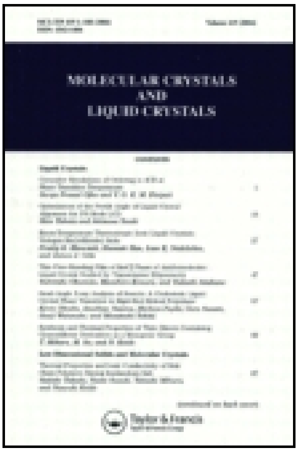

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IDENTIFICATION OF ELECTRONIC TRANSITIONS IN POLYACETYLENE BY ACOUSTIC PHONON SPECTROSCOPY

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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 shown[1] 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.

EXPERIMENT

We used two independent ps dye lasers for the pump and probe beams, synchronously pumped by a frequency-doubled mode-locked Nd:YAG laser at 76 MHz repetition rate. The pump photon energy was fixed at 2.14 eV, whereas the probe was varied between 1.2 and 2.1 eV. The magnitude of the strain-induced change in transmission ($\Delta T/T|_s$) was determined from the oscillation amplitude detected in $\Delta T(t)/T$. Raman spectra were measured in the forward direction using a triple spectrograph with 3 cm^{-1} resolution coupled to a CCD array. A CW Ti:sapphire (Spectra Physics) provided excitation between 700 and 850 nm, and incident power of 100 mW at each wavelength. The antiStokes (AS) to Stokes (S) ratio AS/S was corrected for CCD efficiency, the ω^4 scattering law, exposure time, and self-absorption. The sample was a thin film of Shirakawa cis-rich $(CH)_x$ (1200 Å), which was found, from Raman spectra, to contain a 50/50 mixture of cis/trans $(CH)_x$.

RESULTS AND DISCUSSION

Fig. 1 shows the spectrum of $\Delta T/T|_s$ in cis-rich $(CH)_x$, along with the absorption coefficient $\alpha(\omega)$ and its derivative $\frac{\partial\alpha}{\partial\omega}$. The correspondence between $\Delta T/T|_s$ (ω) and $\frac{\partial\alpha}{\partial\omega}$ follows from[2,6]

$$\left.\frac{\Delta T}{T}\right|_s^i \approx \frac{\partial\alpha}{\partial\omega}\frac{\partial E_i}{\partial\eta} < \eta(t) > \frac{d}{\hbar}, \tag{1}$$

where $\frac{\partial E_i}{\partial\eta}$ is the deformation potential of the $1B_u$ exciton level E_i, η is the strain, d the thickness of the film, and $\hbar$ is Planck's constant (reduced). As seen in Fig.1, though, the agreement between $\Delta T/T|_s$ and $\frac{\partial\alpha}{\partial\omega}$ in cis-rich $(CH)_x$ is poor. For example, $\Delta T/T|_s(1.7\text{ eV})=4*\Delta T/T|_s(2.0\text{ eV})$ even

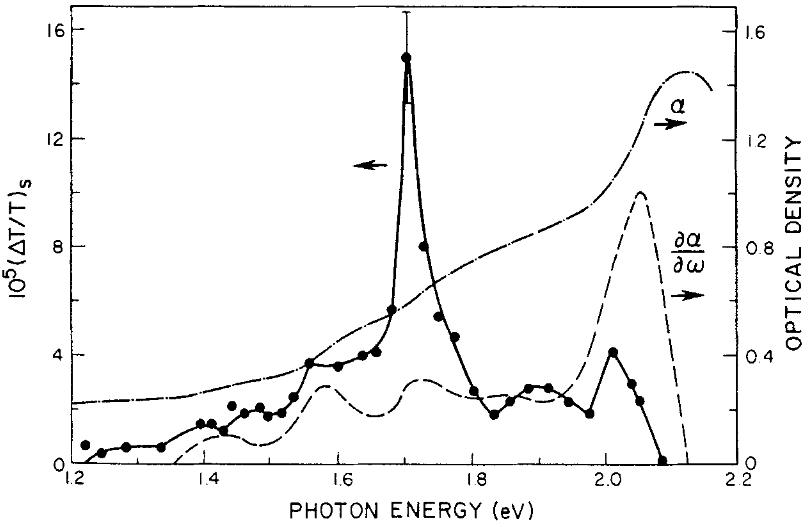

FIGURE 1 The spectra of $\Delta T/T|_s$ (solid line through solid circles), $\alpha(\omega)$, and its derivative $\frac{\partial\alpha}{\partial\omega}$.

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

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

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

$$\Delta n(E) = \left[\frac{\partial \eta}{\partial E} - \frac{1}{2E^2} \ln\left(\frac{E_i - E}{E_i + E} \right) \right] \frac{\partial E_i}{\partial \eta} \eta . \qquad (3)$$

Using Eqs. (2) and (3) we evaluated the effect of ΔR from the real and imaginary parts of the dielectric constant for oriented cis-$(CH)_x$,[9] accounting for a 0.3 eV blue-shift of $\alpha(\omega)$ in stretched cis-$(CH)_x$ from that of our unoriented sample. The result is that the second term in Eq. (2) is negligible compared to the first one, so that $\Delta\alpha(\omega)$, not $\Delta n(\omega)$, is the main contributor to $\Delta T/T|_s$.

Most of the excitations photogenerated on cis linkages migrate toward trans-$(CH)_x$ segments.[10] Thus, features in Fig.1 probably have contributions from both isomers, suggesting that a difference between deformation potentials of E_i in them may account for the discrepancy between $\Delta T/T|_s$ and $\frac{\partial \alpha}{\partial \omega}$. However, the difference in $\frac{\partial E_i}{\partial \eta}$ is not nearly large enough[11] for Eq.(1) alone to accurately describe Fig.1.

We assumed above that the spectrum of Fig.1 is associated solely with transitions that are allowed in the undeformed state, as is the case for piezoreflectance in $(CH)_x$, the features of which are attributed to vibronic structure in the absorption spectrum, which is rigidly shifted upon application of stress.[12] In principle, forbidden transitions can be induced when the crystal symmetry is changed by uniform compression.[13] However, if the stress is nonuniform, possessing an odd parity component, or no symmetry under inversion, then new transitions may appear, regardless of the orientation of the stress, which can mix states of the same parity. In our experiment, for which the stress is thermally generated (with an exponential spatial profile), such transitions, unaccounted for by Eq.(1), may give rise to the peaks in Fig.1. This can be seen from time-independent perturbation theory, which gives

$$|n> = |n^0> + \sum_{m\neq n} \frac{<n^{(0)}|H_s(z)|m^{(0)}>|m^{(0)}>}{E_n^{(0)} - E_m^{(0)}}, \tag{4}$$

where the unperturbed and excited states are $|n^{(0)}>$ and $|m^{(0)}>$, respectively, with energies $E_n^{(0)}$ and $E_m^{(0)}$, and[14]

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

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

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

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 1.7eV. A quantitative comparison between contributions from Eqs. 1 and 6 is not possible, however, without knowing the wavefunctions of the excited states.

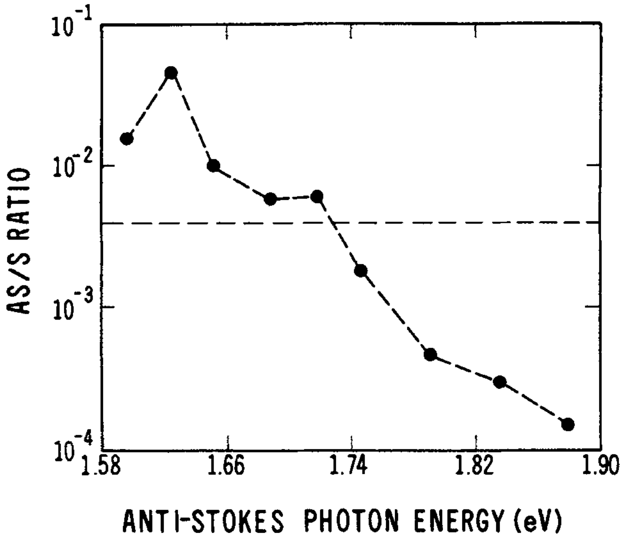

FIGURE 2 Excitation profile of the AS/S ratio for the 1100 cm^{-1} (0.136 eV) C-C stretching mode of trans-$(CH)_x$

The forbidden nature of the 1.7 eV peak may be elucidated by Fig.2, which shows the excitation profile of the AS/S ratio for the 1100 cm^{-1} (0.136 eV) C-C stretching mode of trans-$(CH)_x$. The prominent features are a peak at 1.62 eV and a shoulder at 1.71 eV. These features are indicative of resonances between the outgoing photons and electronic transitions of trans-$(CH)_x$, which should be enhanced only at energies coinciding with allowed transitions.[15] The high intensity of the 1.62 eV resonance and its proximity to the three-photon resonance of trans-$(CH)_x$ at 0.55 eV in THG,[16] suggest that the small shoulder at 1.6 eV (Fig.1) is associated with the (optically allowed) $1B_u$ exciton. Similarly, we attribute the peak at 2 eV (Fig.1) to the $1B_u$ exciton of cis, since this energy is close to three times that of the three photon resonance (0.7 eV) of cis-rich $(CH)_x$.[16] On the other hand, the low intensity of the 1.7 eV outgoing resonance in the AS/S 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 trans-$(CH)_x$,[18] we associate it with the mA_g state. Perhaps this transition is not detected in $(CH)_x$ 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 measurements[20] 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 $(CH)_x$.

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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