

## A MODEL OF ORGANIC THIN FILM ELECTROLUMINESCENCE

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A simple model for thin film organic electroluminescence in single layered one-dimensional cell is developed, assuming direct excitation of luminophor molecules by electron impact. The values and behaviour of calculated curves for brightness and efficiencies correlate with experimental data. For high efficiency, low work function, and high Fermi energy cathodes, and relatively low electric fields should be used.

(Received July 3, 2002; accepted July 22, 2002)

*Keywords:* Organic thin film, Electroluminescence, Electron impact

### 1. Introduction

Organic solid thin film structures are very promising materials for the development of manifold optoelectronic devices. However, fundamental physical processes in such structures and mechanisms of luminophor excited states formation are not clear yet. Many authors assume that organic luminophor excited states appear due to an electron-hole recombination. But luminophor molecules can also be excited by direct "hot" electron impact [1], especially at high electric fields. If we understand all the mechanisms of organic electroluminescence, we can solve their main problems, such as efficiency and durability. The theoretical modeling can essentially clear this question. Some authors tried to solve this problem (see, for example [2, 3]). In this paper a model of processes in organic thin film electroluminescent cell is developed, assuming direct excitation of luminophor molecules by electron impact into singlet, triplet, and ion states and electron-ion recombination.

### 2. Background and model description

Electroluminescent studies of organic substances were earlier held in the gas phase [4]. The molecules in the gas discharge are conclusively excited by an electron impact, because the shape of luminescence spectrum of free molecules strongly depends on the average electron energy, which can be changed by applied voltage [5] or by addition of another gas with different excitation potential [6]. As it is known from the gas discharge physics [7], the condition for electron-ion recombination at high electric field is very bad, because electrons and positive ions are divided spatially and continue to divorce by a field. "Thermal" electrons only take part in the recombination process. A rise of electric field strength increases electron energy and makes recombination process difficult. The conditions of electric excitation in an organic electroluminescent cell and in a gas discharge tube are similar. A value  $E/n=10^{-14}$  V·cm<sup>2</sup> determining the average electron energy is the same both in neon and organic gas discharge ( $E=10^2$  V/cm,  $n=10^{16}$  cm<sup>-3</sup> [7, 8]) and in organic electroluminescent cell ( $E\sim 10^6$ - $10^7$  V/cm [9],  $n=10^{21}$  cm<sup>-3</sup>). Particularly, many amorphous organic thin films conserve their properties in monomolecular state. It is known that electrons are ejected from the cathode as a result of tunneling in a high electric field, where they are also accelerated. The ejected electrons energy approximately equals the Fermi energy. The real energy received by electron from electric field between inelastic collisions in this field equals to  $eEd=eE/n\sigma$  and can reach 10 – 100 eV (here  $n$  is about  $10^{21}$  cm<sup>-3</sup>, and  $\sigma$  is the cross section of inelastic collisions (about  $10^{-16}$  cm<sup>2</sup>),  $d=100$  nm is the thickness of the cell). But the excitation threshold of molecules is about 2-3 eV. Note that the way between two inelastic

collisions  $d=1/n\sigma$  is about 100 nm, i.e. one inelastic collision occurs in the thickness of electroluminescent cell, and we can consider the excitation only near surface region. The above presented data show that we have to take into consideration the process of direct excitation by “hot” electrons. It is interesting to describe the organic electroluminescence on the basis of this process. Though, charge transport in the bulk of amorphous organic materials is widely described as a hopping process with low mobilities, it can strong differ in thin near interface films due to dipole layer. It should be also noted that with only recombination description of organic electroluminescence the calculated electroluminescent intensity is around one order of magnitude higher than experimental [2,3], the recombination cross section much exceeds geometrical one [3], recombination zone is supposed to be near cathode surface [10], near the anode surface [11], at the interface [12], or in the volume [13].

The typical electroluminescent cell consists of three organic layers sandwiched between two electrodes. They are so called electron transporting, emitting, and hole transporting. However, the real role of the additional transporting layers is not clear yet. It is known that diamine based antioxidants gives the possibility for organic electroluminescent devices to work in contact with oxygen and air, at rising in temperature and radiation level, in contacts with metals, etc., as well as to reduce molecular aggregation increasing luminescence quantum yield. Such substances can accept charge or energy and prevent destruction of molecules due to dissociation or chemical reaction. This is possibly one of the functions of additional organic charge transporting layer. On the other hand, it is well known [14] that a thin dielectric film of electronegative substance placed on the cathode surface results in decreasing of the cathode work function. Thus, the additional layers are the part of electrodes. The very low drop of potential on additional layer [15] corroborates this conclusion. As a result, the real thickness of electroluminescent cell consists of the thickness of radiating layer. Moreover, we can consider the reduced work function of the cathode metal. As a rule, on the cathode surface there always are microscopic edges of  $h$  height and  $r$  radius, and electric field strength is  $h/r$  times more than a mean value in the space between electrodes. The field increase can be 100 times and more, as it was earnestly shown in the gas discharge [14]. Note, that tunnelling process is very inertial [16] due to charge accumulation at the interface [17]. It really determines the electroluminescence response.

Taking into account the above assumptions, for single layered electroluminescent cell the rate of excitation of organic molecules with the  $x$  coordinate  $F(x)$  was calculated using the standard expression

$$F(x) = \int_0^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \sigma(p_x, p_y, p_z) \frac{j(p_x, p_y, p_z)}{e} dp_x dp_y dp_z = \frac{2}{mh^3} \int_0^{\infty} \int_0^{2\pi} \sigma(p, \rho, \alpha) D(p_0, E) p_0 \rho dp_0 d\rho d\alpha \quad (1)$$

where  $\sigma(p_x, p_y, p_z)$  is the excitation cross section,  $j(p_x, p_y, p_z)$  is the current density,  $D(p_0, E)$  is the tunneling probability. The right part is written in cylindrical coordinates. In the one-dimensional approximation the tunneling probability for a triangular barrier is:

$$D(p, E) = \exp\left[-\frac{8\pi\sqrt{2m}}{3h} \frac{(\Psi + E_f - \frac{P_0^2}{2m})^{3/2}}{eE} \theta(y)\right] \quad (2)$$

where  $\Psi$  is the work function,  $E_f$  is the Fermi energy (chemical potential) of the metal,  $E$  is the electric field strength, and  $\theta(y)$  is the Schottky function. Then the excitation rate is:

$$F(x) = \frac{4\pi}{mh^3} \int_0^{\sqrt{2mE_f}} \int_0^{\sqrt{2mE_f - p_0^2}} \sigma(p, \rho) \exp\left[-\frac{8\pi\sqrt{2m}}{3h} \frac{(\Psi + E_f - \frac{P_0^2}{2m})^{3/2}}{eE} \theta(y)\right] p_0 \rho dp_0 d\rho d\alpha \quad (3)$$

because momentum changes from zero to  $\sqrt{2mE_f}$ . The same formula without cross section multiplier was used for current density calculation.

The energy dependence of cross section of organic luminophor excitation into singlet states was approximated by Born formula, which behaviour is similar to molecular fluorescence excitation function [18, 19]  $\sigma(p, \rho) = \alpha p^{-2} \ln(\beta p^2)$ , where  $p = \sqrt{(p_0 + (2 m e E - W_1 \sigma_1 N) x)^2 + \rho^2}$ ,  $W_1$  is the averaged energy which loses the electron after one collision,  $\sigma_1$  is the averaged cross section of the process,  $\alpha$  and  $\beta$  are the coefficients for the studied molecule. The energy dependence of triplet states excitation was calculated using formulae  $\sigma_t(E) = \sigma_t^{\max} E_{th}/E$ , where  $\sigma_t^{\max}$  is the maximal value of cross section,  $E_{th}$  is the threshold energy. For ionization the Born approximation with threshold at ionization energy (7.5 eV) was used. The weakening of the electron flux was taken into account by multiplying of expression in (3) by  $\exp(-\sigma_2 N x)$ , where  $\sigma_2$  is the cross section of this process. The values of excitation rates were found by means of numerical integration. Using this value, the electroluminescence brightness can be easily calculated. Electron concentration,  $N_e$ , was calculated by

integration over  $x$  coordinate the expression  $N_e(p_{x_0}, x) = \frac{j(p_{x_0}, x)}{ev(x)}$  (see formula 2). Maximal

values of cross sections  $\sigma_t^{\max}$  and  $\sigma_1^{\max}$  were varied from  $10^{-17}$  to  $10^{-16}$  cm<sup>2</sup>. Electron-ion recombination rate  $K_{rec} = 10^{-6}$  cm<sup>3</sup>/sec, singlet and triplet excited molecules (1:3) are formed after recombination.

The full number of luminescent molecules in the volume was found by  $F_v = (N\eta V/d) \int_0^d F(x) dx$ , where  $V$  and  $d$  is the volume and the thickness of the cell,  $\eta$  is the quantum yield of luminescence,  $h\nu$  is the averaged energy of luminescence quantum. The energy efficiency was defined as  $\Phi = F_v h\nu / (W_k + jSU)$ , and quantum efficiency  $\varphi = F_v / jS$  (the ratio of radiated quanta to a number of electrons), where  $W_k$  is the energy of ejected electrons.

We consider organic diode fabricated using indefinite organic phosphor with  $\eta=0.8$ , excited state lifetime  $\tau=10^{-9}$  sec, the energy of excited state 3.4 eV, and the maximal value of excitation cross section to be  $10^{-16}$  cm<sup>2</sup>. We take  $N=10^{21}$  cm<sup>-3</sup>,  $d=100$  nm. Some calculations are made for host-guest system with effective energy transfer from host molecules to guest. The effects of space charge, polarization of luminophor layer, and electron-electron cooling are not taken into consideration, though they are very essential at high fields. The electrical field is supposed to be homogeneous and directed along the  $x$  axis. Intramolecular processes are described by the system of standard equations in the four-level approximation.

### 3. Results and discussion

In Fig. 1 the calculated dependences of distribution of excitation rate on the cell thickness for different values of work functions and Fermi energies (11.8 eV for Al, and 3 eV for Ca [20]) are presented. Here all the curves are normalized on the maximal values. This characteristic strongly depends on Fermi energy, which can change from 11.8 eV for Al to 2.5 eV for Na, especially at low work functions. It is connected with the energy dependence of excitation cross section, which rises from threshold  $E_{th}$  at excitation potential to a maximal value  $\sigma^{\max}$  at 3-4  $E_{th}$  and then decays slowly. If  $E_f$  is less or more than the energy of  $\sigma^{\max}$  or after acceleration by electric field, electrons are not optimal for excitation of luminophor molecules. So, for defined conditions there is an optimal thickness of emitting layer. The very intensive electroluminescence is observed in rather narrow thickness range nearby the cathode surface, in compliance with the experimental data [21]. If we use the real energy dependence of excitation cross section [22], this range will be narrower.

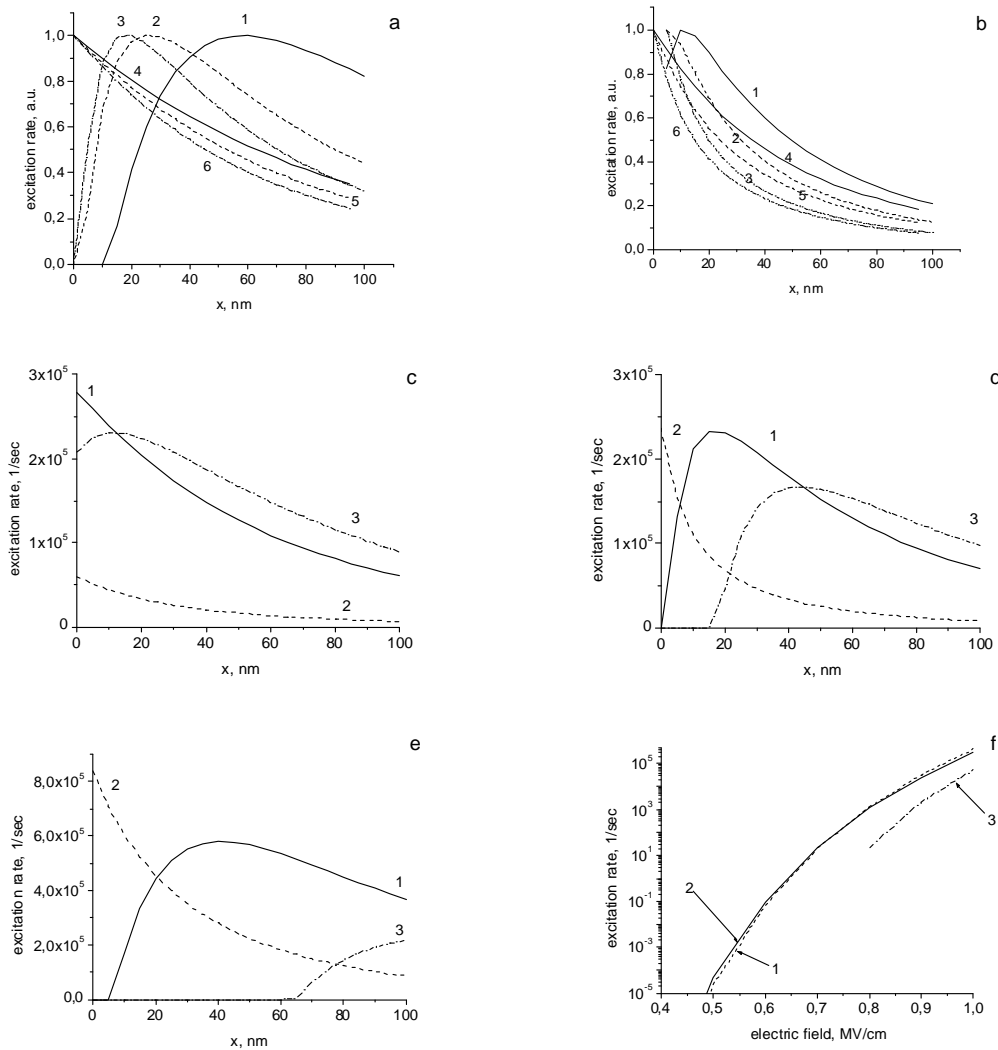


Fig. 1. The dependences of distribution of excitation rate on the cell thickness for different values of work functions and Fermi energies: a)  $\psi=1$  eV (1-6),  $E_f=3$  (1-3), 11.8 eV (4-6),  $E=1$  (1, 4), 2 (2, 5), 3 MV/cm (3, 6), b)  $\psi=3$  eV (1-6),  $E_f=3$  (1-3), 11.8 eV (4-6),  $E=5$  (1, 4), 10 (2, 5), 20 MV/cm (3, 6).

Fig. 1c-f show the relative rates of considered processes. The dependences of volume averaged rates on electric field (f) and their depth distribution for luminophor molecule singlet state  $S_1$  F (1), triplet  $F_T$  (2) and ion  $F_I$  (3) are presented for cathodes with different Fermi energies and work functions. If  $E_f$  is relatively high (Fig. 1c), electrons excite triplet states with approximately one order lower efficiency than singlet. Both curves (1, 3) decrease quickly with depth (for triplets two times quicker), the curve 2 for ions changes more slowly. Taking into consideration recombination process, at high fields recombination rate is strongly increased and excitation rates for singlets and triplets are comparable. For cathodes with low Fermi energy (Fig. 1d) at cathod-luminophor interface the most intensive rates are for triplet excitation, ionization process is negligible. Maximal values singlet excitation and ionization are reached at 20 and 40 nm, correspondingly. Triplet excitation is quickly decreased. Ionization process is essential at fields higher than 1 MV/cm (Fig. 1f). It occurs at depth more than 60 nm.

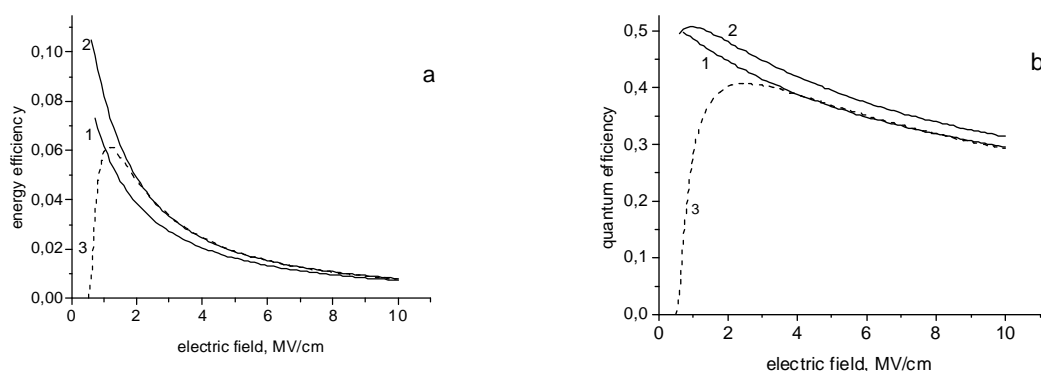


Fig. 2. The dependence of energy (a) and quantum (b) efficiency on electric field.  $\psi=1-3$  eV,  $E_f=11.8$  (1), 7 (2), 3 eV (3).

Fig. 2 illustrates the behaviour of energy and quantum efficiency with electric field. It can be noted that the behaviour of these curves are similar. Both the energy and the quantum yield are very sensitive to the Fermi energy at relatively low electric fields. Moreover, there is an optimal framework for electrical field to reach the maximal efficiency. Its value decreases with the further enhancing of electrical field. It is also connected with the acceleration of electrons to energies exceeding the energies of maximal excitation cross section. For our molecules this energy equals to 10 eV. The value of quantum efficiency is agreed with our estimation [27]. The value of energy efficiency and its energy behaviour are in a good accordance with the experimental data [1, 28]. Thus, the best maximal energy efficiency is nowadays about 4%. We have also to take into consideration that quantum yield of luminescence in our calculations is 0.8, but really it is essentially lower.

#### 4. Conclusion

In conclusion, we have shown that the operation of organic electroluminescent device could be described by a simple model based on tunneling injection of electrons and direct electron impact excitation of molecules. For high efficiency, low work function and high Fermi energy cathodes and relatively low electric fields should be used. The further development of this model is in progress.

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