Mirrorless optical bistability of linear molecular aggregates

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The bistable response of linear molecular aggregates modeled as linear chains of two-level systems is shown. We carry out analytical and numerical calculations of the aggregate population by means of the system of coupled nonlinear equations for the density matrices of individual molecules. Our conclusion is that bistable behavior of the population results from the dependence of resonance frequency of the aggregate on the number of excited molecules.

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I. INTRODUCTION

During the last decade, nonlinear optical properties of the so-called nanostructures—for instance, linear molecular aggregates (see [1], and references therein)—have been widely observed. Among the most attractive features of optical response of these objects we have the N-fold enhancement of the spontaneous emission rate and the N^2 scaling of the cubic hyperpolarizability, where N is the number of molecules in the aggregate. The reason is the collective (excitonic) character of aggregate eigenfunctions.

The aim of our work is to show that mirrorless bistable response happens for a linear molecular aggregate modeled as a linear chain of two-level molecules. In order to achieve the task, we will assume the one-molecule density-matrix formalism formerly used in [2–4] to treat Dicke superradiance and in [5] to look at bistability of an ensemble of two-level atoms inside a λ^3 volume. In this formalism (Sec. II), we have a set of coupled equations for the density matrices of individual molecules, where the field acting on each molecule consists of the external field plus the field generated by the rest of molecules in the chain. This last field is responsible for the bistability phenomenon (Secs. III and IV) because the resonance frequency of the aggregate depends linearly on the number of excited molecules in the aggregate.

Bistable behavior of the aggregate population is restrained by some critical parameters. We will find these parameters (Sec. III) and discuss the validity of the one-molecule density-matrix formalism in our physical problem (Sec. V).

II. FORMALISM

We shall consider the molecular aggregate as an assembly of N identical two-level molecules equally spaced along a straight line. In the one-molecule density-matrix formalism [2,3], the set of differential equations for the density-matrix elements ($\rho_{ij}^{(k)}; i,j = 1,2$) of kth molecule may be written as

$$\dot{\rho}_{11}^{(k)} = -i\frac{\vec{\mu} \cdot \vec{E}_k}{\hbar}[\rho_{12}^{(k)} - \rho_{21}^{(k)}],$$

$$\dot{\rho}_{22}^{(k)} = i\frac{\vec{\mu} \cdot \vec{E}_k}{\hbar}[\rho_{12}^{(k)} - \rho_{21}^{(k)}],$$

$$\dot{\rho}_{21}^{(k)} = -i\omega_{21}\rho_{21}^{(k)} + i\frac{\vec{\mu} \cdot \vec{E}_k}{\hbar}[\rho_{11}^{(k)} - \rho_{22}^{(k)}],$$ (1)

$$\rho_{12}^{(k)} = \rho_{21}^{(k)*}$$

where $\vec{\mu}$ is the transition matrix element of dipole operator for any molecule (we assume all dipoles are parallel and the angle between $\vec{\mu}$ and the axis of the chain is θ), ω_{21} is the resonance frequency of a single molecule, $\vec{E}_k$ is the electric field acting on the kth molecule, and includes the external field $\vec{E}_k^{\text{ext}}$ and the field induced by the rest of the molecules in the location of the kth molecule

$$\vec{E}_k = \vec{E}_k^{\text{ext}} + \sum_{\substack{l=1 \\ l \neq k}}^{N} \vec{E}_{lk}.$$ (2)

We assume the incident field to be a plane wave (ω_0, k_0) traveling perpendicular to the linear-chain axis and polarized parallel to the dipole vector of molecules in the chain, so $\vec{E}_k^{\text{ext}}(t) = \vec{E}^{\text{ext}}(t)$ for any k.

The field emitted by the lth molecule is regarded as the field radiated by a classical dipole with momentum equal to the mean value of quantum dipole momentum $\vec{d}_l(t) = \vec{\mu}[\rho_{12}^{(l)}(t) + \rho_{21}^{(l)}(t)]$. Therefore, at the position of the kth molecule, it is (see, for instance, [6])

$$\vec{E}_{lk}(t) = \left[\frac{3d_l(t')}{r_{lk}^5} + \frac{3\dot{d}_l(t')}{cr_{lk}^4} + \frac{\ddot{d}_l(t')}{c^2 r_{lk}^3}\right](\vec{n} \cdot \vec{r}_{lk})\vec{r}_{lk}$$

$$- \left[\frac{d_l(t')}{r_{lk}^3} + \frac{\dot{d}_l(t')}{cr_{lk}^2} + \frac{\ddot{d}_l(t')}{c^2 r_{lk}}\right]\vec{n},$$ (3)

where $t' = t - r_{lk}/c$, $\vec{n} = \vec{\mu}/\mu$, and $\vec{r}_{lk} = (l-k)\vec{a}$.

We apply the rotating wave approximation, assuming the optical period $2\pi/\omega_0$ to be the shortest characteristic time of the problem, and then splitting the fast and slow time dependent variables in the following way:

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$$\rho_{21}^{(k)}(t) = \tfrac{1}{2} R_k(t) e^{-i\omega_0 t},$$

$$\vec{E}^{\text{ext}}(t) = \tfrac{1}{2} \vec{\varepsilon}^{\text{ext}}(t) e^{-i\omega_0 t} + \text{c.c.},$$

(4)

$$\vec{E}_{lk}(t) = \tfrac{1}{2} \vec{\varepsilon}_{lk}(t) e^{-i\omega_0 t} + \text{c.c.},$$

$$\vec{E}_k(t) = \tfrac{1}{2} \vec{\varepsilon}_k(t) e^{-i\omega_0 t} + \text{c.c.}$$

Substituting these expressions in Eqs. (2) and (3), one can get the amplitudes $\vec{\varepsilon}_{lk}(t)$ and $\vec{\varepsilon}_k(t)$

$$\vec{\varepsilon}_{lk}(t) = \left\{ \left[\frac{3}{r_{lk}^5} - \frac{3ik_0}{r_{lk}^4} - \frac{k_0^2}{r_{lk}^3} \right] (\vec{\mu} \cdot \vec{r}_{lk}) \vec{r}_{lk} \right.$$
$$\left. - \left[\frac{1}{r_{lk}^3} - \frac{ik_0}{r_{lk}^2} - \frac{k_0^2}{r_{lk}} \right] \vec{\mu} \right\} R_l(t') e^{ik_0 r_{lk}},$$

(5)

$$\vec{\varepsilon}_k(t) = \vec{\varepsilon}^{\text{ext}}(t) + \sum_{\substack{l=1 \\ l \neq k}}^{N} \vec{\varepsilon}_{lk}(t).$$

Furthermore, we shall neglect the retardation effect in the amplitudes ($t' = t - r_{lk}/c \to t$), because the customary chains are not very large.

Replacing the magnitudes in Eqs. (1) by those of Eqs. (4) and skipping the rapidly oscillating terms, the system of equations for the slowly varying (in time) amplitudes arises,

$$\dot{R}_k = -i\Delta R_k + i \sum_{\substack{l=1 \\ l \neq k}}^{N} (\Delta_{lk} - i\gamma_{lk}) R_l Z_k - i\Omega Z_k,$$

(6)

$$\dot{Z}_k = \frac{i}{2} \sum_{\substack{l=1 \\ l \neq k}}^{N} \Delta_{lk} (R_k R_l^* - R_k^* R_l)$$
$$- \frac{1}{2} \sum_{\substack{l=1 \\ l \neq k}}^{N} \gamma_{lk} (R_k R_l^* + R_k^* R_l) + i\frac{\Omega}{2} (R_k^* - R_k),$$

where $\Delta = \omega_{21} - \omega_0$ is the detuning, $\Omega = \mu \varepsilon^{\text{ext}}/\hbar$ is the Rabi frequency of external field, $Z_k = \rho_{22}^{(k)} - \rho_{11}^{(k)}$ is the population difference, and matrices Δ_{lk} and γ_{lk} are given by the formulas

$$\Delta_{lk} = \frac{\mu^2}{\hbar a^3} \left\{ \left[\frac{\cos(k_0 a |l-k|)}{|l-k|^3} + k_0 a \frac{\sin(k_0 a |l-k|)}{|l-k|^2} \right] \right.$$
$$\left. \times (1 - 3 \cos^2\theta) - (k_0 a)^2 \frac{\cos(k_0 a |l-k|)}{|l-k|} \sin^2\theta \right\},$$

(7)

$$\gamma_{lk} = \frac{\mu^2}{\hbar a^3} \left\{ \left[k_0 a \frac{\cos(k_0 a |l-k|)}{|l-k|^2} - \frac{\sin(k_0 a |l-k|)}{|l-k|^3} \right] \right.$$
$$\left. \times (1 - 3\cos^2\theta) + (k_0 a)^2 \frac{\sin(k_0 a |l-k|)}{|l-k|} \sin^2\theta \right\}.$$

(8)

The sum of matrices $\Delta_{lk} - i\gamma_{lk}$ may be identified with the matrix of intermolecular retarded interaction. Its imaginary part γ_{lk} results from the molecular interaction through the transverse field [3,7]. In the particular case of an aggregate with a length as small as that compared with the wavelength of the incident field ($L = Na \ll \lambda$), these matrices have the following forms:

$$\Delta_{lk} = \frac{\mu^2}{\hbar r_{lk}^3} (1 - 3 \cos^2\theta),$$

(9)

$$\gamma_{lk} = \frac{2\mu^2 k_0^3}{3\hbar} = \tfrac{1}{2} \gamma_0.$$

(10)

Thus, Δ_{lk} in Eq. (9) is the usual dipole-dipole molecular interaction, and γ_{lk} in Eq. (10) equals the half of the radiative constant γ_0 of an isolated molecule.

From (7), it is straightforward to get N integrals of motion,

$$|R_k|^2 + Z_k^2 = \text{const}$$

(11)

which means the Bloch vector length conservation law of the kth molecule with components $X_k = \text{Re}[R_k]$, $Y_k = \text{Im}[R_k]$ and Z_k. If every molecule in the chain is initially in the ground-state ($R_k = 0$, $Z_k = -1$), then the right-hand side of (11) equals unity.

III. HOMOGENEOUS APPROXIMATION

The simplest model that includes the dipole-dipole interaction assumes that density matrices of all molecules are identical [3]. Such approximation simplifies drastically the system of differential Eqs. (6) and sheds light on the physical origin of bistability in linear aggregates. We should note that this model is exact for an infinite linear chain as well as for cyclic aggregates.

Let $R_k = R$ and $Z_k = Z$ in Eqs. (6). Then, the system of equations changes into

$$\dot{R} = [-i(\Delta - \Delta_L Z) + \gamma_R Z]R - i\Omega Z,$$

(12)

$$\dot{Z} = -\gamma_R |R|^2 + i\frac{\Omega}{2}(R^* - R),$$

where

$$\Delta_L = \frac{3\gamma_0}{2(k_0 a)^3} \sum_{l=1}^{N/2} \left\{ \left[\frac{\cos(k_0 a l)}{l^3} + k_0 a \frac{\sin(k_0 a l)}{l^2} \right] \right.$$
$$\left. \times (1 - 3 \cos^2\theta) - (k_0 a)^2 \frac{\cos(k_0 a l)}{l} \sin^2\theta \right\},$$

(13)

$$\gamma_R = \frac{3\gamma_0}{2(k_0 a)^3} \sum_{l=1}^{N/2} \left\{ \left[k_0 a \frac{\cos(k_0 a l)}{l^2} - \frac{\sin(k_0 a l)}{l^3} \right] \right.$$
$$\left. \times (1 - 3 \cos^2\theta) + (k_0 a)^2 \frac{\sin(k_0 a l)}{l} \sin^2\theta \right\}.$$
(14)

In the limit of high density ($k_0 a \ll 1$) and large number of molecules ($N \gg 1$), the summation of the series in Eqs. (13) and (14) gives

$$\Delta_L = \frac{3\gamma_0}{2(k_0 a)^3} \zeta(3)(1 - 3\cos^2\theta), \quad (15)$$

$$\gamma_R = \frac{3\pi\gamma_0}{8(k_0 a)} \sin^2\theta \quad \text{if} \quad k_0 L \gg 1, \quad (16)$$

$$\gamma_R = \frac{\gamma_0}{2} N \quad \text{if} \quad k_0 L \ll 1, \quad (17)$$

with accuracy of $k_0 a$. Here, $\zeta(3) = 1.202$ is the third-order Riemann ζ function.

It is remarkable that in the limit $k_0 a \ll 1$, the inequality $|\Delta_L| \gg \gamma_R$ is valid independently of the value of $k_0 L$ except the narrow range of values of θ that makes the factor $(1 - 3\cos^2\theta)$ very close to zero. In our analysis, we shall assume Δ_L to be negative as corresponds to J aggregates [1].

The system of Eqs. (12) is similar to that describing the nonlinear response of a thin film to a short resonant pulse [8,9]. The quantity Δ_L has the same meaning as the Lorenz correction $4\pi P/3$ for bulk media (where P is the electric polarization) and γ_R is the collective radiative constant (superradiance constant [3]).

According to Eqs. (12), Δ_L determines the magnitude of resonance frequency shift, which depends also on the population difference Z. The Lorenz correction turns the resonance frequency ω_{21} into $\omega'_{21} = \omega_{21} - |\Delta_L|$ and the condition for resonance into $\Delta' = \Delta - |\Delta_L| = 0$ for the aggregate in the ground state.

As it was shown in [8,9], the dependence of resonance frequency on the population difference leads to bistable behavior of the stationary solution of Eqs. (12). In the limit $|\Delta_L| \gg \gamma_R$, the driving parameter of bistability is the new resonance detuning $\Delta' = \Delta - |\Delta_L|$. It follows from the analysis of [8,9] that bistability occurs when $\Delta' < -\sqrt{3}\gamma_R$.

Let us remember the main statements of that analysis. Applying the steady-state conditions to Eq. (12), we have a fourth-order equation for the population difference

$$(1 - Z^2)\{[\Delta' + |\Delta_L|(1+Z)]^2 + \gamma_R^2 Z^2\} = \Omega^2 Z^2. \quad (18)$$

Under the condition $|\Delta_L| \gg \gamma_R$, the bistable behavior may take place for $|\Delta'| \ll |\Delta_L|$ and therefore $Z \approx -1$. In this case, we may reduce the order of Eq. (18) by making the following substitutions: $1 - Z \to 2$, $1 + Z \to 2\rho_{22}$, and $Z^2 \to 1$. Then, we have

$$4\rho_{22}\{(\Delta' + 2|\Delta_L|\rho_{22})^2 + \gamma_R^2\} = \Omega^2. \quad (19)$$

The interesting solution is that assigning three values of ρ_{22} to each value of Ω. As it follows from examining the zeros of derivative $d[\Omega^2]/d\rho_{22}$, this kind of solution requires $\Delta' < -\sqrt{3}\gamma_R$. In this case, each value of the external field Rabi frequency within the interval (Ω_1, Ω_2) produce three different solutions of Eq. (19) (see Fig. 1), but only lower and upper branches are stable [10]. The values of population ρ_{22} and Rabi frequency Ω that correspond to the threshold value of detuning $\Delta' = -\sqrt{3}\gamma_R$ are
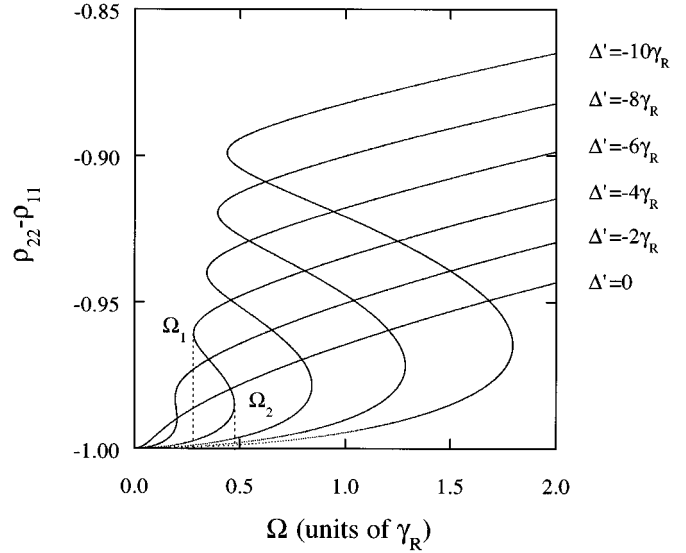

FIG. 1. Dependence of population difference on Rabi frequency of the external field $\Omega = \mu \varepsilon^{\text{ext}}/\hbar$ for different values of the detuning Δ' calculated for the homogeneous model under steady-state conditions. The ratio $|\Delta_L|/\gamma_R$ equals 100.

$$\rho_{22} = \frac{1}{\sqrt{3}} \frac{\gamma_R}{|\Delta_L|} \ll 1,$$

$$\left(\frac{\Omega}{\gamma_R}\right)^2 = \frac{16}{3\sqrt{3}} \frac{\gamma_R}{|\Delta_L|} \ll 1. \quad (20)$$

The conclusion arising from these results is that bistability may appear even for a low degree of excitation of our system, and consequently for small ratios of the Rabi frequency of an external field over the collective radiative constant γ_R. For higher values of the detuning $|\Delta'| \approx |\Delta_L|$, we need Rabi frequencies comparable to $|\Delta_L|$ to get bistability, but in this case our approach does not work (see Sec. V). Rather, we shall consider detuning close to the threshold value.

It is easy to check from Eq. (18) that for $\Delta_L = 0$ there is no bistability effect. Thus, the physical origin of bistability is the dependence of resonance frequency on population difference.

We have performed some numerical calculations of Eq. (12) in order to study the evolution of population difference $Z(t)$. It is evident from Fig. 2 the sudden change of kinetics as we choose values of the Rabi frequency in the vicinity of the critical value Ω_2 (see Fig. 1). The relaxation time to the stationary value of $Z(t)$ is some units of γ_R^{-1}.

In Fig. 3 we present the solution of Eq. (12) as we slowly scan the Rabi frequency up and down in time, in order to show the possibility of optical hysteresis for molecular aggregates. The scanning rate of Rabi frequency was $10^{-3}\gamma_R^2$. Obviously, the intermediate branch of the population difference does not appear as it is unstable.

IV. NUMERICAL SOLUTION OF EXACT EQUATIONS

We have solved the exact system of Eqs. (6) to show the presence of bistable behavior for the general case (Sec. II)
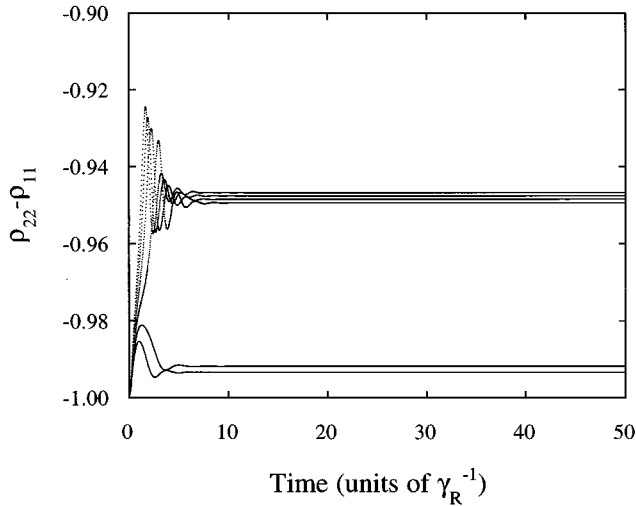
FIG. 2. Kinetics of the population difference $Z(t)$ for Rabi frequencies of the external field around the critical value Ω_2 (see Fig. 1) in the frame of the homogeneous model. From bottom to top, Ω/γ_R ranges from 0.403 with constant step 0.027. The detuning Δ' is $-4\gamma_R$. The ratio $|\Delta_L|/\gamma_R$ equals 100.

when the variables Z and R depend on the molecule location. The results for averaged population difference over the linear chain $\bar{Z}(t) = (1/N)\Sigma_k Z_k(t)$ are presented in Figs. 4–7.

Figure 4 shows the same sudden change in the kinetics of the averaged population difference as in the homogeneous model by increasing slightly the Rabi frequency near the critical value. The number of molecules in the linear chain was 50 and $k_0 a = 0.1$. The initial detuning in these calculations was $-4\gamma_R$ [Fig. 4(a)] and $-10\gamma_R$ [Fig. 4(b)], respectively.

Please, pay attention to the fact that all values of the physical magnitudes of our interest (critical Rabi frequencies

FIG. 4. Kinetics of the average population difference $\bar{Z}(t)$ calculated with the exact Eqs. (6) for different Rabi frequencies. (a) $\Delta' = -4\gamma_R$ and from bottom to top, Ω/γ_R ranges from 0.403 with constant step 0.027. (b) $\Delta' = -10\gamma_R$ and from bottom to top, Ω/γ_R ranges from 0.645 with constant step 0.054. The ratio $|\Delta_L|/\gamma_R$ equals 100. The linear chain consists of 50 molecules with $k_0 a = 0.1$.
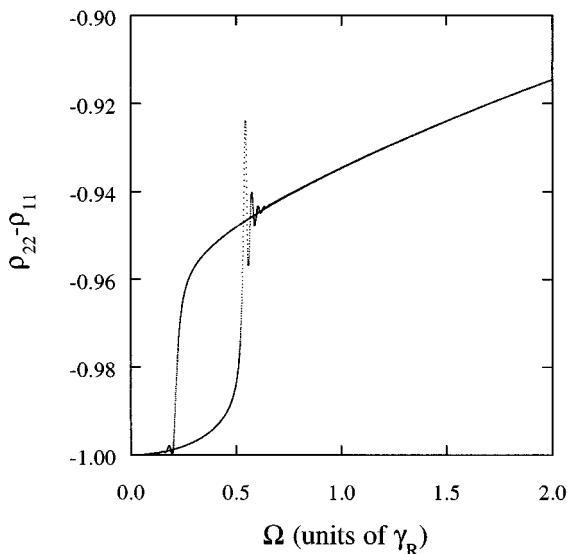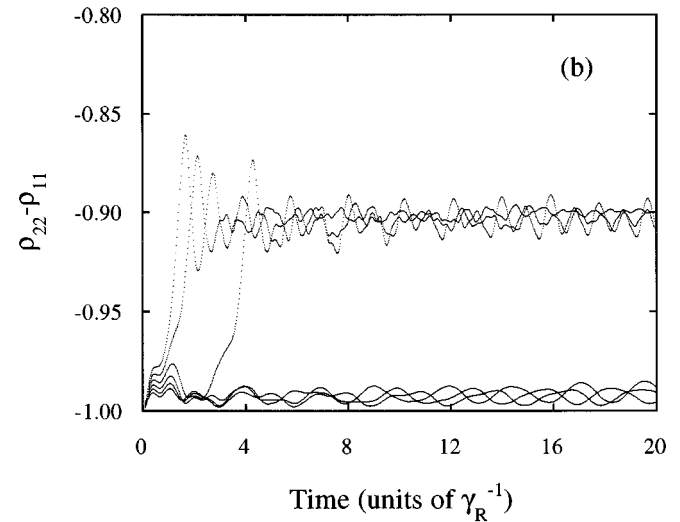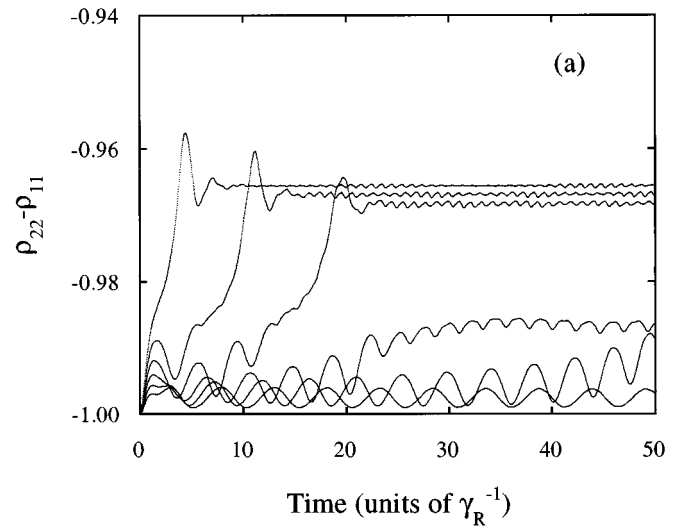

FIG. 3. The optical hysteresis loop calculated in the frame of the homogeneous model by scanning up and down the Rabi frequency in time. The scanning rate is $10^{-3}\gamma_R^2$. The detuning Δ' equals $-4\gamma_R$.

and population differences) fit quite well in the analogous ones of the homogeneous model (see Sec. II). The most obvious discrepancy is that the population difference does not reach its stationary value and oscillates slightly in time. The spatial distributions of population along the same chain are depicted in Fig. 5 for two different points in time evolution. These two figures clarify the origin of such instability. The inhomogeneous distributions of population and consequently its redistribution in time among the different sites of the chain are responsible for the oscillations of the averaged population difference.

Surprisingly, we have not found such a sudden change in the kinetics of the averaged population for linear chains with small lengths, much less than the emission wavelength. In Fig. 6 we present analogous calculations of the solution of
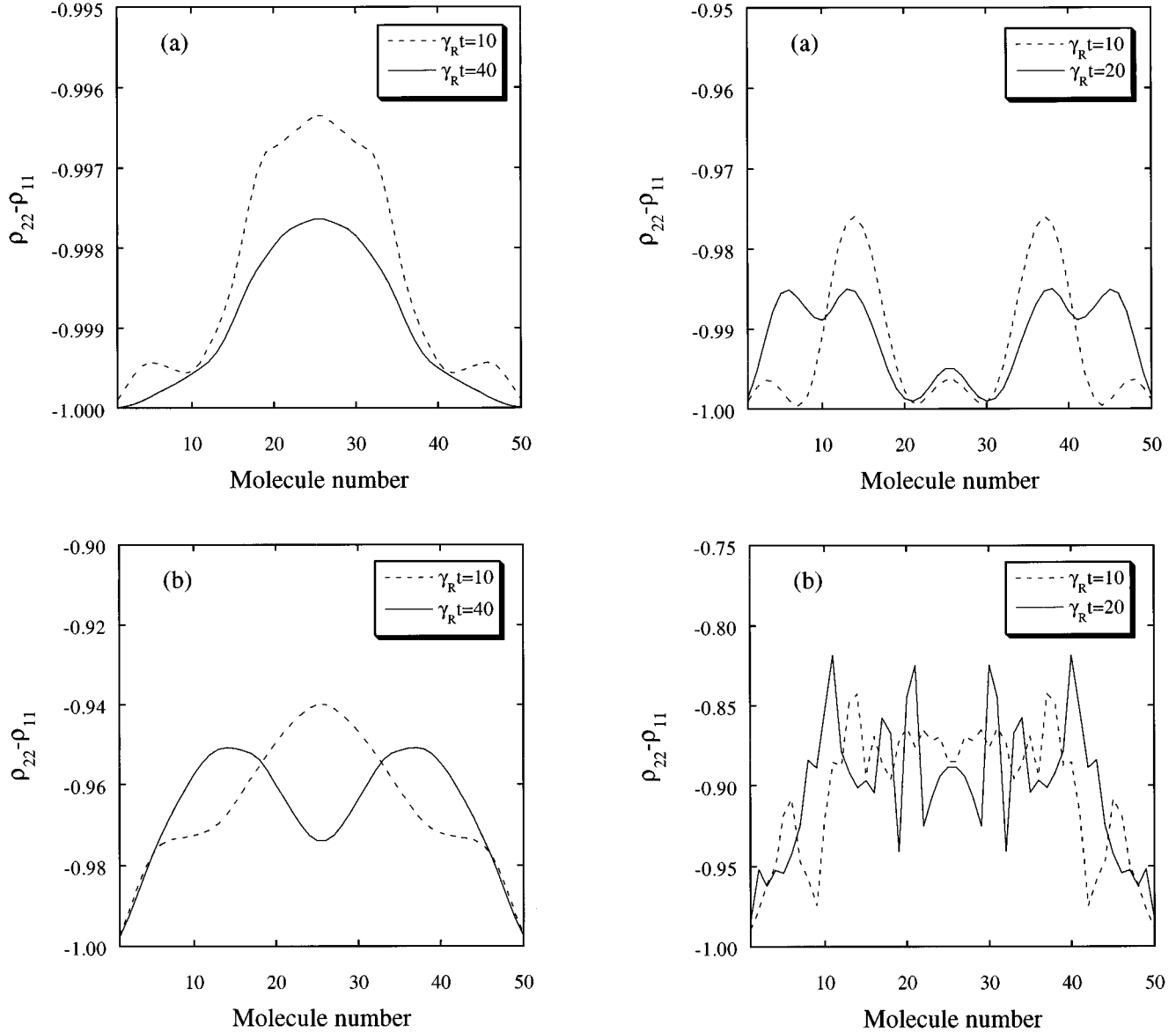
FIG. 5. Spatial distribution of population difference for two points in time evolution and the minimum (a) and maximum (b) values of Rabi frequency of the external field used in Figs. 4(a) and 4(b). The detunings are (left) $\Delta' = -4\gamma_R$ and (right) $\Delta' = -10\gamma_R$.

Eqs. (6) for a linear chain with $N = 10$ and $k_0 a = 0.1$, and initial detunings $-4\gamma_R$ [Fig. 6(a)] and $-10\gamma_R$ [Fig. 6(b)]. Observe the monotonical increase of excited population as we increase the Rabi frequency of the external field. Figure 7 shows the spatial distribution of population along the chain. Probably, the spatial inhomogeneity of the population difference in the case of the short aggregates masks the steplike dependence of $\bar{Z}(t)$ on Ω due to the small jump of $\bar{Z}(t)$ in the vicinity of the threshold value of detuning $\Delta' = -\sqrt{3}\gamma_R$.

V. JUSTIFICATION OF THE ONE-MOLECULE DENSITY-MATRIX APPROACH

The aim of this section is to discuss the validity of the one-molecule density-matrix approximation in our study. It is possible to derive Eqs. (6) by means of the Heisenberg equation of motion for molecular operators [5]. The key approxi-

mation in this method leading to Eqs. (6) is the factorization of the expectation values of the product of two molecular operators into the product of the individual ones. For instance, $\langle \hat{d}_k \hat{d}_l \rangle = \langle \hat{d}_k \rangle \langle \hat{d}_l \rangle$, where $\hat{d}_k$ and $\hat{d}_l$ are the dipole operators for the kth and lth molecule, respectively. This factorization is rigorously true whenever the density matrix of the whole system is represented as the direct product of density matrices of individual molecules rather than those for collective excitations of the whole system, i.e., one-dimensional (1D) Frenkel excitons.

Therefore, the one-molecule density-matrix approach does not allow for spatial quantum correlations of dipoles belonging to different sites of the linear aggregate. This statement is the reference to study the validity of the one-molecule density-matrix approach when considering nonlinear optical properties of linear molecular aggregates.

Turning to the collective basis means the renormalization of the energy spectrum of the aggregate. In the case of linear
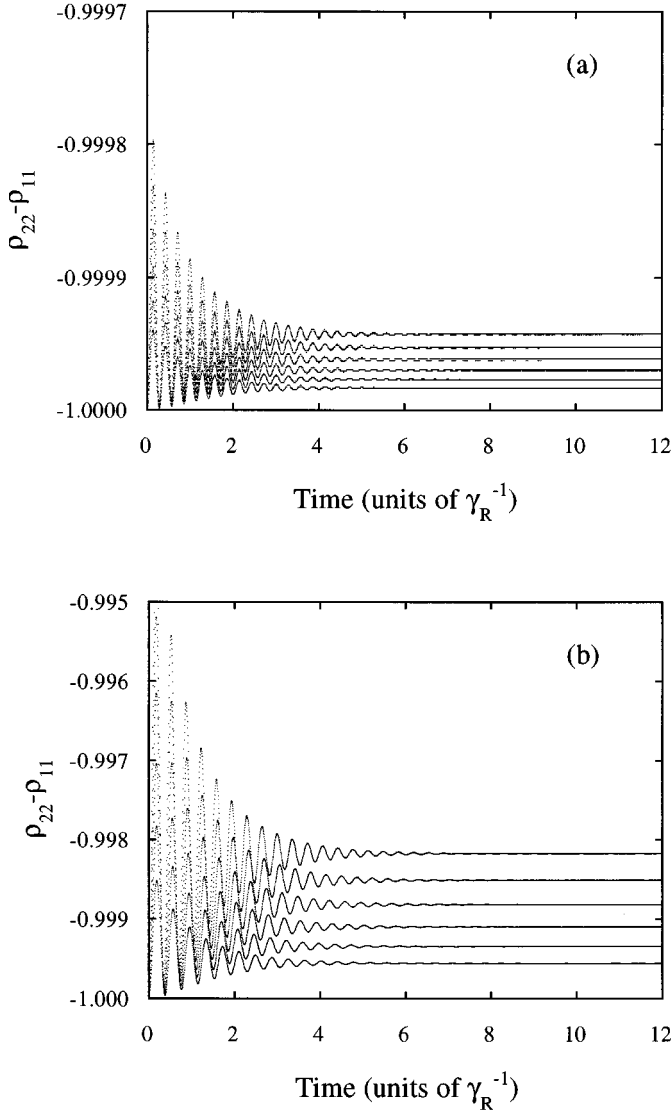
$W = \Sigma_{k=1}^{N} W_k n_k$, where W_k is the energy spectrum of 1D exciton and $n_k = 0,1$ denotes the occupation of the k-th state. W_k is given by the formula

$$W_k = \hbar \omega_{21} + 2V \cos \frac{\pi k}{N+1} \quad \text{with} \quad k = 1,2, \ldots ,N, \quad (21)$$

where $V = (\mu^2/a^3)(1-3 \cos^2 \theta)$. To simplify we assume $1-3 \cos^2 \theta = -1$. For negative values of V the states in the bottom of multiexciton bands are the most active in optical transitions [4]. The bottom energy of the n-exciton band equals $\Sigma_{k=1}^{n} W_k$, where n is the number of excitons ($1 \leq n \leq N$). Therefore, the transition energy between $(n-1)$-th and n-th exciton bands is W_n, i.e., exactly the energy of n-th exciton state. This quantity ranges from W_1 for the transition into one-exciton band, to W_N for the transition into the band with N excitons (all molecules in the excited state). These energies exactly correspond to the limits of resonance frequency change in the one-molecule picture.

Nevertheless, the transition energies does not change continuously as predicted by the one-molecule theory. They are quantized and the minimal energy mismatch is $W_2 - W_1$. According to Eq. (21), in the limit of large N it is $3\pi^2 |V|/(N+1)^2$.

So far, we may conclude that our matter of interest is precisely those conditions when quantization of the 1D exciton energy spectrum is not important. Otherwise, if the collective radiative constant γ_R can exceed the energy intervals of the 1D exciton spectrum. If so, the spectrum looks like an inhomogeneously broadened band.

First, we should compare $\hbar \gamma_R$ with the minimal energy interval of the 1D exciton spectrum $W_2 - W_1$. In the particular case of aggregate length less than the emission wavelength $\lambda (k_0 L \ll 1)$, we get

$$\frac{(W_2 - W_1)}{\hbar \gamma_R} = \frac{9\pi^2}{2(k_0 L)^3} \gg 1, \quad (22)$$

using Eq. (17) and $|V| = 3\hbar \gamma_0/4(k_0 a)^3$, i.e., the energy intervals of 1D exciton spectrum are always larger than radiative broadening.

On the contrary, when $L \gg \lambda$ or $k_0 L \gg 1$, by means of Eq. (16), we get the following expression:

$$\frac{(W_2 - W_1)}{\hbar \gamma_R} = \frac{18\pi}{(k_0 L)^2}. \quad (23)$$

Therefore, there is a characteristic length $L^* = \lambda (9/2\pi)^{1/2}$ for which $W_2 - W_1 = \hbar \gamma_R$. For larger L the inequality $W_2 - W_1 < \hbar \gamma_R$ we are seeking is always satisfied.

On the other hand, if we compare the maximal value of $W_k - W_{k-1} = 2\pi |V|/(N+1)$—which is reached in the middle of 1D exciton band ($k \cong N/2$)—with the collective radiative width $\hbar \gamma_R$ in the limit of large aggregates, we will get

$$\frac{(W_k - W_{k-1})}{\hbar \gamma_R} = \frac{12}{N(k_0 a)^2}. \quad (24)$$

FIG. 6. Kinetics of the average population difference $\bar{Z}(t)$ calculated with the exact Eqs. (6) for different Rabi frequencies. (a) $\Delta' = -4\gamma_R$ and from bottom to top, Ω/γ_R ranges from 0.135 with constant step 0.022. (b) $\Delta' = -10\gamma_R$ and from bottom to top, Ω/γ_R ranges from 0.506 with constant step 0.112. The ratio $|\Delta_L|/\gamma_R$ equals 425. The linear chain consists of ten molecules with $k_0 a = 0.1$.

aggregates, we have 1D exciton bands whose energy scale is determined by the aggregate length. This quantization is absent if we use the one-molecule density-matrix approximation. This approach traces adequately the resonance frequency shift from ω_{21} to $\omega_{21}' = \omega_{21} - |\Delta_L|$ for the nonexcited aggregate, which corresponds exactly to the band bottom energy of the 1D Frenkel exciton (see [1]). It also depicts the dependence of resonance frequency on the population difference. In fact, while the excited state population grows from zero to unity the resonance frequency changes from $\omega_{21} - |\Delta_L|$ to $\omega_{21} + |\Delta_L|$. The reason is that 1D Frenkel excitons are weakly interacting fermions (they are rigorously fermions only if nearest-neighbor interaction is considered, [1,4,11–13]). Assuming nearest-neighbor approximation the energy of 1D exciton gas may take the values
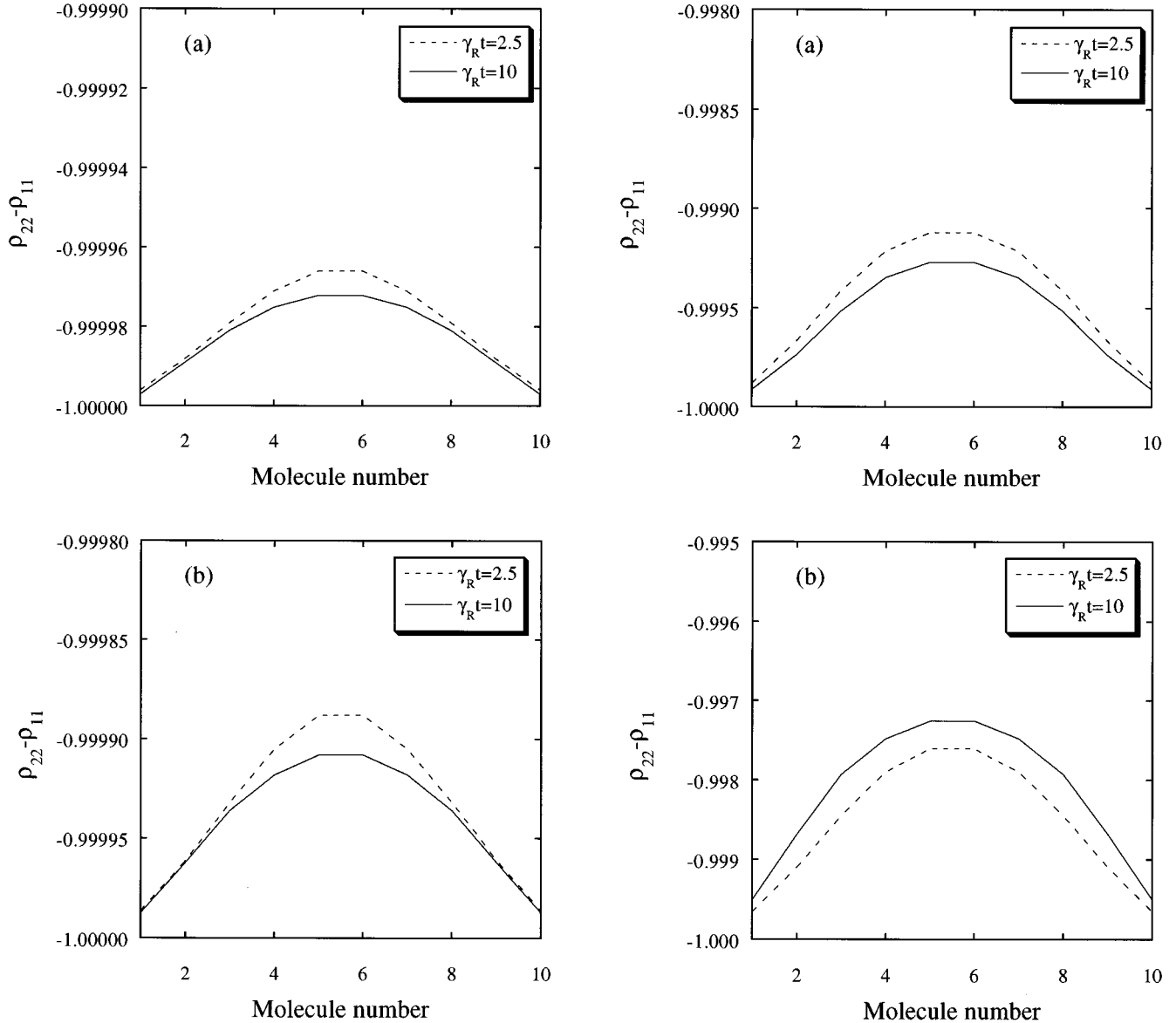
FIG. 7. Spatial distribution of population difference for two points in time evolution and the minimum (a) and maximum (b) values of Rabi frequency of the external field used in Figs. 6(a) and 6(b). The detunings are (left) $\Delta' = -4\gamma_R$ and (right) $\Delta' = -10\gamma_R$.

It follows from Eq. (24) that satisfying the inequality $(W_k - W_{k-1})/\hbar\gamma_R < 1$ for actual values of $k_0 a$ (≈ 0.01) requires too many molecules making up the aggregate.

In short, the one-molecule density-matrix approach is appropriate for the problem under consideration in the case of large aggregates ($k_0 L \gg 1$) whenever we work in the low-energy region of the 1D exciton spectrum.

One could associate the approach we use with the local-field approximation (LFA) in the theory of nonlinear response of linear molecular aggregates [14,15] (see also [1] and references therein). Our study differs in the sense that we take into account the whole field (near and far zones) while the mentioned previous works included only the near zone part. The validity of LFA was widely discussed in connection with the *perturbative* problem of the two-photon absorption spectrum of 1D excitons. It was shown both for infinite [14] and short [15] aggregates that LFA breaks down for an interval of resonance detunings of the order of the 1D exciton

band. It seems that this observation is in contradiction with ours, at least when considering the large aggregates. The question only is if the restrictions found in Refs. [14] and [15] affect our *nonperturbative* analysis of bistable response of linear aggregates. We are not able to assert that these conclusions arise also from our work. We are only sure of the fact that the condition of breaking down the 1D exciton energy quantization is absolutely necessary for applying the one-molecule density-matrix approach to the problem considered above.

VI. CONCLUSION

We have shown mirrorless bistable response of large linear molecular aggregates ($L \gg \lambda$) and found that this behavior results from the dependence of resonance frequency on the number of excited molecules in the aggregate.

The formalism for describing this phenomenon should be

based on the equation for the density matrix of collective excitations, i.e., 1D Frenkel excitons. However, this formalism is not helpful as we consider effects of many excitons (see [1], where difficulties of applying this method are discussed).

A simpler and more useful formalism is that making use of the one-molecule density matrices. Our analysis shows that this approach is satisfactory if aggregate lengths are more than the emission wavelength. The resulting system of coupled nonlinear equations includes exactly the intermolecular retarded interaction. The real part of this interaction is responsible for the dynamical shift of resonance frequency of the aggregate while the imaginary one describes the collective radiative relaxation. It is remarkable that this last one is much faster (approximately 100 times) than the spontaneous relaxation of an isolated molecule. Therefore we may have the optical switching of a linear molecular aggregate with a characteristic time of the order of 100 ps.

About the possibilities of an experimental probe of the linear aggregates bistable response, we suggest measuring the field dependence of transmittivity for the linear aggregate thin layer in the spectral domain just above the absorption line. According to our predictions, the transmittivity should change sharply for a given value of the incident light intensity.

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