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Optical properties of highly oriented fibrous polyacetylene

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The optical reflectivity of thick-film (20–30 μm) polyacetylene, highly oriented by mechanical stretching, has been measured using polarized light. A Kramers-Kronig analysis of the data has been used to determine the optical absorption coefficient for polarization parallel and perpendicular to the chain axis. These novel optical data for fibrous polyacetylene are compared with those already reported on Durham polyacetylene. We have worked out a tight-binding model, extended to include the electronic coupling between neighboring chains within a three-dimensional periodic lattice. From a rough evaluation of the transverse hopping integral derived from the width of the vibronic absorption peaks an estimate of the number of the interchain photocarriers generated by radiation polarized perpendicular to the chain direction is provided. A comparison between calculated and experimental optical anisotropies indicates that the measured optical response perpendicular to the chain direction originates entirely from the chain misalignment.

INTRODUCTION

The evaluation of the anisotropy of the optical properties of polyacetylene is in principle quite important for a better understanding of the optical transitions and of the mechanism of photogeneration of the carriers in a three-dimensional polymer lattice using polarized light.[1–4] Moreover it has been recently shown[5] that for oriented polyacetylene, like any other anisotropic crystal, the true Raman cross sections can be inferred from the measured intensities in the various scattering configurations only if the optical reflectivity and absorption coefficient and their anisotropies are known.

So far an accurate investigation of the optical properties of fully oriented polyacetylene has been carried out only on the nonfibrous crystalline material obtained by orientation of a precursor polymer during the thermal conversion to polyacetylene.[6] We have felt that in consideration of its different morphology, the measure of the optical constants of the stretch-oriented Shirakawa polyacetylene could yield an additional insight on the nature of the interband transition of this prototype semiconducting polymer. Also we will concentrate our attention on the *cis* isomer of polyacetylene, which exhibits a well-defined pattern of vibronic structure and has been less studied than the *trans* isomer. In a way the *cis* isomer of polyacetylene is a better system from which to obtain information, since its optical spectra are quite sample independent, and inhomogeneous broadening of the spectra due to a distribution of electronic energies does not occur. As a matter of fact, it is well established that the thermal *cis-trans* isomerization is associated with a production of defects (cross links, deviations from planarity, etc.) which originate a distribution of conjugation lengths and therefore of the electronic and vibrational energies in *trans*-polyacetylene. For this reason, in the case of *trans*-polyacetylene, it might be difficult to single out the broadening of the peaks in the optical spectra caused by interchain interactions.

The data obtained in the present paper will also be discussed in connection with the still ongoing discussion concerning the direct photoproduction of interchain excitations which, being long lived, are assumed to dominate the photoconductive response of polyacetylene.

The aim of this work is to detect the effects of the interchain interactions on the optical response of polyacetylene. With this in mind we have worked out a tight-binding model extended to include the effect of the interchain interactions on the electronic energies and on the transition moments. However, we anticipate at this point that a theoretical interpretation of the optical data in terms of three-dimensional effects is complicated by the fact that the observed anisotropy originates from both an electronic transition moment perpendicular to the chains and to the small but not negligible sample misalignment.

EXPERIMENT

Highly oriented (draw ratio 7) films were a gift by Enichem Research Laboratories. The polymerization procedure adopted[7] uses a Ti-based catalyst and yields a pristine *cis*-polyacetylene film, 2–4 μm thick, which can be stretched up to seven–eight times its original length. The as-synthesized film exhibits a fibrillar morphology as detected from scanning electron microscopy technique. The overall density of the oriented film is 1.0–1.1 g/cm^3 thus approaching the theoretical crystallographic density (1.15 g/cm^3).[7] X-ray measurements carried out on this sample[8] indicate a degree of crystallinity of 97% and a misalignment angle of 10 deg.

The polarized reflectivity and transmission measurements in the wave-number range between 500 (0.062 eV) and 5000 cm^{-1} (0.62 eV) were performed by a Bruker 113v Fourier-transform spectrometer, equipped with a KRS5 polarizer. A Perkin Elmer 330 automatic spectrophotometer was used in the energy range from 0.5 to 4.2 eV, with dichroic sheet polarizers in the sample and reference beams. Special accessories for both instruments allowed us to carry out the reflectivity measurements at near-normal incidence in vacuum for the infrared region and in inert atmosphere in the visible-to-ultraviolet region.

The reflectivity of the samples, shown in Fig. 1, was obtained relative to the reflectivity of an aluminum mirror, which was previously carefully measured by a V-W absolute-reflectivity accessory, in order to normalize our spectra. A further check of reflectivity measurements was performed with collimated laser light ($\lambda=634$, 514, 488, and 457 nm) on very small (< 1 mm diameter) and particularly smooth sample regions. In this way we were able to account for the surface unhomogeneities, whose dimensions were found to be of the same order of the spectrophotometer light spot. As to the infrared region, this check was made by an infrared microscope with 15× objective and a light-spot diameter of about 100 μm.

The complex refraction index $\tilde{n}(\omega)=n(\omega)+ik(\omega)$, obtained by Kramers-Kronig (KK) analysis on the experimental reflectivity spectra for both the light polarizations, is shown in Fig. 2. It has to be pointed out that in the energy region where multiple reflection and interference effects are present (infrared region), the reflectivity data for KK transformations (R_0) could not be taken as measured. In fact, R_0 was deduced from the relations[9] between the measured reflectivity R and the transmission T_0:

$$R_0=R+\frac{(1-R)^2Re^{-2\alpha d}}{1-R^2e^{-2\alpha d}} ,$$

$$T_0=\frac{(1-R)^2e^{-\alpha d}}{1-R^2e^{-2\alpha d}} ,$$

where T_0 is the transmission averaged on the period of interference fringes, α is the absorption coefficient, and d is the sample thickness.

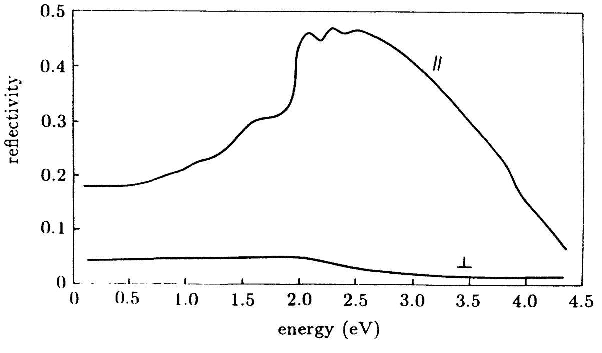

FIG. 1. Optical reflectivity measured with light parallel and perpendicular to the stretching direction.

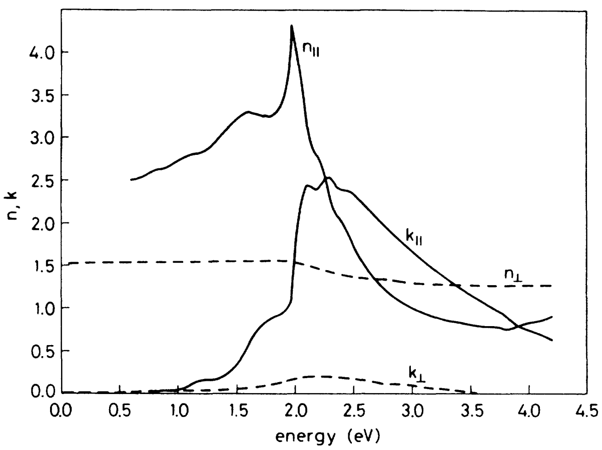

FIG. 2. Real and imaginary parts of the refractive index, as obtained by KK analysis of the experimental reflectivity spectra for both the light polarizations.

The integral required in KK analysis calls for the reflectivity over an infinite range of energies, so it has been necessary to introduce an extrapolation procedure. In our analysis a tail[10] $R(\omega)=R(\omega_2)(\omega_2/\omega)^s$ was used beyond the last experimental energy ω_2; such extrapolation is expected to give quite good results if the parameter s can be adjusted to reproduce the value of some optical functions independently known at one or more selected energies. With that purpose we deduced the value of the refraction index n in the infrared region by the well-known relation[11]

$$n=\frac{N_f}{2d(\nu_1-\nu_2)} ,$$

where N_f is the number of fringes in the wave-number interval $\nu_1-\nu_2$ considered. The values so obtained and employed as fixed points in KK analysis were $n=2.52$ at 0.62 eV for parallel light polarization, and $n=1.51$ at 0.496 eV for perpendicular light polarization (in both cases the extinction coefficient k was ≈ 0).

THEORETICAL EVALUATION OF THE OPTICAL PROPERTIES

The calculation of the electronic absorption spectrum of a conjugated carbon chain has been carried out by Flytzanis *et al.*[12] using the one-electron tight-binding approach to describe the π electronic states. These authors have considered the case of a one-dimensional crystal consisting of a single or two coupled infinite polyenic chains made of collinear carbon atoms. Because of this assumption only the components of the electronic transition parallel to the chain can be evaluated.

In this section the optical transitions of a three-dimensional crystal of polyacetylene (again made of chains of collinear atoms) will be studied by extending the formalism developed by Flytzanis *et al.* to include the effects of the interchain coupling. It is expected that interchain interactions will have three effects on the optical response of a one-dimensional chain, namely the removal of the inverse-square-root singularity, the reduction of the band-gap energy, and the appearance of a transition moment perpendicular to the chain. According to Refs. 12 and 13, the electronic transition moment is given by

$$\mathbf{M}_{nn'} \propto \frac{1}{V}\int u_{n'\mathbf{k}}(\mathbf{r})\nabla_{\mathbf{k}} u_{n\mathbf{k}}(\mathbf{r})d\tau \ , \tag{1}$$

where $\mathbf{k}$ is the wave vector corresponding to the vertical optical transition, V is the volume of the unit cell, $d\tau$ is the infinitesimal volume element, and $u_{n'\mathbf{k}}$ is the unit-cell periodic part of the Bloch wave function Φ:

$$\Phi_{n\mathbf{k}}(\mathbf{r})=e^{i\mathbf{k}\cdot\mathbf{r}}u_{n\mathbf{k}}(\mathbf{r}) \ . \tag{2}$$

The crystal structure of *trans*-polyacetylene[14] is shown in Fig. 3. The unit cell contains two inequivalent matching[14] chains. The wave-function Φ is constructed as a linear combination of the atomic orbitals belonging to the two chains:

$$\begin{aligned}\Phi_{s\mathbf{k}}(\mathbf{r})&=(N_1N_2N_3)^{-1/2}\sum_{l=1}^{N_1}\sum_{m=1}^{N_2}\sum_{n=1}^{N_3} e^{A(l,m,n)}B(l,m,n) \ ,\\ A&=\mathbf{k}\cdot[(l-1)a\mathbf{i}+(m-1)b\mathbf{j}+(n-1)c\mathbf{k}] \ , \qquad (3)\\ B&=c_1^{s\mathbf{k}}\varphi_{4l-3,4m-3,4n-3}+c_2^{s\mathbf{k}}\varphi_{4l-2,4m-2,4n-2}\\ &\quad +c_3^{s\mathbf{k}}\varphi_{4l-1,4m-1,4n-1}+c_4^{s\mathbf{k}}\varphi_{4l,4m,4n} \ ,\end{aligned}$$

where the φ's are the atomic wave functions for the p_z electrons, and $c^{s\mathbf{k}}$ are the expansion coefficients which can be determined by minimizing the total π electronic energy of the crystal. By inserting Eq. (3) into Eq. (1) and using the relation

$$\int \varphi_i^* x \varphi_j d\tau=\delta_{ij}x_i \ , \tag{4}$$

one obtains for the x component of the electronic transition moment

$$M_{ss'}^x(\mathbf{k})=\sum_{p=1}^{4}\left[-ic_p^{s'*}c_p^s+c_p^{s'*}\frac{\partial}{\partial k_x}c_p^s\right] \ , \tag{5}$$

with analogous expressions holding for the y and z components. Evaluation of Eq. (5) requires analytical expressions for the expansion coefficients. With reference to Fig. 3, three interchain transfer parameters are seen to be relevant in polyacetylene, namely β_x, β_y (the transfer integrals between translationally equivalent chains in the x and y directions), and β' (the transfer integral between chains in the unit cell). Neglecting β_y because $b \gg a$, and using the Bloch theorem, we obtain the following set of equations for the $c's$:

$$(\alpha_1-\epsilon)c_1+\beta c_2+\gamma c_3+(\gamma+\beta' e^{-i\theta_c})c_4=0 \ , \tag{6a}$$

$$\beta^* c_1+(\alpha_1-\epsilon)c_2+(\gamma+\beta' e^{i\theta_c})c_3+\gamma c_4=0 \ , \tag{6b}$$

$$\gamma^* c_1+(\gamma^*+\beta' e^{-i\theta_c})c_2+(\alpha_1-\epsilon)c_3+\beta c_4=0 \ , \tag{6c}$$

$$(\gamma^*+\beta' e^{i\theta_c})c_1+\gamma^* c_2+\beta' c_3+(\alpha_1-\epsilon)c_4=0 \ , \tag{6d}$$

where

$$\alpha_1=\alpha+2\beta_x\cos\theta_a \ , \tag{7a}$$

$$\beta=\beta_1+\beta_2 e^{-i\theta_c}+2\beta_x\cos\theta_a \ , \tag{7b}$$

$$\gamma=\beta'(1+e^{-i\theta_a})(1+e^{-i\theta_b}) \ , \tag{7c}$$

$$\theta_a=k_x a; \quad \theta_b=k_y b; \quad \theta_c=k_z c \ . \tag{7d}$$

Only if we neglect the terms $\beta' e^{\pm i\theta_c}$ can a four-band analytical solution of Eqs. (7) be found. For the moment, however, we shall be content with the two-band solution, which is obtained by putting $\beta'=0$ (no interactions within the cell). In this way the problem becomes a two-dimensional one, $M_{cv}(k)$ having only x and z components. Their expressions are given by

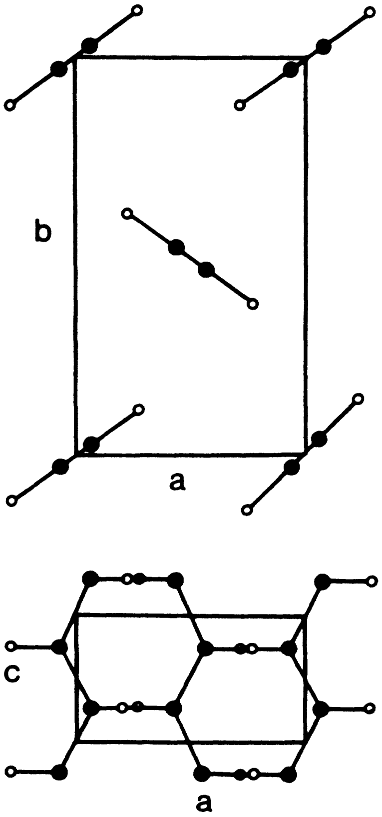

FIG. 3. Two schematic projections of the structure of *trans*-CH$_x$. $a=4.24$ Å; $b=7.32$ Å; $c=2.46$ Å, and $\beta=91.5°$ (from Ref. 14).

$$M^x_{cv}(\mathbf{k})=\frac{ia}{4\epsilon^2}(\epsilon^2-\epsilon_0^2+\beta_x^2)\ , \tag{8}$$

$$M^z_{cv}(\mathbf{k})=\frac{ic}{4\epsilon^2}[\epsilon_0^2-\epsilon^2+\beta_2^2-\beta_1^2+\beta_2\beta_x\cos(\theta_c-\theta_a)]\ , \tag{9}$$

where

$$\epsilon_0^2=\beta_1^2+\beta_2^2+2\beta_1\beta_2\cos\theta_c\ , \tag{9a}$$

$$\epsilon^2=\epsilon_0^2+\beta_x^2+2\beta_1\beta_x\cos\theta_a+2\beta_2\beta_x\cos(\theta_c-\theta_a)\ . \tag{9b}$$

Once the components of the transition moment are known, the contribution to the optical susceptibility coming from the π electrons can be evaluated using the relation[13]

$$\chi_\pi=\frac{2e^2}{\pi\hbar}\int_{-\pi/c}^{\pi/c}dk_z\int_{-\pi/a}^{\pi/a}dk_x\frac{\omega_{cv}(\mathbf{k})|M_{cv}(\mathbf{k})|^2}{\omega_{cv}^2(\mathbf{k})-[\omega-(i/\tau_0)]^2}\ , \tag{10}$$

where e is the electronic charge, $\omega_{cv}(\mathbf{k})$ is the transition frequency, and τ_0 is the lifetime of the optical excitation. Optical properties are obtained through the following standard relations, in which the local-field corrections to the perpendicular component of the dielectric constant have been taken into account:

$$\epsilon_\parallel=1+4\pi\chi_\parallel\ , \tag{11a}$$

$$\epsilon_\perp=\frac{1+2\pi\chi_\perp}{1-2\pi\chi_\perp}\ , \tag{11b}$$

$$\chi_\parallel=\chi_\pi^\parallel+\chi_\sigma^\parallel\ , \tag{11c}$$

$$\chi_\perp=\chi\sigma^\perp+\chi_\pi^\perp\ , \tag{11d}$$

$$n=\{\tfrac{1}{2}[(\epsilon_1^2+\epsilon_2^2)^{1/2}+\epsilon_1]\}^{1/2}\ , \tag{11e}$$

$$k=\{\tfrac{1}{2}[(\epsilon_1^2+\epsilon_2^2)^{1/2}-\epsilon_1]\}^{1/2}\ , \tag{11f}$$

$$\alpha=\frac{2\omega k}{c}\ , \tag{11g}$$

$$R=\frac{(n-1)^2+k^2}{(n+1)^2+k^2}\ . \tag{11h}$$

The contribution coming from the σ electrons is easily evaluated within the bond-polarizability theory.[15] The following values have been obtained elsewhere:[16] $\chi_{\sigma\parallel}=1.87$, and $\chi_{\sigma\perp}=1.98$.

Figure 4 shows the optical properties calculated within the framework of the model previously sketched. The effect of the interchain interactions on the joint density of states is shown in Fig. 5. It is quite apparent that the inverse-square-root-type singularity of the purely one-dimensional case is replaced by a rounded peak and a shoulder separated by $4\beta_x$. The width of the vibronic peaks observed in the reflectivity spectra (Fig. 4), about 400 cm^{-1}, is incompatible with a value for β_x greater than 0.1 eV.

All in all, the optical properties calculated using a tight-binding model appear in reasonable agreement with the experimental data. It should be noticed that, since in the model the electron-phonon interaction has not been

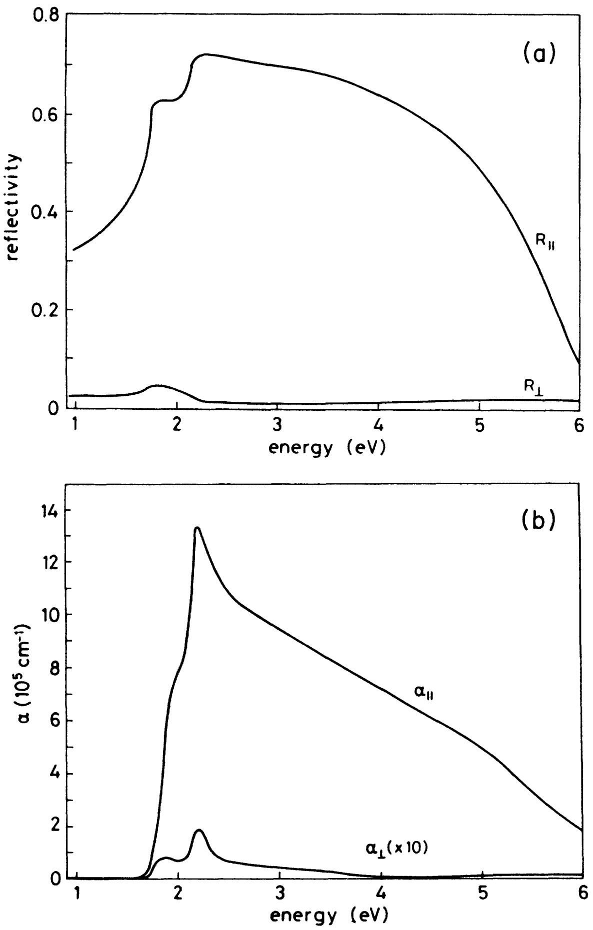

FIG. 4. Reflectivity (a) and absorption coefficient (b) as calculated for both the polarizations of light within the framework of the theoretical model [$\beta_1=3$ eV; $\beta_2=4$ eV; $\beta_x=0.1$ eV].

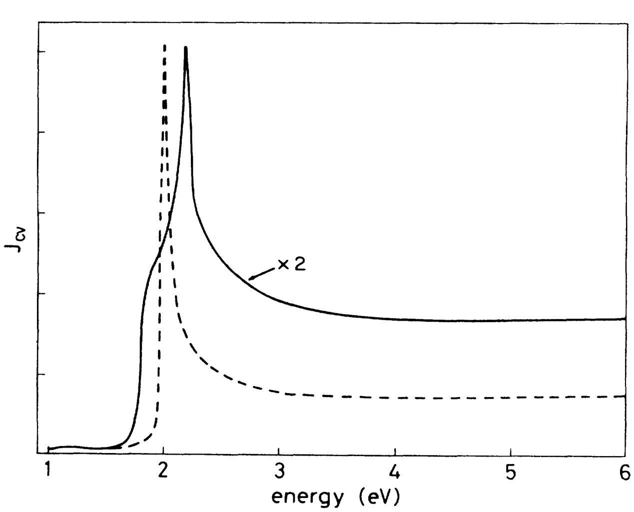

FIG. 5. Joint density of states for the one- (— — —) and three- (———) dimensional model.

included, the vibronic structure (experimentally observed as three distinct peaks separated by an average phonon frequency of 1300 cm^{-1}) is not accounted for by the calculations.

The peak value of the reflectivity ($R_{\parallel}=0.75$) is somewhat higher than the observed value. However, it should be noticed that the poor optical quality of our sample, which exhibits grooves due to the stretching process, is possibly responsible for this discrepancy. As a matter of fact, $R_{\parallel}$ measured on samples of Durham polyacetylene,[17] which certainly possess a smoother surface, is closer to the calculated value. Also, the peak absorption coefficient α is calculated to the correct order of magnitude.

The inclusion of the interchain coupling β_x results, as anticipated, in a lowering of the gap energy, in the appearance of a perpendicular component of the absorption, and in a broadening and splitting of the joint density of the states.

An estimate of β_x has been given by Moses *et al.*[18] by examining the pressure dependence of the photoabsorption in polyacetylene. These authors have concluded that $\beta_x=0.1$ eV can be regarded as the upper limit of the interchain interactions. By using this value we have calculated in the gap region an anisotropy $\epsilon_{2\parallel}/\epsilon_{2\perp}=135$, to be compared with the experimental value of 27.5.

Some caution should, however, be exerted in comparing the calculated and experimental anisotropies. In fact, a contribution to the perpendicular absorption and reflectivity comes from the small (but not negligible in this context) sample misalignment, detected from the breadth of the azimuthal x-ray diffraction peak. We have measured a half-width (at half-maximum intensity) of 10° for the samples of *cis*-$(\text{CH})_x$ used in the present study. The tensor $\underline{\epsilon_2}$ associated with a single chain which has the form

$$\begin{bmatrix} \epsilon_{2\perp} & 0 & 0 \\ 0 & \epsilon_{2\perp} & 0 \\ 0 & 0 & \epsilon_{2\parallel} \end{bmatrix} \qquad (12)$$

should therefore be averaged over the possible orientations of the chain with respect to the stretching direction. The mean value of the components of ϵ_2 can be written[19]

$$\begin{aligned} \overline{\epsilon_{2\parallel}} &= \epsilon_{2\perp}\overline{\sin^2\theta}+\epsilon_{2\parallel}\overline{\cos^2\theta} \, , \\ \overline{\epsilon_{2\perp}} &= \frac{\epsilon_{2\perp}}{2}(1+\overline{\cos^2\theta})+\frac{\epsilon_{2\parallel}}{2}\overline{\sin^2\theta} \, . \end{aligned} \qquad (13)$$

Assuming $\overline{\cos^2\theta}=0.503$ we get $\overline{\epsilon_{2\parallel}}/\overline{\epsilon_{2\perp}}=43.7$, which corresponds to $k_{\parallel}/k_{\perp}=11.3$, to be compared with the experimental value of 10.1. This implies that sample misalignment accounts almost entirely for the absorption anisotropy.

The results obtained in the present paper can be discussed with reference to the origin of the anisotropy in the photoexcitation. Indeed it has been shown by various groups[1,20] that for the oriented sample both the photoinduced absorption and the photoconductivity exhibit higher intensity when the exciting light is polarized perpendicularly to the chain direction. Even after correction for the reflectivity anisotropy, perpendicular photoexcitation is found to be at least several times (2–5) larger than that of the parallel excitations.

A number of explanations has been offered to account for this fact. One possibility suggested for the first time by Siddiqui in the case of polydiacetylenes[21] is that, because of the smaller penetration depth, excitation with light polarized parallel to the chain direction produces a higher density of carriers than in the case of perpendicular polarization. The possibility of bimolecular recombination of photogenerated carriers is therefore reduced in the latter case.

An alternative explanation is based on the existence of an absorption perpendicular to the chain. If this is the case, excitation by perpendicular light produces carriers on different chains, which are likely to possess lifetimes greater than those of the carriers generated on the same chain by parallel excitation. These long-lived carriers will therefore control the overall photoconductive response.

In an attempt to provide an answer to this question, in the present investigation we have tried to detect the existence of an intrinsic perpendicular absorption. However, as has been previously discussed, this is hampered by the fact that the possible intrinsic absorption is hidden by the features originated by the sample misalignment.

The theoretical model worked out in the present paper predicts a small but not vanishing interchain absorption which possibly accounts for the existence of long-lived photocarriers. The theoretical knowledge of the optical response function of the chain together with the measured chain misalignment allows an estimate of the number of the interchain photocarriers. Assuming a linear recombination regime, the number of steady-state photocarriers is given by

$$N = A\tau(\eta\Phi)I(1-e^{-\alpha d}) \, , \qquad (14)$$

where A is the area of the illuminated surface, τ is the time for the carrier lifetime, $\eta\Phi$ is the quantum efficiency for free-carrier generation, I is the laser intensity, α is the absorption coefficient, and d is the sample thickness.[22] The ratio $N_{\parallel}/N_{\perp}$ between the number of intrachain and interchain photocarriers is then given by

$$\frac{N_{\parallel}}{N_{\perp}} = \frac{(1-e^{-\alpha_{\parallel}d})}{(1-e^{-\alpha_{\perp}d'})}\frac{(\tau\Phi)_{\parallel}}{(\tau\Phi)_{\perp}} \, , \qquad (15)$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the intrinsic (no misalignment) absorption coefficients of the chain, and d' is the penetration depth when the radiation is polarized perpendicular to the stretch, and which is controlled by the sample misalignment $d'=1/(\alpha_{\parallel}/10)$.

Using Eq. (15) and the calculated values for α ($\alpha_{\parallel}=13\times10^{5}$ cm^{-1}, $\alpha_{\parallel}/\alpha_{\perp}=65$ for $\beta_x=0.1$, and $\alpha_{\parallel}/\alpha_{\perp}=4.3\times10^{3}$ for $\beta_x=0.01$), we get

$$\frac{N_{\parallel}(\tau\Phi)_{\perp}}{N_{\perp}(\tau\Phi)_{\parallel}} \simeq 5$$

with $\beta_x = 0.1$ eV, and

$$\frac{N_{\parallel}(\tau\Phi)_{\perp}}{N_{\perp}(\tau\Phi)_{\parallel}} \simeq 3\times 10^2$$

with $\beta_x = 0.01$ eV. As we have previously discussed, the measured anisotropy of the photoinduced absorptions upon changing the laser polarizations is $I_{\perp}/I_{\parallel} \sim 2-5$. If the origin of this anisotropy is entirely related to the existence of interchain excitation, this implies that the quantum efficiency for free carrier generation is $15-10^3$ times (for the two limiting cases of $\beta_x = 0.1$ and 0.01 eV, respectively) higher when the laser is polarized perpendicularly to the chains. This is not surprising since intrachain carriers are more likely to undergo a quick geminate recombination than carriers created on different chains. We believe that these remarks could stimulate further experimental work on the time evolution of the photoexcitation in oriented samples upon changing the polarization of the light pump.

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