

## ESTIMATION OF RESONANT THIRD-ORDER HYPERPOLARIZABILITY OF BETA-CAROTENE FROM RAMAN AND ABSORPTION SPECTROSCOPY\*

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**Abstract.** A theoretical link based on two-level system is developed that permits the estimation of third-order hyperpolarizabilities from parameters measured by linear spectroscopic techniques of Raman resonance and absorption spectroscopy. In an attempt to gain experimental evidence for the proposed link, we have examined  $\beta$ -carotene in different organic solvents.

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### 1. Introduction

Third-order nonlinear optical properties of organic molecules have been subject of intense investigation recently because of their potential applications in frequency generation, optical switching and nonlinear spectroscopy [1]. Conjugated organic molecules have emerged as the most widely studied group because of the delocalization behaviour of their  $\pi$ -electrons which gives rise to large optical nonlinearities. Till recently, the structure, property relations for linear polarizabilities and third-order hyperpolarizabilities have been treated separately. Earlier attempts to predict hyperpolarizabilities of organic molecules from linear spectroscopic properties were made by Maloney et al. [2]. Recently Marder et al. [3] have developed derivative relations which provide a unified picture of the dependence of the polarizability and hyperpolarizability on the structure in organic polymethine dyes. We consider here the link that permits the estimation of third-order hyperpolarizabilities from parameters measured from linear spectroscopic techniques of Raman and absorption spectroscopy. Furthermore the experimental evidence will be presented that confirms this link.

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## 2. Connection Between Linear and Nonlinear Properties

The description of resonant optical process in organic systems is greatly simplified by using a two-level model. Using such a model, we consider here the connection between two photon-resonant third-order nonlinearity and linear optical properties measured from resonance Raman and absorption spectra. Under the condition of resonant enhancement, the intensity required to observe the nonlinear process is greatly reduced. This allows the nonlinear process to operate at lower power levels.

The third-order nonlinear susceptibility  $\chi^3$ , which describes stimulated Raman scattering is given in [4]

$$\chi^{(3)} = \frac{-N}{\omega_{eg} + i\Gamma_{eg} - \omega_p + \omega_s} \frac{6\hbar\epsilon_0}{|\alpha_{eg}|^2} \quad (1)$$

where  $\omega_{eg}$  denotes the transition frequency between a molecular ground state ( $g$ ) and a final excited state ( $e$ ).  $\omega_p$  is the incident pump frequency.  $\omega_s$  is the Stokes frequency,  $\Gamma_{eg}$  is the damping parameter which corresponds to the dephasing parameter. The estimation of the damping constant  $\Gamma_{eg}$  is somewhat more difficult than it is when considering pure electronic effect, because now contributions from vibration relaxation is also involved. The width  $\Delta\omega_s$  of the Stokes line may be taken as an estimate for  $\Gamma_{eg}$ .  $N$  is the number density,  $\alpha_{eg}$  is the first-order transition hyperpolarizability. The two-level model describes well the link that exists between the classical resonance Raman scattering and stimulated Raman scattering (a two-photon resonant third-order process). This procedure shows that  $\alpha_{eg}$  is equivalent to the Raman polarizability  $\alpha_R$  [4]. In the Born-Oppenheimer approximation, the Raman polarizability near resonance for a molecular transition states  $g$  and  $e$  is given by the dispersion relation [5]

$$(\alpha_R)_{eg} = \frac{1}{\hbar} \mu_e^2 \sum_v \frac{\langle j|v\rangle\langle v|i\rangle}{\omega_{eg} - \omega_p + i\Gamma_{eg}} \quad (2)$$

where the electronic wavefunctions appear in  $\mu_e$ , which is the pure electronic transition moment from the ground to the  $e$ -th excited electronic state.  $i, j$  are the vibrational levels associated with  $g$  and  $v$  is a vibrational level associated with  $e$ .  $\langle j|v\rangle\langle v|i\rangle$  are the Frank Condon factors (the vibrational overlap integral between the nuclear wavefunctions of the states  $g$  and  $e$ ). An analytical form of the integrals was developed by Keil [6]

$$\langle j|v\rangle = \exp\left(-\frac{z^2}{2}\right) \sqrt{\frac{v!}{j!}} (-z)^{j-v} L_j(z^2) \quad j \geq v \quad (3)$$

where  $L_j(z^2)$  is a generalized Laguerre polynomial and  $z$  is a dimensionless parameter related to the displacement of the ground and excited state potentials  $D$  by  $Z = \left(\frac{2\pi m\nu}{h}\right)^{1/2} D$ . The reduced mass and frequency for the normal mode are  $m$  and  $\nu$

respectively. The transition dipole moment  $\mu_e^2$  is calculated from the absorption spectra as

$$\mu_e^2 = \frac{3fe^2\hbar}{2m_e\omega_{eg}} \quad (4)$$

where  $f$  is the oscillator strength calculated as

$$f = 4.6 \times 10^{-9} \epsilon_{\max} \Delta\nu_{1/2} \quad (5)$$

$\epsilon_{\max}$  is the maximum extinction coefficient and  $\Delta\nu_{1/2}$  is the full width at half-height in  $\text{cm}^{-1}$ . Combining Eqs (1), (2) and (4) and extracting the imaginary part (since the imaginary part represents absorption), we get

$$\text{Im } \chi^{(3)} = \frac{3Nf^2e^4 |\langle j|v\rangle\langle v|i\rangle|^2 \Gamma_{eg}}{8m_e^2\omega_{eg}^2 \hbar\epsilon_0 [(\Delta^2 - \omega_s)^2 + \Gamma_{eg}^2] (\Delta^2 + \Gamma_{eg}^2)} \quad (6)$$

where  $\Delta$  is the detuning factor defined as  $\Delta = \omega_{eg} - \omega_p + \omega_s$ .

The third-order hyperpolarizability is related to  $\chi^{(3)}$  by [2]

$$\gamma = \frac{\text{Im } \chi^{(3)}}{L_L^4 N} \quad (7)$$

where  $L_L$  is the Lorentz field factor. The final expression for third order hyperpolarizability becomes

$$\gamma = \frac{3f^2e^4 |\langle j|v\rangle\langle v|i\rangle|^2 \Gamma_{eg}}{8m_e^2\omega_{eg}^2 L_L^4 \hbar\epsilon_0 [(\Delta^2 - \omega_s)^2 + \Gamma_{eg}^2] (\Delta^2 + \Gamma_{eg}^2)} \quad (8)$$

Equation (8) permits the estimation of third-order hyperpolarizability from parameters measured by linear spectroscopic techniques of Raman resonance and absorption spectroscopy. In an attempt to gain experimental evidence for the proposed relation, we examined  $\beta$ -carotene (a conjugate  $\pi$ -electron organic system). The particular choice of  $\beta$ -carotene was made because the delocalization behaviour of the  $\pi$ -electrons makes the  $\pi$ -electron distribution highly deformable in conjugate electronic system, which also gives rise to large value of hyperpolarizabilities. The nonlinear polarization of the  $\pi$ -electrons is large even for frequencies of radiation far away from electronic resonances.

### 3. Experimental

$\beta$ -carotene was purchased from Sigma. The concentration of  $\beta$ -carotenoid was kept at  $5 \mu\text{M}/\text{l}$  of the various organic solvents used. The samples were subjected to laser Raman spectrophotometer (Jasco model NR-1000) consisting of a photomultiplier unit (R-464) and an argon ion laser at 488 nm, 200 mW power, having a scan speed of  $5 \text{ cm}^{-1}\text{s}^{-1}$ . An average of 10 scans were taken by the computer. Time constant was 0.5 s. The frequency expansion was  $10 \text{ cm}^{-1}\text{div}^{-1}$ . Absorption measurements were made on a double beam Shimadzu (model UV-260) UV-VIS spectrophotometer. Fused

silica cells of path length 1 cm were maintained at a constant temperature of 25 °C during the experiment using a Julabo water bath (model F-40).

## 4. Results and Discussion

$\beta$ -carotene gives a strong absorption ( $\pi \rightarrow \pi^*$ ) spectrum at  $\approx 476$  nm. Consequently resonance enhancement is prominent because the electronic absorption band of  $\beta$ -carotene overlaps the wavelength of the exciting laser light of 488 nm. The following characteristics have been observed in a typical Raman spectrum of  $\beta$ -carotene: strong Raman bands at  $1520 \text{ cm}^{-1}$  ( $\nu_{\text{C}=\text{C}}$ ) and  $1160 \text{ cm}^{-1}$  ( $\nu_{\text{C}-\text{C}}$ ) corresponding to C=C and C-C stretching vibrations respectively and a moderately strong band at  $1005 \text{ cm}^{-1}$  corresponding to C-CH<sub>3</sub> stretching and/or C-H in plane bending mode.

The C=C stretch is an important marker band and its frequency is a genuine measure of the degree of conjugation through the  $\pi$ -electron chain [7], hence can be used to follow the nonlinear polarization of the  $\pi$ -electrons.

Consequently the value of the dimensionless parameter  $z$  for  $\nu_{\text{C}=\text{C}}$  band was taken to be 0.77 from Ref. [5]. To calculate  $L_L$ , the formula for spherical molecules  $L_L = (\epsilon(\omega) + 2)/3$  was used, which under near resonance conditions and for the concentration used here ( $N < 10^{18} \text{ m}^{-3}$ ) tends to unity as  $\epsilon(\omega) \rightarrow 1$ . Table 1 lists the linear experimental parameters measured from Raman resonance and absorption spectra along with the third order hyperpolarizability predicted by Eq. (8). No appreciable change is observed in  $\nu_{\text{C}=\text{C}}$  for  $\beta$ -carotene in different solvents, while shifts in  $\lambda_{\text{max}}$  is noticed. The unchanged  $\nu_{\text{C}=\text{C}}$  shows that the ground state remains essentially unperturbed and that the shifts in  $\lambda_{\text{max}}$  must be a property of the excited state alone the values of  $\gamma$  estimated from Eq. (8) clearly decrease with increasing detuning factor, therefore pointing to a resonantly enhanced nonlinearity. The predicted values of  $\gamma$  from linear spectroscopic techniques agree remarkably to within one-order of magnitude with Degenerate Four Wave Mixing (DFWM) and Third Harmonic Generation (THG) measurements on  $\beta$ -carotene. The values reported by Hermann et al. [8], obtained from THG measurements in benzene solution with wavelength of pump laser of  $1.89 \mu\text{m}$ , is  $4.8 \times 10^{-33}$  esu. Maloney et al. [2] used DFWM technique at wavelength  $1.064 \mu\text{m}$  in ethanol solution. They reported a value of  $7.2 \times 10^{-31}$  esu. Meredith et al. [9] reported a value of  $1.1 \times 10^{-32}$  esu using a fundamental wavelength of  $1.908 \mu\text{m}$  for THG.

**Table 1.** Linear experimental parameters measured from Raman resonance and absorption spectroscopy along with the third-order hyperpolarizability predicted from Eq. (8)

Solvent	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}} \times 10^5$	$\Delta\nu_{1/2}$ ( $\text{cm}^{-1}$ )	$f$ ( $\text{cm}^{-1}$ )	$\omega_s$ (C=C) ( $\text{cm}^{-1}$ )	$\Gamma$ ( $\text{cm}^{-1}$ )	$\Delta$ ( $\text{cm}^{-1}$ )	$\gamma$ (esu)
Benzene	452	1.13	4100	2.13	1520	20	3152	$3.93 \times 10^{-34}$
Methanol	473	1.23	4150	2.35	1520	20	2170	$7.44 \times 10^{-33}$
Ethanol	480	1.08	4200	2.09	1522	20	1863	$2.46 \times 10^{-32}$

## 5. Conclusion

In this paper we have shown the close connection that exists between linear and non-linear properties of conjugate organic molecules. Such an approach to predict nonlinear parameters from linear spectroscopic data will enable the selection of potential conjugate systems from the already existing large amount of linear spectroscopic data for use in nonlinear applications.

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