

EXCITON-EXCITON INTERACTIONS IN MOLECULAR ORGANIC CRYSTALS

M. TRLIFAJ

*Institute of Physics, Czechoslovak Academy of Sciences, Prague 8,
Na Slovance 2, Czechoslovakia*

The main results of the theory of exciton-exciton interaction processes in molecular organic crystals are reviewed and discussed.

1. INTRODUCTION

The study of multiple exciton interactions in organic molecular crystals has been intensively pursued in recent years. This has been due to the fact that the exciton-exciton interactions can lead to different processes resulting in observable effects in organic crystals especially at high-exciton concentrations.

In this paper we review and discuss the exciton-exciton interactions leading to the formation of new excited states of the crystal represented by bound states of two or more excitons moving as a whole through the crystal, analogous to the Bethe spin wave complexes¹ and to the mutual non-radiative bimolecular annihilation of a pair of excitons resulting in one-electron excitation with higher excitation energy, especially at high-exciton concentrations.

The possibility of the existence of bound states of two excitons, called biexciton, has been formulated and theoretically discussed², but these have not yet been detected experimentally in organic molecular crystals.

The mutual non-radiative bimolecular annihilation of a pair of excitons due to their interaction is a well-established phenomenon. Its existence for singlet excitons was conjectured³ in an attempt to interpret the production of charge carriers in anthracene crystals and it has been invoked for this purpose by many workers since then^{4,5}. Although this mechanism of charge-carrier production is not proven, the presence of the annihilation process for singlet excitons in anthracene crystals has been demonstrated⁷. Dynamic interactions between pairs of excitons do not necessarily lead to the charge-carrier production and may result in a higher exciton state. These processes of mutual annihilation of triplet excitons with one resulting singlet exciton have been observed in naphthalene and phenanthrene crystals in the form of the observation of delayed fluorescence⁸, although the interpretation was suggested later^{9,10}. The conclusive evidence for explaining the delayed fluorescence in terms of triplet-triplet exciton annihilation in anthracene crystals was presented in 1963¹¹. Since then triplet-triplet exciton annihilation has been verified in anthracene crystals by others¹² and it has been observed in pyrene crystals¹³, naphthalene

crystals^{13, 14} and a number of mixed crystals^{10, 14, 15}. As an intermediate state, involved in this annihilating process of a pair of triplet excitons, a real¹⁶ or a virtual^{16, 17} charge-transfer exciton, formed by bound states of a positive and negative molecular ion pair, was considered.

The fluorescence quenching in anthracene crystals under high intensities of excitation was discovered and ascribed to singlet-singlet exciton annihilation resulting in one exciton with higher excitation energy^{18, 19}. The main process of quenching of fluorescence of the anthracene crystal under long illumination was interpreted¹⁹ as a mutual annihilation of a pair of singlet and triplet excitons leading to the formation of a triplet exciton with higher exciton energy.

We begin the review and discussion of the theory of the biexciton and non-radiative bimolecular annihilation processes of excitons with a brief description of the Frenkel molecular and charge-transfer excitons, with a brief description of their parent electron excitons of the crystal-molecular and charge transfer electron excitons and with an introduction of the crystal Hamiltonian describing the exciton-exciton interaction processes.

2. MOLECULAR AND CHARGE-TRANSFER ELECTRON EXCITATIONS OF THE CRYSTAL

We will consider a simple model of an organic crystal consisting of neutral molecules in a periodic arrangement with one molecule per unit cell held together by weak van der Waals forces, whose sites in the crystal are denoted by lattice vectors \mathbf{p} . There are N unit cells with volume v_0 in the crystal.

Because of the weakness of the intermolecular interactions the energy levels of the excited states of the electrons of the crystals are traceable to parent excited molecular states²⁰⁻²³. Assuming that each molecule of the crystal may be divided into π electrons and the core, the excited states of the isolated molecules can be described in a one-electron approximation. Using this model of excited states of the isolated molecule we will consider two types of parent electron excitations of the crystal.

As the first type we will consider the electron excitation constructed by the promotion of one π electron from the highest filled orbital $\psi_{\mathbf{p}0}(\mathbf{r})$ with energy ε_0 to all possible unfilled orbitals of the same molecule $\psi_{\mathbf{p}f}(\mathbf{r})$ with energies $\varepsilon_f > \varepsilon_0$ ($f > 0$) and quantum indices $f > 0$ in the ground state configuration of the molecule. These neutral electron excitations are called molecular electron excitations and are characterized with regard to the singlet or triplet spin states by the quantum indices f and $S = 0, 1$; $M = -S, \dots, +S$. Their quasi-boson^{22, 23} creations and annihilation operators at the \mathbf{p} th molecule of the crystal by $B_{\mathbf{p}f}^+(S, M_S)$, $B_{\mathbf{p}f}(S, M_S)$. These molecular electron excitations have the same excitation energy $E_f(S)$ independent of their location in the crystal.

As the second type of parent electron excitations we will consider a positive and a negative molecular ion pair constructed by the transfer of a π electron from the highest filled orbital of one neutral molecule of the crystal into an orbital $\psi_{\mathbf{p}\mu}(\mathbf{r})$ with energy ε_μ and quantum index μ in the Hartree field of another neutral molecule of the crystal. The creation and annihilation quasi-boson operators of this charge-transfer electron excitation

with excitation energy E_μ and with an excess electron and hole localized at the \mathbf{p}_1 th and \mathbf{p}_2 th molecules of the crystal are characterized with regard to the singlet ($S = M_S = 0$) or triplet ($S = 1; M_S = -1, 0, 1$) spin states by $B_{\mathbf{p}_1\mu, \mathbf{p}_2}^+(S, M_S), B_{\mathbf{p}_1\mu, \mathbf{p}_2}(S, M_S)$.

3. CRYSTAL HAMILTONIAN IN ELECTRON EXCITATION SECOND-QUANTIZED REPRESENTATION

Using the introduced models of parent electron excitations and Refs. 22, 23, and neglecting the interaction between the charge-transfer electron excitations, it is possible to write the crystal Hamiltonian describing the processes which we shall examine in the form

$$H = W_0 + {}^{\text{exc}}H_1 + {}^{\text{exc}}H_2 + {}^{\text{exc}}H_4 + H_3 + {}^{\text{ch}}H_0 \quad (1)$$

where W_0 is the energy of the quasi-vacuum of the electron excitations of the crystal, ${}^{\text{exc}}H_1$ is the Hamiltonian of the non-interacting molecular electron excitations given by

$${}^{\text{exc}}H_1 = \sum_{\mathbf{p}} \sum_f \sum_{S, M_S} E_f(S) B_{\mathbf{p}f}^+(S, M_S) B_{\mathbf{p}f}(S, M_S) \quad (2)$$

and

$${}^{\text{exc}}H_2 = \sum_{\mathbf{p}_1 \neq \mathbf{p}_2} \sum_f \sum_{S, M_S} {}^{\text{exc}}L_{fS}(\mathbf{p}_1 - \mathbf{p}_2) B_{\mathbf{p}_1 f_1}^+(S, M_S) B_{\mathbf{p}_2 f_2}(S, M_S) \quad (3)$$

describes the migration of the molecular electron excitations from one molecule to another through electrostatic and exchange interaction between molecules for singlet spin state $S = 0$ and through exchange interaction between molecules only for triplet state $S = 1$. The matrix elements ${}^{\text{exc}}L_{fS}(\mathbf{p}_1 - \mathbf{p}_2)$ characterize the electrostatic and exchange mechanism of the migration²²⁻²⁴.

The operator ${}^{\text{exc}}H_4$ contains quartic products of molecular electron excitation operators and describes the collision and reaction processes between pairs of molecular electron excitations:

$${}^{\text{exc}}H_4 = \frac{1}{2} \sum_{\mathbf{p}_1 \neq \mathbf{p}_2} \sum_{S_1, M_{S_1}, S_2, M_{S_2}} \sum_{f_1, f_1'} \sum_{f_2, f_2'} {}^{\text{exc}}U_{f_2 f_2'; f_1 f_1'}(\mathbf{p}_1 - \mathbf{p}_2) \times B_{\mathbf{p}_2 f_2'}^+(S_2, M_{S_2}) B_{\mathbf{p}_2 f_2}(S_2, M_{S_2}) B_{\mathbf{p}_1 f_1'}^+(S_1, M_{S_1}) B_{\mathbf{p}_1 f_1}(S_1, M_{S_1}) \quad (4)$$

where ${}^{\text{exc}}U_{f_2 f_2'; f_1 f_1'}(\mathbf{p}_1 - \mathbf{p}_2)$ are the matrix elements of the dynamic interaction between molecular electron excitations given in Ref. 25.

The Hamiltonian H_3 contains cubic products of the operators of the molecular electron excitations or the products of operators of two molecular electron excitations and of one operator of the charge-transfer electron operator of the form:

$$H_3 = \sum_{\left\{ \begin{smallmatrix} f \\ \mu \end{smallmatrix} \right\}} \sum_{\mathbf{p}_1 \neq \mathbf{p}_2} \sum_{f_1/2} \sum_{S_1, S_2} \sum_{S = |S_1 - S_2|}^{S_1 + S_2} \sum_{M_S} \{ U_{\left\{ \begin{smallmatrix} p_1 f_1 \\ p_2 \mu \end{smallmatrix} \right\}; \mathbf{p}_1 f_1, \mathbf{p}_2 f_2} \} (S_2 S_2 | S) \times B_{\left\{ \begin{smallmatrix} p_1 f_1 \\ p_2 \mu, \mathbf{p}_1 \end{smallmatrix} \right\}}^+(S, M_S) \left[\sum_{M_{S_1}} \sum_{M_{S_2}} (S_1 S_2 M_{S_1} M_{S_2} | S M_S) \times \delta_{M_{S_2}, M_S - M_{S_1}} B_{\mathbf{p}_2 f_2}(S_2, M_{S_2}) B_{\mathbf{p}_1 f_1}(S_1, M_{S_1}) \right] + \text{herm conj.} \} \quad (5)$$

where the first term describes the simultaneous non-radiative annihilation of two molecular electron excitations and creation of one molecular electron excitation or of one charge-transfer electron excitation, and the second hermite conjugate term describes the inverse process, i.e. the non-radiative decay of one molecular electron excitation or of one charge-transfer electron-excitation into a pair of molecular electron excitations. The well-known Condon-Shortley coefficients²⁶ $(S_1 S_2 M_{S_1} M_{S_2} | S M_S)$ couple the total spin angular momentum (S, M_S) with the spin angular momentum (S_1, M_{S_1}) and (S_2, M_{S_2}) of two molecular electron excitations and

$$U_{\substack{\{p_1, f_1\}, p_1, f_1, p_2, f_2 \\ \{p_2, f_2\}, p_1, f_1, p_2, f_2}}^{\text{elstat}} (S_1 S_2 | S) = \delta_{S,0} \text{elstat} U_{\substack{\{p_1, f_1\}, p_1, f_1, p_2, f_2 \\ \{p_2, f_2\}, p_1, f_1, p_2, f_2}} (S_1 S_2 | S) + \text{exch} U_{\substack{\{p_1, f_1\}, p_1, f_1, p_2, f_2 \\ \{p_2, f_2\}, p_1, f_1, p_2, f_2}} (S_1 S_2 | S) \quad (6)$$

Here

$$\text{elstat} U_{\substack{\{p_1, f_1\}, p_1, f_1, p_2, f_2 \\ \{p_2, f_2\}, p_1, f_1, p_2, f_2}} (S_1 S_2 | S) \quad \text{and} \quad \text{exch} U_{\substack{\{p_1, f_1\}, p_1, f_1, p_2, f_2 \\ \{p_2, f_2\}, p_1, f_1, p_2, f_2}} (S_1 S_2 | S)$$

are the matrix elements characterizing the electrostatic and the exchange mechanisms of the non-radiative fusion of two molecular electron excitations (f_1, S_1) , (f_2, S_2) into one molecular electron excitation (f', S) localized at the p th molecule of the crystal, or into one charge-transfer electron excitation with the excess hole localized at the p_1 th molecule of the crystal and with the excess electron in the state μ localized at the p_2 th molecule of the crystal, both fulfilling the condition:

$$\begin{matrix} \{\text{elstat}\} \\ \{\text{exch}\} \end{matrix} U_{\substack{\{p_1, f_1\}, p_1, f_1, p_2, f_2 \\ \{p_2, f_2\}, p_1, f_1, p_2, f_2}} (S_1 S_2 | S) = \begin{matrix} \{\text{elstat}\} \\ \{\text{exch}\} \end{matrix} U_{\substack{\{p_1, f_1\}, p_1, f_1, p_2, f_2 \\ \{p_2, f_2\}, p_1, f_1, p_2, f_2}} (S_2 S_1 | S) \quad (7)$$

The Hamiltonian:

$$\begin{aligned} \text{eh}H_0 = & \sum_{p_1, \mu} \sum_{p_2} \sum_{S, M_S} E_{\mu} B_{p_1, \mu, p_2}^+ (S, M_S) B_{p_1, \mu, p_2} (S, M_S) \\ & + \sum_{p_1, \mu, p_2} \sum_{p, \mu, p} \sum_{S, M_S} [\text{eh}L_{p_1, \mu, p_2'; p_1, \mu, p_2} + \text{eh}U_{p_1, \mu, p_2'; p_1, \mu, p_2} (S)] \\ & \times B_{p_1, \mu, p_2'}^+ (S, M_S) B_{p_1, \mu, p_2} (S, M_S) \quad (8) \end{aligned}$$

describes the behaviour of the charge-transfer electron excitations migrating through the crystal. Here $\text{eh}L_{p_1, \mu, p_2'; p_1, \mu, p_2}$ are the matrix elements of the migration of the charge-transfer electron excitation through the transfer of the excess electron ($p_2' = p_2$) and the excess hole ($p_1' = p_1$) from one molecule to another, and $\text{eh}U_{p_1, \mu, p_2'; p_1, \mu, p_2} (S)$ is the matrix element characterizing the electrostatic and exchange interaction^{2b} between the excess electron, the hole being different from zero for $p_1' = p_1, p_2' = p_2$ or $p_1' = p_2, p_2' = p_1$.

4. MOLECULAR AND CHARGE-TRANSFER EXCITONS

(a) Molecular excitons

Using the translational symmetry of the crystal, the Hamiltonian $\text{exc}H_0 = \text{exc}H_1 + \text{exc}H_2$, describing the behaviour of the migrating molecular electron excitations, can be diagonalized in the form^{22, 23}:

$${}^{\text{exc}}H_0 = \sum_{kf} \sum_{SM_S} E_{fS}(\mathbf{k}) B_{kf}^+(S, M_S) B_{kf}(S, M_S) \quad (9)$$

$$B_{kf}^+(S, M_S) = \frac{1}{N^{\frac{1}{2}}} \sum_{\mathbf{p}} \exp [i(\mathbf{k} \cdot \mathbf{p})] B_{\mathbf{p}f}^+(S, M_S) \quad (10)$$

$$E_{fS}(\mathbf{k}) = E_f(S) + {}^{\text{exc}}L_{fS}(\mathbf{k}) \quad (11)$$

$${}^{\text{exc}}L_{fS}(\mathbf{k}) = \sum_{\mathbf{p} \neq 0} {}^{\text{exc}}L_{fS}(\mathbf{p}) \exp [i(\mathbf{k} \cdot \mathbf{p})] \quad (12)$$

Here $B_{kf}^+(S, M_S)$, $B_{kf}(S, M_S)$ are the creation and annihilation operators of the coherent electron excitation wave with spin (S, M_S) and with quasi-wave vector \mathbf{k} assuming any of N values in the first Brillouin zone of the reciprocal space of the crystal. This collective electron excitation is called the Frenkel or molecular exciton and, according to equations 11 and 12, its energies form a band containing N states. This description of the behaviour of the molecular electron excitation in the crystal is correct if the mean free path l_{fS} of the molecular exciton, determined through incoherent colliding with the thermal or other fluctuations of the crystal, is considerably larger than the lattice spacing characterized by the quantity

$$R_0 = v_0^{\frac{1}{2}} \quad (13)$$

But if $l_{fS} \approx R_0$, the quasi-wave vector \mathbf{k} is not a good quantum number and the migration of the molecular electron excitation must be described in the random-walk model as a random incoherent hopping from one molecule to another with the probability per second determined by the transfer matrix element ${}^{\text{exc}}L_{fS}(\mathbf{p})$ ^{17, 27}. In the diffusion approximation this motion is that of the molecular electron excitation characterized by the diffusion coefficient^{17, 27};

$$D_{fS}(i, j) = \frac{1}{2} \sum_{\mathbf{p} \neq 0} w_{fS}(\mathbf{p})(\mathbf{p} \cdot \mathbf{e}_i)(\mathbf{p} \cdot \mathbf{e}_j); i, j = 1, 2, 3 \quad (14)$$

Here $w_{fS}(\mathbf{p})$ is the probability per second of the non-radiative transition of the molecular electron excitation fS from the reference molecule to the molecule at the distance \mathbf{p} under the intermolecular interaction characterized by the matrix element ${}^{\text{exc}}L_{fS}(\mathbf{p})$, and \mathbf{e}_i ($i = 1, 2, 3$) are the unit vectors of the Cartesian coordinate axis.

(b) Charge-transfer excitons

Using translational symmetry of the crystal and the results and the methods described in Ref. 28, the Hamiltonian ${}^{\text{eh}}H_0$, describing the behaviour of the charge-transfer electron excitations in the crystal, takes the following diagonalized form:

$${}^{\text{eh}}H_0 = \sum_{\alpha, \lambda} \sum_{\mu, \mathbf{K}} \sum_{SM_S} E_{\alpha\lambda; \mu S}(\mathbf{K}) B_{\alpha\lambda\mu; \mathbf{K}}^+(S, M_S) B_{\alpha\lambda\mu; \mathbf{K}}(S, M_S) \quad (15)$$

$$\begin{aligned} B_{\alpha\lambda\mu; \mathbf{K}}^+(S, M_S) = & \frac{1}{2N^{\frac{1}{2}}} \sum_{\mathbf{p}_1 \neq \mathbf{p}_2} \exp \left[i \left(\frac{\mathbf{K}}{2} \cdot \mathbf{p}_1 + \mathbf{p}_2 \right) \right] D_{\rho}(\alpha\lambda\mathbf{K}; \mu SM_S) \\ & \times \{ B_{\mathbf{p}_1\mu, \mathbf{p}_2}^+(S, M_S) + (-1)^{\alpha} B_{\mathbf{p}_2\mu, \mathbf{p}_1}^+(S, M_S) \}; \alpha = 0, 1 \end{aligned} \quad (16)$$

Here $B_{\alpha\lambda\mu; \mathbf{K}}^+(S, M_S)$, $B_{\alpha\lambda\mu; \mathbf{K}}(S, M_S)$ are the creation and annihilation operators

of the coherent excitation wave with spin (S, M_S) and with quasi-wave vector \mathbf{K} characterizing the motion of the charge-transfer electron excitation in the crystal as a whole, $E_{\alpha\lambda; \mu S}(\mathbf{K})$ is the excitation energy of this wave, $\alpha = 0, 1$ are the parity quantum numbers and $\boldsymbol{\rho} = \mathbf{p}_1 - \mathbf{p}_2$ is the distance between the excess electron and hole. The coefficients $D_{\boldsymbol{\rho}\alpha\lambda\mathbf{K}; \mu SM_S}$ fulfilling the normalization condition

$$\sum_{\boldsymbol{\rho} \neq 0} |D_{\boldsymbol{\rho}\alpha\lambda\mathbf{K}; \mu SM_S}|^2 = 1 \quad (17)$$

and the conditions

$$D_{-\boldsymbol{\rho}}(\alpha\lambda\mathbf{K}; \mu SM_S) = (-1)^2 D_{\boldsymbol{\rho}}(\alpha\lambda\mathbf{K}; \mu SM_S) \quad (18)$$

$$D_{\boldsymbol{\rho}=0}(\alpha\lambda\mathbf{K}; \mu SM_S) = 0 \quad (19)$$

are the wave functions of the relative motion of the excess electron and hole, the stationary states of which are characterized by the quantum indices λ .

Let us introduce the energy $\varepsilon_{\mu}(\boldsymbol{\kappa}, \mathbf{K})$ of the non-interacting excess electron-hole pair with the help of the relationship:

$$\begin{aligned} \varepsilon_{\mu}(\boldsymbol{\kappa}, \mathbf{K}) = \frac{1}{2} \left[\varepsilon_{\mu} \left(\boldsymbol{\kappa} + \frac{\mathbf{K}}{2} \right) - \varepsilon_0 \left(\boldsymbol{\kappa} + \frac{\mathbf{K}}{2} \right) \right] \\ + \frac{1}{2} \left[\varepsilon_{\mu} \left(\boldsymbol{\kappa} - \frac{\mathbf{K}}{2} \right) - \varepsilon_0 \left(\boldsymbol{\kappa} - \frac{\mathbf{K}}{2} \right) \right] \quad (20) \end{aligned}$$

Here the quasi-wave vector $\boldsymbol{\kappa}$ characterizes the relative motion of the non-interacting excess-electron hole pair as a good quantum number, $\varepsilon_{\mu}(\mathbf{k})$ is the energy of the excess electron with quasi-wave vector \mathbf{k} belonging to the parent orbital of the negative molecular ion with quantum index μ , and $\varepsilon_0(\mathbf{k})$ is the energy of the excess hole with quasi-wave vector \mathbf{k} belonging to the parent orbital $f = 0$ of the positive molecular ion. The explicit expressions for the energies $\varepsilon_{\mu}(\mathbf{k})$, $-\varepsilon_0(\mathbf{k})$ are given for example in Ref. 29. The energies of a non-interacting excess electron-hole pair for a given quasi-wave vector \mathbf{K} , describing its motion as a whole, form a band between the minimum value $\min \varepsilon_{\mu}(\boldsymbol{\kappa}, \mathbf{K})$ and the maximum value $\max \varepsilon_{\mu}(\boldsymbol{\kappa}, \mathbf{K})$ ²¹.

Then using the results of the mathematical analysis²⁸, we conclude that for the given \mathbf{K} :

(i) There exist stationary states of the interacting and migrating excess electron-hole pair which for $N \rightarrow \infty$ have a continuous energy spectrum in the range:

$$\min \varepsilon_{\mu}(\boldsymbol{\kappa}, \mathbf{K}) \leq E_{\gamma\lambda; \mu S}(\mathbf{K}) \leq \max \varepsilon_{\mu}(\boldsymbol{\kappa}, \mathbf{K}) \quad (21)$$

i.e. in the band of the energies of the non-interacting excess electron-hole pair. These states describe the scattering of the excess electron and hole caused by their dynamic interaction and they may also be called 'ionization continuum' states²⁸. In these scattering states, the excess electron and hole may become freely moving when an electric field is applied.

(ii) Because of attractive long-ranged forces between the excess electron and hole, for $N \rightarrow \infty$ there also exist stationary states with a discrete

spectrum of energies in the range:

$$E_{\alpha\lambda; \mu S}(\mathbf{K}) < \min \varepsilon_{\mu}(\boldsymbol{\kappa}, \mathbf{K}) \quad (22)$$

These states belong to the bound states of the relative motion of the excess electron and hole. In this case the bounded excess electron-hole pair moves as a whole through the crystal in the form of a coherent excitation wave with quasi-wave vector \mathbf{K} called charge-transfer exciton. The corresponding energies $E_{\alpha\lambda; \mu S}(\mathbf{K})$ for given α, λ, μ, S form a band containing N states.

The occurrence of charge-transfer excitons in molecular organic crystals has been discussed³⁰. Experimental evidence for the existence of charge-transfer excitons is meagre. The only reported experimental determination of the energies of charge-transfer exciton states is that of Pope *et al.*³¹.

5. MOLECULAR BIEXCITONS

If the cubic and quartic anharmonicity interaction terms H_3 and ${}^{\text{exc}}H_4$ of the molecular electron excitations are taken into consideration, and if we use the translational symmetry of the crystal, the creation and annihilation operators $B_{\beta\nu\mathbf{K}; f_1S_1, f_2S_2}^+(S, M_S)$ and $B_{\beta\nu\mathbf{K}; f_1S_1, f_2S_2}(S, M_S)$ of two interacting and migrating molecular electron excitations f_1S_1, f_2S_2 with total spin quantum numbers (S, M_S) , diagonalizing approximately the Hamiltonian ${}^{\text{exc}}H = {}^{\text{exc}}H_1 + {}^{\text{exc}}H_2 + {}^{\text{exc}}H_3 + {}^{\text{exc}}H_4$ in the subspace of two exciton states, can be written in the form:

$$B_{\beta\nu\mathbf{K}; f_1S_1, f_2S_2}^+(S, M_S) = \frac{1}{2[N(1 + (-1)^\beta \delta_{f_1f_2} \delta_{S_1S_2})]^\frac{1}{2}} C_{\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S) \\ \times \left\{ \sum_{M_{S_1} M_{S_2}} (S_1S_2M_{S_1} M_{S_2} | SM_S) \delta_{M_{S_2}, M_S - M_{S_1}} [B_{\rho_1f_1}(S_1, M_{S_1})^+ \right. \\ \times B_{\rho_2f_2}(S_2, M_{S_2}) + (-1)^{\beta+S_1+S_2-S} B_{\rho_1f_2}(S_2, M_{S_2}) B_{\rho_2f_1}(S_1, M_{S_1})] \left. \right\}; \\ \beta = 0, 1 \quad (23)$$

Here $\boldsymbol{\rho} = \boldsymbol{\rho}_1 - \boldsymbol{\rho}_2$ is the coordinate of the relative motion of the interacting pair of molecular electron excitations, \mathbf{K} is the quasi-wave vector characterizing the motion of the interacting pair of molecular electron excitations as a whole and $\beta = 0, 1$ are the parity quantum numbers. The set of coefficients $C_{\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S)$ for all $\boldsymbol{\rho} \neq 0$ is the wave function of the relative motion of the interacting pair of molecular electron excitations, the stationary states of which are characterized by the quantum indices ν and it fulfils for given \mathbf{K} the following important conditions and relationships:

$$\sum_{\rho \neq 0} |C_{\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S)|^2 = 1 \quad (24)$$

$$C_{\rho=0}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S) = 0 \quad (25)$$

$$C_{-\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S) = (-1)^{\beta+S_1+S_2-S} C_{\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S) \quad (26)$$

$$C_{\rho}(\beta\nu\mathbf{K}; f_2S_2, f_1S_1; SM_S) = (-1)^{\beta} C_{\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S) \quad (27)$$

Using the Fourier transformation, we can derive for the coefficients $C_{\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S)$ the following set of difference equations:

$$C_{\rho}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S) = \sum_{\rho'} G_{\beta\nu\mathbf{K}; f_1S_1, f_2S_2}(\rho - \rho') \times \text{exc}U_{\beta; f_1S_1, f_2S_2}(\rho') C_{\rho'}(\beta\nu\mathbf{K}; f_1S_1, f_2S_2; SM_S) \quad (28)$$

where

$$\text{exc}U_{\beta; f_1S_1, f_2S_2}(\rho) = 2[1 + (-1)^{\beta} \delta_{f_1f_2} \delta_{S_1S_2}]^{-1} \times \{ \text{exc}U_{f_1f_1; f_2f_2}(\rho) + (-1)^{\beta} \delta_{S_1S_2} \text{exc}U_{f_1f_2; f_2f_1}(\rho) \} \quad (29)$$

is the matrix element of the adiabatic interaction between two molecular electron excitations f_1S_1, f_2S_2 , localized at the ρ_1 th and ρ_2 th molecules of the crystal, and

$$G_{\beta\nu\mathbf{K}; f_1S_1, f_2S_2}(\rho - \rho') = N^{-1} \sum_{\mathbf{\kappa}} \frac{\exp[i(\mathbf{\kappa} \cdot \rho - \rho')]}{[E_{\beta\nu; f_1S_1, f_2S_2; S}(\mathbf{K}) - E_{f_1S_1, f_2S_2}(\mathbf{\kappa}, \mathbf{K})]} \quad (30)$$

In this expression, $E_{\beta\nu; f_1S_1, f_2S_2; S}(\mathbf{K})$ is the excitation energy of the interacting pair of molecular excitations and

$$E_{f_1S_1, f_2S_2}(\mathbf{\kappa}, \mathbf{K}) = \frac{1}{2} \left[E_{f_1S_1} \left(\mathbf{\kappa} + \frac{\mathbf{K}}{2} \right) + E_{f_2S_2} \left(\mathbf{\kappa} + \frac{\mathbf{K}}{2} \right) \right] + \frac{1}{2} \left[E_{f_1S_1} \left(\mathbf{\kappa} - \frac{\mathbf{K}}{2} \right) + E_{f_2S_2} \left(\mathbf{\kappa} - \frac{\mathbf{K}}{2} \right) \right] \quad (31)$$

are the energies of two non-interacting molecular excitons f_1S_1, f_2S_2 ; the relative motion of these is characterized by the quasi-wave vector $\mathbf{\kappa}$ as a good quantum number. Energies (equation 31) form a band ranging for the given \mathbf{K} from the minimum value $\min E_{f_1S_1, f_2S_2}(\mathbf{\kappa}, \mathbf{K})$ to the maximum value $\max E_{f_1S_1, f_2S_2}(\mathbf{\kappa}, \mathbf{K})$.

The excitation energies $E_{\beta\nu; f_1S_1, f_2S_2; S}(\mathbf{K})$ are determined by the secular equation of equation 29, i.e. by the equation:

$$\det \{ \delta_{\rho\rho'} - G_{\beta\nu\mathbf{K}; f_1S_1, f_2S_2}(\rho - \rho') \text{exc}U_{\beta; f_1S_1, f_2S_2}(\rho') \} = 0 \quad (32)$$

Equations 28 and 32 are similar in form to the one derived for the study of stationary states of two interacting magnons³². Using the results of the general mathematical analysis³², it can be shown that equation 32 for the given \mathbf{K} has N roots in the range of energies:

$$\min E_{f_1S_1, f_2S_2}(\mathbf{\kappa}, \mathbf{K}) \leq E_{\beta\nu; f_1S_1, f_2S_2; S}(\mathbf{K}) \leq \max E_{f_1S_1, f_2S_2}(\mathbf{\kappa}, \mathbf{K}) \quad (33)$$

passing over for $N \rightarrow \infty$ into the continuous band spectrum of energies of two non-interacting excitons. These solutions correspond to the scattering states of two interacting molecular electron excitations or of two interacting molecular excitons.

Equation 32 can also have singular and discrete roots for $N \rightarrow \infty$ in the

range of energies :

$$\left. \begin{aligned} E_{\beta\nu; f_1S_1, f_2S_2; S}(\mathbf{K}) &< \min E_{f_1S_1, f_2S_2}(\boldsymbol{\kappa}, \mathbf{K}) \\ E_{\beta\nu; f_1S_1, f_2S_2; S}(\mathbf{K}) &> \max E_{f_1S_1, f_2S_2}(\boldsymbol{\kappa}, \mathbf{K}) \end{aligned} \right\} \quad (34)$$

i.e. under and above the energy band of two non-interacting excitons. Because of short-ranged interaction forces between the molecular excitations, the number of discrete roots is at most finite. The solutions with a discrete energy spectrum belong to the bound states of the relative motion of two interacting electron excitations. In this case, a bound pair of interacting molecular electron excitations moves as a whole through the crystal in the form of a coherent excitation wave called molecular biexciton. The energies of this molecular biexciton as a whole form, according to equation 32, a band containing N states. The number of these bands for given β , f_1S_1 , f_2S_2 and S is determined by the number of discrete roots of equation 32.

The intensity of the absorption band of the molecular biexciton is mainly determined by the matrix element of the radiative transition from the ground state of the crystal to its excited state with one molecular biexciton. To calculate this matrix element a second-order time-perturbation theory is used, treating the sum of Hamiltonians $H_3 + H_{\text{rad}}$ as perturbation causing the radiative transition, where H_{rad} is the Hamiltonian of the interaction of the molecular and charge-transfer electron excitations with the radiation field. In carrying out these calculations we drew the following conclusions which were also partly reached by other workers^{2c, 2h}.

(i) The one-phonon excitation process creates singlet molecular biexcitons formed by two singlet or triplet molecular electron excitations. This excitation process goes through the excitation of virtual singlet molecular or charge-transfer excitons and it is this process which governs the absorption polarization in the corresponding frequency region.

(ii) The two-photon excitation process creates singlet molecular biexcitons formed only by two singlet molecular electron excitations. This excitation process goes stepwise through the virtual excitation of two molecular electron excitations. In this case, the absorption polarization is determined by the absorption polarization of single molecular excitons forming the molecular biexciton.

The coherent biexcitons in organic molecular crystals have been studied theoretically^{2c-e, g-i}, but, as was said in the introduction, they have not yet been detected experimentally.

The description of a molecular biexciton in the form of a coherent excitation wave equation 23 is possible, provided that the mean free paths $l_{f_1S_1}$, $l_{f_2S_2}$ of the molecular excitons forming the molecular biexciton are very large compared with the lattice spacing R_0 . If one of the molecular excitons, say the f_2S_2 forming molecular biexciton, moves in its free state in incoherent form, i.e. $l_{f_2S_2} \approx R_0$, then under suitable conditions the motion of the molecular biexciton as a whole is best viewed as an incoherent random hopping of the molecular electron excitation f_2S_2 with the bound molecular electron excitation f_1S_1 from one molecule to another (incoherent molecular biexciton)³³.

If both molecular excitons move in their free state in an incoherent form,

i.e. if $l_{f_1S_1} \approx l_{f_2S_2} \approx R_0$, the interaction between them can lead generally to the dependence of their hopping rates on their separation. But neglecting this dependence does not lead to serious errors because of short-ranged interaction forces between the excitons, especially at higher temperatures.

6. GAS KINETIC AND DIFFUSION THEORY OF TWO EXCITON NON-RADIATIVE ANNIHILATION

All mutual non-radiative annihilation processes of a pair of molecular excitons through their interaction, mentioned in the introduction, are conveniently described by the equations:

$$\frac{dn_{f_iS_i}(t)}{dt} = -\gamma n_{f_1S_1}(t)n_{f_2S_2}(t); \quad i = 1, 2 \quad (35)$$

where $n_{f_iS_i}(t)$ ($i = 1, 2$) are the concentrations of annihilating molecular excitons at the time t , and γ is the overall bimolecular annihilation rate constant. The aim of the theory is to calculate the bimolecular constant γ for all possible channels of the non-radiative annihilation.

The first-order processes determine the following channels of the non-radiative annihilation of a pair of molecular excitons: (i) the formation of a real molecular exciton with a higher excitation energy¹⁷, (ii) the formation of one real charge-transfer exciton followed by its transformation into one molecular exciton³⁴ and (iii) the formation of a real 'ionization continuum' state of the charge-transfer exciton³.

The two exciton non-radiative annihilation processes may also have an intermediate stage—the formation of real or virtual bound states of two molecular electron excitons. If we neglect this intermediate effect of the binding energy of two molecular excitons known to be very small³⁵, then it is necessary for the calculation of the rate constants γ_i ($i = 1, 2, 3$) for the channels mentioned to consider two rate-determining processes governing the magnitude of γ_i ^{7, 34, 36}: (a) the diffusive migration of the two excitons towards (as well as away from) one another, and (b) the non-radiative annihilation of the two excitons through spontaneous non-radiative transition to the final state once they are at sufficiently close relative distance R_{ef} to interact.

If the condition

$$R_0 \leq R_{ef} \ll l_{f_1S_1}, l_{f_2S_2} \quad (36)$$

is fulfilled, then, (i) the diffusive migration of the two excitons can be neglected and the rate-determining step is the process (b), and (ii) the rate constant γ is determined through the non-radiative spontaneous transition of the crystal from the initial state with one coherent molecular biexciton in a 'dissociation continuum' state into the final state with one of the electron excitations determining the annihilation channels.

Using in this gas kinetic limit the first-order time-dependent perturbation theory with H_3 as the perturbation operator and denoting the initial and final energies and state vectors of the channels determining the excited electron states of the crystal by E_{in} , $|in\rangle$ and ${}^iE_{fin}$, $|fin\rangle$ ($i = 1, 2, 3$) respectively

we obtain the following formulae for the two molecular exciton annihilation processes:

$$\gamma_{i\text{trans}} = \frac{2\pi N v_0}{\hbar} \sum_{(\text{fin})} \sum_{(\text{in})} g_{\text{in}} |{}^i\langle \text{fin} | H_3 | \text{in} \rangle|^2 \sigma({}^i E_{\text{fin}} - E_{\text{in}}) \quad i = 1, 2, 3 \quad (37)$$

Here the sum $\sum_{(\text{fin})}$ is the summation over all possible one molecular exciton states for $i = 1$, over all possible charge-transfer exciton states with λ belonging to the discrete states for $i = 2$ and to the continuous states for $i = 3$. The sum $\sum_{(\text{in})}$ is the thermodynamic average over all possible 'dissociation continuum' states of the molecular biexciton in the initial state of the crystal, and g_{in} is the weight factor of the initial excited electron state of the crystal. The quantity $\sigma({}^i E_{\text{fin}} - E_{\text{in}})$ is the effective density of the final excited electron states, determined through the incoherent interaction of electron excitations with thermal or other fluctuations of the crystal, this interaction giving a finite non-radiative lifetime as well as a non-zero width of absorption and emission lines^{34,37}.

Constructing the state vectors $|\text{in}\rangle, |\text{fin}\rangle^i$ of the initial and final states with the help of the operators of equations 23 and 26, the transition matrix elements ${}^i\langle \text{fin} | H_3 | \text{in} \rangle$ for the single channels ($i = 1, 2, 3$) can be written in the form:

$${}^1\langle \text{fin} | H_3 | \text{in} \rangle = U_{\beta\nu; \mathbf{K}}(f_1 S_1, f_2 S_2; SM_S) + U_{\beta\nu; \mathbf{K}}(f_2 S_2, f_1 S_1; SM_S) \quad (38)$$

$${}^{2,3}\langle \text{fin} | H_3 | \text{in} \rangle = U_{\alpha\lambda; \beta\nu; \mathbf{K}}(f_1 S_1, f_2 S_2; SM_S) + U_{\alpha\lambda; \mathbf{K}}(f_1 S_1, f_2 S_2; SM_S) \quad (39)$$

where

$$U_{\beta\nu; \mathbf{K}}(f_1 S_1, f_2 S_2; SM_S) = \sum_{\rho \neq 0} \exp\left[-i\left(\frac{\mathbf{K}}{2} \cdot \boldsymbol{\rho}\right)\right] \times C_{\rho}(\beta\nu\mathbf{K}; f_1 S_1, f_2 S_2; SM_S) U_{\mathbf{p}_1 f_1; \mathbf{p}_1 f_1, \mathbf{p}_2 f_2}(S_1 S_2 | S) \quad (40)$$

and

$$U_{\alpha\lambda; \beta\nu; \mathbf{K}}(f_1 S_1, f_2 S_2; SM_S) = \sum_{\rho \neq 0} C_{\rho}(\beta\nu\mathbf{K}; f_1 S_1, f_2 S_2; SM_S) \times D_{\rho}^*(\alpha\lambda\mathbf{K}; \mu SM_S) U_{\mathbf{p}_2 \mu; \mathbf{p}_1 f_1, \mathbf{p}_2 f_2}(S_1 S_2 | S) \quad (41)$$

From these formulae we conclude that exclusive of the effective density of the final excited electron states: (i) the generation of a singlet molecular or charge-transfer exciton via two singlet molecular exciton interaction and of a triplet molecular or charge-transfer exciton via the interaction of a singlet molecular exciton with a triplet molecular exciton takes place with identical rates through the electrostatic and exchange mechanism of the non-radiative transfer of excitation energy; and (ii) the generation of a singlet molecular exciton or of a charge-transfer exciton, or the generation of a triplet or charge-transfer exciton via interaction of two triplet molecular excitons takes place with identical rates through the exchange mechanism of the non-radiative transfer of excitation energy only.

The approximate calculations of the rate constants $\gamma_{i\text{trans}}$ ($i = 1, 2, 3$), according to equation 37 with a simplified model for the effective density

$\sigma(E)$ of the final state, were performed for the following two molecular exciton annihilation processes: (i) The non-radiative annihilation of a singlet coherent molecular exciton on an incoherent triplet molecular electron excitation resulting in one incoherent triplet molecular exciton³⁸. As the effective density of the final states $\sigma(E)$, the effective density of states of an incoherent, hopping triplet molecular exciton in a strong interaction with the vibrations of the crystal was used. The rough estimate $\gamma_{1\text{trans}}$ for the anthracene crystal gives the value $\gamma_{1\text{trans}} = 5 \times 10^{-8} \text{ cm}^3 \text{ s}^{-1}$ which is not too far from the experimental value $\gamma_{1\text{trans}} = (7 \pm 4) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ¹⁹. (ii) The non-radiative generation of a pair of charge carriers—of free excess electron with high kinetic energy, and a hole moving incoherently in the crystal—as a result of the annihilation of two coherent singlet molecular excitons^{4a, b, 33}. The density of the final states of the free electron in vacuum was taken as the effective density of the final states^{4a, 39}. The calculated rate constant $\gamma_{3\text{trans}} = 2.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ for the anthracene crystal is in good agreement with the experimental value of $\gamma_{3\text{trans}} = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ^{5a}. The theory presented by Kearns^{4b} was extended to triplet–triplet and triplet–singlet coherent molecular exciton annihilation^{4a, 39}.

The rate constant γ for the charge-transfer exciton annihilation channel of two triplet molecular excitons, as the transition rate to the final state, was calculated³⁴ under the assumption that:

$$I_{f_1S_1} \approx I_{f_2S_2} \approx R_0 \approx R_{\text{ef}} \quad (42)$$

i.e. that the propagation of the triplet molecular excitons can be described in the random-walk model. The effective density of the final states was calculated assuming that only the totally symmetric intramolecular C–C stretching modes are active, including intermolecular vibrations phenomenologically. Under the same condition 42 the matrix element of the annihilation process of two triplet molecular excitons was calculated as a second-order process involving the charge-transfer exciton states as virtual states¹⁷.

If condition 42 is fulfilled, the diffusive motion of the molecular excitons must be taken into consideration in an estimation of γ . The first estimate of γ on condition that the diffusion encounter process of triplet molecular excitons constitutes the rate-determining step, was given by Jortner *et al.*¹⁷, and was based on the assumption that the annihilations occur whenever two triplet molecular excitons are on nearest neighbour lattice sites, i.e.

$$\gamma_{\text{dif}} = 8\pi D_T R_0 \quad (43)$$

where D_T is the isotropic macroscopic diffusion constant of triplet molecular exciton. This estimate clearly places an upper limit on γ if annihilation of two adjacent triplet molecular excitons is sufficiently fast. But the measurement of the dependence of γ on the magnetic field for the triplet–triplet molecular exciton annihilation process^{41b, d}, indicates that both the rate-determining processes—the encounter and transition processes—occur at comparable rates. Therefore a stronger diffusion theory for the calculation of γ was developed^{34, 36}. These theories analyse qualitatively and quantitatively the dependence of the rate constant γ on the rate of encounter of two triplet molecular excitons and the transition rate to the final state. A relatively

simple form of the formula for γ was derived³⁶, which for the three-dimensional crystal is roughly given by:

$$\gamma = \frac{\gamma_{\text{dif}} \gamma_{\text{trans}}(R_0)}{\gamma_{\text{dif}} + \gamma_{\text{trans}}(R_0)} \quad (44)$$

Here γ_{dif} is the encounter rate of diffusing triplet molecular excitons given by equation 43 and $\gamma_{\text{trans}}(R_0)$ is the transition rate constant to the final state at the relative distance of molecular excitons R_0 . The rate constant has been calculated for naphthalene, anthracene and tetracene crystals³⁴. The calculated value $\gamma = 4 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for the anthracene crystal is in good agreement with the experimental value of $\gamma = (2 \text{ to } 5) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$.

It should be emphasized that this diffusion theory of rate constant γ ^{34, 36} is applicable on the following assumptions: (i) the molecular excitons satisfy the hopping equation of motion, (ii) the effects of the binding process—of biexcitons—can be neglected. Both these assumptions can be fulfilled for triplet molecular excitons at high temperatures, but not for molecular excitons with a larger length of coherence and not for all types of molecular excitons at low temperatures. Therefore the inclusion of binding and band effects would necessitate a new development of the diffusion theory.

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