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Interaction of Triplet Excitons with Neutral and Charged Electron Excitations in Organic Crystals

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Theory of nonradiative decay processes of triplet and singlet excitons and theory of new combined excited electron states in organic crystals connected with the triplet exciton-charged and uncharged electron excitations interactions is reviewed, discussed and developed. Theoretical results are compared with experimental results for anthracene crystal.

I. Introduction

The study of the interaction of the triplet excitons with neutral and charged electron excitations i.e. with excitons and excess electrons and holes has been intensively pursued in recent years. This has been due to the fact, that the triplet excitons can undergo different triplet — charged or uncharged electron excitation processes resulting in observable effects in organic crystals.

It is well known, that the production of charge carriers in organic crystals can be a result of the interaction of the triplet excitons with singlet excitons [1]. The collision of two triplet excitons due to their interaction gives rise to a singlet exciton state, which decay radiatively in the form of the observable delayed fluorescence from the singlet exciton state in crystal [2], [3], [4], [5], [6]. The fluorescence quenching of the singlet exciton states under high intensities and longer illumination was discovered and ascribed to the nonradiative annihilation of the singlet excitons through their interaction with triplet excitons [7]. The excess electrons introduced into the crystal by means of space-charged-limited (SCL) currents causes a decrease of the triplet exciton lifetime [8]. This decrease is interpreted as the result of the nonradiative destruction of the triplet exciton by interaction with excess electrons.

The production of charge carriers through triplet — singlet exciton interaction was examined theoretically by Kearns [1]. He considered the following reaction: an anitial state in which the crystal contains one triplet and one singlet exciton; a final state in which the excitons have annihilated one another to yield a hole in the lowest hole band and electron in a highly excited, essentially plane wave level. The rate of this auto-ionization process of the double singlet-triplet exciton state was calculated from first — order time-dependent perturbation theory. Using the results of this calculation Kearns concluded, that the triplet — singlet process can predominate over the singlet-singlet process for steady photocurrents proposed some

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years ago by Northrop and Simpson [9] to explain their data on surface photoconduction in anthracene. But Silver et al. [10] in an ingenious double lightpulse experiment found in the anthracene crystal the singlet — singlet process only.

The process of the collision of two triplet excitons resulting in a higher singlet exciton state was investigated theoretically by Jortner et al. [11]. The theoretical and experimental studies of the diffusion coefficient of triplet exciton states in organic crystals yield strong support for the proposal that the rate — determining step in the above triplet-triplet annihilation process involves the production of two adjacent excited molecules. Therefore Jortner et al. considered the mentioned triplet-triplet annihilation as a bimolecular annihilation reaction, which is diffusion controlled. The rate constant is then given by the rate for the encounter of two triplet excitons

$$\gamma_{\text{theor}} = 8\pi \eta D_{\text{T}} \langle R \rangle. \tag{1}$$

Here D_{T} is the diffusion coeficient of the triplet exciton, $\eta = 1/9$ represents the probability for the formation of a singlet state from two triplet states and $\langle R \rangle$ is an average crystal spacing. Setting $D_{\text{T}} = 2 . 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ and $\langle R \rangle = 6 \text{ Å}$ we get $\gamma_{\text{theot}} = 2 . 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$ which is in good agreement with the experimental observations in the anthracene crystal ($\gamma_{\text{exp}} = 2 . 10^{-11} \text{ cm}^3 \text{ sec}^{-1}$).

In the following I report on theoretical studies of the non-radiative annihilation of the singlet excitons on the triplet excitons and of the nonradiative destruction of the triplet excitons by excess electrons made by me in the last years. For simplicity I focus attention on organic molecular crystals with one molecule per unit cell and assume that each molecule of the crystal may be divided into π-electrons and the rest.

2. Basic Model of Electron Excitations of the Crystal

In the following considerations we have need of characterize the excited states of the excess electrons i.e. charged electron excited states and the excited states of the molecules remaining allways neutral i.e. neutral electron excitations.

We describe the neutral excited electron states of the molecule in one-electron approximation and characterize the one-electron states by the quantum index f. We denote the corresponding wave functions and energies of the $\vec{p}$ -thmolecule of the crystal by $\psi_{\text{pf}} (\vec{r})$ and ε_f, where $\vec{r}$ is the position vector of the π-electron and $\vec{p}$ is the lattice vector denoting the position of the molecule in the crystal. In this one-electron approximation, we consider the neutral electron excitations of the molecule generated through the transitions of one π-electron from the one-electron state with the highest energy occupied by π-electrons in the electron ground state of the molecule, which we denote by the quantum index $f \equiv O$ into all possible one-electron states with higher energy $\varepsilon_f > \varepsilon_0$ (with $f > O$ briefly). We characterize these electron excitations by the quantum index f and we denote their quasiboson creation and annihilation operators with regard to the spin states at the $\vec{p} - th$ molecule of the crystal by $B_{\text{pf}}^{+}(S, M_{\text{S}})$, $B_{\text{pf}}^{-} (S, M_{\text{S}})$, where $S = O, 1$; $M_{\text{S}} = -S,..., + S$ are the

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spin quantum numbers. These neutral electron excitations have the same excitation energy $E_t(S)$ independent of the location in the crystal and in the presence of the intermolecular interaction migrate as a coherent or incoherent exciton through the crystal [11]. In this description of the excited states of the inner electrons of the crystal we consider the triplet exciton in incoherent random walk model as a neutral triplet electron excitation ($S = 1$; $M_S = -1$, 0, 1) hopping randomly from one molecule to another [11]. On the other hand in the following we consider the singlet exciton in the coherent model as a singlet electron excitation moving through the crystal in the form of the coherent excitation wave, the travelling time of which between two adjacent molecules of the crystal is much shorter than that one of the triplet exciton.

We describe the excited states of the excess electrons in one-electron approximation under the assumption, that the inner electrons of the crystal in the neutral excited states of the molecules follow the motion of the excess electron adiabatically. This approximation allows us to express the interaction of the excess electrons with the inner electrons of the crystal in the form of the appropriate elected potential field depending on the excited states of the inner electrons of the crystal. When we denote by ν the set of the quantum numbers characterizing the excited states of the inner electrons of the crystal given by the number of the neutral electron excitations situated at the individual molecules of the crystal, we obtain the following equation for the wave function $\varphi_{\lambda\gamma}(\vec{r})$ and energy $E_{\lambda\gamma}$ of the excess electron under the above assumptions

$$\left[-\frac{\hbar}{2m}\Delta + U_0(\vec{r}) + U_\nu(\vec{r}) \right] \varphi_{\lambda\gamma}(\vec{r}) = E_{\lambda\nu}\,\varphi_{\lambda\gamma}(\vec{r}). \qquad (2)$$

Here m is the mass of the excess electron and $U_0(r)$ is the potential energy of the excess electron in the periodic field of all molecules of the crystal in their electron ground state. The source of the additional potential energy $U_\nu(\vec{r})$ of the excess electron is the change of the charge distribution of the inner electrons of the crystal caused by the excitation of the crystal from the electron ground state to the excited electron state ν. The λ in (2) are the quantum numbers characterizing the stacionary states of the excess electron. We denote the fermion creation and annihilation operators of the excess electrons in the quantum state $\lambda_{\gamma\nu}$ by $a_{\lambda\nu}(s)$, $a_{\lambda\nu}^+(s)$ where $s = \pm 1/2$ (in units $\hbar$) are the spin quantum numbers of the excess electron.

A. Nonradiative annihilation of the singlet exciton on triplet exciton

3. Model of the Nonradiative Annihilation of the Singlet Exciton on the Triplet Exciton

According to [12], the encounter rate of the singlet and triplet exciton is given by

$$\gamma_{\text{dif}} = 4\pi \left(D_S + D_T\right) R_{ST} \tag{3}$$

where D_S and D_T are the diffusion coefficients of the singlet and triplet exciton and where R_{ST} denote the distance to which singlet and triplet exciton must approach in order that the annihilation process of singlet exciton takes place. Taking for anthracene crystal $D_S \approx 1 \text{ cm}^2 \text{ sec}^{-1}$ [11], $D_T \approx 2 \cdot 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ and the minimum value $R_{ST} \approx 6 \cdot 10^{-8}$ cm we get

$$\gamma_{\text{dif}} = 7{,}5 \cdot 10^{-7} \text{ cm}^3 \text{ sec}^{-1}. \tag{4}$$

This value of the encounter rate of the singlet and triplet exciton in anthracene crystal is two orders of magnitude larger than the observed value $\gamma_{\text{exp}} \times (7 \pm 4) \cdot 10^{-9} \text{ cm}^3 \text{ sec}^{-1}$. Therefore the annihilation process of the singlet exciton on the triplet exciton cannot be considered as a diffusion controlled process and we must to determine the annihilation rate by the transition probability of the crystal from the initial state with one singlet exciton and one triplet exciton in dynamical interaction to the final state with one triplet exciton with higher excitation energy.

Our model of the triplet and singlet exciton and the fact that $D_T \ll D_S$ allows us to treat the stationary states of the singlet and the triplet exciton in dynamical interaction in the initial state of the crystal as the stationary sates of the singlet electron excitation moving in the potential field of the triplet electron excitation fixed on some molecule of the crystal. These stacionary states are determined by the Schrödinger equation

$$H \,|> \,= W \,|>, \tag{5}$$

where W is the energy and $|>$ is the state vector of the stationary states and H is the operator energy of our system. This operator can be written in the form:

$$H = W_0 + \sum_S \sum_M \sum_{\vec{p}} \sum_{f>0} E_f(S) B^{+}_{\vec{p}f}(S, M_S) B_{\vec{p}f}(S, M_S) +$$

$$+ \sum_S \sum_{M_S} \sum_{\vec{p}' \neq \vec{p}} \sum_{f>0} L_f(\vec{p}' - \vec{p}) B^{+}_{\vec{p}f}(S, M_S) B_{\vec{p}f}(S, M_S) + \tag{6}$$

$$+ \sum_{\vec{p}' \neq \vec{p}} \sum_{f>0} \sum_{f'>0} \sum_M U_{f'f}(\vec{p}' - \vec{p}) B^{+}_{\vec{p}'f'}(0,0) B_{\vec{p}'f'}(0,0) B^{+}_{\vec{p}f}(1, M) B_{\vec{p}f}(1, M).$$

On the right side of (6), the first term is the energy of the quasivacuum of the electron excitations of the crystal, the second term is the operator energy of the

electron excitations without interaction and the thirth term describes the migration of singlet electron excitations from one molecule to another with the help of the virtual emission and reabsorption of the quantum of the coulombic and exchange interaction. This process of the migration is characterized in one-electron approximation by the matrix element

$$L_t(\vec{p'} - \vec{p}) = 2 \int \psi_{\vec{p'}f}^*(r_1)\, \psi_{\vec{p}o}^*(r_2)\, \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \times$$

$$\times\ \psi_{\vec{p}f}(\vec{r_2})\, \psi_{\vec{p'}o}(\vec{r_1}) d^3\vec{r}_1 d^3\vec{r}_2 - \int \psi_{\vec{p'}f}^*(r_1)\, \psi_{\vec{p}o}^*(r_2)\, \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} + \quad (7)$$

$$+\ \psi_{\vec{p'}o}(\vec{r_2})\, \psi_{\vec{p}f}(\vec{r_1}) d^3\vec{r}_1 d^3\vec{r}_2\ .$$

The third term on the right side of (6), is the operator energy of the dynamical interaction between singlet and triplet electron excitation where $U_{f'f}(\vec{p'} - \vec{p})$ is the potencial energy of the dynamical interaction between the $f' - th$ singlet electron excitation localized at the $\vec{p} - th$ molecule of the crystal and the f, M triplet electron excitation localized at the $\vec{p}$-th molecule of the crystal. The potential energy $U_{f'f}(\vec{p'} - \vec{p})$ is determined by the change of the electrostatic and exchange or dispersive forces between the $\vec{p'}$-th and $\vec{p}$-th molecule of the crystal caused by its excitation from the electron ground state to the excited state with one singlet electron excitation f' and one triplet electron excitation f localized at the $\vec{p'}$-th and $\vec{p}$-th molecule.

Now suppose, that we have one singlet electron excitation f_1 in the dynamical interaction with the triplet electron excitation f_2, M fixed at the $\vec{p}_2$-th molecule of the crystal. Then the state vectors $|f_1, f_2 M\rangle$ describing the stationary states of the singlet electron excitation in the potential field of the fixed triplet electron excitation can be written in the form:

$$|f_1, f_2\, M\rangle = \sum_{\vec{\varrho}\,\neq\,0} C(f_1, f_2\, M; \vec{\varrho}) B_{\vec{p},f_1}^+(0,0) B_{\vec{p},f_2}^+(1, M)|\,\mathrm{vac}\rangle_{\mathrm{el}}\ . \quad (8)$$

Here $|\mathrm{vac} >_{\mathrm{el}}$ is the normalized state vector of the quasivacuum of the electron excitations, $\vec{p}_1$ is the position vector of the singlet electron excitation in the crystal and $\vec{\varrho} = \vec{p}_1 - \vec{p}_2$ is the vector of the singlet-triplet electron excitation separation. The set of coefficient $C(f_1, f_2 M; \vec{\varrho})$ for all $\vec{\varrho} \neq 0$ is the wave function of the singlet electron excitation in the field of the fixed triplet electron excitation in the $\vec{\varrho}$-representation.

Inserting (8) in (5) and using (6), we obtain for the wave function $C(f_1, f_2 M; \vec{\varrho})$ the set of difference equations:

$$E_{f_1}(o) + U_{f_1 f_2}(\vec{\varrho}) - W\, C(f_1, f_2 M; \vec{\varrho}) + \sum_{\vec{\varrho'}\,\neq\,\vec{\varrho}\,\neq\,o} L_{f_1}(\vec{\varrho'} - \vec{\varrho})\, C(f_1, f_2 M; \vec{\varrho'}) = 0. \quad (9)$$

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The solutions of this set of difference equations with corresponding bound conditions determine the stationary states of the singlet and triplet exciton in dynamical interaction in the initial state of the crystal.

4. Incoherent Singlet — Triplet Biexciton

Before we calculate the nonradiative annihilation rate of the singlet exciton on the triplet exciton in our model, we discuss the solutions of the set difference equations (9) determining the behaviour of a pair of singlet and triplet exciton in dynamical interaction.

If we use the Fourier transformation, we can rewrite the set of difference equation (9) in the form:

$$C(f_1, f_2 M; \vec{\varrho}) = \sum_{\vec{\varrho}} G(W; \vec{\varrho} - \vec{\varrho'}) U_{f_1 f_2}(\vec{\varrho}) \, C(f_1 f_2 M; \vec{\varrho'}); \; \vec{\varrho}, \vec{\varrho'} \neq 0. \tag{10}$$

Here
$$G(W; \vec{\varrho} - \vec{\varrho'}) = \frac{1}{N} \sum \frac{\exp[i(\vec{k} \cdot \vec{\varrho} - \vec{\varrho'})]}{W - E_{f_1}(\vec{k})}, \tag{11}$$

where N is the number of the unit cells in the crystal and $E_{f_1}(\vec{k})$ is the excitation energy of the free coherent singlet exciton f_1 with the wave vector $\vec{k}$.

The set of equations (10) is similar in form to that derived by Takenti [13] for the stationary states of a pair of electron and hole in the crystal. Therefore we can apply the results of Takenti's mathematical analysis to the discussion our set of the difference equation (10).

As has been shown by Takenti, the set of the difference equations (10) has solutions with continous spectrum of energies io the range of the energies

$$O \leq W - E_{f_1 \min} \leq \Delta E_{f_1}, \tag{12}$$

where $E_{f_1 \min}$ is the minimum energy of the coherent singlet exciton f_1 and ΔE_{f_1} is the bandwith of its band of energies. These solutions correspond to the scattering states of the singlet electron excitation in the potential field of the fixed triplet electron excitation. In this case for vanishing interaction between singlet and triplet electron excitation, the wave function $C(f_1, f_2 M ; \vec{\varrho})$ of the singlet electron excitation passes over into the wave function of a coherent singlet exciton f_1 with wave vector $\vec{k}$ and with energy $E_{f_1}(\vec{k})$ i.e.

$$C(f_1, f_2 M; \vec{\varrho}) = \frac{1}{\sqrt{N}} \exp[i(\vec{k} \cdot \vec{\varrho})]. \tag{13}$$

Now suppose, that the condition

$$\sum_{\vec{p}} |U_{ff}(\vec{p})| > \frac{1}{3} \Delta E_{f_1} \tag{14}$$

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is fulfilled. Here the sum is taken over all separations of the singlet and triplet excit-
ation for which $U_{f_1 f_3} < O$ i.e. for which the forces of the interaction between singlet
and triplet electron excitation are attractive. Then the set of difference equations
(10) has solutions with discrete spectrum energies in the range

$$W \leq E_{f_1 \, \mathrm{min}}. \tag{15}$$

Because the dynamic interaction between singlet and triplet electron excitation is
short — ranged always, the number of the solutions with the discrete spectrum of
energies is at most finite.

The solutions with discrete spectrum of energies correspond to the bound states
of the singlet electron excitation in the potential field of the fixed triplet electron
excitation. In this case we have a bound pair of singlet and triplet exciton — singlet-
-triplet biexciton, whose localization determines the localization of the triplet electron
excitation.

The transition probability $\omega_{a; \, f_1 f_3}(\varrho)$ of the triplet electron excitation with bound
singlet electron excitation from one molecule to another is given approximately by

$$\omega_{a; \, f_1 f_3}(\varrho) = \omega_{f_3}(\varrho) \mid Q_{f_1}(\varrho) \mid^2 . \tag{16}$$

Here $\omega_{f_3}(\vec{\varrho})$ is the probability of the nonradiative transition of the triplet electron
excitation from the reference molecule to the molecule separated by lattice vector
$\vec{\varrho}$ and $Q_{a \, f_1}(\vec{\varrho})$ is the corresponding overlap integral of the wave functions of the singlet
electron excitation f_1 in the bound state α in the field of the triplet electron excitation.
Because $\mid Q_{a f_1}(\vec{\varrho}) \mid < 1$ for all $\vec{\varrho} \neq 0$, the transition probability of the triplet electron
excitation with bound singlet electron excitation from one molecule to another is
always smaller than that one of the triplet incoherent exciton. Therefore in our model
the motion of the singlet-triplet biexciton as a whole must be analyzed in terms
of a incoherent random walk model and we can call this type of the singlet-triplet
biexciton — incoherent singlet-triplet biexciton. In diffusion approximation the
behaviour of the incoherent singlet-triplet biexcitons in the crystal is described by
the diffusion coefficient tensor, whose components $D_{\mathrm{ST}}(i, j)$ $(i, j = 1, 2, 3)$ in analogy
with the diffusion theory of the triplet exciton can be written in the form:

$$D_{\mathrm{ST}}(i, j) = \frac{1}{2} \sum_{\vec{\varrho} \, \neq \, 5} \omega_{a; \, f_1 f_3} (\vec{\varrho})(\vec{\varrho} \cdot \vec{e})(\vec{\varrho} \cdot \vec{e}) \tag{17}$$

Here $\vec{e}_i(i = 1, 2, 3)$ are the unit vectors of the Cartesian axies.

5. Nonradiative Annihilation Rate of the Singlet Exciton on the Triplet Exciton

Now we calculate the nonradiative annihilation rate of the singlet exciton on the
triplet exciton in our model described in Ch.3.

As the initial state of the crystal, we take the state described by the state vec-
tor (8).

As the final state of the crystal, we take in agreement with our model of triplet exciton, the state with one triplet electron excitation f_2', M localized on the p_2'th molecule of the crystal. The corresponding state vector of the crystal $| f_2'M'; p_2 >$ is given by the expression:

$$| f_2'M'; p_2' \rangle = B^+_{\vec{p}_2'f_2'}(1, M') \, | \text{ vac } \rangle_{\text{el}} . \tag{18}$$

As perturbation operator H' causing the nonradiative annihilation of the singlet exciton on the triplet exciton, we take in our model of neutral electron excitations the operator of the nonradiative conversion of a pair of singlet and triplet electron excitation into one triplet electron excitation. The operator H' can be expressed in the form:

$$H' = \sum_{\substack{\vec{p}', \vec{p} \\ p' \neq p}} \sum_{M} \sum_{f > 0} \sum_{f' > 0} \sum_{f'' > 0} \{ V_{1f_1f'f''}(\vec{p} - \vec{p}') B^+_{\vec{p}f}(1, M) \, B_{\vec{p}f'}(1, M) B_{\vec{p}f''}(0, 0) +$$

$$+ V_{2f_1f'f''}(\vec{p} - \vec{p}') B^+_{\vec{p}f_3}(1, M) B_{\vec{p}f'}(0,0) B_{\vec{p},f''}(1, M) \} \tag{19}$$

with

$$V_{1f_1f'f''}(\vec{p} - \vec{p}') = \sqrt{2} \left\{ \int \psi^*_{\vec{p}f}(\vec{r}_1) \, \psi^*_{\vec{p}o}(\vec{r}_2) \, \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \, \psi_{\vec{p}'f'}(\vec{r}_2) \, \psi_{\vec{p}f''}(\vec{r}_1) d^3\vec{r}_1 d^3\vec{r}_2 - \right.$$

$$\left. - \delta_{f'f''} \int \psi^*_{\vec{p}o}(\vec{r}_1) \, \psi^*_{\vec{p}'o}(\vec{r}_2) \, \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \, \psi_{\vec{p}'f'}(\vec{r}_2) \psi_{\vec{p}o}(\vec{r}_1) \, d^3\vec{r}_1 d^3\vec{r}_2 \right\} + V_{2f_1f'f''}(\vec{p} - \vec{p}) \tag{20}$$

$$V_{2f_1f'f''}(\vec{p} - \vec{p}') = -\frac{1}{\sqrt{2}} \left\{ \int \psi^*_{\vec{p}f}(\vec{r}_1) \, \psi^*_{\vec{p}'o}(\vec{r}_2) \, \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \, \psi_{\vec{p}f}(\vec{r}_2) \psi_{\vec{p}'f''}(\vec{r}_1) d^3\vec{r}_1 d^3\vec{r}_2 - \right.$$

$$\left. - \delta_{ff'} \int \psi^*_{\vec{p}o}(\vec{r}_1) \psi^*_{\vec{p}o}(\vec{r}_2) \, \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \, \psi_{\vec{p}o}(\vec{r}_2) \psi_{\vec{p}'f''}(\vec{r}_1) d^3\vec{r}_1 d^3\vec{r}_2 . \right\} \tag{21}$$

From (20), (21) we see, that $V_{1f_1f'f''}(\vec{p} - \vec{p}')$ ($i = 1, 2$) are the matrix elements of the nonradiative conversion of the pair of f'-th singlet and f''-th triplet electron excitation localized on the $\vec{p}$-th and $\vec{p}'$-th molecule of the crystal into one triplet electron excitation f, M localized on the $\vec{p}$-th molecule of the crystal through electrostatic and exchange interaction ($i = 1$) or through exchange interaction only ($i = 2$). Therefore on the right side of (19) the first term describes the nonradiative annihilation of the singlet exciton on the triplet exciton as nonradiative transfer of excitation energy from singlet exciton to the triplet exciton through electrostatic and exchange interaction i.e. as absorption of the singlet exciton by triplet exciton. The second term on the same side of the equation describes the nonradiative annihilation of the singlet exciton on the triplet exciton as nonradiative transfer of the excitation energy from the triplet exciton to the singlet exciton i. e. as the absorption of the triplet excion by the singlet exciton. This second process of nonradiative annihilation takes place through exchange interaction only.

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Let us use the state vectors (8) and (18) of the initial and final state of the crystal and the perturbation operator (19) and let us take into consideration the broadening of the emission and absorption lines of the incoherent triplet exciton in the crystal. Then we derive for the transition probability of the crystal from the initial state to the final state with all possible localizations of the triplet electron excitation $f_2 M'$ and with all possible triplet electron excited states $f_2' M'$ the following expression:

$$\omega_{ST} = \omega_{ST}^{(1)} + \omega_{ST}^{(2)} . \tag{22}$$

Here

$$\omega_{ST}^{(1)} = \frac{2\pi}{3\hbar} \sum_M \sum_{f_2'} \sum_a | \overline{\sum_{\vec{\varrho} \neq 0}} C_a(f_1 f_2' M; \vec{\varrho}) V_{1f_{2'} f_1 f_2}(\vec{\varrho}) |^2 \sigma_{f_2 f_{2'}}^{(a)}(W_a) \tag{23}$$

is the probability of the absorption of the singlet exciton by the triplet exciton and

$$\omega_{ST}^{(2)} = \frac{2\pi}{3\hbar} \sum_M \sum_{f_2'} \sum_a \sum_{\vec{\varrho} \neq 0} | C_a(f_1 f_2' M; \vec{\varrho}|^2 | V_{2f_{2'}; f_1 f_2}(\vec{\varrho}) |^2 \times$$

$$\times \int \sigma_{f_2}^{(a)}(W_a + E) \sigma_{f_1}^{(e)}(E) dE \tag{24}$$

is the probability of the absorption of the triplet exciton by the singlet exciton.

In these formulae, $\overline{\sum_a}$ means to take average over all initial states α with continuous and discrete spectrum of energies of the singlet electron excitation in the field of the triplet electron excitation, $\sigma_{f_2'}^{(a)}(E)$ is the absorption line shape factor of incoherent triplet exciton f_2, $\sigma_{f_1}^{(e)}(E)$ is the emission line shape factor of the incoherent triplet exciton f_2 and $\sigma_{f_2 f_{2'}}^{(a)}(E)$ is the absorption line shape factor belonging to the optical transition of the molecule in the crystal from triplet excited state f_2 to the triplet excited state f_2'. We suppose, that all mentioned line shape factors are normalized to unity.

Suppose first, that there are not bound states of the singlet electron excitation in the field of the fixed triplet electron excitation, i.e. that the average in (23), (24) is taken over initial scattering states of the coherent singlet exciton in the field of the fixed triplet exciton. Then neglecting the interaction between singlet and triplet electron excitation and using (13) and (22), (23), (24) we can derive for the nonradiative annihilation rate γ_{ST} of the singlet exciton on the triplet exciton the expression

$$\omega_{ST} = \omega_{ST}^{(1)} + \omega_{ST}^{(2)} \tag{25}$$

Here

$$\omega_{ST}^{(1)} = \frac{2\pi \, v_0}{\hbar} \sum_{f_2'} \overline{\sum_{\vec{k}}} V_{1f_{2'}; f_1 f_2}(\vec{k}) |^2 \sigma_{f_2 f_{2'}}^{(a)} [E_{f_1}(\vec{k})] , \tag{26}$$

$$\gamma_{ST}^{(2)} = \frac{2\pi_0 \, v_0}{\hbar} \sum_{f_2'} \overline{\sum_{\vec{k}}} \sum_{\vec{\varrho} \neq 0} | V_{2f_{2'}; f_1 f_2}(\vec{\varrho}) |^2 \int \sigma_{f_2}^{(a)}(E_{f_1}(\vec{k}) + E) \sigma_{f_1}^{(e)}(E) dE , \tag{27}$$

where v_0 is the volume of the unit cell of the crystal and

$$V_{1f_{2}';\,f_1f_2}(\vec{k}) = \sum_{\vec{\varrho}\,\neq\,0} V_{1f_{2}';\,f_1f_2}(\vec{\varrho}) \exp\left[i(k \cdot \vec{\varrho})\right]. \tag{28}$$

For the estimate of the order of the magnitude of the nonradiative annihilation rate given by (25), (26), (27), we use the dipole-dipole approximation for the coherent singlet exciton f_1 and for the matrix elements $V_{1f_{2}';\,f_1f_2}(\vec{\varrho})$ and neglect all exchange term in $V_{1f_{2}';\,f_1f_2}(\vec{\varrho})$ $(i = 1, 2)$. Then we obtain for the nonradiative annihilation rate of the singlet exciton on the triplet excitons at low temperatures the approximate formula:

$$\omega_{\text{ST}} = \frac{8\pi^2}{3\hbar\,R_o^3}\,|\,(\vec{\mu}_{of_1} \cdot \vec{\mu}_{f_2f_{2}'})\,|^2\,\sigma_{f_2f_{2}'}^{(a)}(E_{f_1\,\text{min}}). \tag{29}$$

Here R_0 is given by

$$\frac{4\pi}{3}\,R_o^3 = v_0 \tag{30}$$

and $\vec{\mu}_{ff'}$ are the transition dipole moments corresponding to the optical transitions $f \to f'$ of the molecule in crystal.

Assume that $\vec{\mu}_{of_1} \,||\, \vec{\mu}_{f_2f_2}$, and that the energy $E_{f_1\,\text{min}}$ of the coherent singlet exciton is in the resonance with the energy of the maximum of the absorption band $f_2 \to f_2'$ with bandwith $\Delta E_{f_2f_{2}'}$. Then taking for anthracene crystal $|\,\vec{\mu}_{of_1}\,| \approx |\,\vec{\mu}_{f_2f_2}\,| \approx$ $\approx 10^{-1}\,eR_0$ [14], $\sigma_{f_2f_{2}'}^{(a)}\,(E_{f_1\,\text{min}}) \approx 1/\Delta E_{f_2f_{2}'}$ with $\Delta E_{f_2f_{2}'} \approx 10^{-1}$ e Volt and $R_0 =$ $= 6 \cdot 10^{-8}$ cm we get $\omega_{\text{ST}} = 5 \cdot 10^{-8}$ cm^3 sec^{-1}. This overestimated value of the nonradiative annihilation rate of the singlet exciton on the triplet exciton is not too far from the experimental value $\gamma_{\text{ST exp}} = (7 \pm 4) \cdot 10^{-8}$ cm^3 sec^{-1} mentioned in § 2.

When the bound states of a pair of singlet and triplet exciton existe, then the nonradiative annihilation of the singlet exciton on the triplet exciton can go through formation of the incoherent singlet-triplet biexciton also i.e. triplet exciton can act as a trap for the singlet exciton. Thus the proper nonradiative annihilation process takes place in the second step after the trapping of the singlet exciton by the triplet exciton as a monomolecular nonradiative decay of the singlet-triplet biexciton with probability given by (22), (23) and (24). In this case we must add to the general cinetic schema of the fluorescence of the singlet excitons given in [7], the singlet — triplet biexcitons rate equations of the following form:

$$\frac{\partial n_{\text{ST}}(\vec{r},\,t)}{\partial t} = \sum_{i,\,j} D_{\text{ST}}(i,j)\,\frac{\partial^2 n_{\text{ST}}(\vec{r},\,t)}{\partial x_i\,\partial x_j} - \omega_{\text{ST}}\,n_{\text{ST}}(\vec{r},\,t) - \beta_{\text{ST}}\,n_{\text{T}}(\vec{r},\,t)n_{\text{S}}(\vec{r},\,t). \tag{31}$$

Here $n_{\text{ST}}(\vec{r},\,t)$, $n_{\text{S}}(\vec{r},\,t)$ $n_{\text{T}}(\vec{r},\,t)$ are the concentrations of the singlet-triplet biexcitons, singlet excitons, triplet excitons at the point of the crystal $\vec{r} = \{x_1, x_2, x_3\}$ at the time t and β_{ST} is the rate for the trapping of the singlet exciton by the triplet exciton.

B. Nonradiative destruction of triplet excitons by excess electrons

6. Model of the Destruction of Triplet Excitons by Excess Electrons

Now, we examine theoretically the nonradiative destruction of the triplet excitons by the excess electrons in our model of the triplet exciton and of the excited states of the excess electrons.

First we consider the process of the nonradiative destruction of the triplet excitons by the excess electrons as a multiphonon nonradiative transition of the crystal from initial state with one excess electron moving in the potential field of the triplet electron excitation fixed on some molecule of the crystal to be final state with one excess electron with higher excitation energy. Suppose, that in initial state the triplet electron excitation f, M is localized at the $\vec{p}$-th molecule of the crystal and denote the potential energy of the excess electron in the field of the localized triplet electron excitation by $U_{\mathrm{pf}}^{\rightarrow}(\vec{r})$. Then according to the (2), the wave function $\varphi_{\lambda}(\vec{r})$ and the energy E_{λ} of the excess electron moving in the potential field of the electron excitation are determined by the equation:

$$\left[-\frac{\hbar^2}{2m} \Delta_{\vec{r}} + U_0(\vec{r}) + U_{\mathrm{pf}}(\vec{r}) \right] \varphi_{\lambda}(\vec{r}) = E_{\lambda}\, \varphi_{\lambda}(\vec{r}) . \tag{32}$$

Here λ are the quantum indexes of the stationary states of the excess electron in the field of the localized triplet electron excitation f, M. The additional potential energy $U_{\mathrm{pf}}^{\rightarrow}(r)$ is given through the change of the electrostatic and exchange or dispersive forces of the interaction of the excess electron with the molecules of the crystal at the excitation of the crystal from the inner electron ground state to the excited state with one triplet electron excitation f localized on the $\vec{p}$-th molecule of the crystal. The additional potential energy $U_{\mathrm{pf}}^{\rightarrow}(\vec{r})$ is different from zero in the vicinity of the molecule with localized triplet electron excitation and wanishes for electron ground state of the inner electrons of the crystal. Therefore setting $U_{\mathrm{pf}}^{\rightarrow}(\vec{r}) = 0$ for all $\vec{r}$, we can also use the equation (32) for the determination of the stationary states of the excess electrons in the final state of the transition of the crystal.

Generally the equation (32) for $U_{\mathrm{pf}}^{\rightarrow}(\vec{r}) \neq 0$ has the solutions with continuous spectrum of the energies and can have the solutions with discrete spectrum of energies also.

The solutions with the continuous spectrum of energies belong to the scattering states of the excess electron in the field of the localized triplet electron excitation. For vanishing additional potential energy $U_{\mathrm{pf}}^{\rightarrow}(r)$, the equation (32) determines the stationary states of the excess electron in the potential field with the periodic potential energy $U_0(r)$. Therefore in this case the excess electron motion is to be described in terms of the band structure of the crystal and the quantum numbers are identical with the wave vector $\vec{k}$ and the band energy $E_{\mu}(\vec{k})$ with band index μ. Then the

normalized and orthogonalized wave function of the excess electron $\varphi_{\mu\vec{k}}(\vec{r})$ is given by the expression:

$$\varphi_{\mu\vec{k}}(\vec{r}) = \frac{1}{\sqrt{N}} \exp [i(\vec{k} \cdot \vec{r})] u_{\mu\vec{k}}(\vec{r}) , \tag{33}$$

where the function $u_{\mu\vec{k}}(\vec{r})$ is periodic in the lattice of the crystal. This description of the motion of the excess electron is exact for the inner electron ground state because in this case is $U_{\text{pf}}(\vec{r}) = 0$ for all $\vec{r}$.

The solutions of the equation (32) with discrete spectrum of the energies correspond to the bound states of the excess electron in the potential field of the localized triplet electron excitation. In this case we have a bound complex of excess electron and triplet exciton whose localization in the crystal determines the localization of the triplet electron excitation. Using similar arguments as for the bound states of the singlet and triplet excitons we can conclude that as a whole the bound complex of the excess electron and triplet exciton moves through the crystal in the incoherent form i.e. through random hopping from one molecule to another. In diffusion approximation the behaviour of the bound complex of the excess electron and triplet exciton is to be described by diffusion coefficient tensor whose components $D_{\text{eT}}(i, j)$ $(i, j = 1, 2, 3)$ can be written in the form:

$$D_{\text{eT}}(i, j) = \frac{1}{2} \sum_{\vec{\varrho} \neq 0} \omega_\lambda(\vec{\varrho}) (\vec{\varrho} \cdot \vec{e}_1)) (\vec{\varrho} \cdot \vec{e}_j) , \tag{34}$$

where $\omega_\lambda(\vec{\varrho})$ is the transition probability of the triplet electron excitation with bound excess electron from one molecule to another.

As a mechanism of the nonradiative destruction of the triplet exciton by excess electron we consider the nonradiative transfer of the excitation energy from the triplet exciton to the excess electron, which takes place through exchange interaction only. In our model, we can describe this mechanism as a nonradiative recombination with the hole at the molecule with localized triplet electron excitation resulting in the transition of the π-electron from the excited state of the same molecule to the state of the free excess electron. The operator H'' describing this process of nonradiative destruction of the triplet exciton can be represented in the form:

$$H'' = \sum_{s} \sum_{f > 0} \sum_{\mu'} \sum_{\vec{k}'} \sum_{\lambda} V_{\mu'\vec{k}'; \lambda} +$$
$$+ \left\{ a^+_{\mu'\vec{k}'}(s) \frac{1}{3} \left[\sqrt{2} a_\lambda(-s) B_{\text{pf}}(1, 2s) + 2s a_\lambda(s) B_{\text{pf}}(1,0) \right] \right\} . \tag{35}$$

Here $V_{\mu'\vec{k}'; \lambda}$ are the matrix elements of the nonradiative destruction of the triplet exciton by excess electron given explicity by the expression:

$$V_{\mu'\vec{k}'; \lambda} = - \sqrt{\frac{3}{2}} \int \varphi_{\mu'\vec{k}'}(\vec{r}_1) \psi_{\text{po}}(\vec{r}_2) \frac{e^2}{|\vec{r}_1 - \vec{r}_2|} \varphi_\lambda(\vec{r}_2) \psi_{\text{pf}}(\vec{r}_1) d^3\vec{r}_1 d^3\vec{r}_2 . \tag{36}$$

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7. Probability and the Rate of the Nonradiative
Destruction of the Triplet Exciton by Excess Electron

Now we calculate the probability of the nonradiative destruction of the triplet exciton by the excess electron within the framework of the first order time-dependent perturbation theory. The problem is to calculate quantum mechanically the probability of the multiphonon spontaneous nonradiative transition of the crystal from initial state with one excess electron in quantum state and with one triplet exciton f localized at the $\vec{p}$-th molecule of the crystal characterized by the state vector

$$|\vec{p}f; s> = \frac{1}{\sqrt{3}}\left[\sqrt{2}\,a_\lambda^+(-s)B_{\mathrm{pf}}^+(1, 2s) + 2sa_\lambda^+(s)B_{\mathrm{pf}}^+(1,0)\right]. \tag{37}$$

to the final state with one excess electron in the quantum state $k', E_{\mu'}(k')$ characterized by the state vector

$$|\mu'k'; s> = a_{\mu'\vec{k}'}^+(s)\,|\,\mathrm{vac}>_{\mathrm{el}}; s = \pm\frac{1}{2} \tag{38}$$

caused by the perturbation characterized by the operator H'' in (35).

Using the state vector (37), (38) and operator (35) and taking into consideration the broadening of the emission line of the incoherent triplet exciton caused by its incoherent interaction with various modes of lattice vibrations, we derive for the probability of the nonradiative destruction of the triplet exciton by the excess electron through the absorption of the triplet exciton by the excess electron the following expression:

$$\gamma_e = \frac{2\pi}{\hbar}\overline{\sum_\lambda}\sum_{\mu'}\sum_{\vec{k}'}|\,V_{\mu'\vec{k}'\lambda}|^2\sigma_f^{(e)}(E(k') - E_\lambda), \tag{39}$$

where $\overline{\sum_\lambda}$ means to take overage over all initial states of the excess electron in the field of the localized triplet electron excitation.

Let us suppose, that there are not bound states of the excess electron in the field of the localized triplet electron excitation and neglect the interaction between excess electron and triplet electron excitation. Then assuming, that in the initial state the excess electron is in its lowest energy band with band index $\vec{\mu}$ and with wave vector $\vec{k}$ and using (39), we obtain for the nonradiative destruction rate γ_e of the triplet exciton by excess electron following formulae:

$$\gamma_e = \frac{2\pi V}{\hbar}\overline{\sum_{\vec{k}}}\sum_{\mu'}\sum_{\vec{k}'}|\,V_{\mu'\vec{k}'; \lambda}|^2\,\sigma_f^{(e)}(E(k') - E(k)). \tag{40}$$

Here V is the volume of the crystal.

According to (40), the main contribution to the nonradiative destruction rate of the triplet exciton by excess electrons arises from the difference of energies $E_{\mu'}(\vec{k}') - E_\mu(\vec{k})$ of the excess electron in the initial and final state near the energie

$E_f^{(e)}$ of the maximum of the emission band of the triplet exciton. Usually, the excitation energy $E_f^{(e)}$ is much higher than the electron affinity of the molecule A_g and the lowest energy band of the excess electron has relatively small band with [11]. Therefore in its final state the excess electron has a large kinetic energy and the energy band $E_{\mu'}(k')$ contributing most to the γ_e must belong to highly excited states with a large bandwith. In this case assuming that the matrix element $V_{\mu'\vec{k'};\,\mu\vec{k}}$ as function of $\vec{k'}$ varies slowly in the range of energies near the maximum of the emission band of the triplet exciton and summing over all $\vec{k}$ in the first Brillouin zone, we get the following approximate formula for γ_e:

$$\gamma_e = \frac{V^2}{4\pi^2\,\hbar} \sum_{\vec{k}} \int_F \frac{|\,V_{\mu'\vec{k'};\,\mu\vec{k}}\,|^2}{|\,\text{grad}_{\vec{k'}} E_{\mu'}(\vec{k'})\,|}\, dF \,. \tag{41}$$

In this formula, the integral is taken over the surface F of constant energy in the first Brillouin zone defined by the equation

$$E_{\mu'}(\vec{k'}) - E_{\mu\,\min} = E_f^{(e)} \,, \tag{42}$$

where $E_{\mu\,\min}$ is the minimum energy of the excess electron in its lowest energy band.

When the bound states of the excess electron in the field of the localized triplet electron excitation existe, we must consider the process of the nonradiative destruction of the triplet exciton by excess electrons as two step process with formation of the bound complex of the excess electron and triplet exciton. In this case the proper destruction process takes place in the second step as a monomolecular nonradiative decay of the bound complex of the excess electron and triplet exciton with the probability given by (39). Therefore we must consider in the general kinetic scheme of the time rate of the change of triplet excitons the time rate of the change of bound complexes of the excess electron and triplet exciton also.

8. Calculation of the Nonradiative Destruction Rate of the Triplet Exciton by Excess Electrons in the Anthracene Crystal

In order to obtain a rough estimate of the rate constant of the nonradiative destruction of the triplet exciton by excess electrons in the anthracene crystal, we use formula (41) under the assumptions listed below.

1) We suppose the molecule of the anthracene crystal to be planar. We assume the one-electron functions $\psi_{pf}(\vec{r})$ to be Hückel molecular orbitals represented as a linear combination of atomic orbitals with magnetic axis normal to the plane of the molecule.

Thus

(all atoms i of the p-th molecule)

$$\psi_{of}(\vec{r}) = \sum_i C_{if}\, \xi_i(\vec{r}) \tag{43}$$

where

$$\xi_i(r) = \left(\frac{a^5}{\pi}\right)^{1/2} r_i \cos \delta_i \exp\left(-a r_i\right) \tag{44}$$

is the known Slater $2p_z$ atomic orbital centered on the i-th atom of the molecule and C_{if} are the coefficients determined by the symmetry of the molecule. These coefficients for the anthracene molecule are given in [15].

2) We neglect all overlap integrals between atomic orbitals of the different atoms in the molecule.

3) We take the wave function of the excess electron with large kinetic energy in the final state to be the free electron wave function in a vacuum normalized in the volume V of the crystal. We express the energy of the excess electron in this vacuum plane wave state in the form [16]:

$$E_{\mu'}(k') = \frac{\hbar^2}{2m} k'^2 + 2I_c - I_g .$$

(45)

Here I_c is the ionisation energy of the crystal and I_g is the ionisation energy of the molecule in the gas phase. For simplicity we take the wave function of the excess electron in the initial state also to be normalized free electron plane wave and we write the enegy $E_{\mu \, \text{min}}$ in the form [16]:

$$E_{\mu \, \text{min}} = 2I_c - I_g - A_g .$$

(46)

4) We suppose the following unequalities to be fulfilled:

$$\frac{k_0}{a} \ll 1 ,$$

(47)

$$\frac{k'}{a} \ll 1 ,$$

(48)

$$ad \gg 1.$$

(49)

Here d is the minimum distance between the atoms in the molecule and k_0 is given by the expression

$$k_0 = \left(\frac{6\pi^2}{v_0} \right)^{1/3} .$$

(50)

5) We assume, that there is thermal equilibrium at temperature τ in the initial state. Then supposing, that this temperature is not too high, we carry out the sum and the average over initial states in (41) with the help of the approximate formula:

$$\overline{\sum_{\vec{k}}} \ldots = \frac{1}{8\pi^3} \left(\frac{2\pi \hbar^2}{m_\mu \varkappa \tau} \right)^{3/2} \int \exp \left(- \frac{\hbar^2 k^2}{2 m_\mu \varkappa \tau} \right) \ldots d^3\vec{k} .$$

(51)

Here m_μ is the effective mass of the excess electron at the bottom of its lowest energy band and $\varkappa$ is the Boltzmann constant.

Under all these assumptions and suppositions, we derive from (41) the approximate formula for the rate constant of the nonradiative destruction of the triplet exciton by the excess electrons in anthracene crystal:

$$\gamma_e = \frac{98e^4 m \, k_0'}{a^4 \hbar^3} \, G_{of}(\tau) .$$

(52)

Here
$$G_{of}(\tau) = \sum_{i=1}^{14} \sum_{j=1}^{14} C_{io}C_{if} \left\{ \exp\left[-\frac{m\mu\varkappa\tau}{2\hbar^2} d_{ij}^2 \right] j_0(k_0'd_{ij}) \right\}, \tag{53}$$

where $k_0'^2$ is determined by the expression for the conservation of energy

$$\frac{\hbar^2}{2m} k_0'^2 = E_f^{(e)} - A_g, \tag{54}$$

j_0 is the spherical Bessel function of the zeroth order and d_{ij} is the distance between the i-th and j-th atom in the molecule.

We see that for the values $E_f^{(e)} = 1.83$ eV [17], $a = 3.08 \cdot 10^8$ cm [18], $d = 1.39 \cdot 10^{-8}$ cm [15], $A_g = 0.55$ eV [16] of the anthracene crystal, the conditions (47), (48), (49) are good fulfilled at room temperature $\tau = 293$-K. Inserting these values in (52) and using the coefficients C_{io} and C_{if} for the highest filled and for the lowest unfilled orbital in the ground configuration of the anthracene molecule given in [15], we get:

$$\gamma_e = 2 \cdot 10^{-9} \text{ cm}^3 \text{ sec}^{-1} \tag{55}$$

for $m_\mu = 10^{-25}$ gr [17].

Considering the nonradiative destruction process of the triplet exciton by excess electrons as a diffusion controlled process we can derive according to [12], the following expression for the nonradiative destruction rate of the triplet exciton by excess electrons:

$$\gamma_{e \text{ dif}} = 4\pi(D_e + D_T) R_{eT}. \tag{56}$$

Here D_e is the diffusion coefficient of the excess electron and R_{eT} denote the distance to which the excess electron and triplet exciton must approach in order the destruction process of the triplet exciton takes place.

Taking $D_e \approx 1.3 \cdot 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$ [16], $D_T = 2 \cdot 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ [11] and $R_{eT} = R_0 = 4.8 \cdot 10^{-8}$ cm [11] we get with the help of the formula (56)

$$\gamma_{e \text{ dif}} \approx 8 \cdot 10^{-9} \text{ cm}^3 \text{ sec}^{-1}. \tag{57}$$

This value of $\gamma_{e \text{ dif}}$ may be considered as the lower limit because it is always $R_{eT} > R_0$.

The experimental value of γ_e according to [8] is

$$\gamma_{e \text{ exp}} = 1.1 \cdot 10^{-9} \text{ cm}^3 \text{ sec}^{-1}. \tag{58}$$

We see from (55), (57) and (58), that the calculated value of the rate constant γ_e and $\gamma_{e \text{ dif}}$ are in the agreement with the experimental)value within a factor 10 and that the rate constant γ_e calculated according to (55) is nearer to the experimental value (58) than minimum value of $\gamma_{e \text{ dif}}$ calculated according to (57). Therefore our calculations support the interpretation of the decrease of the triplet exciton lifetime in anthracene crystal in terms of the triplet exciton nonradiative destruction by excess electrons. From these calculations we can also conclude, that the determining process of the nonradiative destruction of the triplet exciton by excess electron is the

spontaneous nonradiative transition of the crystal from the initial state with one excess electron and one triplet exciton to the final state with one excess electron with higher excitation energy.

References

[1] KEARNS D. R.: J. Chem. Phys. **39** (1963), 2697.

[2] KEPLER R. G., CARIS I. C., AVAKIAN P., ABRAMSON E.: Phys. Rev. Letters **10** (1963), 400.

[3] HALL I. L., JENNINGS D. A., McCLINTOCK R. M.: Phys. Rev. Letters **11** (1963), 364.

[4] WEISZ S. Z., ZAHLAN A. B., SILVER M., JARNAGIN R. C.: Phys. Rev. Letters **12** (1964), 71.

[5] AVAKIAN P., ABRAMSON E., KEPLER R. G., CARIS I. C.: J. Chem. Phys. **39** (1963), 1127.

[6] SINGH S., JONES W. I., SIEBRAND W., STOICHEFT B. P., SCHNEIDER W. G.: J. Chem. Phys. **42** (1965), 330.

[7] BABENKO S. D., BENDERSKIJ V. A., GOLDANSKIJ V. I., LAVRUSHKO A. G., TYCHINSKIJ V. P.: Phys. stat. sol. (b) **45** (1971), 91.

[8] HELTRICH W.: Phys. Rev. Letters **16** (1966), 401.

[9] NORTHROP D. C., SIMPSON O.: Proc. Roy. Soc. (London) **A244** (1958), 377.

[10] SILVER M., WEISZ S. Z., KIM I. S., IARNAGIN R. C.: J. Chem. Phys. **39** (1963), 3163.

[11] JORTNER I., RICE S. A., KATZ L., CHOI S.: J. Chem. Phys. **42** (1965), 309.

[12] CHANDRASEKHAR S.: Rev. Mod. Phys. **15** (1943), 1.

[13] TAKENTI Y.: Progr. Theor. Phys. **18** (1957), 421.

[14] DAVYDOV A. S.: Soviet. Phys.-Uspekhi **82** (1964), 393.

[15] PARISER R.: J. Chem. Phys. **24** (1956), 250.

[16] LeBLANC O. H.: Physics and Chemistry of the Organic Solid State, Vol. III. J. Wiley & Sons-New York-London-Sydney 1967.

[17] GUTMANN F., LYONS L. E.: Organic Semiconductors, I. Wiley & Sons, New York – London – Sydney, 1967.

[18] SLATER I. C.: Phys. Rev. **36** (1930), 57.