Intense extraresonant signals in four-wave mixing triggered by resonance-enhanced three-photon scattering

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It is shown that intense collisionless Raman-type extraresonant signals in four-wave mixing can be obtained by exciting a strongly fluorescent atomic or molecular eigenstate which is not directly connected to the states coupled by the Raman transition. The process which triggers the extraresonant signal is associated with resonance-enhanced three-photon scattering or, equivalently, with excited-state Raman scattering.

I. INTRODUCTION

In contrast to collision-triggered extra Raman-type resonances in four-wave mixing (FWM), where high signal-to-background ratios (S/B) have been reported,[1] the values of S/B predicted for extra resonance in FWM triggered by radiative relaxation, in the absence of collision, are rather low.[2] Since this may prevent the observation of collisionless extra resonances in FWM, we propose here to enhance S/B by saturating the three-photon scattering process using to trigger the collisionless extraresonant signal.

In previous publications, observations on Raman-type[1] and Rayleigh-type[3] extra resonances in FWM have been interpreted[2,4] in terms of transitions starting from the virtual or "dressed-atom" state $|a'\rangle$ with energy $E_{a'}=E_b-\hbar\omega_1$ or $E_{a'}=E_c-\hbar\omega_2$. This state can be populated by collision-induced transitions from the ground state.[1-4] The energy difference $\hbar|\tilde{\Delta}|=E_{a'}-E_a=E_b-E_a-\hbar\omega_1$ is supplied by quasielastic dephasing collisions (see Fig. 1).

An alternative method for obtaining FWM extra resonances has been proposed in a previous paper.[2] The key conclusion of this paper was that at sufficiently high laser intensity, the energy detuning $\hbar\tilde{\Delta}$ can be supplied, even in the absence of collisions, by means of a light-scattering process. In this process, which is also depicted in Fig. 1, the nonresonant absorption of a laser photon of frequency ω is followed by the emission of a scattered photon at the three-photon or hyper-Raman frequency $\omega'=\omega+\omega_1-\omega_{ba}=\omega-\tilde{\Delta}$. The absorption of a second laser photon at frequency ω_1 leads to the population of the excited state $|b\rangle$ allowing the emission of a Raman-type FWM signal at the frequency $\omega_{\rm FWM}=\omega_1-\omega_{cb}$ provided $\omega_2-\omega_1=\omega_{cb}$. It is important to note that the absorption of the second photon is already part of the FWM process, and also that none of the incident laser frequencies are in resonance with the transition frequencies ω_{ba} and ω_{ca} of the atomic system. The peak signal-to-background ratio for the Raman-type extraresonant FWM signal was found to be

$$\frac{S}{B}\simeq 1+\frac{4}{\tilde{\Delta}^2(1/T_2)_{bc}}[(1/T_2)_{ab}V_{ab}^2+(1/T_2)_{ac}V_{ac}^2]\ , \tag{1}$$

where $(T_2)_{ij}$ is the transverse relaxation time (coherence damping) of the off-diagonal density-matrix element ρ_{ij}; $V_{ab}=\mu_{ab}|\mathscr{E}_1|/2\hbar$ and $V_{ac}=\mu_{ac}|\mathscr{E}_2|/2\hbar$ are the Rabi frequencies, μ_{ij} are transition-dipole moments, and $\mathscr{E}_{1,2}$ are the laser-field envelopes. Equation (1) is only valid provided

$$\tilde{\Delta}\gg(1/T_2)_{ab},(1/T_2)_{ac},V_{ab},V_{ac}\ , \tag{2}$$

and under these conditions, we see that

$$(S-B)/B\ll 1\ . \tag{3}$$

Under resonance and saturation conditions, where Eq. (2) and hence Eq. (3) are no longer valid, larger values for S/B may be expected but then the contribution to the Raman-resonance signal at $\omega_2-\omega_1=\omega_{cb}$ arising from the two-step, excited-state coherent Stokes-Raman scattering (ES CSRS)[2,5,6] will become dominant, thereby masking the one-step process of Fig. 1. Note that in the two-step process, the absorption of the second laser photon of fre-

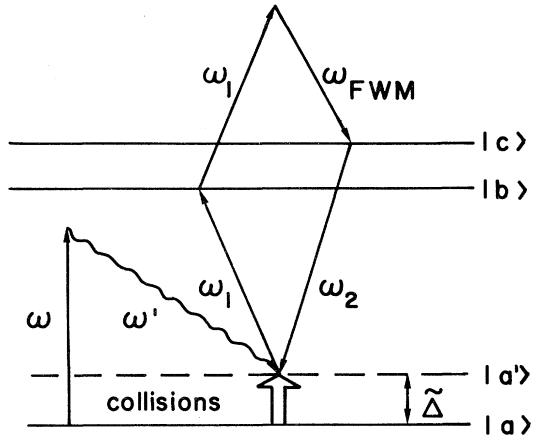

FIG. 1. Extraresonant four-wave mixing signal at the Raman frequency $\omega_{\rm FWM}\equiv 2\omega_1-\omega_2=\omega_1-\omega_{cb}$, with initially unpopulated states $|b\rangle$ and $|c\rangle$, is triggered either collisionally or by radiative relaxation via the emission of a photon at the three-photon or hyper-Raman scattering frequency $\omega'=\omega+\omega_1-\omega_{ba}$. None of the pump-laser frequencies ω_1, ω_2, or ω (which may be identical to ω_1 or ω_2) may by exactly resonant with the $|a\rangle\rightarrow|b\rangle$ or $|a\rangle\rightarrow|c\rangle$ transition frequencies, ω_{ba} and ω_{ca}, so that $\tilde{\Delta}=\omega_{ba}-\omega_1=\omega_{ca}-\omega_2\neq 0$. Only the rotating term of Eq. (5) is depicted.

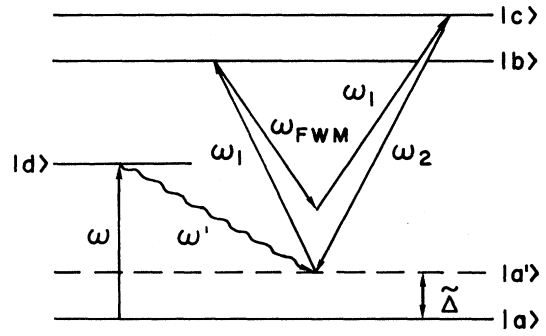

FIG. 2. Extraresonant FWM signal triggered by resonance-enhanced three-photon scattering. The three-level system of Fig. 1 is replaced by a four-level system. Pump-laser frequency ω is exactly resonant with ω_{da}, the $|a\rangle \rightarrow |d\rangle$ transition frequency. State $|d\rangle$ should be chosen to fluoresce to the ground state $|a\rangle$ at least as strongly as the states $|b\rangle$ and $|c\rangle$. Frequencies ω_1, ω_2, ω_{FWM}, and $\tilde{\Delta}$ are defined as in Fig. 1. Only the counter-rotating term of Eq. (5) is depicted.

quency ω_1 does *not* constitute the first step in the FWM process as in Fig. 1, but simply populates the excited state $|b\rangle$ as shown in Fig. 3 of Ref. 2.

In order to obtain an unequivocal resonance- or saturation-enhanced extraresonant signal, the physical situation described by the three-level system of Fig. 1 is replaced in the present approach by that depicted in Fig. 2 where a four-level system is considered. An additional pump laser of frequency ω is introduced such that $\omega \simeq \omega_{da}$. This increases the intensity of the photons at the three-photon, or hyper-Raman,[7] scattering frequency $\omega' = \omega + \omega_1 - \omega_{ba}$ (see Fig. 2), and hence also that of the FWM signal. We then obtain [cf. Eq. (1)]

$$\frac{S}{B} \simeq 1 + 4\frac{(1/T_2)_{ad}}{(1/T_2)_{bc}} + 4\frac{(1/T_2)_{ad}^2}{(1/T_2)_{bc}^2} , \tag{1'}$$

which, when the state $|d\rangle$ is at least as strongly fluorescent as the states $|b\rangle$ and $|c\rangle$ together, gives

$$(S-B)/B \gtrsim 8 \tag{3'}$$

so that the signal is readily observable.

The transition from the process depicted in Fig. 1, and discussed previously,[2] to that described by Fig. 2 consists of replacing the weak triggering mechanism of extraresonant FWM, involving scattering of nonresonant radiation, by a much more efficient fluorescencelike process which follows the absorption of saturating resonant radiation.

Inspection of Eqs. (1) and (1') shows that the appearance of the collisionless extraresonant signal in FWM depends on the transverse relaxation times of purely radiative origin. This "radiative dephasing" replaces the effect of collisional dephasing discussed by Bloembergen.[1,3] Of course, the radiative transverse relaxation times are due only to radiative lifetimes and therefore the measurements proposed in this paper should provide a direct method of obtaining these lifetimes. In particular, Eq. (24) shows that $(1/T_2)_{bc}$ can be determined from the linewidth of the extraresonant signal. Once $(1/T_2)_{bc}$ is found, the radiative lifetime of state $|d\rangle$ is obtained from the peak S/B ratio given by Eq. (1'). Thus very fast relaxation times, which are difficult to measure in the time domain, can be determined from measurements carried out in the frequency domain. The preceding remarks indicate that the information on radiative dephasing, obtained from the collisionless triggering of Raman-type FWM extra resonances proposed in this paper, complements the information on collisional dephasing obtained from the pressure-induced Raman-type extra resonances in FWM of Bloembergen and co-workers.[1,3]

A theoretical description of the model in terms of the four-level Bloch equations is given in Sec. II and the new qualitative and quantitative aspects of this model are discussed in Sec. III. We show, using the alkali metals as an example, that S/B can be of order 10^2–10^3, provided we choose the $|a\rangle \rightarrow |d\rangle$ transition to be a valence transition and the $|a\rangle \rightarrow |b\rangle$ and $|a\rangle \rightarrow |c\rangle$ transitions to be Rydberg transitions.

II. THE MODEL

Consider the four-level system shown in Fig. 2: $|a\rangle$ is the ground state of the atomic or molecular system, $|b\rangle$ and $|c\rangle$ are excited states connected by the extra Raman-type resonance, and $|d\rangle$ is another excited state. The system is irradiated by four laser beams: one with frequency ω and wave vector $\vec{k}$ that interacts near resonantly with the $|a\rangle \rightarrow |d\rangle$ transition, two with frequency ω_1 and wave vectors $\vec{k}_1$ and $\vec{k}'_1$ that interact with the $|a\rangle \rightarrow |b\rangle$ transition, and one with frequency ω_2 and wave vector $\vec{k}_2$ that interacts with the $|a\rangle \rightarrow |c\rangle$ transition. The state $|d\rangle$ is chosen such that $\mu_{bd} = \mu_{cd} = 0$, and may be either above or below the states $|b\rangle$ and $|c\rangle$. The electric field intensity is given by

$$\vec{E} = \vec{x}\{ |\mathscr{E}| \cos(\omega t - \vec{k}\cdot\vec{r} + \phi) + |\mathscr{E}_1| [\cos(\omega_1 t - \vec{k}_1\cdot\vec{r} + \phi_1) + \cos(\omega_1 t - \vec{k}'_1\cdot\vec{r} + \phi_1)] + |\mathscr{E}_2| \cos(\omega_2 t - \vec{k}_2\cdot\vec{r} + \phi_2)\} , \tag{4}$$

where we have assumed all the beams to be plane polarized with the unit-polarization vector $\vec{x}$. As discussed previously,[2,8] the component of the polarization $\vec{P}$ that oscillates with the CSRS frequency $\omega_{\mathrm{CSRS}} = 2\omega_1 - \omega_2$, propagates with wave vector $\vec{k}_1 + \vec{k}'_1 - \vec{k}_2$, and has the polarization $\vec{x}$, is given by

$$P = \frac{N}{2\hbar} \left[\sum_k \rho'_{bc} \mu_{bk} \mu_{kc} |\mathscr{E}_1| \left[\frac{1}{\omega_{kc} + \omega_1} + \frac{1}{\omega_{kb} - \omega_1} \right] \exp[-i(2\omega_1 - \omega_2)t + i(\vec{k}_1 + \vec{k}'_1 - \vec{k}_2)\cdot\vec{r} - i(2\phi_1 - \phi_2)] + \text{c.c.} \right] , \tag{5}$$

where

$$\rho'_{bc}=\rho_{bc}\exp[i\Delta_{cb}t+i(\vec{k}_2-\vec{k}_1)\cdot\vec{r}-i(\phi_2-\phi_1)] \tag{6}$$

and Δ_{cb} is the two-photon detuning

$$\Delta_{cb}=\omega_{cb}-\omega_2+\omega_1 \, . \tag{7}$$

We note that the first term in the large parentheses in Eq. (5) is counter-rotating whereas the second is rotating.

In order to determine ρ'_{bc}, we solve the following Bloch equations for the four-level system:

$$\dot{\rho}_{aa}=iV_{ab}(\rho'_{ba}-\rho'_{ab})+iV_{ac}(\rho'_{ca}-\rho'_{ac})+iV_{ad}(\rho'_{da}-\rho'_{ad})+(1/T_1)_{ba}\rho_{bb}+(1/T_1)_{ca}\rho_{cc}+(1/T_1)_{da}\rho_{dd} \, , \tag{8a}$$

$$\dot{\rho}_{bb}=-iV_{ab}(\rho'_{ba}-\rho'_{ab})-(1/T_1)_b\rho_{bb}+(1/T_1)_{cb}\rho_{cc}+(1/T_1)_{db}\rho_{dd} \, , \tag{8b}$$

$$\dot{\rho}_{cc}=-iV_{ac}(\rho'_{ca}-\rho'_{ac})-(1/T_1)_c\rho_{cc}+(1/T_1)_{dc}\rho_{dd} \, , \tag{8c}$$

$$\dot{\rho}_{dd}=-iV_{ad}(\rho'_{da}-\rho'_{ad})-(1/T_1)_d\rho_{dd} \, , \tag{8d}$$

$$\dot{\rho}'_{ab}=iV_{ab}(\rho_{bb}-\rho_{aa})+iV_{ac}\rho'_{cb}+iV_{ad}\rho'_{db}-[(1/T_2)_{ab}-i\Delta_{ba}]\rho'_{ab} \, , \tag{8e}$$

$$\dot{\rho}'_{ac}=iV_{ab}\rho'_{bc}+iV_{ac}(\rho_{cc}-\rho_{aa})+iV_{ad}\rho'_{dc}-[(1/T_2)_{ac}-i\Delta_{ca}]\rho'_{ac} \, , \tag{8f}$$

$$\dot{\rho}'_{ad}=iV_{ab}\rho'_{bd}+iV_{ac}\rho'_{cd}+iV_{ad}(\rho_{dd}-\rho_{aa})-[(1/T_2)_{ad}-i\Delta_{da}]\rho'_{ad} \, , \tag{8g}$$

$$\dot{\rho}'_{bc}=-iV_{ac}\rho'_{ba}+iV_{ab}\rho'_{ac}-[(1/T_2)_{bc}-i\Delta_{cb}]\rho'_{bc} \, , \tag{8h}$$

$$\dot{\rho}'_{bd}=iV_{ab}\rho'_{ad}-iV_{ad}\rho'_{ba}-[(1/T_2)_{bd}-i\Delta_{db}]\rho'_{bd} \, , \tag{8i}$$

$$\dot{\rho}'_{cd}=iV_{ac}\rho'_{ad}-iV_{ad}\rho'_{ca}-[(1/T_2)_{cd}-i\Delta_{dc}]\rho'_{cd} \, , \tag{8j}$$

where

$$V_{ab}=\mu_{ab}\,|\,\mathscr{E}_1\,|\,/2\hbar, \quad V_{ac}=\mu_{ac}\,|\,\mathscr{E}_2\,|\,/2\hbar, \quad V_{ad}=\mu_{ad}\,|\,\mathscr{E}\,|\,/2\hbar \tag{9}$$

are the one-photon Rabi frequencies,

$$\begin{aligned}
&\rho'_{ab}=\rho_{ab}\exp[i(\Delta_{ba}t+\vec{k}_1\cdot\vec{r}-\phi_1)] \, , \\
&\rho'_{ac}-\rho_{ac}\exp[i(\Delta_{ca}t+\vec{k}_2\cdot\vec{r}-\phi_2)] \, , \\
&\rho'_{ad}=\rho_{ad}\exp[i(\Delta_{da}t+\vec{k}\cdot\vec{r}-\phi)] \, , \\
&\rho'_{bd}=\rho_{bd}\exp\{i[\Delta_{db}t+(\vec{k}-\vec{k}_1)\cdot\vec{r}-(\phi-\phi_1)]\} \, , \\
&\rho'_{cd}=\rho_{cd}\exp\{i[\Delta_{dc}t+(\vec{k}-\vec{k}_2)\cdot\vec{r}-(\phi-\phi_2)]\} \, ,
\end{aligned} \tag{10}$$

are the rotated off-diagonal elements of the density matrix in the interaction picture, and

$$\begin{aligned}
&\Delta_{ba}=\omega_{ba}-\omega_1, \quad \Delta_{ca}=\omega_{ca}-\omega_2, \quad \Delta_{da}=\omega_{da}-\omega, \quad \Delta_{db}=\Delta_{da}-\Delta_{ba}=\omega_{db}-\omega+\omega_1 \, , \\
&\Delta_{dc}=\Delta_{da}-\Delta_{ca}=\omega_{dc}-\omega+\omega_2 \, ,
\end{aligned} \tag{11}$$

are the one- and two-photon frequency offsets; $(1/T_1)_{ij}$ is the rate of transition from state $|\,i\,\rangle\rightarrow|\,j\,\rangle$, $(1/T_1)_i$ is the total rate of transitions from state $|\,i\,\rangle$ to all other states, and $(1/T_2)_{ij}$ is the rate of decay of ρ_{ij}.

The steady-state solution of Eqs. (8) to first order in V_{ab} and V_{ac} and to all orders in V_{ad} is given by

$$\begin{aligned}
\rho'_{bc}=\frac{V_{ab}V_{ac}}{\Delta_{cb}+i(1/T_2)_{bc}}\Bigg[&\frac{\rho_{aa}-\rho_{bb}}{\Delta_{ba}-i(1/T_2)_{ab}}+\frac{\rho_{cc}-\rho_{aa}}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{V_{ad}^2}{[\Delta_{dc}-i(1/T_2)_{cd}][\Delta_{ca}+i(1/T_2)_{ac}]+V_{ad}^2} \\
&\times\left[\frac{\rho_{dd}-\rho_{aa}}{\Delta_{da}-i(1/T_2)_{ad}}-\frac{\rho_{cc}-\rho_{aa}}{\Delta_{ca}+i(1/T_2)_{ac}}\right]-\frac{V_{ad}^2}{[\Delta_{db}+i(1/T_2)_{db}][\Delta_{ba}-i(1/T_2)_{ab}]+V_{ad}^2} \\
&\times\left[\frac{\rho_{dd}-\rho_{aa}}{\Delta_{da}+i(1/T_2)_{ad}}-\frac{\rho_{bb}-\rho_{aa}}{\Delta_{ba}-i(1/T_2)_{ab}}\right]\Bigg] \, .
\end{aligned} \tag{12}$$

When the intensity of the additional pump laser (frequency ω) is very low, $\rho_{aa}\simeq\rho_{aa}^{\mathrm{eq}}$, and ρ_{dd} (and hence ρ_{bb} and ρ_{cc}) is negligible. The expression for ρ'_{bc} given in Eq. (12) then reduces to that of Bogdan *et al.*[1]

$$\rho'_{bc}=\frac{V_{ab}V_{ac}\rho_{aa}^{\mathrm{eq}}}{[\Delta_{ba}-i(1/T_2)_{ab}][\Delta_{ca}+i(1/T_2)_{ac}]}\left[1+\frac{i[(1/T_2)_{ac}+(1/T_2)_{ab}-(1/T_2)_{bc}]}{\Delta_{cb}+i(1/T_2)_{bc}}\right] \, . \tag{13}$$

From this expression, it can be deduced that an extra resonance will be observed at $\omega_2-\omega_1=\omega_{cb}$ when the pressure is suf-

ficiently high so that $(1/T_2)_{ac}+(1/T_2)_{ab}-(1/T_2)_{bc}\neq 0$. The signal-to-background ratio at the peak of the extra resonance is given by

$$\left[\frac{S}{B}\right]_{\Delta_{cb}\simeq 0}=1+\frac{[(1/T_2)_{ac}+(1/T_2)_{ab}-(1/T_2)_{bc}][(1/T_2)_{ac}+(1/T_2)_{ab}+(1/T_2)_{bc}]}{(1/T_2)_{bc}^2} . \tag{14}$$

For Na, where $|a\rangle=3^2S_{1/2}$, $|b\rangle=3^2P_{1/2}$, and $|c\rangle=3^2P_{3/2}$, the maximum value of this ratio is four.[1]

We now evaluate ρ'_{bc} in the collisionless regime. Assuming that

$$\rho_{aa}+\rho_{bb}+\rho_{cc}+\rho_{dd}=\rho_{aa}^{eq} , \tag{15}$$

where ρ_{aa}^{eq} is the population of state $|a\rangle$ at thermal equilibrium, we find from Eqs. (8a) and (8d), that to first order in V_{ab} and V_{ac},

$$\rho_{aa}=\rho_{aa}^{eq}\left[\frac{\Delta_{da}^2+(1/T_2)_{ad}^2+V_{ad}^2}{\Delta_{da}^2+(1/T_2)_{ad}^2+2V_{ad}^2}\right] \tag{16}$$

and

$$\rho_{dd}-\rho_{aa}=-\rho_{aa}^{eq}\left[\frac{\Delta_{da}^2+(1/T_2)_{ad}^2}{\Delta_{da}^2+(1/T_2)_{ad}^2+2V_{ad}^2}\right] . \tag{17}$$

In writing Eqs. (16) and (17) we have used the fact that $(1/T_1)_d=(1/T_1)_{da}$ and $2(1/T_2)_{ad}/(1/T_1)_{da}=1$ in the collisionless regime. Recalling that at low pressures $(1/T_2)_{ac}+(1/T_2)_{ab}-(1/T_2)_{bc}\simeq 0$, Eq. (12) now becomes

$$\begin{aligned}\rho'_{bc}=&\frac{V_{ab}V_{ac}\rho_{aa}^{eq}}{[\Delta_{ba}-i(1/T_2)_{ab}][\Delta_{ca}+i(1/T_2)_{ac}]}\frac{\Delta_{da}^2+(1/T_2)_{ad}^2+V_{ad}^2}{\Delta_{da}^2+(1/T_2)_{ad}^2+2V_{ad}^2}\\
&\times\left\{1+\frac{V_{ad}^2}{\Delta_{cb}+i(1/T_2)_{bc}}\left[\frac{\Delta_{ba}-i(1/T_2)_{ab}}{[\Delta_{dc}-i(1/T_2)_{cd}][\Delta_{ca}+i(1/T_2)_{ac}]+V_{ad}^2}-\frac{\Delta_{ca}+i(1/T_2)_{ac}}{[\Delta_{db}+i(1/T_2)_{bd}][\Delta_{ba}-i(1/T_2)_{ab}]+V_{ad}^2}\right]\right.\\
&-\frac{V_{ad}^2}{\Delta_{cb}+i(1/T_2)_{bc}}\frac{\Delta_{da}^2+(1/T_2)_{ad}^2}{\Delta_{da}^2+(1/T_2)_{ad}^2+V_{ad}^2}\\
&\times\left[\frac{[\Delta_{ba}-i(1/T_2)_{ab}][\Delta_{ca}+i(1/T_2)_{ac}]}{[\Delta_{da}+i(1/T_2)_{ad}]\{[\Delta_{dc}-i(1/T_2)_{cd}][\Delta_{ca}+i(1/T_2)_{ac}]+V_{ad}^2\}}\right.\\
&\left.\left.-\frac{[\Delta_{ba}-i(1/T_2)_{ab}][\Delta_{ca}+i(1/T_2)_{ac}]}{[\Delta_{da}+i(1/T_2)_{ad}]\{[\Delta_{db}+l(1/T_2)_{bd}][\Delta_{ba}-i(1/T_2)_{ab}]+V_{ad}^2\}}\right]\right\} .\end{aligned} \tag{18}$$

When the additional pump laser is in resonance with the $|a\rangle\rightarrow|d\rangle$ transition ($\Delta_{da}\simeq 0$), the value of ρ'_{bc} at the peak of the extra resonance is given by

$$\begin{aligned}(\rho'_{bc})_{\Delta_{cb}\simeq 0}=&\frac{V_{ab}V_{ac}\rho_{aa}^{eq}}{\tilde{\Delta}^2}\frac{(1/T_2)_{ad}^2+V_{ad}^2}{(1/T_2)_{ad}^2+2V_{ad}^2}\\
&\times\left\{1+\frac{iV_{ad}^2}{(1/T_2)_{bc}}\left[\frac{\tilde{\Delta}-i(1/T_2)_{ab}}{[\tilde{\Delta}+i(1/T_2)_{cd}][\tilde{\Delta}+i(1/T_2)_{ac}]-V_{ad}^2}-\frac{\tilde{\Delta}+i(1/T_2)_{ac}}{[\tilde{\Delta}-i(1/T_2)_{bd}][\tilde{\Delta}-i(1/T_2)_{ab}]-V_{ad}^2}\right]\right.\\
&+\frac{V_{ad}^2(1/T_2)_{ad}}{(1/T_2)_{bc}[(1/T_2)_{ad}^2+V_{ad}^2]}\left[\frac{[\tilde{\Delta}-i(1/T_2)_{ab}][\tilde{\Delta}+i(1/T_2)_{ac}]}{[\tilde{\Delta}+i(1/T_2)_{cd}][\tilde{\Delta}+i(1/T_2)_{ac}]-V_{ad}^2}\right.\\
&\left.\left.+\frac{[\tilde{\Delta}-i(1/T_2)_{ab}][\tilde{\Delta}+i(1/T_2)_{ac}]}{[\tilde{\Delta}-i(1/T_2)_{bd}][\tilde{\Delta}-i(1/T_2)_{ab}]-V_{ad}^2}\right]\right\} ,\end{aligned} \tag{19}$$

where

$$\tilde{\Delta}=\Delta_{ba}=\Delta_{ca}=-\Delta_{db}=-\Delta_{dc} . \tag{20}$$

We now examine the behavior of $(\rho'_{bc})_{\Delta_{cb}\simeq 0}$ as a function of the intensity of the additional pump laser. Clearly, when $V_{ad}\ll(1/T_2)_{ad}$, no extraresonant signal will be observable above the background. When, however, the $|a\rangle\rightarrow|d\rangle$ transition is saturated, that is $V_{ad}\gg(1/T_2)_{ad}$, we can distinguish three regimes (i) $V_{ad}\ll|\tilde{\Delta}|$, (ii) $V_{ad}\simeq|\tilde{\Delta}|$, and (iii) $V_{ad}\gg|\tilde{\Delta}|$. In order to simplify the discussion, we shall assume throughout that

$$|\tilde{\Delta}|\gg(1/T_2)_{ab},(1/T_2)_{ac},(1/T_2)_{bd},(1/T_2)_{cd} . \tag{21}$$

In regime (i), which is the only really interesting regime, Eq. (19) reduces to

TABLE I. Data required for an experimental verification of Eq. (23) using alkali-metal atoms.

Atom	$\|a\rangle$	$\|b\rangle$	$\|c\rangle$	$\|d\rangle$	ω_{ba} (cm^{-1})	ω_{ca} (cm^{-1})	ω_{da}[a] (cm^{-1})	Calculated[b] $\frac{(1/T_2)_{ad}}{(1/T_2)_{bc}}$	Calculated S/B
Na	$3^2S_{1/2}$	$4^2P_{1/2}$	$5^2P_{1/2}$	$3^2P_{1/2}$	30267	35040	16956	16.34	1134
K	$4^2S_{1/2}$	$5^2P_{1/2}$	$6^2P_{1/2}$	$4^2P_{1/2}$	24701	28999	12985	14.38	886
Rb	$5^2S_{1/2}$	$6^2P_{1/2}$	$7^2P_{1/2}$	$5^2P_{1/2}$	23715	27835	12579	9.68	415

[a]C. E. Moore, *Atomic Energy Levels,* Natl. Bur. Stand. Circ. No. 467 (U.S. GPO, Washington, D.C., 1949).
[b]Calculated from oscillator-strength tables of R. B. Miles and S. E. Harris, IEEE J. Quantum Electron. QE-9, 470 (1973).

$$(\rho'_{bc})_{\Delta_{cb}\simeq 0}\simeq\frac{V_{ab}V_{ac}\rho^{eq}_{aa}}{2\tilde{\Delta}^2}[1+2(1/T_2)_{ad}/(1/T_2)_{bc}] \tag{22}$$

so that

$$\left[\frac{S}{B}\right]_{\Delta_{cb}\simeq 0}\simeq 1+4\frac{(1/T_2)_{ad}}{(1/T_2)_{bc}}+4\frac{(1/T_2)^2_{ad}}{(1/T_2)^2_{bc}}\ . \tag{23}$$

Thus, we see that when the rate of radiative decay from state $|d\rangle$ is at least as great as the sum of the rates of decay from states $|b\rangle$ and $|c\rangle$, that is, $(1/T_1)_{da}\gtrsim(1/T_1)_{ba}+(1/T_1)_{ca}$, we obtain $S/B\gtrsim 9$ which is readily observable.[1]

In the more general case ($\Delta_{cb}\neq 0$) we have in regime (i)

$$\frac{S}{B}\simeq 1+\frac{4(1/T_2)_{ad}[(1/T_2)_{bc}+(1/T_2)_{ad}]}{[\Delta^2_{cb}+(1/T_2)^2_{bc}]}\ , \tag{24}$$

which shows that linewidth measurements of the FWM extra resonances in the collisionless regime provide a direct measurement of the lifetimes of the states involved in the extraresonant Raman transition. What is remarkable here is that the linewidth in regime (i) is *not* influenced by power broadening although the effect is produced under saturating conditions.

In regime (ii), very large values of S/B can be obtained but these are not interesting from the point of view of extra resonances, since they derive from tuning the $|a\rangle\rightarrow|b\rangle$ and $|a\rangle\rightarrow|c\rangle$ transitions into resonance with the lasers of frequencies ω_1 and ω_2 by means of the ac Stark effect.[9,10]

In regime (iii), $S/B\rightarrow 0$ since here the ac Stark effect is so strong that the $|a\rangle\rightarrow|b\rangle$ and $|a\rangle\rightarrow|c\rangle$ transitions are now far from resonance with the incident lasers.

III. DISCUSSION

We have shown in the preceding section that intense collisionless Raman-type extraresonant FWM signals can be obtained, provided we populate a fluorescent molecular or atomic eigenstate $|d\rangle$ which decays radiatively to the ground state $|a\rangle$, at least as fast as the states $|b\rangle$ and $|c\rangle$ coupled by the extraresonant transition (see Fig. 2). The same collisionless enhancement can of course be achieved in other extraresonant processes discussed by Bloembergen and co-workers, such as the Rayleigh-type

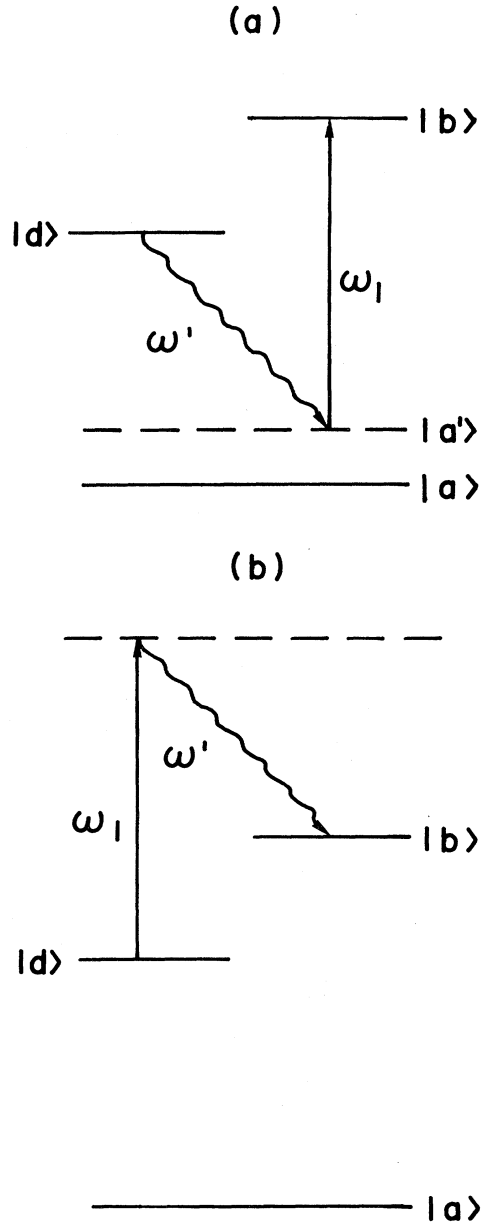

FIG. 3. ES RS as a possible mechanism for population of an excited state in the absence of resonant radiation. Frequencies are defined as in Fig. 1.

resonances observed by Bogdan *et al.*[3] and the "two-photon quasiresonant coherent signal" predicted by Dagenais.[11] For all these cases, S/B will be given in regime (i) by equations similar to Eq. (23). An experimental verification of this equation, within the framework of the level scheme of Fig. 2, could be obtained by choosing the states $|a\rangle$, $|b\rangle$, $|c\rangle$, and $|d\rangle$ to be the $|3^2S_{1/2}\rangle$, $|4^2P_{1/2}\rangle$, $|5^2P_{1/2}\rangle$, and $|3^2P_{1/2}\rangle$ states of the sodium atom, or the corresponding states of the other alkali-metal atoms (see Table I). By choosing the state $|d\rangle$ to be the strongly fluorescent alkali-metal valence state $|n^2P_{1/2}\rangle$ and states $|b\rangle$ and $|c\rangle$ to be the weakly fluorescent Rydberg states $|(n+1)^2P_{1/2}\rangle$ and $|(n+2)^2P_{1/2}\rangle$, we ensure that

$$(1/T_2)_{ad} \gg (1/T_2)_{bc} \ . \tag{25}$$

As shown in Table I, Eq. (23) then leads to values of the order of 10^2—10^3 for S/B of the alkali metals.

It is interesting to note that the expression for S/B obtained here [see Eq. (23)] is independent of the degree of detuning $\tilde{\Delta}$ [defined in Fig. 2 and Eq. (20)] provided Eq. (21) holds. This is in contrast to the expression [Eq. (1)] obtained previously[2] which decreases rapidly with $\tilde{\Delta}$. In the case of pressure-induced extraresonant signals in FWM (PIER 4), S/B also appears to be independent of $\tilde{\Delta}$ [see Eq. (19)]. However, this is only true in the impact limit where the collision time τ_{coll} is smaller than $\tilde{\Delta}^{-1}$. When $\tau_{\text{coll}} > \tilde{\Delta}^{-1}$, it has been shown experimentally by Carlsten *et al.*[12] and theoretically by Burnett *et al.*[13] that the transverse relaxation times $(T_2)_{ij}$ become dependent on $\tilde{\Delta}$.

The resonance-enhanced three-photon scattering considered here is a two-step process. In the first step, the state $|d\rangle$ is populated (see Fig. 2). In the second step, a photon is emitted at the three-photon or hyper-Raman frequency $\omega+\omega_1-\omega_{ba}$, followed by the absorption of a laser photon at frequency ω_1. (As shown in Fig. 2, the absorption of this second photon is already part of the FWM process.) Clearly, only the second step of the three-photon scattering process causes the appearance of the extraresonant FWM signal. The mechanism responsible for the occupation of the fluorescent state $|d\rangle$ is therefore unimportant. Now, the second step is just an excited-state Raman scattering (ES RS) process [see Fig. 3(a)]. Therefore, we see that, in addition to collisional redistribution[1,3,11,12,13] and three-photon scattering,[2,12] ES RS may be invoked as a mechanism leading to population of an excited state in the absence of resonant incident radiation. We note, however, that although both the processes depicted in Figs. 3(a) and 3(b) contribute to ES RS and to the population of the state $|b\rangle$, only the process of Fig. 3(a) contributes to the extraresonant FWM signal since only here does the absorption of the laser photon of frequency ω_1 constitute the first step in the FWM process. By contrast, the mechanism depicted in Fig. 3(b) leads to ES CSRS.[5] The ordinary resonant Raman-type signal obtained in this way can easily be distinguished from the extraresonant one since it requires an additional photon of frequency ω_1 and, consequently, the ES CSRS signal depends on a higher power of the corresponding pump-laser intensity.

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