Extraresonances in degenerate four-wave mixing induced by sequential decay

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Collisionless extraresonances (ER) in degenerate four-wave mixing (DFWM) are predicted when the upper state $|b\rangle$ of the $|a\rangle \rightarrow |b\rangle$ transition, excited by near-resonant incident laser beams, decays to the lower state $|a\rangle$ both directly ($|b\rangle \rightarrow |a\rangle$) and via one or two intermediate states: $|b\rangle \rightleftarrows |d\rangle \rightarrow |a\rangle$ or $|b\rangle \rightarrow |c\rangle \rightarrow |d\rangle \rightarrow |a\rangle$. The width of the new ER, which depends on the relative decay rates in the cascade process, may be very narrow leading to very strong DFWM signals. Dephasing collisions affect the intensity of the new ER and also produce the usual, pressure-induced ER.

I. INTRODUCTION

Bogdan *et al.*[1,2] have observed that four-wave mixing (FWM) exhibits a sharp extraresonance at $\omega_2=\omega_1$ in the presence of dephasing collisions despite the fact that the incident laser frequencies, ω_1 and ω_2, were detuned with respect to the atomic transition frequency ω_{ba}. The width of the pressure-induced extraresonance in the degenerate FWM (PIER-D4) signal was found to be determined by the decay rate Γ_b of the upper state $|b\rangle$ of the $|a\rangle \rightarrow |b\rangle$ transition excited by the incident radiation. We have shown[3] that when the lower state $|a\rangle$ of the transition is also allowed to relax at a rate Γ_a, via collision-induced transitions to states that do not interact directly with the incident radiation, an additional Rayleigh-type extraresonant feature at $\omega_2=\omega_1$ with width Γ_a is introduced into PIER-D4. Experimental confirmation of PIER-D4 due to ground-state relaxation has been obtained recently.[4]

At low pressures, the relaxation rate Γ_a can be made arbitrarily small leading to extremely narrow and intense PIER-D4 peaks which may be important for use in phase conjugation. It is interesting to note that in the presence of ground-state relaxation, dephasing collisions are no longer necessary to produce the extraresonances although they may influence their intensities.

In the present paper, we show that two extraresonant features can be obtained in the degenerate FWM (DFWM) signal even in the absence of ground-state relaxation. Here, again, we assume that the lasers with frequencies ω_1 and ω_2 are tuned near the transition frequency ω_{ba}. However, in addition to its direct decay to the ground state $|a\rangle$, the upper state $|b\rangle$ also decays to $|a\rangle$ via an intermediate state $|d\rangle$. This sequential decay scheme

$$|b\rangle \rightarrow |d\rangle \rightarrow |a\rangle \tag{1}$$

is illustrated in Fig. 1(a).

Examples of such three-level systems are the green absorption band of ruby[5] and alexandrite.[6] These systems have been investigated experimentally[5,6] and theoretically[7] in connection with the related problem of population oscillations of state $|a\rangle$ at the frequency difference $\omega_1-\omega_2$ between pump frequency ω_1 and probe frequency ω_2. Both systems are characterized by rapid decay from the excited state $|b\rangle$ to the storage state $|d\rangle$, followed by the slow recovery of the ground state:

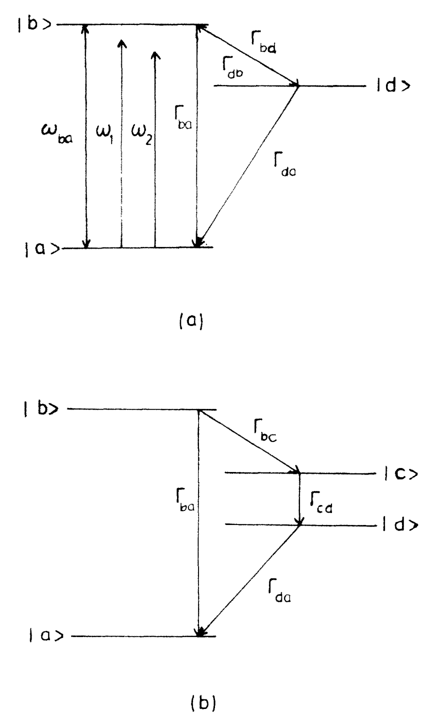

FIG. 1. Energy levels and decay rates Γ_{ij} for (a) three-level system and (b) four-level system. The incident lasers at frequencies ω_1 and ω_2 are nearly resonant with the $|a\rangle \rightarrow |b\rangle$ transition. Both direct decay ($|b\rangle \rightarrow |a\rangle$) and cascade decay processes [(a) $|b\rangle \rightleftarrows |d\rangle \rightarrow |a\rangle$ and (b) $|b\rangle \rightarrow |c\rangle \rightarrow |d\rangle \rightarrow |a\rangle$] are allowed.

$$\Gamma_{bd} \gg \Gamma_{ba}, \Gamma_{da} \ , \tag{2}$$

where Γ_{ij} is the rate of decay from state $|i\rangle$ to state $|j\rangle$.

Pump-probe and phase-conjugation experiments have been performed on another three-level system: fluorescein-doped boric acid.[8] Here an additional process of return to the excited state $|b\rangle$ from the storage state $|d\rangle$ contributes as the temperature is raised. The decay scheme for such systems is

$$|b\rangle \rightleftarrows |d\rangle \rightarrow |a\rangle \ . \tag{3}$$

For the particular case of fluorescein-doped boric acid, the following inequalities hold:

$$\Gamma_{bd} \gg \Gamma_{ba} \gg \Gamma_{db} \gg \Gamma_{da} \ . \tag{4}$$

The scheme of Eq. (3) is a generalization of the relaxation scheme of Eq. (1) which was also considered by Boyd and Mukamel.[7] It is an idealization of the more realistic situation where $|d\rangle$ is replaced by an ensemble of many states $\{|d\rangle\}$ with transitions among them. Treating $|d\rangle$ as a single state is valid provided $\{|d\rangle\}$ can be subdivided into two sets. In the first set, the states $\{|d(\mathrm{I})\rangle\}$ are characterized by relaxation constants such that

$$\Gamma_{d_1(\mathrm{I})b} = \Gamma_{d_2(\mathrm{I})b} = \cdots = \Gamma_{db}$$

and

$$\Gamma_{d_1(\mathrm{I})a} = \Gamma_{d_2(\mathrm{I})a} = \cdots = \Gamma_{da} \ .$$

In the second set, the states $\{|d(\mathrm{II})\rangle\}$ are characterized by relaxation constants such that

$$\Gamma_{d_1(\mathrm{II})b} = \Gamma_{d_2(\mathrm{II})b} = \cdots = 0$$

and

$$\Gamma_{d_1(\mathrm{II})a} = \Gamma_{d_2(\mathrm{II})a} = \cdots = 0 \ .$$

In addition it is required that rapid equilibrium be established between the two sets.

We find two extraresonant peaks for these three-level systems at frequency $\omega_2 = \omega_1$, one weak, broad peak with width $\Gamma_b + \Gamma_{db} - x \simeq \Gamma_b + \Gamma_{db}$ and one narrow, intense peak of width $\Gamma_{da} + x$ where

$$x = \Gamma_{db}(\Gamma_{ba} - \Gamma_{da})/(\Gamma_{db} + \Gamma_{bd} + \Gamma_{ba} - \Gamma_{da}) \ .$$

Preliminary results on phase conjugation in fluorescein-doped boric acid[8] show high reflectance at very low laser pump intensity and are therefore in qualitative agreement with this conclusion.

For gas-phase atoms, we find similar extraresonance peaks when decay schemes (1) and (3) are replaced by the four-level scheme

$$|b\rangle \rightarrow |c\rangle \rightarrow |d\rangle \rightarrow |a\rangle \tag{5}$$

which is illustrated in Fig. 1(b).

For the purposes of the present paper which demonstrates the existence of Rayleigh-type resonances in FWM due to sequential decay, we treat only two extreme cases where the Bloch equations for the four-level system $|a\rangle$, $|b\rangle$, $|c\rangle$, and $|d\rangle$ reduce mathematically but not physically to those of a three-level system. The general solution of the four-level system will not introduce additional physical insight into this particular problem. In the first case,

$$\Gamma_{cd} \gg \Gamma_{bc} \tag{6}$$

so that the population in level $|c\rangle$ rapidly reaches its steady-state value and in the second case,

$$\Gamma_{da} \gg \Gamma_{cd} \tag{7}$$

so that the population in level $|d\rangle$ rapidly reaches its steady-state value. The limiting case of Eq. (7) is relevant to the example discussed in Sec. III. When Eq. (6) holds, the two peaks appear at $\omega_2 = \omega_1$, with widths $\Gamma_b = \Gamma_{ba} + \Gamma_{bc}$ and Γ_{da} and when Eq. (7) holds, the peaks are characterized by widths Γ_b and $\Gamma_{da}\Gamma_{cd}/(\Gamma_{da} + \Gamma_{cd}) \simeq \Gamma_{cd}$. As in the experiments of Bloembergen and co-workers,[2,4] the extraresonant feature with width Γ_b only appears in the presence of dephasing collisions. By contrast, the second extraresonant feature whose width is characterized by Γ_{da} (or Γ_{cd}) appears even in the absence of collisions provided the decay scheme is purely radiative. Thus in a low-pressure gaseous system that decays according to Eq. (5), one expects a single extraresonant feature with width Γ_{da} (or Γ_{cd}). As the pressure is increased, the extraresonant feature with width Γ_b will also become important, leading to an increase or decrease in the width of the signal, according to the relative values of Γ_b and Γ_{da} (or Γ_{cd}). The pressure may also lead to an increase in the intensity of both extraresonant peaks.

II. THE MODEL

We consider the level schemes depicted in Fig. 1 and assume that the electric field intensity is given by

$$\mathbf{E} = \tfrac{1}{2}[(\boldsymbol{\epsilon}\mathscr{E}_1 e^{-i\omega_1 t} + \boldsymbol{\epsilon}\mathscr{E}_2 e^{-i\omega_2 t}) + \mathrm{c.c.}] \ , \tag{8}$$

where

$$\mathscr{E}_1 = |\mathscr{E}_1|(e^{i\mathbf{k}_1\cdot\mathbf{r}} + e^{i\mathbf{k}_1'\cdot\mathbf{r}}) \qquad \mathscr{E}_2 = |\mathscr{E}_2| e^{i\mathbf{k}_2\cdot\mathbf{r}} \ , \tag{9}$$

$\boldsymbol{\epsilon}$ is the complex polarization unit vector, $\mathbf{k}_1$ and $\mathbf{k}_1'$ are the wave vectors of the incident fields at frequency ω_1, and $\mathbf{k}_2$ is the wave vector of the incident field at frequency ω_2. Then further assuming that

$$\rho_{aa} + \rho_{bb} + \rho_{cc} + \rho_{dd} = \rho_{aa}^{eq} \ , \tag{10}$$

we obtain the following equations of motion for the density-matrix elements:

$$\begin{aligned} i\hbar\dot{\rho}_{aa} &= -V_{ba}\rho_{ab} + \rho_{ba}V_{ab} - i\hbar\Gamma'(\rho_{aa} - \rho_{aa}^{eq}) + i\hbar\Gamma''\rho_{bb} \ , \\ i\hbar\dot{\rho}_{bb} &= V_{ba}\rho_{ab} - \rho_{ba}V_{ab} - i\hbar(\Gamma_b + \Gamma_{db})\rho_{bb} \\ &\quad - i\hbar\Gamma_{db}(\rho_{aa} - \rho_{aa}^{eq}) \ , \\ i\hbar\dot{\rho}_{ab} &= -\hbar(\omega_{ba} + i\gamma)\rho_{ab} + V_{ab}(\rho_{bb} - \rho_{aa}) \ , \end{aligned} \tag{11}$$

where Γ_{ij} is the rate of decay from level $|i\rangle$ to $|j\rangle$;

$$\Gamma_b = \Gamma_{ba} + \Gamma_{bd} \quad \text{(three-level system)} \tag{12a}$$

or

$$\Gamma_b = \Gamma_{ba} + \Gamma_{bc} \quad \text{(four-level system)} \tag{12b}$$

is the total rate of decay from level $|b\rangle$;

$$\gamma = \tfrac{1}{2}\Gamma_b + \gamma^* \tag{13}$$

is the rate of decay of the off-diagonal density-matrix element ρ_{ab}; and γ^* is the rate of phase-changing collisions,

$$\Gamma' = \Gamma_{da}, \quad \Gamma'' = \Gamma_{ba} - \Gamma_{da} = \Gamma_{ba} - \Gamma' \tag{14a}$$

for the three-level system,

$$\Gamma' = \Gamma_{da}, \quad \Gamma'' = \Gamma_{ba} - \Gamma_{da}(1 + \Gamma_{bc}/\Gamma_{cd}) \simeq \Gamma_{ba} - \Gamma' \tag{14b}$$

for the four-level system when the condition of Eq. (6) holds, and

$$\Gamma' = \Gamma_{da}\Gamma_{cd}/(\Gamma_{da} + \Gamma_{cd}) \simeq \Gamma_{cd}, \quad \Gamma'' = \Gamma_{ba} - \Gamma' \tag{14c}$$

for the four-level system when Eq. (7) holds. The matrix elements of the interaction Hamiltonian are written in the electric-dipole and rotating-wave approximations as

$$V_{ba} = -\tfrac{1}{2}\mu_{ba}(\mathscr{E}_1 e^{-i\omega_1 t} + \mathscr{E}_2 e^{-i\omega_2 t}) = V_{ab}^* \tag{15}$$

with electric-dipole matrix element $\mu_{ba} = \langle b \,|\, \boldsymbol{\epsilon}\cdot\boldsymbol{\mu} \,|\, a\rangle$.

The equations for the Fourier components of the density-matrix elements that must be solved in order to determine $\rho_{ab}(\omega_2 - 2\omega_1)$, the Fourier component of ρ_{ab} oscillating at frequency $\omega_2 - 2\omega_1$, to first order in $|\mathscr{E}_2|$ and to all orders in $|\mathscr{E}_1|$, are given by[3]

$$\begin{aligned}
&(\omega_2 - 2\omega_1 + \omega_{ba} + i\gamma)\rho_{ab}(\omega_2 - 2\omega_1) = -\mathscr{V}_1^*(\rho_{bb} - \rho_{aa})^{(\omega_2 - \omega_1)}, \\
&(\omega_2 - \omega_{ba} + i\gamma)\rho_{ba}(\omega_2) = \mathscr{V}_2(\rho_{bb} - \rho_{aa})^{dc} + \mathscr{V}_1(\rho_{bb} - \rho_{aa})^{(\omega_2 - \omega_1)}, \\
&(\omega_{ba} - \omega_1 + i\gamma)\rho_{ab}(-\omega_1) = -\mathscr{V}_1^*(\rho_{bb} - \rho_{aa})^{dc}, \\
&(\omega_2 - \omega_1 + i\Gamma')\rho_{aa}(\omega_2 - \omega_1) = -\mathscr{V}_1^*\rho_{ba}(\omega_2) + \mathscr{V}_2\rho_{ab}(-\omega_1) + \mathscr{V}_1\rho_{ab}(\omega_2 - 2\omega_1) + i\Gamma''\rho_{bb}(\omega_2 - \omega_1), \\
&(\omega_2 - \omega_1 + i\Gamma_b + i\Gamma_{db})\rho_{bb}(\omega_2 - \omega_1) = \mathscr{V}_1^*\rho_{ba}(\omega_2) - \mathscr{V}_2\rho_{ab}(-\omega_1) - \mathscr{V}_1\rho_{ab}(\omega_2 - 2\omega_1) - i\Gamma_{db}\rho_{aa}(\omega_2 - \omega_1),
\end{aligned} \tag{16}$$

where

$$\mathscr{V}_1 = \tfrac{1}{2}\mu_{ba}\mathscr{E}_1/\hbar, \quad \mathscr{V}_2 = \tfrac{1}{2}\mu_{ba}\mathscr{E}_2/\hbar. \tag{17}$$

From Eqs. (16), we find that

$$\rho_{ab}(\omega_2 - 2\omega_1) = \frac{-\mathscr{V}_1^{*2}\mathscr{V}_2(\omega_2 - \omega_1 + 2i\gamma)(\rho_{bb} - \rho_{aa})^{dc}}{D(\omega_2)(\omega_{ba} - \omega_1 + i\gamma)}, \tag{18}$$

where

$$D(\omega_2) = -2|\mathscr{V}_1|^2(\omega_2 - \omega_1 + i\gamma) + \frac{(\omega_2 - \omega_{ba} + i\gamma)(\omega_2 - 2\omega_1 + \omega_{ba} + i\gamma)[\omega_2 - \omega_1 + \frac{1}{2}i(\Gamma' + \Gamma_b + \Gamma_{db}) + \frac{1}{2}X][\omega_2 - \omega_1 + \frac{1}{2}i(\Gamma' + \Gamma_b + \Gamma_{db}) - \frac{1}{2}X]}{2(\omega_2 - \omega_1) + i(\Gamma' + \Gamma_b + 2\Gamma_{db} - \Gamma'')} \tag{19}$$

with

$$X = [-(\Gamma_{db} + \Gamma_b - \Gamma')^2 + 4\Gamma_{db}\Gamma'']^{1/2}, \tag{20}$$

and $(\rho_{bb} - \rho_{aa})^{dc}$ is the steady-state solution of Eqs. (11) when only the field with frequency ω_1 is considered. We note that to first order in $|\mathscr{E}_1|^2$, taking $\Gamma_{db} = 0$ and making the necessary transformations on Eqs. (18) and (19), we obtain full agreement with the expression for $\chi^{(3)}(-\omega_2, \omega_2, -\omega_1, \omega_1)$ needed for the calculation of probe absorption in the presence of a pump beam. [See Eq. (34) of Ref. 7.]

In order to elucidate the physics let us consider the case where the $|a\rangle \rightarrow |b\rangle$ transition is *not saturated*. We consider two cases: $\Gamma_{db} = 0$ and $\Gamma_{db} \neq 0$.

A. $\Gamma_{db} = 0$

When there is no return from level $|d\rangle$ to level $|b\rangle$ Eq. (18) reduces to

$$\rho_{ab}(\omega_2 - 2\omega_1) = C(1 + A + B) \tag{21}$$

where

$$\begin{aligned}
A &= \frac{\frac{1}{2}i(2\gamma - \Gamma')}{\omega_2 - \omega_1 + i\Gamma'}\left[1 - \frac{\Gamma''}{\Gamma_b - \Gamma'}\right], \\
B &= \frac{i\gamma^*}{\omega_2 - \omega_1 + i\Gamma_b}\left[1 + \frac{\Gamma''}{\Gamma_b - \Gamma'}\right], \\
C &= \frac{2\mathscr{V}_1^{*2}\mathscr{V}_2\rho_{aa}^{eq}}{(\omega_{ba} - \omega_1 + i\gamma)(\omega_2 - \omega_{ba} + i\gamma)(\omega_2 - 2\omega_1 + \omega_{ba} + i\gamma)}.
\end{aligned} \tag{22}$$

In the absence of collisions, one obtains

$$A=\frac{\frac{1}{2}i(\Gamma_b-\Gamma'-\Gamma'')}{\omega_2-\omega_1+i\Gamma'},\quad B=0 \tag{23}$$

so that a single extraresonant feature with width Γ' appears at $\omega_2=\omega_1$. In the presence of collisions, two extraresonant features appear at $\omega_2=\omega_1$, one with width Γ' and one with width Γ_b. The amplitudes of the features are pressure-dependent but their widths are independent of pressure provided collision-induced depopulation of the states $|b\rangle$, $|c\rangle$, and $|d\rangle$ is negligible. We note that when the indirect decay schemes are either absent or very slow compared to the direct decay so that $\Gamma_b\simeq\Gamma_{ba}$, only the extraresonant peak with width Γ_b survives and we return to the situation discussed by Bloembergen and coworkers.[1,2,4] Only if Γ_b differs significantly from Γ_{ba} will there be an important contribution from the new extraresonant feature. Even then the contribution will disappear if $\Gamma'\gg\Gamma_b$, that is, if the decay from $|b\rangle$ is the rate-determining step in the decay scheme. Thus the new extraresonant peak disappears whenever the population that leaves level $|b\rangle$ rapidly returns to level $|a\rangle$ leaving no residual population stored in levels $|c\rangle$ or $|d\rangle$.

B. $\Gamma_{db}\neq 0$

When the rate of return from state $|d\rangle$ to state $|b\rangle$ is significant, Eq. (21) reduces to

$$\rho_{ab}(\omega_2-2\omega_1)=C(1+A'+B')\ , \tag{24}$$

where C is defined in Eq. (22) and

$$A'=\frac{1}{2}\frac{2i\gamma-\frac{1}{2}i(\Gamma'+\Gamma_b+\Gamma_{bd})+\frac{1}{2}X}{\omega_2-\omega_1+\frac{1}{2}i(\Gamma'+\Gamma_b+\Gamma_{db})-\frac{1}{2}X}\times\left[1-\frac{i(\Gamma''-\Gamma_{db})}{X}\right],$$

$$B'=\frac{1}{2}\frac{2i\gamma-\frac{1}{2}i(\Gamma'+\Gamma_b+\Gamma_{db})-\frac{1}{2}X}{\omega_2-\omega_1+\frac{1}{2}i(\Gamma'+\Gamma_b+\Gamma_{db})+\frac{1}{2}X}\times\left[1+\frac{i(\Gamma''-\Gamma_{db})}{X}\right]. \tag{25}$$

When X is real, two extraresonant peaks characterized by the width $\frac{1}{2}(\Gamma'+\Gamma_b+\Gamma_{db})$ appear at $\omega_2=\omega_1\pm\frac{1}{2}X$. When X is purely imaginary, the extraresonant peaks are characterized by the widths $\frac{1}{2}(\Gamma'+\Gamma_b+\Gamma_{db}\pm|X|)$ and both appear at $\omega_2=\omega_1$. We note that in contrast to the case $\Gamma_{db}=0$, discussed above, we obtain here two extraresonant features whose intensities, determined by A' and B', are nonzero even when there are no dephasing collisions.

When Eq. (4) holds, X can be approximated as

$$X\simeq i(\Gamma_{db}+\Gamma_b-\Gamma')-2ix\ , \tag{26}$$

with

$$x=\Gamma_{db}\Gamma''/(\Gamma_{db}+\Gamma_b-\Gamma')\ . \tag{27}$$

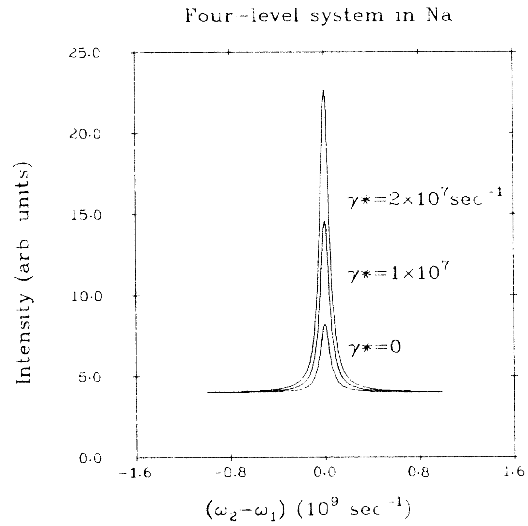

FIG. 2. DFWM signal for atomic Na calculated using Eqs. (21) and (22), where the lasers are tuned near the $3^2S_{1/2}\rightarrow4^2P_{1/2}$ transition and the decay channels are $4^2P_{1/2}\rightarrow3^2S_{1/2}$ (direct) and $4^2P_{1/2}\rightarrow4^2S_{1/2}\rightarrow3^2S_{1/2}$ (cascade). The decay parameters are given in the text and $\omega_{ba}-\omega_1=10^{11}$ s^{-1}. The DFWM signal increases as the rate of dephasing collisions γ^* increases.

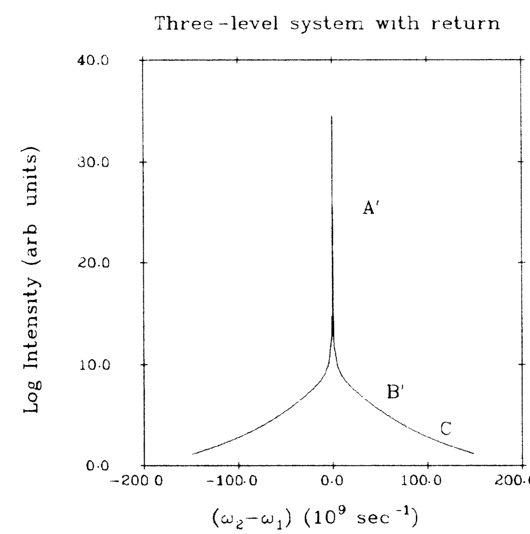

FIG. 3. Near-resonant DFWM signal for a three-level system with the decay channels $|b\rangle\rightarrow|a\rangle$ (direct) and $|b\rangle\rightleftarrows|d\rangle\rightarrow|a\rangle$ (cascade). The decay parameters used are $\Gamma_{ba}=10^8$ s^{-1}, $\Gamma_{bd}=10^{10}$ s^{-1}, $\Gamma_{db}=10^6$ s^{-1} (rate of *return* from the storage state $|d\rangle$ to the excited state $|b\rangle$), $\Gamma_{da}=10^4$ s^{-1}, $\gamma^*=5\times10^{10}$ s^{-1} and the detuning, $\omega_{ba}-\omega_1=10^{-4}$ s^{-1}. The spectrum was calculated from Eqs. (24) and (28). The narrow, intense peak arises from the A' term and the broad, weak peak from the B' term of Eq. (28). The contribution in the wings arises from the resonances in the C factor of Eq. (24) with width γ.

Then Eq. (25) simplifies to

$$A'=\frac{1}{2}\frac{i(2\gamma-\Gamma')-ix}{\omega_2-\omega_1+ix+i\Gamma'}\left[1-\frac{\Gamma''-\Gamma_{db}}{\Gamma_b+\Gamma_{db}-\Gamma'-2x}\right], \tag{28}$$

$$B'=\frac{1}{2}\frac{i(2\gamma^*-\Gamma_{db})+ix}{\omega_2-\omega_1-ix+i(\Gamma_b+\Gamma_{db})}\times\left[1+\frac{\Gamma''-\Gamma_{db}}{\Gamma_b+\Gamma_{bd}-\Gamma'-2x}\right].$$

We thus obtain two extraresonant peaks at $\omega_2=\omega_1$ with widths determined by $\Gamma_{da}+x$ and by $\Gamma_b+\Gamma_{db}+x\simeq\Gamma_b+\Gamma_{db}$, respectively. The peak whose width is determined by $\Gamma_{da}+x$ may be very narrow and become very intense if $\Gamma_{da}+x\ll\gamma$ as is the case in fluorescein.[8] Because of the very small value of $\Gamma_{da}+x$ for fluorescein, DFWM is easily saturated [see Eq. (19)]. This has recently been observed.[8]

III. EXAMPLES

In a numerical calculation, we apply Eqs. (21) and (22) to the case of DFWM with cascade decay in atomic Na where the (frequency-doubled) dye lasers are tuned near the $3^2S_{1/2}\rightarrow4^2P_{1/2}$ transition frequency. Here $|a\rangle=3^2S_{1/2}$, $|b\rangle=4^2P_{1/2}$, $|c\rangle=4^2S_{1/2}$, and $|d\rangle=3^2P_{1/2}$. The linewidths due to radiative decay were calculated from the oscillator strengths of Miles and Harris.[9] Thus $2\pi/\Gamma_{da}=16.2$ ns, $2\pi/\Gamma_{ba}=323$ ns, $2\pi/\Gamma_{bc}=154$ ns, and $2\pi/\Gamma_{cd}=117$ ns. Since here $\Gamma_{da}\gg\Gamma_{cd}$, the expressions for Γ' and Γ'' given in Eq. (14c) are appropriate. In Fig. 2, we show the extraresonance at $\omega_2=\omega_1$ in the absence and presence of phase-changing collisions. Since $\Gamma_b\gtrsim\Gamma'\simeq\Gamma_{cd}$, no significant change in the width of the extraresonance is observed on the introduction of phase-changing collisions.

We now use Eqs. (24) and (28) to calculate the near-resonance ($\omega_1\simeq\omega_{ba}$) DFWM spectrum for a system similar to fluorescein-doped boric acid. For convenience, we have chosen the lifetime of state $|d\rangle$ to be much shorter than the "several seconds" quoted for the fluorescein system[8] but still much longer than all other radiative lifetimes in the system in accord with Eq. (4). In Fig. 3, the sharp, intense peak arises from the A' term in Eq. (28) and the broad, weak peak arises from a superposition of contributions from the C term [Eq. (24)] and B' term [Eq. (28)].

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