Optical characteristics of the nanoparticle coupled to a quantum molecular aggregate

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Optical characteristics of a single nanoparticle, coupled to the one-dimensional quantum molecular aggregate is studied. Depending on the values of the coupling of the particle and its own frequency, with respect to the own frequency of the aggregated molecules, and the strength of the aggregation, the dynamical relative permittivity of the nanoparticle manifests the contribution from the exciton band, or/and the ones from the local level(s) caused by the particle. The refractive index and the extinction coefficient of the nanoparticle is also calculated.

Low-dimensional optical materials like quantum wells and wires, and organic systems like conjugated polymers, photosynthetic complexes of plants and bacteria, and molecular aggregates were extensively studied during last years. The interest to them is connected with their special optical properties, such as the fast transport of the electromagnetic energy, the strong (and color-tunable) optical absorption, optical switching, and fluorescence [1]. Light in such molecular systems is collectively absorbed by many molecules and their optical properties reveal the collective coherent behavior [2]. The changes of the shape of organic molecule, when such molecules aggregate can help to understand the nature of the interaction between monomers in such molecular aggregates, and to determine the strength of such an interaction. Aggregates of organic molecules are supra-molecular complexes with the strong interactions between electronic transitions. So called *J*-aggregates [3] manifest the red shift and narrowing of the absorption spectrum for many molecular aggregates, e.g., for cyanine dyes with strong inter-monomer coupling caused by the dipole-dipole interaction. Unlike well-known concentration effects [4] (that manifest themselves in broadening of optical spectra and decay of the fluorescence of organic molecules for their chaotic associa-tion), *J*-aggregates reveal ordered aggregation of molecules with the new narrow absorption band, being shifted compared to the monomer absorption. *J*-aggregates are related to the class of large nanoclusters with the length $L \geq 100$ nM, with the translation symmetry [5]. This is why, exciton excitations of quantum molecular aggregates are used to be described by the band theory [6].

It is known that optical properties of an excited atomic state is not only the function of that single atom, but of its environment [7]. That feature was observed, e.g., for atoms closed to plane interfaces, in cavities and photonic crystals [8]. For molecules, it was shown [9] that the strong interaction of a molecule to the band exciton states can yield the essential transformation of optical properties of the molecule itself. However, the results of the experiments regarding fluorescence of single molecules/particles coupled to the environment are not consistent: Some of them demonstrate the fluorescence enhancement, while others report fluorescence quenching [10]. Nanoplasmonics is the branch of the modern optical science devoted to the optical phenomena of the nanoscale in nanostructured systems [11]. Molecules (or nanoparticles) coupled to the *J*-aggregate can serve as a good example of such nanostructured subjects. Recently it

was observed that the fluorescence of metallic nanoparticles coupled to molecular aggregates strongly depends on the distance between them [12].

The permittivity of nanoparticles is often used to describe the behavior of optical characteristics of such systems [13]. In this paper we study the optical characteristics of a metallic nanoparticle (or a molecule) coupled to the exciton band of a one-dimensional molecular aggregate: the permittivity and the refractive index. We show that both can manifest contributions from the local levels (caused by the coupling of that single particle to the aggregate), and from the exciton band states of the aggregate chain.

In molecular aggregates one usually deals with Frenkel excitons, because the charge overlap in neighboring molecules is small [14]. For Frenkel excitons the typical separation between electron and hole is essentially zero, i.e., an electron and a hole occur at the same molecule, and their binding energy is large. The main contribution to the exciton physics comes from interactions between transition dipoles, which form the exciton band. The Hamiltonian of a Frenkel exciton in a single quantum molecule can be written as the one for the two-level system $\mathcal{H}_{\text{sing}} = \hbar\omega_g \mid g\rangle\langle g \mid + \hbar(\omega_e)\mid e\rangle\langle e\mid$, where $\mid g, e\rangle$ and $\hbar\omega_{g,e}$ are the wave function and the energy of the ground (excited) state of the Frenkel exciton. It is useful to denote the difference as $\omega_0 = \omega_e - \omega_g$, where ω_0 is the transition frequency. The optical absorption of such a system is the delta-function peak situated at the frequency of the light $\omega = \omega_0$. For the ensemble of interacting quantum molecules one can neglect couplings between ground states and singly and doubly excited states etc., and the interaction Hamiltonian can be written as

$$\mathcal{H}_{\text{int}} = \sum_{n,m} J_{n,m}(\mid e_n g_m\rangle\langle g_n e_m \mid + \mid g_n e_m\rangle\langle e_n g_m \mid),$$

where $g_{n,m}$ and $e_{n,m}$ corresponds to the ground and excited states of the nth (mth) molecule. Also the energy of a single exciton can be renormalized due to the interaction. The interaction between excitons in molecular aggregates is of Coulomb nature, and it is dominated by the dipole-dipole coupling between molecular transition dipoles. Within the Hartree–Fock approximation the excited state of the exciton is formed by the creation of an electron in an unoccupied (excited) orbital and simultaneous destruction of an electron state of the occupied (ground state) orbital, neglecting intermolecular charge transfer. Such creation and annihilation of the nth two-level molecule can be described in terms of Pauli creation and destruction operators, $b_n^\dagger$ and b_n, which satisfy the following commutation relations at the same site $b_n^\dagger b_n + b_n b_n^\dagger = 1$, with $(b_n)^2 = (b_n^\dagger)^2 = 0$, and at different sites $[b_n, b_j] = 0$, with $[b_n, b_j^\dagger] = 0$ (for $n \neq j$). The problem with the quantum mechanical description of such an ensemble of Frenkel excitons is in these commutation relations, which are bosonic for different molecules and fermionic for the same molecule. That produces so-called kinematic interaction between excitons. The number of excitons of the

same molecule is $n_n = b_n^\dagger b_n$. Using these notations the Hamiltonian of the ensemble of excitons can be written as

$$\mathcal{H}_0 = \sum_n [(\hbar\omega_0 + D_n)b_n^\dagger b_n -$$
$$-\sum_j J_{n,j}(b_n^\dagger b_j + b_j^\dagger b_n)] + H_{\text{int}} + E_g ,\qquad(1)$$

where D_n is the difference between the ground state in the Coulomb interaction of the first interacting molecule and the excited state of the other interacting molecule, or vice versa (we assume that molecules are situated symmetrically), $\mathcal{H}_{\text{int}}$ is the part of the Hamiltonian, which contains higher-order in b_n and $b_n^\dagger$ operators ($\mathcal{H}_{\text{int}}$ is called the dynamic interaction), and E_g is the ground-state energy. Within dipole approximation the dynamic interaction part $\mathcal{H}_{\text{int}}$ can be neglected. However, the kinematic interaction persists, so the quadratic form of Pauli creation and destruction operators still describes an interacting system. It follows then that in linear optics one can only examine properties of one-exciton states.

The molecules, forming aggregates, interact with electromagnetic fields in the optical range and the absorbed energy of the latter transforms to excitons on a sub-micron scale.

From now on we limit ourselves with the one-dimensional quantum molecular aggregates, and suppose the interaction $J_{n,j}$ to be limited to the nearest neighboring molecules. Also we neglect D_n, i.e., consider homogeneous aggregates. In such a case we can write the Hamiltonian of the one-dimensional ensemble of excitons as

$$\mathcal{H}_0 = \sum_n [\hbar\omega_0 b_n^\dagger b_n - J(b_n^\dagger b_{n+1} + \text{H.c.})].\qquad(2)$$

Using the Jordan–Wigner transformation [15] $b_n^\dagger = \prod_{m<n}(1-2a_m^\dagger a_m)a_n$, and $b_n = a_n^\dagger \prod_{m<n}(1-2a_m^\dagger a_m)$, where a_n ($a_n^\dagger$) are destruction (creation) operator of a fermion in the nth molecule, we can re-write the Hamiltonian $\mathcal{H}_0$ as $\mathcal{H}_0 = \sum_n [\hbar\omega_0 a_n^\dagger a_n - J(a_n^\dagger a_{n+1} + \text{H.c.})]$. The advantage of the transition to fermion operators is in the absence of the kinematic interaction, present in the ensemble of Pauli operators. Then the Hamiltonian $\mathcal{H}_0$ can be diagonalized using the Fourier transform, and we obtain $\mathcal{H}_0 = \sum_k \varepsilon_{k'} a_{k'}^\dagger a_{k'}$. The one-exciton eigenstates in the open aggregate chain can be written as $\mid k\rangle = \sqrt{2/L+1}\sin(\pi k'/L+1)a_n^\dagger \mid g\rangle$ with the energy $\varepsilon_{k'} = \hbar\omega_0 - 2J\cos(\pi k'/L+1)$ and integer $k' = 1, 2, ..., L$, L being the number of molecules in the chain. For $L \to \infty$ the one-exciton state is a band centered around $\hbar\omega_0$ with the bandwidth $4\mid J\mid$. The energy distance between band states is $\Delta E = 2\mid J\mid \pi/(L+1)$. Notice that the case $J > 0$ the absorption of the molecular aggregate is red-shifted comparing to the monomer absorption (the case is called J-aggregates), and for $J < 0$ it is blue-shifted (H-aggregates).

Suppose that the one-dimensional molecular aggregate is coupled to a single nanoparticle (or a molecule) (which we enumerate with the number 0). Considering the main effect we can model the Hamiltonian of the total system as

$$\mathcal{H} = \mathcal{H}_0 + \hbar\omega_1 b_0^\dagger b_0 - J'(b_0^\dagger b_1 + b_1^\dagger b_0),\qquad (3)$$

where ω_1 denotes the transition frequency of that single particle, and J' is the coupling strength of that single particle to the aggregate chain. Here we assume that the single particle is coupled to the first molecule of the chain. One can see that the single molecule differs in our model from other molecules of the chain by ω_1 and J'. Obviously, the case with $\omega_1 = \omega_0$ and $J' = J$ results in the same Hamiltonian $\mathcal{H}_0$ with $L \to L+1$. For the infinite chain ($L \to \infty$) it is possible to obtain the characteristics of all states of the Hamiltonian $\mathcal{H}$, see, e.g., Ref. 16 using the unitary transformation $a_n = (2/L)\sum_\lambda u_{n,\lambda} a_\lambda$ (for the homogeneous case $J' = J$ and $\omega_1 = \omega_0$ it is the Fourier transformation), where λ denotes either band eigenstates, or possible localized levels. Analysis shows that there can exist band states and localized states. The band states (with their wave functions renormalized due to the coupled single molecule) have the energy $\varepsilon_k = \hbar\omega - 2J\cos k$, where $-\pi \le k \le \pi$. The localized states appear if the following conditions hold. Let us define $\Delta = \hbar(\omega_1 - \omega_0)/2J$ and $f = J'/J$. Then the local level

with the energy ε_1 and the local level with the energy ε_2 are split from the upper/lower edge of the band if $f^2 > 2 - 2\Delta$, or $f^2 > 2 + 2\Delta$, respectively. The energies are [16] $\varepsilon_{1,2} = \hbar\omega_0 - J(f^2-1)^{-1}[\Delta(2-f^2) \pm f^2\sqrt{\Delta^2 + f^2 - 1}]$. The localization lengths for those local levels are $\xi_{1,2} = \ln[(\Delta \pm \sqrt{\Delta^2 + f^2 - 1})/(f^2 - 1)]$. For $f = 1$, we have only one level with $\varepsilon = \hbar\omega_0 + J(1+\Delta^2)/\Delta$ with the localization length $\xi = -\ln(-2\Delta)$.

The imaginary part of the dynamical susceptibility of the particle can be written as $\chi'' = \chi''_{(b)} + \chi''_{(l)}$, where the imaginary part of the susceptibility due to the band states of the molecular aggregate is

$$\chi''_{(b)} = \frac{1}{|J|}\tanh\left[\frac{\hbar\omega}{2k_BT}\right] \times$$

$$\times \frac{2f^2\sqrt{1-x^2}}{4(\Delta+x)^2 - 4f^2 x(\Delta+x) + f^4}\Theta(1-|x|),\qquad (4)$$

where $x = \hbar(\omega_0 - \omega)/2J$, Θ is the Heaviside step function, T is the temperature, and k_B is Boltzmann's constant. On the other hand, the imaginary part of the susceptibility, caused by the local levels, is

$$\chi''_{(l)} = \tanh\left[\frac{\hbar\omega}{2k_BT}\right]\left[\delta(\varepsilon_1 - \hbar\omega)\Theta(f^2 - 2 + 2\Delta)\left(-\frac{1}{f^2-1} + \frac{f^2}{2(\Delta^2 + f^2 - 1 + \Delta\sqrt{\Delta^2 + f^2 - 1})}\right)\right.$$

$$\left. + \delta(\varepsilon_2 - \hbar\omega)\Theta(f^2 - 2 - 2\Delta)\left(-\frac{1}{f^2-1} + \frac{f^2}{2(\Delta^2 + f^2 - 1 - \Delta\sqrt{\Delta^2 + f^2 - 1})}\right)\right],\qquad (5)$$

where $\delta(x)$ is the Dirac delta-function. One can see that for $J' = 0$ (i.e., for $f = 0$) the contribution to the imaginary part of the susceptibility from the second local level is zero, while the one from the first level becomes $\chi''_{(l)} \sim \delta(\omega_1 - \omega)$, i.e., it is the imaginary part of the susceptibility of a single nanoparticle (a single molecule), and the contribution from the band exciton states is zero. On the other hand, for $f = 1$ and $\Delta = 0$ we obtain the imaginary part of the susceptibility $\chi''_{(b)}$ being the one of the homogeneous one-dimensional J-aggregate chain, $\chi''_{(b)} \sim \sqrt{1-x^2}\Theta(1-|x|)$. Using the Kramers–Kronig relations we can obtain the real part of the dynamical susceptibility $\chi'(\omega) = \pi^{-1}\mathcal{P}\int d\omega' \chi''(\omega')/(\omega - \omega')$, where $\mathcal{P}$ denotes the principal part of the integral. Then using the relation

$$\epsilon(\omega) = 1 + \chi(\omega)\qquad (6)$$

we obtain the dynamical permittivity caused by the nanoparticle coupled to the exciton system of the one-dimensional J-aggregate (we normalize everything by the vacuum permittivity ϵ_0, so we deal with the relative dynamical permittivity). Notice that the imaginary part of the dynamical permittivity is related to the dynamical conductivity σ via $\epsilon'' = \sigma/\omega$. Figures 1 and 2 present the real and imaginary parts of that permittivity (here and below we present the results as the function of the light wavelength $\lambda = 2\pi c/\omega$, where c is the speed of light). In our calculations we used the fact that the relaxation rate in J-aggregates is usually much larger than in a single molecule (or in a nanoparticle) γ_0 [17].

For calculation of the results, presented in Figs. 1 and 2, we used the following set of parameters: $\lambda_0 = 2\pi c/\omega_0 = 513$ nm, $\lambda_1 = 2\pi c/\omega_1 = 556$ nm, $\lambda_T = 2\pi\hbar c/T = 20000$ nm, $\lambda_J = 2\pi\hbar c/|J| = 11111$ nm and $f = 5$ (the strong cou-
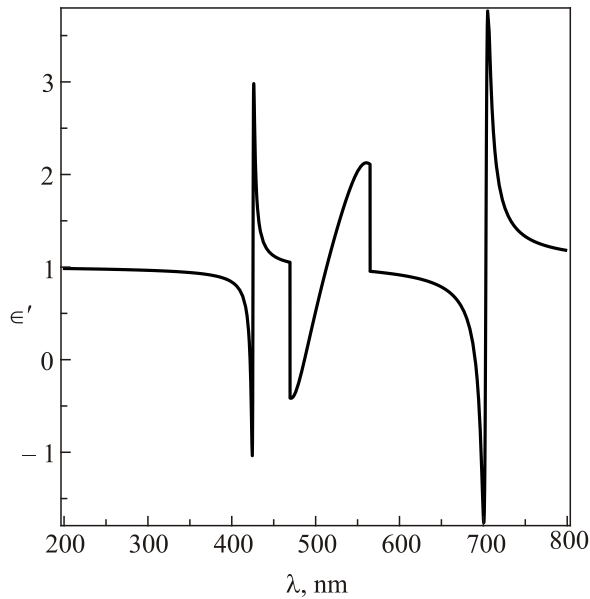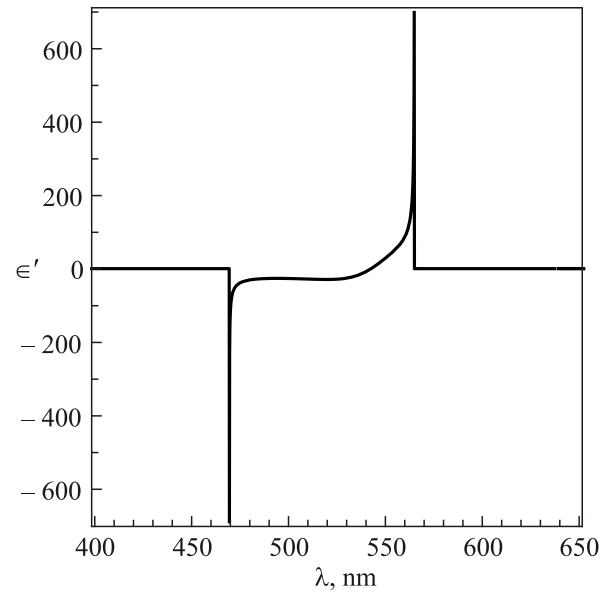
Fig. 1. The real part of the relative dynamical permittivity (in arbitrary units) of the nanoparticle (a molecule) strongly interacting with the one-dimensional *J*-aggregate as a function of the wavelength of the electromagnetic field λ. One can see the contributions from the band exciton states and from the local levels split below and above the band states.

Fig. 3. The real part of the relative dynamical permittivity (in arbitrary units) of the nanoparticle (a molecule) weakly interacting with the one-dimensional *J*-aggregate as a function of the wavelength of the electromagnetic field λ. Only band exciton states contribute.
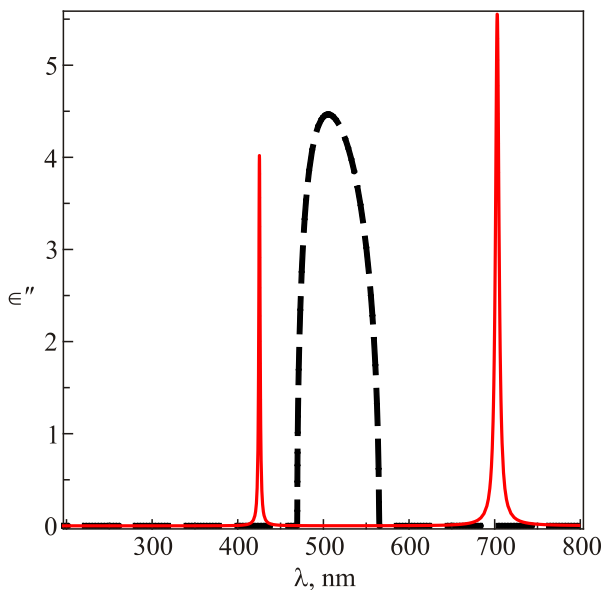

Fig. 2. The imaginary part of the relative dynamical permittivity (in arbitrary units) of the nanoparticle (a molecule) strongly coupled to the one-dimensional *J*-aggregate as a function of the wavelength of the electromagnetic field λ with the contributions from the band exciton states (the dashed line) and from the local levels (the solid line).
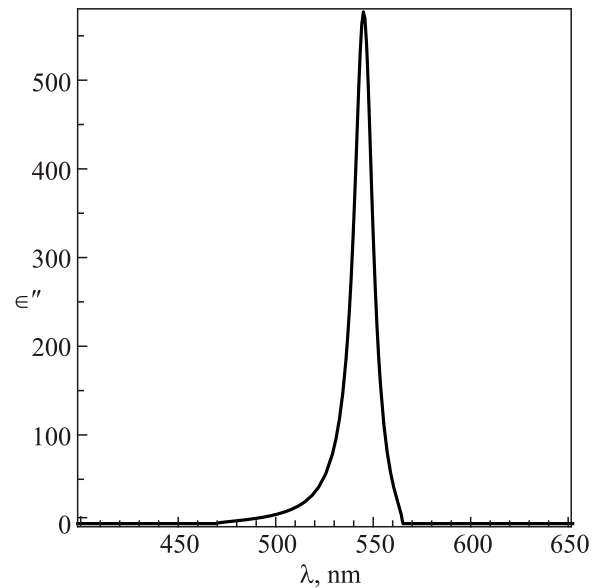

Fig. 4. The imaginary part of the relative dynamical permittivity (in arbitrary units) of the nanoparticle (a molecule) weakly coupled to the one-dimensional *J*-aggregate as a function of the wavelength of the electromagnetic field λ with the contributions from the band exciton states only.

pling of the nanoparticle to the *J*-aggregate). Notice that the wavelengths, related to the local levels, are very different from λ_1 (425 and 703 nm) due to the strong coupling of the particle to the *J*-aggregate. For comparison, in Figs. 3 and 4

we present the results of calculation of the relative dynamical permittivity for the nanoparticle, weakly coupled to the *J*-aggregate chain. In this case we use $f = 0.5$ with $\lambda_1 = 541$ nm and $\lambda_J = 7143$ nm (all other parameters are the same as in Figs. 1 and 2).
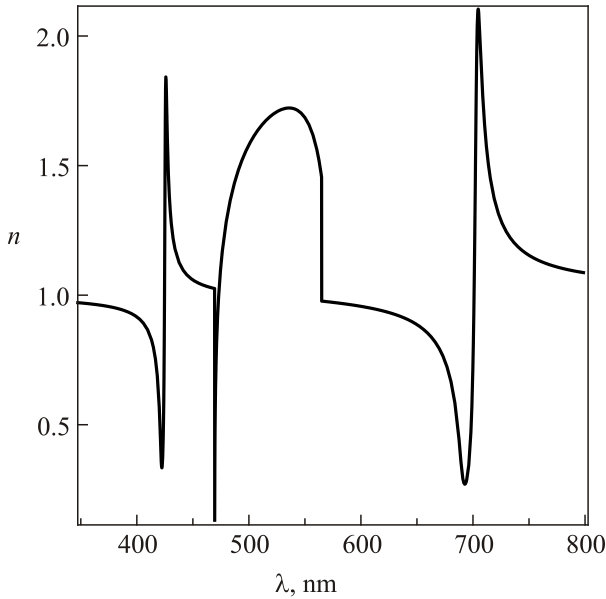
Fig. 5. The dynamical refractive index (in arbitrary units) of the nanoparticle (a molecule) strongly interacting with the one-dimensional *J*-aggregate as a function of the wavelength of the electromagnetic field λ.
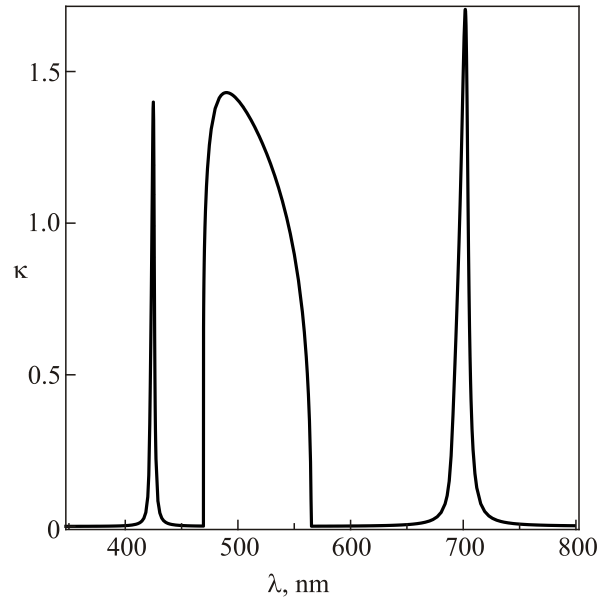

Fig. 6. The dynamical extinction coefficient (in arbitrary units) of the nanoparticle (a molecule) strongly coupled to the one-dimensional *J*-aggregate as a function of the wavelength of the electromagnetic field λ.

For this set of parameters there are no local levels, and the dynamical permittivity of the nanoparticle is determined only by the exciton band states of the *J*-aggregate chain. Notice that both the real and the imaginary parts of the dynamical permittivity in this case is much larger than the ones for the strong coupling case, see Figs. 1 and 2.

Then we calculate the dynamical refractive index $n(\omega)$ caused by the nanoparticle (or a molecule) coupled to the *J*-aggregate chain $\epsilon(\omega) = n^2(\omega)$. (Notice that the refractivity is $N = 1 - n$.) The real part of the refractive index (which indicates the phase velocity) is related to the relative permittivity as

$$n = 2^{-1/2}\left[\epsilon' + \sqrt{(\epsilon')^2 + (\epsilon'')^2}\right]^{1/2}. \tag{7}$$

The imaginary part of the refractive index κ (also known as the extinction coefficient, or the mass attenuation coefficient, is related to the absorption coefficient α via $\kappa = c\alpha / 2\omega$) can be written as

$$\kappa = \frac{\epsilon''}{2^{1/2}\left[\epsilon' + \sqrt{(\epsilon')^2 + (\epsilon'')^2}\right]^{1/2}}. \tag{8}$$

The absorption coefficient is connected with the penetration depth $\delta_p = \alpha^{-1}$, i.e., it shows how deep the light can penetrate into the material. Notice that the skin depth δ_e is twice bigger than the penetration depth. The refractive index and the extinction coefficient are related to the phase con-

stant β and the attenuation constant α (the imaginary and the real part of the propagation constant γ), respectively.

In Figs. 5 and 6 we present the results of calculation of the dynamical refractive index and the extension coefficient for the nanoparticle (a molecule) strongly coupled to the one-dimensional *J*-aggregate. We used the same parameters as in Figs. 1, 2.

In summary, we have shown that a nanoparticle (a single molecule), coupled to the one-dimensional quantum molecular aggregate manifests special features of its optical characteristics, like the dynamical permittivity and the refractive index. Depending on the values of the coupling of the particle and its own frequency, with respect to the own frequency of the aggregated molecules, and the strength of the aggregation, the real and imaginary parts of the dynamical permittivity and the refractive index of the molecule manifest the contribution from the exciton band, or/and the ones from the local level(s) caused by the nanoparticle (or a single molecule). It is very different from the dynamical characteristics of the single nanoparticle (or a molecule). Hence, the optical characteristics of the nanoparticle coupled to Frenkel excitons of the *J*-aggregate are stronly affected by the environment. In some cases, only the exciton band contributes to the optical characteristics of the nanoparticle (a molecule).

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