Raman scattering in an atomic gas in the presence of depolarizing collisions

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A general expression for the cubic susceptibility tensor of an atomic gas is derived by taking into account level degeneracy, thermal motion, and depolarizing collisions. The expression is used to investigate the influence of depolarizing collisions and of the Doppler effect on Raman scattering in the presence of single, double, or triple resonances and also its influence on two-photon absorption and phase conjugation. Some methods are proposed for the determination of the relaxation constants of atomic multipole moments and for the identification of forbidden transitions. The methods are extended to include Raman scattering from excited states and to spectroscopy free of Doppler broadening.

Raman scattering (RS) is extensively used to study solids, liquids, and gases.[1-5] Principal attention in the investigation of gases is usually given to the study of molecular systems. Atomic gases, however, have their own attractive features and admit of a rigorous quantum-mechanical description of RS with account taken of depolarizing collisions and of the form of the interatomic potential. Light interaction with atoms and relaxation processes in gases in the presence of depolarizing collisions are described by using the multipole moments that appear when the density matrix is expanded in periodic tensor operators. Multipole moments of various ranks are indicative of the population, orientation, and alignment of the atoms. They determine the polarization of the spontaneous emission and the properties of the spectral line, and enter directly in many physical experimentally observed quantities.[6,7] The damping of multipole moments by depolarizing collisions is studied by various methods based on depolarization of the fluorescence, broadening of the Hall-effect signal, level crossing, and quantum beats,[6-8] and also photon echo[9] and quasistationary RS.[10] All these methods, however, have limited applicability regions and can find only some of multipole-moment relaxation constants, so that the search for new effective methods is a timely problem.

In the present paper we obtain the atom's multipole-moment relaxation and other spectroscopic information by using stationary RS produced in various excitation regimes that differ in the location of the resonance levels of the atom, and also in the number and character of the resonances. To this end, we solve first the general-physics problem of calculating for an atomic gas a cubic-susceptibility tensor that is valid in the presence of thermal motion, depolarizing collisions, and any possible number of resonances, since the earlier calculations[13,2,4,5] of this tensor are not valid for our problem (other papers are cited in Ref. 4). Owing to the obtained cubic-susceptibility tensor, many optical four-wave mixing phenomena, such as light scattering in the presence of single, double or triple resonances, the generation of new waves, two-photon absorption, and phase conjugation are represented as various manifestations of RS. With the traditional excitation scheme, using Raman (or two-photon) resonance and an arbitrary trial pulse, we formulate a general approach to the investigation of the depolarizing collisions with the aid of stationary RS. On the basis of the law governing the variation of the intensity and polarization properties of RS we propose a method of determining three relaxation constants for a homogeneously broadened forbidden transition, and also their derivatives with respect to the pressure of the buffer gas. We determine in addition the collisional shifts of the spectral lines and the ratios of the cubic-susceptibility tensor parameters, and identify the forbidden transition. Furthermore, the proposed method can be generalized to include the case when both levels of a forbidden transition are excited and are coupled to the ground level by two allowed transitions resonant to the pump-wave frequencies. The RS amplitude depends here on two resonances, one of which belongs to the allowed transition, so that it is possible to determine in addition to the indicated spectroscopic information also the homogeneous width and the width of the spectral line of the allowed transition. For comparison are shown the capabilities of the method of coherent anti-Stokes scattering (CARS)[2,3,5] in the investigation of the depolarizing collisions in an atomic gas. We consider next other modifications of the stationary RS, since the obtained cubic-susceptibility tensor can be used for all excitation regimes of atoms used for single resonance as well as for a combination of different resonances. In particular, in the two-photon absorption regime in the presence of frequency degeneracy, the range of validity of Doppler-free RS spectroscopy[14,2,5] has been extended to the case of depolarizing collisions. This has made it possible to determine the relaxation constants for the forbidden transition regardless of the character of its broadening. Also determined are the spectral-line collisional shifts needed for the calculation of exact positions of the resonance levels. It follows from the results that a new field of research is opened for the spectroscopy of stationary RS in an atomic gas, which includes, together with the determination of the exact positions of the energy levels of the atoms, the emission of the depolarizing collisions and their influence on the shape, width, and shifts of the lines in the RS spectra. Furthermore, a comparison of the theoretical conclusions with experiment will permit a verification of the universally accepted model of depolarizing collisions.[15]

1. CUBIC SUSCEPTIBILITY TENSOR

If three light waves are incident on an atomic gas new waves are formed in it by four-photon interaction. The total electric field has therefore the form

$$\mathbf{E}=\sum_{n}\mathbf{a}_{n}\exp[i(\mathbf{k}_{n}\mathbf{r}-\omega_{n}t)]+\text{c.c.} \tag{1}$$

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where the indices $n = 1, 2, 3$ correspond to three incident waves, while $n = 4, 5, \ldots$ correspond to the newly formed waves. Here the frequencies ω_n and the wave-vector directions $\mathbf{k}_n$ with indices $n = 1, 2, 3$ are given while those with other indices $n = 4, 5, \ldots$ are to be determined. Amplitude $\mathbf{a}_n$ is a slow function in comparison with $\exp(i\mathbf{k}_n \cdot \mathbf{r})$. Gas-atom behavior in the electric field (1) in the presence of depolarizing collisions is described by means of a density matrix ρ which satisfies the equation

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

where H is the Hamiltonian of a free atom which is moving with the velocity $\mathbf{v}$,$\mathbf{d}$ is the dipole operator and $\Gamma\rho$ is the collisions integral. Since the state of the atom is characterized by an energy E, a total angular momentum J, and its projection M on the quantization axis, it is convenient to write (2) in JM-presentation. However, it takes the simplest form after expanding it in $6j$-symbols and at $\mathbf{E} = 0$ it yields

$$\left[\frac{\partial}{\partial t} + \mathbf{v}\nabla + i\left(\omega_{fg} + \Delta_{fg}^{(\varkappa)}\right) + \gamma_{fg}^{(\varkappa)}\right]\rho_q^{(\varkappa)}(J_f J_g) = \gamma_g N_g f(v)\,\delta_{fg}\delta_{0\varkappa}\delta_{0q}, \tag{3}$$

$$\rho_q^{(\varkappa)}(J_f J_g) = (2J_f + 1)^{1/2}\sum_{M_f M_g}(-1)^{J_f - M_g}\begin{pmatrix} J_f & J_g & \varkappa \\ M_f & -M_g & q \end{pmatrix}\rho_{M_f M_g},$$

$$\omega_{fg} = (E_f - E_g)\hbar^{-1}, \qquad \gamma_{fg}^{(\varkappa)} = \gamma_{fg} + \Gamma_{fg}^{(\varkappa)},$$
$$f(v) = (\pi^{1/2}u)^{-3}\exp(-v^2/u^2),$$

where $\rho_{M_f M_g}$ is the density matrix in JM-presentation, $\rho_q^{(\varkappa)}(J_f J_g)$ is a multipole moment of rank K and $\gamma_{fg}^{\varkappa}$ is the relaxation constant of this multipole moment. The constant γ_g describes radiation decay and gaskinetic collisions, while $\Gamma_{fg}^{(\varkappa)}$ and $\Delta_{fg}^{(\varkappa)}$ are determined by depolarizing collisions, with $\Delta_{gg}^{(\varkappa)} = \Gamma_{gg}^{(\varkappa)} = 0$ and $\Delta_{fg}^{(\varkappa)} = -\Delta_{gf}^{(\varkappa)}$ (see, for example, Refs. 15 and 10). Next, $f(v)$ is Maxwell's distribution function, u the most probable speed, and N_g the stationary density of atoms on the E_g level in the absence of the field (1). The indices f and g independently run through a number of values which correspond to all atomic levels.

To calculate the vector $\mathbf{P} = \int \mathrm{Sp}(\rho\mathbf{d})d\mathbf{v}$ of the dielectric polarization of a gas in the stationary case the equation (2) along with the equation (3) was solved by perturbation theory in the cubic approximation in the field (1). This permits the vector $\mathbf{P}$ to be written as a sum of linear $\mathbf{P}^L$ and nonlinear $\mathbf{P}^{NL}$ parts

$$\mathbf{P}(\mathbf{r}, t) = \mathbf{P}^L(\mathbf{r}, t) + \mathbf{P}^{NL}(\mathbf{r}, t),$$

$$\mathbf{P}^L(\mathbf{r}, t) = \sum_n \varkappa(\omega_n, \mathbf{k}_n)\mathbf{a}_n\exp[i(\mathbf{k}_n\mathbf{r} - \omega_n t)] + \text{c.c.},$$

$$\varkappa(\omega_n, \mathbf{k}_n) = \sum_{fg}\frac{N_{fg}|d_{fg}|^2}{3\hbar}\int\frac{f(v)\,d\mathbf{v}}{\omega_n - \mathbf{k}_n\mathbf{v} - \omega_{fg} - \Delta_{fg}^{(1)} + i\gamma_{fg}^{(1)}}, \tag{4}$$

$$\mathbf{P}^{NL}(\mathbf{r}, t) = \mathbf{P}(\omega_+)\exp[i(\mathbf{k}_+\mathbf{r} - \omega_+ t)] + \mathbf{P}(\omega_-)\exp[i(\mathbf{k}_-\mathbf{r} - \omega_- t)]$$
$$+ \mathbf{P}(\bar\omega_+)\exp[i(\bar{\mathbf{k}}_+\mathbf{r} - \bar\omega_+ t)] + \mathbf{P}(\bar\omega_-)\exp[i(\bar{\mathbf{k}}_-\mathbf{r} - \bar\omega_- t)] + \text{c.c.}, \tag{5}$$

$$\omega_\pm = \omega_3 \pm (\omega_1 - \omega_2),\ \bar\omega_\pm = \omega_3 \pm (\omega_1 + \omega_2),$$
$$\mathbf{k}_\pm = \mathbf{k}_3 \pm (\mathbf{k}_1 - \mathbf{k}_2),\ \bar{\mathbf{k}}_\pm = \mathbf{k}_3 \pm (\mathbf{k}_1 + \mathbf{k}_2), \tag{6}$$

$$\mathbf{P}(\omega_+) = \chi_1^{(+)}\mathbf{a}_1(\mathbf{a}_2^*\mathbf{a}_3) + \chi_2^{(+)}\mathbf{a}_2^*(\mathbf{a}_3\mathbf{a}_1) + \chi_3^{(+)}\mathbf{a}_3(\mathbf{a}_1\mathbf{a}_2^*),$$
$$\mathbf{P}(\omega_-) = \chi_1^{(-)}\mathbf{a}_1^*(\mathbf{a}_2\mathbf{a}_3) + \chi_2^{(-)}\mathbf{a}_2(\mathbf{a}_3\mathbf{a}_1^*) + \chi_3^{(-)}\mathbf{a}_3(\mathbf{a}_1^*\mathbf{a}_2),$$
$$\mathbf{P}(\bar\omega_+) = \bar\chi_1^{(+)}\mathbf{a}_1(\mathbf{a}_2\mathbf{a}_3) + \bar\chi_2^{(+)}\mathbf{a}_2(\mathbf{a}_3\mathbf{a}_1) + \bar\chi_3^{(+)}\mathbf{a}_3(\mathbf{a}_1\mathbf{a}_2),$$
$$\mathbf{P}(\bar\omega_-) = \bar\chi_1^{(-)}\mathbf{a}_1^*(\mathbf{a}_2^*\mathbf{a}_3) + \bar\chi_2^{(-)}\mathbf{a}_2^*(\mathbf{a}_3\mathbf{a}_1^*) + \bar\chi_3^{(-)}\mathbf{a}_3(\mathbf{a}_1^*\mathbf{a}_2^*),$$

$$\chi_1^{(+)} = {}^1/_2[Q_1(\omega_+, \omega_1, -\omega_2) + Q_2(\omega_+, \omega_1, -\omega_2)$$
$$+ Q_1(\omega_+, \omega_1, \omega_3) + Q_2(\omega_+, \omega_1, \omega_3)]$$
$$+ {}^1/_3[Q_0(\omega_+, \omega_3, -\omega_2) - Q_2(\omega_+, \omega_3, -\omega_2)],$$

$$\chi_2^{(+)} = {}^1/_2[Q_2(\omega_+, \omega_1, -\omega_2) - Q_1(\omega_+, \omega_1, -\omega_2)$$
$$+ Q_2(\omega_+, \omega_3, -\omega_2) - Q_1(\omega_+, \omega_3, -\omega_2)]$$
$$+ {}^1/_3[Q_0(\omega_+, \omega_1, \omega_3) - Q_2(\omega_+, \omega_1, \omega_3)],$$
$$\chi_3^{(+)} = {}^1/_2[Q_1(\omega_+, \omega_3, -\omega_2) + Q_2(\omega_+, \omega_3, -\omega_2)$$
$$+ Q_1(\omega_+, \omega_3, \omega_1) + Q_2(\omega_+, \omega_3, \omega_1)]$$
$$+ {}^1/_3[Q_0(\omega_+, \omega_1, -\omega_2) - Q_2(\omega_+, \omega_1, -\omega_2)],$$

$$Q_\varkappa(\omega, \omega_n, \omega_p) = \sum_{fg}\int d\mathbf{v}\,f(v)\,\Pi_{fg}^{(\varkappa)}(\omega - \mathbf{k}\mathbf{v})$$
$$\times\frac{W_{fg}^{(\varkappa)}(\omega_n - \mathbf{k}_n\mathbf{v}) + (-1)^\varkappa W_{fg}^{(\varkappa)}(\omega_p - \mathbf{k}_p\mathbf{v})}{\omega_n + \omega_p - (\mathbf{k}_n + \mathbf{k}_p)\mathbf{v} - \omega_{fg} - \Delta_{fg}^{(\varkappa)} + i\gamma_{fg}^{(\varkappa)}} \tag{7}$$

$$\Pi_{fg}^{(\varkappa)}(\omega - \mathbf{k}\mathbf{v}) = \frac{1}{\hbar}\sum_s d_{fs}^* d_{sg}^*\begin{Bmatrix} 1 & \varkappa & 1 \\ J_f & J_s & J_g \end{Bmatrix}$$
$$\times\left(\frac{1}{\omega - \mathbf{k}\mathbf{v} - \omega_{fs} - \Delta_{fs}^{(1)} + i\gamma_{fs}^{(1)}} - \frac{(-1)^\varkappa}{\omega - \mathbf{k}\mathbf{v} - \omega_{sg} - \Delta_{sg}^{(1)} + i\gamma_{sg}^{(1)}}\right),$$

$$W_{fg}^{(\varkappa)}(\omega - \mathbf{k}\mathbf{v}) = \frac{1}{\hbar^2}\sum_s d_{fs}d_{sg}\begin{Bmatrix} 1 & \varkappa & 1 \\ J_f & J_s & J_g \end{Bmatrix}$$
$$\times\left(\frac{N_{fs}}{\omega - \mathbf{k}\mathbf{v} - \omega_{fs} - \Delta_{fs}^{(1)} + i\gamma_{fs}^{(1)}} - \frac{(-1)^\varkappa N_{sg}}{\omega - \mathbf{k}\mathbf{v} - \omega_{sg} - \Delta_{sg}^{(1)} + i\gamma_{sg}^{(1)}}\right),$$

$$N_{fs} = N_f/(2J_f + 1) - N_s/(2J_s + 1),$$
$$\varkappa = 0, 1, 2, \quad n, p = 1, 2, 3,$$

where $\chi_i^{(-)}$ with $i = 1,2,3$ is obtained from $\chi_i^{(+)}$ by exchanging of indices $1 \rightleftarrows 2$ in the quantities $\omega_1, \omega_2, \chi_1^{(+)}$, and $\chi_2^{(+)}$ with the simultaneous renotation of index $+ \to -$, while $\bar\chi_i^{(+)}$ is obtained from $\chi_i^{(\pm)}$ with by replacing $\omega_{(\pm)} \to \bar\omega_{(\pm)}$ and $\omega_2 \to -\omega_2$. The quantity $Q_\varkappa(\omega, \omega_n, -\omega_p)$ is equal to the right-hand side of (7) with the replacement $\omega_p - \mathbf{k}_p\mathbf{v} \to -\omega_p + \mathbf{k}_p\mathbf{v}$, the designations, of the $6j$-symbol and of the reduced dipole moment d_{fg} are taken from Ref. 16. Here in (5) are retained only those terms which contain products of all three incident-wave amplitudes.

We introduce the cubic susceptibility tensor χ_{ijkl} according to the equation (Ref. 17)

$$P_i^{NL}(\mathbf{r}, t) = \int_{-\infty}^{t}\chi_{ijkl}(t - t', t - t'', t - t''')$$
$$\times E_j(\mathbf{r}, t')E_k(\mathbf{r}, t'')E_l(\mathbf{r}, t''')$$
$$\times dt'\,dt''\,dt''', \tag{8}$$

where indices i, j, k, and l take on the values x, y, and z marking the vector projections onto the Cartesian axes X, Y, and Z. Substituting expression (1) for the electric field in (8) and retaining terms which describe RS we obtain

$$P_i^{NL}(\mathbf{r}, t) = 6\{\chi_{ijkl}(\omega_+; \omega_1, -\omega_2, \omega_3)a_{1j}a_{2k}^*a_{3l}\exp[i(\mathbf{k}_+\mathbf{r} - \omega_+ t)]$$
$$+ \chi_{ijkl}(\omega_-; -\omega_1, \omega_2, \omega_3)a_{1j}^*a_{2k}a_{3l}$$
$$\times\exp[i(\mathbf{k}_-\mathbf{r} - \omega_- t)] + \ldots\} + \text{c.c.}, \tag{9}$$

where all other terms are omitted to make for brevity and th following notation is used

$$\chi_{ijkl}(\omega_\pm;\pm\omega_1,\mp\omega_2,\omega_3)=\int_0^\infty \chi_{ijkl}(\tau_1,\tau_2,\tau_3)$$
$$\times\exp[i(\pm\omega_1\tau_1\mp\omega_2\tau_2+\omega_3\tau_3)]d\tau_1 d\tau_2 d\tau_3.$$

Comparing (5) and (9) we find the main result

$$\chi_{ijkl}(\omega_\pm;\ \pm\omega_1,\ \mp\omega_2,\ \omega_3)$$
$$={}^1/_6(\chi_1{}^{(\pm)}\delta_{ij}\delta_{kl}+\chi_2{}^{(\pm)}\delta_{ik}\delta_{lj}+\chi_3{}^{(\pm)}\delta_{il}\delta_{jk}). \tag{10}$$

The formula (10) determines the general expression for the cubic susceptibility tensor

$$\chi_{ijkl}(\omega;\ \omega_1,\ \omega_2,\ \omega_3)={}^1/_6(\chi_1\delta_{ij}\delta_{kl}+\chi_2\delta_{ik}\delta_{lj}+\chi_3\delta_{il}\delta_{jk}), \tag{11}$$
$$\chi_1={}^1/_2[Q_1(\omega,\ \omega_1,\ \omega_2)+Q_2(\omega,\ \omega_1,\ \omega_2)$$
$$+Q_1(\omega,\ \omega_1,\ \omega_3)+Q_2(\omega,\ \omega_1,\ \omega_3)]$$
$$+{}^1/_3[Q_0(\omega,\ \omega_2,\ \omega_3)-Q_2(\omega,\ \omega_2,\ \omega_3)],$$
$$\chi_2={}^1/_2[Q_1(\omega,\ \omega_2,\ \omega_1)+Q_2(\omega,\ \omega_2,\ \omega_1)$$
$$+Q_1(\omega,\ \omega_2,\ \omega_3)+Q_2(\omega,\ \omega_2,\ \omega_3)]$$
$$+{}^1/_3[Q_0(\omega,\ \omega_3,\ \omega_1)-Q_2(\omega,\ \omega_3,\ \omega_1)],$$
$$\chi_3={}^1/_2[Q_1(\omega,\ \omega_3,\ \omega_1)+Q_2(\omega,\ \omega_3,\ \omega_1)$$
$$+Q_1(\omega,\ \omega_3,\ \omega_2)+Q_2(\omega,\ \omega_3,\ \omega_2)]$$
$$+{}^1/_3[Q_0(\omega,\ \omega_1,\ \omega_2)-Q_2(\omega,\ \omega_1,\ \omega_2)],$$
$$\omega=\omega_1+\omega_2+\omega_3,\ \mathbf{k}=\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3,$$

where spatial dispersion is determined according to (7) by the Doppler effect just as in the case of dielectric susceptibility (4). The tensor (11) is symmetrical with the reference to any permutation of j, k, and l taken two at a time in case of the simultaneous permutation of the corresponding indices of frequencies ω_m, wave vectors $\mathbf{k}_m$ and quantities χ_m with $m=1,2,3$. If we neglect the dispersion or assume $\omega_1=\omega_2=\omega_3$ (and $\mathbf{k}_1=\mathbf{k}_2=\mathbf{k}_3$) we get $\chi_1=\chi_2=\chi_3$, and the tensor (11) becomes symmetric with respect to any pair of indices from i, j, k, and l according to Kleinman's relations. For $\omega_1=\omega_2$ ($\mathbf{k}_1=\mathbf{k}_2$), $\omega_1=\omega_3$ ($\mathbf{k}_1=\mathbf{k}_3$) and $\omega_2=\omega_3$ ($\mathbf{k}_2=\mathbf{k}_3$) we have respectively $\chi_1=\chi_2$, $\chi_1=\chi_3$ and $\chi_2=\chi_3$ and this results in the symmetry over two pairs of indices i, l (j, k), as well as i, k (l, j) and i, j (k, l). The components of the tensor (11) satisfy all the relations typical of isotropic media, for example, $\chi_{xxxx}=\chi_{xxyy}+\chi_{xyxy}+\chi_{xyyx}$. Besides, we have $\chi_{ijkl}{}^*(\omega;\omega_1,\omega_2,\omega_3)=\chi_{ijkl}(-\omega;-\omega_1,-\omega_2,-\omega_3)$, while in the right side of this equation the corresponding wave vectors reverse their signs too. If we neglect the irreversible relaxation the tensor (11) becomes real and satisfies the permutation symmetry

$$\chi_{ijkl}(\omega;\ \omega_1,\ \omega_2,\ \omega_3)=\chi_{jikl}(-\omega_1;\ -\omega,\ \omega_2,\ \omega_3)$$
$$=\chi_{kjil}(-\omega_2;\ \omega_1,\ -\omega,\ \omega_3)=\chi_{ljki}(-\omega_3;\ \omega_1,\ \omega_2,\ -\omega),$$

where frequencies under the integral over the velocity **v** in (7) are permuted together with the Doppler shift.

Thus the tensor (11) meets all necessary requirements and represents a general type of the cubic susceptibility tensor of atomic gas with the Doppler effect and depolarizing collisions taken into account and is correct either with any possible resonances or without them. In this case the formula (11) is still valid when the quantities $\gamma_{fg}^{(\varkappa)}$ and $\Delta_{fg}^{(\varkappa)}$ are functions of the velocity v, as for resonance atoms whose mass is small compared with that of a buffer atom.[10]

It should also be mentioned that the tensor (11) can be written in a short symbolic form

$$\chi_{ijkl}(\omega;\ \omega_1,\ \omega_2,\ \omega_3,)={}^1/_6\hat{P}\{{}^1/_2[Q_1(\omega,\ \omega_1,\ \omega_2)$$
$$+Q_2(\omega,\ \omega_1,\ \omega_2)]\delta_{ij}\delta_{kl}+{}^1/_2[Q_1(\omega,\ \omega_2,\ \omega_1)+Q_2(\omega,\ \omega_2,\ \omega_1)]\delta_{ik}\delta_{lj}$$
$$+{}^1/_3[Q_0(\omega,\ \omega_1,\ \omega_2)-Q_2(\omega,\ \omega_1,\ \omega_2)]\delta_{il}\delta_{jk}\},$$

where the operator $\hat{P}$ acts as follows: terms obtained by means of two cyclic permutations of indices 1, 2, 3 for the frequencies and wave vectors together with the same simultaneous permutation of indices j, k, l are added to the initial expression in the braces.

In order to study RS we use the Maxwell's equations and the obtained dielectric polarization vector (5) while we seek RS waves in (1) with indices $n=4, 5, 6, 7$ in the form

$$\mathbf{E}_{\mathrm{RS}}=\mathbf{a}(\omega_+,\ \mathbf{s}_+)\exp[i(\mathbf{s}_+\mathbf{r}-\omega_+t)]$$
$$+\mathbf{a}(\omega_-,\ \mathbf{s}_-)\exp[i(\mathbf{s}_-\mathbf{r}-\omega_-t)]$$
$$+\mathbf{a}(\bar{\omega}_+,\ \bar{\mathbf{s}}_+)\exp[i(\bar{\mathbf{s}}_+\mathbf{r}-\bar{\omega}_+t)]+\mathbf{a}(\bar{\omega}_-,\ \bar{\mathbf{s}}_-)$$
$$\times\exp[i(\bar{\mathbf{s}}_-\mathbf{r}-\bar{\omega}_-t)]+\mathrm{c.c.}, \tag{12}$$

where the wave frequency for $\omega_3<\omega_1+\omega_2$ is $|\omega_-|=\omega_1+\omega_2-\omega_3$. After that the field (12) amplitudes and vectors $\mathbf{s}_\pm$ ($\bar{\mathbf{s}}_\pm$) are determined by the equations

$$\left[-\frac{i}{2s_\pm}\nabla^2+\frac{1}{s_\pm}\mathbf{s}_\pm\nabla+\alpha(\omega_\pm,\mathbf{s}_\pm)\right]\mathbf{a}(\omega_\pm,\mathbf{s}_\pm)$$
$$=\frac{i2\pi\omega_\pm{}^2}{s_\pm c^2}\left[\mathbf{P}(\omega_\pm)-\frac{\mathbf{s}_\pm\mathbf{P}(\omega_\pm)}{s_\pm{}^2}\mathbf{s}_\pm\right]$$
$$\times\exp[i(\mathbf{k}_\pm-\mathbf{s}_\pm)\mathbf{r}], \tag{13}$$
$$\alpha(\omega_\pm,\ \mathbf{s}_\pm)=\omega_\pm{}^2\varepsilon''(\omega_\pm,\ \mathbf{s}_\pm)/2s_\pm c^2,\ \omega_\pm{}^2\varepsilon'(\omega_\pm,\ \mathbf{s}_\pm)=s_\pm{}^2c^2,$$
$$\varepsilon(\omega_\pm,\ \mathbf{s}_\pm)=1+4\pi\varkappa(\omega_\pm,\ \mathbf{s}_\pm).$$

Here $\alpha(\omega_\pm,\mathbf{s}_\pm)$ is the absorption coefficient, $\varepsilon(\omega_\pm,\mathbf{s}_\pm)$ is the dielectric function, and $\varepsilon'(\omega_\pm,\mathbf{s}_\pm)$ and $\varepsilon''(\omega_\pm,\mathbf{s}_\pm)$ are the real and imaginary parts of $\varepsilon(\omega_\pm,\mathbf{s}_\pm)$. We make next use of the slowly-varying-amplitudes approximation and omit the second-order derivatives in (13). We neglect also the incident-wave exhaustion, considering them to propagate linearly in this nonlinear medium with dispersion law $\omega_n^2\varepsilon'(\omega_n,\mathbf{k}_n)=k_n^2c^2$ where $n=1,2,3$. Besides, we assume that the angles between the vectors $\mathbf{k}_1$, $\mathbf{k}_2$, $\mathbf{k}_3$ (as well as $\mathbf{s}_\pm$ and $\bar{\mathbf{s}}_\pm$) are small in the range between 0 and $\sim10^{-2}$ radian, or large ones ranging between π and $\sim(\pi\sim-10^{-2})$ radian and therefore the term $(\mathbf{s}_\pm\mathbf{P}(\omega_\pm))\mathbf{s}_\pm/s^2_\pm$ may be neglected. Under these assumptions projections of the amplitudes of the field (12) on to the Cartesian axes at the point $\mathbf{r}=\mathbf{s}_\pm L_\pm/s^2_\pm$ at the exit from the gas will have the form

$$a_i(\omega_+,\mathbf{s}_+)=6G(\omega_+,\mathbf{s}_+)\chi_{ijkl}(\omega_+;\ \omega_1,-\omega_2,\ \omega_3)a_{1j}^{(0)}a_{2k}^{(0)*}a_{3l}^{(0)}, \tag{14}$$

$$a_i(\omega_-,\mathbf{s}_-)=6G(\omega_-,\mathbf{s}_-)\chi_{ijkl}(\omega_-;\ -\omega_1,\ \omega_2,\ \omega_3)a_{1j}^{(0)*}a_{2k}^{(0)}a_{3l}^{(0)}, \tag{15}$$

$$G(\omega_\pm,\mathbf{s}_\pm)$$
$$=i\frac{2\pi\omega_\pm{}^2}{s_\pm c^2}\frac{\exp[-(q_\pm+i\Delta_\pm)L_\pm]-\exp[-\alpha(\omega_\pm,\mathbf{s}_\pm)L_\pm]}{\alpha(\omega_\pm.\ \mathbf{s}_\pm)-q_\pm-i\Delta_\pm},$$

$$q_\pm=\sum_{n=1}^{3}\omega_n{}^2\varepsilon''(\omega_n,\ \mathbf{k}_n)\ (\mathbf{k}_n\mathbf{s}_\pm)/2k_n{}^2s_\pm c^2,$$
$$\Delta_\pm=(\mathbf{s}_\pm-\mathbf{k}_\pm)\mathbf{s}_\pm/s_\pm,$$

where $q_\pm$ is the sum of the incident-waves absorption coefficients, $L_{\pm}$ is the gas linear dimension in the $\mathbf{s}_{\pm}$ direction, and the index (0) marks the incident waves amplitudes at the boundary point $r = 0$ on entering the gas for the small convergence angles of these waves. The multiplier $G(\omega_{\pm}, \mathbf{s}_{\pm})$ determines the possible $\mathbf{s}_{\pm}$ while the optimal values of the above vectors are $\mathbf{s}_{\pm} = \mathbf{k}_{\pm}$ and $\bar{\mathbf{s}}_{\pm} = \bar{\mathbf{k}}_{\pm}$. The amplitudes $a_i(\bar{\omega}_{\pm}, \bar{\mathbf{s}}_{\pm})$ are obtained from (13)–(15) by replacing $\omega_{\pm} \to \bar{\omega}_{\pm}$, $\mathbf{s}_{\pm} \to \bar{\mathbf{s}}_{\pm}$, $\omega_2 \to -\omega_2$, $\mathbf{k}_2 \to -\mathbf{k}_2$ and $a_2^{(0)} \to a_2^{(0)*}(a_2^{(0)*} \to a_2^{(0)})$. With the help of (14) and (15) we obtain the intensity $I_{\pm}^{(i)}$ which corresponds to the electric field RS projection on to i-Cartesian axis in the form

$$I_{\pm}^{(i)} = c|a_i(\omega_{\pm}, \mathbf{s}_{\pm})|^2/2\pi, \quad i = x,\ y,\ z. \tag{16}$$

2. SINGLE RAMAN OR TWO-PHOTON RESONANCE

In case of Raman $\omega_1 - \omega_2 = \omega_{cb}$ and two-photon $\omega_1 + \omega_2 = \omega_{cb}$ resonances the incident waves with the frequencies ω_1 and ω_2 are pumping waves, while the third wave with the frequency ω_3—is a probe wave. The physical quantities with + and − indices belong to anti-Stokes (high-frequency) and Stokes (law-frequency) waves. Here the coefficients in the tensor (10) for the Raman resonance have the form

$$\chi_1^{(+)} = {}^1/_2(B_1^{(+)} + B_2^{(+)}),\ \chi_2^{(+)} = {}^1/_2(B_2^{(+)} - B_1^{(+)}),$$
$$\chi_3^{(+)} = {}^1/_3(B_0^{(+)} - B_2^{(+)}), \tag{17}$$

$$\chi_1^{(-)} = {}^1/_2(B_1^{(-)} + B_2^{(-)})^*,\ \chi_2^{(-)} = {}^1/_2(B_2^{(-)} - B_1^{(-)})^*,$$
$$\chi_3^{(-)} = {}^1/_3(B_0^{(-)} - B_2^{(-)})^*, \tag{18}$$

$$B_\varkappa^{(\pm)} = \frac{N_{cb}}{\hbar}\Pi_{cb}^{(\varkappa)}(\pm\omega_{\pm})\Pi_\varkappa(\omega_1, \omega_2)$$
$$\times\int\frac{f(v)\,d\mathbf{v}}{\omega_1 - \omega_2 - (\mathbf{k}_1 - \mathbf{k}_2)\mathbf{v} - \omega_{cb} - \Delta_{cb}^{(\varkappa)} + i\gamma_{cb}^{(\varkappa)}}, \tag{19}$$

$$\Pi_{cb}^{(\varkappa)}(\omega) = \frac{1}{\hbar}\sum_g d_{cg}{}^* d_{gb}{}^* \begin{Bmatrix} 1 & \varkappa & 1 \\ J_c & J_g & J_b \end{Bmatrix}\left(\frac{1}{\omega - \omega_{cg}} - \frac{(-1)^\varkappa}{\omega - \omega_{gb}}\right),$$

$$\Pi_\varkappa(\omega_1, \omega_2) = \frac{1}{\hbar}\sum_g d_{cg} d_{gb} \begin{Bmatrix} 1 & \varkappa & 1 \\ J_c & J_g & J_b \end{Bmatrix}\left(\frac{1}{\omega_1 - \omega_{cg}} - \frac{(-1)^\varkappa}{\omega_2 + \omega_{cg}}\right),$$

$$\varkappa = 0, 1, 2,$$

where nonresonance terms have been omitted.

Since all wave frequencies in this four-wave mixing are nonresonance we can neglect the linear absorption in $G(\omega_{\pm}, \mathbf{s}_{\pm})$, and thus the amplitudes (14) and (15) have the form

$$\mathbf{a}(\omega_+, \mathbf{s}_+) = G_{NR}(\omega_+, \mathbf{s}_+)a_1^{(0)}a_2^{(0)*}a_3^{(0)}$$
$$\times[\chi_1^{(+)}\mathbf{l}_1(\mathbf{l}_2^*\mathbf{l}_3) + \chi_2^{(+)}\mathbf{l}_2^*(\mathbf{l}_3\mathbf{l}_1) + \chi_3^{(+)}\mathbf{l}_3(\mathbf{l}_1\mathbf{l}_2^*)],$$
$$\mathbf{a}(\omega_-, \mathbf{s}_-) = G_{NR}(\omega_-, \mathbf{s}_-)a_1^{(0)*}a_2^{(0)}a_3^{(0)}$$
$$\times[\chi_1^{(-)}\mathbf{l}_1^*(\mathbf{l}_2\mathbf{l}_3) + \chi_2^{(-)}\mathbf{l}_2(\mathbf{l}_3\mathbf{l}_1^*) + \chi_3^{(-)}\mathbf{l}_3(\mathbf{l}_1^*\mathbf{l}_2)],$$
$$G_{NR}(\omega_{\pm}, \mathbf{s}_{\pm}) = 2\pi\omega_{\pm}^2[1 - \exp(-i\Delta_{\pm}L_{\pm})]/s_{\pm}c^2\Delta_{\pm},$$
$$\mathbf{a}_n^{(0)} = a_n^{(0)}\mathbf{l}_n, \quad n = 1, 2, 3,$$

where $\mathbf{I}_n$–the incident wave polarization vector. The amplitudes obtained can be written as sums of three typical parts

$$\mathbf{a}(\omega_+, \mathbf{s}_+) = G_{NR}(\omega_+, \mathbf{s}_+)a_1^{(0)}a_2^{(0)*}a_3^{(0)}$$
$$\times\{{}^1/_3B_0^{(+)}\mathbf{l}_3(\mathbf{l}_1\mathbf{l}_2^*) + {}^1/_2B_1^{(+)}\mathbf{l}_3$$
$$\times(\mathbf{l}_1\times\mathbf{l}_2^*) + {}^1/_2B_2^{(+)}[\mathbf{l}_1(\mathbf{l}_2^*\mathbf{l}_3) + \mathbf{l}_2^*(\mathbf{l}_3\mathbf{l}_1) - {}^2/_3\mathbf{l}_3(\mathbf{l}_1\mathbf{l}_2^*)]\}, \tag{20}$$

$$\mathbf{a}(\omega_-, \mathbf{s}_-) = G_{NR}(\omega_-, \mathbf{s}_-)a_1^{(0)*}a_2^{(0)}a_3^{(0)}$$
$$\times\{{}^1/_3B_0^{(-)}\mathbf{l}_3(\mathbf{l}_1^*\mathbf{l}_2) + {}^1/_2B_1^{(-)}[\mathbf{l}_3[\mathbf{l}_1^*\mathbf{l}_2]]$$
$$+ {}^1/_2B_2^{(-)}[\mathbf{l}_1^*(\mathbf{l}_2\mathbf{l}_3) + \mathbf{l}_2(\mathbf{l}_3\mathbf{l}_1^*) - {}^2/_3\mathbf{l}_3(\mathbf{l}_1^*\mathbf{l}_2)]\}, \tag{21}$$

where the terms proportional to $B_0^{(\pm)}, B_1^{(\pm)}$, and $B_2^{(\pm)}$ describe isotropic, antisymmetric and anisotropic scattering respectively. Here each of relaxation constants $\gamma_{cb}^{(0)}, \gamma_{cb}^{(0)}$ and $\gamma_{cb}^{(0)}$ is connected only with one of the scattering type mentioned. Presenting the amplitudes in the form (20) and (21) permits the use of methods of RS amplitude-polarization spectroscopy[2,5] in the presence of depolarizing collisions, which in their turn will permit to determine $\gamma_{cb}^{(\varkappa)}$ with $\varkappa = 0,1,2$.

Often in experiments the linearly polarized incident waves propagating at small angles of the order of a milliradian fraction are used. In this case we choose X axis along the polarization vector $\mathbf{I}_3$ of the probe wave and we obtain

$$\mathbf{l}_n = \mathbf{l}_x\cos\psi_n + \mathbf{l}_y\sin\psi_n, \quad n = 1, 2, \quad \mathbf{l}_3 = \mathbf{l}_x,$$

where $\mathbf{I}_x$ and $\mathbf{I}_y$ are the unit vectors of Cartesian axes X and Y, Ψ_1 and Ψ_2 are the angles between $\mathbf{I}_3$ and polarization vectors $\mathbf{I}_1$ and $\mathbf{I}_2$ of the pump waves. Under such conditions the amplitudes (20) and (21) can be written in the form

$$\mathbf{a}(\omega_+, \mathbf{s}_+) = G_{NR}(\omega_+, \mathbf{s}_+)a_1^{(0)}a_2^{(0)*}a_3^{(0)}\mathbf{F}_+,$$
$$\mathbf{a}(\omega_-, \mathbf{s}_-) = G_{NR}(\omega_-, \mathbf{s}_-)a_1^{(0)*}a_2^{(0)}a_3^{(0)}\mathbf{F}_-^*, \tag{22}$$

$$\mathbf{F}_{\pm} = {}^1/_3\mathbf{l}_x\{B_0^{(\pm)}\cos(\psi_1 - \psi_2) + B_2^{(\pm)}$$
$$\times[3\cos\psi_1\cos\psi_2 - \cos(\psi_1 - \psi_2)]\}$$
$$+ {}^1/_2\mathbf{l}_y[B_1^{(\pm)}\sin(\psi_1 - \psi_2) + B_2^{(\pm)}\sin(\psi_1 + \psi_2)]. \tag{23}$$

Using the RS polarization properties obtained in (22) and (23) we can choose such values of the angles Ψ_1 and Ψ_2 that the components of amplitudes (22) along the axes X and Y would have only one multiplier of the type (19) with a specific value of the index $\varkappa$. This permits to determine in an experiment one by one the three decay constants $\gamma_{cb}^{(0)}, \gamma_{cb}^{(1)}$ and $\gamma_{cb}^{(2)}$ for a homogeneously broadened forbidden transition if we study the intensity (16) as a function of a tunable frequency ω_1 or ω_2. For example, if $\Psi_1 = -\Psi_2 = \pi/4$, the intensity (16) corresponding to the RS electric field projections on to axes X and Y, is proportional to $|B_1^{(\pm)}|^2$ and $|B_2^{(\pm)}|^2$ respectively and this will give $\gamma_{cb}^{(1)}$ and $\gamma_{cb}^{(2)}$ as well as the collision shifts $\Delta_{cb}^{(1)}$ and $\Delta_{cb}^{(2)}$ of the corresponding lines provided ω_{cb} is known or their difference $\Delta_{cb}^{(1)} - \Delta_{cb}^{(2)}$ if ω_{cb} is not known. If we chose $\Psi_1 = \Psi_2 = \arccos(3^{-1/2})$ then the intensity (16) with the index $i = x$ is proportional to $|B_0^{(\pm)}|^2$ and this permits to find $\gamma_{cb}^{(0)}$ and $\Delta_{cb}^{(0)}$. However, we should bear in mind that in case of forbidden transition $J_b - J_c = \pm 2$ we have $B_0^{(\pm)} = B_1^{(\pm)} = 0$, therefore only $\gamma_{cb}^{(2)}$ and $\Delta_{cb}^{(2)}$ are being determined. In case of $J_b - J_c = \pm 1$ we have $B_0^{(\pm)} = 0$ so that only $\gamma_{cb}^{(\varkappa)}$ and $\gamma_{cb}^{(\varkappa)}$ are being determined with $\varkappa = 1,2$. In case when $J_b - J_c = 0\gamma_{cb}^{(\varkappa)}$ and $\Delta_{cb}^{(\varkappa)}$ are being determined with all possible indices $\varkappa$. In the examined cases the intensities ratio permits to calculate

$$|\Pi_{cb}^{(\varkappa+1)}(\pm\omega_{\pm})\Pi_{\varkappa+1}(\omega_1, \omega_2)/\Pi_{cb}^{(\varkappa)}(\pm\omega_{\pm})\Pi_\varkappa(\omega_1, \omega_2)|$$

with the corresponding values of $\varkappa$.

The proposed methods of determining $\gamma_{cb}^{(\varkappa)}$ is valid if buffer atoms are added to the resonance atoms. In this case the decay constants $\gamma_{cb}^{(\varkappa)}$ acquire terms proportional to the buffer-atom concentration or to the buffer-gas pressure p and it is possible to write

$$\gamma_{cb}^{(\varkappa)} = p\, d\gamma_{cb}^{(\varkappa)}/dp + b_\varkappa,$$

where $b_\varkappa$ is a certain constant independent of p. Determining $\gamma_{cb}^{(\varkappa)}$ at the same temperature of gas and different values of p it is not difficult to calculate the derivative $d\gamma_{cb}^{(\varkappa)}/dp$ connected with the effective cross section of the atomic collisions. In this case the dielectric function corresponding to the buffer atoms should be added to $\varepsilon(\omega_n, \mathbf{k})$ and $\varepsilon(\omega_\pm, \mathbf{s}_\pm)$.

The coefficients (19) contain $6j$-symbols which take into account the selection rules for the total angular momentum of the forbidden transition $J_b - J_a$. This makes it possible to choose the polarization features in (20)–(22) which are determined only by the forbidden transition type and which do not depend on depolarizing collisions and other factors. For the transitions $J_b - J_c = \pm 2$ in (23) we have $B_0^{(\pm)} = B_1^{(\pm)} = 0$, therefore wave polarizations in (22) is linear for arbitrary angles Ψ_1 and Ψ_2. The angle between the vector $\mathbf{I}_3$ and RS electric field is determined by the formula

$$\operatorname{tg}\chi_{\mathrm{RS}} = 3\sin(\psi_1+\psi_2)/[3\cos(\psi_1+\psi_2)+\cos(\psi_1-\psi_2)]. \qquad (24)$$

For $J_b - J_c = \pm 1$ and $J_b + J_c > 1$ we have $B_0^{(\pm)} = 0$ and therefore RS wave polarization in (22) is either elliptical for $\Psi_1 \neq \Psi_2$ or linear for $\Psi_1 = \Psi_2 = \Psi$ and $\tan \Psi_{\mathrm{RS}} = 3 \sin 2\Psi/2\ (3 \cos^2\Psi - 1)$. The exceptions are transitions $J_b = 1 \to J_c = 0$ and $J_b = 0 \to J_c = 1$ for which $B_0^{(\pm)} = B_2^{(\pm)} = 0$ and therefore in case of the real $\mathbf{I}_3$ polarization of the RS waves according to (20) and (21) is linear, orthogonal to $\mathbf{I}_3$ for arbitrary linear and elliptical polarizations of pumping waves. For $J_b - J_c = 0$, the RS waves polarization in (22) is elliptical for any Ψ_1 and Ψ_2, and in the case $J_b = 0 \to J_c = 0$ we have $B_1^{(\pm)} = B_2^{(\pm)} = 0$, and thus the polarization according to (20) and (21) coincides with the probe wave polarization either linear or elliptical one. The found polarization rules permit to identify experimentally the forbidden transitions.

In case of the two-photon resonance $\omega_1 + \omega_2 \approx \omega_{cb}$ coefficients $\chi_i^{(+)}$ in (5) are obtained from (17) and (18) by the replacements $\omega_{(\pm)} \to \bar{\omega}_{(\pm)}$, $\omega_2 \to -\omega_2$ and $\mathbf{k}_2 \to -\mathbf{k}_2$, while anti-Stokes and Stokes wave amplitudes are described by the formulas (20)–(22) with substitutions $a_2^{(0)} \to a_2^{(0)*}$ $(a_2^{(0)*} \to a_2^{(0)})$ and $\mathbf{I}_2 \to \mathbf{I}_2{}^*$ as well as with substitutions $\omega_\pm \to \bar{\omega}_\pm$, $\omega_2 \to -\omega_2$ and $\mathbf{k}_2 \to -\mathbf{k}_2$ in the expression (19). That is why the proposed methods for determination of $\gamma_{cb}^{(\varkappa)}, \Delta_{cb}^{(\varkappa)}$ and $d\gamma_{cb}^{(\varkappa)}/dp$ as well as the method of forbidden-transitions identification are still valid in case of the two-photon resonance.

3. CARS IN THE PRESENCE OF DEPOLARIZING COLLISIONS

Together with the scattering of the third (probe) incident wave described by the formulas (20) and (21) the other types of RS independently take place when the probe wave's role is played by the first of the second pumping wave. In this case scattered waves are separated in the space due to the space synchronism.[6] If the first impulse of pumping with the frequency $\omega_1 > \omega_2$ acts as a probe wave there appear the types of RS at anti-Stokes $\omega_+ = 2\omega_1 - \omega_2$ and Stokes $\omega_- = \omega_2$ frequencies. The former is used in CARS spectroscopy in the absence of the third incident wave.[2,3,5] For CARS an additional multiplier 1/2 appears in the above obtained vector $\mathbf{P}(\omega_+)$, and in (9) for the anti-Stokes wave the multiplier 6 is replaced by 3, while for the Stokes signal the formulas will remain the same with the third impulse replaced by the first. Therefore in this case the cubic susceptibility tensor for both Stokes and anti-Stokes waves is given by the expression (10) with the index 3 replaced by 1 in all physical quantities. In the case of CARS the expressions (20) and (22) for the amplitudes of the anti-Stokes wave remain valid after index 3 is replaced by 1 in all quantities and $\Psi_1 = 0$ in (23). Hence in the CARS method the quantities $B_\varkappa^{(\pm)}$ with $\varkappa = 0,1,2$ for the forbidden transitions $J_b - J_c = 0$ and $J_b - J_c = \pm 1$ exist in the anti-Stokes wave amplitude in the form of such sums which make it difficult to determine $\gamma_{cb}^{(\varkappa)}$ with $\varkappa = 0,1,2$ experimentally. The difficulty mentioned above disappears in case of transitions $J_b - J_c = \pm 2$, for which the amplitudes (20) and (22) contain only $\gamma_{cb}^{(2)}$ and $\Delta_{cb}^{(2)}$, as well as in case of transitions $J_b \to J_c$ with small angular momenta $0 \to 1$ $(1 \to 0)$, $1/2 \to 1/2$ and $1/2 \to 3/2$ $(3/2 \to 1/2)$ for which each of the constants $\gamma_{cb}^{(\varkappa)}$ and $\Delta_{cb}^{(\varkappa)}$ has only one value $\gamma_{cb}^{(\varkappa)} = \gamma_{cb}^{(1)}$ and $\Delta_{cb}^{(\varkappa)} = \Delta_{cb}^{(1)}$ for each possible $\varkappa$ (the same in case of transition $0 \to 0$, where $\gamma_{cb}^{(\varkappa)} = \gamma_{cb}^{(0)}$). For transitions of that type a widely developed method of CARS in atomic gas in the presence of depolarizing collisions can be used without any additional complication.

4. ON RS SUB-DOPPLER SPECTROSCOPY

In case of the two-photon resonance $\omega_1 + \omega_2 \approx \omega_{cb}$ there are special conditions of excitation which make it possible to carry out Doppler-free spectroscopical investigations. These conditions are realized when all three incident wave frequencies are equal $\omega_1 = \omega_2 = \omega_3 = \omega$, while pumping waves are propagating in opposite directions $\mathbf{k}_1 + \mathbf{k}_2 = 0$. Then the Stokes signal can be described by formulas (21)–(23) with replacing $\omega_1 \to \omega, \omega_2 \to -\omega$, $\mathbf{k}_2 \to -\mathbf{k}_2$, $\mathbf{I}_2 \to \mathbf{I}_2^*, a_2^{(0)} \to a_{(2)}^{(0)*}$ and $B_1^{(\pm)} = 0$. Since in this case the Stokes signal on frequency ω is propagating in the direction opposite to the probe wave it can easily be separated from the other waves if the vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ are not collinear. In this case of the two-photon absorption in the presence of frequency degeneracy the denominator in (19) is equal to the sum $2\omega - \omega_{cb} - \Delta_{cb}^{(\varkappa)} + i\gamma_{cb}^{(\varkappa)}$ which does not contain a Doppler shift and this permits to carry out the experimental investigation of collision relaxation independently from the type of the forbidden transition $J_b \to J_c$ broadening. While we scan the frequency near the two-photon resonance $2\omega \approx \omega_{cb}$ and study the intensity (16) as a function of the resonance detuning with the rational choice of the angles Ψ_1 and Ψ_2 it is easy to determine $\gamma_{cb}^{(\varkappa)}, \Delta_{cb}^{(\varkappa)}$ and $d\gamma_{cb}^{(\varkappa)}/dp$ with $\varkappa = 0,2$ by means of the method proposed above for both homogeneous or non-homogeneous forbidden transition $J_b - J_c = 0$. Together with it the ratio of the parameters $|\Pi_{cb}^{(2)}(\omega)\Pi_2(\omega_1 - \omega)/\Pi_{cb}^{(0)}(\omega)\Pi_0(\omega, -\omega)|$ is being calculated. In case of $J_b - J_c = \pm 1, \pm 2$ $\gamma_{cb}^{(2)}, d\gamma_{cb}^{(2)}/dp$ and $\Delta_{cb}^{(2)}$ are being determined except for the transitions $J_b = 0 \to J_c = 1$ and $J_b = 1 \to J_c = 0$ where the Stokes wave does not exist.

To identify forbidden transitions one must recognize that in case of $J_b - J_c = \pm 1, \pm 2$ only anisotropic light scattering appears while in case of $J_b - J_c = 0$ both isotropic and anisotropic scattering take place simultaneously except for the cases of transitions $J_b = 0 \to J_c = 0$, $J_b = 1/2 \to J_c = 1/2$ where the scattering is isotropic. If incident waves are polarized linearly the formula (24) is valid for $J_b - J_c = \pm 1, \pm 2$ while for $J_b - J_c = 0$ the Stokes wave is polarized elliptically except for the transitions $J_b = 0 \to J_c = 0$, $J_b = 1/2 \to J_c = 1/2$ where its polarization coincides with that of the probe wave either linear or elliptical. This permits us to distinguish $J_b - J_c = 0$ from $J_b - J_c = \pm 1, \pm 2$ in experiment.

It is worth to note that in case of linearly polarized incident waves $\mathbf{l}_1 = \mathbf{l}_2 = \mathbf{l}_3$ or $\mathbf{l}_1 = \mathbf{l}_2$ and $\mathbf{l}_1 \mathbf{l}_3 = 0$ the Stokes wave is reversed related to the probe wave, and in case of transitions $J_b = 0 \to J_c = 0$ and $J_b = 1/2 \to J_c = 1/2$ this feature remains also in case of elliptical polarization. The obtained rules can be used to transfer optical information using the well known method (18) in the presence of depolarizing collisions.

5. AN EXAMPLE OF THE DOUBLE RESONANCE

RS from excited states is of great interest when the frequencies of pumping impulses satisfy the conditions of resonances $\omega_1 \approx \omega_{ca}$, $\omega_2 \approx \omega_{ba}$, and $\omega_1 - \omega_2 \approx \omega_{cb}$ while the probe wave frequency ω_3 is nonresonant. In this case the formulas (17)–(24) are still valid after substituting $G_{\mathrm{NR}}(\omega_\pm, \mathbf{s}_\pm)$ for $G(\omega_\pm, \mathbf{s}_\pm)$ and also $B_\varkappa^{(\pm)}$ for the following expression

$$U_\varkappa^{(\pm)} = \frac{1}{\hbar^2} d_{ca} d_{ab} \Pi_{cb}^{(\varkappa)} (\pm\omega_\pm) \begin{Bmatrix} 1 & \varkappa & 1 \\ J_c & J_a & J_b \end{Bmatrix}$$

$$\times \int \Bigg(\frac{N_{ca}}{\omega_1 - \mathbf{k}_1 \mathbf{v} - \omega_{ca} - \Delta_{ca}^{(1)} + i\gamma_{ca}^{(1)}} - \frac{N_{ba}}{\omega_2 - \mathbf{k}_2 \mathbf{v} - \omega_{ba} - \Delta_{ba}^{(1)} - i\gamma_{ba}^{(1)}} \Bigg)$$

$$\times \frac{f(v)\,d\mathbf{v}}{\omega_1 - \omega_2 - (\mathbf{k}_1 - \mathbf{k}_2)\mathbf{v} - \omega_{cb} - \Delta_{cb}^{(\varkappa)} + i\gamma_{cb}^{(\varkappa)}}$$

Here both levels E_c and E_b of the forbidden transition are excited and the RS intensity increases considerably because every term in the amplitudes (20)–(22) has two resonances. The constants $\gamma_{ca}^{(1)}(\Delta_{ca}^{(1)})$ and $\gamma_{ba}^{(1)}(\Delta_{ba}^{(1)})$ are determined independently with the help of RS using a single one-photon resonance. After that with the help of the method described above one can determine experimentally $\gamma_{cb}^{(\varkappa)}$ and $\Delta_{cb}^{(\varkappa)}$ for the forbidden transition with two excited levels, and one can also calculate the ratio of the parameters $|\Pi_{cb}^{(\varkappa+1)}(\pm\omega_\pm)/\Pi_{cb}^{(\varkappa)}(\pm\omega_\pm)|$ with $\varkappa = 0,1$ provided the values of J_a, J_b, and J_c are known. Here the forbidden transitions $J_b \to J_c$ identification method described above is valid.

6. DISCUSSION

Depolarizing collision's influence on some types of RS has been investigated above. However, the obtained cubic susceptibility tensor describes all possible RS including those caused by the interference effects of resonant and nonresonant parts. In this connection we point out some other general rules. When three waves resonant to two adjacent transitions are interacting with the medium there is no sense in separating them into pumping waves and a probe wave, both in the absence of the resonance and in the presence of single one-photon resonance. The reason is that two of these three waves have the same frequencies and the total electric field (12) of scattered waves does not change in case of rearrangement of the physical values related to these two waves. For example, in case $\omega_1 = \omega_3 \approx \omega_{ca}$ and $\omega_2 \approx \omega_{ba}$ $(E_a < E_b < E_c)$ two scattered waves with the frequencies $\omega_+ = 2\omega_1 - \omega_2$ and $\omega_- = \omega_2$ are formed. After passing through the gas they separate from each other due to the different directions of their wave vectors. The former corresponds to the double resonance and the latter—to the triple resonance. In this case the gas polarization nonlinear vector is described by the formula (5) with $\mathbf{P}(\bar{\omega}_+) = 0$. According to the calculations all types of scattering in this case—isotropic, antisymmetric and anisotropic depend on two or three constants $\gamma_{cb}^{(0)}, \gamma_{cb}^{(1)}$ and $\gamma_{cb}^{(2)}$ at the same time, unlike (20) and (21), and this makes it difficult to determine them experimentally. The same problem will be easier in case of forbidden transitions $J_b - J_c$ with small angular momenta $0 \to 0$, $1 \to 0$ $(0 \to 1)$, $1/2 \to 1/2$, $1/2 \to 3/2$ $(3/2 \to 1/2)$ as well as in case of transitions $J_b - J_c = \pm 2$ with arbitrary momenta.

In cases when three incident waves have different frequencies and are resonant to the three different adjacent transitions any two of them may be considered as pumping waves and the remaining one as a probe wave. The scattered waves in this case interfere in such a way that experimental determination of the relaxation constants is as difficult as in the previous case.

Finally we note that polarizational self-action for the wave with frequency $\omega \approx \omega_{\mathrm{ba}}$, wave vector $\mathbf{k}$ and polarization vector $\mathbf{l}$ is also described with the help of the formula (5) with $\mathbf{P}(\bar{\omega}_+) = 0$, $\omega_1 = \omega_2 = \omega_3 = \omega$, $\mathbf{k}_1 = \mathbf{k}_2 = \mathbf{k}_3 = \mathbf{k}$ and $\mathbf{l}_1 = \mathbf{l}_2 = \mathbf{l}_3 = \mathbf{l}$. In a gas which is dense enough to satisfy the condition $\gamma_{bb}^{(\varkappa)} \gg \gamma$ the resonance term in (5) coincides with that obtained in (19), where $\gamma = 4|d_{ba}|^2 \omega_{ba}^3 / 3\hbar c^3 (2J_b + 1)$ is a probability of the spontaneous emission for the quantum $\hbar\omega_{ba}$ by the single atom. In this case the term $\mathbf{P}(\bar{\omega}_+)$ in (5) describes the third harmonic generation in the presence of depolarizing collisions.

[1] *Nonlinear Spectroscopy*, edited by N. Bloembergen, International School of Physics "Enrico Fermi," Amsterdam, NY, North Holland, 1977.

[2] S. A. Akhmanov and N. I. Koroteev, *Methods of Nonlinear Optics in the Spectroscopy of Light Scattering*, Nauka, Moscow, 1981.

[3] *Raman Spectroscopy of Gases and Liquids* (edited by A. Weber), Springer-Verlag, 1979.

[4] J. F. Reintjes, *Nonlinear Optical Parametrical Processes in Liquids and Gases*, Academic Press, N.Y., 1984 (Russ. transl., Mir, Moscow, 1987).

[5] Y. R. Shen, *The Principles of Nonlinear Optics*, J. Wiley, N. Y., 1984 (Russ. transl., Mir, Moscow, 1989).

[6] M. P. Chaika, *Interference of Degenerate Atomic States*, Len. Gos. Univ., Leningrad, 1975.

[7] K. Blum, *Density Matrix Theory and Applications*. Plenum Press, N. Y., 1981 (Russ. transl., Mir, Moscow, 1983).

[8] E. B. Aleksandrov, N. I. Kaliteevskii and M. P. Chaika, Usp. Fiz. Nauk **155**, 129, 1979 [Sov. Phys. Usp. **22**, 760 (1979)].

[9] A. I. Alekseev and A. M. Basharov, Izv. Akad. Nauk SSSR, Ser. Fiz. **46**, 557, 1982, Bull. Acad. Sci. USSR, Phys. Ser. **46**(3), 130, 1982.

[10] A. I. Alekseev, V. N. Beloborodov, and O.V. Zhemerdeev, J. Phys. B. **20**, 3571 (1987); **22**, 143 (1989); **22**, 2393 (1989).

[11] A. I. Alekseev and O. V. Zhemerdeev, Zh. Eksp. Teor. Fiz. **93**, 71, 1987 (Sov. Phys.—JETP **66**, 40, 1987.

[12] V. D. Vedenin, F. Sh. Ganikhanov, S. Dinev *et al.*, Opt. Lett. **113**, 14, 1989.

[13] N. Bloembergen, *Nonlinear Optics. Series Frontiers in Physics*, Reading, Mass., Benjamin, 1964 [Russ. transl. Mir, Moscow (1966)].

[14] L. M. Humphrey, J. P. Gordon, and P. F. Ziao, Opt. Lett. **56**, 5, 1980.

[15] A. Omont, Prog. Quant. Electron. **69**, 5, 1977.

[16] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of the Angular Momentum*, Nauka, Leningrad, 1975.

[17] L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media*, Nauka, Moscow, 1982.

[18] B. Ya. Zeldovitch, N. F. Pipiletzkii, and V. V. Shkunov, Phase Conjugation [in Russian], Nauka, Moscow, 1985.

[19] A. I. Alekseev, Zh. Eksp. Teor. Fiz. **94** (7), 130, 1988 [Sov. Phys.—JETP **67**, 1370 (1988)].

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