Cubic susceptibility tensor of gas atoms with a hyperfine level structure

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The cubic susceptibility tensor is derived for a gaseous medium consisting of atoms with a hyperfine level structure. This tensor can describe all the nonlinear phenomena involving four-wave mixing and self-interaction of optical waves. It is shown that each nonlinear phenomenon corresponds to terms in this tensor that give rise to single, double, or triple resonances at the frequencies of incident optical waves as well as at difference and sum frequencies of these waves. The tensor is used to investigate the characteristic features due to the hyperfine splitting of the atomic levels in Doppler-free two-photon absorption spectroscopy and also in Raman light scattering. The relationships obtained are suggested as the basis of methods which can be used to determine the decay constants of electron–nuclear multipole moments of atoms and to identify the transitions forbidden in respect of the electron angular momentum and the total momentum.

Hundreds of experimental and theoretical investigations have been made of the nonlinear phenomena of four-wave mixing and self-interaction of optical waves in gases and condensed media (many references can be found in the books listed as Refs. 1–4). The interest in these phenomena is due to their general physical importance and extensive practical applications. The greatest attention has been paid to the Raman light scattering (RLS), coherent anti-Stokes Raman scattering (CARS), phase conjugation, self-diffraction, and Doppler-free two-photon absorption spectroscopy. Studies of these nonlinear phenomena in atomic gases, rather than in other media, have been particularly popular because the experimental results can be explained theoretically in a convincing manner by adopting a quantum-mechanical approach.

The fullest theoretical investigation of the degenerate four-wave mixing under steady-state conditions in a gas of atoms with the zero nuclear spin in the presence of level degeneracy and thermal motion was that given in Ref. 5, whereas the treatments allowing for elastic depolarizing collisions were provided in Refs. 6–8. In the case of arbitrary frequencies of the incident cw optical waves the cubic susceptibility tensor for the four-wave mixing in a gas of atoms with zero nuclear spin in the presence of other depolarizing collisions was calculated in Ref. 9 and was used to investigate RLS, CARS, and Doppler-free two-photon absorption spectroscopy.

However, experimental studies of the nonlinear phenomena of four-wave mixing and self-interaction of optical waves under cw conditions are usually carried out on atoms with a nonzero nuclear spin and the description of the experimental results is usually made employing a model of a two-level atom or a quantum-mechanical approach which ignores the hyperfine structure of the atomic levels (see, for example, Refs. 1–4). Such a description of nonlinear phenomena ignores their specific features associated with the hyperfine splitting of the atomic levels when the nuclear spin is present.

In view of this gap, the present paper reports a calculation of the cubic susceptibility tensor of gas atoms with a nonzero nuclear spin and the use of this tensor in describing all the nonlinear phenomena of four-wave mixing and self-interaction of optical waves. Calculations are made below on the basis of a quantum-mechanical equation for a density matrix and the Maxwell equations allowing for an arbitrary nuclear spin, as well as for the level degeneracy, thermal motion, elastic depolarizing collisions, and linear absorption of incident optical waves of arbitrary polarization.

The cubic susceptibility tensor found below applies both in the absence of resonances and in the presence of any number of resonances of hyperfine sublevels. The explicit form of this tensor can be obtained for each specific nonlinear effect by retaining in the general expression those terms representing resonances and corresponding to a given nonlinear effect. By way of example, the cubic susceptibility tensors are given below for the Raman scattering with a single Raman or two-photon resonance, as well as for a double resonance corresponding to the Raman scattering of atoms in excited states. These tensors describe different types of the Raman light scattering, as well as different variants of two-photon absorption, CARS, and Stokes scattering used in Doppler-free two-photon absorption spectroscopy. This spectroscopy is considered in a search for methods that can be used to determine the decay constants of electron–nuclear multipole moments of atoms and to identify the forbidden transitions between hyperfine sublevels.

In view of its uniqueness the method of Doppler-free two-photon absorption spectroscopy is superior to other spectroscopic techniques in determination of the decay constants predicted by the model of elastic depolarizing collisions. However, in the identification of the transitions forbidden in respect of the electron angular momentum and the total momentum, it is more convenient to adopt some variety of the RLS. This is due to the fact that in the absence of degeneracy in respect of the frequencies of the incident optical waves the hyperfine structure of the atomic levels influences the polarization properties of the RLS more strongly than in the two-photon absorption spectroscopy utilizing incident optical waves with identical frequencies. Away from a resonance with hyperfine sublevels of the upper level of a forbidden transition it is found that these hyperfine sublevels become locked together and behave as a single upper level, and transitions from this level to any hyperfine sublevel of the lower level of a given transition are determined by

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the selection rules governing the electron angular momentum, which makes it possible to identify the transitions forbidden only in respect of this momentum. Then, the transitions forbidden in respect of the total momentum can be found by scanning the frequency of one of the optical pump waves near a resonance with one of the hyperfine sublevels and investigating the RLS polarization.

If a nonlinear effect is due to a resonance at zero frequency and also due to two other resonances within the width of a one-photon absorption line, the polarization of the new waves which are then formed also depends strongly on the hyperfine structure of the atomic levels even if the frequencies of the incident waves are degenerate. This is true also of self-diffraction, phase conjugation, and self-interaction of optical waves. General properties of all the nonlinear phenomena of four-wave mixing and self-interaction of optical waves in a gas of atoms with a nonzero nuclear spin are a major change in the polarization properties and in densities of the newly formed optical waves, which appears away from a resonance with the hyperfine sublevels, and a gradual transformation to the corresponding nonlinear phenomena for atoms with zero nuclear spin, which occurs when the deviations from all the resonances with the hyperfine sublevels of the resonant levels become sufficiently large.

1. PRINCIPAL EQUATIONS AND NOTATION

We shall consider a gas containing atoms with a nonzero nuclear spin. The hyperfine interaction splits an energy level of an atom into hyperfine levels with energies[10]

$$E_F=E+\hbar\Delta_F,\quad \hbar\Delta_F={}^1/_2AC+BC(C+1),$$

$$C=F(F+1)-J(J+1)-I(I+1),$$

where E is the energy of an atom without allowance for the nuclear spin; $\hbar\Delta_F$ is the energy of the hyperfine interaction; A and B are the constants of the magnetic and quadrupole hyperfine splitting of the level; F, J, and I are the quantum numbers representing the total momentum $\mathbf{F}=\mathbf{J}+\mathbf{I}$, the electron angular momentum $\mathbf{J}$, and the nuclear spin $\mathbf{I}$. Therefore, the state of an atom is characterized not only by E_F, but also by the quantum numbers J, I, F, and by the projection M_F of the vector $\mathbf{F}$ along the quantization axis.

The interaction of gas atoms with an electric field $\mathbf{E}$ can be represented, based on the usual model of elastic depolarizing collisions,[11] using the density matrix equation:

$$\left(\frac{\partial}{\partial t}+\mathbf{v}\nabla-\hat{\Gamma}\right)\rho=\frac{i}{\hbar}[\rho(H-\mathbf{Ed})-(H-\mathbf{Ed})\rho], \tag{1}$$

where H is the Hamiltonian of the investigated atom; $\mathbf{v}$ is the velocity of this atom; $\mathbf{d}$ is the dipole moment operator; $\hat{\Gamma}\rho$ is the collision integral. The integral assumes its simplest form if we expand the density matrix, written in the FM_F representation, as a series in terms of the $3j$ symbols:

$$\rho_{F_fM_{F_f},F_gM_{F_g'}}=\frac{(-1)^{F_f-M_{F_g'}}}{(2F_f+1)^{1/2}}\sum_{\varkappa q}(2\varkappa+1)$$
$$\times\begin{pmatrix}F_f & F_g' & \varkappa\\ M_{F_f} & -M_{F_g'} & q\end{pmatrix}\rho_q^{(\varkappa)}(F_fF_g'), \tag{2}$$

where $\rho_q^{(\varkappa)}(F_fF_g')$ is the electron–nuclear multipole moment of rank $\varkappa$, whereas the indices f and g assume independently infinite series of values corresponding to all the atomic levels with the energy E_f (E_g). Substituting Eq. (2) into Eq. (1) and assuming that $\mathbf{E}=0$, in order to represent more clearly the collision-integral contribution, we obtain

$$\left\{\frac{\partial}{\partial t}+\mathbf{v}\nabla+i[\omega_{F_fF_g'}+\Delta_{fg}^{(\varkappa)}(F_fF_g')]\right.$$
$$\left.+\theta_{fg}^{(\varkappa)}(F_fF_g')\right\}\rho_q^{(\varkappa)}(F_fF_g')=0,$$

$$F_f\neq F_g'\quad\text{for}\quad f=g, \tag{3}$$

$$\omega_{F_fF_g'}=(E_{F_f}-E_{F_g'})\hbar^{-1}=\omega_{fg}+\Delta_{F_f}-\Delta_{F_g'},$$

$$\omega_{fg}=(E_f-E_g)\hbar^{-1},$$

$$\theta_{fg}^{(\varkappa)}(F_fF_g')+i\Delta_{fg}^{(\varkappa)}(F_fF_g')$$
$$=(2F_f+1)(2F_g'+1)\sum_{\varkappa'\varkappa''}(2\varkappa'+1)(2\varkappa''+1)$$
$$\times\begin{Bmatrix}J_f & I & F_f\\ J_g & I & F_g'\\ \varkappa' & \varkappa'' & \varkappa\end{Bmatrix}^2(\gamma_{fg}^{(\varkappa')}+i\Delta_{fg}^{(\varkappa')}), \tag{4}$$

$$\gamma_{fg}^{(\varkappa)}=\gamma_{fg}+\Gamma_{fg}^{(\varkappa)},\quad \gamma_{fg}=(\gamma_f+\gamma_g)/2,$$

$$\gamma_{fg}^{(\varkappa)}=\gamma_{gf}^{(\varkappa)},\quad \Delta_{fg}^{(\varkappa)}=-\Delta_{gf}^{(\varkappa)},\ \Gamma_{gg}^{(0)}=0,$$

$$\left[\frac{\partial}{\partial t}+\mathbf{v}\nabla+i(\Delta_{F_g}-\Delta_{F_g'})+\gamma_g\right]\rho_q^{(\varkappa)}(F_gF_g')$$
$$+(2F_g+1)^{1/2}\sum_{F_g''F_g'''}(2F_g''+1)^{-1/2}\tau_g^{(\varkappa)}$$
$$\times(F_gF_g',F_g''F_g''')\rho_q^{(\varkappa)}(F_g''F_g''')$$
$$=\gamma_gN_gf(v)(2F_g+1)(2J_g+1)^{-1}(2I+1)^{-1}\delta_{F_gF_g'}\delta_{0\varkappa}\delta_{0q},$$

$$\tau_g^{(\varkappa)}(F_gF_g',F_g''F_g''')=(2F_g+1)^{1/2}(2F_g'+1)^{1/2} \tag{5}$$
$$\times(2F_g''+1)^{1/2}(2F_g'''+1)^{1/2}$$
$$\times\sum_{\varkappa'\varkappa''}(2\varkappa'+1)(2\varkappa''+1)\begin{Bmatrix}J_g & I & F_g\\ J_g & I & F_g'\\ \varkappa' & \varkappa'' & \varkappa\end{Bmatrix}\begin{Bmatrix}J_g & I & F_g''\\ J_g & I & F_g'''\\ \varkappa' & \varkappa'' & \varkappa\end{Bmatrix}\Gamma_{gg}^{(\varkappa')},$$
$$f(v)=(\pi^{1/2}u)^{-3}\exp(-v^2/u^2),$$

where the terms in Eqs. (3) and (5) containing $\theta_{fg}^{(\varkappa)}(F_fF_g')$, $\Delta_{fg}^{(\varkappa)}(F_fF_g')$, $\tau_g^{(\varkappa)}(F_gF_g',F_g''F_g''')$ and $f(v)$ are due to the collision integral. Here, $\theta_{fg}^{(\varkappa)}(F_fF_g')$ is the electron—nuclear decay constant representing the rate of relaxation of the relevant multipole moment of an atom, whereas the real quantity $\Delta_{fg}^{(\varkappa)}(F_fF'_g)$ allows for the shift of the hyperfine sublevels by depolarizing collisions. In particular, $\Delta_{fg}^{(1)}(F_fF'_g)$ describes the shift of a spectral line of the $J_fF_f\rightarrow J_gF_g$ transition. The quantities $\gamma_{fg}^{(\varkappa)}$ and $\Delta_{fg}^{(\varkappa)}$ have a similar physical meaning for the electron subsystem without allowance for the interaction with the nuclear spin, when the electron subsystem is described in the *JM* representation and when we can use the expansion of Eq. (2) with the substitutions $F_f\rightarrow J_f(F'_g\rightarrow J_g)$ and $M_{Ff}\rightarrow M_f(M_{F'_g}\rightarrow M_g)$, and the electron multipole moment $\rho_q^{(\varkappa)}(J_fJ_g)$ of an atom satisfies the equation

$$\left[\frac{\partial}{\partial t}+\mathbf{v}\nabla+i(\omega_{fg}+\Delta_{fg}^{(\varkappa)})+\gamma_{fg}^{(\varkappa)}\right]\rho_q^{(\varkappa)}(J_fJ_g)=\gamma_gN_gf(v)\delta_{fg}\delta_{0\varkappa}\delta_{0q},$$

which replaces both Eqs. (3) and (5). Here, N_g is the steady-state density of atoms at a level E_g in the absence of an external field; $f(v)$ is the Maxwellian distribution; u is the most probable velocity; $\hbar\gamma_g$ is the width of the level E_g, due to radiative decay and inelastic collisions; $\Gamma_{fg}^{(\varkappa)}$ and $\Delta_{fg}^{(\varkappa)}$ allow for the contributions of elastic depolarizing collisions (see, for example, Ref. 12, where a description is given of the usual model of depolarizing collisions using the notation $\theta_{gg}^{(\varkappa)}(F_gF'_g)=\theta_g^{(\varkappa)}(F_gF'_g)$, $\Gamma_{gg}^{(\varkappa)}=\Gamma_g^{(\varkappa)}$ and $\gamma_{gg}^{(\varkappa)}=\gamma_g^{(\varkappa)}$ with identical lower indices). In the case of some types of interatomic interaction the quantities $\Gamma_{fg}^{(\varkappa)}$ and $\Delta_{fg}^{(\varkappa)}$ are defined theoretically in Ref. 13, and references to other calculations of these quantities can be found in Refs. 11 and 12.

In the case of the $J_fF_f\rightarrow J_gF_g$ transitions with small electron angular momenta $J_f=J_g=1/2$, $J_f=1/2$ $(3/2)$ and $J_g=3/2$ $(1/2)$, and also $J_f=0$ (1) and $J_g=1$ (0), the relationship (4) can be reduced, because of the properties of the $9j$ symbols and the electron decay constants $\gamma_{fg}^{(\varkappa)}$, to $\theta_{fg}^{(\varkappa)}(F_fF'_g)=\gamma_{fg}^{(1)}$ and $\Delta_{fg}^{(\varkappa)}(F_fF'_g)=\Delta_{fg}^{(1)}$ for any possible values of $\varkappa$, F_f, and F_g. Moreover, if $J_f=0$ and $J_g=J$ or $J_g=0$ are arbitrary and $J_f=J$ is also arbitrary, we find that $\theta_{fg}^{(\varkappa)}(F_fF'_g)=\gamma_{fg}^{(J)}$ and $\Delta_{fg}^{(\varkappa)}(F_fF'_g)=\Delta_{fg}^{(J)}$. If there are no elastic depolarizing collisions, then the principal equations (3) and (5) should be modified by the substitutions

$$\theta_{fg}^{(\varkappa)}(F_fF_f')=\gamma_{fg}^{(\varkappa)}=\gamma_{fg},\qquad \Delta_{fg}^{(\varkappa)}(F_fF_g')=\Delta_{fg}^{(\varkappa)}=\Gamma_{fg}^{(\varkappa)}=0. \tag{6}$$

2. CUBIC SUSCEPTIBILITY TENSOR OF A GAS

Let us assume that an atomic gas is subjected to an arbitrary number n_0 of *cw* plane optical waves of frequencies ω_n, wave vectors $\mathbf{k}_n$, complex amplitudes $\mathbf{a}_n$, where $n=1, 2,\ldots, n_0$. The intensities of these incident waves are assumed to be sufficiently low to allow us to use perturbation theory. The four-photon interaction of such optical waves with atoms in a gas creates new waves, so that the combined electric field is

$$\mathbf{E}(\mathbf{r},t)=\sum_n\mathbf{a}_n\exp[i(\mathbf{k}_n\mathbf{r}-\omega_nt)]+\text{c.c.}, \tag{7}$$

where the terms with the indices $n=1,2,\ldots,n_0$ represent the incident waves, and the other terms with $n=n_0+1, n_0+2,$ ... describe new waves and nonlinear corrections to the incident waves representing their self-interaction. The complex amplitude $\mathbf{a}_n$ is now a slow function of the coordinates compared with $\exp(i\mathbf{k}_n\mathbf{r})$.

Each new wave forms, in combination with the corresponding three incident waves, a four-wave mixing set which is described by the vector

$$\mathbf{P}=\int\mathrm{Sp}(\rho\mathbf{d})\,d\mathbf{v}$$

representing the electric polarization of the gas in the approximation which is cubic in terms of the field of Eq. (7). It covers also the cases of the four-wave mixing with double participation of one of the incident waves and the wave self-interaction processes. The linear $\mathbf{P}^L$ and nonlinear $\mathbf{P}^{NL}$ terms of the vector $\mathbf{P}$ can be calculated by solving Eq. (1) in combination with Eqs. (3) and (5), applying perturbation theory, which yields results in their general form suitable for the application to all the cases of four-wave mixing and self-interaction of optical waves:

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

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

$$\varkappa(\omega_n,\mathbf{k}_n)=\sum_{fgF_fF_g}\frac{N_{fg}|d_{F_fF_g}|^2}{3\hbar(2I+1)}$$

$$\times\int\frac{f(v)\,d\mathbf{v}}{\omega_n-\mathbf{k}_n\mathbf{v}_n-w_{F_fF_g}-\Delta_{fg}^{(1)}(F_fF_g)+i\theta_{fg}^{(1)}(F_fF_g)}, \tag{8}$$

$$N_{fg}=N_f/(2J_f+1)-N_g/(2J_g+1),$$

$$d_{F_fF_g}=(-1)^{J_f+F_g+I+1}(2F_f+1)^{1/2}(2F_g+1)^{1/2}\begin{Bmatrix}J_f & F_f & I\\ F_g & J_g & 1\end{Bmatrix}d_{fg},$$

$$\begin{aligned}P_i^{NL}(\mathbf{r},t)=\sum_{nmp}\{&\chi_{ijkl}(\omega_n+\omega_m+\omega_p;\ \omega_n,\omega_m,\omega_p)a_{nj}a_{mk}a_{pl}\\ &\times\exp[i((\mathbf{k}_n+\mathbf{k}_m+\mathbf{k}_p)\mathbf{r}-(\omega_n+\omega_m+\omega_p)t)]\\ &+3\chi_{ijkl}(\omega_n+\omega_m-\omega_p;\ \omega_n,\omega_m,-\omega_p)a_{nj}a_{mk}a_{pl}^*\\ &\times\exp[i((\mathbf{k}_n+\mathbf{k}_m-\mathbf{k}_p)\mathbf{r}-(\omega_n+\omega_m-\omega_p)t)]\}+\text{c.c.},\end{aligned} \tag{9}$$

$$\begin{aligned}\chi_{ijkl}(\omega;\ \omega_n,\omega_m,\omega_p)={}&{}^1/_6[\chi(\omega;\ \omega_n,\omega_m,\omega_p)\delta_{ij}\delta_{kl}\\ &+\chi(\omega;\ \omega_m,\omega_p,\omega_n)\delta_{ik}\delta_{lj}+\chi(\omega;\ \omega_p,\omega_n,\omega_m)\delta_{il}\delta_{jk}],\\ \chi(\omega;\ \omega_n,\omega_m,\omega_p)={}&{}^1/_2[Q_1(\omega,\omega_n,\omega_m)+Q_2(\omega,\omega_n,\omega_m)\\ &+Q_2(\omega,\omega_p,\omega_n)-Q_1(\omega,\omega_p,\omega_n)]\\ &+{}^1/_3[Q_0(\omega,\omega_m,\omega_p)-Q_2(\omega,\omega_m,\omega_p)],\end{aligned} \tag{10}$$

$$Q_\varkappa(\omega,\omega_n,\omega_p)=\sum_{fgF_fF_g'}\int d\mathbf{v}f(v)\,\Pi_{F_fF_g'}^{(\varkappa)}(\omega-\mathbf{k}\mathbf{v})$$

$$\times\frac{W_{F_fF_g'}^{(\varkappa)}(\omega_n-\mathbf{k}_n\mathbf{v})+(-1)^\varkappa W_{F_fF_g'}^{(\varkappa)}(\omega_p-\mathbf{k}_p\mathbf{v})}{\omega_n+\omega_p-(\mathbf{k}_n+\mathbf{k}_p)\mathbf{v}-\omega_{F_fF_g'}-\Delta_{fg}^{(\varkappa)}(F_fF_g')+i\theta_{fg}^{(\varkappa)}(F_fF_g')},$$

$$\Pi_{F_fF_g}^{(\varkappa)}(\omega-\mathbf{k}\mathbf{v})=\frac{1}{\hbar}\sum_{hF_h}d_{F_fF_h}^*d_{F_hF_g}^*\begin{Bmatrix}1 & \varkappa & 1\\ F_f & F_h & F_g\end{Bmatrix}$$

$$\times\left(\frac{1}{\omega-\mathbf{k}\mathbf{v}-\omega_{F_fF_h}-\Delta_{fh}^{(1)}(F_fF_h)+i\theta_{fh}^{(1)}(F_fF_h)}-\frac{(-1)^\varkappa}{\omega-\mathbf{k}\mathbf{v}-\omega_{F_hF_g}-\Delta_{hg}^{(1)}(F_hF_g)+i\theta_{hg}^{(1)}(F_hF_g)}\right),$$

$$W^{(\varkappa)}_{F_fF_g}(\omega_n-\mathbf{k}_n\mathbf{v})=\frac{1}{\hbar^2(2I+1)}\sum_{hF_h} d_{F_fF_h}d_{F_hF_g}\begin{Bmatrix}1 & \varkappa & 1\\ F_f & F_h & F_g\end{Bmatrix}$$

$$\times\left(\frac{N_{fh}}{\omega_n-\mathbf{k}_n\mathbf{v}-\omega_{F_fF_h}-\Delta^{(1)}_{fh}(F_fF_h)+i\theta^{(1)}_{fh}(F_fF_h)}-\frac{(-1)^{\varkappa}N_{hg}}{\omega_n-\mathbf{k}_n\mathbf{v}-\omega_{F_hF_g}-\Delta^{(1)}_{hg}(F_hF_g)+i\theta^{(1)}_{hg}(F_hF_g)}\right),$$

$$Q_\varkappa(\omega,\ \omega_p,\ \omega_n)=(-1)^\varkappa Q_\varkappa(\omega,\ \omega_n,\ \omega_p),$$

$$Q_\varkappa(-\omega,\ -\omega_n,\ -\omega_p)=Q_\varkappa^*(\omega,\ \omega_n,\ \omega_p),\quad \varkappa=0,\ 1,\ 2,$$

where the first argument ω in the tensor of Eq. (10) is equal to the sum of three other arguments $\omega=\omega_n+\omega_m+\Omega_p$ (this applies also to $\mathbf{k}=\mathbf{k}_n+\mathbf{k}_m+\mathbf{k}_p$). The repeated vector indices i, j, k, and l always imply summation. They assume the values x, y, and z, representing the projections a_{nj}, a_{mk}, and a_{pl} of the vectors $\mathbf{a}_n$, $\mathbf{a}_m$, and $\mathbf{a}_p$ along Cartesian axes. The definitions of the $6j$ symbol and of the reduced dipole moment d_{fg} of the $J_f\to J_g$ atomic transition are taken from Ref. 14.

The four-wave mixing and self-interaction of optical waves will be described by the cubic susceptibility tensor introduced with the aid of the familiar relationship[15]

$$P_i^{NL}(\mathbf{r},t)=\int\limits_{-\infty}^{t}\chi_{ijkl}(t-t',t-t'',t-t''')E_j$$

$$\times\ (\mathbf{r},t')E_k(\mathbf{r},t'')E_l(\mathbf{r},t''')\,dt'\,dt''\,dt''',\qquad(11)$$

which for an isotropic gas remains symmetric under the transposition of any pair of indices from the triplet j, k, and l, or under the same transposition of t', t'', and t'''. Substituting the electric field of Eq. (7) into Eq. (11), and adopting

$$\int\limits_0^\infty\chi_{ijkl}(\tau_1,\tau_2,\tau_3)\exp[i(\omega_n\tau_1+\omega_m\tau_2+\omega_p\tau_3)]\,d\tau_1\,d\tau_2\,d\tau_3$$

$$=\chi_{ijkl}(\omega_n+\omega_m+\omega_p;\ \omega_n,\ \omega_m,\ \omega_p),\qquad(12)$$

we obtain an expression which is apparently similar to Eq. (9). A comparison of these equations shows that Eq. (10) now represents the cubic susceptibility tensor (12) of an atomic gas in the presence of a hyperfine level structure, which is suitable for tackling all the problems of the four-wave mixing and self-interaction of optical waves. The spatial dispersion of this tensor and of the linear electric susceptibility of Eq. (8) is due to the Doppler effect, so that when we use the transposition symmetry of the tensor (10), we must—in addition to the frequencies—transpose also the corresponding wave vectors. In this connection it should be stressed that the tensor (10) can be written in a compact symbolic form reflecting its transposition symmetry:

$$\chi_{ijkl}(\omega;\ \omega_n,\ \omega_m,\ \omega_p)={}^1/_6\hat{P}\{{}^1/_2[Q_1(\omega,\ \omega_n,\ \omega_m)$$

$$+{}^1/_2[Q_2(\omega,\ \omega_n,\ \omega_m)-Q_1(\omega,\ \omega_n,\ \omega_m)]\delta_{ik}\delta_{lj}$$

$$+{}^1/_3[Q_0(\omega,\ \omega_n,\ \omega_m)-Q_2(\omega,\ \omega_n,\ \omega_m)]\delta_{il}\delta_{jk}\},$$

where the operator $\hat{P}$ means that the initial expression in the braces must be supplemented by terms obtained as a result of two cyclic transpositions of the arguments ω_n, ω_m, and ω_p (and also $\mathbf{k}_n$, $\mathbf{k}_m$, and $\mathbf{k}_p$) accompanied by a simultaneous identical transposition of the indices j, k, and l. The quantities $Q_\varkappa(\omega,\omega_n,\omega_m)$ with $\varkappa=0,1,2$ assume the forms $Q_\varkappa(\omega,\omega_m,\omega_p)$ and $Q_\varkappa(\omega,\omega_p,\omega_n)$ after, respectively, the first and second cyclic transpositions of the arguments ω_n, ω_m, and ω_p.

The linear electric susceptibility of Eq. (8) and the cubic susceptibility tensor of Eq. (10) are valid both in the absence of a resonance and in the presence of any possible number of resonances of the hyperfine atomic sublevels. However, the contribution of a resonance at zero frequency in the case of atoms with a hyperfine level structure is allowed for correctly in the tensor (10) only in the absence of elastic depolarizing collisions when Eq. (6) is obeyed, which is due to the mathematical difficulties encountered in solving Eq. (5) in the presence of the field described by Eq. (7). In the case of atoms with zero nuclear spin, Eqs. (8) and (10) obtained for $I=0$ are identical with those reported in Ref. 9. Moreover, if in $Q_\varkappa(\omega,\omega_n,\omega_p)$, $\Pi^{(\varkappa)}_{F_fF_g}(\omega-\mathbf{kv})$ and $W^{(\varkappa)}_{F_fF_g}(\omega_n-\mathbf{k}_n\mathbf{v})$ we make the substitutions $\omega_{F_fF_g}\to\omega_{fg}$, $\theta^{(\varkappa)}_{fg}(F_fF_g)\to\gamma^{(\varkappa)}_{fg}$ and $\Delta^{(\varkappa)}_{fg}(F_fF_g)\to\Delta^{(\varkappa)}_{fg}$ for any value of I and then sum over the hyperfine levels, we find that $Q_\varkappa(\omega,\omega_n,\omega_p)$ assumes the form calculated in Ref. 9 for atoms with zero nuclear spin. Consequently, far from resonances with hyperfine sublevels occurring simultaneously at all the frequencies $\omega_n,\omega_m,\omega_p$ and $\omega_n\pm\omega_p$, the tensor (10) is identical with the cubic susceptibility tensor of a gaseous medium consisting of atoms with zero nuclear spin.

A gas containing two or more species of atoms can be described if the principal equations (8) and (10) are modified by the substitutions $N_{fg}\to N^{(\lambda)}_{fg}$, $f(v)\to f^{(\lambda)}(v)$ and $I\to I^{(\lambda)}$, and if in addition to summation over the levels $E_f(E_g)$ and over the hyperfine sublevels, we sum over the index λ that allows for all the varieties of the gas atoms.

By way of example, we shall apply the general expression (10) to the RLS problems in which two pump pulses with off-resonance frequencies ω_1 and ω_2 as well as an off-resonance probe pulse of frequency ω_3 are used. The difference between the frequencies of the pump pulses satisfies the Raman resonance condition $\omega_1-\omega_2\approx\omega_{cb}$. Retaining in Eq. (10) the terms with a Raman resonance, we obtain the cubic susceptibility tensor for the RLS by atoms with a hyperfine level structure:

$$\chi_{ijkl}(\omega_\pm;\ \pm\omega_1,\ \mp\omega_2,\ \omega_3)={}^1/_6(\chi_1{}^{(\pm)}\delta_{ij}\delta_{kl}$$

$$+\chi_2{}^{(\pm)}\delta_{ik}\delta_{lj}+\chi_3{}^{(\pm)}\delta_{il}\delta_{jk}),\qquad(13)$$

where $+Q_2(\omega,\ \omega_n,\ \omega_m)]\delta_{ij}\delta_{kl}$

$$\chi_1{}^{(+)}={}^1/_2(B_1{}^{(+)}+B_2{}^{(+)}),\quad \chi_2{}^{(+)}={}^1/_2(B_2{}^{(+)}-B_1{}^{(+)}),$$

$$\chi_3{}^{(+)}={}^1/_3(B_0{}^{(+)}-B_2{}^{(+)}),$$

$$\chi_1{}^{(-)}={}^1/_2(B_1{}^{(-)}+B_2{}^{(-)})^*,\quad \chi_2{}^{(-)}={}^1/_2(B_2{}^{(-)}-B_1{}^{(-)})^*,$$

$$\chi_3{}^{(-)}={}^1/_3(B_0{}^{(-)}-B_2{}^{(-)})^*,$$

$$B_\varkappa^{(\pm)}=\frac{N_{cb}}{\hbar(2I+1)}\Pi_{cb}^{(\varkappa)}(\pm\omega_\pm)\Pi_\varkappa(\omega_1,\omega_2)$$

$$\times\sum_{F_bF_c}(2F_b+1)(2F_c+1)\begin{Bmatrix} J_b & J_c & \varkappa \\ F_c & F_b & I\end{Bmatrix}^2 \tag{14}$$

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

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

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

$$\omega_\pm=\omega_3\pm(\omega_1-\omega_2),\quad \mathbf{k}_\pm=\mathbf{k}_3\pm(\mathbf{k}_1-\mathbf{k}_2),\quad \varkappa=0,1,2,$$

where the indices " + " and " − " of all these quantities represent the anti-Stokes and Stokes waves, respectively, and the tensor (13) does not have the transposition symmetry of the original expression (10), since the off-resonance terms are omitted.

Equations (13) and (14) allow us to use the familiar methods of amplitude—polarizaton spectroscopy[1] in the presence of a hyperfine level structure. However, we must bear in mind the characteristic features of the RLS due to the hyperfine splitting of the levels. One of them is manifested when $|\Delta_{F_c}|\ll|\Delta_{F_b}|$ far from a Raman resonance with hyperfine sublevels of the upper level E_c, in which case the following inequalities are satisfied in the homogeneous broadening case when $\bar\theta_{cb}^{(\varkappa)}(F_b)\gg(k_1-k_2)u$:

$$|\omega_1-\omega_2-\omega_{cb}+\Delta_{F_b}|\gg|\Delta_{F_c}+\Delta_{cb}^{(\varkappa)}(F_cF_b)-\bar\Delta_{cb}^{(\varkappa)}(F_b)|,$$

$$\bar\theta_{cb}^{(\varkappa)}(F_b)\gg|\theta_{cb}^{(\varkappa)}(F_cF_b)-\bar\theta_{cb}^{(\varkappa)}(F_b)|,$$

whereas in the inhomogeneous broadening case $\bar\theta_{cb}^{(\varkappa)}(F_b)<(k_1-k_2)u$, we find that

$$|\omega_1-\omega_2-\omega_{cb}+\Delta_{F_b}-(k_1-k_2)u|\gg|\Delta_{F_c}+\Delta_{cb}^{(\varkappa)}(F_cF_b)-\bar\Delta_{cb}^{(\varkappa)}(F_b)|,$$

$$(k_1-\mathrm{k}_2)u\gg|\theta_{cb}^{(\varkappa)}(F_cF_b)-\bar\theta_{cb}^{(\varkappa)}(F_b)|,$$

where $\bar\theta_{cb}^{(\varkappa)}(F_b)$ and $\overline{\Delta}_{cb}^{(\varkappa)}(F_b)$ are the results of arithmetic averaging of $\theta_{cb}^{(\varkappa)}(F_cF_b)$ and $\Delta_{cb}^{(\varkappa)}(F_cF_b)$ over F_c. When these inequalitites are obeyed, we can readily carry out the summation over F_c in Eq. (14) using the expression

$$\sum_{F_c}(2F_c+1)\begin{Bmatrix} J_b & J_c & \varkappa \\ F_c & F_b & I\end{Bmatrix}^2=\frac{1}{2J_b+1}.$$

The result is the conclusion that far from a resonance with hyperfine levels of the upper level E_c we can expect these hyperfine sublevels to lock together and behave as a single level, and transitions from this level to any possible lower sublevel E_{F_b} are restricted only by the selection rule applicable to the electron angular momentum $|J_b-J_c|\leqslant\varkappa\leqslant J_b+J_c$, while the spectral line of such a transition is described by a new denominator in Eq. (14), which is

$$\omega_1-\omega_2-\mathbf{kv}-\omega_{cb}+\Delta_{F_b}-\bar\Delta_{cb}^{(\varkappa)}(F_b)+i\bar\theta_{cb}^{(\varkappa)}(F_b).$$

Far from a Raman resonance with the hyperfine sublevels of the upper E_c and lower E_b levels we can modify Eq. (14) by the substitutions $\omega_{F_cF_b}\to\omega_{cb}$, $\theta_{cb}^{(\varkappa)}(F_cF_b)\to\gamma_{cb}^{(\varkappa)}$ and $\Delta_{cb}^{(\varkappa)}(F_cF_b)\to\Delta_{cb}^{(\varkappa)}$, and we can sum over F_c and F_b. This means that the locking together of the hyperfine sublevels occurs in the upper E_c and lower E_b levels, so that the quantities described by Eqs. (13) and (14) reduce to those calculated earlier[9] for atoms with zero nuclear spin.

If the pump-wave frequencies satisfy a two-photon resonance $\omega_1+\omega_2\approx\omega_{cb}$, the resonance terms of the cubic susceptibility tensor (10) become

$$\chi_{ijkl}(\overline{\omega}_\pm,\pm\omega_1,\pm\omega_2,\omega_3)$$

$$={}^1\!/_6(\bar\chi_1{}^{(\pm)}\delta_{ij}\delta_{kl}+\bar\chi_2{}^{(\pm)}\delta_{ik}\delta_{lj}+\bar\chi_3{}^{(\pm)}\delta_{il}\delta_{jk}), \tag{15}$$

where

$$\overline{\omega}_\pm=\omega_3\pm(\omega_1+\omega_2),\quad \overline{\mathbf{k}}_\pm=\mathbf{k}_3\pm(\mathbf{k}_1+\mathbf{k}_2),$$

and the quantities $\bar\chi_s^{(\pm)}$ with $s=1$, 2, and 3 are obtained from$\chi_s^{(\pm)}$ by the substitutions $\omega_\pm\to\overline{\omega}_\pm$, $\mathbf{k}_\pm\to\overline{\mathbf{k}}_\pm$, $\omega_2\to-\omega_2$, and $\mathbf{k}_2\to-\mathbf{k}_2$, and the Stokes wave frequency in the case when $\omega_1+\omega_2>\omega_3$ is $|\overline{\omega}_-|=\omega_1+\omega_2-\omega_3$. These comments about locking together of the hyperfine levels apply also to a two-photon resonance.

3. FORMATION OF NEW WAVES

Propagation of optical waves of the kind described by Eq. (7) in a gas can be described using the Maxwell equations

$$\mathrm{rot\,rot}\,\mathbf{E}+\frac{1}{c^2}\frac{\partial^2\mathbf{E}}{\partial t^2}=-\frac{4\pi}{c^2}\frac{\partial^2\mathbf{P}}{\partial t^2},\quad \mathrm{div}(\mathbf{E}+4\pi\mathbf{P})=0,$$

where the required field **E** consists, in accordance with Eq. (7), of two parts, which—for the sake of convenience—are written in a different notation:

$$\mathbf{E}(\mathbf{r},t)=\mathbf{E}_0(\mathbf{r},t)+\mathbf{E}^{NL}(\mathbf{r},t),$$

$$\mathbf{E}_0(\mathbf{r},t)=\sum_{n=1}^{n_0}\mathbf{a}_n\exp[i(\mathbf{k}_n\mathbf{r}-\omega_nt)]+\text{c.c.},$$

$$\mathbf{E}^{NL}(\mathbf{r},t)=\sum_f\{\mathbf{b}_f\exp[i(\mathbf{s}_f\mathbf{r}-\Omega_ft)]$$

$$+\tilde{\mathbf{b}}_f\exp[i(\tilde{\mathbf{s}}_f\mathbf{r}-\tilde\Omega_ft)]\}+\text{c.c.},$$

$$\Omega_f=\omega_n+\omega_m+\omega_p,\quad \tilde\Omega_f=\omega_n+\omega_m-\omega_p,$$

where the summation over f replaces the summation over $n=n_0+1$, n_0+2, ... in Eq. (7), and the index f assumes different values, when the indices n, m, and p run independently through all possible values from the set 1, 2, ..., n_0.

The first part $\mathbf{E}_n(\mathbf{r},t)$ includes incident waves with a given frequency ω_n, a given polarization, and a given direction of the wave vector $\mathbf{k}_n$. They propagate in a gas linearly with the dispersion law $\omega_n^2\varepsilon'(\omega_n,\mathbf{k}_n)=k_n^2c^2$ and the absorption coefficient $\alpha_n=\omega_n^2\varepsilon''(\omega_n,\mathbf{k}_n)/2k_nc^2$, where $\varepsilon'(\omega_n,\mathbf{k}_n)$ and $\varepsilon''(\omega_n,\mathbf{k}_n)$ are, respectively, the real and imaginary parts of the permittivity

$$\varepsilon(\omega_n,\mathbf{k}_n)=1+4\pi\varkappa(\omega_n,\mathbf{k}_n)=\varepsilon'(\omega_n,\mathbf{k}_n)+i\varepsilon''(\omega_n,\mathbf{k}_n).$$

The second part $\mathbf{E}^{NL}(\mathbf{r},t)$ contains nonlinear corrections to the incident waves, which describe the self-interaction of these waves and includes also new waves which form because of the four-photon interaction of the incident waves with the gas atoms. The frequencies Ω_f and $\overline{\Omega}_f$ of these waves assume different values, depending on ω_n, ω_m, and ω_p, and the wave vectors $\mathbf{s}_f$ ($\tilde{\mathbf{s}}_f$) and the complex amplitudes $\mathbf{b}_f$($\tilde{\mathbf{b}}_f$) are found by solving the Maxwell equations using perturbation theory. In solving the equations we shall use the approximation of slowly varying amplitudes $\mathbf{b}_f$($\tilde{\mathbf{b}}_f$), according to which the second derivatives with respect to the coordinates can be ignored. Moreover, we shall assume that the angle of convergence of the incident waves is of the order of a milliradian or differs little from π, so that the terms containing $s_f\mathbf{P}^{NL}$ and $\tilde{s}_f\mathbf{P}^{NL}$ can be dropped. Under these conditions, it follows from the Maxwell equations that

$$\left(\frac{\mathbf{s}_f\nabla}{s_f}+\alpha_f\right)b_{fi}=\frac{i12\pi\Omega_f^2}{s_fc^2}\chi_{ijkl}(\Omega_f;\Omega_n,\omega_m,\omega_p)$$
$$\times a_{nj}a_{mk}a_{pl}\exp[i(\mathbf{k}_n+\mathbf{k}_m+\mathbf{k}_p-\mathbf{s}_f)\mathbf{r}], \tag{16}$$

where

$$\Omega_f^2\varepsilon'(\Omega_f,\mathbf{s}_f)=s_f^2c^2, \quad \alpha_f=\Omega_f^2\varepsilon''(\Omega_f,\mathbf{s}_f)/2s_fc^2.$$

The equation for the amplitude $\tilde{\mathbf{b}}_f$ is obtained from Eq. (16) by the substitutions

$$b_{fi}\to\tilde{b}_{fi}, \quad \Omega_f\to\tilde{\Omega}_f, \quad \mathbf{s}_f\to\tilde{\mathbf{s}}_f, \quad \omega_p\to-\omega_p,$$
$$\mathbf{k}_p\to-\mathbf{k}_p, \quad a_{pl}\to a_{pl}^*, \tag{17}$$

whereas in the study of the self-interaction of the waves we must make the substitutions of Eq. (17) and multiply the right-hand side of Eq. (16) by the factor 1/2.

We have to distinguish here the case when the same modes are found at the exit and at the entry to the gas from the case when new waves are formed at the exit. In the latter case the right-hand side of Eq. (16) should be supplemented by a similar term in which the values of Ω_f and s_f are characterized by a different set of indices n, m, and p, whereas in the former case Eq. (16) is not affected.

The projection of the amplitude $\mathbf{b}_f$ along the ith Cartesian axis at the point $\mathbf{r}=s_fL_f/s_f$ at the exit from the gas can be written as follows:

$$b_{fi}=6G(\Omega_f,\mathbf{s}_f)a_n(0)a_m(0)a_p(0)\chi_{ijkl}(\Omega_f;\omega_n,\omega_m,\omega_p)l_{nj}l_{mk}l_{pl}, \tag{18}$$

where

$$G(\Omega_f,\mathbf{s}_f)=\frac{i2\pi\Omega_f^2\{\exp[-(q_f+i\Delta_f)L_f]-\exp(-\alpha_fL_f)\}}{s_fc^2(\alpha_f-q_f-i\Delta_f)}$$
$$q_f=[\alpha_n\mathbf{k}_n/k_n+\alpha_m\mathbf{k}_m/k_m+\alpha_p\mathbf{k}_p/k_p]\mathbf{s}_f/s_f,$$
$$\Delta_f=(\mathbf{s}_f-\mathbf{k}_n-\mathbf{k}_m-\mathbf{k}_p)\mathbf{s}_f/s_f, \quad \mathbf{a}_n=a_n(0)\mathbf{l}_n, \quad \mathbf{l}_n\mathbf{l}_n^*=1,$$

a_n (0) is the amplitude of the incident wave at the boundary point $r=0$ in the entry plane of the gas, and the optical path L_f is the modulus of the vector $\mathbf{L}_f=\mathbf{s}_fL_f/s_f$. Unit complex polarization vectors $\mathbf{l}_n$, $\mathbf{l}_m$, and $\mathbf{l}_p$ of the incident waves are not modified inside the gas and their projections along the Cartesian axes are l_{nj}, l_{mk}, and l_{pl}. The factor $G(\Omega_f,\mathbf{s}_f)$ shows that the generation of new waves is optimal along the direction corresponding to the phase matching: $\mathbf{s}_f=\mathbf{k}_n+\mathbf{k}_m+\mathbf{k}_p$.

The difference between the directions of propagation of the new waves is usually employed to separate them spatially. Sometimes this is achieved by adding a suitable impurity gas, which alters greatly the refractive index of the selected wave, so that $\Omega_f^2\varepsilon'(\Omega_f,\mathbf{s}_f)=s_f^2c^2$ and $\mathbf{s}_f=\mathbf{k}_n+\mathbf{k}_m+\mathbf{k}_p$ are satisfied, resulting in the amplification and suppression of other waves.[3,4] The intensity $I_f^{(i)}$ corresponding to the projection of an electric field of this wave along the ith Cartesian axis is

$$I_f^{(i)}=c|b_{fi}|^2/2\pi, \quad i=x,y,z. \tag{19}$$

The projection $\tilde{b}_{fi}$ of the amplitude $\tilde{\mathbf{b}}_f$ is obtained from Eq. (18) by replacing Eq. (17) subject to the condition that the term $\alpha_p\mathbf{k}_p/k_p$ in q_f remains unaltered.

4. DOPPLER-FREE HYPERFINE SPECTROSCOPY

In Doppler-free coherent two-photon absorption spectroscopy[15,16,1,4] use is made of three incident waves (7) with identical frequencies $\omega_1=\omega_2=\omega_3=\omega$. The pump waves then propagate in opposite directions $\mathbf{k}_1+\mathbf{k}_2=0$ and they satisfy the condition $2\omega\approx\omega_{cb}$ for a two-photon resonance; the wave vector $\mathbf{k}_3$ of a probe wave makes a small angle, of the order of a fraction of a milliradian, with $\mathbf{k}_2$. We shall assume specifically that the first, second, and third waves enter the gas at the boundary points $\mathbf{r}=0$, $\mathbf{r}=\mathbf{r}_s$, and $\mathbf{r}=\mathbf{r}_3$. Using Eqs. (15), (17), and (18) we can readily determine the electric field $E_{\mathrm{RLS}}(\mathbf{r},t)$ of a Stokes wave at a boundary point $\mathbf{r}=\mathbf{s}L/s$ at the exit from the gas:

$$\mathbf{E}_{\mathrm{RLS}}(\mathbf{r},t)=\mathbf{b}\exp[i(\mathbf{sr}-\omega t)]+\text{c.c.}, \tag{20}$$

where

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

$$G_{NR}^*(\omega,\mathbf{s})=2\pi\omega^2[1-\exp(i\Delta L)]/sc^2\Delta,$$
$$\Delta=(\mathbf{s}+\mathbf{k}_3)\mathbf{s}/s, \quad \mathbf{a}_n(\mathbf{r}_n)=a_n(\mathbf{r}_n)\mathbf{l}_n, \quad n=2,3, \tag{22}$$

$$B_\varkappa=\frac{N_{cb}}{\hbar(2I+1)}\Pi_{cb}^{(\varkappa)}(\omega)\Pi_\varkappa(\omega,-\omega)$$

$$\times\sum_{F_bF_c}(2F_b+1)(2F_c+1)\begin{Bmatrix}J_b & J_c & \varkappa\\ F_c & F_b & I\end{Bmatrix}^2$$

$$\times[2\omega-\omega_{F_cF_b}-\Delta_{cb}^{(\varkappa)}(F_cF_b)+i\theta_{cb}^{(\varkappa)}(F_cF_b)]^{-1}, \tag{23}$$

$$\Pi_\varkappa(\omega,-\omega)=\frac{2}{\hbar}\sum_g d_{cg}d_{gb}\begin{Bmatrix}1 & \varkappa & 1\\ J_c & J_g & J_b\end{Bmatrix}\frac{1}{\omega-\omega_{cg}}, \quad \varkappa=0,2,$$

where a_n ($\mathbf{r}_n$) is the amplitude of the incident wave at the entry to the gas; L is the optical path of the Stokes wave of Eq. (20) in the gas. In writing down Eq. (22), the linear absorption of off-resonance optical waves is omitted. The terms containing B_0 and B_2 in Eq. (21) describe the isotropic and anisotropic scattering processes, respectively.

In the optimal direction ($\mathbf{s}=-\mathbf{k}_3$) the Stokes wave of Eq. (20) is reversed relative to the probe wave for specially selected linearly polarized incident waves $\mathbf{l}_1=\mathbf{l}_2=\mathbf{l}_3$ or

$\mathbf{l}_1 = \mathbf{l}_2$ and $\mathbf{l}_1 = \mathbf{l}_2$ and $\mathbf{l}_1\mathbf{l}_3 = 0$, in full agreement with the results reported in Refs. 2 and 4 and obtained by spectroscopy within the width of a one-photon absorption line without allowance for the hyperfine structure of the levels. In the case of the $(J_c = 0)F_c \to (J_b = 0)F_b$ and $(J_c = 1/2)F_c \to (J_b = 1/2)F_b$ or $J_c(F_c = 0) \to J_b(F_b = 0)$ and $J_c(F_c = 1/2) \to J_b(J_b = 1/2)$ transitions this phase conjugation of a probe wave occurs for any elliptic polarization of the incident light waves, as in the case of atoms without the nuclear spin.[17]

In the case of linearly polarized incident waves with arbitrary polarization planes, we have

$$\begin{gathered}\mathbf{b}=G_{NR}{}^{*}(\omega, \mathbf{s})a_1(0)a_2(\mathbf{r}_2)a_3{}^{*}(\mathbf{r}_3)\mathbf{F},\\ \mathbf{F}={}^1/{}_3\mathbf{l}_x\{B_0\cos(\psi_1-\psi_2)+B_2[3\cos\psi_1\cos\psi_2-\cos(\psi_1-\psi_2)]\}\\ +{}^1/{}_2\mathbf{l}_yB_2\sin(\psi_1-\psi_2),\end{gathered} \tag{24}$$

where $\mathbf{l}_x$ and $\mathbf{l}_y$ are the unit vectors along the Cartesian axes x and y, and the z axis is directed along $\mathbf{k}_1$. The angles ψ_1 and ψ_2 are measured from the polarization plane of a probe pulse in the plane of polarization, respectively, in the first and second pump pulses in the clockwise direction if we view the system along the wave vector $\mathbf{k}_1$.

In contrast to Eq. (14), where the fine structure of the levels is masked by the Doppler broadening, the denominators in B_0 and B_2 do not contain the Doppler shift. Therefore the amplitudes in Eqs. (21) and (24) allow us to study relaxation and the hyperfine structure of the levels irrespective of the nature of broadening of the forbidden transition and this can be done by scanning the frequency 2ω near a two-photon resonance and investigating the intensity of the Stokes wave of Eq. (20) as a function of detuning from this resonance.

We shall assume that the separations between the hyperfine components of the levels E_b and E_c are sufficiently large:

$$|\Delta_{F_b}|\gg\theta_{cb}^{(\varkappa)}(F_cF_b),\quad |\Delta_{F_c}|\gg\theta_{cb}^{(\varkappa)}(F_cF_b),\quad \varkappa=0,2. \tag{25}$$

Then, the contribution to the amplitude of (24) comes only from two hyperfine sublevels $E_{F_b} = E_b + \hbar\Delta_{F_b}$ and $E_{F_c} = E_c + \hbar\Delta_{F_c}$, which satisfy the condition for the appearance of a two-photon resonance $2\omega \approx \omega_{F_cF_b}$ and the selection rule $|F_b - F_c| \leqslant \varkappa \leqslant F_b + F_c$. In this case the intensity of Eq. (19), corresponding to the projection of the electric field of Eq. (20) along the y axis, is proportional to $|B_2|^2$, which makes it possible to determine $\theta_{cb}^{(2)}(F_cF_b)$. Moreover, the measured position of the spectral line allows us to calculate $\Delta_{cb}^{(2)}(F_cF_b)$ when $\omega_{F_cF_b}$ is known. If in Eq. (24) we assume that $\psi_1 = \psi_2 = \cos^{-1}(3^{-1/2})$, then the intensity of Eq. (19) corresponding to the projection of the electric field (20) along the x axis is proportional to $|B_0|^2$, which gives $\theta_{cb}^{(0)}(F_cF_b)$ and also allows us to find $\Delta_{cb}^{(0)}(F_cF_b)$ at a given frequency $\omega_{F_cF_b}$ or the difference $\Delta_{cb}^{(0)}(F_cF_b) - \Delta_{cb}^{(2)}(F_cF_b)$ when $\omega_{F_cF_b}$ is not known. In addition, the ratio of these intensities allows us to calculate

$$|\Pi_{cb}^{(2)}(\omega)\Pi_2(\omega,-\omega)/\Pi_{cb}^{(0)}(\omega)\Pi_0(\omega,-\omega)|,$$

if J_b, J_c, F_b, and F_c are known.

In the case of the forbidden $J_bF_b \to J_cF_c$ transitions with small electron angular momenta $J_b = J_c = 1/2$, $J_b = 1/2$ $(3/2)$, $J_c = 3/2$ $(1/2)$, and also $J_b = J(0)$ and $J_c = J(0)$ where $J = 0$ or 2, each of the required relaxation constants $\theta_{cb}^{(\varkappa)}(F_cF_b)$ and $\Delta_{cb}^{(\varkappa)}(F_cF_b)$ has only one value $\gamma_{cb}^{(1)}$ and $\Delta_{cb}^{(1)}$ or $\gamma_{cb}^{(J)}$ and $\Delta_{cb}^{(J)}$ for all possible values of $\varkappa$, F_c, and F_b. This makes it possible to use the experimentally determined positions of the two spectral lines under the conditions of (25) and calculate $\Delta_{F_b} - \Delta_{F_c}$ for the appropriate values of F_b and F_c, and to determine in the case of atoms with the nuclear spin $I = 1/2$ the difference $A_c - A_c$ between the magnetic hyperfine splitting constants of the levels E_b and E_c. We can determine experimentally Δ_{F_b}-$\Delta_{cb}^{(1)}$ and $\Delta_{F_c} - \Delta_{cb}^{(1)}$ or $\Delta_{F_b} - \Delta_{cb}^{(J)}$ or $\Delta_{F_c} - \Delta_{cb}^{(J)}$ separately if we investigate all the transitions between the hyperfine sublevels of the upper and lower levels.

In the case of the transitions with other electron angular momenta the quantities $\theta_{cb}^{(\varkappa)}(F_cF_b)$ and $\Delta_{cb}^{(\varkappa)}(F_cF_b)$ assume a range of values. Variation of the frequency 2ω shows that the two-photon resonance $2\omega \approx \omega_{F_cF_b}$ is satisfied by hyperfine sublevels with different values of F_c and F_b. This allows us to determine $\theta_{cb}^{(\varkappa)}(F_cF_b)$ with all possible values of F_c and F_b satisfying the selection rule $|F_c - F_b| \leqslant \varkappa \leqslant F_c + F_b$ when $\varkappa = 0$ or 2. However, we must bear in mind that in the case of the $J_bF_b \to J_cF_c$ transitions with $J_b = J_c$ or $F_b = F_c$ we determine $\theta_{cb}^{(\varkappa)}(F_cF_b)$ for $\varkappa = 0$ or 2, whereas in the case $J_b - J_c = \pm 1, \pm 2$, or $F_b - F_c = \pm 1, \pm 2$ only $\theta_{cb}^{(2)}(F_cF_b)$ is determined. In the case of the $[J_b = 1(0)]F_b \to [J_c = 0(1)]F_c$ and $J_b[F_b = 1(0)] \to J_c[F_c = 0(1)]$ transitions the Stokes wave (20) does not form.

We can identify the forbidden transitions $J_bF_b \to J_cF_c$ in the case (25) by using the fact that for $J_b - J_c = \pm 1, \pm 2$ and any possible values of F_b and F_c, and also for $F_b - F_c = \pm 1, \pm 2$ and any values of J_b and J_c, we have $B_0^{(\pm)} = 0$. Therefore, only the anisotropic scattering of light appears and in the case of linearly polarized waves the Stokes wave of Eq. (20) is linearly polarized and it obeys

$$\operatorname{tg}\psi_{\mathrm{RLS}}=3\sin(\psi_1+\psi_2)/[3\cos(\psi_1+\psi_2)+\cos(\psi_1-\psi_2)], \tag{26}$$

where ψ_{RLS} is the angle between the plane of polarization of the probe pulse and the Stokes wave of Eq. (20). In contrast, if $J_b - J_c = 0$ or $F_b - F_c = 0$, isotropic and anisotropic scattering proceed simultaneously. In the case of the linearly polarized quantities the Stokes wave of Eq. (20) is elliptically polarized. Exceptions are the transitions $J_bF_b \to J_cF_c$ characterized by $J_b = 0 \to J_c = 0$ and $J_b = 1/2 \to J_c = 1/2$, and also by $F_b = 0 \to F_c = 0$ and $F_b = 1/2 \to F_c = 1/2$, if the scattering is isotropic and the Raman scattering polarization is identical with the polarization of a probe wave which may be linear or elliptic.

If the separations between the hyperfine components of the upper level E_c are small $|\Delta_{F_c}| \ll |\Delta_{F_b}|$, it is interesting to consider the Stokes wave of Eq. (20) far from a two-photon resonance with the hyperfine components of the upper level E_c:

$$\begin{gathered}|2\omega-\omega_{cb}+\Delta_{F_c}|\\ \gg(|\Delta_{F_c}+\Delta_{cb}^{(\varkappa)}(F_cF_b)-\Delta_{cb}^{(\varkappa)}(F_b)|,\ |\theta_{cb}^{(\varkappa)}(F_cF_b)-\bar{\theta}_{cb}^{(\varkappa)}(F_b)|),\end{gathered}$$

where $\bar{\theta}_{cb}^{(\varkappa)}(F_b)$ and $\overline{\Delta}_{cb}^{(\varkappa)}(F_b)$ are the arithmetic averages of $\theta_{cb}^{(\varkappa)}(F_cF_b)$ and $\Delta_{cb}^{(\varkappa)}(F_cF_b)$, when the averaging is carried out with respect to F_c. In this case we can sum over F_c in Eq. (23) and then the quantity given by Eq. (23) contains selection rules only for the electron angular momentum $|J_b - J_c| \leqslant \varkappa \leqslant I_b + J_c$, and the denominator of Eq. (23) becomes

$$2\omega-\omega_{cb}+\Delta_{F_b}-\bar{\Delta}_{cb}^{(\varkappa)}(F_b)+i\bar{\theta}_{cb}^{(\varkappa)}(F_b). \qquad (27)$$

This allows us to determine the constants $\bar{\theta}_{cb}^{(\varkappa)}(F_b)$ and $\bar{\Delta}_{cb}^{(\varkappa)}(F_b)$, and also to identify the transitions in accordance with the electron angular momentum by the methods described above using Eqs. (20)–(24), (26), and (27).

5. CHARACTERISTICS OF THE RAMAN LIGHT SCATTERING IN THE PRESENCE OF HYPERFINE SUBLEVELS

When two pump pulses with off-resonance frequencies ω_1 and ω_2 ($\omega_1 - \omega_2 \approx \omega_{cb}$) and an off-resonance probe pulse of frequency ω_3 propagate in a medium, the result is formation of anti-Stokes $\mathbf{E}_+(\mathbf{r},t)$ and Stokes $\mathbf{E}_-(\mathbf{r},t)$ waves:

$$\mathbf{E}_\pm(\mathbf{r},t)=\mathbf{b}_\pm \exp[i(\mathbf{s}_\pm\mathbf{r}-\omega_\pm t)]+\text{c.c.} \qquad (28)$$

The amplitudes of these waves at the exit from the gas are given by the following expressions obtained from Eqs. (13), (14), (17), and (18):

$$\begin{aligned}\mathbf{b}_+={}&G_{NR}(\omega_+,\mathbf{s}_+)a_1(0)a_2^*(0)a_3(0)\\&\times\{{}^1/{}_3B_0^{(+)}\mathbf{l}_3(\mathbf{l}_1\mathbf{l}_2^*)+{}^1/{}_2B_1^{(+)}[\mathbf{l}_3[\mathbf{l}_1\mathbf{l}_2^*]]\\&+{}^1/{}_2B_2^{(+)}[\mathbf{l}_1(\mathbf{l}_2^*\mathbf{l}_3)+\mathbf{l}_2^*(\mathbf{l}_3\mathbf{l}_1)-{}^2/{}_3\mathbf{l}_3(\mathbf{l}_2^*\mathbf{l}_1)]\},\end{aligned} \qquad (29)$$

$$\begin{aligned}\mathbf{b}_-={}&G_{NR}(\omega_-,\mathbf{S}_-)a_1^*(0)a_2(0)a_3(0)\\&\times\{{}^1/{}_3B_0^{(-)*}\mathbf{l}_3(l_1^*\mathbf{l}_2)+{}^1/{}_2B_1^{(-)*}[\mathbf{l}_3[\mathbf{l}_1^*\mathbf{l}_2]]\\&+{}^1/{}_2B_2^{(-)*}[\mathbf{l}_1^*(\mathbf{l}_2\mathbf{l}_3)+\mathbf{l}_2(\mathbf{l}_3\mathbf{l}_1^*)-{}^2/{}_3\mathbf{l}_3(\mathbf{l}_2\mathbf{l}_1^*)]\},\end{aligned} \qquad (30)$$

$$G_{NR}(\omega_\pm,\mathbf{s}_\pm)=2\pi\omega_\pm^2[1-\exp(-i\Delta_\pm L_\pm)]/s_\pm c^2\Delta_\pm,$$
$$\Delta_\pm=(\mathbf{s}_\pm-\mathbf{k}_\pm)\mathbf{s}_\pm/s_\pm,$$

where $L_\pm$ is the linear size of the gas in the direction of the vector $\mathbf{s}_\pm$, and the terms with $B_0^{(\pm)}$, $B_1^{(\pm)}$, and $B_2^{(\pm)}$ describe the isotropic, antisymmetric, and anisotropic scattering processes, respectively.

In the case of linearly polarized incident waves these amplitudes are different:

$$\begin{aligned}\mathbf{b}_+&=G_{NR}(\omega_+,\mathbf{s}_+)a_1(0)a_2^*(0)a_3(0)\mathbf{F}_+,\\ \mathbf{b}_-&=G_{NR}(\omega_-,\mathbf{s}_-)a_1^*(0)a_2(0)a_3(0)\mathbf{F}_-^*,\end{aligned} \qquad (31)$$

$$\begin{aligned}\mathbf{F}_\pm={}&{}^1/{}_3\mathbf{l}_x\{B_0^{(\pm)}\cos(\psi_1-\psi_2)+B_2^{(\pm)}\\&\times[3\cos\psi_1\cos\psi_2-\cos(\psi_1-\psi_2)]\}\\&+{}^1/{}_2\mathbf{l}_y[B_1^{(\pm)}\sin(\psi_1-\psi_2)+B_2^{(\pm)}\sin(\psi_1+\psi_2)],\end{aligned} \qquad (32)$$

where the angles between the wave vectors $\mathbf{k}_1$, $\mathbf{k}_2$, and $\mathbf{k}_3$ of the incident waves and the z Cartesian axis are of the order of a fraction of a milliradian.

If the frequencies of the pump pulses satisfy the condition for a two-photon resonance $\omega_1 + \omega_2 \approx \omega_{cb}$, then we have to make in Eqs. (28)–(32) the substitutions $\omega_\pm \to \bar{\omega}_\pm$, $\mathbf{k}_\pm \to \bar{\mathbf{k}}_\pm$, $\omega_2 \to -\omega_2$, $\mathbf{k}_2 \to -\mathbf{k}_2$, $a_2(0) \to a_2^*(0)$ ($a_2^*(0) \to a_2(0)$), $\mathbf{l}_2 \to \mathbf{l}_2^*$ ($\mathbf{l}_2^* \to \mathbf{l}_2$).

The relaxation constants of the electron–nuclear multipole moments of an atom in the cases of the Raman and two-photon resonance conditions can be determined as described above, by varying the frequency ω_1 or ω_2 and by investigating the intensity (19) of the scattered waves after allowing for their polarization characteristics. However, in the case of an inhomogeneous broadening of the $J_bF_b \to J_cF_c$ forbidden transition the fine structure of the levels is usually masked by the Doppler broadening, which makes it difficult to study relaxation. Therefore, we shall consider only the method for identification of the forbidden transitions, which is valid irrespective of the nature of broadening of these transitions.

The polarization characteristics of the Stokes and anti-Stokes waves are given by Eqs. (29)–(32) where the coefficients $B_\varkappa^{(\pm)}$ with $\varkappa = 0,1,2$ contain $6j$ symbols which allow for the selection rules governing the electron $|J_b - J_c| \leqslant \varkappa \leqslant J_b + J_c$ and total $|F_b - F_c| \leqslant \varkappa \leqslant F_b + F_c$ momenta of the $J_bF_b \to J_cF_c$ forbidden transition. These inequalities should be satisfied independently. We can therefore formulate the following method for the identification of the transitions forbidden in respect of the electron and total momenta.

The forbidden transitions can be identified on the basis of the electron angular momentum if we consider the Raman scattering of light far from a Raman or two-photon resonance with hyperfine sublevels of both levels E_c and E_b in the case of Eq. (25) or only the upper level E_c if $|\Delta_{F_c}| \ll |\Delta_{F_b}|$, which allows us to sum over F_c in Eq. (14). As a result, Eq. (14) contains the selection rule which applies only to the electron angular momentum $|J_b - J_c| \leqslant \varkappa \leqslant J_b + J_c$ of the investigated transitions $J_bF_b \to J_cF_c$ with all possible values of F_b and F_c. Therefore, identification of the forbidden transitions $J_b \to J_c$ is carried out following the same procedure as for atoms with zero nuclear spin.[9]

After the transition $J_b \to J_c$ forbidden in respect of the electron angular momentum is identified by the above (or some other) method, we can identify the $J_bF_b \to J_cF_c$ transition using the total angular momentum by investigating the Raman scattering of light near a Raman or a two-photon resonance involving hyperfine levels when the inequalities $|J_b - J_c| \leqslant \varkappa \leqslant J_b + J_c$ and $|F_b - F_c| \leqslant \varkappa \leqslant F_b + F_c$ are satisfied simultaneously for $\varkappa = 0$, 1, and 2.

We shall assume that the forbidden transition $J_b \to J_c$, included in $J_bF_b \to J_cF_c$, is known and is of the $J_b - J_c = 0$ type. Then, if $J_b = J_c = 0$, we find that $B_1^{(\pm)} = B_2^{(\pm)} = 0$ and it follows from Eqs. (29) and (30) that the scattering is isotropic. If $J_b = J_c = 1/2$, we find that $B_2^{(\pm)} = 0$, so that the $F_b - F_c = 0, \pm 1$ transitions are possible. In the case of the $F_b - F_c = \pm 1$ transitions, since $B_0^{(\pm)} = 0$, the scattering is antisymmetric, whereas for $F_b - F_c = 0$ it consists of an isotropic and an antisymmetric component. If $J_b = J_c \geqslant 1$, the $F_b - F_c = 0, \pm 1, \pm 2$ transitions are possible, which makes it necessary to consider each of them separately.

In the case of the $F_b - F_c = \pm 2$ transitions we have $B_0^{(\pm)} = B_1^{(\pm)} = 0$ and the polarization of the scattered waves of Eq. (28) in the case described by Eq. (31) is linear for any angles ψ_1 and ψ_2, whereas the angle ψ_{RLS} between the vector $\mathbf{l}_3$ and the electric field of the Raman scattering is given by Eq. (26). It follows that if $\psi_1 = \psi_2$, the plane of polarization of the waves of Eq. (28) lies within an obtuse angle formed by the planes of polarization of a probe pulse and of the pump pulses. If $\psi_1 = -\psi_2$, it coincides with the polarization of a probe pulse, whereas for $\psi_1 \neq 0$ and $\psi_2 = 0$ ($\psi_1 = 0$ and $\psi_2 \neq 0$) it lies within an acute angle.

If $F_b - F_c = \pm 1$ and $F_b + F_c > 1$, we find that $B_0^{(\pm)} = 0$, so that the polarization of the waves is elliptic if $\psi_1 \neq \psi_2$ and linear if $\psi_1 = \psi_2 = \psi$, where

$$\mathrm{tg}\,\psi_{\mathrm{RLS}} = 3\sin 2\psi / 2(3\cos^2\psi - 1).$$

The exceptions are the transitions $F_b = 1 \rightarrow F_c = 0$ and $F_b = 0 \rightarrow F_c = 1$ for which we have $B_0^{(\pm)} = B_2^{(\pm)} = 0$ so that for real values of $\mathbf{l}_s$ the polarization of the waves is, according to Eqs. (29) and (30), linear and orthogonal to $\mathbf{l}_s$ irrespective of the polarization of the pump waves if $[\mathbf{l}_1\mathbf{l}_2^*] \neq 0$.

Finally, if $F_b - F_c = 0$ the polarization of the waves of Eq. (28) in the case defined by Eq. (31) is elliptic for all angles ψ_1 and ψ_2, whereas for $F_b = 0 \rightarrow F_c = 0$ we obtain $B_1^{(\pm)} = B_2^{(\pm)} = 0$, so that—according to Eqs. (29) and (30)—the polarization is identical with the polarization of a probe wave, which may be linear or elliptic. It should also be noted that if $F_b = F_c = 1/2$, the axes of the polarization ellipse of the waves of Eq. (28) depend in the case (31) on $\psi_1 - \psi_2$ in such a way that if $\psi_1 - \psi_2 = 0$, the polarization ellipse becomes elongated forming a segment of the x axis and if $\psi_1 - \psi_2 = \pi/2$, it forms a segment of the y axis. These polarization relationships allow us to identify the $J_bF_b \rightarrow J_cF_c$ transitions when $J_b = J_c$.

In the other case, when $J_b - J_c = \pm 1$, we have to substitute $B_0^{(\pm)} = 0$ in Eqs. (29)–(32) so that the $J_bF_b \rightarrow J_cF_c$ transitions become possible and they involve a change in the total angular momentum amounting to $F_b - F_c = 0, \pm 1, \pm 2$. If $J_b = 0$ (1) and $J_c = 1$ (0), then $B_0^{(\pm)} = B_2^{(\pm)} = 0$ and we have the transitions characterized by $F_b - F_c = 0, \pm 1$, for which the scattering is antisymmetric. If $J_b + J_c > 1$, then $B_2^{(\pm)} \neq 0$ and Eq. (26) is valid for $F_b - F_c = \pm 2$ and becomes invalid for $F_b - F_c = 0, \pm 1$, if $\psi_1 \neq \psi_2$. This circumstance allows us to distinguish experimentally the transitions characterized by $F_b - F_c = 0, \pm 1$ from those characterized by $F_b - F_c = \pm 2$. Then, for $F_b = F_c = 1/2$ and for $F_b = 0$ (1) and $F_c = 1$ (0), we have $B_0^{(\pm)} = B_2^{(\pm)} = 0$, which is responsible for the antisymmetric scattering.

Finally, for $J_b - J_c = \pm 2$ we find that only $B_2^{(\pm)}$ differs from zero in Eqs. (29)–(32) and that $B_0^{(\pm)} = B_1^{(\pm)} = 0$, so that the scattering is entirely anisotropic and Eq. (26) is valid for all possible $F_b - F_c = 0, \pm 1, \pm 2$ transitions with the exception of $F_b = F_c = 0$ and $F_b = F_c = 1/2$, and those characterized by $F_b = 0$ (1) and $F_c = 1$ (0).

It follows from these relationships that the method for identification of forbidden transitions using Raman scattering of light provides more opportunities than the Doppler-free spectroscopic method, which is due to the occurrence in the amplitudes (29)–(31) of the coefficient $B_1^{(\pm)}$ in addition to the coefficients $B_0^{(\pm)}$ and $B_2^{(\pm)}$.

6. DISCUSSION

When cw plane optical waves are incident on an atomic gas, the cubic susceptibility tensor of Eq. (10) describes, in the absence of resonances, all the resultant nonlinear phenomena of four-wave mixing and self-interaction of waves, which are represented on equal footing in the electric polarization vector of Eq. (9) when the intensities of the resultant optical waves are of the same order of magnitude. However, in the case of single, double, or triple resonances at the frequencies of the incident optical waves or in the case of resonances corresponding to the differences or sums of these frequencies, certain terms in the cubic susceptibility tensor of Eq. (10) become the dominant ones and they describe the relevant specific nonlinear effect. The other terms in Eq. (10) create a background against which the main nonlinear effect takes place and they participate in interference effects. This makes it possible to draw a number of general conclusions.

When the Raman light scattering involves excited states belonging to adjacent $J_aF_a \rightarrow J_cF_c$ and $J_aF_a \rightarrow J_bF_b$ transitions, which are in resonance with the frequencies of the pump waves $\omega_1 \approx \omega_{ca}$ and $\omega_2 \approx \omega_{ba}$ ($\omega_1 - \omega_2 \approx \omega_{cb}$) and an off-resonance probe pulse of frequency ω_3 is also applied, the tensor of Eq. (10) should still have terms with double resonances, which leads to Eqs. (13) and (14), which instead of $B_\varkappa^{(\pm)}$ contain

$$U_\varkappa^{(\pm)} = \frac{\Pi_{cb}^{(\varkappa)}(\pm\omega_\pm)}{\hbar^2(2I+1)}$$

$$\times \sum_{F_aF_bF_c} (-1)^{I-J_b-F_c-\varkappa} d_{F_cF_a} d_{F_aF_b} (2F_b+1)^{1/2}(2F_c+1)^{1/2}$$

$$\times \begin{Bmatrix} J_b & J_c & \varkappa \\ F_c & F_b & I \end{Bmatrix} \begin{Bmatrix} 1 & \varkappa & 1 \\ F_c & F_a & F_b \end{Bmatrix}$$

$$\times \int \biggl(\frac{N_{ca}}{\omega_1 - \mathbf{k}_1\mathbf{v} - \omega_{F_cF_a} - \Delta_{ca}^{(1)}(F_cF_a) + i\theta_{ca}^{(1)}(F_cF_a)}$$

$$- \frac{N_{ba}}{\omega_2 - \mathbf{k}_2\mathbf{v} - \omega_{F_bF_a} - \Delta_{ba}^{(1)}(F_bF_a) - i\theta_{ba}^{(1)}(F_bF_a)} \biggr)$$

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

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

Consequently, after the substitution of $B_\varkappa^{(\pm)} \rightarrow U_\varkappa^{(\pm)}$ Eqs. (28)–(32) describe the Raman scattering of light by excited states and the method described above for the identification of the $J_bF_b \rightarrow J_cF_c$ forbidden transitions can be used if there are double Raman scattering resonances at frequencies $\omega_1 \approx \omega_{ca}$ and $\omega_1 - \omega_2 \approx \omega_{cb}$ and also at $\omega_2 \approx \omega_{ba}$ and $\omega_1 - \omega_2 \approx \omega_{cb}$.

In the familiar CARS spectroscopic method use is made of two pump waves of frequencies ω_1 and ω_2 ($\omega_1 - \omega_2 \approx \omega_{cb}$) and then the first pump wave frequency ω_1 acts as a probe pulse.[1,18] Therefore, in the CARS case the cubic susceptibility tensor of Eq. (13) should be modified by the substitution $\omega_3 \rightarrow \omega_1$. Consequently, the scattering at the anti-Stokes ($\omega_\pm = 2\omega_1 - \omega_2$) and Stokes ($\omega_- = \omega_2$) frequencies is described by Eqs. (28)–(32), where the index substitution $3 \rightarrow 1$ is made for all the physical quantities and it is assumed that $\psi_1 = 0$ in Eq. (32).

Equation (5) is simplified by omitting the term that allows for the arrival of atoms at the lower level due to spontaneous radiation emitted by the upper levels. Therefore, the cubic susceptibility tensor of Eq. (10) is valid in the case of those nonlinear effects for which this physical process makes no contribution. Examples are the Doppler-free two-photon absorption spectroscopy discussed above, as well as the RLS and CARS methods and several variants of the process of third harmonic generation. There are, however, some nonlinear effects due to a resonance at zero frequency, in addition to resonances at nonzero frequencies. They involve self-diffraction, phase conjugation, and self-interaction of optical waves which appear when one, two, or more optical waves which are in resonance with one transition frequency ω_{ba} traverse a gas. In this case the arrival of atoms at the lower level because of spontaneous decay at the upper level may be a significant effect. However, in the case of a sufficiently dense gas, the probability

$$\gamma=4|d_{ba}|^2\omega_{ba}{}^3/3\hbar c^3(2J_b+1)$$

of spontaneous emission of a photon $\hbar\omega_{ba}$ by a single atom is low compared with γ_a and γ_b, so that the arrival of atoms at the lower level as a result of spontaneous emission by the upper level can be ignored. Then, the cubic susceptibility tensor for self-diffraction, phase conjugation, and self-interaction of optical waves under the conditions described in (6) can be obtained from the tensor (10) if we retain the terms with the triple resonance and then two resonances occur at frequencies corresponding to the set $\omega_n \approx \omega_{ba}$, $\omega_m \approx \omega_{ba}$, and $\omega_p \approx \omega_{ba}$, whereas the third resonance occurs at zero frequency. The frequencies ω_n, ω_m, and ω_p may then coincide or have different values within the limits of the width of a one-photon absorption light, as is true in the approximate degenerate four-wave mixing process.[19,20,3]

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