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Background information for talk on New possibilities of ultrahigh resolution laser spectroscopy on the basis of the coherent population trapping

"ON THE SELECTIVE PHOTOEXCITATIN OF MOLECULES WITHIN THE HOMOGENEOUS WIDTH OF OPTICAL LINES"

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On the selective photoexcitation of molecules within the homogeneous width of optical lines

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Abstract

We investigate the photoexcitation of molecules of a gas, caused by the change of the state of the coherent population trapping of the open Λ-system of quantum levels at the sharp change of phase and amplitude parameters of the two-frequency laser pumping. Analysis is carried out both on the basis of the Schrödinger equation and in the formalism of the density matrix of molecules in the case of homogeneously broadened spectral lines. The maximum photoexcitation takes place at the two-quantum resonance between lower long-lived states of the Λ-system. It is shown, that the narrow, high-contrast peak of the photoexcitation appears on the comparatively low and wide background, caused by collisions of molecules. Conditions are determined, when the influence of this background is minimum and the spectral width of the photoexcitation peak is much less than the homogeneous widths of the optical lines of resonance transitions in the Λ-system. Such photoexcitation may be used in the technology of isotope (isomer) separation, selective photochemistry and photobiology even at essential overlap of optical spectra of different molecules. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

At the phenomenon of coherent population trapping (CPT) a multilevel quantum system subject to decay processes is coherently driven into a superposition state immune from further excitation, and in which the system population is trapped. CPT was first observed as dark line resonances in fluorescence emission in a laser optical pumping experiment by Alzetta et al. [1] and then explained theoretically by Arimondo and Orriols [2]. In these experiments the atomic states on which the trapped state is based are connected by two photon processes, and CPT requires the condition of two photon resonance to be

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satisfied. Since its discovery, CPT effects have been studied in a variety of situations, leading to the considerable literature on the subject referenced in the review articles by Arimondo [3] and Agap'ev et al. [4]. CPT is the basis of a number of important scientific applications: ultra-high resolution spectroscopy, coherent laser cooling, lasers without inversion, electromagnetically induced transparency, and a number of others described, for example, in reviews [3–5]. Treatments of CPT have been mainly restricted to closed atomic multilevel systems, where the total atomic population is constant. Molecular systems, on the other hand have excited states which may radiatively decay to numerous sublevels (vibrational, rotational) of the ground molecular term, so the levels involved in the CPT process do not form a closed system. Theoretical studies of CPT in open three level systems have been carried out by Knight et al. [6,7] and several works about possible CPT applications in molecules have appeared. For example, velocity selection of molecules subject to stationary optical pumping has been predicted by Izmailov et al. [8,9]. The features of CPT in a highly degenerate open system have been analysed by Milner et al. [10].

Recently we have shown the possibility of the selective photoexcitation of molecules of a gas within the homogeneous width of resonance optical lines on the basis of CPT [11,12]. Indeed, let us consider the quantum Λ-system (Fig. 1), which is formed by lower long-lived nondegenerate states $|1\rangle$ and $|2\rangle$ (for example, sublevels of the ground molecular term) and the excited level $|3\rangle$. The Λ-system interacts with two monochromatic optical fields with frequencies ω_1 and ω_2, which are closed to centers Ω_{31} and Ω_{32} of electrodipole transitions $|1\rangle - |3\rangle$ and $|2\rangle - |3\rangle$, respectively. For molecules such Λ-system (Fig. 1) is open because of a probability of the radiative decay of the excited state $|3\rangle$ on a large number of nonabsorbing sublevels of the ground term [13]. Therefore the population of the Λ-system almost completely vanishes at the sufficiently intensive optical pumping [13,14]. However a fraction of molecules may remain in long-lived states $|1\rangle$ and $|2\rangle$ at the following condition of the CPT [3,4]:

$$|\Delta| = |(\omega_2 - \omega_1) - (\Omega_{32} - \Omega_{31})| \leq W, \qquad (1)$$

where the value W is determined by relaxation rates of populations and coherence of states $|1\rangle$ and $|2\rangle$ and also by intensities of light fields. At definite conditions the value $W(1)$ may be much less than homogeneous widths of spectral lines of resonance optical transitions $|1\rangle - |3\rangle$ and $|2\rangle - |3\rangle$ (Fig. 1). Therefore the CPT condition (1) may be selectively realized even when the effectiveness is low of known methods of the selective laser action [15], based on distinctions of optical spectra of various molecules (for example, isotopes or isomers). It is especially important at sufficiently dense gas media. Selective realization of the CPT condition (1) is possible, for example, owing to the distinction of the hyperfine structure of the ground term for different isotopes (isomers) [13]. The quantum states of the Λ-system at the CPT depends on intensities and phases of pumping waves [3,4]. Therefore the definite change of phase and amplitude parameters of these waves (at their fixed frequencies) leads to the change of the CPT state and to the excitation of trapping molecules from levels $|1\rangle$ and $|2\rangle$ to the state $|3\rangle$ (Fig. 1) with the selectivity determined by the value $W \ll \gamma$ (1).

Such high selective photoprocesses may be used in the spectroscopy, photochemistry and photobiology. Therefore after description of the mechanism of these processes in our short communications [11,12], it is necessary to carry out the detailed investigation of the dynamics, spectrum and selectivity of the photoexcitation of molecules within homogeneous widths of spectral lines of resonance optical transitions $|1\rangle - |3\rangle$ and $|2\rangle - |3\rangle$ (Fig. 1). Such theoretical analysis is carried out in the present paper both

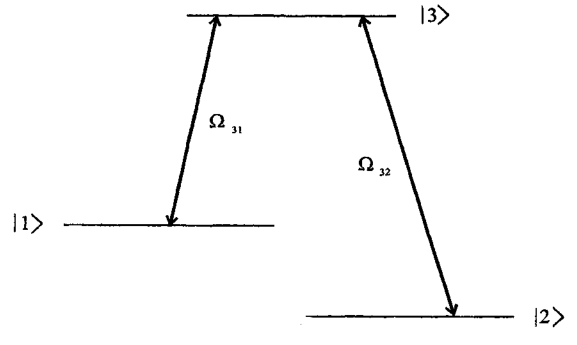

Fig. 1. The Λ-system of optical transitions $|1\rangle - |3\rangle$ and $|2\rangle - |3\rangle$ (with central frequencies Ω_{31} and Ω_{32}) between the excited level $|3\rangle$ and long-lived states $|1\rangle$ and $|2\rangle$.

on the basis of the Schrödinger equation and in the formalism of the density matrix of molecules taking into account characteristic relaxation processes in the gas. Conditions are determined, when this photoexcitation of molecules is effective and recommendations are elaborated of its applications in practice.

2. Calculation of the photoexcitation on the basis of the Schrödinger equation

A number of important peculiarities of interaction of the Λ-system (Fig. 1) with the resonance two frequency laser radiation may be determined on the basis of the Schrödinger equation [3,4]:

$$i\hbar\frac{\partial|\psi\rangle}{\partial t} = \left\{\hat{H}_0 - \sum_{j=1}^{2} I_j^{0.5}\left[\left(e_j\hat{d}\right)\exp(i\omega_j t) + \text{c.c.}\right]\right\}|\psi\rangle, \tag{2}$$

where $\hat{H}_0$ is the nonperturbed Hamiltonian of a motionless molecule, and the second component in Eq. (2) is the Hamiltonian of interaction of this molecule (having the operator $\hat{d}$ of the dipole moment) with monochromatic optical fields 1 and 2, having frequencies ω_1 and ω_2, intensities I_1 and I_2, complex polarization vectors e_1 and e_2, respectively. The wave function $|\psi\rangle$ (2) of the Λ-system may be represented as the following superposition of states $|1\rangle$, $|2\rangle$ and $|3\rangle$:

$$|\psi\rangle = \sum_{m=1}^{3} b_m(t)\exp(-iE_m t/\hbar)|m\rangle, \tag{3}$$

where E_m are energies of nonperturbed states of the Λ-molecule and eigenfunctions $|m\rangle$ are determined by the relationship:

$$\hat{H}_0|m\rangle = E_m|m\rangle \quad (m = 1,2,3). \tag{4}$$

After substitution of the function $|\psi\rangle$ (3) in the Schrödinger equation (2) we receive the following system of equations for probability amplitudes $b_1(t)$, $b_2(t)$ and $b_3(t)$ at the resonance approximation:

$$\begin{aligned} \frac{\partial b_1}{\partial t} &= i g_1 b_3 \exp[i(\delta_1 t + \phi_1)], \\ \frac{\partial b_2}{\partial t} &= i g_2 b_3 \exp[i(\delta_2 t + \phi_2)], \\ \frac{\partial b_3}{\partial t} &= i g_1 b_1 \exp[-i(\delta_1 t + \phi_1)] \\ &\quad + i g_2 b_2 \exp[-i(\delta_2 t + \phi_2)] - \gamma b_3(t), \end{aligned} \tag{5}$$

where $\Omega_{3j} = (E_3 - E_j)\hbar^{-1}$, $\delta_j = (\omega_j - \Omega_{3j})$ is the frequency detuning from the center of the resonance transition $|j\rangle - |3\rangle$ (Fig. 1) for the field $j (j = 1,2)$. Values g_j and ϕ_j in Eqs. (5) are the absolute value and argument of the complex Rabi frequency G_j, respectively:

$$G_j = g_j\exp(i\phi_j) = I_j^{0.5}(e_j d_j)\hbar^{-1} \quad (j = 1,2), \tag{6}$$

where d_j is the matrix element of the dipole moment for the transition $|j\rangle - |3\rangle$ (Fig. 1). The phenomenological last item in the third Eq. (5) describes the decay of the excited state $|3\rangle$ with the rate 2γ out of the open Λ-system (Fig. 1). In Eqs. (5) we don't take into account the radiative decay of the excited level $|3\rangle$ on long-lived states $|1\rangle$ and $|2\rangle$. The upper level $|3\rangle$ will not be populated at the CPT of the Λ-system. According to Eqs. (5) such situation is possible only at simultaneous realization of following equalities:

$$\delta_1 = \delta_2, \tag{7}$$

$$g_1\exp(-i\phi_1)b_1 + g_2\exp(-i\phi_2)b_2 = 0. \tag{8}$$

The dynamics of establishment of the CPT in the open Λ-system (Fig. 1) under the action of the two frequency radiation was investigated in detail on the basis of the Schrödinger equation in the paper [6]. We will analyse the excitation of trapped (at the CPT) molecules by means of an instantaneous change of phase and amplitude parameters of light fields. Indeed, according to relationships (3), (7) and (8), at the CPT the Λ-system of levels (Fig. 1) transits to the nonabsobing state $|NC\rangle$, which is the superposition of lower states $|1\rangle$ and $|2\rangle$:

$$|NC\rangle = \frac{g_2}{G}\exp\left(-\frac{\mathrm{i}E_1 t}{\hbar}\right)|1\rangle - \frac{g_1}{G}\exp\left[-\frac{\mathrm{i}E_2 t}{\hbar} + \mathrm{i}(\phi_2 - \phi_1)\right]|2\rangle, \quad (9)$$

where $G = (g_1^2 + g_2^2)^{0.5}$. The state $|C\rangle$, orthogonal with respect to $|NC\rangle$ (9), may be represented in the form:

$$|C\rangle = \frac{g_1}{G}\exp\left(-\frac{\mathrm{i}E_1 t}{\hbar}\right)|1\rangle + \frac{g_2}{G}\exp\left[-\frac{\mathrm{i}E_2 t}{\hbar} + \mathrm{i}(\phi_2 - \phi_1)\right]|2\rangle. \quad (10)$$

Unlike the state $|NC\rangle$ (9), particles in the state $|C\rangle$ (10) will intensive interact with the pumping radiation [3]. Therefore the two frequency pumping radiation will deplete the state $|C\rangle$ (10) in the open Λ-system (Fig. 1). However molecules will remain in the state $|NC\rangle$ (9) because of the CPT. Given molecules may be then excited on the level $|3\rangle$ (Fig. 1) by means of the change of phase and amplitude pumping parameters, leading to the change of the function $|NC\rangle$ (9). We note that it is possible to realize the mutual transformation of states $|NC\rangle \leftrightarrow |C\rangle$ (9), (10) at fixed frequency detunings (7) of light fields by the replacement of absolute values of Rabi frequencies $g_2 \leftrightarrow g_1$ and also by the change of the phase difference $(\phi_2 - \phi_1)$ of fields on π. Values g_1 and g_2 (6) are equal at the definite ratio of fields intensities. Then it is possible to realize the mutual transformation $|NC\rangle \leftrightarrow |C\rangle$ (9), (10) only by the change of the value $(\phi_2 - \phi_1)$ (6) on π. Further we will investigate the excitation of molecules to the level $|3\rangle$ (Fig. 1) from the state $|NC\rangle$ (9) at the step change of parameters g_1, g_2, ϕ_1 and ϕ_2 (6) on new values $\tilde{g}_1$, $\tilde{g}_2$, $\tilde{\phi}_1$ and $\tilde{\phi}_2$ at the moment $t = t_0$. Then the CPT again will restore in the Λ-system of levels (Fig. 1) in the definite time, however already in the new nonabsorbing quantum state $|\widetilde{NC}\rangle$:

$$|\widetilde{NC}\rangle = \frac{\tilde{g}_2}{\tilde{G}}\exp\left(-\frac{\mathrm{i}E_1 t}{\hbar}\right)|1\rangle - \frac{\tilde{g}_1}{\tilde{G}}\exp\left[-\frac{\mathrm{i}E_2 t}{\hbar} + \mathrm{i}\left(\tilde{\phi}_2 - \tilde{\phi}_1\right)\right]|2\rangle, \quad (11)$$

where $\tilde{G} = (\tilde{g}_1 + \tilde{g}_2)^{1/2}$. The following fraction of the population, trapped in the state $|NC\rangle$ (9), will pass over the excited level $|3\rangle$ during the conversion $|NC\rangle \to |\widetilde{NC}\rangle$ (11):

$$\alpha = |\langle C|\widetilde{NC}\rangle|^2 = \frac{|\tilde{g}_1 g_2 - g_1 \tilde{g}_2 \exp\left[\mathrm{i}\left(\phi_{21} - \tilde{\phi}_{21}\right)\right]|^2}{\left(g_1^2 + g_2^2\right)\left(\tilde{g}_1^2 + \tilde{g}_2^2\right)}, \quad (12)$$

where $\phi_{21} = \phi_2 - \phi_1$and $\tilde{\phi}_{21} = \tilde{\phi}_2 - \tilde{\phi}_1$. According to the expression (12) the process of the optical repumping will be complete $(\alpha = 1)$, when the state $|\widetilde{NC}\rangle$ (11) coincides with the state $|C\rangle$ (10), that is

$$\exp\left[\mathrm{i}\left(\tilde{\phi}_{21} - \phi_{21}\right)\right] = -1, \quad g_1\tilde{g}_1 = g_2\tilde{g}_2. \quad (13)$$

For the description of the dynamics of the open Λ-system at the conversion $|NC\rangle \to |\widetilde{NC}\rangle$ (9), (11) under consideration, it is necessary to solve Eqs. (5) with new values $\tilde{g}_1$, $\tilde{g}_2$, $\tilde{\phi}_1$ and $\tilde{\phi}_2$ at the following starting conditions (at the moment t_0 of the change of pumping parameters):

$$b_1(t_0) = b_{10}, \quad b_2(t_0) = b_{20}, \quad b_3(t_0) = 0, \quad (14)$$

where, according to conditions (7) and (8) of the CPT, probability amplitudes are connected by the relationship $b_{20} = (-g_1/g_2)\exp(\mathrm{i}\phi_{21})b_{10}$ if $\delta_1 = \delta_2$. Then it is not difficult to receive following simple expressions for populations $\rho_{33} = |b_3|^2$ of the excited state $|3\rangle$ for the time interval $\tau = (t - t_0) > 0$ at zero frequency detunings $\delta_1 = \delta_2 = 0$:

$$\rho_{33} = \frac{R}{2\xi^2}\{\exp[-0.5(\gamma + \xi)\tau] - \exp[-0.5(\gamma - \xi)\tau]\}^2,$$

$$\text{if} \quad \left(\tilde{g}_1^2 + \tilde{g}_2^2\right) < \frac{\gamma^2}{4}, \quad (15)$$

$$\rho_{33} = \frac{R\exp(-\gamma\tau)}{\xi^2}[1 - \cos(\xi\tau)],$$

$$\text{if} \quad \left(\tilde{g}_1^2 + \tilde{g}_2^2\right) > \frac{\gamma^2}{4}, \quad (16)$$

where

$$R = 2\alpha\left(\tilde{g}_1^2 + \tilde{g}_2^2\right)\left[|b_{10}|^2 + |b_{20}|^2\right], \quad (17)$$

$$\xi = 2|0.25\gamma^2 - \tilde{g}_1^2 - \tilde{g}_2^2|^{1/2}. \quad (18)$$

At sufficiently low pumping intensities the population ρ_{33} (15) is maximum at the moment $\tau^\star = \xi^{-1}\ln[(\gamma+\xi)/(\gamma-\xi)]$. Then the exponential decrease of the photoexcitation (15) occurs. The characteristic time of such photoexcitation pulse (15) may be determined by the value $T \simeq 2/(\gamma-\xi)$, which decrease up to the quantity $(2/\gamma)$ (when $\tilde{g}_1^2+\tilde{g}_2^2=0.25\gamma^2$) at the growth of the pumping intensity. If $(\tilde{g}_1^2+\tilde{g}_2^2)>0.25\gamma^2$, then the maximum population ρ_{33} (16) takes place at the moment $\tau^\star = 2\xi^{-1}\arctan(\xi/\gamma)$ with the following exponential decrease of the excitation during the characteristic time $T \simeq 2/\gamma$, which may be accompanied by oscillations with the frequency ξ (18) if $\xi>\gamma$. One can show from relationships (15), (16), that the fraction of the population of the Λ-system, which will pass through the excited state $|3\rangle$ during the conversion $|NC\rangle \to |\tilde{NC}\rangle$ (9), (11) under consideration, is determined by the value α(12):

$$2\gamma\int_0^\infty \rho_{33}(\tau)\,\mathrm{d}\tau=\alpha\left(|b_{10}|^2+|b_{20}|^2\right). \qquad (19)$$

We can see also from relationships (12), (15)–(18), that the maximum photoexcitation of the Λ-system takes place at the conditions (13), when states $|NC\rangle$ (9) and $|\tilde{NC}\rangle$ (11) are orthogonal. Let us assume, that the noncoherent ensemble of motionless molecules was in the equilibrium state with average populations $\rho_{11}^{(0)}$, $\rho_{22}^{(0)}$ and $\rho_{33}^{(0)}$ of quantum levels $|1\rangle$, $|2\rangle$ and $|3\rangle$ (Fig. 1), respectively, before the switching of the pumping radiation. Then it is not difficult to show [6], that following averaged populations remain on lower levels $|1\rangle$and $|2\rangle$ at the establishment of the CPT state $|NC\rangle$ (9):

$$\langle|b_{10}|^2\rangle=\frac{g_2^2\left(\rho_{11}^{(0)}g_2^2+\rho_{22}^{(0)}g_1^2\right)}{\left(g_1^2+g_2^2\right)^2}, \qquad (20)$$

$$\langle|b_{20}|^2\rangle=\frac{g_1^2}{g_2^2}\langle|b_{10}|^2\rangle. \qquad (21)$$

Values (20) and (21) may be used in the expression (17) for relationships (15), (16) at the analysis of the photoexcitation of an ensemble of motionless molecules from the CPT state at a change of pumping parameters.

The Schrödinger Eq. (2) does not take into account an influence of molecular collisions in the gas. Therefore it is necessary further to use the formalism of the density matrix [16].

3. Calculation of coherences and populations of levels in the formalism of the density matrix

Let us consider the interaction of molecules of the gas on levels of the open Λ-system (Fig. 1) with two plane running monochromatic light waves, whose electric components have the form:

$$\boldsymbol{E}=\sum_{j=1}^{2} I_j^{1/2}\boldsymbol{e}_j\exp\left[\mathrm{i}\left(\omega_j t-\boldsymbol{K}_j\boldsymbol{r}\right)\right]+\text{c.c.}, \qquad (22)$$

where ω_j is the frequency, $\boldsymbol{K}_j$ is the wave vector, $\boldsymbol{e}_j$ is the unit polarization vector and I_j is the intensity of the wave $j,(j=1,2)$. Further we will use the following system of equations for elements of the density matrix of the open Λ-system of molecular levels (Fig. 1), taking into account characteristic relaxation processes in the gas medium [16]:

$$\frac{\mathrm{d}\rho_{11}}{\mathrm{d}t}=\mathrm{i}g_1\rho_{31}\exp(\mathrm{i}f_1)+\text{c.c.}+2\gamma_1\rho_{33}-\left(\rho_{11}-\rho_{11}^{(0)}\right)\Gamma_1, \qquad (23)$$

$$\frac{\mathrm{d}\rho_{22}}{\mathrm{d}t}=\mathrm{i}g_2\rho_{32}\exp(\mathrm{i}f_2)+\text{c.c.}+2\gamma_2\rho_{33}-\left(\rho_{22}-\rho_{22}^{(0)}\right)\Gamma_2, \qquad (24)$$

$$\frac{\mathrm{d}\rho_{33}}{\mathrm{d}t}=-\mathrm{i}g_1\rho_{31}\exp(\mathrm{i}f_1)-\mathrm{i}g_2\rho_{32}\exp(\mathrm{i}f_2)+\text{c.c.}-2\gamma_3\rho_{33}, \qquad (25)$$

$$\frac{\mathrm{d}\rho_{13}}{\mathrm{d}t}=\mathrm{i}g_1(\rho_{33}-\rho_{11})\exp(\mathrm{i}f_1)-\mathrm{i}g_2\rho_{12}\exp(\mathrm{i}f_2)-\gamma_{13}\rho_{13}, \qquad (26)$$

$$\frac{\mathrm{d}\rho_{23}}{\mathrm{d}t}=\mathrm{i}g_2(\rho_{33}-\rho_{22})\exp(\mathrm{i}f_2)-\mathrm{i}g_1\rho_{21}\exp(\mathrm{i}f_1)-\gamma_{23}\rho_{23}, \qquad (27)$$

$$\frac{\mathrm{d}\rho_{12}}{\mathrm{d}t}=\mathrm{i}g_1\rho_{32}\exp(\mathrm{i}f_1)-\mathrm{i}g_2\rho_{13}\exp(-\mathrm{i}f_2)-\Gamma_{12}\rho_{12}, \qquad (28)$$

where $f_j=\delta_j t-\boldsymbol{K}_j\boldsymbol{r}+\phi_j$; $\delta_j=(\omega_j-\Omega_{3j})$ is the frequency detuning from the resonance for the wave

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$j,(j=1,2)$; values g_j and ϕ_j are determined in relationships (6); the value $2\gamma_3$ in Eq. (25) is the relaxation rate of the excited state $|3\rangle$(Fig. 1); values $2\gamma_1$ and $2\gamma_2$ in Eqs. (23) and (24) are partial rates of the radiative decay from the level $|3\rangle$ to the states $|1\rangle$ and $|2\rangle$, $(\gamma_3 > \gamma_1 + \gamma_2)$. The value $\Gamma_j(j=1,2)$ in Eqs. (23) and (24) describes the relaxation of the population of the long-lived level $|j\rangle$ to the equilibrium value $\rho_{jj}^{(0)}$ because of molecular collisions. The value Γ_{12} in Eq. (28) is the relaxation rate of the light-induced coherence ρ_{12} between states $|1\rangle$ and $|2\rangle$. Values γ_{13} in Eq. (26) and γ_{23} in Eq. (27) are half-widths of spectral lines for transitions $|1\rangle - |3\rangle$ and $|2\rangle - |3\rangle$ (Fig. 1), respectively. Further we will consider the case, when these optical lines are homogeneously broadened. Such situation may take place for the comparatively dense gas medium or for the short-living excited state $|3\rangle$ and sufficiently heavy polyatomic molecules [13]. It is suggested, that the relationship $|\Omega_{32} - \Omega_{31}| \ll \Omega_{31}$ takes place for frequencies of the Λ-system (Fig. 1) and wave numbers $|\boldsymbol{K}_1|$ and $|\boldsymbol{K}_2|$ of the resonance light field (22) are approximately equal. Further we will consider the case of unidirectional pumping waves (22). It is convenient to use following replacements for nondiagonal elements of the density matrix in Eqs. (23)–(28) [4]:

$$\rho_{j3}(\boldsymbol{r},t) = \tilde{\rho}_{j3}(t)\exp\left[\mathrm{i}(\delta_j t - \boldsymbol{K}_j \boldsymbol{r})\right] \quad (j=1,2),$$
$$\rho_{12}(\boldsymbol{r},t) = \tilde{\rho}_{12}(t)\exp\left[\mathrm{i}(\delta_1 - \delta_2)t - (\boldsymbol{K}_1 - \boldsymbol{K}_2)\boldsymbol{r}\right]. \tag{29}$$

Then we receive the system of linear equations:

$$\begin{aligned}
\frac{\partial \rho_{11}}{\partial t} &= \mathrm{i}G_1\tilde{\rho}_{31} - \mathrm{i}G_1^{\star}\tilde{\rho}_{13} + 2\gamma_1\rho_{33} \\
&\quad - (\rho_{11} - \rho_{11}^{(0)})\Gamma_1, \\
\frac{\partial \rho_{22}}{\partial t} &= \mathrm{i}G_2\tilde{\rho}_{32} - \mathrm{i}G_2^{\star}\tilde{\rho}_{23} + 2\gamma_2\rho_{33} \\
&\quad - (\rho_{22} - \rho_{22}^{(0)})\Gamma_2, \\
\frac{\partial \rho_{33}}{\partial t} &= -\mathrm{i}G_1\tilde{\rho}_{31} - \mathrm{i}G_2\tilde{\rho}_{32} + \mathrm{i}G_1^{\star}\tilde{\rho}_{13} \\
&\quad + \mathrm{i}G_2^{\star}\tilde{\rho}_{23} - 2\gamma_3\rho_{33}, \\
\frac{\partial \tilde{\rho}_{13}}{\partial t} &= -(\gamma_{13} + \mathrm{i}\delta_1)\tilde{\rho}_{13} + \mathrm{i}G_1(\rho_{33} - \rho_{11}) \\
&\quad - \mathrm{i}G_2\tilde{\rho}_{12}, \\
\frac{\partial \tilde{\rho}_{23}}{\partial t} &= -(\gamma_{23} + \mathrm{i}\delta_2)\tilde{\rho}_{23} + \mathrm{i}G_2(\rho_{33} - \rho_{22}) \\
&\quad - \mathrm{i}G_1\tilde{\rho}_{21}, \\
\frac{\partial \tilde{\rho}_{12}}{\partial t} &= -\left[\Gamma_{12} + \mathrm{i}(\delta_1 - \delta_2)\right]\tilde{\rho}_{12} + \mathrm{i}G_1\tilde{\rho}_{32} \\
&\quad - \mathrm{i}G_2^{\star}\tilde{\rho}_{13},
\end{aligned} \tag{30}$$

where $G_j = g_j\exp(\mathrm{i}\phi_j)$ (6). Let us at first analyse stationary solutions of Eqs. (30). Then we receive the balanced relationship between populations of levels of the open Λ-system (Fig. 1):

$$\rho_{33} = \frac{\Gamma_1(\rho_{11}^{(0)} - \rho_{11}) + \Gamma_2(\rho_{22}^{(0)} - \rho_{22})}{2(\gamma_3 - \gamma_1 - \gamma_2)}. \tag{31}$$

One can see, that the stationary population ρ_{33} (31) of the excited state $|3\rangle$ is caused by the supplement of lower levels $|1\rangle$ and $|2\rangle$ (Fig. 1) because of molecular collisions. Stationary nondiagonal elements of the density matrix in Eqs. (30) also are determined by levels populations ρ_{11}, ρ_{22} and ρ_{33}:

$$\tilde{\rho}_{13} = \left[\mathrm{i}G_1(\rho_{33} - \rho_{11}) - \mathrm{i}G_2\tilde{\rho}_{12}\right]L_1, \tag{32}$$

$$\tilde{\rho}_{23} = \left[\mathrm{i}G_2(\rho_{33} - \rho_{22}) - \mathrm{i}G_1\tilde{\rho}_{21}\right]L_2, \tag{33}$$

$$\tilde{\rho}_{12} = \frac{G_1G_2^{\star}\left[(\rho_{33} - \rho_{22})L_2^{\star} + (\rho_{33} - \rho_{11})L_1\right]}{\left[\Gamma_{12} + g_1^2L_2^{\star} + g_2^2L_1 + \mathrm{i}(\delta_1 - \delta_2)\right]}, \tag{34}$$

where $L_j = (\gamma_{j3} + \mathrm{i}\delta_j)^{-1}$, $(j=1,2)$. It is easy to receive expressions for stationary populations ρ_{11} and ρ_{22} from the system of linear Eqs. (30). We don't cite these expressions here because they are sufficiently unwieldy in general case.

We will assume that following relationships take place for relaxation parameters of the Λ-system (Fig. 1) under consideration in Eqs. (23)–(28):

$$\gamma_{13}, \gamma_{23}, (\gamma_3 - \gamma_1 - \gamma_2) \gg \Gamma_1, \Gamma_2, \Gamma_{12}, \tag{35}$$

that is relaxation rates of populations and coherence of sublevels $|1\rangle$ and $|2\rangle$ of the ground molecular term are comparatively small. Let us also consider following relationships between these parameters:

$$\gamma_{13} = \gamma_{23} = \gamma\,, \quad \Gamma_1 = \Gamma_2 = \Gamma\,. \tag{36}$$

Then expressions for populations of levels of the Λ-system essentially simplify at such intensities of the radiation, when relationships take place:

$$\gamma \geq \frac{2g_1^2}{\gamma} \gg \Gamma, \Gamma_{12}\,, \quad \gamma \geq \frac{2g_2^2}{\gamma} \gg \Gamma, \Gamma_{12}\,. \tag{37}$$

Restrictions (37) correspond to such intensities of waves (22), when the effective repumping of the population occurs from lower levels $|1\rangle$ and $|2\rangle$ (Fig. 1), however the saturation of resonance optical transitions $|1\rangle - |3\rangle$ and $|2\rangle - |3\rangle$ is not essential. For example, conditions (37) may be realized at intensities of radiation of CW lasers $(I_1 + I_2) \sim 0.1–1$ W/cm^2 if relaxation rates $\Gamma, \Gamma_{12} \sim 1$ MHz and $\gamma \sim 10^3$ MHz and oscillator strengths of resonance optical transitions $f \sim 0.1–1$. It is not difficult to receive from Eqs. (30) following simple formulas for stationary populations ρ_{11} and ρ_{22} of lower levels of the open Λ-system (when $\gamma_1, \gamma_2 \ll \gamma$) for comparatively small frequency detunings $|\delta_1| \ll \gamma$, $|\delta_2| \ll \gamma$ and $|\delta_1 - \delta_2| \leq (g_1^2 + g_2^2)/\gamma$ at conditions (36), (37):

$$\rho_{11} = \frac{0.5\Gamma(1 + g_2^2 g_1^{-2})(\rho_{11}^{(0)} g_2^2 + \rho_{22}^{(0)} g_1^2)}{\gamma(0.25W^2 + \Delta^2)}\,, \tag{38}$$

$$\rho_{22} = \frac{g_1^2}{g_2^2}\rho_{11}\,, \tag{39}$$

where $\Delta = (\delta_2 - \delta_1)$ and the characteristic width W (1) of dependences $\rho_{11}(\Delta)$ (38) and $\rho_{22}(\Delta)$ (39) has the form:

$$W = 2\sqrt{(g_1^2 + g_2^2)\left[\frac{\Gamma_{12}}{\gamma} + 0.5\left(\frac{g_1^2}{g_2^2} + \frac{g_2^2}{g_1^2}\right)\frac{\Gamma}{\gamma}\right]}\,. \tag{40}$$

We note, that the width (40) depends not only on absolute values of intensities of the pumping waves (22) but also on their ratio (g_1^2/g_2^2). For the fixed sum $(g_1^2 + g_2^2)$, the minimum width W (40) takes place at equal values $g_1 = g_2$ (6). Thus the relationship $2\gamma \gg W \geq \Gamma, \Gamma_{12}$ may be realized at pumping intensities (37) under consideration. Then the frequency interval $|\Delta| \leq (g_1^2 + g_2^2)/\gamma$ exists, where the peak of the CPT arises, in fact, on the negligible background. Therefore it is possible to realize the CPT for the definite type of molecules with the selectivity determined by the value $W \ll 2\gamma$ (1), (40).

Molecules trapped at the CPT , may be then excited to the state $|3\rangle$ (Fig. 1) at the sharp change of phase and amplitude parameters of waves (with fixed frequencies and polarizations) (22). It is necessary to solve Eqs. (30) for the density matrix by numerical methods for analysis of such nonstationary photoexcitation.

4. Analysis of dynamics, spectrum and selectivity of the photoexcitation

Let us, at first, analyse dependences of stationary populations of levels of the Λ-system (Fig. 1) on the difference of frequency detunings $\Delta = \delta_2 - \delta_1$ of waves (Fig. 2). One can see, that the essential decrease of populations ρ_{11} and ρ_{22} of lower levels occurs already at comparatively low intensities of pumping waves (curves 1 in Figs. 2a, 2b) because of the process of the optical repumping from the open Λ-system. At the same time the narrow peak appears in dependences $\rho_{11}(\Delta)$ and $\rho_{22}(\Delta)$ with the center at the point $\Delta = 0$, which is caused by the CPT. The width of such CPT resonance is determined by the relaxation rate Γ_{12} of the coherence between lower states $|1\rangle$ and $|2\rangle$ at sufficiently low pumping intensities, when $(g_1^2 + g_2^2) \ll \Gamma_{12}\gamma$ [3,4]. According to the formula (31), the narrow dip appears in the dependence $\rho_{33}(\Delta)$ (curve 1 in Fig. 2c), which is caused by the resonance weakening of the photoexcitation at the CPT. Populations of lower levels decrease at intensification of the optical pumping, while the CPT peaks increase in dependences $\rho_{11}(\Delta)$ and $\rho_{22}(\Delta)$ (curves 1 and 2 in Figs. 2a, 2b). These dependences are well described by obtained expressions (38)–(40) in the frequency interval $|\Delta| \leq (g_1^2 + g_2^2)/\gamma$ at sufficiently high pumping intensities (37). One can see, that the population of the excited state is negligible in comparison with populations of lower levels at the CPT condition $|\Delta| \leq W$ (1) under the stationary pumping of the open Λ-system (Figs. 2a, 2b, 2c).

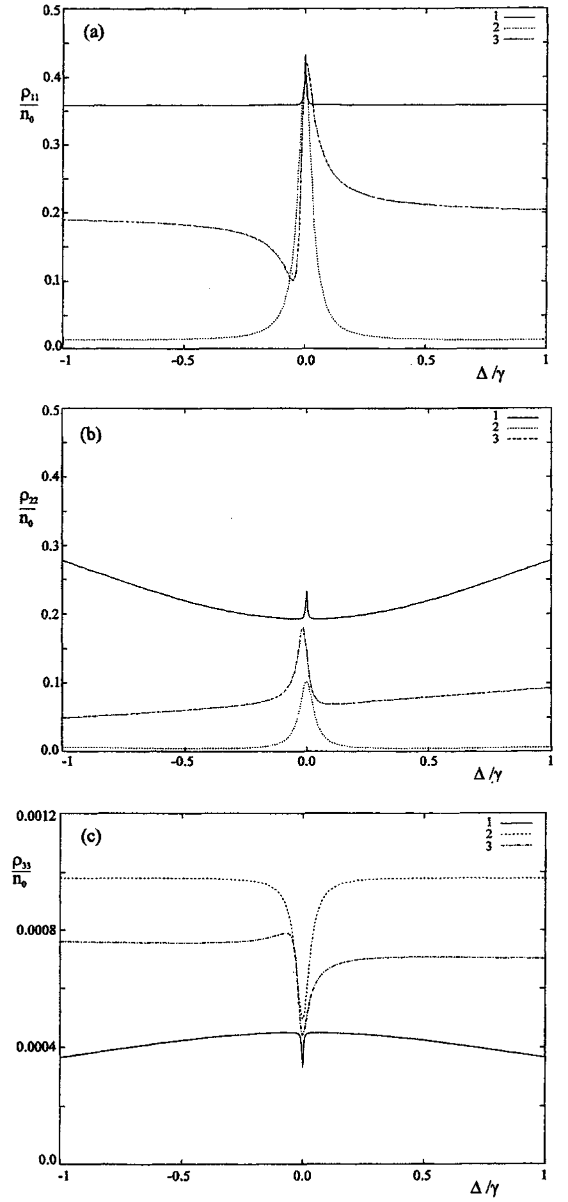

Fig. 2. Dependences of stationary populations of levels $\rho_{11}(a)$, $\rho_{22}(b)$, and $\rho_{33}(c)$ on the value $\Delta=(\delta_2-\delta_1)$, when $\gamma_3=\gamma$, $(\gamma_1+\gamma_2)\ll\gamma$, $\Gamma_{12}=\Gamma=0.002\gamma$, $\rho_{11}^{(0)}=\rho_{22}^{(0)}=0.5n_0$, $\delta_1/\gamma=0(1,2),5(3)$, $g_1=0.02(1),0.2(2,3)$, $g_2=2g_1$.

We note that dependences 1 and 2 in Figs. 2a, 2b, 2c, obtained at the fixed zero frequency detuning $\delta_1=0$ of the wave 1, are symmetric with respect to the value $\Delta=0$. At the same time light shifts occur of quantum levels $|1\rangle$ and $|2\rangle$ in the case of frequency detunings of waves (22) from centers of resonance transitions $|1\rangle-|3\rangle$ and $|2\rangle-|3\rangle$ (Fig. 1) [14,16]. Such shifts may cause the essential antisymmetry of CPT resonances in dependences $\rho_{11}(\Delta)$, $\rho_{22}(\Delta)$ and $\rho_{33}(\Delta)$ (curves 3 in Figs. 2a, 2b, 2c) at the large frequency detuning $|\delta_1|\gg\gamma$. Fig. 3 displays the dynamics of levels populations of the Λ-system (Fig. 1) at the switching of the pumping radiation (22) at the moment $t=0$ and the momentary change of amplitude and phase parameters of waves (with fixed frequencies and polarizations) at the moment $t=t_0=400\gamma^{-1}$. One can see the sharp decrease of the total population of lower levels ($\rho_{11}+\rho_{22}$) at the condition $\Delta=(\delta_2-\delta_1)=0$ at initial time (curves 1 and 2 in Fig. 3b). In consequence, the

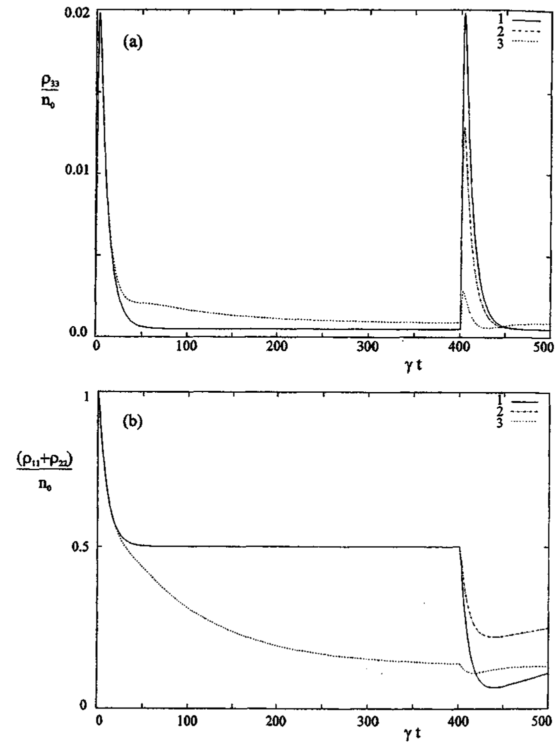

Fig. 3. Dynamics of the population ρ_{33} of the excited levels $|3\rangle$ (a) and the summary population ($\rho_{11}+\rho_{22}$) of lower levels $|1\rangle$ and $|2\rangle$ (b) at the pumping switching (at the moment $t=0$) and following changes (at the moment $t=t_0=400\gamma^{-1}$) of waves parameters $g_1\to\tilde{g}_1$, $g_2\to\tilde{g}_2$, $\phi_1\to\tilde{\phi}_1$, and $\phi_2\to\tilde{\phi}_2$, when $\gamma_3=\gamma$, $(\gamma_1+\gamma_2)\ll\gamma$, $\Gamma_{12}=\Gamma=0.002\gamma$, $\rho_{11}^{(0)}=\rho_{22}^{(0)}=0.5n_0$, $\delta_1=0$, $\delta_2/\gamma=0(1,2),0.04(3)$, $g_1=0.1$, $g_2=2g_1$, $\tilde{g}_1=g_2(1),g_1(2,3)$, $\tilde{g}_2=g_1(1),g_2(2,3)$, $\tilde{\phi}_1=\phi_1$, $\tilde{\phi}_2=\phi_2+\pi$.

Λ-system transits to the nonabsorbing quantum state $|NC\rangle$ (9). The characteristic time $T \simeq 2/(\gamma - \xi) \ll \Gamma^{-1}, \Gamma_{12}^{-1}$ of photoexcitations jumps in Fig. 3a may be received from the expression for the population ρ_{33} (15) of the excited level. At $\delta_1 \neq \delta_2$ populations of lower levels will repump out of the Λ-system from the starting moment $t = 0$ up to the establishment of the equilibrium value (curve 3 in Fig. 3b). Thus stationary populations establish in some time $\tau \geq \Gamma^{-1}$ after the switching of the optical pumping, which are described by formulas (38) and (39) at conditions (37). Molecules, trapped on lower levels, may be then excited by means of the change of amplitude and phase parameters of waves (22). Curves 1 in Figs. 3a, 3b were received at such change of wave parameters, when the conversion realizes of the Λ-system from the quantum state $|NC\rangle$ (9) to the orthogonal state $|\widetilde{NC}\rangle = |C\rangle$ (10), (11), according to relationships (13), and the most complete depletion occurs of populations of levels $|1\rangle$ and $|2\rangle$. Unlike curves 1, dependences 2 in Figs. 3a, 3b correspond to the change (at the moment $t = t_0$) only of the phase difference $(\phi_2 - \phi_1)$ on π at constant values $g_1 \neq g_2$ (6). Then the Λ-system transits to the quantum state $|\widetilde{NC}\rangle$ (11) nonorthogonal to the state $|NC\rangle$ (9). Therefore the photoexcitaion peak (at $t \rangle t_0$) for the dependence 2 is less than for the curve 1 in Fig. 3a. The dynamics of the population of the excited state $|3\rangle$ (Fig. 3a) corresponds to the dynamics of the fluorescence of the gas medium, which may be registered directly at experiments. One can see from dependences 2 and 3 in Fig. 3a in the time interval $t > t_0$, that the essential weakening of the photoexcitation peak occurs already at the difference of frequency detunings $|\Delta| = |\delta_2 - \delta_1|$ much less than the homogeneous width 2γ of spectral lines of optical transitions $|1\rangle - |3\rangle$ and $|2\rangle - |3\rangle$. Indeed, stationary populations of lower levels establish under the action of the two-frequency radiation (22), which are described by formulas (38) and (39) at conditions (36) and (37) (curves 2 in Figs. 2a, 2b). Therefore the excitation occurs, in the main, of trapped molecules, which satisfy the CPT condition $|\Delta| \leq W$ (1) with the small width $W \ll \gamma$ (40) at the following sharp change of waves parameters. Thus Fig. 4 displays the dependence of the population ρ_{33} of the excited level $|3\rangle$ on the value $\Delta = (\delta_2 - \delta_1)$ for different fixed moments $t > t_0$.

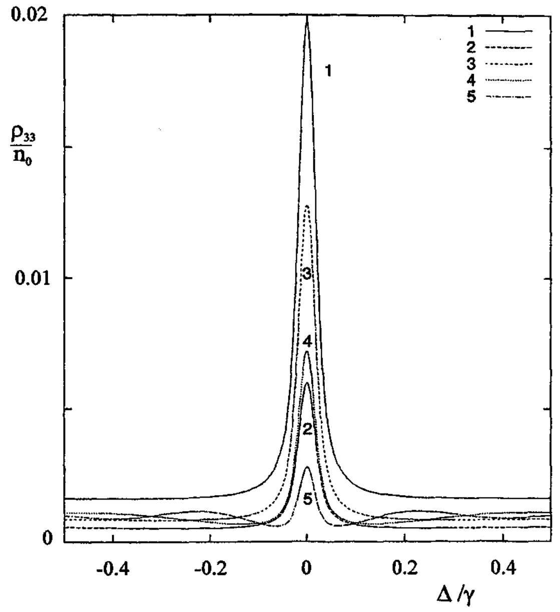

Fig. 4. Dependence of the population ρ_{33} of the excited level $|3\rangle$ on the value $\Delta = (\delta_2 - \delta_1)$ at fixed moments t after change (at the time $t_0 = 400\gamma^{-1}$) of waves parameters $g_1 \to \tilde{g}_1$, $g_2 \to \tilde{g}_2$, $\phi_1 \to \tilde{\phi}_1$ and $\phi_2 \to \tilde{\phi}_2$, when $(t - t_0)\gamma = 1(2)$, 3 (1,3), 10 (4), 20 (5), $\gamma_3 = \gamma$, $(\gamma_1 + \gamma_2) \ll \gamma$, $\Gamma_{12} = \Gamma = 0.002\gamma$, $\rho_{11}^{(0)} = \rho_{22}^{(0)} = 0.5 n_0$, $\delta_1 = 0$, $g_1 = 0.1$, $g_2 = 2 g_1$, $\tilde{g}_1 = g_2(1)$, $g_1(2-5)$, $\tilde{g}_2 = g_1(1)$, $g_2(2-5)$, $\tilde{\phi}_1 = \phi_1$, $\tilde{\phi}_2 = \phi_2 + \pi$.

One can see, that dependences $\rho_{33}(\Delta)$ have high-contrast peak with the center in the point $\Delta = 0$. Characteristic spectral width of this peak is determined by the value W (40) at conditions (36), (37). At the same time the dependence $\rho_{33}(\Delta)$ has the background at $|\Delta| \rangle W$, which is caused by the supplement of populations of lower levels (Fig. 1), because of molecular collisions. Such background does not change essentially in the case of the switching only of the phase difference of waves (curves 2–5 on Fig. 4), because the light-induced coherence between levels $|1\rangle$ and $|2\rangle$ essentially weakens in the frequency region $|\Delta| \rangle W$ (1). Curves 1 and 3 in Fig. 4 correspond to such moment $t > t_0$ when the maximum photoexcitation of molecules takes place at zero frequency detunings $\delta_1 = \delta_2 = 0$ (Fig. 3a). Unlike dependence 3, curve 1 in Fig. 4 was obtained at the change not only of the phase difference $(\phi_2 - \phi_1)$ on π but also amplitude parameters of waves $g_1 \to g_2$, $g_2 \to g_1$, according to conditions (13), when the strongest photoexcitation occurs. However in this case growth takes place not only for the photoexcitation peak but also for the background of the dependence $\rho_{33}(\Delta)$ in the frequency region $|\Delta| \gg W$.

It is necessary side by side with the described selective photoexcitation of definite molecules to carry out their further transitions to another energy states for required transformations (ionization, dissociation or chemical reaction) [14,15]. Then the additional electromagnetic field must be applied on the medium during the characteristic time T of the photoexcitation under study. Therefore it is important to analyse also the population P_3 of the excited state $|3\rangle$, averaged over the time interval T (after the moment t_0):

$$P_3 = \frac{1}{T}\int_{t_0}^{t_0+T} \rho_{33}(t)\mathrm{d}t. \tag{41}$$

Fig. 5 displays the dependence $P_3(\Delta)$ of such population (41) on the value $\Delta = \delta_2 - \delta_1$. Then the averaging time $T = 2/(\gamma - \xi)$ was used in the formula (41), when the most essential photoexcitation of molecules occurs at pumping intensities under consideration, according to relationships (15), (17), (18). One can see, that the growth of waves intensities causes the increase both the amplitude and the width W of the photoexcitation peak (curves 1 and 2 in Fig. 5). At the same time the background of given functions $P_3(\Delta)$ feebly depends on pumping intensities in the region $\gamma > |\Delta| \gg W$ at the conditions (37). Such background may be estimated from the stationary population (31) of the excited level $|3\rangle$ at the depleted lower levels $|1\rangle$ and $|2\rangle$, that is:

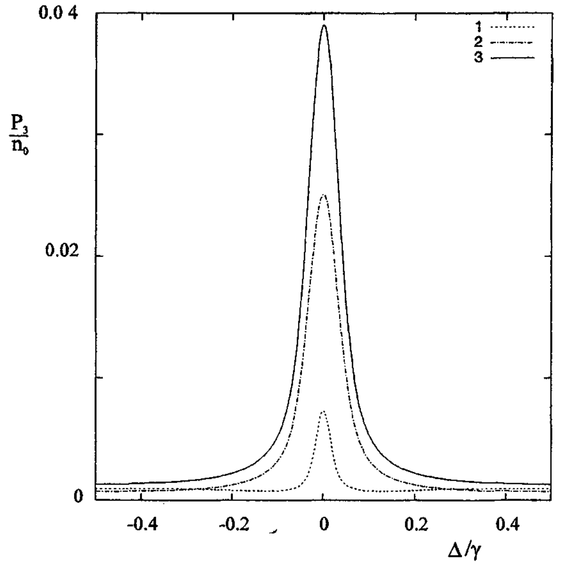

Fig. 5. Dependence of the averaged population P_3 of the excited level $|3\rangle$ on the value $\Delta = (\delta_2 - \delta_1)$ at the change (at moment $t_0 = 400\gamma^{-1}$) of waves parameters $g_1 \to \tilde{g}_1$, $g_2 \to \tilde{g}_2$, $\phi_1 \to \tilde{\phi}_1$ and $\phi_2 \to \tilde{\phi}_2$, when $\gamma_3 = \gamma$, $(\gamma_1 + \gamma_2) \ll \gamma$, $\Gamma_{12} = \Gamma = 0.002\gamma$, $\rho_{11}^{(0)} = \rho_{22}^{(0)} = 0.5n_0$, $\delta_1 = 0$, $g_1 = 0.1(1), 0.2(2,3), g_2 = 2g_1$, $\tilde{g}_1 = g_1(1,2), g_2(3)$, $\tilde{g}_2 = g_2(1,2), g_1(3)$, $\tilde{\phi}_1 = \phi_1$, $\tilde{\phi}_2 = \phi_2 + \pi$.

$$P_3(\gamma > |\Delta| \gg W) \simeq \frac{\Gamma_1 \rho_{11}^{(0)} + \Gamma_2 \rho_{22}^{(0)}}{2(\gamma_3 - \gamma_1 - \gamma_2)}. \tag{42}$$

At the simultaneous change of amplitude and phase parameters of waves (22), in accordance with conditions (13), the growth occurs both of the peak and the background of the photoexcitation spectrum $P_3(\Delta)$ (curve 3 in Fig. 5). We note, that the maximum value of the photoexcitation P_3 (41), reached at zero detunings $\delta_1 = \delta_2 = 0$ (Fig. 5), may be estimated on the basis of formulas (15)–(21) for the population ρ_{33} of the level $|3\rangle$.

In Figs. 4 and 5 dependences of the population of the excited level on the value $\Delta = \delta_2 - \delta_1$ were obtained at the fixed zero detuning $\delta_1 = 0$ of the wave 1 (22). Our calculations show, that given dependences don't change qualitatively at the small detuning $|\delta_1| < \gamma$. However the essential antisymmetry takes place in dependences of photoexcitation peaks on the value Δ at the large frequency detuning $|\delta| \gg \gamma$. Indeed such antisymmetry is characteristic for dependences $\rho_{11}(\Delta)$ and $\rho_{22}(\Delta)$ of stationary populations of lower levels (curves 3 on Figs. 2a, 2b).

The process of the selective photoexcitation under consideration is especially important in the case of a gas mixture of different molecules (for example, isotopes or isomers) with overlapping homogeneously broadened spectral lines of optical transitions from the ground term to excited states. Then we can realize the interaction of two-frequency radiation (22) with such Λ-systems of levels for different molecules, where the photoexcitaion occurs, in the main, for the definite type of molecules. It is possible because of distinctions of the energy structure of the ground term for different types of molecules. Let us consider, for example, the gas mixture of molecules a and b with densities n_a and n_b, respectively. Then it is convenient to introduce the following characteristic of the selectivity S_a of the photoexcitation of molecules a:

$$S_a = \frac{P_3^{(a)}\left(\delta_1^{(a)}=0,\delta_2^{(a)}=0\right)n_b}{P_3^{(b)}\left(\delta_1^{(b)},\delta_2^{(b)}\right)n_a}, \tag{43}$$

where $P_3^{(j)}(\delta_1^{(j)},\delta_2^{(j)})$ is the averaged (over the time) population (41) of the excited level $|3j\rangle$, $\delta_1^{(j)}=(\omega_1-\Omega_{31}^{(j)})$ and $\delta_2^{(j)}=(\omega_2-\Omega_{32}^{(j)})$ are detunings of fixed frequencies ω_1 and ω_2 of waves (22) from centers of resonance transitions for the Λ-system of molecules of the type $j,(j=a,b)$. The situation is especially interesting, when relationships $|\delta_1^{(b)}|<\gamma_{13}$, $|\delta_2^{(b)}|<\gamma_{23}$ and $|\delta_1^{(b)}-\delta_2^{(b)}|>W$ take place, where $W\ll\gamma_{13},\gamma_{23}$ is the characteristic width of the photoexcitation peak. In this case the value S_a (43) directly describe the selectivity of the photoexcitation of molecules a within homogeneous widths of spectral lines of resonance optical transitions.

Selective photoexcitation of molecules under consideration may be repeated by the next sharp change of phase and amplitude parameters. Indeed, after such photoexcitation and the following depletion of the Λ-system, stationary populations of lower levels $|1\rangle$ and $|2\rangle$ again restore in the time $\tilde{\tau}\geq\Gamma^{-1}$, because of the optical pumping and mixing of quantum states at molecular collisions.

The change of phase and amplitude parameters of pumping waves is not instantaneous in practice. However obtained in this paper dynamic dependences are correct if the characteristic time $T^{\star}$ of such change is much less than relaxation times of the excited state $|3\rangle$ and optical coherences of the Λ-system of levels (Fig. 1), that is if $T^{\star}\ll\gamma_3^{-1},\gamma_{13}^{-1},\gamma_{23}^{-1}$. Our investigations also showed that the amplitude and selectivity of the photoexcitation essentially decrease at a growth of this time $T^{\star}$ when $T^{\star}>\gamma_3^{-1},\gamma_{13}^{-1},\gamma_{23}^{-1}$

5. Conclusions

The selective photoexcitation of molecules under consideration occurs during the conversion of the open Λ-system of levels (Fig. 1) from one quantum CPT state $|NC\rangle$ to another CPT state $|\tilde{NC}\rangle$, caused by the sharp change of intensities and the phase difference of the two-wave pumping (with fixed frequencies). The maximum photoexcitation realize at the condition of the two-quantum resonance between lower long-lived nondegenerate states of the Λ-system. The growth of the pumping intensities causes the increase of the amplitude and spectral width but decrease of the duration of such photoexcitation. The high-contrast peak appears in the photoexcitation spectrum on the comparatively wide and low background, caused by a mixing of quantum sublevels of the ground term of molecules at collisions. The influence of this background on the selectivity of the photoexcitation is minimum in the case of the change only of the phase difference (on π) of waves at their constant intensities. The width W (1) of the photoexcitation peak is determined by comparatively low relaxation rates of the coherence and populations of lower levels of the Λ-system. Therefore the value W may be essentially less than homogeneous widths of spectral lines of resonance optical transitions at sufficiently low pumping intensities. The process of such selective photoexcitation may be repeated in the characteristic time of the collisional relaxation of populations of sublevels of the ground molecular term.

Photoprocesses under consideration may be realized in practice by means of two laser waves with stable frequency difference and controllable phases. This photoexcitation is effective, when the time of the change of parameters of given waves is less than relaxation times of the excited state and optical coherences of the Λ-system. Such sharp change of pumping parameters may be realized by fast-acting electrooptic modulators.

This high selective photoexcitation is possible owing to a distinction of energy structure of the ground term for different molecules (for example, isotopes or isomers) even at an essential overlap of spectra of their optical transitions. Thus given selective photoprocesses may be used in the technology of isotope (isomer) separation, photochemistry and molecular biology, especially in cases of comparatively dense gas media and also for polyatomic molecules with short-living excited states [13,14].

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