Effects of Electron-Vibrational Interaction in Exciton-Polariton Luminescence and Relaxation. Time-dependent Polariton Luminescence Spectrum.

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The non-equilibrium polariton luminescence spectrum is calculated within the framework of the non-Markovian molecular relaxation model. The model accounts for both the high-frequency (HF) and the low frequency (LF) optically active (OA) molecular vibrations. For the calculation of the composite vibration-polariton operators, we employ the Lang-Firsov transformation for the HFOA vibration mode and account for the classical LFOA vibrations stochastically. We also propose a polariton fluorescence mechanism in which the spreading of the two-particle polariton expectation value outside the nano-sample is considered as the decay of the composite polariton particle. This opens a way for observation of the hot exciton-polaritons luminescence in organic-based nano-devices in analogy with the hot luminescence of molecules and crystals. The theory provides a clear simple physical picture of the polariton luminescence line-shape relaxation and, as it is demonstrated, agrees with the experiment.

I. INTRODUCTION

The emission of light by Frenkel excitons in organic excitonic materials, e.g. dye molecules, polymers and biological structures, is used in many photonic applications, including wave guiding, lasers etc.\textsuperscript{[11]} Frenkel excitons are formed by the Coulomb interaction between molecules, so that in the majority of cases photoemission from excitons is accompanied by the exciton annihilation and the photon creation where two (quasi-) particles (exciton and photon) can be considered separately. In contrast, in ordered materials with large oscillator strength possessing strong absorption, excitons that determine the medium polarization and photons (transverse field) are strongly coupled forming new elementary excitations: polaritons. Exciton polaritons (EPs) possess properties of both light and matter. Cavity EPs have a mass thanks to their excitonic part that enables us to consider them as an interacting Bose gas leading to Bose-Einstein condensation. The latter results in macroscopic coherence of the condensate and superfluidity. In addition, polariton condensation enables us to realize low threshold polariton lasing without population inversion achieved with conventional nanosecond excitation. Recently topological insulators in EP systems organized as a lattice of coupled semiconductor microcavities in magnetic field were suggested and implemented.

Furthermore, electron-vibrational interactions in molecular systems have a pronounced effect on EPs, resulting among other things in decay and their instability. One way of taking the decay into account is the introduction of complex frequencies with the imaginary part describing phenomenologically constant damping rates (Markovian relaxation). In general, taking the effect of strong electron-vibrational interactions on the EPs into account is a challenge. The point is that in this case both the interaction with radiation field and electron-vibrational interaction should be considered as strong\textsuperscript{[10]}. La Rocca et al.\textsuperscript{[22,23]} studied polariton dispersion in organic-based microcavities taking a single high-frequency (HF) optically active (OA) intramolecular vibration into account introducing also complex exciton replicas frequencies (see above).

However, in real situations the relaxation of molecular, exciton and polariton systems is non-Markovian\textsuperscript{[24]} and cannot be described using constant decay rates resulting in the Lorentzian shape of spectra. Using such a description, one may simulate a separate spectrum of an exciton or even polaritonic luminescence using fitting parameters, but cannot describe the transformation of spectra when for example monomers form an aggregate\textsuperscript{[25]} (see also\textsuperscript{[26]}) as, for example monomer spectrum has Lorentzian shape, the aggregate spectrum is simply shifted monomer spectrum. At the same time, other shapes that non-Markovian theory leads to are able to describe the transformation of spectra including strong narrowing the J-aggregate absorption spectrum with respect to that of a monomer\textsuperscript{[20]}. It is worth noting that actual dissipative properties of the vibrational system are very important for EPs, in particular, for EP fluorescence propagating in organic nanofibers. In Refs\textsuperscript{[25,27]} we developed a mean-field electron-vibrational theory of Frenkel EPs in organic dye structures including the systems with spatial symmetry (like organic molecular crystals), and applied it to the aggregate absorption, luminescence and the EPs with spatial dispersion. The matter is that ordered structures include among other things also organic dye nanofibers that are synthesized by self-assembly of thiacyanine (TC) dye molecules in solution. The theory is non-Markovian and is able to describe the transformation of absorption spectra on molecular aggregation. We obtained the correspondence between manifestation of electron-vibrational interaction in monomers, molecular aggregates and exciton-polaritons in nanofibers. With the same description of material parameters we calculated both the absorption and luminescence of molecular ag-
ggregates and the EP dispersion in nanofibers. Our results show that the Coulomb interaction between molecules stronger affects the absorption line-shape of H-aggregates than their luminescence spectrum. This is consistent with the experiment.

In Ref.\textsuperscript{27} we restricted ourselves to the exciton luminescence. Polariton luminescence in cavity was calculated using numerical solution of coupled equations of motion\textsuperscript{28} balance equations\textsuperscript{29} or Langevin approach where dissipation is added as Lindblad terms\textsuperscript{30}. However, actual dissipative properties of the vibrational system become more important when calculating polariton luminescence. In this work we use non-Markovian model of molecular relaxation, Refs.\textsuperscript{25,27} to calculate non-equilibrium polariton luminescence, i.e. the polariton luminescence line-shape during relaxation. We consider both HF and the low frequency (LF) OA molecular vibrations. The LFOA vibrations give the main contribution to that of the exciton luminescence that agrees with experiment 1. This observation is taken into account by introducing the annihilation and creation operators $c_{im}$ and $c_{im}^\dagger$ of the vibration mode $i$, respectively. The quantity $X_{im}$ ($i=0, s$) describes a shift in the equilibrium position of the OA vibration after excitation of the molecule $m$.

The light-matter interaction in the dipole approximation can be written equivalently in two ways, by using $\mathbf{r} \cdot \mathbf{E}$ or $\mathbf{p} \cdot \mathbf{A}$ Hamiltonians\textsuperscript{31} with $\mathbf{E}$ being the electric field, $\mathbf{A}$ - the vector potential, and $\mathbf{p}$ - the electronic momentum operator. Though both Hamiltonians for the light-matter interaction are formally equivalent, they can lead to different results\textsuperscript{32} and thus have to be used with a care. Since the exciton-polariton problem was first formulated with the aid of the vector potential\textsuperscript{11,12} (see also\textsuperscript{23}), we also stick to the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian. In this case the electromagnetic-field and the light-matter interaction Hamiltonians are

$$H_{\text{ph+int}} = \hbar \sum_q \omega_q a_q^\dagger a_q - \frac{e}{Mc} \sum_m A(\mathbf{r}_m) \cdot \mathbf{p}(\mathbf{r}_m),$$

(1)

with $e$ and $M$ being the electron charge and mass, respectively, $c$ - the light velocity,

$$A(\mathbf{r}_m) = \sum_{q,e_q} \sqrt{\frac{2\pi\hbar^2}{V \omega_q}} e_q [a_q \exp(i \mathbf{q} \cdot \mathbf{r}_m) + H.c.],$$

(2)

$$\mathbf{p}(\mathbf{r}_m) = -\frac{iD \omega_{\text{el}}}{e} (b_m - b_m^\dagger).$$

(3)

Here $H.c.$ denotes Hermitian conjugate, $\mathbf{D}$ is the electronic transition dipole moment, $e_q$ is the unit photon polarization vector, $V$ is the photon quantization volume. In the rotating-wave approximation, Hamiltonian $H_{\text{ph+int}}$ can be written as

$$H_{\text{ph+int}} = \hbar \sum_q \omega_q a_q^\dagger a_q$$

$$+ -i\hbar \sum_m \sum_q \frac{g \exp(-i \mathbf{q} \cdot \mathbf{r}_m)}{\sqrt{\omega_q}} b_m a_q^\dagger + H.c.,$$

II. MODEL, HAMILTONIAN AND ITS TRANSFORMATION

We consider ensemble of identical molecules having two electronic states each. The system is described by the Hamiltonian

$$H_0 = \hbar \sum_m \left\{ \left[ \omega_{\text{el}} + \sum_s \omega_s X_{ms}^2 + \omega_0 X_{m0}^2 \right. \right.$$
using Eqs. (1), (2) and (3). Here parameter

\[ g = -\omega_{cl} \sum_{e_q} \sqrt{\frac{2\pi}{\hbar V}} (e_q \cdot D) \]  

(4)

In what follows we assume that \( \hbar \omega_s \ll k_B T \), so that the LF vibrational subsystem can be considered semiclassically, such that after optical excitation of a molecule the vibration subsystem relaxes semiclassically from some excited state. In accordance with the Franck-Condon principle, an optical electronic transition takes place at a fixed nuclear configuration. Therefore, the quantity \( \alpha_m = \sum_x \omega_x X_{mx} (c_x^\dagger + c_x) \), which represents the electronic-vibration coupling, can be considered as a disturbance of the electronic transition under nuclear motion. In other words, the LFOA vibrations can be seen as some stochastic modulation of the electronic transition frequency, such that \( \tilde{\omega}_{21}(t) = \omega_{cl} + \omega_{st}/2 - \alpha_m(t) \) where \( \omega_{st} = 2 \sum_x \omega_x X_{mx} = \hbar K(0)/(k_B T) \) is the contribution of the LFOA vibrations to the Stokes shift of the equilibrium absorption and luminescence spectra, and \( \alpha_m(t) \) is a stochastic process. In that case \( H_0 \) becomes a stochastic Hamiltonian and can be written as

\[ H_0(\alpha) = \hbar \sum_m \left\{ (\omega_{cl} + \omega_{st}/2 + \omega_0 X_{m0}^2 - \alpha_m \right\} 
- \omega_0 X_{m0} (c_{0m}^\dagger + c_{0m}) b_m^\dagger b_m + \omega_0 c_{0m}^\dagger c_{0m} \} \]

The electronic transition relaxation stimulated by LFOA vibrations we describe\(^{25,27}\) by a one-parametric Gaussian-Markovian process with \( \langle \alpha_m(t) \rangle_1 = 0 \) and exponential correlation function with a characteristic attenuation time \( \tau_s \), \( K_m(t) = \langle \alpha_m(0) \alpha_m(t) \rangle_1 = K(0) \exp(-|t|/\tau_s) \), where \( \langle \cdot \rangle_1 \) stands for the trace operation over the reservoir variables in the ground electronic state 1.

In this work we focus on polariton luminescence bearing in mind two types of molecular systems based on organic dyes: H-aggregates and enhanced green fluorescent protein (eGFP). Experimental\(^{11}\) and theoretical\(^{27}\) results show that the dipole-dipole interaction between molecules,

\[ H_{int} = \hbar \sum_{m \neq n} J_{mn} b_m^\dagger b_n \]  

(5)

where \( J_{mn} \) is the resonant exciton coupling, more strongly affects the absorption line-shape of H-aggregates (due to redistribution of intensities of vibronic transitions related to the HFOA vibration) than their luminescence spectrum. Fast relaxation of the HFOA vibration leads to the fact that only 0–0 vibronic transition with respect to the HFOA vibration contributes to the polariton luminescence (see below), and the intensity redistribution related to the HFOA vibration becomes unimportant. As for eGFP, the actual fluorophore of FP's is enclosed by a nano-cylinder that consists of eleven \( \beta \)-sheet\(^{31,35}\) This protective shell acts as natural ‘bumper’ and prevents close contact between fluorophores of neighbouring FP's limiting intermolecular energy migration even at the highest possible concentration. Thus, as a first approximation, one can exclude the dipole-dipole interactions between molecules from our consideration. Nevertheless, in this paper we will discuss a generalization of the theory to including the intermolecular interactions in the framework of the mean-field theory\(^{25,27}\).

Hamiltonian \( H_0(\alpha) \) can be diagonalized with respect to the HFOA vibration using unitary Lang-Firsov transformation \( \exp(-S) H_0(\alpha) \exp(S) \)

\[ S = \sum_m X_{m0} (c_{0m}^\dagger - c_{0m}) b_m^\dagger b_m \]  

(6)

As a result one get for \( \tilde{H}_0(\alpha) = \exp(-S) H_0(\alpha) \exp(S) \)

\[ \tilde{H}_0(\alpha) = \hbar \sum_m [(\omega_{cl} + \omega_{st}/2 - \alpha_m) b_m^\dagger b_m + \omega_0 c_{0m}^\dagger c_{0m}] \]  

(7)

Next fast relaxation of the HFOA vibrations (~10–100 fs) should be taken into account. We believe that the intramolecular relaxation related to the HFOA vibrations takes place in a time shorter than the relaxation of the LFOA system\(^{25,33}\). Therefore, only vibrationless state \( v = 0 \) with respect to the HFOA vibration will be populated in the ground electronic state, and only \( |10\rangle \rightarrow |2v\rangle \) vibronic transitions can couple to light creating polariton\(^{23}\). In this case Hamiltonian \( \tilde{H}_0(\alpha) \) can be rewritten as

\[ \tilde{H}_0(\alpha) = \hbar \sum_m \sum_{v=0} (\omega_{2v} + \omega_{st}/2 - \alpha_m) b_m^\dagger b_m \]  

(8)

where \( \omega_{2v} = \omega_{cl} + v \omega_0 \), \( b_m^\dagger b_m = |m2v\rangle \langle m10| \) and \( b_m^\dagger b_m^\dagger \) can be regarded as bosons

\[ [b_m^\dagger, b_{m'}^\dagger] = \delta_{mm'} b_{2v} \]  

(9)

In the new representation Hamiltonian of the photons and the light-matter interaction can be written as

\[ \tilde{H}_{ph+int} = \hbar \sum_{m, q} \omega_q a_q^\dagger a_q - i \hbar g \sum_{m, q} \left\{ \frac{\exp(-i \mathbf{q} \cdot \mathbf{r}_m)}{\sqrt{\omega_q}} \tilde{b}_m a_q^\dagger - \frac{\exp(i \mathbf{q} \cdot \mathbf{r}_m)}{\sqrt{\omega_q}} \tilde{b}_m^\dagger a_q \right\} \]  

(10)

in terms of the coherent states\(^{10}\)

\[ |2X_{0m}/m10\rangle = \exp(-X_{0m}/2) \sum_{v=0} X_{0m}/\sqrt{v!} |m2v\rangle \]  

(11)

Here the operator \( \tilde{b}_m^\dagger = |2X_{0m}/m10\rangle \) describes creation of an excitation of molecule \( m \) to the level 2 and into the coherent vibrational state \( |X_{0m}\rangle \), and the operator
\( \hat{b}_m = |m10\rangle \langle 2X_{0m}| \) describes annihilation of the excitation in the molecule \( m \) and the coherent vibrational state. The operators \( \hat{b}_m \) and \( \hat{b}_m^\dagger \) can also be considered as bosons since they satisfy the bosonic commutative relation \( [\hat{b}_m, \hat{b}_n^\dagger] = 1 \), and expressed in terms of \( b_{mv} \) and \( b_{mv}^\dagger \) by means of Eq. (11).

\[
\left( \begin{array}{c}
\hat{b}_m \\
\hat{b}_m^\dagger
\end{array} \right) = \exp(-X_{0m}^2/2) \sum_{v=0} X_{0m}^v \left( \begin{array}{c}
b_{mv} \\
b_{mv}^\dagger
\end{array} \right)
\]

(12)

III. POLARITONS AND THEIR DISPERSION TAKING ELECTRON-VIBRATIONAL INTERACTIONS INTO ACCOUNT

The bilinear Hamiltonian of the system

\[
\hat{H} = \hat{H}_0(\alpha) + \hat{H}_{ph+int}
\]

(13)

can be diagonalized by introducing polariton operators \( p_s \) as linear combination of operators \( b_{mv} \) and \( a_q \)

\[
p_s = \sum_q v_s(q) a_q + \sum_{mv} u_{smv} b_{mv}
\]

(14)

Here \( p_s \) denotes the annihilation operator for a polariton in branch \( s \). The polariton operators have to obey the Bose commutation relations

\[
[p_s, p_s^\dagger] = \sum_q |v_s(q)|^2 + \sum_{mv} |u_{smv}|^2 = 1
\]

(15)

We now choose the unknown coefficients \( u_{smv} \) and \( v_s(q) \) so that the Hamiltonian (13) becomes diagonal in the polariton operators

\[
(\Omega_s - \omega_q)v_s(q) = \exp(-X_0^2/2) \sum_{vq'} X_{0}^{2v} \sum_{q'} \frac{\zeta[\Omega_s-(\omega_{2q}+\omega_{st}/2)+\alpha]}{\zeta[\Omega_s-(\omega_{2q}+\omega_{st}/2)+\alpha]} g^2 v_s(q') \sum_m \exp[i(q - q') \cdot \mathbf{r}_m]
\]

(16)

The transformation coefficients \( u_{smv} \) and \( v_s(q) \) obey the following equations (see Appendix A)

\[
u_{smv} = -i\zeta[\Omega_s-(\omega_{2q}+\omega_{st}/2)+\alpha] \sum_q \frac{g}{\sqrt{\omega_q}} v_s(q) \times \exp(-X_0^2/2) \frac{X_{0}^{2v}}{\sqrt{v!}} \exp(-i\mathbf{q} \cdot \mathbf{r}_m)
\]

(17)

and

\[
(\Omega_s - \omega_q)v_s(q) = \frac{i g}{\sqrt{\omega_q}} \sum_{mv} \exp(-X_0^2/2 + i\mathbf{q} \cdot \mathbf{r}_m) \frac{X_{0}^{2v}}{\sqrt{v!}} u_{smv}
\]

(18)

where

\[
\zeta[\Omega_s-(\omega_{2q}+\omega_{st}/2)+\alpha] = \frac{P}{\Omega_s-(\omega_{2q}+\omega_{st}/2)+\alpha} - i\pi \delta[\Omega_s-(\omega_{2q}+\omega_{st}/2)+\alpha],
\]

(19)

\( P \) is the symbol of the principal value, and we omitted subscript \( m \) near \( X_0 \) since all shifts are equal, \( X_{0m} = X_0 \). Substituting \( u_{smv} \) from Eq. (17) into Eq. (18), we find the relation determining the polariton frequencies \( \Omega_s \) and amplitudes \( v_s(q) \)

For systems with spatial symmetry like organic dye nanofibers synthesized by self-assembly of TC dye molecules in solution, the sum on the right-hand side of Eq. (20) is equal to \( \sum_m \exp[i(q - q') \cdot \mathbf{r}_m] = N \delta_{qq'} \) where \( N \) is the number of molecules. Then Eq. (20) turns into the dispersion equation for the polaritons

\[
(\Omega_s - \omega_q) = N \frac{g^2}{\omega_q} \exp(-X_0^2) \sum_v X_{0}^{2v} \zeta[\Omega_s-(\omega_{2q}+\omega_{st}/2)+\alpha].
\]

(21)

For the systems without spatial symmetry like eGFP molecules in diluted protein solution the photon amplitude \( v_s(q) \) enters on the right-hand side of Eq. (20) with all possible values of its argument \( q' \). However, those values of the argument, which differ from \( q \) appearing on the left-hand side of Eq. (20), just describe the scattering of light by the inhomogeneities in the medium. If this scattering is neglected, then only the term with \( q' = q \) survives in the sum over \( q' \), and the zero-order relation which determines the dispersion equation for the polaritons is the same as Eq. (21). In that case the polariton frequency \( \Omega_s \) and exciton amplitude \( u_{smv} \) become functions of \( q, \Omega_s = \Omega_s(q) \) and \( u_{smv} = u_{smv}(q) \), and one can introduce polariton operators \( p_{sq} \)

\[
p_{sq} = v_s(q) a_q + \sum_{mv} u_{smv}(q) b_{mv}
\]

(22)
where $p_{sq}$ denotes the annihilation operator for a polaron with wave vector $q$ in branch $s$. Then Eq. (16) takes a form

$$\hat{H} = \hbar \sum_{sq} \Omega_s(q)p_{sq}^\dagger p_{sq}$$

(23)

where polaron operators $p_{sq}$ obey the Bose commutation relation

$$[p_{sq}, p_{sq}^\dagger] = |v_s(q)|^2 + \sum_{mv} |u_{smv}(q)|^2 = 1$$

(24)

Since $\alpha$ is a stochastic Gaussian variable, one can average amplitudes $u_{smv}(q)$ and the dispersion equation for the polaritons, Eq. (21), over the stochastic process using the density matrix

$$\rho_{11}^{(0)}(\alpha) = [2\pi K(0)]^{-1/2} \exp[-\frac{\alpha^2}{2K(0)}]$$

(25)

The averaging is reduced to the calculation of the integral

$$W_{av}[\Omega_s(q)] = \frac{i}{\pi} \int_{-\infty}^{\infty} d\alpha \rho_{11}^{(0)}(\alpha) \zeta(\Omega_s(q) - (\omega_{2v} + \omega_{st}/2) + \alpha)$$

(26)

representing the spectrum of $0 \to v$ vibronic transition with respect to the HFOA vibration. The imaginary part of $-iW_{av}[\Omega_s(q)]$ with sign minus, $-\text{Im}\{-iW_{av}[\Omega_s(q)]\} = \text{Re}W_{av}[\Omega_s(q)]$, describes the absorption lineshape of the vibronic transition $0 \to v$, and the real part, $\text{Re}\{-iW_{av}[\Omega_s(q)]\} = \text{Im}W_{av}[\Omega_s(q)]$, describes the corresponding refraction spectrum. For the “slow modulation” limit used in this work, $K(0)\tau_s^2 >> 1$, quantities $W_{av}[\Omega_s(q)]$ and $F_{av}[\Omega_s(q)]$ are given by

$$W_{av}[\Omega_s(q)] = \sqrt{\frac{1}{2\pi K(0)}} w(\Omega_s(q) - (\omega_{2v} + \omega_{st}/2) + \frac{\alpha}{\sqrt{2K(0)}})$$

(27)

where $w(z) = \exp(-z^2)[1 + i\text{erf}(z)]$ is the probability integral of a complex argument and

$$F_{av}[\Omega_s(q)] = \frac{1}{\sqrt{2\pi K(0)}} \exp\left\{-\frac{[\Omega_s(q) - (\omega_{2v} + \omega_{st}/2) + \frac{\alpha}{\sqrt{2K(0)}}]^2}{2K(0)}\right\}$$

(28)

The spectrum of $0 \to v$ vibronic transition with respect to the HFOA vibration, $W_{av}[\Omega_s(q)]$, calculated in the slow modulation limit, Eq. (27), is valid only near the central frequency $\omega_{2v} + \omega_{st}/2$. However, $W_{av}[\Omega_s(q)]$ can be calculated exactly beyond the slow modulation limit.

$$W_{av}[\Omega_s(q)] = \frac{\tau_s}{\pi} \Phi(1, 1 + x_{av}; K(0)\tau_s^2)$$

(29)

where $x_{av} = K(0)\tau_s^2 + i\tau_s(\omega_{2v} + \omega_{st}/2 - \Omega_s)$, $\Phi(1, 1 + x_{av}; K(0)\tau_s^2)$ is a confluent hypergeometric function. It is worthy to note that Eq. (29) is valid for both small and large detunings from the central frequency. Eq. (29) will be used for numerical calculations.

Furthermore, using Eqs. (17), (21) and (26), we obtain for the averaged value of $u_{smv}(q)$

$$u_{smv}(q) = \int u_{smv}(q)\rho_{11}^{(0)}(\alpha) d\alpha = -\pi \exp(-X_0^2/2)$$

(30)

and for the averaged dispersion equation for the polaritons

$$\Omega_s(q) - \omega_q = -\frac{ig'N}{\omega_q} \pi W_a[\Omega_s(q)]$$

(31)

where

$$W_a[\Omega_s(q)] = \exp(-X_0^2) \sum_v \frac{X_v^2}{v!} W_{av}[\Omega_s(q)]$$

(32)

is the equilibrium molecular spectrum in the presence of both HF and LF OA vibrations. Using Eq. (4), we get for the value

$$g'N = \omega_c^2 Q$$

(33)

where parameter $Q = 4\pi N D_{ph} D_{el} h$ corresponds to notation $q$ used in Refs. 25,27. $N = N/V$ is the density of molecules. When deriving Eq. (33), we took two independent polarization directions of $\mathbf{q}$ for each $\mathbf{q}$ into account. Therefore, the factor 2 appears due to two possible states of polarization in Eq. (33).

The averaged dispersion equation for the polaritons, Eq. (31), can be reduced to the equation for the transverse eigenmodes of the medium, $c^2 q^2 = \Omega_s^2(\Omega_s)$ in Refs. 25,27,28. Indeed, bearing in mind that $\omega_q = q\nu/\sqrt{\varepsilon_0}$ where $\nu$ is the background refraction index of the medium, one gets from Eqs. (31) and (33) in the rotating-wave approximation when $\Omega_s\approx \Omega_s^0$ and $\omega_q^0/\Omega_s^0 \approx 1$

$$c^2 q^2 / \Omega_s^2 = \varepsilon_0[1 + Q/\pi W_a[\Omega_s]]$$

(34)

Here the right-hand side of Eq. (34) presents the dielectric function $\varepsilon(\Omega_s)$ in the absence of the dipole-dipole interaction between molecules. It is worthy to note that the dispersion equation for the polaritons can be recast in the form $c^2 q^2 = \Omega_s^2(\Omega_s)$ if non-resonant terms and the $A_2$ term in the light-matter interaction part of Hamiltonian $H_{ph+int}$ are also taken into account. Therefore, below we will use Eq. (34) since both Eq. (31) and Eq. (34) have the same accuracy in the rotating-wave approximation.

Fig. 1 shows EP dispersion of an ordered ensemble of TC dye molecules calculated using Eq. (34). In order
FIG. 1: (a) The polariton dispersion curves, $\Omega_s(q)$, without (black solid) and with (gray dashed) accounting of intermolecular dipole-dipole interactions; (b) Imaginary part of the wavevector as a function of polariton frequency. The model parameters are obtained by fitting the experimental absorption spectrum of TC dye in Ref. 27: $K(0)\tau_s = 80$, $Q\tau_s = 84$, $\omega_{st}\tau_s = 28$, $\omega_0\tau_s = 20$, $X^2_0 = 0.454$, $\omega_{el}\tau_s = 303.2$, $J(0)\tau_s = 7$, $1/\tau_s = 75 cm^{-1}$.

to satisfy this equation, the wave number $q$ should be complex $q = q' + iq''$. The polariton dispersion shows the leaky part in the splitting range between lower and upper polariton branches. The imaginary part of wave number $q''$ as a function of the polariton frequency can be considered as a polariton absorption spectrum.

Eq. (34) can be extended to the presence of the intermolecular dipole-dipole interaction using the mean-field theory.

$$c^2q'^2/\Omega_s^2 = \varepsilon_0 \left\{ 1 + Q\pi \frac{W_a[\Omega_s(q)]}{1 + i\pi W_a[\Omega_s(q)]} \right\}$$

Here $J(0) \equiv J(k = 0)$, $J(k) = \sum_{n\neq m} J_{mn} \exp[i\mathbf{k} \cdot (\mathbf{r}_n - \mathbf{r}_m)]$ is the lattice Fourier transform of the intermolecular interaction strength matrix. One can see that the dispersion taking intermolecular dipole-dipole interaction into account, Eq. (35), (dashed curve in Fig 1a) is similar to the dispersion calculated without intermolecular dipole-dipole interaction. This supports the approach used in our paper.

Furthermore, from Eqs. (24, 30, 31) we derive the Hopfield coefficients

$$|v_s(q)|^2 = \omega_q$$
$$\times \left[ \omega_q + \pi^2 \omega_{el}^2 Q \exp(-X_0^2) \sum_v \frac{X_v^2}{v!} |W_{av}[\Omega_s(q)]|^2 \right]^{-1}$$

(36)

$$\sum_m |\tilde{u}_{smv}(q)|^2 = \pi^2 \omega_{el}^2 Q \exp(-X_0^2) \frac{X_v^2}{v!} |W_{av}[\Omega_s(q)]|^2$$
$$\times \left[ \omega_q + \pi^2 \omega_{el}^2 Q \exp(-X_0^2) \sum_{v'} \frac{X_{v'}^2}{v'!} |W_{av'}[\Omega_s(q)]|^2 \right]^{-1}$$

(37)

The Hopfield coefficients calculated by Eqs. (36) and (37) as functions of the lower branch polariton frequency $\Omega_L$ are shown in Fig 2.

FIG. 2: The Hopfield coefficients as functions of $\Omega_L$. (a) $|v_L(\Omega_L)|^2$ (red solid line) and $\sum_m |u_{Lmv}^{\Omega_L}|^2$ (dashed blue line); (b) coefficients $\sum_m |u_{Lmv}^{\Omega_L}|^2$ plotted for various excitations, $v = 0, 1, 2$, of the HFOA vibration mode; (c) Product of the Hopfield coefficients $|v_L(\Omega_L)|^2 \sum_m |\tilde{u}_{Lnm}^{\Omega_L}|^2$ (see Eqs. (51), (55) and (56) below) as a function of $\Omega_L$. Other parameters are identical to those as in Fig 1.
IV. LUMINESCENCE SPECTRUM OF POLARITON

A. General formulas

The frequency spectrum of a light emitting system

\[ I(\omega) = 2\Re \int_0^\infty d\tau \langle E^-(t)E^+(t-\tau) \rangle \exp(-i\omega\tau) \]  

(38)

is calculated from the two-times correlation function of the quantum electric field\[43]\]

\[ \tilde{E}(r, t) = E^+(t) + E^-(t) = \sum_q \sqrt{2\pi \hbar \omega_q} \]

\[ \times [ia_q u_q(r) \exp(-i\omega_q t) - ia_q^\dagger u_q^*(r) \exp(i\omega_q t)], \]  

(39)

where \( \langle \ldots \rangle \) indicates the trace over the density matrices of the phonon bath and polariton, \( u_q(r) \) describes a space dependence of the field amplitude. For plane waves, \( u_q(r) = e^{i\mathbf{q} \cdot \mathbf{r}} \sqrt{V^{-1/2}} \). Substituting Eq.(39) into Eq.(38), we obtain

\[ I(\omega) = 4\pi \Re \sum_q \hbar \omega_q |u_q(r)|^2 \]

\[ \times \int_0^\infty d\tau \langle a_q^\dagger(t)a_q(t-\tau) \rangle \exp(-i\omega\tau) \]  

(40)

Consider first the polariton luminescence. Then the photon and exciton operators can be expressed in terms of the polariton operators using inverse polariton transformation\[40]\]

\[ a_q = \sum_s v_s^\dagger(q)p_{s,q}, \quad b_{mv} = \sum_s u_{sv^\dagger,q}p_{s,q}. \]  

(41)

Using Eq.(41), we get for polariton luminescence from Eq.(40)

\[ I_p(\omega) = 4\pi \Re \sum_{ss'} \hbar \omega_q |u_q(r)|^2 \]

\[ \times \int_0^\infty d\tau \langle v_s(q)v_{s'}^\dagger(q)p_{s,q}(t)\rangle \exp(-i\omega\tau) \]  

(42)

where averaging with respect to the phonon bath includes both amplitudes \( v_s(q) \) and polariton variables, and we ought to identify frequency \( \omega \) with polariton frequencies \( \Omega_s(q) \).

If the electron-vibrational interaction is weak, one can first calculate amplitudes \( v_s(q) \) and \( u_{sv^\dagger}(q) \) for the electron system only (interaction with radiation field), and then take the interaction of polaritons with vibrational system into account using perturbation theory\[112]. In that case the averaging indicated by \( \langle \ldots \rangle \) in Eq.(42) applies only to the polariton variables. In contrast, we consider here strong electron-vibrational interaction. That is why we took the interaction with the HF and LFOA vibrations into account when calculated amplitudes \( v_s(q) \) and \( u_{sv^\dagger}(q) \) in Section III. Moreover, we averaged these amplitudes with respect to variable \( \alpha \) related to the LFOA vibrations that enabled us to reduce the obtained dispersion equation for the polaritons to that of the dielectric theory of polaritons. This indicates the correctness of the procedure used. Therefore, we factorize the expectation value

\[ \langle v_s(q)v_{s'}^\dagger(q)p_{s,q}(t)\rangle \]

\[ = \langle v_s(q)v_{s'}^\dagger(q)\rangle \langle p_{s,q}(t)\rangle, \]  

(43)

since the averaging of the amplitudes \( v_s(q) \) and \( u_{sv^\dagger}(q) \) has been already performed in Section III. Additional arguments in favour of such factorization will be advanced in Section IV.B below.

Furthermore, due to large splitting between the upper (U) and lower (L) polariton branches in molecular systems based on organic dyes (\( \sim 6000-8000 \text{ cm}^{-1}\)), the terms with \( s = s' \) will give the main contribution to the polariton luminescence in Eqs.(42) and (43). Since the pump energy was smaller than that of the higher branch, we will consider only the lower branch contribution to the luminescence. Then Eq.(41) becomes

\[ I_p[\Omega_L(q)] = 4\pi \hbar \omega_q |u_q(r)|^2 |v_L(q)|^2 \]

\[ \times \Re \int_0^\infty d\tau \langle p_{L,q}(t)p_{L,q}(t-\tau) \rangle \exp(-i\Omega_L(q)\tau) \]  

(44)

B. Calculation of the polariton two-particle expectation value

Since \( \langle \ldots \rangle \) on the right-hand side of Eq.(44), among others, indicates the trace over the phonon bath density matrix, it is convenient to calculate it by using the excitonic (molecular) operators,

\[ \Re \int_0^\infty d\tau \langle p_{L,q}(t)p_{L,q}(t-\tau) \rangle \exp(-i\Omega_L(q)\tau) = \sum_m |\tilde{b}_{L,m0}(q)|^2 \]  

\[ \times \Re \int_0^\infty d\tau \langle \tilde{b}_{L,m0}^\dagger(t)\tilde{b}_{L,m0}(t-\tau) \rangle \exp(-i\Omega_L(q)\tau) = \sum_m |\tilde{u}_{L,m0}(q)|^2 \]

\[ \times \Re \int_0^\infty d\tau \text{Tr}\{\tilde{b}_{L,m0}^\dagger\tilde{b}_{L,m0}\tilde{b}_{L,m22}(\alpha,t) \exp[i(\tilde{\omega}_{21} - \alpha - \Omega_L(q))]\} \]  

(45)

where \( \tilde{b}_{L,m0}^\dagger(t) = b_{L,m0}^\dagger \exp[i(\tilde{\omega}_{21} - \alpha)t], \quad b_{L,m0}(t-\tau) = b_{L,m0} \exp[-i(\tilde{\omega}_{21} - \alpha)(t-\tau)], \quad \tilde{\omega}_{21} = \omega_{20} + \omega_{21}/2 \) is the frequency of Franck-Condon transition \( 1 \to 2 \) for the LFOA vibrations, and we took the fast relaxation of the HFOA vibrations into account (see Section II). Therefore, since other OAHF vibration states with \( \nu \geq 1 \) relax very fast, only vibrationless state \( v = 0 \) with respect to the HFOA vibration will contribute to the polariton luminescence.
Then the trace on the right-hand side of Eq. (45) is

\[ \text{Tr} \{ b_{\alpha m}^\dagger b_{\alpha 0} \rho_{22}(\alpha, t) \exp[i(\bar{\omega}_2 - \alpha - \Omega_L)\tau] \} \]

\[ = \int_{-\infty}^{\infty} b_{\alpha m}^\dagger b_{\alpha 0} \rho_{22}(\alpha, t) \exp[i(\bar{\omega}_2 - \alpha - \Omega_L)\tau] d\alpha \quad (46) \]

where \( \rho_{22}(\alpha, t) \) is the partial density matrix of the molecular excited state.

Substitution of Eq. (46) into Eq. (45) and integration with respect to \( \tau \) yield

\[ \text{Re} \int_0^\infty \! dr \{ q_{Lq}(t) p_{Lq}(t) \} \exp(-i\Omega_L \tau) = \pi \sum_m |\bar{u}_{Lm0}(\mathbf{q})|^2 \times \int_{-\infty}^{\infty} \! d\alpha \langle b_{\alpha m}^\dagger b_{\alpha 0} \rangle \delta(\Omega_L(\mathbf{q}) + \alpha - \bar{\omega}_2) \quad (47) \]

where the average exciton population is equal to \( \langle b_{\alpha m}^\dagger b_{\alpha 0} \rangle = \rho_{22}(\alpha, t) \). The density matrix element \( \rho_{22}(\alpha, t) \) satisfy the evolution equation

\[ \frac{d}{dt} \rho_{22}(\alpha, t) = L_{22} \rho_{22}(\alpha, t) \]

\[ + P_L(t) \rho_{11}^{(0)}(\alpha) \delta(\bar{\omega}_2 - \Omega_L(\mathbf{q}_0) - \alpha) \quad (48) \]

with the operator

\[ L_{22} = \tau_s^{-1} \left[ 1 + \left( \frac{\alpha - \omega_{st}}{\partial(\alpha - \omega_{st})} \right) + K(0) \frac{\partial^2}{\partial(\alpha - \omega_{st})^2} \right]. \quad (49) \]

The equation (48) describes diffusion of the excited electronic state density matrix element \( \rho_{22}(\alpha, t) \) in the \( \alpha \)-coordinate space after excitation caused by the pumping term \( P_L(t) \rho_{11}^{(0)}(\alpha) \delta(\bar{\omega}_2 - \Omega_L(\mathbf{q}_0) - \alpha) \).

Having in mind Eqs. (48) and (47) and using \( \rho_{22}(\alpha, t) \), one writes

\[ \text{Re} \int_0^{\infty} \! dr \{ q_{Lq}(t) p_{Lq}(t) \} \exp(-i\Omega_L \tau) \]

\[ = \pi \sum_m |\bar{u}_{Lm0}(\mathbf{q})|^2 \rho_{22}(\bar{\omega}_2 - \Omega_L(\mathbf{q}), t) \quad (50) \]

Then the frequency spectrum of the light emitting polariton system, Eq. (44), takes the form

\[ I_p[\Omega_L(\mathbf{q})] = 4\pi^2 \hbar |u_{L}(\mathbf{r})|^2 |v_{L}(\mathbf{q})|^2 \times \sum_m |\bar{u}_{Lm0}(\mathbf{q})|^2 \rho_{22}(\bar{\omega}_2 - \Omega_L(\mathbf{q}), t) \quad (51) \]

It is worthy to note that the factorization, Eq. (43), can be justified by follows. The amplitudes \( v_s(\mathbf{q}) \) and \( u_{sme}(\mathbf{q}) \) are calculated using averaging with respect to the ground electronic state (see Section III). At the same time, \( \langle p_{Lq}^0(t) p_{Lq}(t - \tau) \rangle \) is calculated for the emission using \( \rho_{22}(\alpha, t) \) that involves relaxation in the excited electronic state. Between these events, rapid dephasing occurs, in particular due to HFOA vibrations. Therefore, averagings of amplitudes \( v_s(\mathbf{q}) \), \( u_{sme}(\mathbf{q}) \) and \( \langle p_{Lq}^0(t) p_{Lq}(t - \tau) \rangle \) can be carried out separately.

The Green’s function of the Eq. (48) has the form

\[ G(\alpha, t; \alpha', t') = \frac{1}{\sqrt{2\pi \sigma (t - t')}} \times \exp \left\{ - \frac{[\alpha - \omega_{st} - (\alpha' - \omega_{st}) S(t - t')]^2}{2\sigma (t - t')} \right\} \quad (52) \]

where \( \sigma (t - t') = K(0) \left[ 1 - S^2(t - t') \right] \), and \( K(t)/K(0) \equiv S(t) = \exp(-|t|/\tau_s) \). Therefore, we derive

\[ \rho_{22}(\alpha, t) = \int_0^t \! dt' \int_{-\infty}^{\infty} \! d\alpha' G(\alpha, t; \alpha', t') \rho_{L}(t') \rho_{11}^{(0)}(\alpha') \delta(\bar{\omega}_2 - \Omega_L(\mathbf{q}_0) - \alpha') = \rho_{11}^{(0)}(\bar{\omega}_2 - \Omega_L(\mathbf{q}_0)) \int_0^t \! \frac{dt' P_L(t')}{\sqrt{2\pi \sigma (t - t')}} \exp \left\{ - \frac{[\alpha - \omega_{st} - (\bar{\omega}_2 - \Omega_L(\mathbf{q}_0) - \omega_{st}) S(t - t')]^2}{2\sigma (t - t')} \right\}, \quad (53) \]

which gives the time-dependent luminescence spectrum. From Eq. (51) we obtain

\[ I_p[\Omega_L(\mathbf{q}), t] = 4\pi^2 \hbar |u_{L}(\mathbf{r})|^2 |v_{L}(\mathbf{q})|^2 \sum_m |\bar{u}_{Lm0}(\mathbf{q})|^2 \rho_{11}^{(0)}(\bar{\omega}_2 - \Omega_L(\mathbf{q}_0)) \int_0^t \! \frac{dt' P_L(t')}{\sqrt{2\pi \sigma (t - t')}} \times \exp \left\{ - \frac{[\bar{\omega}_2 - \Omega_L(\mathbf{q}) - \omega_{st} - (\bar{\omega}_2 - \Omega_L(\mathbf{q}_0) - \omega_{st}) S(t - t')]^2}{2\sigma (t - t')} \right\} \quad (54) \]
Time $t$ corresponds to the time of the polariton exit from the sample. In case of a short pump, i.e. $P_L(t') = P_L \lim_{t' \to 0} \delta(t' + \varepsilon)$, the expression for intensity simplifies to
\[
I_p[\Omega_L(q), t] = 4\pi^2 P_L \hbar \omega_q |u_q(r)|^2 |v_L(q)|^2 \sum_m |\bar{u}_{Lm0}(q)|^2
\times \rho_{11}^{(0)}(\bar{w}_{21} - \Omega_L(q_0)) G(\bar{w}_{21} - \Omega_L(q), t; \bar{w}_{21} - \Omega_L(q_0), 0)
\]
\[
\text{Eq. (55)}
\]

Since $S(0) = 1$, in the limit $t \to 0$ the spectrum is centred around the frequency $\Omega_L(q_0)$ and is very narrow, $I_p[\Omega_L(q), 0] \propto \delta(\Omega_L(q_0) - \Omega_L(q))$. However, remind that Eq. (55) is derived using the slow modulation limit where time $t$ may be smaller than $\tau_s$ but must be larger than the irreversible dephasing time of the vibronic transition $0 \to 1$, $T' = |r_s/K(0)|^{1/3} < 50\mathrm{ps}$.

The Green’s function $G(\bar{w}_{21} - \Omega_L(q), t; \bar{w}_{21} - \Omega_L(q_0), 0)$ entering the right-hand side of Eq. (55) describes the time-dependent Gaussian spectrum, which center is moving along the dispersion curve $\Omega_L(q)$ from the initial frequency $\Omega_L(q_0)$ to the frequency $\Omega_L(q) = \bar{w}_{21} - \omega_s t$, and broadens over time. For long times $t >> \tau_s$, the spectrum tends to its equilibrium value
\[
I_p[\Omega_L(q), \infty] = 4\pi^2 \hbar \omega_q |u_q(r)|^2 |v_L(q)|^2
\times \sum_m |\bar{u}_{Lm0}(q)|^2 \rho_{11}^{(0)}(\bar{w}_{21} - \Omega_L(q_0))
\times \frac{P_L}{2\pi K(0)} \exp \left\{ \frac{[\bar{w}_{21} - \Omega_L(q) - \omega_s t]^2}{2K(0)} \right\}
\]
\[
\text{Eq. (56)}
\]

if the polariton does not leave the crystal before this time.

To deal with this issue, we will also evaluate the spectrum of the polariton two-particle expectation value, Re $\int_0^\infty dt \bar{p}_{Lq}(t) p_{Lq}(t - \tau) \exp(-i\Omega_L\tau)$, using Eqs. (55) and (53). If the pump is short, we get similar to Eq. (55)
\[
\text{Eq. (57)}
\]

Spectrum, Eq. (57), plotted as a function of the wave number $q$ allows us to estimate the spreading of the polariton two-particle expectation value in real space $x$ due to relation $\Delta x \sim 1/\Delta q$ can reach the value of the height of a nanofiber $100 - 200 \mathrm{nm}$ both during relaxation of the polariton and after its completion. In these cases polariton emission can occur. The polariton emission mechanism based on the spreading of another quantity, the polariton wave package, beyond the nanosystem was considered in Ref. 44.

By this means our consideration opens up a way for observing hot luminescence of the exciton-polaritons in organic nanosystems by analogy with the hot luminescence of molecules and crystals [16]. To detect the effect in experiments of the type reported in Ref. 3 the measurement should be carried out with a high time resolution.

VI. CONCLUSION

In this work we calculated non-equilibrium polariton luminescence, i.e. the polariton luminescence line-shape during the relaxation, using the non-Markovian model of molecular relaxation [14, 22]. Both HF and LF OA molecular vibration modes were considered in the model. To calculate the spectra we applied the Lang-Firsov canonical transformation to the HFOA vibration degrees of freedom, while for the LFOA modes we used a stochastic description. To this end, the modified stochastic po-

V. APPLICATION TO EXCITON-POLARITON EXPERIMENT IN NANOFIBER

In this section we apply the above theory to the experimental fluorescence spectrum of the fiber-shaped TC dye H-aggregates measured at room temperature [3]. The spectrum is shown in Fig. 3. The polariton spectrum with the spectrum of exciton luminescence [29, 30] we observe that the experimental fluorescence spectrum may be considered as a composition of both the exciton luminescence (peak B) and the blue shoulder A. We address the latter to the polariton luminescence, which contribution to the total spectrum is described by Eqs. (54), (55), and (56). It is worthy to note that all those light-matter processes, which do not contribute to the polariton formation, i.e. the molecular photoluminescence transitions, were also considered in Ref. 23.

The time dependent spectrum of the light emitting polariton system, Eq. (55) is shown in Fig. 4. As one can see from Fig. 4 b, the spectrum at large time has maximum at the frequency about $\Omega_L \tau_s \approx 297$. This frequency is bluer than the theoretical value of the exciton luminescence frequency maximum $\Omega_L \tau_s \approx 280$, Fig. 4 c. The spectrum of the light emitting polariton system differs from the excitonic one by the factor $|v_L|^2 \sum_m |\bar{u}_{Lm0}|^2$, which shown in Fig. 2 c. This factor decreases sharply in the frequency range $\Omega_L \tau_s = 270 - 310$, in particular, in the range of the exciton luminescence ($\Omega_L \tau_s \approx 280$). Therefore, the spectrum of the light emitting polariton system is blue-shifted with respect to the spectrum of exciton luminescence. In other words, the excitonic component of the polariton ($\sim \sum_m |\bar{u}_{Lm0}|^2$) must be large enough for the polariton emission to be effective. This agrees with experiment [3] (peak A and spectrum B in Fig. 3).

Fig. 5 shows the spectrum of the polariton two-particle expectation value, Eq. (57), plotted as a function of time $t$ and the wave number $q$. Evaluation of $\Delta q$ from Fig. 5 shows that $\Delta x \sim 1/\Delta q$ can reach the value of the height of a nanofiber $100 - 200 \mathrm{nm}$ both during relaxation of the polariton and after its completion. In these cases polariton emission can occur. The polariton emission mechanism based on the spreading of another quantity, the polariton wave package, beyond the nanosystem was considered in Ref. 44.

By this means our consideration opens up a way for observing hot luminescence of the exciton-polaritons in organic nanosystems by analogy with the hot luminescence of molecules and crystals [16]. To detect the effect in experiments of the type reported in Ref. 3 the measurement should be carried out with a high time resolution.

VI. CONCLUSION

In this work we calculated non-equilibrium polariton luminescence, i.e. the polariton luminescence line-shape during the relaxation, using the non-Markovian model of molecular relaxation [22, 23]. Both HF and LF OA molecular vibration modes were considered in the model. To calculate the spectra we applied the Lang-Firsov canonical transformation to the HFOA vibration degrees of freedom, while for the LFOA modes we used a stochastic description. To this end, the modified stochastic po-
FIG. 3: Experimental fluorescence spectrum of fiber-shaped H-aggregates of TC dye (solid black), the best fitted curves (dashed and dot-dashed blue lines A and B), and theoretical absorption spectra of a monomer, the real part of Eq. (32) (dashed green), polariton without Coulomb interaction (dot-dashed green) and the polariton with taking Coulomb interaction into account (dotted red). Curve B is the sum of curves B, C and D of Fig. 4 of Ref. 3. The model parameters for the theoretical absorption spectra are the same as in Fig. 1.

FIG. 4: The time-dependent spectrum of the light emitting polariton system (eq. 35) plotted as a function of time $t$ and (a) frequency $\Omega_L$, and its cross-sections (b) at various instants of time. The gray-dashed line (B) corresponds to the theoretical spectrum of molecular luminescence and is shown for comparison. The model parameters are the same as in Fig. 1.

Polariton operators have been defined and their quantum and the stochastic average have been calculated. The latter allowed us to find expression of the polariton fluorescent spectrum. As we demonstrated, the polariton fluorescence is proportional to the quantum expectation value and stochastic averaging of the product of photon amplitudes, which enter the polariton operator, and the polariton operators themselves. Factorization of this expectation value, which has been justified in the text, allowed us to derive the final expression for the fluorescent intensity. It is proportional to the two-particle polariton average and to the averaged amplitudes.

The obtained result has a clear simple physical interpretation: due to interaction with the vibration modes, the two-particle polariton average diffuses along the lower polariton dispersion branch. During the diffusion process, the polariton luminescence spectrum broadens in the frequency domain. As the polariton frequency approaches the energy of the molecular luminescence, the polariton relaxation stops. The maximum of the polariton luminescence, however, stays blue-shifted with respect to that of the exciton luminescence, which agrees with the experiment. This blue shift is explained by decreasing the excitonic component of the polariton in the range of the exciton luminescence. We proposed the polariton emission mechanism in which the spreading of the two-particle polariton expectation value onto the range of small wave-vectors is prevented by the finite size of the nanofiber.

The theory presented in the article can be also applied to various problems of polariton chemistry, condensation of polaritons and polariton lasing in molecular systems based on organic dyes, J- and H-aggregates, and eGFP in microcavities.

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VII. APPENDIX A

The transformation coefficients $u_{smv}$ and $v_{sq}(q)$ in Eq. (14) and the polariton spectrum $\Omega_s$ can be found by evaluating the commutator $[\hat{p}_s, \hat{H}] / \hbar$ once directly using Eq. (16) and once using Eq. (14) together with the total
Hamiltonian \[\{13\}\]. We obtain

\[
\Omega_s p_s = \Omega_s \left[ \sum_q v_s(q) a_q + \sum_{mv} u_{smv} b_{mv} \right] - \sum_q \int \frac{d^3 r_m}{(2\pi)^3} e^{i r_m \cdot q} \left[ \sum_{lm} u_{smv}^{lm} \left( e^{-\frac{X_{lm}^2}{2 \omega q^2}} \right) + \sum_{lm} u_{smv}^{lm} \left( e^{-\frac{X_{lm}^2}{2 \omega q^2}} \right) \right] b_{mv} (58)
\]

Comparing the coefficients of \(a_q\) and \(b_{mv}\), we find

\[
(\Omega_s - \omega) v_s(q) = \frac{ig}{\omega q} \sum_{mv} e^{-\frac{X_{lm}^2}{2 \omega q^2} + i q \cdot r_m} u_{smv}^{lm} X_{lm}^v (59)
\]

and

\[
u_{smv} = \frac{-i}{\Omega_s - (\omega + \omega_{st}/2 + \alpha_m)} \times \sum_q g_q \left( -\frac{X_{lm}^v}{2 \omega q^2} - \frac{X_{lm}^v}{\omega q^2} \right) e^{-\frac{X_{lm}^2}{2 \omega q^2} - i q \cdot r_m} (60)
\]

Introducing a small decay, the term \(1/|\Omega_s - (\omega + \omega_{st}/2 + \alpha_m)|\) in the right-hand side of Eq. (60) can be

written as

\[
\lim_{\gamma \to 0} \frac{1}{\Omega_s - (\omega + \omega_{st}/2 + \alpha_m + i \gamma)} = \zeta[\Omega_s - (\omega + \omega_{st}/2 + \alpha_m)] (61)
\]

where \(\zeta[\omega] = P - i \pi \delta[\omega]\), and \(P\) stands for the principal value. Substituting Eq. (61) into Eq. (60), we get Eq. (17) of the main text.
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52 Absorption and luminescence spectra in our theory have mirror symmetry. In contrast, the experimental luminescence spectrum is broader than the absorption one, and the corresponding Stokes shift is slightly larger than one expects from the absorption spectrum bandwidth [11,21]. However, the relative position of the polariton and the exciton luminescence spectra in experiment and theory stays the same.