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The Coupled Coherent and Incoherent Exciton Motion and its Influence on Optical Absorption, Electron Spin Resonance and Nuclear Spin Resonance

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The coupled coherent and incoherent motion of Frenkel excitons is treated by a model calculation comprising both its coherent and its incoherent motion. The coherent motion is determined by the exchange interaction integral J whereas the incoherent motion is described by the strengths of the local (γ_0) and non-local (γ_1) fluctuations. Calculation of the optical absorption of systems with two differently oriented molecules per unit cells results in the Davydow-splitting given by $\Delta = 8J$ and the linewidth given by $\Gamma = \gamma_0 + \gamma_1$. From the equation of motion of the density matrix we derive a diffusion equation. The comparison with data of optical absorption and diffusion measurements allows to determine all parameters of the system. Using these numerical values and the criterium of Haken and Strobl, we derive that at room temperature the exciton motion is incoherent and may be described by a hopping process whereas at low temperature it is coherent. The interaction of the spin of the triplet exciton with its surroundings is described by the usual spin-Hamiltonian which is, however, simplified to a spin 1/2 particle. We solve exactly the two limiting cases of completely coherent and incoherent motion for two molecules. In the incoherent case, the influence of the exchange interaction integral is taken into account by perturbation theory. We find expressions which are immediately comparable with ESR-experimental data. This comparison and additional information derived from optical absorption also yields the parameters of our model. Finally, we have calculated the longitudinal relaxation time and the correlation time of proton spin resonance, when triplet excitons are present in the crystal. The parameters of the model derived from NSR-experiments are consistent with those obtained in the two manners described above.

I. Introduction

Since many years, the experimental and theoretical study of excitons in molecular crystals is meeting an ever increasing interest. Among many other things, excitons play a role in sensitized luminescence and, more generally, in energy transport in solids. The detailed study of excitonic energy transfer may give insight into the energy transport in macromolecules. In this way, but probably also in other ways, energy transfer by excitons may also be of importance for the understanding of energy transport in biological systems [1].

While the existence of excitons in molecular crystals is well established, the

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nature of its motion was not so clear up to now. For the description of the exciton motion two different models have been proposed, namely that of coherent [2] and that of incoherent motion [3, 4]. In the coherent case the exciton is assumed to move through the lattice in complete analogy to a Bloch wave which is eventually scattered by phonons. In the incoherent case it is assumed that the phase of the wave function of the exciton is very quickly destroyed by the interaction with the vibrations of the crystal so that the exciton undergoes a hopping process. In mathematical terms this process may be described by a master equation in its narrow sense or in the limit of a continuum by a diffusion equation.

Sometime ago, Haken and Strobl [5] developed a stochastic model which allows to treat not only both limiting cases but also the whole range in between. The coherent contribution to the energy transport is described by the transition matrix element between the molecules of the crystal containing the Coulomb and the exchange
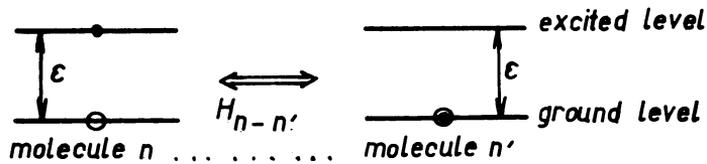
Fig. 1. Energy levels and coherent interaction of the molecules

interaction integral. The phonons destroy the coherence, and their influence is taken into account by letting fluctuate the transition matrix element and the energy of the localized excitation. This model allowed to derive an exact criterium for the occurrence of the coherent or the incoherent motion depending on the parameters of the system. Now, this model is developed further in order to get results comparable with those of experiments. Thus, contact to optical absorption measurements is made by calculating the influence of the coupled coherent and incoherent exciton motion on the absorption line shape. Furtheron, starting from the exact equation for the density matrix of the model, it is possible to derive a diffusion equation for the motion of the exciton which is valid within a certain range of the parameters of the model. Using results of optical absorption and diffusion measurements, from the theoretical expressions for the optical line shape and the diffusion constant all parameters of the model are determined.

But the model of the coupled coherent and incoherent exciton motion renders useful results also in the completely different fields of electron-spin resonance and nuclear magnetic resonance. We investigate the influence of the exciton motion on the ESR-line shape of triplet excitons. The expression for the line shape takes also into account the influence of the coherent exciton motion and, in the limit of the hopping model, it is identical to Anderson's result [6]. Furtheron, we consider the influence of the motion of triplet excitons on the longitudinal relaxation time and the correlation time of NSR-measurements done at the protons of organic crystals.

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The results of both spin resonance experiments, in connection with the results of the optical absorption experiments mentioned above, enable us also to derive all parameters of the model from our theoretical expressions. The parameters determined in this way are consistent with those derived from optical and diffusion experiments.

2. Model of the Coupled Coherent and Incoherent Exciton Motion

a) The Coherent Motion of the Exciton

Haken and Strobl[5]) consider an arbitrary arrangement of molecules whose sites are denoted by the index n (see Fig. 1). It is assumed that each molecule may be divided into a Leucht-electron and the rest and that each molecule has only two equally spaced electronic energy levels, a ground level and an excited level an energy ε above the ground level. Thus the electron of each molecule may be either in the ground level or in the excited level. As one wants to consider Frenkel excitons, only such excitations are allowed, where the electron and the hole are situated at the same molecule, therefore the molecules always remain neutral. It is allowed, however, that the electron and its hole move together to the other molecule. This motion may either be coherent or incoherent. The coherent part of the motion is described by the matrix element $H_{n-n'}$ of the interaction between the molecules.

It is advantageous to use second quantization in describing our system. b_n^+ and b_n are the creation and annihilation operators for a localized electron-hole pair at molecule n. Thus we obtain for the coherent part of the Hamiltonian the expression (2.1).

$$H_1 = \sum_n \varepsilon b_n^+ b_n + \sum_{n \neq n} H_{n-n} b_n^+ b_n \qquad (2.1)$$

The terms of the first sum represent the energy of the exciton when sitting on the molecule at site n. The terms of the double sum annihilate an exciton at site n' and generate one at site n; therefore, these terms are responsible for the coherent energy transport. Under the assumptions of the model, the matrix element H_{n-n} contains the Coulomb and the exchange interaction integral. When considering triplet excitons, the Coulomb integral is zero and the only contribution to H_{n-n} stems from the exchange interaction integral which, as usually, will be denoted by $J_{n-n'}$.

b) The Incoherent Motion of the Exciton

The influence of the vibrations within and between the molecules is taken into account by letting fluctuate the energy of the exciton at the molecule and the transition matrix element.

By doing this the molecular vibrations are treated as a heat-bath pushing the excitonic system in a stochastic manner. This procedure may be justified, if the molecules are not too small and the temperature is not too low. However, it is not

possible to take into account the reaction of the exciton on the molecular vibrations. The Hamiltonian of this part of the motion is given by eq. (2.2).

$$H_2 = h(t) = \sum_{n,\,n'} h_{nn'}(t) b_n^+ b_{n'} \qquad (2.2)$$

$h_{nn}(t)$ is assumed to be a Gaussian Markov process. Physically this means that the fluctuations are generated by many independent molecular vibrations with broad frequency spectrum.

The correlation functions of the stochastic process $h(t)$ are given by these expressions

$$\langle h_{nn'}(t) = 0 \rangle \qquad (2.3)$$

$$\langle h_{nn'}(t) h_{n''n'''}(t') \rangle = [\delta_{nn''}\delta_{n'n'''} + \delta_{nn'''}\delta_{n'n''}(1 - \delta_{nn'})]2\hbar\gamma_{n-n'}\delta(t - t') \qquad (2.4)$$

$$\gamma_m = \gamma_{-m} \qquad (2.5)$$

The first expression means, that the mean value of the fluctuations disappears or that a possibly existing mean value is taken into account in the coherent part of the Hamiltonian given by (2.1). Furtheron, the meaning of the correlation functions may be elucidated by considering two examples. The disappearance of the correlation function of the diagonal elements $\langle h_{nn}(t)\, h_{n'n'}(t') \rangle$ for $n \neq n'$ means that energy fluctuations at different molecules are not correlated. Finally, from $\langle h_{nn'}(t)\, h_{n''n'''}(t) \rangle = 0$ we see that fluctuations between different pairs of molecules, namely between n and n' and between the pair n'' and n''', are not correlated.

c) The Equation of Motion

From the total Hamiltonian

$$H = H_1 + H_2 \qquad (2.6)$$

we obtain the equation of motion for the density operator of the system

$$i\hbar\dot{\tilde{\varrho}} = [H, \tilde{\varrho}] = [H_1, \tilde{\varrho}] + [H_2, \tilde{\varrho}]. \qquad (2.7)$$

The first term of the equation of motion describes the coherent motion, the second term represents the fluctuating part. One is not interested in the operator $\tilde{\varrho}$ still containing the fluctuations of the heat bath, but in the quantity ϱ averaged over the fluctuations. Taking into account that only H_2 contains fluctuations, we arrive at the equation of motion for the averaged quantity:

$$i\hbar\dot{\varrho} = [H_1, \varrho] + \langle [H_2, \tilde{\varrho}] \rangle \qquad (2.8)$$

What one wants to have is ϱ instead of $\tilde{\varrho}$ also in the second term. This requires some lengthy calculation. It may be done either by using perturbation theory to infinite order and summing up the series again as was the procedure by Haken and Strobl[5]. Another possibility uses Feynman's time ordering operator and the charac-

teristic functional of the stochastic process.[5a] The latter procedure is due to Kubo [7] and allows to write the equation of motion in operator form:

$$\langle [H_2, \tilde{\varrho}] \rangle = - \frac{i}{2} \sum_n \sum_{n'} \sum_{n''} \sum_{n'''} \Lambda\{n\} .$$

$$\{b_n^+ b_{n''} b_n^+ b_{n'} \varrho(t) - b_n^+ b_{n'} \varrho(t) b_n^+ b_{n''} - b_n^+ b_{n''} \varrho(t) b_n^+ b_{n'} +$$
$$+ \varrho(t) b_n^+ b_{n'} b_n^+ b_{n''} + b_n^+ b_{n'} b_n^+ b_{n''} \varrho(t) - b_n^+ b_{n'} \varrho(t) b_n^+ b_{n''} -$$
$$- b_n^+ b_{n''} \varrho(t) b_n^+ b_{n'} - \varrho(t) b_n^+ b_{n''} b_n^+ b_{n'} \} \qquad (2.9)$$

$$\Lambda\{n\} = \gamma_{n'-n}[\delta_{nn''}\delta_{n'n''} - \delta_{nn''}\delta_{n'n''}(1 - \delta_{nn'})] \qquad (2.10)$$

For the representation of the density matrix, we use as basis functions the states $| 0 \rangle$ with no exciton in the crystal and $| n \rangle = b_n^+ | 0 \rangle$ with the exciton sitting at molecule n. The equation of motion for the density matrix may then be written in the following form

$$i\hbar\dot{\varrho} = L\varrho \qquad (2.11)$$

Here L is the Liouville-Operator. Explicitly the equations for the diagonal and non-diagonal elements are given by the following two equations

$$\hbar\dot{\varrho}_{nn} = - i[H_1, \varrho]_{nn} - 2\Gamma\varrho_{nn} + 2\sum_{n'}\gamma_{n-n'}\varrho_{n'n'}$$
$$\hbar\dot{\varrho}_{nn'} = - i[H_1, \varrho]_{nn'} - 2\Gamma\varrho_{nn'} + 2\gamma_{n-n'}\varrho_{n'n} \qquad (2.12)$$

The first term on the right side of each equation describes the coherent, the following terms stand for the incoherent part of the motion.

At this point it is illustrative to consider instead of the arbitrary arrangement of molecules a two-molecule model. The equations of motion then simplify to these expressions

$$\hbar\dot{\varrho}_{11} = -2\gamma_1\varrho_{11} + 2\gamma_1\varrho_{22} - iJ(\varrho_{21} - \varrho_{12})$$
$$\hbar\dot{\varrho}_{22} = -2\gamma_1\varrho_{22} + 2\gamma_1\varrho_{11} - iJ(\varrho_{12} - \varrho_{21}) \qquad (2.13)$$

$$\hbar\dot{\varrho}_{12} = -2(\gamma_0 + \gamma_1)\varrho_{12} + 2\gamma_1\varrho_{21} - iJ(\varrho_{22} - \varrho_{11})$$
$$\hbar\dot{\varrho}_{21} = -2(\gamma_0 + \gamma_1)\varrho_{21} + 2\gamma_1\varrho_{12} - iJ(\varrho_{11} - \varrho_{22}) \qquad (2.14)$$

The first two equations describe the change of the occupation numbers of the excitons at the two molecules. From the last equation we may get the change of the phase relation between the two molecules.

Let us first consider the situation, where the exchange interaction integral J vanishes, that is we consider the complete incoherent case. Then the equations for the diagonal elements of the density matrix ϱ_{11} and ϱ_{22} are completely decoupled from the equations for the non-diagonal elements ϱ_{12} and ϱ_{21}. The equations for the diagonal elements represent a set of rate equations for the occupation numbers of the excitons. The transition probability for an exciton between the two molecules is given by $W = \frac{2\gamma_1}{\hbar}$, which means that it is determined by non-local fluctuations.

On the other hand, from the equations for the non-diagonal elements $\varrho_{nn'}$ of the density matrix we see, that the phase of the excitons decays exponentially with the exponent given by $2(\gamma_0 + \gamma_1)$. Thus the phase of the exciton is destroyed both by local and non-local fluctuations.

Now we consider the situation of non-vanishing exchange interaction integral. Then the equations for the diagonal and non-diagonal matrix elements are coupled and we have to solve a four-dimensional eigenvalue problem. In this way, we get the occupation probability for molecule number 1 with the exciton initially sitting at this molecule as the expression (2.15).

$$\varrho_{11}(t) = \frac{1}{2} + \frac{1}{4}\left(1 + i\frac{\gamma_0}{\sqrt{4J^2 - \gamma_0^2}}\right)\exp\left\{-\frac{1}{\hbar}R_8 t\right\} +$$

$$+ \frac{1}{4}\left(1 - i\frac{\gamma_0}{\sqrt{4J^2 - \gamma_0^2}}\right)\exp\left\{-\frac{1}{\hbar}R_9 t\right\} \qquad (2.15)$$

The exponents, describing the behaviour in time, are written down here

$$\frac{1}{\hbar}R_{\substack{8\\9}} = \frac{1}{\hbar}(\gamma_0 + 4\gamma_1) \pm \frac{i}{\hbar}\sqrt{4J^2 - \gamma_0^2} \qquad (2.16)$$

From (2.16) we remark that for small values of the local fluctuations γ_0, i.e. for $\gamma_0 < 2J$, the occupation number exerts damped oscillations. For values of γ_0 in this range, it is reasonable to denote the exciton motion as coherent. On the other hand, when $\gamma_0 > 2J$ the occupation number decreases exponentially and for such values of γ_0 the motion of the exciton is called incoherent. The transition from coherent to incoherent motion happens, when $\gamma_0 = 2J$.

3. Optical Absorption

a) The Line Shape of the Optical Absorption

Now we wish to consider the influence of the motion of the exciton on the line shape of optical absorption. To that end, we treat a model consisting of two molecules at the sites 1 and 2 each having two energy levels with distance ε. The coherent interaction between the molecules is described by the exchange interaction matrix element J.

The Hamiltonian of this system is the sum of two parts H_1 and H_2. H_1 describes the coherent, H_2 the incoherent part of the motion in the above explained way. The sum of both is denoted as H_0 and considered as the unperturbed part when investigating optical absorption.

$$H_0 = H_1 + H_2. \qquad (3.1)$$

When the two-molecule system is perturbed by a time dependent electric field represented in this way

$$\vec{E} = 2\vec{E}_1 \cdot \cos \omega t \qquad (3.2)$$

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the system will absorb energy. In addition to the unperturbed Hamiltonian H_o describing the exciton motion, we have to consider this perturbation

$$H_s = -2\vec{p} \cdot \vec{E}_1 \cdot \cos \omega t. \tag{3.3}$$

Here $\vec{p}$ is the operator of the dipole moment of the two-molecule system. In second quantization, it is given by eq. (3.4).

$$\vec{p} = \vec{\mu}_1 b_1^+ + \vec{\mu}_1^* b_1 + \vec{\mu}_2 b_2^+ + \vec{\mu}_2^* b_2 \tag{3.4}$$

$$\mu_n = (\varphi_{n1} \mid \vec{er} \mid \varphi_{no}) \tag{3.5}$$

b_n^+, b_n are creation and annihilation operators for excitons and $\vec{\mu}_n$ is the dipole matrix element between the ground and the excited states of the molecule. It is assumed that optical transitions between different molecules are not possible.

The absorbed energy per second is given by the expression (3.6).

$$P = 2\omega \cdot \vec{E}_1 \cdot \chi''(\omega) \cdot \vec{E}_1 \tag{3.6}$$

and thus proportional to the imaginary part of the dielectric susceptibility.

Using Kubo's formalism [8], it is easy to show that the imaginary part of the tensor of the dielectric susceptibility is given by the following expression:

$$\chi_{kl}''(\omega) = \frac{1}{2\hbar} \int\limits_{-\infty}^{+\infty} d\tau e^{-i\omega\tau} \mathrm{Tr}_S[\langle \varrho(-\infty)\, p_k(0)p_l(\tau)\rangle - \langle \varrho(-\infty)p_l(\tau)p_k(0)\rangle] \tag{3.7}$$

The p_k's are the cartesian components of the dipole moment operator, Tr_S means trace over the states of the two-molecule system and the brackets $\langle \cdots \rangle$ averaging over the fluctuations.

The calculation of the correlation function is done according to a theorem of Haken and Weidlich [9] using a generalized density matrix ϱ, which is a function of some parameters α_1, α_1^*, β_1, β_1^*. The correlation functions are then given as the second derivatives of the generalized density matrix according to these parameters.

$$\mathrm{Tr}_S\langle \varrho(-\infty)\, p_l(t'')\, p_k(0)\rangle = \mathrm{Tr}_S \left(\frac{\partial^2}{\partial\alpha_k \partial\beta_e^*}\, \varrho(t'',\{\alpha_1, \alpha_1^*, \beta_1, \beta_1^*\}) \right)_{\{\alpha = \beta = 0\}} \tag{3.8}$$

$$\mathrm{Tr}_S\langle \varrho(-\infty)p_k(0)p_l(t'')\rangle = \mathrm{Tr}_S \left(\frac{\partial}{\partial\alpha_k^* \partial\beta_1}\, \varrho(t'',\{\alpha_1, \alpha_1^*, \beta_1, \beta_1^*\}) \right)_{\{\alpha = \beta = 0\}} \tag{3.9}$$

The generalized density matrix is defined by

$$\varrho(t, \{\alpha_1^*, \alpha_1, \beta_1, \beta_1^*\}) = \langle \tilde{\varrho}(t, \{\alpha_1^*, \alpha_1, \beta_1, \beta_1^*\})\rangle =$$

$$\left\langle \left(T \exp \left\{ -\frac{i}{\hbar} \int\limits_{-\infty}^{t} H_o(\tau)d\tau - i\sum_j \alpha_j p_{jt'} - i\sum_j \beta_j p_{jt'} \right\} \right) \cdot \varrho(-\infty). \right. \tag{3.10}$$

$$\left. \cdot \tilde{T} \exp \left\{ +\frac{i}{\hbar} \int\limits_{-\infty}^{t} H_o(\tau)d\tau + i\sum_j \alpha_j^* p_{jt} + i\sum_j \beta_j^* p_{jt''} \right\} \right) \right\rangle$$

T and $\tilde{T}$ are time ordering operators ordering later times to the left and right, respectively. H_0 is the unperturbed Hamiltonian; the $p_{jt'}$ are the components of the dipole moment operator and the index t' means that it is operating at time t'. It is not very difficult to show that the generalized density matrix has to satisfy the same equation of motion as the original density matrix together with additional jump conditions at the times t' and t'' introducing the parameters α_i and β_i.

The result of the calculation of the correlation functions [10] by this method may be simplified by the assumption that the dipole moments of the two molecules have the same amounts, lie in the x-z-plane and are symmetrically arranged as referred to the z-axes (see Fig. 2). In this case we have

Fig. 2.
Directions of the molecular dipole moments

$$\vec{\mu}_1 + \vec{\mu}_2 = 2\mu_z \quad \text{and} \quad \vec{\mu}_1 - \vec{\mu}_2 = -2\mu_x$$

For the components of the tensor of the dielectric susceptibility we then have these expressions:

$$\chi''_{xx}(\omega) = \left[\frac{\Gamma}{\Gamma^2 + [\omega - (\varepsilon - J)]^2} - \frac{\Gamma}{\Gamma^2 + [\omega - (-\varepsilon + J)]^2}\right]\mu_x^2 \Delta\varrho \quad (3.11)$$

$$\chi''_{zz}(\omega) = \left[\frac{\Gamma}{\Gamma^2 + [\omega - (-\varepsilon + J)]^2} - \frac{\Gamma}{\Gamma^2 + [\omega - (-\varepsilon - J)]^2}\right]\mu_z^2 \Delta\varrho \quad (3.12)$$

The two expressions show that a light field polarized in x-direction causes absorption at $\omega = \varepsilon - J$ and a light field polarized in z-direction generates a line at $\omega = \varepsilon + J$. Thus the distance of the lines in the two-molecule model is $\Delta = 2$ J. Furtheron

$$\Gamma = (\gamma_0 + \gamma_1) \quad (3.13)$$

describes the linewidth of the Lorentzian lines. Thus from the distance of the centers of the absorption lines we obtain the exchange integral J and from the linewidth the parameter Γ which is a measure for the strength of the fluctuations. The linewidth is determined both by the strength of the local fluctuations γ_0 and by the non-local fluctuations γ_1, because both processes destroy the phase of the exciton as shown in the last section.

c) Comparison with Experiments

We wish to compare our results with the polarized excitation spectra for triplet excitons in anthracene crystals. These measurements were reportet by Avakian et al. [4], Ern et al. [11] and by Hochstrasser and Clark [12].

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But before applying the results of our two-molecule model to measurements at real crystals, we must remember that in anthracene and naphtalene crystals each molecule has four neighbours instead of one which are relevent for the Davydov-splitting. Thus instead of $\Delta = 2J$ we have for the Davydov-splitting $\Delta = 8J$. Furtheron, from our model we have got a Lorentzian line shape, and there arises the problem how to define the linewidth and the Davydov-splitting Δ, if the line shapes of the absorption lines are not Lorentzian but have a more complicated structure. For the determination of these two quantities, Merrifield and Suna have proposed a procedure which, in the case of Lorentzian line shapes, reduces to the usual definition of the Davydov-splitting and the linewidth [11]. From the comparison of the experimental results of the above mentioned papers with our theoretical expressions we have the values in table 1.

Table 1. Values for the exchange interaction integral J and the fluctuation parameter Γ for various values of the temperature infered from the experimental values of (a) Avakian et al. [4], (b) Ern et al. [11] and (c) Clarke and Hochstrasser [12]

T/°K	Δ/cm⁻¹	J/cm⁻¹	Γ/cm⁻¹	
371	19	2.4	65 ‖ a 62 ‖ b	b
298	17	2.1	51 ‖ a 54 ‖ b	b
160	18	2.25	30 ‖ a 26 ‖ b	b
118	18	2.25	14 ‖ a 14 ‖ b	b
4	22	2.7	< 1	c
room temperature	17	2.1	70	a

The first column gives the temperatures for which we have found values in the literature. In the second column the Davydov-splittings are given. From there we may calculate the exchange interaction integrals, represented in the third column. The fourth column represents the half width at half maximum of the optical absorption lines. All values are given in units of cm⁻¹. The numbers in the last column finally refer to the authors of the experimental values.

From the table we see, that with decreasing temperature the exchange integral increases and the parameter Γ describing the fluctuations becomes smaller. This is easy to understand because with decreasing temperature the molecules are packed more densely and therefore the overlap between the wave functions and thus the

exchange integral increases. At the same time with decreasing temperature the thermal motion of the particles constituting the crystal becomes smaller and by this the fluctuations of the exciton energy and of the exchange integral decrease. But until now we don't know which of the two quantities γ_0 and γ_1 is the reason for the strong temperature dependence of the optical linewidth, because in the linewidth they enter only as the sum $\Gamma = \gamma_0 + \gamma_1$.

In order to get the values of γ_0 and γ_1 separately, we must have additional information. To that end, we may use information derived from diffusion or from spin resonance experiment. What we want first to do now, is to consider diffusion experiments.

4. Diffusion

a) Derivation of a Diffusion Equation

In order to get a diffusion equation, we start from our equation of motion for the density matrix. Separating for diagonal and non-diagonal elements, we have these two equations

$$\hbar \dot{\varrho}_{nn} = -i \sum_{n' \neq n} H_{nn'} \varrho_{n'n} + i \sum_{n' \neq n} \varrho_{nn'} H_{n'n} - 2\Gamma \varrho_{nn} + 2 \sum_{n'} \gamma_{n-n'} \, \varrho_{n'n'} \qquad (4.1)$$

$$\hbar \dot{\varrho}_{nn'} = -i \sum_{n'' \neq n} H_{nn''} \varrho_{n''n'} + i \sum_{n'' \neq n'} \varrho_{nn''} H_{n''n'} - 2\Gamma \varrho_{nn'} + 2\gamma_{n-n'} \varrho_{n'n} \qquad (4.2)$$

We wish to consider diffusive motion and from our previous considerations of the model of coupled coherent and incoherent motion in § 2 we know, that in the case of diffusive motion $\gamma_0 \gg 2J$. Then phase relations are destroyed after a very short time. If we consider only time intervals longer than these decay times of the phase, in the equations for the non-diagonal elements we may neglect $\dot{\varrho}_{nn'}$ compared to $\varrho_{nn'}$. After solving for $\varrho_{nn'}$ and inserting into the equation for $\dot{\varrho}_{nn}$ we may neglect all non-diagonal elements compared to the diagonal ones and arrive at an equation, containing only diagonal elements.

$$\hbar \dot{\varrho}_{nn} = \sum_{n'} \frac{1}{2} \left\{ \frac{\gamma_{n'-n}}{\gamma_{n'-n}^2 - \Gamma^2} H_{nn'} + \frac{\gamma_{n-n'}}{\gamma_{n-n'}^2 - \Gamma^2} H_{n'n} \right\} (\varrho_{n'n'} - \varrho_{nn}) -$$

$$- \sum_{n'} \frac{1}{2} \left\{ \frac{\Gamma}{\gamma_{n'-n}^2 - \Gamma^2} |H_{nn'}|^2 + \frac{\Gamma}{\gamma_{n'-n}^2 - \Gamma^2} |H_{nn'}|^2 \right\} (\varrho_{n'n'} - \varrho_{nn}) - \qquad (4.3)$$

$$- 2\Gamma \varrho_{nn} + 2 \sum_{n'} \gamma_{n-n'} \, \varrho_{n'n'}$$

The first two lines of this equation have their origin in the coherent interaction, the terms in the third line follow from the stochastic part of the Hamiltonian. Now we assume that the density of the excitons varies only slowly in space, so that we may expand $\varrho_{n'n'} \equiv \varrho(\vec{X}_{n'})$ in a Tylor series in $(\vec{X}_{n'} - \vec{X}_n)$ and neglect terms higher than second order:

$$\varrho(\vec{X}_{n'}) = \varrho(\vec{X}_n) + (\vec{X}_{n'} - \vec{X}_n) \nabla \varrho(\vec{X}_n) + \frac{1}{2} [(\vec{X}_{n'} - (\vec{X}_n) \nabla]^2 \varrho(\vec{X}_n) \qquad (4.4)$$

After inserting this into the above equation and regarding that the curly brackets depend only on the amount of $\vec{X}_{n'} - \vec{X}_n$ we arrive at this diffusion equation:

$$\dot{\varrho}(\vec{X}) = \sum_{i,j} D_{ij} \frac{\partial}{\partial X_i} \frac{\partial}{\partial X_i} \varrho(\vec{X}) \tag{4.5}$$

with the diffusion tensor given by this expression.

$$D_{ij} = \sum_{m \neq 0} \frac{1}{\hbar} \left(\gamma_m + \frac{1}{2} \frac{H_m^2}{\gamma_m + \Gamma} \right) X_{mi} X_{mj} \tag{4.6}$$

Starting from our model this from of the diffusion tensor has also been published by Ern and coworkers [11].

The first term in the bracket of the diffusion tensor stems from the non-local fluctuations, the second from the coherent interaction in connection with the fluctuating terms of the Hamiltonian. X_{mi} and X_{mj} are the i and j components of the lattice vector of molecule m and the sum runs over all lattice points.

b) Comparison with Directly Measured Diffusion Tensors

In order to get the parameters of the system, we use the D_{aa} component of the diffusion tensor of triplet excitons, measured by Ern et al. [11] in anthracene crystals at various temperatures. It is very easy to evaluate the sum in the diffusion tensor for triplet excitons. For triplet excitons the coherent interaction matrix element contains only the exchange interaction integral, which decreases exponentially with increasing distance. Thus, for triplet excitons, the sum runs only over nearest neighbours as regards the coherent interaction and the same is assumed for the fluctuation parameters γ_m. Int hese crystals the interaction between translationally inequivalent molecules is much larger than between equivalent ones. Therefore, after summing over the four nearest neighbours of fig. 3, we arrive at the diffusion constant given by the following expression:

Fig. 3. The four nearest neighbours of a molecule in anthracene crystals

$$D_{aa} = \frac{1}{2} \frac{1}{\hbar} \left(\frac{a}{2} \right)^2 \cdot 4 \left(2\gamma_1 + \frac{J^2}{\Gamma + \gamma_1} \right) = \frac{1}{2} \, l^2 \, W \tag{4.7}$$

Here a is the lattice constant in a direction, and γ_1 and J are the interactions between the above defined nearest neighbours. We see that the diffusion constant has the general structure of the second expression of eq. (4.7), where 1 is the distance in one jump and W the hopping rate.

Using the results of the diffusion measurements together with the values for J

and Γ derived from optical absorption experiments and a $= 8.6\text{Å}$ we may calculate the values for the non-local fluctuations γ_1. The results of this evaluation are represented in table 2.

Table 2. Values of the parameters of the system infered from diffusion measurements of (a) Avakian et al. [4], and (b) Ern et al. [11]

T/°K	J/cm^{-1}	Γ/cm^{-1}	D$_{aa}$ $\dfrac{\text{cm}^2}{\text{sec}}$	γ_1/cm^{-1}	$\dfrac{1}{2}\dfrac{J^2}{\Gamma+\gamma_1}$/cm^{-1}	
371	2.4	65	$1.6 \cdot 10^{-4}$	0.07	0.04	b
298	2.1	51	$1.5 \cdot 10^{-4}$	0.07	0.04	b
160	2.25	30	$2.5 \cdot 10^{-4}$	0.10	0.08	b
118	2.25	16	$4 \cdot 10^{-4}$	0.11	0.18	b
4	2.7	< 1	—	—	—	c
room tempe- rature	2.1	70	$2 \cdot 10^{-4}$	0.11	0.03	a

The first column of this table again gives the temperatures for which we have found experimental values. In the second and third columns we have represented once more the values for the exchange interaction integral J and the fluctuation parameter Γ derived from optical absorption experiments. The fourth column gives values for the diffusion constant measured by Ern and coworkers [11]. The following column shows the values for the non-local fluctuation parameter γ_1 derived with the aid of our expression for the diffusion tensor. Finally, in the last column we have gathered the values for the second term in the diffusion constant. From the table we may infer several interesting facts.

1. On account of $\Gamma = \gamma_0 + 4\gamma_1$ and $\gamma_1 \ll \Gamma$ we see that $\gamma_0 \approx \Gamma$. Using now the criterium of Haken and Strobl for the occurrence of coherent exciton motion, namely $\gamma_0 < 2J$, we see that at all temperatures with the exception of 4°K, $\gamma_0 > 2J$. Thus the motion of the exciton at these temperatures is incoherent and may be described by a hopping process. On the other hand, at 4°K we find $\gamma_0 < 2J$, so that the exciton motion now should be coherent.

2. We may see that the temperature dependence of the optical linewidth, described by Γ, is primarily determined by the local fluctuations γ_0 on account of $\gamma_0 \gg \gamma_1$.

3. The exciton transport, on the other hand, is determined by the sum of the two quantities γ_1 and $1/2J^2/(\Gamma + \gamma_1)$. From the table we see, that at all temperatures considered, except at the lowest temperature of 118°K, the contribution of the non--local fluctuations is even more important than that of the term explicitly containing the exchange interaction integral.

From the comparison with data of optical absorption and diffusion measurements in anthracene crystals we could determine all parameters of our model and show that at room temperature the exciton undergoes a hopping process, whereas at 4°K the motion takes place in a coherent fashion. There are, however, more data available of excitons in organic crystals, especially those of electron spin resonance [13, 14] and nuclear spin resonance [15, 16], particularly by Wolf and his coworkers. In order to exploit these experimental data we have extended our former model so that it includes the spin Hamiltonian.

a) The Spin-Hamiltonian

Triplet excitons have a total spin angular momentum $S = 1$. The two π-electrons forming the triplet state in naphtalene or anthracene molecules have a dipole-dipole interaction on account of the magnetic moments connected with their spin angular momenta. This interaction is described by the fine structure Hamiltonian [17]

$$H_F = S \cdot F \cdot S \tag{5.1}$$

Here F is a tensor. The orientation of its principle axes depends on the local orientation of the molecule in the crystal lattice.

The two molecules in the unit cells of naphtalene and anthracene crystals are oriented differently. As we want to compare our results of the model calculation with measurements done at these crystals, we assume that the two molecules of our model are oriented differently too. Therefore, for both molecules we obtain the following total fine structure Hamiltonian

$$H_F = b_1^+ b_1 S \cdot F_1 \cdot S + b_2^+ b_2 S \cdot F_2 \cdot S \tag{5.2}$$

F_1 is the fine-structure tensor of molecule 1, and F_2 the fine structure tensor of the second molecule which has a different orientation.

We wish to replace this Hamiltonian by a simpler one, containing the essential feature that the triplet exciton sees different magnetic fields when sitting at the two differently oriented molecules. Confining for simplicity on excitons with spin 1/2, we get the following spin Hamiltonian

$$H_3 = b_1^+ b_1 \vec{H}(1) \cdot \vec{\mu} + b_2^+ b_2 \vec{H}(2) \cdot \vec{\mu} \tag{5.3}$$

H(1) and H(2) respectively are the effective magnetic fields at molecule 1 and at molecule 2, $\mu = \dfrac{\gamma \hbar}{2} \sigma$ is the operator of the magnetic moment expressed by the spin operator σ and the gyromagnetic ratio γ. The Hamiltonian may thus be written as

$$H_3 = b_1^+ b_1 A \sigma^+ + b_2^+ b_2 (B\sigma^+ + C\sigma^+ + C^* \sigma^+) \tag{5.4}$$

where σ_z, σ^+ and σ^- are Paulioperators.

The coordinate system is oriented in such a manner that the total magnetic field at molecule 1, including external magnetic fields, points in z-direction. At molecule 2, however, the magnetic field has a component orthogonal to the z-direction, too (see fig. 4). This Hamiltonian has the effect that the excitonic spin rotates with different velocities when the exciton is sitting at sites 1 and 2 respectively. Furtheron the z-component of the spin is altered by the terms at molecule 2 containing the flipflop-operators and this together with the incoherent exciton motion leads to relaxation.
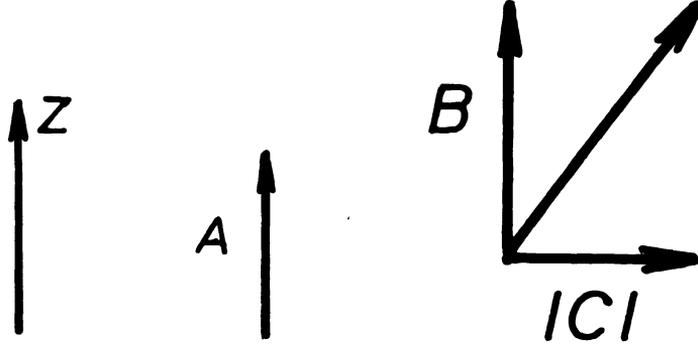
Fig. 4. Orientation of the effective magnetic fields at the two molecules

b) The Equation of Motion of the Two-Molecule-Model with Spin

The total Hamiltonian of the system is now given by

$$H_0 = H_1 + H_2 + H_3. \qquad (5.5)$$

where H_1 and H_2 are defined by (2.1) and (2.2), respectively. After averaging over the fluctuations, we obtain for the equation of motion of the density operator this expression

$$i\hbar\dot\varrho = [H_1, \varrho] + \langle[H_2, \tilde\varrho]\rangle + [H_3, \varrho] \qquad (5.6)$$

The first two terms are known from § 2. The evaluation of the third term is not difficult and we shall represent the result in matrix form after having introduced a suitable basis in Hilbert space.

Calculating the absorption line we consider H_0 as the unperturbed operator and the time dependent magnetic field as the perturbation. The number of excitons is not altered by H_0 and also the magnetic perturbation is not able to change the number of excitons but only to reverse the direction of the magnetic moment.

Thus when an exciton is generated it can not disappear but must sit either at molecule 1 or 2. Therefore, we have not to consider the ground state with no exciton,

but may describe our system by states $|$ n, s$\rangle$ where n denotes, if the exciton is at molecule 1 or 2 and s describes the direction of the spin.

Using this basis and the notation $\varrho_{ns,\ n's'}$ for the matrix element $\langle ns\ |\ \varrho\ |\ n's'\rangle$ of the density operator ϱ, furtheron $\Gamma = \gamma_0 + \gamma_1$, the equation of motion of the density matrix reads

$$i\hbar\dot{\varrho}_{ns;\ n's'} = \{\delta_{n1} \cdot \mathbf{J} \cdot \varrho_{2s;\ n's'} + \delta_{n2} \cdot \mathbf{J} \cdot \varrho_{1s;n's'} - \delta_{n'2} \cdot \mathbf{J} \cdot \varrho_{ns;\ 1s'} - \delta_{n'1} \cdot \mathbf{J} \cdot \varrho_{ns;\ 2s'}\} +$$

$$+ \{\delta_{n1} \cdot \mathbf{A} \cdot \mathbf{s} \cdot \varrho_{1s;\ n's'} + \delta_{n2} \cdot \mathbf{B} \cdot \mathbf{s} \cdot \varrho_{2s;\ n's'} + \delta_{n2} \cdot \delta_{s1} \cdot \mathbf{C} \cdot \varrho_{2,\ -1;\ n's'} +$$

$$+ \delta_{n2} \cdot \delta_{s,\ 1} \cdot \mathbf{C}^* \cdot \varrho_{21;\ n's'} - \delta_{n'1} \cdot \mathbf{A} \cdot \mathbf{s}' \cdot \varrho_{ns;\ 1s'} - \delta_{n2} \cdot \mathbf{B} \cdot \mathbf{s}' \cdot \varrho_{ns;\ 2s'} -$$

$$- \delta_{n'2} \cdot \delta_{s',\ -1} \cdot \mathbf{C} \cdot \varrho_{ns;\ 21} - \delta_{n'2} \cdot \delta_{s'1} \cdot \mathbf{C}^* \cdot \varrho_{ns;\ 2,\ -1}\} +$$

$$+ \{i \cdot 2(1\delta_{nn'})\gamma_{n'-n} \cdot \varrho_{n's;\ ns'} - i2\Gamma \cdot \varrho_{ns;\ n's} + i \cdot 2\delta_{nn'} \sum_m \gamma_{m-n} \cdot \varrho_{ms;\ ms}\} \quad (5.7)$$

This system of differential equations looks rather complicated but nevertheless has a very simple structure. The terms of the first curled bracket describe the coherent motion of the exciton. The third bracket stems from the incoherent part of the Hamiltonian and taken alone represents the random walk process. Finally, the second bracket represents the coherent motion of the spin in the fields at the two molecules. In our model there exists no direct coupling of the spin to a heat bath. But an indirect coupling is given by the spin being transported by the exciton and the exciton being pushed by the heat bath.

The ansatz

$$\varrho(t) = e^{1/\hbar\ (Rt)} \cdot \varrho \quad (5.8)$$

reduces the solution of the system of differential equations to that of an eigenvalue problem which may be written in the form

$$R\varrho = L\varrho. \quad (5.9)$$

The coefficients of the Liouville operator L form a square matrix. R are the eigenvalues and ϱ the eigenvectors of the eigenvalue problem. Generally, when all coefficients being unequal zero, we obtain a 16-dimensional eigenvalue problem which we have solved by computer calculation [18]. But two special cases may be solved analytically [19].

If we have very strong fluctuations, phase relations between the two molecules are destroyed rather quickly. Then the exciton motion occurs via a hopping process and the influence of the exchange integral J may be neglected in zero's approximation. Thus for J = 0 and with the additonal assumption that the magnetic fields at the two molecules are parallel but have different amounts, the eigenvalue problem may be solved exactly. The influence of the exchange interaction integral is afterwards taken into account by perturbation calculation. But first it is instructive, to consider the other limiting case with no fluctuations at all, that is we consider $H_2(t)$ and thus the fluctuation parameters γ_0 and γ_1 as zero.

c) Solution of the Equation of Motion in the Limit of Vanishing Fluctuations

In this case it is not necessary to solve the equation of motion for the density matrix. Instead all information about the system is contained in the wave function ψ, satisfying the usual Schrödinger equation

$$i\hbar\dot{\psi} = (H_1 + H_3)\psi \tag{5.10}$$

By the ansatz $\psi(t) = e^{-(i/\hbar) Et}$ we arrive at the time independent Schrödinger equation

$$(H_1 + H_3)\psi_i = E_i\psi_i \tag{5.11}$$

for the eigenvalues E_i and eigenfunctions ψ_i. The influence of a time dependent magnetic field, applied in the plane orthogonal to the static field, leads to the following perturbation of the Hamiltonian

$$H_s = \vec{\mu} \cdot \vec{H}(t) = \gamma(\sigma^+ + \sigma^-) H_x(t) \tag{5.12}$$

Then transitions between the above stationary states are possible. According to time-dependent perturbation theory, the transition probability between the states ψ_i and ψ_j is given by

$$P_{ij} = \frac{2\pi}{\hbar} | \langle \psi_i | H_s | \psi_j \rangle |^2 \, \delta(E_i - E_j - \hbar\omega) \tag{5.13}$$

and thus proportional to the second power of the amount of this matrix element

$$M_{ij} = (\psi_i | \sigma^- + \sigma^- | \psi_j) \tag{5.14}$$

In figs. 5 and 6 the eigenvalues E_i and the transition matrix elements $| M_{ij} |^2$ are represented as a function of the exchange interaction integral J for the values $A = B = | C | = 1$ of the parameters describing the magnetic field strengths. From Fig. 5 we see that for $J = 0$, which means that there is no interaction and thus no transition of the exciton between the two molecules, we have the energy levels $+A$ and $-A$ belonging to the two possible alignment of a spin $1/2$ in the magnetic field of molecule number 1. Correspondingly at molecule number 2 we have the two levels $\pm \sqrt{B^2 + | C |^2}$.

On the other hand, for large values of J, that is rapid exchange, the energy levels E_1 and E_2 and the levels E_3 and E_4 are parallel. The dashed lines represent the asymptotic behaviour for large values of J. The energy difference is given by $\Delta E = \sqrt{(A + B)^2 + | C |^2}$. As indicated in the figure, the levels E_1 and E_2 belong for large J to the same Davydov-component, where E_1 has the spin mainly in $+z$-direction and E_2 mainly in $-z$-direction. The levels E_3 and E_4 belong to the other Davydov-component. Fig. 6 shows the squares of the matrix elements M_{ij}, being proportional to the transition probabilities between the states i and j. At $J = 0$ only

the transitions between E_1 and E_4 and between E_2 and E_3 are allowed with transition energies given by $E_1 - E_4 = 2\sqrt{B^2 + |C|^2}$ and $E_2 - E_3 = 2A$ respectively. In spin resonance experiments, thus we should see two lines. With increasing exchange between the two molecules there appear two further lines, one stemming from the transition between E_1 and E_3 and between E_2 and E_4 and the other having its origin
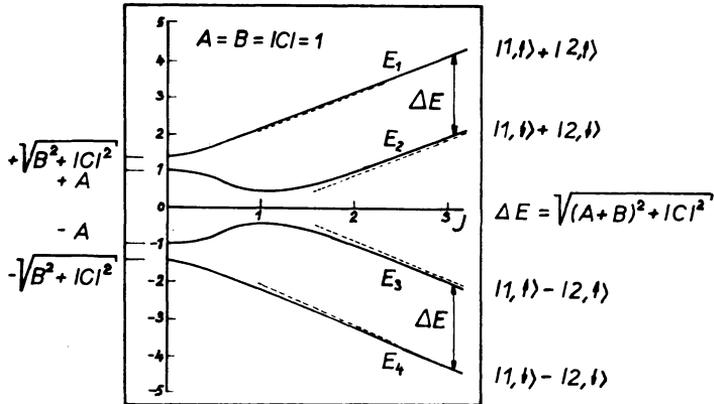
Fig. 5. *Energy levels as a function of the exchange interaction integral J n the pure coherent case*
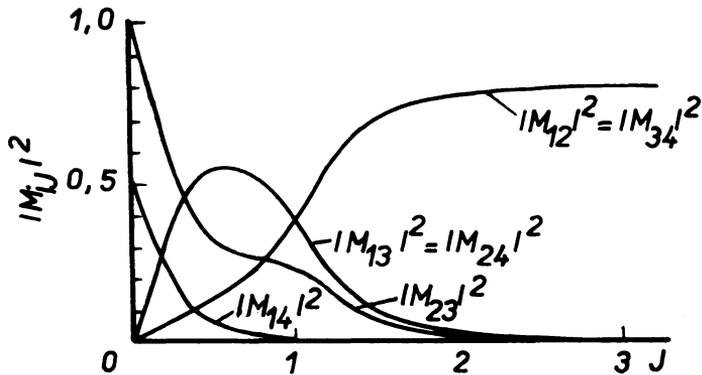
Fig. 6. *Squares of the transition matrix element M_{ij} as a function of the exchange interaction integral J*

from transitions between E_1 and E_2 and between E_3 and E_4. Both transitions leading to one line have the same transition probability. When further increasing J, only transitions between the pairs belonging to the same Davydov-component, namely between E_1 and E_2 and between E_3 and E_4 remain. All other transition probabilities disappear. The transition probabilities and energy differences for the two transitions still allowed are equal and in spin resonance we expect only one line at

$$\Delta E = \sqrt{(A + B)^2 + |C|^2}.$$

d) Solution of the Equation of Motion in the Limit of Strong Fluctuations

Let us now turn to the other case of very strong fluctuations, where the energy between the molecules is transferred by a hopping process. Furtheron, for the analytical calculation we have assumed that the magnetic fields at the two molecules be parallel. The matrix L in the resulting non-hermitian eigenvalue equation will be split into two parts

$$L\varrho = L_0\varrho + L_1\varrho = R\varrho \qquad (5.15)$$

Here $L_0\varrho$ contains the terms describing the spin motion and those stemming from the fluctuating part of the Hamiltonian. In $L_1\varrho$ we have gathered the terms containing the exchange interaction integral describing the coherent exciton motion. Our further procedure is, to consider $L_0\varrho_0 = R^0\varrho_0$ as the unperturbed problem and to treat L_1 by perturbation theory to second order.

From the 16 eigenvalues corresponding to the 16-dimensional eigenvalue problem only the following four are important as regards ESR:

$$R^\circ = \pm i(A + B) - 2\gamma_1 \pm \sqrt{4\gamma_1^2 - (A - B)^2} \qquad (5.16)$$

Now it depends on the magnitude of γ_1, if the square root is real or imaginary, that is, if the square root contributes to the damping or results in a frequency shift.

Expanding for $2\gamma_1 \ll |A - B|$ and $2\gamma_1 \gg |A - B|$ we get for the eigenvalues the expressions:

$$R^\circ = i\,2A - 2\gamma_1 \qquad R^\circ = i2B - 2\gamma_1 \qquad (2\gamma_1 \ll |A - B|) \quad (5.17)$$

$$R^\circ = -i(A + B) - \frac{(A - B)^2}{4\gamma_1} \qquad (2\gamma_1 \gg (A - B|) \qquad (5.18)$$

$2\gamma_1 \ll |A - B|$ means slowly moving excitons. In this case, the imaginary parts of the eigenvalues, which describe the spectral position of the absorption lines, are given by 2A and 2B, respectively. The absorption lines are thus at the positions of the lines of the isolated molecules. The real part of the eigenvalues, describing the linewidth of the ESR-line is given by $2\gamma_1$.

On the other hand, when $2\gamma_1 \gg |A - B|$, i.e. rapid motion of the exciton, from the imaginary part of the eigenvalue we expect a single absorption line at $(A + B)$ with the linewidth given by $\dfrac{(A - B)^2}{4\gamma_1}$. In deriving an explicit expression for the line shape of ESR, we again use Kubo's formalism. Thus the spectral distribution of the absorbed energy, i.e. the line shape of spin resonance absorption, is given by

$$\chi''(E) = \frac{1}{2} \int d\tau e^{-(i/\hbar)E} \operatorname{Tr}_{BS} [\varrho(-\infty) M_x(0)M_x(\tau) - \varrho(-\infty) M_x(\tau)M_x(0)] \quad (5.19)$$

Here M_x is the operator of the magnetic moment and Tr_{BS} means averaging over the fluctuations and trace over the states of the system introduced in section 5.b. These

correlation functions are again calculated using the theorem of Haken and Weidlich in complete analogy to the method used in treating optical absorption.

We shall evaluate $\chi''(E)$ first in the limit $J = 0$. The influence of the exchange interaction integral will be considered lateron.

The calculation of $\chi''(E)$ results in

$$\chi''(E) = -\frac{8\gamma_1\hbar(A-B)^2 \cdot \Delta P}{(E-2A)^2(E-2B)^2 + 16\gamma_1^2(E-A-B)^2} +$$
$$+ \frac{8\gamma_1\hbar(A-B)^2 \cdot \Delta P}{(E+2A)^2(E+2B)^2 + 16\gamma_1^2(E+A+B)^2} \qquad (5.20)$$

This expression is well known since many years and describes the line shape of ESR, when the spin is moving stochastically between two different fields. We have evaluated this general expression for $A = 1$, $B = 2$. The result is given in fig. 7. In this figure, γ_1 is growing when going downward. For small values of $2\gamma_1$, we obtain two lines at $E = 2A$ and $E = 2B$, whose linewidth becomes wider with increasing γ_1. For $2\gamma_1 = (A-B)$, the two original lines have grown together to one single broad line, which becomes smaller and smaller with increasing γ_1. In order to get analytical expressions for the line shapes in the two limiting cases $2\gamma_1 \ll |A-B|$ and $2\gamma_1 \gg |A-B|$, we may expand the general expression for $\chi''(E)$ and obtain simple Lorentzian lines:

$$\chi''(E) = -\hbar\Delta P \left\{ \frac{4\gamma_1}{(E-2A)^2 + 4\gamma_1^2} + \frac{4\gamma_1}{(E-2B) + 4\gamma_1^2} \right\} \quad (2\gamma_1 \ll |A-B|) \ (5.21)$$

$$\chi''(E) = -2\hbar\Delta P \cdot \frac{\frac{(A-B)^2}{2\gamma_1}}{(E-A-B)^2 + \frac{(A-B)^4}{16\gamma_1^2}} \quad (2\gamma_1 \ll |A-B|) \ (5.22)$$

These expressions confirm our earlier considerations that for slow energy transfer the resonance lines are at $E = 2A$ and $E = 2B$ and that the linewidth is given by $2\gamma_1$. When the exciton, however, moves very quickly between the molecules, we have a single absorption line at $E = A + B$ with the width $(A-B)^2/4\gamma_1$. Taking now into account the influence of the coherent interaction, that is of the exchange interaction integral on the linewidth by perturbation theory, we obtain

$$\frac{(A-B)^2}{2\left(2\gamma_1 + \frac{J^2}{\gamma_1 + \Gamma}\right)} \qquad (5.23)$$

In the denominator, we have now the additional term containing the exchange interaction integral. We know that $2\gamma_1$ represents the probability for an exciton jump to a neighbouring molecule. But in anthracene and naphtalene crystals we have four nearest neighbours. Thus we must replace the jump probability by an expression

which is four times as great. For the linewidth of ESR instead of the left expression, derived from our two molecule model, in the crystal we have the expression on the right side of eq. (5.24).

$$\frac{(A - B)^2}{2\left(2\gamma_1 + \dfrac{J^2}{\Gamma + \gamma_1}\right)} \quad \text{crystal} \Longrightarrow \quad \delta = \frac{(A - B)^2}{4 \cdot 2\left(2\gamma_1 + \dfrac{J^2}{\gamma_1 + \Gamma}\right)} \qquad (5.24)$$

Using the diffusion constant D_{aa}, derived in § 4.b we may write δ as shown in the next line

$$\delta = \frac{(A - B)^2}{4 D_{aa}} \cdot \frac{1}{\hbar} \left(\frac{a}{2}\right)^2 \qquad (5.25)$$

Introducing the jump probability W and the correlation time τ_c, the linewidth may be written alternatively in the manners given by eq. (5.26)

$$\delta = \frac{(A - B)^2}{2W} = (A - B)^2 \tau_c \qquad (5.26)$$

We see that the linewidth is a linear function of $(A - B)^2$. Forming now the derivative

$$\frac{d\delta}{d(A - B)^2} = \frac{1}{2W} \qquad (5.27)$$

we see that the slope of the straight line $\delta = \delta[(A - B)^2]$ determines the jump probability W.

e) Comparison with Experiment

Now we wish to compare this result with the experiment. In our calculation we have got the secular linewidth, that is the linewidth on account of the difference in the Larmor-frequencies at the two molecules. Thus we have to compare our theoretical expression with the secular part of the total linewidth. The ESR-measurements of Haarer and Wolf [14, 20] at anthracene crystals show that the secular linewidth indeed is a linear function of

Fig. 7. Line shapes of the ESR in the pure incoherent case for $A = 1$, $B = 2$ and different values of the fluctuation parameter γ_1

$(A - B)^2$, where $(A - B)$ is the difference in the local magnetic fields. From eq. (5.27) we may calculate the jump probability W as

$$W = \frac{1}{2} \left[\frac{d\delta}{d(A - B)^2} \right]^{-1} \tag{5.28}$$

The comparison with the experiment results in

$$W = 0.76 \cdot 10^4 G = 0.76 \, cm^{-1} = 1.43 \cdot 10^{11} \, sec^{-1}.$$

Using this numerical value for W and the values of J and Γ determined from optical absorption measurements at room temperature (Table 1)

$$J = 2.1 \, cm^{-1}, \qquad\qquad \Gamma = 51 \, cm^{-1}$$

we arrive at

$$\gamma_1 = 0.06 \, cm^{-1}.$$

This value is in good agreement with $\gamma_1 = 0.07 \, cm^{-1}$ determined from optical absorption together with diffusion measurements.

6. Influence of Exciton Motion on Nuclear-Spin-Resonance Absorption

Finally, we use the model of coherent and incoherent exciton motion in order to derive quantities, which are measurable by nuclear spin resonance. Investigating anthracene crystals using NSR one observes a shortening of the longitudinal relaxation time, if the crystal is irradiated by light. This may be understood as follows: The irradiation by light generates triplet excitons in the crystal. Their magnetic moments interact with those of the protons leading to hyperfine structure interaction, which is time dependent on account of the exciton migration and in this way causes relaxation processes. The longitudinal relaxation time of this process is obtained by a model calculation.

In order to investigate NSR one applies a constant external magnetic field H_{oz} in which the proton spins may align. This field is assumed to point in z-direction. If the crystal is irradiated by light, triplet excitons are generated. The magnetic moments, connected with the spin of the triplet excitons generate an additional magnetic field at the sites of the protons. This magnetic field is time dependent on account of two reasons: Firstly, the magnetic moments of the excitons rotate in the external magnetic field with their Larmor-frequency $\omega_e = \gamma_e \cdot H_{oz}$. Thus the additional magnetic field $\vec{H}(t)$ generated by the excitonic spins oscillates with this frequency ω_e.

$$H_x(t) = H_\perp \cos \omega_e t, \qquad H_y(t) = H_\perp \sin \omega_e t, \qquad H_z = H_z . \tag{6.1}$$

H_z is the component of this field in the z-direction, and $H_\perp$ the component in the x-y-plane. Secondly, the exciton may only generate a magnetic field at a certain molecule, if it is really sitting at this molecule. But on account of the interaction between the molecules, the excitons migrate from molecule to molecule. Therefore,

the probability ϱ_n of finding an exciton at a certain molecule depends on time. This time dependence is calculated within our two-molecule model. With the initial condition of finding the exciton at t = 0 at the molecule n, this probability is given by

$$\varrho_n(t) = \frac{1}{2} + \frac{1}{4}\left\{1 + i\frac{\gamma_0}{\sqrt{4J^2 - \gamma_0^2}}\right\}e^{-(i/\hbar)R_8 t} +$$

$$+ \frac{1}{4}\left\{1 - i\frac{\gamma_0}{\sqrt{4J^2 - \gamma_0}}\right\}e^{-(i/\hbar)R_9 t} \tag{6.2}$$

and R_8 and R_9 are represented by (2.16).
Assuming furtheron that these time dependencies are equal for all molecules occupied by an exiton, we have as total Hamiltonian:

$$H = - \sum_n H_{oz}\,\mu_{nz} - \sum_{n,i} \varrho_n(t)H_i(t)\mu_{ni} . \tag{6.3}$$

Here the first term represents the energy of the protons in the external magnetic field H_{oz}. The second term stems from the time dependent magnetic fields generated by the motion of the excitonic spins. $\varrho_n(t) = 0$ for protons whose molecules are not occupied by an exciton.

Assuming that the proton spins don't interact, we may separate the equation of motion of the density matrix of the protons

$$i\hbar\dot\varrho = [H, \varrho] \tag{6.4}$$

by a product ansatz into the equations of motion of the single proton spins. Using second order perturbation theory we obtain in the interaction representation for $\dfrac{d\tilde\varrho}{dt}$ the usual expression

$$\frac{d\tilde\varrho}{dt} = -\frac{i}{\hbar}[\tilde{\mathscr{H}}(t), \tilde\varrho(0)] + \left(\frac{i}{\hbar}\right)^2 \int_0^t \left[[\tilde\varrho(0), \tilde{\mathscr{H}}(t')], \tilde{\mathscr{H}}(t)\right]dt' \tag{6.5}$$

where $\tilde{\mathscr{H}}(t)$ is given in the following line

$$\tilde{\mathscr{H}}(t) = -\varrho_n(t)\frac{\hbar\gamma_p}{2}\{H_\perp(\sigma^+ e^{i(\omega_p - \omega_e)t} + \sigma^- e^{-i(\omega_p - \omega_e)t} + H_z\sigma_z\} \tag{6.6}$$

and $\omega_p = \gamma_p H_{oz}$ is the Larmor-frequency of the protons. Multiplication of the equation for $\tilde\varrho$ with the operator of the z-component of the proton spins and using trace operation, as usual we arrive at an equation of motion for the z-component of the magnetization. Now, not all molecules are occupied by an exciton. N_e be the number of molecules with excitons and N the total number of molecules. Thus N_e/N is the density of the excitons. Furtheron, there is also some relaxation when the crystal is not irradiated, which means, when there are no excitons in the crystal. We denote this relaxation time by T_1'.

Taking these two facts still into account, we arrive at this equation of motion for the z-component of the total spin:

$$\frac{d}{dt} \langle \sigma_z \rangle = \left\{ \frac{N_e}{N} \frac{1}{T_1'} + \frac{1}{T_1'} \right\} \langle \sigma_z \rangle. \tag{6.7}$$

The first expression in the curly bracket is the relaxation rate having its origin in the presence of the excitons. It will be denoted by $1/T_{1, ex}$. For $\gamma_0 \gg 2J$, that is for incoherent motion of the exciton, we obtain

$$\frac{1}{T_{1, ex}} = \frac{N_e}{N} \frac{1}{T_1'} = \frac{N_e}{N} \frac{\gamma_p^2 H_\perp^2}{2} \cdot \frac{1}{2} \cdot \frac{2\tau_c}{1 + \Omega^2 \tau_c^2} \quad (\gamma_0 \gg 2J) \tag{6.8}$$

Capital Ω is the difference in the Larmor-frequencies of the exciton and proton spins and approximately equal to the Larmor-frequency of the exciton spin. The correlation time τ_c is given by

$$\tau_c = \frac{\hbar}{2 \left(2\gamma_1 + \dfrac{J^2}{\gamma_0} \right)} \tag{6.9}$$

Taking now into account that in a real crystal of anthracene we have four neighbours which are relevant for the interaction between the molecules, instead of the left expression we have that one on the right side of eq. (6.10).

$$\frac{\hbar}{2 \left(2\gamma_1 + \dfrac{J^2}{\gamma_0} \right)} \overset{\text{crystal}}{\Longrightarrow} \frac{\hbar}{2 \cdot 4 \left(2\gamma_1 + \dfrac{J^2}{\gamma_0} \right)}, \quad (\gamma_0 \gg 2J) \tag{6.10}$$

NSR-measurements of Wolf and coworkers [15, 16] done were at room temperature. There the assumption $\gamma_0 \gg 2J$ is well fulfilled and we may use the above expression for τ_c in evaluating experimental data.

At room temperature, Wolf and coworkers got

$$\tau_c = 5 \cdot 10^{-12} \text{ sec .}$$

Furtheron, we know J and γ_0 from optical absorption measurements:

$$J = 2.1 \text{ cm}^{-1} \qquad \gamma_0 = 54 \text{ cm}^{-1}$$

The evaluation of the above expression then results in

$$\gamma_1 = 0.03 \text{ cm}^{-1}$$

This value is in satisfying agreement with $\gamma_1 = 0.06$ cm^{-1} known from the other experiments if we remember the rough assumptions, made in evaluating NSR--experiment: the interaction between the spins of the protons and the excitons was treated classically, the fine structure interaction was neglected, and instead of the two-dimensional motion of the exciton we have considered the motion of the exciton between two molecules.

7. Summary

Let us now summarize. We have presented a model, which tries to describe the coupled coherent and incoherent motion of Frenkel excitons. The coherent motion was described by the Coulomb and the exchange interaction integral, whereas the incoherent motion was represented by a Gaussian Markov process. After discussing the properties of the model using a two molecule system, we have investigated the influence of the coupled coherent and incoherent exciton motion on the line shape of the optical absorption. Starting from the equation of motion for the density matrix, in the limit of very strong fluctuations we have arrived at a diffusion equation. Then we have extended the model in order to allow the comparison with data obtained from electron and nuclear spin resonance.

Table 3. Comparison of the local fluctuation parameter γ_1 infered from various experiments at room temperature

optical absorption		diffusion	ESR	NSR
J/cm^{-1}	Γ/cm^{-1}	γ_1/cm^{-1}	γ_1/cm^{-1}	γ_1/cm^{-1}
2.1	51	0.07	0.06	0.03

In table 3 we have collected the data derived from these experiments at room temperature. In the first two columns we have represented the data derived from optical absorption experiments. In the last three columns, the values for γ_1 are given obtained by using the data known from optical absorption and from diffusion, electron spin resonance and nuclear spin resonance, respectively.

Taking into account the rough assumptions made in evaluating NSR, we may say that the data for γ_1 are in satisfying agreement. Thus using our model, we may describe completely different experiments in a consistent manner.

Furtheron, from the values of the parameters and the criterium of Haken and Strobl we could infer that the exciton motion in anthracene at room temperature is incoherent. On the other hand, at 4°K it should be coherent. The temperature behaviour of the parameters has been derived from optical absorption and diffusion measurements, covering the range from 371°K to 118°K.

ESR and NSR measurements, however, are only available at room temperature and at 77°K. Thus, for the future, it seems to be useful to have more and exact enough data also from these measurements.

From the theoretical point of view, it seems useful to extend those calculations which have been based on the two-molecule model to a larger arrangement of molecules, because in anthracene crystals the excitons move mainly in the a-b-plane. Furtheron, the application of this model to perturbed crystals should deliver results comparable with sensibilisized flourescence measurements. On the other hand, it would be interesting to treat explicitely the coupling of excitons to molecular and

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lattice vibrations and thus to derive the model of coupled coherent and incoherent exciton motion from first principles.

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