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Pressure-induced extra resonances in nonlinear spectroscopy

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We present three examples of pressure-induced extra resonances that can be observed in nonlinear spectroscopy: fluorescence of a "three-level atom" driven by two laser fields, two-photon ionization of a "three-level atom" (plus continuum) driven by two laser fields, and excitation of a "four-level atom" driven by four laser fields. We show that all these extra resonances can be interpreted in terms of quantum pathways, each pathway involving a collisionally aided excitation. We also demonstrate that the two first extra resonances can be obtained with incoherent fields, while relatively coherent fields are required in the last example.

INTRODUCTION

The field of extra resonances triggered by collisional relaxation has for a long time mainly concentrated on the resonances occurring in four-wave mixing generation.[1] However, similar resonances have also been predicted in nonlinear spectroscopy,[2–4] the main differences being that in this case, the signal originates from atomic state populations rather than from a coherent collective emission.

The aim of this paper is to present other examples of pressure-induced extra resonances (PIER) occurring in nonlinear spectroscopy. We examine PIER which arise in (a) the fluorescence of a "three-level" atom driven by two laser fields, (b) the two-photon ionization of a "three-level" atom driven by two laser fields, and (c) the excitation of a "four-level" atom driven by four laser fields.

Apart from their intrinsic interest, we show that each of these examples allows one to specify the role of the relaxation process in the generation of extra resonances. In particular, we show that the extra resonances can be understood in terms of quantum-mechanical interference between two pathways, each of these pathways involving a collisionally aided excitation. In addition, the influence of the phase of the applied fields will be stressed. We show that some extra resonances can be obtained with number states for the applied fields while, in other cases, relatively coherent fields are required.

I. NOTATION AND ASSUMPTIONS

Let us first consider a three-level atom with a ground state a and two excited states b and b' (see Fig. 1). This atom interacts with two electromagnetic fields of frequencies ω_1 and ω_2. The first field is nearly resonant with the a-b transition and we denote by $\Delta_1=\omega_1-\omega_0$ the frequency detuning from resonance. The second field is nearly resonant with the a-b' transition and we define its detuning $\Delta_2'=\omega_2-\omega_0'$. The amplitudes of these two fields, and their associated resonance Rabi frequencies, are denoted by E_1 and E_2, and Ω_1 and Ω_2' ($\Omega_1=-d_{ab}E_1/\hbar$, $\Omega_2'=-d_{ab'}E_2/\hbar$, where d_{ab} and $d_{ab'}$ are dipole-moment matrix elements).

The radiative lifetimes of the excited states b and b' are Γ_b^{-1} and $\Gamma_{b'}^{-1}$, respectively. Apart from radiative relaxation, the atoms undergo collisional relaxation. We assume that the active atoms are perturbed by a buffer gas and that the collisions are dephasing in nature, inducing a decay of the atomic state coherences, but not of the atomic state population. The relaxation rate of the atomic state coherence i-j due to collisions is denoted by γ_{ij}. We assume that the conditions of the impact approximation are satisfied and, in particular, that $|\Delta_1|$ and $|\Delta_2'|$ are small compared to τ_c^{-1}, where τ_c is the typical duration of a collision. On the other hand, we assume that $|\Delta_1|$ and $|\Delta_2'|$ are large compared to the widths of the a-b and a-b' transitions, but that $|\Delta_1-\Delta_2'|$ remains small compared to $|\Delta_1|$ and $|\Delta_2'|$. To simplify matters somewhat, we shall also assume that $|\Omega_1/\Delta_1|$ and $|\Omega_2'/\Delta_2'|$ are very small compared to unity. With this assumption, the density-matrix equations can be solved using a perturbative approach.[5]

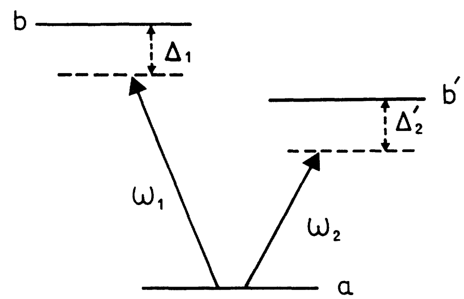

FIG. 1. Three-level atom driven by two laser fields.

The calculations are carried out using either a semiclassical approach (classical fields and quantum-mechanical atoms) or a (fully quantized) dressed-atom picture. In the first case, the atomic density-matrix elements evolve as[6]

$$\frac{d}{dt}\rho_{ij}=\frac{1}{i\hbar}[H,\rho]_{ij}-\Gamma_{ij}\rho_{ij}+(\Gamma_b\rho_{bb}+\Gamma_{b'}\rho_{b'b'})\delta_{ia}\delta_{ja}\ , \tag{1}$$

where

$$\Gamma_{ij}=\tfrac{1}{2}(\Gamma_i+\Gamma_j)+\gamma_{ij} \tag{2}$$

is the sum of the radiative and collisional relaxation rates and

$$H=H_0+V \tag{3a}$$

is the Hamiltonian for the system without relaxation. The quantity H_0 is the free-atom Hamiltonian and V is the electric dipole interaction between the atom and the field

$$V=-\mathbf{d}\cdot\mathbf{E}_T\ . \tag{3b}$$

$\mathbf{d}$ is the atomic dipole operator and $\mathbf{E}_T$ is the sum of the incident fields.

To second order in the incident fields, we find that the populations and the coherence of the excited states are

$$\rho_{bb}^{(2)}=\frac{\Omega_1^2}{4\Delta_1^2}\left[1+\frac{\gamma_{ba}+\gamma_{ba}^*}{\Gamma_b}\right]\ , \tag{4a}$$

$$\rho_{b'b'}^{(2)}=\frac{\Omega_2'^2}{4\Delta_2'^2}\left[1+\frac{\gamma_{b'a}+\gamma_{b'a}^*}{\Gamma_{b'}}\right]\ , \tag{4b}$$

$$\rho_{bb'}^{(2)}=\frac{\Omega_1\Omega_2'}{4\Delta_1\Delta_2'}\left[1+\frac{\gamma_{ba}+\gamma_{ba}^*-\gamma_{bb'}}{\Gamma_{bb'}-i\delta}\right]e^{-i(\omega_1-\omega_2)t}e^{i(\theta_1-\theta_2)}\ , \tag{4c}$$

$$\rho_{b'b}^{(2)}=\rho_{bb'}^{(2)*}\ , \tag{4d}$$

where

$$\delta=\Delta_1-\Delta_2'\ . \tag{5}$$

In these expressions, θ_1 and θ_2 correspond to the phase of the fields E_1 and E_2. If these fields propagate in the $\mathbf{k}_1$ and $\mathbf{k}_2$ directions, we have $\theta_1=\mathbf{k}_1\cdot\mathbf{r}+\varphi_1$ and $\theta_2=\mathbf{k}_2\cdot\mathbf{r}+\varphi_2$, where φ_1 and φ_2 are some additional phases associated with fields 1 and 2, respectively. The quantities ρ_{bb} and $\rho_{b'b'}$ appear as the sum of a collision-free term and a collisionally aided term. The collision-free term has been shown to be connected with Rayleigh scattering at the laser frequency while the collisionally aided terms leads to fluorescence at the resonance frequency.[7] A similar separation exists for $\rho_{bb'}$, the collisionally aided term being proportional to the factor $(\gamma_{ba}+\gamma_{b'a}^*-\gamma_{bb'})$, which has been originally introduced by Bloembergen, Loten and Lynch.[8]

Another approach uses a dressed-atom basis. In the perturbative limit the eigenstates of the dressed-atom Hamiltonian are[9]

$$|1(N_1,N_2)\rangle=-\frac{\Omega_1}{2\Delta_1}|a,N_1+1,N_2+1\rangle+|b,N_1,N_2+1\rangle\ , \tag{6a}$$

$$|2(N_1,N_2)\rangle=-\frac{\Omega_2'}{2\Delta_2'}|a,N_1+1,N_2+1\rangle+|b',N_1+1,N_2\rangle\ , \tag{6b}$$

$$|3(N_1,N_2)\rangle=|a,N_1+1,N_2+1\rangle+\frac{\Omega_1}{2\Delta_1}|b,N_1,N_2+1\rangle+\frac{\Omega_2'}{2\Delta_2'}|b',N_1+1,N_2\rangle\ , \tag{6c}$$

where $|i,N_1,N_2\rangle$ describes an atom in state $|i\rangle$ with N_1 photons of frequency ω_1 and N_2 photons of frequency ω_2. The quantities Ω_1 and Ω_2' are evaluated at $\overline{N_1}$ and $\overline{N_2}$, where $\overline{N_1}$ and $\overline{N}_2$ are the mean number of photons in these two modes of the field. (Ω_1 and Ω_2' should be replaced by $\Omega_1e^{i\theta_1}$ and $\Omega_2'e^{i\theta_2}$ to describe propagation effects. Since the paper is devoted to single atom effects, we omit the phase factors). Within the approximations made in this paper, the stages $|1(N_1,N_2)\rangle$, $|2(N_1,N_2)\rangle$, and $|3(N_1,N_2)\rangle$ are very close in energy, the separation between $|1(N_1,N_2)\rangle$ and $|3(N_1,N_2)\rangle$ being $-\hbar\Delta_1$ and the separation between $|2(N_1,N_2)\rangle$ and $|3(N_1,N_2)\rangle$ being $-\hbar\Delta_2'$. In the dressed-atom approach, collisions induce transitions between the dressed states. The steady-state values ρ_{11} and ρ_{22} of the populations of the levels $|1(N_1,N_2)\rangle$ and $|2(N_1,N_2)\rangle$ and of the coherence ρ_{12} between $|1(N_1,N_2)\rangle$ and $|2(N_1,N_2)\rangle$ are[10]

$$\rho_{11}=\frac{\Omega_1^2}{4\Delta_1^2}\frac{\gamma_{ba}+\gamma_{ba}^*}{\Gamma_b}\ , \tag{7a}$$

$$\rho_{22}=\frac{\Omega_2'^2}{4\Delta_2'^2}\frac{\gamma_{b'a}+\gamma_{b'a}^*}{\Gamma_{b'}}\ , \tag{7b}$$

$$\rho_{12}=\frac{\Omega_1\Omega_2'}{4\Delta_1\Delta_2'}\frac{\gamma_{ba}+\gamma_{b'a}^*-\gamma_{bb'}}{\Gamma_{bb'}-i\delta}\ . \tag{7c}$$

One recognizes in (7c) the collisional factor $(\gamma_{ba}+\gamma_{b'a}^*-\gamma_{bb'})$, which is associated with the creation of a coherence between dressed states through collisional excitation.[9] The values of ρ_{11} and ρ_{22} result from an equilibrium between the collisional excitation of the level and decay by spontaneous emission.[7]

Actually, the results presented above are only valid for stationary atoms. For a Doppler broadened medium, the detuning δ appearing in Eqs. (4c) and (7c), as well as elsewhere in this paper, should be replaced by $[\delta-(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{v}]$, where $\mathbf{v}$ is the atomic velocity. For the time being, we assume that $|(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{v}|\ll\Gamma_{bb'}$ for all atoms in the sample, justifying our neglect of the residual Doppler shift $(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{v}$. The modifications of the results that would occur if $|(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{v}|>\Gamma_{bb'}$ is discussed in the Conclusion.

II. FLUORESCENCE OF A THREE-LEVEL ATOM

A. PIER resonance in atomic states populations

The aim of this section is to show how the fluorescence originating from level b is modified by the field E_2 acting on the a-b' transition. Consequently, we seek a term in the population of level b which depends on both E_1 and E_2. Furthermore, we are interested only in the PIER resonance occurring around $\delta=0$. This term should originate from $\rho_{bb'}^{(2)}$ given in (4c).

Solving the density-matrix equation to fourth order, we find that the term of interest is equal to

$$\rho_{bb}^{(I)}=\frac{\Omega_1^2\Omega_2'^2}{16\Delta_1^2\Delta_2'\Gamma_b}\, i\left[\frac{(\gamma_{bb'}^a)^*}{\Gamma_{bb'}^*+i\delta}-\frac{\gamma_{bb'}^a}{\Gamma_{bb'}-i\delta}\right], \tag{8}$$

where $\gamma_{bb'}^a$ is the collisional factor of PIER 4

$$\gamma_{bb'}^a=\gamma_{ba}+\gamma_{b'a}^*-\gamma_{bb'} . \tag{9}$$

Equation (8) is valid in the limit that

$$\left|\frac{\Omega_1\Omega_2'}{\Delta_1(\Gamma_{bb'}-i\delta)}\right| \ll 1 . \tag{10}$$

Let us split $\gamma_{bb'}^a$ into its real and imaginary parts

$$\gamma_{bb'}^a=(\gamma_{bb'}^a)'+i(\gamma_{bb'}^a)'' .$$

We also assume that the imaginary part of $\Gamma_{bb'}$ (which corresponds to a shift of the line) is included in δ. We thus take $\Gamma_{bb'}$ real and obtain for $\rho_{bb}^{(I)}$

$$\rho_{bb}^{(I)}=\frac{\Omega_1^2}{8\Delta_1^2}\frac{\Omega_2'^2}{\Delta_2'\Gamma_b}\left[\frac{(\gamma_{bb'}^a)'\delta}{\Gamma_{bb'}^2+\delta^2}-\frac{(\gamma_{bb'}^a)''\Gamma_{bb'}}{\Gamma_{bb'}^2+\delta^2}\right] . \tag{11}$$

This pressure-induced contribution to the fluorescence from state b can have either a positive or negative sign (of course, the *total* fluorescence from level b is positive). The ratio of the relative magnitude of the PIER given by (11) and of the background given by (4a) is

$$\frac{\rho_{bb}^{(I)}}{\rho_{bb}^{(2)}}\sim\frac{\Omega_2'^2}{\Delta_2'\Gamma_{bb'}} . \tag{12}$$

Although it is assumed that $|\Omega_2'/\Delta_2'| \ll 1$, the ratio (12) is not necessarily very small compared to unity[11] since Ω_2' can be larger than $\Gamma_{bb'}$. Furthermore, when Δ_2' varies, the background remains constant while $\rho_{bb}^{(I)}$ exhibits a narrow resonance around $\Delta_2'-\Delta_1=0$. Thus the PIER should be observable on the fluorescence from the excited state. To have an image of how such resonance should appear, we have plotted in Fig. 2 the variation of the fluorescence I_F emitted from level b versus the frequency ω_2 for several values of the buffer-gas pressure. The frequency ω_1 of the first source is assumed to remain constant and I_F is calculated from the sum $\rho_{bb}^{(2)}+\rho_{bb}^{(I)}$.

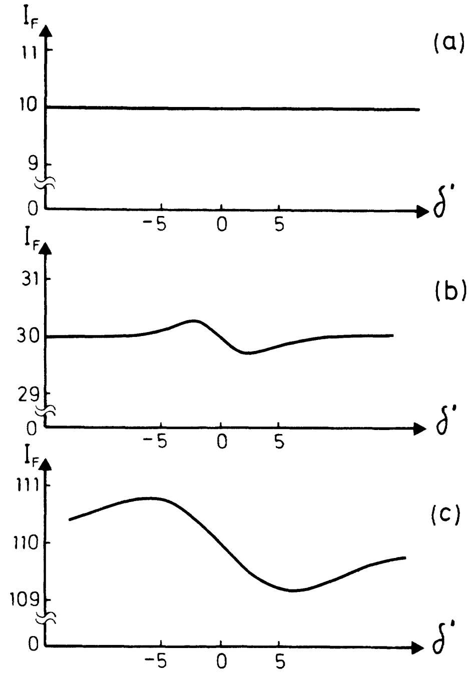

FIG. 2. Variation of the fluorescence I_F emitted from the level b vs the frequency ω_2 for various buffer-gas pressures. The curves have been obtained by assuming that $\gamma_{bb'}^a$, γ_{ba}, $\gamma_{b'a}$, and $\gamma_{bb'}$ are real and by taking $\gamma_{bb'}^a=\gamma_{b'a}=\gamma_{ba}$. We have $\Omega_1 \ll \Omega_2'$ and $|\Omega_2'/\Delta_2'|=10^{-2}$. We take $\Gamma_b=\Gamma_{b'}$ and $\Omega_2'/\Gamma_{b'}=20$. The curve a is obtained in absence of buffer gas ($\gamma_{bb'}=0$). The curve b is obtained for a pressure of buffer gas such that $\gamma_{bb'}=\Gamma_b$ and the curve c for a higher pressure ($\gamma_{bb'}=5\Gamma_b$). The same arbitrary unit is used on the vertical axis of the three curves. The abscissa corresponds to $\delta'=(\omega_2-\omega_1-\omega_0'+\omega_0)/\Gamma_b$. One can note that in the range of pressure considered here the signal and the background increases with pressure. For higher pressure, the signal saturates while the background still increases.

B. Interpretation in the uncoupled states basis

We first interpret this resonance in terms of interference between transition amplitudes. A transition amplitude will be represented by a diagram which, at this stage, should be considered a qualitative method for understanding the physics rather than a complete method for calculating the signal. If we consider the excitation of level b, two possible paths can be considered. The first possibility [Fig. 3(a)] is a direct collisionally aided excitation with absorption of one photon ω_1. The population of level b resulting from this process is proportional to the intensity of the field having frequency ω_1, i.e., to Ω_1^2. In fact, it is this process that leads to the collision-induced component of formula (4a) [or to formula (7a)]. A second possibility is a collisionally aided excitation of level b' followed by a two-photon transition from b' to b [Fig. 3(b)]. This process alone would lead to a population of the level b proportional to the square of the intensity of the field having frequency ω_2 multiplied by the intensity of the field having frequency ω_1, i.e., proportional to $\Omega_2'^4\Omega_1^2$. To get the population ρ_{bb}, however, one must also consider the possibility of an interference between these two pathways. Indeed, the quantum states of the fields and of the internal degrees of freedom of the atom are the same in the initial ($|a,N_1,N_2\rangle$) and final ($|b,N_1-1,N_2\rangle$) states

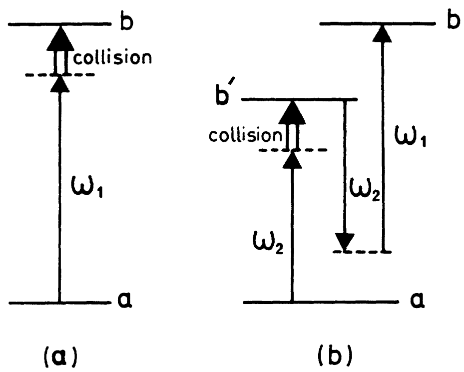

FIG. 3. Collisionally aided excitation of level b. (a) Direct pathway and (b) pathway with intermediate excitation of level b'. The pressure-induced extra resonance on the population of level b comes from the interference between these two pathways.

(in the second pathway the absorption of a photon ω_2 is followed by an emission of a photon ω_2 with the net result that N_2 is not changed). The transition amplitude for the second pathway should exhibit a resonance when the two-photon transition from b' to b becomes resonant, i.e., when $\delta=0$ [see Fig. 3(b)]. This resonance should also appear in the interference term. In some sense, the interference between the two pathways of Fig. 3 has an effect similar to that of an heterodyne detection since the effect associated with the pathway of Fig. 3(b) appears at a lower order of perturbation because of the interference with the pathway of Fig. 3(a).

The origin of the PIER resonance at $\delta=0$ can also be interpreted by a complementary argument. To have interference effect between the two pathways of Fig. 3, we should also consider the external degrees of freedom since the atom is not isolated but undergoes a collision. Indeed, energy is exchanged between the active atom and its collision partner. In the pathway shown in Fig. 3(a), the energy received by the atom is $E_{ba}-\hbar\omega_1$. In the pathway shown in Fig. 3(b), the energy received is $E_{b'a}-\hbar\omega_2$. In order to have the same change of kinetic energy of the colliding atoms for each pathway, we must have

$$E_{ba}-\hbar\omega_1=E_{b'a}-\hbar\omega_2 , \tag{13}$$

i.e.,

$$\delta=0 . \tag{14}$$

Thus the interference between the two pathways of Fig. 3 only occurs around $\delta=0$.

C. Interpretation in the dressed-state basis

We can also interpret this resonance using the dressed-state basis. More precisely, when the two-photon coupling between $|b,N_1,N_2+1\rangle$ and $|b',N_1+1,N_2\rangle$ becomes important, the states $|1(N_1,N_2)\rangle$ and $|2(N_1,N_2)\rangle$ should be written[9]

$$\begin{aligned}|1(N_1,N_2)\rangle=&-\left[\frac{\Omega_1}{2\Delta_1}\cos\theta+\frac{\Omega_2'}{2\Delta_2'}\sin\theta\right]\\&\times|a,N_1+1,N_2+1\rangle\\&+(\cos\theta)|b,N_1,N_2+1\rangle\\&+(\sin\theta)|b',N_1+1,N_2\rangle ,\end{aligned} \tag{15a}$$

$$\begin{aligned}|2(N_1,N_2)\rangle=&-\left[\frac{\Omega_2'}{2\Delta_2'}\cos\theta-\frac{\Omega_1}{2\Delta_1}\sin\theta\right]\\&\times|a,N_1+1,N_2+1\rangle\\&-(\sin\theta)|b,N_1,N_2+1\rangle\\&+(\cos\theta)|b',N_1+1,N_2\rangle ,\end{aligned} \tag{15b}$$

with

$$\tan 2\theta=\frac{\Omega_1\Omega_2'}{2\Delta_1\delta} . \tag{16}$$

Let us now assume that initially, the system is in the state $|3(N_1,N_2)\rangle$. We calculate the probability of finding the system in the state $|1(N_1,N_2)\rangle$ after a collision, our demonstration being very similar to the one originally done for the PIER resonances in four-wave mixing.[9] We call Φ and Φ' the phase factors due to a collision of relative velocity v and impact parameter b on the transitions a-b and a-b', respectively. The state $|\psi\rangle$ of the system after a collision is

$$\begin{aligned}|\psi\rangle=&|a,N_1+1,N_2+1\rangle+\frac{\Omega_1}{2\Delta_1}e^{-i\Phi}|b,N_1,N_2+1\rangle\\&+\frac{\Omega_2'}{2\Delta_2'}e^{-i\Phi'}|b',N_1+1,N_2\rangle .\end{aligned} \tag{17}$$

From (15a) and (17), we deduce the transition amplitude to find the system in the state $|1(N_1,N_2)\rangle$ after a collision,

$$\begin{aligned}\langle 1(N_1,N_2)|\psi\rangle=&\frac{\Omega_1}{2\Delta_1}(\cos\theta)(e^{-i\Phi}-1)\\&+\frac{\Omega_2'}{2\Delta_2'}(\sin\theta)(e^{-i\Phi'}-1) .\end{aligned} \tag{18}$$

The transition probability is thus

$$\begin{aligned}|\langle 1(N_1,N_2)|\psi\rangle|^2=&\frac{\Omega_1^2}{2\Delta_1^2}(\cos^2\theta)(1-\cos\Phi)\\&+\frac{\Omega_1\Omega_2'}{4\Delta_1\Delta_2'}(\cos\theta)(\sin\theta)\\&\times[(1-e^{-i\Phi})(1-e^{i\Phi'})+\text{c.c.}]\\&+\frac{\Omega_2'^2}{2\Delta_2'^2}(\sin^2\theta)(1-\cos\Phi') .\end{aligned} \tag{19}$$

When we average the various phase factors over all possible collisions, we find[9]

$$\langle 1-e^{-i\Phi}\rangle=\gamma_{ba}\ , \tag{20a}$$

$$\langle (1-e^{-i\Phi})(1-e^{i\Phi'})\rangle=\gamma_{ba}+\gamma^{*}_{b'a}-\gamma_{bb'} \\ =\gamma^{a}_{bb'}\ , \tag{20b}$$

$$\langle 1-e^{-i\Phi'}\rangle=\gamma_{b'a}\ . \tag{20c}$$

Thus the mean collisionally aided excitation of level $|1(N_1,N_2)\rangle$ in steady state is

$$\Lambda_1=\frac{\Omega_1^2}{4\Delta_1^2}(\cos^2\theta)(\gamma_{ba}+\gamma^{*}_{ba}) + \frac{\Omega_1\Omega_2'}{4\Delta_1\Delta_2'}(\cos\theta)(\sin\theta)(\gamma^{a}_{bb'}+\gamma^{a*}_{bb'}) + \frac{\Omega_2'^2}{4\Delta_2'^2}(\sin^2\theta)(\gamma_{b'a}+\gamma^{*}_{b'a})\ . \tag{21}$$

In the secular approximation $|\delta|\gg\Gamma_{bb'}$, the steady-state population of state $|1(N_1,N_2)\rangle$, denoted by ρ_{11}, is equal to Λ_1/Γ_b. To compare this result with Eq. (11), we note that the validity condition for Eq. (11) [Eq. (10)] is equivalent to $\theta\ll 1$ when $|\delta|\gg\Gamma_{bb'}$. In the limit $\theta\ll 1$, we obtain

$$\rho_{11}=\frac{\Omega_1^2}{4\Delta_1^2}\frac{(\gamma_{ba}+\gamma^{*}_{ba})}{\Gamma_b}+\frac{\Omega_1^2\Omega_2'^2}{16\Delta_1^2\Delta_2'\delta}\frac{(\gamma^{a}_{bb'}+\gamma^{a*}_{bb'})}{\Gamma_b}\ . \tag{22}$$

The second term of (22) coincides with the result of formula (11) for $|\delta|\gg\Gamma_{bb'}$. This shows that, in this approach, the PIER resonance results from the contamination of the dressed state $|1(N_1,N_2)\rangle$ by a small amount of the state $|b'\rangle$. The contamination is maximum when the two uncoupled states $|b',N_1+1,N_2\rangle$ and $|b,N_1,N_2+1\rangle$ have the same energy, i.e., when the resonance condition for the two-photon transition is fulfilled.[12]

Finally, we note that the phase of the fields does not appear in the formula (11), which give $\rho_{bb}^{(I)}$. This is an indication that the observation of this effect does not require coherent fields. This indication is supported by the physical discussion given above, which is done in terms of number states for the field.

III. TWO-PHOTON IONIZATION

We still consider the three-level atom a,b,b', but now consider the possibility that a second photon is absorbed to a state k in the continuum. More precisely, we study the case where an absorption of a photon ω_2 from state b or an absorption of a photon ω_1 from state b' leads to ionization of the atom (Fig. 4).

In the dressed-state basis, we have to add to the states given by formulas (6) the states $|k(N_1,N_2)\rangle$ corresponding to the continuum (see Fig. 5)

$$|k(N_1,N_2)\rangle=|k,N_1,N_2\rangle\ . \tag{23}$$

With respect to $|3(N_1,N_2)\rangle$, the state $|k(N_1,N_2)\rangle$ has an energy

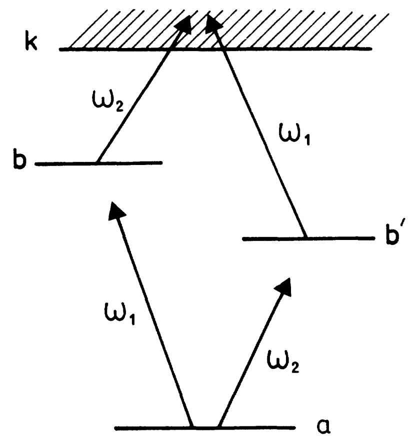

FIG. 4. Three-level atom plus continuum driven by two laser fields.

$$-\hbar\Delta_k=E_{ka}-\hbar(\omega_1+\omega_2)\ . \tag{24}$$

The coupling between $|1(N_1,N_2)\rangle$, $|2(N_1,N_2)\rangle$ and $|k(N_1,N_2)\rangle$ is produced by the electric dipole interaction having matrix elements

$$\langle k(N_1,N_2)|V|1(N_1,N_2)\rangle=-\frac{d_{kb}E_2}{2}=\hbar\frac{\Omega_2}{2}\ , \tag{25a}$$

$$\langle k(N_1,N_2)|V|2(N_1,N_2)\rangle=-\frac{d_{kb'}E_1}{2}=\hbar\frac{\Omega_1'}{2}\ . \tag{25b}$$

Recall that states $|1(N_1,N_2)\rangle$ and $|2(N_1,N_2)\rangle$ are populated only in the presence of collisions.

The state $|3(N_1,N_2)\rangle$ is also coupled to $|k(N_1,N_2)\rangle$ through its small components depending on the atomic states b and b' [see formula (6c)]

$$\langle k(N_1,N_2)|V|3(N_1,N_2)\rangle=\frac{\hbar}{4}\left[\frac{\Omega_1\Omega_2}{\Delta_1}+\frac{\Omega_2'\Omega_1'}{\Delta_2'}\right]\ . \tag{26}$$

This term corresponds to the direct coupling between the dressed state $|3(N_1,N_2)\rangle$ (adiabatically connected to the atomic ground state) and the continuum. In the absence of collisions, the photoionization results from this two-

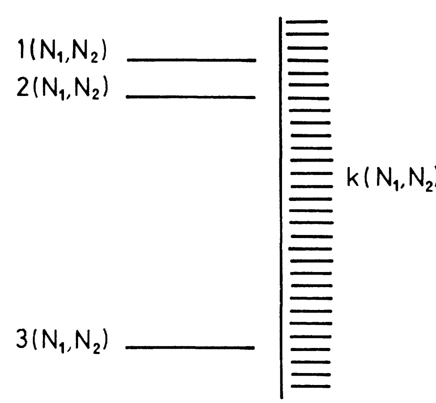

FIG. 5. Energy levels in the dressed-state picture.

photon coupling. The states of the continuum that are reached by this direct photoionization mechanism are those that have the same energy as $|3(N_1,N_2)\rangle$, i.e., those for which

$$E_{ka}=\hbar(\omega_1+\omega_2) . \tag{27}$$

On the other hand, in presence of collisional damping, two other photoionization processes are possible. First, we can have a collisionally aided excitation of $|1(N_1,N_2)\rangle$ followed by an absorption of a photon $\hbar\omega_2$ [Fig. 6(a)]. The states of the continuum that are reached by this process have energies

$$E_{k'b}=\hbar\omega_2 . \tag{28}$$

The second process [Fig. 6(b)] is a collisionally aided excitation of $|2(N_1,N_2)\rangle$ followed by an absorption of a photon $\hbar\omega_1$. The states of the continuum that are reached by this process have energies

$$E_{k''b'}=\hbar\omega_1 . \tag{29}$$

If we compare the states of the continuum that can be reached by the different processes, we find, by comparing formulas (27) and (28) on one hand and formulas (27) and (29) on the other hand,

$$E_{kk'}=\hbar\omega_1-\hbar\omega_0=\hbar\Delta_1, \tag{30a}$$

$$E_{kk''}=\hbar\omega_2-\hbar\omega_0'=\hbar\Delta_2' . \tag{30b}$$

Thus it can be deduced from the assumptions of our model that the states of the continuum reached by direct photoionization and by collisionally aided photoionization are well separated in energy and can be (at least theoretically) distinguished by measuring the kinetic energy of the ejected electron. On the other hand,

$$E_{k''k'}=\hbar(\Delta_1-\Delta_2')=\hbar\delta \tag{31}$$

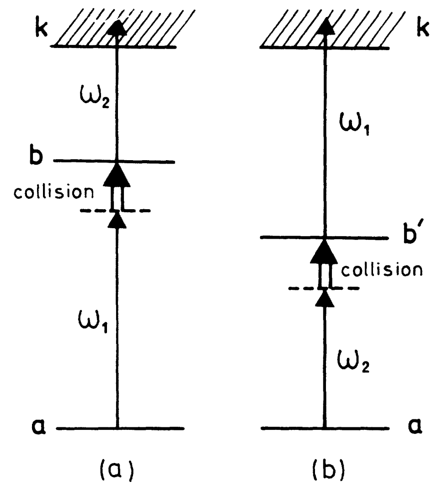

FIG. 6. Collisionally aided two-photon ionization. The pathway (a) involves the intermediate excitation of level b and the pathway (b) the intermediate excitation of level b'. Note that one photon of each mode is absorbed in each process. The pressure-induced extra resonance in two-photon ionization comes from the interference between the pathways (a) and (b).

is a small quantity and the two collisionally aided photoionization processes have to be handled together. In the following, we consider only the electrons that originate from the collisionally aided processes.

Let us consider a time interval t which is large compared to the time necessary to reach the steady-state values for ρ_{11}, ρ_{12}, and ρ_{22} [formula (7)]. We assume that the states of the field are number states. The number of photoelectrons of energy E_k generated is equal to

$$\rho_{kk}=\frac{\Omega_2^2}{4}\rho_{11}\frac{\sin^2[(\Delta_1-\Delta_k)t/2]}{[(\Delta_1-\Delta_k)/2]^2}+\frac{\Omega_1'^2}{4}\rho_{22}\frac{\sin^2[(\Delta_2'-\Delta_k)t/2]}{[(\Delta_2'-\Delta_k)/2]^2}+\frac{\Omega_1'\Omega_2}{4}\left[\rho_{12}\int_0^t dt'e^{-i(\Delta_k-\Delta_1)t'}\int_0^t dt''e^{i(\Delta_k-\Delta_2')t''}+\text{c.c.}\right] . \tag{32}$$

If we call $\rho(E_k)$ the density of states in the continuum, the total number of photoelectrons obtained through a collisionally aided process is

$$N^{(\text{coll})}=\int dE_k\rho(E_k)\rho_{kk} . \tag{33}$$

We assume that the continuum is sufficiently flat so that we can replace $\rho(E_k)$ by $\rho(\bar{E})$ with $\bar{E}\simeq E_b+\hbar\omega_1\simeq E_{b'}+\hbar\omega_2$. The integration of formula (33) with ρ_{kk} given by formula (32) then leads to

$$N^{(\text{coll})}=\frac{2\pi}{\hbar}\rho(\bar{E})\left[\left[\frac{\Omega_2^2}{4}\rho_{11}+\frac{\Omega_1'^2}{4}\rho_{22}\right]t+\frac{\Omega_1'\Omega_2}{4}\left[\rho_{12}\int_0^t dt'e^{i\delta t'}+\text{c.c.}\right]\right] . \tag{34}$$

The two first terms of formula (34) (proportional to ρ_{11} and ρ_{22}) correspond to the photoionization processes described by the diagrams of Figs. 6(a) and 6(b), respectively. The last term of formula (34) describes the interference between these two diagrams. Here again, we see that an interference occurs around $\delta \simeq 0$, i.e., in a situation where the energy exchanged with the collision partner is the same for the two pathways of Fig. 6.

More precisely, when $|\delta| t \gg 1$ the interference term contributes negligibly and we obtain, using formulas (7) and (34),

$$\frac{N^{(\text{coll})}}{t} = \frac{2\pi}{\hbar}\rho(\bar{E})\left[\frac{\Omega_1^2\Omega_2^2}{16\Delta_1^2}\frac{\gamma_{ba}+\gamma_{ba}^*}{\Gamma_b} + \frac{\Omega_1'^2\Omega_2'^2}{16\Delta_2'^2}\frac{\gamma_{b'a}+\gamma_{b'a}^*}{\Gamma_{b'}}\right] . \tag{35}$$

On the other hand, when $|\delta| t \ll 1$, there is an interference between the two pathways and we find

$$\frac{N^{(\text{coll})}(\delta=0)}{t} = \frac{2\pi}{\hbar}\rho(\bar{E})\left[\left[\frac{\Omega_1^2\Omega_2^2}{16\Delta_1^2}\frac{\gamma_{ba}+\gamma_{ba}^*}{\Gamma_b} + \frac{\Omega_1'^2\Omega_2'^2}{16\Delta_2'^2}\frac{\gamma_{b'a}+\gamma_{b'a}^*}{\Gamma_{b'}}\right] + \frac{\Omega_1\Omega_1'\Omega_2\Omega_2'}{16\Delta_1\Delta_2'}\left[\frac{\gamma_{bb'}^a}{\Gamma_{bb'}}+\text{c.c.}\right]\right] . \tag{36}$$

Here again, the initial state $|a,N_1+1,N_2+1\rangle$ and the final state $|k,N_1,N_2\rangle$ of the excitation processes shown in Fig. 6 correspond to pure number states for the field. The pressure-induced extra resonance predicted in two-photon ionization does not require coherent fields.

We should also note that the effect calculated here would probably not be easy to observe. It is essentially a "gedanken" experiment suited to show the influence of the interference between collisionally aided diagrams. Even if the interference process appears more intelligible in Fig. 6 than in Fig. 3, we think that the process described in Sec. II is more suited to an experimental investigation.

IV. TWO-PHOTON ABSORPTION OF A FOUR-LEVEL ATOM

The last example that we will consider is a four-level atom (Fig. 7) driven by four laser fields. The new fields E_3 and E_4 (having frequencies ω_3 and ω_4, respectively) drive the b-c and b'-c transitions, respectively.[13] The detunings from resonance are denoted by Δ_3 and Δ_4',

$$\hbar\Delta_3 = \hbar\omega_3 - \hbar\omega_{cb} , \tag{37a}$$

$$\hbar\Delta_4' = \hbar\omega_4 - \hbar\omega_{cb'} . \tag{37b}$$

We assume that the single-photon detunings $|\Delta_3|$ and $|\Delta_4'|$ and the two-photon detunings $|\Delta_1+\Delta_3|$ and $|\Delta_2+\Delta_4'|$ are much smaller than τ_c^{-1}. For the sake of simplicity, we also assume that

$$\omega_1+\omega_3=\omega_2+\omega_4 . \tag{38}$$

The detunings from the two-photon resonance are thus the same for the two possible excitation paths $(\Delta_1+\Delta_3=\Delta_2'+\Delta_4')$. We calculate the population $\rho_{cc}^{(4)}$ to fourth order in the field amplitudes. We denote by Ω_3 and Ω_4' the Rabi frequencies for the b-c and b'-c transitions $(\Omega_3=-d_{bc}E_3/\hbar,\ \Omega_4'=-d_{b'c}E_4/\hbar)$. Besides the terms proportional to $\Omega_1^2\Omega_3^2$, which correspond to the excitation through level b, and those proportional to $\Omega_2'^2\Omega_4'^2$, which correspond to the excitation through b', there are terms depending on $\Omega_1\Omega_2'\Omega_3\Omega_4'$ which correspond to an interference between these two pathways. It is those terms, denoted by $\rho_{cc}^{(I)}$, that we consider now. Using perturbation theory, we find

$$\rho_{cc}^{(I)} = \frac{\Omega_1\Omega_2'\Omega_3\Omega_4'}{16\Gamma_c}e^{i(\theta_1+\theta_3-\theta_2-\theta_4)}\left[\frac{1}{\Gamma_{ba}-i\Delta_1}\frac{1}{\Gamma_{ca}-i(\Delta_1+\Delta_3)}\frac{1}{\Gamma_{cb'}-i\Delta_4'} + \frac{1}{\Gamma_{b'a}^*+i\Delta_2'}\frac{1}{\Gamma_{ca}^*+i(\Delta_2'+\Delta_4')}\frac{1}{\Gamma_{cb}^*+i\Delta_3} + \left[1+\frac{\gamma_{bb'}^a}{\Gamma_{bb'}-i\delta}\right]\frac{1}{\Gamma_{ba}-i\Delta_1}\frac{1}{\Gamma_{b'a}^*+i\Delta_2'}\left[\frac{1}{\Gamma_{cb'}-i\Delta_4'}+\frac{1}{\Gamma_{cb}^*+i\Delta_3}\right]\right]+\text{c.c.} \tag{39}$$

Regrouping the terms, this expression can be written

$$\rho_{cc}^{(I)} = \frac{\Omega_1\Omega_2'\Omega_3\Omega_4'}{16\Gamma_c}e^{i(\theta_1+\theta_3-\theta_2-\theta_4)} \times\left[\frac{1}{\Gamma_{ba}-i\Delta_1}\frac{1}{\Gamma_{cb'}-i\Delta_4'}\left[\frac{1}{\Gamma_{ca}-i(\Delta_1+\Delta_3)}+\frac{1}{\Gamma_{b'a}+i\Delta_2'}\right] + \frac{1}{\Gamma_{b'a}^*+i\Delta_2'}\frac{1}{\Gamma_{cb}^*+i\Delta_3}\left[\frac{1}{\Gamma_{ca}^*+i(\Delta_2'+\Delta_4')}+\frac{1}{\Gamma_{ba}-i\Delta_1}\right] + \frac{\gamma_{bb'}^a[\Gamma_{cb'}+\Gamma_{cb}^*+i(\Delta_3-\Delta_4')]}{(\Gamma_{bb'}-i\delta)(\Gamma_{ba}-i\Delta_1)(\Gamma_{b'a}^*+i\Delta_2')(\Gamma_{cb'}-i\Delta_4')(\Gamma_{cb}^*+i\Delta_3)}\right]+\text{c.c.} \tag{40}$$

Using the relation $(\Delta_3-\Delta_4')=-(\Delta_1-\Delta_2')=-\delta$, we finally obtain

$$\rho_{cc}^{(I)}=\frac{\Omega_1\Omega_2'\Omega_3\Omega_4' e^{i(\theta_1+\theta_3-\theta_2-\theta_4)}}{16\Gamma_c(\Gamma_{ba}-i\Delta_1)(\Gamma_{b'a}^*+i\Delta_2')}\left[\frac{2\Gamma_{ca}}{(\Gamma_{ca})^2+(\Delta_1+\Delta_3)^2} + \frac{\gamma_{cb'}^a}{[\Gamma_{ca}-i(\Delta_1+\Delta_3)][\Gamma_{cb'}-i\Delta_4']} + \frac{(\gamma_{cb}^a)^*}{[\Gamma_{ca}^*+i(\Delta_1+\Delta_3)][\Gamma_{cb}^*+i\Delta_3]} + \frac{\gamma_{bb'}^a}{(\Gamma_{cb'}-i\Delta_4')(\Gamma_{cb}^*+i\Delta_3)}\left[1+\frac{\Gamma_c+\gamma_{bb'}^c}{\Gamma_{bb'}-i\delta}\right]\right]+\text{c.c.}\ , \tag{41}$$

where $\gamma_{cb'}^a$ and γ_{cb}^a are defined by expressions similar to formula (9) and

$$\gamma_{bb'}^c=\gamma_{cb}^*+\gamma_{cb'}-\gamma_{bb'}\ . \tag{42}$$

Let us now discuss Eq. (41). In the absence of collisions, all the γ_{ij}^k are equal to zero and the only term that remains is the two-photon term centered at $\Delta_1+\Delta_3=0$.[14] This term represents the interference between the two pathways for two-photon excitation via fields $\omega_1+\omega_3$ or $\omega_2+\omega_4$. Once collisions occur, there are several new resonant features centered at $\Delta_4'=0$, $\Delta_3=0$, and $\delta=0$. Let us first note that the second term of formula (41) is related to a collisionally aided excitation of the coherence between levels c and b' (see Fig. 8) identical to the one used in the four-wave mixing generation of Ref. 15. In other words, the two pathways that interfere are associated with a collisionally aided two-photon absorption [Fig. 8(a)] and a collisionally aided single-photon absorption followed by the absorption of a photon ω_4 [Fig. 8(b)]. Similarly, the third term of formula (41) is related to an interference between the two pathways shown in Fig. 9.

Finally, we find that the resonance centered at $\delta=0$ (which is analogous to the PIER 4 resonance[1]) arises from the last term of formula (41). In particular, if we assume that the fields are detuned from the single-photon and two-photon resonances ($|\Delta_3|\gg\Gamma_{cb}$, $|\Delta_4'|\gg\Gamma_{cb'}$, $|\Delta_1|\gg\Gamma_{ba}$, $|\Delta_2'|\gg\Gamma_{b'a}$, $|\Delta_1+\Delta_3|\gg\Gamma_{ca}$) we find that Eq. (41) reduces to

$$\rho_{cc}^{(I)}=\frac{\Omega_1\Omega_2'\Omega_3\Omega_4' e^{i(\theta_1+\theta_3-\theta_2-\theta_4)}}{16\Gamma_c\Delta_1\Delta_2'\Delta_3\Delta_4'}\left[A+\gamma_{bb'}^a\frac{\Gamma_c+\gamma_{bb'}^c}{\Gamma_{bb'}-i\delta}\right], \tag{43}$$

where

$$A=2\Gamma_{ca}\frac{\Delta_3\Delta_4'}{(\Delta_1+\Delta_3)^2}+\gamma_{bb'}^a-\gamma_{cb'}^a\frac{\Delta_3}{\Delta_1+\Delta_3}-\gamma_{cb}^{a*}\frac{\Delta_4'}{\Delta_1+\Delta_3}\ . \tag{44}$$

The background term A grows linearly with the pressure. The term exhibiting a resonance at $\delta=0$ has a numerator which grows quadratically with the pressure, while the width of the resonance increases linearly with pressure.

The resonance at $\delta=0$ is also obtained if we consider the situation where the two single-photon transitions from b to c and from b' to c are nearly resonant, but that $|\Delta_1|$ and $|\Delta_2'|$ are very large. In this case, the resonance at $\delta=0$ is very similar to the one described in Sec. III for the two-photon ionization. However, there are some different features. In particular, there is a phase dependence in formulas (41) and (43) that was not present in formula (36). Let us first note that $\rho_{cc}^{(I)}$ is a function of the point $\mathbf{r}$ unless one assumes that

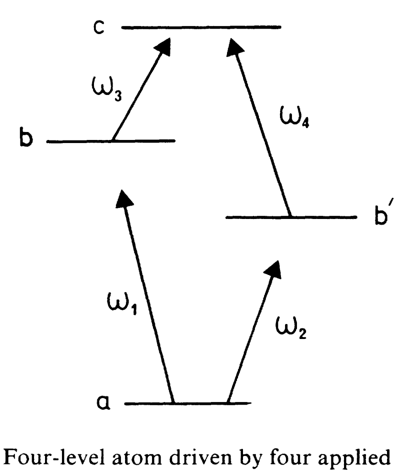

FIG. 7. Four-level atom driven by four applied laser fields.

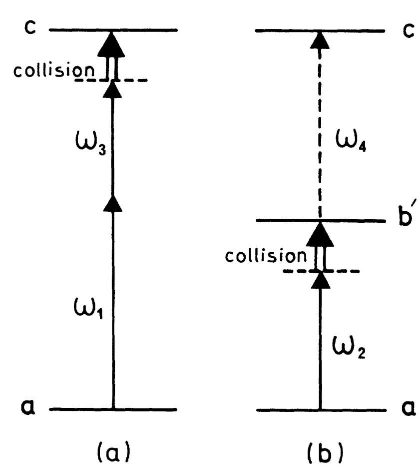

FIG. 8. Collisionally aided excitation of level c. The pathway (a) corresponds to a collisionally aided two-photon excitation, while the pathway (b) is associated to a collisionally aided two-step process with intermediate excitation of level b'. The interference between these pathways leads to a pressure-induced extra resonance centered at $\Delta_4'=0$.

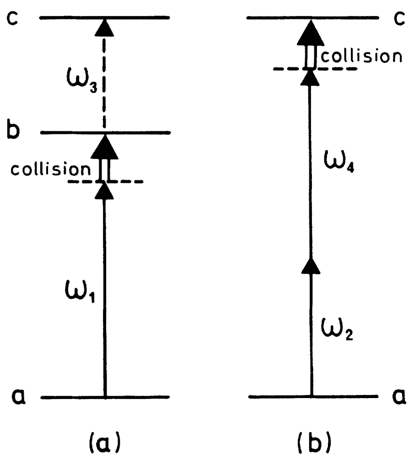

FIG. 9. Collisionally aided excitation of level c. The interference between the two pathways leads to a pressure-induced extra resonance centered at $\Delta_3=0$.

$$\mathbf{k}_1+\mathbf{k}_3=\mathbf{k}_2+\mathbf{k}_4 \; .$$

If this condition (similar to the phase-matching condition of four-wave mixing generation) is fulfilled, $\rho_{cc}^{(I)}$ is independent of $\mathbf{r}$, but still remains a function of the phases of the field through a factor $e^{i(\varphi_1+\varphi_3-\varphi_2-\varphi_4)}$. This means that the resonance centered at $\delta=0$ vanishes unless the fields are relatively coherent.

This feature can be understood if we try to describe the resonance at $\delta=0$ as an interference between quantum pathways similar to the one of Fig. 6. Let us first assume that all the fields are in number states and that the initial state of the system is $|a,N_1,N_2,N_3,N_4\rangle$. The two pathways that should be considered now are associated with the absorption of one photon ω_1 and one photon ω_3 [Fig. 10(a)] or with the absorption of one photon ω_2 and one photon ω_4 [Fig. 10(b)]. In the first case, the final state is $|c,N_1-1,N_2,N_3-1,N_4\rangle$, while in the second case, the final state is $|c,N_1,N_2-1,N_3,N_4-1\rangle$. Since the final state is not the same for the two pathways, there is no possible interference between these pathways.[16] On the other hand, if the nondiagonal matrix elements for the density matrix of the fields are not zero (as it is the case for quasiclassical fields),[17] then the number of photons is not fixed in the initial state and the interference can be restored. For example, let us assume that the initial state is

$$|\psi_i\rangle=\sum_{N_1',N_2',N_3',N_4'} c_1(N_1')c_2(N_2')c_3(N_3')c_4(N_4') \times|a,N_1',N_2',N_3',N_4'\rangle \; . \tag{45}$$

The probability of finding the system in the final state $|\psi_f\rangle=|c,N_1,N_2,N_3,N_4\rangle$ is proportional to

$$\begin{aligned}|\langle\psi_f|U|\psi_i\rangle|^2\sim|&c_1(N_1+1)c_2(N_2)c_3(N_3+1)\\ &\times c_4(N_4)[(N_1+1)(N_3+1)]^{1/2}\\ &+c_1(N_1)c_2(N_2+1)c_3(N_3)c_4(N_4+1)\\ &\times[(N_2+1)(N_4+1)|^2]^{1/2} \; .\end{aligned} \tag{46}$$

To obtain the probability to find the atom in state c, we have to sum formula (46) over N_1, N_2, N_3, and N_4. We see that the interference term is equal to zero unless we have $c_i(N_i)$ and $c_i(N_i+1)$ simultaneously different from zero for the four fields.

In other words, to obtain a resonance on the population of the c level, we have to start with a coherence

$$\langle A,N_1+1,N_2,N_3+1,N_4|\rho|A,N_1,N_2+1,N_3,N_4+1\rangle \; ,$$

where $|A,N_1,N_2,N_3,N_4\rangle$ is the dressed state adiabatically connected to the uncoupled state $|a,N_1,N_2,N_3,N_4\rangle$. Then collisions act on this coherence to create

$$\langle B,N_1,N_2,N_3+1,N_4|\rho|B',N_1,N_2,N_3,N_4+1\rangle \; ,$$

where $|B,N_1,N_2,N_3,N_4\rangle$ and $|B',N_1,N_2,N_3,N_4\rangle$ are the dressed states connected to $|b,N_1,N_2,N_3,N_4\rangle$ and $|b',N_1,N_2,N_3,N_4\rangle$, respectively. Finally, the action of the fields 3 and 4 leads to a population $\langle c,N_1,N_2,N_3,N_4|\rho|c,N_1,N_2,N_3,N_4\rangle$. In this approach, which is essentially similar to the one already developed in Ref. 4, the resonance at $\delta=0$ arises from the collisionally aided excitation of the coherence between the dressed states B and B'.

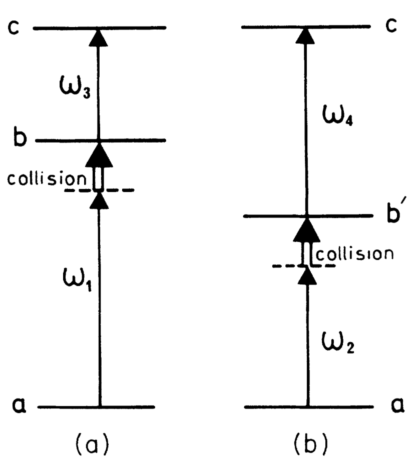

FIG. 10. Collisionally aided excitation of level c. The pathway (a) corresponds to a collisionally aided two-step excitation with intermediate excitation of level b. The pathway (b) is associated to a similar process with intermediate excitation of level b'. The interference between these pathways leads to a pressure-induced extra resonance centered at $\delta=0$.

CONCLUSION

In conclusion, we have presented three different examples of pressure-induced extra resonances that can be observed in nonlinear spectroscopy. We have shown that all these resonances can be qualitatively interpreted in terms of interference between quantum pathways, each pathway involving a collisionally aided excitation. Finally, we have shown that the resonances can be obtained in some cases with incoherent fields while, in other cases, coherent fields are required.

Implicit in our approach has been the neglect of any effects arising from the atoms' velocity. As long as the single-photon and two-photon detunings $|\Delta_1|$, $|\Delta_2'|$, $|\Delta_3|$,

$|\Delta_4'|$, $|\Delta_1+\Delta_3|$ are all much greater than the Doppler widths associated with their corresponding transitions, one is at liberty to neglect the Doppler shifts associated with these terms. On the other hand, $|\delta|$ is a small quantity compared with $|\Delta_1|$ or $|\Delta_2'|$, consequently, one should include any effects of residual Doppler shifts in all terms containing δ. The results are then modified by replacing δ by $\delta-(\mathbf{k}_1-\mathbf{k}_2)\cdot\mathbf{v}$ and averaging over a Maxwellian distribution of velocities having most probable speed u. If $Ku \ll \Gamma_{bb'}$ ($\mathbf{K}=\mathbf{k}_1-\mathbf{k}_2$), none of the results are changed. If $Ku \gg \Gamma_{bb'}$, the results are modified as follows: (a) In Eq. (11), the first term no longer contributes and the second term becomes a Gaussian of width Ku; (b) in Eq. (34), the PIER contribution no longer varies as t for $\delta \sim 0$; (c) in Eq. (43), the PIER contribution is again proportional to a Gaussian having width Ku. The ratio $Ku/\Gamma_{bb'}$ is determined in a large part by the energy separation of levels b and b'. To observe PIER, it is thus best to have two nearby energy levels.

ACKNOWLEDGMENTS

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[5]In fact, the conditions $|\Omega_1/\Delta_1| \ll 1$ and $|\Omega_2'/\Delta_2'| \ll 1$ are necessary conditions to justify a perturbative expansion, but they are not sufficient. Other conditions [see formula (10) and Ref. 11) should also be verified.

[6]In the relaxation terms, we neglect the coupling between the coherence $\rho_{bb'}$ and the population ρ_{aa}. Such an assumption is generally justified because the term that has been neglected leads to nonsecular contributions. However, there are a few cases where this term should be kept [see G. Grynberg and M. Pinard, Europhys. Lett. **1**, 129 (1986)].

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[10]Actually the coherences given by Eqs. (7) are the reduced coherences, which are related to the real coherences $\langle i(N_1,N_2)|\rho|j(N_1,N_2)\rangle$ by the relation $\rho_{ij} = \sum_{N_1,N_2} \langle i(N_1,N_2)|\rho|j(N_1,N_2)\rangle$.

[11]The ratio (12) should, however, remain smaller than 1 if one wants the perturbation expansion to be correct. In particular, the higher-order terms are negligible only if the ratio (12) is smaller than unity.

[12]The calculation for $\delta \sim 0$ in the dressed-state basis requires one to solve the coupled equations of evolution in the subspace generated by $|1(N_1,N_2)\rangle$ and $|2(N_1,N_2\rangle$.

[13]A practical way to realize such an excitation would be to have two light sources of frequencies ω_1 and ω_3 and two acousto-optic modulators to obtain the other frequencies ω_2 and ω_4 by shifting the frequencies ω_1 and ω_3. Because of the small value of $|\omega_1-\omega_2|$ and $|\omega_3-\omega_4|$, the levels b and b' would be fine or hyperfine sublevels, or even Zeeman sublevels whose degeneracy can be shifted by applying a static magnetic field.

[14]The shift of the two-photon resonance due to the imaginary part of Γ_{ca} has been included in $(\Delta_1+\Delta_3)$ when we have written formula (41).

[15]E. Giacobino and P. R. Berman, Phys. Rev. Lett. **58**, 21 (1987).

[16]The same argument can be applied for the diagrams of Figs. 7 and 8.

[17]See, for example, R. J. Glauber, in *Quantum Optics and Electronics,* edited by C. de Witt, A. Blandin, and C. Cohen-Tannoudji (Gordon and Breach, New York, 1965), p. 63.