6

EXCITON ANNIHILATION
6.1 Introduction

Up to now, we focussed on limited sections of the chains of aggregated molecules: the delocalization length. The size of this area could be determined in the pump-probe experiment, and appeared to be approximately 15 monomers. However, the physical size of the studied aggregate consists of thousands of molecules, so it may well be possible that on the same aggregate chain several excitations are present, separated by more than their delocalization length. In a formal sense, multiple single excitons on the same chain can be described as one multiple-exciton. But excitations on the same chain that are separated by more than the exciton delocalization length, do not interact and it therefore makes more sense to think of them as independent one-excitons. These excitons will propagate in a diffusive way along the chain, driven by thermal fluctuations on the molecular energy levels. As will be discussed in this chapter, this influences the lifetime of an optical excitation on the chain.

The purpose of this chapter is to study the excited state dynamics and energy transport in J-aggregates at room temperature. It is not only of great fundamental interest to study these processes, but in addition, strongly coupled chromophores, like those in J-aggregates, also exist in biological systems. Most photobiological processes, including photosynthesis, rely on aggregates for energy or charge transfer processes. Thus, in order to learn more about natural systems it may be useful to study J aggregates, which are simpler systems.

For many aggregates, several population relaxation times have been reported. It is now well-established that the experimental excitation intensity strongly influences the observed decay rate [1-3]. It was shown that the measured lifetimes are shortened by exciton-exciton annihilation if too high excitation intensities are used [3], but the physics of the annihilation process was never specified. To investigate the role of exciton annihilation in J-aggregates we have therefore measured the population decay of the excitons under various excitation conditions, by means of ultrashort grating scattering experiments and time-resolved single-photon counting.

In this chapter the results are presented of an experimental study on the population decay of TDBC in water. These will be interpreted in terms of two different versions of a simple kinetic model, based on population dynamics among the various exciton bands. The multi-exciton bands act as doorway states in the exciton-exciton annihilation process. These bands thereby determine the population decay of the Frenkel excitons at high excitation densities.

The simple kinetic model is based on the fact that the studied J-aggregates have a linear, quasi-one-dimensional structure [4,5]. In such low-dimensional systems, reactants have a limited freedom of motion and consequently the diffusion of excitons has to be explicitly taken into account. In fact, the dynamics of the annihilation reaction between photo-generated excitons is expected to be diffusion-limited. This aspect was ignored in our first kinetic model. We will present an extended kinetic model in which the transport properties of excitons play a crucial role in the annihilation process. In addition, Monte Carlo calculations are performed to simulate a diffusion-limited annihilation reaction on a one-dimensional chain.

This chapter is organized as follows: In sec. 6.2, the experimental conditions of the various exciton lifetime experiments will be briefly described. In sec. 6.3 and 6.4 results of
these exciton lifetime experiments will be presented and discussed. The relaxation time is observed to be non-exponential, which may indicate a distribution of relaxation times. But the relaxation time is shown to depend also on the excitation density. This points to contributions from higher exciton bands to the observed decay, or exciton-exciton annihilation of one-excitons as a decay channel. In sec. 6.3 a simple kinetic picture of this process is presented, in which the multi-exciton bands act as doorway states in the annihilation process. A tacit assumption in this model is that diffusion does not limit the reaction rate. However, the excitons which we studied are restricted to a one-dimensional space. Therefore, the annihilation reaction is in fact expected to be diffusion-limited. In sec. 6.4 a more advanced kinetic model is used in order to analyze annihilation under these conditions. In sec. 6.5, the diffusion-limited annihilation reaction on a one-dimensional chain is simulated via Monte Carlo calculations in order to get a better sight on this process. In sec. 6.6 we discuss the results of these simulations. Finally, in sec. 6.7, our findings are summarized and conclusions are drawn.

6.2 Experiments

The optical set-up, used for the grating scattering and time-correlated single-photon counting experiments, has already been described in chapter 2 (sec. 2.3). Also the detection in the two types of population decay experiments was described extensively in sec. 2.3. In the grating scattering experiment the time resolution is determined solely by the pulse duration. In the time-correlated single photon counting experiment the overall response time of the set-up is determined by the speed of electronics, which gives a resolution of about 40 ps.

Details about the excitation characteristics are given in sec. 2.4. Here only a short summary is given. Depending on the requirements of the experiments, either one pulse (in the single-photon counting experiment) or three excitation and probe pulses (in the grating scattering experiment) were employed. At the sample, the energy of each 10 fs pulse was about 0.2 nJ (≈ 6×10⁸ photons pulse⁻¹). In case of the grating scattering experiment, excitation is performed in focus, so that the initial excitation density nₑ(0) can be calculated accurately. With the optical density of the sample being 0.8, this density is nₑ(0)= 1.55×10¹⁵ excitations pulse⁻¹cm⁻³. Focussed with a 75 mm focal length lens, this gives a (two-level) pulse angle of more than Θ= π/2 on the strongest aggregate exciton transition. One can calculate that in this situation there exists one excitation per 50 monomers. At times neutral-density filters were used to limit the pulse energy to the small-angle (perturbative) limit. To maintain short pulse durations at the sample, the pulse compressor was then readjusted to precompensate for the optical dispersion in the filters.

6.3 Exciton population decay
For many aggregates, several population relaxation times have been reported. TDBC is no exception to this rule: Makio et al. reported an exciton lifetime of 62 ps [4], while Lindrum et al. concluded that this lifetime was 96 ps [5]. It is now well-established that the experimental excitation intensity strongly influences the observed decay rate [1-3]. This is usually interpreted phenomenologically in terms of exciton-exciton annihilation [3], without further specification of the physics of the annihilation process. Also, multi-exponential decay is often observed [5-7], which can in principle be explained in terms of a distribution of exciton delocalization lengths in the sample [8]. However, since the decay times of the multi-exponent may differ considerably [5-7], it is more likely that fundamentally different states contribute to the observed decay. In this section results are presented on the population decay of TDBC in water. These are interpreted in a simple kinetic model, based on population dynamics among the various exciton bands. Both exciton-exciton annihilation and multi-exponential population decay can be explained in this model when the proper limits of the decay parameters are taken.

In fig. (6.1) the result is shown of a population-grating scattering experiment. Here, two femtosecond excitation pulses, with wave vectors $k_1$ and $k_2$, are crossed with an angle of ca. 5° in the sample, in order to induce a spatially modulated distribution of excited aggregates. This is shown schematically in the inset of fig. (6.1). A third pulse, with wave vector $k_3$, scatters from the resulting amplitude hologram in the phase-matched direction $k_3 = k_1 \pm (k_2 - k_1)$. When the delay of this pulse is varied, the scattered intensity reflects the dynamics of all exciton states that are involved in the formation of the population grating [9,10].

The result of fig. (6.1) shows a maximum in the signal when the third pulse overlaps in time with the excitation pulses. This effect is partly due to coherent coupling of all optical beams. It is related to the coherent artefact of the pump-probe experiment discussed in chapter 3, but, as discussed in chapter 5 on stimulated photon echo experiments, it is not fully understood, yet. When the third pulse is well-separated in time from the excitation beams, a

![Figure 6.1: Grating scattering signal of TDBC in water, measured with 10 fs optical pulses. The grating (hologram), induced by two crossing beams, is shown in the inset. A delayed third beam scatters from this interference pattern. The smooth solid curve is a calculation, based on the exciton-exciton annihilation model of eqs. (6.4) with parameters mentioned in the text. The grating scattering signal is proportional to $|n_{\tau}(0)|^2$.](image-url)
fast decay of the scattering signal of about 1.4 ps is observed. The interpretation seems to be clear: the population lifetime of the Frenkel excitons on the aggregate is 2.8 ps (the factor of 2 is due to the fact that the signal is proportional to the spatially modulated population density squared). However, the fact that the trace deviates significantly from being mono-exponential, indicates that this interpretation is not sufficient for a full description of the population decay process.

In fig. (6.2) the solid curve shows the result of a fluorescence lifetime experiment. The dashed curve in the figure shows the time response of the system, which was approximately 40 ps. In this single-photon counting experiment the population dynamics of the excitons is studied as well, but now on a much longer timescale. The measured response contains a long component, which decays with a (close to mono-exponential) time constant of 220 ps, and a short one that cannot be time-resolved by our set-up, but that could very well be the 2.8 ps derived from the grating scattering experiment. The long component only makes up about 1% of the overall decay. Both components are emitted in the spectral range of the aggregate transitions; monomer emission or pump-pulse stray-light does not contribute to these signals.

In fig. (6.3) another interesting aspect of the measured fluorescence decays is shown. Here grating scattering signals are displayed for different excitation intensities. The peaks of the signals are rescaled to fall on top of each other. It is clearly visible that the decay times of the observed signals are strongly dependent on the excitation intensity. When the pulses are attenuated, the observed decay becomes slower.

To connect the results of the grating scattering experiment with that of the single-photon counting experiment, we consider a simple kinetic model for the population dynamics in the one- and two-exciton bands. The exciton bands are depicted in fig. (6.4). The level structure in each band is neglected (the emission is dominated by the strongest transition in each band), and higher multi-exciton bands are not considered either. Extensions of the model which

![Figure 6.2: Time-resolved single-photon counting decay of TDBC in water. The solid curve is the experiment and the dashed one the time response of the system, as measured from a non-absorbing scattering medium. The smooth solid curve is a convolution of the system response with the exciton-exciton annihilation theory of eqs. (6.4). The photon counting signal is proportional to n₁(t).](image-url)
include these bands and the level structure are easily constructed. Here we concentrate on the essential features. The simplified population kinetics can thus be expressed in terms of the following differential equations:

\[
\begin{align*}
\frac{dn_g}{dt} &= +\gamma_{1e-g} n_{1e} + \gamma_{2e-g} n_{2e} \\
\frac{dn_{1e}}{dt} &= -\gamma_{1e-g} n_{1e} - \gamma_{coll} n_{1e}^2 + (\gamma_{2e-1e} + 2\gamma_{diss}) n_{2e} \\
\frac{dn_{2e}}{dt} &= +\frac{\gamma_{coll}}{2} n_{1e}^2 - (\gamma_{2e-1e} + \gamma_{2e-g} + \gamma_{diss}) n_{2e}
\end{align*}
\] (6.1)

Here, \(n_g\), \(n_{1e}\) and \(n_{2e}\) are the densities of excitons in the ground state and one- and two-exciton bands, respectively. All rate constants of eqs. (6.1) are depicted in fig. (6.4). The rates \(\gamma_{1e-g}\), \(\gamma_{2e-1e}\) and \(\gamma_{2e-g}\) hold for the spontaneous relaxation processes of the exciton bands, in which photons are emitted or energy is released as heat to the material. The rate \(\gamma_{coll}\) describes a process in which the higher exciton band is populated from the lower one. In a formal sense, two single excitations on the same chain can be described as a two-exciton. But in this picture, two excitations on the same aggregate chain, that are separated by more than the exciton delocalization length, are thought of as two independent one-excitons. These excitons propagate in a diffusive way along the chain, with a velocity that is probably to a large extent
diffusion of excitations is very slow, the rate constants directly connect between the dephasing of the excitons, discussed in chapters 4 and 5, and

Two limiting cases of eqs. (6.1) give analytical solutions that were used previously in the analysis of decay profiles of population relaxation in aggregates [1-3,5,7]. In both cases non-exponential intensity dependent decays are predicted. When it is assumed that the spatial propagation characteristics are determined by the fluctuations of the molecular energy levels. A "collision" between two propagating one-excitons may then occur with a rate $\gamma_{\text{coll}}$ and a probability proportional to the one-exciton density squared. When this happens, two one-excitons are converted into one two-exciton. The inverse process is also taken into account, in which one two-exciton is converted into two one-excitons, separated by more than the delocalization length. The rate constant for this "dissociation" process is $\gamma_{\text{diss}}$, which is also expected to be governed (in an as yet unknown way) by the energy fluctuations in the aggregate chain. In this way there is a direct connection between the dephasing of the excitons, discussed in chapters 4 and 5, and their propagation characteristics.

Two limiting cases of eqs. (6.1) give analytical solutions that were used previously in the analysis of decay profiles of population relaxation in aggregates [1-3,5,7]. In both cases non-exponential intensity dependent decays are predicted. When it is assumed that the spatial diffusion of excitations is very slow, the rate constants $\gamma_{\text{coll}}$ and $\gamma_{\text{diss}}$ approach zero and the corresponding terms in eqs. (6.1) can be neglected. The solution of eqs. (6.1) for the excited state exciton densities $n_{1e}$ and $n_{2e}$ of the one- and two-exciton bands then is:

$$n_{1e}(t) = n_{1e}(0) \exp[-\gamma_{1e-g} t] + \frac{\gamma_{2e-1e} n_{2e}(0)}{\gamma_{2e-1e} + \gamma_{2e-g} - \gamma_{1e-g}} \left\{ \exp[-\gamma_{1e-g} t] - \exp[-(\gamma_{2e-1e} + \gamma_{2e-g}) t] \right\}$$

$$n_{2e}(t) = n_{2e}(0) \exp[-(\gamma_{2e-1e} + \gamma_{2e-g}) t]$$

(6.2)

In this limit bi-exponential behavior is observed, with the relative magnitude of both components determined by the excitation efficiency and emission cross section of both the one- and two-exciton band. Since the excitation efficiency of the two-exciton band is non-linear, while that of the one-exciton band is linear, the observed decay is expected to be
intensity dependent. When more bands are included in the model, this result generalizes to multi-exponential decays.

Our results from the grating scattering experiment and the single-photon counting can thus be interpreted in the following way: the excitation pulses populate both the one- and two-exciton bands. These relax according to eqs. (6.2) with a total decay constant \((\gamma_{2e-1e}+\gamma_{1e-g})^{-1}\) = 2.8 ps for the two-exciton band, and a decay constant \((\gamma_{1e-g})^{-1}\) = 220 ps for the one-exciton band. However, the experimentally observed ratio of the two contributions (99% of the single-photon counting decay occurs in 2.8 ps) can only be explained when the quantum yield for emission from the one-exciton band is much lower than for emission from the two-exciton band. This seems not very likely.

Another limit, in which eqs. (6.1) can be solved analytically, is obtained when the lifetime of the two-exciton band is assumed to be very short, and dominated by the relaxation rate \(\gamma_{2e-1e}\). At high excitation density, the population decay of the one-exciton band is then determined by collisional population of the two-exciton band, which subsequently rapidly relaxes back to the one-exciton band. In this process one of the two original colliding one-excitons is "annihilated". The differential equation for the one-exciton population of eqs. (6.1) then simplifies to:

\[
\frac{dn_{1e}}{dt} = -\gamma_{1e-g} n_{1e} - \frac{1}{2} \gamma_{\text{coll}} n_{1e}^2
\]  

(6.3)

This form was extensively used in the interpretation of fluorescence decays of PIC aggregates [3]. In this limit \((\gamma_{2e-1e} \rightarrow \infty)\), the solution of eqs. (6.1) for the excited state exciton densities \(n_{1e}\) and \(n_{2e}\) of the one- and two-exciton bands is:

\[
n_{1e}(t) = \frac{2\gamma_{1e-g} n_{1e}(0) \exp\left[-\gamma_{1e-g} t\right]}{2\gamma_{1e-g} + \gamma_{\text{coll}} n_{1e}(0) \left[1-\exp\left[-\gamma_{1e-g} t\right]\right]} \\
n_{2e}(t) \approx 0
\]  

(6.4)

In this model intensity dependent population relaxation is expected as well, since the annihilation process depends on the square of the population density of one-excitons.

Our results from the grating scattering experiment and the single-photon counting can now be interpreted in a different way: the optical pulses cause multiple excitations on each aggregate. Due to the limited exciton delocalization length of about 15 monomers, these excitations can be considered as independent one-excitons. The two-exciton band is also populated (two single-molecule excitations within the delocalization length), but relaxation from this band is extremely fast due, for instance, to coupling with highly excited single-molecule states or the conduction band of the aggregates. Therefore, population in this band is negligible and does not contribute to either the grating scattering signals or the single-photon counting decay (except perhaps around zero-delay, where it contributes to the observed
additional peaks in figs. (6.1) and (6.2)). Since the one-excitons propagate in a diffusive manner, they may meet each other with a probability equal to the population density squared. Rapid depopulation then follows via excitation and decay of the two-exciton band.

At long times, when the concentration of one-excitons has become so low that the collision probability vanishes, eq. (6.4) predicts single-exponential decay: \( n_{e}(t) \sim \text{exp}(-\gamma_{1e-g} t) \). The mono-exponential time constant of 220 ps found by fitting the tail of the single-photon counting signal, is in this limit the spontaneous lifetime \( (\gamma_{1e-g})^{-1} \approx 220 \text{ ps} \) of the one-exciton band. At short times, in the grating scattering experiment, the annihilation process dominates the decay \( (\gamma_{1e-g}<1) \) and eqs. (6.4) can then be simplified to:

\[
    n_{e}(t) = \frac{n_{e}(0)}{1 + \frac{1}{2} \gamma_{\text{coll}} n_{e}(0) t} \tag{6.5}
\]

This offers a way to obtain the collisional decay rate \( \gamma_{\text{coll}} \) from the fit of the grating scattering signal. To this end, the initial excitation density \( n_{e}(0) \) must be known. This can be calculated from the optical density of the sample and the beam parameters of the optical pulses, when it is assumed that for every absorbed photon a one-exciton arises. This is most accurately done for the grating scattering experiment, because there the excitation is performed in focus (see sec. 2.4 and 6.2). The collisional rate for the annihilation process is then derived to be \( \gamma_{\text{coll}} = 1.02 \times 10^{-3} \text{ cm}^3 \text{s}^{-1} \). This rate is about a factor of 2 smaller than the annihilation values reported for PIC aggregates by Gagel et al. [7] and Sundström et al. [3].

Since aggregates in liquids are assumed to have a one-dimensional structure, the dimension of the collisional rate constant per volume unit has no direct physical meaning. Instead, the rate constant should be calculated per unit of length, so that it can be related to the mobility of one-excitons. In order to transfer volume to length, we place all the aggregates in succession on a single long chain. Then: \( n'_{e} = n_{e}/c \Delta L \), in which \( n'_{e} \) is the number of one-excitons per unit of length, \( c \) is the number of monomers per cm\(^3\) and \( \Delta L \) is the length per monomer. If \( n_{e} \) is then substituted in eq. (6.3) in terms of \( n'_{e} \), this leads to:

\[
    \frac{dn'_{e}}{dt} = -\gamma_{1e-g} n_{e}' - \frac{1}{2} \gamma_{\text{coll}}' n_{e}'^2 \tag{6.6}
\]

in which \( \gamma_{\text{coll}}' \) now is the collisional rate per unit of length, defined as: \( \gamma_{\text{coll}}' = c \Delta L \gamma_{\text{coll}} \). When we use \( c = 9 \times 10^{16} \text{ molecules/cm}^3 \) and \( \Delta L = 3.5 \text{ Å} \) [4], we can calculate \( \gamma_{\text{coll}}' = 3.21 \times 10^6 \text{ cm} \text{s}^{-1} \).

The solid curves in figs. (6.1) and (6.2) are calculated with the annihilation model of eqs. (6.4). In fig. (6.5) is shown how the decay of one-excitons occurs at a certain density. With our parameters one can calculate that the excitation intensity of the grating experiment should be a factor of 10\(^4\) less than the intensities used here, in order to do experiments free from annihilation. With our detection sensitivity this limit could not be reached.
In order to determine whether the annihilation limit of eqs. (6.4) truly holds for TDBC, decay curves were calculated as a function of intensity and compared with the intensity dependent population relaxation experiments as displayed in fig. (6.3). Because $\gamma_{col}$ and the variation in $n_e(0)$ for the different experimental curves are known, the intensity dependent grating scattering signals can be calculated exactly with eq. (6.5). The calculations are displayed as solid curves in fig. (6.3) and are seen to describe the experimental curves very well. Thus, the intensity dependence can completely be explained in the model of eqs. (6.4).

It can be stated that the annihilation picture describes all population relaxation features well, with the exception of the strong grating scattering and photon counting signals around zero-delay. As stated above, coherent coupling between the optical beams will certainly contribute to the grating scattering signal when all pulses overlap in time, as well as emission from the two-exciton band. It is also possible that incoherent population relaxation from the higher exciton bands contributes to these signals as well. However, as discussed in chapter 5 on stimulated photon echoes, the transients around zero delay cannot be fully explained, yet.

6.4 Diffusion-limited population decay

So far, transport properties of excitons were not explicitly considered in the kinetic model described in the previous paragraph. But in principle, diffusion of reaction particles will be influenced by the surroundings in which the particles move. Obvious examples for this are the situations in which reactants are spatially constrained on the microscopic level by either walls, phase boundaries, or force fields, i.e., are restricted in their freedom of motion by dimensional constraints. Numerous theoretical works describe the properties of excitons restricted to a one-dimensional space [16,18,19,21]. Diffusion of reacting particles in such space-limited structures is different from that in bulk materials. Experimentally, such excitons have been observed in polymers [11,12], J-aggregates [3,13], columnar phases of phthalocyanines [14], and some other materials consisting of linear chains, where probabilities

![Figure 6.5: Decay characteristics of one-excitons in the annihilation model of eqs. (6.4). The sensitivity of our grating scattering set-up is insufficient to detect a signal from exciton densities low enough to make annihilation negligible ($n_e < 10^{13} \text{ cm}^{-3}$). The dashed curve represents an exponential decay with a time constant of 220 ps.](image)
of intra- and interchain hopping are very different.

Aggregates dissolved in water presumably have a linear, quasi-one-dimensional structure [4,5]. This assumption underlies the theoretical treatment presented in chapter 3, and was used in subsequent chapters to discuss our experimental results. However, we did not take into account that due to this dimensional constraint, diffusion of the photo-generated excitons is expected to be influenced, which affects the dynamics of the annihilation process. Despite the fact that the experimental results were simulated very well with the model of sec. 6.3, a more advanced model is needed in order to describe the dynamics of one-dimensional exciton annihilation properly. This will be the purpose of this paragraph.

In order to incorporate the diffusion of excitons in the annihilation process, aggregates can be considered to be diffusion-reaction systems, in which the reactants are transported by diffusion [15]. Two fundamental timescales characterize these systems: the diffusion time, which is the time that elapses between collisions of reacting particles, and the reaction time, the time that particles take to react when in proximity. If the reaction time is much larger than the diffusion time, the process is reaction-limited. The kinetics of such systems is described by well-known classical rate equations. This approach underlies our treatment of the annihilation dynamics of the previous section.

On the contrary, in diffusion-limited processes the reaction timescale is negligible compared to the diffusion time. In practice, any closed diffusion-reaction system may exhibit diffusion-limited behavior: as the concentration of the reactants decreases, the time between collisions of the reactants increases, and at very low concentrations, the diffusion time is larger than the characteristic reaction time. A diffusion-limited reaction is in particular expected to occur when the reactants are restricted in their movement by the above mentioned dimensional constraints.

The essential difference between reaction-limited and diffusion-limited reactions concerns the spatial distribution of the reactants [11,16,17]. In the annihilation reaction, a “hole” is created in an originally uniform distribution of excitons. Diffusive transport of reactants in three dimensions is well able to eliminate this “hole”, i.e., to create a spatially uniform “random” concentration of reactants. However, in systems where diffusive transport is limited to less than two dimensions, the distribution of reactants tends to become “less random”, that is, it is actually more ordered. Classical rate equations such as eqs. (6.3) and (6.6), where implicitly a uniformly random distribution in space is assumed, are then no longer valid. When the diffusion of reactants is, by lack of space, not sufficiently rapid compared to the reaction rate, the fluctuations in spatial concentration grow in time as a consequence of the reactions. This process has been described as a dynamic self-ordering of the spatial distribution of reactants [18,19].

This effect is related to the compactness of a low-dimensional random walk. In low dimensions a random walker is likely to stay at its original vicinity and will eventually recross its starting point. So diffusion-limited kinetics is a “compact” kinetics, the random walkers mostly “oscillate” around their original positions. In higher dimensions (i.e., two and higher) the random walker has a finite “escape probability” and may never return to the starting point [18]. It will therefore be able to eliminate spatial fluctuations in the concentration much more easily. In one-dimensional systems the influence of the developing inhomogeneous spatial
distribution of reactants on the reaction kinetics is therefore most pronounced.

In the *diffusion-limited single species annihilation model* [18-20] the particles are localized on a single site and are able to hop to neighboring sites. When two particles meet, they are subject to an irreversible annihilation reaction: \( A + A \rightarrow \text{products} \). The most relevant difference with the kinetic model discussed in the previous section, is that the diffusive transport of the particles is now the rate-limiting step, instead of the rate of the annihilation reaction. Annihilation is assumed to take place instantaneously whenever two particles meet (the extreme diffusion limit [21]). The model accurately describes the time evolution of the distribution of particles on a chain.

Kopelman and coworkers [18], and ben-Avraham and coworkers [19] presented the solution of this process in one spatial dimension. The mathematical analysis of the chosen systems is surprisingly simple: the problem is reduced to a linear partial differential equation, and can therefore serve as a basic model for various phenomena in diffusion-reaction systems. The model has been used to describe for example excitation trapping in photo-biological systems [22], exciton fusion in composite materials [20,23] and charge recombination in colloids and clouds. However, up to now the model was never used to describe the annihilation process in J-aggregates in solution.

When the lifetime of the two-excitons is very short, and spontaneous population relaxation of the one-excitons can be neglected, the model applies directly to our annihilation process. At long times and fixed temperature, the annihilation process in the diffusion limit obeys the rate equation [18,25]:

\[
\frac{dn_{1e}}{dt} = -\frac{1}{2} \gamma_{\text{anh}}(t) n_{1e}^2 \quad (t \to \infty)
\]  

(6.7)

in which \( n_{1e} \) is the density of one-excitons and \( \gamma_{\text{anh}}(t) \) is the macroscopic rate “constant”. The most important difference with the classical situation is that the rate constant \( \gamma_{\text{coll}} \) (in eq. (6.6)) is now replaced by a time-dependent rate “constant” \( \gamma_{\text{anh}}(t) \). The time-dependence is due to the process of dynamic self-ordering, by which the distribution of excitons is not random anymore.

The form of the time-dependence of \( \gamma_{\text{anh}}(t) \) is related to the random walker’s exploration space \( S(t) \), i.e., the mean number of distinct sites visited by the random walker [18]: \( \gamma_{\text{anh}}(t) = [dS(t)/dt] \). The expression for \( S(t) \) strongly depends on the dimensionality of the system [24,25]. For a one-dimensional system is \( dS(t)/dt \propto t^{-1/2} \). Thus eq. (6.7) becomes:

\[
\frac{dn_{1e}}{dt} = -\frac{1}{2} \gamma_{\text{anh}} t^{-1/2} n_{1e}^2(t)
\]  

(6.8)

with the time-independent rate constant [21]:
\[
\gamma_{\text{anh}} = \sqrt{\frac{\pi (\Delta L)^2}{\tau_{\text{hop}}}} \tag{6.9}
\]

where \(\Delta L\) is the spacing between neighboring sites and \(\tau_{\text{hop}}\) is the average time an exciton remains on one site in between two consecutive hops. The general solution of eq. (6.8) is [16,21]:

\[
\frac{n_{1e}(t)}{n_{1e}(0)} = (1 + \gamma_{\text{anh}} n_{1e}(0) \sqrt{t})^{-1} \tag{6.10}
\]

in which \(n_{1e}(0)\) represents the initial exciton density created under pulsed excitation at \(t=0\). One should realize that here, with writing down eq. (6.7), the evolution of the exciton density of a stationary system is described. So \(n_{1e}(0)\) is not the real initial exciton density, but represents some equilibrated distribution in which start-up effects have disappeared.

The fluorescence intensity \(I(t)\) in the photon counting experiment is proportional to the instantaneous exciton density \(n_{1e}(t)\). Then eq. (6.10) leads to:

\[
\ln \left( \frac{I(0)}{I(t)} \right) = 0.5 \ln(t) + \ln(\gamma_{\text{anh}} n_{1e}(0)) \tag{6.11}
\]

The grating scattering intensity is proportional to the exciton density squared, so for this experiment \(I(t)\) represents the square root of the signal.

Up to here it is assumed that the excitations are localized on a single monomer. However, in J-aggregates in solution, we know that excitations are delocalized over approximately 15 molecules. As a result, free space is reduced which in turn reduces the motional freedom of excitons on the same aggregate chain. In order to describe the reaction kinetics of the annihilation reaction properly, one needs to correct for this fact. Therefore we replace in the differential equation (6.8) the particle density \(n_{1e}\) by \(D/L\), in which \(D\) is the total number of one-excitons per aggregate and \(L\) is the total length of the aggregate chain. One can then take the space reduction of excitations into account, by replacing \(L\) by a reduced length \(L' = L - D(N-1)\), where \(N\) is the delocalization length. Both \(N\) and \(L\) are expressed in terms of the number of monomers involved. The solution of the new differential equation is then found to be:

\[
\frac{n_{1e}(t)}{n_{1e}(0)} = \left(1 + \gamma_{\text{anh}} n_{1e}(0) \sqrt{t} + (N-1) n_{1e}(0) \log \frac{n_{1e}(0)}{n_{1e}(t)} \right)^{-1} \tag{6.12}
\]
Note that for localized excitations, i.e., \( N=1 \), one obtains again eq. (6.10). The net effect is that the annihilation process for delocalized excitations becomes less effective compared to the situation where the excitations are localized.

The theory leading to eq. (6.7) describes the annihilation reaction in a one-dimensional system that has proceeded long enough, so that it is diffusion controlled. In reality, the absorption of light from a short optical pulse generates a randomly distributed ensemble of excitations. Hence, in order to treat the annihilation problem properly, one should therefore start with a completely random distribution of particles. Kopelman \[18\] and ben-Avraham \[19\] described the evolution of such a system. The initial interparticle distribution function (IPDF, closest neighbor distance distribution, i.e., the probability density function for finding the nearest particle at distance \( x \) on one side of a given excitation) then has the exponential form:

\[
p(x,0) = n_{1e}(0) \exp[-n_{1e}(0)x]
\]

(6.13)

This IPDF is pictured in fig. (6.6a). For this situation, the exact result for the decay of the survival fraction in the annihilation reaction is:

\[
\frac{n_{1e}(t)}{n_{1e}(0)} = \left[ 1 - \text{erf} \left( \sqrt{\frac{n_{1e}^2(0)\gamma^{anh}}{\pi t}} \right) \right] \exp \left( \frac{n_{1e}^2(0)\gamma^{anh}}{\pi} \right)
\]

(6.14)

By the fact that annihilation occurs when two excitations meet, the distribution is modified when the reaction has proceeded for some time. The ensemble of particles achieves a
stable, self-ordered distribution. This is characterized by a change of the exponential IPDF to a stationary skewed Gaussian form, depicted in fig. (6.6b):

\[
p(x,t) = \frac{\pi}{2} n_{1e}^2(t) x \exp\left[ -\frac{\pi}{2} \frac{n_{1e}^2(t)}{2} \frac{(x)^2}{2} \right]
\]  

(6.15)

The decay of the survival fraction in the annihilation reaction for this IPDF can be calculated exactly [18,19]:

\[
\frac{n_{1e}(t)}{n_{1e}(0)} = \left( 1 + \frac{\gamma_{anh}^2 n_{1e}(0)}{2} t \right)^{-1/2}
\]

(6.16)

which has the same long-time behavior as eq. (6.10).

However, the derivation of eqs. (6.14) and (6.16) is not so straightforward. The starting point for the analysis is a master equation for the state probability [19]. Apart from very special cases, such master equations pose a formidable mathematical problem and approximate techniques are needed. The approach used here assumes a steady state situation in the distribution of excitations on the chain, so that the system can be described simply by the linear differential equation (6.7) [18]. The solutions of this differential equation, eqs. (6.10), (6.11) and (6.12), are used in this chapter in order to study the annihilation reaction in aggregates.

In order to judge whether the used approximation is useful, in fig. (6.7) the time evolution is shown of the excitation concentration in the annihilation reaction for the three different approaches in the diffusion-limited annihilation model. The solid and dashed curves

Figure 6.7: Survival probability \[n_{1e}(t)/n_{1e}(0)\] versus dimensionless time for the single species annihilation model. The initial conditions for the curves are (solid line) a totally random distribution and (dashed and dotted line) a stationary skewed Gaussian distribution for the excitations on a chain. It is shown that the initial reaction rate strongly depends on the exact shape of the initial IPDF. The universal behavior at long times is apparent. The difference between the dashed and dotted line is that the dashed line is the result of an exact calculation (eq. (6.16)), while the dotted line is an approximation as described in eq. (6.10), and used in the analysis of the experimental results.
represent the situations for different initial distributions for the excitations on a chain. The universal behavior at long times is apparent, but the reaction proceeds at strikingly different rates at early times, depending on the exact shape of the initial IPDF. For particles distributed on a chain according to an exponential IPDF (solid line, eq. (6.14)), the initial reaction rate is 100 times larger than for a skewed Gaussian initial IPDF (dashed line, eq. (6.16)), at identical particle density [20]. This is not too surprising when one considers that the initial condition for a random exponential distribution places many particles very close together. Excitations near their neighbors react quickly, leaving the more isolated excitations to achieve the stationary skewed Gaussian distribution. So the macroscopic behavior of a fully non-linearly interacting many-particle system can depend on the microscopic initial conditions of the system.

The dashed and dotted curves represent the situation for particles distributed on a chain according to a skewed Gaussian initial IPDF. The dashed line is the result of an exact calculation (eq. (6.16)), while the dotted line is an approximation as described in eq. (6.10), and used in the analysis of the experimental results. It is clear that compared to the solid curve, which describes the annihilation system in the most realistic way, the dotted approximation is the best one. One finds the results of eq. (6.10) and (6.14) to be identical within 16%. In units of the dimensionless time used in fig. (6.7), the timescale of our experiments is so large that differences between the different approaches in the single species annihilation model have completely disappeared. Therefore eq. (6.10), (6.11) and (6.12) are useful approximations for the interpretation of our experimental results.

6.5 Monte Carlo simulations

In the previous section, it was shown that in the exciton-exciton annihilation process in J-aggregates diffusion has to be taken explicitly into account. However, the used diffusion-limited single species annihilation model is a simplification of a complex process. In order to describe the annihilation reaction in a more realistic way, we have simulated the A+A→A annihilation reaction on a one-dimensional chain via the Monte Carlo technique. This technique simulates the actual motion and reaction of (de)localized excitations [25], and is an improvement of the diffusion-limited single species annihilation model on two points. First, when two excitons collide in the Monte Carlo simulation, they can annihilate with a probability smaller than one, which can be related to a finite lifetime of the two-exciton band. Second, the annihilation process starts now from a completely random distribution of excitons, so that start-up effects are included.

The Monte Carlo simulations are performed as follows. The aggregate is represented by a chain of variable length, but with a maximum of 15,000 sites. Chains are used with periodic spatial boundary conditions, simulating an aggregate of infinite length. The initial state of the system at time t₀ is prepared by distributing excitations on the chain. This can be done one by one, which simulates localized excitations, or by filling repeatedly N neighboring sites, simulating excitations delocalized over a delocalization length N of molecules. The (de)localized excitations are displaced from each other at an average random distance, determined by the random exponential IPDF (see fig. (6.6a)).

Then, the state of the system is calculated at times tₙ₊₁=tₙ+Δt, where Δt is the steptime. During each time step we allow the excitations to hop, either to the left or to the right.
neighboring site, with a fixed hop probability. This simulates the diffusive motion of the excitations. At the completion of a hop, we check for annihilation of two excitations. If the target site is already occupied by another excitation, one of the two excitations has a chance, the annihilation probability, to be removed from the chain, decreasing the total number of excitations by one. For delocalized excitations the annihilation probability is proportional to the overlap of the delocalization areas, in such a way that the probability gets its maximum value with complete overlap of the areas. Decreasing the annihilation probability will slow down the self-ordering of the distribution of reactants, such that diffusion can become sufficiently rapid to eliminate spatial fluctuations in the concentrations of reactants. This will tend to diminish the diffusion limitation of the annihilation reaction.

For all simulations we use a very low hop probability, in order to prevent the so-called hop artefact to occur. This artefact is the effect that, above some critical hop probability, the decay of population becomes slower instead of faster. It is caused by the fact that for a hop probability close to one, neighboring particles will pass each other during a time step and therefore never can annihilate. Decay of population will then be retarded with an increasing hop probability. It was tested that this effect is already occurring above a hop probability per time step of 0.3. Therefore, we take a hop probability per time step of 0.1 in all simulations.

The simulation is averaged over 50 chains, in order to ensure proper statistics. Output of the simulations is the survival fraction \( n_x(t)/n_x(0) \) versus time in units of the step time. The step time can be placed optionally on a linear or logarithmic scale. One has to keep in mind that in the latter representation the y-value at step time 0 is not the real population due to the initial distribution of excitons, but is the survival fraction after one step. The survival fraction from the logarithmic calculation is converted to a double logarithmic plot, reproduced corresponding to the form of eq. (6.11), where we take the first y-value of the linear calculation as the initial luminescence intensity \( I(0) \). In this way it is easily checked whether the simulation predicts indeed a linear dependence with slope 0.5, indicative for a diffusion-limited reaction on a one-dimensional chain (eq. (6.11)), or slope 1, which holds for the reaction-limited case (eq. (6.5)). This provides a critical test for the dimensionality of the aggregate model as employed in this thesis.

6.6 Discussion

The diffusion-limited single species annihilation model describes the kinetics of a diffusion-limited annihilation reaction in one dimension. We used this model to test the one-dimensional character of the aggregate model as employed in this thesis.

A double logarithmic plot of the experimental grating scattering decay curve is reproduced corresponding to the form of eq. (6.11) and plotted in fig. (6.8). Note that in eq. (6.11) it is assumed that the fluorescence intensity \( I(t) \) is proportional to the exciton density \( n_{ex}(t) \), while in the grating scattering experiment the measured intensity is proportional to \( (n_{ex}(t))^2 \). In fig. (6.8) the square root of the experimental grating scattering decay signal is therefore taken. The diffusion-limited model predicts a linear dependence with slope 0.5 (dotted line), representing the time dependence \( t^{-0.5} \) of the reaction rate. Instead, a decay of the
experimental curves with slope 1 (dashed line) is observed, i.e., the reaction rate is time independent. This means that our annihilation reaction is not diffusion-limited in the frame of a one-dimensional system.

Monte Carlo simulations of the annihilation reaction can help us to get an idea in what way the diffusion-limited annihilation model fails to describe the experimental results. First we will perform Monte Carlo simulations for single-particle excitations (sec. 6.6.1). Then we enlarge the spatial extension of the excitons and observe the effect of delocalization. In sec. 6.6.2 the results are described of Monte Carlo simulations on the aggregate chain for excitations delocalized over 5 or 15 monomers.

### 6.6.1 Annihilation of localized excitations

We first simulated the annihilation behavior of localized excitations. The results for different annihilation probabilities per time step are plotted in fig. (6.9a) on a double logarithmic scale, corresponding to the form of eq. (6.11), as a function of step time. In the situation that the annihilation probability equals one, the diffusion-limited annihilation model predicts a linear dependence with slope 0.5, according to eq. (6.11). This is indeed true for the Monte Carlo simulation in the figure, but only after a considerable number of step times. The deviation from slope 0.5 at the start of the simulation is caused by the fact that the initial distribution of excitons is random. However, in the annihilation model it is assumed that the distribution is stationary self-ordered, characterized by a skewed Gaussian interparticle distribution function. In the Monte Carlo simulations, and also in the actual experiments, the ensemble needs some time to achieve this self-ordered distribution. At the start of the simulation, the reaction rate will therefore be faster than predicted in the annihilation model:

![Figure 6.8: Double logarithmic plot of the grating scattering signal of TDBC in water, measured with 10 fs optical pulses, reproduced corresponding to the form of eq. (6.11). The maximum in the signal is probably due to a coherent artefact, and not to real dynamics. Therefore, I(0) (and the matching t=0) was not chosen at the maximum of the signal, but 300 fs later. The dotted line is a plot with slope 0.5, identifying a diffusion-limited annihilation reaction with a reaction rate ~t^-\(1/2\). The dashed line has a slope of 1, representing a time-independent reaction rate.](image-url)
many excitons react quickly, because they are placed very close together. After some time the reaction then really becomes diffusion-limited. It is seen in the figure that this is only achieved after a considerable number of steps. Due to the low hop probability a lot of hops, or hop possibilities, are needed before the stationary distribution has arisen.

In contrast to the annihilation model, in the Monte Carlo simulations it is possible to incorporate a finite reaction probability of excitations, by using an annihilation probability per time step lower than one. It is seen in fig. (6.9a) that, going to lower annihilation probabilities, the slope of the plots is shifting from 0.5 to 1. A slope of 1 represents the situation in which the reaction rate has become time-independent, i.e., the annihilation process is not diffusion-limited anymore. The low annihilation probability causes the spatial distribution of excitons to become more homogeneous, by moving from the pure diffusion-limited case towards the situation where the reaction process becomes rate-limiting.

In fig. (6.9b) the effect of different excitation densities on the annihilation reaction is studied with a Monte Carlo simulation. The annihilation probability is fixed at 0.05. The curve calculated with a large initial exciton distance, approaches quickly a slope of 0.5. The larger
“holes” in this distribution apparently cannot be filled, so that already after a few steps an inhomogeneous distribution of excitons arises, leading to the diffusion-limited annihilation reaction. After more time steps it is seen that for the different excitation densities there exist no differences anymore in the annihilation rate. The concentration of excitons is now reduced and the average distances between the excitons have become so large, that the original differences in excitation density have disappeared.

The experimental results, shown in fig. (6.8), can be simulated for the case of localized excitations, provided that the annihilation probability is chosen very low: 0.05. The agreement between calculation and experiment does not improve for lower probabilities. By comparing this Monte Carlo simulation with the experimental results, one can derive two parameters for the TDBC aggregates: the hop time of the one-excitons and the lifetime of the two-exciton state.

We will first consider the conversion of the abstract step time of the one-excitons to a real, physical hop time. The step time-axis of a calculated curve with annihilation probability of

![Graph](image_url)

*Figure 6.9: Monte Carlo simulations (solid lines) for localized excitations. The results are plotted on a double logarithmic scale, corresponding to the form of eq. (6.11), as a function of time in units of step time. The hop probability is always taken to be 0.1 per time step. A dotted line with slope 0.5 is also shown, identifying a diffusion-limited annihilation reaction with a reaction rate $-t^{-0.5}$. The dashed line has a slope of 1, representing a time-independent reaction rate (eq. (6.5)). (a) Monte Carlo simulations performed for different annihilation probabilities. The initial exciton distance is 2 monomers on average. The annihilation probabilities per time step are, from top to bottom: 1, 0.05 and 0.005 respectively. (b) The calculation for an annihilation probability of 0.05 is now performed for different initial excitation densities. The average initial excitation probability of 0.05 is now performed for different initial excitation densities. The average initial excitation probability of 0.05 is now performed for different initial excitation densities. The average initial excitation probability of 0.05 is now performed for different initial excitation densities. The average initial excitation probability of 0.05 is now performed for different initial excitation densities. The average initial excitation probability of 0.05 is now performed for different initial excitation densities. The average initial excitation probability of 0.05 is now performed for different initial excitation densities. The average initial excitation probability of 0.05 is now performed for different initial excitation densities.
0.05 (in fig. (6.9a)), is superimposed on the experimental curve of fig. (6.8) (also displayed on a double logarithmic scale). Both axes should extend over the same order of magnitude. The step time-axis is then moved relative to the experimental time axis, in such a way that both curves have a maximal overlap. This is done in fig. (6.10) for an annihilation probability of 0.05. The step time is then calculated to be approximately 10 fs. The hop probability per time step in these simulations was 0.1. This means that the hop time, i.e., the average time an exciton remains on one site in between two consecutive hops, will be approximately 10 times as large and is 100 fs. This hop time tells us something about the mobility of the one-excitons. By lowering the annihilation probability in the simulations, the hop time becomes smaller and in this situation the excitons “run” faster over the chain, in order to get the same overall decay rate by increasing the number of collisions. With the hop time of 100 fs, one can calculate a hopping rate constant (in unit of length), defined as $\Delta L/\gamma_{\text{hop}} = 0.35 \times 10^6 \text{ cm s}^{-1}$ (for $\Delta L$ the same value as in sec. 6.3 is used), which we can compare with the collisional rate $\gamma_{\text{coll}} = 3.21 \times 10^5 \text{ cm s}^{-1}$, calculated in sec. 6.3. Although the physical picture is completely different (diffusion is explicitly taken into account or ignored completely), they are of comparable magnitude.

Next, we turn to the lifetime of the two-exciton state. This can be calculated from the annihilation probability used in the simulation. The survival probability per time step for two excitons on the same site, i.e., in a two-exciton state, is 1 minus the annihilation probability of a one-exciton. The lifetime $1/\gamma_{2e}$ of the two-exciton state is then defined as the time (or the number of simulation steps) after which the population has decayed to $1/e$ of the initial value, so: $(1-\text{annihilation probability})^{1/\gamma_{2e}} = 1/e$, in which $1/\gamma_{2e}$ is expressed in terms of the step time, and the initial population is normalized to unity. For an annihilation probability per time step of 0.05, and a step time of 10 fs, the lifetime of the two-exciton state is thus found to be approximately 200 fs. This very short lifetime of two-excitons was already assumed in writing down eq. (6.7).

![Figure 6.10: Scaling of a Monte Carlo simulation of figure 6.9 (dotted line), for an annihilation probability of 0.05, on the experimental curve of figure 6.8 (solid line). The scale on top of the figure is the experimental timescale. The scale on the bottom of the figure is the timescale of the Monte Carlo simulation. From this plot, the hop time is found to be 100 fs.](image-url)
6.6.2 Annihilation of delocalized excitations

The Monte Carlo simulations discussed above were performed for localized excitations. However, we know that the excitations in TDBC are delocalized over approximately 15 monomers. To study the effect of the delocalization on the annihilation properties, we also performed Monte Carlo simulations for delocalized excitations.

The result is shown in fig. (6.11). A double logarithmic plot, as a function of some abstract step time, is displayed here for delocalized excitations. The delocalization lengths are five and fifteen monomer units and for each length calculations are performed with different initial exciton densities. The annihilation probability was taken proportional to the overlap of the delocalization areas, with the maximum value of 0.5 for total overlap.

Most striking in the figure is the fact that the Monte Carlo calculations for delocalized excitations never resemble the experimental results. The slope of the double logarithmic plot is always, as predicted in the diffusion-limited single species annihilation model, approximately 0.5, except for short times. It never really becomes 1, as observed in the experiments. By taking the annihilation probability proportional to the overlap of the delocalization areas, the effective annihilation probability is low. Despite this, the delocalized excitations are apparently not “dynamic” enough to maintain a homogeneous distribution, in contrast to single-particle excitations as we saw in sec. 6.6.1. The simulated annihilation reaction in one-dimension for delocalized excitations is therefore always diffusion-limited, in contrast with the

Figure 6.11: Monte Carlo simulations (solid lines) for delocalized excitations. The delocalization length is 5 (solid) or 15 (solid with squares) monomers. For each delocalization length, calculations with different exciton distances are performed. The results are plotted on a double logarithmic scale, corresponding to the form of eq. (6.11). For a delocalization length of 5 monomers, the upper curve corresponds to exciton distance 5, the lower curve has an exciton distance of 15 monomers. For a delocalization length of 15 monomers, the upper curve has exciton distance 15, the lower curve a distance of 80 monomers. The annihilation probability is 0.5 and is proportional to the overlap of delocalization areas. Also drawn is a dotted line with slope 0.5, identifying a diffusion-limited annihilation reaction with a reaction rate \( -t^{-\frac{1}{2}} \). The dashed line has a slope of 1, representing a time-independent reaction rate.
experimentally observed annihilation reaction. We will return to this point in the next section. Let us consider now another observation in the figure.

For short times the slope of the double logarithmic plots in fig. (6.11) is approximately 1, then quickly flattens, before it eventually becomes 0.5. One possible reason for this “wiggle” is the initial distribution of excitons on the chain. At the start of the simulation, the distribution is homogeneous, leading to a time independent annihilation rate, with slope 1 in the plot. But the delocalization areas are placed randomly on the chain, so that they overlap already at the start. This will cause a very fast decay of population and the distribution of excitons then quickly becomes inhomogeneous. So after a few steps the reaction becomes diffusion-limited, and the slope of the plot will be lowered to 0.5.

This explanation for the “wiggle” is closely related to the fact that by the delocalization of excitations, free space is reduced, which reduces the motional freedom of excitons on the same aggregate chain. Especially at short times this effect plays an important role. At larger times, the concentration of excitons is strongly reduced and then the delocalization length becomes so small compared to the average distances between the excitons, that it has no effect anymore on the diffusion of excitons. An easy way to check the role of this volume effect, is to incorporate the effect of the reduced space into the diffusion-limited single-species annihilation model. This is described in sec. 6.4 and leads to the corrected form eq. (6.12) of eq. (6.10).

In fig. (6.12), Monte Carlo simulations are compared with the corrected annihilation model as described by eq. (6.12), for a delocalization length of 5 monomers. The physical parameters in the annihilation model are taken the same as in the Monte Carlo simulations.

![Figure 6.12](image-url)

Figure 6.12: Monte Carlo simulation (solid line) for delocalized excitations, compared with a curve calculated in the volume corrected annihilation model as described by eq. (6.12) (dashed line). In both curves the delocalization length is 5 monomers, the exciton distance is also 5 monomers, and the annihilation probability per time step is 0.5 and proportional to the overlap of delocalization areas. The different (abstract) timescales of the two calculated curves have been scaled relative to each other, this rescaling has no physical meaning. On top of the figures is the timescale of the (volume corrected) annihilation model, on the bottom is the step timescale for the Monte Carlo simulation. (a) Here the results are plotted on a single logarithmic scale. (b) The same calculations as in figure (6.12a), but now plotted on a double logarithmic scale, corresponding to the form of eq. (6.11).
Then a rescaling of both calculations is necessary, in order to incorporate the different hop- and annihilation probabilities (in the annihilation model these probabilities are always 1) and to compare the abstract timescales in both calculations. One should realize that this scaling has no physical meaning: both timescales have no connection with the experimental timescale. The fact that the calculations are performed with different IPDF’s, is taken into account by slightly changing the initial concentration of excitons on the chain in the annihilation model, such that the overlap of both calculated curves at short times is optimal. The result, after rescaling, is shown in fig. (6.12a). The (logarithmic) fluorescence intensity is plotted here as a function of time. The corrected annihilation model calculations coincide fully with the Monte Carlo simulations. However, when we look more carefully on a double logarithmic scale in fig. (6.12b), reproduced corresponding to the form of eq. (6.11), we can see that the “wiggle” in the Monte Carlo calculations cannot be simulated completely in the volume corrected annihilation model. Therefore, we can conclude that the initial random, and therefore overlapping, distribution of excitons on the chain plays an important role in creating the “wiggle” in the double logarithmic plot of fig. (6.11).

6.7 Summary and conclusions

The population decay of excitons, as measured by time-resolved grating scattering and single-photon counting, can be explained in a satisfactory way by the annihilation model, with a time-independent annihilation rate. But, on a one-dimensional chain diffusion limitations predict time-dependent rate constants. Also Monte Carlo simulations of delocalized excitations in one-dimension predict the annihilation reaction to be diffusion-limited. However, the experimentally studied annihilation reaction in TDBC does not show this diffusion limitation. As we already assumed in the two-exciton band model in sec. 6.3, the annihilation of excitons is apparently not limited by dimensional constraints. Several explanations can be thought of.

First of all, one must keep in mind that the Monte Carlo simulations are based upon a specific physical picture: that of a Brownian random walker on a one-dimensional lattice. It may be possible that we need to consider a more advanced model in order to explain our experimental results. For instance, we assumed that diffusion of excitons is based on random thermal fluctuations. However, it is quite possible that the presence of an exciton on the chain causes a deformation of the linear aggregate, which influences the propagation in some unknown way. In addition, one can wonder if interactions between excitons should be taken into account. Possibly, this can play a role in maintaining a homogeneous distribution of excitons during the annihilation process.

In the previous chapters, we assumed aggregates to be one-dimensional. But in these situations, we focussed on only “one” delocalization length. Here we looked for diffusion on the entire physical size of the aggregated molecules. Not only the length scale is larger, but also the timescale. Then it may become possible that coupling of aggregate chains starts to become important, so that diffusion is extended to more dimensions.
Another consideration is heat. This is a by-product of the annihilation reaction: \( A + A \rightarrow A + \text{heat} \). The exciton that remains after the reaction is in the midst of this “shower” and will feel its influence. Possibly, this enhances the hopping rate. If the annihilation probability is low, this brings about a more homogeneous distribution of excitons, and therefore the reaction will become less diffusion-limited than predicted in the diffusion-limited annihilation model. This would also explain the observed time-independent reaction rate. On the other hand, aggregates may efficiently transfer their thermal energy to the surrounding solvent, long before they have the chance to meet a new exciton. Local heating is therefore expected to be reduced.

In summary, we have studied the dynamics for a diffusion-reaction system, consisting of photogenerated excitons in TDBC. From the grating scattering and photon counting experiments it was concluded that the two-exciton band participated in exciton-exciton annihilation, by serving as a decay channel for the one-exciton band. The reaction process is well described by the two-exciton band model. Despite the fact that TDBC aggregates generally are described as one-dimensional systems, the diffusion of delocalized excitations in the annihilation reaction is found to be not rate-limiting by this single dimension. Explanations for this behavior may be based on possible, but unknown, interactions between the excitons, interchain couplings, or enhanced diffusion by the release of heat in the annihilation process. Or should the conclusion be that aggregates on a molecular scale are not truly one-dimensional?
References