12), in which the slowly varying-envelope functions σ_{ij} were introduced, led to a set of coupled linear differential equations [(13)–(19)] describing the total system, molecules plus applied field. The solution of such a set of equations may be obtained by finding its normal modes, each one having a particular eigenfunction composed of amplitude, frequency, and decay rate. Since our system is described by nine coupled equations [Eqs. (13)-(18) plus the complex conjugates of Eqs. (16)–(18)], there will be nine normal modes, each one oscillating at a given eigenfrequency.[20] In addition, the background populations σ^0_{ij}, which act as inhomogeneous source terms in Eqs. (13)–(19), give rise to constant terms in the σ_{ij} solutions.

In the perturbation solution obtained in Sec. III B approximate values for the eigenfunctions were obtained, and their amplitudes were established by matching the initial conditions. Let us inspect the normal mode frequencies of σ_{13} and σ_{23} more closely. The σ_{j3}'s obtained are of the form

$$\sigma_{j3} = \sum_{n=0}^{9} \Lambda_n e^{\lambda_n t},$$

where the Λ_n's are velocity-dependent amplitudes and the λ_n's, $n = 1$–9, are the corresponding complex eigenfrequencies.

In the first-order solution, Eqs. (33), we have

$$\lambda_0 = 0, \tag{37}$$

$$\lambda_1 = -L_1 = -i(\omega - \omega_{31} - kv) - \gamma_{13}, \tag{38a}$$

$$\lambda_2 = -L_2 = -i(\omega - \omega_{32} - kv) - \gamma_{23}. \tag{38b}$$

The λ_0 contribution is due to the inhomogeneous source terms and describes the steady-state behavior of the system. The other contributions are associated with transient effects, as described in Sec. III B.

In the third order, Eqs. (36), additional eigenfrequencies appear in σ_{j3}:

$$\lambda_{3,4,5} = -\gamma_{1,2,3}, \tag{39}$$

$$\lambda_6 = -L_R = i\omega_{21} - \gamma_{12}, \tag{40a}$$

$$\lambda_7 = -L_R^* = -i\omega_{21} - \gamma_{12}, \tag{40b}$$

$$\lambda_8 = -L_1^* = i(\omega - \omega_{31} - kv) - \gamma_{13}, \tag{41a}$$

$$\lambda_9 = -L_2^* = i(\omega - \omega_{32} - kv) - \gamma_{23}. \tag{41b}$$

The first, second, and third contributions, Eqs. (39) and (40), are due to the coupling of the polarization to the molecular level populations and the sublevel coherence σ_{12}. The last two contributions, Eqs. (41a) and (41b), are due to the couplings of the optical polarization components σ_{13} and σ_{23} with their counterrotating parts σ^*_{13} and σ^*_{23}.

As shown in Sec. II [Eqs. (12) and (20)], the induced polarization and, consequently, the reradiated field, is proportional to

$$\mu_{13}\rho_{13} + \mu_{23}\rho_{23} = (\mu_{13}\sigma_{13} + \mu_{23}\sigma_{23})e^{i(\omega t - kz)}.$$

Therefore the corresponding real frequencies Ω_n and decay rates Γ_n of the induced polarization and reradiated field (as viewed in the laboratory frame) may be obtained by adding $i\omega$ to the λ_n's listed above:

$$\lambda_n + i\omega = i\Omega_n - \Gamma_n. \tag{42}$$

Using the values of λ_n we have the following reradiated frequencies and damping constants:

$$\Omega_0 = \omega, \quad \Gamma_0 = 0, \tag{43}$$

$$\Omega_1 = \omega_{31} + kv, \quad \Gamma_1 = \gamma_{13}, \tag{44a}$$

$$\Omega_2 = \omega_{32} + kv, \quad \Gamma_2 = \gamma_{23}, \tag{44b}$$

$$\Omega_{3,4,5} = \omega, \quad \Gamma_3 = \gamma_1, \quad \Gamma_4 = \gamma_2, \quad \Gamma_5 = \gamma_3, \tag{45}$$

$$\Omega_6 = \omega - \omega_{21}, \quad \Gamma_6 = \gamma_{12}, \tag{46a}$$

$$\Omega_7 = \omega + \omega_{21}, \quad \Gamma_7 = \gamma_{12}, \tag{46b}$$

$$\Omega_8 = 2\omega - \omega_{31} - kv, \quad \Gamma_8 = \gamma_{13}, \tag{47a}$$

$$\Omega_9 = 2\omega - \omega_{32} - kv, \quad \Gamma_9 = \gamma_{23}. \tag{47b}$$

These emission frequencies may also be interpreted in terms of the quantum process depicted in diagrams of the type shown in Fig. 3, which represent the exchange of energy between the em field and molecule in its rest frame.[21] These processes involve both the laser field, which in the molecular rest frame appears Doppler shifted to frequency $\omega' = \omega - kv$, and the forward-scattered light wave, at frequency $\Omega'_n = \Omega_n - kv$ in the molecular frame. In each process the frequency of the reradiated field follows in a straightforward way from the conservation of energy of the total system, molecule plus field:

(a) The normal-mode frequencies Ω_1 and Ω_2 result from emission processes in which a molecule in energy state E_3 undergoes a transition to state E_1 or E_2, accompanied by the emission of a single quantum at frequency Ω' [Fig. 3(a)]. Energy conservation (in the molecular rest frame) then requires that $\hbar\Omega' = E_3 - (E_1 \text{ or } E_2)$, leading to emission in the laboratory frame at frequency

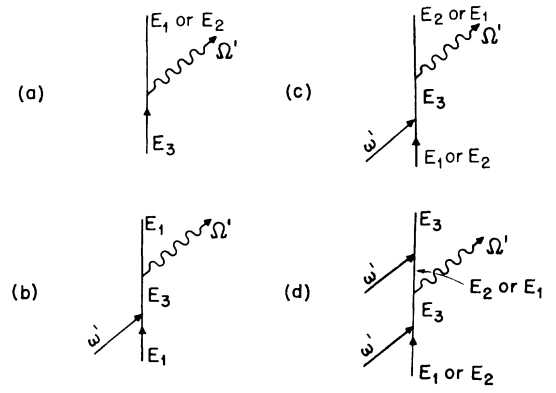

FIG. 3. Typical diagrams depicting the quantum processes responsible for emission of radiation in the transient regime. Laser photons, frequency $\omega' = \omega - kv$, and reemitted photons, frequency $\Omega' = \Omega - kv$, are denoted by straight and wavy lines, respectively. The frequencies in the diagrams, given in the *molecular rest frame*, may be converted to the laboratory frame by adding kv. See text for details. (a) Emission process leading to radiation at the molecular natural frequencies $\Omega' = \omega_{31}$ and ω_{32}. (b) Elastic scattering process leading to emission at the laser frequency $\Omega' = \omega'$. (c) Raman-type process leading to emission at the Raman frequencies $\Omega' = \omega' \pm \omega_{21}$. (d) Three-quantum process leading to emission at $\Omega' = 2\omega' - \omega_{31}$ and $2\omega' - \omega_{32}$.

$$\Omega_1 = \Omega_1' + kv = \omega_{31} + kv ,$$

$$\Omega_2 = \Omega_2' + kv = \omega_{32} + kv .$$

(b) The normal-mode frequencies Ω_0, Ω_3, Ω_4, and Ω_5 result from elastic scattering processes of the type depicted in Fig. 3(b), in which two photons are exchanged with the radiation field, a laser photon being absorbed at frequency $\omega' = \omega - kv$ and a scattered photon being emitted at frequency $\Omega' = \Omega - kv$, leaving the molecule in its initial state. Energy conservation then requires that

$$\Omega_n = \omega, \quad n = 0,\ 3,\ 4, \text{ and } 5 .$$

(c) The normal-mode frequencies Ω_6 and Ω_7 result from the Raman-type processes depicted in Fig. 3(c), in which the molecule makes a transition between states 1 and 2, accompanied by the exchange of two photons with the radiation field, absorption of a photon at the laser frequency, and emission of a photon at a frequency determined by energy conservation:

$$\hbar\Omega' = \hbar\omega' \pm (E_2 - E_1) .$$

This leads to the well-known velocity-independent forward scattering at frequencies

$$\Omega_6 = \omega - \omega_{21}, \quad \Omega_7 = \omega + \omega_{21} .$$

(d) The normal-mode frequencies Ω_8 and Ω_9 result from the quantum process shown in Fig. 3(d), in which the molecule makes a transition between states 1 and 3 or 2 and 3 accompanied by the exchange of three photons with the radiation field, the absorption of two laser photons, and emission of a third photon at frequency Ω' determined by energy conservation:

$$\hbar\Omega' + E_3 - (E_1 \text{ or } E_2) = 2\hbar\omega' .$$

This leads to emission at frequencies

$$\Omega_8 = 2\omega - \omega_{31} - kv \text{ and } \Omega_9 = 2\omega - \omega_{32} - kv .$$

In each process, the frequency spread of the scattered photon is governed by the decay constants associated with the initial and final states, and leads to the decay rates of the corresponding field component Γ_n, as given by Eqs. (43)–(47).

IV. VELOCITY INTEGRATION OF THE INDUCED POLARIZATION

To obtain the net macroscopic polarization and other observable quantities, it is necessary to integrate $\sigma_{ij}(v,t)$ over the velocity distribution $G(v)$:

$$\langle\sigma_{ij}\rangle = \int_{-\infty}^{\infty} \sigma_{ij}(v,t)\,dv . \tag{48}$$

In the fully Doppler-broadened limit, where the natural or homogeneous width is much smaller than the Doppler (inhomogeneous) width, $G(v)$ is a broad function of velocity which is slowly varying compared to the velocity dependence of σ. Accordingly, in doing the integrations one can remove $G(v)$ from inside the integral, evaluating it at the velocity (or velocities) at which σ_{ij} is maximum, e.g.,

$$\langle F(v)\rangle = \int_{-\infty}^{\infty} G(v) f(v,t)\,dv$$

$$\approx G(v_r) \int_{-\infty}^{\infty} f(v,t)\,dv , \tag{49}$$

where $F(v)$ is a typical term of $\sigma_{ij}(v,t)$ which has a resonant denominator at v_r, and such that $F = Gf$. Thus the velocity integrals depend only on $f(v)$, and not on the exact form of $G(v)$, as long as $G(v)$ is broad.[22]

Velocity integrations of the type (49) can be conveniently performed using contour integration, by considering $f(v)$ as an analytic function of the complex variable $\tilde{v}$ with poles in the complex v plane (Fig. 4). The path of integration is then the real axis of the complex v plane, and the contour may be closed at $+\infty$ and $-\infty$ in either half of the complex plane. As can be seen from the expressions for σ_{ij}, Eqs. (33)–(36), in some terms the velocity dependence appears not only in resonant Lorentzian denominators but also, in some terms, in the time-dependent exponentials. In the latter

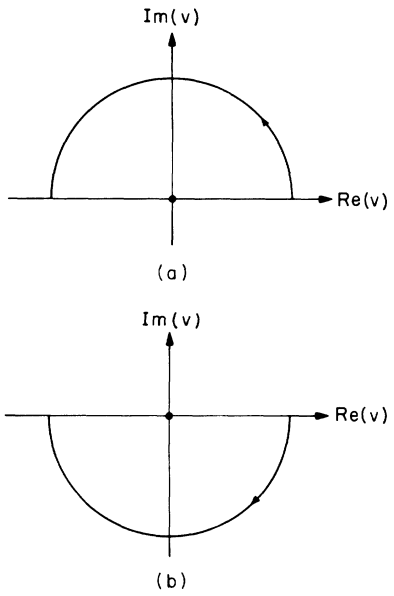

FIG. 4. Contours in the complex v plane used in the velocity integrations. The contours are closed at $v = \pm\infty$. (a) Contour for terms having time dependence of the type $e^{-L_1 t}$ and $e^{-L_2 t}$. (b) Contour for terms having time dependence of the type $e^{-L_1^* t}$ and $e^{-L_2^* t}$. For terms without a velocity-dependent time factor, the contour may be closed in either half-plane.

case the contour must be closed in the half of the complex v plane in which the argument of the real part of the velocity-dependent factor in the exponential is negative for $t > 0$. Thus integrating over velocity is equivalent to evaluating $\sigma_{ij}(v, t)$ at the poles lying in the appropriate part of the complex plane, and in the integration process the velocity groups at which resonant behavior occurs are selected. From this point of view a pole $\tilde{v}_r$ of the complex variable $f(\tilde{v})$ enclosed by the appropriate integration contour corresponds to a resonance of the real variable $f(v)$ centered at $\mathrm{Re}(\tilde{v}_r)$ [and of width $\sim \mathrm{Im}(\tilde{v}_r)$] which has a finite (i.e., nonzero) area in velocity space. The poles lying outside of the contour, which do not contribute to the integration, correspond to resonances in $f(v)$ having zero net area, i.e., either odd functions of velocity or even functions with equal areas above and below the v axis.

Discussion of the various type of terms occurring in the velocity integration are given below. The complete result of the calculation, Eqs. (A9) and (A12)–(A15), and some mathematical details are deferred to the Appendix.

A. Resonant velocities and emission frequencies

In Sec. III it was seen that the coupled equations for σ give rise to a set of eigenfrequencies given by Eqs. (37)–(41). Some of these frequencies are velocity dependent and will be altered in the course of integration over velocity. This comes about because the amplitudes (the Λ_n's of $\sigma_{j3} = \sum_{n=0}^{9} \Lambda_n e^{\lambda_n t}$) multiplying the various oscillating factors are themselves velocity-dependent functions with denominators which undergo resonant behavior at specific values of v. Thus at these velocities the molecular response is enhanced, and in the process of integration the velocity-dependent factors (kvt's) appearing in the exponentials of σ [cf. Eqs. (36)] are replaced by complex frequency factors corresponding to the (complex) velocities at which resonant behavior occurs. Thus the selective enhancement of particular velocities gives rise to "new" frequencies and decay rates.

As can be seen from Eqs. (33)–(36), the resonant denominators are of the form $\lambda_i - \lambda_j$ (including $\lambda_i - \lambda_0 = \lambda_i$). Therefore resonant behavior can occur for a particular value of v when two of the λ_n's become equal.[23] Additional resonant behavior is introduced through the velocity dependence of the initial conditions.

In the following discussion the various terms which comprise $\sigma(v, t)$ will be grouped into categories and analyzed separately. As shall be seen, cancellations occur in certain types of terms leading to a simplified expression for $\langle\sigma\rangle$, as compared to the pre-velocity-integrated expression.

1. Terms in σ with no velocity dependence in their time behavior

These terms have velocity dependence only in their amplitudes. Therefore their emission frequencies will not be altered by velocity integration, nor will their decay constants be modified by Doppler dephasing. Examples of this type of term are the steady-state contributions, the transients with time variations $e^{-\gamma_i t}$, and the ones which vary as $e^{-L_R t}$. The latter terms contribute to the beat signal at ω_{21}.

As shall be seen below other types of terms, after velocity integration, may have exactly the same form as these terms and so can cancel or modify them. This will be the case, for example, with the beat signal at ω_{21}.

2. Terms in σ having velocity-dependent time variations

The remaining terms all have velocity dependence in their time behavior through the exponential factors $L_j(v)t$ and $L_j^*(v)t$. These factors, evaluated at specific velocities v_r at which resonant behavior can occur, result in emission at frequencies $\Omega_1(v_r)$, $\Omega_2(v_r)$ and $\Omega_8(v_r)$, $\Omega_9(v_r)$, respectively [cf. Eqs. (38) and (41), which lead to Eqs. (44) and (47)]. These same factors also give rise to the decay constant associated with Doppler dephasing

effects. Let us now look at these resonant contributions in some detail.

a. Contributions due to velocity groups selected at $t<0$. Due to the initial preparation of the system, σ_{ij} contains terms which become resonant when $L_j^0=0$, that is, when

$$v_0=(\omega-\omega_0)/k\,, \tag{50}$$

where v_0 is the velocity at which the laser frequency is Doppler shifted into resonance with the molecular transition, at frequency ω_0. Thus emission at frequencies $\Omega_j=\omega_{3j}+kv$ is enhanced for $v=v_0$, giving

$$\omega_{3j}+kv_0=\omega+\omega_{3j}-\omega_0\,, \tag{51}$$

leading to beat frequencies at $\delta_j=\omega_{3j}-\omega_0$.[24] The main contribution of this type is due to free-induction decay. However, terms of this form will also occur in optical nutation, as explained in the discussion following Eqs. (35).

As an example, consider the following integral, which appears in $\langle\rho_{13}\rangle=\langle\sigma_{13}\rangle e^{i(\omega t-kz)}$:

$$e^{i(\omega t-kz)}\int_{-\infty}^{\infty}\frac{e^{-L_1 t}\,dv}{L_1|L_2^0|^2}\,. \tag{52}$$

This contribution comes from the coupling of the 1-3 and 2-3 transitions via the common level 3, so that the v_0 group selected in transition 2-3 gives rise to resonant behavior in σ_{13}. The integral (52) may be carried out by closing the integration contour in the upper half of the complex v plane [Fig. 4(a)]. The pole corresponding to $L_2^{0*}=0$, the only pole enclosed by the contour, gives a contribution with time-dependent factor

$$e^{i(\omega_{31}+kv_0)t}e^{-\gamma_{23}t}e^{-\gamma_{13}t}\,. \tag{53}$$

Thus the integration selects the frequency $\omega+\delta_1$. In addition, the damping rate is increased from its original value γ_{13} due to the decay of $\sigma_{13}(v,t)$, by an amount γ_{23}. This additional contribution arises because the excited molecules are spread over a range $\Delta v_0\approx\gamma_{23}/k$ around v_0. Consequently, the transient response of the polarization at $\omega+\delta_1$ is spread over a range of frequencies $\sim\gamma_{23}$, which leads to *Doppler dephasing* of this contribution in a time $\sim\gamma_{23}^{-1}$.

Other terms of this type, all having a beat frequency at $\delta_j=\omega_{3j}-\omega_0$, occur in the integrated expression for $\langle\sigma_{j3}\rangle$, Eq. (A15). In every case there are two contributions to the decay constant, one due to Doppler dephasing and the other to decay.

The remaining terms are all characterized by resonances occurring at $t>0$, after the levels have been Stark split. Therefore they describe the driven transients, i.e., terms of the optical nutation type.

b. Terms in σ leading to cancellations. As mentioned above, some terms having velocity-dependent time factors will cancel one another and, most importantly, will also cancel terms which are free of Doppler-dephasing effects (Sec. IV A 1). As an example, consider a resonance in σ associated with the denominator L_j (or L_j^*). The resonance condition L_j $(L_j^*)=0$ occurs for

$$v_{3j}=(\omega-\omega_{3j})/k\,. \tag{54}$$

At this velocity the laser frequency is Doppler shifted into resonance with the molecular transition at frequency ω_{3j}. Accordingly, the resonant velocity groups v_{3j} will select the emission frequencies $\Omega_{1,2}=\omega_{3j}+kv$ for $v=v_{31}$ and v_{32}:

$$\omega_{31}+kv_{31}=\omega\,, \tag{55a}$$

$$\omega_{32}+kv_{32}=\omega\,, \tag{55b}$$

$$\omega_{31}+kv_{32}=\omega+\omega_{21}\,, \tag{56a}$$

$$\omega_{32}+kv_{31}=\omega-\omega_{21}\,. \tag{56b}$$

The same emission frequencies will result upon substitution of v_{31} and v_{32} into $\Omega_{8,9}=2\omega-\omega_{3j}-kv$. Other denominators leading to the same resonant velocity groups, and thus to the above emission frequencies, are $L_j-\gamma_i$, due to population transients, and L_R-L_1 and $L_R-L_2^*$, due to $\sigma_{12}^{(2)}$ transients [cf. Eqs. (34)–(36)]. In general, the velocity groups v_{3j} occur resonantly in terms related to population saturation and to the nonlinear response of the near-diagonal density matrix elements. Integration of terms of this type is similar to that of Eq. (52), and again we find that the damping constant will have two contributions, one from Doppler dephasing and one from decay.[25]

The resulting components oscillating at frequency ω are optical nutation terms of the two-level type, at either the 1-3 or 2-3 transition. The frequency components at $\omega\pm\omega_{21}$ are due to coupling between the 1-3 and 2-3 transitions, and are thus optical nutation terms of the three-level type. However, these terms are clearly not of the Raman type, since they are due to terms having velocity-dependent time factors, and are therefore sensitive to Doppler dephasing.

As can be seen from Eq. (36), many terms having frequencies (55) and (56) arise in the course of integrating σ_{13} and σ_{23} over velocity. Interestingly enough, for each of the components at frequencies $\omega\pm\omega_{21}$ with two γ's in its damping constant, complete cancellation occurs when the individual terms are summed. In addition, partial cancellation occurs between terms at these frequencies coming from contributions of the type described in Sec. IV A 1, with terms resulting from the $L_j-\gamma_i$ and L_j-L_R resonances, which have only one γ in their time dependence.

In order to explain these cancellations it is necessary to analyze the origin of frequencies (55) and (56) in more detail. The general type of expression which gives a v_{3j} resonance has the factor [cf. Eq. (29)]

$$(1/L_i)[(e^{-\lambda_n t} - e^{-L_j t})/(L_j - \lambda_n)], \tag{57}$$

where the λ_n's, $n=0, 3-7$ [Eqs. (37)–(40)], have either no velocity dependence or the same velocity dependence as that of L_j. However, the contribution to the velocity integral due to the factor in brackets always vanishes, because for these λ_n's the same contour (closed in the upper half-plane) can be used to evaluate both parts of the term in brackets. If the pole of $L_j - \lambda_n = 0$ lies in the lower half-plane, then the contribution will vanish for each term separately. (A particular case of this type is $\lambda_n = \lambda_0 = 0$.) On the other hand, it is possible that the pole lies inside the contour (upper half-plane), in which case each individual term will give a nonzero contribution. However, the sum of the two contributions will exactly cancel, since at the pole, where $L_j = \lambda_n$, the two exponential factors of Eq. (57) are equal. In fact, the bracketed term in Eq. (57) does not contribute a pole, as can be seen from the expansion

$$(e^{-\lambda_n t} - e^{-L_j t})/(L_j - \lambda_n) = e^{-\lambda_n t}[t - (L_j - \lambda_n)t^2/2! + \cdots], \tag{58}$$

and thus no residue can result from the two terms. It should be noted, however, that the factors outside the brackets in Eq. (57) may contribute poles and thus give rise to nonvanishing contributions.

As a specific example of cancellation, consider the term containing the factor

$$(e^{-L_R t} - e^{-L_1 t})/(L_1 - L_R) \tag{59}$$

which appears in Eq. (36). It follows from the preceding discussion that in the velocity integration the terms having time dependence $e^{-L_1(v)t}$ exactly cancels the $e^{-L_R t}$ term, so that the factor (59) does not contribute to $\langle \sigma_{13} \rangle$. This example shows how Doppler dephasing gives rise to oscillation at ω_{21}. Note that the $e^{-L_1 t}$ term in Eq. (59) is not caused by population changes induced by the laser field. Rather, it originates in $\sigma_{12}^{(2)}$, which drives $\sigma_{13}^{(3)}$. Terms of this type are important because, unlike the oscillations at ω_{21} due to population saturation, which completely cancel among themselves in the velocity integration, their velocity-integrated contributions cancel with some of the $e^{-L_R t}$ term. Thus Doppler-dephasing effects modify the resulting amplitude of the beat signal at ω_{21}.

c. Terms in σ giving rise to new contributions. Another type of resonant behavior occurs for terms in σ_{j3} containing factors of the type (57), in which the velocity dependence of λ_n is opposite in sign to that of L_j. These are the cases of $\lambda_n = L_i^*$ (i.e., $n=8, 9$). Factors of this type are important because their poles are such that no cancellation arises in the course of velocity integration.

The most interesting example of this type in σ_{13} is for $L_j = L_1$ and $\lambda_n = L_2^*$, giving a resonant denominator $L_1 - L_2^*$ in (57), because it leads to a contribution oscillating at frequency $\frac{1}{2}\omega_{21}$. Such terms originate from the coupling of $\sigma_{23}^{(1)*}$ to $\sigma_{13}^{(3)}$ via $\sigma_{33}^{(2)}$ and $\sigma_{12}^{(2)}$ (there are analogous terms in $\sigma_{23}^{(3)}$). A resonant-velocity group occurs for $L_2^* - L_1 = 0$, i.e.,

$$v_{12} = [\omega - \tfrac{1}{2}(\omega_{31} + \omega_{32})]/k, \tag{60}$$

the velocity which is halfway between v_{13} and v_{23}.

The physical origin of this new resonant-velocity group is as follows: Due to three quantum processes of the optical nutation type [Fig. 3(d)], the molecules reradiate at frequency Ω_8 (and Ω_9). In the molecular rest frame, this corresponds to an oscillatory component of the induced polarization at frequency $\Omega' = \Omega_8 - kv = 2\omega - \omega_{31} - 2kv$. This oscillation is resonantly enhanced at velocities for which the frequency is tuned into the natural frequency, $\Omega' = \omega_{32}$, i.e., for $v = v_{12}$. This velocity group is a specific feature of the *transient* response of the molecular medium and is absent in the steady-state regime. The reradiation of this velocity group at the Doppler-shifted natural frequencies leads to[26]

$$\omega_{31} + kv_{12} = \omega + \tfrac{1}{2}\omega_{21}, \tag{61a}$$

$$\omega_{32} + kv_{12} = \omega - \tfrac{1}{2}\omega_{21}. \tag{61b}$$

Unlike the terms discussed in Sec. IV A 2 b, these terms do not vanish after the velocity integration. Because the velocity-dependent factors in the exponentials are opposite in sign, the integral

$$\int_{-\infty}^{\infty} \frac{1}{L_j}\left[\frac{e^{-L_2^* t} - e^{-L_1 t}}{L_1 - L_2^*}\right] dv \tag{62}$$

cannot be evaluated by closing the contour in the same half-plane for both terms, and so the expansion Eq. (58) cannot be used. Each term has to be integrated separately, closing the contour in the lower half-plane for the first exponential and in the upper half-plane for the second one. If $\gamma_{23} > \gamma_{13}$, the pole of $(L_2^* - L_1)^{-1}$ lies in the upper half-plane; there is no contribution from the first term, whereas the second one gives a nonzero contribution. If $\gamma_{23} < \gamma_{13}$, the contributions are exchanged, but the final result is the same, independent of the sign of $\gamma_{23} - \gamma_{13}$. The integration results in a term proportional to

$$\exp\{\tfrac{1}{2}[-(\gamma_{13} + \gamma_{23} - i\omega_{21})t]\}, \tag{63}$$

which oscillates at $\frac{1}{2}\omega_{21}$ and decays at a rate $\frac{1}{2}(\gamma_{13}+\gamma_{23})$.

Another contribution of the same type is due to the resonant denominator $L_j^* - L_j$, which originates from the coupling of $\sigma_{3j}^{(3)}$ with its own counter-rotating part $\sigma_{3j}^{*(1)}$. The corresponding resonant velocity group v_{3j} leads to oscillation at the laser frequency, but with a decay rate γ_{3j}. This term contributes to the two-level optical nutation [cf. Eq. (A15)].

The discussions of this section help explain why the expression for the velocity-integrated induced polarization, Eq. (A15), is much simpler than the preintegrated expression, Eq. (36). The relative importance of the different contributions and their dependence on laser detuning, before and after the levels are split, are discussed in Sec. V.

V. DISCUSSION OF RESULTS

A. Frequency components of the reradiated field

The reradiated field is given by Eq. (20), and thus can be analyzed by inspecting the expressions for σ_{3j}, Eqs. (A9) and (A15) of the Appendix. The following frequency components may be distinguished in the rotating frame:

(a) A constant term, representing the steady-state absorption at $t \gg 1/\gamma_{ij}$. The origin of this term was explained in Sec. IV A 1.

(b) Some purely decaying contributions. The $e^{-\gamma_i t}$ terms describe the transients in the level populations as they approach their new equilibrium values after $t=0$ [Sec. IV A 1]. The contributions having time variations $e^{-\gamma_{3j}t}$ are two-level nutation effects, the origin of which has been explained in Sec. IV A 2 c.

(c) Finally, the most interesting contributions are those oscillating at frequencies different from that of the laser. They lead to beats in the heterodyne signal. One can distinguish three principal frequency components:

(i) The beat at frequency $\delta_j = \omega_{3j} - \omega_0$. As explained in Sec. IV A 2 a, the largest contribution to this term is due to the free-induction decay of the molecules excited before $t=0$.

(ii) The Raman beat at frequency ω_{21}. As discussed in Sec. IV A, it includes the contributions with velocity-independent time factors, as modified by the velocity-dependent Raman-type contributions. The remaining velocity-integrated terms oscillating at ω_{21} cancel when combined. Using Eqs. (20) and (A15), the component of the reradiated field envelope oscillating at frequency ω_{21} is given by

$$\mathcal{E}(\omega_{21}) = \frac{gL\mathcal{E}_0\beta^2}{2}\left[\frac{\mathcal{G}(v_0)}{\gamma_{12}}\left(\frac{e^{-(\gamma_{12}+i\omega_{21})t}}{\gamma_{13}+\gamma_{23}-\gamma_{12}+i(\omega_{32}-\omega_0)}+\frac{e^{-(\gamma_{12}-i\omega_{21})t}}{\gamma_{13}+\gamma_{23}-\gamma_{12}+i(\omega_{31}-\omega_0)}\right)\right.$$
$$+\frac{\mathcal{G}(v_{32})e^{-(\gamma_{12}+i\omega_{21})t}}{\gamma_{13}+\gamma_{23}-2\gamma_{12}-i\omega_{21}}\left(\frac{1}{\gamma_{13}+\gamma_{23}-\gamma_{12}+i(\omega_{32}-\omega_0)}-\frac{1}{\gamma_{12}+i\omega_{21}}\right)$$
$$\left.+\frac{\mathcal{G}(v_{31})e^{-(\gamma_{12}-i\omega_{21})t}}{\gamma_{13}+\gamma_{23}-2\gamma_{12}+i\omega_{21}}\left(\frac{1}{\gamma_{13}+\gamma_{23}-\gamma_{12}+i(\omega_{31}-\omega_0)}-\frac{1}{\gamma_{12}-i\omega_{21}}\right)\right], \tag{64}$$

where

$$gL = +4\pi^{3/2}N_0\mu_{13}^2L/\hbar u$$

is the usual expression for the linear gain coefficient of the Doppler-broadened 3-1 transition at line center, u is the Boltzmann velocity factor (see the Appendix), and

$$\mathcal{G}(v) = \sqrt{\pi}\,uG(v) = e^{-(v/u)^2}.$$

Accordingly, the reradiated field $\mathcal{E}(\omega_{21})$ is smaller than the incident field by a factor $gL(\beta/\gamma_{ij})^2$. The factor gL was explained in Sec. II A. The extra factor $(\beta/\gamma_{ij})^2$ obtained here results from the perturbation treatment.

As can be seen from Eq. (64), the amplitude of the Raman beat is largest when one of the transitions remains in resonance after $t=0$ (i.e., either $|\omega_{31}-\omega_0|$ or $|\omega_{32}-\omega_0| \ll \gamma_{ij}$). The quantity in brackets in Eq. (64) is then given approximately by

$$\mathcal{G}(v_0)e^{-(\gamma_{12}\pm i\omega_{21})t}/\gamma_{12}(\gamma_{13}+\gamma_{23}-\gamma_{12}), \tag{65}$$

when the condition of observability of the Raman beat, $\omega_{21} \gg \gamma_{12}$, is taken into account. This enhancement occurs because the σ_{12} coherence created before $t=0$ is resonantly enhanced for $v=v_0$ [Eq. (26)]. If $\omega_{32}=\omega_0$, the laser continues to resonate with this velocity group at the 3-2 transition for $t>0$, leading to a maximum contribution to $\langle\sigma_{13}\rangle$.

For the off-resonance case, when both $\omega_{31}-\omega_0$, $\omega_{32}-\omega_0 \gg \gamma_{ij}$ (for simplicity it is assumed that all γ's are of the same order), the quantity in brackets in Eq. (64) becomes

$$\frac{\mathcal{G}(v_0)}{\gamma_{12}}\left(\frac{e^{-(\gamma_{12}+i\omega_{21})t}}{i(\omega_{32}-\omega_0)}+\frac{e^{-(\gamma_{12}-i\omega_{21})t}}{i(\omega_{31}-\omega_0)}\right), \tag{66}$$

which is smaller than Eq. (65) by a factor $\sim\gamma/(\omega_{3j}-\omega_0)$. In this expression it is assumed that $|\omega_{21}| \sim |\omega_{3j}-\omega_0|$. In the case $\omega_{21}^2 \ll |\omega_{3j}-\omega_0|\gamma_{ij}$ the terms in $\mathcal{G}(v_{13})$ and $\mathcal{G}(v_{23})$ in Eq. (64) would give additional contributions to Eq. (66).

The decay rate of the Raman-beat signal, as obtained in Eq. (64), is free of Doppler-dephasing effects. The decay rate is not sensitive to collisions which destroy the phase of the induced optical electric dipole. However, γ_{12} does depend on depolarizing collisions. Accordingly, the Raman beat is affected by the collisions which change the orientation of the induced optical dipole.

According to the discussion following Eq. (65), the influence of velocity-changing collisions on the decay rate of the Raman-beat signal should be very different for the resonance and nonresonance cases, Eqs. (65) and (66). In the resonance case, in which one of the transition frequencies remains unchanged when the Stark field is applied, such collisions can transfer the σ_{12} coherence induced in the v_0 velocity group to other velocity groups. This should reduce the amplitude of the beat signal, since these new velocities do not satisfy the resonance condition. Accordingly, the damping rate of the beat signal should include a contribution equal to the rate of velocity-changing collisions. On the other hand, in the nonresonance case the transfer of the initial σ_{12} coherence to other velocity groups is of no significance, so that collisions of this type should not lead to a reduction of the amplitude of the beat signal. Thus in the resonance case the decay rate of the Raman-beat signal will be increased by velocity-changing collisions, whereas in the nonresonance case it will not be. This point might be used to advantage in experiments.

(iii) The polarization exhibits a beat at frequency $\frac{1}{2}\omega_{21}$, which has been interpreted in Sec. IV A as originating from molecules of velocity $v_{12}=\frac{1}{2}(v_{31}+v_{32})$. The envelope of reradiated field due to this beat is given by

$$\mathcal{E}(\tfrac{1}{2}\omega_{21}) = \frac{gL\mathcal{E}_0\beta^2}{2}\left[\frac{i8\mathcal{G}(v_{12})(\gamma_{13}+\gamma_{23}-\gamma_{12}-\gamma_3)}{\gamma_{13}+\gamma_{23}+i(\omega_{31}+\omega_{32}-2\omega_0)}\left(\frac{(\omega_{32}-\omega_0)e^{-i\omega_{21}t/2}}{(\gamma_{13}+\gamma_{23}+i\omega_{21})(\gamma_{13}+\gamma_{23}-2\gamma_3+i\omega_{21})(\gamma_{13}+\gamma_{23}-2\gamma_{12}-i\omega_{21})}\right.\right.$$
$$\left.\left.+\frac{(\omega_{31}-\omega_0)e^{i\omega_{21}t/2}}{(\gamma_{13}+\gamma_{23}-i\omega_{21})(\gamma_{13}+\gamma_{23}-2\gamma_3-i\omega_{21})(\gamma_{13}+\gamma_{23}-2\gamma_{12}+i\omega_{21})}\right)e^{-(\gamma_{13}+\gamma_{23})t/2}\right]. \tag{67}$$

Several features of this expression are noteworthy. First, the beat disappears if there are no collisions which either dephase or disorient the polarization without changing the level population [i.e., $\mathcal{E}(\frac{1}{2}\omega_{21})\to 0$ if $\gamma_{ij}=\frac{1}{2}(\gamma_i+\gamma_j)$, so that $\gamma_{13}+\gamma_{23}=\gamma_{12}+\gamma_3$]. Secondly, the beat amplitude is maximum when $\omega_0=\frac{1}{2}(\omega_{31}+\omega_{32})$. In this case, setting $\omega_{21}\gg\gamma_{12}$, the expression in brackets in Eq. (67) is approximately equal to

$$-\frac{8\mathcal{G}(v_0)(\gamma_{13}+\gamma_{23}-\gamma_{12}-\gamma_3)}{(\gamma_{13}+\gamma_{23})\omega_{21}^2}\cos\left(\frac{\omega_{21}t}{2}\right)e^{-(\gamma_{13}+\gamma_{23})t/2}, \tag{68}$$

and is thus a factor γ/ω_{21} smaller than the Raman-beat amplitude [cf. Eq. (66)]. Thirdly, the decay rate of this signal is sensitive to Doppler-dephasing effects, in contrast to that of the Raman beat.

B. Relative importance of the beats for molecular levels with Zeeman structure

Up to now, an idealized three-level system has been considered. In the actual experiments[9] the molecular levels have degeneracies and the above conclusions have to be modified. Let us assume that the levels are split by a Zeeman or Stark field perpendicular to the polarization of the laser field. The coupling between the magnetic sublevels is then as indicated in Fig. 5.

a. Both levels have similar Zeeman splitting. In the case of similar splittings for both levels ($g_{\text{upper}}\simeq g_{\text{lower}}$) or for $J=1$-0 transitions all of the three-level subsystems coupled by $\Delta M=\pm 1$ transitions are identical and satisfy the condition

$$\omega_{31}-\omega_0=-(\omega_{32}-\omega_0)=\tfrac{1}{2}\omega_{21}. \tag{69}$$

The discussion of Sec. V A then applies. Note that in this case the free-induction beat of every subsystem has the same frequency, $\frac{1}{2}\omega_{21}$, and its amplitude is of the same order as that of the Raman beat at frequency ω_{21}.

b. Zeeman splittings of the two levels differ. When the splittings of the upper and lower levels of the molecular transition are unequal ($g_{\text{upper}}\neq g_{\text{lower}}$), the beat frequencies of the free-induction-decay signals, $\omega_{31}-\omega_0$ and $\omega_{32}-\omega_0$, will be different for each subsystem. In this case the net free-induction-decay signal tends to vanish because of

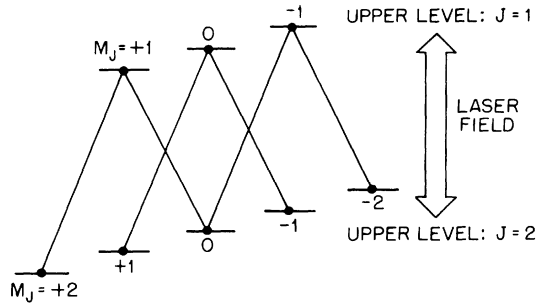

FIG. 5. Example of level scheme for a molecular transition with Zeeman structure. The case shown is for $J = 2 \longleftrightarrow J = 1$.

destructive interference.[27] However, this is not the case for the beat signals at ω_{21} and $\frac{1}{2}\omega_{21}$, which occur at the same frequency for all three-level subsystems. Therefore at these frequencies the contributions of all of the subsystems add. Accordingly, the net effect of the Zeeman structure is to enhance these beats. As mentioned earlier, however, the principal contributions to the beat at ω_{21} come from those transitions whose frequencies are nearly unchanged by the splitting of the sublevels (ω_{31} or $\omega_{32} \simeq \omega_0$). In contrast, the most important contribution to the oscillations at $\frac{1}{2}\omega_{21}$ come from the transitions which are symmetrically split $[\omega_0 \simeq \frac{1}{2}(\omega_{31} + \omega_{32})]$.

C. Comparison with previous work

The present study is directly applicable to the experiments of Shoemaker and Brewer.[9] Previous theoretical analyses of these experiments have been given by Hopf, Shea, and Scully[10] and Brewer and Hahn.[11]

These treatments clearly show that the beat at frequency ω_{21} originates in the transient response of ρ_{12}. However, they are all incomplete in various ways, and none gives an explicit expression for the velocity-integrated polarization and reradiated field.[28]

As pointed out in Sec. V A-B, such an expression is essential for analyzing the physical origin of the various contributions and assessing the relative importance of various experimental factors, such as velocity-changing collisions.

The three-level-beat effect is closely related to the quantum-beat phenomena.[4] In fact, three-level beats may be considered to be "stimulated quantum beats." That effect is usually observed as the interference beat produced in the fluorescence arising from a system with coupled closely spaced transitions, excited by a pulse whose bandwidth is sufficiently wide to resonate with both transitions simultaneously. However, the same effect can be observed in a three-level-beat system by studying the fluorescence to a fourth lower level (Fig. 6). Our analysis may be extended to this kind of experiment by calculating the frequency-integrated side fluorescence from levels 1 and 2 to a lower level 4.

The expression for the frequency-integrated fluorescence is well known.[29,30] For the (1-2)→4 transitions it depends only on the velocity-integrated density matrix elements of levels 1 and 2,[30]

$$I \propto |\mu_{41}|^2 \langle \sigma_{11} \rangle + |\mu_{42}|^2 \langle \sigma_{22} \rangle + 2\,\mathrm{Re}(\mu_{41}\,\mu_{24} \langle \sigma_{12} \rangle), \tag{70}$$

where the μ_{4j} are the dipole matrix elements connecting levels 1 and 2 to level 4. The expressions for $\langle \sigma_{ii} \rangle$ in Eq. (70) are given in the Appendix, Eqs. (A12)–(A14), up to second order in the laser field.

From Eq. (A14) it can be seen that the $\langle \sigma_{12} \rangle$ term in Eq. (70) exhibits a quantum beat at frequency ω_{21}. There are two contributions to this signal, the one with coefficient $G(v_0)$ being due to free decay and the one with coefficient $G(v_{32})$ being due to optical nutation. (Note that the optical nutation term is smaller than the free-decay term by a factor $\sim \gamma_{12}/\omega_{21}$.) Also note the relative simplicity of the expression. There is no beat signal at $\frac{1}{2}\omega_{21}$, nor are there any cross terms between optical nutation and free-induction decay of the type present in the three-level-beat expression. These other contributions to the quantum beat should appear in the fluorescence signal only at the fourth order. The only additional second-order terms,

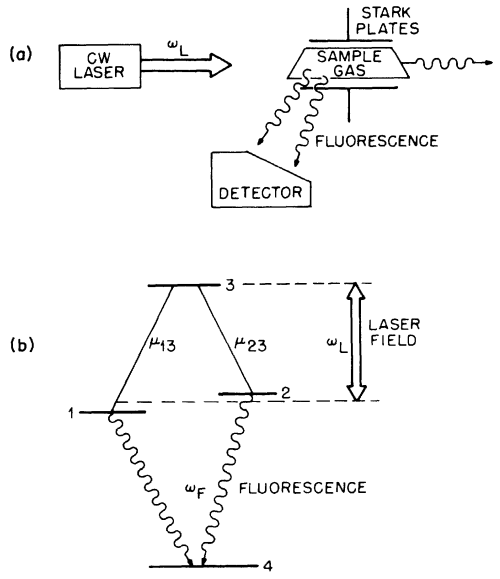

FIG. 6. Quantum-beat fluorescence experiment. The Stark field is applied at $t = 0$. (a) Experimental setup. (b) Energy-level diagram.

the $\langle\sigma_{ii}^{(2)}\rangle$ terms in Eq. (70), can, at most, contribute an exponential signal decaying at the population decay rates. (This occurs for a Stark splitting large compared to the Doppler width. With a small splitting these terms remain constant.) Therefore it appears that the interpretation of the quantum-beat experiments would be simpler than that of the coherent three-level beat effect.

APPENDIX: VELOCITY INTEGRATION OF THE ENVELOPE FUNCTIONS IN THE DOPPLER LIMIT

This appendix presents the details of the velocity integration of the $\sigma_{ij}(v,t)$, Eqs. (33)–(36), in the Doppler limit. The required velocity integrals are of the form [cf. Eqs. (48) and (49)]

$$\langle\sigma_{ij}\rangle = N_0 \int_{-\infty}^{\infty} G(v) \sum_n f_{ij}^{(n)}(v,t)\, dv\,, \tag{A1}$$

where $f_{ij}^{(n)}$ is a particular term of the corresponding σ_{ij}, defined by

$$\sigma_{ij} = N_0 G(v) \sum_n f_{ij}^{(n)}(v,t)\,. \tag{A2}$$

The velocity distribution will be taken to be Maxwellian at temperature T:

$$G(v) = e^{-(v/u)^2}/u\sqrt{\pi}\,, \tag{A3}$$

where $u = (2KT/M)^{1/2}$, with K the gas constant and M the molecular mass. In the general case an exact expression for the velocity-integrated lineshape must be given in terms of the plasma dispersion function.[31] However, in the Doppler-broadened limit, where

$$ku \gg \gamma_{ij}, \gamma_i, \alpha, \beta\,, \tag{A4}$$

the form of the expressions simplifies considerably. The velocity dependence of $G(v)$ will then be slow, as compared to that of $f(v,t)$, and we can write

$$\langle\sigma_{ij}\rangle = N_0 \sum_n G(v_n) \int_{-\infty}^{\infty} f_{ij}^{(n)}(v,t)\, dv\,, \tag{A5}$$

where v_n is the velocity at which the denominator of $f_{ij}^{(n)}$ is resonant. As discussed in the text, the remaining integrals in Eqs. (A5) can be conveniently performed by means of contour integration in the complex v plane. Thus in this limit $\langle\sigma_{ij}\rangle$ will consist of a set of narrow resonances superimposed upon a broad Gaussian background of width ku (full width at the $1/e$ points) in units of rad/sec.

Approximation (A5) is a great convenience which considerably simplifies the integration process. However, since Eq. (A5) represents the limiting case of $ku \to \infty$, it inherently contains two assumptions: (i) the laser is tuned close to the molecular center frequencies (i.e., $|\omega - \omega_{3j}| \ll ku$); and (ii) the inverse time $(ku)^{-1} \to 0$. Before proceeding with the integrations, it is worth investigating further the validity of Eq. (A5). In any term having two or more factors of the type $L_j(v)^{-1}$, (A5) gives rise to all of the leading terms (i.e., the terms of lowest order in γ/ku) in $\langle\sigma_{ij}\rangle$ in second and higher orders in α, β. However, it omits first-order contributions to $\langle\sigma\rangle$ in α, β, which may be important even in the Doppler limit. For example, as will now be seen, use of Eq. (A5) leads to the neglect of transient terms in $\langle\sigma_{3j}^{(1)}\rangle$ which decay in a time $(ku)^{-1}$, leading to an apparent discontinuity in the linear signal at $t=0$.

Using Eq. (33a) and approximation (A5), $\langle\sigma_{13}^{(1)}\rangle$ is given by

$$\langle\sigma_{13}^{(1)}\rangle = N_0 \left(G(v_0) \int_{-\infty}^{\infty} \frac{e^{-L_1 t}}{L_1^0}\, dv - G(v_{31}) \int_{-\infty}^{\infty} \frac{1 - e^{-L_1 t}}{L_1}\, dv \right). \tag{A6}$$

The integral occurring in the steady-state contribution (the second term in the large parentheses) is π/k. The remaining integrals both vanish, as can be seen by contour integration. This approximation (A5) leads to (for $t > 0$)

$$\langle\sigma_{13}^{(1)}\rangle = (i\alpha\pi N_0/k) G(v_{13})\,, \tag{A7}$$

which gives rise to an apparent discontinuity at $t=0$, since

$$\langle\sigma_{13}^{(1)}(t \leq 0)\rangle = (i\alpha\pi N_0/k) G(v_0)\,. \tag{A8}$$

However, if instead $\langle\sigma_{13}^{(1)}\rangle$ is calculated directly from Eq. (A1), additional terms appear which remove this apparent discontinuity. In the Doppler-broadened limit one obtains, using the properties of the plasma dispersion function,[31]

$$\langle\sigma_{13}^{(1)}\rangle = \frac{i\alpha\pi N_0}{k} \left[G(v_{31}) \left(1 + \frac{2i}{\sqrt{\pi}} \int_0^{v_1} e^{y^2}\, dy \right) + G(v_0) \left(1 + \frac{2i}{\sqrt{\pi}} \int_0^{v_0 + ikut/2} e^{y^2}\, dy \right) e^{i(\omega_{31} - \omega_0)t} - G(v_{31}) \left(1 + \frac{2i}{\sqrt{\pi}} \int_0^{v_1 + ikut/2} e^{y^2}\, dy \right) \right], \tag{A9}$$

where ν_1 and ν_0 are equal to $(\omega_{31}-\omega)/ku$ and $(\omega_0-\omega)/ku$, respectively. Several additional terms appear in this expression. The additional contribution to the steady-state part of $\langle\sigma_{13}^{(1)}\rangle$ (the first term in the brackets) gives rise to the usual linear refractive index in the Doppler-broadened limit. (It does not contribute to the gain.) The last two terms, associated with the transient behavior, do not have simple exponential decay but will decay rapidly in a time of the order of $(ku)^{-1}$.[32] This fast decay is due to the fact that the steady-state preparation of the molecules at frequency ω_0, followed by a sudden shift of the molecular center frequency at time $t=0$, is equivalent to a broad frequency spectrum whose Fourier components can excite the complex polarization over the entire velocity distribution. The dispersive part of σ plays an important role in this process, since it varies as $(\omega-\omega_{31}-kv)^{-1}$ and therefore falls more slowly than the absorptive part.[33] Although the dispersive term is purely real at $t=0$ and so cannot directly contribute to the reradiated signal at that time, it can contribute at time $t\gtrsim 1/kv$, since its phase becomes complex then due to the phase factor e^{ikvt}. Thus the use of approximation (A5) in calculating $\langle\sigma_{13}\rangle$ to first order leads to omission of terms comparable in magnitude to those obtained from (A5), which are important when either assumption (i) or (ii) does not hold.

In contrast, in second and higher orders in α, β, approximation (A5) leads to expressions for $\langle\sigma\rangle$ which are complete to lowest order in γ/ku. For example, the velocity integration of any steady-state term containing two or more factors of the type $L_j^{-1}(v)$ using approximation (A5) gives the same result as that obtained starting from (A1) and keeping only lowest-order terms in γ/ku.[34] The same is true for transient terms containing at least two Lorentzian factors. In the transient terms for the higher-order components, the use of approximation (A5) leads to neglect of terms decaying in a time of the order of $(ku)^{-1}$. However, even for times near $t=0$ it can be shown that these terms are smaller by a factor γ/ku than the ones which decay at a rate γ.

Let us now proceed with the velocity integration of the higher-order terms, using approximation (A5). For the second-order elements of σ [Eqs. (34) and (35)] we can write

$$\sigma_{11}^{(2)}=2\alpha^2N_0G(v)\left\{\frac{\gamma_{13}e^{-\gamma_1 t}}{\gamma_1 L_1^0 L_1^{0*}}+\frac{\gamma_{13}(1-e^{-\gamma_1 t})}{\gamma_1 L_1 L_1^*}+\mathrm{Re}\left[\frac{e^{-L_1 t}-e^{-\gamma_1 t}}{\gamma_1-L_1}\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)\right]\right\}, \tag{A10a}$$

$$\sigma_{22}^{(2)}=2\beta^2N_0G(v)\left\{\frac{\gamma_{23}e^{-\gamma_2 t}}{\gamma_2 L_2^0 L_2^{0*}}+\frac{\gamma_{23}(1-e^{-\gamma_2 t})}{\gamma_2 L_2 L_2^*}+\mathrm{Re}\left[\frac{e^{-L_2 t}-e^{-\gamma_2 t}}{\gamma_2-L_2}\left(\frac{1}{L_2^0}-\frac{1}{L_2}\right)\right]\right\}, \tag{A10b}$$

$$\sigma_{12}(v,t)=\alpha\beta N_0G(v)\left[\frac{\gamma_{13}+\gamma_{23}}{\gamma_{12}L_1^0L_2^{0*}}e^{-L_R t}+\frac{\gamma_{13}+\gamma_{23}-i\omega_{21}}{L_R L_1 L_2^*}(1-e^{-L_R t})\right.$$
$$\left.+\frac{e^{-L_1 t}-e^{-L_R t}}{L_R-L_1}\left(\frac{1}{L_1^0}-\frac{1}{L_1}\right)+\frac{e^{-L_2^* t}-e^{-L_R t}}{L_R-L_2^*}\left(\frac{1}{L_2^{0*}}-\frac{1}{L_2^*}\right)\right]. \tag{A11}$$

Using approximation (A5) and evaluating the integrals along the contours of Fig. 4 by means of the residue theorem, one obtains

$$\langle\sigma_{11}^{(2)}\rangle=(2\pi\alpha^2N_0/k\gamma_1)\times[G(v_0)e^{-\gamma_1 t}+G(v_{31})(1-e^{-\gamma_1 t})], \tag{A12}$$

$$\langle\sigma_{22}^{(2)}\rangle=(2\pi\beta^2N_0/k\gamma_2)\times[G(v_0)e^{-\gamma_2 t}+G(v_{32})(1-e^{-\gamma_2 t})], \tag{A13}$$

$$\langle\sigma_{12}^{(2)}\rangle=\frac{2\pi\alpha\beta N_0}{k}\left(G(v_0)\frac{e^{-(\gamma_{12}-i\omega_{21})t}}{\gamma_{12}}+G(v_{32})\frac{1-e^{-(\gamma_{12}-i\omega_{21})t}}{\gamma_{12}-i\omega_{21}}\right). \tag{A14}$$

Note that a small transient, proportional to $G(v_0)-G(v_{31})$, occurs in the velocity-averaged population of level 1, corresponding to a new group of molecules at v_{31} going into resonance while the old group at v_0 undergoes free decay. A similar transient occurs for $\langle\sigma_{22}^{(2)}\rangle$. However, since the Gaussians are slowly varying $[G(v_0)\simeq G(v_{31})]$, these terms will usually be small. In any case, the populations do not exhibit oscillations of the type observed in strong-field optical nutation. As mentioned in the text, this is a consequence of the perturbation treatment. The near-diagonal element $\langle\sigma_{12}\rangle$ exhibits a quantum beat at the Raman frequency ω_{21} independent of the relative values of $G(v_0)$ and $G(v_{32})$. This beat is essentially the same as that observed in the well-known quantum-beat

fluorescence experiments (see Sec. V C and Ref. 4).

For the third order-contributions to $\langle\sigma\rangle$, again each term consists of the product of at least two velocity-dependent Lorentzians. Accordingly, approximation (A5) is valid, and the contour integration can be performed as discussed in Sec. IV. The final result for $\langle\sigma_{13}^{(3)}\rangle$ is

$$\begin{aligned}\langle\sigma_{13}^{(3)}(t)\rangle = -\frac{i\alpha\pi N_0}{k}\Bigg\{ & G(v_0)\left[\alpha^2\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_3}\right)\frac{e^{-(2\gamma_{13}-i\delta_1)t}}{\gamma_{13}} + 2\beta^2\left(\frac{1}{\gamma_3}+\frac{1}{\gamma_{12}}\right)\frac{e^{-(\gamma_{13}+\gamma_{23}-i\delta_1)t}}{\gamma_{13}+\gamma_{23}}\right] \\ & + \frac{\alpha^2 G(v_{31})}{\gamma_{13}}\left(\frac{1}{\gamma_1}+\frac{1}{\gamma_3}\right) + \frac{2\beta^2 G(v_{32})}{\gamma_{13}+\gamma_{23}-i\omega_{21}}\left(\frac{1}{\gamma_3}+\frac{1}{\gamma_{12}-i\omega_{21}}\right) \\ & + \frac{2i\beta^2 G(v_{32})\delta_2 e^{-\gamma_3 t}}{\gamma_3(\gamma_{13}+\gamma_{23}-2\gamma_3-i\omega_{21})(\gamma_{13}+\gamma_{23}-\gamma_3-i\delta_1)} \\ & + iG(v_{31})\left[\frac{\alpha^2\delta_1}{\gamma_{13}-\gamma_1}\left(\frac{e^{-\gamma_1 t}}{\gamma_1(2\gamma_{13}-\gamma_1-i\delta_1)} - \frac{e^{-\gamma_{13}t}}{\gamma_{13}(\gamma_{13}-i\delta_1)}\right)\right. \\ & \left. + \frac{\alpha^2\delta_1}{\gamma_{13}-\gamma_3}\left(\frac{e^{-\gamma_3 t}}{\gamma_3(2\gamma_{13}-\gamma_3-i\delta_1)} - \frac{e^{-\gamma_{13}t}}{\gamma_{13}(\gamma_{13}-i\delta_1)}\right)\right] \\ & - \alpha^2 G(v_{31})\left[\frac{2\gamma_{13}-\gamma_3-2i\delta_1}{\gamma_3(2\gamma_{13}-\gamma_3-i\delta_1)} + \frac{2\gamma_{13}-\gamma_1-2i\delta_1}{\gamma_1(2\gamma_{13}-\gamma_1-i\delta_1)}\right]\frac{e^{-(2\gamma_{13}-i\delta_1)t}}{\gamma_{13}-i\delta_1} \\ & - 2\beta^2 G(v_{32})\left[\frac{\gamma_{13}+\gamma_{23}-\gamma_3-i(\delta_1+\delta_2)}{\gamma_3(\gamma_{13}+\gamma_{23}-\gamma_3-i\delta_1)} + \frac{\gamma_{13}+\gamma_{23}-\gamma_{12}-i(\delta_1+\delta_2)}{\gamma_{12}(\gamma_{13}+\gamma_{23}-\gamma_{12}-i\delta_2)}\right]\frac{e^{-(\gamma_{13}+\gamma_{23}-i\delta_1)t}}{\gamma_{13}+\gamma_{23}-i(\delta_1+\delta_2)} \\ & + \frac{2\beta^2 G(v_0)e^{-(\gamma_{12}-i\omega_{21})t}}{\gamma_{12}(\gamma_{13}+\gamma_{23}-\gamma_{12}-i\delta_2)} + \frac{2\beta^2 G(v_{32})e^{-(\gamma_{12}-i\omega_{21})t}}{\gamma_{13}+\gamma_{23}-2\gamma_{12}+i\omega_{21}}\left(\frac{1}{\gamma_{13}+\gamma_{23}-\gamma_{12}-i\delta_2} - \frac{1}{\gamma_{12}-i\omega_{21}}\right) \\ & - \frac{16\beta^2 G(v_{12})(\gamma_{13}+\gamma_{23}-\gamma_{12}-\gamma_3)i\delta_2 e^{-(\gamma_{13}+\gamma_{23}-i\omega_{21})t/2}}{[\gamma_{13}+\gamma_{23}-i(\delta_1+\delta_2)](\gamma_{13}+\gamma_{23}-i\omega_{21})(\gamma_{13}+\gamma_{23}-2\gamma_3-i\omega_{21})(\gamma_{13}+\gamma_{23}-2\gamma_{12}+i\omega_{21})}\Bigg\}. \end{aligned} \tag{A15}$$

In Eq. (A15) δ_j is equal to $\omega_{3j}-\omega_0$. The result for $\langle\sigma_{32}\rangle$ is the same, with the interchange of α, β and 1, 2 everywhere. The physical meaning of the terms of Eq. (A15) is discussed in detail in Sec. V A.

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[12]Raman-type processes in steady-state systems are discussed in Ref. 7.

[13]The three-level model is directly applicable to $J=0 \longleftrightarrow 1$ and $1 \longleftrightarrow 1$ molecular transitions. Molecular systems with larger J values (Fig. 5) cannot be decomposed into isolated three-level systems. Although an exact treatment of a system with more than three levels would give rise to additional details, the major features of the effect should be contained in a three-level model.

Moreover, in experiments in which the third-order approximation is satisfied, a complete description can be based on a three-level model, since in this limit the e.m. field couples a particular level only to the two adjacent optically connected levels. Accordingly, in the third-order limit any multilevel system can be decomposed into a set of independent three-level subsystems. See Sec. V for further discussion.

[14]See, for example, A. Icsevgi and W. E. Lamb, Jr., Phys. Rev. 185, 517 (1969).

[15]The precise condition is that the linear absorption coefficient of the sample has to be small compared to unity ($gL \ll 1$, where g is the absorption coefficient per unit length).

[16]Equation (8) is derived by B. J. Feldman and M. S. Feld, Phys. Rev. A 1, 1375 (1970), Sec. II, and in Ref. 14.

[17]See, for example, M. S. Feld and A. Javan, Phys. Rev. 177, 540 (1969). The approximation leading to Eqs. (13)–(18) is equivalent to going into the "rotating frame," well known in nuclear magnetic resonance.

[18]Note the factor $\partial/\partial t$ appearing on the left-hand sides of Eqs. (13)–(18). Strictly speaking, one should write $\partial/\partial t + v\,\partial/\partial z$, but in the present problem $\sigma(z, t>0)$ is a function only of t, not of z, since the initial conditions on σ (uniform Stark field applied at $t=0$) are independent of z. Similarly, in the case of a medium prepared by an optical pulse propagating down the sample the initial conditions will be of the form $\sigma_0(z, ct)$, and so the terms in $\partial/\partial z$ will be smaller than those in $\partial/\partial t$ by a factor of v/c, and thus may be neglected.

[19]C. L. Tang and B. D. Silverman, in *Physics of Quantum Electronics*, edited by P. L. Kelly, B. Lax, and P. Tannenwald (McGraw-Hill, New York, 1966), pp. 280–293.

[20]In the exact solution the eigenfrequencies depend on the laser field intensity. However, in the third-order approximation they are all intensity independent.

[21]Diagrams of this type have been used to calculate emission line shapes of an atomic system subjected to an intense laser field. See, for example, C. Cohen-Tannoudji, in *Frontiers in Laser Spectroscopy*, Les Houches Summer School, July 1975, Session XXVII, edited by R. Balian, S. Haroche, and S. Liberman (North-Holland, 1976) (to be published).

[22]The limits of validity of approximation (49) are discussed in the Appendix.

[23]As can be seen from Eqs. (33)–(36), not every combination $\lambda_i - \lambda_j$ occurs as a resonant denominator in σ. The combinations which do occur as resonant denominators are determined by the coupling in Eqs. (13)–(18).

[24]The frequencies calculated correspond to $\Omega_1(v_0)$ and $\Omega_2(v_0)$. One might also expect contributions at $\Omega_8(v_0)$ and $\Omega_9(v_0)$, but each of these vanishes when integrated over velocity. Mathematically this results from the fact that for the factors $e^{-L_j^{*}t}$ (i.e., Ω_8 and Ω_9 contributions) the poles of terms $L_j^{0*}=0$ always lie outside of the integration contour [Fig. 4(b)].

[25]For resonant denominators of the type $L_j - \gamma_i$ and $L_1 - L_R$ the damping constants associated with Doppler dephasing will be differences between two γ's.

[26]Note that $\Omega_{8,9}(v_{12})$ [Eq. (47)] also leads to frequencies (61a) and (61b). This is due to the fact that v_{12} results from $\lambda_{1,2}=\lambda_{8,9}$ and, as seen in Sec. III C, the emission frequencies associated with these λ's are $\Omega_{1,2}$ and $\Omega_{8,9}$, respectively.

[27]In some cases the free-decay signal can exhibit a train of sharp pulses regularly spaced in time as a result of repetitive interference between the various emission frequencies [see Foster *et al.*, Phys. Rev. A 10, 2318 (1974), for the case of π transitions]. However, in general, owing to the collisional dephasing of the optical dipole and to the power broadening during the preparative step [Refs. 2, 10, and 11(b)], the decay time of this signal will be very short compared to the one of the ω_{21} beat. We wish to thank R. G. Brewer for bringing this point to our attention.

[28]In the first place it is assumed in Ref. 11(a) that at $t=0$ the Stark field "switches the transitions 1-3 and 2-3 out of resonance with the laser frequency," which, evidently, implies $|\omega_{3j}-\omega_0| \gg$ (Doppler width). This would be the extreme limit of our off-resonance case (Sec. V A), which holds whenever $|\omega_{3j}-\omega_0| \gg \gamma_{ij}$, and would give rise to signals of negligible amplitude [see Eq. (66)]. However, this assumption does not describe the experimental conditions of Ref. 9, where it was recognized that the major contributions to the Raman beats (from both upper and lower levels) come from the three-level subsystems in which one of the transition frequencies is *unchanged* by the Stark field (see Fig. 3 of Ref. 9). This is confirmed in the present analysis, which shows that the Raman beat is maximum when one of the transitions remains in resonance after $t=0$ (either $\omega_{31}\simeq\omega_0$ or $\omega_{32}\simeq\omega_0$). Secondly the velocity integration of the signal $E_T E_T^*$ calculated in Ref. 11(a) [see Eqs. (35) and (36) therein] would raise difficulties, because the form of the resulting expression depends on the relative importance of the decay time associated with ρ_{12}, $\tau_2 = 1/\gamma_{12}$, as compared to the other decay times $T_2 = 1/\gamma_{j3}$. Indeed, the location of some poles of $E_T E_T^*$ [Eq. (35) of Ref. 11(a)] in the upper or lower half of the complex v plane and, consequently, their contributions to the velocity integration, depend on the sign of $1/T_2 - 1/\tau_2$. Accordingly, when Eq. (19) of Ref. 11(a) is integrated over velocity to obtain $E_T E_T^*$ one gets different expressions, depending on the sign of $1/T_2 - 1/\tau_2$, whereas the actual expression is in fact independent of the relative importance of the various decay constants (see the Appendix). This incorrect result is due to omission of important terms in $\rho_{j3}(v, t)$ having velocity dependence in their time-dependent exponents. See Sec. IV A for further discussion of this point.

[29]W. Heitler, *The Quantum Theory of Radiation* (Oxford U. P., London, 1960), Sec. 20; C. Cohen-Tannoudji, Ann. Phys. (Paris) 7, 423 (1962).

[30]For a derivation of Eq. (70) especially suited to laser-induced fluorescence studies, see M. S. Feld and B. J. Feldman, Phys. Rev. A 12, 1015 (1975).

[31]See, for example, *Handbook of Mathematical Functions*, edited by A. Abramowitz and I. A. Segun (Dover, New York, 1965), p. 297.

[32]For instance, when $\nu \simeq 0$ ($ku \gg \omega_0 - \omega$, $\omega_{31} - \omega$), the function

$$1 + \frac{2i}{\sqrt{\pi}} \int_0^{v + ikut/2} e^{+y^2} dy = 1 - \frac{2}{\sqrt{\pi}} \int_0^{kut/2} e^{-y^2} dy .$$

This function is reduced by half for $t \simeq 0.96/ku$ (Ref. 31).

[33]The authors wish to thank Stig Stenholm for an interesting discussion on this point.

[34]M. S. Feld and A. Javan, Ref. 17, Appendix D.