

## TWO-PHOTON DISPERSION IN CONJUGATED POLYMERS

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The frequency dependence of the dispersive and absorptive parts of a strongly allowed two-photon transition is determined in a series of conjugated polymer solutions. The data analysis yields the energy and width of the two-photon transition, symmetry assignment for the two-photon transition ( $A_g \rightarrow A_g$ ), and oscillator strengths for both the one-photon and two-photon transitions.

A complete characterisation of two-photon dispersion in a series of conjugated polymer solutions has been obtained with three wave mixing (3WM) spectroscopy. The two-photon hyperpolarizability  $\gamma_T = \gamma'_T + i\gamma''_T$  is determined over a broad frequency range which encompasses the region of the two-photon transition. One-photon resonance effects on  $\gamma_T$  dispersion are strongly evident in the experimental results and are completely explained theoretically with a single intermediate state. Theoretical analysis of the  $\gamma_T$  dispersion curve yields the energy and width of the two-photon transition as well as oscillator strengths for the transitions from ground state to intermediate state and from intermediate state to two-photon final state. This analysis constitutes the first determination from experiment of the two oscillator strengths involved in a two-photon transition in organic molecules. In addition, polarization studies allow an unambiguous symmetry assignment for the two-photon state. These results have important implications regarding the use of conjugated polymers in nonlinear optical devices [1].

3WM spectroscopy has received considerable attention recently in the study of two-photon absorption (TPA) of organic molecules in solution [2-6]. Though 3WM has been used in a few instances to determine  $\gamma_T$

over limited frequency ranges [3,6], the results presented here are by far the most extensive yet obtained with 3WM in solution. Such extensive results are possible because the properties of the materials under investigation here (large  $\gamma_T$  and no significant solute-solute interactions) allow a relatively simple analysis procedure based on concentration dependence.

The polymer solutions under investigation here provide a unique system for the study of excited state energetics, since large variations in optical properties can be accomplished in a controlled manner without any fundamental change in the nature of the excited states [7] (fig. 1). The polymers are polydiacetylenes with repeat unit  $[-RC-C\equiv C-CR-]_k$  where R is  $-(CH_2)_m OCONHCH_2 COOC_4H_9$ . The two polymers considered here are 3BCMU ( $m = 3$ ) and 4BCMU ( $m = 4$ ) [7]. Though the chain length  $k$  is  $\approx 1000$  repeat units [8], the conjugation length  $l_c$  (i.e., the length over which backbone planarity is maintained without interruption) will generally be substantially smaller in solution ( $l_c \approx 6$  units with  $CHCl_3$  solvent). However, variations in the solvent system can substantially increase  $l_c$  [7]. 3BCMU in  $CHCl_3$ /hexane (blue solution, fig. 1) corresponds to essentially infinite conjugation length [9]. Our most extensive measurements have

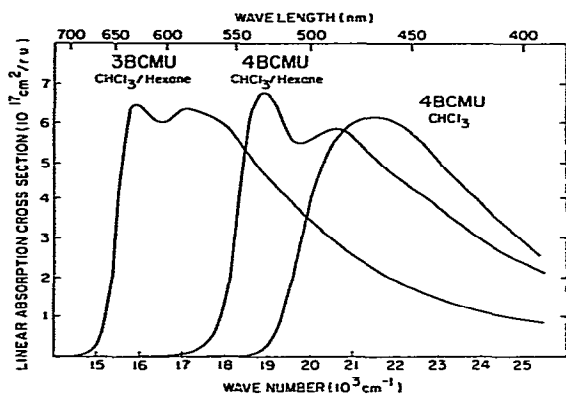


Fig. 1. Linear absorption spectra for polymer solutions investigated here. The three solutions are referred to in the text as "blue" (3BCMU in 1 : 1  $\text{CHCl}_3$ /hexane mixture), "red" (4BCMU in 1 : 2  $\text{CHCl}_3$ /hexane mixture), and "yellow" (4BCMU in pure  $\text{CHCl}_3$ ).

been conducted in the yellow solution (4BCMU in  $\text{CHCl}_3$ ) due to the large range of transparency and the absence of detectable intermolecular interactions even at relatively high polymer concentrations — up to  $1.2 \times 10^{19}$  r.u./ $\text{cm}^3$ . These results will be presented in some detail. The red and blue solution results are briefly summarized. The 3WM apparatus and experimental procedure are described elsewhere [10].

3WM is accomplished by focusing two laser beams with frequencies  $\omega_1$  and  $\omega_2$  in the polymer solution. The beam generated at  $\omega_3 = 2\omega_1 - \omega_2$  in the polymer solution has an intensity  $I^{s+p} \propto |\chi_{\text{tot}}|^2$  where  $\chi_{\text{tot}}$  is the total nonlinear susceptibility of the medium (solvent + polymer)

$$\chi_{\text{tot}} = \chi_s + \chi_p + \chi_R^{s,p} + \chi_T^p, \quad (1)$$

where  $\chi_s$  and  $\chi_p$  are the nonresonant susceptibilities of the solvent and polymer.  $\chi_R^{s,p}$  is the Raman resonance term which yields enhancement of  $I^{s+p}$  when  $|\omega_1 - \omega_2|$  is near a Raman active molecular vibration in the solvent or polymer. The final term  $\chi_T^p$  is the two-photon resonance term for the polymer. There are no two-photon resonances in the solvents in the frequency range of interest here [5].

This experiment can be more conveniently discussed in terms of the two-photon hyperpolarizability of the

polymer,  $\gamma_T = \chi_T^p/N^{\frac{1}{2}}$ , where  $N$  is the polymer concentration in r.u./ $\text{cm}^3$ . Previous determinations of  $\chi_T$  have utilized the interference effects between  $\chi_T$  and  $\chi_R$  evident in line shape analysis of the Raman resonance [2–6,10]. We have developed an alternate technique which is considerably less complicated. In particular,  $|\omega_1 - \omega_2|$  has been chosen away from Raman resonances, so that  $\chi_R^{s,p} = 0$ . Also, it can be safely assumed [10] that  $\chi_p \ll \chi_T$  so that the  $\omega_3$  intensity for the polymer solution  $I^{s+p}$  divided by that of the solvent alone  $I^s$  takes the simple form

$$I^{s+p}/I^s = 1 + 2N\gamma_T'/\chi_s + N^2[(\gamma_T'/\chi_s)^2 + (\gamma_T''/\chi_s)^2], \quad (2)$$

where  $\gamma_T \equiv \gamma_T' + i\gamma_T''$ . Therefore,  $\gamma_T$  can be determined from the  $N$  dependence of  $I^{s+p}$ . Further details of this procedure are given in ref. [10] along with single frequency results for the yellow and red solutions. The successful application of this method generally requires that  $|\chi_T| \gtrsim \chi_s$  be achievable experimentally without any significant solute–solute interaction, as is the case for the polymer solutions discussed here.

The  $\gamma_T$  dispersion curve for the yellow solution is given in fig. 2. These data are by far the most extensive obtained with 3WM (or any other technique) for two-photon dispersion in solution. One-photon resonance effects on the  $\gamma_T$  dispersion are immediately evident as the source of the asymmetric  $\gamma_T''$  curve shape and the lack of inversion symmetry in  $\gamma_T'$  around the  $\gamma_T' = 0$  frequency ( $\approx 30500 \text{ cm}^{-1}$ ). This qualitative observation is borne out by our theoretical analysis.

A complete theoretical analysis of the data in fig. 2 requires assignment of the excited state symmetries. The molecular symmetry for the polymer repeat unit is  $C_{2h}$ . We define a molecular coordinate system so that  $x$  is the chain direction with  $z$  perpendicular to the polymer plane ( $xy$ ). The ground state is labelled  $g$  and the two-photon-accessible final state is labelled  $f$ . We assume a single intermediate one-photon state labelled  $i$ , as suggested by the linear absorption data in fig. 1. The symmetry assignment for the  $f \leftarrow g$  transition is made by measurement of  $\gamma_T^{1111}$  (all beams polarized

\* A local field correction factor  $L$  is frequently included in the definition of  $\gamma$  ( $\gamma \equiv \chi/NL$  [4]) to account for solvent effects.  $L$  is usually approximated as  $(n^2 + 2)/3$ , where  $n$  is the refractive index of the solvent. However, this relation is known to be a poor approximation for linear absorption strengths.

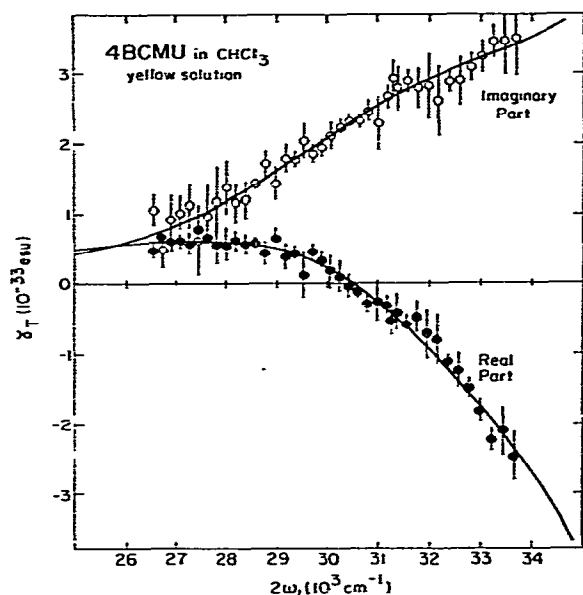


Fig. 2. Dispersion of the real (●) and imaginary (○) parts of the two-photon hyperpolarizability for the yellow solution (4BCMU in  $\text{CHCl}_3$ ). The data are obtained by fitting eq. (3) to the concentration dependence of the  $\omega_3$  intensity. The error bars represent 90% confidence limits. All data are taken in a 1111 geometry (all beams polarized parallel). The solid lines are theoretical fits of eq. (3) to the dispersion curves.

parallel) and  $\gamma_T^{1221}$  ( $\omega_1$  perpendicularly polarized with respect to  $\omega_2$  and  $\omega_3$ ) where superscript numerals refer to perpendicular laboratory axes. Since the  $i \leftarrow g$  transition is  $x$  polarized ( $B_u \leftarrow A_g$ ) [11], the only possibilities for the two-photon case are  $xx$  ( $A_g \leftarrow A_g$ ),  $xy$  ( $A_g \leftarrow A_g$ ), and  $xz$  ( $B_g \leftarrow A_g$ ). Our polarization measurements yield  $|\gamma_T^{1111}|/|\gamma_T^{1221}| = 3.19 \pm 0.33$  independent of frequency; a ratio of 3 is expected for the  $xx$  case and 2 for the  $xy$  or  $xz$  case. Therefore, both the  $i \leftarrow g$  and  $f \leftarrow i$  transitions are polarized along the chain, so that the spatially averaged hyperpolarizability  $\gamma_T^{1111}$  equals  $\frac{1}{2}\gamma_T^{xxxx}$ .

Given the symmetry assignments for the excited states of the polymer backbone and, again, with the assumption of a single intermediate state, the theoretical form for the  $\gamma_T$  dispersion curve is [2]

$$\gamma_T^{1111} = \frac{3e^4}{80\hbar m^2} \frac{f_{gi}f_{if}}{\omega_{gi}\omega_{if}} \frac{1}{\omega_{gi} - \omega_1} \times \left[ \frac{1}{\omega_{gi} - \omega_2} + \frac{1}{\omega_{gi} - \omega_3} \right] G(\omega_{gf} - 2\omega_1), \quad (3)$$

where  $e$  and  $m$  are the electron charge and mass and  $\omega_{jk}$  and  $f_{jk}$  are the  $k \leftarrow j$  transition frequency and oscillator strength<sup>‡</sup>.  $G(\omega_{gf} - 2\omega_1)$  is the line shape function for the two-photon transition which in the usual lorentzian approximation is  $G(\omega_{gf} - 2\omega_1) = (\omega_{gf} - 2\omega_1 - i\Gamma_{gf})^{-1}$ . Since  $\omega_{gi}$  and  $f_{gi}$  are known from linear absorption (fig. 1;  $f_{gi} = 1.5$ ,  $\omega_{gi} = 21300 \text{ cm}^{-1}$ ), the fit parameters for eq. (3) are  $f_{if}$ ,  $\omega_{gf}$ , and  $\Gamma_{gf}$ . The results of this fitting procedure for the data in fig. 2 are given in table 1, which also includes the results of a similar procedure for the red solution and a single frequency result for the blue solution.

Several important conclusions can be drawn from the results in table 1. The two-photon transition energy  $\omega_{gf}$  scales approximately to the one-photon transition energy  $\omega_{gi}$  with  $\omega_{gf}/\omega_{gi} \approx 1.3-1.5$ . No theoretical description of two-photon transitions in polydiacetylenes is available. However, such a description is easily formulated for the analogous polyene backbone  $\{\text{HC}=\text{CH}\}_K$ , which has linear optical properties that are very similar to the polydiacetylenes [9]. In the polyene case a simple Hückel description for chains of finite length can be constructed to relate  $\omega_{gf}$  and  $\omega_{gi}$ . The two resonance integrals necessary in this treatment are estimated from linear absorption experiments for short chain polyenes. This model results in

$$\omega_{gf} = 1.78 \omega_{gi} - 9200 \text{ cm}^{-1}, \quad (4)$$

which yields  $\omega_{gf} = 28700, 24400$ , and  $19100 \text{ cm}^{-1}$  for the yellow, red, and blue solutions, respectively, in reasonable agreement with the experimental results in table 1.

The  $\Gamma_{gf}$  values in table 1 represent the widths of the entire two-photon absorption bands. Large values are observed for  $\Gamma_{gf}$  (as well as for the corresponding one-photon widths,  $\approx 2500 \text{ cm}^{-1}$ ) due principally to vibrational sidebands and the distribution of conjugation lengths.

The oscillator strengths for the  $f \leftarrow i$  transition are  $\approx 2.5$  for all three solutions and indicate a strongly allowed transition. This result is consistent with our assignment of this transition as  $A_g \leftarrow B_u$  based on polarization studies. It is also found that  $f_{if} > f_{gi}$  for all three solutions, though the differences are not that large.

<sup>‡</sup> Note that we have assumed in writing eq. (3) that  $\omega_1$ ,  $\omega_2$ , and  $\omega_3$  are far enough removed from  $\omega_{gi}$  so that the one-photon width  $\Gamma_{gi}$  may be neglected. This approximation is reasonable, since our closest approach is  $\omega_3 - \omega_{gi} \approx 3000 \text{ cm}^{-1}$ .

Table 1

Energies, widths, and oscillator strengths for one- and two-photon absorption in polydiacetylene solutions (energies and widths in  $\text{cm}^{-1}$ )

Solution	$\omega_{gi}$	$f_{gi}^{a)}$	$\omega_{gf}$	$\Gamma_{gf}$	$f_{if}^{a)}$
yellow	21300	1.5	30500	4600	2.7
red	18900	1.6	28100	4000	2.5
blue b)	15900	1.4	{ 23200 20500	{ 2200 4000	{ 2.3 2.7

a) Both  $f_{gi}$  and  $f_{if}$  represent oscillator strengths for polarization parallel to the chain direction.

b) Experiments in the blue solution were limited to a single frequency ( $2\omega_1 = 26554 \text{ cm}^{-1}$ ) by our dye laser range and by linear absorption. The only restriction we can reasonably impose on the three parameters necessary in eq. (3) is that the measured ratio  $\gamma_T''/\gamma_T''$  for the blue solution ( $-1.52$ ) equal  $(\omega_{gf} - 2\omega_1)/\Gamma_{gf}$ . The two sets of values for  $\omega_{gf}$  and  $\Gamma_{gf}$  given in the table are presented as bounds on the actual value and are derived from the following two restrictions implied by the red and yellow results:  $\omega_{gf}/\omega_{gi} \approx 1.46$  and  $\Gamma_{gf} < 4000 \text{ cm}^{-1}$ . Note that  $f_{if}$  is reasonably well determined, nevertheless.

A very large TPA cross section  $\beta$  has been reported previously for one of these polymers [10].  $\beta$  is related to  $\gamma_T''$  by

$$\beta = 48\omega^2 h \gamma_T'' / n^2 c^2, \quad (5)$$

which yields  $\beta \approx 10^{-46} \text{ cm}^4 \text{ s photon}^{-1} \text{ r.u.}^{-1}$  for all three solutions. This value is by far the largest ever reported. However, from the preceding data analysis it is clear that these surprisingly large  $\beta$  values are due to the large value of the product  $f_{gi}f_{if}$ , coupled with the one-photon resonance effects. These results clearly demonstrate that strong TPA is a fundamental property of the polydiacetylene backbone and is not chain defect related as had been suggested previously [12]. This conclusion has important implications regarding applications of conjugated polymers in nonlinear optical devices suggested by previous work [1].

## References

- [1] C. Sauteret, J.-P. Hermann, R. Frey, F. Pradore, J. Ducuing, R.H. Baughman and R.R. Chance, Phys. Rev. Letters 36 (1976) 956; J.-P. Hermann and J. Ducuing, J. Appl. Phys. 45 (1974) 5100.
- [2] M.D. Levenson and N. Bloembergen, Phys. Rev. B10 (1974) 447.
- [3] H. Lotem and R.T. Lynch, Phys. Rev. Letters 37 (1976) 334.
- [4] R.T. Lynch, S.D. Kramer, H. Lotem and N. Bloembergen, Opt. Commun. 16 (1976) 372.
- [5] H. Lotem, R.T. Lynch and N. Bloembergen, Phys. Rev. A14 (1976) 1748.
- [6] R.T. Lynch and H. Lotem, J. Chem. Phys. 66 (1977) 1905.
- [7] G.N. Patel, R.R. Chance and J.D. Witt, J. Polymer Sci. Polymer Letters Ed. 16 (1978) 607.
- [8] G.N. Patel and E.K. Walsh, J. Polymer Sci. Polymer Letters Ed. 17 (1979) 203.
- [9] R.H. Baughman and R.R. Chance, J. Polymer Sci. Polymer Phys. Ed. 14 (1976) 2037.
- [10] M.L. Shand and R.R. Chance, J. Chem. Phys. 69 (1978) 4482.
- [11] R.R. Chance, unpublished; R.R. Chance, R.H. Baughman, H. Müller and C.J. Eckhardt J. Chem. Phys. 67 (1977) 3616.
- [12] M. Lequime and J. Hermann, Chem. Phys. 26 (1977) 431.