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Cooperative effects in radiation processes (multilevel particles and second-order perturbation theory)

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The Dicke theory of coherent spontaneous emission is generalized by means of group-theoretical methods. Effects of superradiation and the structure of coherent responses of an equilibrium medium to pulsed excitation are considered. A method of calculating cooperative effects in second-order perturbation theory is developed. The role of collective properties of a system of radiators in experiments with high power exciting radiation is discussed. Some "anomalous" features of stimulated Raman scattering are accounted for.

I. INTRODUCTION

As is well known, when a many-particle system undergoes spontaneous emission of radiation, the individual atoms or molecules composing the system do not emit independently of one another. Rather, there are cooperative effects, due to the common radiation field, that can amplify or suppress the emission above or below the intensity of independently radiating particles. The pioneering theory of such coherent spontaneous emission was expounded by Dicke,[1] who considered a system of two-level particles, interacting by means of a radiation field, and showed that the system behaves as a single coherent entity. The Dicke theory allowed one to predict and investigate a number of first-order radiation effects connected with the collective behavior or particles, e.g., photon echo[2] and self-induced transparency.[3]

In recent years different aspects of the Dicke problem have been studied by many authors (see, e.g., Refs. 4–6 and references therein), but the treatment has rarely gone beyond the two-level idealization and first-order perturbation theory. The two-level idealization is a satisfactory approximation to real systems only in those cases when the interaction with the field has a strong resonance character. However, it is essential to take into account the "multilevelness" of the particles in a number of situations of practical importance, such as the action on a medium of several resonance pulses with different frequencies, the case of molecules with equidistant spectra, and the description of the interaction of a medium with intense fluxes of radiation. Furthermore, in this last case it is necessary to utilize higher orders of perturbation theory to calculate Raman scattering effects, harmonic generation, and so on. Here, relaxation processes do not have time to return the medium to its initial equilibrium state, and hence, as was pointed out in Ref. 7, it is necessary to consider the perturbation of the medium by earlier scattering when calculating transition probabilities. As a result, the molecules of the medium act as a single cooperative system, leading to off-diagonal elements in the density matrix of the medium (in the energy representation), in turn giving rise to a number of peculiarities of scattering processes. In view of these examples, the removal of the above-mentioned limitations of the Dicke theory is a necessity.

We shall refer to a system of multilevel particles interacting by means of a radiation field as the generalized Dicke problem. This generalized problem has been considered by several authors. Apanasevitch and Cruglick[8] have interpreted it from the point of view of permutation groups. Shelepin[9] and Teplitsky[10] discussed the possibility of direct generalization of the energy-spin method to a system of multilevel radiators. Methods of calculating coherent responses of matter to several external pulses, using a matrix generalization of the Dicke formula [Eq. (72) in Ref. 1], have been developed in Ref. 11. Several authors have extended the domain of applicability of the Dicke theory, not by considering the generalized problem, but by making *ad hoc* additions to the basic theory. Thus in Ref. 12, equations have been found for the scattering intensity when a photon beam passes through a medium. Cooperative effects were taken into account by terms proportional to the square of the density of scattering particles. Walls[13] obtained scattering probabilities for a molecular system in the Dicke state with a maximal cooperation number.

In the present paper, we develop the generalized Dicke theory further with the purpose of expanding its domain of applicability. In Sec. II we describe the system of multilevel particles, using group-theoretical techniques. In Sec. III we then use these techniques to calculate quantities of interest for coherent spontaneous emission. Features of this emission peculiar to the multilevel description are considered briefly in Sec. IV. Cooperative effects in second-order perturbation theory are considered in Sections V–VII. In particular, we find in Sec. V the probabilities of single Stokes and anti-Stokes scattering events on pure coherent states. In Sec. VI the scattering probabilities on a molecular system that has been subjected beforehand to a short intense laser pulse are calculated. The results of our theoretical considerations are compared with experimental data on stimulated Raman scattering (SRS) in Sec. VII, where we see that a number of peculiarities of SRS are accounted for by taking into consideration cooperative effects.

II. GROUP-THEORETICAL FORMULATION

Let us consider at first a system of radiators, each with three unequally spaced nondegenerate energy levels. An ensemble of particles occupies a volume with linear dimensions small compared with the wavelengths of the radiation. We shall neglect inelastic collisions (a gas of low density). Then, the internal and center-of-mass variables separate. It is convenient to write the Hamiltonian by means of the generators of the group SU_3 (see, for example, Ref. 14; the notation introduced there is used below). The internal energy operator of the jth molecule has eigenvalues $\epsilon_1=-\frac{1}{2}\epsilon$, $\epsilon_2=\frac{1}{2}\epsilon$, ϵ_3 and we will represent it as

$$H_1^{(j)}=\epsilon I_3^{(j)}+\epsilon_3(\tfrac{1}{3}-Y)^{(j)},\quad j=1,2,\ldots,N. \tag{1}$$

The eigenfunctions of this operator, $\chi_i^{(j)}$, $i=1,2,3$, correspond to the eigenvalues $(-\frac{1}{2},\frac{1}{3})$, $(\frac{1}{2},\frac{1}{3})$, $(0,-\frac{2}{3})$ of "isospin" $I_3^{(j)}$ and "hypercharge" $Y^{(j)}$ operators and describe the molecule in its first, second, and third levels. The functions $\chi_i^{(j)}$ transform according to the representation $\mathfrak{D}(1,0)$ of the group SU_3; that is, each molecule is characterized by its unitary spin in energy space. The unperturbed Hamiltonian of a system of N radiators can be written as

$$H=H_0(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)+\epsilon I_3+\epsilon_3(\tfrac{1}{3}-Y), \tag{2}$$

where H_0 describes the energy of translational motion and intermolecular interaction, $I_3=\sum_j I_3^{(j)}$, $\frac{1}{3}-Y=\sum_j(\frac{1}{3}-Y)^{(j)}$. This Hamiltonian acts only on the molecules' center-of-mass coordinates $\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N$. The operators H_0 and $H_1=\sum_j H_1^{(j)}$ commute with each other. The unperturbed Hamiltonian eigenfunctions are

$$\Psi_{g,N_1,N_2,N_3}=U_g(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)\chi_{p_1}^{(1)}\chi_{p_2}^{(2)}\cdots\chi_{p_N}^{(N)}. \tag{3}$$

Here, $U_g(\vec{r}_1,\vec{r}_2,\ldots,\vec{r}_N)$ is the space coordinate part of the wave function $(H_0U_g=E_gU_g)$; the functions $\chi^{(j)}$ show what level each molecule occupies, and N_i is the level population. The eigenvalues I_3 and $\frac{1}{3}-Y$ are equal to $\frac{1}{2}(N_2-N_1)$ and $\frac{1}{3}(N_1+N_2-2N_3)$, respectively.

The operator

$$H_{\text{int}}=-\vec{\mathfrak{a}}\{[(\vec{e}_1-i\vec{e}_2)I_+ +(\vec{e}_3+i\vec{e}_4)K_- +(\vec{e}_5+i\vec{e}_6)L_-] + (\text{Hermitian conjugate})\} \tag{4}$$

describes in the dipole approximation the interaction of the molecules with the radiation field. Here $\vec{\mathfrak{a}}$ is the vector potential of the field at the point at which the system is located. The vectors $\vec{e}_i$ are connected with the dipole moment matrix elements by the relation $(\hbar=c=1)$

$$\vec{e}_1-i\vec{e}_2=-i\epsilon\vec{d}_{12},\quad \vec{e}_3-i\vec{e}_4=i(\epsilon_3-\tfrac{1}{2}\epsilon)\vec{d}_{32},$$
$$\vec{e}_5-i\vec{e}_6=i(\epsilon_3+\tfrac{1}{2}\epsilon)\vec{d}_{31}.$$

Thus, the transition probabilities are determined by matrix elements of the nondiagonal generators of the group SU_3 (Fig. 1). In analogy with the two-level scheme,[1] instead of using states (3) as initial states, it is necessary to form appropriate linear combinations so that H_{int} connects a given state with the smallest possible number of other states. The basis $|P,Q,I,I_3,Y\rangle$ of the irreducible representation $\mathfrak{D}(P,Q)$ of the group SU_3 is such a set of suitable states. (For brevity, here and further, the coordinate part of the wave function is not written out.)

The electromagnetic transitions conserve the quantum numbers P and Q. (The complete Hamiltonian is formed linearly from the group generators with which the Casimir operators commute.) It can be shown[6] that for given N_1, N_2, N_3, I the numbers $s=\frac{1}{3}(N-P+Q)$ and $a=\frac{1}{3}(N-P-2Q)$ take values satisfying the system of inequalities

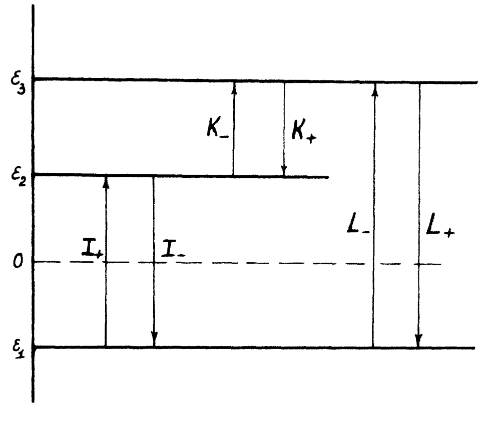

FIG. 1. Diagram of transitions between energy levels. The transition between each pair of levels is described by nondiagonal generators of the group SU_3.

$$I_M - I \leqslant s \leqslant I_M + I, \quad a \leqslant I_M - I, \quad s + a \leqslant I_M - I + N_3, \tag{5}$$

where

$$I_M = \tfrac{1}{2}(N_1 + N_2), \quad \tfrac{1}{2}|N_2 - N_1| \leqslant I \leqslant \tfrac{1}{2}(N_1 + N_2).$$

The treatment given above allows one, in principle, to calculate the transition probabilities to any order of perturbation theory.

III. COHERENT SPONTANEOUS EMISSION IN A SYSTEM OF MULTILEVEL PARTICLES

The intensities of spontaneous emission from the state $|s, a, I, I_3, Y\rangle$, calculated to first order, are equal to

$$\mathcal{T}_{ik} = \mathcal{T}_{ik}^{(0)} f_{ik}(s, a, I, I_3, Y), \tag{6}$$

where $\mathcal{T}_{ik}^{(0)}$ are the spontaneous-emission intensities of an isolated molecule for the transition $i \to k$. The functions f_{ik} are defined by matrix elements of the nondiagonal generators,[6]

$$f_{21} = (I + I_3)(I - I_3 + 1), \quad f_{32} = \gamma_1(I + I_3 + 1) + \gamma_2(I - I_3),$$
$$f_{31} = \gamma_1(I - I_3 + 1) + \gamma_2(I + I_3),$$

where

$$\gamma_1 = (I_M + I - s + 1)(I_M + I - a + 2) \times (I_M - I - s - a + N_3)[(2I + 1)(2I + 2)]^{-1},$$
$$\gamma_2 = (I - I_M + s)(I_M - I - a + 1) \times (I_M + I - s - a + N_3 + 1)[2I(2I + 1)]^{-1}.$$

Thus, the intensities depend upon three quantum numbers, s, a, and I, one of which (I) changes in the transitions $3 \to 1$ and $3 \to 2$. These numbers are cooperative characteristics of the system of molecules, determining its radiation decay rates. In the particular cases when the number of particles at one of the levels is zero, the correlation between the two other levels is described in the same way as in the case of the two-level scheme with a corresponding isospin (I, K, or L). The emission through other channels is proportional to the number of particles at the level, the transition from which is under consideration. For example, if $N_2 = 0$, one has from (5),

$$I = -I_3 = \tfrac{1}{2}N_1, \quad a = 0, \quad 0 \leqslant s \leqslant \min(N_1, N_3).$$

By means of (6) one gets

$$\mathcal{T}_{31} = \mathcal{T}_{31}^{(0)}(L + L_3)(L - L_3 + 1), \quad \mathcal{T}_{32} = \mathcal{T}_{32}^{(0)} N_3, \quad \mathcal{T}_{21} = 0,$$

where

$$L = \tfrac{1}{2}(N_1 + N_3) - s, \quad |L_3| \leqslant L \leqslant \tfrac{1}{2}(N_1 + N_3),$$
$$L_3 = \tfrac{1}{2}(N_3 - N_1).$$

If $s = 0$, then $\mathcal{T}_{31} \simeq \mathcal{T}_{31}^{(0)} N^2$ (the superradiant Dicke state). In Ref. 6 we give a detailed discussion of formulas (6). Let us dwell here on the most interesting case of superradiance through all frequencies. When $I = I_M$ it follows from (5) that

$$a = 0, \quad 0 \leqslant s \leqslant \min(N_1 + N_2, N_3).$$

If $s = 0$, then

$$\mathcal{T}_{ik} = \mathcal{T}_{ik}^{(0)} N_i(N_k + 1). \tag{10}$$

In particular, when the populations are equal, the emission intensity through all channels is proportional to the square of the total number of molecules. This case corresponds to the totally symmetric wave function, transforming by means of the representation $\mathfrak{D}(N, 0)$.

One can excite such states by starting with the gas in its ground state, for which $I = -I_3 = \tfrac{1}{2}N$, $s = a = 0$. After the action of two pulses with frequencies ω_{12} and ω_{13}, the gas goes to the superradiant state because with absorption of the first pulse the number I does not change, whereas with absorption of the second pulse it remains maximal.[6] The system in the state, thus attained, radiates with intensities calculated according to (10). For a system initially in a state of thermodynamic equilibrium, superradiance will also be observed after the two-pulse excitation [see formulas (14) with $\Gamma(\vec{k}_{12}, \vec{k}') = \Gamma(\vec{k}_{13}, \vec{k}''') = \Gamma(\vec{k}_{13} - \vec{k}_{12}, \vec{k}'') = 1$].

In the optical range the linear dimensions of the system, as a rule, exceed the wavelengths of spontaneous emission. In this case the molecules can be correlated in such a manner that coherent emission is observed at different frequencies in directions connected by certain geometric relations. The Hamiltonian of the molecules' interaction with the field can be written in a form

$$H_{\text{int}} = -\sum_{\vec{k}, \lambda} \left[\left(\frac{1}{2\omega V} \right)^{1/2} a_{\vec{k},\lambda} \vec{e}_{\vec{k},\lambda} \cdot [(\vec{e}_1 - i\vec{e}_2) I_+(\vec{k}) + (\vec{e}_3 + i\vec{e}_4) K_-(\vec{k}) + (\vec{e}_5 + i\vec{e}_6) L_-(\vec{k})] \right]$$
$$+ (\text{Hermitian conjugate}), \tag{11}$$

where $a^{\dagger}_{\vec{k},\lambda}$, $a_{\vec{k},\lambda}$ are, respectively, the photon creation and annihilation operators. The operators appearing in (11) are defined by formulas

$$I_\pm(\vec{k}')=\sum_j I_\pm^{(j)}e^{\pm i\vec{k}'\cdot\vec{r}_j},$$

$$K_\pm(\vec{k}'')=\sum_j K_\pm^{(j)}e^{\mp i\vec{k}''\cdot\vec{r}_j}, \qquad (12)$$

$$L_\pm(\vec{k}''')=\sum_j L_\pm^{(j)}e^{\mp i\vec{k}'''\cdot\vec{r}_j},$$

and under the condition

$$\vec{k}'+\vec{k}''=\vec{k}''', \qquad (13)$$

satisfy the commutation relations of the Lie algebra SU_3. The wave functions of the system of molecules can be chosen simultaneously to be eigenfunctions of the unperturbed Hamiltonian (2) and the Casimir operators $F^2(\vec{k}',\vec{k}'',\vec{k}''')$, $G^3(\vec{k}',\vec{k}'',\vec{k}''')$, constructed from (12) if the condition (13) is fulfilled. Under these circumstances the Casimir operators do not commute with operators of type (12), having wave-vector indices different from the one already chosen. In analogy with the considerations leading to (6), one discovers that the constructed wave functions are states of a system for which the radiation, emitted in the directions $\vec{k}',\vec{k}'',\vec{k}'''$ $(\vec{k}'+\vec{k}''=\vec{k}''')$ at frequencies ω_{12}, ω_{23}, ω_{13}, is coherent. Spontaneous-emission intensities in these directions are given by formulas (6), where $\mathcal{T}_{21}$, $\mathcal{T}_{21}^{(0)}$; $\mathcal{T}_{32}$, $\mathcal{T}_{32}^{(0)}$; $\mathcal{T}_{31}$, $\mathcal{T}_{31}^{(0)}$ are now to be interpreted as the photon emission rates per unit solid angle in the directions $\vec{k}'$, $\vec{k}''$, $\vec{k}'''$, respectively. The emission in $\vec{k}'$, $\vec{k}''$, $\vec{k}'''$ directions does not change the quantum numbers s and a, while the emission in other directions leads to their change and to the destruction of coherence with respect to $\vec{k}'$, $\vec{k}''$, $\vec{k}'''$.

IV. PULSE-INDUCED COHERENT RADIATION

Let us calculate the intensities of coherent responses to the action of pulses with frequencies ω_{12} (wave vector $\vec{k}_{12}$) and ω_{13} (wave vector $\vec{k}_{13}$) on a medium in equilibrium. It follows from formulas (6) that for mixed states,

$$\mathcal{T}_{21}(\vec{k}')=\mathcal{T}_{21}^{(0)}(\vec{k}')\,\mathrm{Tr}I_-(\vec{k}')\rho I_+(\vec{k}'),$$

$$\mathcal{T}_{32}(\vec{k}'')=\mathcal{T}_{32}^{(0)}(\vec{k}'')\,\mathrm{Tr}K_+(\vec{k}'')\rho K_-(\vec{k}''),$$

$$\mathcal{T}_{31}(\vec{k}''')=\mathcal{T}_{31}^{(0)}(\vec{k}''')\,\mathrm{Tr}L_+(\vec{k}''')\rho L_-(\vec{k}'''),$$

where ρ is the density matrix of a system of molecules after the action of the pulses.

The action of a pulse on a molecule is described by a unitary transformation on the molecules' energy space.[1,6] In the case under consideration one has

$$\rho(t)=e^{-iH_1t}T\rho_0T^{-1}e^{iH_1t},$$

where ρ_0 is the initial density matrix, $T=T_{13}\cdot T_{12}$,

$$T_{12}=\exp\{i\tfrac{1}{2}\theta_1[\alpha I_-(\vec{k}_{12})+\alpha^*I_+(\vec{k}_{12})]\},$$

$$T_{13}=\exp\{i\tfrac{1}{2}\theta_2[\beta L_-(\vec{k}_{13})+\beta^*L_+(\vec{k}_{13})]\},$$

$$(|\alpha|=|\beta|=1).$$

Here the parameters θ_1 and θ_2 are proportional to the product of the amplitude and duration of the first and the second pulses, respectively, $\sin^2\frac{1}{2}\theta_1$ and $\sin^2\frac{1}{2}\theta_2$ are the excitation probabilities of the molecules by the first and the second pulses to the second and the third level, respectively. The calculations give

$$\begin{aligned}
\mathcal{T}_{21}(\vec{k}')&=\mathcal{T}_{21}^{(0)}(\vec{k}')N\{(\sigma_1\sin^2\tfrac{1}{2}\theta_1+\sigma_2\cos^2\tfrac{1}{2}\theta_2)+\tfrac{1}{4}(\sigma_1-\sigma_2)^2\sin^2\theta_1\cos^2\tfrac{1}{2}\theta_2[N\Gamma(\vec{k}_{12},\vec{k}')-1]\},\\
\mathcal{T}_{31}(\vec{k}''')&=\mathcal{T}_{31}^{(0)}(\vec{k}''')N\{\sigma_3\cos^2\tfrac{1}{2}\theta_2+\sin^2\tfrac{1}{2}\theta_2(\sigma_1\cos^2\tfrac{1}{2}\theta_1+\sigma_2\sin^2\tfrac{1}{2}\theta_1)\\
&\qquad+\tfrac{1}{4}\sin^2\theta_2(\sigma_3-\sigma_1\cos^2\tfrac{1}{2}\theta_1-\sigma_2\sin^2\tfrac{1}{2}\theta_1)^2[N\Gamma(\vec{k}_{13},\vec{k}''')-1]\},\\
\mathcal{T}_{32}(\vec{k}'')&=\mathcal{T}_{32}^{(0)}(\vec{k}'')N\{\sigma_3\cos^2\tfrac{1}{2}\theta_2+\sin^2\tfrac{1}{2}\theta_2(\sigma_1\cos^2\tfrac{1}{2}\theta_1+\sigma_2\sin^2\tfrac{1}{2}\theta_1)\\
&\qquad+\tfrac{1}{4}\sin^2\theta_1\sin^2\tfrac{1}{2}\theta_2(\sigma_1-\sigma_2)^2[N\Gamma(\vec{k}_{13}-\vec{k}_{12},\vec{k}'')-1]\},
\end{aligned} \qquad (14)$$

where $\sigma_i=\bar{N}_i/N$, $\bar{N}_i$ is the equilibrium population of the ith level; $\Gamma(\vec{p}_1,\vec{p}_2)=|\langle\exp[i(\vec{p}_1-\vec{p}_2)\cdot\vec{r}]\rangle|^2$, and the symbol $\langle\,\rangle$ signifies the average over all the molecules. For systems of large extent, $\langle\exp[i(\vec{p}_1-\vec{p}_2)\cdot\vec{r}]\rangle=\delta_{\vec{p}_1,\vec{p}_2}$. From here it follows that superradiation will be observed in the directions $\vec{k}_{12}$ (frequency ω_{12}), $\vec{k}_{13}-\vec{k}_{12}$ (frequency ω_{23}), and $\vec{k}_{13}$ (frequency ω_{13}). A single pulse induces an intense response in the same direction. Here, however, the radiation at other frequencies is not coherent.

So far, relaxation processes have been excluded from consideration. Therefore the intensities obtained have not depended on time and have determined immediate coherent responses of the system to the exciting pulses. In order to analyze the time development of these responses, it is necessary to include the effect of inhomogeneous broadening, caused by differences in the resonance frequencies of individual radiators as a result of the inhomogeneity of the field within the sample under investigation (see also Ref. 11). For instance, calculations analogous to those in Ref. 2 show that when two pulses of frequencies ω_{12} and ω_{13} act on the medium, there arises an echo signal of frequency ω_{32} at time $t+(\omega_{31}|\omega_{32})\tau$, in addition to the coherent responses at frequencies ω_{12} and ω_{13} immediately after the pulses at times t and $t+\tau$. The time τ is much less than that for the irreversible relaxation of the system. The intensities of the signals as before are determined by formulas (14). The time delay of the response at frequency ω_{32} is present only if $(\omega_{31}^{(j)}/\omega_{32}^{(j)}) = (\mathrm{const.})$ $(j=1,2,\ldots,N)$ and is absent in the case of an arbitrary two-dimensional Gaussian distribution of the molecules about the frequencies ω_{32} and ω_{31}, when their correlation coefficient is different from unity.

Analysis of the case $n=3$ allows one to exhibit the main peculiarities of the multilevel problem. The states of a system of molecules with n levels are classified according to the irreducible representations $\mathfrak{D}(p_1,p_2,\ldots,p_{n-1})$ of the group SU_n. Indices of the irreducible representations serve as cooperative labels of the system. Representations $\mathfrak{D}(N,0,\ldots,0)$ correspond to the superradiant states; wave functions of such states are totally symmetric. If the system is in the superradiant state, the intensities of emission at all frequencies are proportional to N^2. The superradiant states can be excited by pulsed action on the medium. If wavelengths are less than the dimensions of the system, the intensities of responses are easily found by means of the generalization of the above formalism. Thus, reducing the n-level problem with respect to the subgroup SU_2 of SU_n, we easily find the angular distribution of the coherent responses from the geometric relations between the wave vectors. In Table I we present the angular distributions of superradiant responses to pulsed excitation for the four-level unequidistant radiators. (In the table instead of wave vectors we indicate only their indices. For example, the notation 12 + 14 means $\vec{k}_{12}+\vec{k}_{14}$.) Those cases in which the angular distribution does not depend upon the succession of pulses are considered here. Other aspects of the multilevel Dicke problem (the classical limit, oscillatory systems) are considered by the authors in Refs. 6 and 15.

V. CALCULATION OF COOPERATIVE SCATTERING EFFECTS

The generalization of the Dicke technique to the case of multilevel particles allows one to consider the influence of the collective properties of a system of molecules on processes, described by higher orders of perturbation theory. The influence of this collective behavior on the Raman scattering of light (RS) is calculated below.

It is usually considered that the scattering of radiation on individual particles (atoms and molecules) takes place independently. Such processes are studied sufficiently well within the framework of quantum electrodynamics. Meanwhile, physical conditions are possible (e.g., the case of such intense incident radiation, that one may neglect relaxation processes), under which the phase correlation among individual radiators becomes substantial. In this case it is necessary to consider for scattering calculations the electromagnetic field interaction with the whole ensemble of par-

TABLE I. Angular distributions of superradiant responses to pulsed excitation for the four-level unequidistant radiators. (Instead of wave vectors, we indicate only their indices. For example, the notation 12 + 14 means $\vec{k}_{12}+\vec{k}_{14}$.)

	Exciting pulses						Superradiant responses					
Frequencies	ω_{12}	ω_{23}	ω_{13}	ω_{14}	ω_{24}	ω_{34}	ω_{12}	ω_{23}	ω_{13}	ω_{14}	ω_{24}	ω_{34}
I	12	⋯	13	14	⋯	⋯	12	13 − 12	13	14	14 − 12	14 − 13
II	12	23	⋯	14	⋯	⋯	12	23	23 + 12	14	14 − 12	14 − 12 − 23
III	12	⋯	⋯	14	⋯	34	12	14 − 34 − 12	14 − 34	14	14 − 12	34
IV	12	23	⋯	⋯	⋯	34	12	23	12 + 23	12 + 23 + 34	34 + 23	34
V	12	⋯	⋯	⋯	24	34	12	24 − 34	12 + 24 − 34	24 + 12	24	34
VI	12	23	⋯	⋯	24	⋯	12	23	12 + 23	12 + 24	24	24 + 23
VII	12	⋯	13	⋯	⋯	34	12	13 − 12	13	13 + 34	34 + 13 + 12	34
VIII	12	⋯	13	⋯	24	⋯	12	13 − 12	13	12 + 24	24	24 − 13 + 12
IX	⋯	23	⋯	14	⋯	34	14 − 23 − 34	23	14 − 34	14	23 + 34	34
X	⋯	23	⋯	14	24	⋯	14 − 24	23	23 + 14 − 24	14	24	24 − 23
XI	⋯	23	13	⋯	⋯	34	13 − 23	23	13	13 + 34	23 + 34	34
XII	⋯	23	13	⋯	24	⋯	13 − 23	23	13	13 + 24 − 23	24	24 − 23
XIII	⋯	23	13	14	⋯	⋯	13 − 23	23	13	14	23 + 14 − 13	14 − 13
XIV	⋯	⋯	13	14	24	⋯	14 − 24	13 + 24 − 14	13	14	24	14 − 13
XV	⋯	⋯	13	⋯	24	34	13 + 34 − 24	24 − 34	13	13 + 34	24	34
XVI	⋯	⋯	⋯	14	24	34	14 − 24	24 − 34	14	14	24	34

ticles as a single entity.

Let us consider at first the problem of calculating transition probabilities for coherent RS processes in the case when the wavelengths of the initial and final photons are large compared with the linear dimensions of the scattering system. An adequate formalism to describe coherent interactions of a medium with light to higher orders of perturbation theory is the one developed in Sec. II, according to which, the eigenstates and operators for n-level molecules are classified by means of the group SU_n. With the cooperative effects taken into account, the molecules behave as a single quantum-mechanical system characterized by the cooperation numbers introduced above. To make a connection between the generalized Dicke method, describing cooperative effects in first-order radiation processes, and the earlier treatments of cooperative scattering,[12,13] let us consider scattering on pure cooperative states. This treatment illustrates the nature of the effect and allows one to go over to the case of mixed states (Sec. VI).

We will calculate the probability of a single scattering event on the indicated states (the process of the type n_L, $n_S \rightarrow n_L - 1$, $n_S + 1$, where n_L, n_S are the occupation numbers of laser and scattered photons). Without loss of generality we restrict ourselves, for simplicity, to the case of three-level molecules. The formulas derived below in Sections VI and VII remain justified by taking into account an arbitrary number of discrete levels and a continuous spectrum. The Hamiltonian of the system can be written as follows:

$$H + H_{\text{int}}, \tag{15}$$

where H and H_{int} are defined by formulas (2) and (4). In (15) the terms that describe relaxation processes are omitted. It is assumed further that the characteristic times of these processes τ_{rel} are large compared to the characteristic time τ_{RS} of perturbation of a medium (changing of its density matrix) as a result of the RS processes. In the reverse case the effect of cooperation disappears. This is the case when low-power sources are used for the exciting radiation, because the medium has time to return to equilibrium after each scattering event. When intense laser radiation is applied and stimulated processes become essential, the assumption $\tau_{\text{RS}} \ll \tau_{\text{rel}}$ is apparently justified experimentally.[16,17]

We shall use the basis $|s, a, I, I_3, Y\rangle$ of the irreducible representations of the group SU_3 as eigenfunctions of the unperturbed Hamiltonian H. Insofar as in the calculation of RS probabilities, the level "3" is virtual, we get from (5) at once $a = 0$, $s = \frac{1}{2}N - I$. The probability amplitude for a scattering process with the formation of a Stokes photon [(Fig. 2(a)] can be written as

$$\mathcal{A}_S = \frac{\langle 2|H'_{\text{int}}|3\rangle\langle 3|H_{\text{int}}|1\rangle}{-\frac{1}{2}\epsilon - \epsilon_3 + \omega} + \frac{\langle 2|H_{\text{int}}|3\rangle\langle 3|H'_{\text{int}}|1\rangle}{-\frac{1}{2}\epsilon - \epsilon_3 - \omega_S}, \tag{16}$$

where $\langle |H_{\text{int}}| \rangle$ are matrix elements for absorption of a photon with wave vector $\vec{k}$ and polarization $\vec{e}$:

$$\begin{aligned} \langle 3|H_{\text{int}}|1\rangle &= -i(2\pi\omega n_L)^{1/2} \\ &\quad\times[\vec{e}\cdot(\vec{e}_5 + i\vec{e}_6)]\langle 3|L_-|1\rangle, \\ \langle 2|H_{\text{int}}|3\rangle &= -i(2\pi\omega n_L)^{1/2} \\ &\quad\times[\vec{e}\cdot(\vec{e}_3 - i\vec{e}_4)]\langle 2|K_+|3\rangle. \end{aligned} \tag{17}$$

$\langle |H_{\text{int}}| \rangle$ are matrix elements for emission of the Stokes photon $(\vec{k}_S, \vec{e}_S)$:

$$\begin{aligned} \langle 2|H'_{\text{int}}|3\rangle &= i[2\pi\omega_S(n_S + 1)]^{1/2} \\ &\quad\times[\vec{e}_S^{\,*}\cdot(\vec{e}_3 - i\vec{e}_4)]\langle 2|K_{\mp}|3\rangle, \\ \langle 3|H'_{\text{int}}|1\rangle &= i[2\pi\omega_S(n_S + 1)]^{1/2} \\ &\quad\times[\vec{e}_S^{\,*}\cdot(\vec{e}_5 + i\vec{e}_6)]\langle 3|K_-|1\rangle. \end{aligned} \tag{18}$$

Using formulas (6) we get for the probability of Stokes scattering on the system of molecules (the indices s, a in what follows are omitted)

$$w_S = w_S^{(0)}(I - I_3)(I + I_3 + 1), \tag{19}$$

where $w_S^{(0)}$ is the usual expression for the scattering probability of an isolated molecule, $w_S = \mathcal{A}_S^* \mathcal{A}_S$,

$$\mathcal{A}_S = 2\pi[\omega\omega_L n_L(n_S + 1)]^{1/2} \times \sum_g \left(\frac{[\vec{e}_S^{\,*}\cdot(\vec{e}_3 - i\vec{e}_4)][\vec{e}\cdot(\vec{e}_5 + i\vec{e}_6)]}{\epsilon_1 - \epsilon_g + \omega} + \frac{[\vec{e}\cdot(\vec{e}_3 - i\vec{e}_4)][\vec{e}_S^{\,*}\circ(\vec{e}_5 + i\vec{e}_6)]}{\epsilon_1 - \epsilon_g - \omega_S} \right).$$

For $I_3 = 0$ and $I = I_{\max}$, w_S is proportional to the square of the total number of scattering molecules (superscattering). It is clear (see Sec. VI), that for a system of molecules in equilibrium, the scattering probability is always proportional to N_1; that is, the scattering process takes places, as is to be expected, incoherently. The cooperative effect is manifested only in nonstationary systems.

Analogously, for the probability of anti-Stokes photon scattering [the mechanism of the process is depicted in Fig. 2(b)] we have

$$w_{a-S} = w_{a-S}^{(0)}(I + I_3)(I - I_3 + 1). \tag{20}$$

It should be noted that the ratio of the probabilities of Stokes and anti-Stokes processes from the state $|I, I_3\rangle$ is expressed by the quantity

$$\frac{(I-I_3)(I+I_3+1)}{(I+I_3)(I-I_3+1)},$$

which, when $I=\frac{1}{2}N$, yields $N_1(N_2+1)[N_2(N_1+1)]^{-1}$. The latter result is derived in Ref. 11. In the general case, when a state of the system is represented by a superposition of states with different I and I_3, we have

$$w_S = w_S^{(0)} \sum_{I,I_3} P_{I,I_3}(I+I_3)(I-I_3+1) = w_S^{(0)} \langle L_+K_-K_+L_-\rangle, \tag{21}$$

where P_{I,I_3} is the probability for a system to be in the state $|I,I_3\rangle$ at the moment of scattering.

In the case when the linear dimensions of the system exceed the wavelengths of the initial and final photons ($\lambda \ll a$), which usually takes place under real conditions, the system may be correlated in such a way that the scattering process with a given wave vector of the scattered photon goes on coherently for some direction or another. Then for the scattering amplitude we have formula (16), where instead of the matrix elements in the right-hand sides of formulas (17) and (18) now should appear, respectively,

$$\langle 3|L_-(\vec{k})|1\rangle,\ \langle 2|K_-(\vec{k})|3\rangle,$$
$$\langle 2|K_+(\vec{k}_S)|3\rangle,\ \langle 3|L_-(\vec{k}_S)|1\rangle \tag{22}$$

($\vec{k}$ is the wave vector of the incident photon, $\vec{k}_S$ is the wave vector of the scattered photon). According to (22) the scattering amplitude contains operators from two sets (12), corresponding to the following values of the parameters in (12):

$$\text{(i)}:\ \vec{k}'=\vec{k}-\vec{k}_S,\quad \vec{k}''=\vec{k}_S,\quad \vec{k}'''=\vec{k};$$
$$\text{(ii)}:\ \vec{k}'=\vec{k}-\vec{k}_S,\quad \vec{k}''=-\vec{k},\quad \vec{k}'''=-\vec{k}_S.$$

The Casimir operators, constructed from the two indicated sets of operators, commute if their domain of definition includes only the functions $|s,a,I,I_3,Y\rangle$, with $s=\frac{1}{2}N$, $a=0$, $Y=\frac{1}{3}N$. The wave function of our system may be chosen simultaneously to be an eigenfunction of the unperturbed Hamiltonian H and the Casimir operators, constructed by means of the first and the second sets of operators.

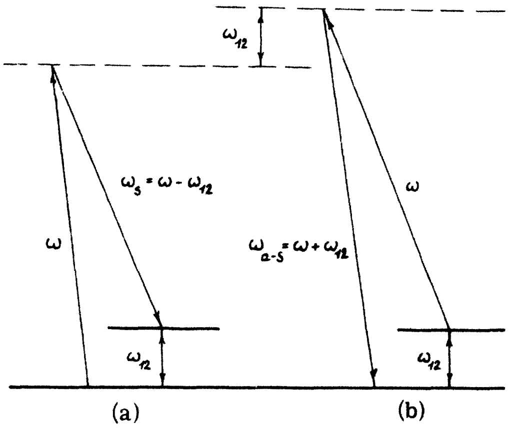

FIG. 2. Diagrams of (a) Stokes and (b) anti-Stokes scattering processes.

The states thus introduced are the states of a system for which the scattering in the direction $\vec{k}_S$ is coherent. The degree of coherence is given by a single quantum number I, which is related to the chosen wave vectors ($\vec{k}$ and $\vec{k}_S$). By virtue of (16) and (22), the calculation of scattering amplitudes reduces to the calculation of matrix elements of the operators

$$K_+(\vec{k}_S)L_-(\vec{k}) = I_+(\vec{k}-\vec{k}_S) + \sum_{j\neq j'} K_+^{(j)} L_-^{(j')} e^{i(\vec{k}\cdot\vec{r}_j-\vec{k}_S\cdot\vec{r}_{j'})},$$
$$K_+(-\vec{k})L_-(-\vec{k}_S) = I_+(\vec{k}-\vec{k}_S) + \sum_{j\neq j'} K_+^{(j)} L_-^{(j')} e^{i(\vec{k}\cdot\vec{r}_{j'}-\vec{k}_S\cdot\vec{r}_j)}.$$

Since the second terms in these formulas when acting on the functions $|\frac{1}{2}N-I,0,I,I_3,\frac{1}{3}N\rangle$ do not contribute to the matrix elements, the scattering probabilities for such states are calculated by formulas (19), where w_S, $w_S^{(0)}$ are to be interpreted as the scattering rates per unit solid angle in the $\vec{k}_S$ direction, when a photon with wave vector $\vec{k}$ is incident on the system

$$w_S(\vec{k},\vec{k}_S) = w_S^{(0)}(\vec{k},\vec{k}_S)(I-I_3)(I+I_3+1). \tag{23}$$

In Sections VI and VII the scattering of an intense light beam passing through a system of molecules in equilibrium will be considered. Such consideration, in distinction with the case of pure states, requires the use of the density-matrix formalism. In this connection we present a formula, following from (23) and generalizing (21) for the case of a system of large extent:

$$w_S(\vec{k},\vec{k}_S) = w_S^{(0)}(\vec{k},\vec{k}_S)\langle O^\dagger O\rangle,$$
$$O=\tfrac{1}{2}[K_+(\vec{k}_S)L_-(\vec{k})+K_+(-\vec{k})L_-(-\vec{k}_S)]. \tag{24}$$

VI. LASER PULSE SCATTERING IN THE ABSENCE OF RELAXATION PROCESSES

Under real conditions cooperative effects can be induced by perturbations of a medium as a result of a light beam passing through it. It will be seen, further, that for a medium in equilibrium, the scattering occurs in the ordinary way (the probability of scattering is equal to a sum of scattering probabilities of each molecule); but if a medium is described by a nonstationary density matrix (having off-diagonal elements in the energy representation) the scattering is at least partially coherent. It is essential that in the experimentally realized case $\lambda \ll a$, to be investigated further, coherent scattering is nonisotropic and is responsible for the asymmetry of the scattering indicatrix of the first Stokes component as well as other peculiarities of the angular distributions. The presence of cooperative terms in scattering probabilities brings about a number of energy and spectral peculiarities of scattered emission as well.

In calculating scattering probabilities, we shall consider, that a single-model laser pulse (plane wave with a frequency ω and wave vector $\vec{k}$) is incident on the medium in equilibrium at temperature T. The intense field, acting on the molecules as the pulse passes, can be described classically, whereas RS probabilities will be calculated quantum mechanically. For simplicity we shall neglect the changing of the molecules' positions during the passage of the pulse.

By virtue of formula (24) the probability of formation of a Stokes photon with a wave vector $\vec{k}_S$ for a mixed state can be written as follows:

$$w_S(\vec{k},\vec{k}_S) = w_S^{(0)}(\vec{k},\vec{k}_S)\,\mathrm{Tr}\,O\rho O^\dagger, \tag{25}$$

where ρ is the density matrix of the molecules at the time of scattering. Let us find the explicit form which the density matrix assumes at some time t after a pulse of duration τ has passed (in part or completely) through a given length of the medium. As a result of preceding scattering events some of the molecules jump from the first to the second level and the medium departs from equilibrium.

The density matrix can be calculated in the following way. Let $\Psi(0)$ be the wave function of the system before the passage of the pulse. At time t we have

$$\Psi'(t) = e^{-iH_1 t}\,T\Psi(0). \tag{26}$$

Here T is the unitary transformation, describing the perturbation of the medium after passage of a part of the pulse. We can establish the most general form of the operator T by considering the action of the pulse on an individual molecule. The field, acting on the jth molecule differs from zero in the time interval $t_j \leq t \leq t_j + \tau$, where t_j is the arrival time of the pulse at the jth molecule. The unitary transformation, describing the scattering on a given molecule, can be represented as two successive rotations in the L and K subspaces, which, as is easy to see, reduce to rotations in I-spin space: first about an axis, normal to the axis of quantization (3-axis), and second about the 3-axis. Hence the operator T assumes the form of a product

$$\begin{aligned} T = {} & \exp\Bigl(i \sum_j H_1^{(j)} t_j\Bigr) \\ & \times \prod_{s=1}^{N} \exp\bigl[i\tfrac{1}{2}\varphi_s(\alpha_s I_+^{(s)} + \alpha_s^* I_-^{(s)}) + i\varphi_s' I_3^{(s)}\bigr] \\ & \times \exp\Bigl(i \sum_j H_1^{(j)} t_j\Bigr). \end{aligned} \tag{27}$$

Here φ_s and φ_s' are parameters of the first and the second rotation, respectively, in the energy space of the sth molecule. The position of the axis, around which the first takes place, is determined by a phase of α_s ($|\alpha_s| = 1$). The parameters φ_s' vanish in further calculations, which is why in the following they will be assumed equal to zero from the outset. The quantity $\sin^2\frac{1}{2}\varphi_s$ is the transition probability of a molecule from the first level to the second one, as a result of preceding scattering events. In the present problem we are taking into account stimulated scattering, so φ_s are not equal for different molecules (at a given time $\sin^2\frac{1}{2}\varphi_s$ attains a larger value at the end of the section of the medium in question, where the role of stimulated RS is maximal). After substitution of $t_j = \vec{k}\cdot\vec{r}_j/\omega$ in (27) we get

$$\begin{aligned} T = \exp\Bigl(i \sum_j \bigl[& \alpha_j \tfrac{1}{2}\varphi_j I_+^{(j)} e^{i(\omega_{12}/\omega)\vec{k}\cdot\vec{r}_j} \\ & + \alpha_j^* \tfrac{1}{2}\varphi_j I_-^{(j)} e^{-i(\omega_{12}/\omega)\vec{k}\cdot\vec{r}_j}\bigr]\Bigr) \quad (\omega_{12} = \epsilon_2 - \epsilon_1). \end{aligned}$$

Going over from (26) to the density-matrix description, one finds

$$\rho(t) = e^{-iH_1 t}\,T\rho_0 T^{-1} e^{iH_1 t}, \tag{28}$$

where ρ_0 is the equilibrium density matrix:

$$\rho_0 = \frac{e^{-H_1/kt}}{\mathrm{Tr}\,e^{-H_1/kt}} = \prod_j (\sigma_1 P_1^{(j)} + \sigma_2 P_2^{(j)}),$$

$$\sigma_i = \frac{\overline{N}_i}{N} = \frac{1}{2}\Bigl(1 + (-1)^{i-1}\tanh\frac{\epsilon}{2kT}\Bigr) \quad (i = 1, 2),$$

$$P_1^{(j)} = 2L_3^{(j)} + (\tfrac{1}{3} - Y)^{(j)}, \quad P_2^{(j)} = 2K_3^{(j)} + (\tfrac{1}{3} - Y)^{(j)}.$$

In what follows, it is convenient to represent $T\rho_0 T^{-1}$ in the form $\prod_j A_j$, where

$$\begin{aligned} A_j = {} & (\sigma_1 \cos^2\tfrac{1}{2}\varphi_j + \sigma_2 \sin^2\tfrac{1}{2}\varphi_j) P_1^{(j)} \\ & + (\sigma_1 \sin^2\tfrac{1}{2}\varphi_j + \sigma_2 \cos^2\tfrac{1}{2}\varphi_j) P_2^{(j)} \\ & + \tfrac{1}{2} i \sin\varphi_j (\sigma_1 - \sigma_2)(\alpha_j I_+^{(j)} e^{i(\omega_{12}/\omega)\vec{k}\cdot\vec{r}_j} \\ & - \alpha_j^* I_-^{(j)} e^{-i(\omega_{12}/\omega)\vec{k}\cdot\vec{r}_j}). \end{aligned} \tag{29}$$

For illustration, let us calculate one out of the four terms included in (25); for example, the quantity

$$\begin{aligned}\mathrm{Tr}\rho L_+(\vec{k})K_-(\vec{k}_s)K_+(\vec{k}_s)L_-(\vec{k}) &= \sum_{j_1 j_2 l_1 l_2} \mathrm{Tr}\prod_j A_j L_+^{(j_1)} K_-^{(j_2)} K_+^{(l_1)} L_-^{(l_2)} \\ &\quad \times e^{i\vec{k}\cdot(\vec{r}_{l_2}-\vec{r}_{j_1})} e^{i\vec{k}_s\cdot(\vec{r}_{j_2}-\vec{r}_{l_1})}. \qquad (30)\end{aligned}$$

With the help of (29) it is easy to see that in (30) the only terms differing from zero are those with $j_1 = j_2 = l_1 = l_2$ and $j_1 = j_2 \neq l_1 = l_2$. Taking into consideration that φ is a slowly changing function of the coordinate, one gets an equation equal to Eq. (30):

$$\begin{aligned}& N(\sigma_1\langle\cos^2\tfrac{1}{2}\varphi\rangle + \sigma_2\langle\sin^2\tfrac{1}{2}\varphi\rangle) + N(\sigma_1 - \sigma_2)^2 \\ & \quad \times [N\langle\sin\varphi\rangle^2 \delta_{\vec{k}_S,(\omega_S/\omega)\vec{k}} - \langle\sin^2\varphi\rangle].\end{aligned}$$

Here, because of the condition $\lambda \ll a$ is taken,

$$\langle\exp\{i[\vec{k}_S - (\omega_S/\omega)\vec{k}]\cdot\vec{r}\}\rangle = \delta_{\vec{k}_S,(\omega_S/\omega)\vec{k}}.$$

The quantity

$$\langle\sin\varphi\rangle^2 = \left(\frac{1}{N}\sum_j \sin\varphi_j\right)^2$$

is an integral characteristic of the medium, determining the degree of perturbation at a given time. The function $\varphi(\vec{r}, t)$ varies from zero (at the time $t = 0$) to its maximum value $\varphi_{\max}$, which is determined by the intensity of the incident beam and in real cases depends on the rate of relaxation processes. Other terms in (25) are calculated analogously. Finally, for the probability of Stokes scattering we obtain

$$\begin{aligned}w_S(\vec{k}, \vec{k}_S) &= w_S^{(0)}(\vec{k}, \vec{k}_S) \\ &\quad \times \{N(\sigma_1 \cos^2\tfrac{1}{2}\varphi + \sigma_2 \sin^2\tfrac{1}{2}\varphi) \\ &\quad + N\sin^2\varphi(\sigma_1 - \sigma_2)^2\ [N\delta_{\vec{k}_S,(\omega_S/\omega)\vec{k}} - 1]\}. \qquad (31)\end{aligned}$$

Here the condition $\langle\sin\varphi\rangle^2 \ll 1$ confirmed by experiment is used (see Sec. VII). When $\varphi = 0$ (the medium in equilibrium), (31) leads to the usual result $w_S(\vec{k}, \vec{k}_S) = w_S^{(0)}(\vec{k}, \vec{k}_S) N\sigma_1$. In a similar way, an expression for the probability of anti-Stokes scattering is obtained:

$$\begin{aligned}w_{a-S}(\vec{k}, \vec{k}_{a-S}) &= w_{a-S}^{(0)}(\vec{k}, \vec{k}_{a-S}) \\ &\quad \times \{N(\sigma_1 \sin^2\tfrac{1}{2}\varphi + \sigma_2 \cos^2\tfrac{1}{2}\varphi) \\ &\quad + N\sin^2\varphi(\sigma_1 - \sigma_2)^2 \\ &\quad \times [N\delta_{\vec{k}_{a-S},(\omega_{a-S}/\omega)\vec{k}} - 1]\}. \qquad (32)\end{aligned}$$

We shall discuss the obtained formulas (31) and (32) in connection with available experimental information.

VII. APPENDIX TO STIMULATED RAMAN SCATTERING PHENOMENON

Collective processes in Raman scattering are intimately connected with the question of so called "anomalies" in stimulated Raman scattering (SRS), which have been observed after using intense light beams from laser sources as exiting radiation (see, for example, Refs. 16 and 18). Here the most relevant are anomalous angular distributions of the scattered light, extremely sharp dependence of the scattered-light intensity on the power of the exiting radiation, and appearance in the SRS spectra of only a small number of frequencies of the ordinary RS of the given substance.

These anomalies are poorly accounted for by existing quantum theories of SRS, but are explained naturally by consideration of cooperative effects. These effects play a crucial role in processes with intense incident beams where it is necessary, when calculating transition probabilities, to take into account the change in properties of the medium due to the preceding RS. The necessity of studying problems of this sort on the basis of the coherent interaction of light with matter was first put forth by Sushtchinsky.[18]

Conditions under which cooperative scattering plays a crucial role, apparently are actually found in experiments on SRS.[16,17] The use of powerful laser sources makes stimulated processes essential. As a result, characteristic scattering times τ_{RS} are two to three orders of magnitude less than characteristic relaxation times τ_{rel}. After the forward front of a laser pulse passes through a given section of the medium, further scattering occurs in the already perturbed medium, which does not have time to relax. It is essential that with the use of the usual low-power sources (the case of ordinary Raman scattering) τ_{rel} is less than τ_{RS}, and in this case cooperative effects do not play any role (output intensities and scattering probabilities have the usual concentration and angular dependences).

Scattering on a nonequilibrium medium means qualitatively that in every scattering event participate all molecules of the sample located in a volume of height equal to that of the cuvette and of cross-sectional area equal to that of the incident beam. On considering relaxation processes, one can make the estimate $N_{\mathrm{eff}} = N(l_{\mathrm{rel}}/l)$ for the number of molecules participating in the scattering, where l is the sample length, l_{rel} is the characteristic relaxation length, and N is the number of molecules in the active layer of the sample. An estimation of $\sin^2\varphi_{\max}$ is provided by the relative fraction of molecules excited by scattering, multiplied by the ratio of the characteristic relaxation time to the duration of the pulse. This quantity is usually small. Thus, under the conditions of the experiment described in Ref. 17, the relative fraction of excited molecules was $\sim 10^{-6}$. For $\varphi^2_{\max}$ from here one obtains the estimate $\varphi_{\max} \sim 10^{-9}$ to 10^{-10}. However from (31) and (32) it follows that cooperative effects play an important role at values of φ^2 exceeding the magnitude $N^{-1}_{\mathrm{eff}} \sim 10^{-16}$. From here it is evident that it is the off-diagonal structure of the density matrix which is essential, not the variation of level populations.

From the scattering probabilities obtained in Sec. VI follow the peculiarities of the complete integral response, which can be compared with experimental data. The transition from local probabilities to the output intensity of scattered light is achieved in the usual manner (see, for example, Ref. 16). The intensity of scattering on outlet of a cell is equal to $\mathcal{I} = \hbar\omega_S c n_S^{\mathrm{out}} S/\bar{n}$ (S is the cross section of a channel, along which the radiation propagates, n_S^{out} is the number of scattered photons at the end of cuvette, $\bar{n}$ is the index of refraction for the scattered light). Considering the increments of the number of photons n and n_S of exciting and scattered radiation with the passage of a pulse through a layer of thickness dx, one obtains

$$\frac{dn}{dx} = -k_1 n n_S - k_2 n, \quad \frac{dn_S}{dx} = k_1 n n_S + k_2 n, \tag{33}$$

where the scattering probability is written in the form $w_S = k_1 n n_S + k_2 n$. Expressions for k_1 and k_2 in the case of the medium in equilibrium ($\varphi = 0$) are proportional to the number of particles N_0 in a unit volume and are given in Ref. 16. Taking into consideration cooperative effects, k_1 and k_2 have a quadratic dependence on N_0:

$$k_i = \alpha_i N_0 + \beta_i N_0^2 . \tag{34}$$

The solution of system (33) under the simplifying assumption that β_i is independent of coordinates [$\beta_i(\vec{r})$ is a slowly varying function] has the form

$$n_S^{\mathrm{out}} = \frac{k_2}{k_1}\left(e^{k_1 l (n_0 + k_2/k_1)} - 1\right) \times \left(1 + \frac{k_2}{k_1 n_0} e^{k_1 l (n_0 + k_2/k_1)}\right)^{-1}, \tag{35}$$

where n_0 is the number of photons with a frequency ω entering the cell. Formula (35) defines (outside the saturation region, where $n_S^{\mathrm{out}} \simeq n_0$) a sharper dependence of output intensity upon N_0 compared with the case when *no* cooperative effects are present and transition probabilities are proportional to N_0 ($\beta_i = 0$). This fact implies a sharp increase of scattering intensity if cooperative effects are present. Thus, from expressions for scattered probabilities follow the peculiarities of the complete integral response of the medium.

Let us consider, for example, the angular distribution of Stokes emission. Formula (31) for $w_S(\vec{k}, \vec{k}_S)$ contains the δ symbol, describing forward emission. When the cooperative term in (31) dominates, which happens with transition to integral responses of the medium, the intensity of forward scattering also dominates, because it has a sharper dependence upon N_0, than that of intensities in other directions. (The reason for this is that quadratic terms in the expressions for scattering probabilities are absent. Below, when considering other features of SRS, the transition described here from scattering probabilities to output intensities is implied.) In accordance with the estimate for $\varphi^2_{\max}$ given above, formula (31) confirms the dominance of forward Stokes scattering.[16]

From (31) it can also be seen that with increase in the thickness of the active layer (length of the cuvette) the asymmetry of the scattering indicatrix must grow, since increasing the role of stimulated processes brings about larger values of $\varphi^2_{\max}$. This is in agreement also with experimental data.[19]

Let us consider the angular distribution of the first anti-Stokes component. The mechanism of Fig. 2(b) by virtue of (32) gives rise to dominance of forward emission. Anti-Stokes axial scattering has been observed, in Refs. 20–24. Axial emission is realized either with sufficiently low input beam power, or with a thin active layer, when perturbation of the medium is connected mainly with the passage of the exciting pulse. Axial anti-Stokes emission (without Townes rings) is actually observed in experiments with cuvettes of short length and small input power.[23,24] With increase of incident radiation intensity (or of cuvette length), when considering anti-Stokes scattering, one should take into account also perturbation of the medium by Stokes radiation from the reverse process of that shown in Fig. 2(a). When calculating the density matrix, one should realize that the operator T in (28) is a product of two rotation operators in energy space. The first operator corresponds to the passage of the exciting pulse and the second one to the passage of a plane wave with frequency ω_S (wave vector $\vec{k}_S$). A calculation shows that the probability of the process of Fig. 2(b) for a medium, described by such a density matrix, contains a coherent term of order N^2_{eff} with an angular dependence leading (with small angles between vectors $\vec{k}$ and $\vec{k}_S$) to phase synchronism $\vec{k} + \vec{k}_S = 2\vec{k}$. Thus with increase of the intensity of the incident radiation (or cuvette length), anti-Stokes emission appears on a conical surface, in accordance with the

Townes condition, the intensity of which increases and becomes greater than that of forward emission. The transition from axial to conical emission also was observed, in Ref. 23.

Let us consider the energy dependences of SRS. Formula (35), with $\beta_i = 0$, describes exponential growth of intensity when n_0 is small. Then, the intensity approaches the saturation level. However, experimental curves reveal a dependence on n_0 significantly stronger than exponential.[17,18] This sharp increase is most probably a consequence of the cooperation terms in the expressions for k_1 and k_2 in formula (34). Under sufficiently large n_0, cooperative scattering plays a dominant role; and hence, formula (35) leads to the correct qualitative description of the dependence in question.

It was shown in numerous experiments that only few frequencies out of the complete spectrum of ordinary RS of a given substance are exhibited in SRS spectrum. This is connected with the fact that higher Stokes and anti-Stokes components of scattering occur by means of step mechanisms.[16] These mechanisms lead to the appearance of the following frequencies in the SRS spectrum:

$$\omega_S^{(n)} = \omega - n\omega_{12}, \quad \omega_{a-S}^{(n)} = \omega + n\omega_{12}, \quad n = 1, 2, \ldots .$$

At the same time, components are not formed with frequencies

$$\tilde{\omega}_S^{(n-1)} = \omega - \omega_{1n}, \quad \tilde{\omega}_{a-S}^{(n-1)} = \omega + \omega_{1n},$$
$$\approx\!\!\!\!\omega_S^{(n-1)} = \omega_S^{(1)} - \omega_{1n}, \quad \approx\!\!\!\!\omega_{a-S}^{(n-1)} = \omega_{a-S}^{(1)} + \omega_{1n},$$
$$n = 3, 4, \ldots, \tag{36}$$

corresponding to transition from the ground level to the second, third, and other excited levels. This behavior of higher SRS components has been confirmed in experiments with unharmonic molecules. Although, as a rule, individual molecule transition probabilities to the first vibrational level (transitions A) are larger than those to higher levels (transitions B), this can not serve as a reason for the absence (at least, within the sensitivity of the detector) of component (36) from the SRS spectra. However, because the probabilities of transitions A are usually larger than those transition B, the excitation of the medium is expressed mathematically by the comparatively large magnitude of the off-diagonal density matrix elements connecting the ground and first excited states. As a result of this density-matrix structure, cooperative effects between the ground and first excited levels are enhanced. During the passage of the pulse these effects become stronger. From here it follows that the probabilities of processes connecting the pair of levels mentioned above are much greater than probabilities of other processes. Just because of this, the step mechanism for the appearance of the new SRS components is significantly intensified.

We shall note in conclusion that an experiment with a simultaneous exciting SRS pulse and resonance pulse of frequency ω would be of interest. The density matrix of the medium, after a resonance pulse has passed, has the form, analogous to (29),

$$\rho(t) = e^{-iH_1 t} \prod_j A_j e^{iH_1 t},$$
$$A_j = (\sigma_1 \cos^2 \tfrac{1}{2}\theta + \sigma_2 \sin^2 \tfrac{1}{2}\theta) P_1^{(j)} + (\sigma_1 \sin^2 \tfrac{1}{2}\theta + \sigma_2 \cos^2 \tfrac{1}{2}\theta) P_2^{(j)} + \tfrac{1}{2} i \sin\theta (\sigma_1 - \sigma_2) [\alpha_j I_+^{(j)} e^{i\vec{k}_{12}\cdot\vec{r}_j} - \alpha_j^* I_-^{(j)} e^{-i\vec{k}_{12}\cdot\vec{r}_j}],$$

where $\sin^2 \frac{1}{2}\theta$ is the probability of excitation of a molecule by the resonance pulse with wave vector $\vec{k}_{12}$.

Substituting (37) in (25), one will get for Stokes scattering a formula, analogous to (31), where $\delta_{\vec{k}_S, (\omega_S/\omega)\vec{k}}$ is substituted for $\delta_{\vec{k}_S, \vec{k}-\vec{k}_{12}}$. From here it follows that the resonance pulse can significantly lower the threshold and increase the energy of all SRS spectral components. If vectors $\vec{k}$ and $\vec{k}_{12}$ are not collinear, the angular distributions of scattered light change; for instance, the first Stokes component will have a maximum in the direction $\vec{k}_S = \vec{k} - \vec{k}_{12}$. We note that a resonance pulse with a frequency corresponding to some other molecular transition is used, these off-diagonal elements of the density matrix related to the resonating levels will be enhanced. As a result, one might observe a change in SRS spectrum, stemming from the intensification of step mechanism between the new resonance level. The influence of a resonance pulse on scattering intensity has apparently been mentioned also in Ref. 25.

We wish to call attention to the qualitative character of the treatment of coherent SRS effects presented here. We feel that more quantitative treatments will have to consider the dynamics of a pulse passing through a medium.

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