Effects of higher exciton manifolds and exciton-exciton annihilation on optical bistable response of an ultrathin glassy film comprised of oriented linear Frenkel chains

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We theoretically analyze the optical response from an ultrathin film built up of oriented molecular aggregates, the operating states of which are represented by Frenkel exciton states. A four-level model, involving transitions between the ground, one-exciton and two-exciton states, exciton-exciton annihilation from the two-exciton state as well as relaxation from the annihilation level back to the one-exciton and ground states, is used for describing the film optical response. It is proved that the exciton-exciton annihilation may act not as a destructive but, on the contrary, as a constructive factor tending towards the occurrence of bistability. In particular, the effect of inhomogeneous broadening of the exciton optical transition, preventing the bistable behavior, may be suppressed considerably due to a fast exciton-exciton annihilation.

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I. INTRODUCTION

In the middle of the 1930s Jelley [1] and Scheibe [2] discovered the effect of aggregation of polymethine dye molecules in solutions into long linear chains and, as a result, drastic changes of their optical spectra: considerable narrowing and a red shift. Since that time, these objects received much attention. In the beginning of the 1990s if was found that the spontaneous emission time of *J*-aggregated systems could be dropped by cooling to several tens to hundreds of picoseconds [3–5]. Similar effects were found to appear in conjugated polymers [6]. In addition, it was recognized that *J*-aggregated systems show extremely high magnitudes of nonlinear susceptibilities [7,8] (see for a comprehensive review Refs. [9] and [10]). In recent years, cooperative emission in π-conjugated polymer thin films [11–13] and superradiant lasing from *J*-aggregated cyanine dye molecules adsorbed onto colloidal silica [46] and silver [14,15] were reported. All these findings make these objects to be very promising species from the viewpoint of laser and optoelectronic applications (see a recent review in Ref. [16]).

Another intriguing option that would be highly desirable is observation of a bistable optical response from assemblies of molecular aggregates. The theoretical aspect of this problem was intensively discussed [17–25]. The conditions for such a behavior to occur for a dimer [17,20,22], for a single aggregate built up of many molecules [18,19,21] as well as for a collection of aggregates [23–25] were analyzed. However, there has been no experimental report of this effect as concerned aggregated (organic) molecular system. Only an observation of optical bistability in cooperative luminescence of the Yb^{3+}-ions pairs in inorganic crystalline $Cs_3Y_2Br_9$: Yb^{3+} was reported in Refs. [26,27]. The authors attributed the observed effect to a dimerlike bistability [28].

It is worth mentioning that optical bistability discussed in all of these papers is intrinsic in nature: it does not require an optical resonator. On the contrary, in the initial theoretical prediction [29] and experimental demonstration [30] of optical bistability, namely, the resonator configuration was used. The latter served for creating a feedback that, combined with the nonlinearity of the material, led to bistability of the optical response (for an extensive review of this type of optical bistability, see Refs. [31] and [32]). The fact that a collection of identical two-level atoms placed into a volume of linear size less that an emission wavelength may manifest the optical bistable behavior without external feedback, e.g., *mirrorless* optical bistability, was first pointed out in Ref. [33]. A mirrorless configuration is much favored in many cases as compared to that using an optical resonator [34].

It is now well established that the unusual properties of *J*-aggregated systems outlined above are due to the fact that the states coupled to the light are Frenkel exciton states. In our recent papers [23] we argued that the blueshift of the one-to-two exciton optical transition with respect to the zero-to-one exciton optical transition in *J*-aggregates [35] gives the opportunity to consider a *J*-aggregated sample as an ensemble of inhomogeneously broadened two-level systems. Based on this model, we found that an ultrathin film made up of oriented *J*-aggregates may behave in a bistable manner, displaying an abrupt switching of both reflectivity and transmittivity.

The two-level model seems to be applicable until the system follows the lower branch of the bistable output-input characteristics where the corresponding Rabi frequency of the operating field is smaller than the blueshift. Under such a condition, populating the two-exciton state as well as the accompanying process of exciton-exciton annihilation can be neglected. However, after passing the critical point of the bistable curve, where the reflection of the film drops abruptly (the transmission, on the contrary, rises up), the field amplitude inside the film increases in favor of population of the two-exciton state and initiation of the exciton-exciton annihilation process. In our previous short communication [25], we showed that a fast exciton-exciton annihilation may even act towards improving the conditions for bistability to occur. The goal of the present paper is to analyze in detail the influence of the one-to-two exciton optical transitions, the exciton-exciton annihilation from the two-exciton state and relaxation from the annihilation level back to the one-exciton

and ground states on bistability of the optical response from an ultrathin film built up of oriented *J*-aggregates. The reminder of the paper is organized as follows. In Sec. II, we describe the four-level model of the system and derive a set of truncated equations for the density-matrix elements. In Sec. III, the comprehensive steady-state analysis of this set is performed in order to find the possible branches of the output-input characteristic of the film. The estimations of driving parameters and the discussions of the experimental data are presented in Section IV. We conclude in Sec. V.

II. FOUR-LEVEL MODEL

In spite of the fact that the number of molecules in a real molecular aggregate, $\mathcal{N}$, may achieve thousands [36,37], it is a widely adopted concept now that only a subsystem of rather short aggregate segments (constituted of the so-called coherently bound molecules) contributes to the optical response of the aggregate. The origin of this peculiarity lies in localization of the exciton states resulted from disorder. Because of the disorder, the exciton wave functions, being extended over the whole aggregate in an ideal chain, reduce their extension to a (localization) segment of size $N \ll \mathcal{N}$ [38]. This quantity is fluctuating and characterized by a rather broad distribution [43]. The typical magnitude of N, denoted hereafter as N^*, depends on the degree of disorder and usually does not exceed 100 [3–5,7,8,39,40].

An important finding is that the exciton, localized within a particular segment, has the low-energy structure that is similar to the structure of an ideal linear chain of length N [41–43]. Hence, for our purposes, we will model a *J*-aggregated sample by an ensemble of noninteracting short (with length smaller than the emission wavelength) ideal linear chains consisting of N (assumed to be much larger than unity) *three-level* molecules, with N being distributed stochastically within some interval. The lowest levels of molecules form the ground state of a chain (when all molecules occupy those levels). The intermediate molecular level is assumed to form the Frenkel multiexciton bands due to a strong resonant inter-molecular dipole-dipole coupling. The highest level is an electronic-vibrational molecular term through which the exciton-exciton annihilation occurs [44–48]: we suppose that the two-exciton optical state is resonantly coupled by an interaction V to one of the electronic-vibrational levels which, in turn, undergoes an efficient phonon-assisted relaxation with the rate Γ to the ground vibronic state, Fig. 1. The latter can further relax either to the lowest state of the molecule or to the intermediate state. The annihilation process itself consists of transferring the energy from the two-exciton state to the high-lying molecular term. The possible channel of annihilation employing two excitons created within two different chains will be neglected as much less probable under the conditions we will be dealing with [47,48].

Within the nearest-neighbor approximation we will adopt hereafter, one-dimensional Frenkel excitons appear to be noninteracting fermions [49–52]. Therefore, any state with a fixed number of excitons n_{ex} can be constructed as a Slater determinant of n_{ex} one-exciton states represented by

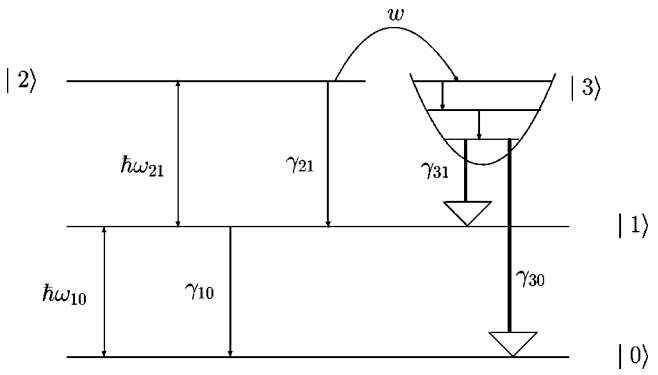

FIG. 1. Schematic representation of all transitions contributing to the optical response of the film. The input field populates the one-exciton (1) and two-exciton (2) states. The population of the latter is transferred (annihilates) with a rate w to a high-lying electronic-vibrational molecular term (3). The next step employs the fast vibrational relaxation within high-lying electronic-vibrational sublevels towards the ground vibrational state. Further, this level undergoes a multiphonon relaxation to the one-exciton and ground states with the rates γ_{31} and γ_{30}, respectively.

$$|k\rangle = \left(\frac{2}{N+1}\right)^{1/2} \sum_{n=1}^{N} \sin\frac{\pi k n}{N+1} |1n\rangle, \qquad k = 1,2,\ldots,N, \tag{1}$$

where $|1n\rangle$ is the ket vector of the excited state (1) of the nth molecule. The energies of the one-dimensional exciton gas may take the values $W = \Sigma_{k=1}^{N} n_k E_k$, where $n_k = 0,1$ is the occupation number of the kth one-exciton state and E_k is the corresponding energy given by

$$E_k = \hbar\omega_0 - 2U\cos\frac{\pi k}{N+1}. \tag{2}$$

Here, ω_0 is the frequency of the transition between the lowest and intermediate states in an isolated molecule; U (chosen to be positive as it is in the case of *J*-aggregates) is the magnitude of the nearest-neighbor dipole-dipole coupling.

In our present paper, we will restrict ourselves to the case when not more than two excitons per chain are created by the pump. This means that only the ground, one-exciton, and two-exciton states should be involved into the scheme. Recall further that the optical transition from the ground state of the chain to the bottom state of the one-exciton band $|k=1\rangle$ has the dominating oscillator strength (81% of the entire one; see, for instance, Ref. [4]). Nearly the same statement is true relative to the transitions between the bottoms of the one-exciton and two-exciton bands, $|k=1\rangle \rightarrow |k=1,k'=2\rangle$, carrying 70% of the entire oscillator strength [51,53]. Therefore, in what follows, we take into account only these two strongest optical transitions, neglecting the others. It is important to note that the transitions of interest are not resonant to each other. Indeed, the energies of the one-exciton and two-exciton band bottom states equal E_1 and E_1+E_2, respectively. Thus, the one-to-two exciton transition is blue-shifted with respect to the zero-to-one exciton transition by the energy

$$E_2 - E_1 = 2U\left(\cos\frac{2\pi}{N+1} - \cos\frac{\pi}{N+1}\right) \approx \frac{3\pi^2 U}{N^2}, \qquad N \gg 1. \tag{3}$$

We will consider an ensemble of linear chains oriented in the same direction and forming an ultrathin film with thickness less that the emission wavelength. The latter gives us a great advantage in the mathematical description of the model taking away the propagation effects along the film normal. The dipole moments of all transitions are considered to be parallel to each other as well as to the film plane. Such conditions are achievable for thin films prepared by the spin-coating method [54]. Regarding the incoming field ε_i the quasi-resonance and normal incidence conditions are chosen. In addition, we assume that the field polarization is directed along the transition dipole moment. Then, all the observables can be considered as scalars.

Under the above limitations, the time evolution of the film can be described in terms of the 4×4 density matrix $\rho_{\alpha\beta}, \alpha,\beta=0$ (ground state), 1 (one-exciton state), 2 (two-exciton state), and 3 (high-lying molecular state), which determines the state of a single chain of size N, together with the Maxwell equation for the total field $\mathcal{E}$, including the secondary field produced by the film. They read

$$\dot{\rho}_{00} = i\frac{d_{10}\mathcal{E}}{\hbar}(\rho_{10}-\rho_{01}) + \gamma_{10}\rho_{11} + \gamma_{30}\rho_{33}, \tag{4a}$$

$$\dot{\rho}_{11} = -\gamma_{10}\rho_{11} + i\frac{d_{21}\mathcal{E}}{\hbar}(\rho_{21}-\rho_{12}) - i\frac{d_{10}\mathcal{E}}{\hbar}(\rho_{10}-\rho_{01}) + \gamma_{21}\rho_{22} + \gamma_{31}\rho_{33}, \tag{4b}$$

$$\dot{\rho}_{22} = -(\gamma_{21}+w)\rho_{22} - i\frac{d_{21}\mathcal{E}}{\hbar}(\rho_{21}-\rho_{12}), \tag{4c}$$

$$\dot{\rho}_{33} = -\gamma_3\rho_{33} + w\rho_{22}, \tag{4d}$$

$$\dot{\rho}_{10} = -(i\omega_{10}+\Gamma_{10})\rho_{10} + i\frac{d_{10}\mathcal{E}}{\hbar}(\rho_{00}-\rho_{11}) + i\frac{d_{21}\mathcal{E}}{\hbar}\rho_{20}, \tag{4e}$$

$$\dot{\rho}_{21} = -\left(i\omega_{21}+\Gamma_{21}+\frac{1}{2}w\right)\rho_{21} + i\frac{d_{21}\mathcal{E}}{\hbar}(\rho_{11}-\rho_{22}) - i\frac{d_{10}\mathcal{E}}{\hbar}\rho_{20}, \tag{4f}$$

$$\dot{\rho}_{20} = -\left(i\omega_{20}+\Gamma_{20}+\frac{1}{2}w\right)\rho_{20} + i\frac{d_{21}\mathcal{E}}{\hbar}\rho_{10} - i\frac{d_{10}\mathcal{E}}{\hbar}\rho_{21}, \tag{4g}$$

where the dots denote time derivatives; d_{10} and d_{21} are the transition dipole moments (assumed to be real) of the zero-to-one exciton and one-to-two exciton optical transitions, respectively; ω_{10}, ω_{21}, and ω_{20} stand for the frequencies while Γ_{10}, Γ_{21}, and Γ_{20} for the dephasing rates of the corresponding transitions; γ_{10}, γ_{21}, $\gamma_3=\gamma_{30}+\gamma_{31}$ are the population relaxation constants of the one-exciton, two-exciton, and high-lying states, respectively. The excitonic nature of the states 1 and 2 imposes a certain N scaling of the transition dipole moments, $d_{10}, d_{21} \sim \sqrt{N}$, as well as the radiative relaxation constants, $\gamma_{10}=0.81\gamma_0 N, \gamma_{21}=1.27\gamma_0 N$ [51,53], where γ_0 is the radiative rate of a monomer. The exciton-exciton annihilation is described by the rate w given by [47]

$$w = \xi\frac{w_0}{N^3}, \tag{5}$$

where $w_0 = 4\pi V^2/\hbar\Gamma$ is the annihilation rate for a chain consisting of only two molecules and $\xi = 5\pi^6/18 \approx 270$.

The field inside the film consists of the incident field $\mathcal{E}_i$ plus the field produced by the molecular dipoles, $\mathcal{E}_D$, which in the case of an ultrathin film does not depend on spatial coordinates. It is calculated as (see, for instance, Refs. [55–57])

$$\mathcal{E}_D = -\frac{2\pi L}{c}\dot{\mathcal{P}}, \tag{6}$$

where L and c stand for the slab thickness and the speed of light, respectively; $\mathcal{P} = n\Sigma_N p(N)(d_{10}\rho_{10} + d_{21}\rho_{21} + \text{c.c.})$ represents the electric polarization with n being the number concentration of chains and $p(N)$ being the distribution of chains over sizes. Thus, the Maxwell equation for the field inside the film reads

$$\mathcal{E} = \mathcal{E}_i - \frac{2\pi L}{c}\dot{\mathcal{P}}. \tag{7}$$

The incident field is assumed to be of the form $\mathcal{E}_i = E_i(t)\cos\omega_i t$, where ω_i is the frequency and $E_i(t)$ is the amplitude, slowly varying in scale of the optical period $2\pi/\omega_i$. We look for a solution to the set of Eqs. (4) and (7) by passing to the rotating frame: $\rho_{10}=(-i/2)R_{10}\exp(-i\omega_i t)$, $\rho_{21}=(-i/2)R_{21}\exp(-i\omega_i t)$, $\rho_{20}=(-i/2)R_{20}\exp(-i2\omega_i t)$, $\mathcal{E}=(1/2)E\exp(-i\omega_i t)+\text{c.c.}$, where R_{10}, R_{21}, R_{20}, and E are the complex slowly varying (in scale of $2\pi/\omega_i$) amplitude of the off-diagonal density-matrix elements and the field, respectively. Substitution of these expressions into Eqs. (4) and (7) and neglecting the counter-rotating terms gives us the following set of truncated equations:

$$\dot{\rho}_{00} = \frac{1}{4}\mu_{10}[\Omega R_{10}^* + \Omega^* R_{10}] + \gamma_{10}\rho_{11} + \gamma_{30}\rho_{33}, \tag{8a}$$

$$\dot{\rho}_{11} = -\gamma_{10}\rho_{11} - \frac{1}{4}\mu_{10}[\Omega R_{10}^* + \Omega^* R_{10}] + \frac{1}{4}\mu_{21}[\Omega R_{21}^* + \Omega^* R_{21}] + \gamma_{21}\rho_{22} + \gamma_{31}\rho_{33}, \tag{8b}$$

$$\dot{\rho}_{22} = -(\gamma_{21}+w)\rho_{22} - \frac{1}{4}\mu_{21}[\Omega R_{21}^* + \Omega^* R_{21}], \tag{8c}$$

$$\dot{\rho}_{33} = -\gamma_3 \rho_{33} + w\rho_{22}, \tag{8d}$$

$$\dot{R}_{10} = -(i\Delta_{10} + \Gamma_{10})R_{10} - \mu_{10}\Omega(\rho_{00} - \rho_{11}) + \frac{i}{2}\mu_{21}\Omega^* R_{20}, \tag{8e}$$

$$\dot{R}_{21} = -\left(i\Delta_{21} + \Gamma_{21} + \frac{1}{2}w\right)R_{21} - \mu_{21}\Omega(\rho_{11} - \rho_{22}) - \frac{i}{2}\mu_{10}\Omega^* R_{20}, \tag{8f}$$

$$\dot{R}_{20} = -\left(i\Delta_{10} + i\Delta_{21} + \Gamma_{20} + \frac{1}{2}w\right)R_{20} - \frac{i}{2}\mu_{10}\Omega R_{21} + \frac{i}{2}\mu_{21}\Omega R_{10}, \tag{8g}$$

$$\Omega = \Omega_i + \gamma_R \sum_N p(N)(\mu_{10}R_{10} + \mu_{21}R_{21}), \tag{8h}$$

where the notations introduced are: $\Omega = dE/\hbar$, $\Omega_i = dE_i/\hbar$ with $d = \sqrt{(d_{10}^2 + d_{21}^2)/2}$; $\mu_{10} = d_{10}/d$, $\mu_{21} = d_{21}/d$; $\Delta_{10} = \omega_{10} - \omega_i$, $\Delta_{21} = \omega_{21} - \omega_i$; and $\gamma_R = 2\pi d^2 n k_i L/\hbar$ with $k_i = \omega_i/c$.

Recall that γ_R describes the collective radiative (superradiant) damping of an ensemble of two-level molecules [58] (see for more details the monograph [57]) and determines also the characteristic amplitude of the super-radiance field emitted by the molecules. Being expressed through the mean spontaneous emission constant of an isolated chain, defined as $\gamma = 4d^2k^3/3\hbar = (\gamma_{10} + \gamma_{21})/2$ with $k = \omega_{10}/c \approx \omega_{21}/c \approx k_i$, it reads $\gamma_R = (3/8\pi)\gamma n \lambda^2 L$, where $\lambda = 2\pi/k$. The ratio γ_R/Γ_{10} represents the crucial parameter in the case of the two-level problem driving bistable behavior. In particular, at $\gamma_R/\Gamma_{10} < 8$, no bistability is manifested by the film built up of two-level molecules [23,59,60].

The set of Eqs. (8) forms a basis for 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 built up of oriented *J*-aggregates.

III. STEADY-STATE ANALYSIS

In order to find the stationary states of the system, we have to analyze the steady-state solutions to Eqs. (8), setting, respectively, the time derivatives equal to zero. In our analysis, we will use the fact that the bistability effect results from the saturation of the exciton transition by the field inside the film, i.e., when $|\Omega| \sim (\gamma_{10}\Gamma_{10})^{1/2}$. Let us estimate this magnitude using the known experimental data. In particular, for *J*-aggregates of pseudoisocyanine $\gamma_{10} \approx (1/70\ \text{ps})$ or $0.5\ \text{cm}^{-1}$ in wave numbers [3,4]. Taking $\Gamma_{10} \sim \gamma_{10}$, the saturation amplitude of the field is estimated as $|\Omega| \sim 0.5\ \text{cm}^{-1}$. On the other hand, the offset Δ_{21} is of the order of $30\ \text{cm}^{-1}$ (see, for instance, Ref. [9]), i.e., 60 times as large. Even after the system is saturated and the field inside the film increases by an order of magnitude, $|\Omega|$ will not exceed the offset Δ_{21}. This relationship allows us to derive a rather simple equation for the "intensity" of the field inside the film, $|\Omega|^2$, and to study the tendency of changes caused by the population of the two-exciton state and by the exciton-exciton annihilation.

From Eq. (8g) it follows that $|R_{20}| \sim |\Omega/(i\Delta_{21} + \Gamma_{20} + w/2)| \ll 1$ under the restrictions adopted. Respectively, the terms proportional to R_{20} can be neglected in Eqs. (8e) and (8f) as they are much smaller as compared to the others. Taking this into account, one arrives at the following equation for $|\Omega|^2$:

$$|\Omega|^2 \left\{ \left[1 + \gamma_R \sum_N p(N) \left(\mu_{10}^2 \frac{\Gamma_{10}}{\Gamma_{10}^2 + \Delta_{10}^2}(\rho_{00} - \rho_{11}) + \mu_{21}^2 \frac{\Gamma_{21} + w/2}{(\Gamma_{21} + w/2)^2 + \Delta_{21}^2}(\rho_{11} - \rho_{22}) \right) \right]^2 + \left[\gamma_R \sum_N p(N) \left(\mu_{10}^2 \frac{\Delta_{10}}{\Gamma_{10}^2 + \Delta_{10}^2}(\rho_{00} - \rho_{11}) + \mu_{21}^2 \frac{\Delta_{21}}{(\Gamma_{21} + w/2)^2 + \Delta_{21}^2}(\rho_{11} - \rho_{22}) \right) \right]^2 \right\} = \Omega_i^2. \tag{9}$$

The populations ρ_{00}, ρ_{11}, and ρ_{22} are found from the following set of equations:

$$-S_{10}\rho_{00} + (1 + S_{10})\rho_{11} + \frac{\gamma_{30}}{\gamma_{10}}\rho_{33} = 0, \tag{10a}$$

$$-S_{21}\rho_{11} + (1 + S_{21})\rho_{22} = 0, \tag{10b}$$

$$w\rho_{22} - \gamma_3\rho_{33} = 0, \tag{10c}$$

$$\rho_{00} + \rho_{11} + \rho_{22} + \rho_{33} = 1, \tag{10d}$$

where the notation introduced are

$$S_{10} = \frac{\mu_{10}^2 |\Omega|^2}{2\gamma_{10}} \frac{\Gamma_{10}}{\Delta_{10}^2 + \Gamma_{10}^2}, \tag{11a}$$

$$S_{21} = \frac{\mu_{21}^2 |\Omega|^2}{2(\gamma_{21} + w)} \frac{\Gamma_{21} + w/2}{\Delta_{21}^2 + (\Gamma_{21} + w/2)^2}. \tag{11b}$$

Resolving Eqs. (10), one gets

$$\rho_{00}-\rho_{11}=\frac{1+(1+w\gamma_{30}/\gamma_{10}\gamma_3)S_{21}}{1+2S_{10}+(1+w\gamma_{30}/\gamma_{10}\gamma_3)S_{21}+(3+w/\gamma_3)S_{10}S_{21}}, \tag{12a}$$

$$\rho_{11}-\rho_{22}=\frac{S_{10}}{1+2S_{10}+(1+w\gamma_{30}/\gamma_{10}\gamma_3)S_{21}+(3+w/\gamma_3)S_{10}S_{21}}. \tag{12b}$$

In our previous paper [25], we neglected in Eq. (9) the terms proportional to $\rho_{11}-\rho_{22}$. This approximation is valid if the exciton-exciton annihilation rate w is large compared to the other rates and detunings. In other cases, the corresponding terms must be kept in Eq. (9) because they affect considerably the final result (see below).

The analytical evaluation of sums presented in Eq. (9) is unlikely in a general case, i.e., when taking into account the N dependence of all variables. Therefore, we set several simplifications allowing us to perform the average over segment sizes analytically. First, it can be argued that within the spectral region close to the one-exciton resonance, which is of our primary interest, the main contribution to the N dependence of the summands comes from the N dependence of the one-exciton resonance detuning Δ_{10}. From the theoretical point of view, it is simply due to the fact that all the relaxation constants and dipole moments squared scale linearly with N, while Δ_{10} is inversely proportional to N^2. Numerically, this assumption has been proven in Ref. [61]). Thus, in what follows, we consider the detuning Δ_{10} as the only N-dependent variable, setting the other variables to their respective means. This also concerns the offset Δ_{21}. The latter approximation is valid if the width of the Δ_{10} distribution is smaller than Δ_{21}.

Furthermore, we replace the average over size by the average over detuning using a Lorentz-shaped distribution function

$$\sum_N p(N)\rightarrow\int_{-\infty}^{\infty}d\Delta_{10}p(\Delta_{10})$$

$$=\int_{-\infty}^{\infty}d\Delta_{10}\frac{G}{\pi}\frac{1}{(\Delta_{10}-\Delta_0)^2+G^2}.$$

The parameters G and $\Delta_0=\omega_0-\omega_i$ mimic here the J-band width and the deviation of the input field frequency ω_i on the pick frequency of the J band, respectively.

After the simplifications adopted, it is straightforward to evaluate the integrals in Eq. (9): all of them represent the overlap integrals of Lorentzians. For the sake of simplicity, we present here the result of integration only for a particular case of $\Delta_0=0$, which holds as well if $\Delta_0\ll G$). It reads

$$y\left\{\left[1+a\frac{1+dy}{\sqrt{1+(1+c)y+by^2}[g\sqrt{1+cy}+\sqrt{1+(1+c)y+by^2}]}\right]^2+a^2\frac{e^2y^2}{[1+(1+c)y+by^2][g\sqrt{1+cy}+\sqrt{1+(1+c)y+by^2}]^2}\right\}=x, \tag{13}$$

where $y=\mu_{10}^2|\Omega|^2/\gamma_{10}\Gamma_{10}$ and $x=\mu_{10}^2\Omega_i^2/\gamma_{10}\Gamma_{10}$ are the dimensionless ''intensities'' of the output and input fields, respectively. The other notations introduced are

$$a=\mu_{10}^2\frac{\gamma_R}{\Gamma_{10}},\quad g=\frac{G}{\Gamma_{10}}, \tag{14a}$$

$$b=\frac{1}{4}\left(3+\frac{w}{\gamma_3}\right)\frac{\gamma_{21}}{\gamma_{21}+w}\frac{\Gamma_{10}(\Gamma_{21}+w/2)}{\Delta_{21}^2+(\Gamma_{21}+w/2)^2}, \tag{14b}$$

$$c=\frac{1}{2}\left(1+\frac{w\gamma_{30}}{\gamma_{10}\gamma_3}\right)\frac{\gamma_{21}}{\gamma_{21}+w}\frac{\Gamma_{10}(\Gamma_{21}+w/2)}{\Delta_{21}^2+(\Gamma_{21}+w/2)^2}, \tag{14c}$$

$$d=\frac{1}{2}\left(1+\frac{w\gamma_{30}}{\gamma_{10}\gamma_3}+\frac{\gamma_{21}+w}{\gamma_{10}}\right)\frac{\gamma_{21}}{\gamma_{21}+w}\frac{\Gamma_{10}(\Gamma_{21}+w/2)}{\Delta_{21}^2+(\Gamma_{21}+w/2)^2}, \tag{14d}$$

$$e=\frac{1}{2}\frac{\gamma_{21}}{\gamma_{10}}\frac{\Gamma_{10}\Delta_{21}}{\Delta_{21}^2+(\Gamma_{21}+w/2)^2}. \tag{14e}$$

When deriving expressions for the constants b, c, d, and e, we used the relationship $\mu_{21}^2\gamma_{10}/\mu_{10}^2\gamma_{21}=1$.

By setting b, c, d, and e in Eq. (13) equal to zero one obtains an equation corresponding to the two-level model studied previously [23]. Keeping the $bcde$ terms, as is seen, gives rise to a stronger nonlinearity in Eq. (13), originating from the y^2 term.

A. Effect of the one-to-two-exciton transition

First, we intend to gain insight into how the one-to-two-exciton transition itself influences the bistable behavior. In line with this, we neglect the exciton-exciton annihilation ($w=0$) and assume no dispersion of chain sizes, $G=0$. Under these restrictions, Eq. (13) takes the form

$$y\left\{\left[1+a\frac{1+dy}{1+(1+c)y+by^2}\right]^2+a^2\frac{e^2y^2}{[1+(1+c)y+by^2]^2}\right\}=x, \tag{15}$$

where the parameters b, c, d, and e now are

$$b=\frac{3}{4}\frac{\Gamma_{10}\Gamma_{21}}{\Delta_{21}^2+\Gamma_{21}^2}\approx\frac{3}{4}\frac{\Gamma_{10}\Gamma_{21}}{\Delta_{21}^2}, \tag{16a}$$

$$c=\frac{1}{2}\frac{\Gamma_{10}\Gamma_{21}}{\Delta_{21}^2+\Gamma_{21}^2}\approx\frac{1}{2}\frac{\Gamma_{10}\Gamma_{21}}{\Delta_{21}^2}, \tag{16b}$$

$$d=\frac{1}{2}\left(1+\frac{\gamma_{21}}{\gamma_{10}}\right)\frac{\Gamma_{10}\Gamma_{21}}{\Delta_{21}^2+\Gamma_{21}^2}\approx\frac{1}{2}\left(1+\frac{\gamma_{21}}{\gamma_{10}}\right)\frac{\Gamma_{10}\Gamma_{21}}{\Delta_{21}^2}, \tag{16c}$$

$$e=\frac{1}{2}\frac{\gamma_{21}}{\gamma_{10}}\frac{\Gamma_{10}\Delta_{21}}{\Delta_{21}^2+\Gamma_{21}^2}\approx\frac{1}{2}\frac{\gamma_{21}}{\gamma_{10}}\frac{\Gamma_{10}}{\Delta_{21}}. \tag{16d}$$

It is important to notice that b, c, and d are of the second order while e is of the first order of magnitude with respect to the ratio relaxation-rate/Δ_{21}. Because of that, the e term cannot be neglected in Eq. (15) whenever $w=0$. A similar term would appear within the two-level model at a nonzero detuning Δ_{10} [see. Eq. (9) at $\mu_{21}=0$]. Thus, the e term in the present model is effectively equivalent to introducing a nonzero detuning into the two-level model. Recall that in the latter case, any detuning tends to prevent bistability [23]. This fact determines the role which plays the e term in the effect we are dealing with: it will result in rising the critical value of the parameter a driving the bistability.

The first term inside the braces in Eq. (15) also differs from that in the two-level model due to the presence of the b, c, and d terms. In order to analyze the (bcd) effect, we simplified Eq. (15), neglecting the e term

$$y\left[1+a\frac{1+dy}{1+(1+c)y+by^2}\right]^2=x. \tag{17}$$

According to Eqs. (16a)–(16b), the parameters a, b, and c are proportional to each other. After setting b as a variable parameter, the other can be expressed through b as follows: $c=(2/3)\,b$, $d=(2/3)(1+\gamma_{21}/\gamma_{10})\,b$, where $\gamma_{21}/\gamma_{10}=1.27/0.81\approx1.57$.

Plot (a) in Fig. 2 shows the computed dependence of the threshold value of a as a function of b. Within the range of pairs (a,b) above the curve, Eq. (17) has three-valued real solutions implying the bistable behavior. Below the curve, this equation has only a single-valued real solution and thus no bistability is present in the system response. As is seen, the b dependence of a_c is not monotonous. The critical parameter a_c, first, slightly increases (from 8 to approximately 11) at small values of b and then goes down upon further increasing b even below the threshold for the two-level model $a_c=8$. It is easy to check out, taking formally the limit of b large compared to unity, that Eq. (17) is equivalent to the corresponding equation of the two-level model (at $b=c=d=0$), only with a renormalized parameter a. Indeed, keeping in the fraction of Eq. (17) only the terms proportional to b and rescaling the variables as follows: $y'=(b/c)y=(3/2)y$, $x'=(b/c)x=(3/2)x$, and $a'=(d/c)a=(1+\gamma_{21}/\gamma_{10})a=2.57a$, we obtain

$$y'\left[1+a'\frac{1}{1+y'}\right]^2=x'. \tag{18}$$

This equation has a three-valued real solution whenever $a'\geqslant a_c'=8$ [59,60] or, in terms of the original parameter a, whenever $a\geqslant 8/(1+\gamma_{21}/\gamma_{10})=3.12$. This explains decreasing a_c upon increasing b.

In our general analysis of Eq. (15), i.e., taking into account (bcd) and e terms, we selected e as a variable parameter as well as assumed that $\Gamma_{10}=\Gamma_{21}$. Then the other parameters can be expressed through e as follows: $b=3(\gamma_{10}/\gamma_{21})^2e^2=1.22e^2$, $c=2(\gamma_{10}/\gamma_{21})^2e^2=0.81e^2$, and $d=2(1+\gamma_{21}/\gamma_{10})(\gamma_{10}/\gamma_{21})^2e^2=2.09e^2$. Plot (b) in Fig. 2 presents e dependence of the threshold value of a. As previously, the curve $a_c(e)$ divides the space of pairs (a,e) into two regions: bistable (above the curve) and stable (below the curve). We see that including the e term drastically affects the occurrence of bistability when e ranges within $0.063<e<0.225$. First of all, there appear two branches of a_c. This means that above both curves (the shaded area) one gets ''double'' bistability. Panel (c), in which we plotted a solution to Eq. (15) computed at particular values of $a=35$ and $e=0.175$, illustrates this case. As is seen, the y vs x dependence shows two S-shaped fragments formed each one by three-valued real solutions of Eq. (15). Note that the regions of ranging x, where these solution exist, are not overlapped.

Another effect of the e term within the region $0.063<e<0.225$ is that the threshold value a_c increases gradually with e, indicating the dominated role of this term as compared to the bcd terms. It is not surprising because b,c, and d, being proportional to e^2, are very small for those values of e. Out of that region, however, a_c goes down and becomes smaller than the threshold value for the two-level model, $a_c=8$, whenever e approaches unity. Here, on the contrary, the bcd terms start to play major role, and a_c follows, in fact, the curve presented in plot (a) for largest b.

It is to be noted that $b,e\sim1$ corresponds in physical quantities to $\Gamma_{10}\sim\Delta_{21}$, which means that the zero-to-one and one-to-two exciton transitions are nearly in resonance due to the homogeneous broadening. Thus, making these two transitions resonant to each other works towards improving the conditions for bistability to occur.

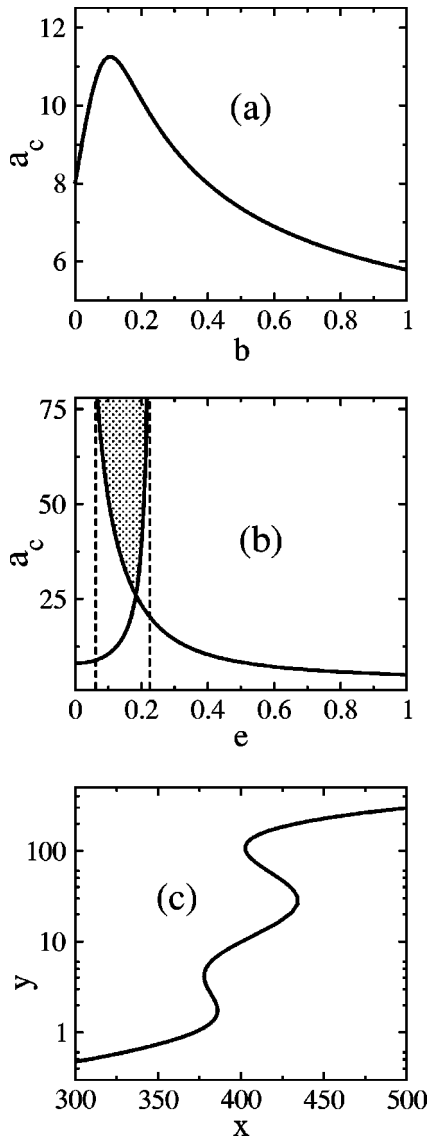

FIG. 2. Effect of the one-to-two exciton transition on feasibility of the bistable behavior in the film optical response. (a) b dependence of the threshold value (a_c) of the driving parameter $a=\mu_{10}^2\gamma_R/\Gamma_{10}$ showing the effect of (bcd) terms on the appearance of three-valued real solutions to Eq. (17) at $e=0$. $b=3\Gamma_{10}\Gamma_{21}/4\Delta_{21}^2$, $c=(2/3)b$, and $d=(2/3)(1+\gamma_{21}/\gamma_{10})b$. (b) e dependence of the threshold value (a_c) of the driving parameter $a=\mu_{10}^2\gamma_R/\Gamma_{10}$. $e=\gamma_{21}\Gamma_{10}/2\gamma_{10}\Delta_{21}$, $b=1.22e^2$, $c=0.81e^2$, and $d=2.09e^2$. (c) An example of the solution to Eq. (15) at $e=0.175$ and $a=35$. $y=\mu_{10}^2|\Omega|^2/\gamma_{10}\Gamma_{10}$ and $x=\mu_{10}^2\Omega_i^2/\gamma_{10}\Gamma_{10}$. The other parameters set in the calculation are: $b=1.22e^2=0.037$, $c=0.81e^2=0.025$, and $d=2.09e^2=0.064$.

B. Effect of a fast exciton-exciton annihilation

We turn now to the question to what extent a fast exciton-exciton annihilation from the two-exciton states may influence the bistable behavior of the ultrathin film optical response. We assume that the rate of exciton-exciton annihilation w is large compared to any relaxation rate (γ_{10}, γ_{21}, Γ_{10}, and Γ_{21}) as well as the offset Δ_{21}. Keeping then in Eqs. (14b)–(14c) only the terms proportional to w, one obtains

$$b=\frac{\gamma_{21}\Gamma_{10}}{2\gamma_3 w}, \tag{19a}$$

$$c=\frac{\gamma_{21}\gamma_{30}\Gamma_{10}}{\gamma_{10}\gamma_3 w}, \tag{19b}$$

$$d=\left(1+\frac{\gamma_{30}}{\gamma_3}\right)\frac{\gamma_{21}\Gamma_{10}}{\gamma_{10}w}, \tag{19c}$$

$$e=\frac{2\gamma_{21}\Gamma_{10}\Delta_{21}}{\gamma_{10}w^2}. \tag{19d}$$

As is seen, the parameters b, c, and d now are of the first order while e is of the second order of magnitude with respect to the ratio relaxation-rate/w. This allow us to neglect the e term in Eq. (15). The resulting equation is of the form

$$y\left[1+a\frac{1+dy}{1+(1+c)y+by^2}\right]^2=x. \tag{20}$$

In analyzing this equation, we assume that there is no drastic difference between the rates γ_{30} and γ_{31}, so that $\gamma_{30}/\gamma_3\sim 1$, and take also into account that $\gamma_{10}\sim\gamma_{21}$. Then we find that $c\ll 1$ as a result of smallness of Γ_{10}/w. Due to this fact, the corresponding terms in Eq. (20) can be neglected. Whether the coefficient b is small or not depends on the relationship between the rates γ_{21} and γ_3. If $\gamma_{21}\simeq\gamma_3$ then $b\ll 1$, and the corresponding term in Eq. (20) is also negligible. In such a case, Eq. (20) is equivalent to the equation found within the two-level model. Thus, a fast exciton-exciton annihilation compensates the negative effect of the one-to-two exciton transition, however, it does not give any advantage over the two-level model in the limit we are discussing: $\gamma_{21}\sim\gamma_{30}\sim\gamma_{31}$. It is not surprising because if the relationship $\gamma_{21}\sim\gamma_{30}\sim\gamma_{31}$ is held, the population, taken out of the operating channel $1\leftrightarrow 0$, will be returned back despite a fast annihilation process.

In the limit of $\gamma_3\ll\gamma_{21}$ (a slow depopulation of the high-lying molecular level), one may in principle arrive at values of b of the order of magnitude of unity and even larger. If so, the b term has to be kept in Eq. (20). Figure 3 illustrates the b effect. Plot (a) of this figure shows an example of the y vs x dependence obtained by solving Eq. (20) at $a=6$ (below the two-level-model threshold, $a_c=8$) and choosing $c=d=0$ and $b=1$. As is seen, within some domain of changing x, Eq. (20) has three-valued real solutions implying a bistable behavior. Plot (b) show the b dependence of the threshold value of a. Again, within the region of pairs (a,b) above the curve the system is bistable, while below the curve it is stable. It is remarkable that a_c may be dropped considerably due to the combining action of a fast exciton-exciton annihilation and a slow depopulation of the high-lying molecular level. The physical meaning of such a behavior is rather simple and consists of transferring a large amount of population from the ground state to the slow relaxing state. Then, the system can be much easier made transparent.

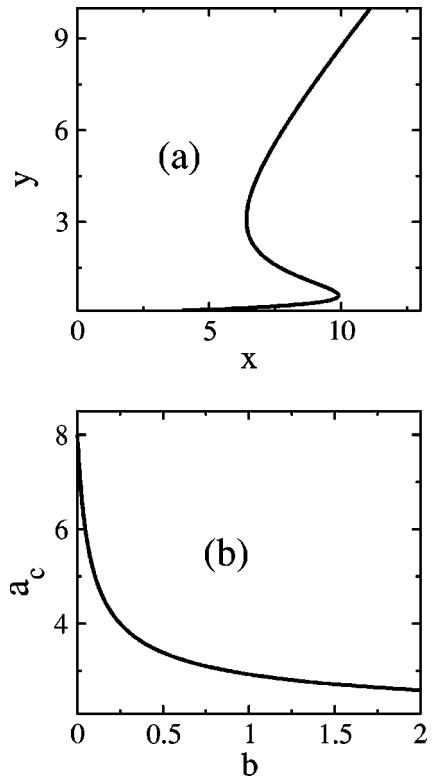

FIG. 3. Effect of the exciton-exciton annihilation on feasibility of the bistable behavior in the film optical response. (a) A sample of the numerical solution to Eq. (20) obtained at $a=6$ and setting $b=\gamma_{21}\Gamma_{10}/2\gamma_3 w=1$. The other parameters are $c=d=0$. (b) b dependence of the threshold value (a_c) of the driving parameter $a=\mu_{10}^2\gamma_R/\Gamma_{10}$ at $c=d=0$.

The lower limit for the critical value a_c as a function of b can be found analytically. At large, compared to unity values of b, Eq. (20) is simplified as follows:

$$y\left[1+\frac{a}{1+by^2}\right]^2=x. \tag{21}$$

The critical value of a is found from equalizing the derivative dx/dy to zero. In doing so, we obtain $a_c=16/9$.

C. Effect of the chain size distribution

The chain size fluctuations (a nonzero inhomogeneous width g) are expected to tend towards worsening the conditions for bistable behavior to occur, similar to what occurs within the two-level model [23]. We present here the results of numerical solutions of Eq. (13) dependent on the inhomogeneous width g under the condition of the combining action of a fast exciton-exciton annihilation and a slow depopulation of the high-lying level 4. When making calculations, we set $b=1$ and $c=d=e=0$. The solid curve in Fig. 4 shows the g dependence of the critical value of the driving parameter a within the generalized model. The system response behaves in a bistable and stable fashion within the regions above and below the curve, respectively. For comparison, we

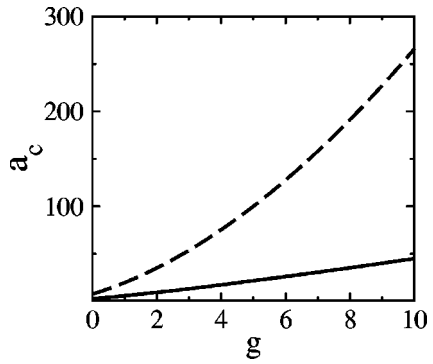

FIG. 4. Effect of the inhomogeneous broadening on feasibility of the bistable behavior in the film optical response. The curves were obtained by the numerical solution of Eq. (13) and represent the inhomogeneous width ($g=G/\Gamma_{10}$) dependence of the critical value (a_c) of the driving parameter $a=\mu_{10}^2\gamma_R/\Gamma$. The solid line—the three-level model at $b=1, c=d=e=0$; the dashed line—the two-level model ($b=c=d=e=0$).

also depicted in Fig. 4 the similar dependence (the dashed curve) obtained within the two-level model ($b=c=d=e=0$).

Observing the results presented in Fig. 4, we see first of all that the minimal value of a_c (at $g=0$) drops off from eight (the critical value of a in the two-level model) to approximately three for this particular magnitude of $b=1$ used in the calculations. However, the main conclusion, which can be derived from the data depicted in Fig. 4, is that the effect of inhomogeneous broadening, being fairly strong within the two-level model (the dashed curve a_c vs g goes gradually up), is considerably suppressed within the generalized version of the theory: a_c rises much slower upon increasing the inhomogeneous width g as compared to the two-level model. In other words, the combining action of a fast exciton-exciton annihilation from the two-exciton states and a slow depopulation of the high-lying molecular level, populated due to the annihilation, works towards improving the conditions for the occurrence of bistable behavior in the film optical response.

IV. ESTIMATES OF THE PARAMETERS

First, we estimate the super-radiant damping constant $\gamma_R=(3/8\pi)\gamma n\lambda^2 L$ basing our considerations on the low-temperature experimental data for J-aggregates of polymethine dyes. For these species, typically $\gamma\approx 0.01\ \mathrm{ps}^{-1}$ and $\lambda\approx 0.500$ nm. Choosing $L=\lambda/2\pi$ (or $kL=1$) that guarantees the applicability of the mean-field approach for the description of the thin-film optical response (see, for instance, Ref. [55]), we arrive at the following estimate: $\gamma_R\approx 2\times 10^{-17} n\ \mathrm{cm^3 ps^{-1}}$. Recall that n is the number density of the linear chains (or of the localization segments). It is related to the number density of molecules n_0 as $n_0=nN^*$, where N^* is the mean size of the chain (or the localization segment). At low temperature the quantity N^* is of the order of several tens [3–5,39,40]. Using these data in the estimate obtained above we now get $\gamma_R\approx 10^{-18} n_0\ \mathrm{cm^3 ps^{-1}}$. The typical width of the J band (and the blueshift as well) is of

the order of several tens of cm^{-1} or approximately 1 ps^{-1} in frequency units. In particular, the *J*-band of pseudoisocyanine bromide at the temperature of liquid helium is of inhomogeneous nature and of 34 cm^{-1} in magnitude. Hence, according to the results shown in Fig. 4, the observation of optical bistability in such species requires the number density of molecules to be of the order or even larger than 10^{19} cm^{-3}. We note that it is a rather high value. In principle, it can be reduced by raising the film thickness *L*, however, in this case the mean-field approximation is no longer an adequate approach (see Ref. [24]).

For estimating the annihilation rate *w* we need the data for the parameters *V*, N^*, and Γ. As we have no information relative to the magnitude of interaction in the annihilation channel *V*, we assume it as being of the dipole-dipole nature and consider *V* of the same order of magnitude as the dipole-dipole interaction *U* responsible for the formation of the *J* band. The value $U \sim 1000$ cm^{-1} is usually reported for *J*-aggregates of polymethine dyes [3–5,9,39,40]. The size of a localization segment N^* varies within the interval 20–50 [3–5,9,39,40]. As an estimate for the relaxation constant Γ, the interaction *V* itself can be adopted [39,40]. From Eq. (5) we then find that the annihilation rate varies from approximately 100 fs^{-1} to 1 ps^{-1} indicating in fact the fast annihilation limit. It is worth noting that the low-temperature femtosecond-scale experiments performed in Refs. [39] and [40] identified, namely, such a behavior. To the best of our knowledge, the experimental data relative to the relaxation rate γ_3 of high-lying molecular states responsible for the annihilation process are unknown. One may believe that it turns out to be relatively slow ($\gamma_3 \ll \gamma_{21}$) to get the constant *b* in Eq. (13) of the order of unity. This would then allow one to drop the number concentration of molecules n_0 to a reasonable level at which optical bistability is indeed realizable.

V. SUMMARY AND CONCLUDING REMARKS

In this paper, we considered the four-level model for the bistable optical response of an ultrathin film consisting of oriented molecular aggregates, including the ground, one-exciton and two-exciton states as well as the high-lying molecular level through which the annihilation of two excitons occurs. From our analysis the following conclusions can be drawn:

(i) The one-to-two exciton transition may result in a stronger limitation to the occurrence of bistability as compared to the two-level model, involving only the ground-to-one-exciton transition, whenever the exciton-exciton annihilation is slow.

(ii) A fast exciton-exciton annihilation may tend towards improving the conditions for the occurrence of bistability as compared to the two-level model: the critical value of the parameter driving the bistable behavior of the system response can be dropped off considerably. Respectively, the switching intensity of the input signal also does so. This comes into role if the rate of depopulation of the high-lying level, through which annihilation occurs, is low. This finding is important from the viewpoint of the experimental verification of our theoretical predictions.

(iii) Inhomogeneous broadening of the exciton absorption band acts strongly towards worsening the conditions for the occurrence of bistability. Its effect, however, may be considerably suppressed due to a fast exciton-exciton annihilation from the two-exciton state.

Any source of reducing the inhomogeneous broadening seems to be highly desirable. From this point of view, thin films comprised of different types of oligomers, the sizes of which can be precisely controlled [62–65], represent very promising candidates to achieve this goal: at least one of the important sources of inhomogeneity (dispersion of sizes) may be dropped down. It is also to be noted that the authors of Ref. [66] reported the room-temperature formation of polariton states in ordered thin films built up of the cyanine dye 1,7-bis(dimethylamino)heptamethine, BDH^+. This fact unambiguously means that dye molecules are strongly coupled to each other by the electromagnetic field, the property being crucial for the mechanism of optical bistability we are dealing with [23]. Thus, these species can also be put into the list of promising, from the viewpoint of our findings, objects.

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