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Transient picosecond photoconductivity in polyacetylene

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We present the results of transient photoconductivity measurements on highly oriented *trans*-polyacetylene. Using a photoconductive switching method utilizing picosecond optical pulses we have improved the temporal resolution of the photoresponse by one order of magnitude. We observe a fast temperature-independent photocurrent, which decays within a few picoseconds and reflects the intrinsic motion of charge carriers along the chains. Estimation of the mobility yields values of the order 1 cm^2/V s, in good agreement with theoretical calculations. By comparison of the data to that obtained from recent transient photoinduced midgap absorption experiments, we conclude that the fast photocurrent is mainly due to polarons.

I. INTRODUCTION

During the past ten years the dynamics of photogenerated charge-carrier transport in conjugated polymers has been extensively investigated.[1-6] Especially the measurement of the temporal evolution of these photoinduced excitations on short time scales has received much attention, since it offers the possibility of studying the intrinsic motion of charge carriers along the chains before their transport becomes limited by the morphology of the samples.

Among the conducting polymers *trans*-polyacetylene is still considered a prototype of this class of materials. Impressive improvements in synthesis and processing have led to well-characterized fully dense, high-quality samples.[17-21] Due to the chainlike structure, which leads to a strong electron-phonon coupling and anisotropic quasi-one-dimensional electronic properties, photoexcitations across the Peierls gap ($E_g \approx 1.5-1.8$ eV) are fundamentally different from the photoinduced electron-hole pairs in conventional inorganic semiconductors. After absorption of photons the created electrons in the conduction band and holes in the valence band distort the lattice so strongly that actually new quasiparticles, which are described as solitons and polarons, are formed with their associated electronic states deep inside the semiconducting gap.[22]

Of special interest and importance are the lifetime and the mobility of these photoexcited carriers. Polaron and soliton transport along the chains have been studied theoretically by Jeyadev and Conwell,[23-25] who found the mobility in *trans*-polyacetylene to be ≈ 3 cm^2/V s and ≈ 1.5 cm^2/V s at 300 K due to scattering by acoustic phonons, respectively. It was inferred that the short-time photoconductivity represents the transport of freely moving solitons and polarons, but until now the corresponding experiments suffered from their limited temporal resolution of about 100 ps.[3,5-7,9] Since it is well known that the photoresponse consists of a fast and a slow component, a higher temporal resolution of the measuring system is clearly desirable to avoid averaging the two components. That this is true has been demonstrated by recent transient photoinduced absorption measurements in the mid-infrared,[26,27] which revealed a very rapid generation as well as a rapid initial decay of the quasiparticles on a (sub)picosecond time scale, thus confirming the proposed Su-Schrieffer mechanism[22] about the formation of self-localized charge carriers.

In this paper we present a detailed study on transient photoconductivity in oriented Durham polyacetylene with a highly improved temporal resolution of about 5 ps by using the photoconductivity cross-correlation technique.[28] We measured the temperature, bias, polarization, and intensity dependences of the fast photocurrent dynamics. Analyzing our results we obtain a relaxation time of several picoseconds, which we assign to the initial intrinsic motion of the charge carriers along the chains. To the best of our knowledge we believe this to be the first measurements on transient phototransport in a conducting polymer with such a high temporal resolution.[15]

II. EXPERIMENT

The development of ultrafast photoconductive switches for measuring transient photoconductivity has been pioneered by Auston.[28,29] Usually, the switch is fabricated on a semiconducting film with a high density of defects, thus leading to a short free-carrier lifetime. The cross-correlation technique uses one photoconductor as a pulse generator and a second photoconductor as a sampling gate in a broadband microstrip line. The time resolution of such an arrangement is determined by the convolution of the response of the two photoconductors with the *RC* response of the interconnecting circuit of the device.

Initial attempts to measure photoconductivity in polyacetylene using this technique were not successful due to the low light-induced conductance. However, since the applicability of the technique is not restricted to identical photoconductors, we used polyacetylene as the pulse generator together with a polycrystalline Si film, damaged by heavy ion bombardment, as the fast sampling gate. The correlation circuit is shown in Fig. 1.

The substrate employed was cut from a silicon on sapphire (SOS) wafer with a 0.6-μm-thick silicon film grown by chemical vapor deposition on the 350-μm-thick sapphire. The samples were damaged at room temperature with $^{28}Si^{+}$ ions of different energies (40, 120, and 320 keV) and different doses (0.2×10^{14}, 0.6×10^{14}, and 2.2×10^{14} cm^{-2}) in order to achieve a homogeneous distribution of defects across the thickness of the Si film.[30] The created defects act as trapping and recombination centers and effectively reduce the free-carrier lifetime in the extended band states, i.e., they prevent long-lived background currents. After the implantation, part of the silicon film was removed by reactive ion etching. For reference purposes we omitted the etching process after the implantation for an otherwise identical SOS sample. The Au electrode configuration (2000 Å thick) was evaporated in the form of two crossing microstrip transmission lines (characteristic impedance $Z_0=50$ Ω) with 300-μm-wide center conductors and gap widths of 20 μm. The evaporation was performed in such a way that one of the gaps was positioned on the etched part of the substrate, the second gap on the implanted part of the Si film [see Fig. 1(a)].

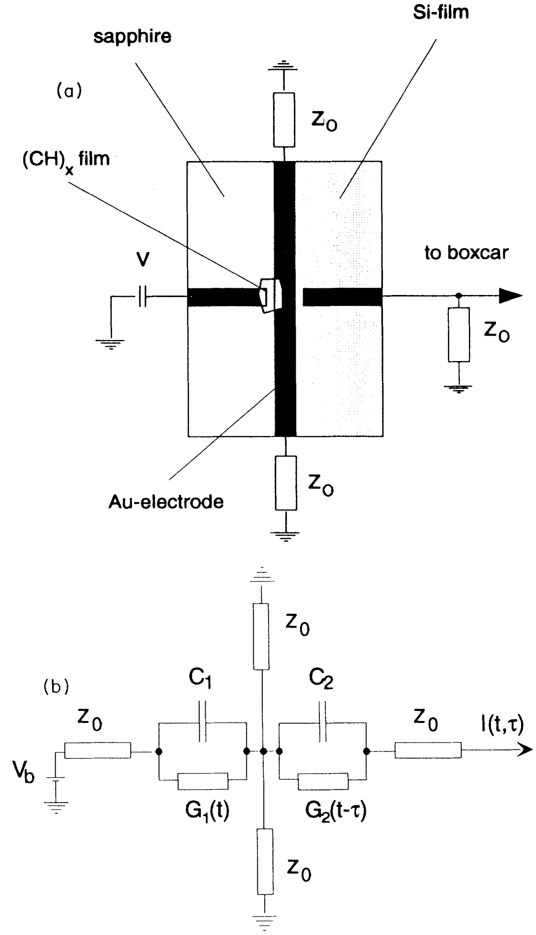

FIG. 1. (a) Schematic diagram of the correlation circuit for photoconductivity cross-correlation measurement in $(CH)_x$ on broadband microstrip lines. (b) Corresponding circuit diagram. The switches are modeled using the approximation of lumped elements with a static capacitance C_g and a resistor having a time-dependent conductance $G(t)$ in parallel. Z_0 is the characteristic impedance of the transmission lines.

The stretch-aligned polyacetylene samples were grown by the Durham route[17,18] with a stretching ratio of approximately 10:1. The thickness of the free-standing films was about 1–2 μm, sufficiently large for almost all of the incident light with polarization perpendicular to the polymer chains at 590 nm to be absorbed. A small piece of the film was placed onto the gap on the etched side of the substrate with the chains oriented parallel to the applied electric-field direction. The two microstrip contacts were underneath the sample which was illuminated from above. All sample handling was performed under inert argon atmosphere in a glovebox to avoid oxygen contamination. Measurements were carried out in an optical cryostat under vacuum of 10^{-5} mbar or less.

For the optical excitation we used the picosecond pulses of a Rh6G dye laser operating at a wavelength of 590 nm, synchronously pumped by a cw mode-locked (76 MHz), frequency-doubled Nd:YAG laser (where YAG denotes yttrium aluminum garnet). The dye laser pulses were amplified with a regenerative frequency-doubled Nd:YAG laser in combination with a three-stage dye amplifier to produce 5-ps pulses at a repetition rate of 30 Hz. The low repetition rate allows the recovery of the ground state between successive pulses. Running the dye laser with an additional absorber jet (DODCI) leads to a shortening of the pulses to about 1 ps. We routinely obtain ~1 mJ/pulse at 590 nm containing $\leq5\%$ amplified spontaneous emission.

The experiments were performed in a typical pump-probe arrangement, i.e., the output was split into two beams and a variable time delay between the excitation and probe pulse was introduced with a translation stage. The beams were focused through the same lens on the $(CH)_x$ and Si film, respectively. Measuring the exact spatial profile of the pulses using a knife-edge technique allowed for the determination of the photon fluxes. The incident light was linearly polarized with a dichroic polarizer and subsequently rotated via a half-wave plate. In most of the experiments we used light polarized perpendicular to the stretch direction of the $(CH)_x$ film due to the large anisotropy $\alpha_{\parallel}/\alpha_{\perp}$ of about 25 in the Durham material.[4,31] This provides a better possibility to excite carriers across the full thickness of the sample, thereby achieving a well-controlled excitation density in the region of the contacts underneath the sample.

A dc voltage was applied to the polyacetylene gap, which acts as a pulser upon excitation and biases the second gap. The quantity measured is the total charge at the output of the Si gap as a function of the relative delay between the two light pulses. The signal was amplified with a broadband preamplifier and integrated with a fast-sampling module of a boxcar system.

To minimize any influence of a photoinduced space-charge buildup in the photoconductive gaps, they were illuminated homogeneously, i.e., the laser beams were focused to distinctly larger spots than the areas of the gaps. By careful adjustment there was no indication of a built-in field due to charge accumulation near the contacts, opposing and screening the external field, thus resulting in a smaller correlation signal. Although it is well known that the electric-field distribution in the case of two semi-infinitely extended, infinitely thin electrodes separated by a small gap is inhomogeneous,[32] the results of a numerical study by Marcuse[33] indicate the existence of an almost uniform electric field near the surface of the sample. For the thin films used in our experiments we can therefore neglect the deviation from a uniform field distribution. Furthermore, the same study reveals that the electric potential does not vary strongly over the thickness of our films, i.e., to a first approximation the dc fields the carriers are experiencing are not very different for parallel or perpendicular optical excitation.

III. RESULTS

Before presenting the results of the cross-correlation experiments in this section we show in Fig. 2 the normalized photoresponse of stretch-aligned Durham $(CH)_x$, which has been measured using the conventional single-gap microstripline switch technique.[34] The data were taken from Ref. 6. The overall electronic resolution of the apparatus is about 50–60 ps, which clearly limits the rise time of the photocurrent wave form. The authors determined from the observed decay a relaxation time for the fast component of about 100 ps. No attempt to deconvolute the data has been made.

By assuming the system response to be Gaussian with a rise time of 50 ps we deconvoluted the material response. Best fits were obtained with a double exponential decay of the form

$$I_{\mathrm{ph}}(t)=A\exp\left[-\frac{t}{\tau_1}\right]+(1-A)\exp\left[-\frac{t}{\tau_2}\right], \qquad (1)$$

as is shown by the solid line in Fig. 2 with the following values for the parameters: $A=0.9$, $\tau_1=10$ ps, and $\tau_2=170$ ps. The photoresponse is clearly dominated by an initial fast component which decays on a picosecond time scale, much faster than the reported 100 ps. This indicates that single-gap measurements are not very reliable for an accurate determination of the short carrier lifetime in polyacetylene. Although it is tempting to associate the long component with the parameter τ_2, one should be cautious with the value since the slow decay of the photovoltage in single gap experiments is very sensitive to imperfections of the 50-Ω matching condition and to reflections at connectors; i.e., the true long component can already be buried under the noise.

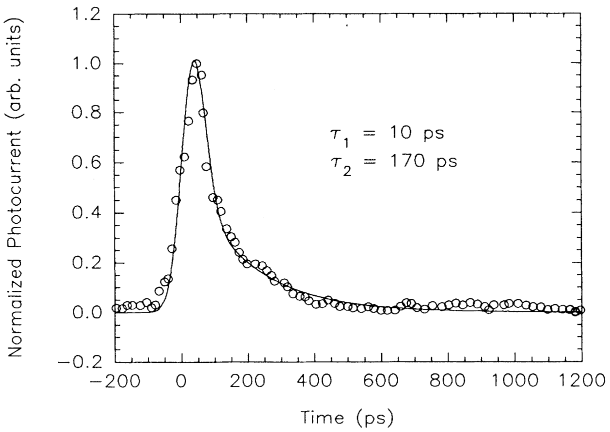

FIG. 2. Normalized fast component of the photocurrent in oriented Durham *trans*-$(CH)_x$ excited with 25-ps laser pulses (532 nm) at room temperature. Data were taken from Ref. 6. The energy of the incident light pulses with polarization perpendicular to the stretch direction is 0.95 μJ at a sample area of 200 μm × 330 μm. The integral under the peak corresponds to 1.5×10^6 electronic charges. ($U_0=100$ V.) The solid line represents the best fit to the curve obtained by convoluting the photoconductivity response [Eq. (1)] with the overall system response (assumed to be Gaussian).

As already mentioned a far better temporal resolution is achievable with the cross-correlation technique. To check the resolution of our experimental arrangement we performed first some characterizing measurements on the reference sample consisting of two ion-implanted SOS switches (see Sec. II). Conductivity measurements yield a linear current-voltage relationship over all voltages of interest and a dark conductivity of 2.5×10^{-5} S/cm, consistent with a hopping transport mechanism due to the large density of defects near the Fermi level.[35] Typically, a voltage of 60 V was applied and the incident photon fluxes were about 3×10^{16} cm^{-2} per pulse with energy of 2.1 eV and a pulse duration of 1 ps. The repetition rate was 30 Hz.

In Fig. 3 we have plotted the normalized correlation signal at room temperature. The two curves were obtained by simply interchanging the bias voltage and the measuring electronics (see Fig. 1). This corresponds to a time reversal and allows for a precise determination of zero delay between the two light pulses. Both curves are nearly symmetric by reflection with a full width at half maximum (FWHM) of about 15 ps. From the distance between the two maxima the value for the gap capacitance C_g can be determined. Following the analysis of Auston[34] we obtain $C_g\approx65$ fF, which is in good agreement with comparable data in the literature.[35,36] Assuming a simple exponentially decaying photoconductivity for the SOS switches allows for a fit of the experimental curves where the only free parameter is the relaxation time τ and where the RC-limited response of the device as well as the finite duration of the light pulses have been taken into account.[34] Figure 3 also contains the best fit we obtained with a value of $\tau\approx2.5$ ps, again in good agreement with the results reported by other authors.[35,37]

We have repeated the measurements with light pulses roughly three orders of magnitude lower in intensity by using the output of the dye laser without amplification at 76 MHz and detecting the signal with a lock-in amplifier at a chopper frequency of 1.5 kHz. The results were essentially the same, again leading to an average relaxation time of about 2.5 ps. Additionally, from the aver-

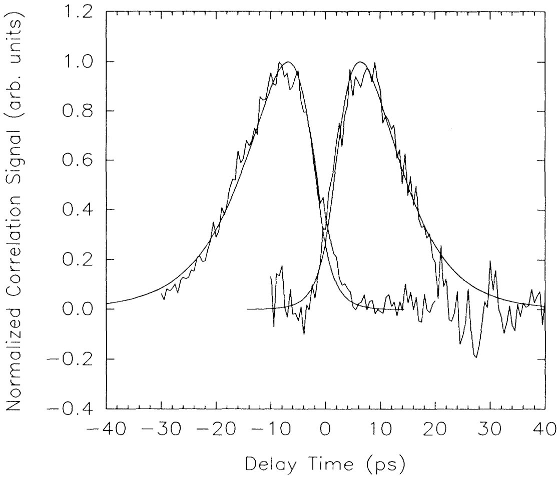

FIG. 3. Photoconductivity correlation measurement in a SOS/Si$^+$ sample with an implantation dose of 3×10^{14} cm^{-2} at ambient temperature. Interchanging bias voltage and detection system corresponds to a time reversal of the correlation and allows for the determination of the gap capacitance C_g. The solid lines show the fit to the experimental curves from which a relaxation time for the photoconductivity in SOS/Si$^+$ of $\tau\approx2.5$ ps was deduced.

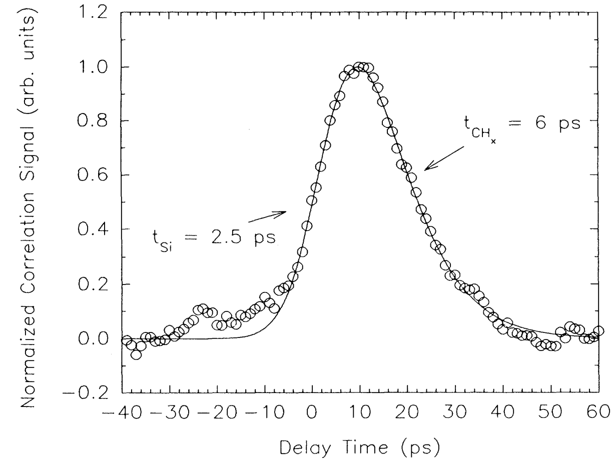

FIG. 4. Cross-correlation signal observed from a stretched *trans*-$(CH)_x$ sample and an ion-implanted Si film. The FWHM is about 22 ps. The solid line represents the calculated pulse profile assuming exponentially decaying photoconductivities where the *RC* response of the device and the finite light pulses have been taken into account.

aged peak current of the correlation we estimated the mobility of the carriers to be about 1.6 cm^2/V s, which is within the same order of magnitude as the mobility found in amorphous silicon (≈1 cm^2/V s).[38] Furthermore, the correlation signal is directly proportional to the applied bias voltage in the range of 20–100 V without any change in the temporal behavior. Together with the results for the different light intensities it follows that the relaxation of carriers is independent of the applied electric field and intensity as well as independent of temperature for the high implantation dose used, as has been shown in detail in Ref. 37.

After having established the properties of the SOS switches we turn now to the cross-correlation measurements in *trans*-polyacetylene. The correlation device was prepared as described in Sec. II. The dark conductivity in polyacetylene was about 10^{-6} S/cm, with a nearly Ohmic current-voltage relationship. Figure 4 shows a typical correlation signal for $(CH)_x$ sampled with the Si gate at room temperature due to a 0.6-μJ incident pulse of 2.1 eV polarized perpendicular to the stretch-direction with a bias field of 6×10^4 V/cm. This corresponds to a photon flux of $\sim1.9\times10^{16}$ cm^{-2} per pulse whereas the Si gap was excited with $\sim1.3\times10^{16}$ cm^{-2} per pulse.

The FWHM of the trace is about 22 ps, where the rising part reflects the temporal behavior of the sampling gap and the falling part that of the pulsing gap. Using the values for the parameters obtained from the measurements on the reference sample one can determine the lifetime of the photogenerated mobile carriers in $(CH)_x$. Thus, setting $C_g=65$ fF and $\tau_{Si}=2.5$ ps and following the theoretical analysis given by Auston[34] we obtain a value $\tau_{CH}=6$ ps. The resulting fit to the experimental data points is shown in Fig. 4 as a solid line, where the finite duration of the amplified light pulses has been taken into account.

Again, we assumed a simple exponentially decaying photoconductance with a single time constant as well as no change in the gap capacitance by placing the polymer film onto the gap. Since the capacitance is mainly determined by the dielectric constant of sapphire (for fixed dimensions) and since $\varepsilon_{saph}\gg\varepsilon_{CH}$, we believe this to be a valid assumption to first order. Repeating the measurements under similar experimental conditions with different samples taken from the same batch yield a slight scatter in the resulting deconvoluted value for the relaxation time in the range of 3.5–7 ps.

This confirms clearly, and quantifies explicitly, the picosecond photoconductivity component in $(CH)_x$, which was already implied by the deconvolution procedure for evaluating the results of the single-gap measurements (see Fig. 2).

Figure 5 shows the temperature dependence of the correlation signal in the range of 80–295 K, where we have plotted the peak values on both a linear and an Arrhenius-type scale. As can be seen in the figure these values are nearly independent of temperature, scattering within a factor of 2. The FWHM of the correlation traces were not affected within the experimental errors. From the slope of the Arrhenius plot (see inset) we deduce an activation energy of only 4 meV. It follows that the decay of the initial photocurrent and therefore the relaxation mechanism for the mobile charge carriers is independent of temperature, a result which has also been confirmed by a number of authors.[3,5–7]

The field dependence of the maximum correlation signal is displayed in Fig. 6, where the applied dc voltage varied between 40 and 180 V. The result is a roughly linear relationship, leading to a slope of 0.9 on a log-log plot. Again, the widths of the traces were not influenced

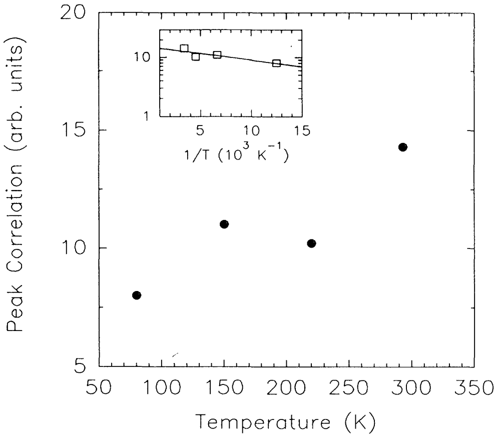

FIG. 5. Temperature dependence of the maximum correlation signal plotted on a linear and an Arrhenius-type scale (see inset). The slope yields an activation energy of only 4 meV, indicating a temperature-independent photocurrent. The applied field was 2×10^4 V/cm with a direction parallel to the chains; the incident light pulses were polarized perpendicular to the chains with a photon flux of $\sim1.6\times10^{16}$ cm^{-2} per pulse.

by the field. We obtained a similar result for the dependence of the correlation as a function of light intensity (Fig. 7). The maximum absorbed photon flux was 2×10^{16} cm^{-2} per pulse, whereas the incident intensity on the Si gap was kept constant ($\approx1\times10^{16}$ cm^{-2}). The dependence was found to be slightly sublinear with a slope of 0.9. On the other hand, within the experimental errors the data are also compatible with a slope of 1.0.

These results are in accordance with those obtained from investigations of the temporally unresolved fast component by other authors.[2,3,5–7,9] Bleier *et al.*[6] reported a linear intensity dependence and a slightly superlinear field dependence ($\sim E^{1.1}$) in stretch-oriented Durham material; Phillips and Heeger[7] observed roughly linear relationships for both dependences in oriented Naarmann-Theophilou polyacetylene. Also, Walser *et al.*[9] found a linear intensity dependence in oriented polyacetylene synthesized following a modified Shirakawa method. The maximum absorbed photon flux in their experiment is approximately one order of magnitude lower than the maximum flux used in our case. This linear behavior, showing no indication of saturation, rules out bimolecular recombination of the charge carriers on early time scales. With perpendicular polarization and a maximum flux of $\sim2\times10^{16}$ cm^{-2} the density of charge carriers is about 7.4×10^{20} cm^{-3} (where we assumed a quantum yield $\eta=1$). Since the density of carbon atoms is $\approx5\times10^{22}$ cm^{-3} ($\rho_{\rm CH}=1.1$ g/cm^3) it follows that on the average one excitation exists per ~70 carbon atoms. An undisturbed conjugated segment in Durham $({\rm CH})_x$ has a typical length of about 30–40 CH units.[39,40] Thus, at most every second segment carries an excitation which can principally contribute to the photocurrent. Obviously the excitation density is lower than the regime where the picosecond transport is affected by bimolecular recombination. One possible explanation could be that for this kind of recombination to become important on the average every segment has to carry an excitation. On longer time scales it can play a role at lower carrier densities, since the carriers have then enough time to reach a neighboring segment or chain and find a proper partner. Of course, another reason could be the quantum yield where values smaller than unity lead to fractions of free mobile carriers.

Finally, we turn to the behavior for different polarizations of the incident light. Due to the high degree of orientational order in stretch-aligned Durham samples, the polymer films have strong anisotropic optical and electrical properties.[6,39–41] Various experimental investigations have revealed an anisotropy of the photoresponse with respect to the pump polarization favoring slightly the perpendicular case.[4,6,7,42] On the other hand, due to the large anisotropy $\alpha_\parallel/\alpha_\perp\approx25$ and the corresponding

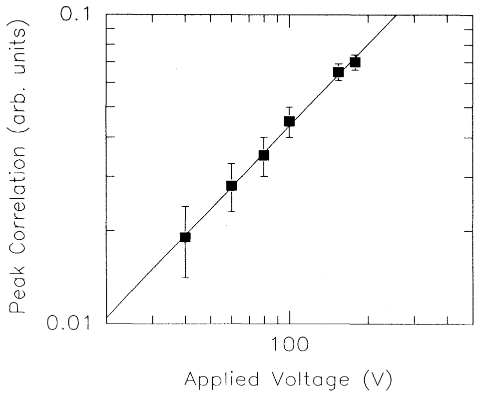

FIG. 6. Field dependence of the correlation signal on a log-log scale. The signal is nearly proportional to the electric field with a slope of 0.9. The photon flux incident on the $({\rm CH})_x$ gap was $\sim8.5\times10^{15}$ cm^{-2} with perpendicular polarization, the corresponding flux incident on the Si film being $\sim1\times10^{16}$ cm^{-2}.

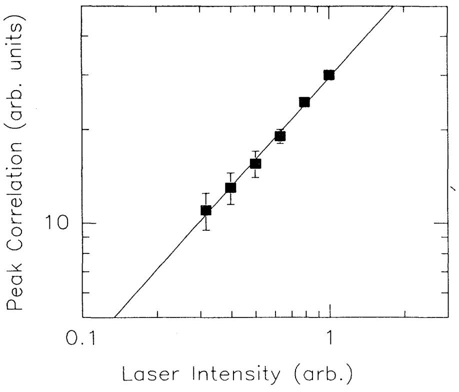

FIG. 7. Intensity dependence of the correlation signal on a log-log scale with the optical electric field perpendicular to the chains for an applied voltage of 100 V. The relationship is almost linear with a slope of 0.9. The maximum photon flux incident on the $({\rm CH})_x$ film was 2×10^{16} cm^{-2} where the values have been corrected for reflection and transmission.

different values for the penetration depths ($d_{\parallel} \approx 0.014$ μm, $d_{\perp} \approx 0.27$ μm at 2.1 eV) it is far more difficult to obtain results in the parallel pump case. This is especially true for the cross-correlation measurements since the penalty paid for the higher temporal resolution is, of course, a lower sensitivity, thus requiring higher excitation densities compared to single-gap measurements. This limits the applicability of the cross correlation for polarization-dependent studies. In a restricted series of experiments we have investigated the response for the parallel pump case, where the incident photon flux was about 8×10^{15} cm^{-2} per pulse and the applied voltage was 100 V. From the evaluation of the experimental data we deduce a relaxation time of $\tau \approx 4-6$ ps, which lies within the same range as in the perpendicular pump case. A comparison of the maximum measured signal amplitudes for both directions after correction for the absorbed number of photons yields an isotropic behavior within the experimental errors.

However, since the reported anisotropies for oriented Durham $(CH)_x$ (Ref. 6) and Naarmann-Theophilou $(CH)_x$ (Ref. 7) are only 1.8 and 1.7, respectively, the observed response is comparable with these values, taking into account the notorious difficulties in determining the absolute number of photons for such a pulsed laser system as well as the strong inhomogeneous excitation of the sample. More important is the experimental fact that for both polarization directions the temporal behavior of the relaxation of the carriers is the same.

Nevertheless, for the high photon fluxes used the thermal heating of the sample, especially for the parallel pump case, is not negligible since for each pulse a substantial amount of energy is deposited into a small volume. Neglecting heat diffusion and assuming an instantaneous energy transfer from the electronic system to the phonon system the increase in temperature is given by[43]

$$\Delta T = \frac{(1-R)\alpha N h\nu}{\rho c_p} , \tag{2}$$

where $(1-R)N$ is the number of absorbed photons per cm^2, α is the absorption coefficient, ρ is the density (1.1 g/cm^3), and c_p is the specific heat (~ 1 J/gK at room temperature[44,45]). Inserting the appropriate values in Eq. (2) leads to a rather high increase of about 600 K for parallel pumping. Although Eq. (2) is only an approximation and represents an upper limit, it demonstrates the huge thermal load of the sample. Even in the perpendicular pump case the observed and well-documented temperature independence of the photosignal (see Fig. 5 and Refs. 3, 6, and 7) may be influenced by thermal heating. Using Eq. (2) the rise for the maximum illumination (2×10^{16} cm^{-2}) is about 230 K, sufficiently high to mask a slight dependence on temperature.

IV. DISCUSSION

After having quantified the picosecond response in $(CH)_x$ we turn now to the discussion of the transport properties and recombination mechanisms of the carriers. A direct estimation of the mobility from the cross-correlation signal is not readily possible since the absolute value of the peak current flowing at the maximum of the observed signal is not known precisely. A far better method is to combine the results of the single-gap measurements and the correlation measurements. Integrating the trace of the photocurrent obtained in a single-gap experiment yields the total charge flow during the lifetime τ of the carriers. Assuming a simple exponentially decaying current the following expression holds:

$$Q = \eta\phi(1-R)(1-\exp[-\alpha d])\frac{e}{h\nu}\frac{U_0}{l^2}E_p\mu\tau , \tag{3}$$

where $E_p/h\nu$ is the number of incident photons, l is the width of the gap, U_0 is the applied voltage, R is the reflectivity, and α is the absorption coefficient. Thus Q is proportional to the quantity $\eta\phi\mu\tau$, where $\eta\phi$ denotes the product of the primary quantum efficiency and the probability to escape fast geminate recombination and $\mu\tau$ represents the typical mobility lifetime product. Inserting the corresponding values from Ref. 6 (see Fig. 2) yields $\eta\phi\mu\tau = 2.4 \times 10^{-12}$ cm^2/V. Together with the average lifetime $\tau \approx 4.5$ ps deduced from the cross-correlation measurement it is now possible to decouple the $\mu\tau$ product, obtaining a value $\eta\phi\mu = 0.53$ cm^2/V s. The only uncertain quantity is the effective quantum yield $\eta\phi$.

Measurement of time-resolved photoinduced absorption (PA) allows for an estimation of the quantum yield. These experiments are complementary to photoconductivity since the latter is proportional to the product of the number and lifetime of the charged excitations and their mobility, while the PA signal is sensitive to the number and lifetime of all charged and neutral excitations.

It is well known that in polyacetylene the PA spectrum consists of two absorption peaks, the so-called low-energy (LE) peak at 0.45 eV and the high-energy (HE) peak at about 1.4 eV, where the LE peak is attributed to charged excitations ($S^+\bar{S}^-$ pairs), while the HE peak is due to neutral soliton pairs ($S^0\bar{S}^0$).[46,47] Thus, with respect to photoconductivity the LE peak is of particular interest for comparison with our experimental data.

Recently, Rothberg *et al.*[26] have performed transient photoinduced midgap absorption experiments on oriented Durham *trans*-$(CH)_x$ with subpicosecond time resolution. The sample was excited with intense pump pulses at 575 nm and probed with synchronized tunable mid-infrared pulses (2.5–5.5 μm), covering the spectral range of the LE peak. Measuring the dynamics of the induced subgap absorption the authors observed a short-lived component for both parallel and perpendicular polarizations of the pump light. This short-lived component was assigned to directly photogenerated charged intrachain (Su-Schrieffer) soliton pairs, equilibrating on a femtosecond time scale and recombining geminately in about 1 ps. Thus, even with light polarized perpendicular to the chains the primarily created excitations are intrachain carriers with substantial quantum yield, in agreement with the prediction by Baeriswyl and Maki.[48] Furthermore, in the case of perpendicular pumping the fast component is followed by a sizable tail with a lifetime of at least 300 ps. The long-lived absorption signal, which is absent in the parallel case, was assigned to interchain electron-hole pair excitation occurring with fairly high quantum yield and leading to polaron formation. Further evidence for this interpretation comes from the fact that the spectra obtained at long pump-probe delays are not the same as the charged soliton spectra.[26] From the intensity dependence of the photoinduced signal Rothberg *et al.*[26] estimated the relative quantum yield for solitons and polarons. For the parallel pump configuration they obtain a value near unity for the generation of charged solitons which reduces drastically for higher intensities due to the volume filling effect of the solitons. For perpendicular pumping they estimate a charged soliton yield of 0.6 ± 0.3, implying a yield for polarons of 0.4 ± 0.3 under the assumption that polarons are the only other excitation.

A comparison of these results with our photoconductivity studies leads to a striking discrepancy concerning the long-lived photoinduced absorption signal for perpendicular pumping, from which one would expect an easily detectable and temporally resolvable contribution to the photocurrent with our cross-correlation arrangement. Since this absorption is assigned to polarons which are in principle mobile, one would further expect a marked anisotropic behavior of the fast photoconducting response, since the lifetime of the solitons is far shorter (~1 ps) and they decay geminately, i.e., there is no net contribution to the photocurrent. In contrast, the results presented in Sec. III have revealed the same mean lifetime and response for both polarizations.

Considering for the moment only the perpendicular polarization and assuming that the contribution of charged solitons to the photocurrent is negligible it follows that polarons exist for quite a long time but are mobile only for a very short period before they are effectively trapped for the first time. They are released at later times contributing to the current on longer time scales which we are not able to resolve within our experimental sensitivity, but which can in principle be detected in single-gap experiments. Setting $\eta\phi=0.4$ leads to a mobility of $\mu\sim1.3$ cm^2/V s, where this value can also vary between 0.75 and 5.3 cm^2/V s within the given experimental uncertainties. With $l=\mu E\tau$ and setting $\tau=4.5$ ps, where E is the applied field of typically 2×10^4/V/cm, we get a mean migration distance $l\approx12$ Å, which again within the errors can reach 50 Å. We consider τ as the characteristic time for the mean free drift of the carriers rather than a recombination time. Comparing the estimated traveling distance and the typical conjugation length in Durham material (30–40 CH units[39,40]) it is obvious to assign the observed picosecond photocurrent to the intrinsic motion of polarons along the chain segments. Chain ends serve as very effective, not necessarily very deep traps or barriers hindering the further transport.

Calculation of the phonon-limited mobility of polarons drifting along a chain in *trans*-polyacetylene has been performed by Jeyadev and Conwell.[23] They find the room-temperature mobility of polarons to be ~3 cm^2/V s, which is in remarkable accordance with our experimental results. Since only acoustic-phonon scattering is considered and scattering by defects and impurities is neglected the calculated value represents an upper limit. Also, the mobility is found to be only slightly temperature dependent for the range 150–300 K which, considering the heating effect by the laser pulses, can explain quite well the observed temperature independence of the correlation signal. Furthermore, Jeyadev and Conwell have shown that the photocurrent is not due to hot carriers, i.e., $E_{\text{kin}}\gg k_BT$, since the thermalization process itself is very rapid through the generation of acoustic phonons occurring within a fraction of a picosecond.

Thus the experimental results reported in Sec. III and the theoretical investigations confirm without contradiction the interpretation that polarons are responsible for the photocurrent in the perpendicular pump configuration.

We turn now to the discussion of the photoconductivity following parallel polarized excitation. The results of Rothberg *et al.*[26] show that for this case solitons are predominantly generated decaying geminately within 1 ps. From their data the authors estimate that fewer than 5% of the photogenerated solitons remain 5 ps after the pump pulses. Due to the geminate recombination most solitons are therefore ruled out from a net contribution of the photocurrent (see below). Setting $\eta\phi=5\%$ and assuming that polarons play no role we get a mobility $\mu\sim10$ cm^2/V s. This value is considerably larger than the theoretical result reported by Jeyadev and Conwell,[24] who have performed a similar calculation for solitons. At room temperature they obtain $\mu_{\text{sol}}\sim1.5$ cm^2/V s. Inversely, to get the theoretical result the yield for solitons escaping geminate recombination should be $\eta\phi\approx0.35$, which appears highly unlikely by inspection of Fig. 1 in Ref. 26.

The main experimental difficulty lies in the large absorption coefficient $\alpha_\parallel$ leading easily to a saturation in the generation of charged solitons due to the volume filling of the lattice by these excitations. In our experiments the absorbed intensity was already high enough to induce saturation. This implies that, although the material continues to absorb light within the penetration depth, the generated electron-hole pairs do not fully evolve into charged solitons before recombining. These carriers may be responsible for the similar observed behavior in the photoresponse.

If it is feasible to perform photoconductivity measurements with such high temporal resolution by using distinctly lower intensities, it should be possible to isolate any contribution from the solitons to the fast photocurrent in the first few picoseconds. Furthermore, since solitons decay geminately a marked anisotropy with respect to the polarization of the light is to be expected on the order of $I_{\text{ph},\perp}:I_{\text{ph},\parallel}\approx8:1$, which, on the other hand, may be reduced within the experimental error to a ratio 2:1.[26]

A further mechanism for separating charge carriers on different chains is due to the finite interchain interaction. An electron-hole pair may be separated on two neighboring chains within a typical time $\tau\sim h/2\pi t_\perp$. With a transfer integral $t_\perp\approx25$ meV, a value $\tau\sim2\times10^{-14}$ s follows, i.e., a time far shorter than the self-trapping time

($\sim$150–350 fs) of the electron-hole pair into solitons. A fraction of the photogenerated intrachain carriers may escape via this channel and relax into polarons on different chains. On the other hand, this fraction should be lower than 5% since Rothberg *et al.* do not see any indication for a long-lived absorption in the parallel pump configuration. Considering the experimental uncertainties in determining the anisotropy of the photoresponse (see Sec. III) this process may be responsible for the isotropic behavior. But again we have to stress that we are not really able to distinguish between a truly isotropic or an anisotropic response with a ratio of the order 2:1 or so with our arrangement.

Finally, we address the question of displacement currents due to geminately recombining charged solitons and their possible role in explaining our experimental data. Since the dielectric constant is low in organics geminate recombination probabilities are quite high in comparison with inorganic semiconductors. Assuming for the moment that the observed photoconductivity is due to separation and geminate recombination of charged solitons and antisolitons created on and confined to the same conjugated chain segment, we would expect to observe a photovoltage signal whose temporal integral (within a time interval of 5 ps) vanishes since the initial and final states are the same and no net charge has flown in the outer circuit. Only solitons (or antisolitons) reaching the contacts within their lifetime τ, i.e., carriers generated within a distance $\Delta l = \mu E \tau$ from the electrodes can consequently only contribute. We estimate the ratio of this fraction to the total number of generated carriers in the sample by taking the ratio of Δl and the gap width (20 μm). Inserting the appropriate mean value for Δl e.g., the typical conjugation length since the carriers are confined, leads to a ratio of the order 10^{-4}. Assuming that only this fraction carries the photocurrent would lead to unreasonable values for the appropriate physical quantities in Eq. (3). Furthermore, if the observed photosignal would be solely due to solitons-antisolitons, we would anticipate an anisotropy in the photoconductivity which shows a crossover with intensity. According to the data of Rothberg *et al.* solitons are generated with a quantum yield ratio of roughly 2:1 at low intensities, favoring the parallel polarization. At higher intensities the quantum yield for soliton pair formation falls off dramatically in the parallel case thereby favoring the perpendicular polarization. Attributing the signals to displacement currents due to separation and geminate recombination of charged solitons would therefore not explain the data—neither the detected photovoltage nor the isotropic or slightly anisotropic response. Also it would seem quite implausible to exclude totally the polaronic contribution since polarons are created together with solitons at the same time—at least in the perpendicular case—with a reasonable quantum yield and are not constrained—like solitons and antisolitons—to the same segment.

Summarizing the results obtained it seems obvious that separation of charge carriers on different chains is necessary and that, consequently, polarons are responsible for the picosecond photocurrent. On longer time scales polarons may, of course, undergo all the known interactions with neutral solitons and polarons converting thereby into charged solitons. These interactions, whose progress and temporal behavior depend sensitively on material properties like crystallinity, purity, morphology, etc., are reflected in the typical spectra of charged solitons observed in the corresponding photoinduced absorption experiments on microsecond or millisecond time scales.[47,49]

Thus there exist at least three different time regimes with respect to photoconductivity. As we have shown in this paper the photocurrent is dominated by polarons on a picosecond time scale drifting along the chains before getting trapped for the first time. The second regime which begins on a subnanosecond time scale and lasts until microseconds is characterized by trapping, conversion of polarons into solitons and their subsequent pinning, hopping between chains and traps, etc., while recombination represents the dominant process for the microsecond regime and later times. Most interestingly, within this picture charged solitons play a role only for a very short time after their creation due to their geminate decay and reappear again at far later times via indirect processes. In the meantime polarons are the important excitations carrying the picosecond photocurrent.

V. CONCLUSION

In summary, we have investigated the transient photoconductivity and its dependence on temperature, light intensity, electric field, and polarization of the light in Durham/Graz *trans*-polyacetylene by using a cross-correlation method. We find a fast temperature-independent picosecond component decaying with a mean relaxation time $\tau \approx 4.5$ ps representing the intrinsic drift of carriers along the chains. Estimation of the mobility leads to $\mu \approx 1.3$ cm^2/V s, which is in good agreement with the theoretically predicted drift mobility. By comparison of the data to that of photoinduced absorption measurements we conclude that polarons are carrying the picosecond photocurrent, while solitons yield no net contribution due to their geminate decay within 1 ps.

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[1] S. Etemad, T. Mitani, M. Ozaki, T. C. Chung, A. J. Heeger, and A. G. MacDiarmid, Solid State Commun. **40**, 75 (1981).

[2] Y. Yacoby, S. Roth, K. Menke, F. Keilmann, and J. Kuhl, Solid State Commun. **47**, 869 (1983).

[3] M. Sinclair, D. Moses, and A. J. Heeger, Solid State Commun. **59**, 343 (1986).

[4] P. D. Townsend and R. H. Friend, Synth. Met. **17**, 361 (1987).

[5] M. Sinclair, D. Moses, R. H. Friend, and A. J. Heeger, Phys. Rev. B **36**, 4296 (1987).

[6] H. Bleier, S. Roth, Y. Q. Shen, D. Schäfer-Siebert, and G. Leising, Phys. Rev. B **38**, 6031 (1988).

[7] S. D. Phillips and A. J. Heeger, Phys. Rev. B **38**, 6211 (1988).

[8] D. D. C. Bradley, Y. Q. Shen, H. Bleier, and S. Roth, J. Phys. C **21**, L515 (1988).

[9] A. D. Walser, R. Dorsinville, R. Tubino, and R. R. Alfano, Phys. Rev. B **43**, 7194 (1991).

[10] D. Moses and A. J. Heeger, J. Phys. Condens. Matter **1**, 7395 (1989).

[11] K. J. Donovan and E. G. Wilson, J. Phys. Condens. Matter **2**, 1659 (1990).

[12] J. Reichenbach, J. Anders, S. Roth, I. Belaish, and D. Davidov, Mol. Cryst. Liq. Cryst. **194**, 317 (1990).

[13] K. J. Donovan, J. W. P. Elkins, and E. G. Wilson, J. Phys. Condens. Matter **3**, 2075 (1991).

[14] N. E. Fisher and D. J. Willock, J. Phys. Condens. Matter **4**, 2517 (1992).

[15] J. Reichenbach, M. Kaiser, J. Anders, H. Byrne, and S. Roth, Europhys. Lett. **18**, 251 (1992).

[16] D. Comoretto, G. Dellepiane, G. F. Musso, R. Tubino, R. Dorsinville, A. Walser, and R. R. Alfano, Phys. Rev. B **46**, 10 041 (1992).

[17] J. H. Edwards and W. J. Feast, Polymer **21**, 595 (1980).

[18] G. Leising, Polymer Bull. **11**, 401 (1984).

[19] H. Naarmann and N. Theophilou, Nature **327**, 403 (1987).

[20] K. Akagi, M. Suezaki, H. Shirakawa, H. Kyotani, M. Shimomura, and Y. Tanabe, Synth. Met. **28**, D1 (1989).

[21] J. Tsukamoto, A. Takahashi, and K. Kawasaki, Jpn. J. Appl. Phys. **29**, 125 (1990).

[22] W. P. Su and J. R. Schrieffer, Proc. Natl. Acad. Sci. U.S.A. **77**, 5626 (1980).

[23] S. Jeyadev and E. M. Conwell, Phys. Rev. B **35**, 6253 (1987).

[24] S. Jeyadev and E. M. Conwell, Phys. Rev. B **36**, 3284 (1987).

[25] E. M. Conwell and S. Jeyadev, Mol. Cryst. Liq. Cryst. **160**, 443 (1988).

[26] L. Rothberg, T. M. Jedju, P. D. Townsend, S. Etemad, and G. L. Baker, Phys. Rev. Lett. **65**, 100 (1992).

[27] L. Rothberg, T. M. Jedju, S. Etemad, and G. L. Baker, Phys. Rev. B **36**, 7529 (1987).

[28] D. H. Auston, A. M. Johnson, P. R. Smith, and J. C. Bean, Appl. Phys. Lett. **37**, 371 (1980).

[29] D. H. Auston, in *Picosecond Optoelectronic Devices,* edited by C. H. Lee (Academic, New York, 1984).

[30] J. R. Denis and E. B. Hale, J. Appl. Phys. **43**, 1119 (1978).

[31] G. Leising, Phys. Rev. B **38**, 10 313 (1988).

[32] S. Ramo, J. R. Whinnery, and T. van Deuzer, *Fields and Waves in Communication Electronics,* 2nd ed. (Wiley, New York, 1984).

[33] D. Marcuse, IEEE J. Quantum Electron. **QE-25**, 939 (1989).

[34] D. H. Auston, IEEE J. Quantum Electron. **QE-19**, 639 (1983).

[35] R. J. Manning and J. R. Hill, Appl. Phys. B **38**, 17 (1985).

[36] N. H. Koster and R. H. Jansen, IEEE Trans. Microwave Theory Tech. **MTT-30**, 1273 (1982).

[37] T. Pfeiffer, Ph.D. thesis, University of Stuttgart, 1986.

[38] A. M. Johnson, D. H. Auston, P. R. Smith, J. C. Bean, J. P. Harbinson, and A. C. Adams, Phys. Rev. B **23**, 6816 (1981).

[39] P. D. Townsend, C. M. Pereira, D. D. C. Bradley, M. E. Horton, and R. H. Friend, J. Phys. C **18**, L283 (1985).

[40] G. Leising, R. Uitz, B. Ankele, W. Ottinger, and F. Stelzer, Mol. Cryst. Liq. Cryst. **117**, 327 (1985).

[41] R. Tubino, R. Dorsinville, A. Seas, J. Birman, and R. R. Alfano, Phys. Rev. B **38**, 8318 (1988).

[42] R. H. Friend, D. D. C. Bradley, and P. D. Townsend, J. Phys. D **20**, 1367 (1987).

[43] J. R. Meyer, F. J. Bartoli, and M. R. Kruer, Phys. Rev. B **21**, 1559 (1980).

[44] G. Leising and H. Kahlert, J. Phys. (Paris) Colloq. **44**, C3-111 (1983).

[45] N. Mermilliod, L. Zuppiroli, and B. François, J. Phys. (Paris) **41**, 1453 (1980).

[46] J. Orenstein and G. L. Baker, Phys. Rev. Lett. **49**, 1043 (1982).

[47] J. Orenstein, in *Handbook of Conducting Polymers,* edited by T. A. Skotheim (Dekker, New York, 1986), Vol. 2, p. 1297.

[48] D. Baeriswyl and K. Maki, Phys. Rev. B **38**, 8135 (1988).

[49] R. H. Friend, H. E. Schaffer, A. J. Heeger, and D. C. Bott, J. Phys. C **20**, 6013 (1987).