Optical bistable response of an open linear Frenkel chain: Exciton-exciton annihilation and boundary effects

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A numerical study of the optical bistable response of an open linear Frenkel chain of three-level molecules is carried out, making use of the one-molecule density-matrix approach. We analyze the joint effect of the presence of boundaries and of the exciton-exciton annihilation on the bistable behavior of a chain. The former is going to destroy such behavior due to the spatial inhomogeneity of the population growing with time. The latter resists a preferable creation of the population at a certain segment of the chain stabilizing the system and, thus, provides the conditions for bistability to be realized. [S1050-2947(98)03907-9]

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I. INTRODUCTION

During the 1990s, the interest of many scientific groups addressed studies of quasi-one-dimensional structures manifesting features quite different from those of bulk materials. In particular, *J* aggregates of polymethine dyes as well as conjugated polymers, which can be approximately modeled by a linear Frenkel chain, display extraordinary peculiarities of their photoresponse [1–4] (see also Refs. [5,6], and references therein), caused mainly by the collective (excitonic) character of the excitations. Recently, possibilities of observing a bistable behavior in the optical response of linear aggregates [7,8] and even of a dimer [7,9] were discussed. The bistability effect originates from a dynamical resonance frequency shift with the population of the system, and consists of a sudden switching of the population from a low level to a higher one with increasing pump intensity. The shift mentioned reflects, in fact, the fermionic character of the excitonic eigenstates [10–13] (see also Refs. [5,6]) and is manifested in spectroscopic data as a blue shift of the one-to-two exciton transitions with respect to the ground-state-to-one-exciton transitions [14,15].

The bistability predicted, unfortunately, can be destroyed for several reasons. In particular, as shown in Ref. [8], the inhomogeneity resulting from the presence of two boundaries in the chain acts in such a way that the bistable behavior disappears for chains of size less than an emission wavelength. The preliminary study showed [16] that even in the opposite limit the lower branch of the population becomes unstable with time, due to growing spatial inhomogeneity, and the system finally passes to the upper stable branch. In addition, the process of excitonic annihilation, which plays a role with increasing pump intensity [15,17–19], can also result in the impossibility of a bistable behavior of photoresponse to be realized. In Ref. [20], a study has been carried out concerning this influence. It has been found, making use of the mean-field approximation, that the bistability of a chain can exist at quite large magnitudes of the annihilation constant (comparable to the dipole-dipole intermolecular coupling) if the relaxation from a molecular level, which is responsible for the annihilation process, is slower than the rate at which the annihilation occurs.

The main goal of the present contribution is to study the mutual influence of both the inhomogeneity and the excitonic annihilation on the manifestation of a bistable behavior in a Frenkel chain. An idea we are going to prove is whether the excitonic annihilation, which does not destroy bistability within a certain range of its rate and acts as a factor of homogenization, can suppress the effect of boundaries. To face the problem, we apply the one-molecule density-matrix formalism as was done in Refs. [8,20]. The resulting system of coupled *nonlinear* equations for the one-molecular density matrix includes exactly the intermolecular retarded interaction whose real part is responsible for the dynamical shift of resonance frequency with an increasing level of excitation, which, in turn, results in the aggregate bistability [7,8]. The imaginary part of the retarded interaction describes the collective radiative damping. Such an approach was previously used to treat Dicke superradiance [21–23], and to show a bistable response of a collection of two-level atoms disposed in a volume with linear dimensions smaller than an emission wavelength [24].

The paper is organized as follows. Section II presents the formalism of the one-molecule density-matrix approach. In Sec. III, we discuss in detail the influence of the excitonic annihilation on the bistability of a chain, making use of the mean-field approximation. Section IV deals with numerical simulations, based on the exact set of coupled nonlinear equations for the one-molecule density matrices. The results of these simulations maintain our idea mentioned above that the excitonic annihilation acts as a stabilizing factor, providing conditions for the bistability to be observed. In Sec. V, we discuss the parameters of some real systems with respect to a realizability of the effect predicted. Finally, Sec. VI summarizes the paper.

II. MODEL AND FORMALISM

As previously, we model a Frenkel chain as an ensemble of *N* identical three-level molecules equally spaced along a

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straight line [8,20]. The states are assumed to have alternate inversion symmetry, so that all transitions are dipole allowed. A possible absorption from the excited state 2 is not accounted for here, due to off-resonance conditions chosen for the optical transition $2\rightarrow 3$. Contrary to that, the dipole-dipole interaction of two excited molecules (responsible for the annihilation process) will be considered rather efficient to populate the higher (third) molecular state, by means of summing the energy of two excitations. Then, the system of differential equations for the amplitude of the off-diagonal matrix element R_k and populations of the levels of the kth molecule in the chain $\rho_{ii}^{(k)}$ $(i=1,2,3)$, accounting for both the intermolecular interaction and the annihilation of excitations, reads [20]

$$\dot{\rho}_{11}^{(k)}=\frac{1}{4}\sum_{l(\neq k)=1}^{N}(\gamma_{lk}+i\Delta_{lk})R_lR_k^*-i\frac{\Omega}{4}R_k^*+\text{c.c.}+\alpha\rho_{22}^{(k)}[\rho_{22}^{(k-1)}+\rho_{22}^{(k+1)}]+\Gamma_1\rho_{33}^{(k)}, \tag{1a}$$

$$\dot{\rho}_{22}^{(k)}=-\frac{1}{4}\sum_{l(\neq k)=1}^{N}(\gamma_{lk}+i\Delta_{lk})R_lR_k^*+i\frac{\Omega}{4}R_k^*+\text{c.c.}-2\alpha\rho_{22}^{(k)}[\rho_{22}^{(k-1)}+\rho_{22}^{(k+1)}]+\Gamma_2\rho_{33}^{(k)}, \tag{1b}$$

$$\dot{\rho}_{33}^{(k)}=-\Gamma\rho_{33}^{(k)}+\alpha\rho_{22}^{(k)}[\rho_{22}^{(k-1)}+\rho_{22}^{(k+1)}], \tag{1c}$$

$$\dot{R}_k=-i\Delta R_k+\sum_{l(\neq k)=1}^{N}(\gamma_{lk}+i\Delta_{lk})R_l[\rho_{22}^{(k)}-\rho_{11}^{(k)}]-i\Omega[\rho_{22}^{(k)}-\rho_{11}^{(k)}]-\alpha R_k[\rho_{22}^{(k-1)}+\rho_{22}^{(k+1)}], \tag{1d}$$

where $\Delta=\omega_{21}-\omega_0$ is the resonance detuning of the external field frequency ω_0, and the molecular transition frequency ω_{21}; $\Omega=\mu\varepsilon^{\text{ext}}/\hbar$ is the Rabi frequency of the external field. The latter was assumed to be a plane wave traveling perpendicularly to the chain axis and polarized parallel to the dipole vector of molecules in the chain, $\boldsymbol{\mu}$. Matrices Δ_{lk} and γ_{lk} are given by formulas [8]

$$\Delta_{lk}=\frac{\mu^2}{\hbar a^3}\left\{\left[\frac{\cos(k_0a|l-k|)}{|l-k|^3}+k_0a\frac{\sin(k_0a|l-k|)}{|l-k|^2}\right]\times(1-3\cos^2\theta)-(k_0a)^2\frac{\cos(k_0a|l-k|)}{|l-k|}\sin^2\theta\right\}, \tag{2a}$$

$$\gamma_{lk}=\frac{\mu^2}{\hbar a^3}\left\{\left[k_0a\frac{\cos(k_0a|l-k|)}{|l-k|^2}-\frac{\sin(k_0a|l-k|)}{|l-k|^3}\right]\times(1-3\cos^2\theta)+(k_0a)^2\frac{\sin(k_0a|l-k|)}{|l-k|}\sin^2\theta\right\}. \tag{2b}$$

Here a is the distance between adjacent molecules and $k_0=\omega_0/c$, and θ is the angle between the dipole vector $\boldsymbol{\mu}$ and the chain axis. The matrix $\Delta_{lk}-i\gamma_{lk}$ may be identified with the matrix of the intermolecular retarded interaction. Its imaginary part γ_{lk} results from the molecular interaction through the transverse field (see, for instance, Ref. [22]). In the problem under consideration, it describes the collective radiative damping. The real part Δ_{lk} gives rise to phase modulation in the optical response of the aggregate, and is responsible for the bistable behavior [8]. In the particular case of a chain with a length small as compared with the emission wavelength ($L=Na\ll\lambda$), γ_{lk} equals half the radiative constant of an isolated molecule $\gamma_0/2$, whereas Δ_{lk} is just the near-zone dipole-dipole interaction $\mu^2(1-3\cos^2\theta)/a^3$ [22].

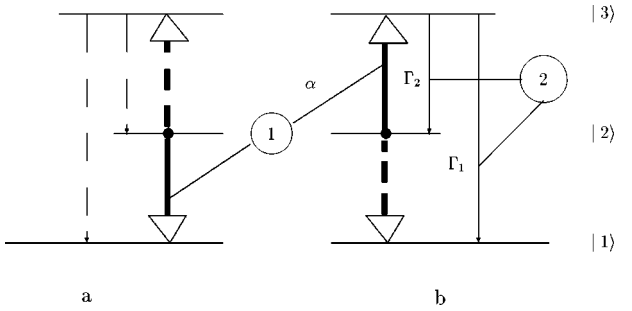

FIG. 1. Scheme of the exciton-exciton annihilation process through a third molecular level. In the first step, the molecule *a* goes to the ground state while the molecule *b* passes to the third level. The second step is the radiationless relaxation of the third level to the ground and excited states of the transition of interest. Dashed arrows indicate the cross-processes.

The parameter α phenomenologically describes the contribution of the exciton-exciton annihilation, in which one excitation passes to the ground state while another one goes up to a third molecular level, due to the dipole-dipole interaction. We assume that two excitations disappear when they are nearest neighbors. The annihilation rate is proportional to the sum of nearest-neighbor population, $\rho_{22}^{(k-1)}+\rho_{22}^{(k+1)}$. Corresponding terms in the equations driving $\rho_{22}^{(k)}$ and R_k differ from one another by the factor of 2. Through the third level, the excitation relaxes to the ground and excited states, with the rates Γ_1 and Γ_2, respectively ($\Gamma=\Gamma_1+\Gamma_2$). So we include into our scheme both the ''Auger'' kind [17,19,15] (described by Γ_2) and the fusion model [18] (associated with Γ_1) of excitonic annihilation (Fig. 1). The magnitudes of Γ vary in several papers from 0.1 ps^{-1} [18] to 5 ps^{-1} [19]. We do not include in our scheme any T_1 and T_2 processes, assuming the exciton-exciton annihilation to be dominant under the conditions we are going to consider.

III. ANALYTICAL RESULTS: MEAN-FIELD APPROACH

In order to gain insight into how the exciton-exciton annihilation influences the bistable behavior of a chain, we restrict our study in this section to the simplest model in which all functions in Eqs. (1) are assumed to be independent of the site number. This gives us the great advantage of the analytical treatment of the problem. The system of equations (1) then transforms into

$$\dot{\rho}_{11}=\frac{\gamma_R}{2}|R|^2+i\frac{\Omega}{4}(R-R^\star)+2\alpha\rho_{22}^2+\Gamma_1\rho_{33}, \tag{3a}$$

$$\dot{\rho}_{22}=-\frac{\gamma_R}{2}|R|^2-i\frac{\Omega}{4}(R-R^\star)-4\alpha\rho_{22}^2+\Gamma_2\rho_{33}, \tag{3b}$$

$$\dot{\rho}_{33}=-\Gamma\rho_{33}+2\alpha\rho_{22}^2, \tag{3c}$$

$$\dot{R}=\{-i[\Delta-\Delta_L(\rho_{22}-\rho_{11})]+\gamma_R(\rho_{22}-\rho_{11})\}R - i\Omega(\rho_{22}-\rho_{11})-2\alpha R\rho_{22}, \tag{3d}$$

where $\Delta_L=2\Sigma_{l-k=1}^{N/2}\Delta_{lk}$ and $\gamma_R=2\Sigma_{l-k=1}^{N/2}\gamma_{lk}$. As in Refs. [8,20], we will assume both that Δ_L is negative (the case of J aggregates, see Refs. [5,6]) and that $|\Delta_L|\gg\gamma_R$.

In order to display clearly the peculiarities of the bistability effect in the presence of excitonic annihilation, one should fulfill a stationary analysis of Eq. (3), substituting the time derivatives in Eqs. (3) by zero. Then an algebraic equation of the fifth order appears, for the population of the second level

$$4\rho_{22}\left(1-\frac{\Gamma_2}{2\Gamma}\right)\left\{\left[1-\rho_{33}-2\left(1-\frac{\alpha}{\gamma_R}\right)\rho_{22}\right]^2+\left[\frac{\Delta-|\Delta_L|(1-\rho_{33})}{\gamma_R}+\frac{2|\Delta_L|}{\gamma_R}\rho_{22}\right]^2\right\}=[1-\rho_{33}-2\rho_{22}]\left(\frac{\Omega}{\gamma_R}\right)^2. \tag{4}$$

Here $\rho_{33}=(2\alpha/\Gamma)\rho_{22}^2$.

First, let us recall the physical origin of the bistability effect in the absence of the exciton-exciton annihilation. Making use in Eq. (4) of the substitution $\Gamma_2\to 0$, $\alpha\to 0$, $1-\rho_{33}\to 1$, we pass to the equation of Ref. [8],

$$4\rho_{22}\left[1+\left(\frac{\Delta'}{\gamma_R}+\frac{2|\Delta_L|}{\gamma_R}\rho_{22}\right)^2\right]=\left(\frac{\Omega}{\gamma_R}\right)^2, \tag{5}$$

where $\Delta'=\Delta-|\Delta_L|$ is the resonance detuning renormalized by the dipole-dipole interaction. Equation (5) has three real roots (and, consequently, demonstrates a bistable behavior) if $\Delta'<-\sqrt{3}\gamma_R$[8]. This means that, in order to observe the effect, one should excite the system slightly above the renormalized resonance $\omega_{21}-|\Delta_L|$. As the current detuning of resonance, according to Eq. (3d), depends on the population difference $\rho_{22}-\rho_{11}$ then the system, when excited by an external field, tends to improve the resonance conditions. The radiative damping, represented by γ_R, competes with this tendency, stabilizing the population at some level. However, at a certain threshold value of the incident field amplitude, the radiative damping can no longer resist the pumping, and the system experiences an abrupt jump to another level of population.

From recent experimental data related to J aggregates [19,15], it follows that usually an inequality $\alpha>\Gamma>\gamma_R$ is satisfied. Nevertheless, to obtain a whole picture of how the excitonic annihilation affects the bistable behavior of a chain, we, first, consider a case of a very high relaxation rate from the third level Γ, so that one can neglect its population. Then, omitting everywhere in Eq. (4) the term ρ_{33}, we obtain

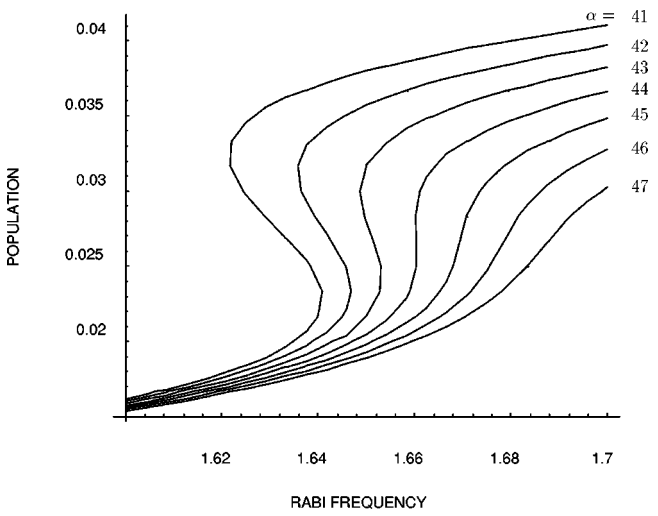

FIG. 2. Results of numerical calculations of Eq. (6) demonstrating the disappearance of the three-valued solution with the annihilation constant α. Bistability exists at $\alpha<\alpha_c=44$ in full correspondence with Eq. (8). The other parameters are $\Gamma/\Gamma_2=2$ ($\Gamma_1,\Gamma_2\gg 1$), $\Delta'=-10$, and $|\Delta_L|=100$. All numbers are in units of γ_R.

$$4\rho_{22}\left(1-\frac{\Gamma_2}{2\Gamma}\right)\left[\left(1+\frac{2\alpha}{\gamma_R}\rho_{22}\right)^2+\left(\frac{\Delta'}{\gamma_R}+\frac{2|\Delta_L|}{\gamma_R}\rho_{22}\right)^2\right]=\left(\frac{\Omega}{\gamma_R}\right)^2. \tag{6}$$

Hereafter, we assume that $\Delta'<-\sqrt{3}\gamma_R$; i.e., as regards the detuning of resonance, we are above the threshold of bistability established in the absence of excitonic annihilation.

In the case of an algebraic equation of third order (6), the conditions of bistability can be derived from examining zeros of the derivative $d\Omega^2/d\rho_{22}$. The appearance of two zeros of $d\Omega^2/d\rho_{22}$ is equivalent to Eq. (6) having three real roots. This takes place when

$$4\left(\frac{\Delta'}{\gamma_R}+\frac{\alpha}{|\Delta_L|}\right)^2\geqslant 3\left[1+\left(\frac{\alpha}{\Delta_L}\right)^2\right]\left[1+\left(\frac{\Delta'}{\gamma_R}\right)^2\right], \tag{7}$$

where the equality means the threshold for bistability to be present. From this, one can find the critical value of the annihilation constant α:

$$\frac{\alpha_c}{|\Delta_L|}=\frac{4(\Delta'/\gamma_R)+\sqrt{3}[(\Delta'/\gamma_R)^2+1]}{3(\Delta'/\gamma_R)^2-1}. \tag{8}$$

If $\alpha>\alpha_c$, inequality (7) is never satisfied and consequently, ρ_{22} monotonically depends on Ω. In the opposite case, $\alpha<\alpha_c$, a three-valued real solution of Eq. (6) appears, which results in a bistable behavior.

Note that α_c, as a function of Δ', has an upper limit at $|\Delta'|/\gamma_R\gg 1$. Taking large values of $|\Delta'|/\gamma_R$, from Eq. (8) one then obtains $\max\{\alpha_c\}=|\Delta_L|/\sqrt{3}$.

In Fig. 2, we have drawn a few examples of the numerical solution of Eq. (6), displaying the disappearence of the chain bistability with increasing α. Figure 3 presents the dependence of the critical annihilation constant α_c on the initial detuning of resonance Δ'. The bistability effect exists where $\alpha<\alpha_c$ (at a fixed Δ'): the shaded part in Fig. 3 shows this region.

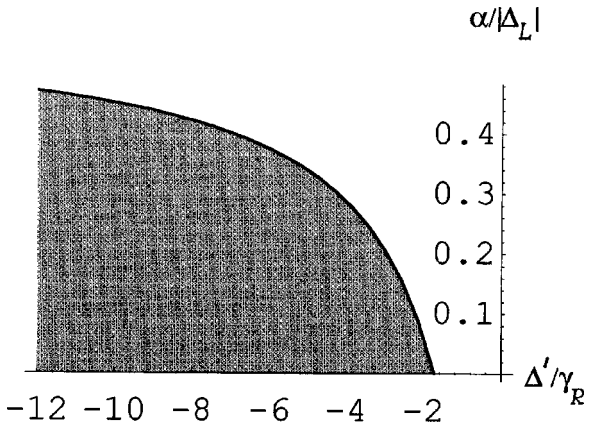

FIG. 3. Dependence of the critical value of the annihilation constant α_c on the initial resonance detuning Δ'. The shaded part corresponds to the existence of aggregate bistability [$\alpha<\alpha_c(\Delta')$].

Now let us discuss a realistic case of the relationship between the annihilation constant α and the relaxation rate Γ: $\Gamma \ll \alpha$. In order to demonstrate the effect of a finite magnitude of Γ upon the realizability of the bistable behavior, in Fig. 4 we plot a family of solutions of the original Eq. (4) obtained at a fixed magnitude of α but varying Γ. From these calculations, it follows that, at $\Gamma \ll \alpha$, the critical value of the annihilation constant increases, providing more favorable conditions for displaying bistability.

Such behavior can be easily explained by the third level population that just takes place at finite magnitudes of Γ. Indeed, comparing Eq. (6) with Eq. (4), one can see that the initial detuning of resonance, $\Delta'=\Delta-|\Delta_L|$ in Eq. (6), is renormalized due to population of the third level, turning to $\Delta-|\Delta_L|(1-\rho_{33})=\Delta'+|\Delta_L|\rho_{33}$ in Eq. (4). This means a better resonance between the pump and the system frequencies and, as a result, more advantageous conditions for bistability to be realized. Note that, the lower the relaxation rate, the higher the critical value of the annihilation constant needed to destroy the effect at hand.

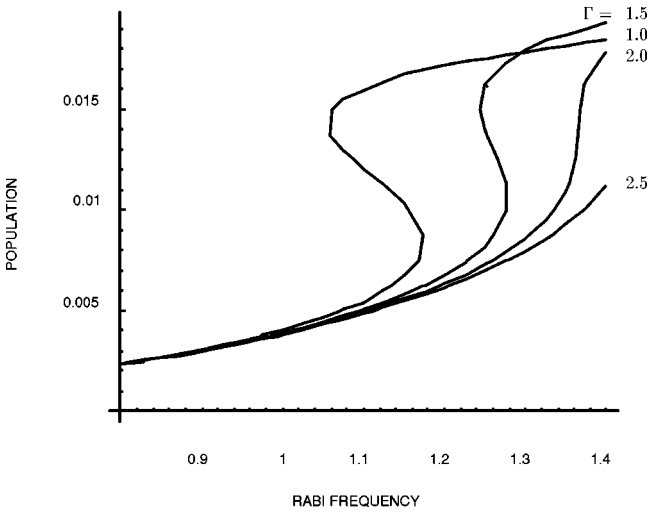

FIG. 4. Results of numerical calculations of Eq. (4) for the population ρ_{22} at a fixed value of the annihilation constant $\alpha=120$ showing the disappearance of the three-valued solution with a growing relaxation rate of the third level Γ. As can be seen, at a relatively slow relaxation rate of the third level (in the sense that $\Gamma \ll \alpha$), the critical value of the annihilation constant α_c increases, providing more suitable conditions for bistability to be present. For the parameters used ($\Delta'=-10$, $|\Delta_L|=100$, and $\Gamma/\Gamma_2=2$), Γ_c equals 2. All numbers are in units of γ_R.

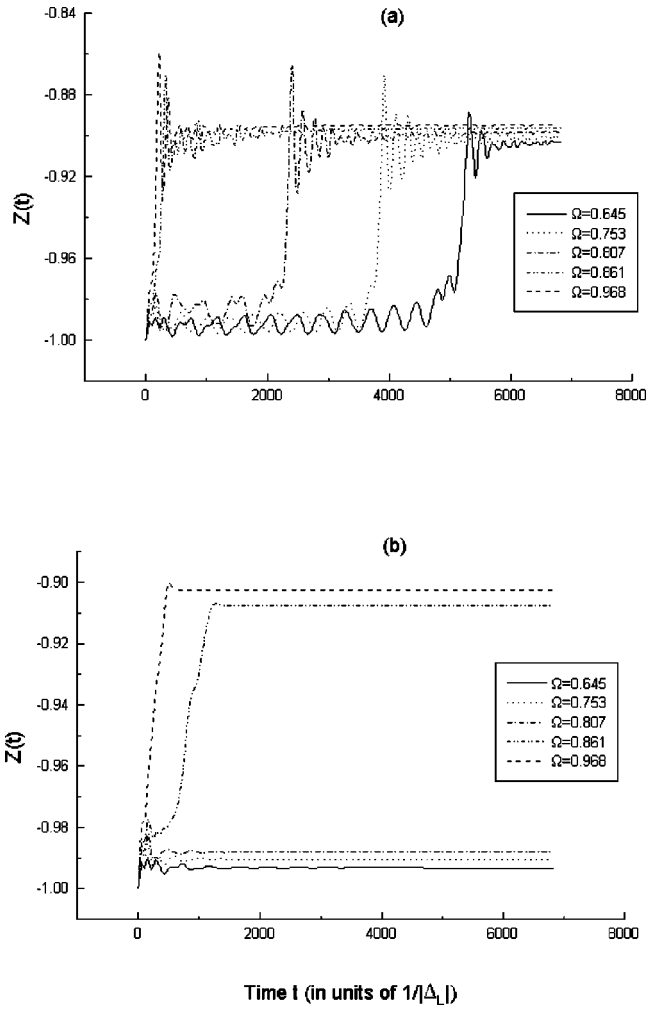

FIG. 5. Kinetics of the average population difference $Z(t)$ for a linear chain of 50 molecules with $k_0a=0.1$ calculated with the exact equations (1): annihilation constants $\alpha=0$ (a) and $\alpha=25$ (b). ($\Delta'=-10$ and $|\Delta_L|=97$.) Insets show the values of the Rabi frequency Ω. All numbers are in units of γ_R.

IV. NUMERICAL SOLUTION OF EXACT EQUATIONS

In reality, the presence of two boundaries in the chain makes the conditions for molecules inside the chain different from those close to the boundaries, in the sense that both the local energy shift $\overline{\Delta}_k=\Sigma_{l\neq k}\Delta_{kl}$ and the local constant of collective radiative damping $\overline{\gamma}_k=\Sigma_{l\neq k}\gamma_{kl}$ now depend on the molecule location k. This naturally leads to a violation of the spatial homogeneity of the one-molecule density-matrix elements, in spite of the fact that it was present at the initial instant of time. As shown in Ref. [8], the spatial inhomogeneity can influence the manifestation of bistable behavior of the linear-chain optical response in such a way that this effect disappears for aggregates of length less than an emission wavelength.

In order to study the joint effects of spatial inhomogeneity

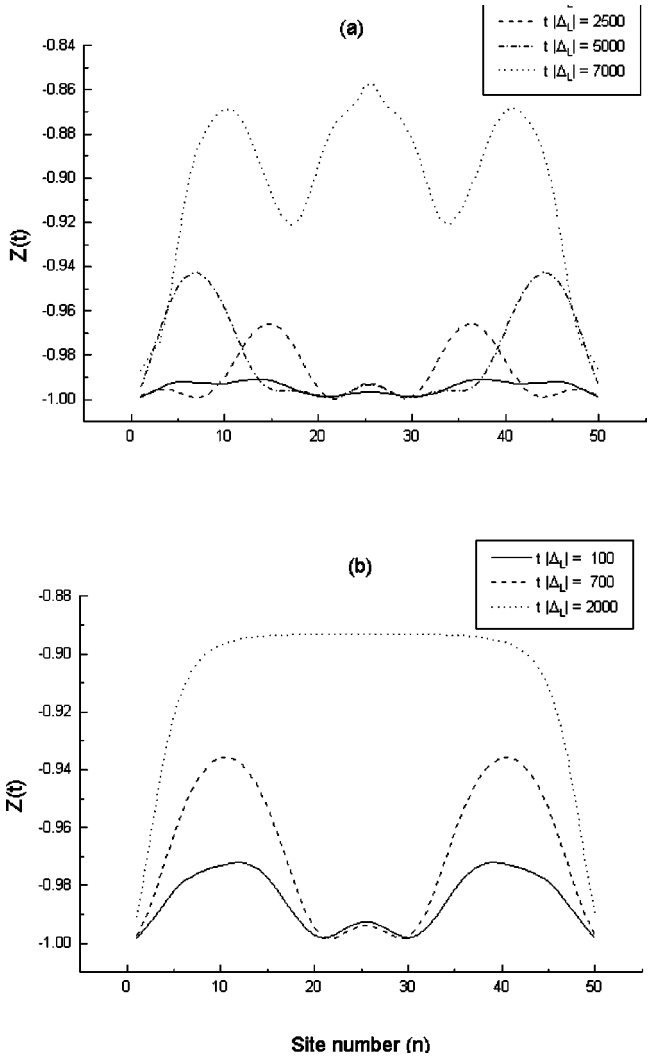

FIG. 6. Spatial distribution of the population difference at several instants in time evolution (shown in the insets). The Rabi frequency is equal to 0.645 (a) and 0.861 (b). The other parameters are the same as in Fig. 5.

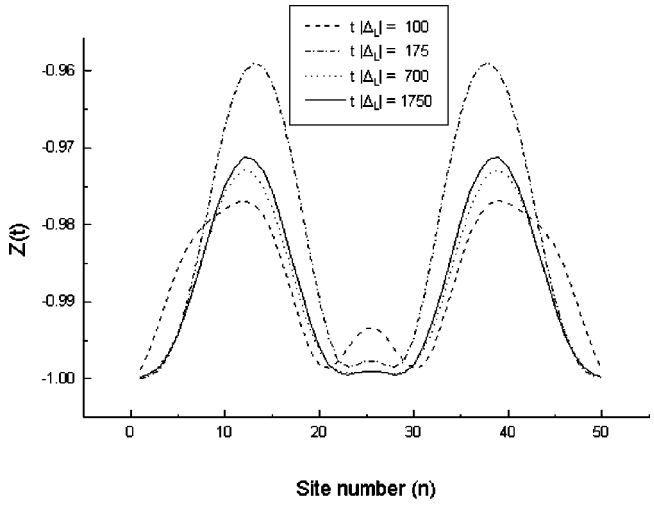

FIG. 7. Spatial distribution of the population difference, corresponding to the lower branch of the possible states of the system, at several instants in time evolution (shown in the insets). The Rabi frequency $\Omega=0.807$, and the annihilation constant $\alpha=25$. The other parameters are the same as in Fig. 5.

and excitonic annihilation upon the bistable response of an open Frenkel chain, we have carried out numerical calculations of the exact system of equations (1). In our numerical experiments, we calculated the time dependence of the average population difference $Z(t)=N^{-1}\Sigma_k[\rho_{22}(t)-\rho_{11}(t)]$, at fixed values of both the resonance detuning (Δ') and the annihilation constant (α), but varying the amplitude of the external field (Ω). In all calculations, a sudden switching on of the field was used. It is also seen in Fig. 6(a) that the inhomogeneity is not created instantaneously. Two sets of calculations have been done, for chains of $N=50$ and 100 molecules at a fixed magnitude of $k_0a=0.1$.

For real systems, magnitudes of the parameter k_0a usually have an order of 0.01. Our choice $k_0a=0.1$ is simply to reduce the computation time to a reasonable limit. The case of matter is that, first, two noticeably different time scales exist in the problem under study, given by the matrices Δ_{kl} and γ_{kl}. The former describes the phase modulation of the electric polarization as well as the redistribution of the population along the chain, while the latter is responsible for the relaxation of the system to a stationary state, which we are interested in. As $\Delta_{kl}\gg\gamma_{kl}$ and, moreover, as this inequality becomes stronger with decreasing k_0a, one should wait a longer and longer time for a stationary state, carefully computing processes occurring within the shorter time scale. Second, as was shown previously [8], a linear chain of length less than an emission wavelength did not manifest any bistable behavior. From this it follows that the parameter $k_0aN=k_0L$, where L is the chain length, should be chosen to be of the order of 2π or more. At a real value of k_0a (~ 0.01), this pushes values of the molecule number N up to 1000. Increasing N also leads to a drastic growth of the computation time, so that finally we have to restrict the number of molecules N to a value of the order of 100. On the other hand, it should be pointed out that the crucial quantities of the problem Δ_{kl} and γ_{kl} scale with $k_0a|k-l|$. Thus the magnitude of k_0a is of no importance at a fixed value of the chain length L: both Δ_{kl} and γ_{kl} look like universal curves in term of the scaling coordinate $\xi=k_0a|k-l|$. The same peculiarity can be attributed to the solutions of Eq. (1). Actually, the magnitude of k_0a affects only the relationship between Δ_{kl} and γ_{kl}, as mentioned above, lowering as a result the critical value of the external field amplitude necessary for a sudden switching of the population from the lower branch to the upper one (see Ref. [8]). In this sense, conclusions obtained for $k_0a=0.1$ can be extended to the more realistic case of $k_0a=0.01$.

The results of numerical simulations are presented in Figs. 5–7 and 11 for $N=50$, and in Figs. 8 and 9 for $N=100$. Observing Figs. 5(a) and 8(a), we come to the first conclusion that the pure bistability (in the absence of excitonic annihilation, $\alpha=0$), in fact, does not exist, at least for the parameters used. The system cannot be stabilized on the lower branch of the population and finally experiences a jump to the upper branch, which is really stable. Such a behavior was not recognized in Ref. [8], since the calculation time in Ref. [8] was within the limits of stability of the lower branch.

As in the frame of the mean-field approach ($\overline{\Delta_k}=\Delta_L$ and

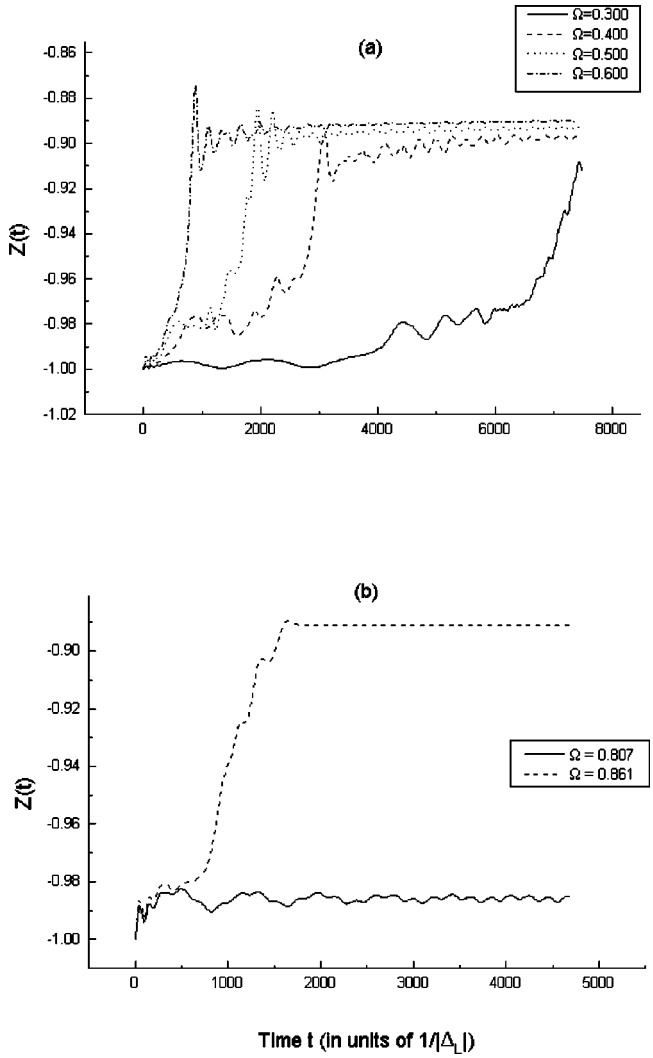

FIG. 8. Same as in Fig. 5, only for a linear chain of 100 molecules; $|\Delta_L|=93$, and the annihilation constants $\alpha=0$ (a) and 15 (b).

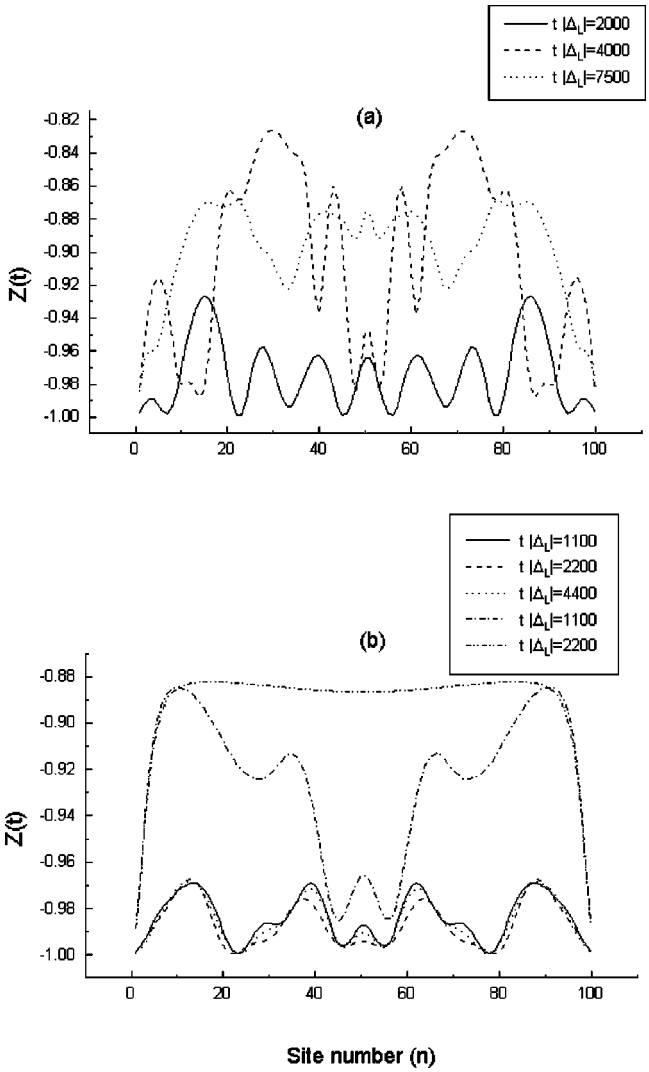

FIG. 9. Same as in Fig. 6, only for a linear chain of 100 molecules. (a) $\Omega=0.400$. (b) $\Omega=0.807$ for the three lower curves, and $\Omega=0.861$ for the two upper curves. The annihilation constant α and all other parameters are the same as in Fig. 8.

$\overline{\gamma_k}=\gamma_R$), the lower branch is stable (see Ref. [8]); an obvious reason for the instability found is the spatial inhomogeneity of the population of the molecules in the chain. As follows from Figs. 6(a) and 9(a), two symmetrically placed regions with a higher level of population arise, close to the boundaries rather than to the center of the chain, which are responsible for the instability of the lower branch found. Evolving in time toward an increasing population, they finally provoke the transition of the system to the stable upper branch.

We relate such preferable creation of population (rather close to the boundaries) to the profile of the local energy-level shift $\overline{\Delta_k}$ depicted in Fig. 10(a). As can be seen from this figure, $\overline{\Delta_k}$ deviates from an analogous value for the mean-field approach, $\Delta_L=\overline{\Delta}_{k=N/2}$, within the regions close to the chain ends. This deviation changes the local detunings of resonance $\Delta_k'=\Delta-\overline{\Delta_k}$ as compared to those at the center of the chain ($\Delta'=\Delta-\Delta_L$). Definitely, two symmetrically located regions can be found with $|\Delta_k'|\leqslant\overline{\gamma_k}$ [$\overline{\gamma_k}$ is depicted in Fig. 10(b)]. The latter means that monomers belonging to such a region are in resonance with the external field, subsequently providing their efficient excitation, which in turn, gives rise to the instability mentioned. It is quite probable that such an instability is present even for a very long chain, except that the time of quasistability may be large as compared to that for a shorter chain.

Note that for a short chain of size less than the emission wavelength [$N=10$ in Fig. 10(a)], $\overline{\Delta_k}$ changes quite steeply with k, resulting subsequently in a high inhomogeneity of the local detuning of resonance Δ_k'. We consider this as a reason for the total absence of a bistable behavior for a short chain [8].

It is remarkable that the bistable behavior of a chain can be revealed provided the presence of the exciton-exciton annihilation. In Figs. 5(b) and 8(b), we present the results of numerical simulations at the same set of parametes as in Figs. 5(a) and 8(a), except for a nonzero value of the annihilation constant ($\alpha=25$ and 15 for chains of 50 and 100 molecules, respectively). As is clearly seen, the excitonic annihilation is able to stabilize the system at the lower branch of population. In Figs. 6(b), 7, and 9(b), we plot the

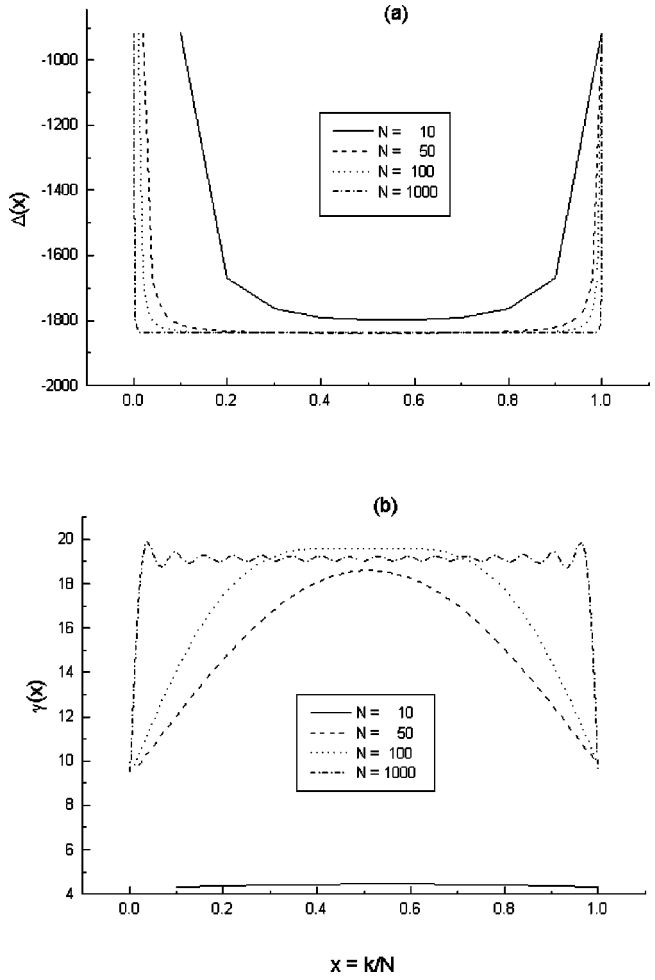

FIG. 10. Dependence of the local energy-level shift $\Delta(x)\equiv\overline{\Delta_k}$ (a) and of the local constant of the collective radiative relaxation $\gamma(x)\equiv\overline{\gamma_k}$, (b) on the position of the molecule in the chain k scaled as $x=k/N$. Insets show the number of molecules in the chain N.

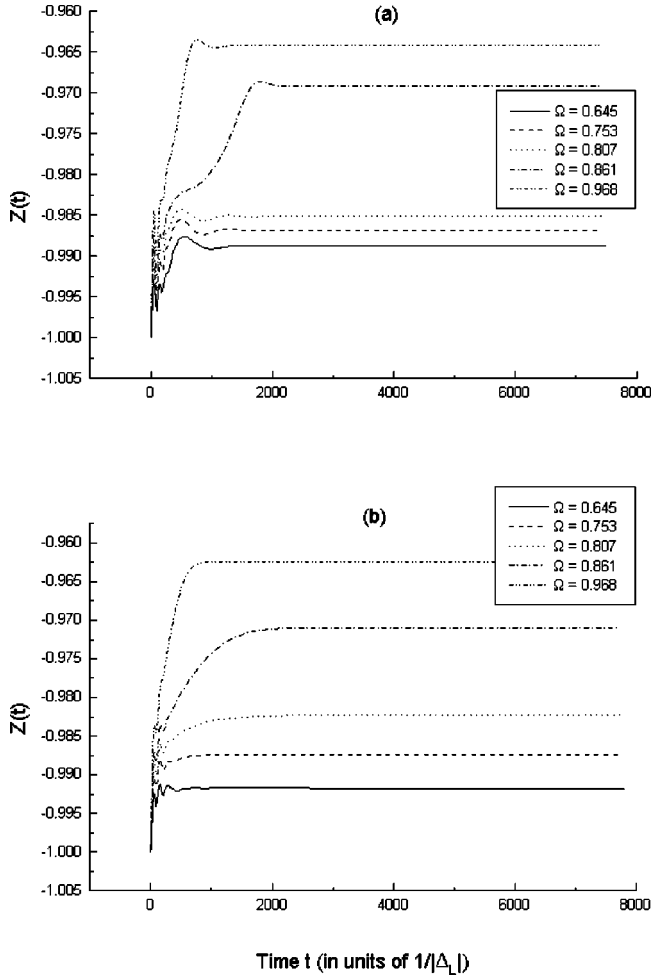

FIG. 11. Kinetics of the average population difference $Z(t)$ for a linear chain of 50 molecules with $k_0a=0.1$ calculated with the exact equations (1). Annihilation constants $\alpha=50$ (a) and $\alpha=100$ (b). Insets show the values of the Rabi Frequency Ω. All numbers are in units of γ_R.

distributions of the molecule population over the chain, taking time as parameter. It follows from these figures that the spatial ingomogeneity of the population at the lower branch does not disappear; nevertheless, its profile is stabilized in time by the annihilation. Analogous distributions of population related to the upper branch behave more smoothly [see Figs. 6(b) and 9(b)]. Nevertheless, with increasing the annihilation rate the bistable behavior disappears again (Fig. 11), in approximate conformity with the mean-field approach.

As in the absence of the excitonic annihilation the bistable behavior fails, it is clear that, in addition to the upper threshold value of the annihilation constant α_c mentioned in Sec. III, a lower one must also exist. In order to find this threshold, a series of calculations was carried out varying the constant α. From these simulations, we obtained that, with the other parameters $(\Delta_L,\Delta',\Gamma_1,\Gamma_2)$ fixed as above, these values are $\alpha=2.5$ and 10 (in units of γ_R) for $N=50$ and 100, respectively.

Summarizing, one can see that the mean-field approach discussed in Sec. III seems to be a very approximate one for describing the optical response of an open Frenkel chain. The spatial inhomogeneity plays a crucial role in forming the behavior of a chain undergoing an on-resonance external field and, what is important, independently of its size.

V. DISCUSSION OF THE EXPERIMENTAL DATA

In this section, we would like to discuss parameters of some real systems, which can be modeled as an open linear chain. In this sense, J aggregates of pseudoisocyanine present one of the most studied objects of such a kind. The value of α can be extracted from the experimental data of both the annihilation constant $\gamma_a\approx 3\times 10^{-3}$ cm^3/s and a typical size of the coherence length of an exciton (about six at room temperatures) [17,18,15]. This gives a value of α of about 10 ps^{-1}. On the other hand, $|\Delta_L|\approx 650$ cm^{-1} ≈ 20 ps^{-1} is accepted as a typical value for J aggregates of pseudoisocyanine [5,6]. Thus, for such kinds of aggregates, we have the magnitude of the annihilation constant less than the maximal threshold value $\max\{\alpha_c\}=|\Delta_L|/\sqrt{3}$, i.e., the case of existence of a bistable behavior. Nevertheless, it is well known that notwithstanding the fact that J aggregates can incorporate thousands of molecules, only a subsystem of localization domains consisting of a part of these (the so-called coherently bound molecules) contribute to the optical response. This is due to localization of the excitonic states. From the experimental data [1,2,15,19], it follows that this number, even at low temperatures, does not exceed 100 mol-

ecules, which means that a typical size of a coherent domain is less than the emission wavelength. Thus these objects can be considered as promising candidates for a realization of the bistability effect we are discussing, provided there is an increase of the size of a localization domain.

It should be noted in this connection that one may suggest another mechanism of bistable behavior of an ensemble of open Frenkel chains (shorter than the emission wavelength) based on the quasifermionic character of the 1D exciton states (see the discussion in Sec. I). Indeed, as the transition from one-to-two exciton bands is blueshifted with respect to that from the ground state to the one-exciton band by some energy gap (ΔE_{21}), they can then be considered as decoupled from one another, if the Rabi frequency of the external field fulfills the condition $\Omega < \Delta E_{21}$. This allows one to model an isolated linear Frenkel chain as a two-level molecule with a renormalized radiative constant $\gamma_R = \gamma_0 N$ describing the radiative relaxation from the one exciton band. Further, it is known [25,26] that an ensemble of two-level molecules elaborated in the form of a thin slab with a thickness L less than an emission wavelength can demonstrate a bistable behavior of both reflectivity and transmittivity resulting from the coupling of molecules via the emission field. This concept seems to be acceptable to an ensemble of J aggregates, taking into account the fact that they can be oriented by a vertical spin-coating method [27]. Another plan for obtaining homogeneously oriented species that look like J aggregates gives us thin films of thiophen oligomers [28,29], the lowest excitations in which are Frenkel excitons [30]. All this gives us hope that it is, in principle, possible to elaborate a thin slab consisting of homogeneously oriented aggregates. The model of such a type of bistability differs from that we considered in our paper. Therefore, from our study, we cannot assert anything as regards the realizability of this kind of bistability. A detailed description will be given in a forthcoming paper.

VI. SUMMARY

The one-molecular density-matrix approach is used to analyze the nonlinear optical response of an open linear Frenkel chain in the presence of exciton-exciton annihilation. The mean-field approximation predicts the possibility of obtaining a bistable behavior in the response, even in the case of large magnitudes of the annihilation constant comparable to the dipole-dipole interaction of monomers composing the chain.

A numerical study based on the exact set of equations for the one-molecule density matrix shows that, in the absence of the annihilation process, the bistable behavior predicted generally fails due to the spatial inhomogeneity of the density matrices of monomers. Growing in time, this inhomogeneity finally provokes the transition of the system from the lower branch of population (becoming thus unstable) to the upper stable branch. Thus one can say that bistable behavior can be observable only over a certain interval of time after the external field is switched on. Exciton-exciton annihilation, the rate of which rises with population, resists an increase of the population at a certain region of the chain, and stabilizes it, in such a way providing conditions for bistability to be revealed.

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