PHYSICAL REVIEW B VOLUME 61, NUMBER 23 15 JUNE 2000-I

Electric field effects on the Davydov components of a strong intramolecular transition: α-sexithiophene single crystals

S. Möller and G. Weiser
Fachbereich Physik und Zentrum für Materialwissenschaften der Philippps-Universität Marburg, D-35032 Marburg, Germany

F. Garnier
Laboratoire des Matériaux Moléculaire, CNRS, 2 rue Henry-Dunant, F-94320 Thiais, France

(Received 16 December 1999)

Low-temperature absorption and electroabsorption spectra of a thin single crystal of α-sexithiophene reveal a distinctly different line shape and sensitivity to electric fields of the Daydov components of the first intramolecular π-π^* transition. The weak component of very small linewidth responds by a quadratic Stark shift which is attributed to a molecular polarizability of 900 Å^3. The strong Davydov component of much larger linewidth responds by an additional effect which dominates its spectrum and results in an electroabsorption spectrum of second derivative line shape. This signal is attributed to coupling of the field to the large transition dipole of the four molecules of the unit cell. The spectra show no response of a charge-transfer state and no Franz-Keldysh effect of a band continuum. The data indicate that Davydov components of the same molecular state are not mixed by the field.

I. INTRODUCTION

Electroabsorption spectra induced by moderate electric fields are a valuable tool to study extended electronic states. The basic effects are the Stark effect, which arises from mixing of discrete states, and the Franz-Keldysh effect,[1,2] which is equivalent to acceleration of a free particle by the electric field through a continuum of states.[3] The latter effect requires high mobility and large spatial coherence over tens of unit cells[4] and has been observed only in cubic semiconductors and in a few cases of highly ordered chains of polydiacetylenes.[5] The Stark effect, on the other hand, is observed in many conjugated polymers as redshift of the fundamental π-π^* transition. Due to the large linewidth of these transitions, either large field or high polarizability of an excited state is needed to obtain measurable shifts. Since the polarizability of an excited state increases with its size, field-modulation spectroscopy selects extended states and is well suited to study π-conjugated polymers. Competing with electric fields is the perturbation of states by potential fluctuations due to short-range disorder, which reduces the size of field effects and alters the line shape of the spectra.[6] As shown by the very different spectra of polydiacetylene single crystals and polydiacetylene films, short-range disorder can mask the intrinsic properties of the material.[7] Significant improvement is observed in the spectra of ladder-type polymers where additional bonds restrict torsion of the polymer units.[8,9] Charge-transfer excitons respond also sensitively to electric fields best seen again in spectra of single crystals of anthracene and pyromellitic acid anhydride (Ac:PMDA).[10,11] Charge-transfer excitons between identical molecules have been observed in partially crystallized films of anthracene.[12] They vanish in absorption spectra under stronger vibronic replica of the intramolecular exciton but are resolved in electroabsorption experiments because of their much larger shift resulting from a large charge-transfer dipole.

A richly structured electroabsorption spectrum has been observed in sexithiophene films.[13] While the signal at the optical gap seems compatible with a quadratic Stark shift of the first transition of this large molecule, several strong features at higher energy show no correspondence to derivatives of the absorption spectrum. They have been attributed to charge-transfer excitons predicted also by theoretical models[14] or to some residual Franz-Keldysh effect of band states. Charge-transfer transitions have also been invoked recently to explain two features of the electroabsorption spectrum of regioregular poly-hexylthiophene films with small interplane distance (3.8 Å) in nanocrystalline films.[15] Encouraged by the observation that disorder alters the absorption spectra even of partially crystallized and oriented samples significantly, we repeated the electroabsorption study on a single crystal of α-sexithiophene. More recent studies show further that a single molecular transition with vibronic satellites determines the absorption spectrum over a range of about 1 eV.[14,16] Crystal fields split this transition into two silent and two optically active Davydov components of very different strength. This simple scheme of energy levels thus provides an excellent opportunity to study the influence of an electric field on well defined eigenstates of a highly ordered oligomer.

II. EXPERIMENTAL DETAILS

A. Crystal structure

The single-crystal platelet was grown by the sublimation technique described by Lipsett.[17] The crystal structure is monoclinic (symmetry $P2_1/n$) (Ref. 18) and some parameters are listed in Table I. The unit cell (Fig. 1) contains four molecules which arrange in two sheets and are related to each other by inversion and a screw axis $2b$. The dipole moment of the fundamental transition $1B_u$ is parallel to the long axis L of the molecule, which shows little deviation

0163-1829/2000/61(23)/15749(7)/$15.00

TABLE I. Lattice parameters of α-$T6$. L and ξ are the length of the long molecular axis and its tilt angle with respect to the c axis (Ref. 18).

a (Å)	b (Å)	c (Å)	β	L (Å)	$\xi(L,c)$
44.708	7.851	6.029	90.76°	21.85	65.0°

from planarity. Dipole interaction splits the molecular state into four Davydov components, two of them optically active with dipole moments parallel and perpendicular to the b axis.[14,19,20] The alignment of the long molecular axis almost parallel to the ac plane results in a very small oscillator strength of the excited state a_u with dipole moment parallel b. Its strength is four orders of magnitude weaker than that of b_u with dipole moment in the ac plane and tilted by 25° with respect to the a axis. Due to the large separation of molecules in different planes, each of the dipole active transitions is near degenerate with a forbidden state a_g and b_g, respectively.[19] If Davydov components are coupled by an external electric field, such degeneracy should lead to large effects in the optical spectra.

B. Optical measurements

The platelet of about 2 mm^2 area and 9μ thickness was mounted in a He flow cryostat. Light of a tungsten halide lamp or of a Xe arc, dispersed by a 0.5-m grating monochromator and polarized by a calcite polarizer, was focused into a 0.3-mm-wide gap between opaque gold contacts which were evaporated onto the bc plane to apply fields parallel to the c axis. The spectral resolution was better than 1 meV in the visible range and about 3 meV in the case of the broader features in the near-uv. A photomultiplier served as a detector of the transmitted light, which was spatially filtered to reduce stray light. A digital voltmeter measured the light intensity, I, while a digital lock-in amplifier recorded simultaneously the change ΔI of the transmitted light intensity induced by a sinusoidal field of about 1 kHz frequency. The field-induced change $\Delta\alpha$ of the absorption constant is derived from the thickness d of the sample and the relative change of the transmitted light intensity:

$$\Delta\alpha = -\frac{1}{d}\frac{\Delta I}{I}. \tag{1}$$

The signal occurred at twice the frequency of the applied field and signals at the fundamental frequency were absent, which is consistent with the inversion symmetry of crystal and electrode configuration.

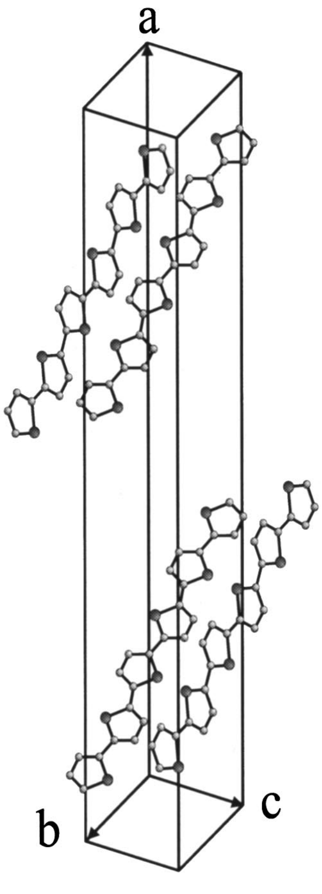

FIG. 1. Unit cell of α-sexithiophene.

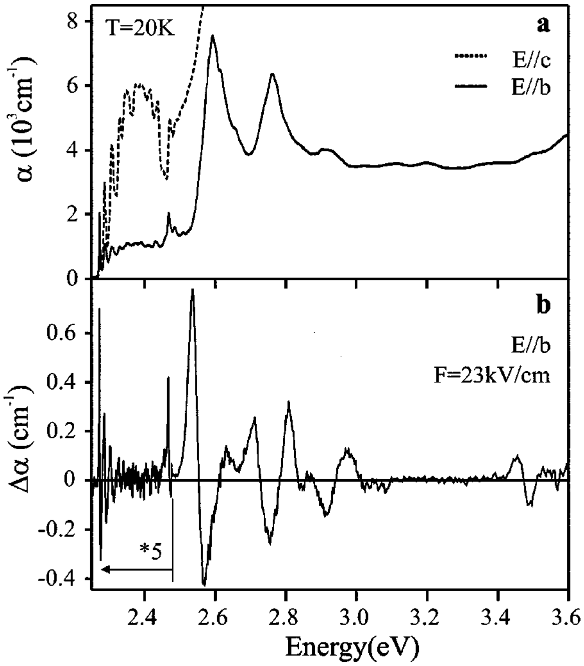

FIG. 2. Survey of (a) the absorption spectra and (b) the electroabsorption spectrum for field $F\|c$ at 20 K. The low-energy signal has been enlarged by a factor of 5.

III. EXPERIMENTAL RESULTS

The highly dichroic absorption spectrum of α sexithiophene is displayed in Fig. 2(a). The spectra show, in agreement with previous studies,[14,21,22] two regions of strikingly different linewidth. The peaks near 2.6 eV and 2.8 eV are relatively broad with a linewidth of about 80 meV. They are attributed to the strong Davydov component b_u, which is polarized in the ac plane blocking all light of polarization $E\|c$. For $E\|b$ the transition is forbidden by symmetry, which keeps the absorption sufficiently low to study this b_u state in a transmission experiment. All features below 2.6 eV have a much narrower linewidth and are related to the weak Davydov component a_u. The same difference of linewidth is

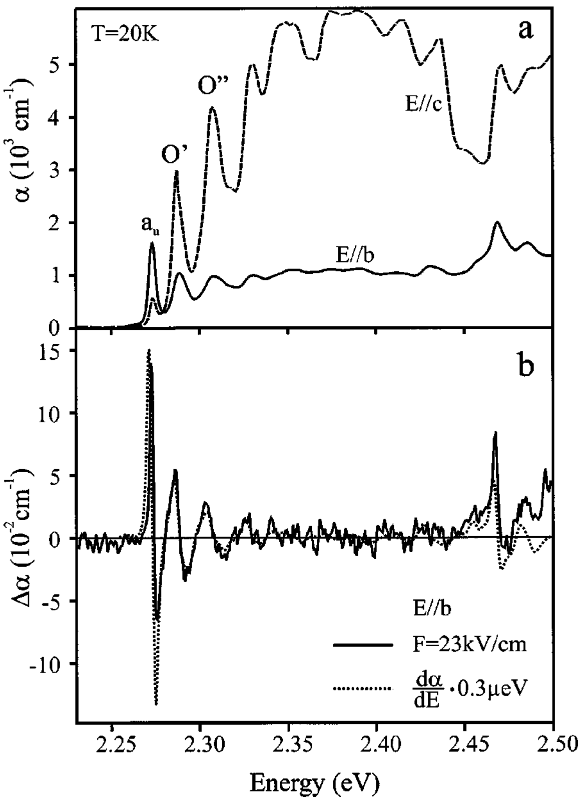

FIG. 3. (a) Absorption spectra of the weak a_u exciton and its vibronic satellites. O' and O'' refer to transitions of false origin (Ref. 14). (b) Electroabsorption spectrum for $F\|c$ and comparison with the first derivative of the absorption spectrum.

found in the field modulated spectrum $\Delta\alpha$ [Fig. 2(b)]. The signal of all transitions increases quadratically with the field strength without change of the spectral shape. It is quite remarkable that despite their small linewidth, all transitions below 2.5 eV give a much smaller electroabsorption signal than the broader transitions at higher energy. The signal at 3.45 eV is attributed to the second intramolecular transition $2B_u$ polarized along the short axis M of the $T6$ molecule.[21] It will not be considered since it does not derive from the molecular $1B_u$ exciton.

Figure 3 shows the spectra of the sharp transitions in more detail. The first absorption peak at 2.275 eV belongs to the exciton of the weak Davydov component a_u followed by vibronic satellites of 39, 82, 158, and 194 meV. Although forbidden, it appears also in the spectrum for $E\|c$, which suggests some imperfection of the crystal. Herzberg-Teller coupling[23] of the a_u exciton to a higher molecular state, probably the state at 3.45 eV, gives rise to two excitons, O' and O'', shifted by 15 meV and 35 meV with respect to a_u to higher energy. They appear in both polarizations although stronger for $E\|c$ and are also accompanied by a series of vibronic states.[14,19,22] The transition energies are listed in Table II.

TABLE II. Transition energies (in eV) of the Davydov components of the fundamental molecular exciton $1B_u$ and their vibronic satellites. O' and O'' are states of Herzberg Teller states of the a_u exciton.

Transition	Exciton	Vibronic states			
a_u	2.273	2.312	2.355	2.431	2.467
O'	2.288	2.330	2.375	2.449	2.486
O''	2.308	2.348	2.391		2.509
b_u	2.593		2.673	2.763	2.800

These narrow transitions respond to a field $F\|c$ by a common quadratic Stark shift to lower energy supporting their assignment to the same electronic excitation. Figure 3(b) shows the spectrum for $E\|b$, but as shown in Fig. 4 the same common shift of all features is observed for $E\|c$ although the latter spectrum is much more noisy due to the low level of transmitted light. The electroabsorption spectrum agrees quite well with the first derivative of the absorption spectrum, which reproduces the positions of all peaks correctly. We see some deviation in the size of the negative peak of the first transition. It is not clear whether this is a real effect or caused by some inaccuracy of the derivative of this very narrow absorption peak of 3 meV width. The spectrum shows no signature of the silent Davydov component a_g, which should be near degenerate to a_u. As observed for the charge-transfer exciton of anthracene-PMDA, such mixing of near degenerate states of different parity results in a linear Stark effect and in field modulated spectra of very different line shape.[10,11] The field $F\|c$ in Fig. 3(b) of 23 kV/cm causes a redshift by 0.3 μeV while the smaller field of 19 kV/cm in Fig. 4 results in a shift of 0.2 μeV as expected for a quadratic field strength dependence. This small shift must result from coupling of the a_u exciton to higher excited states of different parity.[24] We assume that the π electrons are localized to a single molecule so that the shift corresponds to the molecular polarizability of the $1B_u$ state from which the Davydov component derives by combining the four molecular excitons to eigenstates of the crystal. Assuming further that the π electron system is strongly polarizable only along the long molecular axis, only the field component parallel to the molecular axis leads to the redshift

$$\Delta E_{1B_u} = \frac{p}{2}(F\cos\xi)^2. \tag{2}$$

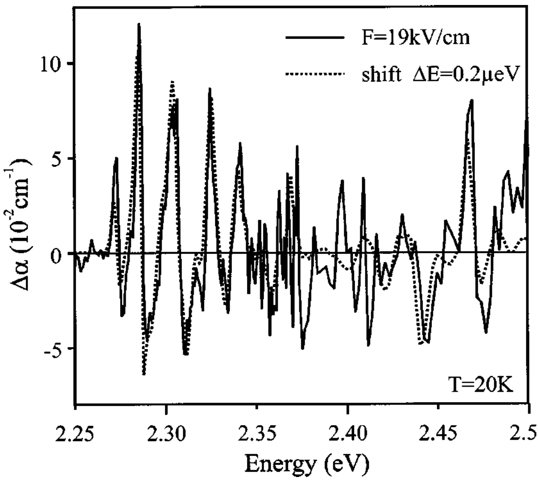

FIG. 4. Electroabsorption spectrum at low energy for polarization of light $E\|c$ in comparison with the first derivative of the absorption spectrum.

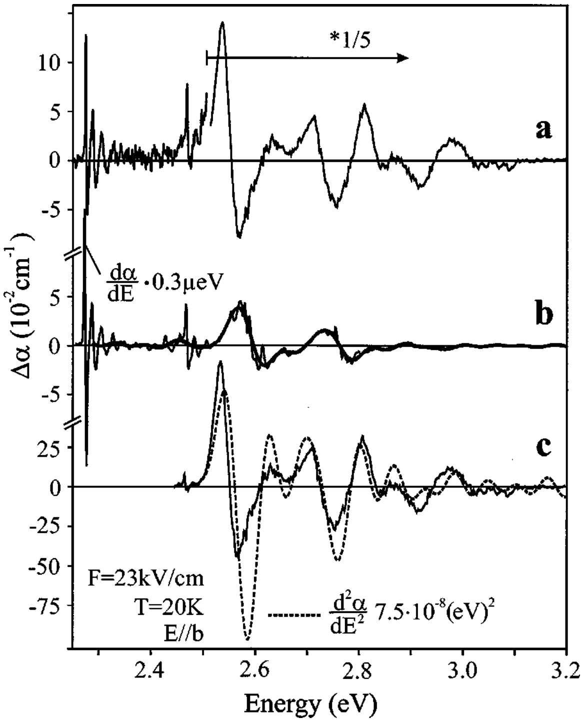

FIG. 5. (a) Electroabsorption spectrum of both Davydov components. The spectrum of the strong b_u exciton at higher energy is reduced in size to fit into the scale. (b) First derivative of the absorption spectrum assuming the same shift by 0.3 μeV for the strong b_u and the weak a_u excitons. The thick line represents the first derivative after Fourier-filtering. (c) Comparison of the second derivative of the absorption spectrum with the electroabsorption spectrum of the strong b_u exciton and its vibronic satellites. Note the different scales of the ordinate.

From the angle $\xi = 65°$ between the molecular axis and field, we obtain a polarizability $p = 915$ Å^3 of the $1B_u$ exciton which is larger than that derived from measurements on films where the relative orientation of molecule and film was neglected.[13] The large polarizability is consistent with the assumption that the $1B_u$ state extends over the full molecule.

Figure 5 show the electroabsorption spectrum of the strong b_u exciton. Since this state originates also from the $1B_u$ molecular exciton, it should show the same quadratic Stark shift as the a_u exciton. However, the first derivative with a shift by 0.3 meV reproduces the electroabsorption spectrum only up to 2.5 eV and fails completely to describe the position and size of the peaks at higher energy. The experimental response above 2.5 eV is an order of magnitude larger than the predicted signal and its spectral line shape is different. It is obvious that a stronger effect of different spectral line shape occurs and masks the Stark shift due to the molecular polarizability. In order to check whether this response of the strong transitions resembles a second derivative of the absorption spectrum, we eliminated the sharp features of the first derivative by Fourier filtering, which otherwise would dominate the second derivative spectrum. The full line [Fig. 5(b)] displays the first derivative after smoothing, which eliminated successfully the narrow features of the a_u exciton and its satellites while maintaining the correct shape and size of the derivative at higher energy in the region of the strong transitions. This derivative is used to produce the second derivative of the absorption spectrum at higher energy [Fig. 5(c)].

This second derivative describes the position of all peaks in the range of the b_u state and reproduces with a common scaling factor the amplitudes of the electroabsorption spectrum within a factor of 2. This agreement is quite satisfactory in view of the uncertainty to distinguish at low light level absorbed and scattered light. Scattered light reduces the negative peaks near 2.6 eV and 2.8 eV of the experimental spectrum, which are observed at the peaks of the absorption spectrum and contributes significantly to the deviation to the second derivative spectrum in that range. The electroabsorption spectrum thus can be described as an expansion of energy shifts to second order:

$$\Delta\alpha = \frac{\partial\alpha}{\partial E}\Delta E_p + \frac{1}{2}\frac{\partial^2\alpha}{\partial E^2}(\Delta E)^2. \tag{3}$$

The first expression corresponds to the shift by ΔE_p due to the molecular polarizability, which is sufficient to explain the spectrum of the weak Davydov component a_u. The second term dominates the spectrum of the strong component b_u but the energy shift ΔE is not related to the molecular polarizability because the square of ΔE_p is negligibly small. The scaling factor which matches the second derivative and electroabsorption spectrum yields the large energy shift by $\Delta E = 0.4$ meV for a field of 23 kV/cm, which applies to all transitions between 2.6 eV and 3.4 eV but not to the a_u state. The uniform scaling suggests again a common electronic origin of all these features. It should be emphasized that this result deviates from the electroabsorption spectrum of $T6$ films which in the high-energy region could not be fitted to a combination of first and second derivatives.[13]

IV. DISCUSSION

A. Polarizability and charge-transfer states

All absorptions peaks below 2.6 eV respond to an electric field with the same shift, which indicates a common electronic origin, namely the weak Davydov component of the $1B_u$ exciton with transition dipole parallel to the long molecular axis, which presumably is also the axis of large polarizability. The field F couples the $1B_u$ exciton to all states of even parity resulting in an energy shift given by

$$\Delta E_{1B_u} = \sum_e \frac{(\vec{\mu}_e \vec{F})^2}{E_{1B_u} - E_e} = \frac{p}{2}(F\cos\xi)^2. \tag{4}$$

Frequently one of the states of energy at E_e dominates, which allows us to derive the dipole moment μ_g between $|e\rangle$ and $1B_u$ from the observed Stark shift. The redshift proves that the strongest coupling state lies at higher energy and we expect it to be below or near the transition $2B_u$ at 3.45 eV, which is sufficiently far above the $1B_u$ to ignore exchange of oscillator strength with respect to the ground state, which would distort the derivative line shape of the electroabsorption spectrum.[24] For an estimated energy difference in the denominator of 1 eV, the redshift of the weak transitions requires the large dipole moment of $\mu_e = 5.6$ eÅ corresponding to a dipole of approximately a quarter of the length of the $T6$ molecule. Such significant redistribution of charge is possible only if the electronic states are delocalized over the molecule.

While the electroabsorption spectrum of the weak Davydov component a_u and its vibronic replica can be explained by the polarizability of the $1B_u$ molecular state, this interpretation fails completely in the case of the stronger Davydov component b_u at 2.593 eV although it is derived from the same molecular state. The response to the field of this state and of the transitions above is much stronger and the line shape agrees with a second derivative of the absorption spectrum. The same line shape applies to the transitions at higher energy and the common scaling factor supports their assignment to vibronic states of the b_u exciton. The transition energies are listed in Table II and within experimental accuracy the vibronic frequencies are the same as for the weak a_u transition. It is quite puzzling that transitions involving the same molecular states show such a difference in spectral line shape of the absorption and electroabsorption spectra and in the size of their response to an electric field.

Similar failure to correlate the electroabsorption spectra of the strong transitions to derivatives of the absorption spectrum was observed for $T6$ films.[13] These spectra show a set of strong oscillations above 2.8 eV, which were attributed to charge-transfer transitions after ruling out Franz-Keldysh oscillations. We exclude the Franz-Keldysh effect also because it is very sensitive to disorder and should be much stronger in a single crystal where the spectrum above 2.6 eV can clearly be assigned to the b_u exciton and its vibronic states. Band structure calculations show only small bandwidth,[25] and coherent acceleration of free carriers through band states is incompatible with mobilities below 1 $\mathrm{cm}^2/\mathrm{V\,s}$.[16]

The most striking property of the electroabsorption spectrum of the strong transition is its second derivative line shape, which can be observed in some cases of charge-transfer excitons. Theoretical calculations predict for α-$T6$ a charge-transfer transition of weak oscillator strength near 3 eV, above the b_u exciton.[14] Partial charge transfer to a neighboring molecule creates a transfer dipole μ_{CT}, which causes a linear shift in an electric field F by $\Delta E = \mu_{\mathrm{CT}} F$. Inserting this shift into Eq. (3) leads to a second derivative line shape of $\Delta\alpha$ because the term linear in ΔE disappears since due to the inversion symmetry of the crystal, charge transfer in opposite directions must have the same probability. Evaluation of the data in Fig. 5(c) yields for charge transfer along c the smallest dipole moment $qc = 1.7\ e\text{Å}$, which corresponds to transfer of 28% of an elementary charge to the next molecule, which seems a reasonable value for charge-transfer excitons. Nevertheless, an interpretation by charge-transfer excitons must be dismissed for several reasons.

The most obvious objection is the lack of a second derivative contribution in the spectrum of the a_u exciton made up of the same molecular states. In addition, the large charge-transfer dipole moment is based on the second derivative of the whole absorption spectrum above 2.5 eV, assuming implicitly that the strongly absorbing b_u state is a charge-transfer exciton. Strong absorption requires large spatial overlap of ground and excited states, which is inconsistent with the interpretation by Davydov components, i.e., molecular states coupled by dipolar interaction and not by exchange coupling. Large spatial overlap between the transitional equivalent molecule corresponds to a large transfer integral resulting in a wide free-carrier band and significant transfer of oscillator strength from exciton to continuum states. None of these consequences is supported by model calculations or optical spectra. Furthermore, an excited state where a pair of molecules exchange charge does not comply with the inversion symmetry of the crystal. Charge-transfer excitons which obey this symmetry could be built up as even and odd combinations of charge transfer to molecules in opposite directions resulting in two eigenstates of different parity.[10] If they are near degenerate, an electric field will redistribute the oscillator strength and both states will split apart by a linear Stark effect. In the case of a small linewidth, the exchange of oscillator strength dominates the spectral line shape as observed in electroreflectance spectra of the CT exciton in Ac:PMDA single-crystals, which cannot be described as second derivative.[11] In this case the electroreflectance signal disappeared already at 30 K below the noise level due to thermal broadening, which mixes the two states of different parity too, thereby diminishing the field effect.

Evaluation of dipole sums in the crystal predicts that the b_u exciton is near degenerate with an even-parity Davydov component b_g.[14] Considering just the parity of the states, a field should mix these Davydov components resulting in a linear Stark effect. The opposite shift of the mixed states causes broadening of the absorption spectrum if the spectral linewidth is larger than the energy splitting and results in a line shape similar to a second derivative. However, the same mixing of Davydov components should apply to the degenerate a_u and a_g states, which do not show a significant contribution of second derivative line shape. We exclude, therefore, that Davydov components of the same molecular state are mixed by an electric field. This result is not surprising since the corresponding matrix element $\langle b_g | qrF | b_u \rangle$ vanishes because it describes transitions between the same molecular state $1B_u$.

B. Interaction of the transition dipole with an external field

The striking difference of linewidth and response to an electric field of two Davydov components of the same molecular excitation cannot be related to properties of the molecular eigenstates. The difference must be caused by a property of the eigenstates a_u and b_u of the crystal. Their most obvious difference is their oscillator strength due to packing of the molecules. This transition dipole should also couple to the field but experimental evidence for such coupling seems not to exist. The transition dipole can be obtained from the oscillator strength of the b_u exciton, which is not known. We therefore derive the oscillator strength, f, from absorption spectra of thiophene solutions by applying the sum rule of the imaginary part of the dielectric function $\mathrm{Im}(\varepsilon) = n\alpha c/\omega$, where n is the refractive index of the solvent and c is the velocity of light:

$$f = 3\frac{4m\varepsilon_0}{he^2}\frac{n}{N}\int \alpha(E)\,dE'. \tag{5}$$

N is the concentration of absorbing molecules while the factor 3 accounts for random orientation of the molecules. Table

TABLE III. Oscillator strength *f*, transition energy E_0, and dipole moment of the fundamental transition in oligo-thiophenes derived from absorption spectra (Ref. 26).

Molecule	$T2$	$T3$	$T4$	$T5$	$T6$
f	1.4	2.22	3.43	3.94	4.44
E_0 (eV)	4.06	3.50	3.16	3.0	2.8
μ (eÅ)	1.15	1.55	2.03	2.24	2.45

III summarizes oscillator strength and peak position E_o of the fundamental absorption band by integrating spectra of several thiophenes[26] solved in methylene chloride with refractive index $n=1.4$. Similar values are obtained from $T3$ and $T5$ solution spectra published earlier.[27] The transition dipole moment is estimated from the relation

$$|\mu|^2=\frac{(e\hbar)^2}{2mE_o}f. \tag{6}$$

The delocalization of the π electrons over the molecule is obvious from the transition energy, which decreases with increasing size of the molecule. Simultaneously we observe an increasing oscillator strength of the $1B_u$ exciton with increasing length of the molecule. Similar large oscillator strength is observed for the strong exciton in polymethine chains such as the streptocyanine dyes,[28] where each double bond contributes about one electron. These spectra show also that packing of the molecules has no noticeable effect on the molecular properties.

From the oscillator strength $f=4.44$ of the $1B_u$ exciton of $T6$ in solution, we obtain transition dipole moments of 4.7 eÅ and 0.05 eÅ for the strong b_u and weak a_u exciton, respectively, by summing up the contribution of the four molecules in the unit cell. The dipole interaction of two b_u excitons in different cells is estimated from the relation

$$U=\vec{\mu}_T\frac{3(\vec{\mu}_T\cdot\vec{r})\vec{r}-r^2\vec{\mu}_T}{4\pi\varepsilon_o r^5}, \tag{7}$$

which yields about 0.6 eV for next neighbors in the c direction. Partial screening by polarization may reduce this energy but the strong exciton b_u should be quite mobile due to Förster transfer, which increases the scattering rate and the linewidth of the strong Davydov component as compared to the immobile weak a_u exciton.

The transition dipole interacts with the static electric field during its coherent lifetime τ. First- and second-order terms of the energy shift of this rapidly oscillating dipole are given as

$$\Delta E=\frac{1}{\tau}\int_0^\tau \vec{\mu}_0\cdot\vec{F}\cos(\omega t)dt,$$
$$(\Delta E)^2=\frac{1}{\tau}\int_0^\tau[\vec{\mu}_0\cdot\vec{F}\cos(\omega t)]^2dt. \tag{8}$$

The first-order term disappears but the second-order term remains finite and broadens the transition quadratically with field strength, resulting in a second derivative line shape [Eq. (3)]. The transition dipole of 4.9 eÅ of the b_u exciton and a field of 23 kV/cm parallel c leads to the large value of $(\Delta E)^2=2.25\times10^{-7}$ (eV)^2, about 50% larger than the shift needed to match the second derivative of the absorption and the electroabsorption spectrum of the strong transitions in Fig. 5(c). This deviation is not significant in view of the uncertainties in obtaining the second derivative of the absorption spectrum and the transition dipole moment from solution spectra. We attribute, therefore, the large electroabsorption signal of the strong Davydov component and its second derivative line shape to coupling of the transition dipole to the electric field. It is obvious that this effect is absent for the weak Davydov component because it requires a very large dipole moment.

V. CONCLUSION

The electroabsorption spectrum for $F\|c$ of the α-sexithiophene single-crystal differs strongly from those of films,[13] which emphasizes the sensitivity of such spectra to disorder. All features can be explained as the response of a single molecular exciton and its vibronic satellites to an electric field, however with striking difference in line shape of the spectra of the weak and strong Davydov components. The weak exciton a_u of very narrow width responds to an electric field by a quadratic Stark shift due to the large polarizability of 900 Å^3 of the molecular exciton $1B_u$. The stronger exciton b_u of much larger linewidth responds much more sensitively to the field by an additional effect of second derivative line shape. This additional effect cannot be explained by charge transfer between molecules since such contribution is absent in the spectrum of the weak exciton a_u, which is derived from the same molecular states. If a charge-transfer state exists, its contribution to the spectra is not resolved and hidden under the signal of the strong Davydov component, which cannot be explained on the basis of molecular eigenstates.

The second derivative electroabsorption signal of the strong b_u exciton results from coupling of its large transition dipole of 4.9 eÅ (23 D), which is the combined moment of the four molecular dipoles in the unit cell. Second-order interaction of the large transition dipole with the external field broadens the exciton resulting in the second derivative line shape of its electroabsorption spectrum. The effect requires large transition dipole moments to compete with the quadratic Stark effect due to the molecular polarizability. It must be sensitive to packing of the molecules and is therefore expected to be sensitive to disorder. The large transition dipole implies strong coupling to exciton states in neighboring cells resulting by Förster transfer in a very mobile b_u exciton, which is a possible reason for its large spectral linewidth. None of these effects occurs for the a_u exciton because its transition dipole moment is two orders of magnitude smaller.

Consistent with small spatial overlap of molecular states, the single crystal shows no trace of the Franz-Keldysh effect, which is expected if a wide band of free-carrier states exists.

The spectra show no mixing of Davydov components of different parity by the field. We conclude that Davydov components derived from the same molecular excitons are not mixed by electric fields unless the molecular eigenstates show significant spatial overlap. The data thus indicate that α-sexithiophene should be considered as a molecular solid.

ACKNOWLEDGMENTS

This work has been supported by the Deutsche Forschungsgemeinschaft (SFB 383). We thank H.-J. Egelhaaf for providing the absorption spectra of the solution and Stefan Koch and Florian Gebhard for valuable discussions.

---

[1] W. Franz, Z. Naturforsch **13**, 484 (1958).
[2] L.V. Keldysh, Zh. Éksp. Teor. Fiz. **34**, 1138 (1958) [Sov. Phys. JETP **7**, 788 (1958)].
[3] D.E. Aspnes, Phys. Rev. **153**, 972 (1967).
[4] A. Jaeger and G. Weiser, Phys. Rev. B **58**, 10 674 (1998).
[5] A. Horváth and G. Weiser, Phys. Rev. B **53**, 13 507 (1996).
[6] A. Horváth, G. Weiser, G.L. Baker, and S. Etemad, Phys. Rev. B **51**, 2751 (1995).
[7] G. Weiser and A. Horváth, Chem. Phys. **227**, 153 (1998).
[8] U. Scherf, Top. Curr. Chem. **201**, 163 (1999).
[9] M.G. Harrison, S. Möller, G. Weiser, G. Urbasch, R.F. Mahrt, H. Bässler, and U. Scherf, Phys. Rev. B **60**, 8650 (1999).
[10] D. Haarer, M.R. Philpott, and H. Morawitz, J. Chem. Phys. **63**, 5238 (1975).
[11] A. Elschner and G. Weiser, Chem. Phys. **98**, 465 (1985).
[12] L. Sebastian, G. Weiser, G. Peter, and H. Bässler, Chem. Phys. **75**, 103 (1983).
[13] L.M. Blinov, S.P. Palto, G. Ruani, C. Taliani, A.A. Tevosov, S.G. Yudin, and R. Zamboni, Chem. Phys. Lett. **232**, 401 (1995).
[14] M. Muccini, E. Lunedei, C. Taliani, D. Beljonne, J. Cornil, and J.L. Bredas, J. Chem. Phys. **109**, 10 513 (1998).
[15] R. Österbacka, C.P. An, X.M. Jiang, and Z.V. Vardeny, Science **287**, 839 (2000).
[16] J.H. Schön, C. Kloc, R.A. Laudise, and B. Batlogg, J. Appl. Phys. **85**, 2844 (1999).
[17] F.R. Lipsett, Can. J. Phys. **35**, 284 (1957).
[18] G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J. Fave, and F. Garnier, Chem. Mater. **7**, 1337 (1995).
[19] M. Muccini, E. Lunedei, A. Bree, G. Horowitz, F. Garnier, and C. Taliani, J. Chem. Phys. **108**, 7327 (1998).
[20] R. Lazzaroni, A. Pal, S. Rossini, G. Ruani, R. Zamboni, and C. Taliani, Synth. Met. **42**, 2359 (1991).
[21] C. Taliani and W. Gebauer, in *Handbook of Oligo- and Polythiophenes*, edited by D. Fichou (Wiley-VCH, New York, 1998).
[22] R.N. Marks, M. Muccini, E. Lunedei, R.H. Michel, M. Murgia, R. Zamboni, C. Taliani, G. Horowitz, F. Garnier, M. Hopmeier, M. Oestreich, and R.F. Mahrt, J. Chem. Phys. **227**, 49 (1998).
[23] G. Herzberg and E. Teller, Z. Phys. Chem. Abt. B **21**, 410 (1933).
[24] G. Weiser, Phys. Rev. B **45**, 14 076 (1992).
[25] R.C. Haddon, T. Siegrist, R.M. Fleming, P.M. Bridenbaugh, and R.A. Laudise, J. Mater. Chem. **5**, 1719 (1995).
[26] H.-J. Egelhaaf, Thesis, Universität Tübingen (1996).
[27] H. Chosrovian, D. Grebner, S. Rentsch, and H. Naarmann, Synth. Met. **52**, 213 (1992).
[28] L. Dähne, A. Horváth, and G. Weiser, Chem. Phys. **196**, 307 (1995).