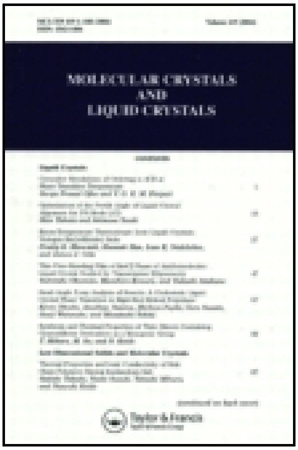

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Z-Scan Studies of Dispersion of the Complex Third-Order Nonlinearity of Nonlinear Absorbing Chromophores

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We have studied dispersion of the cubic nonlinear optical properties of organic and organometallic nonlinear absorbers. The results indicate that a multitude of excited states may be contributing to the resonances seen in the real and imaginary part of the complex hyperpolarizability. Attempts to understand the relation between the real and imaginary part of the hyperpolarizability in terms of a Kramers-Kronig transform are undertaken.

Keywords: hyperpolarizabilities; Kramers-Kronig analysis; nonlinear refraction; two-photon absorption

INTRODUCTION

There is much interest in nonlinear absorbing chromophores and in the determination of their two-photon absorption cross sections. This interest stems from the importance of the nonlinear absorption process for applications in photonics, nanophotonics and biophotonics [1]. Most studies of spectral dependences of the nonlinear absorption use the convenient method of two-photon induced fluorescence [2],

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however, many strong nonlinear absorbers show little or no fluorescence and that method gives no information on the accompanying nonlinear refraction. Investigations of the dispersion of the complex cubic optical nonlinear susceptibility $\chi^{(3)}$ or the molecular second hyperpolarizability γ are rather rare (e.g. [3]). We have performed studies of dispersion of the two-photon absorption cross sections and refractive nonlinearities of various nonlinear chromophores, among them organometallic compounds [4,5], using the technique of Z-scan [6]. This technique has an advantage of measuring the absolute values of the nonlinear absorption, without necessity of knowing the quantum efficiencies of the fluorescence with one-photon and two-photon excitation. However, the sensitivity of the technique is not as good as that for two-photon induced fluorescence which forces one to use amplified short pulse laser systems and high concentrations of two-photon dyes for investigations carried out in solutions. Nevertheless, information on the dispersion of the complex hyperpolarizabilities can be obtained and the emerging experimental data provide a challenge for their interpretation in terms of fundamental rules like eg those considered by Kuzyk *et al*. [7]. Investigations of the dispersion of the cubic nonlinearity are important for assessing the suitability of nonlinear chromophores for the application of their refractive nonlinearity in the presence of nonlinear absorption [8] and for verifying hypotheses like eg one of Peiponen [9] that the negative index behavior of a material (also called left-handed behavior) may be obtained through nonlinear effects.

EXPERIMENTAL

We have carried out our experiments using a laser system consisting of a Clark-MXR CPA-2001 regenerative amplifier operating at 775 nm and a Light Conversion TOPAS optical parametric amplifier. This system is capable of delivering pulses of ~150 fs length and in most measurements was operated at the repetition rate of about 100 Hz to minimize thermal effects [10,11] and photochemical decomposition of samples. The TOPAS was tuned to provide various output wavelengths for the measurements, using the idler – pump mixing, the second harmonic of the signal, the second harmonic of the idler or the signal itself for various wavelength ranges, 520 nm – 1600 nm being the overall wavelength region of interest, however, in practice the region being limited at short wavelengths by excessive one-photon absorption of the investigated dyes and at long wavelengths by low values of the nonlinear optical parameters. The measurements were carried out using the standard Z-scan technique in which the closed-aperture and open-aperture traces are obtained simultaneously and the measurements are carried out on spectroscopic 1 mm path length cells filled with solutions of the investigated chromophores and calibrated by measurements on plates of fused silica [12]. The scans were interpreted by fitting them with theoretical curves computed using the theory of Sheikh-Bahae *et al.* [6] and the real and imaginary part of the cubic hyperpolarizability γ was derived from the difference between the Z-scans for the cell filled with pure solvent and the cell with the solution of the investigated chromophore. Treating the nonlinear phase shift $\Delta\Phi$ as a complex quantity, $\Delta\hat{\Phi} = \Delta\Phi_{real} + i\Delta\Phi_{imag}$, we find the nonlinear refractive index n_2 of the solution from the relation:

$$n_{2,solution} - n_{2,solvent} = \frac{\Delta\Phi_{real,solution} - \Delta\Phi_{real,solvent}}{\Delta\Phi_{silica}} \frac{L_{silica}}{L_{solution}} n_{2,silica} \qquad (1)$$

in which we assume the nonlinear index of silica to be $3 \times 10^{-16}\,\mathrm{cm}^2/\mathrm{W}$ over the whole spectral range (cf [13] for the spectral dependence of n_2 for silica). L stands for the thickness of the active medium. The imaginary part of the complex nonlinear refractive index $\hat{n}_2$, which is related to the nonlinear absorption coefficient β, is also obtained from an analogous relation:

$$\mathrm{Im}(\hat{n}_{2,solution}) = \frac{\lambda\beta}{4\pi} = \frac{\Delta\Phi_{imag,solution}}{\Delta\Phi_{silica}} \frac{L_{silica}}{L_{solution}} n_{2,silica} \qquad (2)$$

The molecular parameters: real and imaginary part of the cubic hyperpolarizability γ and the two-photon cross section, σ_2 can then be obtained by assuming a linear dependence of the nonlinearity of the solution on concentration and using a Lorentz local field factor. Alternatively, it may be convenient to consider the extrapolated (to 100% of the chromophore content) values of the complex third-order susceptibility $\chi^{(3)}$ or the extrapolated values of the complex nonlinear index $\hat{n}_2$. One should note that such extrapolations can only be regarded as approximate, due to uncertainties about influence of different intermolecular interactions on the molecular hyperpolarizabilities and the local field corrections.

DISPERSION OF THE COMPLEX CUBIC NONLINEARITY

We present here three examples of the experimentally obtained dispersion of the complex hyperpolarizability. Although rigorous sum-over-states expressions are available for the hyperpolarizability and for the two-photon absorption cross section, they are not very

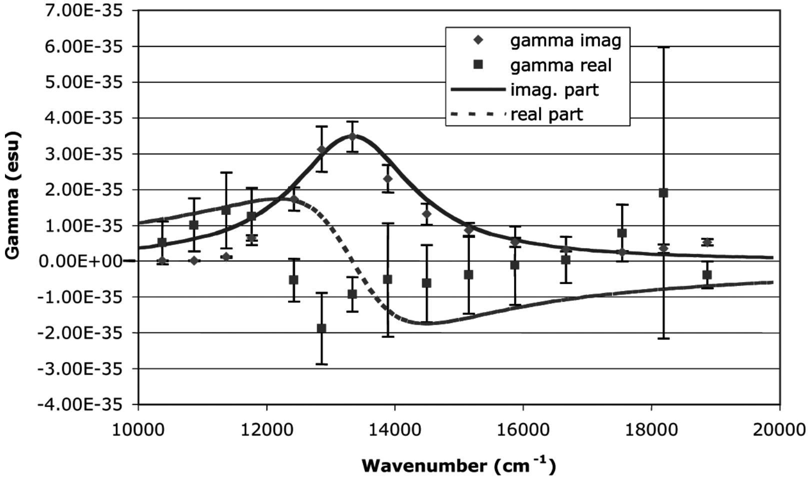

FIGURE 1 Dispersion of the complex hyperpolarizability of Coumarine 307 determined from Z-scan measurements on chloroform solution containing 6.36% of the dye. The full line is the fit by the imaginary part of a simple complex Lorentzian as described in the text and the dashed line is the real part of the same Lorentzian.

useful for interpretation of the experiment because of the large number of resonant terms that may be involved. Therefore, we use here an approach of approximating the nonlinear absorption spectra by simple Lorentz-like resonant terms. Figure 1 shows an example of experimentally determined dispersion curves for Coumarine 307 (Coumarine 503). This dye, one of two-photon absorbers investigated in the seminal paper of Xu and Webb [2], appears to have a very simple nonlinear absorption spectrum dominated by a single peak at about 750 nm, thus it may be taken as a convenient test case for analysing the dispersion of nonlinearity in organic chromophores.

The characteristic features of the dispersion characteristics are the presence of positive real part of the hyperpolarizability at wavelengths longer than ca 850 nm and rather sharp transition to negative values essentially in the whole shorter wavelength part of the spectrum. The Figure also shows an approximate fit of the spectral shape of the imaginary part of γ to a simple Lorentz-type complex expression:

$$\gamma = \frac{A}{\nu_1 - 2\nu - i\Gamma} \tag{3}$$

where the fit parameters are $\mathrm{A} = 8 \times 10^{-32}$, $\nu_1 = 26672\,\mathrm{cm}^{-1}$ and $\Gamma = 2280\,\mathrm{cm}^{-1}$. This approximation does not hold very well in the long wavelength (low energy) part of the spectrum, indicating that a single oscillator approach is not likely to be proper in this case and that the value of Γ responsible for the width of the spectral band is due to the distribution of the oscillator energies rather than to the damping mechanism itself. It is also seen that the real part of γ cannot be satisfactorily described by the real part of the same expression: there is a substantial frequency shift between the experimental and calculated dispersion curves, although the basic shapes of the dependences are similar and the magnitude of the experimental γ_{real} is quite well predicted.

Figure 2 shows a more complicated case of the dispersion of the hyperpolarizability in Rhodamine B chloride. In this case the two-photon absorption spectrum shows two overlapping bands which we approximate as a sum of two Lorentzians ($A_1 = 4.6 \times 10^{-31}$, $\nu_1 = 24600\,\mathrm{cm}^{-1}$ and $\Gamma_1 = 1480\,\mathrm{cm}^{-1}$, $A_2 = 5.0 \times 10^{-31}$, $\nu_2 = 28350\,\mathrm{cm}^{-1}$ and $\Gamma_2 = 1100\,\mathrm{cm}^{-1}$). At higher energies there is a reversal of sign of the nonlinear absorption coefficient, which becomes negative at 600 nm ($16667\,\mathrm{cm}^{-1}$): due to the presence of absorption bleaching. We have seen a similar behavior also in other chromophores investigated by us. The dashed line in the Figure denotes again the real part of the same sum of the two complex Lorentzians. It is clear that the

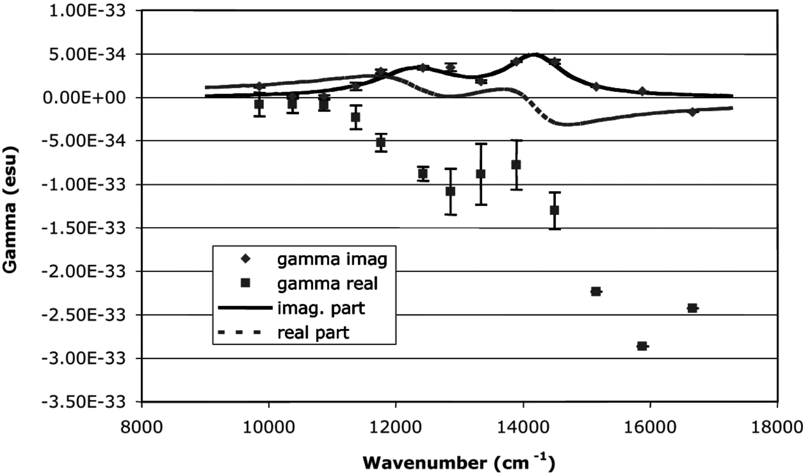

FIGURE 2 Dispersion of the complex hyperpolarizability of Rhodamine B chloride determined from Z-scan measurements on ethanol solution containing 1.0% of the dye. The full line is the fit by the imaginary part of a sum of two complex Lorentzians as described in the text and the dashed line is the real part of the same sum of Lorentzians.

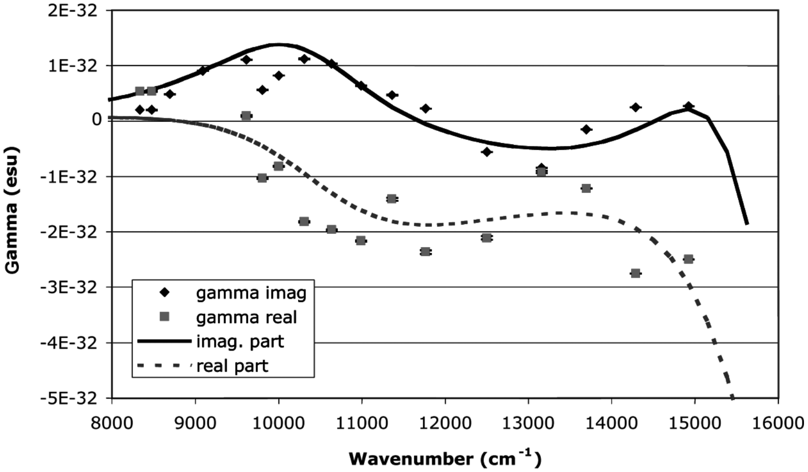

FIGURE 3 Dispersion of the complex hyperpolarizability of a nitro decorated organometallic dendrimer determined from Z-scan measurements on dichloromethane solution containing 1.0% of the dye. The full line is the fit by the imaginary part of an expression suggested in a previous paper [4] and the dashed line is the real part of the same expression.

experimentally determined real part of γ must contain contributions additional to those due to the two-photon resonances.

In a previous article [4] we have described a more complicated case of dispersion of the complex hyperpolarizability seen in measurements on an organometallic dendrimer. Figure 3 shows those results replotted and compared to the real and imaginary part of the expression suggested by us in the paper and taking into account the presence of two absorption bands capable of multiphoton absorption as well as absorption bleaching by the lower lying one-photon absorption band. In this case we have been able to obtain a reasonably good fit of both the real and the imaginary part of the hyperpolarizability, however, at a cost of using a relatively complicated expression containing many parameters whose values are quite difficult to predict theoretically or confirm in independent experiments.

KRAMERS-KRONIG ANALYSIS

We have shown above that the experimentally obtained dispersion of the complex hyperpolarizability does contain features showing that its real and imaginary parts derive at least in part from the same resonances. Approximating the two-photon spectra in terms of combinations of simple Lorentzians, or even more complicated expression derived from sum-over-states approaches, however, provides a rather limited insight into the origin of the refractive part of the nonlinearity. Another way of looking at the relation between the refractive and absorptive part of the nonlinearity should be in terms of the Kramers-Kronig relation which does not presume any specific functional forms of the dispersion. The linear optics Kramers-Kronig expression relating the imaginary and real part of a susceptibility χ can be written as

$$\mathrm{Re}[\chi(\omega)] = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{Im}[\chi(\omega')]}{\omega'^2 - \omega^2}\,\omega' d\omega \tag{4}$$

As discussed in the literature already in the early 1990s [14–16], with further developments in more recent time [9,17–19], the nonlinear optical analogues of this relation do exist. According to Sheikh-Bahae *et al.* [14,16], a straightforward extension of the relation between the linear susceptibilities is to consider a change of both the real and imaginary parts of the susceptibility at a frequency ω, brought about by the action of an additional field at a frequency ω_1. It follows that to obtain the frequency dependence of the *degenerate* real susceptibility $\mathrm{Re}[\chi^{(3)}(-\omega;\omega,-\omega,\omega)]$ one needs to

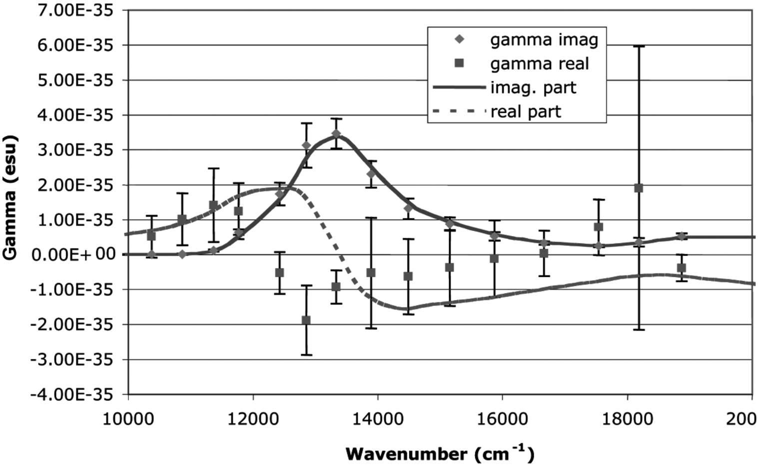

FIGURE 4 Data for Coumarine 307 from Figure 1 interpreted using the Kramers-Kronig transform. The data for the imaginary part of γ were smoothed as shown by the full line in the Figure and transformed as described in the text to give the real part of γ shown as the dashed line.

know the spectrum of the imaginary part of the *nondegenerate* susceptibility $\mathrm{Im}[\chi^{(3)}(-\omega;\omega,-\omega_1,\omega_1)]$. In other words, it is not sufficient to know the spectrum of degenerate two-photon absorption $\beta(2\mathrm{h}\nu)$, what is needed is the 2-D spectrum of absorption coefficient $\beta(\mathrm{h}\nu_1+\mathrm{h}\nu_2)$ i.e. values of the nonlinear absorption coefficient for any combination of the energies of two interacting photons. In terms of the hyperpolarizability the needed relation can be presented as:

$$\mathrm{Re}[\gamma(-\omega;\omega,-\omega,\omega] = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{Im}[\gamma(-\omega';\omega',-\omega,\omega)]}{\omega'^2-\omega^2}\omega' d\omega \tag{5}$$

Following Sheikh-Bahae *et al.* [14] we used the above relation, approximating the needed non-degenerate absorptive nonlinearity at $\omega'+\omega$ by the degenerate value at twice the mean frequency of $(\omega'+\omega)/2$. Figure 4 shows the data for Coumarine 307 interpreted this way. It can be seen that the transform gives results which are quite close to those obtained using a simple Lorentzian in Figure 1.

CONCLUSIONS

Measurements of dispersion of the complex third-order polarizability γ of nonlinear chromophores provide new interesting data and the need for better understanding of the role of various resonances in determining the value of the real part of the hyperpolarizability. It is obvious that to obtain a good description of the dispersion, apart from the two-photon absorption transitions one needs to take into account the presence of other processes such as absorption bleaching, however, they may be difficult to quantify since the determination of the relevant degenerate and nondegenerate nonlinear absorption spectra would require measurements of the effects against the background of strong one-photon absorption.

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