

Intermolecular coupling fluctuation effect on absorption and emission spectra for LH4 ring

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Abstract—Optical properties of the cyclic antenna unit LH4 of the bacterial photosystem from purple bacterium *Rhodospseudomonas palustris* are studied in present paper. Simulated absorption and steady state fluorescence spectra of this molecular system are presented. In addition, localization of exciton states is modeled. The cumulant-expansion method of Mukamel et al. is used for the calculation of spectral responses of the system with exciton-phonon coupling. Dynamic disorder, interaction with a bath, in Markovian approximation simultaneously with two different types of uncorrelated static disorder (the local excitation energy fluctuations and the transfer integral fluctuations) are taking into account in our simulations. For all calculations the software package *Mathematica* was found very useful.

Keywords—LH2, LH4, fluorescence spectrum, absorption spectrum, static and dynamic disorder, exciton states, localization, *Mathematica*

I. INTRODUCTION

Knowledge of optical properties could shed more light on initial ultrafast phases of bacterial photosynthesis. These initial phases start with the absorption of a solar photon by one of the light-harvesting pigment-protein complexes and transferring the excitation energy to the photosynthetic reaction center, where a charge separation is initiated. These ultrafast events have been extensively investigated. Knowledge of the microscopic structure of some photosynthetic systems, e.g., photosynthetic systems of purple bacteria, invokes during last twenty years long and intensive effort of many theoretical and experimental laboratories. No final conclusion about the character of excited states, energy transfer, etc. can be generally drawn.

The antenna systems of photosynthetic units from purple bacteria are formed by ring units LH1, LH2, LH3, and LH4. The geometric structure is known

in great detail from X-ray crystallography, e.g., for the LH2 complex of the purple bacterium *Rhodospseudomonas acidophila* [1], [2]. The bacteriochlorophyll (BChl) molecules are organized in two concentric rings. One ring features a group of nine well-separated BChl molecules (B800) with absorption band at about 800 nm. The other ring consists of eighteen closely packed BChl molecules (B850) absorbing around 850 nm. LH2 complexes from other purple bacteria have analogous ring structures. The similar ring structure but with larger number of BChl molecules is supposed for LH1 rings. The intermolecular distances under 1 nm in rings determine strong exciton couplings between corresponding pigments. Complexes LH3 and LH4 with modified structure (*Rhodospseudomonas palustris*) have been also discovered [3]. While the B850 dipole moments in LH2 ring have tangential arrangements, in the LH4 one they are oriented more radially. Mutual interaction of the nearest neighbour BChls is therefore two times smaller and has opposite sign. Besides ring with sixteen BChl molecules, an additional BChl ring is also present in LH4 complex.

Due to the strong interaction between BChl molecules, an extended Frenkel exciton states model is considered in our theoretical approach. In spite of extensive investigation, the role of the protein moiety in governing the dynamics of the excited states has not been totally clear yet. At room temperature the solvent and protein environment fluctuate with characteristic time scales ranging from femtoseconds to nanoseconds. The simplest approach is to substitute fast fluctuations by dynamic disorder and slow fluctuations by static disorder.

Static disorder effect on the anisotropy of fluorescence for LH2 rings was studied by Kumble and Hochstrasser [4] and Nagarajan et al. [5]–[7]. We extended these investigations by consideration of dynamic disorder. We studied this effect for simple model systems [8]–[10] and then for the models of LH2 rings [11], [12]. Various types of the uncorrelated static disorder (in local excitation energies, in transfer integrals, etc.) and correlated one (e.g., elliptical deformation) were used in the past [12]–[14], [39] and also different arrangements of optical dipole moments were compared [16]–[18].

Recently we have focused on the modeling of the steady state fluorescence and absorption spectra for LH2 complex [20]. In addition, we have investigated the exciton state localization of this complex and also time

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dependence of exciton density matrix [23], [24]. Main goal of this paper is the presentation of the steady state fluorescence and absorption spectra simulations for LH4 ring. In our simulations the dynamic disorder (interaction with the phonon bath) in Markovian approximation is taken into account simultaneously with two different types of Gaussian uncorrelated static disorder (fluctuations of local excitation energies and fluctuations of transfer integrals). We compare the results for two above mentioned types of static disorder.

The remainder of this article is organized as follows. In Section II, we give the model of molecular ring and review the theory we have used. In Section III, we mention computational point of view and used software. In Section IV, we present the results of our absorption and steady state fluorescence spectra simulations. Finally, in Section V, we draw some conclusions.

II. PHYSICAL MODEL

We assume that only one excitation is present on the ring after an impulsive excitation. The Hamiltonian of an exciton in the ideal ring coupled to a bath of harmonic oscillators reads

$$H = H_{\text{ex}}^0 + H_{\text{ph}} + H_{\text{ex-ph}} + H_s^x. \quad (1)$$

Here the first term,

$$H_{\text{ex}}^0 = \sum_{m,n(m \neq n)} J_{mn} a_m^\dagger a_n, \quad (2)$$

corresponds to an exciton, e.g. the system without any disorder. The operator a_m^\dagger (a_m) creates (annihilates) an exciton at site m , J_{mn} (for $m \neq n$) is the so-called transfer integral between sites m and n . The second term,

$$H_{\text{ph}} = \sum_q \hbar \omega_q b_q^\dagger b_q, \quad (3)$$

represents phonon bath in the harmonic approximation (the phonon creation and annihilation operators are denoted by b_q^\dagger and b_q , respectively). The third term in (1),

$$H_{\text{ex-ph}} = \frac{1}{\sqrt{N}} \sum_m \sum_q G_q^m \hbar \omega_q a_m^\dagger a_m (b_q^\dagger + b_q), \quad (4)$$

describes exciton-phonon interaction which is assumed to be site-diagonal and linear in the bath coordinates (the term G_q^m denotes the exciton-phonon coupling constant). The last term in (1), H_s^x , corresponds to static disorder. Influence of uncorrelated static disorder is modeled by:

- I. the local excitation energy fluctuations $\delta \varepsilon_n$ with Gaussian distribution and standard deviation Δ

$$H_s^I = \sum_n \delta \varepsilon_n a_n^\dagger a_n. \quad (5)$$

- II. the transfer integral fluctuations δJ_{mn} (nearest neighbour approximation) with Gaussian distribution and standard deviation Δ_J

$$H_s^{II} = \sum_{m,n(m \neq n)} \delta J_{mn} a_m^\dagger a_n, \quad (6)$$

Inside one ring the pure exciton Hamiltonian can be diagonalized using the wave vector representation with corresponding delocalized "Bloch" states α and energies E_α . Considering homogeneous case with only nearest neighbour transfer matrix elements

$$J_{mn} = J_0(\delta_{m,n+1} + \delta_{m,n-1}) \quad (7)$$

and using Fourier transformed excitonic operators (Bloch representation)

$$a_\alpha = \sum_n e^{i\alpha n} a_n, \quad \alpha = \frac{2\pi}{N} l, \quad l = 0, \pm 1, \dots, \pm \frac{N}{2}, \quad (8)$$

the simplest exciton Hamiltonian in α - representation reads

$$H_{\text{ex}}^0 = \sum_\alpha E_\alpha a_\alpha^\dagger a_\alpha, \quad E_\alpha = -2J_0 \cos \alpha. \quad (9)$$

The cumulant-expansion method of Mukamel et al. [25], [26] is used for the calculation of spectral responses of the system with exciton-phonon coupling. Absorption $OD(\omega)$ and steady-state fluorescence $FL(\omega)$ spectrum can be expressed as

$$OD(\omega) = \omega \sum_\alpha d_\alpha^2 \times \text{Re} \int_0^\infty dt e^{i(\omega - \omega_\alpha)t - g_{\alpha\alpha\alpha\alpha}(t) - R_{\alpha\alpha\alpha\alpha}t}, \quad (10)$$

$$FL(\omega) = \omega \sum_\alpha P_\alpha d_\alpha^2 \times \text{Re} \int_0^\infty dt e^{i(\omega - \omega_\alpha)t + i\lambda_{\alpha\alpha\alpha\alpha}t - g_{\alpha\alpha\alpha\alpha}^*(t) - R_{\alpha\alpha\alpha\alpha}t}. \quad (11)$$

Here $\vec{d}_\alpha = \sum_n c_n^\alpha \vec{d}_n$ is the dipole strength of eigenstate α , c_n^α are the expansion coefficients of the eigenstate α in site representation and P_α is steady state population of the eigenstate α . The inverse lifetime of exciton state $R_{\alpha\alpha\alpha\alpha}$ [27] is given by the elements of Redfield tensor $R_{\alpha\beta\gamma\delta}$ [28]. It is a sum of the relaxation rates between exciton states, $R_{\alpha\alpha\alpha\alpha} = -\sum_{\beta \neq \alpha} R_{\beta\beta\alpha\alpha}$. The g -function and λ -values in (11) are given by

$$g_{\alpha\beta\gamma\delta} = - \int_{-\infty}^\infty \frac{d\omega}{2\pi\omega^2} C_{\alpha\beta\gamma\delta}(\omega) \times \left[\coth \frac{\omega}{2k_B T} (\cos \omega t - 1) - i(\sin \omega t - \omega t) \right], \quad (12)$$

$$\lambda_{\alpha\beta\gamma\delta} = - \lim_{t \rightarrow \infty} \frac{d}{dt} \text{Im} \{ g_{\alpha\beta\gamma\delta}(t) \} =$$

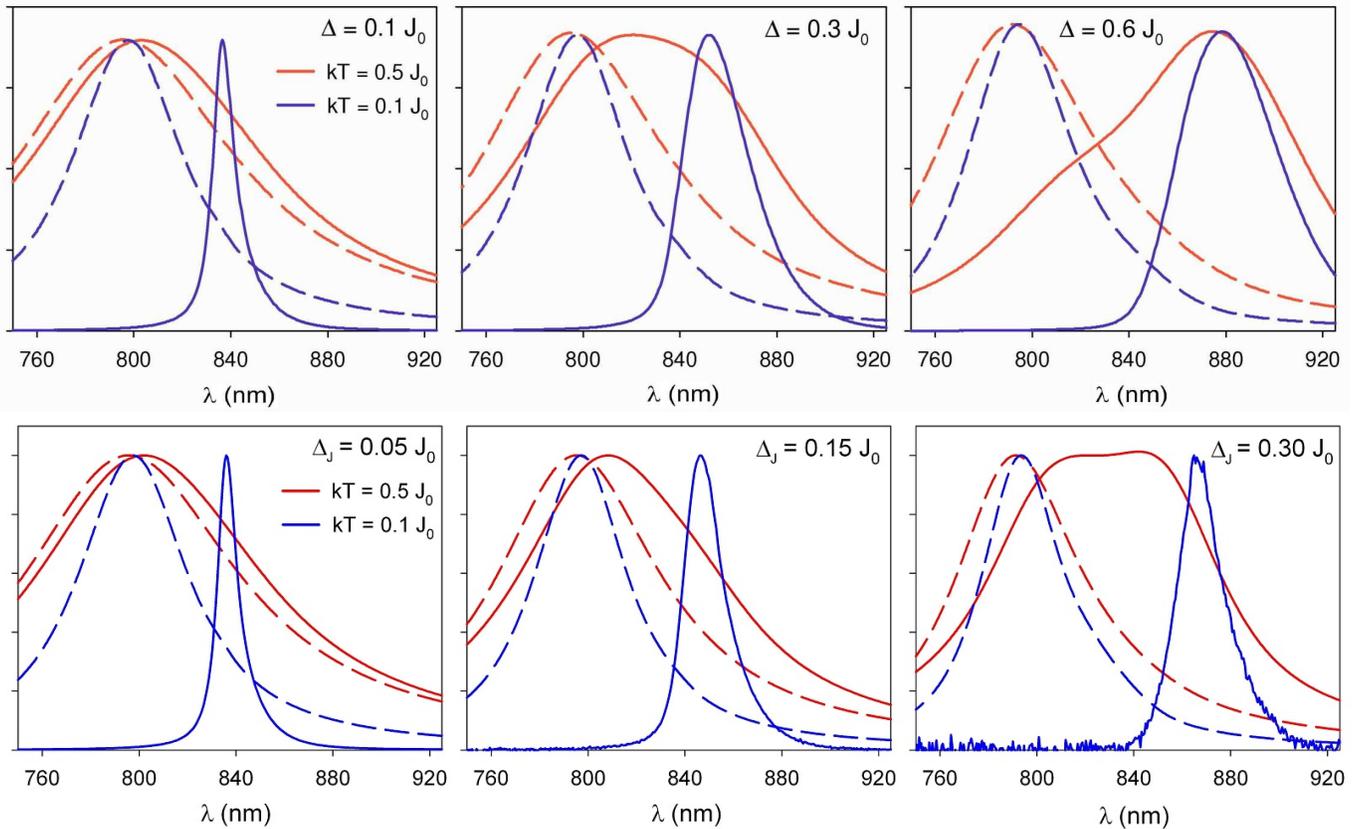


Fig. 1. Resulting absorption $OD(\omega)$ (dashed lines) and steady-state fluorescence $FL(\omega)$ spectra (solid lines) of LH4 at room temperature $kT = 0.5 J_0$ (red lines) and low temperature $kT = 0.1 J_0$ (blue lines), averaged over 2000 realizations of Gaussian uncorrelated static disorder in local excitation energies $\delta\varepsilon$ – three strengths $\Delta = 0.1, 0.3, 0.6 J_0$ (first row) and Gaussian uncorrelated static disorder in nearest neighbour transfer integrals δJ_{mn} – three strengths $\Delta_J = 0.05, 0.15, 0.30 J_0$ (second row).

$$= \int_{-\infty}^{\infty} \frac{d\omega}{2\pi\omega} C_{\alpha\beta\gamma\delta}(\omega). \quad (13)$$

The matrix of the spectral densities $C_{\alpha\beta\gamma\delta}(\omega)$ in the eigenstate (exciton) representation reflects one-exciton states coupling to the manifold of nuclear modes. In what follows only a diagonal exciton phonon interaction in site representation is used (see (1)), i.e., only fluctuations of the pigment site energies are assumed and the restriction to the completely uncorrelated dynamical disorder is applied. In such case each site (i.e. each chromophore) has its own bath completely uncoupled from the baths of the other sites. Furthermore it is assumed that these baths have identical properties [13], [29], [30]

$$C_{mm'm'n'}(\omega) = \delta_{mn}\delta_{mm'}\delta_{nn'}C(\omega). \quad (14)$$

After transformation to exciton representation we have

$$C_{\alpha\beta\gamma\delta}(\omega) = \sum_n c_n^\alpha c_n^\beta c_n^\gamma c_n^\delta C(\omega). \quad (15)$$

Various models of spectral density of the bath are used in literature [27], [31], [32]. In our present investigation

we have used the model of Kühn and May [31]

$$C(\omega) = \Theta(\omega) j_0 \frac{\omega^2}{2\omega_c^3} e^{-\omega/\omega_c} \quad (16)$$

which has its maximum at $2\omega_c$.

Delocalization of the exciton states contributing to the steady state FL spectrum can be characterized by the thermally averaged participation ratio $\langle PR \rangle$, which is given by

$$\langle PR \rangle = \frac{\sum_\alpha PR_\alpha e^{-\frac{E_\alpha}{k_B T}}}{\sum_\alpha e^{-\frac{E_\alpha}{k_B T}}}, \quad (17)$$

where

$$PR_\alpha = \sum_{n=1}^N |c_n^\alpha|^4. \quad (18)$$

III. COMPUTATIONAL POINT OF VIEW

To have steady state fluorescence spectrum $FL(\omega)$ and absorption spectrum $OD(\omega)$, it is necessary to calculate single ring $FL(\omega)$ spectrum and $OD(\omega)$ spectrum for large number of different static disorder realizations created by random number generator. Finally these results have to be averaged over all realizations of static

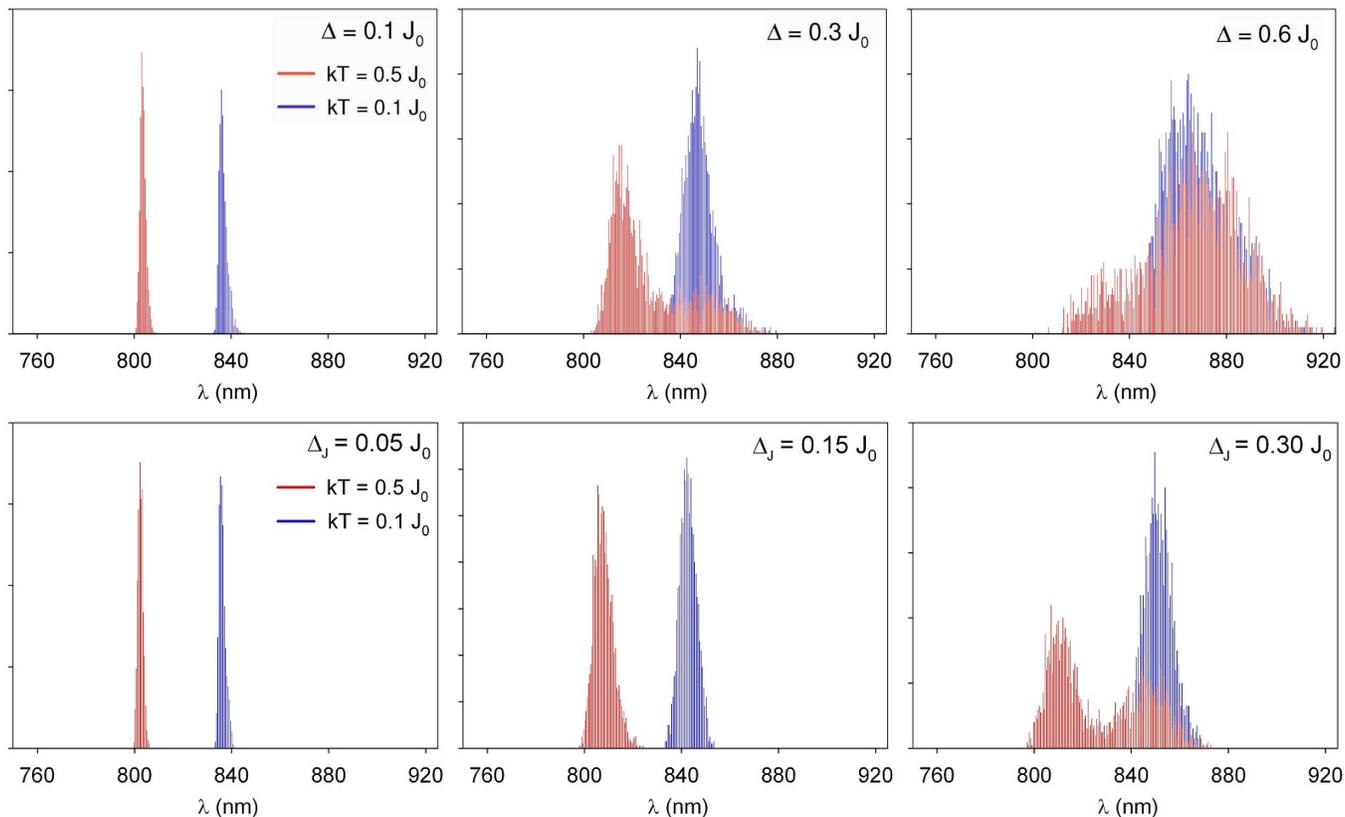


Fig. 2. The peak position distributions of calculated steady-state single ring fluorescence spectra $FL(\omega)$ of LH4 ring at room temperature $kT = 0.5 J_0$ (red lines) and low one $kT = 0.1 J_0$ (blue lines) for 2000 realizations of Gaussian uncorrelated static disorder in local excitation energies $\delta\varepsilon$ – three strengths $\Delta = 0.1, 0.3, 0.6 J_0$ (first row) and Gaussian uncorrelated static disorder in nearest neighbour transfer integrals δJ_{mn} – three strengths $\Delta_J = 0.05, 0.15, 0.30 J_0$ (second row).

disorder. Time evolution of exciton density matrix has to be calculate also for each realization of static disorder. That is why it was necessary to put through numerical integrations for each realization of static disorder (see (11)).

For the most of our calculations the software package *Mathematica* [33] was used. This package is very convenient and has very wide range of applications in different areas of research [34]–[36] not only for symbolic calculations [37] which are needed for expression of all required quantities, but it can be used also for numerical ones [38]. That is why the software package *Mathematica* was used by us as for symbolic calculations as for numerical integrations and also for final averaging of results over all realizations of static disorder.

As concerns the time development of our system, for the solution of the Redfield equation we have used the program written in Fortran and standard Runge-Kutta method.

IV. RESULTS

Two above mentioned types of Gaussian uncorrelated static disorder (fluctuations of local excitation energies

$\delta\varepsilon_n$ and fluctuations of nearest neighbor transfer integrals δJ_{mn}) have been taken into account in our simulations simultaneously with dynamic disorder in Markovian approximation. Dimensionless energies normalized to the transfer integral $J_{12} = J_0$ in LH2 ring and dimensionless time τ have been used. Estimation of J_0 varies in literature between 250 cm^{-1} and 400 cm^{-1} . The values of transfer integrals in LH4 ring differ from that of LH2 ring. Furthermore, stronger dimerization can be found in LH4 in comparison with LH2 [3]. Therefore we have taken the values of transfer integrals in LH4 ring as follows: $J_{12}^{LH4} = -0.5J_{12}^{LH2} = -0.5J_0$, $J_{23}^{LH4} = 0.5J_{12}^{LH4} = -0.25J_0$. All our simulations of LH4 spectra have been done with the same values of J_0 and unperturbed transition energy from the ground state ΔE_0 , that we found for LH2 ring [21].

Contrary to Novoderezhkin et al. [27], different model of spectral density (the model of Kühn and May [31]) has been used. In agreement with our previous results [16], [19] we have used $j_0 = 0.4 J_0$ and $\omega_c = 0.212 J_0$ (see (16)). The strengths of uncorrelated static disorder has been taken in agreement with [20]: $\Delta = 0.1, 0.3, 0.6 J_0$; $\Delta_J = 0.05, 0.15, 0.30 J_0$.

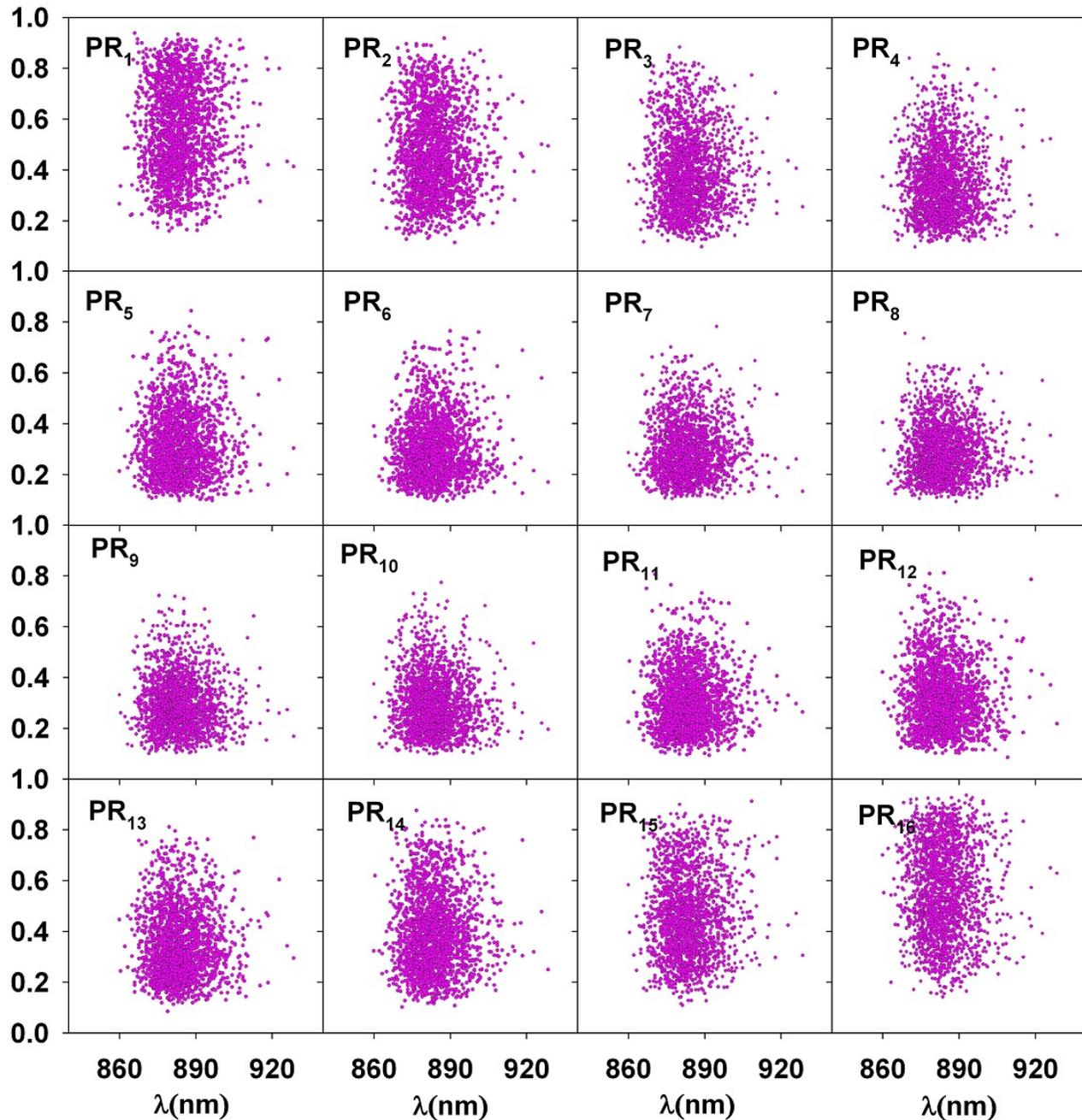


Fig. 3. The distributions of PR_α values ($\alpha = 1, \dots, 16$) of LH4 ring as a function of FL spectrum peak position at room temperature $kT = 0.5 J_0$ calculated for 2000 realizations of Gaussian uncorrelated static disorder in local excitation energies $\delta\varepsilon$, for the highest strength $\Delta = 0.6 J_0$.

Resulting absorption $OD(\omega)$ and steady state fluorescence spectra $FL(\omega)$ for LH4 ring at room temperature ($kT = 0.5 J_0$) and low one ($kT = 0.1 J_0$) averaged over 2000 realizations of static disorder for three strengths Δ and three strengths Δ_J can be seen in Fig. 1.

Peak position of single ring fluorescence spectrum depend on the realization of static disorder and also on the temperature. To investigate this effect we calculate peak position distributions of simulated fluorescence spectra

for above mentioned types of static disorder and for low ($kT = 0.1 J_0$) and room ($kT = 0.5 J_0$) temperature. For each static disorder type we consider three different static disorder strengths (see above). Results are shown in Fig. 2.

The distributions of the participation ratios PR_α for each of sixteen eigenstates α can be seen in Fig. 3 for highest strength of static disorder in local excitation energies $\delta\varepsilon_n$ ($\Delta = 0.6 J_0$) The same but for

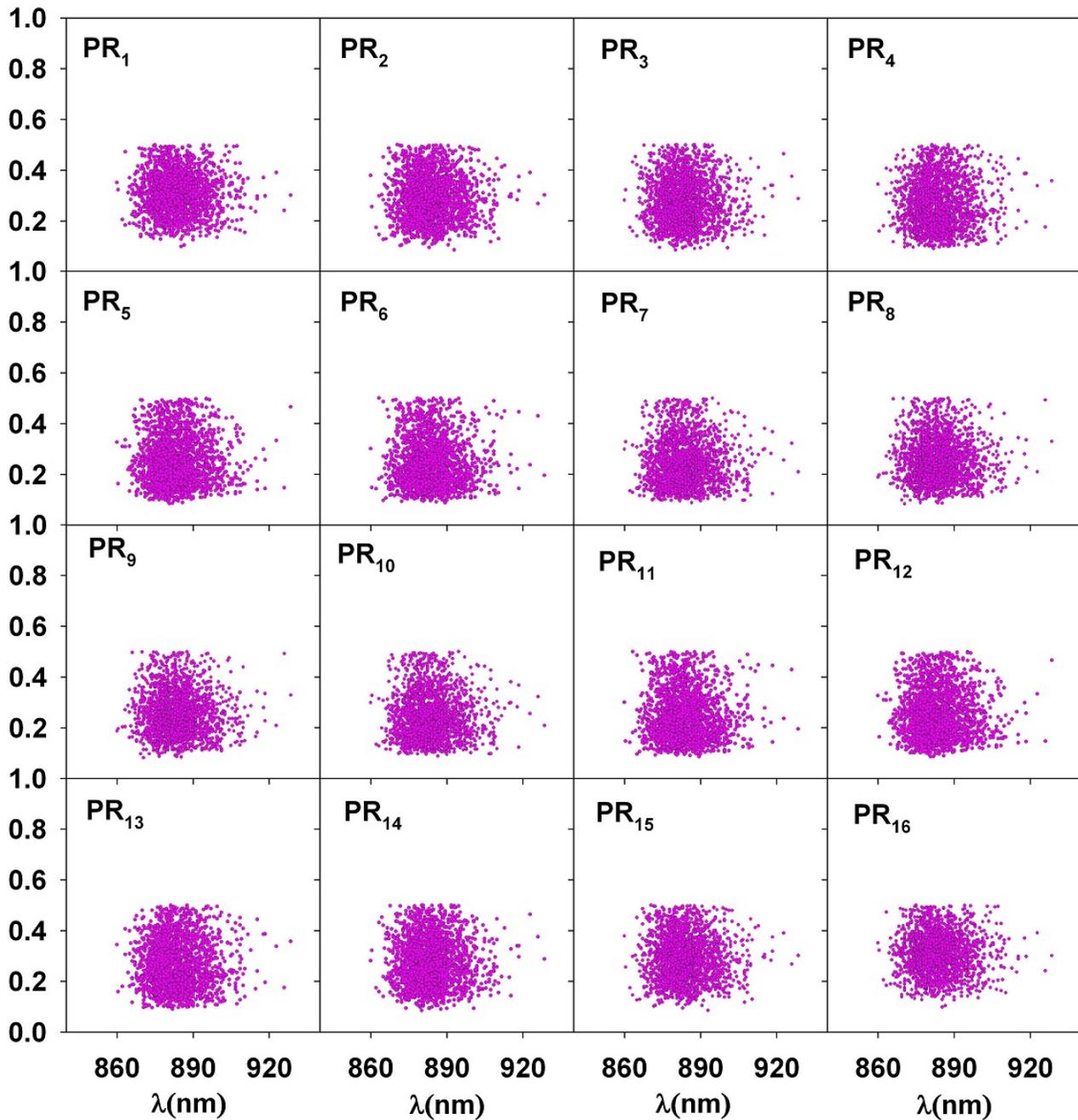


Fig. 4. The distributions of PR_α values ($\alpha = 1, \dots, 16$) of LH4 ring as a function of FL spectrum peak position at room temperature $kT = 0.5 J_0$ calculated for 2000 realizations of Gaussian uncorrelated static disorder in transfer integrals δJ_{mn} , for the highest strength $\Delta_J = 0.30 J_0$.

highest strength of static disorder in transfer integrals $\delta J_{mn}(\Delta_J = 0.30 J_0)$ is presented in Fig. 4.

Fig. 5 and Fig. 6 show the values of thermally averaged participation ratio $\langle PR \rangle$ for LH4 ring as a function of FL spectrum peak position at room temperature $kT = 0.5 J_0$ and low one $kT = 0.1 J_0$ calculated for 2000 realizations of two above mentioned types of Gaussian uncorrelated static disorder.

V. CONCLUSIONS

Software package *Mathematica* has been found by us very useful for the simulations of the molecular ring spectra. Our previous results, simulations of the anisotropy of fluorescence [17], [18], have given the relation between the strengths (Δ , Δ_J) of two above mentioned types of Gaussian uncorrelated static disorder: $2\Delta_J \doteq \Delta$. From the comparison of our present simulations of steady-state fluorescence $FL(\omega)$ and absorption

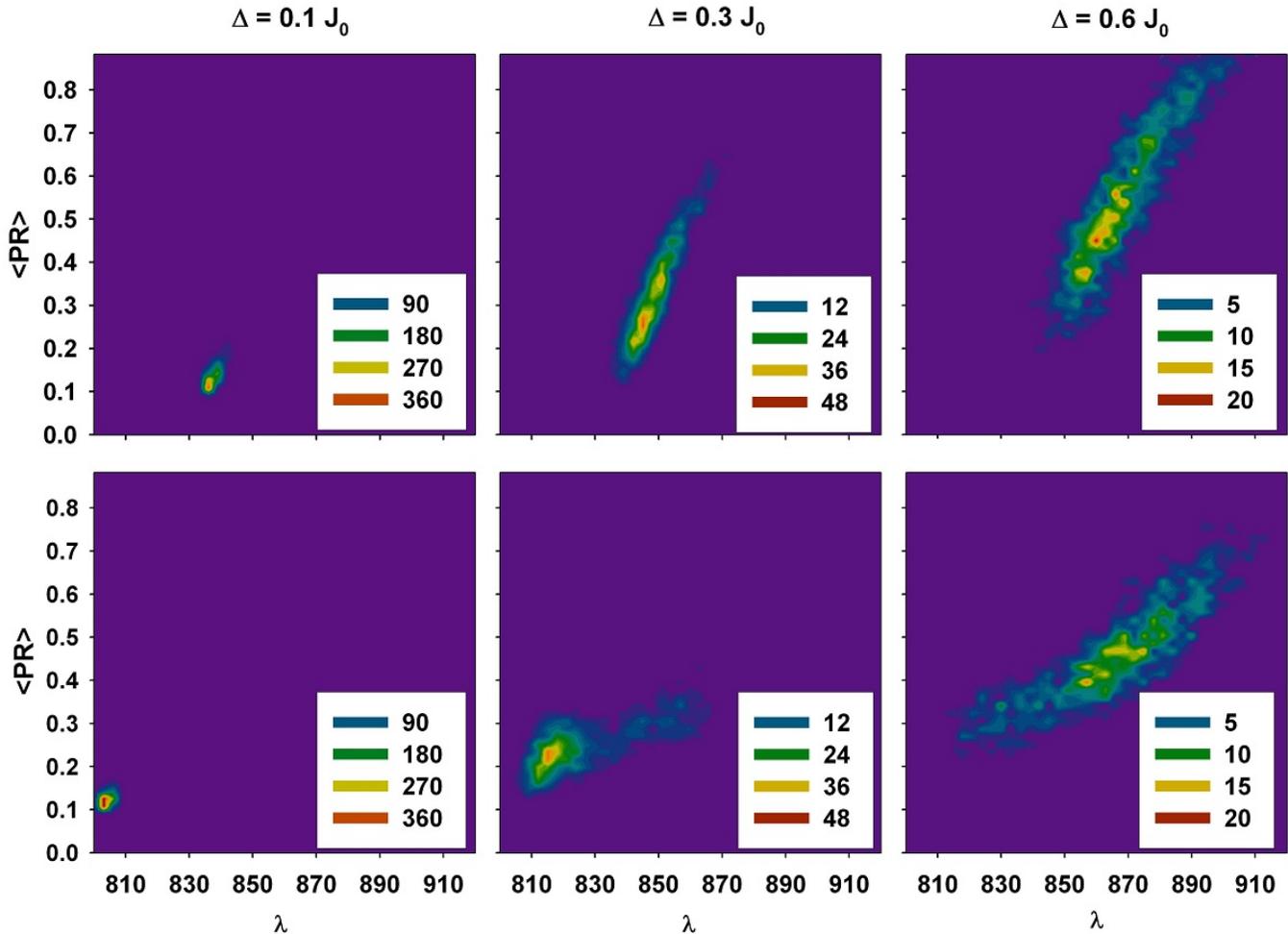


Fig. 5. The distribution of $\langle PR \rangle$ values of LH4 ring as a function of FL spectrum peak position at low temperature $kT = 0.1 J_0$ (first row) and room temperature $kT = 0.5 J_0$ (second row), calculated for 2000 realizations of Gaussian uncorrelated static disorder in local excitation energies $\delta\varepsilon_n$ – three strengths $\Delta = 0.1, 0.3, 0.6 J_0$.

$OD(\omega)$ spectra for LH4 ring (Fig. 1) following conclusions can be done.

At low temperature ($kT = 0.1 J_0$) the fluorescence spectral lines are wider in case of the static disorder type I (fluctuations of local excitation energies $\delta\varepsilon_n$) in comparison with static disorder type II (fluctuations of transfer integrals δJ_{mn}). In case of room temperature ($kT = 0.5 J_0$) this effect is not so visible because of spectral line widening caused by dynamic disorder.

Without any static disorder, optically active states in LH4 are only two high energy degenerate states $\alpha = \pm 7$. For growing strength of static disorder the degeneracy of exciton states is lifted and dipole strength is more and more redistributed among other exciton states. That is why also other exciton states become optically active. Steady state occupation probabilities are higher for exciton states with lower energy. Therefore preferably lower exciton states contribute to steady state fluorescence spectrum. In case of LH4 almost all exciton

states have lower energy than the exciton states $\alpha = \pm 7$. This is the reason of significant fluorescence spectral line shift to higher wavelengths (lower energies) for LH4 ring. This shift is higher in case of static disorder type I and is not visible for absorption lines.

At room temperature ($kT = 0.5 J_0$) the fluorescence spectral lines are shifted to lower wavelengths in comparison with low temperature ($kT = 0.1 J_0$). This is caused by the fact that higher exciton states are occupied more probably at room temperature. The shift is again higher in case of static disorder type I.

From Fig. 1 and Fig. 2 it can be seen the formation of second peak in fluorescence spectrum for higher strengths of static disorder. The transfer to the second peak is faster in case of static disorder type I (fluctuations of local excitation energies $\delta\varepsilon_n$). The formation of second peak is not visible in case of low temperature ($kT = 0.1 J_0$).

If we compare distributions of participation ratios PR_k

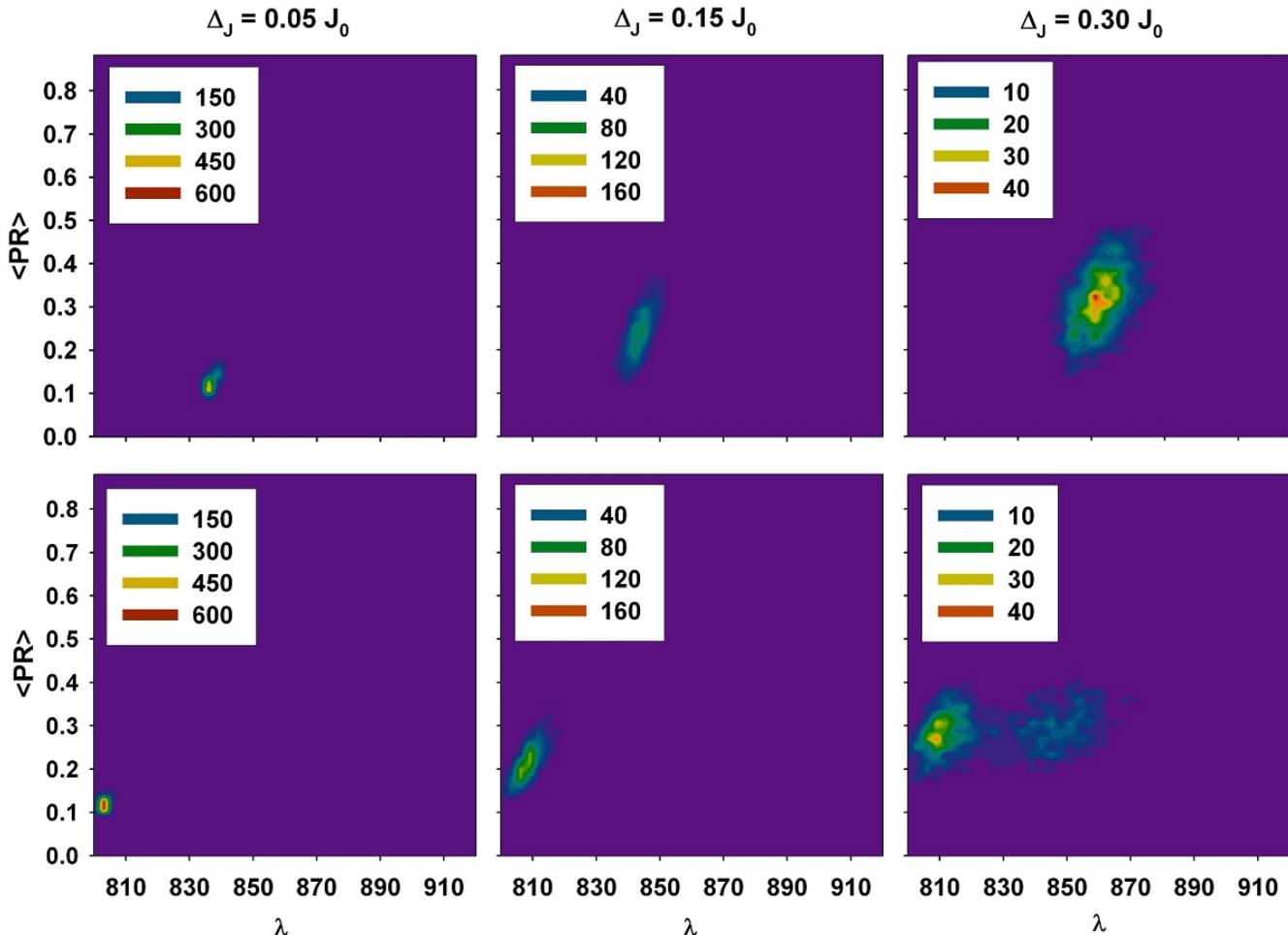


Fig. 6. The distribution of $\langle PR \rangle$ values of LH4 ring as a function of FL spectrum peak position at low temperature $kT = 0.1 J_0$ (first row) and room temperature $kT = 0.5 J_0$ (second row), calculated for 2000 realizations of Gaussian uncorrelated static disorder in transfer integrals δJ_{mn} – three strengths $\Delta_J = 0.05, 0.15, 0.30 J_0$.

for both types of static disorder, we can see higher values of PR_k in case of static disorder type I (fluctuations of local excitation energies $\delta\varepsilon_n$). It means higher localization of exciton states in case of static disorder type I.

From Fig. 5 and Fig. 6 it can be seen growing of $\langle PR \rangle$ values in case of higher strength of static disorder for both types of static disorder. On the other hand, comparison of Fig. 5 and Fig. 6 shows significant differences in $\langle PR \rangle$ values for different types of static disorder. The participation ratio $\langle PR \rangle$ reaches values about 0.9 for highest strength of static disorder type I (fluctuations of local excitation energies $\delta\varepsilon_n$, $\Delta = 0.6 J_0$). Contrary the $\langle PR \rangle$ values are only about 0.5 for highest strength of static disorder type II (fluctuations of transfer integrals δJ_{mn} , $\Delta_J = 0.30 J_0$). It also corresponds to more localized exciton states in case of static disorder type I.

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