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Spectroscopic investigations of the nonlinear response of poly(4-BCMU) films

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Abstract

Two distinct third-order nonlinear optical techniques, third harmonic generator and four-wave mixing, have been used in three independent experiments to probe the frequency dispersion of the nonlinear optical response of thin solid films of a specific π-electron conjugated polydiacetylene polymer, the red form of poly(4-BCMU). Comparison with two molecular models, the essential states and the anharmonic oscillator shows a qualitative agreement, possible reasons for the deviations are discussed.

Polymers with π-electron conjugated backbones have been proposed as candidate nonlinear materials for all-optical applications because they exhibit some of the highest ultrafast nonlinear optical coefficients [1]. Therefore understanding the origin of such large nonlinearities is of paramount importance not only in the field of nonlinear optics but also in biology and quantum physics [2]. Modelling of the nonlinear optical response of one-dimensional π-electron conjugated systems has concentrated on isolated molecules and has evolved into a periodic, one-dimensional, Hückel-like Hamiltonian with electron correlations included [3–5]. It has been shown that the electron correlations are sufficiently strong to affect the positions of the one- (B_u) and two-photon (A_g) active states. It is in the treatment of electron correlation in the ground and excited states that many of the approximations enter the different theories [5,6]. Calculating the nonlinearity from an eigenstate perspective requires diagonalizing the Hamiltonian to identify the global molecular states, calculating the dipole transition moments between different states, leading finally to a nonlinearity in terms of a multiple summation over excited states which results from perturbation theory. A simplified interpretation based on molecules with up to ten double bonds has been used to identify the 'essential states' which contribute the most to the nonlinear optical response in the limit of long polyenes or polymers [7]. It has proven successful in comparing third harmonic generation (THG) spectra to simplified three excited state quantum models [8–11]. However, although there is evidence for all three quantum states in the observed spectra, this is not a stringent test because these spectra are essentially dominated by the resonance between the ground ($1A_g$) and first exciton ($1B_u$) state whose relative location, bandwidth and oscillator strength are obtained from the one-photon absorption spectrum.

A completely different theoretical approach, previously successful in treating semiconductors, was developed recently. The nonlinear response was found

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by mapping the charge excitations onto coupled anharmonic oscillators [13]. We then calculate the elementary excitations of the π-electron conjugated system by deriving equations of motion for two-site nonlocal operators and by solving these equations via Green's function techniques. Electron–electron, hole-hole, as well as exciton responses are inherent to this molecular theory. The starting point of this theory is the PPP model Hamiltonian which depends on the following parameters: β, δ, U, γ. $\beta(1+\delta)$ and $\beta(1-\delta)$ represent the alternate coupling of π electrons along the molecular chain, where δ is the bond alternation parameter. U is the on-site Hubbard interaction energy, and γ is a phenomenological damping constant. The number of double bonds which can be treated is >100, although usually 30 is adequate since the result from the Green function calculation does not change significantly for $N>30$ [13]. The predictions of this theory for resonant four-wave mixing techniques have not been checked in detail against experiment before.

The theories discussed above are molecular in nature and do not include the intermolecular interactions, local field effects and orientational effects, which are known to be very important in neat solid state polymers when homogeneous or inhomogeneous responses are discussed. However, the large nonlinearities needed for all-optical applications require maximum concentrations of nonlinearly active molecules, available only in solid state form [14]. To a good approximation, molecular crystals and amorphous polymers for which the linear and nonlinear optical responses follow a linear dependence with the molecular density can be described respectively by an oriented or randomly disoriented gas phase model. In this Letter, we address the question of how well molecular theories can predict the measured dispersion in the third-order susceptibility of spun films of the conjugated polymer poly(4-BCMU).

Our philosophy for testing the theories is to measure the spectral dependence of different third-order susceptibilities which respond only to virtual electronic mechanisms. Higher-order effects including those due to excited state populations are negligible under our experimental conditions. No intensity or fluence dependence was observed in the results of the experiments presented here. When excited populations can be neglected, for third harmonic generation, the dominant terms in the sum over states expansion are then

$$\frac{\mu_{g\to u}\mu_{u\to g'}\mu_{g'\to u'}\mu_{u'\to g}}{(\omega_{gu}-3\omega)(\omega_{gg'}-2\omega)(\omega_{gu'}-\omega)} - \frac{|\mu_{g\to u}|^2|\mu_{g\to u'}|^2}{(\omega_{gu}-3\omega)(\omega_{gu}-\omega)(\omega_{gu'}-\omega)}, \tag{1}$$

whereas for four-wave mixing (FWM) with output at $2\omega_1-\omega_2$ the dominant terms are

$$-\frac{|\mu_{gu}|^2|\mu_{gu'}|^2}{[\omega_{gu}-(2\omega_1-\omega_2)](\omega_{gu}-\omega_1)(\omega_{gu'}-\omega_1)} - \frac{|\mu_{gu}|^2|\mu_{gu'}|^2}{(\omega_{gu}-\omega_1)(\omega^*_{gu}-\omega_2)(\omega_{gu'}-\omega_1)}, \tag{2}$$

and

$$\frac{\mu_{gu}\mu_{ug'}\mu_{g'u'}\mu_{u'g}}{[\omega_{gu}-(2\omega_1-\omega_2)](\omega_{gg'}-2\omega_1)(\omega_{gu'}-\omega_1)} + \frac{\mu_{gu}\mu_{ug'}\mu_{u'g'}\mu_{u'g}}{(\omega^*_{gu}-\omega_2)(\omega_{gg'}-2\omega_1)(\omega_{gu'}-\omega_1)}. \tag{3}$$

Here $\hbar\omega_{ug}=(E_u-E_g)$ is the energy difference between a one-photon active (u) and the two-photon active ground state (g) and $\mu_{u\to g}$ is the corresponding dipole moment transition element. In the FWM case, ground state Raman contributions have been neglected. In both THG and FWM the positive contribution is due to the presence of a two-photon active oscillator/state while the negative contribution can be seen as the asymptotic tail of a one-photon active oscillator/state acting as a classical saturable absorber. Because the contributions of the different transitions to the third-order susceptibility $\chi^{(3)}$ change with different frequency inputs and outputs, the theories can be tested by performing different types of nonlinear spectroscopic experiments. In our case, we use THG, and FWM with two different fixed frequencies ω_2. To the best of our knowledge, dispersion which yields information about nonlinear mechanisms has only been measured before separately with THG in thin films and electric-field-induced-second-harmonic-generation or coherent-anti-Stokes-spectroscopy in solution experiments [15,16]. The results presented here allow a stringent comparison between experiment on solid state materials and these molecular theories.

Third harmonic generation (THG), governed by

$\chi^{(3)}(-3\omega;\omega,\omega,\omega)$, was measured with a versatile laser system based on an injection seeded Nd:YAG laser. It was used to pump a dye laser, a Raman shifter or a difference frequency mixing system, as needed for producing different wavelengths. The fundamental wavelength (λ_1) was scanned with 10 ns pulses at 10 Hz from 800 nm (1.55 eV) to 1.904 nm (0.65 eV), probing resonances at the second and third harmonic frequencies.

Four-wave mixing probes a different admixture of the nonlinear mechanisms from THG, as discussed above. It was implemented with the same 10 ns source as for THG and allowed measurements of the spectra of $\chi^{(3)}(-2\omega_1+\omega_2;\omega_1,\omega_1,-\omega_2)$. In this case ω_2 was fixed at 1904 nm (0.65 eV) and 1064 nm (1.17 eV) in two separate experiments, while ω_1 was tuned from 680 nm (1.82 eV) to 970 nm (1.28 eV). For these inputs, resonances at $2\omega_1$ as well as $\omega_1-\omega_2$ and $2\omega_1-\omega_2$ were tested.

In both the THG and FWM cases the Maker fringe geometry adopted allowed us to measure both the real and the imaginary parts of $\chi^{(3)}$ [1]. Therefore the dispersion of both the magnitude ($|\chi^{(3)}|$) and the phase ϕ ($\equiv\arctan[\mathrm{Im}(\chi^{(3)})/\mathrm{Re}(\chi^{(3)})]$) are used as probes of the third-order nonlinear susceptibility. For the frequency-shifted techniques, the susceptibilities were measured relative to fused silica and we explicitly assumed that there is no significant dispersion in the fused silica nonlinearity. This is reasonable since the primary absorptions in fused silica occur at wavelengths below 200 nm ($E_g=7.8$ eV) and recent Z-scan measurements have shown little or no dispersion for fundamental wavelengths above 355 nm [17]. Since we are comparing with molecular theories which are lacking in appropriate and consistent treatment of local field factors and orientational effects, we attempt no absolute comparison between experiment and theory. In all of our fits, the amplitude of the calculated spectrum has been scaled to the most prominent feature in each individual experimental spectrum. Note that vibrational substructures which have proven important in finite polyenes and may be at least partially responsible for the poor fits have not been included in either theory to date [10].

The experimental THG results on the red form of poly(4-BCMU) shown in Fig. 1 are partially taken from Ref. [8], augmented by additional data to extend the experiments to shorter wavelengths. The linear absorption and preparation of such thin films can also be found in our previous work [8]. Similar THG results were simultaneously reported by Townsend et al. [9]. Measurements below 700 nm (1.75 eV) appeared impossible with this material system. The double peak near 1500 nm (0.8 eV) has been interpreted previously as identifying transitions between the $1A_g$, and the $1B_u$ (peak at 545 nm, 2.275 eV) and

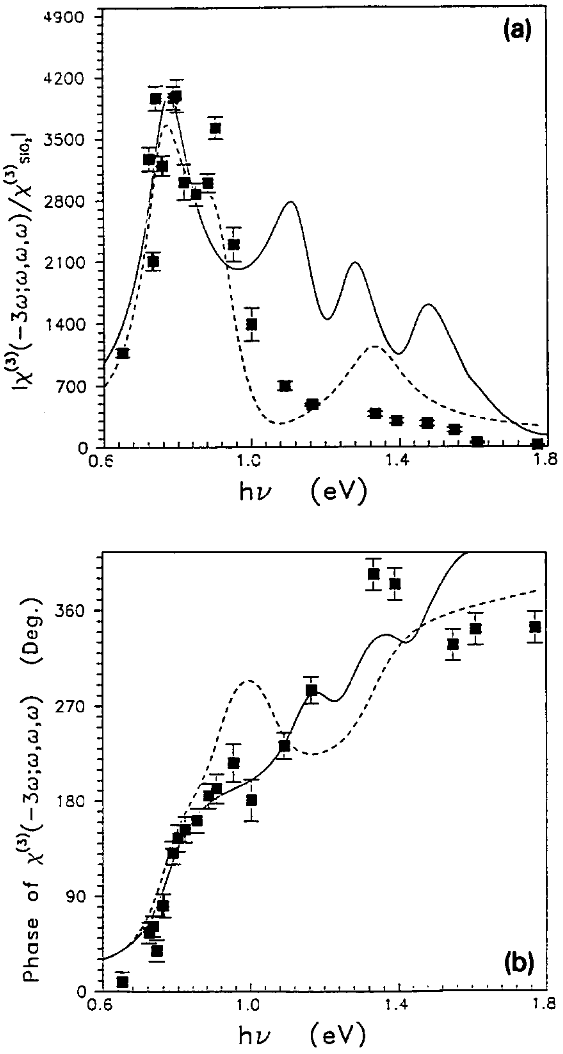

Fig. 1. (a) Magnitude and (b) phase of $\chi^{(3)}(3\omega)$ relative to fused silica. (■) Experimental results; (——) total anharmonic oscillator model calculation; (---) essential state model calculation.

$n\mathrm{B_u}$ (peak at 450 nm, 2.755 eV) states of the four essential states model [10]. Included in the data fitting are contributions from all of the interaction pathways $1\mathrm{A_g}\to\mathrm{B_u}\to\mathrm{A_g}\to\mathrm{B_u}\to 1\mathrm{A_g}$ where the intermediate $\mathrm{B_u}$ states can be $1\mathrm{B_u}$ and/or $n\mathrm{B_u}$ and the intermediate two-photon state can be the $m\mathrm{A_g}$ or the ground state. The energy difference between the $1\mathrm{A_g}$ and $1\mathrm{B_u}$ states was fixed by the measured linear absorption peak. The location of the $n\mathrm{B_u}$ and $m\mathrm{A_g}$ state were free variables, subject to the constraint that $E(n\mathrm{B_u}) > E(m\mathrm{A_g})$. Also fixed by the model were the ratios $\mu_{mg\to nu}/\mu_{1g\to 1u} = -2.0$ and $\mu_{mg\to 1u}/\mu_{1g\to 1u} = 2.2$ and the ratio $\mu_{1g\to nu}/\mu_{1g\to 1u}$ was a free variable predicted by the model to be small relative to the other values just stated [7,10]. The linewidth parameter γ was approximated from the linear absorption spectrum. The best least-squares fit shown in Fig. 1 gave $\mu_{1g\to nu}/\mu_{1g\to 1u} \approx 0.4$ and $\gamma = 2500\ \mathrm{cm^{-1}}$. The resulting fit to the essential states (ES) model is very good, and at the time provided strong evidence for the validity of that theory [10]. Our extended THG spectrum towards the UV shows no strong evidence of the calculated peak in the 800 nm (1.5 eV) range, which is primarily due to the $m\mathrm{A_g}$ state. Our previously reported two-photon-absorption measurements showed such a resonance, which has now been reinterpreted as being produced by excited state absorption and in particular due to triplet species being generated [18,19]. It is worth noting at this point that the two experimental techniques used in this work are insensitive to excited state populations, which is not the case of direct two-photon absorption measurements [8,9,18,19].

The best fit to the anharmonic oscillator (AO) model is also shown. In this model there are three free parameters $+\gamma$. However in this case all the parameters are fixed to the literature values [5]. The only adjusted parameters are the linewidth γ and the scaling factor, which allows to scale the calculations of the microscopic model to the measurement of the macroscopic nonlinear coefficient. The fit to the phase is better than that for the ES model. Note that in this case the scaling parameter vanishes, but the amplitude fit is worse because of the two large peaks predicted for energies above 1 eV. In both cases the experimental results do not show evidence of additional resonances above 1 eV, this is believed to be due to the probable inadequacy of the literature value used for the bond alternation parameter for polydiacetylene. A detailed analysis of the influence of the alternation parameter in the AO approach is in process and will be compared to some recent experimental results in short polyenes [20]. We note that these maxima are 'smoothed out', improving the fit because the inhomogeneous broadening observed in the experimental one-photon peak was also included in the analysis.

The results for the amplitude and phase of $\chi^{(3)}[-(2\omega_1-\omega_2);\omega_1,\omega_1,-\omega_2]$ are shown in Figs. 2 and 3 for the two fixed wavelengths $\lambda_2 = 1064$ nm (1.165 eV) and 1904 nm (0.651 eV). In such experiments many different resonances are expected over a very broad range of wavelengths. For example, the beginning of a resonance in Fig. 3 around 1.4 eV could be interpreted as the expected resonance from the $m\mathrm{A_g}$ state predicted by the ES model, however it could also be due to a ground state Raman contribution. The latter resonance not being reproduced in Fig. 2, where the difference between both input frequencies ($\geqslant 4155\ \mathrm{cm^{-1}}$) excludes the possibility of a two-photon resonance. The enhancement observed in the 1.35 eV range in Fig. 3 can then probably be assigned to a Raman active mode with a resonant frequency approximately equal to $1500\ \mathrm{cm^{-1}}$ corresponding to the carbon double bond stretch [21]. From Figs. 1 and 2 the presence of the previously expected dominant two-photon resonance in the 1.3–1.4 eV range was not found. In all three complex spectra a strong and broad three-photon resonance is present making the deconvolution with additional multiphoton resonances difficult. Fitting all three spectra to a single set of parameters including three or four excited states like the ES model was proven impossible, demonstrating the effectiveness of multiple nonlinear spectroscopic techniques in these molecular systems.

We used the parameters obtained from fitting the THG spectra to generate theoretical FWM spectra for poly(4-BCMU). They are shown as the solid lines for the AO model and dotted lines for the ES model in Figs. 2 and 3. Although the positions of the peaks match well, the fits to the relative amplitudes and phases are unsatisfactory for the ES model, especially the phase. The situation for the AO fit is somewhat better. However, it is clear that there are large differences in relative intensities of spectral features.

We draw a number of conclusions from our results.

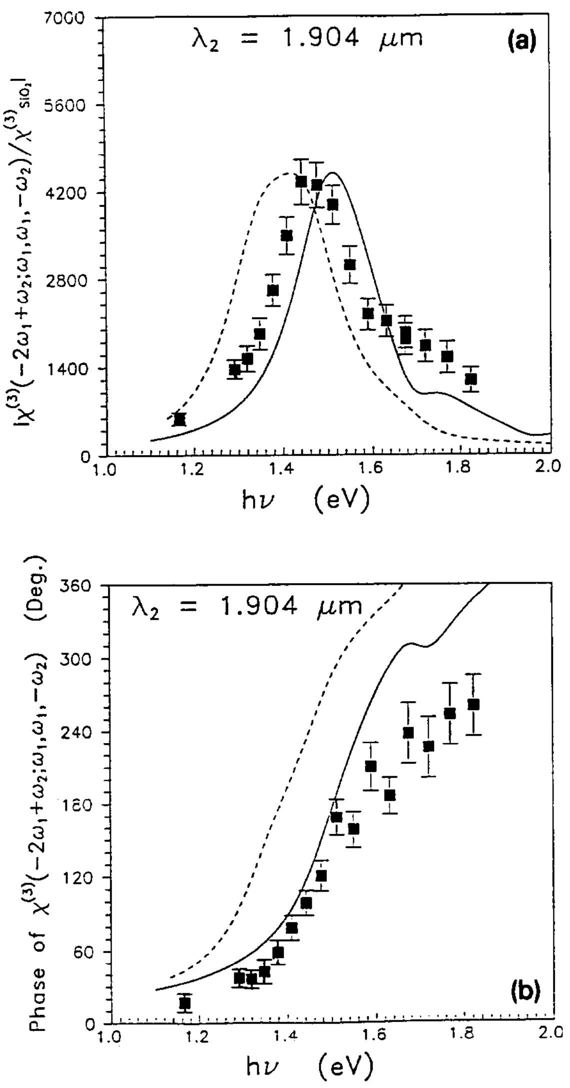

Fig. 2. (a) Magnitude and (b) phase of FWM relative to fused silica (λ_2=1900 nm). (■) Experimental results; (——) anharmonic oscillator model calculation; (- - -) essential states model.

Molecular theories for nonlinearities in polyenes provide just a first approximation to the frequency dispersion of various third-order nonlinearities in the sense that the positions of the dominant spectral features are predicted. However, the fits to the experimental spectra were not satisfactory in detail for either the four essential states or anharmonic oscillator models. Here we report only experiments on poly-(4-BCMU): similar conclusions were reached on polythiophenes which will be published elsewhere. None of the experimental techniques described here could clearly identify a sharp two-photon resonance, otherwise necessary to explain the phase of the susceptibility; the nonlinearities are positive off-resonance. On the other hand because of the poor agreement with existing theories, the spectral position of one or several two-photon oscillators/states is still a question to be answered in polydiacetylenes [9,18,19]. From a theoretical point of view the question of the ade-

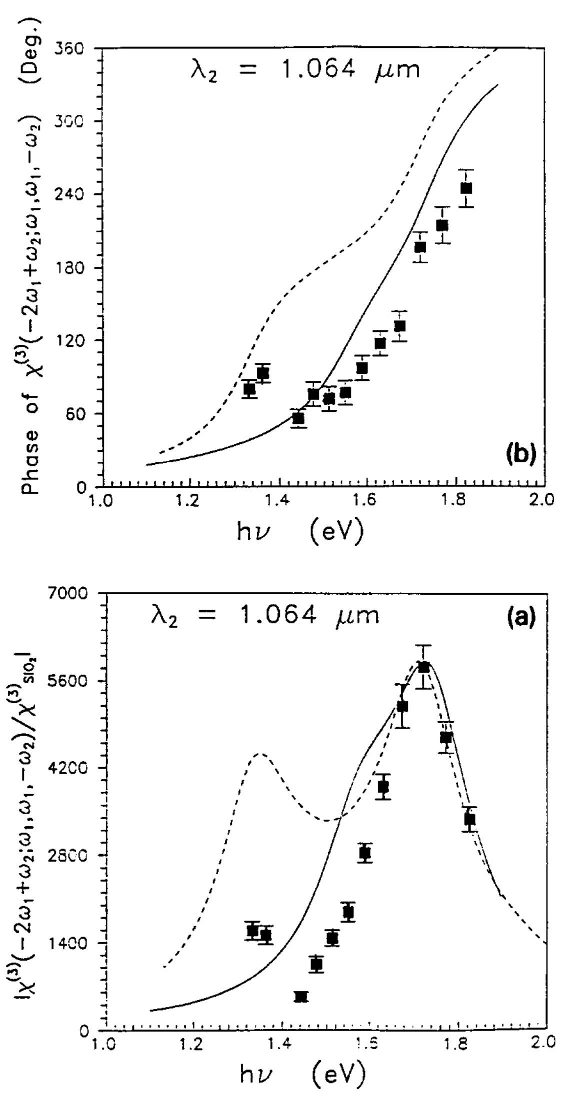

Fig. 3. (a) Magnitude and (b) phase of FWM (λ_2=1064 nm) relative to fused silica. (■) Experimental results; (——) total anharmonic oscillator model calculation; (- - -) essential states model calculation.

quacy of the choice of the Hamiltonian more than the method to solve it has to be raised, in particular in the case of polydiacetylenes. The latter system shows a double periodicity which is not specifically included in the PPP Hamiltonian and somewhat modelled by an arbitrarily large bond alternation parameter. Inclusion of proper broadening mechanism seems to be necessary for an accurate comparison. Besides the experimental evidence of the need of one or several two-photon states, their location and strengths can only be inferred from this work.

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