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Direct observation of the ultrafast electron transfer process in a polymer/fullerene blend

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Published in:

Technical Digest Quantum Electronics and Laser Science Conference, 2000. (QELS 2000)

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2000

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Cerullo, G., Lanzani, G., Silvestri, S. D., Brabec, C. J., Zerza, G., Sariciftci, N. S., & Hummelen, J. C. (2000). Direct observation of the ultrafast electron transfer process in a polymer/fullerene blend. In *Technical Digest Quantum Electronics and Laser Science Conference, 2000. (QELS 2000)* (pp. 245-246). University of Groningen, Stratingh Institute for Chemistry.

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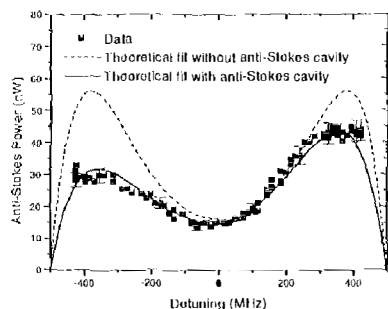
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QFAG Fig. 3. Anti-Stokes emission as a function of detuning from the Raman line-center. The solid (dashed) line shows the predictions with (without) Eqn. 2 included.

Figure 3 shows the anti-Stokes emission as a function of detuning from the Raman resonance line-center for a constant pump power of 3.2 mW ($4 \times$ threshold for detuning = 0). The data is in good agreement with the theoretical predictions of Eqn. 1 when the interferometric effects of Eqn. 2 are included (solid line). Note that the anti-Stokes emission can actually increase with detuning from the Raman resonance since this also raises the laser threshold, thereby allowing more pump to contribute to the four-wave process. We have therefore introduced a theory that accurately describes the behavior of coherent anti-Stokes emission from a cw Raman laser.

This work is supported by NSF under grant #9731602.

*Montana State Univ., U.S.A.

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QFB

8:00 am–9:45 am
Room 270–276

Ultrafast Electronic Dynamics of Molecules

Shaul Makamel, *Univ. of Rochester, USA*,
President

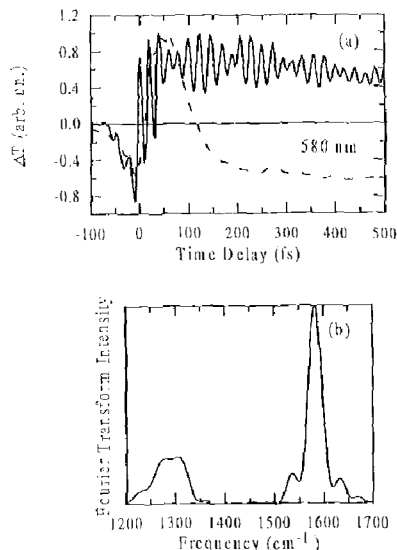
QFB1

8:00 am

Direct observation of the ultrafast electron transfer process in a polymer/fullerene blend

G. Cerullo, G. Lanzani, S. De Silvestri, Ch.F. Bräbe, G. Zerza,* N.S. Saricifci,† J.C. Hummelen,** *Istituto Nazionale per la Fisica della Materia, Milan, Italy*; E-mail: giulio.cerullo@polimi.it

Photoinduced electron transfer in organic molecules is an extensively investigated topic



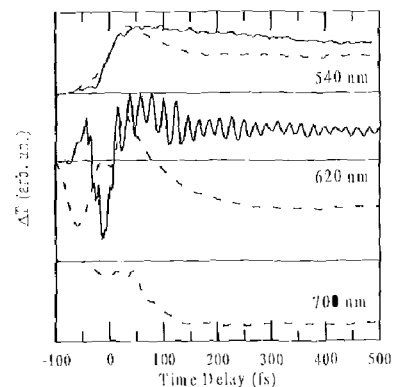
QFB1 Fig. 1. (a) Differential transmission dynamics for pure MDMO-PPV (solid line) and PPV/ C_{60} (dashed line) at the probe wavelength of 580 nm; (b) Fourier transform of oscillatory component of the MDMO-PPV signal.

both because of fundamental interest in the photophysics and for applications to artificial photosynthesis. Highly efficient ultrafast electron transfer from photoexcited conjugated polymers to C_{60} has been reported,¹ the back transfer is heavily hindered, thus providing an intrinsic stabilization mechanism of the photogenerated charges. Although an upper limit for the forward electron transfer time of 1 ps has been reported,² its detailed time resolution is still missing and is highly needed to shed light on the photophysics of the charge transfer mechanism.

In this work we perform ultrafast experiments on conjugated polymer/ C_{60} blends with sub-10-fs time resolution. We are able to time resolve for the first time the charge transfer process, obtaining a forward electron transfer time constant $\tau_{ct} = 45$ fs.

The excitation source is a visible optical parametric amplifier^{3,4} providing ultrabroadband pulses with sub-10-fs duration and spectrum extending from 520 to 720 nm. Pump-probe measurements are performed in a noncollinear configuration and single probe wavelengths are selected using interference filters after the sample. We excite thin films of poly [2-methoxy, 5-(3',7'-dimethyl-octyloxy)]-p-phenylene vinylene (MDMO-PPV) blended with C_{60} , with a 1:1 ratio in molecular concentration; at these high C_{60} concentrations diffusion doesn't influence the dynamics and we measure the intrinsic charge transfer process. We also study, for comparison, pure films of MDMO-PPV.

Fig. 1(a) shows as solid line the differential transmission (ΔT) signal for pure MDMO-PPV at the probe wavelength of 580 nm. The features at negative and near-zero delays at this and other wavelengths are due to coherent artifacts. The ΔT signal has positive sign and, because of negligible ground state absorption at this wavelength, is assigned to stimulated



QFB1 Fig. 2. Differential transmission dynamics for pure MDMO-PPV (solid line) and PPV- C_{60} (dashed line) at different probe wavelengths.

emission from the excited state. The strong oscillations superimposed on the signal are due to the motion of the vibrational wavepacket launched by the pump pulse on the excited state potential energy surface and thus probe the vibrational modes coupled to the excited state. A Fourier transform of the oscillatory component of the signal is shown in Fig. 1(b). By adding C_{60} to the polymer matrix, the signal changes dramatically (dashed line in Fig. 1(a)). The initially positive ΔT changes rapidly sign, indicating the quick formation of a new photoinduced absorption (PA), which remains then stationary on the timescale of the experiment. Based on cw PA measurements, this new absorption is assigned to the MDMO-PPV charged state (polaron) and thus provides a direct signature for the charge transfer process. By an exponential fitting of the PA rise-time, a time constant for the electron transfer process of $\tau = 45$ fs is calculated. Similar results are obtained at other probe wavelengths, as shown in Fig. 2.

Excited state vibrational coherence is not maintained in the charge transfer process, thus indicating evolution of the system on an anharmonic charge transfer potential energy surface, formed immediately after photoexcitation.⁵ Such a fast charge transfer can only be explained by a strong ($\Delta E = \hbar\tau = 90$ meV) exchange integral of the excited state orbitals of donor and acceptor molecules and requires detailed theoretical analysis to clarify its physical mechanism.

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QFB2

8:15 am

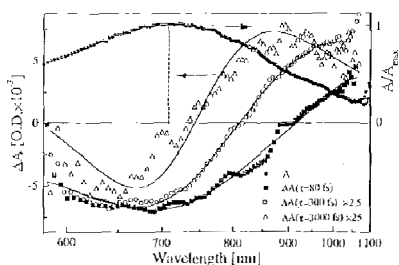
Relaxation dynamics of the hydrated electron studied with 5-fs pulses

A. Baltuška, M.S. Pshenichnikov, D.A. Wiersma, *University of Groningen, The Netherlands*; E-mail: A.Baltuska@chem.rug.nl

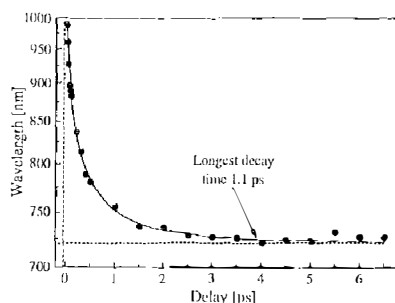
Since its discovery in the early sixties,¹ the hydrated electron has received a continued interest from chemists and physicists alike. Basically, the hydrated electron is an excess electron trapped in a potential well formed by surrounding water molecules, with an *s*-like ground state and three non-degenerate *p*-type excited states.² The electron surrounded by the oriented water molecules is a chemical reactant with an unusually high electron donor capacity as its characteristic chemical feature. On the other hand, it seems to be one of the simplest physical systems to study solvation dynamics and to test mixed quantum-classical theories experimentally. Yet, even after decades of intensive experimentation and calculations on the hydrated electron, understanding of its relaxation dynamics is far from being complete. One of the most important questions is the explanation of an ~ 1 -ps relaxation rate of the photo-excited hydrated electron. This rate has been controversially attributed to the population lifetime of the *p*-state³ or cooling of the ground state after rapid relaxation from the *p*-state.⁴

In this Contribution we present the experimental study of the energy relaxation of the photo-excited hydrated electron. The results of frequency-resolved pump-probe with 5-fs pulses provide sufficient evidence in favor of the hot-ground-state model, outlined above. The initial ultrafast energy relaxation of the photo-excited electron, controlled by the librations of the surrounding water molecules,⁵ takes place during the ~ 50 fs upon the excitation. We show that after the first 100 fs almost the entire population of the *p*-state is transferred to the hot ground state that subsequently cools down on a ps time scale.

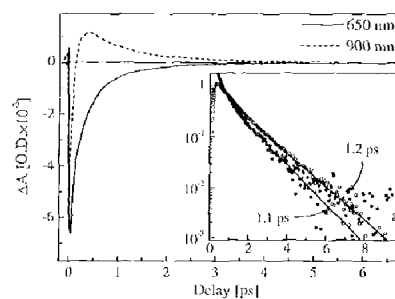
The evolution of the transient absorption spectrum at different pump-probe delays is depicted in Fig. 1. A substantial positive contribution that corresponds to the induced absorption appears at early times. However, this fact alone does not favor any model since the induced absorption may be caused by transitions from the excited *p*-state to continuum. We propose the following method to distinguish the models: One follows the evolution of the wavelength for which $\Delta A = 0$ (zero-crossing point) as a function time (Fig. 2). The longest decay time of this dependence is compared to the longest decays of frequency-resolved transients (Fig. 3). If the former is shorter than the later, then the solvation in the excited state is followed by the population re-



QFB2 Fig. 1. Transient spectra of the hydrated electron obtained at 80 fs (squares), 300 fs (open circles), and 3 ps (open triangles). Solid circles show the absorption spectrum of the equilibrated hydrated electron. Solid curves represent best fits to experimental data, which consists of the ground-state bleach and hot-ground state absorption contributions.



QFB2 Fig. 2. Zero-crossing point as a function of probe and pump delay. Note that its asymptotic value approaches the position of the absorption maximum of fully equilibrated electron (indicated by the dashed horizontal line).



QFB2 Fig. 3. Pump-probe transients at the detection wavelength of 650 nm and 900 nm.

laxation. However, if the two processes have identical decays, we should conclude that the population relaxation is much faster than solvation that takes place in the nonequilibrated ground state.

Our experimental data indicate that the shift of the zero-crossing point in the ΔA signal occurs precisely at the same time scale as detected in the frequency-resolved transients. This corresponds to the movement of the wavepacket down the ground state potential surface with the time of ~ 1 ps. The continuous spectral shift rules out the possibility of a long-lived excited state. Also, the position of zero-crossing in ΔA spectra asymptotically approaches the position of steady-state absorption maximum (Fig. 2). This is a direct prediction of the hot-ground-state model while

in the case of long population lifetime it would be a pure coincidence.

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QFB3

8:30 am

Competition of different ionisation pathways in K_2 investigated by fs pump&probe spectroscopy: experiment and theory

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During the last decade both, experimentalists and theoreticians, began extensively to investigate ultrafast phenomena as wave packet propagation, coherent control, internal vibrational redistribution, structural relaxation and photodissociation in physical, chemical and biological systems. In particular, the wave packet propagation of small molecules as the potassium dimer are studied in great detail.^{1,2} Recent studies of this molecule focused on the ionisation step in ultrafast pump&probe experiments, applying fs-multiphoton ionisation spectroscopy. In these schemes the pump pulse prepares a wave packet in both the $A^1\Sigma_u^+$ and $(2)^1\Pi_g$ state at the inner turning point by means of a one or two-photon process. The delayed probe pulse can transfer the wave packet to an ion state by another two or one-photon process. The generated ions are detected mass-selectively.

We will show, that it is possible to control the transition of the wave packet by changing the applied wavelength of the probe pulse. Two features appear in this context: First the transition pathway can be shifted within the same potential energy surface or, second, in such a way that the ionisation proceeds via different electronic surfaces.

In our investigations on the potassium dimer we used fs-pump&probe spectroscopy in the spectral range of 837 nm and 779 nm. A variety of structures observed (see Fig. 1) reflects the complicated interplay of nuclear dynamics and ionisation processes we will discuss in our report. For the wavelength of 837 nm we find a clear oscillatory structure with a period of ~ 500 fs. The maximum occurs after half a period as was shown in previous experiments at this wavelength.² This indicates an ionisation at the outer turning point. Decreasing the laser wavelength below 816 nm, we find that the peaks of increased ionisation begin to split to form a double peak structure with a slight difference in peak height. This trend is continuous and eventually leads to a frequency