Extra resonances in four-wave mixing triggered by radiative relaxation

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It is predicted that, at sufficiently high laser intensity, the recently observed Raman-type extra-resonant enhancement of four-wave mixing [Y. Prior, A. R. Bogdan, M. Dagenais, and N. Bloembergen, Phys. Rev. Lett. 46, 111 (1981)] should not vanish in the absence of collisions. The collisionless contribution to the extra resonance is associated with a three-photon scattering process which produces an extra-resonant signal intensity which is fourth order in the laser intensity.

I. INTRODUCTION

Recently, pressure-induced extra Raman-type[1,2] and Rayleigh-type[3,4] resonances have been observed in four-wave mixing processes in Na vapor with He buffer gas. Similar, thermally induced, Raman-type resonances have also been reported in solids.[5] The resonances occur between initially unpopulated excited states which are not in resonance with either of the incident laser frequencies. In a related experiment, Dagenais[6] directly populated the $3^2P_{1/2}$ and $3^2P_{3/2}$ excited states of Na with the use of an additional nonresonant pump laser in the presence of helium buffer gas and then performed excited-state coherent Stokes-Raman spectroscopy (CSRS) from these states. In his two-step experiment,[6] the coherent signal depended on the fifth power of the intensity rather than the third power as found by Bloembergen and co-workers[1–4] in their one-step, collision-induced, coherent four-wave mixing processes.

The existence of these resonances and their pressure dependence emerges from the general perturbation-theory expression[1,7] for $\chi^{(3)}$, the third-order nonlinear susceptibility, derived from the four-level Bloch equations. Bogdan *et al.*[2] and Grynberg[8] have given a simple expression for the Raman-type resonances based on the fact that the component of the polarization, $\mathscr{P}$, that oscillates with frequency $\omega_{\text{CSRS}}=2\omega_1-\omega_2$ and propagates with wave vector $\vec{k}_1+\vec{k}_1'-\vec{k}_2$ is proportional to ρ_{bc}, the off-diagonal element of the density matrix connecting the initially unpopulated excited states $|b\rangle$ and $|c\rangle$. (Here, $\vec{k}_1$ and $\vec{k}_1'$ are the wave vectors of the incident laser beams of frequency ω_1 and $\vec{k}_2$ is the wave vector of the incident laser beam of frequency ω_2 with $\omega_1<\omega_2$.) A simple perturbation-theory expression[2] for ρ_{bc} can be derived from the Bloch equations for the three-level system formed by the ground state $|a\rangle$ and excited states $|b\rangle$ and $|c\rangle$.

The relation between the pressure-induced extra resonances and collisional redistribution[9–15] has been pointed out several times.[1,6,8] In collisional redistribution, the difference between the energy required to excite an upper state and the energy of the incident near-resonance light beam is supplied (absorbed) by collisions. The role of collisional redistribution in four-wave mixing is illustrated in Fig. 1. Another process that can lead to excitation of an upper level by a near-resonant laser is three-photon scattering[12,16,17] (sometimes called two-photon sequential absorption[16]) in which two laser photons

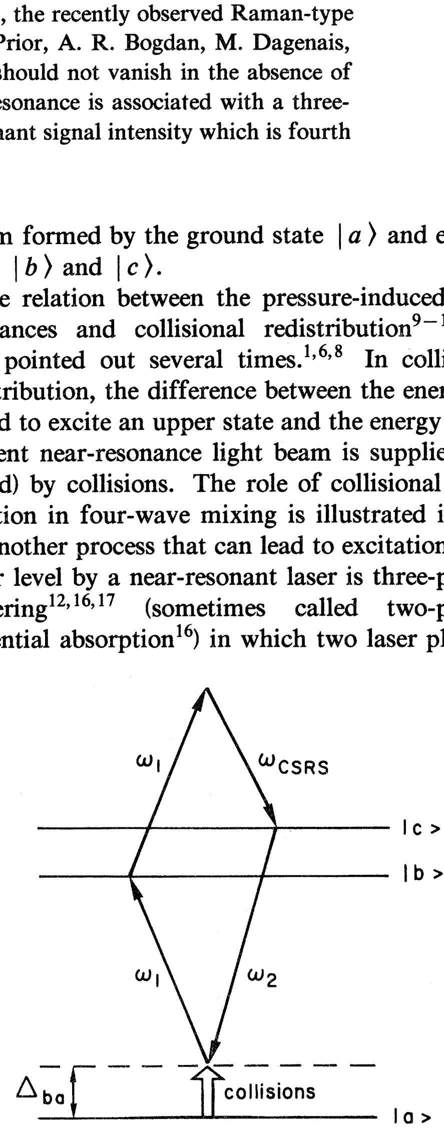

FIG. 1. Collisionally triggered four-wave mixing: Quasielastic collisions supply the energy difference $\Delta_{ba}=\omega_{ba}-\omega_1$ where ω_{ba} is the frequency of the transition from ground state $|a\rangle$ to $|b\rangle$, the lower of the initially unpopulated excited states $|b\rangle$ and $|c\rangle$, and ω_1 is the frequency of two of the three incident laser beams. The coherent signal is emitted at the frequency $\omega_{\text{CSRS}}=2\omega_1-\omega_2$, where ω_2 is the frequency of the third incident laser beam, and an extra resonance is observed at $\omega_{cb}=\omega_2-\omega_1$.

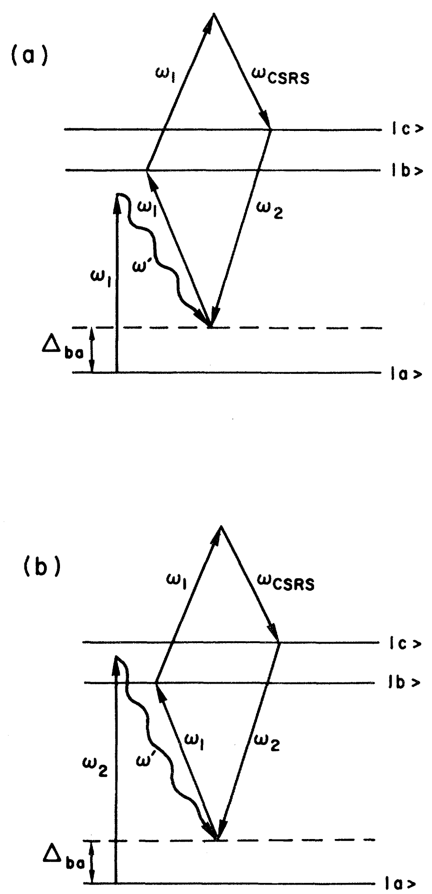

FIG. 2. Four-wave mixing triggered by radiative relaxation: In this process, the energy difference $\Delta_{ba}=\omega_{ba}-\omega_1$ is supplied by the absorption of a laser photon at (a) ω_1 or (b) ω_2 followed by the emission of a scattered photon at frequency (a) $\omega'=2\omega_1-\omega_{ba}$ or (b) $\omega'=\omega_1+\omega_2-\omega_{ba}$. The second absorbed photon in the three-photon scattering process takes part in the four-wave mixing. The leading term in the signal intensity is fourth order in the laser frequency. For nomenclature, see Fig. 1.

are absorbed and one photon is spontaneously emitted. This process has been invoked to explain the origin of the two symmetrical sidebands observed in the scattering of near-resonant light by a two-level system in the absence of collisions.[12] It has also been mentioned in connection with the relative intensities of the two asymmetrical peaks observed in an optical Autler-Townes experiment when the intense incident laser is detuned from resonance with the ac Stark-split transition.[16] A similar three-photon process, involving absorption of two driving-field photons and stimulated emission of one photon at the weak probe-field frequency, has been used to explain the amplification of a weak probe whose frequency is tuned across the resonance frequency of a two-level system in interaction with a strong near-resonant driving field.[17]

In this paper we shall show that the Raman-type resonances detected by Bloembergen and coworkers[1,2] can be observed even in the absence of collisions provided the incident intensities are sufficiently high. The role played by collisional redistribution in the presence of a buffer gas is played here by three-photon scattering (see Fig. 2). The only difference between the present three-photon scattering mechanisms and previous ones[12,16] is that here the two absorbed photons may have different frequencies. In contrast to the pressure-induced effect which depends on the third power of the intensity, the three-photon scattering-induced effect depends on the fourth power of the incident intensity. It is also inversely proportional, at the maximum, to the sixth power of the one-photon detuning.

The mathematical development presented here is analogous to that used to discuss saturation effects in coherent anti-Stokes Raman spectroscopy (CARS).[18] We shall give only the steady-state solution to the three-level Bloch equations, leaving the numerical solution of the transient behavior to a future publication.

II. THE MODEL

Consider the three-level system shown in Figs. 1 and 2: $|a\rangle$ is the ground state of the atomic or molecular system, $|b\rangle$ and $|c\rangle$ are excited states. The system is irradiated by three laser beams, two with frequency ω_1 and wave vectors $\vec{k}_1$ and $\vec{k}_1'$, and one with frequency ω_2 and wave vector $\vec{k}_2$. The electric field strength is thus given by

$$\vec{E}=\vec{x}[\,|\mathscr{E}_1|\cos(\omega_1 t-\vec{k}_1\cdot\vec{r}+\phi_1)+|\mathscr{E}_1|\cos(\omega_1 t-\vec{k}_1'\cdot\vec{r}+\phi_1)+|\mathscr{E}_2|\cos(\omega_2 t-\vec{k}_2\cdot\vec{r}+\phi_2)]\ , \tag{1}$$

where we have assumed all the beams to be plane polarized with unit polarization vector $\vec{x}$. Now assuming the field envelopes $|\mathscr{E}_{1,2}|$ and phases $\phi_{1,2}$ to change slowly in time, we find, by an analogous treatment to that of CARS,[18] that the component of $\mathscr{P}$ that oscillates with frequency $2\omega_1-\omega_2$, propagates with wave vector $\vec{k}_1+\vec{k}_1'-\vec{k}_2$, and has polarization vector $\vec{x}$ is given by[19]

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

where

$$\mu_{ij}=\langle i\,|\,\vec{\mu}\cdot\vec{x}\,|\,j\rangle \quad (3)$$

is the electric-dipole matrix element and ρ'_{bc} is related to ρ_{bc}, the off-diagonal element of the density matrix in the interaction picture, by

$$\rho'_{bc}=\rho_{bc}\exp[-i\Delta t+i(\vec{k}_2-\vec{k}_1)\cdot\vec{r}-i(\phi_2-\phi_1)]\ , \quad (4)$$

where Δ is the two-photon detuning

$$\Delta=\omega_2-\omega_1-\omega_{cb}\ . \quad (5)$$

In order to find ρ'_{bc} we solve the following Bloch equations[18] for the three-level system $|a\rangle$, $|b\rangle$, and $|c\rangle$ on the assumption that the fields with frequencies ω_1 and ω_2 interact only with the $|a\rangle\rightarrow|b\rangle$ and $|a\rangle\rightarrow|c\rangle$ transitions, respectively:

$$\dot{\rho}_{aa}=iV_{ac}(\rho'_{ca}-\rho'_{ac})+iV_{ab}(\rho'_{ba}-\rho'_{ab})+(1/T_1)_{ca}\rho_{cc}+(1/T_1)_{ba}\rho_{bb}\ , \quad (6a)$$

$$\dot{\rho}_{bb}=iV_{ab}(\rho'_{ab}-\rho'_{ba})+(1/T_1)_{cb}\rho_{cc}-(1/T_1)_{ba}\rho_{bb}\ , \quad (6b)$$

$$\dot{\rho}_{cc}=-iV_{ac}(\rho'_{ca}-\rho'_{ac})-[(1/T_1)_{ca}+(1/T_1)_{cb}]\rho_{cc}\ , \quad (6c)$$

$$\dot{\rho}'_{ab}=iV_{ac}\rho'_{cb}-iV_{ab}(\rho_{aa}-\rho_{bb})-[(1/T_2)_{ab}-i\Delta_{ba}]\rho'_{ab}\ , \quad (6d)$$

$$\dot{\rho}'_{ac}=-iV_{ac}(\rho_{aa}-\rho_{cc})+iV_{ab}\rho'_{bc}-[(1/T_2)_{ac}-i\Delta_{ca}]\rho'_{ac}\ , \quad (6e)$$

$$\dot{\rho}'_{bc}=-iV_{ac}\rho'_{aa}+iV_{ab}\rho'_{ac}-[(1/T_2)_{bc}+i\Delta]\rho'_{bc}\ , \quad (6f)$$

where

$$V_{ab}=\mu_{ab}\,|\mathscr{E}_1|\,/2\hbar,\quad V_{ac}=\mu_{ac}\,|\mathscr{E}_2|\,/2\hbar \quad (7)$$

are the one-photon Rabi frequencies;

$$\begin{aligned}&\rho'_{ab}=\rho_{ab}\exp[i(\Delta_{ba}t+\vec{k}_1\cdot\vec{r}-\phi_1)]\ ,\\&\rho'_{ac}=\rho_{ac}\exp[i(\Delta_{ca}t+\vec{k}_2\cdot\vec{r}-\phi_2)]\ ,\\&\rho'_{bc}=\rho_{bc}\exp\{-i[\Delta t+(\vec{k}_1-\vec{k}_2)\cdot\vec{r}-(\phi_1-\phi_2)]\}\ ,\end{aligned} \quad (8)$$

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

$$\Delta_{ba}=\omega_{ba}-\omega_1,\quad \Delta_{ca}=\omega_{ca}-\omega_2,\quad \Delta=\omega_2-\omega_1-\omega_{cb}\ , \quad (9)$$

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

$$(1/T_2)_{ij}=\tfrac{1}{2}[(1/T_1)_i+(1/T_1)_j]+(1/T_2^*)_{ij} \quad (10)$$

is the decay rate of ρ_{ij}, where $(1/T_2^*)_{ij}$ is the rate of dephasing collisions. The dephasing rate can also be written as[1]

$$(1/T_2)_{ij}=(1/T_2)_{ij}^{\text{Sp}}+\eta_{ij}P\ , \quad (11)$$

where $(1/T_2)_{ij}^{\text{Sp}}$ is the contribution from spontaneous emission and the collisional contribution $\eta_{ij}P$ is assumed to be directly proportional to the pressure P.

In the steady state, Eq. (6f) gives

$$\rho'_{bc}=-\frac{V_{ab}V_{ac}}{\Delta'-i(1/T'_2)_{bc}}\left[\frac{\rho_{aa}-\rho_{bb}}{\Delta_{ba}-i(1/T_2)_{ab}}-\frac{\rho_{aa}-\rho_{cc}}{\Delta_{ca}+i(1/T_2)_{ac}}\right], \tag{12}$$

where

$$\Delta'=\Delta+\frac{V_{ab}^2\Delta_{ca}}{\Delta_{ca}^2+(1/T_2)_{ac}^2}-\frac{V_{ac}^2\Delta_{ba}}{\Delta_{ba}^2+(1/T_2)_{ab}^2}, \tag{13}$$

$$(1/T'_2)_{bc}=(1/T_2)_{bc}+\frac{V_{ab}^2(1/T_2)_{ac}}{\Delta_{ca}^2+(1/T_2)_{ac}^2}+\frac{V_{ac}^2(1/T_2)_{ab}}{\Delta_{ba}^2+(1/T_2)_{ab}^2}. \tag{14}$$

On invoking Eqs. (13) and (14) and rearranging, Eq. (12) becomes

$$\rho'_{bc}=\frac{V_{ab}V_{ac}}{\Delta_{ba}-i(1/T_2)_{ab}}\left\{\frac{\rho_{aa}-\rho_{cc}}{\Delta_{ca}+i(1/T_2)_{ac}}\left[1+\frac{i[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{\Delta'-i(1/T'_2)_{bc}}+\left[\frac{V_{ac}^2}{\Delta_{ba}-i(1/T_2)_{ab}}-\frac{V_{ab}^2}{\Delta_{ca}+i(1/T_2)_{ac}}\right]\frac{1}{\Delta'-i(1/T'_2)_{bc}}\right]+\frac{\rho_{bb}-\rho_{cc}}{\Delta'-i(1/T'_2)_{bc}}\right\}. \tag{15}$$

We immediately see that at very low intensity, assuming

$$\rho_{aa}+\rho_{bb}+\rho_{cc}=\rho_{aa}^{\text{eq}}, \tag{16}$$

where ρ_{aa}^{eq} is the population of state $|a\rangle$ at thermal equilibrium in the absence of radiation, Eq. (15) reduces to expression given by Bogdan *et al.*[2]

$$\rho'_{bc}=\frac{V_{ab}V_{ac}\rho_{aa}^{\text{eq}}}{[\Delta_{ba}-i(1/T_2)_{ab}][\Delta_{ca}+i(1/T_2)_{ac}]}\left[1+i\frac{[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{[\Delta-i(1/T_2)_{bc}]}\right]. \tag{17}$$

This expression, when inserted in Eq. (2), and when it is recalled that the intensity of the four-wave mixing signal is proportional to the absolute value squared of the coefficient of $\exp[-i(2\omega_1-\omega_2)]$, predicts an extra resonance at $\omega_2-\omega_1\simeq\omega_{cb}$ provided $(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}\neq0$, that is, provided the pressure is sufficiently high for the collisional part of $(1/T_2)_{ij}$ to be significant [Eq. (11)].

III. HIGHER-ORDER EFFECTS

In order to evaluate ρ'_{bc} to higher order in V^2, it is convenient to rewrite Eq. (15) invoking equalities of the type

$$\frac{1}{\Delta_{ca}+i(1/T_2)_{ac}}=\frac{1}{\Delta_{ba}-i(1/T_2)_{ab}}+\frac{[\Delta'-i(1/T'_2)_{bc}]+\{\Delta-\Delta'+i[(1/T'_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]\}}{[\Delta_{ba}-i(1/T_2)_{ab}][\Delta_{ca}+i(1/T_2)_{ac}]}. \tag{18}$$

We then obtain

$$\rho'_{bc}=\frac{V_{ab}V_{ac}}{\Delta_{ba}-i(1/T_2)_{ab}}\times\left\{\frac{\rho_{aa}-\rho_{cc}}{\Delta_{ca}+i(1/T_2)_{ac}}\left[1+\frac{V_{ac}^2}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\left[-1+\frac{\Delta'-i(1/T'_2)_{bc}}{\Delta_{ba}-i(1/T_2)_{ab}}+\frac{i[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{\Delta_{ba}-i(1/T_2)_{ab}}\right.\right.\right.$$

$$+\frac{(\Delta-\Delta')+i[(1/T_2')_{bc}-(1/T_2)_{bc}]}{\Delta_{ba}-i(1/T_2)_{ab}}\Bigg]$$

$$-\frac{V_{ab}^2}{\Delta_{ba}^2+(1/T_2)_{ab}^2}\Bigg[2+\frac{\Delta'-i(1/T_2')_{bc}}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{2i[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{\Delta_{ca}+i(1/T_2)_{ac}}$$

$$+\frac{2\{(\Delta-\Delta')+i[(1/T_2')_{bc}-(1/T_2)_{bc}]\}}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{2i(1/T_2)_{ab}}{\Delta_{ca}+i(1/T_2)_{ac}}\Bigg]\Bigg]$$

$$+\frac{\rho_{aa}-\rho_{cc}}{\Delta'-i(1/T_2')_{bc}}$$

$$\times\Bigg[\frac{i[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{V_{ac}^2}{\Delta_{ca}^2+(1/T_2)_{ac}^2}$$

$$\times\Bigg\{1-i\frac{[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{\Delta_{ba}-i(1/T_2)_{ab}}$$

$$-\frac{(\Delta-\Delta')+i[(1/T_2')_{bc}-(1/T_2)_{bc}]}{\Delta_{ba}-i(1/T_2)_{ab}}-\frac{2i(1/T_2)_{ac}}{\Delta_{ba}-i(1/T_2)_{ab}}\Bigg\}-\frac{V_{ab}^2}{\Delta_{ba}^2+(1/T_2)_{ab}^2}$$

$$\times\Bigg[1+2i\frac{[(1/T_2)_{bc}-(1/T_2)_{ab}-(1/T_2)_{ac}]}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{2\{(\Delta-\Delta')+i[(1/T_2')_{bc}-(1/T_2)_{bc}]\}}{\Delta_{ca}+i(1/T_2)_{ac}}$$

$$+\frac{2i(1/T_2)_{ab}}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{\{(\Delta-\Delta')+i[(1/T_2')_{bc}-(1/T_2)_{bc}]\}^2}{[\Delta_{ca}+i(1/T_2)_{ac}]^2}$$

$$-\frac{[(1/T_2)_{bc}-(1/T_2)_{ab}-(1/T_2)_{ac}][(1/T_2)_{bc}+(1/T_2)_{ab}-(1/T_2)_{ac}]}{[\Delta_{ca}+i(1/T_2)_{ac}]^2}$$

$$+\frac{2i\{(\Delta-\Delta')+i[(1/T_2')_{bc}-(1/T_2)_{bc}]\}[(1/T_2)_{bc}-(1/T_2)_{ac}]}{[\Delta_{ca}+i(1/T_2)_{ac}]^2}\Bigg]\Bigg]$$

$$+\frac{\rho_{bb}-\rho_{cc}}{\Delta'-i(1/T_2')_{bc}}\Bigg\}. \tag{19}$$

Complete expressions for $\rho_{aa}-\rho_{cc}$ and $\rho_{bb}-\rho_{cc}$ are derived in the Appendix. Here we shall consider only terms valid up to first order in V^2. To this order

$$\rho_{aa}-\rho_{cc}=\rho_{aa}^{\mathrm{eq}}\left[1-\frac{2V_{ab}^2(1/T_2)_{ab}/(1/T_1)_b}{\Delta_{ba}^2+(1/T_2)_{ab}^2}-\frac{2V_{ac}^2(1/T_2)_{ac}/(1/T_1)_c}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\left[2+\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]\right]. \tag{20}$$

$$\rho_{bb}-\rho_{cc}=\rho_{aa}^{\mathrm{eq}}\left[\frac{2V_{ab}^2(1/T_2)_{ab}/(1/T_1)_b}{\Delta_{ba}^2+(1/T_2)_{ab}^2}-\frac{2V_{ac}^2(1/T_2)_{ac}/(1/T_1)_c}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\left[1-\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]\right]. \tag{21}$$

Inserting Eqs. (20) and (21) into Eq. (19) and including, within the curly brackets, only terms up to first order in V^2, we obtain

$$\rho_{bc}'=\frac{V_{ab}V_{ac}\rho_{aa}^{\mathrm{eq}}}{\Delta_{ba}-i(1/T_2)_{ab}}$$

$$\times\Bigg[\frac{1}{\Delta_{ca}+i(1/T_2)_{ac}}\Bigg\{1-\frac{V_{ac}^2}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\Bigg\{1+\frac{2(1/T_2)_{ac}}{(1/T_1)_c}\left[2+\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]-\frac{\Delta-i(1/T_2)_{bc}}{\Delta_{ba}-i(1/T_2)_{ab}}$$

$$-i\left[1-\frac{2(1/T_2)_{ac}}{(1/T_1)_c}\left[2+\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]\right]$$

$$\times\left[\frac{(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}}{\Delta_{ba}-i(1/T_2)_{ab}}\right]\Bigg\}-\frac{V_{ab}^2}{\Delta_{ba}^2+(1/T_2)_{ab}^2}\left[2+\frac{2(1/T_2)_{ab}}{(1/T_1)_b}+\frac{\Delta-i(1/T_2)_{bc}}{\Delta_{ca}+i(1/T_2)_{ac}}\right.$$

$$\left.+\frac{2i[(1/T_2)_{bc}-(1/T_2)_{ab}-(1/T_2)_{ac}]}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{2i(1/T_2)_{ab}}{\Delta_{ca}+i(1/T_2)_{ac}}\right]\Bigg]$$

$$+\frac{1}{\Delta'-i(1/T_2')_{bc}}$$

$$\times\left[\frac{i[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{V_{ac}^2}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\right.$$

$$\times\left\{1-\frac{2(1/T_2)_{ac}}{(1/T_1)_c}\left[1-\frac{(1/T_1)_{cb}}{(1/T_1)_c}\right]-i\left[1+\frac{2(1/T_2)_{ac}}{(1/T_1)_c}\left[2+\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]\right]\right.$$

$$\times\left[\frac{(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}}{\Delta_{ba}-i(1/T_2)_{ab}}\right]$$

$$\left.+\frac{2(1/T_2)_{ac}}{(1/T_1)_c}\left[2+\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]\frac{[(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}]}{[\Delta_{ba}-i(1/T_2)_{ab}][\Delta_{ca}+i(1/T_2)_{ac}]}+\frac{2i(1/T_2)_{ac}}{\Delta_{ba}-i(1/T_2)_{ab}}\right\}$$

$$-\frac{V_{ab}^2}{\Delta_{ba}^2+(1/T_2)_{ab}^2}\left[1-\frac{2(1/T_2)_{ab}}{(1/T_1)_b}+2i\left[1+\frac{4(1/T_2)_{ab}}{(1/T_1)_b}\right]\left[\frac{(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}}{\Delta_{ba}-i(1/T_2)_{ab}}\right]\right.$$

$$+\frac{[1/(T_2)_{bc}-(1/T_2)_{ab}-(1/T_2)_{ac}][(1/T_2)_{bc}+(1/T_2)_{ab}-(1/T_2)_{ac}]}{[\Delta_{ca}+i(1/T_2)_{ac}]^2}$$

$$\left.\left.+\frac{2i(1/T_2)_{ab}}{\Delta_{ca}+i(1/T_2)_{ac}}\right]\right]\Bigg] . \tag{22}$$

At low pressures, $(1/T_2)_{bc}-(1/T_2)_{ac}-(1/T_2)_{ab}=0$, $(1/T_1)_{bc}\ll(1/T_1)_b$, $2(1/T_2)_{ac}/(1/T_1)_c=1$, and $2(1/T_2)_{ab}/(1/T_1)_b=1$. Then Eq. (22) reduces to

$$\rho'_{bc}=\frac{V_{ab}V_{ac}\rho_{aa}^{\text{eq}}}{\Delta_{ba}-i(1/T_2)_{ab}}\left\{\frac{1}{\Delta_{ca}+i(1/T_2)_{ac}}\left[1-\frac{V_{ac}^2}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\left[3-\frac{\Delta-i(1/T_2)_{bc}}{\Delta_{ba}-i(1/T_2)_{ab}}\right]\right.\right.$$

$$\left.-\frac{V_{ab}^2}{\Delta_{ba}^2+(1/T_2)_{ab}^2}\left[3+\frac{\Delta-i(1/T_2)_{bc}}{\Delta_{ca}+i(1/T_2)_{ac}}+\frac{2i(1/T_2)_{ab}}{\Delta_{ca}+i(1/T_2)_{ac}}\right]\right]$$

$$\left.-\frac{2i}{\Delta-i(1/T_2)_{bc}}\left[\frac{V_{ac}^2}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\frac{(1/T_2)_{ac}}{\Delta_{ba}-i(1/T_2)_{ab}}+\frac{V_{ab}^2}{\Delta_{ba}^2+(1/T_2)_{ab}^2}\frac{(1/T_2)_{ab}}{\Delta_{ca}+i(1/T_2)_{ac}}\right]\right\} . \tag{23}$$

We see from Eq. (23) that even at low pressures, an extra resonance at $\Delta\simeq0$ is obtained. The terms that contribute additively to the effect are proportional to $V_{ab}^2(1/T_2)_{ab}$ and $V_{ac}^2(1/T_2)_{ac}$ and correspond to the processes depicted in Figs. 2(a) and 2(b). Equation (22) shows that, at higher pressures, the resonance at $\Delta\simeq0$ can arise either from a purely pressure effect or from a combination of pressure and saturation effects.

From Eqs. (2) and (23) we see that at low pressures, the four-wave mixing signal at frequency $\omega_{\text{CSRS}}=2\omega_1-\omega_2$, omitting terms higher than fourth order in intensity, is given by

$$I_{\text{CRSR}}\propto\frac{I_1^2I_2(\rho_{aa}^{\text{eq}})^2}{[\Delta_{ba}^2+(1/T_2)_{ab}^2][\Delta_{ca}^2+(1/T_2)_{ac}^2]}[A+B(C_1I_1+C_2I_2)] , \tag{24}$$

where $I_{1,2}=\frac{1}{2}c\epsilon_0|\mathscr{E}_{1,2}|^2$ are the intensities of the fields at frequencies $\omega_{1,2}$ and

$$A=1-\frac{1}{c\epsilon_0\hbar^2}\left[\frac{\mu_{ab}^2 I_1}{\Delta_{ba}^2+(1/T_2)_{ab}^2}\left\{3+\frac{[\Delta\Delta_{ca}-(1/T_2)_{bc}(1/T_2)_{ac}+2(1/T_2)_{ab}(1/T_2)_{ac}]}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\right\}\right.$$
$$\left.+\frac{\mu_{ac}^2 I_2}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\left\{3-\frac{[\Delta\Delta_{ca}-(1/T_2)_{bc}(1/T_2)_{ac}]}{\Delta_{ba}^2+(1/T_2)_{ab}^2}\right\}\right], \tag{25}$$

$$B=\frac{2}{c\epsilon_0\hbar^2[\Delta^2+(1/T_2)_{bc}^2][\Delta_{ba}^2+(1/T_2)_{ab}^2]}, \tag{26}$$

$$C_1=\mu_{ab}^2(1/T_2)_{ab}(1/T_2)_{bc}, \tag{27}$$

$$C_2=\frac{\mu_{ac}^2(1/T_2)_{ac}}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\{\Delta[\Delta_{ca}(1/T_2)_{ab}+\Delta_{ba}(1/T_2)_{ac}]+(1/T_2)_{bc}[\Delta_{ba}\Delta_{ca}-(1/T_2)_{ab}(1/T_2)_{ac}]\}. \tag{28}$$

The term proportional to A gives the background, whereas the term proportional to B has a peak at $\Delta\simeq 0$. When $\Delta_{ba}\gg(1/T_2)_{ab}$ and $\Delta_{ca}\gg(1/T_2)_{ac}$, the signal to background ratio at $\Delta\simeq 0$ ($\Delta_{ba}\simeq\Delta_{ca}=\tilde{\Delta}$) is given by

$$\left[\frac{S}{B}\right]_{\Delta\simeq 0}\simeq 1+\frac{2}{c\epsilon_0\hbar^2\tilde{\Delta}^2(1/T_2)_{bc}}[\mu_{ab}^2(1/T_2)_{ab}I_1+\mu_{ac}^2(1/T_2)_{ac}I_2]$$
$$=1+\frac{4}{\tilde{\Delta}^2(1/T_2)_{bc}}[(1/T_2)_{ab}V_{ab}^2+(1/T_2)_{ac}V_{ac}^2]. \tag{29}$$

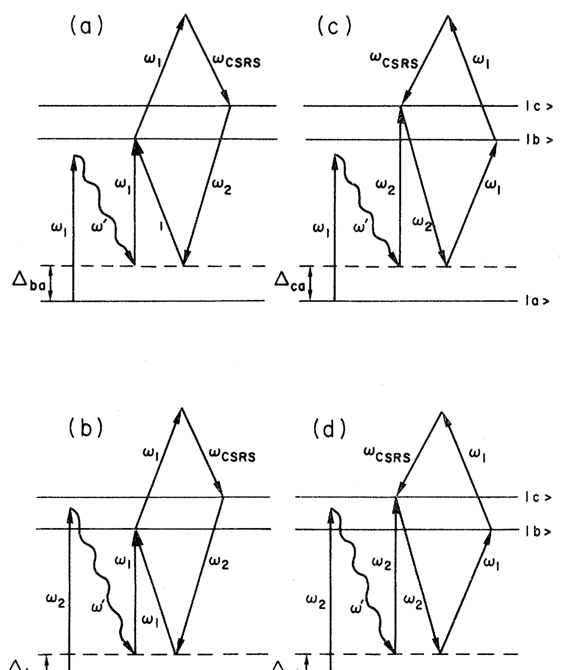

FIG. 3. Excited-state CSRS triggered by a three-photon scattering process: a two-step process in which incoherent excitation of state [(a) and (b)] $|b\rangle$ or [(b) and (c)] $|c\rangle$ is followed by the CSRS process. The leading term in the signal intensity is fifth order in the laser intensity.

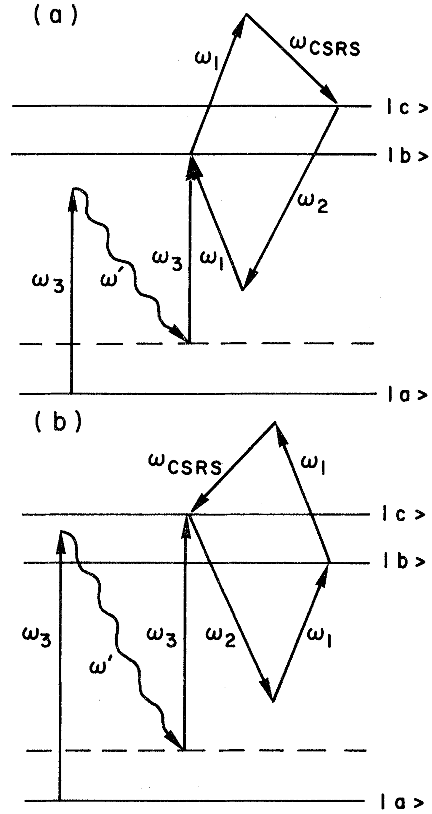

FIG. 4. Excited-state CSRS triggered by a three-photon scattering process: Here, ω_1 and ω_2 are far from resonance with ω_{ba} and ω_{ca}, and ω_3 is near resonance with (a) ω_{ba} or (b) ω_{ca}. The leading term in the CSRS intensity for this two-step process is seventh order in the laser intensity.

Thus, in order for the peak to be observable, we require the ratio of the Rabi frequencies to one-photon detunings to be as large as possible while still fulfilling the condition of Eq. (A10). We also note that the peak height is proportional to $\tilde{\Delta}^{-6}$ whereas the background is proportional to $\tilde{\Delta}^{-4}$.

IV. DISCUSSION

In the previous section we showed that at low pressure the leading term which exhibits the extra resonance behavior is fourth order in intensity. This process, which is depicted in Fig. 2, should be distinguished from excited states (es) four-wave mixing triggered by a three-photon scattering process, which is illustrated in Fig. 3. There, we envisage a two-step process in which incoherent excitation of state $|b\rangle$ (or $|c\rangle$) is followed by the coherent process. The leading term in the intensity dependence of the extra resonance contribution due to this process will be of the form

$$I_{\mathrm{es\,CSRS}} \propto I_1^2 I_2 (C_1' I_1^2 + C_2' I_2^2 + C_3' I_1 I_2) , \tag{30}$$

that is, fifth order in intensity.

If the frequencies ω_1 and ω_2 are chosen to be far from resonance with ω_{ba} and ω_{ca}, and a near-resonance frequency ω_3 is used to populate $|b\rangle$ (or $|c\rangle$) by three-photon scattering, as depicted in Fig. 4, we expect an

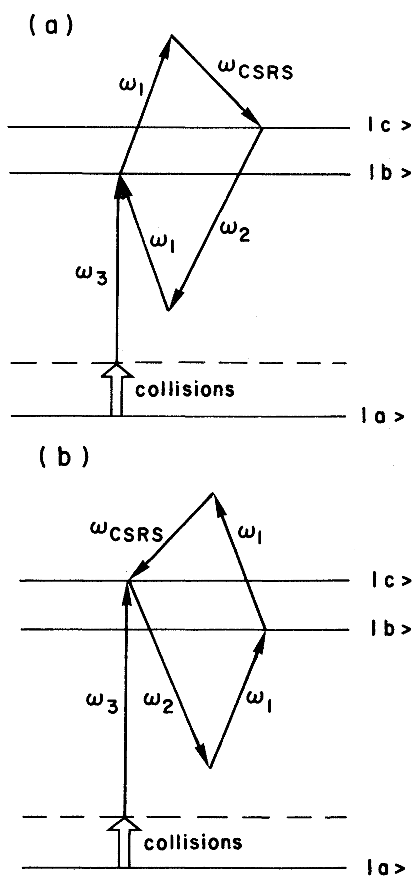

FIG. 5. Collisionally triggered excited-state CSRS: Here, the energy mismatch between ω_3 and (a) ω_{ba} or (b) ω_{ca} is supplied by quasielastic collisions. The other laser frequencies ω_1 and ω_2 are far from resonance with ω_{ba} and ω_{ca}.

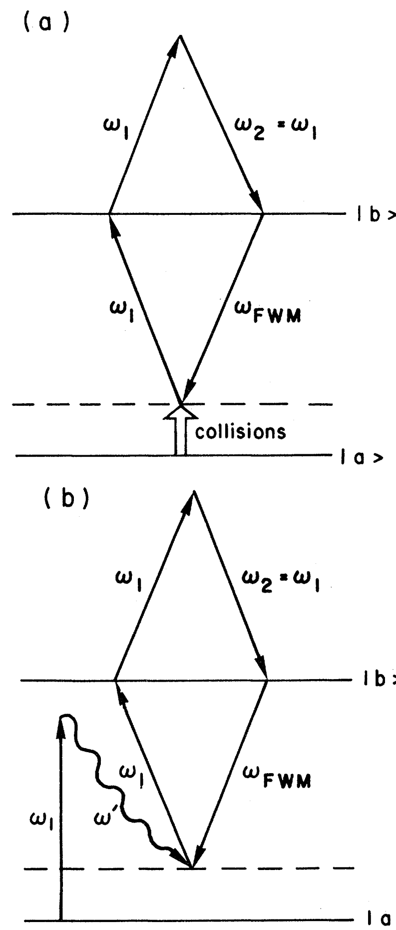

FIG. 6. Rayleigh-type extra resonances in four-wave mixing triggered by (a) quasielastic collisions and (b) radiative relaxation. The input laser frequencies are ω_1 and the coherent signal is emitted at the frequency $\omega_{\mathrm{FWM}} = \omega_1$.

intensity dependence of the form

$$I_{\mathrm{es\,CSRS}} \propto I_1^2 I_2 I_3^4 \tag{31}$$

due to the fact that the ordinary four-mixing process (which is now far off resonance) will be so weak that the interference term will be negligible. This process is analogous to the collisionally triggered exicted-state CSRS experiment of Dagenais,[6] illustrated in Fig. 5.

The Rayleigh-type resonances observed by Bogdan *et al.*,[3,4] and illustrated in Fig. 6(a), can be treated in a similar manner to the Raman-type resonances discussed above. We then expect the effect to be observable even at low pressures provided the intensity is sufficiently high [see Fig. 6(b)].

APPENDIX

In order to evaluate ρ'_{bc} at arbitrary laser intensities, we require expressions for $\rho_{aa}-\rho_{cc}$ and $\rho_{bb}-\rho_{cc}$. Setting the time derivatives of the off-diagonal density-matrix elements in Eqs. (6) equal to zero, and taking Eq. (16) into account, we obtain

$$\dot{P}=UP+V\ , \tag{A1}$$

where

$$P=\begin{bmatrix}\rho_{aa}\\ \rho_{bb}\end{bmatrix}, \tag{A2}$$

$$U=\begin{bmatrix}A+3B+2C-(1/T_1)_{ca} & -A+C-(1/T_1)_{ca}+(1/T_1)_b\\ -A-2B-(1/T_1)_{cb} & A-B-(1/T_1)_b-(1/T_1)_{cb}\end{bmatrix}, \tag{A3}$$

$$V=\rho_{aa}^{\mathrm{eq}}\begin{bmatrix}B+C-(1/T_1)_{ca}\\ -B-(1/T_1)_{cb}\end{bmatrix}, \tag{A4}$$

with

$$\begin{aligned}A&=\frac{2V_{ab}^2V_{ac}^2}{[\Delta'^2+(1/T'_2)_{bc}^2][\Delta_{ba}^2+(1/T_2)_{ab}^2]^2}\{(1/T'_2)_{bc}[(1/T_2)_{ab}^2-\Delta_{ba}^2]-2\Delta'\Delta_{ba}(1/T_2)_{ab}\}-x_{ab}\ ,\\ B&=\frac{2V_{ab}^2V_{ac}^2\{(1/T'_2)_{bc}[(1/T_2)_{ab}(1/T_2)_{ac}+\Delta_{ba}\Delta_{ca}]-\Delta'[\Delta_{ba}(1/T_2)_{ac}-\Delta_{ca}(1/T_2)_{ab}]\}}{[\Delta'^2+(1/T'_2)_{bc}^2][\Delta_{ba}^2+(1/T_2)_{ab}^2][\Delta_{ca}^2+(1/T_2)_{ac}^2]}\ ,\\ C&=\frac{2V_{ab}^2V_{ac}^2}{[\Delta'^2+(1/T'_2)_{bc}^2][\Delta_{ca}^2+(1/T_2)_{ac}^2]^2}\{(1/T'_2)_{bc}[(1/T_2)_{ac}^2-\Delta_{ca}^2]+2\Delta'\Delta_{ca}(1/T_2)_{ac}\}-x_{ac}\ ,\end{aligned} \tag{A5}$$

and

$$x_{ab}=\frac{2V_{ab}^2(1/T_2)_{ab}}{\Delta_{ba}^2+(1/T_2)_{ab}^2},\quad x_{ac}=\frac{2V_{ac}^2(1/T_2)_{ac}}{\Delta_{ca}^2+(1/T_2)_{ac}^2}\ . \tag{A6}$$

We note that A, B, and C contain both one- and two-photon terms. In the steady state we find from Eqs. (A1)–(A4) and (16) that

$$\begin{aligned}\rho_{aa}&=\frac{\rho_{aa}^{\mathrm{eq}}}{D}[(AC-B^2)-(1/T_1)_cA-(1/T_1)_{cb}B-(1/T_1)_bC+(1/T_1)_b(1/T_1)_c]\ ,\\ \rho_{bb}&=\frac{\rho_{aa}^{\mathrm{eq}}}{D}[(AC-B^2)-(1/T_1)_cA-[(1/T_1)_c+(1/T_1)_{cb}]B-(1/T_1)_{cb}C]\ ,\\ \rho_{cc}&=\frac{\rho_{aa}^{\mathrm{eq}}}{D}[(AC-B^2)-(1/T_1)_b(B+C)]\ ,\end{aligned} \tag{A7}$$

where

$$D=3(AC-B^2)-2(1/T_1)_cA-[(1/T_1)_b+(1/T_1)_{ca}+3(1/T_1)_{cb}]B-[2(1/T_1)_b+(1/T_1)_{cb}]C+(1/T_1)_b(1/T_1)_c\ . \tag{A8}$$

Thus we find that

$$\begin{aligned}\rho_{aa}-\rho_{cc}&=\frac{\rho_{aa}^{\text{eq}}}{D}\{-(1/T_1)_cA+[(1/T_1)_b-(1/T_1)_{cb}]B+(1/T_1)_b(1/T_1)_c\}\ ,\\ \rho_{bb}-\rho_{cc}&=\frac{\rho_{aa}^{\text{eq}}}{D}\{-(1/T_1)_cA-[(1/T_1)_c+(1/T_1)_{cb}-(1/T_1)_b]B+[(1/T_1)_b-(1/T_1)_{cb}]C\}\ .\end{aligned} \tag{A9}$$

When the incident intensities are so low so that the two-photon terms in A, B, and C are negligible and, in addition,

$$\frac{x_{ab}}{(1/T_1)_b},\ \frac{x_{ac}}{(1/T_1)_c}\ll 1 \tag{A10}$$

we can write

$$\begin{aligned}\rho_{aa}-\rho_{cc}&=\rho_{aa}^{\text{eq}}\left[1-\frac{x_{ab}}{(1/T_1)_b}-\frac{x_{ac}}{(1/T_1)_c}\left[2+\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]\right]\ ,\\ \rho_{bb}-\rho_{cc}&=\rho_{aa}^{\text{eq}}\left[\frac{x_{ab}}{(1/T_1)_b}-\frac{x_{ac}}{(1/T_1)_c}\left[1-\frac{(1/T_1)_{cb}}{(1/T_1)_b}\right]\right]\ .\end{aligned} \tag{A11}$$

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[19]Equation (2) is valid provided no level $|k\rangle$ exists such that $\omega_1\simeq\omega_{kb}$ or $\omega_1\simeq\omega_{ck}$. Note that only the contributions to four-wave mixing arising from the rotating term in Eq. 2, proportional to $(\omega_{kb}-\omega_1)^{-1}$, are depicted in Figs. 1–5.