PHYSICAL REVIEW A VOLUME 21, NUMBER 3 MARCH 1980

Two-photon near-resonance scattering of a time-dependent light beam

Maciej Kolwas
Institute of Physics of the Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warszawa, Poland

(Received 13 February 1979)

Time-dependent spectra of light emitted after two-photon excitation with nonresonant intermediate state are studied by the perturbation method. Two components are distinguished: a slow one I_s connected with the excited-state population, and a fast one I_f connected with the double-quantum optical coherence. For large detuning of the two-photon frequency from the excited–ground-state energy separation, the fluorescent light is found to be $I_s - |I_f|$, and the Raman-scattered light is I_f. The influence of statistics of light, laser linewidth, spectral bandwidth of the detector, and transfer of coherence from the ground to the excited state are also taken into consideration.

I. INTRODUCTION

In the last few years there has been great interest in the time-dependent phenomena induced by the laser light beam due to the introduction of tunable dye lasers—strong, coherent, narrow-linewidth light sources that can also produce short pulses.

Time-resolved fluorescence and resonance Raman scattering for one-photon excitation were studied by Szöke and Courtens.[1] They confirmed, with the help of the adiabatic-following approximation, that the Raman scattering and two-photon absorption are adiabatic processes, while fluorescence and stepwise two-photon absorption are nonadiabatic ones. Grischkowsky[2] has studied similar problem in the terms of adiabatic states. He divided the excitation into coherent part which maintains a definite phase relationship with the driving field and incoherent part induced by the relaxation processes. However the interpretation of his experiment seems to be more adequate in terms of adiabacity and nonadiabacity rather than coherence versus incoherence.

The problem of the stationary light-induced fluorescence and resonance Raman scattering has been studied by many authors in the one-photon excitation case.[3] In this paper we give as a specific case the spectrum after two-photon excitation.

Two-photon processes in the three-level system for the transient and steady-state cases have been studied by Brewer and Hahn[4] in the Bloch-like model. Their exact solutions were verified experimentally by the radio-frequency transient NMR method.[5]

The adiabatic-following model for two-photon transitions was used by Grischkowsky and Loy[6] to describe two-photon resonant-enhanced parametric-generation processes.

The present paper will deal with time-dependent spectra of spontaneously emitted light after two-photon time-dependent excitation with an off-resonant intermediate state[7]; i.e., we study the time evolution of the spectrum of fluorescence and Raman-scattered light. These phenomena are studied by the perturbation method with respect to the ratio of the electric field of exciting light ϵ (exactly the Rabi frequency) to the detuning of the intermediate state from resonance: Δ_{er} and Δ_{gr}. First, we find the excited-state time-dependent density matrix $\rho_{ee'}(t)$. As a special case we discuss here the experimental situation of Bassini *et al.*,[8] in which the problem of transients produced by Doppler-free two-photon near-resonance excitation was studied.[9]

Then using the quantum regression theorem, we find the time-dependent spectrum of the emitted light. Two components of the spectrum are distinguished: the first, connected with the population of the excited state is called here the slow component I_s, and the second, connected with the double-quantum optical coherence, called the fast component I_f. The fluorescence and Raman part consist generally of both slow and fast components.[10] As an example of the utilization of the fourth-order formulas we discuss three special cases:

(a) the spectrum of emitted light after a stationary excitation; the spectrum consists of two peaks: the fluorescence component and the Raman component;

(b) the time-dependent spectrum of light after step excitation; we show the time development of the spectrum from a nonstationary situation to the stationary state of two peaks; and

(c) the time-dependent spectrum of light after adiabatic excitation—the case of a relatively large detuning Δ of the two-photon frequency from resonance.

The experimental work of Liran *et al.*[11] can be interpreted with the help of our formulas for the time-dependent spectrum.

After the introduction given in this section, we describe in Sec. II the physical basis of this work: the atomic system and light. Then we define the time-dependent spectrum of light in Sec. III. In Sec. IV the total intensity of emitted light, by means of the excited-state density matrix, is calculated. To understand its properties, given in Sec. VI, we discuss first the correlation function of light in Sec. V. The time-dependent spectrum of light and its properties are described in Secs. VII and VIII.

II. ATOMIC SYSTEM AND LIGHT BEAMS

The atomic system (Fig. 1) consists of four states: the ground g, the intermediate r, the excited e, and the final state f. States e, r, and g can have a substructure (e', r', g') and interact with two (or one) laser light beams, with frequencies ω_1 and ω_2. We assume for simplicity that the light with the frequency $\omega_1(\omega_2)$ directly influences optical coherences between e and r (r and g) states only (Fig. 1). In special cases we will restrict ourselves to one-beam excitation, putting $\omega_1=\omega_2$. The two-photon frequency detuning from resonance Δ is assumed to be much smaller than one-photon detunings Δ_{er} and Δ_{rg}; moreover, Δ_{er} and Δ_{rg} are larger than any frequency appearing in this paper except the optical one. Therefore, we assume that the light fields are adiabatic with respect to Δ_{er} and Δ_{rg}, i.e., $|\partial\epsilon/\partial t| \ll \epsilon\Delta_{er}$ and Δ_{rg}. The separation of the final state f and the excited state e is taken to be off-resonant with respect to ω_1 and ω_2. Therefore, we neglect stimulated transitions between e and f states. Hence the Raman effect described here is so called the spontaneous Raman effect in contrast to the stimulated one.

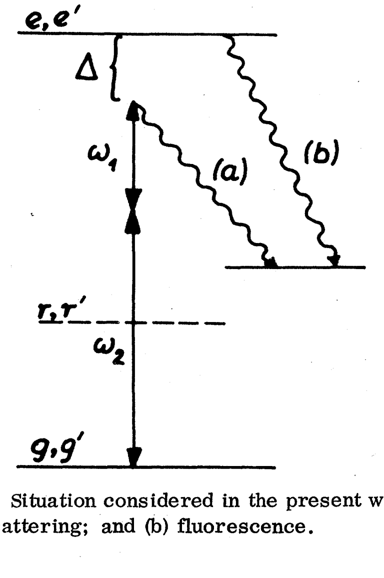

FIG. 1. Situation considered in the present work: (a) Raman scattering; and (b) fluorescence.

III. TIME-DEPENDENT SPECTRUM OF LIGHT

Spectral measurements[1] are made by inserting a frequency-sensitive device, usually a linear filter, in front of the detector. The "spectrum" of light is the record of the detected light signal as a function of the frequency setting of the filter Ω with a certain finite filter bandwidth α. The simplest possible filter is represented by the function

$$F(t)=\exp[-(i\Omega+\alpha)t]\,\theta(t)\,, \tag{1}$$

where $\theta(t)$ is the unit step function starting at $t=0$, and α determines the width of the transfer function with its center at Ω. One can show[12] that this formula describes a Fabry-Perot filter with $\alpha = c(1-r^2)/2d$, where d is the distance between the plates and r is the amplitude-reflection coefficient. The filtered, "observed" field is the convolution of the field $E(t)$ and the filter's transfer function $F(t-t')$:

$$V(t)=\int_{-\infty}^{\infty} dt' E(t')F(t-t')\,. \tag{2}$$

Light intensity detected beyond the filter is given by

$$I(t;\Omega,\alpha)=|V(t)|^2=2\alpha^2\int_{-\infty}^{t} dt' e^{-2\alpha(t-t')} \times \mathrm{Re}\int_0^{\infty} d\tau\, e^{-(i\Omega+\alpha)\tau} E^*(t')E(t'-\tau)\,, \tag{3}$$

The intensity I depends on time t and the frequency Ω, therefore formula (3) describes time-dependent spectrum of light.[1] We are interested in an electric field $E(t)$, which has been emitted by an atomic system. Describing E by its source[13] (atomic dipole moment D), one obtains

$$I(t;\Omega,\alpha)\sim 2\alpha^2\int_{-\infty}^{t} dt' e^{-2\alpha(t-t')} \times \mathrm{Re}\int_0^{\infty} d\tau e^{-(i\Omega+\alpha)\tau}\langle D_+(t')D_-(t'-\tau)\rangle\,, \tag{4}$$

where D_- and D_+ are the lowering ($D_-=d|f\rangle\langle e|$) and the raising ($D_+=d|e\rangle\langle f|$) parts of the electric dipole moment operator of the atom, d being equal to the matrix element $\langle e|D|f\rangle$.

Thus to calculate the time-dependent spectrum, it is necessary to know the two-time correlation function of the atomic dipole moment $\langle D_+(t)D_-(t-\tau)\rangle$. Before studying this problem let us consider a simpler case of the total time-dependent intensity of light emitted by an atomic system.

IV. TOTAL TIME-DEPENDENT LIGHT INTENSITY

In order to have the time-dependent signal not perturbed by a filter it is necessary to have a broadband filter with very large α. The intensity of the detected light is then frequency integrated and can be entirely described by the density matrix[14] of the excited state $\rho_{ee'}(t)$:

$$I(t)\sim\langle D_+(t)D_-(t)\rangle=\sum_{e,e',f}\rho_{ee'}(t)D_{e'f}D_{fe}. \tag{5}$$

Therefore we focus our attention on the equations for the evaluation of the density-matrix elements needed to calculate $\rho_{ee'}$. Under the rotating-wave approximation (RWA) these equations have the form[15]

$$\dot\rho_{ee'}=-(\Gamma_e+i\omega_{ee'})\rho_{ee'} + i\sum_r(D_{er}\rho_{re'}E_1-\rho_{er}D_{re'}E_1^*)\,, \tag{6}$$

$$\dot\rho_{eg}=-(\Gamma_{eg}+i\omega_{eg})\rho_{eg} + i\sum_r(D_{er}\rho_{rg}E_1-\rho_{er}D_{rg}E_2)\,, \tag{7}$$

$$\dot\rho_{er}=-(\Gamma_{er}+i\omega_{er})\rho_{er} + i\sum_{e',r',g'}(D_{er'}\rho_{r'r}E_1-\rho_{ee'}D_{e'r}E_1-\rho_{eg}D_{gr}E_2^*)\,, \tag{8}$$

$$\dot\rho_{rg}=-(\Gamma_{rg}+i\omega_{rg})\rho_{rg} + i\sum_{e,g',r'}(D_{re}\rho_{eg}E_1^*+D_{rg'}\rho_{g'g}E_2-\rho_{rr'}D_{r'g}E_2). \tag{9}$$

Γ_i is the natural width of the ith level, $\Gamma_{ij}=(\Gamma_i+\Gamma_j)/2$.

The light is described classically; so the effect of spontaneous emission was taken into account by adding proper terms to the density-matrix-elements evolution equations.[16] If any nonradiative relaxation exists in the atomic system, it can be described by a modification of Γ_i and Γ_{ij}. Generally the strongest relaxation is due to phase-disturbing (inelastic and quasielastic) collisions. In this case $\Gamma_{ij}>(\Gamma_i+\Gamma_j)/2$. Modification of Γ_i can be caused by the inelastic collisions only.[17]

The electric field of the light E is put in the form

$$E_i=\exp[-i\omega_i t-i\varphi_i(t)]\bar\epsilon_i\,,\quad i=1,2\,, \tag{10}$$

where $\bar\epsilon_i$ is the slowly varying time-dependent envelope of the electric field of ith light beam intensity; $\varphi(t)$ is the phase of the electric field of light, being a stochastic function of time. The introduction of $\varphi(t)$ allows us to generate the spectral width of light. In a general case we will construct the correlation function of light from the complex amplitudes[18] $\epsilon_i=\bar\epsilon_i\exp[-i\varphi_i(t)]$.

Because we have assumed that the intermediate level r is off-resonant, one can transform Eqs. (7) and (8) to nondifferential ones. Performing the transformation to the rotating frame:

$$\sigma_{er}=\rho_{er}e^{i\omega_1 t},\ \sigma_{rg}=\rho_{rg}e^{i\omega_2 t},\quad \sigma_{eg}=\rho_{eg}e^{i(\omega_1+\omega_2)t}\,, \tag{11}$$

we get

$$\dot\rho_{ee'}=-(\Gamma_e+i\omega_{ee'})\rho_{ee'} + i\sum_r(D_{er}\sigma_{re'}\epsilon_1-\sigma_{er}D_{re'}\epsilon_1^*)\,, \tag{12}$$

$$\dot\sigma_{eg}=-(\Gamma_{eg}+i\Delta_{eg})\sigma_{eg} + i\sum_r(D_{er}\sigma_{rg}\epsilon_1-\sigma_{er}D_{rg}\epsilon_2)\,, \tag{13}$$

$$\sigma_{er}(t)=\sum_{e',g',r'}(D_{er'}\rho_{r'r}\epsilon_1-\rho_{ee'}D_{e'r}\epsilon_1 - \sigma_{eg}D_{gr}\epsilon_2^*)/\Delta_{er}\,, \tag{14}$$

$$\sigma_{rg}(t)=\sum_{e,g',r'}(D_{re}\sigma_{eg}\epsilon_1^*+D_{rg}\rho_{g'g}\epsilon_2 - \rho_{rr'}D_{r'g}\epsilon_2)/\Delta_{rg}\,. \tag{15}$$

These equations can be solved now by the successive-approximation method with respect to $\epsilon_1 D_{er}/\Delta_{er}$ and $\epsilon_2 D_{rg}/\Delta_{rg}$, starting from the ground-state density matrix $\rho_{gg'}(t)$ as a zero order. We assume that $\rho_{gg'}$ can be also a function of time. This general choice of the zero order allows one to describe the influence of the transfer of the coherence[19] from the ground state to the observed light emitted by atoms.

We are interested in the second- and fourth-order solutions. In the second order, the double-quantum optical coherences are created. Let us write them for future reference:

$$^{(2)}\sigma_{eg}(t)=\sum_{r,g'}\frac{i}{\Delta_{rg}}\int_{-\infty}^{t}d\tau\,\exp[(\Gamma_{eg}+i\Delta_{eg})(\tau-t)] \times D_{er}D_{rg'}\rho_{g'g}(\tau)\epsilon_2(\tau)\epsilon_1(\tau). \tag{16}$$

In the fourth order, the excited-state density matrix $^{(4)}\rho_{ee'}$ is found to be

$$^{(4)}\rho_{ee'}(t)=\int_{-\infty}^{t}d\tau\int_{-\infty}^{\tau}d\tau'\,e^{-(\Gamma_e+i\omega_{ee'})(t-\tau)}L'(\tau') \times\{g^{(2)}(\tau',\tau)e^{(\Gamma_{eg}-i\Delta_{e'g})(\tau'-\tau)} +g^{(2)}(\tau,\tau')e^{(\Gamma_{eg}+i\Delta_{eg})(\tau'-\tau)}\}\,, \tag{17}$$

where $\omega_{ee'}$ is the energy separation within the excited state,

$$L'(\tau')=\sum_{gg'r}D_{er}D_{rg}\rho_{gg'}(\tau')D_{g'r}D_{re'}/|\Delta_{er}\Delta_{rg}|.$$

A special case of Eq. (17) was given in Ref. 20.

V. CORRELATION FUNCTION OF LIGHT

Because of the assumption that each of the laser beams influences only one optical coherence $(\omega_1 - \rho_{er}, \omega_2 - \rho_{rg})$, the correlation function of the exciting light is given by

$$\mathcal{G}^{(2)}(\tau', \tau)=\epsilon_2^*(\tau')\epsilon_1^*(\tau')\epsilon_2(\tau)\epsilon_1(\tau)=\mathcal{G}^{(2)*}(\tau, \tau'). \quad (18)$$

The over-bar describes the averaging over stochastic phases φ_i.

As a specific case we will consider now excitation by one laser beam; therefore we put $\omega_1=\omega_2$. A number of authors (e.g., Refs. 21, 22) have devised a model of laser light based on the assumption of a fixed field amplitude with a small randomly varying frequency, leading to phase diffusion (one-mode laser working well above threshold). In that model the frequency modulation function $\tilde{\omega}(t)=\dot{\varphi}(t)$ is assumed to be governed by a real stationary joint Gaussian random process with the correlation time much smaller than any other time we need to consider. The first-order correlation function of the light calculated under those assumptions is as follows[21]:

$$\Gamma(t)=Ie^{-i\omega t-b|t|}, \quad (19)$$

where ω is the light frequency. The power spectrum γ of the field is thus a Lorentzian function

$$\gamma(\Omega)=I\{2b/[(\omega-\Omega)^2+b^2]\}, \quad (20)$$

i.e., b is the spectral width of light. The second-order correlation function of the stationary light is in this case given by

$$\mathcal{G}^{(2)}(\tau, \tau')=I^2e^{-4b|\tau-\tau'|}. \quad (21)$$

When the intensity of light is time dependent, $\mathcal{G}^{(2)}(\tau, \tau')$ is not as simple as in Eq. (21). Assuming that the process causing time variation of laser light intensity (e.g., pulsation or modulation) is statistically independent of the stochastic fluctuation of phase (generating the spectral width of the light), one obtains

$$\mathcal{G}^{(2)}(\tau, \tau')=\mathcal{G}_{\text{I}}^{(2)}(\tau, \tau')e^{-4b|\tau-\tau'|}, \quad (22)$$

with

$$\mathcal{G}_{\text{I}}^{(2)}(\tau, \tau')=\tilde{\bar{\epsilon}}_2^*(\tau)\tilde{\bar{\epsilon}}_1^*(\tau)\tilde{\bar{\epsilon}}_2(\tau')\tilde{\bar{\epsilon}}_1(\tau')$$
$$=[I_2(\tau)I_1(\tau)I_2(\tau')I_1(\tau')]^{1/2}. \quad (23)$$

This approximation seems to be good when the light is modulated outside the laser cavity. In other cases one ought to define the joint correlation function of the phase fluctuation and the intensity variation, putting, e.g.,

$$\mathcal{G}^{(2)}(\tau, \tau')=\mathcal{G}_{\text{I}}^{(2)}(\tau, \tau')e^{-4b|\tau-\tau'|}\mathcal{G}_{\varphi,\text{I}}^{(2)}(\tau, \tau'). \quad (24)$$

$\mathcal{G}_{\varphi,\text{I}}^{(2)}(\tau, \tau')$ can be assumed to have the exponential form

$$\mathcal{G}_{\varphi,\text{I}}^{(2)}=e^{-|\tau-\tau'|/\tau_c^{\varphi,I}}.$$

In this case b does not define the spectral width of the laser light.

When the laser is working in the multimode regime (with free-runing modes) the second-order correlation function by analogy to Eq. (22) is

$$\mathcal{G}^{(2)}(\tau, \tau')=2\mathcal{G}_{\text{I}}(\tau, \tau')e^{-2b|\tau-\tau'|}. \quad (25)$$

If one ought to take into consideration the motion of atoms, the excited-state density matrix $\rho_{ee'}$ should be integrated over velocities with a proper velocity distribution of atoms $W(v)$, usually the Maxwellian one:

$$\bar{\rho}_{ee'}(t)=\int_0^\infty \rho_{ee'}(t, \vec{v})\, W(v)d^3v. \quad (26)$$

The density matrix $\rho_{ee'}$ depends in this case on the velocity v through the correlation function of the light:

$$\mathcal{G}_{\text{v}}^{(2)}(\tau, \tau')=\mathcal{G}^{(2)}(\tau, \tau')\exp[2i(\vec{k}_1+\vec{k}_2)\vec{v}(\tau'-\tau)], \quad (27)$$

i.e., the electric field of the light E in the frame moving with the atom is

$$E_i=\epsilon_i\exp[i(\omega_i+\vec{k}_i\vec{v})t], \quad (28)$$

where $\vec{k}\vec{v}$ is the first-order Doppler shift. In the case of Doppler-free experiment,[9] $\vec{k}_1+\vec{k}_2=0$ and $\mathcal{G}^2(\tau, \tau')$, as well as $\rho_{ee'}$, are velocity independent.

VI. PROPERTIES OF THE TOTAL TIME-DEPENDENT LIGHT

Equation (17) describes the time dependence of the coherence $(e'\neq e)$ and population $(e'=e)$ in the excited state induced by the time-dependent light beam. The time dependence of $\rho_{ee'}$ can be induced by:

(a) The time dependence of the ground-state (zero order in our case) density matrix $\rho_{gg'}$, e.g., a double-quantum transfer of coherence from the ground to the excited state. The efficiency of the transfer is resonant and has a maximum for $\omega_{ee'}=\pm|\Delta\pm\omega_{gg'}|$, where $\omega_{gg'}$ is the ground-state frequency

$$\rho_{gg'}=a_{gg'}e^{-i\omega_{gg'}t}. \quad (29)$$

(b) The time dependence of the correlation function of the light $\mathcal{G}^2(\tau, \tau')$. Of course to induce coherence in the excited state, the excited-state frequency $\omega_{ee'}$ ought to be present in the Fourier spectrum of the correlation function of the light and/or in the ground-state density-matrix time evolution.

Equation (17) can be specialized for this case, which has been investigated experimentally by Bassini *et al.*[8]; one only ought to put $e=e'$ (no ex-

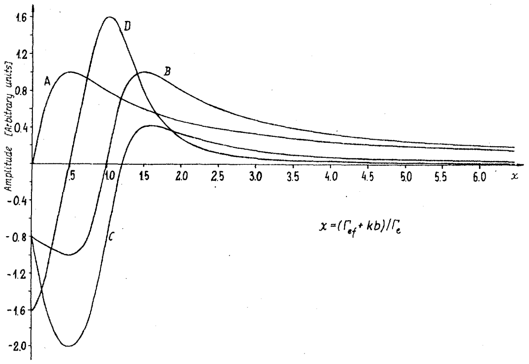

FIG. 2. Dependence of coefficients A, B, C, and D of four terms in the excited-state density matrix $\rho_{ee}=A+B\exp(-\Gamma_e t)+\exp(-\gamma_1 t)\,[C\cos(\Delta t)+D\sin(\Delta t)]$ [See Eq. (30)] on the value of Γ_{eg} (i.e., transverse relaxation) and kb (statistics of light k or spectral light width b) for $\Delta=0.5\,\Gamma_e$.

cited-state structure) and $\omega_1=\omega_2$. In Ref. 8 the laser light was externally and suddenly switched on; the rise time was smaller than the lifetime of the excited state and the inverse of two-photon detuning from the resonance Δ^{-1}, so one can assume that the intensity correlation function $\mathcal{G}_1^2$ is constructed from the step function $\theta(t)$. Under this condition, using Eqs. (22) or (25), Eq. (17) takes the form

$$\rho_{ee}(t)=L'(t)\left[\frac{\gamma_1/\Gamma_e}{\gamma_1^2+\Delta^2}-\frac{\gamma_2/\Gamma_e}{\gamma_2^2+\Delta^2}\exp(-\Gamma_e t)+e^{-\gamma_1 t}\left(\frac{\gamma_1\gamma_2-\Delta^2}{(\gamma_1^2+\Delta^2)(\gamma_2^2+\Delta^2)}\cos(\Delta t)-\frac{(2\gamma_1-\Gamma_e)\Delta}{(\gamma_1^2+\Delta^2)(\gamma_2^2+\Delta^2)}\sin(\Delta t)\right)\right], \quad (30)$$

where $\gamma_1=\Gamma_{eg}+kb$, $\gamma_2=\Gamma_{eg}-\Gamma_e+kb$; $k=4$ for the monomode laser well above threshold, or $k=2$ for multimode one. The formula (30) consists of three terms: the first, independent of time, gives the values of ρ_{ee} reached after a transient regime; it describes the static two-photon Doppler-free resonance; the second, decaying with the lifetime of the excited state (longitudinal relaxation time Γ_e^{-1}); the third, decaying with the lifetime of the optical coherence [transverse relaxation time $\gamma_1^{-1}=(\Gamma_{eg}+kb)^{-1}$] and oscillating with the frequency equal to the detuning Δ.

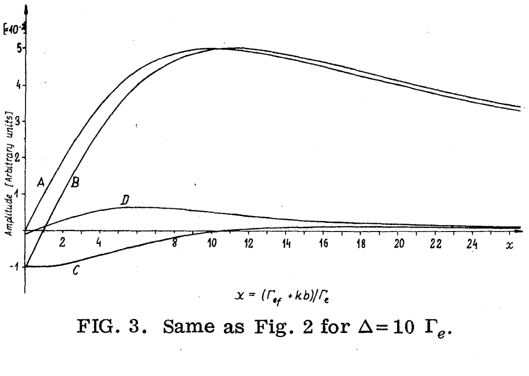

FIG. 3. Same as Fig. 2 for $\Delta=10\,\Gamma_e$.

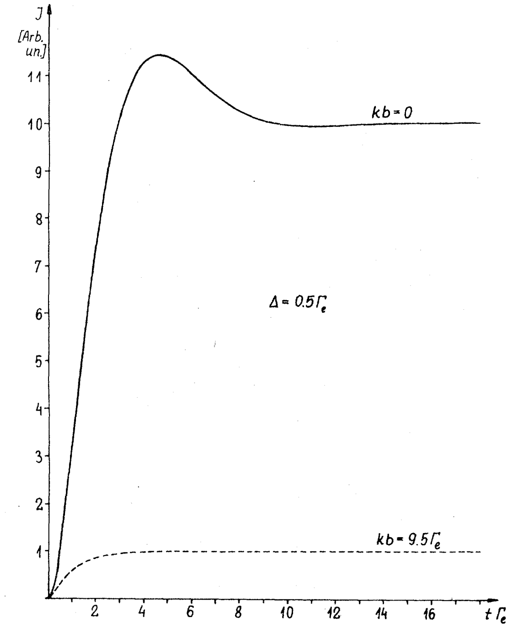

FIG. 4. Time evolution of the total emitted light for two values of exciting light width: $kb=0$ and $kb=9.5$ for $\Delta_{eg}=0.5\,\Gamma_e$.

The dependence of weights of the three terms in Eq. (30) on the exciting light width b (for constant Γ_{eg}) or on transverse relaxation rate Γ_{eg} (b=const) are drawn in Figs. 2 and 3. It seems to be interesting that for the exciting light width b of the order of the natural width Γ_e, the temporal character of ρ_{ee} depends strongly on the value of b (Figs. 4, 5). The oscillations appear because frequency Δ exists in the Fourier spectrum of the exciting

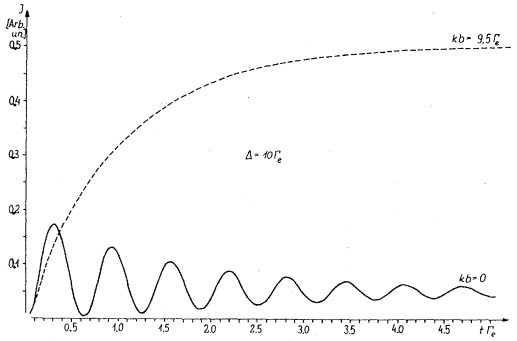

FIG. 5. Time evolution of the total emitted light for two values of exciting light width: $kb=0$ and $kb=9.5$ for $\Delta=10\,\Gamma_e$.

light intensity. It can be said that the oscillations are due to the coherent excitation at $t=0$ and frequency-unresolved observation of the Raman component and the resonance fluorescence component. To end this section let us remark that Eq. (17) also describes:

(i) quantum beats[23] after two-photon excitation, when the intensity of the laser light is changed sufficiently quickly;

(ii) Dodd-Series-type[24] (here double-quantum) experiment, i.e., the creation of excited-state coherence by modulated excitation;

(iii) the transfer of coherence from the ground to the excited state and its influence on time-dependent phenomena; and

(iv) the dependence of the emitted light intensity on the fluctuations, statistical properties, as well as a mode structure of the laser light.

VII. TIME-DEPENDENT SPECTRUM AFTER TWO-PHOTON EXCITATION

To calculate the time-dependent Raman and fluorescence components of emitted light, it is necessary to know the two-time correlation function of the atomic dipole moment $\langle D_+(t')D_-(t'-\tau)\rangle$ [see Eq. (4)]. It follows from the quantum regression theorem, that for $\tau>0$ the two-time average $\langle D_+(t')D_-(t'-\tau)\rangle$ satisfies the same equation of motion as the one-time average $\langle D_+(t')\rangle=\rho_{fe}(t')D_{ef}$ fully described by $\rho_{fe}(t')$. Therefore we have to find the time evolution of ρ_{fe}. Equations for the density-matrix elements, which are necessary to find ρ_{fe}, are

$$\dot{\rho}_{ef}=-(\Gamma_{ef}+i\omega_{ef})\rho_{ef}+i\sum_{r}D_{er}\rho_{rf}E_2, \tag{31}$$

$$\dot{\rho}_{rf}=-(\Gamma_{rf}+i\omega_{rf})\rho_{rf}+i\sum_{eg}(D_{rg}\rho_{gf}E_1+D_{re}\rho_{ef}E_2^*), \tag{32}$$

$$\dot{\rho}_{gf}=-(\Gamma_{gf}+i\omega_{gf})\rho_{gf}+i\sum_{r}D_{gr}\rho_{rf}E_2^*. \tag{33}$$

It ought to be remarked that Eqs. (31)–(33) are independent of Eqs. (6)–(9). Starting from zero-order approximation

$$^{(0)}\rho_{ef}(t)=\exp[-(\Gamma_{ef}+i\omega_{ef})(t-t')]\,\rho_{ef}(t')\,\theta(t-t'), \tag{34}$$

$$^{(0)}\rho_{gf}t=\exp[-(\Gamma_{gf}+i\omega_{gf})(t-t')]\,\rho_{gf}(t')\theta(t-t'), \tag{35}$$

one can find the second-order correction to ρ_{ef}:

$$\begin{aligned}^{(2)}\rho_{ef}(t)=\sum_{rg}\frac{-iD_{er}D_{rg}}{\Delta_{er}}\rho_{gf}(t')\\ &\times\exp[-(\Gamma_{ef}+i\omega_{ef})t]\exp[(\Gamma_{gf}+i\omega_{gf})t']\\ &\times\int_{t'}^{t}d\tau\exp[(\Gamma_{ef}-\Gamma_{gf}+i\omega_{eg})\tau]E_1(\tau)E_2(\tau).\end{aligned} \tag{36}$$

$^{(2)}\rho_{ef}$ was found assuming very large Δ_{er} and remembering that $\omega_{ef}-\omega_{rf}-\omega_2=\Delta_{er}$ and $\omega_{rf}+\omega_2=-\Delta_{er}+\omega_{ef}$. Now using the quantum regression theorem[25] one obtains

$$\begin{aligned}\langle D_+(t')D_-(t'-\tau)\rangle=\exp[-(\Gamma_{ef}-i\omega_{ef})\tau]\langle D_{ef}D_{fe}\rangle(t'-\tau)+\frac{\langle d_{ef}D_{fe}\rangle(t'-\tau)}{i\Delta_{er}}\exp[-(\Gamma_{ef}-i\omega_{ef})t']\\ \times\exp[(\Gamma_{gf}-i\omega_{gf})(t'-\tau)]\int_{t'}^{t}E_1^*(\tau')E_2(\tau')\exp[(\Gamma_{ef}-\Gamma_{gf}-i\omega_{eg})\tau']\,d\tau'.\end{aligned} \tag{37}$$

In Eq. (37) we have one-time correlation functions only,

$$\langle d_{ef}D_{fe}\rangle(t'-\tau)=\sum_{gre'}{}^{(2)}\rho_{eg}(t'-\tau)D_{gr}D_{re'}D_{e'f}D_{fe}, \tag{38}$$

$$\langle D_{ef}D_{fe}\rangle(t'-\tau)=\sum_{e'}{}^{(4)}\rho_{ee'}(t'-\tau)D_{ef}D_{fe}. \tag{39}$$

$^{(2)}\rho_{eg}$ and $^{(4)}\rho_{ee'}$ were found in Sec. III [Eqs. (16) and (17)]. We will call the component of emitted light connected with the double-quantum coherences the fast component I_f, and with the excited-state population, the slow component I_s. It ought to be stressed that both components are of the same (fourth) order in the electric field of light. Now for simplicity we assume that there is no excited-state structure ($e'=e$). In this case the slow component is given by

$$\begin{aligned}I_s(t;\Omega,\alpha)\sim4\alpha^2\,\mathrm{Re}\int_{-\infty}^{t}dt'\exp[-2\alpha(t-t')]\exp(-\Gamma_e t')\int_0^{\infty}d\tau\exp\{[-\alpha-\Gamma_{ef}+\Gamma_e-i(\Omega-\omega_{ef})]\tau\}\\ \times\mathrm{Re}\int_{-\infty}^{t'-\tau}d\tau'\exp[(\Gamma_e-\Gamma_{eg}-i\Delta)\tau']\int_{-\infty}^{\tau'}d\tau''\exp[(\Gamma_{eg}+i\Delta)\tau'']\,L(\tau'')\mathcal{G}^{(2)}(\tau',\tau''),\end{aligned} \tag{40}$$

where

$$L(t)=\sum_{rgg'} D_{er}D_{rg'}\rho_{g'g}(t)D_{gr}D_{re}D_{ef}D_{fe}/|\Delta_{er}\Delta_{rg}|\,.$$

The fast component takes the form

$$I_f(t;\Omega,\alpha)\sim 2\alpha^2\,\mathrm{Re}\int_{-\infty}^{t} dt'\exp[-2\alpha(t-t')]\exp[-(\Gamma_{eg}+\Gamma_{ef}-\Gamma_{gf})t']\int_0^{\infty} d\tau\exp\{[-\alpha-\Gamma_{gf}+\Gamma_{eg}-i(\Omega-\omega_{ef})]\tau\}$$
$$\times\int_{t'-\tau}^{t} d\tau'\exp[(\Gamma_{ef}-\Gamma_{gf}-i\Delta)\tau']\int_{-\infty}^{t'-\tau} d\tau''\exp[(\Gamma_{eg}+i\Delta)\tau'']\,L(\tau'')\mathcal{G}^{(2)}(\tau',\tau'')\,. \tag{41}$$

We remind the reader that Ω is the center frequency and α the spectral bandwidth of the detecting filter (e.g., a spectrometer). We will discuss these formulas later.

Two components similar to I_s and I_f can also be found in the case of one-photon excitation. They were described and observed for three-level free-induction decay[26] (a specific case of the so-called time-delayed laser-saturation spectroscopy). A component similar to I_s was named in[26] the population-driving term and similar to I_f, the Raman-type term.

For the case of stationary excitation, formulas (40) and (41) describe the spectrum of emitted light and reduce to

$$I_s(\Omega,\alpha)\sim 2\alpha LI^2\frac{(\Gamma_{eg}+kb)(\Gamma_{ef}+\alpha)}{\Gamma_e[(\Gamma_{eg}+kb)^2+\Delta^2][(\Gamma_{ef}+\alpha)^2+(\Omega-\omega_{ef})^2]}\,, \tag{42}$$

$$I_f(\Omega,\alpha)\sim\frac{LI^2}{[(\Gamma_{eg}+kb)^2+\Delta^2][(\Gamma_{ef}+\alpha)^2+(\omega_{ef}-\Omega)^2][(\Gamma_{gf}+kb+\alpha)^2+(\omega_{ef}-\Delta-\Omega)^2]}$$
$$\times[(\Gamma_{eg}+kb)(\Gamma_{ef}+\alpha)(\Gamma_{gf}+kb+\alpha)+(\Gamma_{ef}+\alpha)\Delta(\omega_{ef}-\Delta-\Omega)+(\Gamma_{gf}+kb+\alpha)(\omega_{ef}-\Omega)\Delta$$
$$-(\Gamma_{eg}+kb)(\omega_{ef}-\Omega)(\omega_{ef}-\Delta-\Omega)]\,. \tag{43}$$

Fig. 6 shows I_s and I_f vs the center frequency of of the filter Ω for a narrow-band filter ($\alpha\approx 0$). It ought to be remarked that the fluorescence I_F (the light emitted on the frequency ω_{ef}) depends not only on I_s, but is the difference of two terms: $I_F=I_s-|I_f|$. The second peak on Fig. 6, the light emitted on the frequency $\omega_{ef}-\Delta$, depends, for sufficiently large Δ, on I_f only and corresponds to the Raman-scattered light I_R. For a monochromatic excitation ($b=0$) and no nonradiative relaxation in the atomic system ($2\Gamma_{eg}=\Gamma_e$; $\Gamma_{gf}=0$) the fluorescence I_F decreases to zero proportionally to the square of the filter bandwidth α. So, in the absence of nonadiabatic processes, the fluorescence vanishes and only the Raman-scattering part I_R remains. It can be said that the measured fluorescence $I_F(\omega_{ef})$ is connected with nonadiabatic processes such as transverse relaxation, relaxation due to laser phase fluctuation, as well as the detection process.

As an example we have calculated numerically the time-dependent spectrum of light after a step excitation starting at $t=0$ for the two-photon detuning from resonance $\Delta=10\Gamma_e$ and for the filter bandwidth $\alpha=0.6\Gamma_e$ (Fig. 7). At first the Raman-scattered light and the fluorescence are not spectrally resolved (they were coherently excited at $t=0$). Two peaks of incoherent excitation appear after time of the order of Γ_e^{-1}. On Fig. 8 the insity of the light emitted at $\Omega=\omega_{ef}$ (the fluorescence)

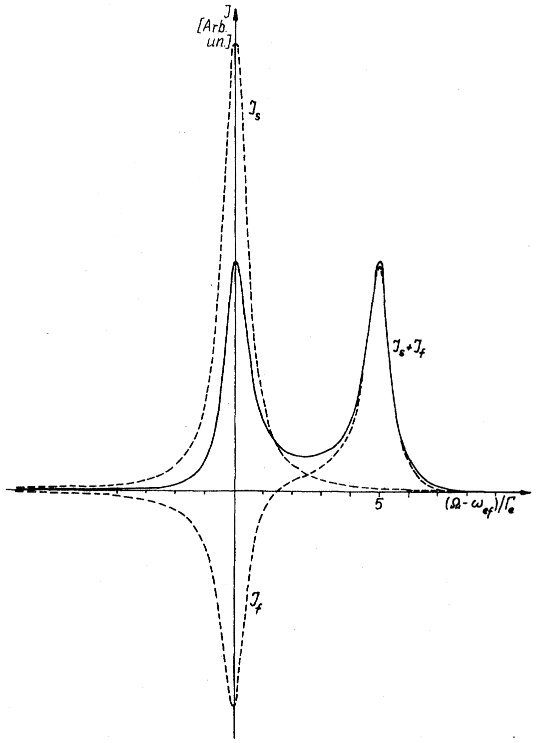

FIG. 6. I_s, I_f, and I_s+I_f vs center frequency Ω of the filter, for the narrow-band filter ($\alpha\simeq 0$). I_s+I_f shows two peaks corresponding to fluorescence ($\Omega=\omega_{ef}$) and Raman-scattered light ($\Omega=\omega_{ef}-\Delta$). $\Gamma_{eg}=0.5\,\Gamma_e$, $\Gamma_{ef}=0.5\,\Gamma_e$, $kb=0.5\,\Gamma_e$, and $\Delta=5\,\Gamma_e$; $\Gamma_{gf}=0$ was assumed.

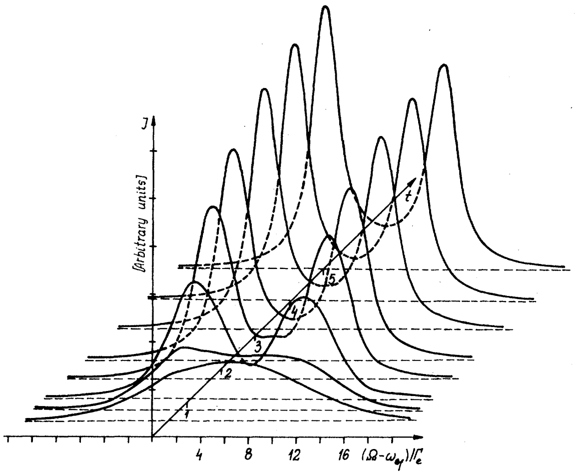

FIG. 7. Time-dependent spectrum of light after step excitation at $t=0$ for two-photon detuning from resonance $\Delta=10\ \Gamma_e$ and the spectral bandwidth of the filter $\alpha=0.6\ \Gamma_e$, $\Gamma_{ef}=0.7\ \Gamma_e$, $\Gamma_{eg}=0.5\ \Gamma_e$, $kb=0.3\ \Gamma_e$, $\Gamma_{gf}=0.2\ \Gamma_e$.

and $\Omega=\omega_{ef}-\Delta$ (the Raman part) are drawn vs time t. Oscillations are due to the coherent excitation of I_R and I_F at $t=0$, and their amplitude decreases in time.

To end this section let us remark that in a general case the atomic motions have to be taken into consideration. To describe this motion as a modification of exciting light frequencies [Eq. (27)], the laboratory frame is changed to the one moving with the atom. However the emitting atom can have a nonvanishing velocity component in the direction of emission. Therefore in Eqs. (40) and (41) we must put "observed" frequency ω_{ef} dependent on the atomic velocity v, which is equivalent to the return to the laboratory frame:

$$\omega_{ef}(v)=\omega_{ef}+\vec{k}\vec{v}\,, \tag{44}$$

where $\vec{k}$ is the wave vector of the field emitted in the direction of the detector. Therefore in order to have the full spectrum of light emitted by "moving" atoms one ought to integrate I_s and I_f over velocities with the proper velocity distribution.

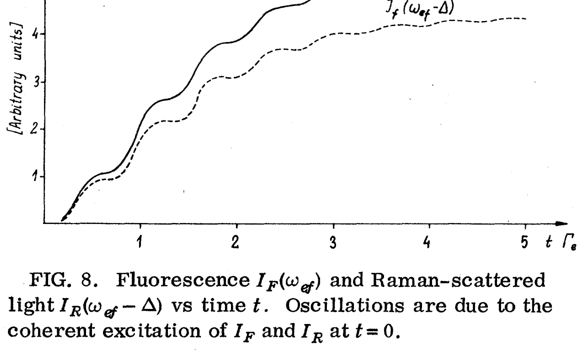

FIG. 8. Fluorescence $I_F(\omega_{ef})$ and Raman-scattered light $I_R(\omega_{ef}-\Delta)$ vs time t. Oscillations are due to the coherent excitation of I_F and I_R at $t=0$.

VIII. SPECTRAL RESOLUTION OF RAMAN-SCATTERED AND FLUORESCENCE LIGHT

In the case of large Δ and large bandwidth of the filter α, both much larger than natural widths, relaxation rates, and characteristic rates as well as frequencies of light intensity changes, one can spectrally resolve two components of the emitted light: the fluorescence I_F and the Raman part I_R, as on Fig. 7. In this section we will study the time dependence of these components. We concentrate on the off-resonance (near-resonance) case, when the emitted light can be well resolved into time-dependent spectral components, and the exciting light satisfies the adiabatic condition

$$\left|\frac{1}{I}\frac{dI}{dt}\right| \ll |\Delta|,\alpha\,, \tag{45}$$

with $\alpha<\Delta$. First, we tune our spectrometer to the fluorescence I_F, putting $\Omega=\omega_{ef}$. In this case $I_F=I_s-|I_f|$, with

$$I_s\sim 2\exp(-\Gamma_e t)\,\mathrm{Re}\int_{-\infty}^{t} d\tau \exp[(\Gamma_e-\Gamma_{eg}-i\Delta)\tau] \times\int_{-\infty}^{\tau} d\tau' \exp[(\Gamma_{eg}+i\Delta)\tau']L(\tau')\mathcal{G}^{(2)}(\tau,\tau')\ ; \tag{46}$$

$$|I_f|\sim[1/(\alpha^2+\Delta^2)]\,L(t)I^2(t)\,, \tag{47}$$

with $I(t)=\mathcal{G}^{(2)}(t,t)$. [As we do not want to specialize the correlation function of light $\mathcal{G}^{(2)}(t,t')$, we cannot take the limit of large Δ in Eq. (46). This can be done only after the double integral.]

The fluorescence is the difference of the slow component and the fast one. I_F (as well as I_s) decays after a pulse excitation with rate Γ_e. Moreover, we find $I_f=0$.

The Raman component $I_R(\Omega=\omega_{ef}-\Delta)$ for large Δ depends on the fast component only $I_R=I_f$; the residual slow component I_s is Δ^2 times smaller than I_f. So the Raman-scattered light I_R follows the temporal behavior of the square of the exciting light intensity. Thus the Raman scattering is an adiabatic process (I_R follows adiabatically the correlation function of the exciting light), and the fluorescence is a nonadiabatic one, as in the one-photon case.[1]

Equations (46) and (47) seem to be appropriate to describe the results of Ref. 11 (see also Ref. 27):

(a) the Raman-scattered light I_R has the temporal characteristics of the "square" of the exciting pulse;

(b) the resonance fluorescence I_F decays with the atomic lifetime when the pulse is over;

(c) the ratio R of the time-integrated intensity of the fluorescence I_F to the time-integrated Raman-scattered light I_R depends linearly (through Γ_{eg}) on the buffer gas pressure;

(d) the relative contributions of I_F and I_R for large Δ are independent of Δ.

From Eqs. (46) and (47) one can also deduce some new properties:

(i) The slow component I_s depends on the second-order correlation function of exciting light and on its characteristic times. Therefore the contribution of I_s to the fluorescent light I_F depends on the shape of the light pulse, the exciting light statistics, and bandwidth. The fluorescence decreases with decreasing of transverse relaxation rates, e.g., the bandwidth of the laser light, while the Raman-scattered light intensity is constant.

(ii) The fast component I_f decreases with the increasing bandwidth of the spectral filter α. So for the broad-band filter one can only observe the slow component I_s, being just the fluorescence.

(iii) The time behavior of the emitted light depends also on the time behavior of the ground-state density matrix $\rho_{gg'}$. Therefore the existance of the ground-state coherence $\rho_{gg'} = a_{gg'} \exp(-i\omega_{gg'}t)$ can also induce oscillations of the fast, as well as the slow, component. These oscillations could be observed as a deformation of the laser light pulse coming to the detector in the Raman scattering or a modulation ("ringing") of the decaying fluorescence, when the light is turned off.

ACKNOWLEDGMENT

The author wishes to thank K. Kolwas, J. Mostowski, and K. Rosiński for useful discussions.

---

[1] A. Szöke and E. Courtens, Phys. Rev. Lett. 34, 1053 (1975); E. Courtens and A. Szöke, Phys. Rev. A 15, 1588 (1977).

[2] D. Grischkowsky, Phys. Rev. A 14, 802 (1976).

[3] J. M. Friedman and D. L. Rousseau, Chem. Phys. Lett. 55, 488 (1978); A. Ron, *ibid.* 58, 329 (1978); R. M. Hochstrasser and C. A. Nyi, J. Chem. Phys. 70, 1112 (1979) and references therein.

[4] R. G. Brewer and E. L. Hahn, Phys. Rev. A 11, 1641 (1975); see also S. Chandra and W. M. Yen, Phys. Lett. A 57, 217 (1976).

[5] D. G. Gold and E. L. Hahn, Phys. Rev. A 16, 324 (1977).

[6] D. Grischkowsky and M. M. T. Loy, Phys. Rev. A 12, 2514 (1975).

[7] M. Kolwas, Phys. Lett. A 69, 15 (1978).

[8] M. Bassini, F. Biraben, B. Cagnac, and G. Grynberg, Opt. Commun. 21, 263 (1977).

[9] G. Grynberg and B. Cagnac, Rep. Prog. Phys. 40, 791 (1977).

[10] If the relaxation times of the system are very short (see Ref. 3) with respect to the rate of exciting light changes, the "slow" component can be emitted more quickly than the "fast" one. However, I prefer to call two components of scattering "fast" and "slow" rather than, e.g., "coherent" and "population," respectively, because the term "coherent" is frequently used for the whole Raman component.

[11] J. Liran, G. Levin, G. Erez, and J. Jortner, Phys. Rev. Lett. 38, 390 (1977).

[12] J. H. Eberly and K. Wódkiewicz, J. Opt. Soc. Am. 67, 1252 (1977).

[13] E.g., B. R. Mollow, Phys. Rev. 188, 1969 (1969).

[14] W. Happer, Rev. Mod. Phys. 44, 169 (1972).

[15] M. Kolwas, J. Phys. B 10, 583 (1977).

[16] J. P. Barrat and C. Cohen-Tannoudji, J. Phys. Radium 22, 329 (1961); 22, 443 (1961).

[17] E.g., D. L. Huber, Phys. Rev. 178, 93 (1969).

[18] E.g., R. J. Glauber, in *Quantum Optics and Electronics* (Gordon and Breach, New York, 1965).

[19] K. Rosiński, Bull. Acad. Pol. Sci. 23, 847 (1965).

[20] A. Ben-Reuven, J. Jortner, L. Klein, and S. Mukamel, Phys. Rev. A 13, 1402 (1976).

[21] B. R. Mollow, Phys. Rev. 175, 1555 (1977).

[22] C. Cohen-Tannoudji and S. Reynaud, J. Phys. B 10, 2311 (1977).

[23] S. Haroche, in *Topics in Applied Physics*, *Vol. 13*, edited by K. Shimoda (Springer-Verlag, Berlin, 1976).

[24] J. N. Dodd, Proc. R. Soc. A 263, 353 (1961).

[25] M. Lax, Phys. Rev. 129, 2342 (1963).

[26] M. Ducloy and M. S. Feld, in *Laser Spectroscopy III*, edited by J. L. Hall and J. L. Carsten (Springer, Berlin, 1977), p. 243.

[27] G. Grynberg, F. Biraben, M. Kolwas, and B. Cagnac, Phys. Rev. A 18, 2387 (1978).