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POLYACETYLENE BY ACOUSTIC PHONON
SPECTROSCOPY

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IDENTIFICATION OF ELECTRONIC TRANSITIONS IN
POLYACETYLENE BY ACOUSTIC PHONON SPECTROSCOPY

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Abstract We have found that a strain-induced oscillation in the decay of the picosecond photoinduced absorption of polyacetylene $(CH)_x$ can be used to identify the allowed and forbidden electronic transitions in that polymer.

INTRODUCTION

Recently, it has been shown¹ that the main contributions to optical nonlinearities in conducting polymers come from four "essential" electronic states, including a two-photon state (mA_g) lying above the lowest optical exciton ($1B_u$). Although the transition from the ground ($1A_g$) state to mA_g is inaccessible in photomodulation experiments with small photon intensities, it can, in principle, be observed via electroabsorption (EA) and third harmonic generation (THG). The energy of mA_g is important because two-photon absorption into this state could limit the performance of nonlinear optical devices in the region where the polymer is ordinarily transparent.

A common feature in photoinduced changes in transmission ($\Delta T/T$) or in reflection ($\Delta R/R$) is a strain-induced oscillation or "phonon echo," respectively, superimposed on the electronic decay,²⁻⁴ which can be used to measure sound velocity and acoustical attenuation,⁵ and the dispersion relation of longitudinal acoustic phonons.⁶ Here we report the results of a new type of strain modulation spectroscopy, revealing a transition in polyacetylene at 1.7 eV, which may be associated with the mA_g state.

FIGURE 1 The spectra of $\Delta T/T|_s$ (solid line through solid circles), $\alpha(\omega)$, and its derivative $\frac{\partial \alpha}{\partial \omega}$.

though $\frac{\partial \alpha}{\partial \omega}(1.7 \text{ eV}) < \frac{1}{2} \frac{\partial \alpha}{\partial \omega}(2.0 \text{ eV})$. One source of the discrepancy may be the neglect of ΔR in Eq. (1). When this is taken into account Eq. (1) becomes

$$\frac{\Delta T}{T}|_s = -\Delta \alpha d - \left(\frac{2}{n} \right) \frac{[(n^2 - \kappa^2 - 1)\Delta n + 2n\kappa\Delta \kappa]}{[(n+1)^2 + \kappa^2]}, \quad (2)$$

where $\Delta \alpha$, $\Delta \kappa$, and Δn , are the strain-induced changes in the absorption, extinction coefficient, and refractive index, respectively. The first term is the same as that in Eq. (1). The second one can be determined from the Kramers-Kronig relation between $\Delta \alpha$ and Δn .⁷ The relevant spectral region in Fig. 1 is below the $1B_u$ exciton of cis-(CH)_x (2.0 eV).⁸ For $E < E_i$, one finds

$$|n\rangle = |n^{(0)}\rangle + \sum_{m \neq n} \frac{\langle n^{(0)} | H_s(z) | m^{(0)} \rangle | m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}, \quad (4)$$

where the unperturbed and excited states are $|n^{(0)}\rangle$ and $|m^{(0)}\rangle$, respectively, with energies $E_n^{(0)}$ and $E_m^{(0)}$, and¹⁴

$$H_s(z) = \eta_{zz}^2(z) \left(\frac{B}{2} + \frac{2}{3} \mu \right) - 3B\beta\Delta\theta(z)\eta_{zz}(z), \quad (5)$$

where η_{zz} is the only nonzero element of the strain tensor,⁵ B and μ are the bulk and shear moduli, respectively, β is the coefficient of thermal expansion, and $\Delta\theta$ is the temperature rise in the film. Thus, following photoexcitation, transitions, from the ground state, for example, have an amplitude proportional to the dipole matrix element

$$M_{0n} = \sum_{m \neq n} \frac{\langle n^{(0)} | H_s(z) | m^{(0)} \rangle \langle n^{(0)} | H_d(z) | m^{(0)} \rangle}{E_n^{(0)} - E_m^{(0)}}, \quad (6)$$

where H_d is the dipole operator. Since $\Delta\alpha \sim |M_{0n}|^2$, and the presence of an oscillation in $\Delta T(t)$ is due to sign changes in $\eta_{zz}(t)$,² only the component proportional to the product of the two terms in Eq. (5) contributes to the oscillation amplitude. For $(CH)_x$, this component is more than an order of magnitude greater than the square of the first term in Eq. (5), but smaller than the square of the second term by the same amount. Nevertheless, the cross-term may still be significant compared to contributions associated with Eq. (1), and, in fact, could be the only source of intensity in $\Delta T/T_s$ at 1.7 eV. A quantitative comparison between contributions from Eqs. 1 and 6 is not possible, however, without knowing the wavefunctions of the excited states.

spectrum indicates that the associated transition is only weakly allowed, by defects,¹⁷ for example. Since this energy is above that of the $1B_u$ exciton, and is close to twice that of the two-photon resonance (0.8 eV) in $\text{trans}-(\text{CH})_x$,¹⁸ we associate it with the mA_g state. Perhaps this transition is not detected in $(\text{CH})_x$ by EA since it is obscured by vibronic sidebands.¹⁹

We contrast the present results with those obtained in PT,⁶ for which $\Delta T/T|_s$ is well described by Eq.(1). According to two-photon absorption measurements²⁰ the lowest A_g states are above the $1B_u$ level ($E_i > 2.1$ eV). Thus, for PT in our energy range we detect only the optically allowed transition and its phonon sidebands; observing forbidden states requires probing at higher energies. Furthermore, from Eqs.(5) and (6), at energies corresponding to optically forbidden transitions, $\Delta T/T|_s$ is nonlinear in the strain. However, for PT, at 2 eV, $\Delta T/T|_s$ is linear in pump pulse energy from 5.4 pJ to 4 nJ, supporting the contention that we detect mainly allowed transitions in that polymer. We have not yet checked the intensity dependence of the 1.7 eV transition in $(\text{CH})_x$.

In conclusion, we have found a potentially useful technique for detecting both allowed and forbidden optical transitions, especially when they cannot be observed by other methods of modulation. It is particularly suitable for conducting polymers, for which the lowest excited A_g states are often at energies accessible to modelocked dye and Ti:sapphire lasers.

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