

Thesis Changes Log

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PhD Program: Physics

Title of Thesis: Polariton lasing in a dye-filled organic microcavities

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Chair of PhD defense Jury: Prof. Nikolay Gippius

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The thesis document includes the following changes in answer to the external review process.

Dear Jury Members,

Thanks for your positive reviews and valuable questions, comments, and suggestions, which improved my thesis a lot. In response to one of the reviewer's comment, the significant changes were made in the thesis by taking into account the role of weakly-coupled molecules. We discovered its contribution to the polariton blueshift by performing Kramers-Kronig analysis of the complex refractive index for the cavity and implemented cavity mode energy renormalization term into the model. Following that analysis, we found that polariton blueshift in organic microcavities is originated from both the vacuum Rabi-quenching and cavity mode energy renormalization of strongly- and weakly-coupled molecules, respectively, caused by the saturation of molecular optical transitions. The appropriate changes were made in the Section 4.4.4 and Appendix part have been added into the thesis.

Please find below both the answers to the questions/comments and a detailed description of modifications made (written with bold) in the final thesis version. The pages here are mentioned according to the final version of the thesis.

I. Based on the Jury Member Report from Professor Simone De Liberato, there are changes made according to the following suggestions:

- 1) I cannot find the definition of ϵ in Eq. 2.7.

The description for the variables ϵ used in Bohr radius formula was included: "...where \hbar is the reduced

Planck constant, ϵ is the permittivity of the medium, ϵ_0 is the vacuum permittivity constant, e is the elementary charge and μ is the effective mass of the exciton.” (Page 29)

- 2) On page 27 Ω_0 should be called Vacuum Rabi Frequency, to distinguish it from the AC-Stark shift case.

The correction was implemented: “...characteristic energy exchange frequency Ω_0 called *vacuum* Rabi frequency.” (Page 30)

- 3) On page 27 it is said that strong coupling is realized if the coupling is **much** larger than the dissipation. The candidate should define what much means in this context.

The following paragraph with a discussion of the coupling strength was added: “...the microcavity photon decay rate γ_1 and the exciton decay rate γ_2 . If the energy exchange between the photons and excitons in microcavity happens much faster than any dissipations in the system, $\Omega_0 \gg (\gamma_1, \gamma_2)$, then the strong coupling regime is realized...

...The strong coupling criterion mentioned above is rather intuitive than strictly defined. The further clarification of strong coupling condition can be considered from the spectroscopic criterion which says that the measurable splitting of two polariton states can be resolved if the frequency splitting is bigger than the sum of the linewidths of loss rates $\Omega_0 > \frac{|\gamma_1 + \gamma_2|}{2}$, according to [35]. Sure, that definition is reasonable in terms of the experimental approach, however, if one wants to access the strength of the coupling, the proper figure of merit would be the ratio $\frac{\Omega_0^2}{\omega_0 \gamma}$, where $\gamma = \frac{(\gamma_1 + \gamma_2)}{2}$ is the loss rate, and ω_0 is the eigenfrequency of the bare oscillators. If the ratio $\frac{\Omega_0^2}{\omega_0 \gamma} > 1$, there is an efficient energy exchange between oscillators and the system appears in the strong coupling regime [36].” (Page 31)

- 4) What are the features appearing on the corners of Fig. 2.5?

Figure 2.5 have been plotted from the stitched reflectivity spectra measured in the range of 460-550 nm at different angles of incidence (from 10° to 60°). The color bar in right bottom corner corresponds to the reflectivity scaling where dark red color corresponds to 100% and dark violet – to 1% of reflection. The features in the top-left and bottom-right corners are the sides of the stopband, where reflectivity drops to $\sim 50\%$. For that clarifications, Figure 2.5 legend was expanded as follows: “...**Color bar is the reflectivity scaling. Note, here the sides of the reflectivity stopband are seen in the corners.**” (Page 34)

- 5) In section 2.2.1 it is stated that condensation and Bose-Einstein condensation are not the same thing. This should be properly discussed.

Sorry for a confusion. The point of this remark was not to state that “polariton condensation is not the same as Bose-Einstein condensation”. It is more about the terminology which is appropriate to use.

There are several disputes on this topic, for example: [Butov, L. V., & Kavokin, A. V. (2012). Nature Photonics, 6(1), 2–2.], [Deveaud-Plédran, B. (2012). Nature Photonics, 6(4), 205–205.], [Tim Byrnes, arXiv:1411.6822v1, 2014], etc. For instance, in the first review the authors conclude the following: “However, there is little agreement in the community regarding the nature and associated terminology of this

condensate: is it a Bose–Einstein condensate (BEC), a laser, or something else? Here we wish to point out that describing polaritons and their condensate in terms of a BEC and superfluidity may be misleading The term ‘polariton laser’ does seem to be appropriate for a polariton condensate. The physics of a polariton condensate, although different from that of a BEC”.

Despite the fact that classification of BEC/polariton condensate/polariton BEC/polariton lasing was not the objective of the study, it is worth to mention, that in our experiments on polariton lasing observation we were not strictly in the thermal equilibrium – the property essential for BEC.

However, it would be good to appoint for readers, that further in the thesis the term “polariton lasing” is used in the meaning of the process which is a result of condensation of bosonic particles, polaritons, but without the necessity of thermal equilibrium. The following remark have been added into the thesis:

“(*Regarding the disputes on the terminology in polaritonics community [42–45], it will be worth to mention that further in the thesis we will use the term polariton condensation, or polariton lasing, in terms of collective behavior of bosonic particles (polaritons), without the strict necessity of the system equilibrium – the property essential for Bose-Einstein condensates).” (Page 35)

6) On page 38 ASE should be properly explained.

The paragraph about ASE has been modified: *“Another essential characteristic of the active medium is a material optical gain. The material gain spectral region is usually indicated by the amplified spontaneous emission (ASE). ASE is a process where spontaneously emitted luminescence is amplified.”* (Page 42)

7) Through the manuscript, there are a number of equations not provided in symbolic terms (e.g., beginning of page 39). This is incorrect. Both the quantities on the left and right hand sides of every equation have to be provided also in symbolic form.

Thanks a lot for correction. The symbolic forms for equations in Chapter 3 were added.

8) On page 43 there is a meV missing.

“The vacuum Rabi splitting $\hbar\Omega_0 = 116 \pm 2$ *meV* was almost invariant...” was corrected. (Page 47)

9) Section 3.4.2 is difficult to understand. It should be rephrased and better explained.

I fully agree with that point. That is why Section 3.4.2 was reformulated. The rudimental part with the integration sphere measurements now moved to the Appendix. The rest text has been modified and adequately described in a clear way.

10) What is the black polygon in Fig. 3.10?

The black polygon on the chromaticity diagram corresponds to the range of the colors, which one can obtain by using the characterized microcavities. Corresponding description and reference have been included. ***“...The black polygon on the chromaticity diagram corresponds to the color range [53], which one can obtain by using the characterized microcavities.”*** (Page 55-56)

11) In Fig 3.10 units are missing from the top right corner

Thanks a lot for mentioning that mistake. Units were added in the top right inset of Figure 3.10.

12) On page 53 a procedure to estimate the threshold incident excitation density is discussed but it is not clear to me whether the data are presented. If they aren't please add them.

The new Figure 3.11 has been added as well as the corresponding description and legend:

“...For a subset of presented wavelengths, we performed the full excitation density dependence, which allowed us to estimate the dependence of the polariton lasing threshold on the exciton–photon gdetuning. We observed a nearly constant condensation threshold across the entire detuning range with an average threshold value of $\approx 6.5 \text{ mJ cm}^{-2}$ (standard deviation of 1.5 mJ cm^{-2}).

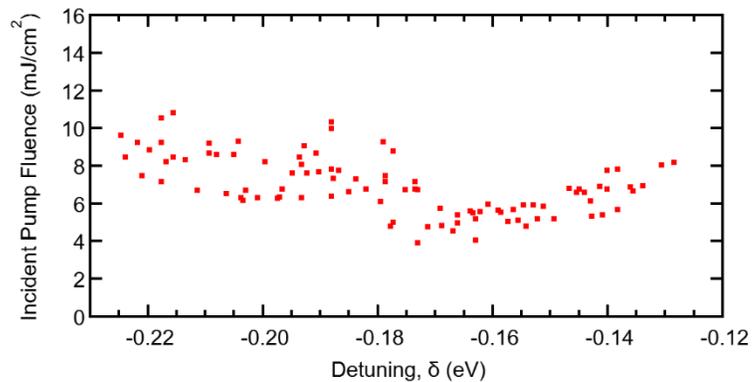


Figure 3.11. Polariton lasing threshold dependence versus the exciton-photon detuning. Nearly constant condensation threshold $\approx (6.5 \pm 1.5) \text{ mJ cm}^{-2}$ observed across the entire detuning range.” (Page 57)

13) In section 3.4.4 I could not find the definition of “d”.

Figure 3.12 has been modified. Now d is the diameter corresponding to the pump spot, and d_{lasing} is the diameter which corresponds to the lasing observed above the threshold. The description of Figure 3.12 has been changed in the text with appropriate definitions for d and d_{lasing} : *“...For estimation, we pumped the microcavity with the pump beam of Gaussian profile with diameter $d = 18 \mu\text{m}$ at one over e^2 level... When we pumped the structure with a single pulse of 320 pJ of absorbed energy ($\sim 1.6 P_{\text{th}}$), the lasing is observed from a small area with diameter $d_{\text{lasing}} \approx 6 \mu\text{m}$ as shown in Figure 3.12(b)”*. (Page 57-58)

14) In Fig. 4.9 it is not clear to me how the data points in panel a) are reduced to these in the other panels.

There is a paragraph in section 4.4.1 which describes the data binning procedures:

“To make the scatter plot dependence trend more pronounced, we performed the binning with the Sturges’ formula [75] which defines an optimal number of binning points for the data scattering reduction. According to the rule, the number of bins is $k = 1 + \log_2(n)$, where n is the total amount of observations. Taking $n = 378$ into account, we got $k = 9.56$, i.e., nine bins of 14.1 meV width for the measured LPB energy range. In Figure 4.6, we superimposed the binned data points for blueshift (black squares) with the amplified spontaneous emission spectrum (red curve).”

In the case of blueshift dependence on exciton fraction (Fig. 4.10), the same binning procedure used. To make the transition to the reduced graphs clear, the following reference to the section 4.4.1 was added in the Figure 4.10 legend:

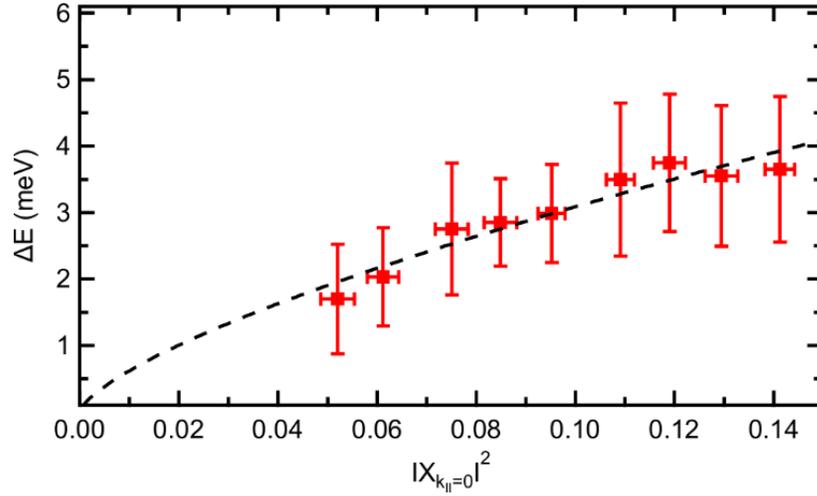


Figure 4.10. The blueshift ΔE versus exciton fraction. The dependence of the blueshift on the exciton fraction is calculated by binning the scattering plot (section 4.3.1) and taking into account the dependence of exciton fraction on the ground polariton state energy (Figure 4.9(d)). The dashed black line is the best-fit result by power-law $\Delta E \sim (|X_{k_{||}=0}|^2)^\beta$ with variable parameter $\beta = 0.7$. (Page 74)

15) This is just a comment on which the candidate should not feel obliged to act, but why between panels b) and c) of Fig. 4.9 the same energy is referred once as 120meV and the other as 0.12eV?

For the sake of unification Figure 4.9 c) has been updated with [meV] units for Rabi splitting. (Page 73)

16) Fig. 4.10 definitely rules out a quadratic dependency, but leaves some space for a linear one. As such the discussion about the clamping of the excitation density presented on page 72 should be expanded and clarified.

Based on the quenching of the vacuum Rabi splitting only, the blueshift dependence is $\Delta E_{LPB}^\Omega = \frac{\xi}{2} \left(\frac{s \cdot \hbar \Omega_0}{\sqrt{1+s^2}} \right)$ where we assume effective saturation parameter $\xi = \frac{(n_x + n_p)}{n_0} \ll 1$ and introduce $s = \frac{\hbar \Omega_0}{|\delta|}$ is being a parameter of strong coupling (Refer to Eq. (4.11) on Page 80 in the thesis). Since we deal with negatively detuned microcavities, we should rewrite the expression of exciton fraction on both detuning and vacuum Rabi splitting, in the following way: $|X_0|^2 = \frac{1}{2} \left(1 - \frac{1}{\sqrt{1+s^2}} \right)$. Now, if we define S as a function of exciton fraction, and introduce it into the ΔE_{LPB}^Ω , we will find the square root dependence for small saturation parameters and exciton fractions, $\xi \ll 1$ and $|X_0|^2 \ll 1$, respectively: $\Delta E_{LPB}^\Omega = \xi \cdot \hbar \Omega_0 \cdot (|X_{k_{||}=0}|^2)^{1/2}$

The graph which shows the blueshift dependence on the exciton fraction (see answer to the question 14) have been updated. By fitting the data with the power law, we found that the best fit parameter was $\beta = 0.7$, while the exciton-polariton and polariton-polariton interactions, if they are present, would

lead to superlinear dependence as characterized by $\beta_{x-p} = 1$ and $\beta_{p-p} = 2$. (Page 74)

The discussion on the sub-linear dependence in case of bare Rabi saturation mechanism is included in the thesis in Appendix 6 (Polariton blueshift versus exciton fraction), (Page 110):

“Here we extend the dependences for a broad range of exciton fractions up to 0.5 and provide a separate analysis of both contributions: the cavity mode energy renormalization and Rabi-quenching. Figure S9 represents polariton blueshifts as the function of exciton fraction.

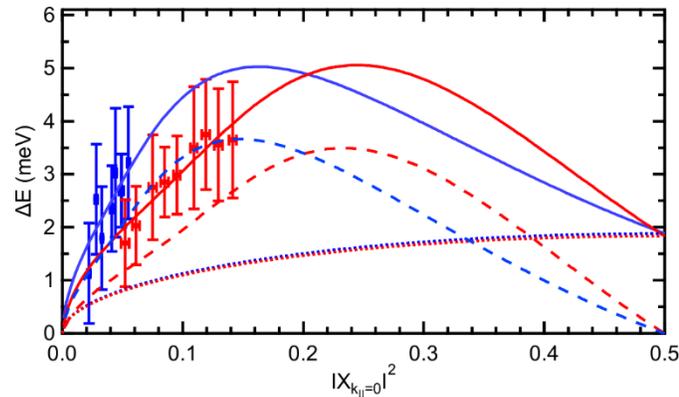


Figure S9. The blueshift ΔE versus exciton-fraction for 5% (blue) and 10% (red) samples. Solid curves show the best-fit results, according to Eq. (4.11). Short dashed curves correspond to the Rabi-quenching term, while the long dashed curves are associated with the cavity mode energy renormalization.

17) The origin of the square root dependence of the vacuum Rabi frequency upon the number of molecules should be discussed.

The square root term appears from the quantum description of the light-matter coupling, when the scaling of the Jaynes–Cummings Hamiltonian is done by Holstein–Primakoff transformation in order to extended model to N oscillators.

The microscopic model of Rabi quenching has been introduced by our collaborator, Ivan Shelykh, who theoretically derived the vacuum Rabi frequency dependence on the number of molecules. In order to satisfy your question, the corresponding theoretical studies were included into the thesis, please, refer to “*Appendix 2. Microscopic model of the quenching of the Rabi splitting*” (Page 93)

18) Fig. 4.14 clearly shows how the steepness of the blueshift increases with the intermolecular energy transfer. Given that all the results of chapter 4 rest on this fact, a better microscopic explanation would be appreciated.

In the investigation I have not done the microscopic model by myself (as was mentioned in the question above), that is why it is not considered. It would be the step for further development of the theory.

19) I am not sure I understand the first equation on page 79. On page 78 F_c is defined by the equation $N_0^{\parallel} = N_0^{\perp} = F_c N_{\text{tot}}$. $N_0^{\{x\}}$ is the number of out-of-plane molecules, but shouldn’t it include also **all** the uncoupled molecules? If that’s the case $N_0^{\{x\}} = N_{\text{tot}}(1 - 2F_c)$. Otherwise what is the difference between

a molecule which is uncoupled because its dipole is orthogonal from one whose dipole has some other form of disorder? Orientational disorder has a role similar to other forms of disorder, as shown for example in PRB **71**, 115320 (2005).

As was mentioned in the very beginning, we changed the concept in the blueshift interpretation, by taking into account the weakly-coupled molecules. Concerning that, the description of the molecules has been changed. In the Appendix 4 (Numerical simulations), all the molecules present in the microcavity and taking place in strong coupling are reading as follows: “*We introduce a coupling coefficient f_c defining the density of coupled molecules as $N_0^{\parallel} = N_0^{\perp} = N_0^{\times} = \frac{f_c N_{tot}}{3}$* ”. They are contributing into the blueshift part which relies on Rabi quenching. (Page 100)

“...Since the cavity energy renormalization term invokes the subset of weakly-coupled molecules, we calculate the time-dependent change in the refractive index $\Delta n_{\parallel, \perp}(t)$ by using the same rate equations above and applying the following boundary conditions: $N_0^{\parallel} = N_0^{\perp} = N_0^{\times} = \frac{(1-f_c)N_{tot}}{3}$...“ (Page 104)

20) Extra suggestion on language improvements:

I did my best and checked the dissertation on the subject of language improvements. Some sentences were corrected, and paragraphs were rewritten in order to make the readability clear. Spellings, articles, typos were corrected as well. In Chapter 4, the structure has been modified following the new data added into the thesis; the explanation now is better.

II. Based on the Jury Member Report from Professor Arkady Shipulin, there are changes made according to the following suggestions:

1. Page 78. Molar absorption coefficient and molecular weight were given without units. The SI unit of the molar absorption coefficient is $\text{m}^2\text{mol}^{-1}$. Also called extinction coefficient, but usually in units of $\text{dm}^3\text{cm}^{-1}\text{mol}^{-1}$. Molecular weight is measured in unified atomic mass units (u or Da);

Thanks a lot for your correction. The units for extinction coefficient and molecular weight have been added in accordance with the dyes specifications: “...molar extinction ratio $\epsilon = 95500 \text{ cm}^{-1} \text{ M}^{-1}$ and molecular weight of the dye $M = 384,18 \text{ g mol}^{-1}$.” (Page 100)

2. Bibliography list consists of only 67 references. It is an unusual number of references for the PhD thesis. The typical number for a PhD thesis is more than one hundred references.

The bibliography list has been expanded. There are 96 references currently in the thesis manuscript.

III. Based on the Jury Member Report from Professor Nikolay A. Gippius, there are changes made according to the following suggestions:

1. I do not have major remarks concerning the thesis. I have noted that the detuning δ and Rabi splitting $\hbar\Omega_0$ sometime are shown in different units (eV and meV, e.g. in Fig.4.9). I suggest to use the same units for them everywhere (e.g. meV).

Thanks a lot for the correction. Figure 4.9 has been updated with [meV] units for Rabi splitting. That correction also implemented in the text where was appropriate. (Page 73)

IV. Based on the Jury Member Report from Professor Sakellaris Mailis, there are changes made according to the following suggestions:

1. I found that the outlook section was rather limited. Perhaps the candidate could offer a more insightful perspective of the future directions that could be followed as a result of this work.

Thanks a lot for the question on Kramers-Kronig mechanisms, which made the outcomes of the thesis stronger. Regarding that mechanism, there are additional perspectives opened for the study of polaritons non-linearities. Corresponding outlooks were included in the Chapter 5.

2. In the discussion about the origin of the blue shift, which is observed in organic polariton condensates, perhaps the effect of the refractive index change in the cavity, as a result of the absorption change (due to the saturated transition) through the Kramers-Kronig relation could be investigated.

In response to the comment, we have significantly revised the manuscript by taking into account the role of weakly-coupled molecules. We discovered its contribution to the polariton blueshift by performing Kramers-Kronig analysis of the complex refractive index for the cavity and implemented cavity mode energy renormalization term into the model. We showed that polariton blueshift in organic microcavities is originated from both the vacuum Rabi-quenching and cavity mode energy renormalization of strongly- and weakly-coupled molecules, respectively, caused by the saturation of molecular optical transitions. Following the new findings, the thesis has been extended with the relevant discussion and analysis, new Figures. Most of them are in the Section 4.4.4 and Appendix.