POLAROM: POLARitons in Organic Microcavities

Leonidas Mouchliadis[1,2]

[1]*Department of Physics, University of Crete, 71003 Heraklion, Crete, Greece*
[2]*Foundation for Research and Technology-Hellas, Institute of Electronic Structure & Laser, 71110 Heraklion, Crete, Greece*

The present report summarizes the main results obtained during my POLATOM research visit at the University of Southampton. In particular, the purpose of the visit is discussed in detail and the work carried out during the visit is described. Consequently, the main results obtained are briefly presented and dissemination of these results is expected to be made both by a publication in Physical Review B and through a talk at an international conference. Finally, the issue of future collaboration with the host institute is addressed and the benefits of close work between theoreticians and experimentalists are discussed.

Purpose of the visit

The principal purpose of the present research visit was to develop a complete theory describing the linear and nonlinear optical properties of polaritons in disordered organic microcavities (J–aggregates) where the influence of the phonon environment into the dynamics of the system should be taken into account in full detail. Realistic systems were considered and experiments were proposed and designed in close collaboration with Prof. Lagoudakis and Dr. Somaschi, the experimentalists at the University of Southampton.

In particular, the aim was to formulate a set of Heisenberg equations of motion for the upper (UP) and lower (LP) polariton branch operators as well as for the exciton reservoir (ER) operators. The nature of these incoherent ER states and their influence on the polariton population buildup and scattering rates was one of the main issues of interest.

Moreover, the environment of molecular vibrations assists intra– and inter–branch scattering, as well as scattering between delocalized polaritons and localized excitons in the ER. The study of these processes and their role in the polariton population buildup times was also of central importance. Furthermore, unlike inorganic semiconductors, polaritons in organic–based structures exhibit a minimum (for both LP and UP branches) and maximum (for the LP branch) value of well–defined wavevector. However, polaritons possessing momentum within this region, are characterized by the their robustness up to room temperature, a feature which renders them unique candidates for the fabrication of lasers with low threshold powers.

In summary, the purpose of the visit was to combine an accurate theoretical description with a state–of–the–art experimental procedure in order to enhance the understanding of both theoreticians and experimentalists on the linear and nonlinear optical properties of J–aggregates inside a microcavity. This was achieved by establishing a two–way communication of prediction/confirmation between theory and experiment achieving in this way the advancement of both.

Description of the work carried out during the visit

During the first weeks of the visit the equations of motion for the polariton and exciton populations were formulated including exciton–exciton interactions and coupling to a phonon bath with both continuous and discrete phonons. Inclusion of the latter required an accurate knowledge of the Raman spectra in order to identify the most prominent molecular vibrations characteristic for the structure studied. Direct access to the experiment and the ability to obtain experimental results on demand not only led to a more concrete theoretical model but also accelerated the whole process of simulation.

Moreover, solution of the organic polariton equations of motion in the presence of an exciton reservoir would be cumbersome without the assistance of the experiment due to the vast parameter space. By proceeding in parallel with the experiment, the majority of the parameters where fixed by realistic values after being measured in experiments particularly designed for this purpose. Indeed, this constitutes a powerful tool in the hands of a theoretician, namely to be able to decide the values of some parameters in the equations not by guessing or being advised the literature but actually performing the experiment.

Establishment and consequent solution of the equations of motion allowed for both testing these equations by reproducing results known from the literature and predicting new effects which could then be confirmed by the experiment. In this way the theoretical results where immediately checked by the experiment and vice versa.

As a first check of the theory the steady state lower polariton photoluminescence was calculated revealing a remarkable agreement with results from previous works. In order to achieve this, the phonon–assisted scattering processes were taken carefully into account by introducing two kinds of phonons: acoustical ones, being responsible for the intra–branch thermalization process of polaritons, and molecular ones, assisting the scattering from the exciton reservoir to the LP branch. Indeed, before considering such kind of processes accurate knowledge of the incoherent ER states was needed and therefore this was the initial step for all of the simulations: to calculate the energies, amplitudes, oscillator strengths and inverse participation ratios of the ER states in the absence of the cavity.

Moving forward, the situation of pump–probe experiments was simulated and in particular the polariton population build–up times with respect to the pump pulse duration. Unlike common belief, the theory was able to predict a delay between pumping the highest energy exciton state and decaying of the lowest polariton state. As a result, a deeper understanding into the polariton formation and decay times was achieved and the sub–100 fs times observed in the experiment were explained by the theory.

Finally, the role of the exciton–exciton interactions reflecting the saturation of oscillator strength in J–aggregates was studied by including nonlinear terms in the Hamiltonian. At this stage, the experimental assistance was necessary to establish the strength of the nonlinear coefficient. In order to achieve this, the experimentalists used a zeta scan technique to determine the $\chi^{(3)}$ nonlinearity coefficient which was then used as an input in the theoretical model. Notably, the contribution of the experiment was of utmost importance as it allowed for limiting the vast parameter space down to a narrow interval of values.

As far as the polariton lasing is concerned, it remains unclear whether there exists a threshold condition in disordered microcavities operating in the strong coupling regime as it is the case for inorganic or organic crystalline systems. Although some speculations can be made, strong theoretical or experimental arguments are still lacking. However, the present incomplete understanding can serve as a motivation for further research and potentially future collaboration between the author and the host institute.

Description of the main results obtained

As mentioned in the previous sections most of the aims of the project were fulfilled successfully while when this was not possible an advancement of the present knowledge also occurred.

Firstly, the polariton population buildup times where theoretically explained and it was shown that following nonresonant excitation, the states in the ER are rapidly populated allowing consequent population of the LP states by means of molecular vibration emission. The role of low wavelength phonons present in noncavity J–aggregates becomes prominent when a microcavity is introduced. This reflects the hybridization of excitons with the fundamental cavity mode which results in the UP and LP splitting and offers new available states for the ER excitons to scatter to/from via emission/absorption of large energy molecular quanta. Identifying the lower polariton population with the photons emitted at these particular energies one is led to the conclusion that the LP population buildup is completed within several tens of fs. As a result, the photoluminescence is characterized by discrete peaks corresponding to transitions from the ER to the LP by emission of a molecular phonon. Indeed, changing the exciton–photon detuning results in different regions of the LP branch being populated, as in this case different molecular vibrations become important. Notably, such an achievement in the theoretical prediction could not be made possible without accurate knowledge of the Raman spectra that dictate which vibrations are important at different detunings.

Along with the buildup time, the decay time of polaritons in the LP branch was also determined. Although this is mainly influenced by the cavity photon lifetime, it was found that when the system is excited nonresonantly the PL does not follow the shape of the pump pulse. The reason for this is that the equilibration of the ER is not instantaneous but a finite amount of time is required before it reaches a thermal distribution. As a result, unlike previous belief the buildup and decay of polaritons occurs with a delay with respect to the pumping pulse and therefore is not directly influenced neither by its shape nor by its duration. The main factor influencing this decay is the decay rate between the ER states.

Finally, the very limited literature reports on nonlinearities in disordered microcavities are going to be enriched by the outcome of the present research and some first results seem very promising for exploitation of these nonlinearities in order to create low threshold organic–based lasers operating at ambient temperature. From a theoretical point of view the nonlinear terms appear when one substitutes the Paulion operators by Bosonic ones using the Agranovich–Toschich transformation. These terms which were neglected in a first approximation in the study of the linear properties, were retained in the last part of the project and their influence on the population buildup was studied.

Remarkably, inclusion of these terms reveals an even faster population buildup time, approaching very close to the experimental values.

Future collaboration with the host institution

In addition to the past common publication with the experimentalists at the host institute and the very fruitful present collaboration which is going to result in another common publication, the future collaboration was ensured thanks to the POLATOM research visit grant. Several fundamental questions regarding polaritons in organic microcavities remain unanswered and there exists a variety of unresolved issues. As a result, the mutual enhancement of understanding obtained during the visit is going to be continued in the future with additional short visits from both sides and potentially a further publication dealing with the problems not addressed in the present work. These include a full understanding of the exciton–exciton nonlinear interactions as well as the ultimate goal of researchers working with organic microcavities in the strong coupling regime: to combine the large binding energy Frenkel excitons in organic systems with the Wannier–Mott excitons in inorganic ones in order to build hybrid nanostructures and exploit in this way the potential of both kinds of excitons.

Projected publications to result from the grant

Dissemination of the results obtained during the visit will proceed through publication in a high–rank international journal, and a talk at an international conference along with seminars at various universities. In particular, a long paper describing in detail the theory will be submitted to Physical Review B. Considering the time needed for completion of the refereeing procedure the paper is expected to appear in printed form in a few months. However, a preprint of the original paper will be available online via the arXiv preprint server immediately after submission. The latter publication will result in collaboration with experimentalists from the Universities of Crete (P.G. Savvidis) and Southampton (P.G. Lagoudakis, N. Somaschi). In this way the longer term collaboration between the host institute and the University of Crete will be enhanced. All projected publications will include an acknowledgement clearly indicating that the results were made possible via POLATOM funding.

Other comments

As a theoretician I would like to stress the priceless benefits of having the opportunity to visit, watch and even participate in a state–of–the–art experiment. Especially nowdays with the overspecialization and extreme fragmentation in science I feel privileged to having been able to access the experiment, participate in its setting up and even obtain results on demand. All these could not be made possible without the POLATOM support and therefore I am indebted to the organizers of the project for this great opportunity.

[1] J. J. Hopfield, *Phys. Rev.* **112**, 1555 (1958).
[2] V. M. Agranovich, *Zh. Eksp. Teor. Fiz.* **37**, 430 (1959) [*Sov. Phys. JETP* **37**, 307 (1960)].
[3] C. Weisbuch, M. Nishioka, A. Ishikawa, and Y. Arakawa, *Phys. Rev. Lett.* **69**, 3314 (1992).
[4] A. V. Kavokin and G. Malpuech, *Cavity Polaritons*, Thin Film and Nanostructures Series Vol. 32 (Elsevier, New York, 2003).
[5] A. V. Kavokin, J. J. Baumberg, G. Malpuech, and F. P. Laussy, *Microcavities*, (Oxford University Press, 2007).
[6] P. Michetti and G. C. La Rocca, *Phys. Rev. B* **79**, 035325 (2009).
[7] P. Michetti and G. C. La Rocca, *Phys. Rev. B* **77**, 195301 (2008).
[8] P. Michetti and G. C. La Rocca, *Phys. Rev. B* **71**, 115320 (2005).
[9] P. Michetti and G. C. La Rocca, *Phys. Rev. B* **82**, 115327 (2010).
[10] L. Fontanesi, L. Mazza, and G. C. La Rocca, *Phys. Rev. B* **80**, 235313 (2009).
[11] L. Mazza, L. Fontanesi, and G. C. La Rocca, *Phys. Rev. B* **80**, 235314 (2009).
[12] H. Zoubi and G. C. La Rocca, *Phys. Rev. B* **72**, 125306 (2005).
[13] H. Zoubi and G. C. La Rocca, *Phys. Rev. B* **71**, 235316 (2005).
[14] D. Coles, P. Michetti, C. Clark, W. C. Tsoi, A. M. Adawi, J. Kim, and D. G. Lidzey *Adv. Func. Mater.* **21**, 3691 (2011).
[15] D. M. Coles, P. Michetti, C. Clark, A. M. Adawi, and D. G. Lidzey *Phys. Rev. B* **84**, 205214 (2011).

[16] T. Virgili, D. Coles, A. M. Adawi, C. Clark, P. Michetti, S. K. Rajendran, D. Brida, D. Polli, G. Cerullo, and D. G. Lidzey *Phys. Rev. B* **83**, 245309 (2011).
[17] T. Virgili, L. Lüer, G. Cerullo, G. Lanzani, S. Stagira, D. Coles, A. J. H. M. Meijer, and D. G. Lidzey *Phys. Rev. B* **81**, 125317 (2010).
[18] T. Kobayashi, in *J-Aggregates*, edited by T. Kobayashi (World Scientific, Singapore, 1996).
[19] J. Chovan, I. E. Perakis, S. Ceccarelli, and D. G. Lidzey, *Phys. Rev. B* **78**, 045320 (2008).
[20] N. Somaschi, L. Mouchliadis, D. Coles, I. E. Perakis, D. G. Lidzey, P. G. Lagoudakis, and P. G. Savvidis *Appl. Phys. Lett.* **99**, 143303 (2011).
[21] V. M. Agranovich, M. Litiskaia, and D. G. Lidzey, *Phys. Rev. B* **67**, 085311 (2003).
[22] V. M. Agranovich and Yu. N. Gartstein, *Phys. Rev. B* **75**, 075302 (2007).
[23] V. M. Agranovich, Yu. N. Gartstein, and M. Litinskaya *Chem. Rev.* **111**, 5179 (2011).
[24] M. Litinskaya, P. Reineker, and V. M. Agranovich, *J. Lumin.* **110**, 364 (2004).
[25] J. R. Tischler, M. S. Bradley, V. Bulović, J. H. Song, and A. Nuromikko, *Phys. Rev. Lett.* **95**, 036401 (2005).
[26] M. S. Bradley and V. Bulović, *Phys. Rev. B* **82**, 033305 (2010).
[27] Q. Zhang, T. Atay, J. R. Tischler, M. S. Bradley, V. Bulović, and A. Nurmikko, *Nat. Nano.* **2**, 555 (2007).
[28] D. G. Lidzey, D. D. C. Bradley, A. Armitage, S. Walker, and M. S. Scolnick, *Science* **288**, 1620 (2000).
[29] D. G. Lidzey, D. D. C. Bradley, M. S. Scolnick, T. Virgili, S. Walker, and M. Whittaker, *Nature* **395**, 53 (1998).
[30] D. G. Lidzey, D. D. C. Bradley, T. Virgili, A. Armitage, M. S. Scolnick, and S. Walker, *Phys. Rev. Lett.* **82**, 3316 (1999).
[31] D. G. Lidzey, A. M. Fox, M. D. Rahn, M. S. Scolnick, V. M. Agranovich, and S. Walker, *Phys. Rev B* **65**, 195312 (2002).
[32] S. Kéna-Cohen and S. R. Forrest, *Nat. Phot.* **4**, 371 (2010)
[33] S. Kéna-Cohen, M. Davanço, and S. R. Forrest, *Phys. Rev. Lett.* **101**, 116401 (2008)
[34] R. J. Holmes and S. R. Forrest, *Phys. Rev. Lett.* **93**, 186404 (2004).
[35] G. H. Lodden and R. J. Holmes, *Phys. Rev. B* **82**, 125317 (2010).
[36] G. H. Lodden and R. J. Holmes, *Phys. Rev. B* **83**, 075301 (2011).
[37] V. Malyshev and P. Moreno, *Phys. Rev. B* **51**, 14587 (1995).
[38] S. M. Vlaming, V. A. Malyshev, and J. Knoester, *Phys. Rev. B* **79**, 205121 (2009).
[39] M. Bednarz, V. A. Malyshev, and J. Knoester, *J. Chem. Phys.* **117**, 6200 (2002).
[40] H. Fidder, J. Knoester, and D. A. Wiersma, *J. Chem. Phys.* **95**, 7880 (1991)
[41] V. V. Egorov and M. V. Alfimov, *Phys. Usp.* **50**, 985 (2007).