In this chapter\textsuperscript{1} we generalize our work on the optical bistability of thin films of molecular aggregates of the previous chapter. We account for the optical transitions from the one-exciton manifold to the two-exciton manifold as well as the exciton-exciton annihilation of the two-exciton states via a high-lying molecular vibronic term. We also include the relaxation from the vibronic level back to both the one-exciton manifold and the ground state. By selecting the dominant optical transitions between the ground state, the one-exciton manifold, and the two-exciton manifold, we reduce the problem to four levels, which simplifies the analysis of the nonlinear optical response of the film. The one- and two-exciton states are obtained by diagonalizing a Frenkel Hamiltonian with uncorrelated on-site (diagonal) disorder. The optical dynamics of the system is evaluated by density matrix equations coupled to the electromagnetic field in the film. We show that the one-to-two exciton transitions followed by fast exciton-exciton annihilation promotes the occurrence of bistability and reduces the switching intensity. We provide estimates of pertinent parameters for actual materials and conclude that the effect can be realized.

\section{Introduction}

The phenomenon of optical bistability has attracted considerable attention for more than thirty years now, starting with the theoretical prediction of

\footnote{This chapter is based on J. A. Klugkist, V. A. Malyshev, and J. Knoester, submitted to J. Chem. Phys.}
McCall [1] in 1974, followed by experimental demonstration of the effect by Gibbs, McCall, and Venkatesan [2] in 1976 (see also Refs. [3, 4], and [5] for an overview). Since then a significant amount of literature has been devoted to explore the topic (an extended bibliography can be found in the previous chapter. The topic is of high scientific interest, because the ability to control the flow of flux with light on the micro- and nano-scale is of great importance for all-optical information processing. More recently, new materials such as photonic crystals [7], surface-plasmon polaritonic crystals [8], and materials with a negative index of refraction [9], have revealed bistable behavior.

In the previous chapter, we theoretically studied the bistable optical response of a thin film of linear molecular J-aggregates. To describe the optical response of a single aggregate, we used a Frenkel exciton model with uncorrelated on-site energy disorder, taking into account only the optically dominant transitions from the ground state to the one-exciton manifold, while neglecting the one-to-two exciton transitions. Within this picture, an aggregate can be viewed as a meso-ensemble of two-level localization segments [10]. Then the optical dynamics can be described by a $2 \times 2$-density matrix. By using a joint probability distribution of the transition energies and the transition dipole moment of the optically dominant Frenkel excitons, we were able to account for the correlated fluctuations of these two quantities, which we obtained by diagonalizing the Frenkel Hamiltonian with disorder. By solving the coupled Maxwell-Bloch equations, we calculated the phase diagram of the possible stationary states of the film (stable, bistable) and the input-dependent switching time. By analyzing the spectral distribution of the exciton population at the switching point, we realized that the field inside the film is sufficient to produce one-to-two exciton transitions, in agreement with a similar statement made in Refs. [11].

The goal of the present chapter is to extend the one-exciton model [6] by including one-to-two exciton transitions. When two excitons are spatially located within the same localization domain, they usually quickly annihilate, transferring their energy to an appropriate resonant monomer vibronic level [12, 13, 14, 15, 16, 17, 18, 19]. Therefore, the generalized model requires the consideration of exciton-exciton annihilation [11]. We will assume that exciton-exciton annihilation prevents the three-exciton states from playing a significant role in the response of the film. The relevant transitions of the model are depicted in Fig. 4.1.
To make the two-exciton model tractable, we will select the optically dominant transitions between the ground state and the one-exciton manifold (see chapter 5), and also between the one- and two-exciton manifolds. We treat the different localization segments independently, which, in combination with the state selection, considerably reduces the computational effort necessary to simulate the optical response. Then, the dynamics of an aggregate segment is described by a 4-level system which consist of a ground state, the optically dominant one- and two-exciton states of the segment, and a high-lying molecular electronic or vibronic state, through which the excitons annihilate. This model was first applied in Ref. [11], using the simplifying assumption that the transition energies and transition dipole moments are correlated perfectly. Following our previous work [6], we will account for the correct joint statistics of both quantities. The optical dynamics of a single localization segment is described within the framework of a $4 \times 4$-density matrix. We derive a steady-state equation for the output field intensity as a function of the input intensity. We calculate the optical response of the film, taking into account the reaction
field produced by the aggregate dipoles. We find that, counter-intuitively, tuning away from resonance may, depending on the dephasing rate, promote bistable behavior. In addition, we show that fast exciton-exciton annihilation combined with slow relaxation from the high-lying vibronic level enhances the tendency towards bistability. The bistability phase diagram of the film is calculated and compared with the one-exciton model. We discuss the possible experimental realization of bistable behavior with actual materials.

This chapter is organized as follows. In the next section, we introduce the model that describes a single aggregate, consisting of a Frenkel Hamiltonian with uncorrelated on-site energy (diagonal) disorder. Our selection procedure of the optically dominant transitions is described in section 4.2.2, and we introduce our model for exciton-exciton annihilation in section 4.2.3. In section 4.2.4, we describe the mathematical formalism, based on $4 \times 4$ density matrix equations combined with the Maxwell equation for a thin film of oriented linear J-aggregates. We present results of our numerical analysis in section 4.3, where we identify the conditions that favor a bistable behavior of the film. In section 4.4, we estimate the driving parameters and the input light flux required for experimental realization of bistability for films of pseudoisocyanine J-aggregates. Finally, in section 4.5 we summarize.

4.2 Model

The geometry of the model system and the assumptions we adopt hereafter are essentially the same as in the previous chapter. In short, we aim to study the transmittivity of an assembly of linear J-aggregates arranged in a thin film (with the film thickness $L$ small compared to the emission wavelength $\lambda'$ inside the film) and aligned in one direction, parallel to the film plane. The aggregates in the film are assumed to be decoupled from each other; their coupling to the environment is treated through phenomenological relaxation rates (see Ref. [6] for a detailed discussion).

4.2.1 A single aggregate

We model a single aggregate as a linear chain of $N$ three-level monomers. The two lower states are assumed to form multi-exciton bands, as a result of strong dipole-dipole excitation transfer interactions between the monomers.
To simplify the treatment of the multi-exciton states, we restrict ourselves to nearest-neighbour interactions. We have assumed that the transition dipole moments between the monomers are equal in magnitude and direction. Then the (Frenkel) exciton part of the aggregate Hamiltonian reads

$$H_0 = \sum_{n=1}^{N} \varepsilon_n b_n^\dagger b_n - J \sum_{n=1}^{N-1} \left( b_{n}^\dagger b_{n+1} + b_{n+1}^\dagger b_{n} \right),$$

(4.1)

where $b_n^\dagger (b_n)$ denotes the creation (annihilation) Pauli operator of an excitation at site $n$. The monomer excitation energies $\varepsilon_n$ between the two lower states are modeled as uncorrelated Gaussian variables with mean $\varepsilon_0$ and standard deviation $\sigma$. The parameter $J$ represents the nearest-neighbour transfer integral, which is positive for J-aggregates. We assume that this quantity does not fluctuate. After applying the Jordan-Wigner transformation, the multi-exciton eigenstates are found as Slater determinants of one-exiton states $\varphi_{\nu n}$ [21, 22, 23]. The multi-exciton eigenenergies are given by $\sum_{\nu=1}^{N} n_\nu \varepsilon_\nu$, with $\varepsilon_\nu$ being the one-exciton eigenenergies and $n_\nu = 0, 1$ depending on whether the $\nu$th state is occupied or not. Particularly, we will be interested in the one- and two-exciton states:

$$|\nu\rangle = \sum_{n=1}^{N} \varphi_{\nu n} |n\rangle,$$

(4.2a)

$$|\mu\nu\rangle = \sum_{m>n}^{N} (\varphi_{\nu m} \varphi_{\mu n} - \varphi_{\nu n} \varphi_{\mu m}) |mn\rangle,$$

(4.2b)

where $|n\rangle = b_n^\dagger |0\rangle$ and $|mn\rangle = b_m^\dagger b_n^\dagger |0\rangle$, and $|0\rangle$ is the ground state of the aggregate (with all monomers in the ground state). We will also need the transition dipole moments from the ground state $|0\rangle$ to a one-exciton state $|\nu\rangle$ and from a one-exciton state $|\nu\rangle$ to a two-exciton state $|\nu_1 \nu_2\rangle$. In units of the single-molecule transition dipole moment, they obtain the dimensionless form

$$\mu_\nu = \sum_{n=1}^{N} \varphi_{\nu n},$$

(4.3a)
\[ \mu_{\nu_1 \nu_2 ; \nu} = \sum_{n_2 > n_1} (\varphi_{\nu n_1} - \varphi_{\nu n_2}) (\varphi_{\nu_1 n_1} \varphi_{\nu_2 n_2} - \varphi_{\nu_1 n_2} \varphi_{\nu_2 n_1}) . \]  

where it was assumed that the aggregate is small compared to an optical wavelength.

### 4.2.2 Selecting the dominant exciton transitions

Despite the fact that the physical size of a molecular aggregate can amount to thousands of monomers (see, e.g., Ref. [13]), most of the optical properties, in particular at low temperatures, are determined by the localized exciton states of much smaller, non overlapping, chain segments. The disordered environment results in Anderson localization of the lowest exciton states in the exciton band [24, 25]. The size of these localization segments is typically much smaller than the physical size of the aggregate. We will denote the typical size of these segments as \( N^* \), often referred to as the number of coherently bound molecules or localization length.

For J-aggregates, the optically dominant localized states reside in the neighbourhood of the bottom of the exciton band. Some of them resemble s-like atomic states: they consist of mainly one peak with no node within the localization segment (see Fig. 4.2a). We will denote the subset of such states as \( S \). To select the s states from the complete set of wave functions \( \varphi_{\nu n} \), we used the rule proposed in Ref. [26], \( \sum_n |\varphi_{\nu n}| \geq C_0 \) with \( C_0 = 0.75 \). The inequality selects the states that consist mainly of one peak. We found numerically that for a wide range of the disorder strength \( \sigma (0.05J < \sigma < J) \), the selected states accumulate on average 73% of the total oscillator strength (equal to \( N \)). Recall that for a disorder-free aggregate, the optically dominant (lowest) exciton state contains 81% of the total oscillator strength of the one-exciton transitions (see, e.g., Refs. [27] and [28]). Furthermore, we have shown that the s states well reproduce the linear absorption spectrum, failing slightly for the blue wing, where higher-energy exciton states contribute as well, see chapter 5 and 7. From this, we conclude that our procedure to select the optically dominant (s-like) one-exciton states works well.
Figure 4.2: (a) The lowest 12 one-exciton states of a chain of length $N = 500$ for a particular disorder realization at the disorder strength $\sigma = 0.1J$. (b) A subset of $s$ states (black) and $p_s$ states (gray) which have the largest ground-state-to-one-exciton and one-to-two exciton transitions. The average single molecule transition energy $\varepsilon_0$ was chosen as the origin of the energy scale.

Similar to the $s$-like states, one may also distinguish states that resemble atomic $p$ states. They have a well defined node within localization segments and occur in pairs with $s$-like states. Each pair forms an $sp$ doublet localized on the same chain segment. The levels within a doublet undergo quantum mechanical level repulsion, resembling the level spacing between the $k = 1$ and $k = 2$ exciton states in a homogeneous chain of size $N^*$ [26]. From studies of the multi-exciton transitions in homogeneous aggregates [29], we know that the transition from the $k = 1$ state to the two-exciton state which is formed by the Slater determinant of the $k = 1$ and $k = 2$ states predominantly contributes to the two-exciton optical response. This gives us a solid ground to believe
that the $s$-like one-exciton states and the two-exciton states composed of $(sp)$ doublets dominate the one-to-two exciton transitions in disordered aggregates (see below).

Usually, well defined $(sp)$ doublets are found below the bare exciton band edge at the energy $-2J$. These doublets are responsible for a hidden level structure of the Lifshits tail [30]. For the $s$ states located close to or above the bare band edge, it is already impossible to assign a $p$-like partner localized on the same segment: higher-energy states have more than one node and spread over segments of size larger than $N^*$ (see Fig. 4.2). To obtain all states that give a major contribution to the one-to-two exciton transitions, the following procedure has been used. First, we select all $s$ states, as described above. Then, we considered the two-exciton states $|sv\rangle$ given by Eq. (4.2b) and calculated the corresponding transition dipole moments $\mu_{sv,s}$. From the whole set of $\mu_{sv,s}$, we took the largest transition, which we denote by $\mu_{sp_s,s}$; the subscript $s$ in $p_s$ indicates its relation with the state $|s\rangle$. This procedure catches all true $sp_s$ doublets and assigns a partner to solitary $s$ states, which does not necessarily look like a proper $p$ state. In Fig. 4.2b, we show the final set of the doublets selected from the states in Fig. 4.2a according to the above procedure, which contribute mostly to the one- and two-exciton transitions.

The average ratio of the oscillator strength of the thus selected transitions $|s\rangle \rightarrow |sp_s\rangle$ and $|0\rangle \rightarrow |s\rangle$ turned out to be approximately 1.4. For a homogeneous chain, this ratio equals 1.57 (then $|s\rangle = |k = 1\rangle$ and $|sp_s\rangle = |k_1 = 1, k_2 = 2\rangle$). The similarity of these numbers supports our selection procedure. Even stronger support is obtained from computing the pump-probe spectrum, using our state selection, and comparing the result to that of the exact calculations, see chapter 5. The comparison revealed that the spectrum using the selected transitions only deviates from the exact spectrum in the blue wing of the induced absorption peak, similarly to the linear absorption spectra.

### 4.2.3 Exciton-exciton annihilation

As was already mentioned in the Introduction, when two excitons are created within the same localization segment, they efficiently annihilate (the intrasegment annihilation in terms of Refs. [31] and [32]). The authors of Ref. [14] studied experimentally the exciton dynamics in J-aggregates of pseudoisocyanine bromide (PIC-Br) at low temperature and found a 200 fs component in the two-exciton state decay. They attributed this decay rate to the annihila-
tion of two-exciton state located within the same chain segment with a typical size of $N^* = 20$. We adopt this mechanism for $|sp_s\rangle$ states described in the preceding section. Note that the exciton annihilation decay time of 200 fs is much shorter than all other population decay times. All other relevant processes, such as radiative decay, occur at times of tens to hundreds of picoseconds.

Two excitons located on different localization segments can also annihilate (the inter-segment annihilation in terms of Refs. [32]). This process, however, is much slower as compared to the intra-segment channel. [32] The thermally activated diffusion of excitons accelerates the annihilation of spatially separated excitons. We consider this diffusion-limited exciton annihilation as irrelevant to our problem, because switching requires the saturation of the majority of the $s$ states (see also section 4.4). Therefore, we neglect this process.

It is usually assumed that the annihilation occurs via transferring the two-exciton energy to a resonant molecular vibronic level (see, e.g., Ref. [12]), which undergoes a fast vibration-assisted relaxation to the ground vibronic state. The population collected in this state then relaxes to the one-exciton state $|1\rangle$ of the segment or to the ground state $|0\rangle$ of the aggregate (cf. Fig 4.1). In this way, respectively one or two excitations are taken from the system. To summarize, we use a four-level model to describe the optical response of the film in the two-exciton approximation, which includes a ground state, one- and two-exciton states, and a molecular vibronic level through which the excitons annihilate.
4.2.4 Truncated density-matrix-field equations

Using the four-level model we introduced in the preceding sections, we describe the optical dynamics of a segment in terms of a $4 \times 4$ density matrix $\rho_{\alpha\beta}$, where the indexes $\alpha$ and $\beta$ run from 0 to 3, where $|1\rangle \equiv |s\rangle$ and $|2\rangle \equiv |sp_s\rangle$. We neglect the off-diagonal matrix elements $\rho_{30}, \rho_{31},$ and $\rho_{32}$, assuming a fast vibronic relaxation within the third molecular level. Within the rotating wave approximation, the set of equations for the populations $\rho_{\alpha\alpha}$ and for the amplitudes of the relevant off-diagonal density matrix elements $R_{\alpha\beta}$, $(\alpha \neq \beta)$ reads \[11\]

\[
\dot{\rho}_{00} = \frac{1}{4} \mu_{10} [\Omega R_{10}^* + \Omega^* R_{10}] + \gamma_{10} \rho_{11} + \gamma_{30} \rho_{33}, \tag{4.4a}
\]

\[
\dot{\rho}_{11} = -\gamma_{10} \rho_{11} + \gamma_{21} \rho_{22} + \gamma_{31} \rho_{33} + \frac{1}{4} \mu_{21} (\Omega R_{21} - \Omega^* R_{21}) - \frac{1}{4} \mu_{10} (\Omega R_{10} - \Omega^* R_{10}), \tag{4.4b}
\]

\[
\dot{\rho}_{22} = - (\gamma_{21} + w) \rho_{22} - \frac{1}{4} \mu_{21} (\Omega R_{21}^* - \Omega^* R_{21}) , \tag{4.4c}
\]

\[
\dot{\rho}_{33} = -\gamma_{3} \rho_{33} + w \rho_{22} , \tag{4.4d}
\]

\[
\dot{R}_{10} = -(i \Delta_{10} + \Gamma_{10}) R_{10} - \mu_{10} \Omega (\rho_{00} - \rho_{11}) + \frac{1}{2} i \mu_{21} \Omega^* R_{20} , \tag{4.4e}
\]

\[
\dot{R}_{21} = - \left( i \Delta_{21} + \Gamma_{21} + \frac{1}{2} w \right) R_{21} - \mu_{21} \Omega (\rho_{11} - \rho_{22}) - \frac{1}{2} i \mu_{10} \Omega^* R_{20} , \tag{4.4f}
\]

\[
\dot{R}_{20} = - \left( i \Delta_{10} + i \Delta_{21} + \Gamma_{20} + \frac{1}{2} w \right) R_{20} + \frac{1}{2} i \mu_{21} \Omega R_{10} - \frac{1}{2} i \mu_{10} \Omega R_{21} . \tag{4.4g}
\]

Here, $\gamma_{10} = \gamma_0 |\mu_{10}|^2$ and $\gamma_{21} = \gamma_0 |\mu_{21}|^2$ are the radiative relaxation rates of the one-exciton state $|1\rangle$ and the two-exciton state $|2\rangle$, respectively, $\gamma_0$ denotes the monomer radiative rate, and $\mu_{10}$ and $\mu_{21}$ are corresponding dimensionless transition dipole moments. Furthermore, $w$ is the annihilation constant of the two-exciton state $|2\rangle$ and $\gamma_{3} = \gamma_{30} + \gamma_{31}$ describe the population relaxation rate of the vibronic state $|3\rangle$. The constants $\Gamma_{10} = \gamma_{10}/2 + \Gamma$ and $\Gamma_{21} = \Gamma_{20} = \gamma_{21}/2 + \Gamma$ correspond to the dephasing rates of the respective transitions. They include a contribution from the population decay as well as a pure dephasing part $\Gamma$, which, for simplicity, we assume equal for all off-diagonal density matrix elements. Finally, $\Delta_{10} = \omega_{10} - \omega_i$ and $\Delta_{21} = \omega_{21} - \omega_i$ denote the detuning between the exciton transition frequencies $\omega_{10}$ and $\omega_{21}$, and the frequency $\omega_i$ of the incoming field. Note that that Eqs. (4.4) auto-
matically conserve the sum of level populations: \( \rho_{00} + \rho_{11} + \rho_{22} + \rho_{33} = 1. \)

The quantity \( \Omega = d_0 E / \hbar \) in Eqs. (4.4) is the amplitude \( E \) of the field inside the film in frequency units, where \( d_0 \) is the transition dipole moment of a monomer and \( \hbar \) is the Planck constant. It obeys the following equation [11]

\[
\Omega = \Omega_i + \Gamma_R \frac{N_s}{N} \left( \mu_{10} R_{10} + \mu_{21} R_{21} \right),
\]

(4.5)

where \( \Omega_i = d_0 E_i / \hbar \) is the amplitude \( E_i \) of the incoming field in frequency units, \( N_s \) is the average number of \( s \)-like states in an aggregate, and \( \Gamma_R = 2\pi n_0 d_0^2 k L / \hbar \) is the superradiant constant, an important parameter of the model [31, 11, 6]. In this expression, \( n_0 \) is the number density of monomers in the film, \( k \) is the field wave number, and \( L \) is the film thickness. The angular brackets in Eq. (4.5) denote the average over disorder realizations.

The set of equations (4.4) forms the basis of our analysis of the effects of one-to-two exciton transitions, exciton-exciton annihilation from the two-exciton state, and relaxation of the annihilation level back to the one-exciton and ground states on the optical bistable response from an ultrathin film of J-aggregates. In the remainder of this chapter, we consider the dependence of the transmitted field intensity \( |\Omega|^2 \) on the input field intensity \( |\Omega_i|^2 \), following from Eqs. (4.4) and (4.5).

### 4.3 Steady-state analysis

#### 4.3.1 Bistability equation

To study the stationary states of the system, we first consider the steady-state regime of the film’s optical response and set the time derivatives in Eqs. (4.4) to zero. We focus on the limit of fast exciton-exciton annihilation, assuming that the annihilation constant \( w \) is the largest of all relaxation constants and also much larger than the magnitude of the field inside the film, \( |\Omega| \). The reason for the last assumption is based on the fact that below the switching threshold, the field magnitude \( |\Omega|^2 \sim (\gamma_0 \sigma^*) \) [6] where \( \gamma_0 \), and \( \sigma^* \) are the radiative decay rate of a monomer and the half width at half maximum (HWHM) of the linear absorption spectrum, respectively. As \( \gamma_0 \ll \sigma^* \), the magnitude of the field is also much smaller than \( \sigma^* \). Above the switching threshold, \( |\Omega| \) becomes comparable to \( \sigma^* \) [6]. The typical HWHM of J-aggregates of PIC at
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at low temperatures is on the order of a few tens of cm$^{-1}$, which in time units corresponds to one picosecond. On the other hand, the time scale of exciton-exciton annihilation is on the order of 200 femtoseconds (see section 4.2.3). This justifies our assumption $|\Omega| \ll w$ and allows us to neglect $R_{20}$ in steady-state Eqs. (4.4), because $|R_{20}| \sim |\Omega|^2/(i\Delta_{21} + \Gamma_{20} + w/2)$. This approximation enables us to derive a closed steady-state equation for the $\Omega$-vs-$\Omega_i$ dependence, which reads

$$|\Omega_i|^2 = \left\{ 1 + \gamma R N_s N \left( \frac{\mu^2_{10}}{\Gamma^2_{10} + \Delta^2_{10}} (\rho_{00} - \rho_{11}) + \frac{\Gamma_{21} + w/2}{(\Gamma_{21} + w/2)^2 + \Delta^2_{21}} (\rho_{11} - \rho_{22}) \right) \right\}^2$$

$$+ \left( \frac{\Delta_{21} + w/2}{(\Gamma_{21} + w/2)^2 + \Delta^2_{21}} (\rho_{11} - \rho_{22}) \right)^2$$

(4.6)

The steady-state populations are given by [11]

$$\rho_{00} - \rho_{11} = \frac{1 + (1 + w\gamma_{03}/\gamma_{10}\gamma_{3}) S_{21}}{1 + 2S_{10} + (1 + w\gamma_{03}/\gamma_{10}\gamma_{3}) S_{21} + (3 + w/\gamma_{3}) S_{10} S_{21}}$$

(4.7a)

$$\rho_{11} - \rho_{22} = \frac{S_{10}}{1 + 2S_{10} + (1 + w\gamma_{03}/\gamma_{10}\gamma_{3}) S_{21} + (3 + w/\gamma_{3}) S_{10} S_{21}}$$

(4.7b)

where

$$S_{10} = \frac{\mu^2_{10}|\Omega|^2}{2\gamma_{10}} \frac{\Gamma_{10}}{\Delta_{10}^2 + \Gamma_{10}^2}$$

(4.8a)

$$S_{21} = \frac{\mu^2_{21}|\Omega|^2}{2(\gamma_{21} + w)} \frac{\Gamma_{21} + w/2}{\Delta_{21}^2 + (\Gamma_{21} + w/2)^2}$$

(4.8b)

The terms proportional to $\mu^2_{21}$ in Eq. (4.6) describe the effects of the two-exciton state, the exciton-exciton annihilation, and the relaxation from the vibronic level back to the one-exciton and ground states. Equation (4.6) reduces to the one-exciton model considered in the previous chapter by setting
\( \mu_{21} = 0 \). Similarly to the one exciton model, Eq. (4.6) contains a small factor \( N_s/N \), absent in an earlier paper, Ref. [11]. This smallness, however, is compensated by the \( N_s \)-scaling of the average in Eq. (4.6): it is proportional to \( (\mu_{10}^2 + \mu_{21}^2)/N_s \approx 2N/N_s \gg 1 \) [6]. Thus, the actual numerical factor in Eq. (4.6) is approximately 2. We stress that, unlike previous work [11], Eq. (4.6) properly accounts for the joint statistics of all transition energies and transition dipole moments.

It is worth to notice that the second term in the first square brackets in Eq. (4.6) represents the imaginary part of the nonlinear susceptibility, while the one in the second square brackets is its real part. Hence, we will refer to these terms as to absorptive and dispersive, respectively, following the convention adapted in the standard theory of bistability of two-level systems in a cavity [2].

We numerically solved Eq. (4.6), with a specific interest in parameters \((\Gamma_R, \sigma^*, \Gamma, \gamma_{31}, \gamma_{30})\) where the output-input dependence becomes S-shaped, which indicates bistable behavior. In all simulations, we used linear chains of \( N = 500 \) sites and the radiative constant of a monomer \( \gamma_0 = 2 \times 10^{-5} J \) (typical for monomers of polymethine dyes). The exciton-exciton annihilation rate was set to \( w = 5000\gamma_0 \), corresponding to an annihilation time of 200 fs. [14] The average single molecule transition energy \( \varepsilon_0 \) was chosen as the origin of the energy scale. 10000 localization segments were considered in disorder averaging.

Figure 4.3 shows the output intensity \( I_{\text{out}} = |\Omega|^2/(\gamma_0 \sigma^*) \) versus the input intensity \( I_{\text{in}} = |\Omega_0|^2/(\gamma_0 \sigma^*) \). Here the superradiant constant \( \Gamma_R \) is increased to find the threshold value needed for optical hysteresis. The relaxation constants \( \gamma_{30} \) and \( \gamma_{31} \) from the state \( |3\rangle \) were taken equal to the radiative rate of a monomer, \( \gamma_0 \), which is the slowest process of our system. The incoming field was tuned to the absorption maximum \( \Delta_{10}^{(0)} = \varepsilon_0 - \omega_i - 2.02J \), which naively speaking is expected to result in the lowest threshold for bistability (see a discussion of the detuning effects in section 4.3.3). The other parameters of the simulations are specified in the figure caption. As follows from Fig. 4.3, for the given set of parameters the bistability threshold is \( \Gamma_{R}^c = 7\sigma^* \).

### 4.3.2 Effects of relaxation from the vibronic level

From the physical point of view, the most favorable conditions for bistability occur when the relaxation from the vibronic state \( |3\rangle \) is slow. This level is
Figure 4.3: Examples of intensity of the transmitted field as a function of the incident field for different values the superradiant constant $\Gamma_R$. The S-shaped hysteresis characteristic in the solution indicates bistable behavior. Simulations were performed for a disorder strength $\sigma = 0.1J$, resulting in an inhomogeneous HWHM $\sigma^* = 0.024J$. The incoming field was tuned to the $J$-band maximum, $\Delta_{10}^{(0)} = \varepsilon_0 - \omega_i - 2.02J$. The population relaxation rates of the vibronic state $|3\rangle$ were taken equal to the monomer decay rate, i.e., $\gamma_{31} = \gamma_{30} = \gamma_0$, while the dephasing constant $\Gamma = 500\gamma_0$. In this figure the superradiant constant $\Gamma_R$ ranges from $\sigma^*$ to $11\sigma^*$ in steps of $\sigma^*$ (left to right). As is seen from this figure, optical bistability requires a superradiant constant which is larger than the threshold value $\Gamma^*_R = 7\sigma^*$.

populated by a fast population transfer from the two-exciton state $|2\rangle$ (fast exciton-exciton annihilation). Indeed, under these conditions, the exciton population is rapidly transferred to the state $|3\rangle$, and, accordingly, the system becomes transparent more easily when compared to the one-exciton model. Clearly, faster relaxation from the state $|3\rangle$ to the ground state $|0\rangle$ will deteriorate the condition for the occurrence of bistability, while slower relaxation improves the situation. This is illustrated in Figure 4.4.
4.3. Steady-state analysis

Figure 4.4: Examples of the output-input characteristics, demonstrating the effect of the relaxation rates \( \gamma_{30} \) and \( \gamma_{31} \) from the vibronic state \( |3\rangle \) on the bistable response. The set of parameters used in the simulations are: \( \sigma = 0.1J \), \( \Delta_{10}^{(0)} = \varepsilon_0 - \omega_i - 2.02J \) (tuning to the J-band maximum), \( w = 5000\gamma_0 \), \( \Gamma = 500\gamma_0 \), and \( \Gamma_R = 10\sigma^* \).
4.3.3 Effects of detuning

As we mentioned in section 4.3.1, one might expect that tuning the incoming field to the absorption maximum gives the lowest threshold for bistability. In this section, we show that in general this expectation is incorrect.

In Fig. 4.5 we plotted the optical response of the film as a function of the detuning, $\Delta_{10}$, obtained for two values of the dephasing constant $\Gamma$. The disorder strength was set to $\sigma = 0.1J$, resulting in an inhomogeneous HWHM $\sigma^* = 0.024J$. From these data, one can distinguish two regimes. First, for a relatively large $\Gamma = 500\gamma_0 \sim \sigma^*$ [panels (a) and (b)] the film’s response behaves according to the naive reasoning: the output-input characteristic looses its S-shaped form upon a deviation of the incoming field frequency from the absorption maximum. In contrast, as is observed in Figs. 4.5 (c) and (d), for $\Gamma = 20\gamma_0 \ll \sigma^*$, when the absorption width is dominated by inhomogeneous broadening $\sigma^*$, tuning away from the resonance favors bistability.

We note that similar behavior has been found for assemblies of inhomogeneously broadened two-level emitters placed in a cavity, [2, 33, 34] where it was suggested that this counterintuitive frequency dependence results from the interplay of absorptive and dispersive contributions to the nonlinear susceptibility. We believe that our model exhibits the same spectral behavior because only the ground-state-to-one-exciton transitions lead to spectral sensitivity. The one-to-two exciton transitions and the relaxation from the molecular vibronic level do not: the former because of the fast exciton annihilation, which washes out all spectral details, and the latter because it occurs from a relaxed state. Thus, all spectral features of the two-exciton model of the film’s bistability are driven by the ground-state-to-one-exciton transitions. In other words, the one-exciton (two-level) model considered in the previous chapter is relevant for explaining the observed spectral behavior. In this case, the bistability equation (4.6) is reduced to

$$|\Omega_i|^2 = \left\{ 1 + \gamma R \frac{N_s}{N} \left( \frac{\mu_{10}^2 \Gamma_{10} - \Delta_{10}^2 + |\Omega|^2 \Gamma_{10} / \gamma_0}{\Gamma_{10}^2 + \Delta_{10}^2 + |\Omega|^2 \Gamma_{10} / \gamma_0} \right) \right\}^2 \left\{ \gamma R \frac{N_s}{N} \left( \frac{\Delta_{10} \Gamma_{10} - \Delta_{10}^2 + |\Omega|^2 \Gamma_{10} / \gamma_0}{\Gamma_{10}^2 + \Delta_{10}^2 + |\Omega|^2 \Gamma_{10} / \gamma_0} \right) \right\} |\Omega|^2.$$ (4.9)
4.3. Steady-state analysis

Figure 4.5: Examples of the output-input characteristics, demonstrating the combined effect of dephasing, $\Gamma$, and detuning, $\Delta_{10}$, on the occurrence of bistability. In the simulations, the following set of parameters were used: a disorder strength $\sigma = 0.1J$ (HWHM $\sigma^* = 0.024J$), the exciton-exciton annihilation rate $w = 5000\gamma_0$, the decay rates of the intermediate vibronic level $\gamma_{31} = \gamma_{30} = \gamma_0$, and the superradiant constant $\Gamma_R = 10\sigma^*$. Panels (a) and (b) represent the results obtained for $\Gamma = 500\gamma_0 \sim \sigma^*$ when changing $\Delta_{10}$ from the absorption maximum at $\Delta_{10}^{(0)} = \varepsilon_0 - \omega_1 - 2.02J$ to the red (a) and to the blue (b) in 20 steps of 0.024$J$. The lighter curves correspond to a larger $\Delta_{10}$. Panels (c) and (d) show similar results obtained for $\Gamma = 20\gamma_0 \ll \sigma^*$. 
In our further analysis we show that, indeed, the interplay of the absorptive and dispersive terms in Eq. (4.9) is responsible for the counterintuitive behavior. First, assume that we are far outside the resonance, i.e., $|\Delta_{10}|$ is large compared to the absorption HWHM, whether the homogeneous ($\Gamma^* = \langle \Gamma_{10} \rangle$) or the inhomogeneous one ($\sigma^*$). Then, the dispersive term drives the bistability, because its magnitude decreases as $|\Delta_{10}|^{-1}$ upon increasing $\Delta_{10}$, while the absorptive term decreases faster, $\propto |\Delta_{10}|^{-2}$. The critical superradiant constant for dispersive bistability has been reported to be $\Gamma^c_R = 4[\Gamma^* + (\Gamma^*^2 + \Delta_{10}^2)^{1/2}]$ (see, e.g., Ref. [2]) which reduces to $\Gamma^c_R \approx 4|\Delta_{10}|$ when $|\Delta_{10}| \gg \Gamma^*$. On the other hand, we found within the one-exciton model [6] that close to the resonance ($|\Delta_{10}| \ll \sigma^*$), where the contribution of the absorptive term is dominant, $\Gamma^c_R$ scales superlinearly with the HWHM, namely as $(\sigma^*/\Gamma^*)^\alpha \Gamma^*$ with $\alpha \approx 1.7$. Similar scaling ($\Gamma^c_R = \sigma^*/\Gamma^*$) has been obtained in Ref. [34] for a collection of inhomogeneously broadened two-level systems placed in a cavity.

The superlinear dependence of $\Gamma^c_R$ for the absorptive type of bistability is a key ingredient in understanding the counterintuitive $\Delta_{10}$ behavior of the film’s optical response. Indeed, let $\Delta_{10} > \sigma^*$ and $\Gamma_R = 4|\Delta_{10}|$, i.e., we are at the (dispersive) bistability threshold. Now, assume that we tune back to resonance, where bistability is of absorptive nature. Choose, for the sake of simplicity, $\Gamma^c_R = \sigma^*/\Gamma^*$ as the critical value. If $4|\Delta_{10}| > \sigma^2/\Gamma^*$, we are still above the (absorptive) bistability threshold, while in the opposite case bistable behavior is not possible. For $\sigma^* \lesssim \Gamma^*$, the line width is almost of homogeneous nature, and tuning away from the resonance deteriorates the conditions for the occurrence of bistability. [2] In our simulations, this holds for the case of $\Gamma = 500\gamma_0$ and $\sigma^* = 0.024J$ [see panels (a) and (b) in Fig. 4.5].

To conclude this section, we note that the detuning effect we found in our simulations is asymmetric with respect to the sign of $\Delta_{10}$: the behavior of $I_{\text{out}}$ versus $I_{\text{in}}$ is different for the incoming frequency tuned to the red or to the blue from the absorption maximum. We believe that this arises from the asymmetry of the absorption spectrum.

4.3.4 Phase diagram

We compare the one- and two-exciton model by considering phase diagrams of the film’s response under the resonance condition, $\Delta_{10}^{(0)} = \epsilon_0 - \omega_i - 2.02J$, see Fig. 4.6. Here we present the critical superradiant constant $\Gamma^c_R$ versus the quantity $W_{1/2} = \sigma^* + \Gamma^*$, where $\Gamma^* = \Gamma + \langle \gamma_{10} \rangle/2$ is the homogeneous
width of the one-exciton transition. The last term denotes the averaged rate of population relaxation from the one-exciton state to the ground state, see Eq. (4.4b). Roughly, $W_{1/2}$ can be interpreted as the HWHM of the absorption spectrum accounting for both inhomogeneous and homogeneous broadening (through $\sigma^*$ and $\Gamma^*$, respectively). The upper (lower) solid curve in both panels was obtained for the dephasing constant $\Gamma = 20\gamma_0$ ($\Gamma = 500\gamma_0$) and varying the disorder strength $\sigma$. For a given $\Gamma$, the film is bistable (stable) above (below) the corresponding curve. To compare these results with previous work [11], we have also plotted $\Gamma_R^c$ versus $W_{1/2}$ taking all transition dipole moments and relaxation constants equal to their averaged values (dotted curves). In this case, the frequency detunings $\Delta_{10}$ and $\Delta_{21}$ are the only fluctuating parameters.

One of the principal conclusions which can be drawn from the data in Fig. 4.6, is that a more efficient dephasing helps the occurrence of bistability: all curves calculated for $\Gamma = 20\gamma_0$ lie above those obtained for $\Gamma = 500\gamma_0$. The physics of this behavior is simple: as the threshold for the absorptive bistability is $\Gamma_R^c = (\sigma/\Gamma^*)^0\Gamma^*$ (see section 4.3.3), a smaller $\Gamma^*$ gives rise to a higher threshold value for $\Gamma_R$. Thus, by adjusting the dephasing constant $\Gamma^*$, we can manipulate the film’s optical response. This conclusion was already drawn in Ref. [10] within the simplified one-exciton model.

Another observation is that the magnitude of the critical superradiant constant $\Gamma_R^c$ is considerably lower in the two-exciton model than in the one-exciton model. This was to be expected from the physical reasoning which we presented above: a fast exciton-exciton annihilation combined with a slow relaxation from the high-lying molecular vibronic level favors bistability. Without showing detailed data, we also note that the critical switching intensity, i.e., the intensity calculated at the bistability threshold, is smaller in the two-exciton model compared to the one-exciton model. In both models, it also decreases upon increasing the dephasing rate.

From the comparison between the solid and dotted curves in Fig. 4.6, it appears that, surprisingly, fluctuating transition dipole moments and relaxation constants improve the conditions for bistability. At first glance this seems counterintuitive. However, inspection of changes in the absorption spectrum obtained when all transition dipole moments are set equal to their averaged value sheds light on this result. We found that upon neglecting the fluctuations, the absorption spectrum, first, acquires a shift which introduces an off-resonant detuning. Secondly, the shape of the absorption spectrum becomes
more asymmetric. As the film’s response is sensitive to both the detuning and asymmetry, the combined effect of these changes produces the observed big difference between the two calculations. In principle, this discrepancy can be reduced by adjusting the detuning; it is impossible, however, to correct for the asymmetry. This comparison shows that to adequately calculate the film’s optical response, fluctuations of all variables should be taken into account.

4.4 Thin film of PIC: Estimates

We analyze low-temperature experimental data of J-aggregates of pseudo-isocyanine (PIC) here, to investigate the feasibility of measuring optical bistability in a thin film of PIC. In particular, we will focus on aggregates of PIC-Br studied experimentally in detail in Refs. [35, 36, 14]. At low temperatures, the absorption spectrum of PIC-Br is dominated by a very narrow absorption band (HWHM = 17 cm\(^{-1}\)) peaked at \(\lambda = 573\) nm and red shifted relative to the main monomer feature (\(\lambda = 523\) nm). For these aggregates, vibration-induced intra-band relaxation is strongly suppressed (no visible Stokes shift of the fluorescence spectrum with respect to the \(J\)-band is observed). This favors a long exciton lifetime, which is desirable from the viewpoint of saturation, and thus for optical bistability. The lifetime of the exciton states forming the \(J\)-band in PIC-Br is conventionally assumed to be of radiative nature. For temperatures below about 40 K, it has been measured to be 70 ps [35].

Within the one-exciton model studied in the previous chapter, we found that the number density of monomers, required for the driving parameter \(\Gamma_R/\sigma^*\) to exceed the bistability threshold, has to obey \(n_0 > 10^{19}\) cm\(^{-3}\). Such densities can be achieved in thin films prepared by the spin-coating method [37, 38]. Within the extended four-level model considered in the present chapter, the critical ratio of \(\Gamma_R/\sigma^*\) may be even lower. Thus, we believe that from the viewpoint of monomer density, J-aggregates of PIC are promising candidates.

Another important requirement for candidates, potentially suitable for bistable devices, is their photostability. J-aggregates are known to bleach if they are exposed for a long time to powerful irradiation. Therefore, it is useful to estimate the electromagnetic energy flux through the film. For the field slightly below the higher switching threshold, the dimensionless intensity inside the film obeys \(I_{\text{out}} = |\Omega|^2/(\gamma_0\sigma^*) \approx 1\) (see, e.g., Fig.4.3). Using the expression for the monomer spontaneous emission rate \(\gamma_0 = 32\pi^3d^2_0/(3\hbar\lambda^3)\),
we obtain \( E_{\text{out}}^2 \approx 32\pi^3 \hbar \sigma^* / (3\lambda^3) \). The electromagnetic energy flux through the film is determined by the Pointing vector, whose magnitude is given by \( S_{\text{out}} = cE_{\text{out}}^2 / (4\pi) \). Being expressed in the number of photons \( S_{\text{out}} / (\hbar\omega_{10}) \), passing per cm\(^2\) and per second through the film, this value corresponds to \( 5 \times 10^{21} \) photons/(cm\(^2\)s). As is seen from Fig. 4.3, above the switching threshold the intensity inside the film rises by an order of magnitude. Hence, above threshold the electromagnetic energy flux reaches a value on the order of \( S_{\text{out}} \approx 5 \times 10^{22} \) photons/(cm\(^2\)s).

Furthermore, the typical time \( \tau \) for the outgoing intensity \( I_{\text{out}} \) to reach its stationary value is on the order of the population relaxation time, which is 70 ps, except for values of \( I_{\text{out}} \) slightly above (below) the higher (lower) switching threshold, where the relaxation slows down [6]. This means that typically, a nanosecond pulse is enough to achieve the steady-state regime. Bearing in mind the above estimates for \( S_{\text{out}} \), we obtain the corresponding flux for a nanosecond pulse \( S_{\text{out}} \approx 10^{13} \) photons/(cm\(^2\) ns). On the other hand, for a thin film of thickness \( L = \lambda / (2\pi) \) and number density of monomers \( n_0 = 10^{20} \) cm\(^{-3}\), the surface density is \( n_0 \lambda / (2\pi) \approx 10^{15} \) cm\(^{-2}\). Combining these numbers, we conclude that only one photon per 20 monomers produces the effect, which is well below the bleaching threshold [38].

### 4.5 Summary and concluding remarks

We theoretically studied the optical response of an ultrathin film of oriented J-aggregates with the goal to examine the effect of two-exciton states and exciton-exciton annihilation on the occurrence of bistable behavior. The standard Frenkel exciton model was used to describe a single aggregate: an open linear chain of monomers coupled by delocalizing dipole-dipole excitation transfer interactions, in combination with uncorrelated on-site disorder, which tends to localize the exciton states.

We considered a single aggregate as a meso-ensemble of exciton localization segments, ascribing to each segment a four-level system consisting of the ground state (all monomers in the ground state), an \( s \)-like exciton state, a two-exciton state constructed as the antisymmetric combination of this \( s \) state and an associated \( p \) state, and a vibronic state of the monomer through which the two-exciton states annihilate. To select the \( s \)- and \( p \)-like states, a new procedure was used which correctly accounts for the fluctuations and correlations.
of the transition energies and transition dipole moments, improving on earlier works [11]. The optical dynamics of the localization segment was described within a $4 \times 4$-density matrix formalism, coupled to the total electromagnetic field. In the latter, in addition to the incoming field, we accounted for a part produced by the aggregate dipoles.

We derived a novel steady-state equation for the transmitted signal and demonstrated that three-valued solutions to this equation exist in a certain domain of the multi-parameter space. Analyzing this equation, we found that several conditions promote the occurrence of a bistable behavior. In particular, fast exciton-exciton annihilation, in combination with a slow relaxation from the monomer vibronic state, favors bistability. In contrast, fast relaxation from the vibronic level to the ground state acts against the effect. Additionally, bistability is also favored by faster dephasing.

We found a counterintuitive interplay between dephasing and tuning from resonance. When homogeneous broadening of the exciton states (associated with the incoherent exciton-phonon scattering) is comparable with the inhomogeneous broadening (resulting from the localized nature of the exciton states), the detuning destroys bistability. Oppositely, for slower dephasing, the bistability effect is favored by tuning away form the resonance. We relate this anomalous behavior to an interplay of the absorptive and dispersive parts of the nonlinear susceptibility, which both contribute to the overall effect.

We found that in general, including one-to-two-exciton transitions promotes bistability. The critical superradiant constant which drives bistability, and the critical switching intensity are lower than in the one-exciton model [6]. Furthermore, bistable behavior is more easily established when the ratio of the inhomogeneous to the homogeneous width is reduced.

Estimates of parameters of our model for aggregates of polymethine dyes at low temperatures indicate that a film with a monomer number density on the order of $10^{20}$ cm$^{-3}$ and a thickness of $\lambda/2\pi$, achievable with the spin coating method [37], is sufficient to realize the effect. Under these conditions, one photon per 20 monomers produces the switching of the film’s transmittivity.

To conclude, we point out that a microcavity arrangement of molecular aggregates [39, 40, 41, 42, 43] in the strong coupling regime is another promising arrangement to realize an all-optical switch. The recent observation of optical bistability in planar inorganic microcavities [45] in the strong coupling regime suggests that organic microcavities can exhibit a similar behavior.
4.5. Summary and concluding remarks

**Figure 4.6:** Phase diagram of the bistable optical response of a thin film in the $(\Gamma_R, W_{1/2})$-space, where $W_{1/2} = \sigma^* + \Gamma + (\gamma_{10})/2$ is used a measure for HWHM of the absorption spectrum accounting for contributions of inhomogeneous and homogeneous broadening (through $\sigma^*$ and $\Gamma + (\gamma_{10})/2$, respectively) to the total width of the $J$ band. The data is obtained by solving Eq. (4.6) for the input field tuned to the $J$-band center, $\Delta_{10}^{(0)} = \varepsilon_0 - \omega_i - 2.02J$ and varying the disorder strength $\sigma$. In both panels, upper and lower curves correspond to $\Gamma = 20\gamma_0$ and $\Gamma = 500\gamma_0$, respectively. The open circles and squares represent the numerical data points, whereas the solid lines are a guide to the eye. The solid lines themselves represent the $W_{1/2}$-dependence of the critical superradiant constant $\Gamma_R^c$. Above (below) the curve for a given $\Gamma$, the film behaves in a bistable (stable) fashion. For comparison, we also plotted $\Gamma_R^c$ versus $W_{1/2}$ taking all transition dipole moments and relaxation constants equal to their averaged values (dotted curves, cf. Ref. [11]).


REFERENCES


[38] R. Augulis, private communication.


