Thesis Changes Log

Name of Candidate: Anton Baranikov
PhD Program: Physics
Title of Thesis: Dynamic polariton condensation in organic microcavities
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Chair of PhD defense Jury: Prof. Nikolay Gippius **Email**: *N.Gippius@skoltech.ru*
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The thesis document includes the following changes in answer to the external review process.

Dear Jury Members,

I am grateful for your helpful suggestions and comments. Here I provide the answers and the thesis modifications.

Reviewer: Prof. Simone De Liberato

1) The description of Fig. 2.4 could be expanded. The origin of the Stoke shift of the zero-phonon line should be explained.

Answer: Usually, organic molecules display Stokes shift of the zero-phonon line due to a lot of factors such as solvent effects, reorganization of the molecular structure in excited states, or inter/intramolecular energy transfer [1]. However, these pure structural processes are often blurred by reabsorption of the highest-energy photons resulting in the redshift of the luminescence. The resulting Stokes shift is observed to be ~0.06 eV in ladder-type polymers like MelPPP [2]. To resolve pure effects, one can perform single-molecule spectroscopy measurements. In this way, it was shown that excited state reorganization causes only a small Stokes shift ~0.01 eV due to the rigid backbone of the MeLPPP polymer [3], while the intramolecular energy transfer affected much stronger (up to 0.04 eV). The latter effect manifests the energy migration towards parts of the molecules with larger wavelength emission resulting in the Stokes shift of the zero-phonon line.

The observed Stokes shift (Figure 3.2a) is attributed to all of three reasons listed above. The corresponding text has been added to the Sections 2.1.2 and 3.2.

2) Eq. 2.9 should be better formatted.

Answer: Corrected.

3) The equation in the text below Eq. 2.9, describing the condition of strong coupling is dimensionally wrong.

Answer: In fact, there is no mistake in the dimensionality. I guess, that the definition of the damping rate of a mechanical oscillator γ could cause the confusion. While the coupling strength Γ has the same dimension as ω: [s^{-1}], γ has dimension [$s^{-1}\cdot kg$]. The latter originates into the equation of motion for a mechanical oscillator where the frictional term is written as $\gamma\cdot\dot{x}$ [4]

4) The reason Eq. 2.13 is different from Eq. 2.9 should be clearly explained (i.e. the use of RWA).

Answer: Thank you very much for this comment. Indeed, Eq. 2.9 can be reduced to Eq. 2.13 taking into account small detuning between the oscillators, i.e., $|\omega_A - \omega_B| \ll \omega_A + \omega_B$. The same approximation (rotating wave approximation or RWA) is made in Jaynes-Cummings model describing the interaction between a two-level system and a cavity field [5]. Under the dipole approximation, the interaction Hamiltonian reads: $\hat{H} = -\hat{d}\cdot\hat{E}$, where $\hat{d}$ is dipole operator, and $\hat{E}$ is a single-mode cavity field. Introducing the creation and annihilation operators for the exciton and the photon, we may integrate the time-dependent Schrodinger equation and omit the terms containing $\omega_A+\omega_B$ in the denominator. Such approximation allows reducing the interaction Hamiltonian to the formula (2.11) of the thesis. The appropriate text has been added to the manuscript.

5) The scaling of the vacuum Rabi frequency with the mode volume below Fig. 2.6 seems wrong to me. Please change it or explain its origin.

Answer: Indeed, there is a typo. According to the usual two-level system – cavity coupling theory $\Gamma \sim (V_{cav})^{-0.5}$ [6]. The appropriate correction has been made in the manuscript.

6) The nature of the three vibronic modes in Fig. 3.2 c should be better discussed.

Answer: Such complicated long-chain polymers as MeLPPP exhibit complex Raman spectra because of the diversity of intermolecular interactions. Each of the vibrational degrees of freedom possesses a resonance resulting in a lot of spectral peaks. The Raman spectrum of MeLPPP was investigated and interpreted in several studies. As depicted in Figure 3.2c, it has three strongest resonances V1, V2, and V3. The former is attributed to interring CC stretching oscillations (i.e., along the line of the chemical bonds). V2 and V3 present aromatic intra-ring CC stretching modes. The discussion on the vibronic modes of MeLPPP has been added to the manuscript.

7) On page 49 the best fits for the two vacuum Rabi frequencies are provided. Can their ratio be verified with a weak coupling (free space) measurement?

Answer: Unfortunately, the sample has not been prepared in our laboratory. It has been provided to us by our collaborators from IBM-Research Zurich. Since it is a strongly-coupled microcavity, we are not able to do weak coupling measurements with this sample.

8) In Fig. 3.4 what are the features in the bottom right corners?

Answer: Note that Figure 3.4b is rescaled displaying the intensity from 0.72 to 1. Owing to a small reflectance (less than 0.72), the bottom right corner is depicted in white color.

9) On page 70, how is the pump value of 180 \muJ/cm^-2 chosen?

Answer: Such value is chosen to be at the saturation regime (~$2P_{th}$) and consequently minimize errors caused by the laser power fluctuations and nonlinear response of the sample. The corresponding sentence is present in the manuscript.

10) In Fig. 5.2 the control beam doesn't reach the spot A.

Answer: This has been done intentionally in order not to obstruct the figure.

11) The presentation of section 5.3 should be improved. Right now it is rather difficult to follow.

Answer: The section 5.3 has been rewritten in more simple words with more detailed explanations.

12) Conclusions should be expanded, and the candidate should develop a bit more his personal vision for the future.

Answer: The conclusions section has been expanded in order to elaborate the author's opinion.

13) In Fig. 4.3 the probe is in resonance with the bare LP mode, while the pump+probe signal is blueshifted. Does this pose a limit to the cascadability of the platform, as each step of the cascade will be more blue-shifted than the previous one? If this is the case such a limitation should be properly discussed and its effect estimated.

Answer: This question is closely related to the recent work of the colleagues [7]. They found out that the blueshift in an organic microcavity is induced by the reduction of the Rabi splitting upon photoexcitation. Following this approach, the Rabi frequency reads:

$$\hbar\Omega = \hbar\Omega_0\sqrt{1-\frac{2(n_x+n_p)}{n_0}}$$

where $n_x + n_p$ is the total number of excitations (sum of excitons and polaritons) and n_0 is the total number of molecules, contributing to the strong-coupling. In this way, the Rabi splitting reduces at higher excitation intensities. Consequently, it renormalizes the lower polariton mode resulting in the blueshift.

Going back to the cascadability experiment, one can note that the pump beam intensity is much higher than the probe. Consequently, at the second amplification step the blueshift will be defined mostly by the total number of excitations induced by Pump 2. A proper adjustment of pump intensities could result in a negligible further blueshift at the second stage.

Reviewer: Prof. Dmitry Gorin

1) page 43. 2.2.3 Inorganic vs organic. It could be useful to give the comparison of inorganic vs organic in the table where disadvantages and advantages organic and inorganic materials will be presented

Answer: The corresponding Table 2.1 has been added.

2) a summary after every chapter including the review would be very useful

Answer: A summary for every chapter has been added.

3) the bibliography list contains only 68 references. It could be useful to increase the number of references;

Answer: The bibliography has been revised and expanded to gain more insight into the past and the future perspectives of organic polaritonics.

4) page 41, Fig.3.1, please add information about the thickness per every layer;

Answer: Added.

5) page 81, chapter 6, please to use THz instead of "Thz".

Answer: Corrected

Reviewer: Prof. Sakellaris Mailis

1) One point of criticism is that the level of citations is probably at a bare minimum given the rich publication pool that is associated with this field. Perhaps the candidate could consider enriching the citation list of the thesis for the benefit of future students that will follow up on this research.

Answer: The bibliography has been revised and expanded to give more insight on the past and the future perspectives of organic polaritonics.

References:

[1] Lakowicz, J. R. *Principles of fluorescence spectroscopy* (Springer Science & Business Media, 2013).

[2] Pope, M. & Swenberg, C. E. *Electronic processes in organic crystals and polymers* (Oxford University Press, New York, 1999).

[3] Muller, J., Anni, M., Scherf, U., Lupton, J. & Feldmann, J. *Vibrational fluorescence spectroscopy of single conjugated polymer molecules.* Physical Review B 70, 035205 (2004).

[4] Novotny, L. *Strong coupling, energy splitting, and level crossings: A classical perspective.* American Journal of Physics 78, 1199-1202 (2010).

[5] Gerry, C., Knight, P. & Knight, P. L. *Introductory quantum optics* (Cambridge university press, 2005).

[6] Fox, M. *Quantum optics: an introduction*, vol. 15 (OUP Oxford, 2006).

[7] Yagafarov, T. et al. *On the origin of blueshifts in organic polariton condensates.* arXiv preprint arXiv:1905.02573 (2019).