

Study of ultra-fast relaxation processes by resonant Rayleigh-type optical mixing. II. Experiment on dye solutions

Tatsuo Yajima, Hirotoishi Souma, and Yuzo Ishida

The Institute for Solid State Physics, The University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

(Received 16 May 1977)

The three-wave optical mixing ($\omega_3 = 2\omega_1 - \omega_2$) of the resonant Rayleigh type ($|\omega_1 - \omega_2| \simeq$ inverse relaxation time, ω_1 and $\omega_2 \simeq$ optical transition frequency) is applied to measure the subpicosecond relaxation times associated with the $S_0 \rightarrow S_1$ electronic transition of 1,1'-diethyl-4,4'-quinocyanine iodide in ethanol and other dye solutions. Two independently tunable dye lasers excited by a nitrogen laser were used as light sources. The measured frequency responses of the nonlinear susceptibility $|\chi^{(3)}|$ as a function of $\omega_1 - \omega_2$ were in good agreement with the theoretical formula based on an inhomogeneously broadened two-level model incorporating the phenomenological relaxation times. We also observed the interference effect between the resonant and nonresonant terms of the nonlinear susceptibility, which agree well with the theory. Thus we were able to determine the transverse relaxation time T_2 in the range of 0.02 ~ 2 psec and the effective relaxation time T_1' (a combination of longitudinal- and cross-relaxation times) in the range of 0.1 ~ 5 psec. These values were found to be largely dependent on the spectral position inside the broad absorption band and the sample preparation and deterioration, as well as on the kinds of dye materials and solvents. Details of the experimental procedure and a discussion of the interpretation of the experimental results are given.

I. INTRODUCTION

In our preceding paper¹ we described a theory of resonant Rayleigh-type optical mixing as a means for measuring ultrashort relaxation times in the frequency domain. In this paper we apply the method and present the results of an experiment which demonstrates the feasibility and the usefulness of this new method.²

As the first material which is most suitable for the above purpose, we selected an organic dye solution. The excellent spatial homogeneity of a liquid sample is quite convenient in this experiment, where stray scattering of intense incident light should be avoided. There are numerous kinds of dye materials, and their solutions offer large flexibility in selection of sample conditions such as center frequency of absorption band, dye concentration, sample length, solvent, and dye mixtures. This makes it easier to find an optimum condition for the experiment. The investigation of excited-state behavior of dye molecules is of importance not only from the standpoint of molecular physics, but also in its essential contribution to quantum electronics as a medium for laser and other optical devices.

With the development of picosecond laser technology, excited-state lifetimes in the picosecond range can be measured directly in the time domain for many dye and other large molecules. However, their measurement with a time resolution of 1 ps or less is quite difficult and we are presently only at the entrance of this extreme time region. The determination of transverse relaxation time (T_2) and spectral-cross relaxation time (T_3) for

electronic-excited states of dye is much more difficult, because they are usually much shorter than fluorescence lifetimes, and, furthermore, they cannot be determined by conventional transient fluorescence or absorption methods. The determination of T_2 is directly connected with the problem of whether a specific electronic transition of a dye material is broadened homogeneously or inhomogeneously. This property has large influences on the dynamical behavior of dye lasers as well as on the interpretation of molecular interactions. When the spectral cross relaxation is very fast, an inhomogeneously broadened transition may exhibit partly or entirely the homogeneouslike behavior in saturation characteristics. In such cases, apparent homogeneous widths are not simply related to the transverse relaxation time. In regard to the experiment aimed at determining T_2 in dye molecules, there are only a hole-burning experiment by Mourou³ and a nonlinear absorption experiment by Vahey and Yariv,⁴ which is based on a more indirect method.

In view of these situations, the application of our new method to dye solutions seems to be worthwhile, because, as shown in paper I, the value of T_2 is expected to be determined more unambiguously by this method, and simultaneously some information on longitudinal and spectral-cross relaxation times can also be obtained.

From many dye materials, a cyanine dye, 1,1'-diethyl-4,4'-quinocyanine iodide was first selected and detailed measurements were made for its singlet-singlet electronic transition $S_0 \rightarrow S_1$ centered at about 6000 Å where powerful dye laser sources can conveniently be used. The broad

width [$\sim 500 \text{ \AA}$ in full width at half maximum (FWHM)] of its absorption band makes it easier to analyze the experimental data. Its nonfluorescent nature^{5,6} is also convenient in eliminating the disturbances resulting from the fluorescent emission and from the possible occurrence of stimulated emission.

The experimental results obtained will be interpreted in the framework of the theory developed in paper I.

II. EXPERIMENTAL APPARATUS

A nonlinear optical spectrometer constructed for the experiment of resonant Rayleigh-type mixing is schematically shown in Fig. 1. The laser sources used are two independently tunable dye lasers simultaneously-excited transversely by a pulsed nitrogen laser with a repetition rate of typically 10 Hz and a maximum peak power of 600 kW. The frequency selection and tuning of the dye lasers were accomplished by a diffraction grating alone or in combination with a Fabry-Perot etalon inside the cavity. The spectral width of the dye laser was narrowed by the use of this Fabry-Perot etalon or by a beam expanding telescope, but they were not simultaneously used because of the reduction of the output power.

This laser system is essentially similar to that used for the experiment of Raman-type optical mixing spectroscopy,⁷ but there is one important difference. The frequencies of the two incident dye lasers are very close to each other in our case, the frequency difference being in the range of $|\omega_1 - \omega_2|/2\pi c = 0.5 \sim 500 \text{ cm}^{-1}$ corresponding to the relaxation-time range of $10^{-11} \sim 10^{-14} \text{ s}$. Accordingly the output light frequency $\omega_3 = 2\omega_1 - \omega_2$ produced by the optical mixing is also very close to the incident one. In such a case, the elimination of a strong stray component of the incident light

is essentially important for the detection of weak output light. In order to overcome this difficulty, we first tried to realize a dye laser with extremely low spectral background. The broad spectral background normally present in dye lasers originates mainly from the superfluorescent emission whose direction is insensitive to the laser-cavity condition. By proper adjustment of the relative positions of the dye cell and other optical components constituting the laser cavity, we were able to shift the direction of the oscillating light output from that of the superfluorescent component so as to minimize the undesirable background. The relative intensity of the spectral background thus obtained was as small as 10^{-6} at a position 20 \AA apart from the laser line center. The operating condition giving the lowest spectral background is generally different from that giving the maximum power. Therefore, the reduction of laser power was inevitable in some extent. With rhodamine 6 G laser dye, the laser output used had typically the peak power of $5 \sim 20 \text{ kW}$ for one laser, the spectral width of $0.2 \sim 1 \text{ \AA}$ and the pulse width of $2 \sim 5 \text{ nsec}$. Because the pulse width was much longer than the picosecond relaxation times of the sample materials under investigation, the laser played essentially the same role as a cw laser in our experiment in spite of its short-pulse operation.

The two dye-laser beams at frequencies ω_1 and ω_2 were weakly focused together by a $f = 20 \text{ cm}$ lens on to a sample cell of 0.1 mm thickness. In a mixing experiment with pulsed laser sources, a careful adjustment is required to accomplish the sufficient overlapping of the two beams at the sample, both temporally and spatially. An optical delay with a movable prism served to make the coincidence between the two pulses from different dye lasers. An auxiliary focusing lens was also

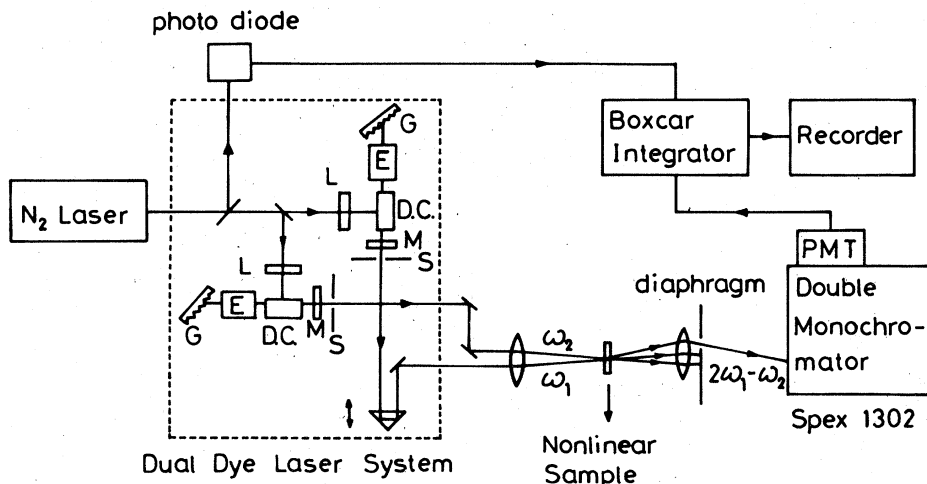


FIG. 1. Schematic diagram of the apparatus for the experiment of resonant Rayleigh-type optical mixing. D.C.: dye cell, G: grating, M: mirror, S: slit, E: beam expander or Fabry-Perot etalon.

used to compensate for the difference in focusing area arising from the slight difference in divergent properties of the two beams. Typical beam size at the focus was 0.2~0.5 mm in diameter.

The two laser beams at ω_1 and ω_2 were not collinear, but incident on the sample cell, with a small angle θ in order to perform the spatial filtering. As discussed in Sec. VII of paper I, the wave vector of the output light wave at $\omega_3 = 2\omega_1 - \omega_2$ is along $2\vec{k}_1 - \vec{k}_2$ whose direction is different from those of both \vec{k}_1 and \vec{k}_2 , the wave vectors of the two noncollinear incident beams. This enables one to separate spatially the weak output beam from the strong incident beams when an appropriate diaphragm is used. In determining the value of θ , however, we must make a compromise between the filtering effect and the output efficiency, because the coherence length l_c of this mixing process decreases rapidly with increasing θ according to the relation $l_c \approx \lambda/2n\theta^2$ (for $\theta \ll 1$), 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 . We have adopted a typical value $\theta \approx 1^\circ$ which gives $l_c \approx 0.7$ mm. In practice, the effective interaction length in our dye solutions has been limited by the absorption length l_a (the reciprocal of the absorption coefficient) rather than by l_c , because both the incident and output light frequencies lie in a strongly absorbing region. It is generally preferable to choose the experimental conditions so that l_c is properly larger than l_a . Under this condition the correction for the wave-propagation effect in deriving the nonlinear susceptibility is accomplished only by considering the linear absorption properties.

The output beam was analyzed by a Spex 1302 double monochromator in order to minimize the scattering effect, and was detected by a photomultiplier. The output spectrum was finally recorded on a pen recorder with the use of a boxcar integrator. The observed intensity of the light output at ω_3 relative to those of the incident light at ω_1 and ω_2 was in the order of 10^{-8} ~ 10^{-5} , and the output light spectrum was observed with good signal-to-noise ratio by the present experimental system.

In the experiments of optical harmonic generation and mixing, it is generally desirable to use a reference nonlinear material in which the same type of nonlinear process occurs. This was impossible in our experiment because of the great difficulty in finding a material with known frequency characteristics and sufficient output efficiency. We therefore always monitored the intensity and the spatial and temporal properties of the incident beams in order to make proper corrections or normalizations for the change of the

incident beam properties.

In order to derive correct dispersion characteristics of nonlinear susceptibility from the measured frequency response of the output beam intensity, the correction for the wave-propagation effect is necessary, as described in Sec. VII of paper I. In the range of small frequency difference $|\omega_2 - \omega_1|/2\pi c$ below about 30 cm^{-1} , the dispersion of linear optical properties of the sample was negligible and the correction was almost unnecessary. In the range of larger values of $|\omega_2 - \omega_1|$, we have made the correction for the variation of absorption coefficient at frequencies ω_1 , ω_2 , and ω_3 by the use of Eq. (56) of paper I.

III. EXPERIMENTAL RESULTS

The measurements were made mostly on a dye solution, 1,1'-diethyl-4,4'-quinocyanine iodide in ethanol as mentioned in Sec. I. Figure 2 shows the measured absorption spectrum of the solution corresponding to the $S_0 \rightarrow S_1$ singlet-singlet transition with which the incident light waves are resonant within its broad bandwidth. In the figure are simultaneously shown the spectra of both the incident and output light waves under a typical experimental condition. For the measurement of nonlinear dispersion, ω_1 was usually fixed and the output light intensity at ω_3 was measured with the scanning of ω_2 . The dye concentration of the solution was adjusted to give an optimum signal-to-noise ratio which depends on the absorption coefficient and the sample length. Typical concentration was $\sim 2 \times 10^{-3} M$ which gave the absorption coefficient of $\sim 2 \times 10^2 \text{ cm}^{-1}$ at 5930 \AA in wavelength. The cell length was nearly equal to the absorption length.

Figure 3 shows a typical measured result of the absolute value of the nonlinear susceptibility $|\chi^{(3)}(\omega_3 = 2\omega_1 - \omega_2)|$ which exhibits a clear feature of the Rayleigh-type resonance enhancement at lower values of $\omega_1 - \omega_2$. In this measurement ω_1 was around the center of the absorption band, and the polarizations of two input light fields were linear and orthogonal. The correction for the wave-propagation effect was negligible, because the change of the linear-absorption coefficient over the scanned range of $\omega_1 - \omega_2$ was very small. It is found that the measured result can well be fitted within the experimental error to the theoretical curve given by

$$|\chi^{(3)}| = \left| \frac{iK}{[1 + i(\omega_2 - \omega_1)T'_1][1 + i(\omega_2 - \omega_1)T_2]} + \chi_{NR}^{(3)} \right|, \quad (1)$$

where T'_1 , T_2 , and $\chi_{NR}^{(3)}/K$ are the adjustable parameters corresponding to the effective longitudinal-

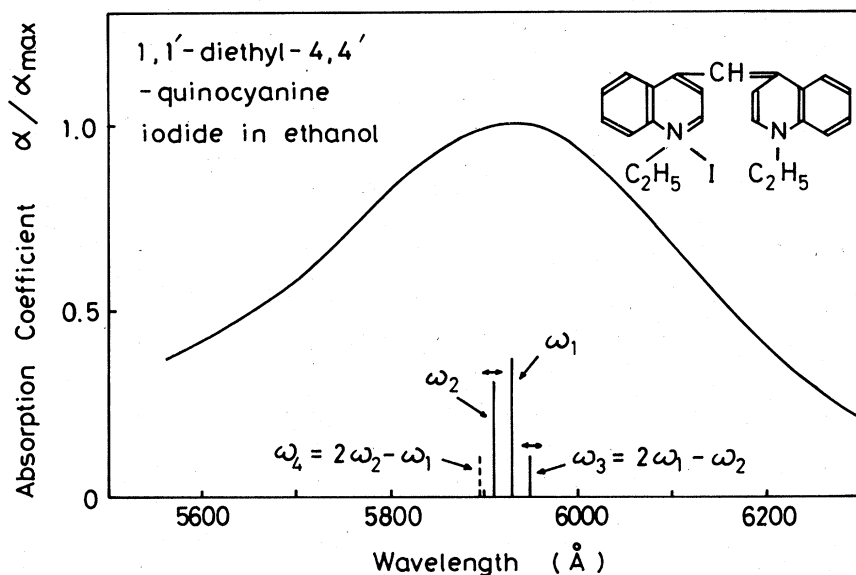


FIG. 2. Absorption spectrum of $S_0 \rightarrow S_1$ electronic transition of cyanine dye solution, 1,1'-diethyl-4,4'-quinocyanine iodide in ethanol. Typical spectral positions of both the incident and output light waves are simultaneously indicated. The constitutional formula of the dye molecule is also shown.

relaxation time, the transverse relaxation time and the ratio of nonresonant to resonant part of the susceptibility, respectively. The Rayleigh-type resonant part of $\chi^{(3)}$ (with $K < 0$) in Eq. (1) has been derived in Secs. II and IV of paper I on the basis of an inhomogeneously broadened two-

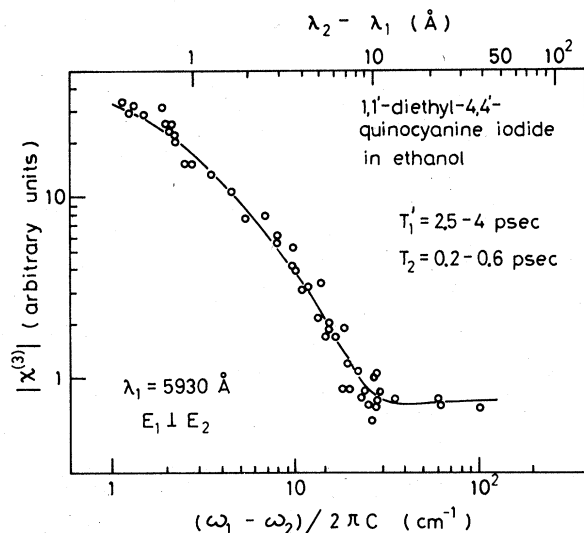


FIG. 3. Typical measured frequency response of the absolute value of the third-order nonlinear susceptibility $|\chi^{(3)}|$ for a dye solution, 1,1'-diethyl-4,4'-quinocyanine iodide in ethanol. The fixed frequency ω_1 (5930 Å in wavelength) is around the center of the absorption band. Two incident light fields are polarized linearly and orthogonally. The open circles indicate the measured points. The solid line denotes the best theoretical fit of Eq. (1) (see text). In consideration of the limited accuracy of the fitting, the values of T_1' and T_2 are determined with the errors as indicated in the figure.

level model. The solid line in Fig. 3 has been calculated by Eq. (1) with $T_1' = 3.5$ ps, $T_2 = 0.35$ ps and $\chi_{NR}^{(3)}/K = 0.02$. In determining these parameters, we must consider the errors originating from the limited accuracy of optimum fitting between the theoretical curve and the experimental points. The ultrashort relaxation times thus determined with this kind of error are indicated in the figure. For the determination of T_1' and T_2 with an improved accuracy, it is necessary to perform the measurements in the range of much lower $\omega_1 - \omega_2$ as well as to reduce the random deviation of the data; but doing so was impractical here due to the instrumental limitations. When the spectral cross-relaxation effect cannot be ignored, the value of T_1' determined here should be interpreted as a combined relaxation time $T_1' = (T_1^{-1} + T_3^{-1})^{-1}$, where T_1 is the pure longitudinal-relaxation time and T_3 is the cross-relaxation time (see Sec. IV of paper I). The additional term of $\chi^{(3)}$ arising from the inverse spectral-diffusion process [Eq. (35) of paper I] may influence, in general, the determination of T_1' . Its contribution cannot be evaluated from the present results, due to the limited experimental accuracy, but it is not expected to affect seriously the result of analysis as discussed in paper I. The result of Fig. 3 shows that the homogeneous width (about 5 Å in wavelength) is much smaller, by about two orders of magnitude, than the total width of the absorption band, which is then found to be highly inhomogeneously broadened. The origins of the inhomogeneous broadening in dye solutions may be attributed partly to the inhomogeneous environmental molecular field and partly to the dense distribution of vibrational and rotational sublevels.

Another feature of measured $|\chi^{(3)}|$ has been obtained for the same dye solution with the two incident laser fields of parallel linear polarizations. In this case a marked interference effect between the resonant and nonresonant terms of the nonlinear susceptibility appeared, as shown in Fig. 4. The spectrum of $|\chi^{(3)}|$ for one sign of $\omega_2 - \omega_1$ is much different from that for the reversed sign of $\omega_2 - \omega_1$, and a dip exists in one of the two spectra. This feature can well be understood based on Eq. (1) if $\chi_{NR}^{(3)}$ takes a real value and the ratio $\chi_{NR}^{(3)}/K$ is fairly large. Equation (1) can be rewritten after a rearrangement as

$$|\chi^{(3)}| = \left\{ \left[\frac{K(T_1' + T_2)\omega_d}{[1 + (\omega_d T_1')^2][1 + (\omega_d T_2)^2]} + \chi_{NR}^{(3)} \right]^2 + \left[\frac{K(1 - T_1' T_2 \omega_d^2)}{[1 + (\omega_d T_1')^2][1 + (\omega_d T_2)^2]} \right]^2 \right\}^{1/2}, \quad (2)$$

where $\omega_d = \omega_2 - \omega_1$. The calculated result of Eq. (2) has been shown as two solid lines in Fig. 4 in which adjustable parameters have been chosen to be $T_1' = 1.0$ ps, $T_2 = 0.30$ ps, and $\chi_{NR}^{(3)}/K = 0.24$ so as to fit the experimental points. The agreement between the theory and the experiment seems to be reasonably good in view of the simplified theoretical model. By taking into account the accuracy of the fitting, the relaxation times T_1' and T_2 were determined with the errors as indicated in the figure. The value of T_2 agrees with that in Fig. 3 within the experimental error as expected. As for the value of T_1' the agreement is not satisfactory. We will discuss this point in the next

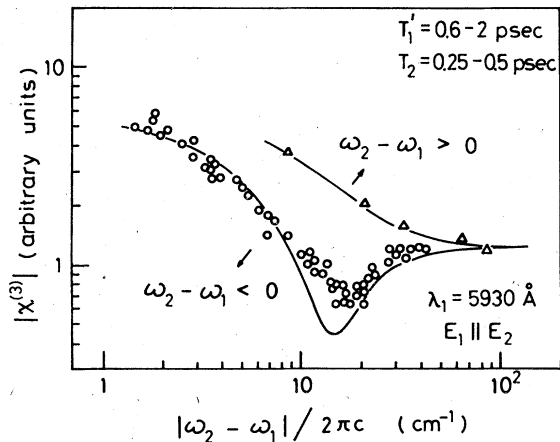


FIG. 4. Measured frequency response of $|\chi^{(3)}|$ for the same dye solution as in Fig. 3 showing the pronounced interference effect between resonant and nonresonant terms. The polarization condition of incident light waves is different from that in the case of Fig. 3. Note the remarkably different spectra for different signs of $\omega_2 - \omega_1$. The solid lines are the best theoretical fit of Eq. (2) (see text). The values of T_1' and T_2 with the errors are determined as indicated in the figure.

section. The large difference of the values of $\chi_{NR}^{(3)}/K$ in Fig. 3 and Fig. 4 may be interpreted thus: the symmetry properties of the energy levels contributing to the resonant and nonresonant terms of $\chi^{(3)}$ might be different, and so cause the different results for the change of polarization properties. The existence of the nonresonant term $\chi_{NR}^{(3)}$ and the resulting interference effect are obstructive to the purpose of the determination of relaxation times. However, the appearance of this effect proves a certain reliability of both the theory and the experiment. In some cases, the interference effect will serve to give new information on the nonlinear susceptibility, as has been demonstrated in the cases involving Raman-type resonance.⁷⁻⁹ In the present case $\chi_{NR}^{(3)}$ was found to have a negative real value.

A problem of common interest in the nonlinear spectroscopy concerned with relaxation processes is the dependence of the homogeneous width or the relaxation time on the spectral position within the inhomogeneous broadening. In the study of saturation spectroscopy of gases,¹⁰ the measurement along this line has been performed. In our mixing experiment this type of behavior has been studied by examining the variation of the frequency response of $|\chi^{(3)}|$ with the change of the center frequency ω_1 which was fixed during the measurement of $|\chi^{(3)}|$ as a function of $\omega_2 - \omega_1$. The results are shown in Fig. 5 for another sample of the same dye solution. The position of ω_1 (λ_1 in wavelength) has been varied over the HWHM (half-width at half maximum) of nearly the entire absorption spectrum. It should be noted in Fig. 5 that different curves have properly been shifted vertically with respect to each other for the ease of observation, and therefore relative magnitudes for different curves are meaningless. This does not affect the determination of relaxation times, which is dependent only on the frequency characteristics of $\chi^{(3)}$. The measurements have been made with $\omega_2 - \omega_1 < 0$ for (a), (b), and (c) and with $\omega_2 - \omega_1 > 0$ for (d) and (e) due to an experimental restriction. This does not complicate the analysis of the results, because the relative contribution of the nonresonant part of $\chi^{(3)}$ in this case was too small to be measured. The scanned range of $|\omega_2 - \omega_1|$ has been extended to a fairly large fraction of the spectral width of the absorption band (~ 760 cm⁻¹ HWHM). In view of this situation the wave-propagation factor (Sec. VII of paper I) has correctly been taken into account in deriving the nonlinear susceptibility $\chi^{(3)}$. Moreover, we must be careful to deduce the relaxation times by fitting the experimental data to the theoretical curve of Eq. (1) which has been derived on the assumption

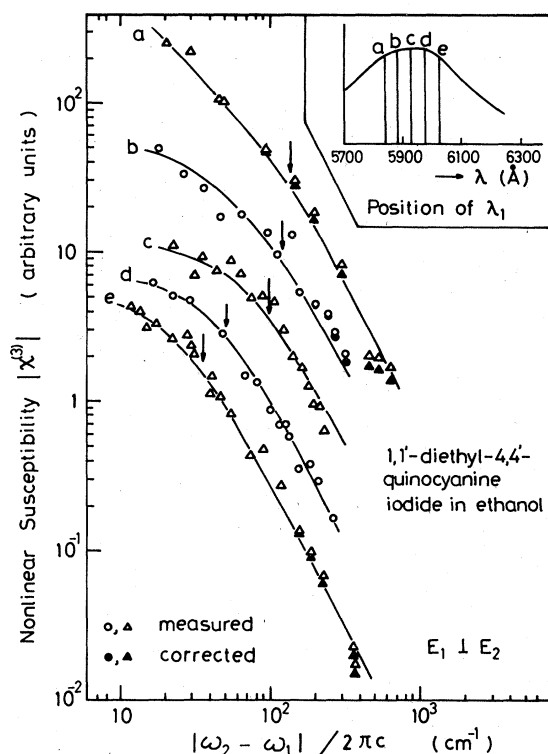


FIG. 5. Change of the frequency response curve of $|\chi^{(3)}|$ when the frequency ω_1 (λ_1 in wavelength) of one incident light is varied within the broad-absorption spectrum of a dye solution, 1,1'-diethyl-4,4'-quinocyanine iodide in ethanol. The corrected points are the results after making the deconvolution of the effect of finite spectral width. The spectral position of λ_1 at which the measurements were made are indicated in the insertion [(a) 5845 Å, (b) 5880 Å, (c) 5930 Å, (d) 5980 Å, (e) 6025 Å]. The solid lines are the best theoretical fit of the resonant part of Eq. (1) (see text). The vertical arrows indicate the positions where $|\omega_2 - \omega_1| = T_2^{-1}$ holds. Because only the frequency response of $|\chi^{(3)}|$ is important for the determination of relaxation times, different curves in Fig. 5 have properly been shifted vertically with respect to each other for the ease of observation. Therefore, relative magnitudes of $|\chi^{(3)}|$ for different curves are meaningless.

$$(T_1')^{-1}, T_2^{-1}, |\omega_2 - \omega_1| \ll (\Delta\omega)_i, \quad (3)$$

where $(\Delta\omega)_i$ is the inhomogeneous width. When the condition of Eq. (3) is not a good approximation, an appropriate correction to the measured frequency characteristic of $|\chi^{(3)}|$ is necessary for the comparison with the curve given by Eq. (1). In the Appendix of the present paper a practical way is shown of doing this task, which corresponds to a deconvolution procedure eliminating the effect of finite width and shape of the resonant absorption spectrum. The experimental points after this correction have been shown as closed symbols in Fig. 5. It is found that the effect of

the correction is very small, being almost within the experimental error, and that the expression of Eq. (1) for the broad-band limit is applicable in a wide range of $|\omega_2 - \omega_1|$. The solid lines are the calculated results of Eq. (1) neglecting $\chi_{NR}^{(3)}$ and with the parameters (a) $T_1' = 2.0$ ps, $T_2 = 0.038$ ps, (b) $T_1' = 0.18$ ps, $T_2 = 0.044$ ps, (c) $T_1' = 0.11$ ps, $T_2 = 0.053$ ps, (d) $T_1' = 0.17$ ps, $T_2 = 0.10$ ps, and (e) $T_1' = 0.37$ ps, $T_2 = 0.15$ ps. The vertical arrows in the figure indicate the positions where the relation $|\omega_2 - \omega_1| = T_2^{-1}$ holds. As mentioned before, the determination of relaxation times is necessarily accompanied by an error originating from the limited accuracy of optimum fitting. The relaxation times thus determined with this error are shown in Fig. 6 as a function of the spectral position. A systematic variation of T_2 and a noticeable variation of the ratio T_1'/T_2 can be recognized. These results will be of value for investigating the detailed nature of molecular interactions and energy transfer within the broad bandwidth of molecular excited states.

In the course of the measurement we have found an unexpected and serious feature of dye solutions, in that the frequency response of the nonlinear susceptibility $|\chi^{(3)}|$ changes largely from sample to sample even for the same kind of dye solution. A prominent feature of this kind is shown in Fig. 7 for three different samples of the same dye compound which have been synthesized at different times. Remarkable differences in nonlinear spectroscopic properties can be seen, although these

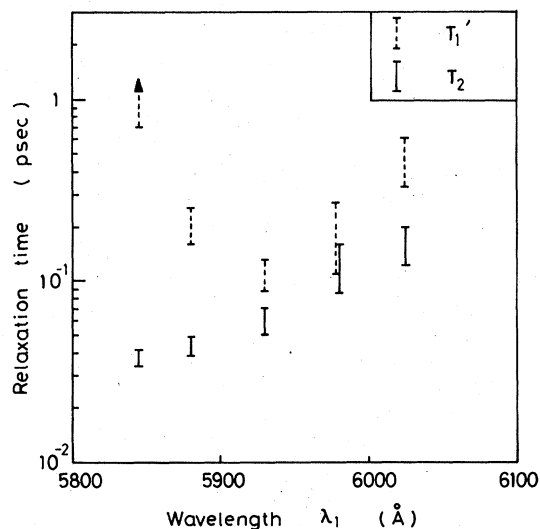


FIG. 6. Variation of the relaxation times (T_1' and T_2) with the spectral position derived from the results of Fig. 5. The errors originate from the limited accuracy of the fitting between theoretical curves and measured points.

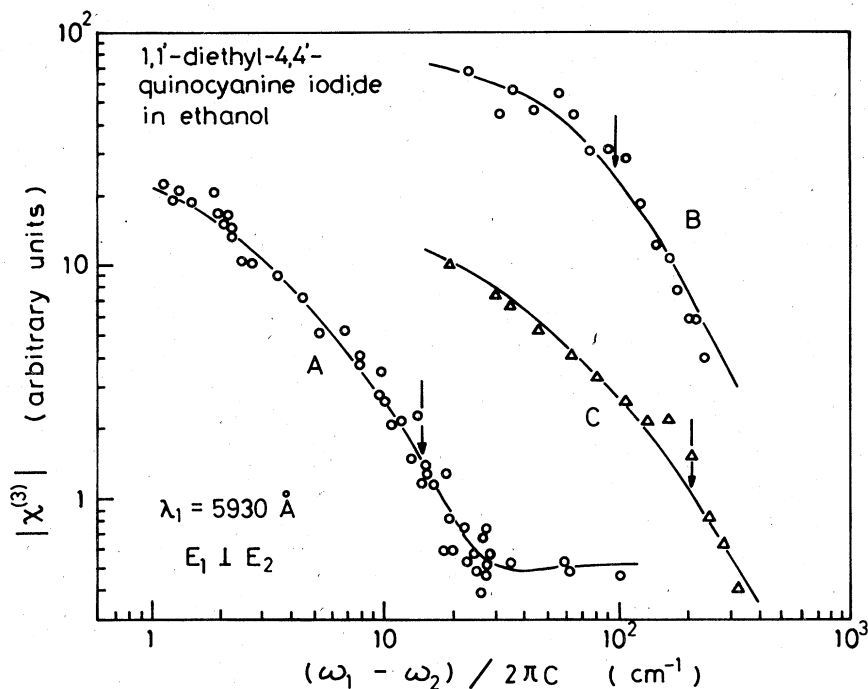


FIG. 7. Frequency response curves of $|\chi^{(3)}|$ which are much different for different samples of the same dye compound but of different origins of preparation. All samples *A* (same as in Fig. 3 and 4), *B* (same as in Fig. 5) and *C* are the dye solution, 1,1'-diethyl-4,4'-quinocyanine iodide in ethanol. The solid lines are the best theoretical fit of Eq. (1), and the vertical arrows indicate the positions of $\omega_1 - \omega_2 = T_2^{-1}$ corresponding to the values of $T_2 = 0.36$ psec (*A*), 0.053 psec (*B*) and 0.025 psec (*C*). Relative magnitudes of $|\chi^{(3)}|$ for different curves are meaningless for the same reason as described in the caption of Fig. 5.

samples showed no appreciable differences in the linear-absorption spectra and the result for a specific sample was sufficiently reproducible. As indicated in the figure, the change of T_2 determined by fitting the theoretical curve extends over about one order of magnitude. A similar kind of change has also been found for a specific sample, when it deteriorates when left either in the state of solution in several weeks, or even in the state of powder for a much longer period. At present we do not know and therefore cannot control the main factors which bring about such changes. This fact makes it difficult to perform a systematic study of relaxation properties of dye molecules and complicates the microscopic interpretation of the experimental results. From another point of view, however, this fact implies a possibility of new applications of nonlinear mixing spectroscopy. A brief discussion of this problem will be given in the next section.

We have also attempted to measure the frequency response of $|\chi^{(3)}|$ for other dye solutions with other solvent and/or other solute such as 1,1'-diethyl-4,4'-quinocyanine iodide in ethylene glycol, cresyl violet in ethanol, DODCI (3,3'-diethyl-oxadicyanocyanine iodide) in ethanol, and rhodamine 6 G in water. Although the available data were rather limited compared with the previous dye solution, these new solutions exhibited a variety of nonlinear spectra. The value of T_2 evaluated from these results covered a wide range of 0.02–2 ps. The variation of relaxation

times with the sample and experimental conditions similar to that described before has also been found even in a specific kind of dye solution. It seems therefore to be difficult or even meaningless to specify a characteristic value of T_2 for a specific dye compound unless main conditions sensitively affecting the nonlinear spectroscopic properties are specified.

IV. DISCUSSION AND CONCLUSION

In the present study we have demonstrated for the first time the feasibility of measuring the frequency characteristics of the nonlinear susceptibility associated with the resonant Rayleigh-type mixing. The main features of the measured frequency response were in good agreement with the theoretical predictions. Thus we were able to determine the ultrashort relaxation times associated with electronic excited states of dye solutions with reasonable accuracies.

The values of the transverse or phase relaxation time T_2 were found to lie mostly in the subpicosecond region and to be distributed over a wide range of 0.02–2 ps depending on the dye materials, solvents, spectral positions, and the conditions of sample preparation and deterioration as described previously. These values can be compared with those of dye solutions determined by other methods. Mourou³ derived the value of $T_2 = 0.6 - 1$ ps for cryptocyanine in methanol by means of spectral hole burning with a mode-locked ruby laser. From the nonlinear absorption

characteristics of an intense laser light, Vahey and Yariv⁴ estimated the value of $T_2 = 0.1 - 1$ ps for cryptocyanine in methanol and $T_2 = 0.4 \pm 0.2$ ps for DDI (1,1'-diethyl-2,2'-dicarbocyanine iodide) in glycerin. Although dye materials in these experiments are different from ours, it seems reasonable that our result gives roughly the same order of magnitude for T_2 as those described above. Garside and Lim¹¹ made a numerical analysis of ultra-short pulse generation in mode-locked dye lasers on the assumption of $T_2 = 0.05$ and 0.065 ps. Our experimental result provides a basis for the existence of such short relaxation times. The value of T_2 in the subpicosecond range has been explained by a simple molecular collision mechanism in liquids.⁴ The results obtainable by the Rayleigh-type mixing method under a variety of experimental conditions may contribute to a more advanced understanding of the relaxation mechanisms. Our method will provide a value of T_2 with improved reliability because it can in principle be determined only from the frequency characteristics of the mixing process without knowing any other physical parameters.

The variation of T_2 shown in Fig. 6 is not easy to interpret, but seems to be physically reasonable, because an excited state with higher energy (shorter transition wavelength) may, in general, tend to have a higher relaxation rate. Although the correct interpretation has not been accomplished, it is suggested that this behavior will be associated with the variation of the nature of different vibrational states in the excited electronic state. A discussion of dephasing mechanism of vibrationally excited molecules in liquids has been given by Fischer and Laubereau.¹² Further investigation of this characteristic will be of value in clarifying the dynamical behavior of excited molecules. This kind of result also provides basic data for advanced studies of the mode-locking behavior of tunable dye lasers and of ultra-short pulse propagation in dye amplifiers and saturable absorbers.

The large dependence of T_2 on the sample preparation and deterioration is much more difficult to interpret. The occurrence of some uncontrollable chemical processes such as polymerization, isomerization, or mixing of impurities might be suggested, but none is conclusive at present. It is well known that most kinds of dye solutions suffer more or less from the deterioration of their quality when they are used as materials in quantum electronic devices. The large sample dependence of $\chi^{(3)}$ described here seems to be related, at least partly, to this general feature of dye solutions. Much effort in both physical and chemical aspects is required to

clarify the underlying mechanisms and to find the conditions under which reproducible results can be obtained. We are convinced, however, that, when this task is accomplished, the nonlinear spectroscopic method of the present type will serve as a sensitive means of discriminating new aspects of molecular states which could not easily be known from other types of experiments.

As for the longitudinal-relaxation time, less accurate information has been achieved here, and a more careful interpretation of the relaxation time is required. The effective longitudinal-relaxation time T'_1 determined by fitting Eq. (1) has been found to be distributed in a range of $0.1 \sim 5$ ps. Because of the relation $T'_1 = (T_1^{-1} + T_3^{-1})^{-1}$, the value of T'_1 gives a lower limit of both T_1 and T_3 , the longitudinal- and spectral cross-relaxation times, respectively. It is known also that the shorter of T_1 and T_3 takes a value between T'_1 and $2T'_1$. Because T_1 corresponds to the fluorescence lifetime and T_3 is expected to have very short value in dye solutions,^{3,4} the relation $T_3 < T_1$ will hold in most situations. It is therefore inferred that measured T'_1 is roughly an indication of the cross-relaxation time. This interpretation is consistent with the fact that the values of T'_1 determined here are much shorter than the fluorescence lifetime of dye solutions which generally lies in the range of $10^{-9} \sim 10^{-11}$ s, and also consistent with the value of T_3 evaluated by Vahey and Yariv.⁴ The dye, 1,1'-diethyl-4,4'-quinocyanine iodide, for which the measurement of $\chi^{(3)}$ was made in detail, is nonfluorescent. This has been explained by a rapid quenching mechanism of excited electronic energy due to the steric effect.^{5,6} For such a dye, both T_1 and T_3 are expected to be very short, which is also consistent with our observations. Because T_1 is usually much longer than T_2 , it can alternatively be measured in some cases by a conventional transient emission or absorption method. The value of T_1 thus determined can be combined with T'_1 determined by the mixing to give a more accurate value of T_3 through the relation $T'_1 = (T_1^{-1} + T_3^{-1})^{-1}$. The introduction of partially transient technique in the mixing experiment will also bring a possibility of separate determination of this kind of combined relaxation times.

It is to be remembered that, as described in paper I, the theoretical result of the nonlinear susceptibility is more model-dependent in the part closely connected to T_1 and T_3 than to T_2 . When a multilevel model is appropriate, the effective longitudinal-relaxation time includes the contribution of energy relaxation to other levels (Sec. V of paper I). In some cases, an additional term of $\chi^{(3)}$ other than that given in Eq. (1) must be taken into account for the reliable determina-

tion of T_1 and T_3 . More relaxation parameters than T_1 , T_2 , and T_3 may be required in certain cases for the more correct description of a material system. The discrepancy of the values of T_1 in Figs. 3 and 4 may arise partly from this model-dependent nature. The correct derivation and interpretation of the longitudinal- and cross-relaxation times depend on how the complicated energy-level structure of real materials can reasonably be approximated by a simple idealized model. This problem must further be explored based on the individual nature of a specific material to be investigated. The study of microscopic relaxation mechanisms involved in T_1 , T_2 , and T_3 thus determined is also a problem remaining to be solved.

Since the basic concept of the resonant Rayleigh-type three-wave mixing is not limited to a specific kind of material group, it can further be applied to investigate relaxation processes associated with excited states of other kinds of materials such as inorganic crystals, although the conquest of additional experimental difficulties and the careful interpretation of results are required.

In conclusion we have shown that the resonant Rayleigh-type three-wave mixing is really a useful spectroscopic means for the determination of ultrashort relaxation times in the range of 10^{-12} – 10^{-14} s. In view of the undeveloped situation of ultrashort pulse laser technique in this extreme time region, the present method will serve as a practical and reliable way for the above purpose with further refinements in both the theory and the experiment.

ACKNOWLEDGMENTS

The authors wish to thank Dr. M. Banno of the Japanese Research Institute for Photosensitizing Dyes Co., Ltd. for his kind facility of providing us with various dyes used in the present experiment. The present work was supported by a Grant-in-Aid for Scientific Research from the Japanese Ministry of Education.

APPENDIX: DISPERSION CHARACTERISTICS OF $\chi^{(3)}$ INCORPORATING SPECTRAL SHAPE

The third-order nonlinear susceptibility $\chi_R^{(3)}(\omega_3 = 2\omega_1 - \omega_2)$ for an inhomogeneously broadened two-level model is generally given by

$$\chi_R^{(3)} = \frac{-2i |\mu_{ba}|^4 N \rho_D^{(0)} \hbar^{-3}}{T_1^{-1} + i(\omega_2 - \omega_1)} \times \left[\frac{I_\alpha}{2[T_2^{-1} + i(\omega_2 - \omega_1)]} - \frac{I_\beta}{i(\omega_2 - \omega_1)} \right], \quad (\text{A1})$$

$$I_\alpha = \int_0^\infty g(\omega_0) \left[\frac{1}{T_2^{-1} + i(\omega_0 - \omega_3)} + \frac{1}{T_2^{-1} - i(\omega_0 - \omega_2)} \right] d\omega_0, \quad (\text{A2})$$

$$I_\beta = \int_0^\infty g(\omega_0) \left[\frac{1}{T_2^{-1} + i(\omega_0 - \omega_3)} - \frac{1}{T_2^{-1} + i(\omega_0 - \omega_1)} \right] d\omega_0, \quad (\text{A3})$$

where T_1 and T_2 are the longitudinal and transverse relaxation times, N is the atomic number density, μ_{ba} is the electric-dipole matrix element, $\rho_D^{(0)} = \rho_{aa}^{(0)} - \rho_{bb}^{(0)}$ is the equilibrium value of the difference of diagonal density-matrix elements, and $g(\omega_0)$ is the normalized distribution function characterizing inhomogeneous broadening (see Sec. II of paper I).

When the variation of $g(\omega_0)$ is not slow enough compared with the remaining part of the integrand of Eqs. (A2) and (A3), the function $g(\omega_0)$ cannot be taken outside the integral, and the integration must be performed on an appropriate assumption of functional form of $g(\omega_0)$.

The shape of the absorption spectrum corresponding to $S_0 - S_1$ electronic transition of dye molecules may be approximated by a Lorentzian shape for the convenience of integration. We therefore assume $g(\omega_0)$ to be of the form

$$g(\omega_0) = \frac{(\Delta\omega)_i}{\pi [(\Delta\omega)_i^2 + (\omega_0 - \omega_c)^2]}, \quad (\text{A4})$$

where ω_c and $(\Delta\omega)_i$ are the center frequency and the HWHM (half-width at half-maximum) of the inhomogeneous broadening, respectively. In view of the conditions $\omega_c/(\Delta\omega)_i \gg 1$, $\omega_j T_2 \gg 1$, $|(\omega_c - \omega_j)/\omega_c| \leq (\Delta\omega)_i$ ($j = 1, 2, 3$), the result of integration of Eqs. (A2) and (A3) can be expressed in good approximation as

$$I_\alpha \approx \frac{1}{(\Delta\omega)_T + i(\omega_c - \omega_3)} + \frac{1}{(\Delta\omega)_T - i(\omega_c - \omega_2)}, \quad (\text{A5})$$

$$I_\beta \approx \frac{1}{(\Delta\omega)_T + i(\omega_c - \omega_3)} - \frac{1}{(\Delta\omega)_T + i(\omega_c - \omega_1)}, \quad (\text{A6})$$

where $(\Delta\omega)_T = (\Delta\omega)_i + T_2^{-1}$ represents the HWHM of the total spectrum.

Inserting the expressions of Eqs. (A5) and (A6) into Eq. (A1) and making some rearrangements of the resulting formulas, we finally obtain the expression for the absolute value of $\chi_R^{(3)}$ as

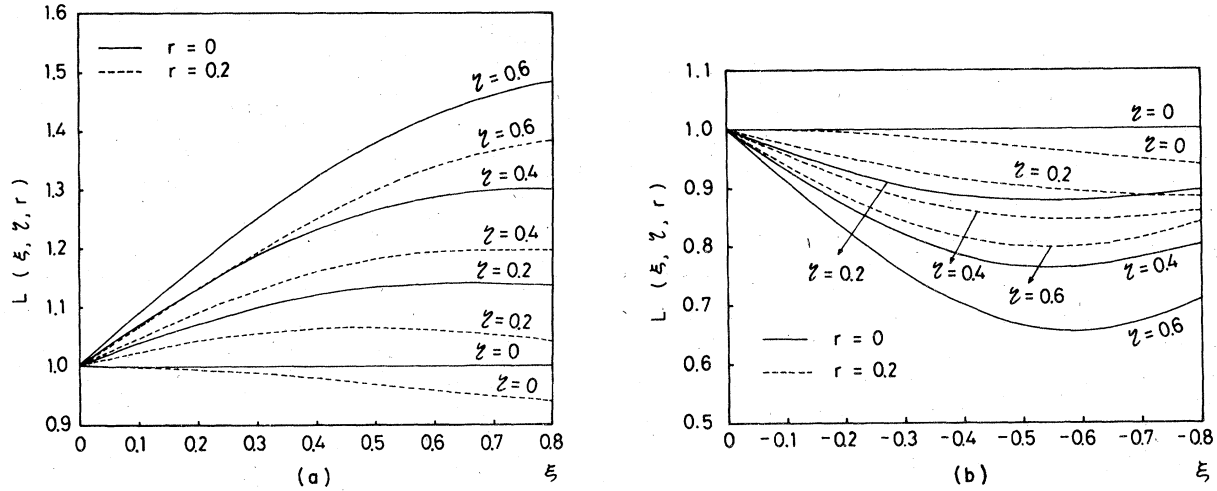


FIG. 8. Calculated curves of $L(\xi, \eta, r)$, a correction factor for the frequency response of the nonlinear susceptibility, representing the effect of finite spectral width of a material transition. $\xi = (\omega_2 - \omega_1)/(\Delta\omega)_T$, $\eta = (\omega_c - \omega_1)/(\Delta\omega)_T$, $r = T_2^{-1}/(\Delta\omega)_T$; ω_c and $(\Delta\omega)_T$ are the central frequency and the HWHM of the absorption band, respectively. (a) $\xi\eta > 0$, (b) $\xi\eta < 0$.

$$\begin{aligned}
 |\chi_R^{(3)}| &= |\chi_{RO}^{(3)}| L(\xi, \eta, r), \\
 |\chi_{RO}^{(3)}| &= \frac{2\pi |\mu_{ba}|^4 N \rho_D^{(0)} T_1 T_2 \hbar^{-3} f}{\{[1 + T_1^2(\omega_2 - \omega_1)^2][1 + T_2^2(\omega_2 - \omega_1)^2]\}^{1/2}}, \\
 f &= \frac{|(1+r)^2 + \eta^2(1-r)^2|^{1/2}}{\pi(\Delta\omega)_T(1+\eta^2)^{3/2}}, \\
 L(\xi, \eta, r) &= (1+\eta^2) \left[\frac{(1+r-\xi^2)^2 + [2\xi + \eta + r(\xi-\eta)]^2}{[(1+r)^2 + \eta^2(1-r)^2][(1+\xi^2 - \eta^2)^2 + 4\eta^2]} \right]^{1/2},
 \end{aligned} \tag{A7}$$

where $\xi = (\omega_2 - \omega_1)/(\Delta\omega)_T$, $\eta = (\omega_c - \omega_1)/(\Delta\omega)_T$ and $r = T_2^{-1}/(\Delta\omega)_T$.

The first factor $|\chi_{RO}^{(3)}|$ shows the same frequency characteristic for the variable $\omega_2 - \omega_1$ as that of the resonant part of Eq. (1) corresponding to the case of broadband limit $[(\Delta\omega)_i \gg T_2^{-1}, |\omega_2 - \omega_1|]$. Therefore, the function $L(\xi, \eta, r)$ represents a correction factor for the finite inhomogeneous width, and it has been normalized so that $L(0, \eta, r) = 1$. In the limit of $r \rightarrow 0$, the factor f becomes $g(\omega_1)$.

The calculated result of $L(\xi, \eta, r)$ is shown in Figs. 8(a) and 8(b). The analysis of the experimental data using this result can be carried out by a successive approximation in the following way. Because $(\Delta\omega)_T$ corresponds approximately to the HWHM of actual absorption band, ξ and η can immediately be known from a given condition

of input light frequencies. Then, we use $L(\xi, \eta, 0)$ as a first approximation to deduce $|\chi_{RO}^{(3)}|$ and to determine T_2 . The value of $r = T_2^{-1}/(\Delta\omega)_T$ thus obtained is used to give a second approximation of $L(\xi, \eta, r)$ which again serves to determine a more correct value of T_2 , and the same procedure is repeated. Actually only one or two cycles of this procedure is sufficient in most cases, because the correction factor L affects little the essential feature of the frequency response curve of $\chi^{(3)}$. The influence of the difference between Lorentzian and actual spectral shapes will therefore be insignificant because it brings about only very small higher-order deviations. As has been shown in Fig. 5, the amount of this correction is almost within the experimental error or within the accuracy of the fitting to theoretical curves in our present experiment.

¹T. Yajima and H. Souma, preceding paper, Phys. Rev. A **17**, 309 (1978). It will be referred to as paper I in the text.

²A part of this work has been presented at the Ninth

International Conference on Quantum Electronics, Amsterdam, 1976 (unpublished).

³G. Mourou, IEEE J. Quantum Electron. **11**, 1 (1975).

⁴D. W. Vahey and A. Yariv, Phys. Rev. A **10**, 1578

- (1974).
- ⁵Y. Miyazoe and M. Maeda, *Opto-Electron.* 2, 227 (1970).
- ⁶L. J. E. Hofer, R. J. Grabenstetter, and E. O. Wiig, *J. Am. Chem. Soc.* 72, 203 (1950).
- ⁷For example, see M. D. Levenson and N. Bloembergen, *Phys. Rev. B* 10, 4447 (1974).
- ⁸M. D. Levenson, C. Flytzanis, and N. Bloembergen, *Phys. Rev. B* 6, 3962 (1972).
- ⁹S. D. Kramer and N. Bloembergen, *Phys. Rev. B* 14, 4654 (1976).
- ¹⁰A. Javan, in *Laser Spectroscopy*, edited by S. Haroche, J. C. Pebay-Peyroula, T. W. Hänsch, and S. E. Harris (Springer-Verlag, New York, 1975), p. 439.
- ¹¹B. K. Garside and T. K. Lim, *Opt. Commun.* 8, 297 (1973); 12, 240 (1974).
- ¹²S. F. Fischer and A. Laubereau, *Chem. Phys. Lett.* 35, 6 (1975).