Raman photon echo

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Coherent nonstationary Raman scattering of light is investigated in a pre-excited medium under conditions when the frequencies of the ultrashort pump pulses are at resonance with atomic or vibrational-rotational molecular transitions, and the long probing pulse is nonresonant. Introduction of a delay time τ between the two pump pulses led to additional damping of the Stokes and anti-Stokes signals as functions of τ. This damping introduces one more relaxation constant compared with the previously developed methods. It is established that excitation of inhomogeneously broadened transitions by two or three pump pulses produces a unique Raman photon echo that contains information on the relaxation of the quantum states. The polarization properties of the nonstationary light scattering and the dependence of the intensity of this scattering on the areas of the pump pulses are described.

Nonstationary Raman scattering (RS) of light is now being exhaustively investigated as a method for determining the relaxation times of ultrafast processes and studying molecular structure.[1,2] Along with other approaches, extensive use is made of methods involving Raman echo,[3,4] two-photon echo,[5] as well as the method of short-time excitation and long-time registration (SELR). The latter consists of pre-exciting the molecule by two picosecond pump-light pulses whose frequency difference is close to the forbidden-transition frequency, followed by investigation of the free relaxation of the excited states in the presence of a prolonged (or short, but delayed in time) nonresonant probing light pulse.[6,7]

We report here a new nonstationary RS phenomenon—Raman photon echo (RPE). It is produced in a gas on inhomogeneously broadened transitions if the usual biharmonic pumping of the SELR method is replaced by application of two pulses separated by a short time interval τ. Their action upsets the coherence of the excited atoms, via the Doppler dephasing mechanism, and weakens drastically the nonstationary RS. If, however, the resonant levels are suitably arranged, the second pump pulse restores the coherence of the radiating atoms, and a sharp spike in the form of a RPE appears against the background of the damped scattering of the light. The time of the spike depends on τ and on the frequencies of the pump plses. If the first pump pulse has a small area and a narrow spectrum, while the second has a broad one, the RPE wavefront is the time-inverted wavefront of the first pump pulse. In contrast to the analogous phenomenon for photon echo in two-level systems,[8] the RPE profile is stretched out or compressed in time, depending on the ratio of the pump-pulse frequency. When the second pump pulse has a small area and a narrow pulse, the RPE form duplicates the profile of this pulse, but stretched out in time. These features are possessed also by the stimulated RPE produced by the action of three pump pulses, and constitutes a six-photon parametric process. The obtained RPE differs substantially from Raman echo[3] and its modifications in media with cubic nonlinearity,[4] from two-photon echo,[5] as well as from three-level echo.[9]

Introduction of the delay time τ has led to a fundamentally new expression for the RS intensity; this expression reduces at $\tau = 0$ to the case of biharmonic pumping. By varying τ one can determine from this expression the relaxation time of the allowed-transition optical coherence, while the damping of the RS intensity as a function of the time t permits an investigation of a forbidden inhomogeneously broadened transition. In contrast to Refs. 6 and 7, where an expansion in powers of the electric field is used, the pump-pulse intensities are fully accounted for here. This shows that, owing to the interference of the atomic states, the RS and RPE intensities oscillate, at fixed t and τ, as functions of the areas under the pump pulses. These oscillations must be taken into account when the experimental conditions are optimized. The obtained RS and RPE polarization properties, for both small and large pump-pulse areas, permit identification of the quantum transitions and make possible, in conjunction with the law that governs the intensity damping, the study of relaxation of rapid processes.

1. POLARIZATION SINGULARITIES AND DAMPING LAW

Let two ultrashort pump pulses

$$\mathbf{E}_n = \frac{1}{2}\mathbf{l}_n a_n \exp(i\Phi_n) + \text{c.c.}, \quad \Phi_n = k_n y - \omega_n t - \varphi_n, \quad n = 1, 2, \tag{1}$$

propagate through the investigated medium occupying the space $0 \leqslant y \leqslant L$. Here $\mathbf{l}_1$ and $\mathbf{l}_2$ are real unit vectors of the wave polarization, a_1 and a_2 are slowly varying amplitudes, φ_1 and φ_2 are constant phase shifts, and ω_1 and ω_2 are the central frequencies connected with the wave-vector moduli $\mathbf{k}_1$ and $\mathbf{k}_2$ by the dispersion law $\varepsilon\omega_{1,2}^2 = c^2 k_{1,2}^2$. The dielectric constant ε takes into account the influence of the nonresonant quantum transitions of the active atoms and impurities. The pulse durations τ_1 and τ_2 are short compared with the irreversible-relaxation times, whereas the time interval τ between them is arbitrary. The leading front of the first pulse crosses the boundary plane $y = 0$ of the medium at the instant of time $t = 0$. The values of ω_1 and ω_2 are close to the

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frequencies ω_{ca} and ω_{bc} of two adjacent transitions between atom or molecule states with energies E_a, E_b, and $E_c (E_a < E_b < E_c)$, angular momenta j_a, j_b, and j_c, as well as projections m, μ, and ν of these angular momenta on the quantization axis. The resonant atoms together with the nonresonant ones make up a gas that acts with respect to the light pulses (1) as an optically thin layer with refractive index $\varepsilon^{1/2}$.

The preceding reasoning holds also for vibrational-rotational molecular transitions

$$vJKM \to v'J'K'M',$$

where v and J are the vibrational and rotational quantum numbers, while K and M are the projections of the total angular momentum on the molecule axis and on the quantization axis. It is assumed here that the K-degeneracy is lifted, i.e., the spacing between neighboring K-split sublevels exceeds the homogeneous and inhomogeneous widths of the spectral lines.

The interaction of the atom with the external field, as well as the free relaxation of the excited states after the passage of each pulse (1), is described by the following quantum-mechanical equation for the density matrix ρ:

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\nabla-\hat{\Gamma}\right)\rho=\frac{i}{\hbar}[\rho(H-\mathbf{Ed})-(H-\mathbf{Ed})\rho], \tag{2}$$

where H is the Hamiltonian of the free atom in its c.m.s., $\mathbf{d}$ is the dipole-moment operator, $\mathbf{v}$ is the atom velocity, $\mathbf{E}$ is the electric field of the propagating field (the subscript n is omitted), and $\hat{\Gamma}\rho$ is the collision integral, which we write for resonant states of the atom in the form

$$(\hat{\Gamma}\rho)_{mm'}=\frac{\gamma_a N_a}{2j_a+1}f(\mathbf{v})\delta_{mm'}-\gamma_a\rho_{mm'},$$
$$(\hat{\Gamma}\rho)_{\nu m}=-\gamma_{ca}\rho_{\nu m}, \quad (\hat{\Gamma}\rho)_{\nu\mu}=-\gamma_{cb}\rho_{\nu\mu}, \quad (\hat{\Gamma}\rho)_{\mu m}=-\gamma_{ba}\rho_{\mu m}. \tag{3}$$

The quantity $(\hat{\Gamma}\rho)_{\mu\mu'}$ is obtained from (3) by the subscript changes $a\to b$, $m\to\mu$, and $m'\to\mu'$, while the other substitutions $a\to c$, $m\to\mu$, and $m'\to\mu'$ yield $(\hat{\Gamma}\rho)_{\nu\nu'}$. Here $\rho_{mm'}$, $\rho_{\mu\mu'}$, and $\rho_{\nu\nu'}$ are density matrices that describe the atom on the different levels, $\rho_{\nu m}$, $\rho_{\nu\mu}$, and $\rho_{\mu m}$ are the optical-coherence matrices, N_a, N_b, and N_c are the stationary densities of the atoms in the absence of an external field, $f(\mathbf{v})=(\pi^{1/2}u)^{-3}\exp(-v^2/u^2)$ is Maxwell's distribution, u is the most probable velocity, while $\hbar\gamma_a$, $\hbar\gamma_b$, and $\hbar\gamma_c$ are the level widths due to the radiative decay, to gaskinetic inelastic collisions, and other possible phenomena. The collision-integral terms proportional to $f(\mathbf{v})$ take into account the arrival due to the Boltzmann distribution over the energy levels, and the others describe the departure due to various relaxation processes.

In Eq. (2) we neglect the irreversible relaxation at each point of the gas in the time interval corresponding to the passage of the ultrashort pump pulse. This is valid under the conditions

$$\gamma_{a,\,b,\,c}\tau_n\ll 1, \quad \gamma_{ca,\,cb,\,ba}\tau_n\ll 1, \quad n=1,\,2. \tag{4}$$

To investigate the free relaxation of the pre-excited atom, we use a long probing pulse of the form (1) with a real polarization vector $\mathbf{l}$, a slow amplitude a, a constant phase shift φ, and a frequency ω not equal to any of the natural atomic frequencies. In the case of resonant SELR, the instant at which the probing pulse is applied is arbitrary and can be chosen to precede or follow the pump pulses, since the coherent emission due to a nonresonant four-photon parametric process is weaker by 6–7 orders and is therefore inessential. The probing pulse induces in a unit volume of the excited gas an electric dipole moment

$$\mathbf{P}=\sum_{\mu\nu}\rho_{\mu\nu}\mathbf{D}_{\nu\mu}+\text{c.c.},$$
$$\mathbf{D}_{\nu\mu}=\frac{1}{2\hbar}\sum_{g\xi}\left[\left(\frac{\mathbf{d}_{\nu\xi}(\mathbf{d}_{\xi\mu}\mathbf{l})}{\omega_{gb}-\omega}-\frac{(\mathbf{d}_{\nu\xi}\mathbf{l})\,\mathbf{d}_{\xi\mu}}{\omega_{cg}-\omega}\right)ae^{i\Phi}+\left(\frac{\mathbf{d}_{\nu\xi}(\mathbf{d}_{\xi\mu}\mathbf{l})}{\omega_{gb}+\omega}-\frac{(\mathbf{d}_{\nu\xi}\mathbf{l})\,\mathbf{d}_{\xi\mu}}{\omega_{cg}+\omega}\right)a^*e^{-i\Phi}\right],$$

where $\Phi=ky-\omega t-\varphi$ is the phase shift of the probing pulse, and the optic-coherence matrix of the Raman transition $j_b\to j_c$ is obtained by solving Eq. (2) by the method described in Ref. 10.

The alternating atomic-polarization vector $\mathbf{P}=\mathbf{P}^{(+)}+\mathbf{P}^{(-)}$ induces an electric field $\mathbf{E}_{RS}$ that takes at the exit from the gas the form

$$\mathbf{E}_{RS}=\mathcal{E}_+(t-k_+y/\omega_+)e^{i\Phi_+}+\mathcal{E}_-(t-k_-y/\omega_-)e^{i\Phi_-}+\text{c.c.},$$
$$\omega_\pm=\omega\pm(\omega_1-\omega_2), \quad k_\pm=k\pm(k_1-k_2), \quad \Phi_\pm=\Phi\pm(\Phi_1-\Phi_2), \tag{5}$$

where the plus and minus signs for all the quantities introduced correspond to the anti-Stokes and Stokes RS signals, while the coordinate y is taken at the gas boundary $y=L$.

The pump pulses frequently used in experiment have arbitrary spectra and small areas

$$\theta_1\ll 1, \quad \theta_2\ll 1, \tag{6}$$

given by the relations

$$\theta_{1,2}=\beta_{1,2}\begin{cases}[j/(j+1)\,(2j+1)]^{1/2} & \text{for the transition } j\to j,\\ [(j+1)/(2j+1)\,(2j+3)]^{1/2} & \text{for the transition } j\leftrightarrow j+1,\ j=0,1,\ldots,\\ [4(j+1)]^{-1/2} & \text{for the transition } j\leftrightarrow j+1,\ j \text{ is half-integer}\end{cases}$$

$$\beta_1=\hbar^{-1}|d_{ca}|\int_0^{\tau_1}|a_1(t)|\,dt, \quad \beta_2=\hbar^{-1}|d_{ba}|\int_{t_2}^{t_2+\tau_2}|a_2(t)|\,dt,$$

where j is the angular momentum, d_{ca} and d_{ba} are the reduced dipole moments of the transitions $j_a \to j_c$ and $j_a \to j_b$ (Ref. 11), t_2 is the time of entry of the second pulse into the gas, while $a_1(t)$ and $a_2(t)$ can be complex if account is taken of the phase modulation of the pump pulses. The last remark pertains also to the slow function $a = a(t)$. Under these assumptions the amplitude $\varepsilon_{\pm}(t)$ of the electric field (5) takes at $t_2 + \tau_2 \leqslant t$ the form

$$\varepsilon_{\pm}(t) = a^{(\pm)}\mathbf{B}^{(\pm)}C^{(\pm)}(t)\exp\left[-\gamma_{cb}(t-\tau)-\gamma_{ca}\tau\right],$$

$$a^{(+)} = a(t), \quad a^{(-)} = a^*(t),$$

$$\mathbf{B}^{(\pm)} = {}^1/_3\mathbf{l}_z\left[M_0^{(\pm)}\cos(\psi_1-\psi_2)+M_2^{(\pm)}\right.$$

$$\left.\times(3\cos\psi_1\cos\psi_2-\cos(\psi_1-\psi_2))\right]$$

$$+{}^1/_2\mathbf{l}_x\left[M_1^{(\pm)}\sin(\psi_1-\psi_2)+M_2^{(\pm)}\sin(\psi_1+\psi_2)\right],$$

$$M_\varkappa^{(\pm)} = (-1)^{j_a+j_c}\begin{Bmatrix} 1 & \varkappa & 1 \\ j_c & j_a & j_b \end{Bmatrix}\Pi_\varkappa^{(\pm)}, \quad \varkappa = 0, 1, 2,$$

$$\Pi_\varkappa^{(\pm)} = \frac{1}{\hbar}\sum_g d_{bg}d_{gc}(-1)^{j_b+j_c}\begin{Bmatrix} 1 & \varkappa & 1 \\ j_c & j_g & j_b \end{Bmatrix}\left(\frac{1}{\omega_{gb}\pm\omega}+\frac{(-1)^\varkappa}{\omega_{gc}\mp\omega}\right).$$

$$C^{(\pm)}(t) = \pm iC_0^{(\pm)}\frac{|d_{ca}d_{ab}|}{4\hbar^2}\int d\mathbf{v}f(\mathbf{v})\int_0^{\tau_1} d\xi\int_{t_2}^{t_2+\tau_2} d\eta a_1(\xi)a_2^*(\eta)$$

$$\times\exp\left[-i(\mathbf{k}_1\mathbf{v}-\Delta_1)(t-\xi)+i(\mathbf{k}_2\mathbf{v}-\Delta_2)(t-\eta)\right],$$

$$C_0^{(\pm)} = \frac{\pi\omega_\pm^2 d_{ca}d_{ab}N_{ac}L}{c^2k_\pm|d_{ca}d_{ab}|}, \quad N_{ac} = \frac{N_a}{2j_a+1}-\frac{N_c}{2j_c+1},$$

$$\Delta_1 = \omega_1-\omega_{ca}, \quad \Delta_2 = \omega_2-\omega_{ba}, \quad \omega_1 > \omega_2. \qquad (7)$$

Here $\mathbf{l}_z$ and $\mathbf{l}_x$ are the unit vectors of the Cartesian axes, and ψ_1 and ψ_2 are the angles between the polarization vectors of the pump pulses and of the probing pump, and are given by

$$\mathbf{l}_n = \mathbf{l}_z\cos\psi_n+\mathbf{l}_x\sin\psi_n, \quad \mathbf{l} = \mathbf{l}_z, \quad \mathbf{l}_x = \frac{[\mathbf{k}\times\mathbf{l}]}{|[\mathbf{k}\times\mathbf{l}]|},$$

where the positive direction of the angles is from $\mathbf{l}$ to $\mathbf{l}_n$, and $n = 1$ or 2. In the region $0 \leqslant t - t_2 \leqslant \tau$ it is necessary to make in (7) the substitutions

$$\exp\left[-\gamma_{cb}(t-\tau)\right] \to 1, \quad t_2+\tau_2 \to t. \qquad (8)$$

For biharmonic pumping, in a time interval $0 \leqslant t \leqslant \tau_1 = \tau_2$ by pulses (1) with small areas (6), the RS electric field takes the form (5) with the amplitude $\varepsilon_{\pm}(t)$ given in the region $0 \leqslant t$ by Eq. (7) at $\tau = 0$, provided the following substitution is made in the expression for $C^{(\pm)}(t)$

$$\int_0^{\tau_1} d\xi\int_{\tau_1}^{\tau_1+\tau_2} d\eta \to \int_0^t d\eta\int_0^\eta d\xi + \frac{N_{ab}}{N_{ac}}\int_0^t d\xi\int_0^\xi d\eta,$$

$$N_{ab} = N_a/(2j_a+1)-N_b/(2j_b+1).$$

The level degeneracy and the type of the Raman transition $j_b \to j_c$ influence radically the RS polarization. This influence is most strongly reflected in the characteristic dependence of $\varepsilon_{\pm}(t)$ on the angles ψ_1 and ψ_2, as well as in the $6j$ symbols that enter in the expressions for $M_\varkappa^{(\pm)}$ and $\Pi_\varkappa^{(\pm)}$.

For the Raman transitions $j_b - j_c = \pm 2$ (O and S branches) the RS polarization is linear for all angles ψ_1 and ψ_2, since $M_0^{(\pm)} = M_1^{(\pm)} = 0$. The angle ψ_{RS} between the polarization vector of the RS and of the probing pulse is given by

$$\operatorname{tg}\psi_{RS} = \frac{3\sin(\psi_1+\psi_2)}{3\cos(\psi_1+\psi_2)+\cos(\psi_1-\psi_2)}.$$

In the case $j_b - b_c = \pm 1$ (P and R branches) we have $M_0^{(\pm)} = 0$, so that the RS polarization is linear only at $\psi_1 = \psi_2 = \psi$, with

$$\operatorname{tg}\psi_{RS} = \frac{3\sin 2\psi}{2(3\cos^2\psi-1)}.$$

For $j_b - j_c = 0$ (Q branch), on the contrary, the RS polarization is elliptic regardless of the angles ψ_1 and ψ_2, since the quantities Π with $\varkappa = 0$, 1, and 2 are complex because of the factors d_{bg} and d_{gc}. An exception is the transition $j_b = 0 \to j_c = 0$, for which $M_1^{(\pm)} = M_2^{(\pm)} = 0$ and the RS signal is linearly polarized in the polarization plane of the probing pulse. We note also that for the transition $j_b = 1/2 \to j_c = 1/2$ (as well as $j_b = 0 \to j_c = 1$ and $j_b = 1 \to j_c = 0$) we have $M_2^{(\pm)} = 0$ and the polarization-ellipse axes depend on $\psi_1 - \psi_2$ in such a way that the polarization ellipse contracts to a segment on the X axis at $\psi_1 - \psi_2 = \pi/2$ and into a segment on the Z axis at $\psi_1 - \psi_2 = 0$.

The indicated RS polarization properties are the same for homogeneously and inhomogeneously broadened transitions, and will therefore be observed also in RPE. They make it possible to distinguish in experiment between the transitions $j_b - j_c = 0$, $j_b - j_c = \pm 1$, and $j_b - j_c = \pm 2$. The polarization properties can be used, besides for identification of quantum transitions, also to distinguish the RS and RPE signals from other pulses when the intensity damping is investigated as a function of t or τ.

When the pump-pulse areas are arbitrary and the inequalities (6) are violated, the RS and RPE amplitudes are calculated by the method of Ref. 10. In this case the polarization of the RS and RPE waves has a more complicated dependence on the parameters involved than in the case of small areas (6). For the angular momenta j_a, j_b, and j_c, which take on values from the set 1/2, 1/2, and 3/2 as well as 0, 0, and 1 (0, 1, and 1), however, the polarization properties formulated above for the case of small areas (6) remain in force. If the first pump pulse has a small area and the second an arbitrary one, the dependence of the indicated amplitudes on the angles ψ_1 and ψ_2 is considerably simplified.

It must be borne in mind that the intensity

$$I^{(\pm)}(t) = c|\varepsilon_{\pm}(t)|^2/2\pi$$

of the nonstationary RS depend strongly on the areas of the pump pulses. In the optimal case $2\theta_1 = \theta_2 = \theta$ at fixed t and τ the intensity $I^{(\pm)}(t)$ oscillates as a function of θ, with periods and damping rates that vary with the type of resonant transition $j_a \to j_b \to j_c$ (Fig. 1). Thus, for transitions without a

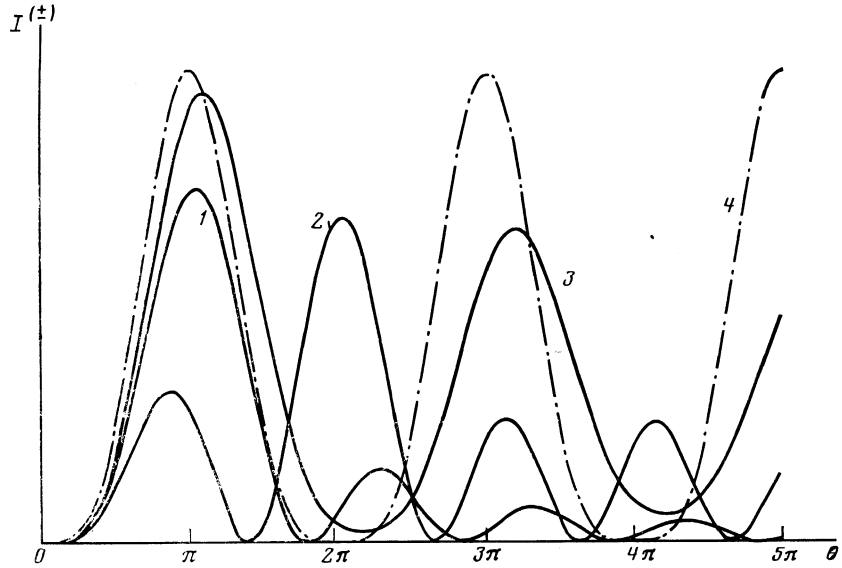

FIG. 1. RS intensity, in arbitrary units, as a function of at fixed t and τ. Curves 1–4 pertain to atomic transitions $j_a \to j_b \to j_c$ of the following respective types: $25\to25\to25$, $25\to24\to24$, $25\to26\to24$ ($25\to24\to26$), $1/2\to1/2\to1/2$ ($3/2\to1/2\to1/2$ and $1\to0\to0$). It is assumed that $2\theta_1 = \theta_2 = \theta$, $\psi_1 = \psi_2$, $|\Delta_n|\tau_n \ll 1$ and $k_n u\tau_n \ll 1$ at $n = 1$ or 2, while the intensity of the xth projection of the RS electric field is shown for the case $j_b = j_c \gg 1$.

change of angular momentum, $j_a = j_b = j_c \gg 1$, the damping is faster than for other transitions. At certain values of θ the RS intensity is zero. A change takes place also in the magnitude and rotation of the polarization ellipse of the scattered waves as functions of θ at fixed ψ_1 and ψ_2, while for different values of θ_1 and θ_2 the polarization of the RS takes a different form as a function of ψ_1 or ψ_2.

At a resonance-level sequence other than $E_a < E_b < E_c$, the electric field $\mathbf{E}_{RS}$ and the amplitude $\varepsilon_\pm(t)$ are described by the previous equations (5) and (7), but with change of notation

$$\Pi_x^{(\pm)} \to \Pi_x^{(\mp)*}, \quad \gamma_{cb} \to \gamma_{bc}$$

and with the following substitutions:

a) for $E_c < E_b < E_a$ and $\omega_1 > \omega_2$:

$$d_{ca}d_{ab} \to -d_{ac}d_{ba}, \quad \Delta_1 \to \omega_1 - \omega_{ac},$$
$$\Delta_2 \to \omega_2 - \omega_{ab}, \quad \gamma_{ca} \to \gamma_{ac};$$

b) for $E_c < E_a < E_b$ and $0 < |\omega_1 - \omega_2|$:

$$\Phi_\pm \to \Phi \pm (\Phi_1 + \Phi_2), \quad d_{ca}d_{ab} \to -d_{ac}d_{ba},$$
$$a_2^*(\eta) \to a_2(\eta), \quad \omega_\pm \to \omega \pm (\omega_1 + \omega_2), \quad k_\pm \to k \pm (k_1 + k_2), \quad \Delta_1 \to \omega_1 - \omega_{ac}, \quad \gamma_{ca} \to \gamma_{ac},$$
$$(\mathbf{k}_2\mathbf{v} - \Delta_2) \to -(\mathbf{k}_2\mathbf{v} - \Delta_2);$$

c) for $E_a < E_c < E_b$ and $\omega_1 < \omega_2$:

$$\Phi_\pm \to \Phi \pm (\Phi_2 - \Phi_1), \quad C^{(\pm)}(t) \to -C^{(\pm)*}(t),$$
$$\omega_\pm \to \omega \pm (\omega_2 - \omega_1), \quad k_\pm \to k \pm (k_2 - k_1).$$

2. RPE IN INHOMOGENEOUSLY BROADENED TRANSITIONS

In the case of inhomogeneously broadened transitions

$$k_1 u > \gamma_{ca}, \quad k_2 u > \gamma_{ba}, \quad |k_1 - k_2| u > \gamma_{cb}$$

the amplitude $\varepsilon_\pm(t)$ of the resonant RS is strongly damped as a function of the time t, owing to the Doppler dephasing of the radiating atoms. This damping is faster than the exponential $\exp[-\gamma_{cb}(t-\tau)]$ that characterizes the irreversible relaxation. For example, for a broad spectrum $k_{1,2}u + |\Delta_{1,2}| \ll 1/\tau_{1,2}$ of the pump pulses and at $E_a < E_b < E_c$ (or $E_c < E_b < E_a$), it follows from Eq. 7 [with account taken of the substitutions (8) and a)] that the amplitude $\varepsilon_\pm(t)$ is proportional to the exponentials

$$\exp\{-[((2k_1 - k_2)t + k_2\tau)u/4]^2\}, \quad 0 \leqslant t - t_2 \leqslant \tau_2;$$
$$\exp\{-[((k_1 - k_2)t + k_2\tau)u/2]^2\}, \quad t_2 + \tau_2 \leqslant t.$$

Consequently the duration of the RS signal is of the order of $1/(k_1 - k_2)/u$, and the modulus of the electric field (5) is strongly decreased.

At $E_c < E_a < E_b$ the decrease of the amplitude $\varepsilon_\pm(t)$ is due to similar exponentials

$$\exp\{-[((2k_1 + k_2)t - k_2\tau)u/4]^2\}, \quad 0 \leqslant t - t_2 \leqslant \tau_2;$$
$$\exp\{-[((k_1 + k_2)t - k_2\tau)u/2]^2\}, \quad t_2 + \tau_2 \leqslant t.$$

If one of the pump pulses has a narrow spectrum $k_1 u + |\Delta_1| \gg 1/\tau_1$ or $k_2 u + |\Delta_2| \gg 1\tau_2$, the duration of the RS signal is of the order of the larger of τ_1 or τ_2. In view of the inequalities (4), the amplitude $\varepsilon_\pm(t)$ attenuates with time in this case more rapidly than $\exp[-\gamma_{cb}(t-\tau)]$.

The resonant RS behaves differently at $E_a < E_c < E_b$ and $\omega_1 < \omega_2$. Just as in the preceding cases, the Doppler dephasing of the excited atoms leads to a considerable weakening of the radiation intensity in the time interval $t_2 \leqslant t$, so that there is practically no resonant RS. Subsequently, however, owing to the unique behavior of the atomic polarization of each group of atoms that have the same velocity v, the resonant RS reappears and reaches a maximum at $t = t_{RS} = \tau_1 + \omega_2(\omega_2 - \omega_1)^{-1}(\tau + \tau_2/2)$, after which it attenuates again (Fig. 2). As a result, passage of the second pump pulse produces an RPE whose amplitude as a function of time is described by Eq. (7) with the substitutions (8) and c). The intensity

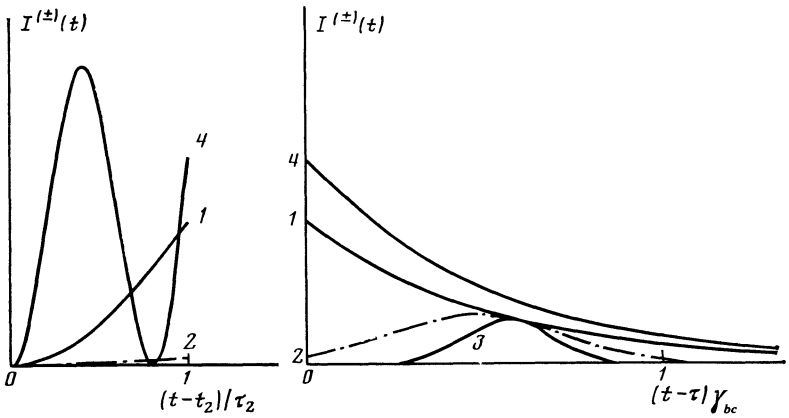

FIG. 2. RS and RPE intensities in arbitrary units. It is assumed that $j_a = j_b = j_c = 1'0$, $\theta_1 = \pi/2$, $k_2 u\tau_1 = 0.1$ and $\gamma_{bc}\tau = 0.6\,(\omega_2 - \omega_1)/\omega_2$. Curves 1, 2, and 3 correspond to $\theta_2 = \pi/2$ and to the parameter $(k_2 - k_1)\cdot\mu/\gamma_{bc}$ equal respectively to 0, 1, 4, and 8, thus illustrating the onset of the RPE as the degree of the inhomogeneous broadening of the transition $j_b \to j_c$ is increased. Curve 4 describes the oscillations of the RS intensity in the time interval $0 \leqslant t - t_2 \leqslant \tau_2$ and the damping at $t_2 + \tau_2 \leqslant t$ for a large area $\theta_2 = 5\pi/2$ and for $(k_2 - k_1)u/\gamma_{bc} = 0.1$.

$$I_e^{(\pm)}(t) = c\,|\mathcal{E}_\pm(t)\,|^2/2\pi$$

of this RPE has at $t = t_{RS}$ a maximum that takes for all values of the areas θ_1 and θ_2 the form

$$I_e^{(\pm)}(t_{RS}) = Q_1^{(\pm)} \exp[-2(\omega_1\gamma_{bc}/(\omega_2-\omega_1)+\gamma_{ca})\tau], \qquad (9)$$

where it is assumed that $k_{1,2}u + |\Delta_{1,2}| \ll 1/\tau_{1,2}$ and the factor $Q_1^{(\pm)}$ is independent of τ. By investigating the attenuation of the intensity (9) as a function of τ with the remaining parameters fixed, it is easy to determine in experiment the sum $\gamma_{ca} + \omega_1\gamma_{bc}/(\omega_2 - \omega_1)$, which permits one of the relaxation constants to be determined if the other is known. The value of γ_{ca} can be determined independently, e.g., by the usual phonon echo (see the reviews[12]).

At small pump-pulse areas (6) the instant when the intensity $I_e^{(\pm)}(t)$ reaches a maximum is shifted relative to $t = t_{RS}$ by the positive quantity Δt_{RS}, as can be easily verified with rectangular pump pulse with $\Delta t_{RS} = \omega_1\tau_1/2(\omega_2 - \omega_1)$ as an example. In view of the inequalities (4), this shift does not influence the investigation of the irreversible relaxation, but affects the location of the KPE at $\tau_1(k_2 - k_1)u > 1$.

Assume that the first pump pulse has a small area $\theta_1 \ll 1$ and a narrow spectrum compared with the Doppler spectral-line width, $k_1 u \gg 1/\tau_1$, while the second has a broad one, $k_2 u \ll 1/\tau_2$. A unique correlation is then observed between the RPE shape and the profile of the first pump pulse. We assume for simplicity that the second pump pulse also has a small area $\theta_2 \ll 1$. Making the necessary transformations in the expression for $C^{(\pm)}(t)$ with allowance for the preceding inequalities and substitution c) in the amplitude (7), we obtain

$$\mathcal{E}_\pm(t) = \frac{\mathbf{Q}^{(\pm)}}{k_1} a_1^*((\omega_2-\omega_1)(\tilde{t}_{RS}-t)/\omega_1) \int_{t_2}^{t_2+\tau_2} a_2(\xi)\exp[i\Delta_2(t-\xi)]\,d\xi \times \exp\left[-i\frac{\omega_2}{\omega_1}\Delta_1(t-t_2) - \gamma_{bc}(t-\tau) - \gamma_{ca}\tau\right],$$

$$\mathbf{Q}^{(\pm)} = \pm i a^{(\pm)} \mathbf{B}^{(\pm)} C_0^{(\pm)*} \frac{\pi^{1/2}|d_{ca}d_{ab}|}{2\hbar^2 u}, \qquad \tilde{t}_{RS} = \frac{\omega_2 t_2}{\omega_2 - \omega_1},$$

where the instant of the onset of the RPE is $t = t_{RS}$. Since the argument t in the function $a_1(t)$ is replaced by $(\omega_2 - \omega_1)(t_{RS} - t)/\omega_1$, the shape of the RPE at $\Delta_1 = \Delta_2 = 0$ and $\gamma_{bc} t \ll 1$ duplicates the profile of the first pump pulse but is reversed in time and subject to a definite elongation at $(\omega_2 - \omega_1)/\omega_1 < 1$ and contraction at $(\omega_2 - \omega_1)/\omega_1 > 1$. A similar deformation and time reversal occurs in the variable phase of the function $a_1(t)$. In addition, in Eq. (5) time reversal takes place also for the principal phase $\Phi_\pm$, which contains the central frequency $\omega_\pm$. If $\mathbf{l} = \mathbf{l}_1 = \mathbf{l}_2$ or $\mathbf{l}\cdot\mathbf{l}_1 = 0$ and $\mathbf{l}_1\cdot\mathbf{l}_2 = 0$, the polarizations of the RPE and of the first pump pulse are identical, so that the RPE constitutes an elongated or compressed wave of the first pump pulse, but inverted in time and propagating in the direction of the vector $\mathbf{k}_\pm = \mathbf{k} \pm (\mathbf{k}_1 - \mathbf{k}_2)$ at a frequency $\omega_\pm$.

In the case of the opposite inequalities $k_1 u \ll 1/\tau_1$ and $k_2 u \gg 1/\tau_2$, the shape of the RPE at $\Delta_1 = \Delta_2 = 0$ and $\gamma_{bc} t \ll 1$ duplicates the profile of the second pump pulse, but is stretched in time because of the factor $(\omega_2 - \omega_1)/\omega_2 < 1$. Also stretched out is the slow phase of the function $a_2(t)$, as can be seen from the following expression:

$$\mathcal{E}_\pm(t) = \frac{\mathbf{Q}^{(\pm)}}{k} a_2((\omega_2-\omega_1)t/\omega_2) \int_0^{\tau_1} a_1^*(\xi)\exp[-i\Delta_1(t-\xi)]\,d\xi \times \exp\left[i\frac{\omega_1}{\omega_2}\Delta_2 t - \gamma_{bc}(t-\tau) - \gamma_{ca}\tau\right],$$

where the instant of the onset of the RPE is $t = t_{RS}$ and the inequality (6) is satisfied, but the argument of the function $a_2 t$ is replaced by $(\omega_2 - \omega_1)t/\omega_2$.

If the atoms are excited by three pump pulses, stimulated RPE is produced regardless of the relative placement of the resonance levels. We assume in this connection that at an instant τ' after the first pump pulse (1) with $n = 1$ there is applied a second duplicating pump pulse at the same frequency ω_1 and the same wave vector $\mathbf{k}_1$, but with different values of $\mathbf{l}_1'$, a_1', τ_1', φ_1', and Φ_1'. Next, after a time interval τ, a third pump pulse (1) with $n = 2$ is sent. The probing pulse produces stimulated RPE, which occurs at $E_a < E_b < E_c$ under the condition $\tau' - \tau > (1 - \omega_2/2\omega_1)\tau_2$, and whose intensity $I_{se}^{(\pm)}(t)$ reaches a maximum at the instant $t = t_e$, where

$$t_e=\tau_1+\tau_1'+\frac{2\omega_1-\omega_2}{\omega_1-\omega_2}\tau'-\frac{\omega_2}{\omega_1-\omega_2}\left(\tau+\frac{\tau_2}{2}\right).$$

If the pump pulses have broad spectra, the intensity is given by

$$I_{se}^{(\pm)}(t_e)=Q_2^{(\pm)}\exp\left[-\frac{\omega_1\gamma_{cb}}{\omega_1-\omega_2}(\tau'-\tau)-\gamma_{ca}(\tau'+\tau)\right],$$

where the factor $Q_2^{(\pm)}$ is independent of τ' or τ. By varying one of the quantities τ' or τ with the other fixed it is possible to obtain from experiment the numerical values of C_1 and C_2 that are contained in the expressions

$$\omega_1\gamma_{cb}/(\omega_1-\omega_2)+\gamma_{ca}=C_1,\quad \omega_1\gamma_{cb}/(\omega_1-\omega_2)-\gamma_{ca}=C_2.$$

In contrast to (9) and to three-phonon echo,[9] both sought constants γ_{cb} and γ_{ca} are determined here simultaneously. If the arrangement of the resonance levels is different, the procedure for determining γ_{cb} and γ_{ca} is similar. Thus, the information obtained with the aid of the considered six-photon parametric process is more complete than in the four-photon case. The intensity of the stimulated RPE can take on quite large values, since $Q_2^{(\pm)}$ and $Q_1^{(\pm)}$ are of the same order for large pump-pulse areas.

3. RS ON HOMOGENEOUSLY BROADENED TRANSITIONS

To investigate homogeneously broadened transitions with

$$k_1u<\gamma_{ca},\quad k_2u<\gamma_{ba},\quad (k_1+k_2)u<\gamma_{cb}$$

it is advantageous to use ultrashort pump pulses with durations $\tau_{1,2}\ll 1/k_{1,2}u$, where $k_{1,2}u\sim 10^{-9}$ sec for a gas. Taking the inequality (4) into account, the durations τ_1 and τ_2 for a nonrarefied gas are of the order of picoseconds. To describe RS on homogeneously broadened transitions it is necessary to make in the preceding equations the substitutions

$$\mathbf{k}_{1,2}\mathbf{v}\to 0,\qquad \int G(\mathbf{v})f(\mathbf{v})\,d\mathbf{v}\to G(0), \tag{10}$$

where $G(\mathbf{v})$ is any of the quantities involved in the calculations. The main formulas are greatly simplified thereby, although the complexity of the expression for the amplitude $\varepsilon_\pm(t)$ is of no importance for the determination of the relaxation time.

It follows from (5) and (7) with allowance for the substitutions a), b) and c) that the intensity $I^{(\pm)}(t)=c|\varepsilon_\pm(t)|^2/2\pi$ of the Stokes or anti-Stokes signals for homogeneously broadened transitions, regardless of the profiles and areas of the pump pulses, takes at any arrangement of the resonance levels the form

$$I^{(\pm)}(t)=Q_3^{(\pm)}\exp[-2\gamma_{cb}(t-\tau)-2\gamma_{ca}\tau],\qquad t_2+\tau_2\leqslant t,$$

where the coefficient $Q_3^{(\pm)}$ is independent of t or τ and is of the same order as $Q_1^{(\pm)}$. In the time interval $0\leqslant t-t_2\leqslant\tau_2$ the intensity $I^{(\pm)}(t)$ increases continuously from zero to a maximum value $I^{(\pm)}(t_2+\tau_2)$ at $\theta_2\lesssim\pi$ or is subject to oscillations at $\pi<\theta_2$, as shown in Fig. 2.

Experimental investigation of the maximum intensity $I^{(\pm)}(t_2+\tau_2)$ as a function of τ yields the relaxation time $1/\gamma_{ca}$ of the optical coherence of the allowed transition $j_a\to j_c$. At the same time, the law governing the damping of $I^{(\pm)}(t)$ as a function of t at fixed τ determines the relaxation time $1/\gamma_{cb}$ of the optical coherence of the forbidden transition $j_b\to j_c$. Thus, the use of a delay time τ between two pump pulses in the SELR method permits also to determine $1/\gamma_{ca}$, a factor not taken into account in the earlier experiments.[6,7]

If the probing pulse has also an ultrashort duration τ_3 and is applied with some delay τ_0 relative to the second pump pulse, the amplitude $\varepsilon_\pm(t)$ is described by the same equations, in which the slow amplitude $a=a(t)$ differs from zero in the time interval $0\leqslant t-t_2-\tau_2-\tau_0\leqslant\tau_3$, and the RS intensity is a separate peak of duration τ_3. The height of this peak is proportional to $\exp(-2\gamma_{cb}\tau_0-2\gamma_{ca}\tau)$, so that γ_{cb} and γ_{ca} can be determined by varying the delays τ and τ_0.

4. CONCLUSION

The described features of RS and RPE were established for three-level systems in the absence of a hyperfine structure, for example for nuclei with zero spin (He, Ne, Ar, Ba, and others). The resonant levels are then quite far from the nonresonant ones, so that the pump pulses can be shortened right down to the picosecond range without violating the chosen three-level approximation. The latter can hold also for molecular systems.

In derivations in Secs. 1–3 were for a gas. In the case of homogeneously broadened transitions, however, all the equations are valid also for resonant impurity atoms in condensed media (liquid and solid) if the substitution (10) is made and each amplitude a_1, a'_1, a_2, and a is multiplied by the Lorentz factor $(\varepsilon+2)/3$ that takes into account the connection between the effective and macroscopic fields. If the atomic transitions are inhomogeneously broadened it is necessary, besides making the substitution (10) and introducing the Lorentz factor, to take into account of the scatter of the resonance levels about a certain mean value. The mechanism and character of this scatter is different for different condensed media, so that the RS problem calls for a separate analysis.

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