Study of second-order nonlinear hyperpolarisability of all-trans-β-carotene in solutions by linear spectroscopic technique*

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This paper demonstrates the second-order nonlinear hyperpolarisability γ of all-trans-β-carotene in different solvents by linear spectroscopic technique that is based on resonance Raman scattering and UV–VIS (Ultraviolet-visible) absorption spectroscopy. Owing to the two-level model well describing the link that exists between the resonance Raman scattering and stimulated Raman scattering, the stimulated Raman polarisability $\alpha_{\rm R}$ can be calculated through the two-photon resonance system. The value of γ of all-trans-β-carotene in carbon bisulfide solution is 6.435×10^{-33} esu (1 esu of resistance = 8.98755×10^{11} Ω) that is close to the true value, because the solution of all-trans-β-carotene in carbon bisulfide satisfies the rigid resonance Raman scattering condition. This method is expected to be worthy of applications to measure the second-order nonlinear hyperpolarisability of a conjugate organic molecule.

Keywords: all-trans-β-carotene, second-order nonlinear hyperpolarisability, rigid resonance Raman scattering, UV–VIS absorption spectroscopy

PACC: 4265B, 3320F, 3320L

1. Introduction

Bond conjugation in the organic molecule has long been known to influence the linear optical properties. The longitudinal molecular polarisability of the conjugated chain molecule does not obey bond additivity rule, but rather exhibits a so-called polarisability exaltation, increasing as the cube of the length of the system.[1−4] Recently the third-order nonlinear optical properties of organic molecules have been the subject of intense investigation because of their potential applications in frequency generation, optical switching and nonlinear spectroscopy.[5−7] Conjugated organic molecules have emerged as the most widely studied group because of the delocalisation behaviour of their π-electrons which gives rise to large optical nonlinearities.[8] Second-harmonic generation has indeed been observed in a number of organic materials presenting a conjugated system.[9−13] However, this effect is not an intrinsic property of the conjugated system but arises from its coupling to a highly inductive group.[12] In fact, Gott, Musgrave, and Murrell[14] have pointed out that because of the pairing properties of the orbitals, π-electron contribution to the third-order polarisability of alternate hydrocarbons vanishes. On the contrary, electron delocalisation should be fully reflected in the third-order optical properties which are insensitive to orbital pairing. The all-trans-β-carotene molecule which belongs to the polyene family, offers with its 11 double bonds an interesting example of a long conjugated chain.[4] Earlier attempts to predict the second-order nonlinear susceptibility were made by degenerate four-wave fixing[15] or interferometric measurement.[16] Marder *et al.*[17] have developed derivative relations which provide a unified picture of the dependence of the polarisability and hyperpolarisability on the structure in organic polymethine dyes. Bhattacherjee used Raman and absorption spectroscopy to estimate the second-order hyperpolarisability, but did not analyse the interaction between the all-trans-β-carotene and solvent.

A theoretical link based on the two-level system is developed between stimulated Raman scattering and resonance Raman scattering. We can obtain the parameters of resonance Raman and UV-VIS (Ultraviolet-visible) absorption spectroscopy and calculate the second-order nonlinear susceptibility $\chi^{(3)}$.

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In addition, the $\chi^{(3)}$ of different all-trans-β-carotene solutions are compared.

2. Experimental

All-trans-β-carotene was purchased from Fluka and used without further purification. It was dissolved in ethanol, methanol, carbon disulfide, carbon tetrachloride and benzene, with the concentrations of all-trans-β-carotene in solvents 9.3×10^{-4} M, 2.8×10^{-3} M, 2.8×10^{-4} M, 7.0×10^{-4} M and 1.4×10^{-3} M ($1\ \mathrm{M}=1\ \mathrm{mol\cdot dm^{-3}}$), respectively. The micro-Raman spectrometer (Renishaw InVia Raman Microscope) was equipped with a 514.5-nm Ar+ ion excitation laser (Spectra Physics 163-M42) with 4.6-mW power. The collimated laser light was focused with a 5×0.12 NA LEICA DMLM microscope objective lens. An exposure time (charge coupled device integration times) of 10 s was used to collect all Raman spectra, and the resolution was 1.4 $\mathrm{cm^{-1}}$. The absorption measurements were made on a Purkinje General TU-1901 UV–VIS spectrophotometer with 0.5 nm step, and fused silica cell of path length 1 cm was used.

3. Theory

We use the two-photon-resonance theory to represent the third-order nonlinearilities, since that is greatly simplified by using a two-level model. Such processes have widespread practical applications; this is because two-photon resonance can significantly enhance the desired nonlinearity, whilst at the same time competing absorption processes can be minimized by avoiding coincidences between the optical frequencies and single-photon resonances. We examine the stimulated Raman scattering, which belongs to the third-order nonlinear effect. This process leads to amplification of a signal at a frequency ω_s in the presence of a strong pump field at ω_p, provided that the two-photon resonance condition $\omega_\mathrm{p}-\omega_\mathrm{s}=\Omega_\mathrm{fg}$ is satisfied (Fig. 1(a)); this condition is known as Raman resonance and ω_s is called the Stokes frequency. Here Ω_fg denotes the transition frequency between a molecular ground state (g) and a higher-lying final state (f).

We can simplify the Raman susceptibility that can be expressed as[18]

$$\begin{aligned}&\chi^{(3)}(-\omega_\mathrm{s};\omega_\mathrm{p},-\omega_\mathrm{p},\omega_\mathrm{s})\\ &=\frac{N/6\hbar\varepsilon_0}{\Omega_\mathrm{fg}+\mathrm{i}\Gamma_\mathrm{fg}-\omega_\mathrm{p}+\omega_\mathrm{s}}\\ &\times\alpha_\mathrm{fg}(-\omega_\mathrm{s};\omega_\mathrm{p})\cdot\alpha_\mathrm{fg}(-\omega_\mathrm{s};\omega_\mathrm{p})^*\ ,\end{aligned}\tag{1}$$

where Γ_fg is the damping factor, which is identified as a dephasing parameter appropriate to weak collisions, and it represents a spectral linewidth for the transition of frequency Ω_fg. So the linewidth $\Delta\omega_\mathrm{s}$ of the Stokes line can be taken as an estimate for Γ_fg. The N is the number density, α_fg is the first-order transition hyperpolarisability, which is equivalent to the resonance Raman polarisability α_R.[18] Because the two-level model describes well the link that exists between the resonance Raman scattering and stimulated Raman scattering.

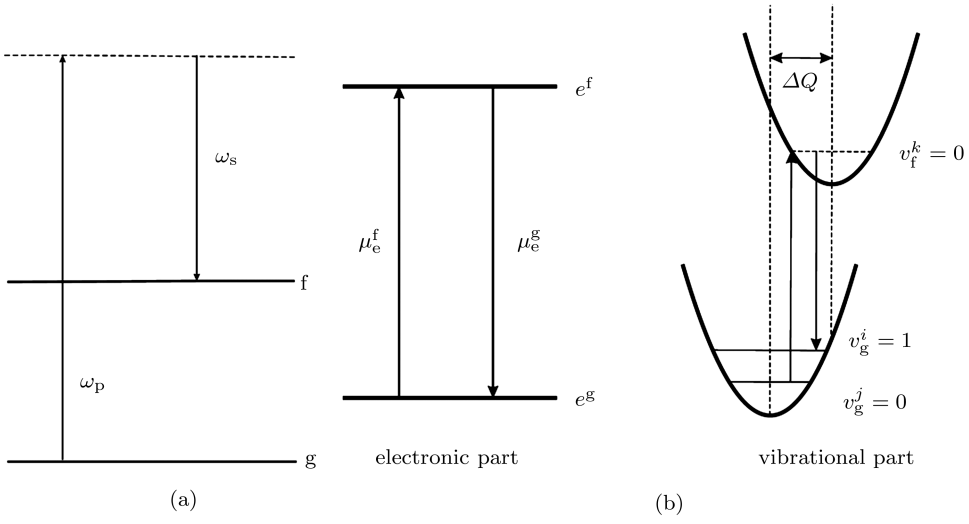


Fig. 1. (a) Molecular energy-level diagram depicting stimulated Raman scattering on the two-photon transition $E_\mathrm{g}\rightarrow E_\mathrm{f}$. (b) The dipole electronic transitions and vibrational overlap integrals involved in α_fg.

The $\alpha_{\rm R}$ component of the vibrational transition polarisability tensor in the resonance case, using perturbation theory, is given by[19]

$$\alpha_{\rm R} = A^{\rm VI} + B^{\rm VI} + C^{\rm VI} + D^{\rm VI}, \tag{2}$$

where, the term $A^{\rm VI}$ is the main contribution to the two-level model, the terms $B^{\rm VI}$, $C^{\rm VI}$, $D^{\rm VI}$ involve the vibronic coupling of excited state to resonant excited state, ground electronic state to excited electronic state and excited electronic state to two other electronic states, respectively. So $\alpha_{\rm R} = A^{\rm VI}$ when we only consider a two-photon resonance system,[19]

$$\alpha_{\rm R} = \frac{1}{\hbar}\mu_{\rm e}^{\rm f}\mu_{\rm e}^{\rm g}\sum_{v_{\rm f}^{\rm k}}\frac{\langle v_{\rm g}^{j}|v_{\rm f}^{k}\rangle\langle v_{\rm f}^{k}|v_{\rm g}^{i}\rangle}{\Omega_{\rm fg}-\omega_{\rm p}-{\rm i}\Gamma_{\rm fg}}, \tag{3}$$

where $\mu_{\rm e}^{\rm f}$ and $\mu_{\rm e}^{\rm g}$ are the transition dipole moments, $\mu_{\rm e}^{\rm f}\cdot\mu_{\rm e}^{\rm g} = 3fe^2\hbar/2m_{\rm e}\Omega_{\rm fg}$ is calculated from the UV–VIS absorption spectra, f is the oscillator strength calculated as $f = 4.33\times10^{-9}\int_0^\infty \varepsilon(\upsilon){\rm d}\upsilon$,[20] $\varepsilon(\upsilon) = A(\upsilon)/CL$ is the extinction coefficient, $A(\upsilon)$ is the absorbance, C is the concentration, $L = 1$ cm, and $\int_0^\infty A(\upsilon){\rm d}\upsilon$ is the area of $c = c$ absorption peak (Fig. 3(b)). When the transition is the complete allowed transition, the $f \to 1$. The $v_{\rm g}^{j}$ and $v_{\rm g}^{i}$ are the vibrational levels associated with g, $v_{\rm f}^{k}$ is a vibrational level associated with f (Fig. 1(b)).

In order to compute the function in Eq. (3), we wish to evaluate the overlap integrals $\langle v_{\rm g}^{j}|v_{\rm f}^{k}\rangle$ which are Frank–Condon factors. It is easily shown that these integrals are given by[21]

$$\langle v_{\rm g}^{j}|v_{\rm f}^{k}\rangle = {\rm e}^{-a^2/4}\left[\frac{k!}{j!}\right]^{1/2}\left(-\frac{a}{2^{1/2}}\right)^{j-k} \times {\rm L}_k^{j-k}\left(\frac{a^2}{2}\right),\ j\geq k, \tag{4}$$

where the ${\rm L}_n^m(z)$ are Laguerre polynomials, and ${\rm L}_0^m(z) = 1$, ${\rm L}_1^m(z) = 1+m-z$, a is a dimensionless constant which characterizes the size of the interaction. The ΔQ in Fig. 1(b) is the displacement of the ground and excited state potential, and $a = 2(\pi m\omega/\hbar)^{1/2}\Delta Q$, $\Delta Q = (m/2)^{1/2}\Delta r$, in these relationships m is the mass of the atom, Δr is the change in the $c = c$ bond length[19] and the change is not appreciable. Combining Eqs. (1), (3) and (4), we can obtain the imaginary part that represents absorption and contributes to the stimulated Raman scattering

$${\rm Im}\chi^{(3)} = \frac{3Nf^2e^4\left|\langle v_{\rm g}^{j}|v_{\rm f}^{k}\rangle\langle v_{\rm f}^{k}|v_{\rm g}^{i}\rangle\right|^2\Gamma_{\rm fg}}{8m_{\rm e}^2\Omega_{\rm fg}^2\hbar\varepsilon_0[(\Delta^2-\omega_{\rm s})^2+\Gamma_{\rm fg}^2](\Delta^2+\Gamma_{\rm fg}^2)}, \tag{5}$$

where $\Delta = \Omega_{\rm fg}-\omega_{\rm p}+\omega_{\rm s}$. The second-order hyperpolarisability is related to χ by Ref. [22],

$$\gamma = \frac{3f^2e^4\left|\langle v_g^{j}|v_{\rm f}^{k}\rangle\langle v_{\rm f}^{k}|v_{\rm g}^{i}\rangle\right|^2\Gamma_{\rm fg}}{8m_{\rm e}^2\Omega_{\rm fg}^2L_{\rm L}^4\hbar\varepsilon_0[(\Delta^2-\omega_{\rm s})^2+\Gamma_{\rm fg}^2](\Delta^2+\Gamma_{\rm fg}^2)}, \tag{6}$$

where $L_{\rm L} = (\varepsilon(\omega)+2)/3$ is the Lorentz field factor, when $N < 10^{18}$ m^{-3}, $\varepsilon(\omega)\to 1$.

4. Results and discussion

All-trans-β-carotene has the delocalisation behaviour of the π-electrons and makes the π-electrons distribution highly deformable in a conjugate electronic system, which also gives rise to a large value of hyperpolarisabilities. The nonlinear polarisation of the π-electrons is large even for frequencies of radiation far away from electronic resonances.[8] The $c = c$ (1520 cm^{-1}) stretch is an important marker band and its frequency is a genuine measure of the degree of conjugation through the π-electrons chain,[23] hence it can be used to follow the nonlinear polarisation of π-electrons. The maximum absorption band ($\pi\to\pi^*$) of all-trans-β-carotene lies at about 487 nm, because the pump laser wavelength of 514.5 nm overlaps the electronic absorption band of all-trans-β-carotene and the resonance enhancement effect is prominent. The local Raman and UV–VIS absorption spectrogram are shown in Figs. 2 and 3(a), respectively. Because the maximum absorption peak is overlapped by the three peaks, we use the Origin software to deal with it, and the area under the curve 2 is the area of the $c = c$ absorption peak in Fig. 3(b). Other solutions spectrograms

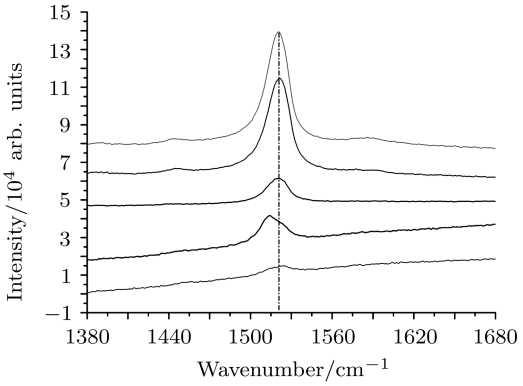


Fig. 2. Local Raman spectrogram of all-trans-β-carotene in solvents, *a* ethanol (1527 cm^{-1}), *b* methanol (1514 cm^{-1}), *c* carbon bisulfide (1520 cm^{-1}), *d* carbon tetrachloride (1520 cm^{-1}), *e* benzene (1520 cm^{-1}).

have not been given. So we can calculate the γ by using the linear experimental parameters, and figure 4 shows the value of the second-order nonlinear hyperpolarisability γ in solutions.

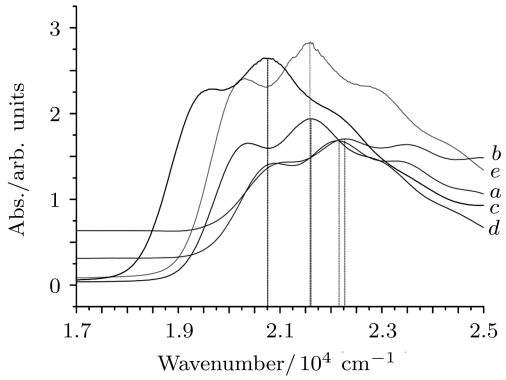


Fig. 3(a). The UV–VIS absorption of all-trans-β-carotene in solvents. Curves a ethanol (452 nm), b methanol (448 nm), c carbon bisulfide (482 nm), d carbon tetrachloride (463 nm), e benzene (464 nm).

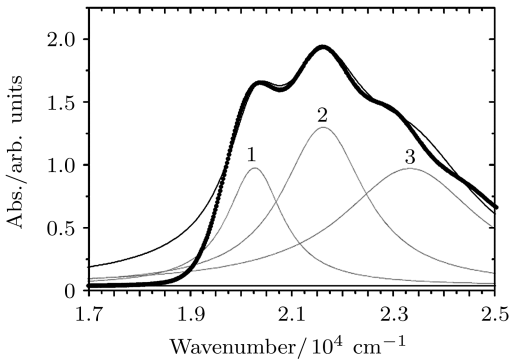


Fig. 3(b). The UV–VIS absorption of carbon tetrachloride has been dealt with using the software Origin. The second peak associates with the $c = c$, and the area is 3583.4. The areas of benzene, carbon bisulfide, ethanol and methanol are 3221.5, 3883.1, 2987.4, and 2875.3, respectively.

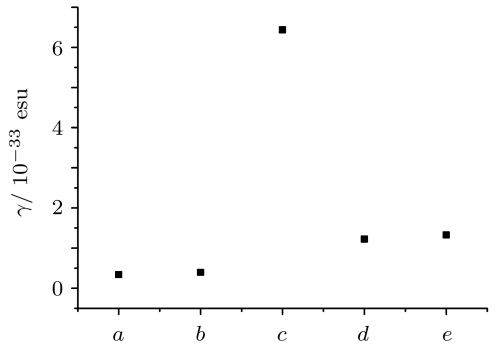


Fig. 4. Calculated results. Symbols a ethanol (0.3375×10^{-33} esu); b methanol (0.3944×10^{-33} esu); c carbon bisulfide (6.435×10^{-33} esu); d carbon tetrachloride (1.226×10^{-33} esu); e benzene (1.328×10^{-33} esu).

In Fig. 4, the hyperpolarisability γ of solution of all-trans-β-carotene in carbon bisulfide is in agreement with the value 7.6×10^{-33} reported by Beljonne *et al.*[24] they used the third harmonic generation and electro-absorption spectra to measure it. However, the values γ of the others are not good. Because the all-trans-β-carotene is the non-polar molecule and the ethanol and the methanol are the polar molecule, their intersolubility with the all-trans-β-carotene is not good, and the all-trans-β-carotenes aggregate together, which leads to the absorption peaks of UV–VIS, and a large red-shift appears. So the rigid resonance Raman effect cannot be satisfied. Benzene, carbon bisulfide and carbon tetrachloride are the nonpolar solvent, the dispersion force is the only acting force between the all-trans-β-carotene and the solvents, which results in the absorption peaks becoming red-shift, the red-shift phenomenon relates to the refractive index of solution, transition intensity and molecular size. Only the absorption peaks of carbon bisulfide lie in rigid resonance Raman band, so the agreement between the experimental result and Hermann's result is remarkably good. Therefore, when calculating the second-order nonlinear hyperpolarisability by the two-level model, the refractive index of solvent, solvent polar, transition intensity and molecular size should be considered.

5. Conclusion

In this paper, we used linear spectroscopic techniques, namely resonance Raman scattering and UV–VIS absorption spectroscopy to measure the second-order nonlinear hyperpolarisability of all-trans-β-carotene. Because the solutions of all-trans-β-carotene in ethanol, methanol, carbon tetrachloride and benzene are not consistent with the rigid resonance Raman condition, and only carbon bisulfide solution is consistent with the resonance condition, the value of hyperpolarisability γ of carbon bisulfide solution is close to true value. Using this method to measure the value of hyperpolarisability of a conjugate organic molecule, we should consider the rigid resonance Raman condition. The second-order hyperpolarisability of a conjugate organic molecule can be calculated by linear spectroscopy rather than by complicated nonlinear means.

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