

Phase Transition to the Conducting State in a System of Charge-Transfer Excitons at a Donor-Acceptor Interface

© V.M. Agranovich, S.A. Kiselev, Z.G. Soos*, S.R. Forrest*

Institute of Spectroscopy of Russian Academy of Sciences,
142092 Troitsk, Moscow region, Russia

*The Princeton Materials Institute, Princeton University,
NJ 08544 Princeton, USA

E-mail: agran@isan.troitsk.ru

We discuss the phase transition to the conducting state in a system of 2D charge-transfer excitons (CTEs) at a donor-acceptor interface. The phase transition arises due to strong dipole-dipole repulsion between CTEs which stimulates the population of free carriers in higher energy states even at low temperature. We use the computer simulations with the random distribution of excitons, and finite lifetime is explicitly taken into account. The critical concentration of CTEs and their energy distribution are calculated. We also discuss the possibility of observing the predicted phenomena.

Two models are employed to classify excitons — the small radius Frenkel exciton model, and the large radius Wannier–Mott exciton model [1]. The charge-transfer exciton (CTE) occupies an intermediate place in the classification based on the exciton internal structure [2]. The lowest energy CTE usually extends over two nearest neighbor molecules. In a CTE, the electron is localized on the acceptor and the hole, on the donor. Such localization in organic crystals is usually stable because the energy of electron-hole attraction is large compared to the corresponding widths of the conduction and valence bands and due to the strong tendency of the CTE to undergo self-trapping [3]. Due to the separation of the electron and the hole in a CTE, the static dipole moment created by positive and negative ions can assume values as large as $10\text{--}25D$. This feature determines the most characteristic properties of the CTE. For example, the CTEs contribute to the large second order nonlinear polarizability χ^2 due to their large dipole moment [4]. As it was recently shown [5], the same feature can be responsible for a new type of photovoltaic effect in asymmetric $D\text{--}A$ superlattices [5a], for unusual intensity dependences of nonlinear polarizabilities of $D\text{--}A$ superlattices [5b], and also for phase transitions to conducting states in the system of CTEs [5c]. In all of these cases, it was assumed that CTEs at $D\text{--}A$ interfaces between alternating layers of donors and acceptors are the lowest energy electronic excited states. These states are usually populated after lattice relaxation from higher energy Frenkel-type electronic or vibronic states. In this work, we investigate the transition from a dielectric to a conducting state in a system of CTEs at a $D\text{--}A$ interface (see also [6]). The realistic possibility to consider such organic crystalline structures appeared recently due to the progress in the development of the organic molecular beam deposition and other related techniques [7]. This opens a wide range of possibilities for creating new types of ordered organic multilayer structures including ordered interfaces.

1. Phase Transition from Dielectric to Conducting State

Consider the CTEs on a single $D\text{--}A$ interface. We assume that they are aligned normal to the interface plane, resulting in mutual repulsion. For example, if the static CTE dipole moment is equal to $20D$ and the distance between them is 5 \AA (the lattice constant at the interface), the repulsion energy is near 1 eV. If the distance between CTEs increases to 10 \AA , the repulsion energy decreases to 0.1 eV. It is important that these energies are of the order of their separation B from the lowest conduction band ($B < 0.5\text{ eV}$, see [8]). Thus, at high CTE concentrations we can expect that repulsion energy populates the higher energy states with free carriers, thus producing photoconductivity even at very low temperature [5c]. In [5c] the photoconductivity was considered under the assumption that the time required for a phase transition to the conducting state is smaller than the CTE life time. Such a phase transition was obtained by minimizing the total energy of the CTEs and dissociated excitations (free carriers). Consider for simplicity a 2D array of self trapped CTEs at $T = 0$. The energy of CTEs (concentration n_1) and the energy of dissociated e–h pairs (concentration n_2), can be calculated by assuming that total number of excitations, determined by the optical pumping intensity, is constant: $n_1 + n_2 = n$. The energy of the CTE array is therefore $E_1 = n_1\Delta + E_{int}$, where E_{int} is the total repulsion energy. This energy can be estimated using the average distance between CTEs, ρ . In the case of dipoles p

$$V = \frac{Ap^2}{\rho^3}, \quad (1)$$

where A is a geometric constant depending on the CTE distribution in the interface plane. For example, for a square lattice $A \approx 10$. Since the CTE concentration by definition is $n_1 = 1/\rho^2$, the electrostatic energy of the interaction between the dipole moments is: $E_{int} = Vn_1/2 = Ap^2n_1^{5/2}/2$. We can approximate the energy of the dissociated pairs as $E_2 = (\Delta + B)n_2$, where the kinetic energy of the free carriers

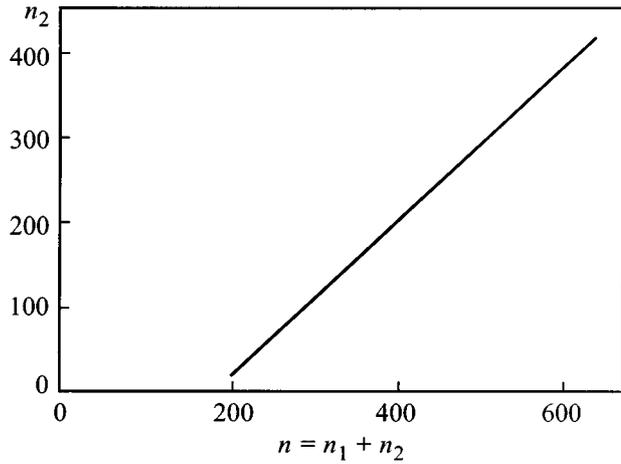


Figure 1. The number of the charge-transfer excitons (n_1) at the donor-acceptor interface and the number of the dissociated excitons (n_2) as the functions of the total number of excitations [according to the simplified analytical model, Ed. (4)].

has been neglected (due to the self-trapping and narrow electronic bands, see above). Near the threshold, where the concentration $n_2 \ll n_1$ and also $n_1 \ll 1$, we can neglect the interaction of the free carriers with the CTEs. The total energy of the system then can be written as

$$E = E_1(n_1) + E_2(n_2) = n\Delta + \frac{Ap^2(n - n_2)^{5/2}}{2} + Bn_2. \quad (2)$$

Minimizing the above expression with respect to n_2 gives

$$n_2 = n - \left(\frac{4B}{5Ap^2} \right)^{2/3}. \quad (3)$$

It is clear from Eq. 3 that n_2 is positive at $n > n_{cr} = [4B/(5Ap^2)]^{2/3}$ (see Fig. 1). The appearance of free carriers at $n > n_{cr}$ is considered to be a phase transition from the dielectric to conducting state. This transition corresponds to photoconductivity at low temperature (i. e., to cold photoconductivity) and is due to long range dipole-dipole interactions between CTEs. In this consideration, we neglected the randomness in the CTE distribution and did not consider the establishment of steady state in ensembles, which is dependent on the pump intensity and the CTE lifetime. These effects are explicitly taken into account in our computer simulations [6].

2. Model for Numerical Simulations and Results

The $D-A$ sites are arranged in a square lattice. The $D-A$ interface is uniformly irradiated with a time-independent source of intensity, I . Only one CTE can be generated at any site. As long as the CT exciton is generated it will stay at the lattice site and it cannot move to other $D-A$ sites because of self-trapping. There are two mechanisms for the

CTE to disappear. First, recombination occurs because of the finite lifetime of the CTE, τ . The second mechanism is dissociation. The CTE exciton dissociates when, due to the dipole-dipole interaction, the energy of the particular exciton exceeds some threshold. If there are n_1 CTEs occupying the $D-A$ interface, the electrostatic energy of the j^{th} exciton in the electric field of the other excitons surrounding this site is

$$V_i = \sum_{j=1}^{n_1} \frac{p^2}{r_{ij}^3}, \quad (j \neq i). \quad (4)$$

The i^{th} CT exciton dissociates when the repulsion energy, V_i , is larger than the energy B . The electrostatic potential energy of the exciton strongly increases when few CTEs occupy the nearest neighbor lattice sites. If this occurs, one or more CTEs will dissociate. Such a mechanism should result in correlations between exciton positions, and ordering of the system of non-mobile CT excitons can be expected. Such a spatial ordering suggests the existence of a critical pump light intensity above which there is an onset of photoconductivity. Thus, just above this threshold, we expect an onset of cold photoconductivity. In simulations, we neglect the process of recombination of free carriers which can result in the creation of CTEs. Near the threshold, where the concentration of free carriers is small, the contribution of this process to the number of CTEs will be small and can be neglected. However, even at higher concentration, the effect of free carrier recombination can be reduced by applying the electric field along the interface. This field will separate electrons and holes and thus will create the photocurrent which has to be measured. Computer simulations were performed for a two-dimensional square lattice containing 600×600 sites. Under continuous pumping of the sample with a constant intensity, the CTEs are generated in the process described above. In order to avoid the influence of boundary conditions, we simulate the evolution of only the central part of the lattice. This square, the central sublattice, consists of 200×200 $D-A$ sites, $N = 40,000$. Next, we replicate the central sublattice by adding 8 square sublattices surrounding the central one. That is, the exciton positions calculated for the central 200×200 sites square lattice is reflected via a mirror symmetry operation to the other surrounding 8 squares. To simulate the time evolution, we run the system through equally spaced time steps separated by the interval Δt . The value of $\Delta t = \tau/50$ is chosen to be much shorter than the CTE lifetime τ . We start the simulations when there are no CTEs at the interface. Under the influence of the pumping the excitons begin to appear. After the time $\approx \tau$, the number of CT excitons occupying the lattice reaches the steady state value. From this time on, the necessary statistical information is collected. The time evolution of the system is simulated as follows. At every time step a few CTEs (depending on the pumping intensity, I) are created at randomly chosen positions at the central sublattice. Then we go over the central sublattice sites and check every $D-A$ molecule. With some probability the exciton at this site can recombine, as explained above. It

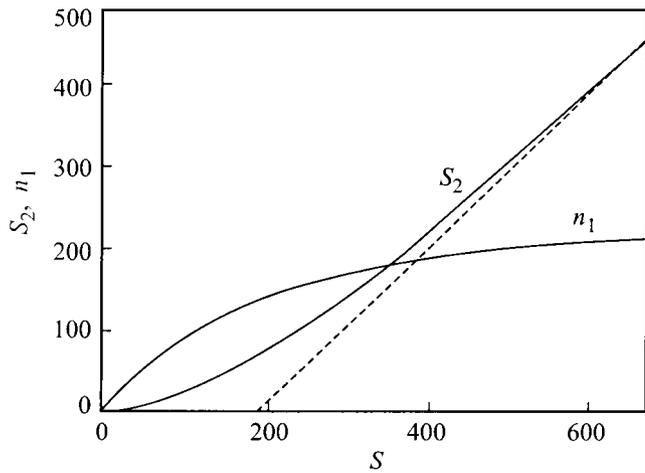


Figure 2. The steady state number of the charge-transfer excitons (n_1) occupying the donor-acceptor interface and the number of the dissociated pairs production (S_2) as the functions of the pump intensity.

also can dissociate if its electrostatic energy is high enough. The rules for these events to happen at one particular $D-A$ site are: 1. If the site is empty, the charge-transfer exciton can be created with the probability $P_c = I\Delta t/N$. 2. If a charge-transfer exciton already occupies this site, it can recombine with the probability $P_r = 1 - \exp(-\Delta t/\tau)$. Next, during the same time step, we calculate the energy of every CTE in the electrostatic field produced by the dipole moments of all other excitons. The energy of the i^{th} CT exciton can be found using the Eq. (4). If this energy is greater than the dissociation threshold, B , the CT exciton dissociates. Finally, we recalculate the energies of the CT excitons that remain at the $D-A$ interface.

All results reported below are collected after steady state is achieved. Fig. 2 shows the dependence of the number of CTEs (n_1) on the value S which is the product of generation intensity of the CTEs I and the CTE's lifetime τ : $S = I\tau$. The steady state number of dissociated pairs is determined by their own lifetime, but we do not estimate here the concentration of carriers and conductivity. Nevertheless, on the Fig. 2 we plotted the value S_2 which is equal to the number of dissociations which take place at given S in steady state during time τ . We find a qualitative agreement with the analytical theory in that the CTEs populate the $D-A$ interface only until some utmost concentration be achieved. Further increase of the pump S results mainly in the dissociation of CTEs into electron-hole pairs. When the number of the CTEs reaches the saturation density, the number of dissociations S_2 increases linearly with S . It is interesting to compare the critical concentration of CTEs derived from analytical model (see Section 2) with the results of computer simulations. Following qualitatively the results of analytical model (Fig. 1), we can take as a critical concentration of CTEs the concentration corresponding to saturation of CTEs at the interface or, what is nearly

the same, the concentration of CTEs which corresponds to intersection of linear S_2 asymptote with the n_1 curve. In Fig. 2, the value of n_1 is approximately 200 and thus the corresponding critical dimensionless concentration $C_{cr} = 200/40000 = 0.5\%$. The curve in Fig. 1 corresponds to the value $M = Ba^3/p^2 = 0.01$. It follows from the analytical theory that for the same M the critical concentration $C_{cr} = (4Ba^3/5Ap^2)^{2/3} = (4M/5A)^{2/3} = 0.85\%$. Thus, a random CTE distribution decreases the critical concentration for the transition to conducting state. This effect could be expected, because, for random distribution, in contrast to analytical model of ordered CTEs, the small distances between CTEs are allowed even at low CTEs concentration. In both approaches the critical concentration strongly depends on the values of B , p and a . For example, for $B = 0.2$ eV, $p = 20D$, and $a = 5 \text{ \AA}$, corresponding — to $M = 0.1$, the analytical model yields $C_{cr} = 4\%$, while the computer simulations $C_{cr} = 2.5\%$. For $M = 0.05$, $C_{cr} = 2.6\%$ (analytical approach) or 1.5% (computer simulations), and so on. Thus, for random CTE distribution at the $D-A$ interface, the critical concentration is almost twice as small as analytical model predicts for ordered CTEs with infinite lifetime. The dissociation prevents the creation of clusters of the closely placed CT excitons and, especially, it prohibits CTEs from occupying adjacent sites at the $D-A$ interface. It cuts off the high energy tail of the CTEs energy distribution function. The peak of energy distribution increases (more details see in [6]) with the number of CTEs and so does the width of the distribution. It is interesting to note that the position of the peak at the repulsion energy distribution (corresponding to the energy of highest probability) varies with the steady state number of CTEs approximately in the way which the theoretical

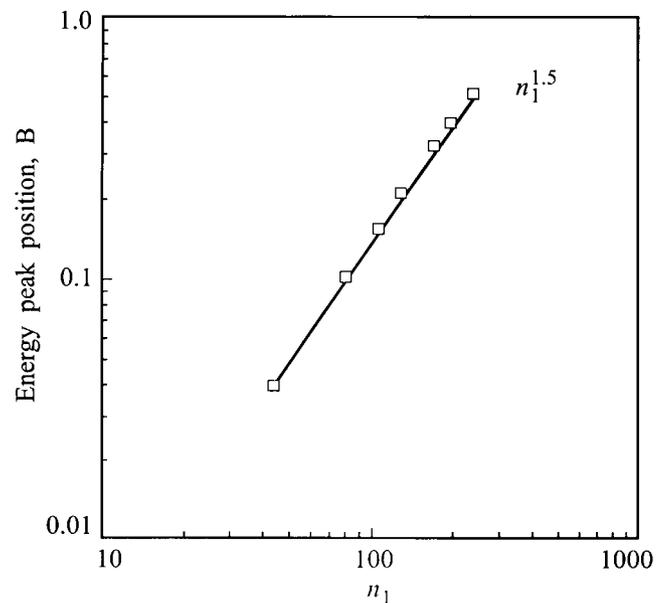


Figure 3. Position of the energy distribution peak as a function of the number of the CT excitons, n_1 .

model of ordered CTEs lattice predicts. As it follows from Eq. (1), the CTE energy as a function of the number of CTEs should vary as $n_1^{3/2}$. Fig. 3 demonstrates that in computer simulations such dependence take place for peak position with high accuracy. At finite temperature, the repulsion also can be important because it decreases the activation energy. This decrease of activation energy depends on the concentration of CTEs. To observe the predicted cold photoconductivity, the methods for observing photoconductivity parallel to the plane of dipoles developed in the investigations of Langmuir–Blodgett films [9] can be used. It is clear also that for such measurements we need to have nearly perfectly ordered crystalline *D–A* multilayers with a large interface area.

Authors are thankful to Martin Pope, Jeffrey Schwartz and Vladimir Yudson for useful discussions.

References

- [1] Excitons. / Ed. by E. Rashba and M. Sturge. North-Holland, Amsterdam (1982).
- [2] M. Pope and C.E. Swenberg, *Electronic Processes in Organic Crystals*. Clarendon Press, Oxford (1982); V.M. Agranovich and M.D. Galanin. *Electronic Excitations Energy Transfer in Condensed Matter*. North-Holland, Amsterdam (1982).
- [3] V.M. Agranovich, A.A. Zakhidov. *Chem. Phys. Lett.* **50**, 278 (1977).
- [4] D.S. Chemla, J. Zyss. *Nonlinear Optical Properties of Organic Molecules and Crystals*. Academic Press, Orlando (1987).
- [5] (a) V.M. Agranovich, G.C. La Rocca, F. Bassani. *JETP Lett.* **62**, 405 (1995). (b) V.M. Agranovich, G.C. La Rocca, F. Bassani. *Chem. Phys. Lett.* **274**, 355 (1995). (c) V.M. Agranovich, K.N. Ilinski. *Phys. Lett.* **A191**, 309 (1994).
- [6] S.A. Kiselev, E. Hartung, Z.G. Soos, S.R. Forrest, V.M. Agranovich. *Chemical Physics* (1998), in press.
- [7] S. Forrest. *Chemical Reviews* **97**, 1793 (1997).
- [8] D. Haarer, M. Philpott. In: *Spectroscopy and Excitation Dynamics of Condensed Molecular Systems* / Ed. by V.M. Agranovich and R.M. Hochstrasser. North-Holland, Amsterdam (1983). P. 27.
- [9] M.C. Petty. *Langmuir–Blodgett Films*. University Press, Cambridge (1996). P. 134.