

# Nonlinear processes in a system of resonantly interacting atoms

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A nonlinear third-order process is considered which is induced by two external monochromatic fields in a system of two unlike atoms, containing energy levels in resonance with the difference frequency of the external fields. It is shown that, at small distances between the atoms, the effective resonant (quadrupole-dipole) interaction may provide an increase of the probability for the process under consideration, the conversion of the frequency to a value corresponding to allowed transitions at all three frequencies. The possibilities of composite optical centers, containing resonantly interacting atoms, are discussed.

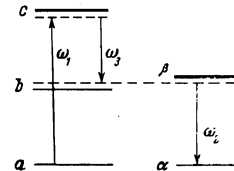
## 1. INTRODUCTION

Emission processes in a system of atoms with coincident or close energy levels have been investigated by many authors.<sup>[1–8]</sup> It was shown that the strong resonant interaction at small distances between the atoms leads to an intensive exchange of excitations between them, as a consequence of which coherent effects arise which substantially modify the characteristics of the spontaneous emission by a system of identical atoms.<sup>[1–5]</sup> Systems of unlike two-level atoms with noncoincident energy levels and different spontaneous decay probabilities were considered in<sup>[6,7]</sup>. It was shown that, just as in the case of identical atoms, the resonant interaction of unlike atoms leads to the collective nature of the emission, altering the probability for decay of the system from the excited state, and leading to a change of the emission spectra associated with spontaneous decay and resonant fluorescence. However, metastable states are not formed in a system of unlike atoms, and the spontaneous decay takes place at the allowed transition rate, provided that for one of the atoms in the system there is no prohibition against the transition from the excited state under consideration to the ground state.

The nonlinear process of downward conversion of a frequency,  $\omega_1 \rightarrow \omega_2 + \omega_3$ , at an optical center containing two resonantly interacting atoms, due to the presence in them of levels with a resonance frequency close to the difference in frequencies  $\omega_1$  and  $\omega_3$  of the external fields, is investigated in the present article. The determination of the steady-state response of a system to periodic external fields is a routine problem in nonlinear optics (see, for example,<sup>[9,10]</sup>). The characteristic feature of the problem being solved is the necessity to take the exchange of excitations between the resonantly interacting atoms into account. In contrast, for example, to magnetic resonance processes where relaxation occurs with the exchange of excitations between identical systems (compare with<sup>[11]</sup>), here it is necessary to take the exchange of excitations between unlike emitters into consideration. The results of the previous work<sup>[6,7]</sup> are utilized in order to solve the problem.

## 2. THE NONLINEAR PROCESS IN RESONANTLY INTERACTING ATOMS

Let us consider a system of two unlike atoms (emitters) placed in stationary, harmonic electromagnetic fields with frequencies  $\omega_1$  and  $\omega_3$  ( $\omega_1 > \omega_3$ ). We shall assume that, in addition to its ground level (a) one of the atoms contains energy levels (b and c) with



resonant transition frequencies  $\omega_0b$  and  $\omega_0c$ , which are close to the external field's frequency  $\omega_1$  and to the difference frequency  $\omega_2 = \omega_1 - \omega_3$ , respectively. The other atom is assumed to be a two-level atom with a resonant transition frequency  $\omega_0\beta$  close to the frequency  $\omega_2$  (see the Figure).

Let us investigate the steady-state response of the system of atoms under consideration to the harmonic external fields  $\omega_1$  and  $\omega_3$  by allowing for resonant dipole-dipole or dipole-quadrupole interactions between the atoms at a frequency  $\sim \omega_2$ , which is possible at small distances between the atoms (compare with<sup>[6,7]</sup>). We shall assume that the following simplifications of the problem are justified. In analogy to the procedure utilized in<sup>[6,7]</sup>, the recoil energy of the nuclei and the motion of the nuclei associated with the emission process are not taken into consideration (the atoms are fixed). We shall assume the distance  $R$  between the atoms to be fixed and comparable to the wavelength  $c/\omega_2$ , so that overlapping of the atomic wave functions is not present. The external fields are rather weak (the effect of level saturation is absent). For simplicity the levels are assumed to be nondegenerate. It is assumed that only the discussed levels (b, c, and  $\beta$ ) fall in the resonant region with regard to the frequencies of the external fields; therefore, the other levels of the system are not considered. The system has six possible states, which correspond to the three states of the three-level atom (atom A) and the two states of the two-level atom (atom B). Transitions between these states may occur due to the presence of the external fields ( $\omega_1, \omega_3$ ), the resonant interaction between the atoms, and due to spontaneous relaxation transitions.

We shall use time-dependent perturbation theory in order to solve the problem, describing the system with the aid of the density matrix. The equation of motion for the density matrix  $\rho_{ijk}$  of the system under consideration can be represented in the form

$$i\hbar\dot{\rho} = [H_0, \rho] + [H_{\text{coh}}, \rho] + [H_{\text{Ab}}, \rho] + i\hbar(\partial\rho/\partial t)_{\text{ran}}, \quad (1)$$

where  $H_0$  is the Hamiltonian determining the unperturbed energy levels of the system;  $H_{\text{coh}}$  is the Hamil-

tonian describing the interaction of the system with the monochromatic fields  $\omega_1, \omega_3$ ;  $H_{AB}$  is the Hamiltonian of the resonant interaction of the atoms with the exchange of excitations;  $(\partial\rho/\partial t)_{\text{ran}}$  is the rate of change of the density matrix due to relaxation processes, determined by the Hamiltonian which describes the interaction of the system with random (electromagnetic and phonon) fields;  $i(k)$  are subscripts indicating a specific state of the system, and in the general case this includes a specification of the energy levels of atom A (a, b, c) and atom B ( $\alpha, \beta$ ).

Taking account of only approximately-resonant terms of the interaction by nonvanishing matrix elements of the Hamiltonian of the external fields will involve only the matrix elements  $H_{ac} \exp(i\omega_1 t)$  and  $H_{bc} \exp(i\omega_3 t)$  (correspondingly  $H_{ca} \exp(i\omega_1 t)$  and  $H_{cb} \exp(-i\omega_3 t)$ ), which cause transitions in atom A. The matrix element of the direct electromagnetic interaction  $H_{AB}$  of the atoms causes transitions between the states  $b\alpha$  and  $a\beta$ . (The specific form of the matrix element  $U_{ik}$  of the dipole-dipole and dipole-quadrupole interactions between unlike atoms, with retardation taken into account, is given in<sup>[6]</sup>).

As is usually done (see, for example,<sup>[9,10]</sup>) one can phenomenologically describe the effect of the random fields, which give rise to relaxation processes in the steady-state regime, with the aid of the attenuation parameters  $\gamma_{ik}$  ("longitudinal" relaxation) and  $\Gamma_{ik}$  ("transverse" relaxation):

$$\begin{aligned} \left(\frac{\partial \rho_{ik}}{\partial t}\right) &= \sum_n \gamma_{in} \rho_{nn} - \sum_n \gamma_{ni} \rho_{ik}; \\ \left(\frac{\partial \rho_{ik}}{\partial t}\right)_{\text{ran}} &= -\Gamma_{ik} \rho_{ik}. \end{aligned} \quad (2)$$

There are no random pumping fields in the problem under consideration; therefore, the  $\gamma_{ik}$  are determined by the probabilities for radiative decays of the atoms (from the levels b, c, and  $\beta$ ). In this connection the decay of atom A from level c does not depend on the state of atom B; therefore,  $\gamma_{ac}$  and  $\gamma_{bc}$  are equal to the corresponding radiative widths of an isolated A atom. As for the levels b and  $\beta$ , it is generally impossible to regard the decays of these states as independent. The resonant interaction leads to an intermixing of the states  $b\alpha$  and  $a\beta$  and to collective, spontaneous decay. However, it is not necessary to know the time behavior of the system's decay law and the spontaneous emission spectrum, which may be substantially altered due to collective effects (see<sup>[2-7]</sup>), in order to determine the steady-state response of the system. It is sufficient to know the total probability for radiative decay of the system. This probability depends on interference between the radiation emitted by the atoms in the system.<sup>[6,7]</sup> But the interference effect disappears at large distances between the resonantly interacting atoms (large in comparison with the wavelength of the radiation) and at small distances for the case of transitions of different multipole character.<sup>[6]</sup> Assuming that these conditions are satisfied, in the first approximation we shall neglect this interference effect, having assigned the radiative widths  $\gamma_{\alpha\beta}$  and  $\gamma_{ab}$  of the levels  $\beta$  and b of isolated atoms to the states  $a\beta$  and  $b\alpha$ .

altogether the system (1) contains 36 equations. One can determine the nonlinear polarization of the system, induced by the external fields  $\omega_1$  and  $\omega_3$ , from the equations:

$$\begin{aligned} -\Delta_{a\beta} \rho_{ca\alpha\beta}^{(-\omega_1)} + H_{ac} e^{i\omega_1 t} \rho_{ca\alpha\beta}^{(\omega_1)} - \rho_{ca\alpha\beta}^{(-2\omega_1+\omega_3)} H_{ca} e^{-i\omega_1 t} - U_{ba\alpha\beta} \rho_{ba\beta\alpha}^{(-\omega_1)} &= 0, \\ -\Delta_{ab} \rho_{ba\beta\alpha}^{(-\omega_1)} + H_{ac} e^{i\omega_1 t} \rho_{ca\alpha\beta}^{(\omega_1)} - \rho_{ca\alpha\beta}^{(-\omega_1)} H_{cb} e^{-i\omega_1 t} - \rho_{ca\alpha\beta}^{(-\omega_1)} U_{ab\beta\alpha} &= 0, \\ -\Delta_{ac} \rho_{ca\alpha\beta}^{(-\omega_1)} - \rho_{ba\beta\alpha}^{(-\omega_1)} H_{bc} e^{i\omega_1 t} + H_{ac} e^{i\omega_1 t} \rho_{ca\alpha\beta}^{(\omega_1)} - \rho_{ca\alpha\beta}^{(-\omega_1)} H_{ca} e^{-i\omega_1 t} &= 0, \end{aligned} \quad (3)$$

where  $\rho_{ik}^{(\omega)}$  is the harmonic component of the matrix element of the scattering matrix at the frequency  $\omega$  ( $\rho_{ik} = \rho_{ki}^*$ );

$$\begin{aligned} \Delta_{a\beta} &= -\omega_2 - \omega_{a\beta} + i\Gamma_{a\beta}, & \Delta_{ab} &= -\omega_2 - \omega_{ab} + i\Gamma_{ab}, \\ \Delta_{ac} &= -\omega_1 - \omega_{ac} + i\Gamma_{ac}, & \Delta_{ik} &= -\Delta_{ki}^*, \end{aligned}$$

and  $\omega_{ik} = (E_i - E_k)/\hbar$  is the resonant frequency of the levels  $E_i$  and  $E_k$ .

Simple calculations lead to the following results, which are valid to the first approximation in the external fields  $\omega_1$  and  $\omega_3$ :

$$\begin{aligned} \rho_{ca\alpha\beta} &= -H_{ac} e^{i\omega_1 t} / \Delta_{ac}, \\ \rho_{ba\beta\alpha} &= \frac{\Delta_{a\beta} H_{ac} H_{cb} e^{i(\omega_1 - \omega_3)t}}{\Delta_{ac} (\Delta_{ab} \Delta_{a\beta} - |U_{ab\beta\alpha}|^2)}, \\ \rho_{a\alpha\beta\beta} &= -\frac{U_{ba\alpha\beta} H_{ac} H_{cb} e^{i(\omega_1 - \omega_3)t}}{\Delta_{ac} (\Delta_{ab} \Delta_{a\beta} - |U_{ab\beta\alpha}|^2)}. \end{aligned} \quad (4)$$

In the derivation of formulas (4) there were no restrictions on the magnitude of the resonant interaction. Therefore, the results are also valid for  $|U_{a\beta b\alpha}| \approx |\Delta_{ik}|$ . Note the structure of the denominator in the expressions for  $\rho_{a\alpha\beta\alpha}$  and  $\rho_{a\alpha\alpha\beta}$ , which is similar to the corresponding expressions for the density matrix in the presence of a strong external field, which equalizes the populations of the states  $b\alpha$  and  $a\beta$  (compare with<sup>[9]</sup>).

The multipole moment of the system at the frequency  $\omega_2$  (the nonlinear polarization), induced by the external fields  $\omega_1$  and  $\omega_3$ , is determined in the first approximation by the obtained matrix elements (4) and the corresponding multipole moments of the transitions from the levels b and  $\beta$  to the ground states of the atoms. In the approximation under consideration (see above), these same moments  $d_{ik}$  determine the radiative widths of the levels,  $\gamma_{ik} \sim |d_{ik}|^2$ .

In practice it is difficult to obtain a completely isolated system of two atoms. In real systems several atoms (emitters) can immediately interact in a resonant manner. In order to understand the effect of surrounding atoms on the investigated two-atom system, let us consider a system consisting of a single three-level atom (with levels a, b, and c) and several two-level atoms (with levels  $\alpha_j$  and  $\beta_j$ ), which are distributed around the first atom at distances  $R_j$  comparable with the wavelength  $c/\omega_2$ . We shall assume that those conditions and restrictions, under which the two-atom system was treated above, are satisfied. We shall characterize the resonant interaction between the three-level atom and the two-level atoms by the matrix elements  $U_{a\beta j b \alpha_j}$ , and the resonant interaction between the two-level atoms j and l by the matrix elements  $W_{\alpha_l \beta_l \beta_j \alpha_j}$  (only the changing subscripts of the states associated with the exchange of excitations are indicated).

The system of equations for the density matrix of a system of several (N + 1) resonantly interacting atoms, permitting us to determine the solution to the first approximation in the external fields  $\omega_1$  and  $\omega_3$  under the initial conditions  $\rho_{a\alpha_j a \alpha_j} = 1$  (for  $j = 1, 2, \dots, N$ ), takes the form

$$\Delta_{ca} \rho_{ca j \alpha \alpha_j} - H_{ca} e^{-i\omega_1 t} \rho_{a \alpha_j a \alpha_j} = 0,$$

$$\Delta_{ab}\rho_{\alpha\alpha, \beta\alpha_j} + H_{cb}e^{-i\omega_1 t}\rho_{\alpha\alpha, \alpha_j} + \sum_{i=1}^N \rho_{\alpha\alpha, \alpha\beta_i} U_{\alpha\beta, \beta\alpha_i} = 0, \quad (5)$$

$$\Delta_{\alpha, \beta_j}\rho_{\alpha\alpha, \alpha\beta_j} - \rho_{\alpha\alpha, \beta\alpha_j} U_{\beta\alpha, \alpha\beta_j} - \sum_{i \neq j}^N \rho_{\alpha\alpha, \alpha\beta_i} W_{\alpha\beta, \beta_i, \alpha_i} = 0.$$

The solution of the system of linear equations (5) appears to be cumbersome in the general case. Let us attempt to understand the main features of the influence of the neighboring two-level atoms for the example of a three-atom system, for which we can explicitly write down the elements of the density matrix:

$$\begin{aligned} \rho_{ac} &= -H_{ac}e^{i\omega_1 t}/\Delta_{uc}, \\ \rho_{\alpha\alpha, \beta\alpha_i} &= \rho_{ac}H_{cb}e^{-i\omega_1 t}\Delta_{ab}\left\{U_{\beta\alpha, \alpha\beta_i}\left(\Delta_{\alpha\beta_i} - \frac{|U_{\beta\alpha, \alpha\beta_i}|^2}{\Delta_{ab}}\right) - U_{\beta\alpha, \alpha\beta_i}\left(W_{\alpha, \beta_i, \beta_i, \alpha_i} - \frac{U_{\beta\alpha, \alpha\beta_i} - U_{\alpha\beta, \beta\alpha_i}}{\Delta_{ab}}\right)\right\} \{(\Delta_{ab}\Delta_{\alpha\beta_i} - |U_{\beta\alpha, \alpha\beta_i}|^2) \times (\Delta_{ab}\Delta_{\alpha\beta_i} - |U_{\beta\alpha, \alpha\beta_i}|^2) - (\Delta_{ab}W_{\alpha\beta, \beta_i, \alpha_i} - U_{\beta\alpha, \alpha\beta_i}U_{\alpha\beta, \beta\alpha_i})(\Delta_{ab}W_{\alpha, \beta_i, \beta_i, \alpha_i} - U_{\beta\alpha, \alpha\beta_i}U_{\alpha\beta, \beta\alpha_i})\}^{-1}. \end{aligned} \quad (6)$$

The expression for  $\rho_{\alpha\alpha, \alpha_2\beta_2}$  is obtained from the expression for  $\rho_{\alpha\alpha, \alpha_1\beta_1}$  by making the following substitution of the indices:  $\alpha_1\beta_1 \rightarrow \alpha_2\beta_2$  and  $\alpha_2\beta_2 \rightarrow \alpha_1\beta_1$ .

The dependence of the cross section for the process involving the absorption of a quantum  $\omega_1$  and the emission of  $\omega_3$  on the frequency difference  $\omega_1 - \omega_3$  gives the shape of the absorption line for level b correct to within interference effects. In actual fact this shape should correspond to the spontaneous emission spectrum of a two-atom system for initial excitation of the single A atom into level b. The absorption line will have a different shape associated with ordinary resonance fluorescence by these levels (b and  $\beta$ ). In this case the absorption cross section will correspond to the spectrum for spontaneous emission from an initial state involving the excitation of both atoms (compare with<sup>[7]</sup>).

### 3. NONLINEAR POLARIZABILITY OF COLLECTIVE CENTERS

From what has been said above it follows that, in the presence of external fields complexes of specifically selected two-level and three-level atoms may behave like collective optical centers owing to the resonant interaction, guaranteeing the exchange of excitations between different atoms in the system. Our goal is a determination of the feasibility of increasing the probability of the nonlinear frequency-conversion process  $\omega_1 \rightarrow \omega_2 + \omega_3$  in the fields  $\omega_1$  and  $\omega_3$  upon using the system of two-level and three-level atoms considered above as active centers. We shall make the comparison with the probability for the same process in active centers, containing "isolated" three-level atoms (without any resonant interaction with the neighboring atoms). In order to be definite, we shall assume that the transitions ac and bc are allowed (in the electric dipole approximation) in the three-level atom, but the transition ba is forbidden, so that spontaneous decay from level b occurs due to the electric quadrupole (magnetic dipole) moment, determining the radiative levelwidth  $\gamma_b$ . In the two-level atoms, which are resonantly interacting with the active three-level atom of the composite optical center, we shall consider the allowed transitions from the levels  $\beta_j$  to the ground level  $\alpha_j$  with the emission of a quantum  $\omega_2$ . We denote the corresponding radiative widths of the levels by  $\gamma_{\beta_j}$ .

Under the influence of the external fields  $\omega_1$  and  $\omega_3$  on the system of emitters, comprising the composite active centers under consideration, the sources of the field  $\omega_2$  are the induced multipole moments which are proportional to the corresponding Fourier components of the matrix elements of the density matrix (see Eqs. (4) and (6)) and to the multipole moments of the transitions in the atoms with a resonant frequency  $\sim \omega_2$ . The latter are in turn determined by the radiative widths of the levels b and  $\beta_j$ . Thus, the expressions  $\gamma_{\beta_j}^{1/2}\rho_{\alpha\alpha, \beta\alpha_j}$  and  $\gamma_b^{1/2}\rho_{ab}$  are subject to comparison.

Let us start with an analysis of a two-atom collective center. Using the solution (4), we find the ratio of the emission probabilities for the two-level atom (PB) and the three-level atom (PA), respectively, of the system in the frequency-conversion process  $\omega_1 \rightarrow \omega_2 + \omega_3$ :

$$\frac{P_B}{P_A} = \frac{\gamma_B}{\gamma_b} \frac{|U_{ba}|^2}{|\Delta_{\alpha\beta}|^2}.$$

Comparison with the probability  $P_3$  for the same reaction in an isolated three-level atom leads to the result

$$\frac{P_B}{P_3} = \frac{\gamma_B}{\gamma_b} \frac{|U_{ba}|^2 |\Delta_{ab}|^2}{|\Delta_{\alpha\beta}\Delta_{ab} - |U_{ab}|^2|^2}.$$

Thus, in order to increase the yield of the reaction  $\omega_1 \rightarrow \omega_2 + \omega_3$  by using a system of resonantly interacting atoms as a collective optical center, it is necessary to fulfil the conditions

$$|U_{ba}| > (\gamma_b/\gamma_B)^{1/2} |\Delta_{\alpha\beta}| \quad (7)$$

or

$$|U_{ba}| > \left(\frac{\gamma_b}{\gamma_B}\right)^{1/2} \frac{||U_{ba}|^2 - \Delta_{ab}\Delta_{\alpha\beta}|}{|\Delta_{\alpha\beta}|}. \quad (7')$$

Let us carry out further analysis for more definite conditions, having in mind impurity optical centers in a solid, containing groups of resonantly interacting atoms of the type considered above. The fact that the actual levels are electronic-vibrational and correspond to relatively broad bands has a substantial effect on the effectiveness of the resonant interaction under consideration, but does not eliminate it completely. The interaction involving the exchange of excitations between the atoms depends on the effective values  $\Gamma_{ik}$  of the widths, which are in turn determined by the phonon widths of the active center's sub-levels. In the case under consideration (for an impurity center) one can assume that the widths  $\Gamma_{ik}$  are primarily determined by their adiabatic part, which is related to the variation of the resonance frequencies (levels) of the system as a result of the interaction with the phonon field. The width  $\Gamma$  of the entire electronic-vibrational band can be regarded as an upper bound on the value of  $\Gamma_{ik}$ . The requirements of coincidence of the resonant frequencies of the interacting levels within the limits of  $\Gamma$  are theoretically possible. In this case the minimum value of  $|\Delta_{ik}|$  turns out to be equal (in order of magnitude) to the width  $\Gamma$ . Taking into consideration that the resonant quadrupole-dipole interaction is small,  $|U_{Qd}| < \Gamma$  (see below), from (7) and (7') we obtain the condition for enhancement of the nonlinear polarizability due to the collective interaction in the form

$$|U_{ba}| > \Gamma(\gamma_b/\gamma_B)^{1/2}. \quad (8)$$

For the quadrupole-dipole interaction of the atoms under consideration,  $|U_{Qd}|(\gamma_{\beta_j}/\gamma_b)^{1/2} \approx |U_{dd}|c/\omega R$ , where  $U_{dd}$  denotes the matrix element of the dipole-dipole interaction between identical (two-level) atoms.

At small distances between the atoms  $|\operatorname{Re} U_{dd}| \gg |\operatorname{Im} U_{dd}|$  (compare with<sup>(6)</sup>); therefore, one can attach the form  $|\operatorname{Re} U_{dd}| > \Gamma\omega R/c$  or  $\gamma_\beta(c/\omega R)^4 > \Gamma$  to condition (8), from which limits for the distances  $R$  between the atoms immediately follow. Having in mind the optical region, in order to make estimates let us assume  $\gamma_\beta \approx 10^8 \text{ sec}^{-1}$  and  $\Gamma \approx 10^{12} \text{ sec}^{-1}$ . As a result we find that distances

$$R \leq 0.1 c/\omega_2, \quad (8')$$

are necessary between the atoms in a center. In the presence of a random (irregular) distribution of the interacting atoms, the necessary distances ( $\lesssim 10^{-6} \text{ cm}$ ) are achieved at quite realistic concentrations ( $n \gtrsim 10^{19} \text{ cm}^{-3}$ ). The gain in the cross section for the nonlinear process under consideration should grow in inverse proportion to the eighth power of the distance between the atoms of the collective center.<sup>(1)</sup>

As has already been mentioned, in real systems several atoms may immediately turn out to be in the region of the resonant interaction. An analysis of the behavior of such systems generally requires the inclusion of the solutions of systems of the type (5). However, one can utilize the solution (6) for estimates. One can easily show that, in view of the fulfillment of the inequalities  $|\operatorname{Im} U_{ab}| < \Gamma$  and  $|\operatorname{Im} W_{ik}| < \Gamma$  it is not possible to obtain an additional increase in the nonlinear susceptibility of a collective center for several atoms in comparison with the two-atom system. The effect of several surrounding atoms is obtained (to order of magnitude) in the same way as for a single nearby two-level atom.<sup>(2)</sup> Thus, the estimates given above can be regarded as valid in the general case for a many-atom center.

Up to now the purely nonlinear processes  $\omega_1 \rightarrow \omega_2 + \omega_3$  without the emission and absorption of phonons ( $\omega_1 = \omega_2 + \omega_3$ ) have been considered. In addition to these, processes involving a change of the vibrational state of the active center and the surrounding medium are possible. The process involving a single transfer of excitation energy from the three-level atom to a two-level atom, accompanied by the emission of phonons, may be an example of such a Raman process in the collective center under consideration in the presence of the fields  $\omega_1$  and  $\omega_3$ , that is, a process of the sensitized-fluorescence type having the special feature that the excitation of the atom-sensitizer is imparted in a nonlinear process (involving the absorption of  $\omega_1$  and the emission of  $\omega_3$ ). One can raise the question of the relative probability of the purely nonlinear process. In particular, on the basis of the Condon principle one can anticipate an increase in the probability for the nonphonon process associated with minimal Stokes' shifts of the resonantly interacting levels ( $\beta$  and  $\beta$ ), at low temperatures, at the exact resonance with regard to the minima of the potential curves, and so forth. For a number of reasons the effective widths of the levels may turn out to be smaller than the width  $\Gamma$  of the entire

electronic-vibrational band. All of these questions require more detailed consideration and investigation. Our goal was to call attention to the theoretical possibility of obtaining composite (compound) impurity centers and an increase of the nonlinear polarizability.

The estimates cited above indicate that, under certain conditions collective impurity centers may possess a substantially larger nonlinear polarizability (for third-order processes) than nonlinear media with inversion symmetry. In the limiting case such a method in principle enables us to obtain nonlinear media of solid solution type with a maximum nonlinear polarizability, corresponding to an allowed transition at all three frequencies.

<sup>1</sup>At distances comparable with atomic dimensions, the two-atom system should behave like a molecule with three levels, with allowed transitions between these levels in the dipole approximation (the system does not possess inversion symmetry). For example, for  $R = 3 \times 10^{-8} \text{ cm}$ , a dipole moment of the atomic transitions  $d = 10^{-18}$  in CGS units and  $\Gamma = 10^{13}$  to  $10^{14} \text{ sec}^{-1}$ , the nonlinear susceptibility tensor of such a quasimolecule may contain terms of the order of  $10^{-28}$  to  $10^{-30} \text{ cm}^3/\text{erg}^{1/2}$ , which is comparable to the maximum nonlinear susceptibility of molecules (compare with [9,12]).

<sup>2</sup>The presence of many two-level atoms around an active three-level atom turns out to be favorable for another reason. These atoms can have several different values for their resonant frequencies (inhomogeneous broadening due to local fields), and therefore the fulfillment of the resonance conditions, which are imposed on the energy levels of the active pair of atoms in the collective center, will be facilitated.

<sup>1</sup>R. H. Dicke, Phys. Rev. 93, 99 (1954).

<sup>2</sup>M. J. Stephen, J. Chem. Phys. 40, 669 (1964).

<sup>3</sup>D. A. Hutchinson and H. F. Hameka, J. Chem. Phys. 41, 2006 (1964).

<sup>4</sup>J. W. Czarnik and P. R. Fontana, J. Chem. Phys. 50, 4071 (1969).

<sup>5</sup>D. D. Hearn and P. R. Fonda, J. Chem. Phys. 51, 1871 (1969).

<sup>6</sup>A. A. Varfolomeev, Zh. Eksp. Teor. Fiz. 59, 1702 (1970) [Sov. Phys.-JETP 32, 926 (1971)].

<sup>7</sup>A. A. Varfolomeev, Zh. Eksp. Teor. Fiz. 62, 111 (1972) [Sov. Phys.-JETP 35, 59 (1972)].

<sup>8</sup>D. F. Smirnov, I. V. Sokolov, and E. D. Trifonov, Zh. Eksp. Teor. Fiz. 63, 2105 (1972) [Sov. Phys.-JETP 36, 1111 (1973)].

<sup>9</sup>N. Bloembergen, Nonlinear Optics, W. A. Benjamin, 1965 (Russ. Transl., Mir, 1966).

<sup>10</sup>V. M. Faïn, Kvantovaya radiofizika, vol. 1, Fonony i nelineĭnye sredy (Quantum Radiophysics, Vol. 1: Phonons and Nonlinear Media), "Sov. radio", 1972.

<sup>11</sup>A. Abragam, The Principles of Nuclear Magnetism, Oxford, Clarendon Press, 1961 (Russ. Transl., IIL, 1965).

<sup>12</sup>R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Letters 14, 681 (1965).

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