Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Martin Pope, Charles E. Swenberg & Alexandre Dourandin (2001): CT Exciton Echoes in Organic Molecular Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 355:1, 77-84

To link to this article: http://dx.doi.org/10.1080/10587250108023655

Mol. Cryst. Liq. Cryst., Vol. 355, pp. 77-84
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CT Exciton Echoes in Organic Molecular Crystals*

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(Received July 01, 1999; In final form January 31, 2000)

The possibility of observing a CT exciton echo in organic molecular crystals and polymers is explored theoretically. Reference is made to the appearance in the literature of two possible examples of this phenomenon.

Keywords: CT excitons; exciton echo; photoemission; geminate recombination; delayed recombination

As a result of the optical (or more energetic) excitation of an organic molecular crystal (OMC) or polymer, a number of mobile electronically excited states are produced that can interact with each other or with the excitation source to cause a photoionization process that may be detected as an increase in external photoemission and/or photoconductivity. In either case, carrier pairs are produced internally that generally recombine geminately. This process can be rapid (≅ ps) or it can take longer, especially if, in the course of recombining, one of the mobile carriers is caught in a trap. In a steady state experiment, such fine details are invisible, but when a pulsed, periodic excitation source is used, it becomes possible to detect the existence and lifetime of such transitory states. The electron-hole pair that is destined to recombine will be referred to herein as a charge-transfer (CT) state or exciton. In other systems, such as in polymers such as polyacetylene, it may be referred to as a polaron-pair.

* We Dedicate this Paper to the Memory of Our Dear Friend, Colleague, and Teacher, Prof. Edgar Silinsh, Whose Scientific Insights and Contributions Lighted the Way for Us, and Whose Integrity and Humanity Served as a Model for his Many Students and Peers All over the World.

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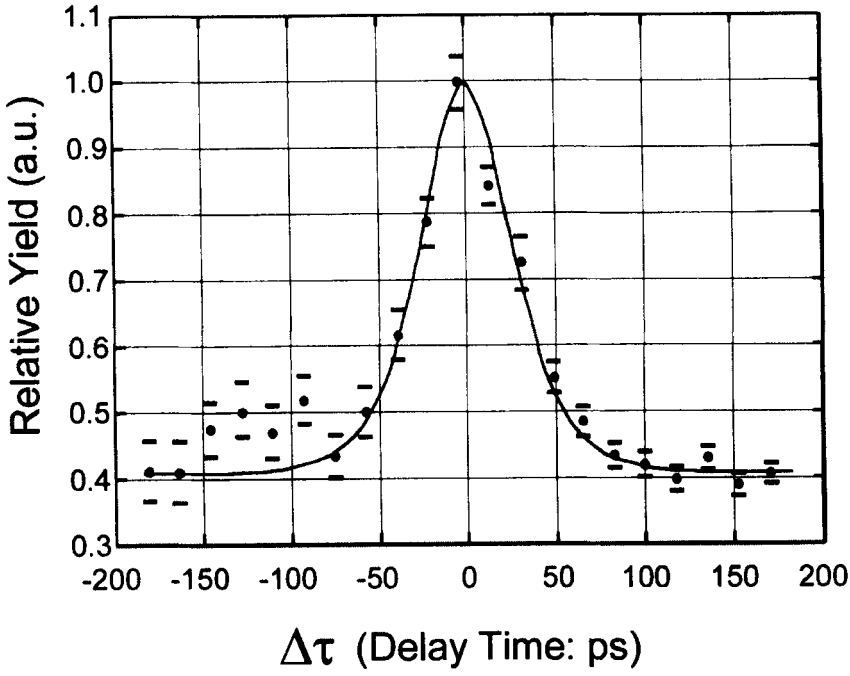

FIGURE 1 Time-resolved photoemission yield from tetracene single crystal as a function of the delay time $\Delta\tau$ between the prompt and delayed light pulse. The prompt and delayed light pulses are interchangeable. Excitation is by the 355nm harmonic of the Nd-Yag laser, the pulse width of which is 20ps fwhm. The solid curve is calculated without the inclusion of the echo hypothesis, from Dourandin et al. [1]

Assume for the moment that a CT exciton has been created in the course of a photoionization process, but that this CT exciton is impacted by one of the other mobile excited states (a Frenkel or singlet exciton as an example) during its lifetime. In that case, the CT exciton will be dissociated to create a more widely separated hole-electron pair, which can either return rapidly, as indicated previously, or it can be delayed. The primary CT exciton will be referred to as a prompt CT (CT_p) exciton and the secondary CT exciton will be referred to as a delayed (CT_d) exciton, or in more picturesque terms, as an exciton echo.

There are two cases in the literature that may be examples of the creation of an exciton echo, although this effect was neither sought for nor identified positively as such. The first (Fig. 1.) describes a photoemission experiment (DLPSG)[1] and the second (Fig. 2) is a photoconductivity experiment (RKR) [2]. The photoemission experiment will be taken as the major example, and the numerical values

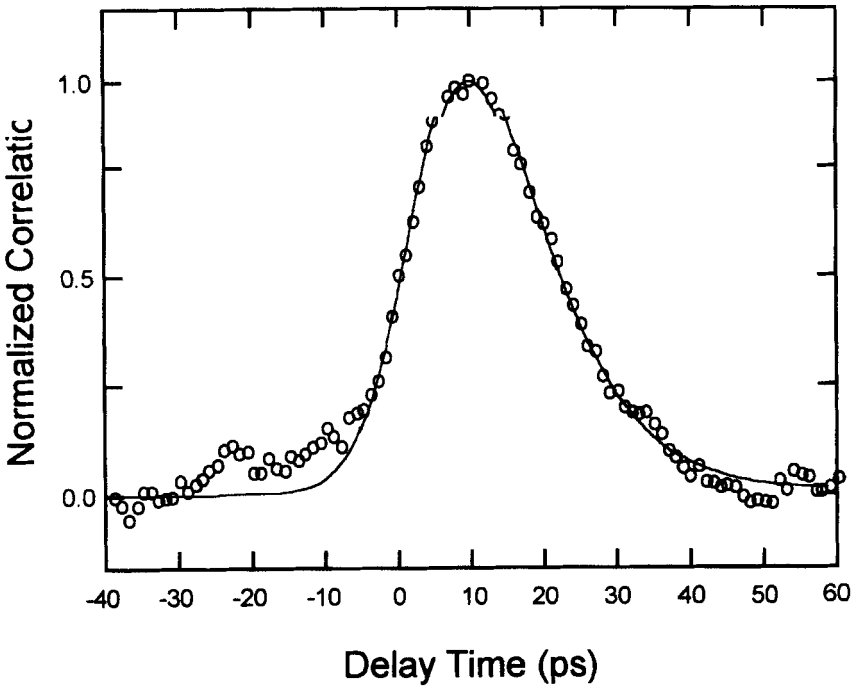

FIGURE 2 A normalized cross-correlation signal observed from a stretched *trans*- $(CH)_x$ sample pulse generator and an ion-implanted Si film gate. The solid line represents the calculated pulse profile assuming exponentially decaying photoconductivities where the RC response of the device and the finite light pulses have been taken into account. See text for details, from Reichenbach et al. [2]

will be chosen to be consistent with the observations made in that experiment. Photoemission from a tetracene crystal was studied by (DLPSG), using the Millikan-Pope-Arnold chamber technique (Altwegg et al.) [3]. Here, a tiny crystal (typically about 50μ in diameter) was suspended electrostatically, and photoionized. The relevant data provided by (DLPSG). are as follows: singlet energy, $E_S = 2.3$eV; CT exciton energy $E_{CT}= 2.9$eV; band gap $E_g = 3.5$eV; ionization energy of the crystal $I_C= 5.3$ eV. The maximum kinetic energy of the emitted electrons was 1.1 eV, and the light intensity dependence of the photoemission was 2.3. These values place a constraint on the possible mechanisms that can be proposed as being plausible. The mechanism used in the (DLPSG) paper will be adhered to without additional justification.

The data and physical constants to be provided are taken in part from the work of (DLPSG). The crystal is tetracene, the light source is a ps laser, operating at a frequency of 20pps. The low repetition rate insures that all excited states have

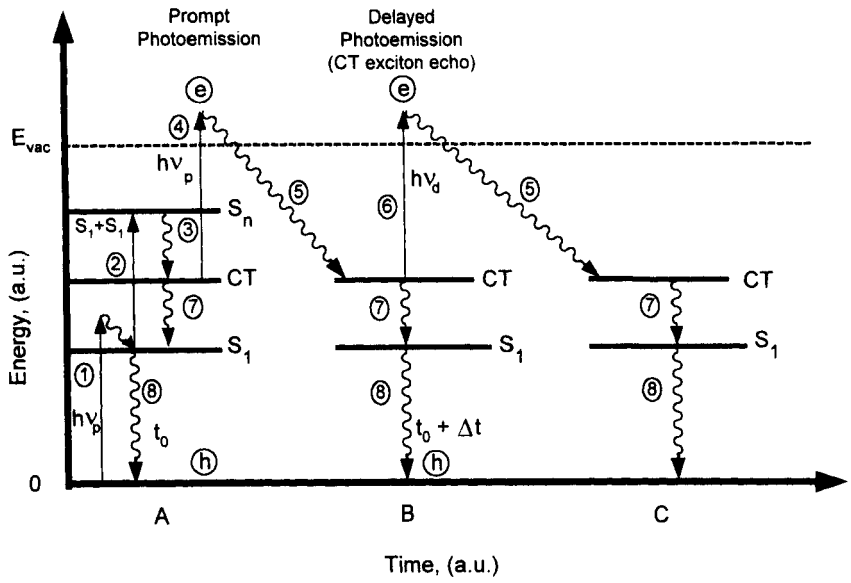

FIGURE 3 Depiction of events described in Eqs. 1–8 (not to scale). (A) represents Eqs. 1–4 in the kinetic scheme. These processes take place within the lifetime of the prompt pulse $h\nu_p$. Eqs. 5–8 are illustrated in (B), and the time delay in the pulse $h\nu_d$ is indicated by Δt_0. (C) represents a possible process that is not considered further

decayed to the ground state before the next pulse arrives. The wavelength used is the 355nm harmonic (photon energy 3.5eV) of a Nd-YAG laser. The kinetic scheme to be described is only one of several that can, in principle, produce an exciton echo. In the (DLPSG) paper, the sequence of events postulated was as follows, and is also depicted in Fig. 3:

1. $h\nu + S_0 \Rightarrow S_1$; excitation of a Frenkel singlet state. Absorption coefficient k.
2. $S_1 + S_1 = S^*$; singlet-singlet fusion producing a superexcited state. Rate constant γ_{SS}.
3. $S^* \Rightarrow CT_p$; decay of S^* into a prompt CT state, CT_p Efficiency η.
4. $h\nu + CT_p \Rightarrow e^* + e\text{-}h$; prompt CT is photoionized producing an emitted electron, and is also dissociated into a geminate hole-electron pair. Efficiency σ.
5. $e\text{-}h \Rightarrow CT_d$; geminate pair recombines after a delay to form the delayed CT_d;
6. $h\nu + CT_d \Rightarrow e^*$; delayed CT is photoionized to produce the CT exciton echo. Efficiency σ.
7. $CT_{p,d} \Rightarrow S_1$; CT decays into the singlet manifold. Rate constant k_{CT}.
8. $S_1 \Rightarrow S_0$; singlet state decays to the ground state. Rate constant k_S.

9. $G(t, \Delta\tau) = kI_0 [\exp(-\frac{1}{2}/ (t/ 7.1)^2) + \exp(-\frac{1}{2}/ ((t - \Delta\tau)/ 7.1)^2)]$; the description of the prompt light pulse and its delayed component when the singlet state is excited. The standard deviation of the half-width of the light pulse is 7.1ps. I_0 is the pulse light intensity. All times are measured in ps and all distances are measured in Angstroms Å.

10. $G'(t, \Delta\tau) = \sigma I_0 [\exp(-\frac{1}{2}/ (t/ 7.1)^2) + \exp(-\frac{1}{2}/ ((t - \Delta\tau)/ 7.1)^2)]$; the description of the prompt light pulse and its delayed component when the CT states are photoionized with an efficiency σ.

The kinetic scheme is as follows:

11. $d[S_1]/dt = G(t, \Delta\tau) - k_S[S_1] - \gamma_{SS}[S_1]^2$

12. $d[CT_p]/dt = \eta\, \gamma_{SS}[S_1]^2 - k_{CT}[CT_p] - \gamma_{SCT}[CT_p][S_1] - G'(t, \Delta\tau)[CT_p]$

13. $d[CT_d]/dt = \gamma_{SCT}[CT_p][S_1] - G'(t, \Delta\tau)[CT_d]$

The various constants used in these processes are:

k = absorption coefficient of tetracene at 355nm $\cong 10^3\ cm^{-1} = 10^{-5}\ Å^{-1}$

k_S = singlet exciton decay rate in tetracene at room temperature = $5\times10^9\ s^{-1} = 5\times10^{-3}\ ps^{-1}$

k_{CT} = decay rate of the nearest neighbor CT exciton $\cong 5\times10^{10}\ s^{-1} = 5\times10^{-2}\ ps^{-1}$

γ_{SS} = singlet-singlet fusion rate constant = $10^{-7} cm^3\ s^{-1} = 10^5\ Å^3\ ps^{-1}$

γ_{SCT} = singlet-CT fusion rate constant = $10^{-7} cm^3\ s^{-1} = 10^5\ Å^3\ ps^{-1}$

η = efficiency of forming a CT state from S^* = 0.01 – 1 at 4.6eV

σ = cross-section for photoemission by the photoionization of a CT exciton $\cong 10^{-18}\ cm^2. = 10^{-2} Å^2$

$I_0 = 10^{27}\ cm^{-2}\ s^{-1}$; light intensity per pulse = $10^{-1}\ Å^{-2}\ ps^{-1}$

Pulse full width at half-height $\cong$ 20ps.

These equations were solved numerically, assuming a Gaussian selection of delay times between the creation of the main pulse by the photoionization of the prompt CT_p, and the photoionization of the delayed CT_d, which shows up as an echo. The Gaussian distribution was peaked at 85ps, with a standard deviation of 5ps. A time delay of 85ps in recombination can be encountered by carrier trapping by a 0.17eV deep trap, ignoring for the moment any other source of delay such as unfavorable Franck-Condon factors for the final fusion of the electron and hole. Twenty separate numerical calculations involving a different choice for a delay time were averaged in order to obtain the smooth curve shown in Fig. 4. The agreement between the calculated curve and the experimental data shown on the left side of Fig. 1 is good.

The absence of a distinct peak on the right side of Fig. 1 can be rationalized. If the intensity of light in the prompt and delayed pulses are not equal, then there will be an asymmetry in the experimental data. To demonstrate this behavior, a

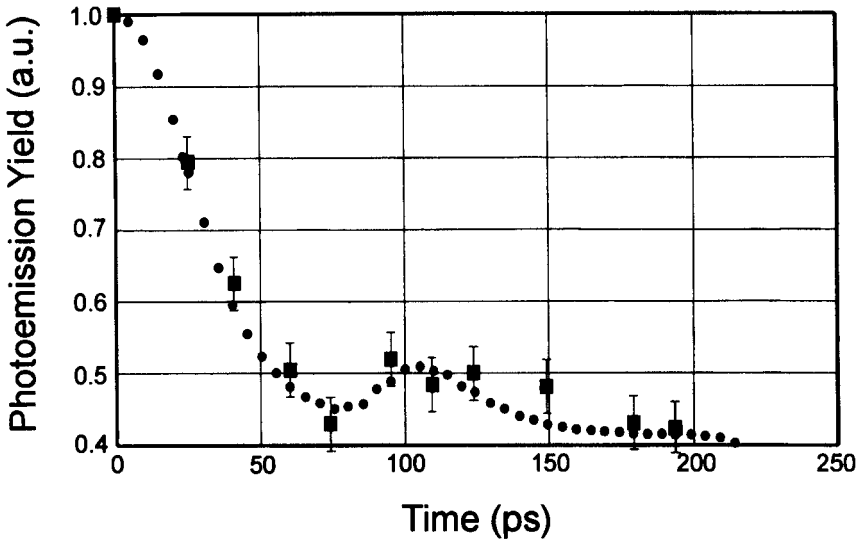

FIGURE 4 The dotted curve is the solution of Eqs. 11–13, and the points are the experimental data from the left side of Fig. 1. The calculated curve is based on the assumption of a CT exciton echo that appears 85ps after the main peak. See text for details

simulation was carried out in which the light intensities of the prompt and delayed pulses on the target were made to differ by a factor of two, and the result is shown in Fig. 5. This factor of two can easily occur if the overlap of the prompt and delayed pulses are not exact.

The other possible example of the observation of an echo is shown in Fig. 2. In this experiment, the lifetime of the fast component of the photoconductive response of an oriented Durham polyacetylene (trans-$(CH)_x$) film to a 1 ps laser pulse is shown. A cross-correlation technique was used to obtain the curve shown in Fig. 2. In this method, one photoconductor (trans-$(CH)_x$) is used as a pulse generator, and the second photoconductor (a heavy ion bombarded Si polycrystalline film) is used as a sampling gate. The lifetime of the Si gate was 2.5 ps. The sampling gate is activated at various delay times in a typical prompt pulse-delayed probe strategy. The conductivity of the gate depends on the total amount of charge placed on the gate as a function of the relative delay between the two light pulses. The full curve is developed by a suitable manipulation of the measuring electronics. The appearance of the delayed peak at ~ 32ps could be due to the detrapping of a shallowly trapped polaron created by the dissociation of the polaron-pair created by the prompt pulse.

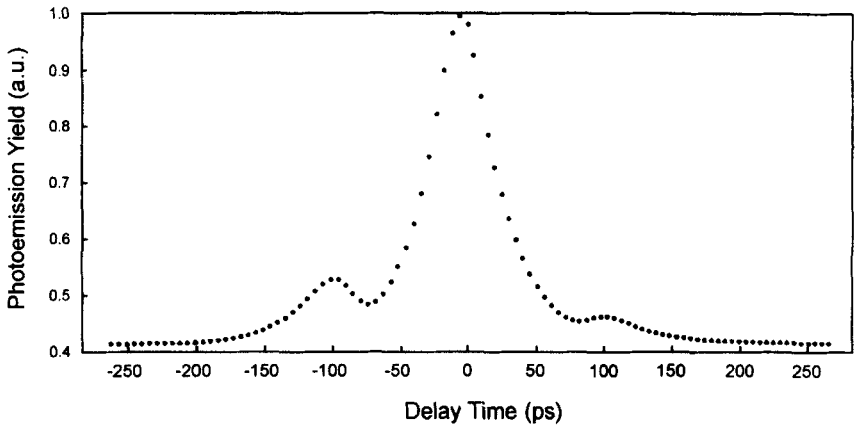

FIGURE 5 Simulated photoemission yield as a function of the delay time between the prompt and delayed light pulses when these pulses differ in intensity by a factor of two, demonstrating the existence of asymmetry when the prompt and delayed pulse differ in intensity on the target

In the (DLPSG) photoemission example cited, a specific average delay time of 85ps for the recombination of the geminate hole-electron pair was taken. In a more detailed analysis, the theory of carrier generation and recombination expounded by Hong and Noolandi [4] would be used to determine the time that would elapse during the process of carrier separation and recombination, as a function of the excess energy delivered to the ionization process. This analysis would provide a time estimate that is free of trapping. In addition, the use of a theory such as that deduced by Marcus [5] might provide an estimate of the rate constant for the fusion of the neighboring hole and electron. By fitting values to the parameters that appear in the Hong and Noolandi[4] development, one should be able to deduce the diffusion coefficient and mobility of the mobile carrier, as well as the microscopic details of the process of carrier separation, and recombination, including the final step of hole-electron annihilation.

In the example chosen a CT exciton was used as a target. In other systems, it could also be the interaction of a photon or exciton with a soliton or polaron, or of these quasi-particles with each other, following their creation by a light flash. The possibilities described herein are part of an ongoing study in our laboratory.

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