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Study of ultra-fast relaxation processes by resonant Rayleigh-type optical mixing. I. Theory

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A comprehensive theory of a new type of three-wave optical mixing ($\omega_3 = 2\omega_1 - \omega_2$) is given for the spectroscopic purpose of determining ultra-short relaxation times (picoseconds or less) associated with excited states of condensed matter. Two incident light frequencies ω_1 and ω_2 are chosen so that they are both resonant with an inhomogeneously broadened optical transition and $|\omega_2 - \omega_1|$ is in the vicinity of inverse relaxation times. The theory is developed for its major application to broad-band electronic transitions. The nonlinear susceptibility $\chi_R^{(3)}$ for this process (named resonant Rayleigh-type mixing) is calculated by a density-matrix formalism with the model of a two-level atomic system incorporating the distribution of resonance frequencies and longitudinal (T_1) and transverse (T_2) relaxation times. The result shows a frequency characteristic depending only on T_1, T_2, and $\omega_2 - \omega_1$ in a broad-band limit, which serves for the determination of T_1 and T_2 in the frequency domain. The analysis is further extended to include the various effects as follows. The calculation of the saturation effect in the lowest order reveals that it modifies the shape of the frequency characteristic of the nonlinear susceptibility but does not affect seriously the determination of relaxation times. The effect of spectral cross relaxation within the inhomogeneous broadening is incorporated by a generalized density-matrix formalism. The resultant $\chi_R^{(3)}$ consists of two terms. The dominant term is the same as before except that T_1 is replaced by a combined relaxation time $T_1' = (T_1^{-1} + T_3^{-1})^{-1}$, where T_3 is the cross-relaxation time. The other term originates from the inverse spectral-diffusion process. The effect of other energy levels located between the two levels under study is analyzed with a simple three-level model. The resultant $\chi_R^{(3)}$ also consists of two terms, the dominant one being the same as that for the two-level model except that T_1^{-1} should be interpreted as total population decay rate of the upper level. For accurate derivation of $\chi_R^{(3)}$ from experiment, we discuss the interference between the resonant and nonresonant susceptibility terms and the light-wave propagation effect. Finally, the close analogy between this type of optical mixing and the photon echo is discussed.

I. INTRODUCTION

The relaxation process associated with excited states of materials is one of the fundamental physical processes determining the dynamical behavior of the light-matter interaction. In condensed matter, relaxation times are generally very short, and often fall far below 1 psec. Their reliable determination is of importance for clarifying photo-physical and chemical processes as well as for the study of quantum-electronic devices, but it has been a very troublesome subject.

There are numerous kinds of relaxation mechanisms depending on the types of materials and excited states. In spite of these varieties they can usually be described in terms of two kinds of phenomenological parameters, the longitudinal relaxation time T_1 and the transverse relaxation time T_2, representing the decay of energy (or population) and phase memory (or polarization) of a material system, respectively.

The development of picosecond laser technology made it possible to determine ultrashort relaxation times directly in the time domain. Recently, the measurements by this technique with a time resolution of 1 psec or less have been reported.[1,2] However, the experiments in this extreme region are feasible only in very limited situations and require a sophisticated technique. For electronic excited states, there have been no reports of time-domain measurement of T_2 in the picosecond range.

The relaxation times can also be determined by means of frequency-domain measurements, because any decay process results in a spectral broadening. However, the spectral widths observable in conventional optical spectra are, in many cases, much larger than the reciprocal relaxation time due to the presence of inhomogeneous broadening. The word "inhomogeneous broadening" used here means, widely, the broadening resulting from all kinds of distribution of atomic transition frequencies caused not only by the variation of environmental microscopic field but also by the multi-energy-level structure of quasicontinuous character. For the study of relaxation, we must overcome the obstacle of this inhomogeneous broadening.

In nonlinear laser spectroscopy there are already various methods developed for this purpose, such as hole burning, the Lamb dip, laser-induced fluorescence narrowing, and Doppler-free two-photon absorption.[3] These are, however, rather suitable to apply to gaseous media which involve much slower relaxation than that in condensed matter. There are a few examples in which the hole-burning[4,5] or the fluorescence-narrowing[6] method are applied to liquid and solid media to determine T_2 in the range of picoseconds or less. These methods are, however, difficult to apply or leave ambiguities in the cases with very fast longitudinal and/or spectral cross relaxations. It is also not easy to determine separately T_1 and T_2 by the existing methods.

In view of these situations, we have proposed[7] and demonstrated experimentally[8] a new nonlinear spectroscopic method which is essentially suitable for the determination of ultrashort relaxation times extending into the range 10^{-14}–10^{-15} sec. The method is based on a new type of three-wave optical mixing[9,10] in which two incident light waves at frequencies ω_1 and ω_2 produce new light waves at $\omega_3 = 2\omega_1 - \omega_2$ and $\omega_4 = 2\omega_2 - \omega_1$ in a material due to third-order nonlinearity.[11] In recent years studies of the dispersion of the nonlinear susceptibility of this process have been performed extensively by many authors[12-23] for spectroscopic purpose under the resonance conditions of Raman-type ($|\omega_1 - \omega_2| \simeq \omega_v$) and/or two-photon-absorption-type ($2\omega_1$ or $2\omega_2 \simeq \omega_e$), where ω_v and ω_e are the vibrational and electronic transition frequencies, respectively. Coherent anti-Stokes Raman scattering[19] (CARS) is synonymous with Raman-type three-wave mixing. Our three-wave mixing is concerned with a different type of resonance condition in which $|\omega_1 - \omega_2|$ is in the vicinity of reciprocal relaxation times and further both ω_1 and ω_2 are resonant with an optical transition within the spectral broadening. Here we shall call this type of doubly resonant process "resonant Rayleigh-type optical mixing." The method is shown to be effective in determining both T_1 and T_2 only from the frequency response of the third-order nonlinear susceptibility, and is applicable to both fluorescent and nonfluorescent transitions and further can be performed on an entirely steady-state basis without requiring partially transient conditions as often used in other methods.

The purpose of the present paper is to give a comprehensive theoretical analysis of this type of mixing incorporating more realistic situations, which have not been considered in the preliminary calculation[7] and must be taken into account for the analysis of experimental results. The experimental method and the results will be described in detail in the succeeding paper (referred to as paper II). The analysis presented here has been made with its application to broad-band electronic transitions of condensed matter borne in mind. The basic concepts and results of the calculations may be applied in certain approximations and, with proper interpretations, to a variety of material transitions such as singlet-singlet transitions of dye molecules, interband transitions of semiconductors, and broad absorption bands of impurity ions in insulators.

Resonant Rayleigh-type mixing is closely related to the optical mixing process occuring automatically within a laser itself in its multimode operation for which some theories have been developed.[24,25] However, the processes in lasers are quite complicated because of the existence of many frequency components, large signal operation, and instabilities. Therefore, the related theories cannot directly be applied to the present situation.

II. BASIC MODEL AND SIMPLIFIED THEORY

To begin we will describe the theory of the nonlinear susceptibility for the resonant Rayleigh-type optical mixing on the basis of the simplest model and with the lowest-order approximation.

When the radiation field is resonant with a material transition, the associated two levels contribute dominantly to the interaction with the field, and therefore the material system can usually be approximated by an effective two-level system. Let us assume that both the two incident radiation fields of frequencies ω_1 and ω_2 are nearly resonant with a two-level atomic system with the ground level a and the excited level b. We further assume inhomogeneous broadening of the system, i.e., the atomic-transition frequency ω_0 varies from atom to atom. We use the word "atom" hereafter as a representative of atoms, molecules, ion, electrons, etc., because the basic concepts and formulas could apply equally well to these with proper interpretations. The nonlinear susceptibility of this system giving rise to a new frequency component at $\omega_3 = 2\omega_1 - \omega_2$ can be obtained in the following way. The atomic nonlinear polarization component at ω_3 is first calculated for a fixed ω_0, and then the result is integrated over ω_0 to give the macroscopic nonlinear polarization.

The basic equation describing the material system under the influences of both the radiation and relaxation is conveniently given by the density matrix formalism in Schrödinger representation as

$$\frac{d\rho}{dt} = -\frac{i}{\hbar}[H_0 + H, \rho] + \left(\frac{\partial\rho}{\partial t}\right)_{\text{rel}}, \tag{1}$$

where H_0 and H are the unperturbed and perturbation Hamiltonians, respectively, and $(\partial\rho/\partial t)_{\text{rel}}$ is the damping term due to relaxation. For the above two-level system in the electric dipole approximation, Eq. (1) can be written in terms of matrix element as[26, 27]

$$\frac{d\rho_D}{dt} = -\frac{2i}{\hbar}(H_{ab}\rho_{ba} - \rho_{ab}H_{ba}) - \frac{1}{T_1}(\rho_D - \rho_D^{(0)}), \quad (2)$$

$$\frac{d\rho_{ba}}{dt} = \frac{d\rho_{ab}^*}{dt} = -\frac{i}{\hbar}H_{ba}\rho_D - \left(\frac{1}{T_2} + i\omega_0\right)\rho_{ba}, \quad (3)$$

$$H_{ba} = H_{ab}^* = -\mu_{ba}[E_1\exp(-i\omega_1 t) + E_2\exp(-i\omega_2 t)] + \text{c.c.}, \quad (4)$$

where $\rho_D = \rho_{aa} - \rho_{bb}$, (0) denotes the equilibrium value, E_1 and E_2 are the electric field amplitudes of the two light waves, μ_{ba} is the electric-dipole matrix element, and T_1 and T_2 are the longitudinal and transverse relaxation times, respectively. The electric field has been treated here as a scalar for simplicity by considering the situation where both fields are linearly polarized in the same direction. In terms of the population decay rates $\gamma(b \to a)$ and $\gamma'(a \to b)$, T_1 is given by $T_1 = (\gamma + \gamma')^{-1}$. For optical transitions γ' and $\rho_{bb}^{(0)}$ can usually be neglected. The absence of μ_{aa} and μ_{bb} has been assumed here. We further assume that $\rho_{aa} + \rho_{bb} = 1$. This means the absence of energy transfer or cross relaxation between atoms having different transition frequencies, and also the absence of population decay to other levels outside the two-level system under consideration.

In the optical region the radiation field should generally be considered as a propagating wave. However, in the calculation of the nonlinear susceptibility, the expression of a simple oscillating field is sufficient, because only the local effect is important. In analyzing a two-level problem, the Bloch-type equation describing the motion of a pseudodipole has widely been used, but it is not convenient in the case involving multiple frequencies of radiation field.

For small perturbation, the steady-state solution of ρ can be expanded in power series of perturbation as

$$\rho = \rho^{(0)} + \rho^{(1)} + \rho^{(2)} + \cdots + \rho^{(n)} + \cdots, \quad (5)$$

where $\rho^{(n)}$ is proportional to the nth power of the electric field intensity of light. The nonlinear terms ($n \geq 2$) contain new frequency components $m\omega_1 \pm n\omega_2 (m, n = 0, 1, 2, \ldots)$ due to the frequency mixing. The Fourier component $\rho^{(n)\delta}$ at the frequency δ can be calculated from the lower-order terms by means of successive approximation with the aid of the recurrence formulas. In the rotating-wave approximation they are given by

$$\rho_{ba}^{(n)\delta} = \frac{[H_{ba}\rho_D^{(n-1)}]_{-\delta}}{i\hbar\{T_2^{-1} + i(\omega_0 - \delta)\}}\exp(-i\delta t), \quad (6)$$

$$\rho_D^{(n)\delta} = \frac{[H_{ab}\rho_{ba}^{(n-1)} - \rho_{ab}^{(n-1)}H_{ba}]_{-\delta}}{2i\hbar(T_1^{-1} - i\delta)}\exp(-i\delta t) + \text{c.c.} \quad (n \geq 2), \quad (7)$$

where $[\ ]_{-\delta}$ means the amplitude of the term proportional to $\exp(-i\delta t)$ within the bracket.

The atomic nonlinear polarization at ω_3 appears first in the third order, and is given by

$$p^{(3)\omega_3} = \mu_{ab}\rho_{ba}^{(3)\omega_3} + \text{c.c.} \quad (8)$$

The matrix element $\rho_{ba}^{(3)\omega_3}$ can be calculated by Eq. (6) from the second-order solution $\rho_D^{(2)\omega_2-\omega_1}$ which has been derived from the first-order solutions $\rho_{ba}^{(1)\omega_1}$ and $\rho_{ba}^{(1)\omega_2}$ through Eq. (7). In this way we have

$$\rho_{ba}^{(3)\omega_3} = \frac{-2i\mu_{ba}|\mu_{ba}|^2\rho_D^{(0)}E_1^2E_2^*}{\hbar^3[T_1^{-1} + i(\omega_2 - \omega_1)]B_3}\left(\frac{1}{B_2^*} + \frac{1}{B_1}\right)\exp(-i\omega_3 t), \quad (9)$$

$$B_j = T_2^{-1} + i(\omega_0 - \omega_j), \quad (j = 1, 2, 3).$$

An additional contribution to $\rho_{ba}^{(3)\omega_3}$ originated from $\rho_D^{(2)2\omega_1}$ has been neglected because of the relation $\rho_D^{(2)2\omega_1} \ll \rho_D^{(2)\omega_2-\omega_1}$. The macroscopic nonlinear polarization is given by taking into account the inhomogeneous broadening as

$$P^{(3)\omega_3} = N\int_0^\infty g(\omega_0)p^{(3)\omega_3}(\omega_0, t)d\omega_0, \quad (10)$$

where N is the density of atoms, and $g(\omega_0)$ is the distribution function satisfying the normalization condition

$$\int_0^\infty g(\omega_0)d\omega_0 = 1. \quad (11)$$

The nonlinear susceptibility $\chi_R^{(3)}$ is then obtained according to the definition

$$P^{(3)\omega_3} = \chi_R^{(3)}E_1^2E_2^*\exp(-i\omega_3 t) + \text{c.c.} \quad (12)$$

If the inhomogeneous width $(\Delta\omega)_i$ is broad enough to satisfy the condition

$$(\Delta\omega)_i \gg T_2^{-1}, T_1^{-1}, |\omega_2 - \omega_1|, \quad (13)$$

the function $g(\omega_0)$ varies slowly compared to $p^{(3)\omega_3}(\omega_0)$, and the integration of Eq. (10) can be performed by extracting $g(\omega_0)$ outside of the integral. The result of integration can further be simplified by neglecting the small terms proportional to the higher powers of $(\omega_1 T_2)^{-1}$ or $|\omega_1 - \omega_2|/\omega_1$ in view of the condition

$$\omega_1, \omega_2 \gg T_2^{-1}, |\omega_2 - \omega_1|. \quad (14)$$

Then the final expression of $\chi_R^{(3)}$ takes a simple form as

$$\chi_R^{(3)} = \frac{iK_3}{(1 + i\omega_d T_1)(1 + i\omega_d T_2)}, \quad (15)$$

where $\omega_d = \omega_2 - \omega_1$ and

$$K_3 = -2\pi\,|\mu_{ba}|^4 N\rho_D^{(0)} g(\omega_1) T_1 T_2 \hbar^{-3}.$$

The real and imaginary parts and the absolute value of $\chi_R^{(3)}$ are given by

$$\chi_r^{(3)} = \frac{K_3(T_1+T_2)\omega_d}{(1+\omega_d^2T_1^2)(1+\omega_d^2T_2^2)}, \tag{16}$$

$$\chi_i^{(3)} = \frac{K_3(1-T_1T_2\omega_d^2)}{(1+\omega_d^2T_1^2)(1+\omega_d^2T_2^2)}, \tag{17}$$

$$|\chi_R^{(3)}| = \frac{|K_3|}{\{(1+\omega_d^2T_1^2)(1+\omega_d^2T_2^2)\}^{1/2}}. \tag{18}$$

Essentially the same result has already been given in our previous note[7] in a slightly different form. Equations (15)–(18) show that the measurement of $\chi_R^{(3)}$ as a function of ω_d gives directly information on both T_1 and T_2 regardless of the magnitude of the inhomogeneous width, because the factor K_3 varies slowly or is nearly constant for the variation of ω_d. Thus, this type of mixing provides a powerful means for determining relaxation times. It is obvious that this method is essentially suitable for the measurement of ultrashort relaxation time. Although T_1 and T_2 contribute to the frequency response of $\chi_R^{(3)}$ in entirely the same form as is seen in the above equations, their origins of appearance are quite different. The factor $(1+i\omega_dT_1)^{-1}$ originates from the modulation of population at the frequency ω_d due to the beating of two incident waves at ω_1 and ω_2, and it appears already in the second-order nonlinearity. On the other hand, the factor $(1+i\omega_dT_2)^{-1}$ does not arise from a simple modulation mechanism, and it appears only at and above the third-order nonlinearity.[28] The appearance of the factor $(1+i\omega_dT_2)^{-1}$ is of importance, because it provides a practical way of determination of T_2, which is extremely difficult or presently impossible in the subpicosecond range by means of coherent transient method.

The output light intensity at ω_3 is proportional to $|\chi_R^{(3)}|^2$. It is found from Fig. 1 that T_1 and T_2 can be determined from the transition regions in the dispersion curve where the slope changes from ω_d^0 to ω_d^{-2} and from ω_d^{-2} to ω_d^{-4}, respectively. When the interference effect between $\chi_R^{(3)}$ and the nonresonant term becomes important, the individual behavor of $\chi_r^{(3)}$ or $\chi_i^{(3)}$ must be considered. This problem will be discussed in Sec. VI. The dispersive behaviors of $\chi_r^{(3)}$ and $\chi_i^{(3)}$ together with $|\chi_R^{(3)}|$ are illustrated in Fig. 2 for $T_1 = T_2$.

In deriving $\chi_R^{(3)}$ from the observed output light intensity at ω_3, the wave-propagation effect should carefully be taken into account as in the case of optical harmonic generation and other types of optical mixing. We discuss this point in Sec. VII.

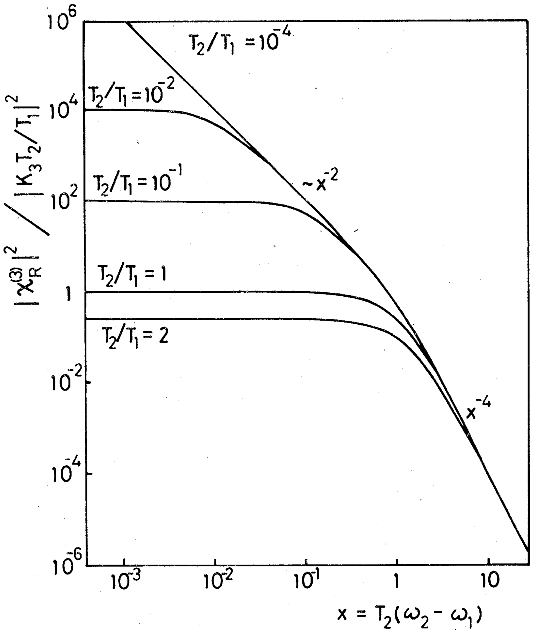

FIG. 1. Frequency characteristics of the square of the normalized nonlinear susceptibility $|\chi_R^{(3)}|^2/|K_3T_2/T_1|^2$ as a function of $\omega_2 - \omega_1$ for several values of T_2/T_1.

When the condition (13) is not satisfied, the situation becomes complicated. The characteristic of $\chi_R^{(3)}$ as a function of ω_d is then influenced by the shape of $g(\omega_0)$, and the deconvolution procedure which separates the effect of $g(\omega_0)$ is generally required to deduce the relaxation times from observed $\chi_R^{(3)}(\omega_d)$. A practical way of this procedure will be described in the succeeding paper (paper II). It will be shown there that the effect of this kind of correction is fairly small, and the expression of Eq. (15) can be used in good approximation for a wide range of inhomogeneous width. The resonant Rayleigh-type mixing serves, therefore,

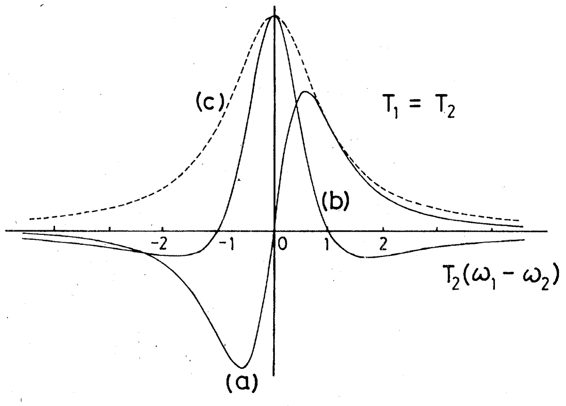

FIG. 2. Dispersion curves of the nonlinear susceptibility for $T_1 = T_2$. (a) Real part $\chi_r^{(3)}$, (b) imaginary part $\chi_i^{(3)}$, and (c) absolute value $|\chi_R^{(3)}|$.

not only to apply to the case of broadly inhomogeneous transitions, but also to decide whether an optical absorption spectrum is broadened homogeneously or inhomogeneously.

III. SATURATION EFFECT

With increasing intensities of incident light waves at ω_1 and ω_2, the saturation effect appears in the resonant Rayleigh-type optical mixing. For the determination of relaxation times, it is necessary to examine how the saturation effect influences the frequency characteristics of this mixing process.

It is difficult to obtain an exact solution for arbitrary strength of incident light fields, but an approximate behavior can be known from the solution expanded in power series of the field intensity as given in Eq. (5). The lowest-order approximation of the saturation effect for the light output at $\omega_3 = 2\omega_1 - \omega_2$ is given by the fifth-order nonlinear polarization $P^{(5)\omega_3}$ to which $\rho_{ba}^{(5)\omega_3}$ contributes. The matrix element $\rho_{ba}^{(5)\omega_3}$ can be obtained by the use of Eq. (6) from the fourth-order solutions $\rho_D^{(4)\omega_d}$ and $\rho_D^{(4)2\omega_d}(\omega_d = \omega_2 - \omega_1)$ which have been derived from the third-order solutions $\rho_{ba}^{(3)\omega_j}(j = 1, 2, 3, 4$ and $\omega_4 = 2\omega_2 - \omega_1)$ through Eq. (7). With this procedure we have

$$\rho_{ba}^{(5)\omega_3} = \frac{i4\mu_{ba}|\mu_{ba}|^4\rho_D^{(0)}E_1^2E_2^*}{\hbar^5[T_1^{-1}+i(\omega_2-\omega_1)]B_3}\left(\frac{1}{B_1}+\frac{1}{B_2^*}\right)\left\{\frac{1}{T_1^{-1}+i(\omega_2-\omega_1)}\left[|E_1|^2\left(\frac{1}{B_3}+\frac{1}{B_2^*}\right)+|E_2|^2\left(\frac{1}{B_1}+\frac{1}{B_4^*}\right)\right]\right.$$
$$\left.+\frac{|E_2|^2}{T_1^{-1}+i2(\omega_2-\omega_1)}\left(\frac{1}{B_3}+\frac{1}{B_4^*}\right)\right\}\exp(-i\omega_3 t), \tag{19}$$

where $B_j = T_2^{-1} + i(\omega_0 - \omega_j)$ $(j = 1, 2, 3, 4)$. In deriving Eq. (19), the small contributions to $\rho_{ba}^{(5)\omega_3}$ originating from other frequency components of $\rho_D^{(4)}$ have been neglected.

The fifth-order macroscopic nonlinear polarization can be obtained by integrating the atomic polarization over ω_0 in the same way as in the third-order problem, and is given by

$$P^{(5)\omega_3} = N\int_0^\infty g(\omega_0)(\mu_{ab}\rho_{ba}^{(5)\omega_3} + \text{c.c.})d\omega_0. \tag{20}$$

The result can be expressed in terms of two kinds of nonlinear susceptibility, $\chi_1^{(5)}$ and $\chi_2^{(5)}$, defined as

$$P^{(5)\omega_3} = (\chi_1^{(5)}|E_1|^2 + \chi_2^{(5)}|E_2|^2)E_1^2E_2^*\exp(-i\omega_3 t) + \text{c.c.} \tag{21}$$

Performing the integration of Eq. (20) on the assumption of Eq. (13) and with the approximation resulting from the condition of Eq. (14) as in the third-order calculation, we finally find

$$\chi_1^{(5)} = \frac{iK_5}{(1+i\omega_dT_1)^2(1+i\omega_dT_2)^2}$$
$$\chi_2^{(5)} = \frac{iK_5}{(1+i\omega_dT_1)(1+i\omega_dT_2)}\left[\frac{1}{1+i\omega_dT_1}\left(\frac{1}{2+i3\omega_dT_2}+\frac{1}{2+i\omega_dT_2}\right)+\frac{1}{1+i2\omega_dT_1}\left(\frac{1}{2+i3\omega_dT_2}+\frac{1}{2+i2\omega_dT_2}\right)\right], \tag{22}$$

where $\omega_d = \omega_2 - \omega_1$ and

$$K_5 = 4\pi|\mu_{ba}|^6\rho_D^{(0)}Ng(\omega_1)T_1^2T_2\hbar^{-5}.$$

The functional form of Eq. (22) with respect to ω_d is different from that of Eq. (15). Therefore the saturation effect modifies the apparent frequency characteristics of the mixing process.

The total nonlinear polarization at ω_3 combining the third- and fifth-order terms can be represented in terms of an intensity-dependent effective nonlinear susceptibility χ_{eff} as

$$\begin{aligned}P_{\text{total}}^{\omega_3} &= (\chi^{(3)} + \chi_1^{(5)}|E_1|^2 + \chi_2^{(5)}|E_2|^2)\\ &\quad\times E_1^2E_2^*\exp(-i\omega_3 t) + \text{c.c.}\\ &= \chi_{\text{eff}}E_1^2E_2^*\exp(-i\omega_3 t) + \text{c.c.}\end{aligned} \tag{23}$$

The behavior of $|\chi_{\text{eff}}|$ indicates how the saturation effect modifies the frequency response of the "apparent" third-order susceptibility which is directly connected to experimental observations. When only E_1 is intense enough to cause the saturation, $|\chi_{\text{eff}}|$ can be written in the form suitable for numerical calculation as

$$|\chi_{\text{eff}}| = |\chi_R^{(3)}|\left(1 + \frac{4S_1(S_1 - 1 + \omega_d^2T_1T_2)}{(1+\omega_d^2T_1^2)(1+\omega_d^2T_2^2)}\right)^{1/2}, \tag{24}$$
$$S_1 = |\mu_{ba}E_1|^2T_1T_2\hbar^{-2},$$

where S_1 is the saturation parameter, being an appropriate measure of the light intensity in this problem. The absorption coefficient at ω_1 including the saturation effect is given by

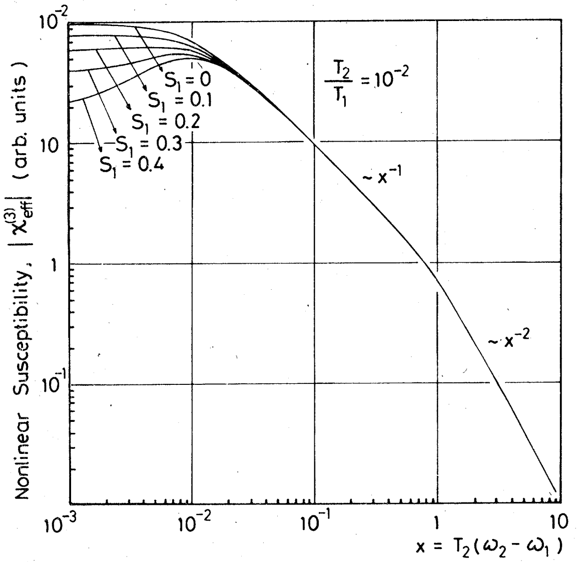

FIG. 3. Frequency characteristics of the effective nonlinear susceptibility $|\chi_{\rm eff}|$ showing the saturation effect. The saturation parameter S_1 is proportional to the light intensity at ω_1.

$$\alpha(\omega_1) = \alpha_0(\omega_1)(1+S_1)^{-1} \simeq \alpha_0(\omega_1)(1-S_1) \quad (\text{for } S_1 \ll 1). \tag{25}$$

Figure 3 shows the frequency response of $|\chi_{\rm eff}|$ calculated from Eq. (24) for several values of S_1 and $T_2/T_1 = 10^{-2}$. The result indicates that the frequency response of $|\chi_{\rm eff}|$ is affected little by the saturation effect in the vicinity of $\omega_2 - \omega_1 \simeq T_2^{-1}$ and some modification of the response curve occurs in the region of $\omega_2 - \omega_1 \lesssim T_1^{-1}$. It is found that under a strong light field the response curve tends to show a clear peak at $\omega_2 - \omega_1 \simeq T_1^{-1}$. These properties are convenient for the present purpose, because the existence of the saturation effect does not seriously prevent but rather helps the determination of relaxation times, although the effect is primarily not necessary. It is to be remembered, however, that the analysis presented here gives only the lowest-order saturation effect. For the more accurate examination of the effect the seventh- or higher-order nonlinear susceptibilities must be evaluated.

IV. EFFECT OF SPECTRAL CROSS RELAXATION

In the previous analysis we have neglected the effect of spectral cross relaxation which occurs within the inhomogeneous broadening. The physical picture of cross relaxation may be different depending on the origins of the inhomogeneous broadening. When impurity ions in a crystal suffer spatially inhomogeneous crystalline fields, the energy exchange between ions in different sites corresponds to the cross-relaxation process. A molecule in liquids can migrate freely to any place to suffer varying environmental molecular fields, which cause the random shift of transition frequencies of the molecule. In this case, the migration process results in the cross relaxation. When the inhomogeneous broadening concept is applied to an energy band with dense sublevels, the cross relaxation corresponds to the nonradiative transition within the band. Because the cross relaxation always exists more or less in a real material system, we must examine how the inclusion of this process in the calculation modifies the frequency response of the nonlinear susceptibility.

Here, we perform the calculation with the model and the assumptions which are essentially the same as those used by Mourou[4] in analyzing the hole-burning behavior of dye solutions. The energy-level diagram of an inhomogeneously broadened two-level system is schematically shown in Fig. 4. It is assumed that an atom can migrate into quantum states of any value of transition frequency within the inhomogeneous width. As to the spectral cross-relaxation rate we will postulate the following assumptions. The probability that one atom changes its transition frequency from ω_0' to a value within $\omega_0 \sim \omega_0 + d\omega_0$ in unit time is $g(\omega_0)T_3^{-1}d\omega_0$, where $g(\omega_0)$ is the atomic distribution function satisfying the normalization condition of Eq. (11), and T_3 is the cross-relaxation time. Then, the rate for an atom to change its transition frequency to any other value becomes T_3^{-1}. We also assume that there are no radiative and nonradiative transitions between a couple of levels such as $a \leftrightarrow b'$ or $a' \leftrightarrow b$.

Under these assumptions the behavior of the whole system can conveniently be described by a generalized density matrix in consideration of the situation that an atom can migrate into any level depicted in Fig. 4. If the distribution of ω_0 is dense enough to be regarded as continuous, we

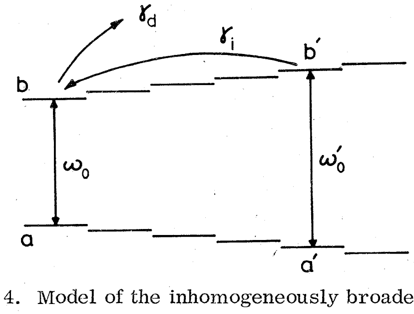

FIG. 4. Model of the inhomogeneously broadened two-level system with cross relaxation. The cross-relaxation rates for spectral diffusion and inverse processes are given by $\gamma_d = T_3^{-1}$ and $\gamma_i = g(\omega_0)\,T_3^{-1}$ (per unit ω_0), respectively.

can define a density matrix per unit frequency interval of ω_0, $\bar{\rho}(\omega_0, t)$. This means that the behavior of a group of atoms with the transition frequency in a limited range of $\omega_0 \sim \omega_0 + d\omega_0$ is determined by $\bar{\rho}(\omega_0, t)d\omega_0$. For example, the upper-level population and the polarization of atoms with $\omega_0 \sim \omega_0 + d\omega_0$ are given by $N\bar{\rho}_{bb}(\omega_0, t)d\omega_0$ and $N[\mu_{ab}\bar{\rho}_{ba}(\omega_0, t) + \text{c.c.}]d\omega_0$, respectively, where N is the total atomic density. Then, the following relation holds:

$$\int_0^\infty [\bar{\rho}_{aa}(\omega_0, t) + \bar{\rho}_{bb}(\omega_0, t)]d\omega_0 = 1. \tag{26}$$

The macroscopic polarization is given by

$$P = N\int_0^\infty [\mu_{ab}\bar{\rho}_{ba}(\omega_0, t) + \text{c.c.}]d\omega_0. \tag{27}$$

We also assume in the same manner as made by Mourou that the atomic distribution $g(\omega_0)$ is independent of the population change of the lower (a) and upper (b) levels so that

$$g(\omega_0) = \bar{\rho}_{aa}(\omega_0, t) + \bar{\rho}_{bb}(\omega_0, t). \tag{28}$$

The density matrix equations describing the system are then written in the form

$$\frac{d\bar{\rho}_{aa}}{dt} = -\frac{i}{\hbar}(H_{ab}\bar{\rho}_{ba} - \bar{\rho}_{ab}H_{ba}) - \bar{\rho}_{aa}\gamma' + \bar{\rho}_{bb}\gamma - \frac{1}{T_3}\bar{\rho}_{aa} + \frac{1}{T_3}g(\omega_0)\int_0^\infty \bar{\rho}_{aa}(\omega_0', t)d\omega_0', \tag{29}$$

$$\frac{d\bar{\rho}_{bb}}{dt} = -\frac{i}{\hbar}(H_{ba}\bar{\rho}_{ab} - \bar{\rho}_{ba}H_{ab}) - \bar{\rho}_{bb}\gamma + \bar{\rho}_{aa}\gamma' - \frac{1}{T_3}\bar{\rho}_{bb} + \frac{1}{T_3}g(\omega_0)\int_0^\infty \bar{\rho}_{bb}(\omega_0', t)d\omega_0', \tag{30}$$

$$\frac{d\bar{\rho}_{ba}}{dt} = \frac{d\bar{\rho}_{ab}^*}{dt} = -\frac{i}{\hbar}H_{ba}(\bar{\rho}_{aa} - \bar{\rho}_{bb}) - \bar{\rho}_{ba}\left(\frac{1}{T_2} + i\omega_0\right), \tag{31}$$

where γ and γ' are the longitudinal relaxation rates as mentioned in Sec. II, and H_{ba} is the same as given by Eq. (4). The abbreviation $\bar{\rho}_{jk} = \bar{\rho}_{jk}(\omega_0, t)$ has also been used for convenience. With the relations $T_1 = (\gamma + \gamma')^{-1}$, $\bar{\rho}_{aa}^{(0)}\gamma' = \bar{\rho}_{bb}^{(0)}\gamma$ and the abbreviation $\bar{\rho}_D = \bar{\rho}_{aa} - \bar{\rho}_{bb}$, Eqs. (29) and (30) can be combined to give

$$\frac{d\bar{\rho}_D}{dt} = -\frac{2i}{\hbar}(H_{ab}\bar{\rho}_{ba} - \bar{\rho}_{ab}H_{ba}) - \frac{1}{T_1}(\bar{\rho}_D - \bar{\rho}_D^{(0)}) - \frac{1}{T_3}\bar{\rho}_D + \frac{g(\omega_0)}{T_3}\int_0^\infty \bar{\rho}_D(\omega_0', t)d\omega_0'. \tag{32}$$

In the absence of cross relaxation ($T_3 \rightarrow \infty$) Eq. (32) reduces to the same form as Eq. (2), but it should be remembered that the meaning of $\bar{\rho}$ is different from that of ρ.

We now derive the third-order nonlinear susceptibility $\chi_R^{(3)}$ giving rise to the light output at $\omega_3 = 2\omega_1 - \omega_2$ on the basis of Eqs. (31) and (32). The calculation can be made in the same way as described in Sec. II by means of successive approximation, although a slight contrivance is required for the treatment of the integral term in Eq. (32). With this procedure [see the Appendix, section (i)] we finally obtain the third-order density-matrix element responsible for the nonlinear polarization at ω_3 in the form

$$\bar{\rho}_{ba}^{(3)\omega_3}(\omega_0, t) = \frac{-i2\mu_{ba}|\mu_{ba}|^2E_1^2E_2^*}{\hbar^3[T_1^{-1} + T_3^{-1} + i(\omega_2 - \omega_1)]B_3}\exp(-i\omega_3 t) \times\left[\bar{\rho}_D^{(0)}(\omega_0)\left(\frac{1}{B_2} + \frac{1}{B_1^*}\right) + \frac{2\pi g(\omega_0)\bar{\rho}_D^{(0)}(\omega_1)}{T_3[T_1^{-1} - i(\omega_2 - \omega_1)]}\right], \tag{33}$$

where $B_j = T_2^{-1} + i(\omega_0 - \omega_j)$ $(j = 1, 2, 3)$. In the derivation of Eq. (33), we have made the approximations based on the conditions of Eqs. (13) and (14). The third-order macroscopic nonlinear polarization at ω_3 is given according to Eq. (27) as

$$P^{(3)\omega_3} = N\int_0^\infty [\mu_{ab}\bar{\rho}_{ba}^{(3)\omega_3}(\omega_0, t) + \text{c.c.}]d\omega_0. \tag{34}$$

After carrying out the integration of Eq. (34), the nonlinear susceptibility $\chi_R^{(3)}$ defined by Eq. (12) is obtained in the form

$$\chi_R^{(3)} = \chi_1^{(3)} + \chi_2^{(3)},$$
$$\chi_1^{(3)} = \frac{iK_3'}{(1 + i\omega_d T_1')(1 + i\omega_d T_2)}, \tag{35}$$
$$\chi_2^{(3)} = \frac{M_3}{(1 + i\omega_d T_1')(1 + i\omega_d T_1)},$$

where $T_1' = (T_1^{-1} + T_3^{-1})^{-1}$, $\omega_d = \omega_2 - \omega_1$, and

$$K_3' = -2\pi|\mu_{ba}|^4\bar{\rho}_D^{(0)}(\omega_1)N\hbar^{-3}T_1'T_2,$$

$$M_3 = -4\pi|\mu_{ba}|^4\bar{\rho}_D^{(0)}(\omega_1)N\hbar^{-3}T_1'T_2 g(\omega_1)T_3^{-1}(J + i\pi).$$

Here, J is a real constant satisfying the condition $J \lesssim \pi$. In the derivation of Eq. (35), we have also made the approximations based on the conditions of Eqs. (13) and (14). [See the Appendix, section (ii) for the derivation of Eq. (35).]

It is seen from Eq. (35) that the first term $\chi_1^{(3)}$ has the same form as Eq. (15) except that T_1 is replaced by T_1'. The second term $\chi_2^{(3)}$ originates from the last integral term in Eq. (32) which represents the population increase due to the inverse process of spectral diffusion. The relative magnitude of the two terms can be examined by the following relation

$$\frac{|\chi_2^{(3)}|}{|\chi_1^{(3)}|}=\left(\frac{T_2^{-2}+\omega_d^2}{T_1^{-2}+\omega_d^2}\right)^{1/2}\left[\frac{2g(\omega_1)}{T_3}(J^2+\pi^2)^{1/2}\right]. \tag{36}$$

In view of the fact that $T_1 \gtrsim T_2$, $T_3 \gtrsim T_2$, $J \lesssim \pi$, and $g(\omega_1) \lesssim (\Delta\omega)_i^{-1} \ll T_2$, the factor $F \equiv 2g(\omega_1)T_3^{-1}(J^2+\pi^2)^{1/2}$ is known to be much smaller than unity. Therefore, in the frequency range of $|\omega_d| \gtrsim FT_2^{-1}$, the relation $|\chi_2^{(3)}| \ll |\chi_1^{(3)}|$ always holds for arbitrary situations of relaxation times, and the second term $|\chi_2^{(3)}|$ can be neglected there. When the relaxation property satisfies the condition $1 \gtrsim T_2/T_1 \gg F$, the relation $|\chi_2^{(3)}| \ll |\chi_1^{(3)}|$ holds in the all range of ω_d.

In summary it is concluded that the cross relaxation does not modify the frequency response of the nonlinear susceptibility in the higher frequency range of ω_d which is effective in the determination of T_2, although the value of T_2 itself is modified by the presence of cross relaxation.[30] Thus, the value of T_2 can unambiguously be determined even in this situation. In the lower range of ω_d, a combined relaxation time T_1' governs dominantly the frequency response of $\chi_R^{(3)}$. However, the determination and interpretation of T_1' from measurements require a careful consideration, because of the possible contribution of $\chi_2^{(3)}$ which complicates the frequency response curve of $\chi_R^{(3)}$.

V. THREE-LEVEL MODEL

In real materials there exist often additional energy levels which lie between the two levels under investigation and are connected to these levels through relaxation processes. This situation commonly occurs when the upper level b is not the lowest but a higher excited state. We will now examine essential features of the frequency response of the resonant Rayleigh-type mixing in this situation on the basis of the simplest three-level model.

Let us consider a three-level system as shown in Fig. 5. Two incident light waves at ω_1 and ω_2 are nearly resonant with the transition $a \longleftrightarrow b$ which is assumed to be inhomogeneously broadened with the width $(\Delta\omega)_i$. The third level c is assumed to be located far from resonance with both ω_1 and ω_2. The population decay rates between the three levels are designated as γ_A, γ_B and γ_C as shown in Fig. 5. The behavior of this three-level system is described by the following set of density matrix equations

$$\frac{d\rho_{aa}}{dt}=-\frac{i}{\hbar}\sum_{j=b,c}(H_{aj}\rho_{ja}-\rho_{aj}H_{ja})+\rho_{bb}\gamma_A+\rho_{cc}\gamma_C, \tag{37}$$

$$\frac{d\rho_{bb}}{dt}=-\frac{i}{\hbar}\sum_{j=a,c}(H_{bj}\rho_{jb}-\rho_{bj}H_{jb})-\rho_{bb}(\gamma_A+\gamma_B), \tag{38}$$

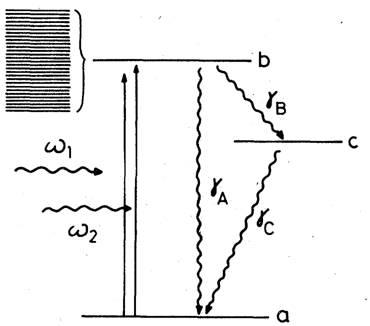

FIG. 5. Model of the three-level system in which one transition ($a \longleftrightarrow b$) is inhomogeneously broadened and is resonant with the light fields at ω_1 and ω_2. Population decay rates are designated as γ_A, γ_B, and γ_C.

$$\frac{d\rho_{cc}}{dt}=-\frac{i}{\hbar}\sum_{j=a,b}(H_{cj}\rho_{jc}-\rho_{cj}H_{jc})-\rho_{cc}\gamma_C+\rho_{bb}\gamma_B, \tag{39}$$

$$\begin{aligned}\frac{d\rho_{ba}}{dt}=-\frac{i}{\hbar}\{&H_{ba}(\rho_{aa}-\rho_{bb})\\&+H_{bc}\rho_{ca}-\rho_{bc}H_{ca}\}-(\Gamma_{ba}+i\omega_{ba})\rho_{ba},\end{aligned} \tag{40}$$

$$\begin{aligned}\frac{d\rho_{ca}}{dt}=-\frac{i}{\hbar}\{&H_{ca}(\rho_{aa}-\rho_{cc})\\&+H_{cb}\rho_{ba}-\rho_{cb}H_{ba}\}-(\Gamma_{ca}+i\omega_{ca})\rho_{ca},\end{aligned} \tag{41}$$

$$\begin{aligned}\frac{d\rho_{bc}}{dt}=-\frac{i}{\hbar}\{&H_{bc}(\rho_{cc}-\rho_{bb})\\&+H_{ba}\rho_{ac}-\rho_{ba}H_{ac}\}-(\Gamma_{bc}+i\omega_{bc})\rho_{bc},\end{aligned} \tag{42}$$

where

$$\begin{aligned}H_{jk}=H_{kj}^*=-\mu_{jk}\{&E_1\exp(-i\omega_1 t)\\&+E_2\exp(-i\omega_2 t)\}+\text{c.c.}\,,\end{aligned}$$

and

$$\rho_{jk}=\rho_{kj}^*\quad(k,j=a,b,c).$$

Here, Γ_{jk} and ω_{jk} are the transverse relaxation rate and the transition frequency for a couple of levels j and k. The meanings of other symbols are the same as in Eqs. (1)–(4). It is also assumed that $\rho_{aa}+\rho_{bb}+\rho_{cc}=1$, i.e., the cross relaxation effect is not considered.

The above equations can be solved without difficulty, if we adopt the successive approximation as in the analysis of the two-level system. The steady-state solution of ρ is expanded in power series of perturbation, and any order of solution can be calculated from the lower-order solutions, although the more complicated recurrence formulas must be used. In this process of calculation, we make the following approximation in addition to the rotating wave approximation. Namely, we neglect the small contributions of nonresonant terms which contain the factors $\omega_{ca}\pm\omega_j$ and $\omega_{bc}\pm\omega_j$ ($j=1,2,3$) in the frequency denominator. In this approximation, ρ_{ca} and ρ_{bc} can be set to be zero, and we need only Eqs. (37), (38), and (40) for the calculation. The third-order solution of ρ giving the atomic nonlinear polarization at the frequency $\omega_3 = 2\omega_1 - \omega_2$ is then obtained in a simple form as

$$\rho_{ba}^{(3)\omega_3} = \frac{-i2\mu_{ba}|\mu_{ba}|^2\rho_D^{(0)}E_1^2E_2^*}{\hbar^3[\gamma_A+\gamma_B+i(\omega_2-\omega_1)]D_3} \times\left(1+\frac{\gamma_B}{2[\gamma_C+i(\omega_2-\omega_1)]}\right)\left(\frac{1}{D_2^*}+\frac{1}{D_1}\right)\exp(-i\omega_3 t) \quad , \tag{43}$$

where $\rho_D = \rho_{aa} - \rho_{bb}$ and $D_j = \Gamma_{ba} + i(\omega_{ba} - \omega_j)$, $(j = 1, 2, 3)$. An additional contribution to $\rho_{ba}^{(3)\omega_3}$ originating from $\rho_D^{(2)2\omega_1}$ has been neglected in Eq. (43) as in the analysis of the two-level system. The corresponding macroscopic nonlinear polarization is given by taking into account the inhomogeneous broadening as

$$P^{(3)\omega_3} = N\int_0^\infty g(\omega_{ba})[\mu_{ab}\rho_{ba}^{(3)\omega_3}(\omega_{ba},t) + \text{c.c.}]d\omega_{ba}, \tag{44}$$

where N is the concentration of atoms, $g(\omega_{ba})$ is the distribution function for ω_{ba} satisfying the condition

$$\int_0^\infty g(\omega_{ba})d\omega_{ba} = 1. \tag{45}$$

The integration of Eq. (44) can be carried out in entirely the same way as Eq. (10) with the same approximations originating from the conditions of Eqs. (13) and (14).

The third-order nonlinear susceptibility $\chi_R^{(3)}$ defined by Eq. (12) is then obtained as

$$\begin{aligned} \chi_R^{(3)} &= \chi_I^{(3)} + \chi_{II}^{(3)}, \\ \chi_I^{(3)} &= \frac{iK_3''}{(1+i\omega_d T_{1b})(1+i\omega_d T_{2A})}, \\ \chi_{II}^{(3)} &= \frac{\gamma_B}{2(\gamma_C + i\omega_d)}\chi_I^{(3)}, \end{aligned} \tag{46}$$

where $\omega_d = \omega_2 - \omega_1$, $K_3'' = -2\pi|\mu_{ba}|^4 N\rho_D^{(0)}g(\omega_1) \times T_{1b}T_{2A}\hbar^{-3}$, $T_{1b} = (\gamma_A + \gamma_B)^{-1}$, and $T_{2A} = \Gamma_{ba}^{-1}$. Here, T_{1b} means the overall population decay time of the level b and T_{2A} means the transverse relaxation time associated with the transition $a \leftrightarrow b$.

It can be seen from Eq. (46) that the first term $\chi_I^{(3)}$ is of the same form as Eq. (15) for the two-level system with the replacement of T_1 by T_{1b} and T_2 by T_{2A}. If the condition $\gamma_B \ll \gamma_C$ is satisfied, the relation $|\chi_I^{(3)}| \gg |\chi_{II}^{(3)}|$ holds in the entire range of ω_d and the first term dominates. In this case, the measurement of the frequency response of $\chi_R^{(3)}$ gives directly the values of T_{1b} and T_{2A} in the same manner as in the case of the two-level system. When $\gamma_B \gg \gamma_C$, the same relation $|\chi_I^{(3)}| \gg |\chi_{II}^{(3)}|$ also holds in the range of $\omega_d \gtrsim T_{2A}^{-1}$ in view of the fact that $T_{2A}^{-1} \gg \gamma_A + \gamma_B$. However, the term $\chi_{II}^{(3)}$ dominates in the lower frequency range of $\omega_d \lesssim \gamma_B$, where the shape of the frequency response of $\chi_R^{(3)}$ is modified from that of $\chi_I^{(3)}$.

These results can be summarized as follows. In the higher-frequency range of $\omega_d \gtrsim T_{2A}^{-1}$, the shape of the frequency response curve of $\chi_R^{(3)}$ is essentially the same as in the two-level model, and therefore the transverse relaxation time T_2 can unambiguously be determined, although its value is modified by the existence of the third level.[30] In the lower-frequency range of ω_d, however, the shape of the frequency response curve is somewhat dependent on the relative magnitude of the longitudinal relaxation rates γ_A, γ_B and γ_C, and a careful interpretation is necessary to deduce the relaxation times from the observed frequency response. Conversely speaking, if this analysis is made properly, it may provide useful information on relaxation processes in such a complicated system.

VI. NONRESONANT TERM AND INTERFERENCE EFFECT

In real materials the third-order nonlinear susceptibility $\chi^{(3)}(\omega_3 = 2\omega_1 - \omega_2)$ includes a nonresonant term $\chi_{NR}^{(3)}$ in addition to the resonant term $\chi_R^{(3)}$ discussed in the preceding sections. The relation is given by

$$\chi^{(3)} = \chi_R^{(3)} + \chi_{NR}^{(3)}. \tag{47}$$

The term $\chi_R^{(3)}$ is characterized by its sensitive variation with respect to $\omega_2 - \omega_1$, while $\chi_{NR}^{(3)}$ is nearly constant for the change of $\omega_2 - \omega_1$. The existence of $\chi_{NR}^{(3)}$ set a limit for the measurement of $\chi_R^{(3)}$, and therefore it is desirable to look for the condition which minimizes the effect of $\chi_{NR}^{(3)}$. The relative magnitudes of $\chi_R^{(3)}$ and $\chi_{NR}^{(3)}$ depend on the specific material transition and the polarization properties of the radiation field. For the measurement of T_2, the magnitude of $|\chi_R^{(3)}|$ at $\omega_2 - \omega_1 = T_2^{-1}$ should be much larger than $|\chi_{NR}^{(3)}|$. However, even when this condition is not satisfied, we can get an upper limit of T_2 from the measurement of frequency response in the region where $\chi_R^{(3)}$ contributes dominantly to $\chi^{(3)}$. Even this kind of limited information is of value in case of the absence of the related data.

The term $\chi_{NR}^{(3)}$ accompanying the resonant Rayleigh-type mixing comes from two origins. One is the contribution of the small terms which are associated with the resonant two-level or three-level system, but are neglected in the preceding calculation in the rotating-wave and other approximations. The other is the contribution from other

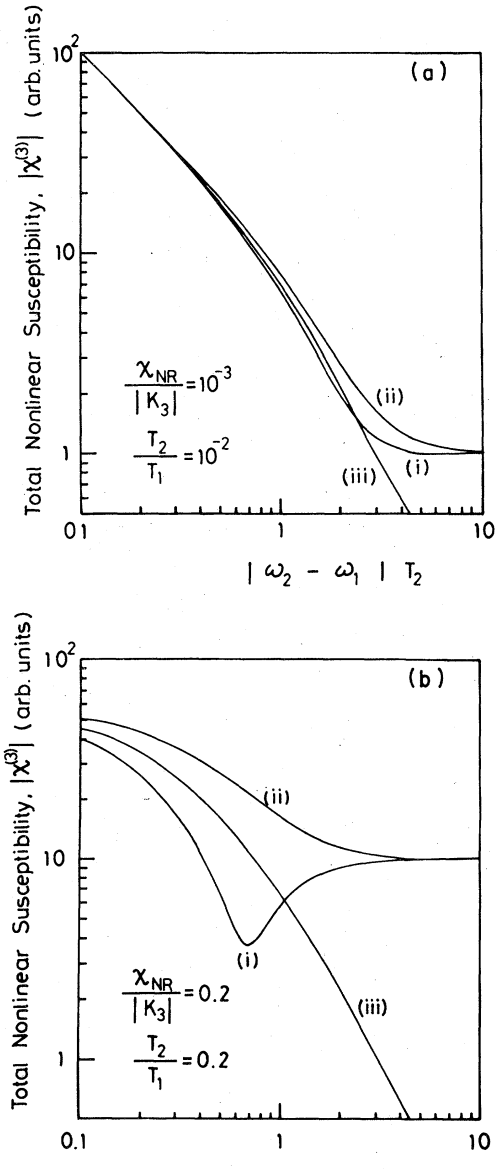

FIG. 6. Frequency characteristics of the total nonlinear susceptibility $|\chi^{(3)}|$ showing the interference effect between resonant ($\chi_R^{(3)}$) and nonresonant ($\chi_{NR}^{(3)}$) terms with $\chi_{NR}^{(3)}>0$. (a) $\chi_{NR}^{(3)}/|K_3|=10^{-3}$, $T_2/T_1=10^{-2}$, and (b) $\chi_{NR}^{(3)}/|K_3|=0.2$, $T_2/T_1=0.2$. (i) $\omega_2-\omega_1>0$, (ii) $\omega_2-\omega_1<0$, and (iii) $\chi_{NR}^{(3)}=0$.

energy levels outside of the levels under consideration. We must now notice about the meaning of the word "nonresonant" named for the term $\chi_{NR}^{(3)}$. The term has been defined only by its character of being almost dispersionless with respect to the variable $\omega_2-\omega_1$. It should be remembered that even in $\chi_{NR}^{(3)}$ the effect of one-photon or two-photon resonance of each radiation frequency ω_j with a broad absorption band has been included. Therefore the nature of $\chi_{NR}^{(3)}$ in the present case is somewhat different from that of the nonresonant term encountered in the cases where all radiation frequencies concerned with the process lie in a transparent region. In the present case $\chi_{NR}^{(3)}$ does not necessarily take a positive real value, but can have a negative real value or even a pure imaginary value depending on the nature of the energy-level system.

When the contribution of $\chi_{NR}^{(3)}$ is important, the interference effect occurs between the resonant and nonresonant terms as has been known in the case of Raman-type three-wave mixing or CARS (coherent anti-Stokes Raman scattering). The nature of the interference also depends on the nature of $\chi_{NR}^{(3)}$ described above. For a real value of $\chi_{NR}^{(3)}$, the intensity of the light output at ω_3 is proportional to

$$|\chi^{(3)}|^2=|\chi_r^{(3)}+\chi_{NR}^{(3)}|^2+|\chi_i^{(3)}|^2, \tag{48}$$

where $\chi_r^{(3)}$ and $\chi_i^{(3)}$ are the real and imaginary parts of $\chi_R^{(3)}$, respectively. The interference brings about the following effects on the frequency response of $|\chi^{(3)}|$: (i) asymmetric behavior with respect to the change of the sign of $\omega_2-\omega_1$, (ii) occurrence of a dip for one sign of $\omega_2-\omega_1$), (iii) slight modification of the slope of $|\chi_R^{(3)}|$. These features are illustrated in Fig. 6 for typical values of T_2/T_1 and $\chi_{NR}^{(3)}/|K_3|$. The features (i) and (ii) arise from the fact that $\chi_{NR}^{(3)}$ combines with $\chi_r^{(3)}$ having antisymmetric character so that the destructive effect occurs on the one side and the constructive effect on the other side. The sign of $\chi_{NR}^{(3)}$ can be determined by observing in which side the dip occurs. For the reliable determination of relaxation parameters from $\chi^{(3)}$, these interference effects should carefully be taken into consideration in the analysis of experimental results.

VII. WAVE PROPAGATION PROPERTIES

In order to obtain the expression of the output light intensity at the frequency $\omega_3=2\omega_1-\omega_2$, we must deal with the wave propagation problem in addition to the calculation of the nonlinear susceptibility. The incident light fields at ω_1 and ω_2 in the plane-wave approximation are given by

$$E_1(t,\vec{r})=\tilde{E}_1\exp[i(\vec{K}_1\cdot\vec{r}-\omega_1 t)]+\text{c.c.} \tag{49}$$

$$E_2(t,\vec{r})=\tilde{E}_2\exp[i(\vec{K}_2\cdot\vec{r}-\omega_2 t)]+\text{c.c.}, \tag{50}$$

where $\vec{K}_j=\vec{k}_j+i\vec{a}_j$ $(j=1,2)$ are the complex wave vectors including the effect of linear absorption. The vector $\vec{a}_j$ is parallel to $\vec{k}_j$, and its absolute value $a_j=|\vec{a}_j|$ represents the linear-absorption coefficient for E_j. The third-order nonlinear polarization at ω_3 is then given by

$$P^{(3)\omega_3}(t,\vec{r})=\chi^{(3)}\tilde{E}_1^2\tilde{E}_2^*\exp[-(2\vec{a}_1+\vec{a}_2)\cdot\vec{r}]\times\exp[i(\vec{k}_p\cdot\vec{r}-\omega_3 t)]+\text{c.c.}, \tag{51}$$

where $\vec{k}_p=2\vec{k}_1-\vec{k}_2$ is the wave vector of the polarization wave. In isotropic media, the light wave at ω_3 produced by $P^{(3)\omega_3}$ is approximated by a plane wave propagating along $\vec{k}_p$. If we designate this direction as z, the light field at ω_3 can be written in the form

$$E_3(t,z)=\tilde{E}_3(z)\exp[i(k_3 z-\omega_3 t)]+\text{c.c.}, \tag{52}$$

where $k_3=|\vec{k}_3|$. The amplitude $\tilde{E}_3(z)$ is determined by the amplitude equation

$$d\tilde{E}_3/dz+a_3\tilde{E}_3=i(2\pi\omega_3^2/c^2k_3)\chi^{(3)}\tilde{E}_1^2\tilde{E}_2^*\times\exp[(-a_p+i\Delta k)z], \tag{53}$$

which has been derived from the Maxwell's wave equation in the slowly-varying amplitude approximation. Here, a_3 is the linear-absorption coefficient at ω_3, a_p is the component of $2\vec{a}_1+\vec{a}_2$ along the direction of $\vec{k}_p$, and $\Delta k=|\vec{k}_p|-k_3$. When the vectors $\vec{k}_1$ and $\vec{k}_2$ are nearly parallel, a_p is nearly equal to $2a_1+a_2$. Solving Eq. (53) with the boundary condition $\tilde{E}_3(0)=0$, we obtain

$$|E_3|^2=(2\pi\omega_3^2/c^2k_3)^2|\chi^{(3)}|^2|\tilde{E}_1^2\tilde{E}_2^*|^2F_p(z), \tag{54}$$

$$F_p(z)=\frac{\exp[-2(2a_1+a_2)z]+\exp(-2a_3z)-2\cos(\Delta kz)\exp[-(2a_1+a_2+a_3)z]}{(a_3-2a_1-a_2)^2+(\Delta k)^2},$$

where $F_p(z)$ is the propagation factor which gives the square of the effective interaction length. The efficiency of light generation at ω_3 can be estimated from Eq. (54) combined with the relation $I_j=n_jc|\tilde{E}_j|^2A_j/2\pi$, where I_j, A_j, and n_j are the light power, the effective beam area and the refractive index at ω_j, respectively.

For the experimental determination of the frequency response of $\chi^{(3)}$ from the measured frequency characteristics of I_3, the frequency dependences of $F_p(z)$ and other factors should carefully be taken into account. When the frequencies ω_1, ω_2, and ω_3 are close enough to each other as in the Rayleigh-type mixing, the linear dispersion within the spread of these frequencies can usually be ignored. In this case, the phase-matching condition $\Delta k=0$ holds for the collinear beam propagation, and a finite phase mismatch Δk arises from the noncollinear beam configuration which is usually adopted in the experiment for the purpose of spatial filtering. For a small angle θ between the two wave vectors $\vec{k}_1$ and $\vec{k}_2$, the coherence length $l_c=\pi/\Delta k$ is calculated by a simple geometrical consideration to be

$$l_c\simeq\lambda/2n\theta^2, \tag{55}$$

where λ and n are the free-space wavelength and the refractive index, respectively, at a mean frequency of ω_1, ω_2, and ω_3. When the coherence length is long enough to satisfy the condition $l_c\gg a_j^{-1}$ $(j=1,2,3)$, the propagation factor $F_p(z)$ is entirely determined by the linear absorption properties as

$$F_p(z)=\left(\frac{t_1\sqrt{t_2}-\sqrt{t_3}}{a_3-2a_1-a_2}\right)^2, \tag{56}$$

where $t_j=\exp(-2a_jz)$ $(j=1,2,3)$ is the transmittance of light waves at respective frequencies. For large values of $\omega_2-\omega_1$, where the frequency dependence of a_j cannot be ignored, Eq. (56) can conveniently be used as a correction factor in obtaining $\chi^{(3)}$.

For the more accurate evaluation of the output light intensity, the effect of finite-beam cross section with, for example, a Gaussian profile must also be taken into account. However, the present consideration will provide practically reasonable results for the analysis of the frequency characteristics of the process.

VIII. ANALOGY WITH PHOTON ECHOS

The three-wave mixing is a process in the frequency domain with two input monochromatic waves, while the photon echo[32,33] is that in the time domain with two input pulses. A close analogy is known to exist between these two phenomena. We discuss here the nature of the resonant Rayleigh-type mixing from this point of view.

As shown in Fig. 7, the two phenomena exhibit quite similar patterns except that there is no echo signal at the time $t_e'=2t_1-t_2$ due to the causality. Dienes[34] has shown that there are strikingly identical relations between the polarization properties of incident and output light waves for these two phenomena. Besides these, there are basic similarities between these two processes. For better

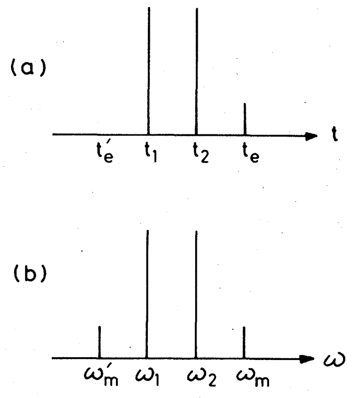

FIG. 7. Photon echo (a) and three-wave mixing (b) showing similar patterns in the time domain and in the frequency domain, respectively.

correspondence to the photon echo, we will deal with the mixing process $\omega_m = 2\omega_2 - \omega_1$ whose nature is the same as that of $\omega'_m = 2\omega_1 - \omega_2$. The direction of propagation of the echo pulse at $t_e = 2t_2 - t_1$ is along the vector $2\vec{k}_{2e} - \vec{k}_{1e}$, where $\vec{k}_{1e}$ and $\vec{k}_{2e}$ are the wave vectors of the first and second excitation pulses, respectively. The direction of propagation of the light wave at ω_m produced by the mixing is also along the vector $2\vec{k}_{2m} - \vec{k}_{1m}$, where $\vec{k}_{1m}$ and $\vec{k}_{2m}$ are the wave vectors of the two input waves at ω_1 and ω_2. The polarization amplitude providing the echo signal is generally given by the relation

$$\begin{aligned} &P_e \propto \sin\theta_1(1-\cos\theta_2), \\ &\theta_j = \mu_{ba}E_j\tau_j\hbar^{-1} \quad (j=1,2), \end{aligned} \tag{57}$$

where E_j and τ_j are the amplitude and the width of each pulse, respectively. Equation (57) indicates that P_e takes a maximum value at $\theta_1 = \frac{1}{2}\pi$ and $\theta_2 = \pi$. The photon echo appears, however, at any field intensities. For weak fields Eq. (57) can be expanded as

$$P_e = K_e E_1 E_2^2 + \cdots, \tag{58}$$

where K_e is a constant. The lowest-order term is the third-order nonlinear polarization which has the same field dependence as that of the three-wave mixing without the saturation effect.

These facts suggest the existence of some analogy also in the relaxation properties associated with these two phenomena. It is well known in the photon echo that the echo intensity as a function of the "pulse separation" $t_2 - t_1$ is governed by the dephasing relaxation time T_2 according to the relation $I_e \propto P_e^2 \propto \exp[-4(t_2 - t_1)T_2^{-1}]$, and it provides a means of measuring T_2. It is therefore expected that in the three-wave mixing the characteristics of the output light intensity as a function of the "frequency separation" $\omega_2 - \omega_1$ will play the same kind of role. In fact this was one of the motives for starting the present study. We have really found this counterpart of analogy in the frequency domain, in that the nonlinear susceptibility $\chi_R^{(3)}$ contains a factor of the form $[1 + i(\omega_2 - \omega_1)T_2]^{-1}$. As has been mentioned in Sec. II, this factor appears only at and above the third-order nonlinearity, and only in the mixing of the type $2\omega_1 - \omega_2$ or $2\omega_2 - \omega_1$.[28] In this sense, this feature is naturally regarded as a manifestation of the analogy with the photon echo. On the other hand, the appearance of the factor $[1 + i(\omega_2 - \omega_1)T_1]^{-1}$ is not peculiar to the third-order or the three-wave mixing, and has no counterpart of analogy in the photon echo. In the higher-order nonlinear processes, the same kind of analogy has also been found in the relationship between the two-photon-resonant Rayleigh-type mixing[35] and the two-photon-resonant (Raman-type) photon echo.[36] Of course, the analogy has its own limitations, and it is dangerous to discuss a problem only on the basis of the analogy. However, as exemplified in the present study, the analogy is very useful in providing a clue to find a solution of a problem or to find a problem itself.

In summary, it can be said that the resonant Rayleigh-type mixing is really a frequency-domain analog of the photon echo. It should be remembered, however, that the two phenomena are independent physical processes, and the one phenomenon is not simply a Fourier transform of the other.

IX. SUMMARY AND DISCUSSION

The present analysis shows that the resonant Rayleigh-type optical mixing provides a powerful spectroscopic means capable of giving potentially much information on ultrafast relaxation dynamics which is not easily obtainable by other experimental technique. However, various precautions are required in the analysis of the experimental data in order to get reliable relaxation rates from this type of measurement technique.

Firstly, for the determination of correct frequency response of the resonant part $\chi_R^{(3)}$, various effects which modify the apparent frequency response should carefully be taken into account. These are the saturation effect, the interference effect, and the wave propagation effect as described in Secs. III, VI, and VII, respectively. It is desirable to choose experimental conditions minimizing these effects, or proper corrections should be performed when these effects are unavoidable.

The second problem is the correct interpretation of the measured frequency response of $\chi_R^{(3)}$ thus obtained. As has been shown, the calculated frequency response is more or less dependent on the energy-level model on which the analysis is based. Even the advanced models presented here are still idealized in comparison with the complicated level scheme of real materials. It is therefore a task to find a reasonably correct model for individual material transition. We found in the present analysis, however, that the frequency response of $\chi_R^{(3)}$ is relatively model-insensitive in the frequency region where the contribution of the transverse relaxation time (T_2) is important. The optical mixing method, therefore, will provide a reliable means for the determination of T_2 which is generally difficult by other methods in the region of picosecond or less. On the other hand, the aspect of how the longitudinal relaxation time contributes to the frequency response of $\chi_R^{(3)}$ is rather complicated and more model-dependent than for T_2. Therefore, we must be more careful to interpret and deduce the longitudinal relaxation rate from the measurement. Auxiliary information on the longitudinal relaxation which, in certain cases, could be available from transient methods, will be of help for the reliable determination of the longitudinal relaxation rates.

It is also a problem to examine how widely the concept of inhomogeneous-broadening model can be applied to a multi-energy-level system with densely distributed sublevels. The interband transition in semiconductors and insulators has often been treated in good approximation as an inhomogeneously-broadened transition, because of the presence of the selection rule $\Delta\vec{k}_e = 0$ where $\vec{k}_e$ is the wave vector of Bloch electrons. The electronic transition of large molecules with dense vibrational and rotational sublevels is another example of an effectively inhomogeneous transition. In order to make clear the exact feature of this kind of level system, more refined treatment of the "inhomogeneous-broadening" than that given here will be required. Further, when the distribution of sublevels is not dense enough to be regarded as continuous, the frequency response of $\chi_R^{(3)}$ will show a complicated behavior which reflects the discrete level structure. Although it makes the analysis difficult, this implies that the resonant Rayleigh-type mixing can also be utilized for the analysis of level structure as well as for the study of relaxation.

A cause of the ambiguity associated with the selection of models arises from the situation that the analysis given here is only a phenomenological theory in which relaxation constants are introduced *a priori* at the beginning. A random perturbation acting on the atomic system under study does not always give the relaxation term characterized by a definite decay constant. This form of relaxation can be deduced only when the perturbation is weak and rapid enough to satisfy the condition $\langle H_r^2\rangle \tau_c^2 \hbar^{-2} \ll 1$, where H_r and τ_c are the amplitude and the correlation time of the random perturbation Hamiltonian, respectively.[26,37] In some cases, a microscopic theory starting from the first principle of particle interactions would be necessary for the correct description of the resonant Rayleigh-type mixing process.

In conclusion, we wish to emphasize that the nonlinear optical spectroscopy is essentially powerful for the study of ultrafast dynamics, although its application has hitherto been oriented rather to high-spectral resolution works where slow processes are involved. One of essential roles of the nonlinear spectroscopy is to distinguish and separate various components constituting spectral broadening. This is commonly true both in high and low spectral-resolution works, the latter being the case involving ultrafast processes. For the slow processes, the same spectroscopic information can also be obtained by a time-domain work without much difficulty, as illustrated in some coherent transient[38] and quantum beat experiments.[39] On the other hand, for the ultrafast processes where time-domain work is extremely difficult or impossible, the nonlinear spectroscopic technique in the frequency domain is the only available means for the above purpose.

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APPENDIX

(i) *Derivation of Eq.* (33). The first-order solution $\bar{\rho}_{ba}^{(1)\omega_j}$ ($j = 1, 2$) gives rise to the second-order solution $\bar{\rho}_D^{(2)\omega_d}(\omega_d = \omega_2 - \omega_1)$ through Eq. (32). In doing this calculation, we first put

$$\int_0^\infty \bar{\rho}_D^{(2)\omega_d}(\omega_0', t)\,d\omega_0' = G\exp(-i\omega_d t) + \mathrm{c.c.}\,. \tag{A1}$$

Then, $\bar{\rho}_D^{(2)\omega_d}(\omega_0, t)$ can be obtained as a function of G by solving Eq. (32). We next insert this solution into the integrand on the left-hand side of Eq. (A1), and then calculate the integral whose result is also a function of G. Then, G can be determined by the condition that the function thus obtained is just equal to the right-hand side of Eq. (A1). In the approximations based on the condition of Eqs. (13) and (14), we have

$$G = \frac{-\pi\,|\mu_{ba}|^2 E_1^* E_2 \rho_D^{(0)}(\omega_1)}{\hbar^2[T_1^{-1} - i(\omega_2 - \omega_1)]}\,, \tag{A2}$$

which completely determines $\bar{\rho}_D^{(2)\omega_d}(\omega_0, t)$. This subsequently gives rise to the third-order solution $\bar{\rho}_{ba}^{(3)\omega_3}(\omega_0, t)$ through Eq. (31). The result is given in Eq. (33).

(ii) *Derivation of Eq.* (35). The part of $\bar{\rho}_{ba}^{(3)\omega_3}$ proportional to the first term in the large bracket [ ] of Eq. (33) can be integrated over ω_0 in completely the same manner as in deriving Eq. (15), and gives the first term $\chi_1^{(3)}$ of Eq. (35).

On the other hand, the integration of the other part of $\bar{\rho}_{ba}^{(3)\omega_3}$ proportional to the second term in the large bracket [ ] requires some contrivance. The distribution function $g(\omega_0)$ cannot be extracted outside of the integral even when the variation of $g(\omega_0)$ is much slower than the remaining factor of this second part, because the integral diverges. Therefore, we carry out the integration by assuming the function $g(\omega_0)$ to be, for example, a Lorentzian shape of the form

$$g(\omega_0) = \frac{(\Delta\omega)_i}{\pi[(\omega_0 - \omega_c)^2 + (\Delta\omega)_i^2]}, \tag{A3}$$

where ω_c is the center frequency and $(\Delta\omega)_i$ is the inhomogeneous width. The result of integration gives rise to the second term $\chi_2^{(3)}$ of Eq. (35) with

$$J = \frac{\omega_c - \omega_3}{(\Delta\omega)_i}\left[\frac{\pi}{2} + \tan^{-1}\left(\frac{\omega_c}{(\Delta\omega)_i}\right)\right] + \frac{1}{2}\ln\left[\frac{\omega_c^2 + (\Delta\omega)_i^2}{\omega_3^2}\right], \tag{A4}$$

which takes a value satisfying $J \lesssim \pi$ in view of the condition $\omega_c - \omega_3 \lesssim (\Delta\omega)_i$ and $(\Delta\omega)_i \lesssim \omega_c$.

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