

Stark effect of one-dimensional Wannier excitons in polydiacetylene single crystals

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Electric-field-modulated reflectivity of three different polydiacetylenes—PTS, poly[2,4-hexadiyne-1,6-diol-bis(*p*-toluene sulfonate)]; PFBS, poly[2,4-hexadiyne-1,6-diol-bis(*p*-fluorobenzene sulfonate)]; and DCHD, poly[1,6-di(*n*-carbazolyl)-2,4-hexadiyne]—has been measured and is analyzed with respect to the underlying mechanism for the observed sensitivity of π - π^* transitions to electric fields. Excitons of high oscillator strength and their vibronic satellites respond to fields along the polymer backbone by a large quadratic Stark shift, revealing a large polarizability for this direction. About 0.5 eV above the excitonic absorption edge, in a region of relatively low absorption, electroreflectance signals of different origin are observed, which, contrary to the excitonic signals, vary strongly in size among different specimens of the same composition. Line-shape analysis and its dependence on the field strength identify this signal as the Franz-Keldysh effect of free-electron states, the continuum of the excitons, and exclude an assignment to forbidden exciton transitions. The large polarizability of the excitonic states, which results from unusually strong coupling to their continuum, is consistent with a Wannier exciton extending over about ten conjugated bonds and with a small reduced mass of the order $0.1m_0$. The large binding energy (0.5 eV) and oscillator strength ($f \approx 0.6$) of the excitons and their extremely strong coupling to continuum states are attributed to the one-dimensional character of the electron states.

I. INTRODUCTION

Polydiacetylenes (PDA), which by solid-state polymerization are available as single crystals,¹ provide an opportunity to study electronic states of a low-dimensional system which, according to band-structure calculations, form wide energy bands.²⁻⁴ Compared with other conjugated polymers such as polyacetylene,⁵ poly(*p*-phenylene),⁶ or polythiophene,⁷ where band-structure calculations have also been performed, the availability of polydiacetylene single crystals offers the unique possibility to verify the validity of such models experimentally without the complications arising from disorder. In three-dimensional solids, disorder leads to localized states at the band edges,^{8,9} and it is expected that this alteration of the density of states is even more severe in low-dimensional electron systems. The low-dimensional character of the π electrons is apparent in highly polarized optical spectra which, for polarization of light parallel to the polymer backbone, are dominated by strong excitons and their vibronic progression.¹⁰⁻¹² Another interesting feature is the sensitivity of the electronic states to an electric field parallel to the polymer, first discovered on poly[2,4-hexadiyne-1,6-diol-bis(*p*-toluene sulfonate)] (PTS),¹³ where field-induced changes of the reflectivity are comparable to those in semiconductors. Later studies on poly[1,6-di(*n*-carbazolyl)-2,4-hexadiyne] (DCHD),^{14,15} poly[5,7-decadiyne-1,12-diol-bis phenylurethane] (TCDU),¹⁶ and fluorobenzene-substituted PDA (Ref. 17) confirmed these results. Different interpretations of these electroreflectance spectra have been given, like a quadratic Stark effect, by mixing a doublet of allowed and forbidden excitons,^{16,17} or a linear Stark effect of almost

degenerate charge-transfer (CT) excitons.¹⁴ Controversial in particular is the interpretation of a signal, about 0.5 eV above the exciton, which has no corresponding feature in the reflectance spectra. While, based on the line shape and field strength dependence, the signal in DCHD is interpreted as the Franz-Keldysh effect of free-electron bands,¹⁵ a corresponding much weaker signal in TCDU has been attributed to a symmetry-forbidden exciton.¹⁶

Large electroreflectance spectra of comparable strength have also been observed in a few other organic materials. In 2-methyl-4-nitroaniline, it results from the linear Stark effect due to a permanent dipole moment,¹⁸ and is related to the Pockels effect of MNA crystals.¹⁸ In PMDA-anthracene, large changes of the reflectivity arise from field-induced transfer of oscillator strength from a dipole-allowed charge-transfer exciton to an almost degenerated forbidden state.^{19,20} The near degeneracy of two CT excitons of different parity, which is related to their very small oscillator strength, is the underlying reason for their strong mixing by the field. The signal disappears if broadening exceeds the splitting of the exciton states. CT excitons have also been invoked in the interpretation of a series of signals, starting 0.25 eV above the onset of π - π^* transitions in Cu phthalocyanine crystals.²¹ Studies on disordered samples result in much smaller signals but, in the case of partially oriented polyacetylene films, electric fields of 25 kV/cm alter the absorption coefficient by $\Delta\alpha \approx 10 \text{ cm}^{-1}$, an effect ascribed to the response of delocalized electron states.²²

In this paper, reflectance and electroreflectance spectra of three polydiacetylenes, which differ only by their side groups, are presented. The interpretation is based on the imaginary part of the dielectric constant, ϵ_2 , which is

most closely related to the density of states, and its field-induced change, $\Delta\epsilon_2$, derived by Kramers-Kronig transformation of the experimental spectra. Line-shape analysis of these spectra will clarify the origin of the weak transitions at higher energies, ruling out its interpretation as a forbidden exciton state.

II. EXPERIMENTAL DETAILS

Single crystals of PTS poly[2,4-hexadiyne-1,6-diol-bis(*p*-toluene sulfonate)], poly[2,4-hexadiyne-1,6-diol-bis(*p*-fluorobenzene sulfonate)] and DCHD poly[1,6-di(*n*-carbazolyl)-2,4-hexadiyne] were obtained by thermal polymerization of the lightly colored monomer crystals.¹ Crystal structure in all cases is monoclinic with the polymer backbone along the *b* axis.²³⁻²⁶ The 4.91-Å short repeat unit of the polymer (Fig. 1) leads to a very small unit cell in this direction. Figure 1 also shows the different side groups *R* which distinguish the polydiacetylenes used in this study.

The reflectance spectra were taken on as-grown (DCHD) or on freshly cleaved (100) faces at nearly normal incidence. The light source was a tungsten iodine lamp, dispersed by a 1 m grating monochromator which provided spectral resolution better than 1 meV at sufficient flux to maintain a large signal-to-noise ratio. The light was polarized by a calcite polarizer and detected with a multiplier. The samples were either immersed in superfluid He or mounted on a He-cooled coldfinger. Additional measurements of the reflectivity in the uv, necessary for the Kramers-Kronig transformation of the reflectivity, were performed with a 0.5 m vacuum monochromator, using a MgF₂ polarizer. This windowless system has also been used to determine absolute reflectivities.

Transverse sinusoidal electric fields of 1-kHz frequency were applied by coplanar evaporated Al contacts with a spacing of 0.5 mm, which is large compared to the

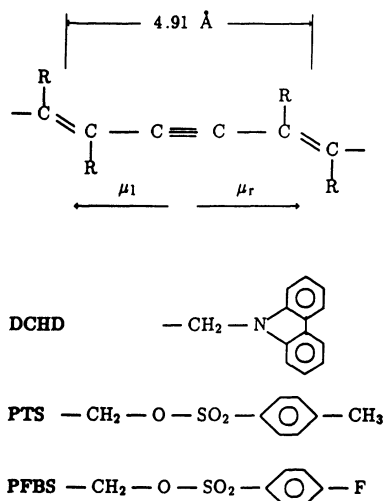


FIG. 1. Repeat unit of the polymer backbone and side groups *R* of the polydiacetylenes.

penetration depth of light. Fields were derived as the ratio of applied voltage and electrode spacing. Space-charge effects are negligible since the signal amplitude of the excitonic transitions was uniform over the sample without any enhancement near the electrodes. The signal, the field-induced change of the reflected intensity, was measured with a lock-in amplifier tuned to twice the frequency of the external field. Consistent with the inversion symmetry of the crystals, signals at the fundamental frequency were absent or very weak, not much above the noise level (range of 10^{-6}).

III. EXPERIMENTAL RESULTS

A. Reflectivity and ϵ_2 spectra

Spectra of the reflectivity *R* for polarization of light $E||b$ and of the imaginary part of the dielectric constant ϵ_2 are shown in Figs. 2-4. The main features of the spectra agree with those published earlier.^{11-15,27} Common to all is the strong excitonic peak ϵ_2 below 2.0 eV, which is related to the $\pi-\pi^*$ transition of the polymer backbone. This transition is followed by a vibronic progression, dominated by stretch modes of the conjugated bonds, the double ($D \approx 180$ meV), and the triple bond ($T \approx 260$ meV). Combination modes involving up to four vibrons of the strongly coupling π bonds are observed in DCHD, where the vibronic spectrum is particularly clearly resolved (Fig. 2). There are differences in the vibronic spectrum at lower energy. PTS and PFBS show satellites at 120-meV energy, close to the energy of C-C bonds (*S*). This peak is absent in DCHD, where the first distinct satellite β corresponds to a vibrational mode of 83 meV. The vibronic energies, derived from the peak energies of ϵ_2 spectra and from the modulated spectra, are listed in Table I together with the transition energy to the exciton ground state and its linewidth.

The spectrum of PTS (Fig. 3) shows even narrower ex-

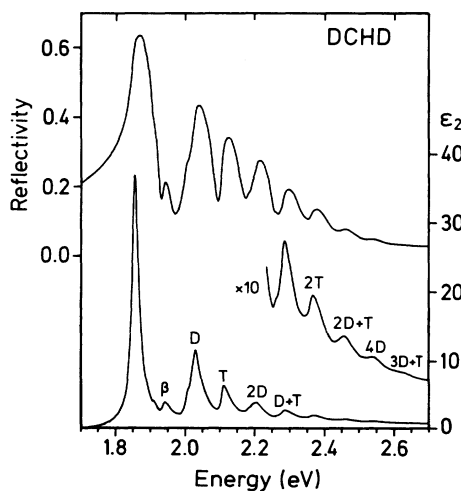
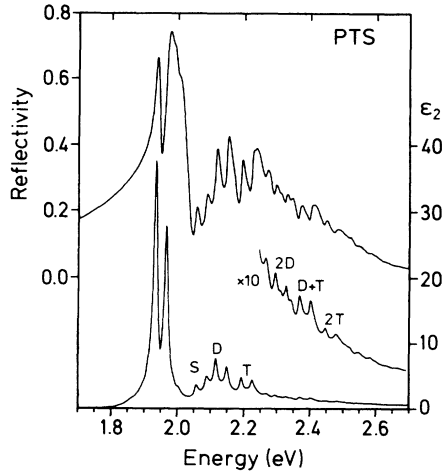
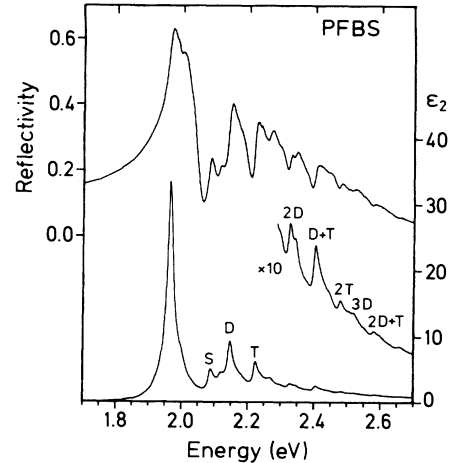


FIG. 2. Reflectivity and ϵ_2 spectra of DCHD, showing a progression of vibrational excitons which is dominated by stretch modes of the conjugated bonds. $T = 8$ K.

FIG. 3. Reflectivity and ϵ_2 spectra of PTS. $T = 7$ K.FIG. 4. Reflectivity and ϵ_2 spectra of PFBS. $T = 12$ K.

citon lines and all features split by 32 meV into doublets. The splitting is related to a phase transition which, below 200 K, leads to inequivalent polymer chains, doubling the size of the unit cell.²⁴ The difference arises from a small rotation of the side groups which slightly affects the π electrons of the polymer chain. The splitting seems to be avoided by replacing the toluene sidegroup with fluorobenzene,²⁷ resulting in the less complicated vibronic spectrum of PFBS (Fig. 4).

The oscillator strength of the π - π^* transitions is obtained from the sum rule

$$n_{\text{eff}}(\hbar\omega) = \frac{8\pi\epsilon_0 m}{e^2 h^2 N} \int_0^{\hbar\omega} E \epsilon_2(E) dE, \quad (1)$$

where N is the density of polymer repeat units and $n_{\text{eff}}(\hbar\omega)$ is the number of electrons per unit which contribute to absorption at energies below $\hbar\omega$. The strong and narrow absorption peak below 2 eV leads to a distinct step at $n_{\text{eff}} \approx 0.6$ (Fig. 5), corresponding to the oscillator f strength of the fundamental exciton which has about 40–50% of the total strength of the π - π^* transitions, including the vibronic excitons. A slightly larger

value is found in PTS, but this difference is probably within the accuracy of the results, limited mainly by the difficulty of measuring absolute reflectivity.

B. Electric-field-modulated spectra

The highly structured electroreflectance spectra $\Delta R/R$ are shown in Figs. 5–7. The magnitude of the field-induced changes is similar for the different samples, with some striking differences in details. We begin with the spectrum of DCHD (Fig. 6). The transition energies, as derived from the ϵ_2 spectra, of the exciton (E) and its main satellites are marked by vertical bars. Six vibrational modes and their combinations are resolved, involving also modes from the carbazole side group.¹⁴ Most striking is the large response above 2.3 eV, which is also followed by a relatively broad vibrational progression. In this particular sample, the signal is one order of magnitude larger than any other feature of the spectrum. In most samples it is smaller and may vary across the same sample, quite in contrast to the spectrum below 2.3 eV, which varies little.

TABLE I. Transition energy E_0 , peak height and width of the exciton, and the energies (in meV) of vibronic components. S , D , and T refer to stretch modes of single, double, and triple bonds, respectively. β , γ , and δ are low-frequency modes observed only in DCHD.

	DCHD	PTS	PFBS
E_0 (eV)	1.856	1.935	1.967
ϵ_{max}	36.6	37.34	27.4
$\hbar\gamma$ (meV)	23.9	14.7	16.8
α	56.3	64.5	63.6
β	87.0		
S		121.2	121.8
γ	153.0		
δ	164.0		
D	176.0	180.7	181.7
T	255.4	257.3	257.9
			122.7
			181.1
			258.6

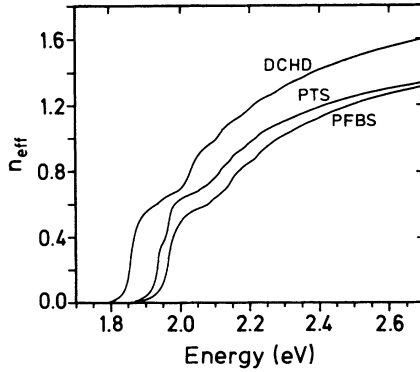


FIG. 5. Application of the sum rule of ϵ_2 spectra [Eq. (1)], yielding the number of electrons per repeat unit, n_{eff} , which contribute to absorption below $\hbar\omega$.

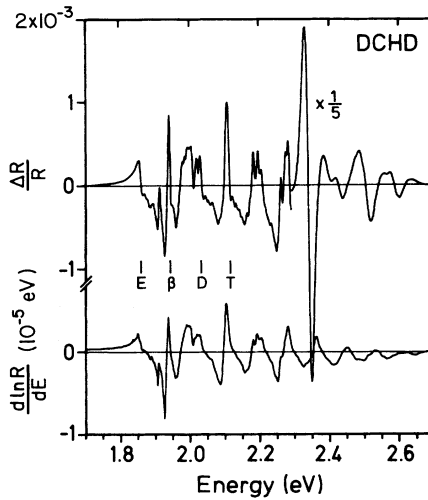


FIG. 6. DCHD: Comparison of the electroreflectance spectrum $\Delta R/R$ and the derivative of the reflectivity $d \ln(R)/dE$ with a redshift by $10 \mu\text{eV}$. $T=2 \text{ K}$, $F=24 \text{ kV/cm}$. Vertical bars mark the position of excitons in the ϵ_2 spectrum. The large signal above 2.3 eV is reduced by a factor of 5.

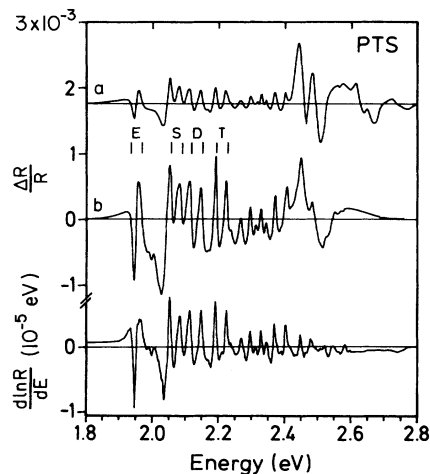


FIG. 7. PTS: Comparison of the electroreflectance spectra $\Delta R/R$ of two samples and the derivative of the reflectivity $d \ln(R)/dE$ with a redshift by $10 \mu\text{eV}$. $T=2 \text{ K}$, $F=22 \text{ kV/cm}$.

This large electroreflectance signal has no counterpart in the reflectance spectrum, which becomes evident by a comparison with the corresponding derivative of the reflectivity, $d \ln(R)/dE$, shown as the lower curve and based on a shift $\Delta E = 10 \mu\text{eV}$, which gives approximately the correct amplitudes. The excitonic part of the electroreflectance spectrum and the derivative of the reflectivity agree well in position and relative size of all peaks. This has also been observed in TCDU.¹⁶ This part of the signal always increases quadratically with the field strength.

The large signal beyond 2.3 eV , however, bears no similarity to the derivative of the reflectivity. Furthermore, its amplitude increases only at low fields quadratically with the field strength. At larger fields it increases more slowly and shows field-induced linewidth broadening, which is completely absent for any signal at lower energy. Based on these observations, the signal has been interpreted as the Franz-Keldysh effect of the free-electron band,¹⁵ an assignment further supported by its coincidence with the threshold of photoconductivity.^{28,29}

Figure 7 compares electroreflectance spectra of two samples of PTS (*a, b*) and the derivative of the reflectivity, again shifting the transitions rigidly by $10 \mu\text{eV}$. Except for the doubling of all spectral features in the low-temperature phase of PTS, the spectrum is less complicated than for DCHD, involving only vibrational modes of the polymer backbone. The derivative of the reflectivity, measured on sample *b*, and electroreflectance spectra agree well for energies below 2.4 eV . The electroreflectance spectrum of sample *a* is exceptionally small, about three times smaller than that of sample *b*. This seems related to a reflectance spectrum which resolves less details than that of sample *b*. In both cases the largest signal occurs 0.5 eV above the exciton, in the region where photoconductivity sets in.³⁰ The signal, again without counterpart in the derivative spectrum of the reflectivity, is much weaker than in DCHD, but splits like the other transitions into a doublet, quite well resolved for sample *a*. All signals increase quadratically with the field and no field-induced broadening is observed.

Electroreflectance spectra of two samples PFBS (*a, b*) are shown in Fig. 8, together with a derivative spectrum of the reflectivity measured on a particularly good sample which did not survive electroreflectance measurements. The experimental spectra represent the range of resolution obtained for this material and most likely reflect variation in crystal quality. The slightly modified side group, compared to PTS, is sufficient to suppress the phase transition at low temperature, resulting in a less complicated spectrum. The features of the excitonic spectra agree with the derivative of the reflectivity. Differences occur again at higher energy, 0.5 eV above the first transitions, in a region where preliminary measurements show the onset of photoconductivity. Sample *b* shows a very strong signal which, as the corresponding feature in DCHD, rises quadratically with field only at low fields, and shows linewidth broadening for fields above 20 kV/cm . This large signal, however, is an exception. From six samples studied, only one gave a clear sig-

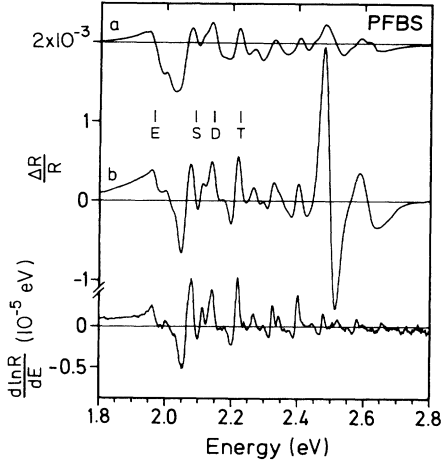


FIG. 8. PFBS: Comparison of the electroreflectance spectra $\Delta R/R$ of two samples and the derivative of the reflectivity $d \ln(R)/dE$ with a redshift by $10 \mu\text{eV}$. $T=2 \text{ K}$, $F=20 \text{ kV/cm}$.

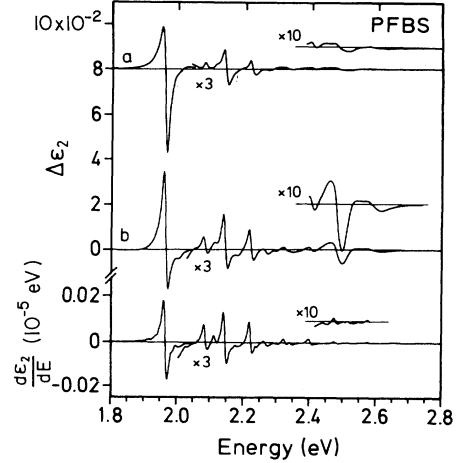


FIG. 11. PFBS: Comparison of the field-induced change $\Delta\epsilon_2$ (data from Fig. 8) and the derivative $d\epsilon_2/dE$ for a redshift by $10 \mu\text{eV}$. All features above 2 eV have been enlarged by the given factors.

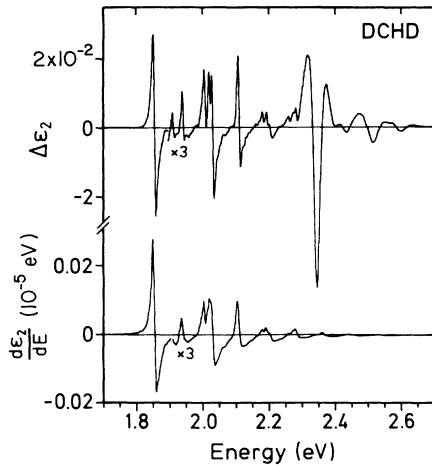


FIG. 9. DCHD: Comparison of the field-induced change $\Delta\epsilon_2$ (data from Fig. 6) and the derivative $d\epsilon_2/dE$ for a redshift by $10 \mu\text{eV}$. All features above 1.9 eV have been enlarged by a factor of 3.

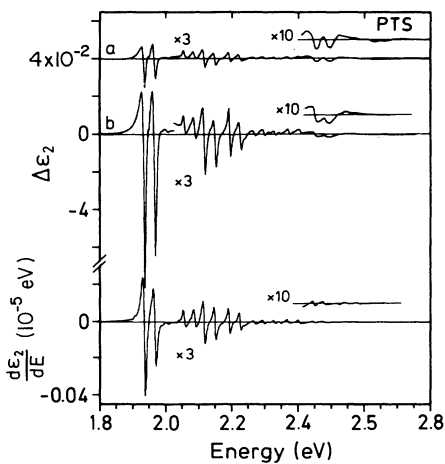


FIG. 10. PTS: Comparison of the field-induced change $\Delta\epsilon_2$ (data from Fig. 7) and the derivative $d\epsilon_2/dE$ for a redshift by $10 \mu\text{eV}$. Features above 2 eV have been enlarged by the given factors.

nal near 2.5 eV ; the others respond to an electric field with spectra like sample *a*.

Quantitative analysis of the field-induced changes of the optical properties will be based on the field-induced change $\Delta\epsilon_2$ of the imaginary part of the dielectric constant. These spectra which most directly show the combined changes of transition matrix elements and density of states are shown in Figs. 9–11, together with the derivative of the ϵ_2 spectra. The difference from the electroreflectance spectra is striking. The most prominent signal now arises from the redshift of the strong exciton peaks. Corresponding changes of the absorption constant are in the range $400\text{--}600 \text{ cm}^{-1}$, almost two orders of magnitude larger than the signal reported for partially oriented polyacetylene.²² The spectrum beyond the fundamental exciton is enlarged by a factor of 3 to enhance its details. Only for DCHD (Fig. 9), the high-energy signal remains large, and the absolute change of $\Delta\epsilon_2$ in this region is still comparable to the signal of the exciton. For PTS (Fig. 10), the peculiar signal around 2.4 eV is recognized only after further enhancement. The strong signal of PFBS (Fig. 11, sample *b*) has a similar line shape to that in DCHD, and is much larger and broader than the features of the derivative of the ϵ_2 spectrum.

IV. DISCUSSION

The striking similarity of the modulated spectra to the energy derivatives of the corresponding spectra, and the quadratic dependence on field strength, suggest an interpretation of the excitonic part of the spectra by a quadratic Stark effect. Fields of 20 kV/cm shift the excitons by approximately $10 \mu\text{eV}$, which corresponds to a very large polarizability p of $\approx 7000 \text{ \AA}^3$, and indicates an extension of the excitons over several unit cells:

$$\Delta E = \frac{1}{2} p F^2 . \quad (2)$$

Because such size implies completely delocalized and

thus mobile excitons, Sebastian and Weiser¹⁴ considered alternatives and explained their results by a linear Stark effect of almost degenerate charge-transfer excitons, following earlier suggestions.³¹ This model also led to the conclusion that the exciton state should be delocalized. The large signal at higher energy was attributed to the response of the band gap between free-electron states.¹⁵ Tokura *et al.* interpreted their results in the frame of Davidov splitting of a pair of Frenkel excitons.^{16,17} Based on the inversion symmetry of the lattice, they proposed that the quadratic Stark shift of the exciton near 2 eV results from coupling to a forbidden exciton state near 2.5 eV, which in turn inherits strength, giving rise to the large response near that energy. Both models explain many details of the spectra, but neither one is fully compatible with all aspects of the spectra.

A. Transition dipole moments and Davidov splitting of excitons

First insight into the electronic excitations is derived from the relationship of oscillator strength and transition dipole moments. Optical excitation of the conjugated bonds of the polymer backbone creates a dipole μ oriented along the chain as indicated by the pronounced selection rules. Transfer of charge, and thus the direction of the dipole, could either be to the left, creating a state $|\varphi_l\rangle$, or to the right, resulting in a state $|\varphi_r\rangle$, which as even and odd combinations provide excited states consistent with the inversion symmetry of the polymer (see Fig. 1)

$$\begin{aligned} |\phi_g\rangle &= (|\varphi_l\rangle + |\varphi_r\rangle)/\sqrt{2}, \\ |\phi_u\rangle &= (|\varphi_l\rangle - |\varphi_r\rangle)/\sqrt{2}. \end{aligned} \quad (3)$$

Only state $|\phi_u\rangle$ carries a dipole moment μ , and gives rise to the strongly absorbing excitons of PDA crystals. Because of their different dipole interaction, the two states split by an energy $2V_0$ which depends on the strength of the transition dipoles μ_l and μ_r and on their spatial separation. If the excited states $|\varphi_l\rangle$ and $|\varphi_r\rangle$ are localized within a unit cell, representing a pair of Frenkel excitons, the zero-field splitting $2V_0$ of the allowed and forbidden exciton $|\phi_u\rangle$ and $|\phi_g\rangle$ is given by³²

$$2V_0 = \frac{16\mu^2}{b^3}. \quad (4)$$

This is a lower limit based on separation of the dipoles μ_l and μ_r by half a repeat unit b , the largest separation within one unit cell.

The transition dipole moment μ can be derived from the sum rule of the ϵ_2 spectra according to the relation

$$f = \frac{2m}{\hbar^2} \frac{\hbar\omega}{e^2} \mu^2. \quad (5)$$

The first step of n_{eff} (Fig. 5) yields a value $f=0.6$ for the oscillator strength of the exciton corresponding to a very large transition dipole moment of $\mu \approx 1 \text{ e}\text{\AA}$. Such a large dipole moment points to considerable redistribution of charge density by the optical excitation, and is quite interesting in view of photochromism and thermochrom-

TABLE II. Transition dipole moment μ and related oscillator strength f to the exciton ground state, its Stark shift $\Delta E/F^2$, and the corresponding polarizability p and dipole moment μ^* .

	DCHD	PTS	PFBS
f	0.61	0.64	0.60
μ (e\AA)	1.12	1.12	1.08
$2V_0$ (eV)	2.44	2.44	2.27
$\Delta E/F^2$ (e\AA ² /V)	285	200	260
p (\AA ³)	8200	5800	7500
μ^* (e\AA)	11.7	10.1	11.6
f^*	17.2	13.6	18.2

ism, reported for Langmuir-Blodgett films,³³⁻³⁵ which are interpreted as photoinduced bond switching from acetylene to butatriene structure.

If the excited state is localized within a unit cell, as presumed in Eq. (4), a zero-field splitting larger than 2 eV results, pushing the forbidden exciton states into the uv region. The values derived from the various spectra are listed in Table II. A splitting of the excitons by only 0.5 eV, as assumed by Tokura *et al.*, requires separation of the dipoles μ_l and μ_r by almost a unit cell, and even larger separation results if contributions of vibronic excitons are taken into account.

The large oscillator strength of the excitons shows clearly that the electroreflectance spectra can be interpreted as mixing an allowed and forbidden exciton-state split by 0.5 eV, only if the exciton states extend over several repeat units of the polymer, which is incompatible with a pair of localized Frenkel excitons.

B. Stark shift of the excitons

The field-induced redshift of the excitons near 2 eV must result from coupling to states at higher energy. Vibrational excitons are ruled out at these upper states because of their very similar redshift. The rigid shift of the whole excitonic spectrum suggests that the strongly interacting states are either in the uv, outside the range studied here, or have very small oscillator strength with respect to the ground state. Except for DCHD, where a small signal near 3.6 eV related to excitonic states of the carbazole group is found, no further electroreflectance signal is observed up to 4.5 eV. Since coupling of states by an electric field decreases with their energy separation, the Stark shift of the excitons most likely results from coupling to those states which are responsible for the electroreflectance signal near 2.5 eV. It will be shown that these weakly absorbing but field-sensitive states are free-electron states above a band gap E_g .

The polarizability p_n of a state $|n\rangle$ is given by virtual transitions to all states $|k\rangle$. Considering only the closest state leads to Eq. (6),

$$p_n = \frac{2|\mu_{nk}|^2}{\hbar\omega_{nk}}, \quad (6)$$

where $\hbar\omega_{nk}$ is the energy gap between $|n\rangle$ and $|k\rangle$ and

μ_{nk} their transition dipole moment. An electric field F increases the separation Δ of the two states,

$$\Delta(F) = 2V_0 \sqrt{1 + (\mu^* F / V_0)^2}, \quad (7)$$

where $\hbar\omega_{nk}$ is replaced by the zero-field splitting $2V_0$ and μ_{nk} by μ^* . The polarizability p then is expressed by

$$p = \frac{\mu^{*2}}{V_0}. \quad (8)$$

The experimental value of p for the excitons in DCHD is $570 \text{ e}\text{\AA}^2/\text{V}$ or 8200 \AA^3 . With a value $V_0 = 240 \text{ meV}$, derived from the separation of exciton and the large electroreflectance response at 2.33 eV , a transition dipole moment $\mu^* = 11.7 \text{ e}\text{\AA}$ is obtained. Similar values are obtained for the other polydiacetylenes (Table II). Such dipole moments correspond to charge transfer over more than two unit cells and exclude localization of the excited states. However, only such large transition dipole moments give virtual transitions over 0.5 eV sufficient strength to explain the observed Stark shift. We estimate from Eq. (5) the oscillator strength for a transition from the exciton state at 1.856 eV (DCHD) to the state at 2.33 eV of $f^* \approx 17$ (Table II).

C. Field-induced transfer of oscillator strength

Coupling of two states leads also to an exchange Δf of oscillator strength. If one state couples only weakly to the ground state, Δf is proportional to the energy shift,

$$\Delta f = f \frac{\Delta E}{2V_0} = f \frac{p}{4V_0} F^2. \quad (9)$$

The exciton below 2 eV must lose some strength, which is gained by the weak transition at higher energy. Based on this considerations Tokura *et al.* interpreted a small positive peak in the $\Delta\epsilon_2$ spectra of TCDU as the growing strength of a symmetry-forbidden exciton, ignoring, however, a subsequent negative peak in their spectra.¹⁶

For DCHD, a field of 24 kV/cm leads to an exchange of oscillator strength $\Delta f = 2.1 \times 10^{-5}$. The amplitude of the correspondingly growing peak in the ϵ_2 spectrum can be estimated from the approximate relation of oscillator strength f , peak position $\hbar\omega_0$, amplitude ϵ_{\max} , and width $\hbar\gamma$:

$$\Delta\epsilon_{\max} \approx \Delta f \frac{\omega_0}{\gamma}. \quad (10)$$

The peak height of the exciton at 1.856 eV should decrease by $\Delta\epsilon_2 = 1.6 \times 10^{-3}$, which is about one order of magnitude smaller than the signal arising from its shift (Fig. 9). The weak transition above 2.3 eV should grow to a peak of $\Delta\epsilon_2 = 2 \times 10^{-3}$, presuming that it has the same linewidth as the allowed transition. The spectrum indeed shows a positive peak but its height, 7×10^{-3} , and its width are far too large. This peak in addition is part of a sequence of negative and positive peaks, which rules out its interpretation as transfer of oscillator strength to a forbidden exciton state.

The spectrum of PFBS (Fig. 11, sample *b*) shows a positive peak of the anticipated strength (10^{-3}) at 2.46 eV , but again it is too broad and is followed by a negative peak of comparable strength. Also, in the case of sample *b* and of PTS (Fig. 10) the line shape of $\Delta\epsilon_2$ contradicts its assignment to a forbidden exciton. In these cases, the height of the positive peak $\Delta\epsilon_2$, reaching at most 2.5×10^{-4} , is even too small to be related to the growth of a narrow exciton absorption peak.

The line shape of the electroreflectance signal at higher energy, with its sequence of positive and negative peaks, indicates that the field redistributes many closely spaced energy levels which begin 0.5 eV above the exciton ground state. Different from all excitonic signals, which up to 80 kV/cm increase quadratically with the field,¹⁴ the strong transitions of DCHD and PFBS show a weaker dependence for larger fields (Fig. 12). In the case of DCHD, the signal becomes, for large fields, independent even of temperature, and its linewidth increases proportional to $F^{2/3}$, the characteristic dependence of the Franz-Keldysh effect on the edge of a free-electron band, which represents the continuum states of the excitons. The analysis yields a band gap at 2.333 eV , and a surprisingly small reduced effective mass, 0.05 of the free-electron mass m_0 , which is consistent with field broadening at moderate fields.¹⁵

Field broadening of the Franz-Keldysh effect is observed only if the perturbation of free-electron states is comparable to lifetime broadening or to broadening by inhomogeneities.³⁶ Scattering processes compete with the field in mixing free-electron states, severely limiting the impact of an external field. The Franz-Keldysh effect is thus rapidly reduced by such processes, and responds to inhomogeneities of the polymer backbone much faster

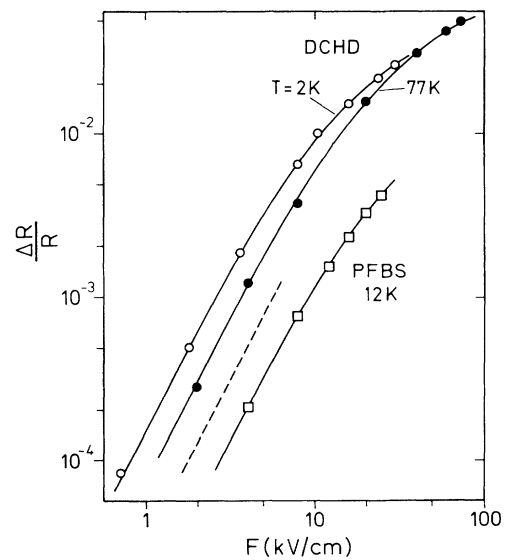


FIG. 12. Dependence on field strength of the peak-to-peak amplitude of the large electroreflectance signals of DCHD and PFBS at 2.33 and 2.48 eV , respectively. The signals increase only at low fields quadratically (dashed line) with the external field, different from the excitonic response which maintains this dependence for all fields.

than the Stark shift of the exciton. This is consistent with the large variation of the high-energy response among different samples. It should be mentioned that in their study of fluorobenzene-substituted samples, Tokura *et al.* observe a large electroreflectance signal at high energy similar to the signal in PFBS, which they attribute to a particularly high quality of this sample.¹⁷

Coupling of the excitons to a continuum of states also explains the small $\Delta\epsilon_2$ signal at high energy in many samples, which fails to show a clear Franz-Keldysh effect. The transferred oscillator strength, a consequence of the Stark effect, is distributed over the wide range of continuum states, and the small gain is masked by the Stark shift of the vibronic excitons in this region.

D. Stark shift of a Wannier exciton

The large polarizability of the excitons, and the Franz-Keldysh effect at the threshold of photoconductivity, point to excited states which extend over several unit cells, suggesting a description of the excitons as Wannier excitons. Electric-field effects on Wannier excitons in isotropic semiconductors have frequently been treated.³⁷⁻⁴⁰ The Stark shift of the exciton ground state due to virtual transitions to higher exciton states and into the continuum, the conduction band, is given as^{39,40}

$$\Delta E \approx \frac{9}{8} E_b \left[\frac{er_0 F}{E_b} \right]^2 \quad (11)$$

E_b is the exciton binding energy and r_0 is the radius of the exciton ground state. This relation, which holds as long as ΔE is small compared with E_b , is the same as Eq. (5) for the pair of Frenkel excitons if the binding energy is replaced by the zero-field splitting $2V_0$ and er_0 is interpreted as the transition dipole moment μ^* . The factor $\frac{9}{8}$ accounts for an enhanced shift due to coupling to higher exciton states.

From the exciton binding energy $E_b = 0.48$ eV, and its Stark shift, an exciton radius of 11 Å is derived for DCHD, similar to the values of the other compounds. Table III summarizes the properties of the Wannier excitons. The electron orbital in the exciton ground state extends over 4–5 unit cells or 8–10 conjugated bonds, justifying its treatment as a Wannier exciton. Equation (12) for the radius r_0 of an isotropic exciton to the Bohr radius a_0 allows an estimate of the reduced mass m^* :

TABLE III. Parameter of the Wannier excitons: E_0 , E_b , and r_0 are the transition energy, the binding energy, and radius of the exciton ground state, E_g is the band gap, derived from the Franz-Keldysh effect, m^* is an upper limit of the reduced mass.

	DCHD	PTS	PFBS
E_0 (eV)	1.856	1.935	1.967
E_g (eV)	2.334	2.442	2.478
E_b (eV)	0.478	0.509	0.515
r_0 (Å)	11.0	9.5	10.9
m^*/m_0	0.14	0.17	0.14

$$\frac{m^*}{m_0} = \frac{\epsilon a_b}{r_0} \quad (12)$$

A value $\epsilon \approx 3$ for the dielectric constant, consistent with the Kramers-Kronig analysis of the reflectivity and with permittivity measurements,⁴¹ yields an effective mass of $m^* = 0.14m_0$. This estimation neglects the quasi-one-dimensional character of the electron states in polydiacetylene, obvious from the small sensitivity of the states to fields perpendicular to the polymer chain.¹⁴ Thus the exciton radius is smaller than the radius of an equivalent three-dimensional exciton because of the enhanced electron-hole interaction in low-dimensional systems. By substituting into Eq. (11) the experimental value of the gap between the exciton state and the continuum, this enhanced electron-hole interaction is included. The exciton radius along the polymer therefore should be correct. The mass derived under the assumption of an isotropic exciton, however, is an upper limit, and can be considerably smaller, coming closer to the value estimated from the Franz-Keldysh effect in DCHD.

An isotropic exciton of a radius of 11 Å in a medium of dielectric constant $\epsilon = 3$ has a binding energy of 210 meV, about 40% of the value observed in the spectra. The difference again is attributed to the low-dimensional character of the excitons. Studies on quantum wells show an increase of the binding energy by 4 going from three- to two-dimensional systems, together with a strong increase of the oscillator strength. The binding energy of a one-dimensional exciton diverges for infinitely high barriers, but remains finite in real systems by tunneling of the electron states into the barrier. The value depends critically on the barrier height and the effective thickness of the so-called quantum wire. In quasi-one-dimensional electron systems, an exciton binding energy of 0.5 eV seems consistent with wide energy bands and small effective masses.

V. CONCLUSIONS

Electric-field-modulated reflectance spectra of polydiacetylenes provide a consistent picture of π - π^* transitions in conjugated polymers and their interaction with an external field. The electron states in polydiacetylene single crystals are delocalized along the polymer backbone, which has a very short repeat unit of 4.91 Å, less than the size of the unit cell of most semiconductors.

Very strong excitons and their vibrational progression respond to an electric field by a quadratic Stark effect with a large redshift similar for all excitonic transitions. The corresponding large polarizability of the order of 8000 Å^3 implies excited states extending over several repeat units. An extremely anisotropic polarizability, about three orders of magnitude smaller for fields perpendicular to the polymer backbone, suggests a description as one-dimensional Wannier excitons. Under this aspect the π electrons in polydiacetylenes can be considered as electrons in a quantum wire of a perfection not yet achieved by structuring semiconductors.

The large Stark shift is due to coupling of the excitons to their continuum, which begins about 0.5 eV at higher

energy. Coupling over such large energies requires large oscillator strength for transitions from discrete exciton states to the continuum. Very large values of $f^* \approx 15$ have been derived, whereas interband transitions from the ground state into the continuum have very small oscillator strength.

The free-electron states respond in some samples very sensitively to an external field, while in others only faint signals are observed. The amplitude of the free-electron states is not related to the Stark effect of the excitons, which varies little among different samples. Neither line shape nor amplitude are consistent with a field-induced transfer of oscillator strength from the excitons. The signal, a series of positive and negative peaks, results from intraband mixing of the continuum states by the field. The line shape and its broadening with increasing fields are in accordance to the Franz-Keldysh effect of free-electron states. Field broadening of the spectra at relatively small fields indicates a small effective mass below $0.1m_0$, consistent with the exciton radius derived from the Stark shift. Studies on semiconductors show that the Franz-Keldysh effect decreases rapidly if scattering broadens the free-electron states. A large response, therefore, is expected only if the polymer strings are perfect over many repeat units, the condition for coherent free-electron states. Defects of the polymer backbone therefore will affect strongly the signal from continuum states whereas the excitonic signal, determined by the Stark shift, decreases only due to some increased linewidth of the excitonic transitions.

The unusual optical properties of polydiacetylenes are closely related to the quasi-one-dimensional character of the π -electron states. Increasing binding energy and oscillator strength of excitons is observed in semiconductor quantum wells when electron states are spatially confined in very thin crystals. Even larger effects are expected if these quantum wells are further structured to quantum wires, leaving only one direction for free motion. The large binding energy and oscillator strength of the excitons is a consequence of their confinement to the polymer backbone, and leaves little strength for direct transitions into continuum states. Spatial confinement also increases the coupling between the excited states, which explains their large response to an external electric field. It seems likely that the field effects presented here, in particular the strong transition dipole between exciton and continuum states, are responsible for the large nonlinear susceptibility $\chi^{(3)}$ of polydiacetylenes.^{42,43}

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