

# Photocurrent autocorrelation of femtosecond laser pulses in poly(*p*-phenylenevinylene)

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**Abstract.** Photoconductive thin-film cells made from a  $\pi$ -conjugated polymer, poly(*p*-phenylenevinylene) (PPV) can be used for diagnostics of femtosecond laser pulses utilizing the phenomenon of photocurrent autocorrelation. In general, the autocorrelation photocurrent signal can be due to the nonlinearity of the primary photogeneration step or to the influence of the existing photogenerated charge carriers on the efficiency of production of further amounts of charges. Experiments with 150 femtosecond pulses from a Ti-sapphire laser at 800 nm show that two-photon induced photocarrier generation is the nonlinear process leading to the autocorrelation in PPV photoconductive cells. There is no indication of the presence of any photogeneration intermediates with picosecond range lifetimes.

The usual technique of measuring the duration of very short laser pulses (in the picosecond and femtosecond regime) employs an autocorrelation principle, i.e. a laser pulse is probed with its replica delayed by a variable amount of time. A nonlinear optical interaction in a medium can be conveniently used for recording the intensity autocorrelation: often the second harmonic generated in a suitable nonlinear crystal is measured as a function of delay between the pulses. We present in this paper a simple autocorrelator based on the photoconductive autocorrelation concept [1–5] and using a thin-film photocell of a conjugated polymer.

The principle of the photocurrent autocorrelation is shown in figure 1. A photoconductive cell is irradiated with a short laser pulse and its time-delayed replica (derived by splitting the intensity of the pulse in half with a beam splitter and passing the two resulting beams through nearly identical beam paths, one of which is adjustable). The time constant of the electrical circuit is much longer than the delay time between the pulse and its replica. If the system is linear, i.e. the amount of charge generated by light is linearly proportional to the number of absorbed photons, then the photocurrent generated by the two beams and integrated over time will not depend on the delay time. This can be also rephrased in terms of the reciprocity law (known e.g. from photography) stating that the magnitude of a photoeffect depends only on the total dose of photons and not the duration of the time period in which they

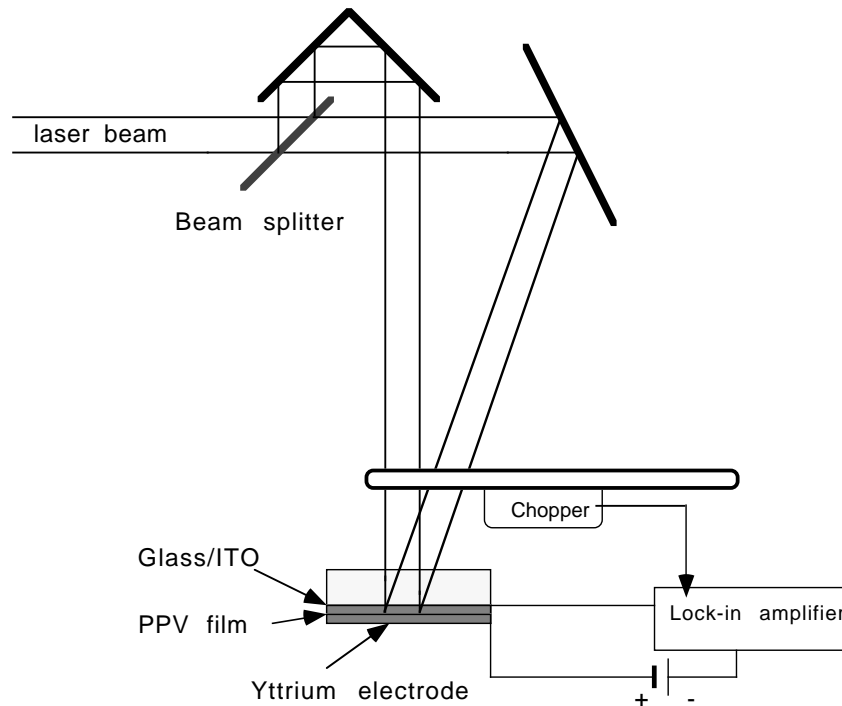
were delivered. Thus, if the reciprocity law holds then the amount of charge collected at the photocell electrodes will be the same whether the pulses arrive at the sample together or are separated in time. Deviations from the reciprocity law will, on the other hand, lead to the appearance of autocorrelation signals.

To discuss how a photoconductive cell can be used for autocorrelation of femtosecond pulses we consider a simple kinetic model of photogeneration and we incorporate two examples of deviations from the reciprocity law. First, we consider that at high light intensities the rate of generation of free charge carriers by photons is a nonlinear function of the light intensity. This nonlinearity of the primary photogeneration process may be due to the nonlinearity of the light absorption as e.g. the presence of two-photon absorption or absorption saturation. Another process which we include in our model is a dependence of the photogeneration rate on the number of charge carriers already present in the photoconductive cell. Such a dependence may be, for example, due to the space charge (screening) effect of the existing carriers on the field-assisted dissociation of charge-transfer excitons. We express therefore the rate of photogeneration of charge carriers in a thin-film photocell by the following equation:

$$\frac{dn(t, \mathbf{r})}{dt} = \eta_1 I(t, \mathbf{r}) + \eta_2 I^2(t, \mathbf{r}) + \dots + \kappa_1 n(t, \mathbf{r}) I(t, \mathbf{r}) + \dots - \frac{n(t, \mathbf{r})}{\tau} \quad (1)$$

where  $n(t, \mathbf{r})$  is the charge carrier density,  $I(t, \mathbf{r})$  stands

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**Figure 1.** A photocurrent autocorrelation setup using a sandwich-type photoconductive cell of poly(*p*-phenylenevinylene).

for the light intensity,  $\tau$  is the carrier lifetime and  $\eta_1$ ,  $\eta_2$ ,  $\kappa_1$  are constants.

The first two terms on the right-hand side of the equation describe the linear and quadratic photogeneration rates. The presence of a term which depends on the square of the light intensity corresponds to an ‘instantaneous nonlinearity’ of the photogeneration process. The third term, on the other hand, describes the dependence of the generation rate on the number of carriers that already exist in the sample and therefore can be called a ‘memory’ effect. Clearly, such ‘memory’ may be due to various physical effects—for example, screening of the external field by the space charge is likely to lead to a decrease of the photogeneration rate (a negative sign of the  $\kappa_1$  coefficient) [1, 5] although in some cases the electric field modification by photogenerated charges may also lead to an increase of the photocurrent [1]. For simplicity, we take this dependence to be linear.

One can note that absorption saturation may also be formally treated in a similar way, although there may be both an instantaneous part of absorption saturation (a negative sign of  $\eta_2$ ) and a longer-lived part. The ‘memory’ effect would then be due to the slow recovery of saturated absorption rather than to a direct effect of charge carriers on the photogeneration. Finally, the fourth term in the equation describes first-order decay of charge carriers. For qualitative discussion it is not important whether the carriers decay by recombination or are mostly discharged at the electrodes, as can be the case for a thin-film cell of a photoconductor with a relatively high electric field applied. We disregard trapping of charge carriers in equation (1). This can be partly justified at least in the case of relatively fast trapping/detrapping events (shallow trapping). We

are not concerned with the temporal evolution of the photocurrent pulse but only with the total charge transferred between the electrodes within a relatively long integration time and therefore it is not important whether the carriers do or do not undergo multiple trapping events on their way to the electrodes.

To calculate model autocorrelation curves we assume that the electric fields of the two beams,  $\mathbf{E}_1$  and  $\mathbf{E}_2$  propagating with wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ , are given by:

$$\mathbf{E}_1(\mathbf{r}, t) = \mathbf{A}(t) \sin(\omega t - \mathbf{k}_1 \mathbf{r}) \quad (2)$$

and

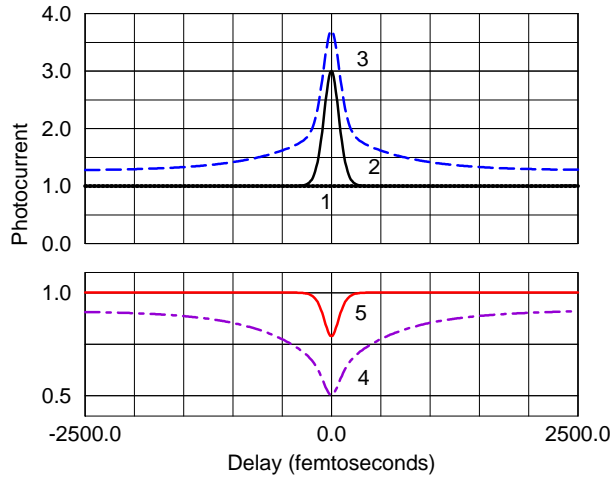
$$\mathbf{E}_2(\mathbf{r}, t) = \mathbf{A}(t - t_D) \sin(\omega t - \mathbf{k}_2 \mathbf{r}) \quad (3)$$

where  $\mathbf{A}(t)$  is the pulse envelope and  $t_D$  is the delay between the pulse and its replica. The time and position dependent light intensity  $I(\mathbf{r}, t)$  is obtained by the summing of these two fields and averaging the square of the field over the oscillation period. The photocurrent measured in an external circuit will depend on the time and space averaged charge carrier density:

$$J(t_D) \propto \left\langle \int_{-\infty}^{\infty} n(t, t_D, \mathbf{r}) dt \right\rangle \quad (4)$$

where the angle brackets denote spatial averaging over the volume of the photoconductor.

For a strictly linear system (that is for the absence of the second and third terms in equation (1)) the integrated photocurrent will be independent of the delay  $t_D$  since the total number of generated charge carriers will only depend on the total number of absorbed photons. Any dependence of the integrated photocurrent on the delay between the two



**Figure 2.** Examples of shapes of autocorrelation curves calculated from equations (1)–(4) for laser pulse duration = 100 fs: 1—linear light intensity dependence of photogeneration, no memory effects:  $\eta_2 = 0$ ,  $\kappa_1 = 0$ ; 2—quadratic light intensity dependence of photogeneration, no memory effects:  $\eta_1 = 0$ ,  $\eta_2 > 0$ ,  $\kappa_1 = 0$ , the value of the lifetime does not influence the curve shape; 3—linear light intensity dependence of photogeneration but with a positive memory effect ( $\eta_2 = 0$ ,  $\kappa_1 > 0$ ) and with a carrier lifetime within the range of the delays scanned (carrier lifetime  $\tau = 500$  fs); 4—a negative memory effect ( $\kappa_1 = 0$ ) with a short lifetime ( $\tau = 500$  fs); 5—as above but with a very long lifetime ( $\kappa_1 < 0$ ,  $\tau = 3$  ns).

halves of the pulsed beam is an indication of the deviation from the reciprocity law.

Figure 2 shows calculated examples of autocorrelation curves which are obtained under various conditions involving nonlinearity and memory effects. These examples have been calculated for the case of the same linear polarization of the two incident beams. The polarization of the beams plays an important role. If both the beams have the same polarization, the sum of the fields taken at delays within the pulse duration will contain terms describing interference fringes varying in space as  $\sin((k_1 - k_2)r)$ . In the presence of the nonlinear effects it will lead to enhanced or reduced (depending on the sign of  $\eta_2$  and  $\kappa_2$ ) efficiency of generation of charge carriers in fringe regions. One should note, however, that the autocorrelation signal will also be present if the beams are of perpendicular polarizations and do not produce interference fringes. The difference will be in the relative magnitude of the autocorrelation photocurrent. As an example, for a quadratic photogeneration rate and no memory effects one can show that the ratio of the peak autocorrelation signal (the integrated photocurrent at the zero time delay between the pulse and its replica) to the out-of-correlation photocurrent background should be 3 for the case of interfering beams (curve 2 in figure 2) and 2 for no interference.

If the nonlinearity of the photogeneration process dominates in equation (1) and there are no memory effects ( $\kappa_1 = 0$ ) then one can expect that the shape of the autocorrelation signal will depend only on the temporal shape of the laser pulse. This is demonstrated

by curve 2 in figure 2. However, the influence of charge carriers on the photogeneration process (memory effects) may be also present for delay times longer than the pulse duration. This is reflected in the ‘wings’ of the autocorrelation signal which are characterized by the lifetime of charge carriers  $\tau$ . Curve 3 in figure 2 shows an example of such a situation. The sign of the signal (i.e. whether it appears as a dip or a hump in the background photocurrent) depends on the sign of the nonlinear and memory terms in equation (1). Curves 4 and 5 are examples of cases when a negative memory effect is present. The ‘wings’ in the autocorrelation signal are only visible when the lifetime of carriers is short enough to detect the changes of the photocurrent within the delay range scanned in an experiment. For very long carrier lifetime the wings are no longer visible although the nonlinearity of the photogeneration can still provide the autocorrelation signal.

The above model is oversimplified but should be an illustration of the general features expected for experimental photocurrent autocorrelation. In fact, the same set of equations can be used to describe an experiment in which autocorrelation is detected e.g. by observation of fluorescence from excited states generated by nonlinear absorption [6]. Such experiments may also be useful for short pulse diagnostics. The photocurrent autocorrelation setup offers, however, the simplicity of the nonlinear photocell providing an electrical signal without the necessity of using additional detectors as in the case of two-photon induced fluorescence.

We show in this paper that a two-photon absorbing  $\pi$ -conjugated polymer such as poly(*p*-phenylenevinylene) (abbreviated PPV) can be conveniently used to observe autocorrelation of femtosecond laser pulses in the vicinity of 800 nm. In a separate communication [6] we have already shown that PPV films are useful for short-laser-pulse diagnostics by third-order autocorrelation, by frequency resolved optical gating (FROG) and by two-photon induced fluorescence autocorrelation. Here, we use another property of PPV, namely its photoconductivity, to measure the pulse duration of femtosecond pulses from a mode locked laser. The photocurrent autocorrelation is not, strictly speaking, a true autocorrelation, since the signal may be related not only to the laser pulse properties but also to the properties of the photoconductive medium. We verify, therefore, whether the the shape of the photocurrent autocorrelation signal from PPV contains indication of ‘memory’ effects.

A major part of the recent research on properties of PPV relates to its ability to act as a light emitting agent in electroluminescent devices. However, it is also known that PPV is a good photoconductor [7–11]. To demonstrate photocurrent autocorrelation in PPV we have used PPV thin-film cells prepared by us for electroluminescence studies. The cells were prepared by spin-coating a PPV sulphonium precursor (LARK Enterprises) onto ITO covered glass slides. The precursor was then converted to the  $\pi$ -conjugated PPV film by heating (a 5 h ramp from room temperature to 210 °C and 5 h at that temperature) under vacuum. The converted material showed an

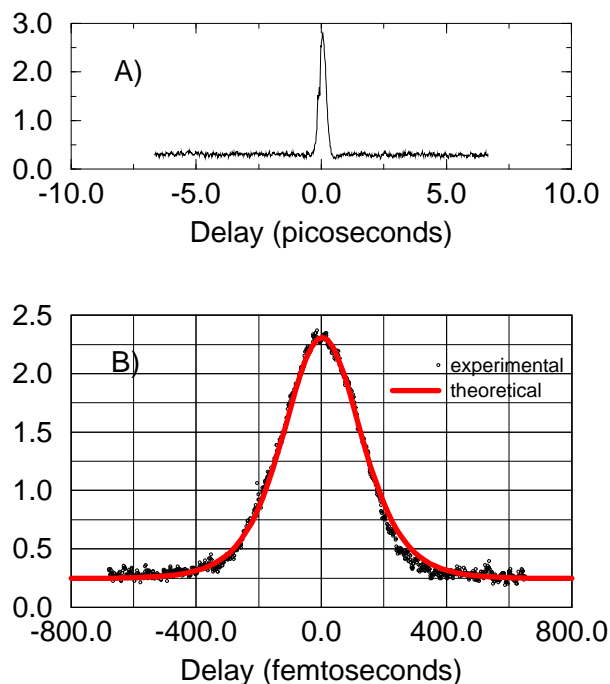
absorption maximum at 428 nm with the absorption coefficient  $\alpha_{max} = 1.3 \times 10^5 \text{ cm}^{-1}$ . The cells were completed by deposition of an yttrium electrode (of about  $10 \text{ mm}^2$ ) onto PPV. Electron beam evaporation was used with the vacuum of  $1 \times 10^{-7}$  Torr and the substrate heated to  $220^\circ\text{C}$ . We found that yttrium is a sufficiently strong electron injecting contact to cause electroluminescence in the ITO–PPV–yttrium structure when forward biased.

For autocorrelation measurement we used reverse bias of the cell (9 volts applied to a 150 nm thick film, ITO contact made negative). The laser system used was a Ti–sapphire Coherent Mira laser pumped with a Coherent Innova Ar ion laser and delivering an 86 MHz mode locked train of approximately 150 fs pulses at 800 nm. The beam was split in two using a 50/50 beam splitter and the two beams were geometrically overlapped on the PPV cell. About 200 mW total power was used and the beams were weakly focused which resulted in a spot size of about  $0.01 \text{ mm}^2$  and a peak light intensity of the order of  $10^8 \text{ W cm}^{-2}$ . Both beams were chopped at 22 Hz and 18.3 Hz, respectively, and the lock-in detection of the photocurrent was performed at the sum of these frequencies. The input resistance of the lock-in was  $1 \text{ M}\Omega$ .

Figure 3 shows an example of the autocorrelation signal obtained by scanning the delay between the pulse and its replica. The absence of signal ‘wings’ indicates that no significant ‘memory’ processes on the picosecond time scale are present. One can conclude that the autocorrelation signal is due to the nonlinearity of the primary photogeneration process. This is to be expected since PPV is a strong two-photon absorber at 800 nm with the two-photon absorption coefficient in the range  $10\text{--}100 \text{ cm GW}^{-1}$  [9]. It is also likely that any memory processes that may contribute to the photogeneration such as for example excited state absorption are characterized by relatively long time constants and therefore do not appear as wings in the autocorrelation scans. The best-fit line shown in figure 3 has been obtained for the simplest case of purely two-photon photogeneration of charge carriers and no memory effects.

We have investigated the light intensity dependences of the photocurrent in PPV cells under the conditions of illumination with a mode locked train at 800 nm from a Ti–sapphire laser. While the intensity dependences of the photocurrent were found to be superlinear, they were always less than quadratic (typically the steady-state photocurrent being proportional to the light intensity in the power 1.5). This suggests that the photoconductivity process may be influenced to a certain degree by e.g. bimolecular recombination of charge carriers. The presence of such a process necessitates modifications to equation (1), i.e. introduction of a bimolecular recombination term.

The model presented in equation (1) may need further modifications. One cannot exclude the possibility that the autocorrelation signal can depend on factors such as the presence of thermal and phototrapping of charge carriers and photoinjection from the electrodes. More detailed studies may be needed to establish the influence of such factors on the signal-to-background ratio of the photocurrent autocorrelation and their importance for



**Figure 3.** The photocurrent autocorrelation signal in a photoconductive PPV cell. The signal was obtained with the use of a chopper modulating both laser beams at two different frequencies. Detection was carried out with a lock-in amplifier at the sum of both modulation frequencies. (A) A wide-range scan showing the absence of signal ‘wings’; (B) a narrower-range scan with a superimposed theoretical autocorrelation curve for a 170 fs  $\text{sech}^2$  laser pulse.

application of the effect for practical laser pulse shape diagnostics. One may note, however, that, as comes from numerical simulations, the halfwidth of the autocorrelation curve (taken as the halfwidth of the autocorrelation signal versus the out-of-correlation background) does not depend on the presence of a background linear photogeneration term (the first term on the RHS of equation (1)) competing with the quadratic photocurrent intensity dependent term (the second term) in equation (1). On the other hand, the presence of photogeneration processes dependent on other powers of light intensity (e.g. cubic) does modify the shape of the autocorrelation curve.

In summary, we have shown that photocurrent autocorrelation in a thin film of a two-photon photoconducting polymer can be used for measuring short-laser-pulse properties. The spectral range of applicability of PPV is probably limited to the strong two-photon absorption region i.e. approximately 500–900 nm. Other photoconducting conjugated polymers may be considered for longer-wavelength operation. We also conclude that, in the case of PPV, there are no detectable wings in the autocorrelation signal on the picosecond time scale. This can be taken to indicate the absence of short-lifetime intermediates in the photogeneration process. Picosecond time scale decay of induced complex susceptibility change was observed in PPV by various techniques, e.g. the time resolved degenerate four-wave mixing [13] gives decay times between 10 and 100 picoseconds,

but the process becomes important only at very high light intensities (higher than approximately  $10 \text{ GW cm}^{-2}$ ) attainable with amplified laser systems. It has been postulated [10] that the photogeneration in PPV involves intermediates having the lifetimes in the 1–10 nanosecond range. Such intermediates would not be seen on the time scale of the present experiment.

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