Collisionally induced coherent signals and collisional redistribution

M. Dagenais
Advance Technology Laboratory, GTE Laboratories, 40 Sylvan Rd., Waltham, Massachusetts 02254
(Received 17 December 1981)

It is demonstrated that, in the presence of collisions and for nonresonant lasers, it is energetically possible to access resonantly excited states and induce a coherence between the states. This situation cannot arise in the absence of collisions if the starting state does not decay. This explains why, when collisions are introduced, a new signal can be generated in a wave-mixing type of experiment. The collisionally induced generation of a coherent signal is intimately related to the process of collisional redistribution. It is shown that all the collisionally induced coherent signals that have been reported up to now involve putting real populations in the excited states. This fact has not always been fully appreciated. No resonance between unpopulated states can exist. The time dependence of these new coherent signals is briefly discussed. In the case of a Raman resonance between equally populated states, it is pointed out that new coherent pathways of equal importance should be considered for explaining the experimental results. A new pressure-induced signal in four-wave mixing is also discussed. It is called "collisionally triggered two-photon quasiresonant coherent signal."

I. INTRODUCTION

Recently, it was demonstrated that collisions can trigger the generation of coherent signals. The experimental evidence took different forms. Pressure-induced extra resonance in four-wave mixing (PIER 4) which exhibits a Raman-type resonance between two excited states,[1,2] pressure-induced degenerate frequency resonance in four-wave mixing,[3,4] four-wave mixing Raman-type resonance between two equally populated states,[4,5] and four-wave mixing from a collisionally populated excited state,[5] are all indisputable experimental facts that demonstrate that an incoherent process can trigger the generation of a coherent signal. For future reference, all these new signals will be designated under the name collisionally induced coherent signals. These signals can be generated every time two coherent pathways interfere destructively in the presence of collisions. Bloembergen and co-workers[6,7] were the first ones to predict the appearance of these remarkable signals. The close connection between these effects and the collisional redistribution process has recently been acknowledged by different authors[1,5,8,9] but not always to its full extent.[2,6,10,11] It is the intention of this paper to discuss all the newly reported collisionally induced coherent signals from the point of view of a transfer of real population by a collisional redistribution process. This has the very important advantage of treating for the first time all these four new signals on an equal footing in a unified way. This is done within the context of the density matrix and the perturbation theory. Even for the PIER 4 signal it is shown that there is a real transfer of population in the excited state responsible for generating the signal. In this treatment, it is proven quite generally that, when a collisionally induced coherent signal is generated, the transfer of population in the excited state is not an artifact but is required in order to generate the signal. For reasons of simplicity Zeeman degeneracies are neglected as they complicate the treatment by possibly altering the pressure dependence of the signal[9] without really changing the basic physics of the process. There is no need for a dressed-atom representation to gain physical insight into the process. This approach makes it possible to gain a physical intuition on the origins and widths of these extra resonances. For the first time, the time dependence of the collisionally induced coherent processes is discussed. Since transfer of real population to excited states is involved, the time required for the whole system to recover completely after a turn-off of the lasers will be relatively long even though the dephasing time of the dipoles can be relatively fast.

In Sec. II of the paper, the collisional redistribution process is fully described by looking at the absorption and emission spectrum. There it is shown that, in the presence of collisions, it becomes energetically possible to access excited states and transfer real populations in these states even though all the incident lasers are detuned from any one-photon resonances. This concept will be useful in explaining why a coherence can be induced resonantly in the excited states when a collisionally induced coherent signal is generated. In Sec. III all the collisionally induced coherent signals are considered. The pressure-induced degenerate frequency resonance and the PIER 4 signal are presented as a Rayleigh and Raman scattering process from a really populated excited state. The scattering amplitudes add up coherently only if the scattered photon frequency satisfies $\omega_{out}=2\omega_2-\omega_2$ and if no momentum is given to the atom for the whole process ($\vec{k}_{out}=2\vec{k}_1-\vec{k}_2$). Four-wave mixing Raman-type resonance between two equally populated states is shown to be possible if the excited state can decay or if collisions are introduced. It is also pointed out that other coherent pathways of equal importance, which have not been considered so far, should be introduced for explaining the experimental results. Four-wave mixing is then discussed from a collisionally populated excited state. Again collisional redistribution plays a dominant role. This particular signal is governed by the fifth-order susceptibility tensor $(X^{(5)})$[12] with correction terms of the same origin as the correction terms for the third-order susceptibility tensor $(X^{(3)})$. Then, a new pressure-induced signal is also discussed. It is called "collisionally triggered two-photon quasiresonant coherent signal." This signal can also be considered as a Rayleigh scattering from a populated excited state with a favored direction where the signal can add up coherently. Finally, it is noted that collisions are not really necessary to generate these new types of resonances. Since all the collisionally induced coherent signals are related to the fact that, in the presence of collisions, it is energetically possible to access the excited states and transfer real population, it should not be too surprising to learn that the same type of signals can be generated in the absence of collisions from an initially populated state broadened by spontaneous emission. Because then it also becomes energetically possible to access other states even though all the lasers are detuned from any one-photon resonances.

II. COLLISIONAL REDISTRIBUTION

Let us consider a gas of two-level atoms all having a natural frequency of oscillation ω_{ba} driven at a slightly off-resonance frequency ω. A buffer gas is introduced. Its constituents, atoms or molecules, can collide with the nearly resonant two-level atoms. By definition, this gas is not able to absorb any light. This can be achieved in practice by choosing a gas such that the resonance frequencies of its constituents are very remote from the driving frequency ω. Any inelastic collisions that can quench the population from the excited state of the two-level atoms will be neglected. We are only interested in dephasing collisions which interrupt the phase of the emitted wave train. During a collision, the energy levels are Stark shifted and the phase of states $|a\rangle$ and $|b\rangle$ suffers a phase shift of ϕ_a and ϕ_b, respectively. The phase shift ϕ_b generally differs from ϕ_a. This implies that for each collision the coherence ρ_{ab} between states $|a\rangle$ and $|b\rangle$ is altered in its phase but not in its magnitude. This change in ρ_{ab} can be expressed in the following way:

$$(\Delta\rho_{ab})_{col}=\langle \exp(i\Delta\phi)-1\rangle\rho_{ab}\ , \tag{1}$$

where the phase shift $\Delta\phi=\phi_b-\phi_a$ is a statistical quantity which depends on the impact parameter and the velocity of the perturbing atom. The bracket symbol implies a statistical average over many collisions. If f designates the collision frequency, Eq. (1) can be written

$$\frac{\delta\rho_{ab}}{\delta t}=f\langle \exp(i\Delta\phi)-1\rangle\rho_{ab}$$
$$=-(\gamma'_{col}-i\gamma''_{col})\rho_{ab}\ . \tag{2}$$

Here γ'_{col} and γ''_{col} are, respectively, the real and imaginary parts of the collisional relaxation rate. γ''_{col} represents a shift of the resonance and γ'_{col} represents a broadening of the transition linewidth. In the limit of low pressure, both γ'_{col} and γ''_{col} are proportional to pressure since only binary collisions are considered. Thus we have $\gamma'_{col}=c'_{12}p$, and $\gamma''_{col}=c''_{12}p$, where p is the buffer gas pressure. As it should be, the longitudinal relaxation rate that controls the decay of population remains unchanged by the phase-changing collisions. From this treatment one can see that the effect of collisions can be phenomenologically taken care of by only adding a quantity $c'_{12}p$ to the transverse damping term, which governs the transition linewidth, and by slightly modifying the resonance frequency by a quantity $c''_{12}p$. These statements are only valid within the impact approximation.[13–15]

The population generated in the excited state in the presence of collisions, is now calculated and the spectrum of the fluorescent light is analyzed as well. In order to evaluate the population in the excited state, the density matrix formalism and the standard technique of perturbation theory[16,17] is used that will be carried up to second order. The following set of equations describes the time evolution of each density matrix element:

$$\frac{\partial\rho_{aa}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{aa}+\gamma_{bb}\rho_{bb}\ , \tag{3a}$$

$$\frac{\partial\rho_{bb}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{bb}-\gamma_{bb}\rho_{bb}\ , \tag{3b}$$

$$\frac{\partial\rho_{ab}}{\partial t}=-i\omega_{ab}\rho_{ab}-\frac{i}{\hbar}[V,\rho]_{ab}-\gamma_{ab}\rho_{ab}\ . \tag{3c}$$

$|a\rangle$ and $|b\rangle$ refer to the ground and excited states, respectively. It is assumed that state $|a\rangle$ does not decay radiatively ($\gamma_{aa}=0$), but it is not necessary. H is the total Hamiltonian of the system, which includes the unperturbed Hamiltonian H_0 of the atomic system and the dipolar interaction $V=-\vec{\mu}\cdot\vec{E}$, where $\vec{\mu}$ is the transition dipole moment and $\vec{E}$ is the applied electric field. γ_{bb} is the spontaneous emission rate from level $|b\rangle$, and γ_{ab} is the dephasing rate of the dipole moment. If spontaneous emission is the only source of dephasing, the transverse damping rate γ_{ab} is related to the longitudinal damping rates γ_{aa} and γ_{bb} by the standard expression:

$$\gamma_{ab}=\tfrac{1}{2}(\gamma_{aa}+\gamma_{bb})\quad\text{(without collisions)}\ . \tag{4}$$

As we have just seen, we can easily modify this expression to account for collisions. Equation (4) then becomes

$$\tilde{\gamma}_{ab}=\tfrac{1}{2}(\gamma_{aa}+\gamma_{bb})+c'_{ab}p\quad\text{(with collisions)}. \tag{5}$$

Solving Eq. (3) to first and second order and using Eq. (5), one finds that a coherence is induced between levels $|a\rangle$ and $|b\rangle$ and that some population is transferred from level $|a\rangle$ to level $|b\rangle$:

$$\rho_{ab}^{(1)}=\frac{\mu_{ab}}{2\hbar}\frac{\rho_{aa}^{(0)}}{(\omega_{ba}-\omega+i\tilde{\gamma}_{ab})}E\ , \tag{6a}$$

$$\rho_{bb}^{(2)}=\left[\frac{\mu_{ab}}{2\hbar}\right]^2\frac{\rho_{aa}^{(0)}}{(\omega_{ba}-\omega)^2+\tilde{\gamma}_{ab}^2}\times\left[1+\frac{\tilde{\gamma}_{ab}-\gamma_{ab}}{\gamma_{ab}}\right]EE^*\ . \tag{6b}$$

Since we are not considering the case where level $|a\rangle$ is very much depleted, we have $\rho_{bb}^{(2)}\ll\rho_{aa}^{(0)}$ and $\rho_{aa}\approx 1$. This means, at least to lowest order, that

$$|\rho_{ab}|^2\le\rho_{aa}\rho_{bb}\ . \tag{7}$$

In fact, this expression is much more general than indicated by the way it has been deduced here. Its validity can be proven very generally, starting from basic concepts of quantum mechanics.[18] It says that we are not able to generate a coherence between two states unless both states are populated. Very generally, this means that we cannot have resonances between unpopulated states. The equality sign holds exactly when no collisions are present. As soon as collisions are introduced, the square of the magnitude of the coherence between two levels is less than the product of the total population involved in each level. It should be noted at this point that before and after each individual collision, the equality holds perfectly since there is only a phase shift involved. It is only when we average over many different collisions that the equality does not hold. This reflects directly the destructive interference between an array of dipoles all oscillating at the same frequency but with different random phases. In the presence of collisions, the square of the magnitude of the coherence between two levels can only be smaller or equal to the product of the population involved. Equation (6b) tells us that in the presence of collisions and for detunings larger than $\tilde{\gamma}_{ab}$ more and more population is transferred in the excited state as the pressure of a buffer gas is increased. In the next section, we shall see that this transfer of population is resonant, which means that real population is transferred in the excited state in the presence of collisions. The absorption coefficient $\alpha(\omega)$ is proportional to the population in level $|b\rangle$ multiplied by the spontaneous emission rate γ_{bb} and is given by

$$\alpha(\omega)\propto 2\left[\frac{\mu_{ab}}{2\hbar}\right]^2\rho_{aa}^{(0)}EE^*\mathcal{A}(\omega)\left[\frac{\gamma_{ab}}{\tilde{\gamma}_{ab}}+\frac{\tilde{\gamma}_{ab}-\gamma_{ab}}{\tilde{\gamma}_{ab}}\right], \tag{8a}$$

where

$$\mathcal{A}(\omega)=\frac{\tilde{\gamma}_{ab}/\pi}{(\omega_{ba}-\omega)^2+\tilde{\gamma}_{ab}^2}\ . \tag{8b}$$

$\mathcal{A}(\omega)$ is called the absorption line shape. As expected, the absorption coefficient is proportional to the laser intensity and decreases as the inverse of the square of the laser detunings from resonance for large detunings. As we shall see, the first term in the second parentheses on the right of Eq. (8a) gives the fraction of the absorbed light which is scattered elastically. The second term in the parentheses gives the fraction of the absorbed light which is scattered inelastically. In fact, the dephasing collisions are not strictly elastic since some kinetic energy can be given to or taken away from the two colliding particles. These collisions are often referred to in the literature as quasielastic collisions.[14]

The spectrum of the fluorescence emitted by a coherently driven two-level atom in the presence of collisions is now discussed. Within the impact approximation, it can be shown that the intensity distribution $I(\omega')$ of the scattered light of frequency ω' integrated over all angles and summed over polarizations, in steady state (in units of photons cm^{-3} sec^{-1}) is given by the following expression[13–15,19]:

$$I(\omega')=\pi\left[\frac{\omega'}{\omega_{ba}}\right]^3\left[\frac{\mu_{ab}}{2\hbar}\right]^2\rho_{aa}^{(0)}\mathscr{A}(\omega)EE^*\left[\frac{\gamma_{ab}}{\tilde{\gamma}_{ab}}\delta(\omega'-\omega)+\frac{\tilde{\gamma}_{ab}-\gamma_{ab}}{\tilde{\gamma}_{ab}}\frac{\tilde{\gamma}_{ab}/\pi}{(\omega_{ba}-\omega')^2+\tilde{\gamma}_{ab}^2}\right], \tag{9}$$

where the prefactors of the delta and the Lorentzian functions give the integrated strengths of the elastic and inelastic contributions. The last contribution is called the inelastic contribution since the emitted light frequency is different from the incident laser frequency. The first term in this equation, which occurs at the incident frequency ω, is known as Rayleigh scattering. Since the ground state has no natural width, the Rayleigh scattering has the same spectral profile as the excitation source. The second term in Eq. (9) is the collision-induced fluorescence. Real population is transferred by collisions in the excited state which then fluoresce with a Lorentzian profile centered at ω_{ba} and of width equal to the sum of the natural and collisional widths. The absorption and the fluorescent processes are represented in Fig. 1. The straight lines designate absorption of the incident laser photons, and the wavy lines designate emission of the fluorescent photons. The figure is broken up into two parts. The elastic part of the process is shown on the left side of Fig. 1. The width of the excited state, due to lifetime broadening, is shown by a solid line. Only $\gamma_{ab}/\tilde{\gamma}_{ab}$ of the atoms that are excited to level $|b\rangle$ goes through a Rayleigh process. From such a representation, one can see directly why the Rayleigh process has the same linewidth as the driving laser if the ground states do not decay. The redistribution part of the process is shown on the right-hand side of Fig. 1. The distribution of possible kinetic energies available for the fraction of atoms $(\tilde{\gamma}_{ab}-\gamma_{ab})/\gamma_{ab}$ that will follow a collisional redistribution process is represented as a dashed line of width $(2\tilde{\gamma}_{ab}-2\gamma_{ab})$ centered around the ground-state energy. Such a representation gives the right absorption profile since

$$\mathscr{A}(\omega)=\frac{1}{\pi^2}\int_{-\infty}^{\infty}\frac{(\tilde{\gamma}_{ab}-\gamma_{ab})}{\omega'^2+(\tilde{\gamma}_{ab}-\gamma_{ab})^2}\times\frac{\gamma_{bb/2}}{(\omega'+\omega-\omega_{ba})^2+(\gamma_{bb/2})^2}d\omega', \tag{10}$$

and also the right emission spectrum since it is correctly centered at ω_{ba} with the right line shape and linewidth. This representation of the complete process is fully consistent with the absorption and the fluorescent spectrum results. This shows that, in the presence of collisions, it is energetically possible to access the excited state even though the laser frequency is detuned from resonance. This concept will be very useful in discussing the collisionally induced coherent signals. As a last point about Fig. 1, it should be noted that if the laser were turned off in a time scale slower than the inverse of the detuning but faster than γ_{bb}^{-1}, it is expected that, after averaging out the interference contribution, the elastic component of the population in state $|b\rangle$ would follow adiabatically the laser pulse; but for the population in state $|b\rangle$ that has followed a collisional redistribution process it is expected that it would decay on a time scale given by the spontaneous emission rate γ_{bb} of the excited state.[20]

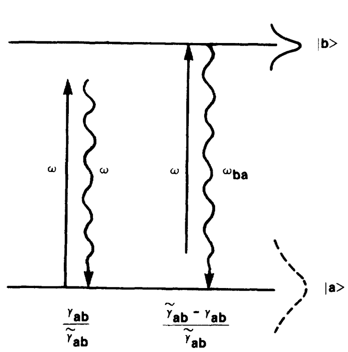

FIG. 1. Representation of the collisional redistribution process. The straight arrows represent the absorption of photons and the wavy arrows stand for the fluorescent photons.

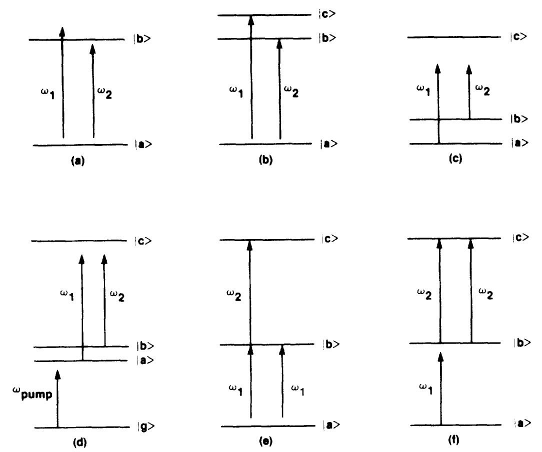

FIG. 2. Tuning of lasers in a wave-mixing experiment for generating a (a) pressure-induced degenerate frequency resonance, (b) pressure-induced extra resonance, (c) Raman resonance between equally populated states, (d) CARS signal from a collisionally populated excited state, (e) collisionally triggered two-photon quasiresonant coherent signal, and (f) a conventional two-photon quasiresonant coherent signal. The prime symbol affixed to ω_1 or ω_2 is used to indicate an identical frequency but a possibly different direction.

III. COLLISIONALLY INDUCED COHERENT SIGNALS

A. Pressure-induced degenerate frequency resonance in four-wave mixing

Recently, a pressure-induced degenerate frequency resonance in Na vapor with He buffer gas was observed.[3,4] The intensity of a four-wave mixing signal at the frequency $2\omega_1-\omega_2$ showed a sharp resonance for $\omega_1=\omega_2$ in the presence of collisions, even though neither incident frequencies nor any of their combinations were resonant with any atomic transitions. The component of the population in level $|b\rangle$ which oscillates at frequency $\omega_1-\omega_2$ in the presence of two lasers of frequencies ω_1 and ω_2 is now evaluated.[21] Figure 2(a) shows the tuning of the lasers. Equations (3a)–(3c) still describe the

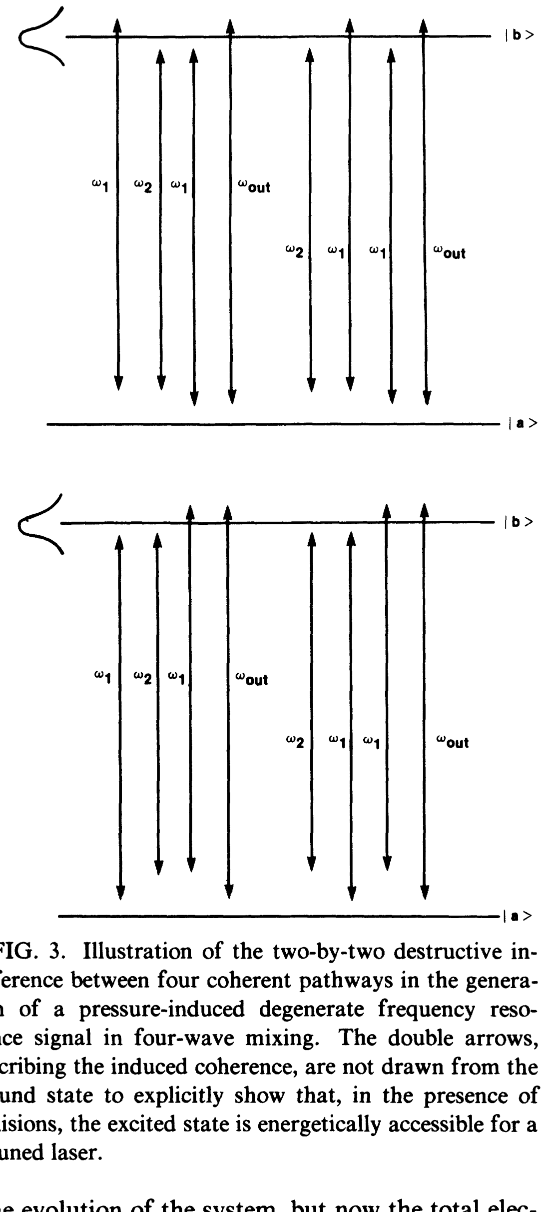

FIG. 3. Illustration of the two-by-two destructive interference between four coherent pathways in the generation of a pressure-induced degenerate frequency resonance signal in four-wave mixing. The double arrows, describing the induced coherence, are not drawn from the ground state to explicitly show that, in the presence of collisions, the excited state is energetically accessible for a detuned laser.

time evolution of the system, but now the total electric field $\vec{E}$ is the sum of two incident fields $\vec{E}_1$ and $\vec{E}_2$. Solving these equations to second order and keeping the components that oscillate at $\omega_1-\omega_2$, we get

$$\rho_{bb}^{(2)}(\omega_1-\omega_2)=-\rho_{aa}^{(2)}(\omega_1-\omega_2)=\left[\frac{\mu_{ab}}{2\hbar}\right]^2\rho_{aa}^{(0)}\frac{E_1E_2^*}{(\omega_{ba}-\omega_2-i\tilde{\gamma}_{ab})(\omega_{ba}-\omega_1+i\tilde{\gamma}_{ab})}\times\left[1-2i\frac{(\tilde{\gamma}_{ab}-\gamma_{bb/2}}{(\omega_1-\omega_2-i\gamma_{bb})}\right]+\text{c.c.} \tag{11}$$

A population grating is generated in the sample from which a laser photon can be scattered off. The intensity of the scattered signal at frequency $\omega_{\text{out}}=2\omega_1-\omega_2$ is proportional to the square of the coherence induced in third order $\rho_{ab}^{(3)}(2\omega_1-\omega_2)$ which is itself proportional to $\rho_{bb}^{(2)}-\rho_{aa}^{(2)}$. As ω_1 is tuned around ω_2 in the presence of collisions, the scattering efficiency has a resonant behavior. When $\omega_1=\omega_2$, we obtain the results deduced before for a one-laser experiment [cf. Eq. (6b)]. The second term in parentheses can then be interpreted as the collisional redistribution term due to the presence of two laser beams. What is remarkable here is that the resonance at $\omega_1=\omega_2$ is not pressure broadened. This provides a completely new technique to measure the lifetime of an excited state. It might not always be possible or easy to measure the lifetime of an excited state in the time domain. However, with a four-wave mixing type of measurement, it is possible to avoid this problem and measure very fast relaxation times in the frequency domain. This technique has already been used by different groups for measuring fast relaxation times in liquids and solids.[11,22] If one is detuned by a quantity much larger than the transition linewidth, it can be proven that this technique gets rid of the inhomogeneous linewidth.[11] We can understand physically the origin of this new resonance by realizing that in the presence of collisions it is energetically possible to access level $|b\rangle$ even if lasers 1 and 2 are detuned from resonance. A very narrow resonance of width γ_{bb} is then expected. The double arrows of Fig. 3 illustrate the coherence generated up to third order and also the two-by-two destructive interference between four coherent pathways. In order to indicate more clearly that there is a transfer of real population to the excited state, the arrows are not drawn from the ground state. Our model has provided us with a physical intuition of why an extra resonance at $\omega_1=\omega_2$ should appear in four-wave mixing experiments in the presence of collisions and why the linewidth of this resonance should be so narrow.

B. Pressure-induced extra resonances in four-wave mixing (PIER 4)

Recently, a coherence was generated between two nearby excited states in sodium in the presence of collisions by tuning the difference of frequencies of two lasers in correspondence to the separation of two excited states, even though none of the lasers were tuned on any one-photon resonances.[1,2] This is illustrated in Fig. 1(b). This gave rise to a Raman resonance between two excited states. It will be shown that this resonance is in fact closely related to the Rayleigh-type of resonance in the excited state we have just discussed. This provided the first experimental evidence for the generation of a coherent signal by an incoherent process. This signal was originally discussed in terms of correction terms in the expression of the third-order susceptibility tensor $X^{(3)}$. Similar types of signal were subsequently observed in liquids and solids.[23] The following set of equations describes the time evolution of the system:

$$\frac{\partial\rho_{aa}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{aa}+\gamma_{cc}\rho_{cc}+\gamma_{bb}\rho_{bb}\ , \tag{12a}$$

$$\frac{\partial\rho_{bb}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{bb}-\gamma_{bb}\rho_{bb}\ , \tag{12b}$$

$$\frac{\partial\rho_{cc}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{cc}-\gamma_{cc}\rho_{cc}\ , \tag{12c}$$

$$\frac{\partial\rho_{ab}}{\partial t}=-i\omega_{ab}\rho_{ab}-\frac{i}{\hbar}[V,\rho]_{ab}-\tilde{\gamma}_{ab}\rho_{ab}\ , \tag{12d}$$

$$\frac{\partial\rho_{ac}}{\partial t}=-i\omega_{ac}\rho_{ac}-\frac{i}{\hbar}[V,\rho]_{ac}-\tilde{\gamma}_{ac}\rho_{ab}\ , \tag{12e}$$

$$\frac{\partial\rho_{bc}}{\partial t}=-i\omega_{bc}\rho_{bc}-\frac{i}{\hbar}[V,\rho]_{bc}-\tilde{\gamma}_{bc}\rho_{bc}\ . \tag{12f}$$

γ_{ii} is the spontaneous emission rate from level i, and $\tilde{\gamma}_{ij}$ is the transition linewidth from level $|i\rangle$ to level $|j\rangle$ in the presence of collisions. The total complex electric field is given by

$$\vec{E}=\vec{E}_1+\vec{E}_2 =\frac{\mathscr{E}_1 e^{i(\omega_2 t-\vec{k}_1\cdot\vec{r})}}{2}+\frac{\mathscr{E}_2 e^{i(\omega_2 t-\vec{k}_2\cdot\vec{r})}}{2}\ .$$

Solving these equations to second order, we find

$$\rho_{bc}^{(2)}=\frac{\mu_{ab}\mu_{ac}}{4\hbar^2}\rho_{aa}^{(0)}\frac{E_1E_2^*}{(\omega_{ca}-\omega_1+i\tilde{\gamma}_{ac})(\omega_{ba}-\omega_2-i\tilde{\gamma}_{ab})}\left[1+i\frac{(\tilde{\gamma}_{ab}+\tilde{\gamma}_{ac}-\tilde{\gamma}_{bc}}{\omega_{cb}-(\omega_1-\omega_2)+i\tilde{\gamma}_{bc}}\right], \tag{13a}$$

$$\rho_{bb}^{(2)}\cong\frac{\mu_{ab}^2}{4\hbar^2}\rho_{aa}^{(0)}\frac{E_2E_2^*}{[(\omega_{ba}-\omega_2)^2+\tilde{\gamma}_{ab}^2]}\left[1+\frac{\tilde{\gamma}_{ab}-\gamma_{ab}}{\gamma_{ab}}\right], \tag{13b}$$

$$\rho_{cc}^{(2)}\cong\frac{\mu_{ac}^2}{4\hbar^2}\rho_{aa}^{(0)}\frac{E_1E_1^*}{[(\omega_{ca}-\omega_1)^2+\tilde{\gamma}_{ac}^2]}\left[1+\frac{\tilde{\gamma}_{ac}-\gamma_{ac}}{\gamma_{ac}}\right]. \tag{13c}$$

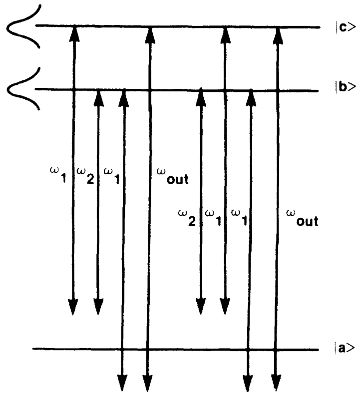

FIG. 4. Illustration of the destructive interference between two coherent pathways in the generation of a pressure-induced extra resonance signal in four-wave mixing. The double arrows, describing the induced coherence, are not drawn from the ground state to explicitly show that, in the presence of collisions, the excited state is energetically accessible for a detuned laser.

The populations transferred in levels $|b\rangle$ and $|c\rangle$, respectively, are mostly due to laser 2 acting alone on level $|b\rangle$ and laser 1 acting alone on level $|c\rangle$. If we only restrict ourselves to dephasing collisions (quasielastic collisions), as has been done up to now, and neglect all inelastic collisions, it is expected that the coherence between levels $|b\rangle$ and $|c\rangle$ will be maximum when ω_1 and ω_2 are adjusted such that $\omega_{cb}=\omega_1-\omega_2$ and when both excited states move at the same rate under the effect of a collision, given that $\gamma_{bb}=\gamma_{cc}$ and $\gamma_{aa}=0$. This implies $\tilde{\gamma}_{cb}-\gamma_{cb}=0$ and $\tilde{\gamma}_{ab}-\gamma_{ab}=\tilde{\gamma}_{ac}-\gamma_{ac}$. For this particular case, $|\rho_{bc}^{(2)}|^2$ is exactly equal to the product of populations in level $|b\rangle$ and $|c\rangle$ as can be seen from Eqs. (13a)–(13c). This is a remarkable result which shows clearly the role of collisional redistribution in establishing a coherence between two excited states. In the more general case, we have $|\rho_{bc}^{(2)}|^2<\rho_{bb}^{(2)}\rho_{cc}^{(2)}$ and a simple knowledge of $\rho_{bb}^{(2)}$ and $\rho_{cc}^{(2)}$ is not sufficient to evaluate the coherence between levels $|b\rangle$ and $|c\rangle$. As explained in Sec. II, before and after each individual collision, we have $|\rho_{bc}|^2=\rho_{bb}\rho_{cc}$. But, when we average over many collisions, we do lose this equality. As explained before, the phases of each separate dipole under the effect of collisions do not add up coherently. In our experimental report of the observation of the generation of a PIER 4 signal in sodium, we had $\gamma_{bb}=\gamma_{cc}$, $\gamma_{aa}=0$, $\tilde{\gamma}_{ab}-\gamma_{ab}=\tilde{\gamma}_{ac}-\gamma_{ac}$ but $\tilde{\gamma}_{cb}-\gamma_{cb}\neq0$, due to fine-structure changing collisions and possibly due to dephasing collisions if levels $|b\rangle$ and $|c\rangle$ are not shifted equally during a collision. It should be noted here that even if the coherence between two excited states can be calculated directly without ever calculating the populations in levels $|b\rangle$ and $|c\rangle$, it does not mean at all that the population generated in the excited state just plays a passive role. In fact, it is just because there is a probability of finding atoms in the excited states that coherence can exist between two excited states. The third-order susceptibility is proportional to $\rho_{bc}^{(2)}(\omega_1-\omega_2)$ and a new wave at $\omega_{\text{out}}=2\omega_1-\omega_2$ can be generated in the phase-matching direction in the presence of collisions. An extra resonance in a four-wave mixing experiment is expected for $\omega_1-\omega_2=\omega_{cb}$. If ω_1 is fixed and if ω_2 is scanned, one can probe the width of any excited state by performing a quasidegenerate four-wave mixing experiment (Fig. 3) or measure the transition linewidth between two excited states by performing a PIER 4 type of measurement (Fig. 4). The two effects are intimately related since they have the same physical origin: Without any collisional redistribution, there would not be any extra resonance in four-wave mixing experiments. There is a build-up of real populations in the excited states when a PIER 4 signal is generated. Again here, strictly speaking, a collisionally induced coherent signal is generated not because collisions destroy the destructive interference between two coherent pathways, but because at the same time as collisions can supply or take away the extra energy required to access a particular level, a coherence between excited states can be induced by two lasers in the presence of collisions. When collisions are introduced, it is not possible to express the coherence between two excited states as a linear superposition with pressure-dependent coefficients of the two interfering coherent pathways existing in the absence of collisions.

C. Raman resonance between equally populated states

The energy level diagram of interest is shown in Fig. 2(c). It is assumed that levels $|a\rangle$ and $|b\rangle$ are initially equally populated ($\rho_{aa}^{(0)}=\rho_{bb}^{(0)}\equiv\rho^{(0)}$) and the two incident lasers are tuned such that $\omega_1-\omega_2=\omega_{ba}$. ω_1 might be detuned from the one-photon resonance. No transition dipole moment exists between levels $|a\rangle$ and $|b\rangle$. The following set of equations describes the time evolution of the system:

$$\frac{\partial\rho_{aa}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{aa}+\Gamma_{ca}\rho_{cc}\ , \qquad (14a)$$

$$\frac{\partial\rho_{bb}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{bb}+\Gamma_{cb}\rho_{cc}\ , \tag{14b}$$

$$\frac{\partial\rho_{cc}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{cc}-(\Gamma_{ca}+\Gamma_{cb})\rho_{cc}\ , \tag{14c}$$

$$\frac{\partial\rho_{ab}}{\partial t}=-i\omega_{ab}\rho_{ab}-\frac{i}{\hbar}[V,\rho]_{ab}-\tilde{\gamma}_{ab}\rho_{ab}\ , \tag{14d}$$

$$\frac{\partial\rho_{ac}}{\partial t}=-i\omega_{ac}\rho_{ac}-\frac{i}{\hbar}[V,\rho]_{ac}-\tilde{\gamma}_{ac}\rho_{ac}\ , \tag{14e}$$

$$\frac{\partial\rho_{bc}}{\partial t}=-i\omega_{bc}\rho_{bc}-\frac{i}{\hbar}[V,\rho]_{bc}-\tilde{\gamma}_{bc}\rho_{bc}\ , \tag{14f}$$

where Γ_{ij} describes the spontaneous emission rate from level $|i\rangle$ to level $|j\rangle$. Here, and later in the text, Γ_{ij} rather than γ_{ii} is used to explicitly take into account the different pathways for spontaneous decay. The second-order coherence induced at $\omega_1-\omega_2$ will have a resonant behavior as ω_2 is scanned around the $\omega_1-\omega_2=\omega_{ba}$ resonance. The resonant coherence induced in third order involves the destructive interference between the two coherent pathways shown in Fig. 5 and is proportional to the second-order coherence induced at $\omega_1-\omega_2$:

$$\rho_{ab}^{(2)}(\omega_1-\omega_2)=\frac{\mu_{ac}\mu_{bc}}{(2\hbar)^2}\rho^{(0)}E_1E_2^*\left[1+i\frac{(\tilde{\gamma}_{ac}+\tilde{\gamma}_{bc}-\tilde{\gamma}_{ab})}{[\omega_{ba}-(\omega_1-\omega_2)+i\tilde{\gamma}_{ab}]}\right]\Big/(\omega_{ca}-\omega_1+i\tilde{\gamma}_{ac})(\omega_{ab}-\omega_2-i\tilde{\gamma}_{bc})\ . \tag{15}$$

The resonance at $\omega_1-\omega_2=\omega_{ba}$ will be sharp unless inelastic collisions play an important role or if the two levels are not shifted equally under the effect of a collision. Using Eqs. (5) and (15), one finds that a four-wave mixing Raman-type resonance between two equally populated states is possible if the excited state can decay or if collisions are introduced.[4,5,10] It should be stressed here that Eq. (15) is not the complete expression for the coherence induced in the medium at $\omega_1-\omega_2$ since the background contribution is not properly taken into account. One must also consider the nonresonant contributions coming from $\rho_{aa}^{(2)}(\omega_1-\omega_2)$, $\rho_{bb}^{(2)}(\omega_1-\omega_2)$, and $\rho_{cc}^{(2)}(\omega_1-\omega_2)$ which involve the destructive interference between many more coherent pathways. If one does so, the exact expression becomes much more complicated and for simplicity will not be considered here. The introduction of other pathways of equal importance contributing to the background should help in getting a better fit to the experimental results of Bloembergen and co-workers.[4,10] In order to explain their measurements, one would also need to consider the effect of optical pumping in more detail.

D. Four-wave mixing from collisionally populated excited states

Work on four-wave mixing from collisionally populated excited states has been reported.[5] The energy level diagram of interest is shown in Fig. 1(d). For simplicity, let us again neglect the inelastic collisions. The following set of equations describes the time evolution of each density-matrix element:

$$\frac{\partial\rho_{aa}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{aa}+\frac{K}{(\omega_{\text{pump}}-\omega_{ag})^2}pI_{\text{pump}}^{(t)}-\Gamma_{aa}\rho_{aa}+\Gamma_{ca}\rho_{cc}\ , \tag{16a}$$

$$\frac{\partial\rho_{bb}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{bb}+\frac{K}{(\omega_{\text{pump}}-\omega_{bg})^2}pI_{\text{pump}}^{(t)}-\Gamma_{bb}\rho_{bb}+\Gamma_{cb}\rho_{cc}\ , \tag{16b}$$

$$\frac{\partial\rho_{cc}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{cc}-(\Gamma_{ca}+\Gamma_{cb})\rho_{cc}\ , \tag{16c}$$

$$\frac{\partial\rho_{ab}}{\partial t}=-i\omega_{ab}\rho_{ab}-\frac{i}{\hbar}[V,\rho]_{ab}-\tilde{\gamma}_{ab}\rho_{ab}\ ,$$

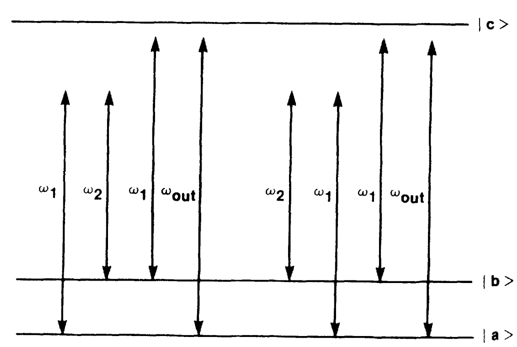

FIG. 5. In generating a Raman resonant signal between equally populated states, the two illustrated coherent pathways interfere destructively and give a resonant contribution for $\omega_{ba}\approx\omega_1-\omega_2$.

$$\frac{\partial\rho_{ac}}{\partial t}=-i\omega_{ac}\rho_{ac}-\frac{i}{\hbar}[V,\rho]_{ac}-\widetilde{\gamma}_{ac}\rho_{ac}\ , \tag{16d}$$

$$\frac{\partial\rho_{bc}}{\partial t}=-i\omega_{bc}\rho_{bc}-\frac{i}{\hbar}[V,\rho]_{bc}-\widetilde{\gamma}_{bc}\rho_{bc}\ .$$

The second term on the right-hand side of Eqs. (16a) and (16b) describes the collisionally assisted transfer of population from the ground state to the two nearest excited states. If we assume that this transfer of population is relatively slow, we can solve these equations to third order. If the populations in levels $|a\rangle$ and $|b\rangle$ stay sufficiently unequal, and if laser 1 is detuned from the ω_{cb} resonance, the major contribution to the induced coherence at $\omega_{\text{out}}=2\omega_1-\omega_2$ for $\omega_1-\omega_2\approx\omega_{ba}$ comes from the interference of the two coherent pathways already shown in Fig. 5. The expression describing the induced coherence at $\omega_{\text{out}}=2\omega_1-\omega_2$ takes the form

$$\rho_{ac}^{(3)}(2\omega_1-\omega_2)=\frac{\mu_{bc}^2\mu_{ac}}{(2\hbar)^3}\frac{E_1E_1E_2^*}{[\omega_{ca}-(2\omega_1-\omega_2)+i\widetilde{\gamma}_{ac}]}\left[\frac{\rho_{aa}^{(0)}}{[\omega_{ba}-(\omega_1-\omega_2)+i\widetilde{\gamma}_{ab}](\omega_{ca}-\omega_1+i\widetilde{\gamma}_{ac})}\right.$$
$$\left.\frac{\rho_{bb}^{(0)}}{[\omega_{ba}-(\omega_1-\omega_2)+i\widetilde{\gamma}_{ab}](\omega_{cb}-\omega_2-i\widetilde{\gamma}_{bc})}\right]\ , \tag{17}$$

where $\rho_{aa}^{(0)}$ and $\rho_{bb}^{(0)}$ are obtained by solving the following two equations:

$$\frac{d\rho_{aa}^{(0)}}{dt}=\frac{kpI_{\text{pump}}(t)}{(\omega_{\text{pump}}-\omega_{ag})^2}-\Gamma_{aa}\rho_{aa}^{(0)}\ , \tag{18a}$$

$$\frac{d\rho_{bb}^{(0)}}{dt}=\frac{kpI_{\text{pump}}(t)}{(\omega_{\text{pump}}-\omega_{bg})^2}-\Gamma_{aa}\rho_{bb}^{(0)}\ . \tag{18b}$$

This expression is similar to the one that was obtained in Ref. 5. If inelastic collisions are progressively introduced to equalize the population between levels $|a\rangle$ and $|b\rangle$, the nonresonant contributions from $\rho_{aa}^{(2)}(\omega_1-\omega_2)$, $\rho_{bb}^{(2)}(\omega_1-\omega_2)$, and $\rho_{cc}^{(2)}(\omega_1-\omega_2)$ become important at high buffer gas pressure and shall also be included.

A physical explanation for the appearance of a coherent signal in the presence of collisions is now given. First, photons from the pump laser are absorbed off resonance, and two nearby excited states are populated by a collisional redistribution process. Then, as the population is increased in these two excited states and in the presence of two lasers of frequencies ω_1 and ω_2, a coherent anti-Stokes Raman scattering signal of frequency $\omega_{\text{out}}=2\omega_1-\omega_2$ is generated in the phase-matching direction and in this sense is triggered by collisions. In the absence of collisions, no resonant enhancement of the four-wave mixing signal for $\omega_{\text{out}}\approx\omega_{ca}$ and $\omega_1-\omega_2=\omega_{ba}$ is seen. Here again collisional redistribution plays a central role in triggering the appearance of the new resonance. From the point of view of nonlinear susceptibilities, it can be shown that the whole process represented in Fig. 1(d) is governed by correction terms in the expression of the fifth-order susceptibility tensor $X^{(5)}$ with the same physical origin as the correction terms in the expression of $X^{(3)}$ that was just discussed.[12] The experimental observation of such a signal then constitutes a proof of the existence of correction terms in $X^{(5)}$.

E. Collisionally triggered two-photon quasiresonant coherent signal

The energy level diagram of interest is shown in Fig. 1(e). The first laser of frequency ω_1 is tuned off the one-photon resonance to the intermediate state, the second laser producing ω_2 is tuned in the vicinity of the one-photon resonance from the intermediate state to the final state. The following set of equations describes the time evolution of the system:

$$\frac{\partial\rho_{aa}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{aa}+\Gamma_{ba}\rho_{bb}\ , \tag{19a}$$

$$\frac{\partial\rho_{bb}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{bb}-\Gamma_{ba}\rho_{bb}+\Gamma_{cb}\rho_{cc}\ , \tag{19b}$$

$$\frac{\partial\rho_{cc}}{\partial t}=\frac{-i}{\hbar}[V,\rho]_{cc}-\Gamma_{cb}\Gamma_{cc}\ , \tag{19c}$$

$$\frac{\partial\rho_{ab}}{\partial t}=-i\omega_{ab}\rho_{ab}-\frac{i}{\hbar}[V,\rho]_{ab}-\widetilde{\gamma}_{ab}\rho_{ab}\ , \tag{19d}$$

$$\frac{\partial\rho_{ac}}{\partial t}=-i\omega_{ac}\rho_{ac}-\frac{i}{\hbar}[V,\rho]_{ac}-\widetilde{\gamma}_{ac}\rho_{ac}\ , \tag{19e}$$

$$\frac{\partial\rho_{bc}}{\partial t}=-i\omega_{ac}\rho_{bc}-\frac{i}{\hbar}[V,\rho]_{bc}-\widetilde{\gamma}_{bc}\rho_{bc}\ . \tag{19f}$$

Some destructive interference between different coherent pathways appears in second and third order of the perturbative treatment. In particular, destructive interference between coherent pathways plays a very important role in the evaluation of ρ_{bc}. This coherence in third order is given by

$$\rho_{bc}^{(3)}=\left[\frac{1}{2\hbar}\right]^3 \mu_{ab}^2\mu_{bc}\rho_{aa}^{(0)}\frac{E_1E_1^*E_2}{[(\omega_{ba}-\omega_1)^2+\tilde{\gamma}_{ab}^2][\omega_{ca}-(\omega_1+\omega_2)+i\tilde{\gamma}_{ac}]}$$

$$\times\left[1-\frac{[\omega_{ca}-(\omega_1+\omega_2)+i\tilde{\gamma}_{ac}]}{(\omega_{cb}-\omega_2+i\tilde{\gamma}_{bc})}\left[\frac{i(\tilde{\gamma}_{bc}-\tilde{\gamma}_{ab}-\tilde{\gamma}_{ac})}{\omega_{ca}-(\omega_1+\omega_2)+i\tilde{\gamma}_{ac}}-\frac{\tilde{\gamma}_{ab}-\gamma_{ab}}{\gamma_{ab}}\right]\right]. \quad (20)$$

As before, when there are no collisions and if state $|a\rangle$ is the ground state, the difference of damping terms just vanish and no extra resonance appears for $\omega_2=\omega_{cb}$. on the other hand, if we increase the pressure of a buffer gas, a new resonance appears and a new coherent signal is triggered by collisions. The interfering coherent pathways are shown in Fig. 6. Again, a new resonance occurs because of the transfer of real population from the ground to the first excited state by a collisional redistribution process. If $\omega_1+\omega_2$ is detuned from the two-photon resonance, and if $\omega_2\approx\omega_{cb}$, then the coherence induced in third order between levels $|b\rangle$ and $|c\rangle$ in the presence of collisions becomes approximately equal to

$$\rho_{bc}^{(3)}\approx\left[\frac{1}{2\hbar}\right]^3 \mu_{ab}^2\mu_{bc}\rho_{aa}^{(0)}\frac{\left[(\tilde{\gamma}_{ab}-\gamma_{ab})/\gamma_{ab}\right]E_1E_1^*}{[(\omega_{ba}-\omega_1)^2+\tilde{\gamma}_{ab}^2]}\frac{E_2}{(\omega_{cb}-\omega_2+i\tilde{\gamma}_{bc})}$$

$$=\rho_{bb}^{(2)}(\text{ laser1})\left[\frac{\mu_{bc}}{2\hbar}\right]\frac{E_2}{(\omega_{cb}-\omega_2+i\tilde{\gamma}_{bc})}\equiv\bar{\rho}_{bc}^{(1)}\,, \quad (21)$$

where $\bar{\rho}_{bc}^{(1)}$ is the coherence that would be established in first order between level $|b\rangle$ and $|c\rangle$ given that the starting population in level $|b\rangle$ is just given by the collisional redistribution expression $\rho_{bb}^{(2)}$ (laser 1) due to laser 1 alone. This is a remarkable result. It means that the collisionally induced two-photon quasiresonant four-wave mixing signal can be seen as a Rayleigh scattering from a populated excited state, and that the signal generated can add up coherently in a direction given by the phase-matching direction $(\vec{k}_1-\vec{k}_1'+\vec{k}_2=\vec{k}_{\text{out}})$. This direction can be different from the direction of $\vec{k}_2$. This type of generation of coherent signal in the presence of collisions is in fact the coherent counterpart of the work done recently by Grischkowsky[20] and by Liao *et al.*[24] on their study of collisional redistribution using two-photon absorption with a nearly resonant intermediate state. The role of collisional redistribution is crucial for generating a new coherent signal. If we were to consider the different process shown in Fig. 1(f), we would not see any new signal generated as we increase the number of collisions because no pair of coherent pathways interfere, or saying it differently, because no collisional redistribution process goes on for the particular represented situation.

IV. CONCLUSION

In this paper, it has been shown that collisions can be used to trigger the generation of different types of coherent signals. The induced coherence describing the generation of such coherent signals can always be broken up in two parts in a way such

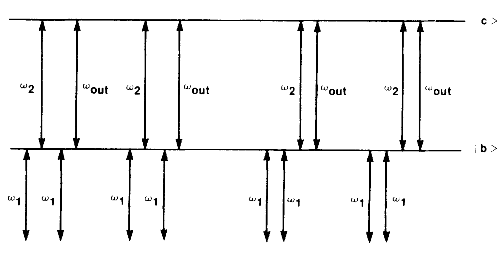

FIG. 6. Illustration of the destructive interference between four coherent pathways in the generation of a collisionally triggered two-photon quasiresonant coherent signal. The double arrows, describing the induced coherence, are not drawn from the ground state to explicitly show that, in the presence of collisions, the excited state is energetically accessible for a detuned laser. $\omega_1=\omega_1'$ but $\vec{k}_1$ is not necessarily equal to $\vec{k}_1'$.

that the second part, involving new resonances, is vanishing in the absence of collisions. All these new signals arise from the fact that, in the presence of collisions, it is energetically possible to access excited states with a detuned laser and generate a coherence between these states. Once a third-order coherence at $2\omega_1-\omega_2$ is generated between two levels, and if the transition dipole moment between these two states is different from zero, a new wave of frequency $\omega_{\rm out}=2\omega_1-\omega_2$ can be generated in the phase-matching direction. All these signals involve the transfer of real population in the excited states by a collisional redistribution process. It is important to realize here that similar types of signals should also appear in solids. Of course, it is necessary to replace the role of collisions by phonons. Interestingly enough, it should also be mentioned that since the requirement for generating the collisionally induced coherent signals is to create the possibility of energetically accessing excited states with a detuned laser, we strictly do not need to introduce collisions or phonons in the physical picture. In fact, as can be seen from Eqs. (4), (5), (11), (13a), and (20), similar types of signal can also be generated in the absence of collisions or phonons if one simply starts the wave-mixing process from an initially populated state with a finite lifetime. This gives a width to the initial level which then makes is feasible to access, resonantly, other states with a nonresonant laser.

ACKNOWLEDGMENTS

The author would like to express his gratitude to Professor N. Bloembergen and Dr. G. Grynberg and Dr. S. Reynaud for very stimulating discussions.

[1]Y. Prior, A. R. Bogdan, M. Dagenais, and N. Bloembergen, Phys. Rev. Lett. 46, 111 (1981).

[2]A. R. Bogdan, M. Downer, and N. Bloembergen, Phys. Rev. A 24, 623 (1981).

[3]A. R. Bogdan, Y. Prior, and N. Bloembergen, Opt. Lett. 6, 82 (1981).

[4]A. R. Bogdan, M. W. Downer, and N. Bloembergen, Opt. Lett. 6, 348 (1981).

[5]M. Dagenais, Phys. Rev. A 24, 1404 (1981).

[6]N. Bloembergen, H. Lotem, and R. T. Lynch, Indian J. Pure Appl. Phys. 16, 151 (1978); N. Bloembergen, in *Laser Spectroscopy IV,* edited by H. Walther and K. W. Rother (Springer, Berlin, 1979), p. 340.

[7]N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965), p. 29.

[8]G. Grynberg, J. Phys. B 14, 2089 (1981); G. Grynberg, in *Laser Spectroscopy V,* edited by A. R. W. McKellar, T. Oka, and B. P. Stoicheff (Springer, New York, 1981), p. 174.

[9]G. Grynberg, Opt. Commun. 38, 439 (1981).

[10]N. Bloembergen, A. R. Bogdan, and M. W. Downer in *Laser Spectroscopy V,* edited by A. R. W. McKellar, T. Oka, and B. P. Stoicheff (Springer, New York, 1981), p. 157.

[11]J. L. Oudar and Y. R. Shen, Phys. Rev. A 22, 1141 (1980).

[12]M. Dagenais (unpublished).

[13]D. L. Huber, Phys. Rev. 178, 93 (1969); A. Omont, E. W. Smith, and J. Cooper, Astrophys. J. 175, 185 (1972); 182, 283 (1973).

[14]J. L. Carlsten, A. Szoke, and M. G. Raymer, Phys. Rev. A 15, 1029 (1977) and references therein.

[15]S. Reynaud and C. Cohen-Tannoudji, in *Laser Spectroscopy V,* edited by A. R. W. McKellar, T. Oka, and B. P. Stoicheff (Springer, New York, 1981), and references therein, p. 166.

[16]N. Bloembergen, *Nonlinear Optics* (Benjamin, New York, 1965).

[17]See Appendix 4 in A. Yariv, *Quantum Electronics* (Wiley, New York, 1975).

[18]See, for instance, C. Cohen-Tannoudji, B. Diu, and F. Laloe, *Quantum Mechanics* (Wiley, New York, 1977), Complement EIII.

[19]R. Loudon, Rep. Prog. Phys. 43, 913 (1980).

[20]D. Grischkowsky, Phys. Rev. A 14, 802 (1976); A. Szöke and E. Courtens, Phys. Rev. Lett. 34, 1053 (1975); M. D. Crisp, Phys. Rev. A 8, 2128 (1973); M. Dagenais (unpublished).

[21]R. W. Boyd, M. G. Raymer, P. Narum, and D. J. Harter, Phys. Rev. A 24, 411 (1981).

[22]T. Yajima and H. Souma, Phys. Rev. A 17, 309 (1978); T. Yajima, H. Souma, and Y. Ishida, *ibid.* 17, 324 (1978); J. J. Song, J. H. Lee, and M. D. Levenson, *ibid.* 17, 1439 (1978); J. H. Lee, J. J. Song, M. A. F. Scarparo, and M. D. Levenson, Opt. Lett. 5, 196 (1980); J. R. Andrews and R. M. Hochstrasser, Chem. Phys. Lett. 76, 213 (1980).

[23]J. R. Andrews and R. M. Hochstrasser, Chem. Phys. Lett. 82, 381 (1981); Chem. Phys. Lett. 83, 427 (1981).

[24]P. F. Liao, J. E. Bjorkholm, and P. R. Berman, Phys. Rev. A 20, 1489 (1979).