



SCOM16

Workshop on Strong Coupling with Organic Molecules

Donostia-San Sebastian, 19th-21st October 2016



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Materials Physics Center
Centro de Física de Materiales



Foreword

Welcome to SCOM16!

During the last years we have witnessed a fascinating development of the fields of nanooptics and molecular spectroscopy that have merged concepts and expertise from a variety of fields ranging from condensed matter physics to quantum chemistry. The increasing complexity of optical cavities in the nanoscale together with that of molecular species expose the need to develop scientific approaches that account for these higher degrees of complexity in the interactions between condensed matter hosts and involved light emitters. We strongly believe that now is the right time to put together many of these initiatives and discuss them deeply, in spite of their different origin, in order to identify a possible roadmap to address the intrinsic complexity of quantum optical and molecular spectroscopy.

This workshop will bring together researchers from different disciplines including: Photonics, Quantum Optics, Materials, Chemistry and Condensed Matter Physics to discuss the latest developments in the study of the strong coupling involving organic molecules and optical cavities. Leaders in the field will discuss recent results on phenomena that involve polaritonic states, molecular excitations, molecular vibrations and their complex interactions, giving rise to a plethora of fascinating effects of both scientific and technological interest. Our aim is that this meeting should act as a catalyst in this emerging field, encouraging discussion of the underlying concepts and promoting new directions and collaborations.

We are very glad to see all of you in Donostia San Sebastian during these days of October 2016 to enjoy an exciting conference in this pleasant city. Donostia-San Sebastian has been awarded to be the European capital of culture in 2016. This award acknowledges the efforts made by the city to show a state-of-the-art cultural agenda, in addition to its astonishing landscape with a wonderful bay surrounded by urban beaches. Gastronomy also plays an important role in the city, and we hope that all the attendees of SCOM16 enjoy both Science and Life in this genuine Basque city.

We wish you a very pleasant conference

The workshop organizers

Bill Barnes, Francisco José García-Vidal, Jaime Gómez-Rivas, Javier Aizpurua

Organizers

Bill Barnes, (University of Exeter, UK)
Francisco José García Vidal, (Universidad Autónoma de Madrid and DIPC, Spain)
Jaime Gómez Rivas, (Dutch Institute for Fundamental Energy Research and Eindhoven University of Technology, The Netherlands)
Javier Aizpurua (Center for Materials Physics, CSIC-UPV/EHU and DIPC, the Basque Country)

Invited speakers

Alberto Amo (Centre de Nanosciences et de Nanotechnologies-CNRS, France)
Harry Atwater (Caltech, USA)
Jeremy J. Baumberg (University of Cambridge UK)
Joël Bellessa (Université Lyon 1 – CNRS, France)
Thomas W. Ebbesen (USIAS, University of Strasbourg and CNRS, France)
Rubén Esteban (DIPC, Spain)
Johannes Feist (Universidad Autónoma Madrid, Spain)
Bert Hecht (Universität Würzburg, Germany)
Jonathan Keeling (University of St. Andrews, UK)
Stéphane Kéna-Cohen (École Polytechnique de Montréal, Canada)
David G. Lidzey (The University of Sheffield, UK)
Christoph Lienau (University of Oldenburg, Germany)
Brahim Lounis (University of Bordeaux CNRS-IOGS , France)
Michel Orrit (MoNOS, Leiden Institute of Physics, The Netherlands)
Martin B. Plenio (Ulm University, Germany)
Said R. K. Rodriguez (Centre de Nanosciences et de Nanotechnologies-CNRS, France)
Daniele Sanvitto (CNR NANOTEC – Institute of Nanotechnology, Italy)
Salvatore Savasta (Università di Messina, Italy)
Timur Shegai (Chalmers University of Technology, Sweden)
Blake Simpkins (Naval Research Laboratory, USA)
Frank Spano (Temple University, USA)
Thilo Stöferle (IBM Research-Zurich, Switzerland)
Costanza Toninelli (European Laboratory for Nonlinear Spectroscopy (LENS), Italy)
Paivi Torma (Aalto University, Finland)
Niek F. Van Hulst (ICFO –ICREA, Spain)
Joel Yuen-Zhou (University of California San Diego, USA)

Invited Oral contributions

Christof P. Dietrich (Universität Würzburg, Germany)
Antonio I. Fernández Domínguez (Universidad Autónoma de Madrid, Spain)
Stephan Götzinger (Max Planck Institute for the Science of Light, Germany)
Virginia Martínez (Universidad del País Vasco, UPV-EHU, Spain)

Program summary

	Wednesday 19 th	Thursday 20 th	Friday 21 st
9:00-9:10	OPENING		
9:10-09:45	Thomas W. Ebbesen	Martin B. Plenio	Harry Atwater
09:45-10:20	David G. Lidzey	Salvatore Savasta	Christoph Lienau
10:20-10:55	Stéphane Kéna-Cohen	Thilo Stöferle	Blake S. Simpkins
10:55-11:30	Alberto Amo	Johannes Feist	Joel Yuen-Zhou
11:30-11:50	COFFEE BREAK	COFFEE BREAK	COFFEE BREAK
11:50-12:25	Daniele Sanvitto	Frank C. Spano	Said R. K. Rodriguez
12:25-13:00	Jonathan Keeling	Timur Shegai	Costanza Toninelli
13:00-13:20	Stephan Götzinger	Jino George	Niek F. Van Hulst
13:20-13:40	Yury P. Rakovich	Claudiu Genes	
13:40-14:00	Mohammad Ramezani	Virginia Martínez	CLOSING
14:00-15:30	LUNCH	LUNCH	LUNCH
15:30-16:05	Jeremy J. Baumberg	Michel Orrit	
16:05-16:40	Bert Hecht	Rubén Esteban	
16:40-17:15	Brahim Lounis	Christof P. Dietrich	
17:15-17:35	Antonio I. Fernández	Matthias Hensen	
17:40-18:00		COFFEE BREAK	
18:00-18:35		Felipe Herrera	
18:35-19:10	COFFEE + POSTER SESSION	Päivi Törmä	
		Joël Bellessa	

Invited talks consist of 30 minutes talks + 5 minutes for discussion.

Oral contributions consist of 17 minutes talks + 3 minutes for discussion.

Program

Wednesday 19th

9:00-9:10 OPENING

9:10-9:45 Invited 1: Thomas W. Ebbesen

Molecular and Material Properties under Strong Coupling to the Vacuum Field

9:45-10:20 Invited 2: David G. Lidzey

Strong coupling in optical microcavities: from fluorescent dyes to living bacteria

10:20-10:55 Invited 3: Stéphane Kéna-Cohen

Room-temperature condensates of light

10:55-11:30 Invite 4: Alberto Amo

Microcavity polaritons in microstructures

11:30-11:50 COFFE BREAK

11:50-12:25 Invited 5: Daniele Sanvitto

Quantum phenomena in polariton systems: from macroscopic to single particle effects

12:25-13:00 Invited 6: Jonathan Keeling

Ground and excited states of vibrationally dressed polaritons

13:00-13:20 Invited Oral Contribution 1: Stephan Götzinger

Coupling single molecules to an ultra-small mode volume cantilever-based Fabry-Perot microcavity

13:20-13:40 Oral 1: Yury P. Rakovich

Strong coupling effects in absorption and photoluminescence spectra of hybrid systems of gold nanorods and J-aggregates

13:40-14:00 Oral 2: Mohammad Ramezani

Plasmon-Exciton-Polariton lasing

14:00-15:30 LUNCH

15:30-16:05 Invited 7: Jeremy J. Baumberg

Single molecule plasmonics, strong coupling, and nanochemistry

16:05-16:40 Invited 8: Bert Hecht

Strong coupling spectroscopy of single nanocrystals with plasmonic resonators at ambient conditions

16:40-17:15 Invited 9: Brahim Lounis

Experimental evidence of plasmonic superradiance

17:15-17:35 Invited Oral Contribution 2: Antonio I. Fernández-Domínguez

Transformation Optics Approach to Plasmon-Exciton Strong Coupling in Nanocavities

17:40-19:10 COFFE+POSTER SESSION

Thursday 20th

- 9:10-9:45 **Invited 10: Martin B. Plenio**
Vibronic Effects in Natural and Artificial Light-Harvesting: Theory and Experiment
- 9:45-10:20 **Invited 11: Salvatore Savasta**
Ultrastrong Coupling of Organic Molecules with Microcavity Photons or Localized Surface Plasmons
- 10:20-10:55 **Invited 12: Thilo Stöferle**
Towards strongly confined exciton-polariton Bose-Einstein condensates at room temperature
- 10:55-11:30 **Invited 13: Johannes Feist**
Extraordinary exciton transport and modifications of molecular structure under strong light-matter coupling
- 11:30-11:50 COFFE BREAK**
- 11:50-12:25 **Invited 14: Frank C. Spano**
Dark Vibronic Polaritons
- 12:25-13:00 **Invited 15: Timur Shegai**
Strong plasmon-exciton coupling on single nanoparticle level
- 13:00-13:20 **Oral 3: Jino George**
Chemistry under Ultra-strong Vibrational Coupling
- 13:20-13:40 **Oral 4: Claudiu Genes**
Cavity-mediated effects in transport
- 13:40-14:00 **Invited Oral Contribution 3: Virginia Martínez-Martínez**
Antenna effect: Energy transfer from monomers to J-Aggregates in 1D systems
- 14:00-15:30 LUNCH**
- 15:30-16:05 **Invited 16: Michel Orrit**
Coupling single molecules to single gold nanoparticles for fluorescence enhancement
- 16:05-16:40 **Invited 17: Rubén Esteban**
Molecular optomechanics: quantum description of Surface Enhanced Raman Spectroscopy
- 16:40-17:00 **Invited Oral Contribution 4: Christof P. Dietrich**
Polariton lasing in microcavities filled with biologically-produced fluorescent proteins
- 17:00-17:20 **Oral 5: Matthias Hensen**
Coherent energy transfer between widely separated nanoantennas coupled via a plasmonic cavity
- 17:20-17:40 COFFE+POSTER SESSION**
- 17:40-18:00 **Oral 6: Felipe Herrera**
Cavity-Controlled Chemistry in Molecular Ensembles
- 18:00-18:35 **Invited 18: Päivi Törmä**
Strong coupling and lasing studies with plasmonic nanoparticles and arrays
- 18:35-19:10 **Invited 19: Joël Bellessa**
Coherence in disordered semiconductors coupled to surface plasmons and long-range plasmons

Friday 21st

9:10-9:45 Invited 20: Harry Atwater

Excited electronic states: mechanisms, prospects and strategies for achieving selective photocatalysis

9:45-10:20 Invited 21: Christoph Lienau

Ultrafast, coherent spectroscopy of strong coupling in semiconductor/metal hybrid systems

10:20-10:55 Invited 22: Blake S. Simpkins

Relaxation dynamics and coherent energy exchange in coupled vibration-cavity polaritons

10:55-11:30 Invited 23: Joel Yuen-Zhou

Molecular polaritonics: topological phases and novel chemical reactivities

11:30-11:50 COFFE BREAK

11:50-12:25 Invited 24: Said R. K. Rodriguez

Polariton Interactions: Optical hysteresis and perspectives for organic molecules

12:25-13:00 Invited 25: Constanza Toninelli

Planar optical antenna to direct light emission

13:00-13:35 Invited 26: Niek F. Van Hulst

Nanoantennas for cavity QED: Nanoscale Control of Coupling Strength g for Bright Single Photon Sources

13:35-14:00 CLOSING

14:00-15:30 LUNCH

Molecular and Material Properties under Strong Coupling to the Vacuum Field

Thomas W. Ebbesen

USIAS, University of Strasbourg and CNRS, Strasbourg, France

While strong coupling has been extensively studied due to the potential it offers in physics such as room temperature Bose-Einstein condensates and thresholdless lasers, the implications for the molecular and material sciences have remained mostly unexplored. Examples of modified properties under strong coupling, such as enhanced charge transport in organic semiconductors and non-radiative energy transfer and chemistry will be given to illustrate the broad potential of hybrid light-matter states for material sciences.

Strong coupling in optical microcavities: from fluorescent dyes to living bacteria

D.G. Lidzey

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We have explored [1] the optical properties of a series of strongly-coupled microcavities containing the fluorescent molecular dye BODIPY-Br (bromine-substituted boron-dipyrromethene). Using temperature-dependent photoluminescence emission, white-light reflectivity and measurements of fluorescence quantum yield, we explore the population of polaritons along the lower polariton branch following non-resonant optical excitation. We find that both the cavity fluorescence quantum efficiency and the distribution of polariton states along the lower polariton branch is a function of exciton-photon detuning. Significantly, we show that in the most negatively detuned cavities, the emission quantum efficiency approaches that of a control (non-cavity) film.

We find that following non-resonant excitation, the population of polariton states along the lower polariton branch in BODIPY-Br microcavities can be most effectively described by a direct 'radiative-pumping' mechanism, in which polaritons are 'pumped' by photons that are spontaneously-emitted by excimer-like states that exist in a weakly-coupled reservoir. Using a simple fitting model we obtain an excellent agreement with measured photoluminescence as a function of temperature and exciton-photon detuning, and qualitative agreement with the measured photoluminescence quantum efficiency.

We explore the optical properties of our cavities following excitation with ps laser pulses, and observe phenomena indicative of lasing, namely linewidth narrowing, a blue-shift of emission, non-linear emission intensity and collapse of emission to states around the bottom of the lower polariton branch.

Finally, we discuss new measurements in which living green sulphur bacteria are placed into a microcavity. We show that strong coupling occurs between the cavity mode and the absorption transition of the chlorosome assembly used by the bacteria in photosynthesis. We believe that this offers new opportunities to modify the function of living bacteria using photonic engineering.

[1] Richard T. Grant, Paolo Michetti, Andrew Musser, Pascal Gregoire, Tersilla Virgili, Eleonora Vella, Marco Cavazzini, Kyriacos Georgiou, Francesco Galeotti, Caspar Clark, Jenny Clark, Carlos Silva, David G. Lidzey, *Advanced Optical Materials* doi: 10.1002/adom.201600337

Room-temperature condensates of light

Stéphane Kéna-Cohen

Department of Engineering Physics, Polytechnique Montréal, Canada

Bose-Einstein condensation of ultracold atoms and superfluidity have been some of the most stunning demonstrations of macroscopic quantum behaviour. We will show how hybrid light-matter particles called polaritons can show similar behaviour, but in simple room-temperature table-top experiment in ambient conditions.

Microcavity polaritons in microstructures

V. Goblot¹, H.-S. Nguyen¹, I. Carusotto², D. Gerace³,
E. Galopin¹, I. Sagnes¹, A. Lemaître¹, J. Bloch¹, A. Amo¹

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Microcavity polaritons in GaAs based heterostructures combine propagation distances that can reach several tens of micrometers with an interparticle interaction strength that can largely exceed the linewidth. The combination of these two elements puts polaritons in this kind of microcavities in the hydrodynamic regime, in which polaritons behave as an interacting fluid showing superfluidity and the nucleation of vortices and solitons. Here we will show two extreme cases of the hydrodynamic behavior of polaritons in a 1D channel.

First, we will report the realization of an acoustic event horizon, at the interface between superfluid to supersonic flow in the channel [1]. This acoustic horizon presents a number of analogies with a cosmic black hole horizon. In the cosmological case, light cannot escape the black hole; in the polariton analogue, density fluctuations cannot propagate beyond the superfluid-subsonic frontier. In both cases, spontaneous emission of Hawking particles is expected [2].

In the second part we will show how the polariton superflow in the 1D channel can be manipulated to nucleate dark solitons, evidencing a novel kind of bistability based activated via the phase of the excitation beam [3].

[1] H. S. Nguyen, D. Gerace, I. Carusotto, D. Sanvitto, E. Galopin, A. Lemaître, I. Sagnes, J. Bloch, and A. Amo, *Phys. Rev. Lett.* 114, 36402 (2015).

[2] P. Grisins, H. S. Nguyen, J. Bloch, A. Amo, and I. Carusotto, *Phys. Rev. B* (to be published), arXiv:1606.02277 (2016).

[3] V. Goblot, H. S. Nguyen, I. Carusotto, E. Galopin, A. Lemaître, I. Sagnes, A. Amo, and J. Bloch, arXiv:1607.03711 (2016).

Quantum phenomena in polariton systems: from macroscopic to single particle effects

Daniele Sanvitto

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In this talk we will focus on the quantum behavior of polaritons, construed as quasi-particles arising from the strong coupling between an electromagnetic mode and excitons in any kind of semiconductor materials. In particular we will see both macroscopic quantum phenomena—observed in a condensed state of organic polaritons—[1] as well as entanglement in microcavity polaritons excited by a quantum of light [2]. Furthermore we will discuss the possibility of generating arrays of quantum electrodynamic nanocavities, with optimized Q/V, by coupling localized gap plasmons, diffractive surface waves and organic excitons.

[1] G. Lerario, A. Fieramosca, et al., Room-temperature superfluidity in a polariton condensate, arXiv:1609.03153 (2016).

[2] A. Cuevas, B. Silva, et al., Entangling a polariton with one photon: effect of interactions at the single-particle level, arXiv:1609.01244 (2016).

Ground and excited states of vibrationally dressed polaritons

Jonathan Keeling

University of St. Andrews, United Kingdom

Molecular polaritonics, strong matter-light coupling where the matter is made of organic molecules, prompts a range of new theoretical questions. In particular, it requires understanding the interplay of vibrational coupling and optical coupling to electronic states, i.e. molecular cavity optomechanics. A particular challenge arises because such systems involve many molecules, and so one is forced to address a many body problem. I will present our recent work exploring the nature of the ground and excited states of a model of such a system [1,2]. In particular, I will focus on the connections to optomechanics in other systems, and changes in the optical properties that can arise from coupling to vibrational modes.

1. M. A. Zeb, P. G. Kirton, J. Keeling, arXiv:1608.08929
2. J. A. Cwik, P. Kirton, S. De Liberato, and J. Keeling, Phys. Rev. A 93, 033840 (2016).

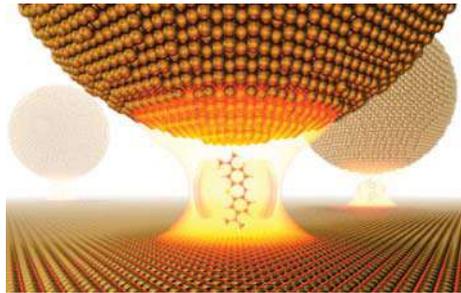
Single molecule plasmonics, strong coupling, and nanochemistry

Professor Jeremy J. Baumberg, FRS

NanoPhotonics Centre, Cavendish Laboratory, University of Cambridge, UK

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Coupling between plasmonic nano-components generates strongly red-shifted resonances combined with intense local field amplification on the nanoscale. This allows directly seeing molecules as well as excitations in semiconductors. We have recently explored plasmonic coupling which can be tuned dynamically, through reliable bottom-up self-assembly using the nanoparticle-on-mirror geometry (NPoM). We recently demonstrated how individual molecules can be strongly coupled to these ultralow volume plasmonic cavities.[12]



We also demonstrate the possibility to track few molecules using the extreme enhancements. We show how the new generation of 2D semiconductors can couple to such nano-scale gaps utilizing our nanoparticle on mirror geometry. We find that changing just a single atom on each molecule of a self-assembled monolayer can shift the plasmon by over 50nm, and produce surprising vibrational signatures.[4-8] These have encouraging prospective applications in (bio)molecular sensing as well as fundamental science.[9-15] The ability to track and watch molecules interact and react opens up the ability to study chemistry molecule-by-molecule and potentially to control single reaction pathways.

- [1] *Nature* **491**, 574 (2012); Revealing the quantum regime in tunnelling plasmonics,
- [2] *ACS Nano* **5**, 3878 (2011); Precise sub-nm plasmonic junctions within Au NP assemblies,
- [3] *Nano Lett* **13**, 5033 (2013); Controlling sub-nm plasmonic gaps using graphene
- [4] *ACS Nano* **9**, 825 (2014); Monitoring Morphological Changes in 2D Monolayer Semiconductors ...
- [5] *Nano Letters* **15**, 669 (2015); Nano-optics of molecular-shunted plasmonic nanojunctions
- [6] *Science Reports* **4**, 5490 (2014); Watching individual molecules flex within lipid membranes using SERS
- [7] *Nature Comm.* **5**, 4568 (2014); Threading plasmonic nanoparticle strings with light
- [8] *Nature Comm.* **5**, 3448 (2014); DNA origami based assembly of gold nanoparticle dimers for SERS detection
- [9] *Scientific Reports* **4**, 6785 (2014); Quantitative multiplexing with nano-self-assemblies in SERS
- [10] *Nano Lett* **13**, 5985 (2013); In-situ SERS monitoring of photochemistry within a nano-junction reactor
- [11] *Opt.Exp* **23**, 33255 (2015); A generalized circuit model for coupled plasmonic systems
- [12] *Nano Lett* **15**, 2600 (2015); Demonstrating PL from Au is Electronic Inelastic Light Scattering ...
- [13] *Phys.Rev.A* **92**, 053811 (2015); Hybridization of plasmonic antenna and cavity modes: Extreme optics...
- [14] *Sci.Rep.* **5**, 16660 (2015); Size Dependent Plasmonic Effect on BiVO₄ Photoanodes for Solar Water Splitting
- [15] *Nano Letters* **15**, 7452 (2015); Controlling Nanowire Growth by Light
- [16] *Nature* **535**, 127 (2016); Single-molecule strong coupling at room temperature in plasmonic nanocavities

Strong coupling spectroscopy of single nanocrystals with plasmonic resonators at ambient conditions

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We show that a weakly radiating plasmonic slit resonator at the apex of a scanning probe tip can strongly couple to a single colloidal quantum dot at room temperature (Fig. 1). By varying the distance between the emitter and the resonator on a nanometerscale the coupling strength can be dynamically and reversibly adjusted. Consecutive spectra recorded while traversing the strong coupling regime give detailed insight into the coupling mechanism as well as the rich electronic structure of the employed colloidal nanocrystals. Since a broadband plasmon resonance can overlap with different excitonic transitions simultaneously, we conclude that strong coupling bares the potential for a new type of spectroscopy.

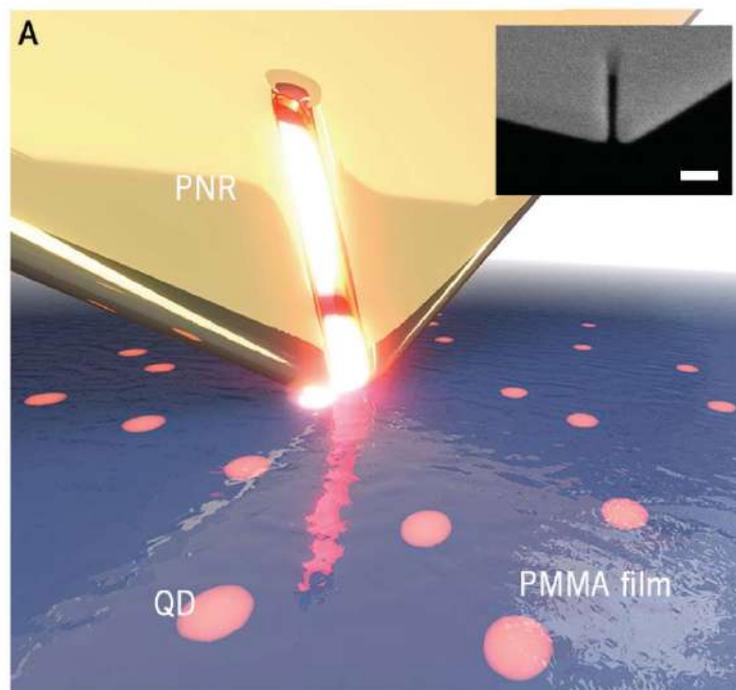


Fig. 1 Artistic illustration of a plasmonic resonator in contact with embedded nanocrystals on a glass substrate. Inset: SEM micrograph of a nanoslit resonator. Scale bar: 100 nm.

Experimental evidence of plasmonic superradiance

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Hybridization of quantum emitters and plasmonic nanostructures has attracted much attention over the last years, due to their interest in the design of plasmon-based nanolasers [1,2] or to achieve long-range qubit entanglement [3]. Recent theoretical studies [4,5] suggest that the plasmonic field mainly acts as a communication bus allowing for intense cross-talking between emitters, and leading to the formation of collective states known as superradiant states. In such regime the synchronized dipoles radiate at an increased rate which scales with the number of emitters, as in the case of the Dicke superradiance [6]. Yet, experimental evidence of plasmonic superradiance is still lacking mainly because of difficulties to engineer systems with precise control of the number and positions of emitters around a metallic nanostructure.

In this work, we experimentally investigate the plasmonic superradiance in nanohybrids constituted of a gold core capped with a silica shell grafted with fluorescent dyes. Single particle studies performed on more than 1000 nanohybrids with controlled core-shell sizes and numbers of grafted emitters revealed that the average decay rate scales with the number of grafted emitters, in agreement with theoretical predictions [4]. The dependence is more prominent when the emitters get closer to the core. These results constitute a direct evidence of plasmonic superradiance. Observation of plasmonic superradiance at room temperature opens questions about the robustness of collective states against decoherence processes in the condensed matter.

[1] J.G. Bohnet, Z. Chen, J.M. Weiner, D. Meiser, M.J. Holland, and J.K. Thompson, *Nature* **484**, 78–81 (2012).

[2] M.A. Noginov, G. Zhu, A.M. Belgrave, R. Bakker, V.M. Shalaev, E.E. Narimanov, S. Stout, E. Herz, T. Suteewong, and U. Wiesner, *Nature* **460**, 1110–2 (2009).

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[4] V.N. Pustovit, T.V. Shahbazyan, *Phys. Rev. Lett.* **102**, 077401 (2009).

[5] D. Martín-Cano, L. Martín-Moreno, F. J. García-Vidal, and E. Moreno, *Nano Letters* **10**, 3129–3134 (2010).

[6] R.H. Dicke. *Phys. Rev.* **93**, 99-11

Vibronic Effects in Natural and Artificial Light-Harvesting: Theory and Experiment

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The coupling of vibrational motion, coherent and incoherent, to excitonic and electronic dynamics is a central element of our understanding of excitation energy and charge transport as well as charge separation dynamics in natural and artificial light-harvesting systems [1]. In this talk I will discuss our work in this area including the concept of noise-assisted transport [2] and the proposal of the central role of the coupling of long-lived vibrations and electronic motion to long-lived coherent signals and transport [3]. I will report both theoretical work and recent experimental efforts towards the demonstration of vibronic coupling in artificial light harvesting [4, 5].

References

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- [2] M.B. Plenio and S.F. Huelga, *New J. Phys.* **10**, 113019 (2008); F. Caruso, A.W. Chin, A. Datta, S.F. Huelga and M.B. Plenio, *J. Chem. Phys.* **131**, 105106 (2009); M. del Rey, A.W. Chin, S.F. Huelga and M.B. Plenio, *J. Phys. Chem. Lett.* **4**, 903 (2013); N. Killoran, S.F. Huelga and M.B. Plenio, *J. Chem. Phys.* **143**, 155102 (2015)
- [3] J. Prior, A.W. Chin, S.F. Huelga and M.B. Plenio, *Phys. Rev. Lett.* **105**, 050404 (2010); A.W. Chin, J. Prior, R. Rosenbach, F. Caycedo-Soler, S.F. Huelga and M.B. Plenio, *Nature Physics* **9**, 113 (2013); M.B. Plenio, J. Almeida and S.F. Huelga, *J. Chem. Phys.* **139**, 235102 (2013)
- [4] J. Lim, D. Palecek, F. Caycedo-Soler, C.N. Lincoln, J. Prior, H. v. Berlepsch, S.F. Huelga, M.B. Plenio, D. Zigmantas, and J. Hauer, *Nature Comm.* **6**, 7755 (2015)
- [5] A. De Sio, F. Troiani, J. Rehault, E. Sommer, J. Lim, S.F. Huelga, M.B. Plenio, M. Maiuri, G. Cerullo, E. Molinari, and Ch. Lienau. Under Review

Ultrastrong Coupling of Organic Molecules with Microcavity Photons or Localized Surface Plasmons

Salvatore Savasta

Università di Messina, Dipartimento MIFT, Messina - Italy

Light-matter interaction in the strong-coupling regime is a coherent reversible process in which a photon is absorbed and reemitted by an electronic transition at a rate equal to the coupling energy divided by the Planck constant [1]. Reaching the light-matter strong-coupling regime has been a major focus of research in atomic and solid state physics, and quantum optics for several decades. It occurs when an electronic transition is resonantly coupled to an optical resonator and the coupling rate exceeds the rates of relaxation and decoherence of both the electronic transition and the field.

Recently, a new regime of cavity QED, where the coupling rate becomes an appreciable fraction of the unperturbed frequency of the bare systems, has been experimentally reached in a variety of solid state systems (see, e.g., [2]). In this so-called ultrastrong-coupling (USC) regime, the routinely invoked rotating-wave approximation is no longer applicable and the counter-rotating terms in the interaction Hamiltonian significantly change the standard cavity QED scenarios (see, e.g., [3]).

Here we discuss experiments in organic semiconductor microcavities where a Rabi splitting up to the 60% of the material band gap was achieved [4]. It has also been shown that these systems can be used to realize monolithic organic light emitting diodes working in the USC [6].

Strong light matter interaction can also be obtained by replacing conventional microcavities with metallic micro- or nano-structures supporting surface plasmons. I also analyze the possibility to achieve the USC regime at nanoscale dimensions by exploiting localized surface plasmons [6]. Specifically I discuss how this regime can be reached in nanoshells constituted by a core of organic molecules surrounded by a silver or gold shell.

Very recently it has been shown that in this light matter regime, one photon can simultaneously excite two or more atoms with high probability [7]. I discuss the possibility to observe this intriguing effect in organic microcavities.

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Towards strongly confined exciton-polariton Bose-Einstein condensates at room temperature

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We create exciton-polaritons with a conjugated polymer inside an optical microcavity at ambient conditions where we observe thermalization and non-equilibrium Bose-Einstein condensation. This is evidenced through nonlinear emission, interaction-induced blue-shift and long-range macroscopic coherence that can be studied even with single-shot measurements. Furthermore, we discuss recent experiments with tunable nanoscale defect cavities to produce zero-dimensional polaritons and polaritonic molecules for strongly confined condensates and possible ways towards quantum simulation.

Extraordinary exciton transport and modifications of molecular structure under strong light-matter coupling

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We will discuss our recent work exploring the influence of strong coupling on organic molecules, focusing on two main effects: Exciton transport, and the modification of molecular structure and chemical reactions.

Exciton transport plays a crucial role in natural phenomena such as photosynthesis and in artificial devices such as organic solar cells, but is inefficient in many organic materials. We will discuss how the formation of collective polaritonic modes can dramatically enhance exciton conductance when the molecules are strongly coupled to an electromagnetic mode [1], which can be exploited to “harvest” and direct excitations to specific positions by tuning the spatial distribution of the EM mode [2]. We then show that in systems with a discrete EM mode spectrum, strong-coupling-enhanced exciton transport can proceed through “dark” modes that have no photonic component, but which nonetheless acquire a delocalized character in the strong-coupling regime [3].

In the second part, we discuss the influence of strong coupling on internal molecular structure and chemical reactions. While most models of strong coupling are based on simple two-level models, pioneering experiments have shown modifications of chemical reaction rates under strong coupling [4]. In order to address this mismatch, we have developed a first-principles model that fully takes into account both electronic and nuclear degrees of freedom [5]. We will first discuss the applicability of the Born-Oppenheimer approximation, which is challenged by the introduction of the new intermediate timescale of energy exchange between the molecule and the field. Based on these findings, we then show how photochemical reactions such as photoisomerization can be almost completely suppressed under strong coupling [6]. Finally, we show that this suppression works more efficiently when many molecules are coupled to a single light mode due to a “collective protection” effect in the delocalized polaritonic state.

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Dark Vibronic Polaritons

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Optical microcavities containing organic molecules and aggregates¹ continue to attract attention due to the very large Rabi splittings ($\sim 1\text{eV}$) demonstrated so far² and the substantial deviations between organic films and crystals, which support Frenkel type excitations strongly coupled to nuclear degrees of freedom, and the more commonly investigated inorganic materials which support Wannier excitons in a more rigid lattice. In this talk we show that an ensemble of vibronic chromophores in an optical microcavity can support “dark” polaritons which have no oscillator strength yet can radiate light. Hence, such unusual states are undetectable by reflection or absorption spectroscopy, yet appear prominently in the photoluminescence spectrum. The conditions necessary for dark polariton formation and the relationship to experiments^{3,4} are discussed.

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Strong plasmon-exciton coupling on single nanoparticle level

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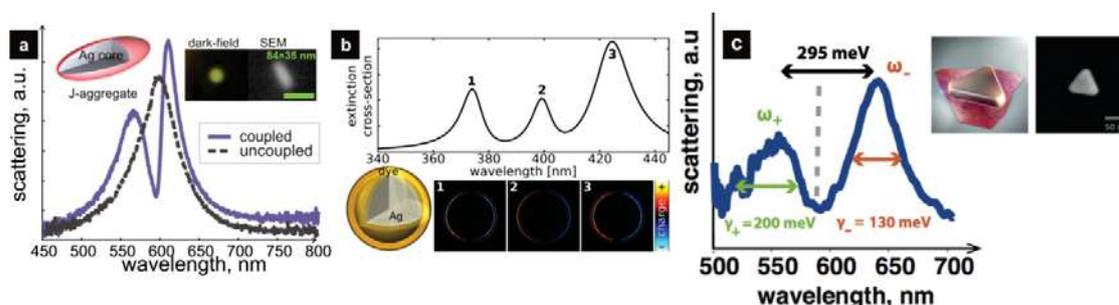


Figure 1. (a) Single silver nanorod strongly interacting with a J-aggregate before and after photodegradation of the molecules [1]. (b) Theoretically studied plasmon-exciton interaction in core-shell geometry. In the limit of high oscillator strength a 3-peaked spectrum emerges [2]. (c) Single silver nanoprism gives rise to Rabi splitting of 300 meV at room temperature [3].

We have studied nanoparticle plasmons coupled to molecular excitons in J-aggregates on a single nanoantenna level [1, 3]. For the case of silver nanorods (Fig. 1a) strong suppression of scattering at the J-aggregate absorption line has been observed, implying strong plasmon-exciton interactions. Upon photodegradation of chromophores under laser illumination, a recovery to a single peak plasmon resonance of a nanorod occurred. We have further reduced the nanoparticle volume and thus suppressed radiative losses by using silver nanoprisms (Fig. 1c). In this study we have shown that individual nanoparticle plasmons can reach the strong coupling limit with about 70-80 excitons in molecular J-aggregates at room temperature [3]. Moreover, we have discussed the possibility to lower the number of excitons down to truly quantum regime.

In addition to these elastic scattering observations, we demonstrated Rabi splitting in photoluminescence of individual hybrid nanosystems [6], which manifests a direct proof of strong coupling in plasmon-exciton nanoparticles (as opposed to dark-field scattering [4, 5]). We achieve these results due to saturation of the mode volume with molecular J-aggregates, resulting in Rabi splitting up to 400 meV on single nanoparticle level, i.e. ~20% of the resonance energy. We correlate between scattering and photoluminescence and find that splitting in photoluminescence is considerably less than in scattering, which sets minimal requirements on the strong coupling limit. Moreover, we find that splitting in both photoluminescence and scattering signal increases upon cooling to cryogenic temperatures.

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COUPLING SINGLE MOLECULES TO SINGLE GOLD NANOPARTICLES FOR FLUORESCENCE ENHANCEMENT

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The enhanced optical near field close to the tips of gold nanorods enhances coupling to optical waves, both for excitation and for emission. These two effects strongly resonate at the plasmon frequency of the rod and enable detecting single molecules of a weakly fluorescent dye, with quantum efficiency of 1% or less [1]. This method generalizes single-molecule spectroscopy to a broad class of “bad” fluorophores, with either low quantum yields or long fluorescence lifetimes. Comparison to finite-element calculations [2] indicate that excitation and emission enhancements critically depend on the spectral overlap between the dye’s absorption and fluorescence and the nanorod’s surface plasmon resonance.

The coupling of the light to molecules is weak in these experiments because of the fairly weak confinement of the field around the tips of the rods (typical dimension 30 nm). However, this has the advantage that the near field is accessible to comparatively large molecules and to biomolecules without steric hindrance or disruptive interactions with metal surfaces. Moreover, these mode volumes are well adapted to typical concentrations in many biochemical reactions, around micromolar, and to diffusion times between microseconds and milliseconds.

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Molecular optomechanics: quantum description of Surface Enhanced Raman Spectroscopy

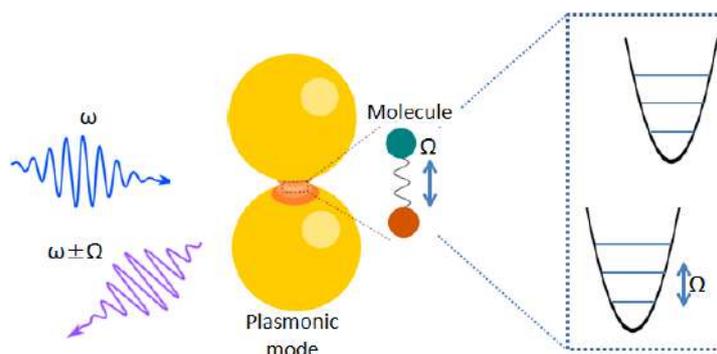
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Surface Enhanced Raman Spectroscopy (SERS) has been one of the main drivers of advances in plasmonics in the last decades. In this technique, the Raman fingerprint of the vibrational and rotational phonons of a molecule is enhanced by many orders of magnitude due to the presence of a nearby metallic particle supporting a plasmonic mode. In a simple description, the strong Raman emission can be explained by the classical enhancement of the near field intensity at both the illumination and frequency wavelengths.

The recent suggestion that off-resonant SERS is analogous to quantum optomechanical systems suggests that new phenomena could be accessible[1,2], and may already be behind some recent experiments[3,4]. I present our recent results treating SERS in a fully quantized manner for scenarios where the illumination is off-resonant or resonant with respect to the electronic levels of the molecule (see Figure). In particular, our treatment reveals unexpected non-linearities on the response of the signal, large correlations of the emitted photons and coherent interference features that emerge when the Mollow triplet peak is tuned to the frequency of the Raman lines. The results do not only have implications to optimize the Raman Signal, but it can open new parameter regimes to work on quantum optomechanics, and the control of the phonon populations may have implications for chemistry



Scheme of the Raman process, where the incoming light mediated by the strong plasmonic enhancement interacts with the vibration of a molecule at frequency Ω , resulting in a photon at smaller (Stokes process) or larger (anti-Stokes) energy. In resonant SERS the incoming light is nearly resonant with respect to an electronic transition of the system

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Strong coupling and lasing studies with plasmonic nanoparticles and arrays

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We discuss some general aspects of strong coupling in plasmonics [1], and briefly mention our results on strong coupling between organic dye molecules and collective surface lattice resonance modes of plasmonic nanoparticle arrays [2,3]. We focus on describing our results on lasing in such arrays in the weak coupling regime [4]. Especially the lasing observed in a dark mode offers interesting prospects for lasing also in the strong coupling regime. We then present studies of coupling between plasmonic nanoparticle modes and excitons in light harvesting complexes [5]. Intriguingly, it seems that plasmon-exciton coupling is sensitive to the specific presentation of the pigment molecules.

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Coherence in disordered semiconductors coupled to surface plasmons and long-range plasmons

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Localized and delocalized plasmons in metallic nanoparticles are associated with a strongly confined electromagnetic field, inducing an enhanced interaction with emitters located in the close environment of the metal. When the plasmon/emitter interaction becomes predominant compared to the damping in the system, the system is in strong coupling regime leading to light matter hybridization. This strong coupling has been observed with a large number of materials, in particular disordered materials. These materials are constituted by a collection of independent emitters (molecules, semiconductor quantum dots...). The hybrid light/matter state can be described by considering a homogeneous absorbing system using coupled oscillator model. But if the microscopic structure of the molecular film close to a metallic film is considered, collective effects between the delocalized plasmon and the set of molecules are present. The spatial and dynamic properties of a set of molecules in strong coupling are dramatically modified compared to the same molecules in weak coupling (the usual configuration of emission). The excitations are not localised in a single particle anymore but delocalised on a large number of particles due to the formation of an extended hybridised state on several microns. We will describe some properties of disordered systems strongly coupled to surface plasmons and experimental demonstrations of the collective phenomena associated with the strong coupling. The system studied consists of J-aggregated dye (TDBC) in interaction with a surface plasmon on silver. To clearly separate the coherence induced by the plasmon/excitons hybridization from the apparent extension related to the propagation of the surface plasmon, the samples in strong coupling have been compared to molecules in weak coupling regime with the plasmon. The extension of the coherent state will also be discussed. The coherence length is limited by the plasmon losses. A way to increase this parameter would be to use modes with reduced losses. We will show that strong coupling can be achieved with long range surface plasmon and organic dyes. The parameters of these modes will be discussed to optimize the interaction with the organic material.

Excited electronic states: mechanisms, prospects and strategies for achieving selective photocatalysis

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Excited electronic states in semiconductors and metals have the potential to alter the rate and selectivity of molecular reduction and oxidation reactions in Doing so requires an accurate description and understanding of resonant optical absorption, excited carrier generation, relaxation and interfacial charge transfer processes, so as to understand what the are prospects for directing catalytic processes with optically generated excited carriers. I will discuss our strategy for approaching this problem and discuss available tools that have been developed to control excited carrier generation, relaxation and interfacial charge transfer. I will also try to summarize what is known and unknown at present in order to complete this picture, with an eye toward both model systems for mechanistic understanding, and also systems that may alter pathways for technologically important reactions, such as selective photocatalytic reduction of carbon dioxide.

Ultrafast, coherent spectroscopy of strong coupling in semiconductor/metal hybrid systems

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Over the past several years we have used fairly advanced coherent, ultrafast spectroscopy tools to study the coupling between excitons in organic and inorganic semiconductors and dielectric or plasmonic resonator modes. We have observed Rabi oscillations, i.e., the periodic exchange of energy between the excitonic and the resonator mode, directly in the time domain [2,6], have discovered optical Stark effects [3], measured the lifetimes of the strongly coupled exciton-plasmon modes [5], probed the line broadening mechanisms of these resonances [4,5] and demonstrated ultraefficient and ultrafast all-optical switching of such coupled modes [7].

This naturally raises the important question whether such ultrafast measurements provide conceptually new insight into the functionality of hybrid nanostructures. In my talk, I will try to address this question and present new and unpublished results which reveal surprising and possibly rather unexpected effects of strong coupling between excitons in organic semiconductors and plasmonic resonator modes. By means phase-resolved coherent optical spectroscopy, I will present first evidence for a coupling-induced motional narrowing of excitonic resonances that transforms the inherently inhomogeneously broadened excitonic resonances of organic semiconductors into a homogeneously system. Our results not only give evidence for a spatial delocalization of the excitonic modes due to their coupling to the plasmonic resonator but also suggest a significant modification of exciton-phonon coupling as a consequence of exciton-plasmon interactions. I will argue that such interactions not only have profound implications on optoelectronic applications of strongly coupled hybrid systems, but may also have significant effects on charge and energy transfer processes in other organic semiconductor systems such as, e.g., organic solar cells. If time permits, I will introduce a powerful technique, two-dimensional electronic spectroscopy with 10-fs time resolution [8], that is capable of studying such processes in real time.

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Relaxation dynamics and coherent energy exchange in coupled vibration-cavity polaritons

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Coupling vibrational transitions to resonant optical modes creates vibrational polaritons shifted from the uncoupled molecular resonances and provides a convenient way to modify the energetics of molecular vibrations. This approach is a new and viable method to explore controlling chemical reactivity.¹ Here, we demonstrate both static and dynamic results for *vibrational* bands strongly coupled to optical cavities. We experimentally and numerically describe strong coupling between a Fabry-Pérot cavity and several molecular species (e.g., poly-methylmethacrylate, thiocyanate, hexamethyl diisocyanate).² We investigate strong and weak coupling regimes through examination of cavities loaded with varying concentrations of a urethane monomer. Rabi splittings are in excellent agreement with an analytical description using no fitting parameters.

We also report pump-probe infrared spectroscopy of the cavity-coupled C-O stretching band of W(CO)₆ and the first direct measurement of the lifetime of a vibration-cavity polariton.³ The upper polariton relaxes ten times more quickly than the uncoupled vibrational mode. Tuning the polariton energy changes the polariton transient spectra and relaxation times. We also observe quantum beats, so-called vacuum Rabi oscillations, between the upper and lower vibration-cavity polaritons. In addition to establishing that coupling to an optical cavity modifies the energy-transfer dynamics of the coupled molecules, this work points out the possibility of systematic and predictive modification of the excited-state kinetics of vibration-cavity polariton systems. Opening the field of polaritonic coupling to vibrational species promises to be a rich arena amenable to a wide variety of infrared-active bonds that can be studied in steady state and dynamically.

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Molecular polaritonics: topological phases and novel chemical reactivities

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Molecular polaritonics lies at the intersection of physical chemistry, quantum optics, and condensed matter physics. It opens new opportunities for the nontrivial control of energy transport in the nano and mesoscales, but also of controlling physico-chemical properties of molecular assemblies. In this talk, I'll showcase some of these opportunities that we have been exploring in the past few years. First, I'll show that topologically nontrivial phases can be realized in excitonic and polaritonic systems of organic dye molecules that support Frenkel excitations [1,2]. Next, I will discuss some intriguing optical properties of plexcitons (surface plasmon-exciton polaritons) associated with van Hove singularities [3]. Finally, I will end my talk discussing how not only kinetics, but also thermodynamics of chemical reactions can be controlled via ultrastrong coupling to a set of confined optical modes [4].

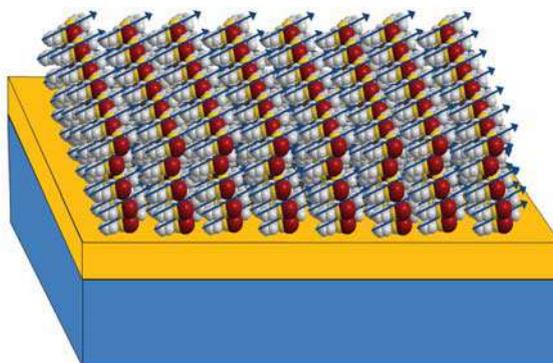


Fig. Topological plexciton: From Ref. [2]

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Polariton Interactions: Optical hysteresis and perspectives for organic molecules

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Strong exciton-photon coupling in organic and inorganic materials has inspired many efforts in two communities which could greatly benefit from a greater mutual overlap. In this talk, I will highlight some of the strengths of polaritons based on two complementary systems: inorganic semiconductor cavities and organic molecules coupled to plasmonic lattices.

First, I will discuss room-temperature strong coupling between excitons in organic molecules and collective resonances in metallic nanoparticle arrays [1-3]. The emergent polaritons are a mixture of diffracted photons, excitons, and localized surface plasmons. The composition, effective mass, and lifetime of these polaritons can be tuned through the geometry and the dimensions of the plasmonic lattice.

The second part of the talk will be devoted to polaritons in semiconductor microcavities at low temperatures. I will focus on polariton-polariton interactions and on the associated optical hysteresis in continuously driven systems. I will briefly show how the phase acquired by polaritons hopping between two coupled microcavities can be controlled through nonlinear interactions [4]. Mainly, I will discuss the influence of quantum fluctuations on optical hysteresis [5,6]. Quantum fluctuations lead to a double power law decay of the hysteresis area as a function of the sweep rate of the driving power. Recently, we have measured the critical exponents associated with this double power law decay [6]. The results in Ref. [6] demonstrate the emergence of quantum dynamics on a time scale vastly greater than the polariton lifetime, and how this time scale depends dramatically on the polariton-polariton interaction strength. I will conclude with perspectives for exploring critical phenomena of driven-dissipative systems, which could comprise either inorganic or organic polaritons.

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Planar optical antenna to direct light emission

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Abstract

The efficient collection of light from single emitters is critical for quantum optics and nanophotonics. We introduce a planar antenna that strongly beams the radiation pattern, we discuss the physical concepts and provide experimental demonstration.

Fluorescence detection covers a broad and bustling area of modern optics. During the last decades, great efforts have been spent in improving the collection of light from single quantum emitters, such as solid-state sources [1] and molecules [2], for example. Recently, novel collection strategies have been introduced, where high efficiencies are achieved either by coupling high numerical-aperture (NA) objectives with planar dielectric structures [5], or using optical micro- and nano-antennas that beam the radiation pattern [3, 4, 6]. Both cases pose serious problems: the former because of the need for high N.A. collection optics, the latter since at optical frequencies, however, require that radio-frequency antenna concepts be reset to the nanometer scale, making the device fabrication and the coupling with the emitter hard to control [7].

Here, we present a planar structure based on the concept of a Yagi-Uda antenna, but similar in its configuration to a Fabry-Perot cavity antenna (Fig. 1a), which strongly beams light radiated by quantum emitters (Fig. 1b and 1c). Our antenna makes use of passive planar elements working as reflector and director to modify the radiation pattern. The working parameters mainly depend on the emission wavelength and the refractive indices of the thin films constituting the structure and are therefore easy to tailor for different light sources [8].

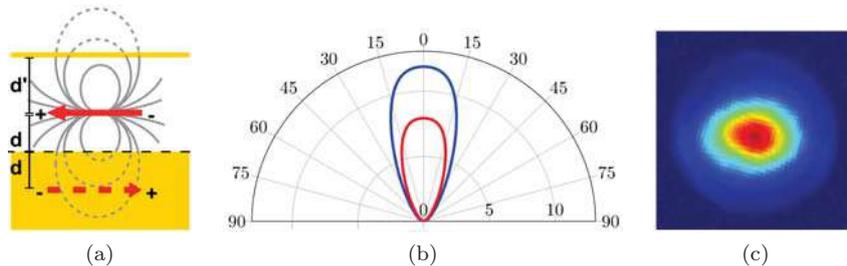


Figure 1: (a) Schematic view of a Hertzian dipole embedded inside our directional planar antenna. (b) Calculated radiation pattern for a Hertzian dipole with horizontal (blue curve) and random (red curve) orientation with respect to the planar interfaces. (c) Experimental back-focal-plane image obtained from a single DBT molecule placed in our antenna structure. See text for details.

A theoretical study has been carried out in order to understand the behaviour of the radiation pattern, first as a function of the distance d between the emitter and the reflector, and then as a function of the distance d' from the emitter to the director. Optimizing such parameters, constructive interference occurs in the direction of beaming, while destructive interference takes place at large angles, as it can be inferred from the narrow radiation pattern of Fig. 1b. We would like to remark that for our configuration we do not take advantage of a cavity resonance. Therefore, the emission rate of the source is not substantially modified by the antenna.

An experimental study has been performed with single molecules to demonstrate and assess the performances of our planar directional antenna. The results are shown in Fig. 1c, which displays a back-focal-plane image of the fluorescence of a single Dibenzoterrylene (DBT) molecule in a thin Anthracene (Ac) crystalline film, placed at the desired distances from a gold reflector and director through Hydrogen silsesquioxane (HSQ) and Polyvinyl alcohol (PVA) films. This particular system exhibit a strong and narrow zero phonon line ($\lambda=785$ nm) and dipole orientation along the crystal surface [9], hence facilitating the demonstration of our antenna concept [10]. The agreement between the theoretical predictions and the experimental results is found to be very good.

We have experimentally achieved a half width at half maximum that is less than 20° for the emission profile of a single molecule at room temperature. Our planar directional antenna hence provides a significant gain in collection efficiency for small NA optics, even in free space. Moreover, it is simple to fabricate, robust, scalable to different wavelengths, broadband and it can be applied to a wide range of quantum emitters.

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Nanoantennas for cavity QED: Nanoscale Control of Coupling Strength g for Bright Single Photon Sources

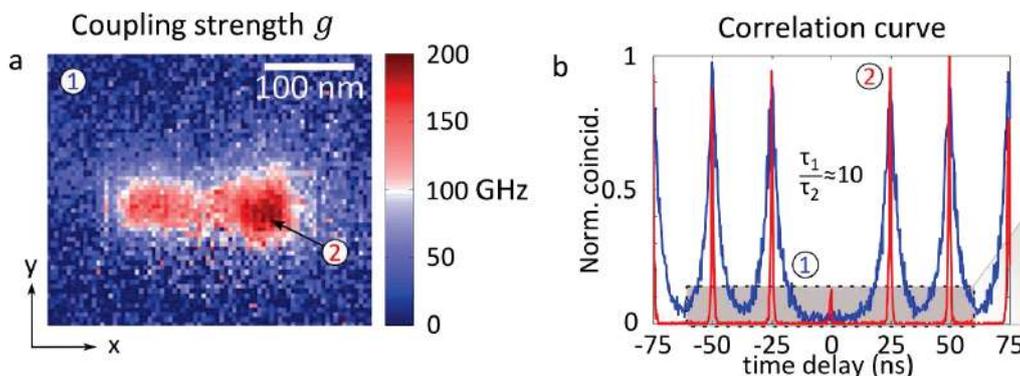
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Cavity QED explores enhanced light-matter interactions between photon emitters and cavities, with opportunities for sensing, quantum information and energy capture technologies. To boost emitter-cavity interaction, i.e. coupling strength g , ultrahigh quality cavities have been concocted yielding photon trapping times of μs to ms . Yet with such strong coupling comes poor photon output which prevents the route to applications. To preserve high photon output and rapid response it is advantageous to strive for highly localised electric fields in lossy cavities. Plasmonics nanoantennas are ideal candidates combining low quality factors Q with deeply localised mode volumes, while still displaying large g , provided the emitter is positioned correctly within the nanoscale mode volume. Here, with nanometre resolution, we map and optimise the coupling strength of a plasmonic dipole nanoantenna to a single molecule at various orientations, obtaining maximum coupling rate of $2g_{\text{max}} = 400 \text{ GHz}$. This provides ideal conditions for fast and pure non-classical photon emission, enabling a pulsed single photon source with brightness exceeding 10^9 photons/sec. Plasmonic nanoantennas thus present a unique opportunity in single emitter cavity QED to provide bright and ultrafast single photon sources for quantum technologies.



Coupling strength g -map and second-order intensity correlations $g^2(t)$, for a single molecule and resonant dipole nanoantenna cavity

Coupling single molecules to an ultra-small mode volume cantilever-based Fabry-Perot microcavity

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Novel concepts aiming at an efficient processing of information require a strong and controlled coupling of single photons with single atomic quantum systems. In recent years we have shown how tight focusing in combination with the large scattering cross section of single organic molecules at cryogenic temperatures can lead to strong linear and nonlinear interactions of photons with a single emitter [1, 2, 3].

Here we will present our latest results where we combine tight focusing with a scannable cantilever-based Fabry-Perot microcavity to achieve an even stronger light-matter interaction at cryogenic temperatures. The cavity consists of a carefully designed distributed Bragg reflector and a highly curved metal mirror at the end of an AFM tip [4]. We are able to controllably couple single dibenzoterrylene molecules to a cavity with a quality factor of 1000 and a mode volume of about $2\lambda^3$. In this configuration a single molecule can extinguish a weak laser beam by 38%. By employing a second laser, we obtain a transistor functionality and thus amplify a laser beam by stimulated emission from a single molecule coupled to the microcavity.

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Transformation Optics Approach to Plasmon-Exciton Strong Coupling in Nanocavities

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We present a theoretical description of the electromagnetic coupling between a quantum emitter and the localized modes supported by the most paradigmatic plasmonic cavity: a pair of metallic spheres separated by a nanometric gap. Our method exploits the invariance of Maxwell's Equations under geometric transformations [1] to obtain analytical expressions for the spectral density in the surroundings of this nanostructure. We use this tool to perform a thorough analysis of the Wigner-Weisskopf problem for this system, which allows us to reveal that by placing the emitter away from the cavity center, its coupling to multipolar dark modes increases remarkably [2]. This mechanism leads to the emergence of reversible dynamics in the population of the quantum emitter in feasible implementations of this nanocavity.

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Antenna effect: Energy transfer from monomers to J-Aggregates in 1D systems

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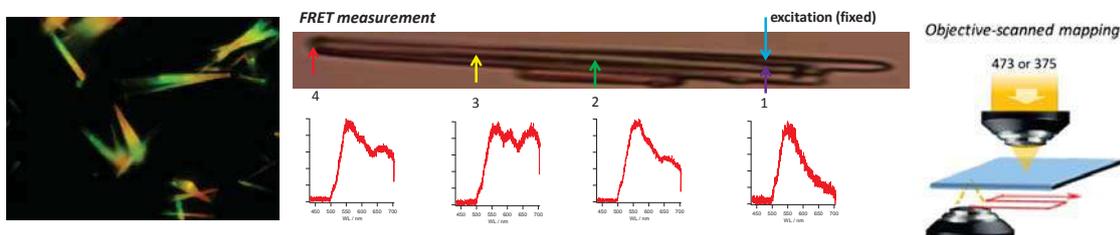
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In this work, several fluorescent dyes are encapsulated into the 1-D elliptical nano-channels of magnesium Aluminofosphate-36, “MgAPO-36” (ATS structure with pore size of 6.7 Å x 7.5 Å similar to the molecular dimension of the dyes) by crystallization inclusion method. The smaller dimensions of the ATS channels avoid the formation of bulkier H-dimers but instead red emissive J-type aggregates are observed. As a result, dye/ATS shows crystals with an organized multicolor emission, due to the strategic distribution of the dye species along the 1D-channels: monomers at one end, and J-type aggregates at the other end, offering an interesting material susceptible to be used as an artificial photonic antenna and interesting for energy transport [1]. The design of these photonic antenna system is based on a very efficient one-dimensional energy-transfer process (FRET: Förster Resonance Energy Transfer) between identical chromophores that have suffered an exciton splitting of their excited states due to the same type of dipole-dipole interactions, as described by Davydov, being the monomers and J-aggregates, the donor and acceptor entities, respectively. In this work is shown experimental evidences of how the excitation energy can be transported along the particle in one direction, by recording fluorescence images in single crystals using remote excitation microscopy technique, *i.e.* the detection spot is scanned over the crystal, while the excitation spot is fixed to monomer region[2]



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Polariton lasing in microcavities filled with biologically-produced fluorescent proteins

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There is an increasing interest in using biologically produced materials for photonic applications. Recent research impressively illustrates the broad potential of biological materials for providing optical gain [1]. In particular, fluorescent proteins like eGFP retain a special position within the quickly growing family of biologically produced laser materials. Fluorescent proteins have a barrel-like molecular structure that prevents concentration-induced quenching of the fluorescence by suppressing Förster and Dexter energy transfer [2] and drastically reduces singlet-singlet annihilation (SSA) at high excitation densities (outperforming common synthetic laser materials). Thus, fluorescent proteins are perfectly suitable for application as optical gain material in microcavities.

By using suitably designed resonators and increasing the concentration of fluorophores, we are able to observe polariton lasing at room temperature. Beyond this, we demonstrate the first two-threshold behavior of the microcavity emission indicating the onset of polariton condensation as well as photon lasing for an active organic material because of the high molecular photon stability of fluorescent proteins. This second threshold has previously not been within reach due to pronounced SSA at high excitation densities.

We further present different approaches capable of tailoring the in-plane confinement in planar optical microcavities filled with an active protein layer and thus creating three-dimensionally confined micro- and nanostructures. The respective confinement affects both the photonic and excitonic part of the microcavity and has therefore direct influence on weak [3] and strong light-matter interactions [4]. The approaches include: (i) organic imprint lithography, (ii) direct lasing writing above bleaching threshold and (iii) hemispherical mirrors in open microcavities. For all different techniques, we achieve confinement potentials on the order of several meV up to several tens of meV. The variety, versatility and moreover the compatibility of the applied techniques gives us the opportunity to tailor the photonic and excitonic part of organic cavities jointly and individually and paves the way towards complex photonic structures such as photonic chains and lattices.

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Strong coupling effect in absorption and photoluminescence spectra of hybrid systems of gold nanorods and J-aggregates

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We investigated the interactions between localized plasmons in gold nanorods and excitons in J-aggregates and were able to track an anticrossing behavior of the hybridized modes both in the extinction and in the photoluminescence (PL) spectra of this hybrid system. We followed the evolution of the two PL peaks as the plasmon energy was detuned from the excitonic resonance. Both extinction and PL results are in good agreement with the theoretical predictions obtained for a model of two modes.

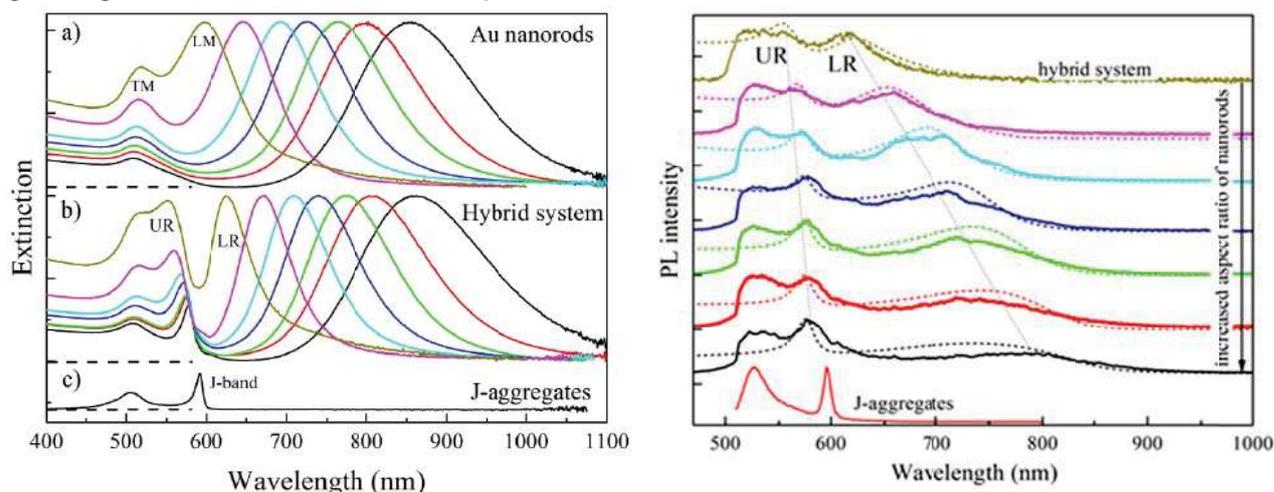


Figure 1 Left panel: Extinction spectra of gold nanorods of different aspect ratio (a), hybrid J-aggregates/gold nanorods complexes (b) and pure J-aggregates (c). Right panel: Normalized PL spectra of the hybrid systems. Dashed curves are results of the theoretical calculations.

Plasmon-Exciton-Polariton lasing

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Strong light-matter interaction leads to the appearance of new states, i.e. exciton-polaritons, with photophysical properties rather distinct from their constituents. Recent developments in fabrication techniques allow us to make metallic structures with strong electric field confinement in nanoscale mode volumes, allowing for facile assembly of strongly coupled systems at room temperature based on a hybrid organic-plasmonic architecture. In this research, a planar array of metallic nano-antennas is covered by a polymer layer doped with organic molecules, where we use photoluminescence spectroscopy to measure an onset in nonlinear emission. At increasing doping levels we observe an enlargement of the Rabi splitting caused by strong coupling and concomitant decrease in lasing threshold, this in spite of a strong reduction in photoluminescence lifetime and quantum yield for the dye. Moreover, using angular resolved photoluminescence we record the thermalization of polaritons in the nonlinear regime, into a mode which is dark in the linear regime. These measurements point towards signatures of stimulated scattering of plasmon-exciton-polaritons at room temperature in an open cavity [1,2].

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Chemistry under Ultra-strong Vibrational Coupling

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Strong light-matter interaction has much potential for modifying the chemical and physical properties of molecular materials. ^[1] Recently we have shown for the first time that molecular vibrational transitions can be coherently coupled to vacuum states in the infrared region. ^[2] Inspired from the previous work on excited state chemical reactivity^[1a] we strongly coupled molecular liquid in a micro-fluidic system, a first step in that direction to control the kinetics and thermodynamics of a given chemical reaction under the vibrational strong coupling (VSC) conditions. ^[3] Very recently, we experimentally proved this to be true by studying a ground state de-protection reaction of an alkynyl silane molecule under VSC of the *C-Si* stretching mode. ^[4] We have also managed to achieve ultra-strong vibrational coupling regime (Rabi splitting >25 % of the fundamental transition energy of a vibrational band) in molecular liquids. ^[5] This results in very interesting physical properties like polaritonic band gap opening which should have important consequence on the reactivity energy landscape.

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Cavity-mediated effects in transport

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Transport properties of materials (transport of charge, energy, correlations, etc) can be considerably altered in the presence of strong light-matter interactions manifested in the strong coupling regime of cavity quantum electrodynamics. Recent experiments show that enhanced charge transport in organic semiconductor materials can occur [3] that can be simulated via a two-band model where the inter-band transitions are coupled to the confined light modes of a micro-cavity and consequent delocalized hybrid light-matter states participate in the transport.

In a simplified quantum optical model, where a single cavity light mode is equally coupled to a chain of two-level systems, we study the modification of the typical nearest neighbor hopping transport below and inside the strong coupling regime. We find in [1] (in agreement with [3]) that the polariton-enhanced transport can show polynomial instead of exponential suppression with the system size in the presence of disorder.

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Coherent energy transfer between widely separated nanoantennas coupled via a plasmonic cavity

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Rather diverse phenomena such as light harvesting in photosynthesis, nanoscale quantum entanglement, or photonic mode hybridization rely on efficient photonic coupling mediated via optical near-fields. Usually, these coupling phenomena are efficient only for separations much shorter than the optical wavelength.

Here, we demonstrate in theory (finite-difference time-domain simulations) and experiment (time-resolved PEEM) an all-plasmonic device which facilitates coherent coupling between selectively addressable nanoantennas (whispering gallery mode resonators [1]) separated over a distance of twice the exciting light wavelength. Placing the nanoantennas in the focal spots of a surface plasmon mode confined within the metallic walls of an elliptic arena cavity [2] results in a rather strongly coupled system: We find a coupling-induced splitting of the new eigenmodes of 17 THz (36 nm). The experimental observations are described by a coupled oscillator model which depicts an all-plasmonic analogue of the quantum mechanical Tavis-Cummings model [3].

Combining hybridized properties of localized and extended plasmon modes, i.e. field enhancement and longevity, with selective addressability of single constituents represents a step towards coherently controlled energy routing in plasmonic circuits and towards strong coupling of few quantum emitters and single plasmons.

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Cavity-Controlled Chemistry in Molecular Ensembles

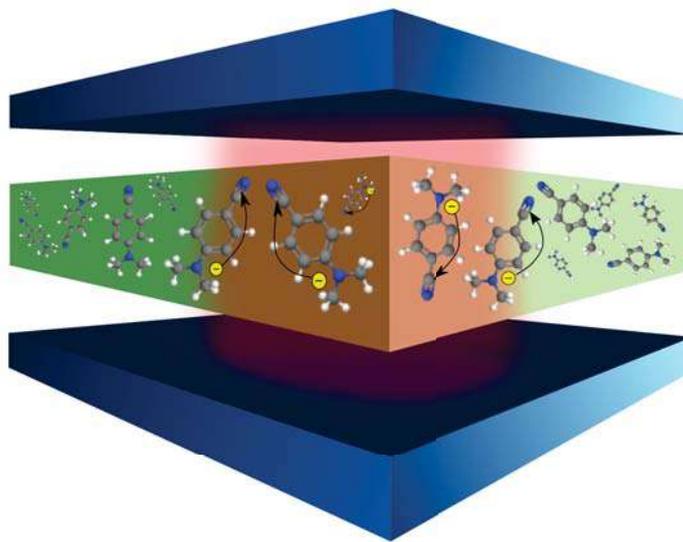
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The demonstration of strong and ultrastrong coupling regimes of cavity QED with organic molecules has opened new routes to control chemical dynamics at the nanoscale. We prove analytically and confirm numerically that strong resonant cavity-molecule coupling can effectively decouple electronic and nuclear degrees of freedom in a disordered molecular ensemble. This type of polaron decoupling effectively prevents nuclear reorganization in the excited electronic state. By reducing the inner-sphere reorganization energy, the rate of intramolecular electron transfer (ET) between cavity-dressed donor and acceptor groups is enhanced, in the language of Marcus theory. We show that polaron decoupling can lead to an exponential enhancement of ET reaction rates in comparison with free-space reactions having the same donor-acceptor energy gap. We also discuss the scaling of intramolecular and bimolecular ET reaction rates with the number of molecules in the ensemble. Finally, we propose novel optoelectronic devices based on cavity-controlled chemistry.



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Poster 1

Strong coupling of localized surface plasmons with a whispering gallery cavity

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Several attempts have tried to spectrally narrow the plasmon resonance of metal nanoparticles, which could benefit the application of the localized surface plasmon resonance (LSPR) for sensing and nonlinear conversion. For example, squeezing the linewidth can be accomplished by coupling a metal nanoparticle with a photonic microcavity [1] or using Fano interference in a nanoparticle cluster [2]. Up to now, the narrowest line-width in a nanoparticle plasmon is still larger than 5 nm. Also, this approach requires complex fabrication with tight control of size, shape, and position arrangement.

Here we demonstrate substantial reduction in the LSPR linewidth of an Au nanorod by depositing it onto the surface of a tapered fiber. Dark field spectroscopy is used to investigate scattering light from single Au particle coupled to a tapered fiber (see the schematic illustration of the dark-field setup in Fig. 1a). In order to avoid the scattering light from the fiber itself, we choose angled illumination along the fiber axis instead of the normal illumination [3].

When the tapered fiber diameter is reduced to about 1-3 μm , we observe signatures of strong coupling between the LSPR modes and the whispering gallery modes of the tapered fiber. Figure 1c is a typical scattering spectrum of a strongly coupled nanorod-microfiber system. This results in a very narrow hybrid plasmon-fiber resonance of the single Au nanorod, with a much higher quality factor Q (over 200) when compared with that of an Au nanorod (see the scattering spectrum of a single Au rod in Fig. 1b) or an uncoated fiber with the same diameter. Meanwhile, the strong coupling leads to a significant enhancement of the peak scattering intensity at plasmon resonance when compared to an uncoupled Au nanorod. Nonlinear optical processes such as second-harmonic generation should therefore be possible in such a simple system with extremely high conversion efficiency, as it scales with Q^4 .

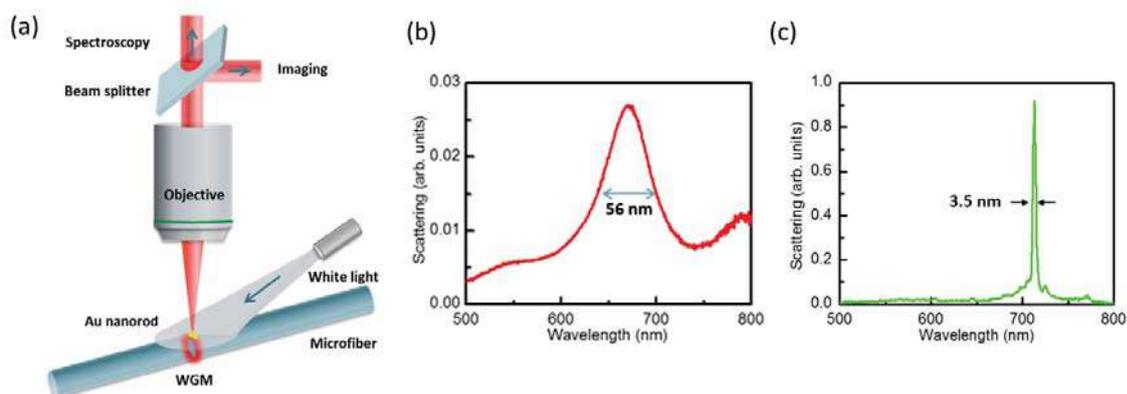


Fig. 1. (a) Schematic illustration of the dark-field setup for light scattering spectroscopy of nanorod-microfiber system. (b) Typical scattering spectrum of an Au nanorod deposited on a glass slide. (c) Scattering spectrum of single Au nanorod coupled to tapered fiber with diameter of 1.6 μm .

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Ultrastrong coupling in a nonlinear organic microcavity

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Cavity polaritons are hybrid light-matter quasiparticles that arise when the interaction between cavity photons and excitons exceeds their individual damping rates. In these strongly coupled systems, polariton-polariton interactions have allowed for the demonstration of a number of interesting nonlinear phenomena such as Bose-Einstein condensation, superfluidity, optical parametric oscillation and amplification. Although most experiments have been limited to low temperatures, the high stability of Frenkel excitons has already enabled a few room-temperature demonstrations of the same nonlinear effects¹. Further demonstrations can benefit from materials that combine large resonant or near-resonant third order nonlinear susceptibilities, large oscillator strengths, low linear and nonlinear optical losses and enhanced photostability. We investigated an organic microcavity containing one such material – a novel polymethine dye – embedded between a pair of silver mirrors². From reflectivity measurements, we obtained a Rabi energy of 0.69 eV, corresponding to 60% of the exciton energy at 1.16 eV - matching the highest ratios reported to date³. This demonstration of ultrastrong coupling using one of the best organic nonlinear materials paves the way for several new opportunities in room-temperature polaritonics.

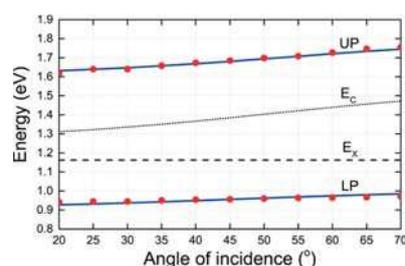


Figure 1. Dispersion relations (solid lines) obtained by a least-squares fit of the experimental reflectivity minima (dots) to the full Hopfield Hamiltonian. Dashed (dotted) lines correspond to the exciton (cavity) energies.

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Generation of Rabi frequency radiation using exciton-polaritons

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Strong coupling between a photon and an electric dipole leads to the formation of mixed light-matter quasiparticles called polaritons. Their dispersion relation is split into upper and lower branches, with an energetic separation termed the vacuum Rabi splitting. It can span from a few meV in inorganic semiconductors to ~1 eV in organic ones [1]. Transitions between the upper and lower polariton branches can therefore provide a simple route towards tunable infrared and terahertz generation. Due to selection rules, however, radiative transitions between these two branches are typically forbidden. In this work, we study the use of semiconductors possessing a second-order susceptibility $\chi^{(2)}$, thus breaking centrosymmetry and allowing for radiative transitions at the Rabi energy through difference-frequency generation (DFG) [2]. This contrasts strongly with conventional optical microcavities, where phase-matching requires maximizing the overlap of the interacting fields and thus some breaking of mode orthogonality [3]. Because exciton-polaritons arise from coupling to a single cavity mode, they naturally display high modal overlap, which relaxes design constraints. Using a simple classical model based on nonlinear transfer matrices in the undepleted pump regime, we calculate the Rabi splitting and the DFG irradiance enhancement for an organic microcavity composed of a poled nonlinear optical polymer and for an inorganic microcavity composed of (111) GaAs. In the first case, by using triple-resonance of the Rabi frequency with the fundamental cavity mode, we obtain a Rabi splitting of 0.68 eV ($\lambda=1.819 \mu\text{m}$) and a DFG enhancement of 2.8×10^2 , as compared to a bare polymer film. For the second case, a Rabi splitting of 5.52 meV ($\lambda=224.5 \mu\text{m}$) and an enhancement of 8.8×10^3 are found, as compared to a bare GaAs slab. In addition, both structures show high wavelength tunability. Our results indicate that the typical Rabi splitting values found in organic and inorganic microcavities make the use of polaritonic modes extremely promising for infrared and terahertz generation.

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Single-molecule optomechanics in picocavities

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We show how atom-sized features in a plasmonic hotspot – *picocavities* – can greatly enhance the optomechanical coupling strength of molecular vibrations of single molecules to plasmonic cavity modes. As an example system we use the nanoparticle-on-mirror geometry, which consists of gold nanoparticles placed on a molecular spacer layer on gold (Fig. 1A). To avoid thermal contributions to the phonon population the samples were cooled to 10 K. The phonon population can be investigated by recording both anti-Stokes and Stokes emission of the molecular spacer layer. We find the characteristic behavior of vibrational pumping with the anti-Stokes emission showing a quadratic laser power dependence and the phonon population increasing linearly with the laser power (Fig. 1B). This observed behavior is described in terms of the optomechanical theory of SERS recently introduced by Schmidt *et al.* [1,2].

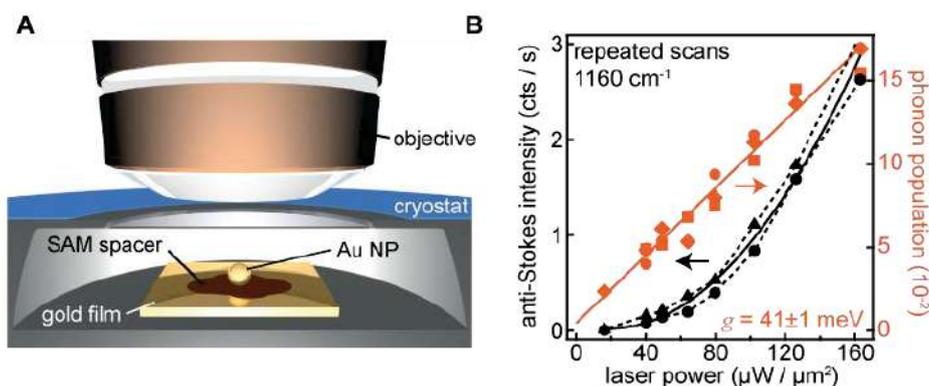


Figure 1. **A**, Illustration of a nanoparticle-on-mirror sample placed in a cryostat. **B**, Example of vibrational pumping: the phonon population increases linearly with laser power.

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Radiative Enhancement of Single-molecule Strongly Coupled to Plasmonic Nanocavity

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Excited optical emitters placed close to a metal decay via non-radiative channels which is generally termed as quenching. Emitters in nanocavities made from metal nanoparticles suffer from high quenching rates. This process has so far prevented the study of many exciting linear & non-linear optical phenomenon of emitters in a cavity. Here, we use reliable self-assembled metal nanoparticle-on-mirror constructs to couple collective oscillation of free electrons (plasmons) with molecular emitters (Fig.1a). By scaling the mode volume below 100 nm^3 and using host-guest chemistry to align 1-10 protectively-isolated dye molecules, we reach the strong-coupling regime at room temperature and in ambient conditions [1]. We find that the coupling strengths and radiative emission have a strong correlation with the position of the molecule in the gap (Fig.1b) [2]. This suggests that it is possible to overcome the high quenching rates by using metal nanocavities with high Purcell factors, resulting in observation of strong coupling with single-emitters [3].

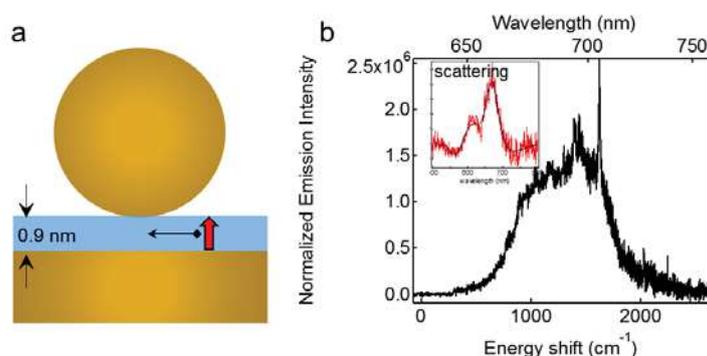


Fig1. Radiative emission from Nanocavity. (a) Schematic of nanoparticle on mirror constructs, with dye molecules in a 0.9 nm gap. (b) Emission from molecule and corresponding dark-field scattering obtained from the nanocavity.

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Exploiting Vibrational Strong Coupling to make an Optical Parametric Oscillator out of a Raman Laser

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When the coherent interaction between a confined light mode and vibrational matter excitations becomes faster than the relevant decoherence processes, the system can enter into vibrational strong coupling (VSC). The fundamental excitations of the two systems then become inextricably linked and can be described as hybrid light-matter quasiparticles, so-called vibro-polaritons, that combine the properties of both ingredients. In particular, the use of vibrational modes that are both IR- and Raman-active allows to probe vibro-polaritons through Raman scattering mediated by their material component [1, 2]. On the other hand, while the cross sections for Raman scattering are typically small, the process can become highly efficient under strong driving if the scattered Stokes photons accumulate sufficiently to lead to stimulated Raman scattering (SRS). The effective energy conversion from input to output beam can then be exploited to fabricate a highly tunable *Raman laser*.

We present theoretical results demonstrating that the hybrid light-matter nature of vibro-polaritons can be exploited to widen the capabilities of Raman laser devices, reducing the threshold and obtaining photon emission from the vibrationally excited final states of the Raman scattering. We consider the system sketched in Fig. 1, consisting of a material with a vibrational transition that is both IR- and Raman-active, placed inside a resonator (e.g., a microcavity). The resonator supports at least two confined modes, a mid-IR mode used to achieve VSC with the vibrational transition, and an optical mode (frequency ω_S) used to accumulate the scattered Stokes photons. A single-output Raman laser device then becomes analogous to an *optical parametric oscillator* (OPO) with output beams both in the visible and in the mid-IR, relevant for many spectroscopic applications [3]. In addition to obtaining two coherent beams with a stable phase relation (and possibly nonclassical correlations) spanning very different frequency regions, this approach has the further advantage of effectively getting rid of the energy deposited into material vibrations; instead of being dissipated as heat, this energy is emitted in the form of photons.

Finally, we show that the coexistence of the upper and lower polariton modes with very similar properties can be exploited to produce an all-optical switch. Here, one (gate) pump beam can be used to switch Raman lasing of a second

(signal) pump beam. These findings are thus an example of the great potential that hybrid light-matter states possess in both manipulating light fields and modifying material properties.

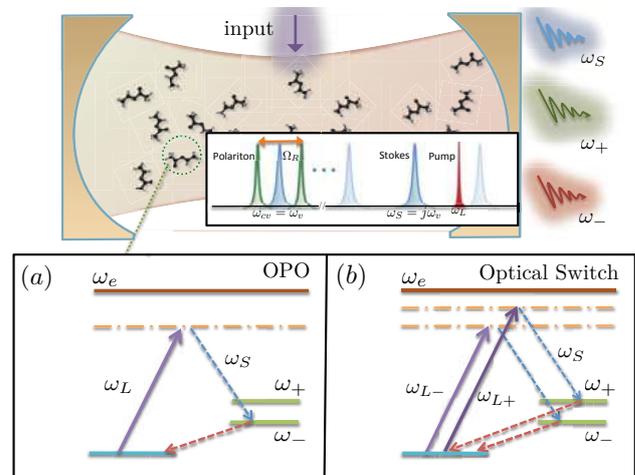


FIG. 1. Upper panel: sketch of the system to convert a Raman laser into an OPO through vibrational strong coupling (see main text). The input fields (purple arrows) can be chosen to achieve (a) OPO operation with a single pump frequency ω_L , or (b) an all-optical switch with two pump fields $\omega_{L\pm}$. The vibro-polariton frequencies are denoted by ω_{\pm}

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Light Emission Statistics as a Local Probe for Structural Phase Switching

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In this work we show that the statistics of emission rates in correlated disordered media is extremely sensitive to the details of the radial distribution function around the emitter. We analyze the emission statistics for single emitter embedded in a finite cluster of resonant particles. However, instead of generate random configurations of scatterers, we compute the emission rates as the system evolves with time under equilibrium conditions. Assuming a standard Lennard-Jones (L-J) interaction between particles, this system is known to present a peculiar solid-liquid-like phase transition at finite temperature: Due to finite-size effects, the two phases cannot coexist at the melting temperature and the whole cluster presents an interesting dynamical behavior, switching between an amorphous solid-like phase and liquid-like phases [1]. This makes it an ideal model system to analyze the effects of local order on the emission rates. In the solid phase at low temperatures, the equilibrium positions are close to those corresponding to a face-centred-cubic (FCC) lattice, and the spectrum of emission rates present a strong chromatic dispersion reminiscent of the band structure of an infinite crystal of resonant dipoles, including spectral windows where the emission is enhanced and pseudo-gaps where it is dramatically inhibited. At the melting temperature, the total scattering cross section of the system does not present significant differences between the two phases while the emission rate jumps following the dynamics of the system. While light scattering measurements would be blind to such dynamical changes, the lifetime statistics would then provide a direct signature of a phase switching behavior [2].

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Structured Organic Layers and Strong-Coupling in a Fabry-Pérot Microcavity

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We present a study of the interaction between the optical field confined in a Fabry-Pérot microcavity and an organic dye embedded within it. In particular we explore the effect of different distributions of dye within the cavity under the strong coupling regime, exploiting the variation of field strength of the mode across the cavity.

Our research brings together experiment and theory. For the organic dye we use TDBC [(5,6-dichloro-2-[[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)-benzimidazol-2-ylidene]-prophenyl]-1-ethyl-3-(4-sulphobutyl)-benzimidazolium hydroxide)] in a J-aggregate form with Poly Vinyl Alcohol (PVA) as a polymer host matrix. Microcavity mirrors are formed by thermal evaporation of metallic layers. The PVA-TDBC films are deposited by spin coating. SiO₂ films are used as spacer layers between the metallic mirrors and the organic dye. We measure both transmission and reflection of our microcavities, thereby allowing absorption spectra to be acquired as a means to demonstrate strong coupling. For the modeling we make use of the Fresnel formulation and the transfer matrix method. The permittivity of the materials have been modelled using the Drude model for the silver metal films [1] and using the Lorentz model for the organic dye [2].

We find that the cavity mode splitting is greater when the organic film is placed at the position where the cavity mode has more intensity. We correlate these observations with calculations of the field profiles within the cavity. We also model the way in which the 2D material WS₂ may be used as the excitonic layer for strong coupling, focusing on what happens as such a layer is brought into close proximity with one of the metal layers. Finally we explore the way in which multilayer excitonic structures, which may support a hyperbolic response, are modified by strong coupling, thereby combining strong coupling with metamaterials.

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Suppressing photochemical reactions with quantized light fields

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Strong coupling in quantum electrodynamics is a well-known phenomenon achieved when coherent energy exchange between a confined light mode and a quantum emitter becomes faster than the decoherence processes in the system. The modes of the coupled system are hybrid light-matter excitations called polaritons. Organic molecules are a particularly favorable case for achieving strong coupling at room temperature due to their excitons with large transition dipole moments and binding energies. Most pictures of strong coupling are based on two-level models for the organic molecules, and do not take into account the many nuclear (rovibrational) degrees of freedom of these systems. However, recent pioneering experimental studies demonstrating modifications of material properties and chemical reaction rates under strong coupling show that strong coupling can indeed affect these “internal” degrees of freedom [1].

In order to treat the nuclear degrees of freedom in more detail, we have recently combined the well-known picture of molecules potential energy surfaces (PES) based on the Born-Oppenheimer approximation with the tools of cavity quantum electrodynamics [2]. This allows us to describe nuclear motion on strongly coupled polaritonic PES, providing a straightforward approach to understanding and manipulating molecular properties under strong coupling. In particular, we demonstrate that a wide class of photochemical reactions can be strongly suppressed by modifying the reaction pathway through strong coupling [3]. This suppression is even more pronounced for the experimentally relevant case of collective strong coupling where many molecules couple to one or a few light modes. Using this approach, even molecules that normally undergo extremely rapid photoisomerization can be stabilized, potentially increasing their usefulness for applications that rely on the interaction with external light, such as solar cells or solar energy storage.

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Anticorrelation of photoluminescence with strength of hot-spots between gold bipyramids

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Compared to bulk gold, nanoparticles show a significantly higher quantum yield of photoluminescence (PL) from *d*-band hole recombination. It makes them attractive for cell imaging and biosensing. Although there are numerous reports on single-photon and multi-photon-induced PL of plasmonic particles and nanoparticle systems, the underlying mechanism of the PL is still a subject of intensive debate. Here we report on one-photon photoluminescence from dimers of bipyramids (BP), where the plasmonic coupling can be adjusted by varying interparticle distance and by seesawing the BPs using the tip of an AFM. This nanomanipulation allows us to directly control the interparticle distance, and therefore to tune the strength of the hot-spot in the gap of a dimer. Based on experimentally measured photoluminescence and the scattering spectra of the dimers, two major features were observed. Firstly, the PL emission and scattering spectra show similar redshifts for each interparticle distance. Secondly, while the scattering somewhat increases, the PL intensity decreases with increasing plasmonic coupling. This reveals that the PL is anticorrelated with the local field enhancement in the gap between the two BPs. Finally, we not only observe PL supported by dipolar plasmon resonances, but also measure and simulate PL supported by higher order plasmonic modes. We developed a theoretical model for the calculation of photoluminescence emission, which explains these experimental findings.

Financial support was provided by the European Research Council (ERC Starting Grant 257158 'Active NP') and partially by the Austrian Klima- und Energiefonds (SolarTrap, Grant 843929).

Polarized Scattering versus Unpolarized Photoluminescence from Single Gold Nanosponges

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Complex shaped nanoparticles exhibit multiple plasmon resonances in the visible and near infrared spectral range. In this contribution, we address and discuss the plasmonic properties of a particular kind of complex shaped nanoparticles, namely three-dimensionally gold/air percolated nanoparticles, so called nanosponges. We present the correlation between structural and optical properties of the nanosponges. The scattering spectra depend only weakly on outer diameter and shape, but are decisively influenced by the inner mesoporous structure. Due to the size of the interior filaments which is below 20 nm, the nanosponges provide a three dimensional variation of the local dielectric function on the same scale. [1]

Subsequently, we correlate the single-photon induced photoluminescence with the scattering of the same individual nanosponge. In contrast to other nanoparticles, where the polarization dependence of the photoluminescence and scattering spectra resemble each other, we find that the photoluminescence from nanosponges is substantially less polarized than the scattered light.

Financial support was provided by the European Research Council (ERC Starting Grant 257158 'Active NP') and by Deutsche Forschungsgemeinschaft (DFG, grant SCHA 632/20-1).

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On the Impact of Quenching in 'active' Plasmonic Systems: Spaser, Single Photon Transistor & Strong Coupling in NPoMs

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A promise of 'active' plasmonics is to construct ultra-compact devices with new functionality (e.g., with non-linear reaction). Here, by 'active' plasmonics we think of hybrid systems[1], in which (organic) quantum emitters interact with plasmonic nanostructures. We focus on three (controversially discussed) device types: the spaser[2], the single photon transistor[3]–[5] and strong coupling in resonant nanostructures like nanoparticle on mirror (NPoM) structures[6].

Here we claim, that an accurate incorporation of quenching in theoretical models is of highest importance in order to realistically predict a systems' performance and to interpret experimental findings.

Essential performance characteristics of the above mentioned devices can be modeled semi-classically with the help of classical Maxwell solvers, even for systems in the strong coupling regime[7]. We discuss, that the main figures of merit to understand the three 'active' devices are the 'modal' Purcell factor P_M [8] and the β -factor $\beta = P_M/P_{tot}$. Both factors *combined* describe the coupling of an emitter to a specific mode. Here P_{tot} is the overall Purcell factor including the change of the total local density of states, especially also any quenching process.

In parallel we discuss ways to model realistic emitters. In the lab emitters typically suffer from incoherence, especially in most plasmonic experiments. These sources of incoherence are (i) broadening due to coupling to phonons of the surrounding, (ii) a limited Debye-Waller factor due to coupling to vibrational modes within the emitter and (iii) spectral diffusion due to charge fluctuations in the surrounding (Stark shift).[3], [9] In contrast, in theory emitters are typically described as ideal two level systems (TLS) or spectrally narrow (Fourier limited) point sources.

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Strong Coupling in Plasmonic Nanocavities

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Quantum emitters placed in a plasmonic nanostructure can coherently exchange energy with plasmon modes. When the coherence time of the coupling is longer than the period of energy oscillation, the system reaches the strong coupling regime and shows characteristic Rabi splitting in its far-field spectrum. The recent experiments [Ref 1] have shown that strong coupling can be achieved at room temperature by using a plasmonic nanocavity. Reducing the mode volume to below 40 cubic nanometres, a plasmonic nanocavity sufficiently enhances the coupling strength and the energy oscillation rate. Here, we treat the system semi-classically, using the Maxwell-Bloch approach and study the time dynamic of the strong coupling with dipole and quadrupole plasmonic resonances.

Ultrastrong coupling effects on molecular reactivity

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Cavity quantum electrodynamics (cavity QEDs) have opened up new avenues to introduce strong light-matter interaction. As previous works show [1]-[4], electromagnetic nanostructures allow for the modification of energy landscapes in molecules which can directly affect chemical reactivity and nuclear dynamics. This is done through the coupling of the electric field which is confined in the cavity with the electronic and vibrational degrees of freedom of molecules. Typically, the magnitude of single-particle couplings are of the order of 1×10^{-3} meV to a few meV for typical organic molecules [3]. Under this regime, the ground state energy of the particles is unaffected compared with higher excitation manifolds, which exhibit strong hybridization of light and matter modes. However, in the so-called ultrastrong coupling regime, the ground state also acquires photonic character and its energy is lowered as a consequence of its coupling to higher-energy states through counter-rotating terms of the system's Hamiltonian. Although the influence of this regime on the ground state has been mentioned in previous works [1][3], there is no current study showing the modification of chemical reactivity under this regime. In this work, we address the effects of ultrastrong coupling in the kinetics and thermodynamics of the isomerization of a model molecule. Our approach reveals that the rate of a chemical reaction can be tuned in a cavity QED, and demonstrates the capability of cavity nanostructures to control the chemistry of molecules in the ground state.

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Strong coupling between vibrational modes and optical micro-cavity modes: the challenges of combining infrared and Raman spectroscopy

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Abstract:

The coherent coupling between confined cavity modes and the vibrational modes of molecules within the cavity gives rise to new hybrid modes which can be observed in the infra-red spectrum. Here we present results from an experimental and numerical study that explores how different experimental approaches, infrared (IR) absorption spectroscopy and Raman spectroscopy, may be used to probe the underlying physics. Figure 1 shows Fourier transform infrared spectroscopy (FTIR) experimental data from the strong coupling between cavity modes and the C=O vibrational mode of polymethylmethacrylate (PMMA), consistent with previous work [1], [2]. We will discuss how cavities may be optimised to allow both IR and Raman techniques to yield useful though somewhat complimentary information. Control over vibrational modes shows promise for modifying chemical reaction rates and to control material properties [3].

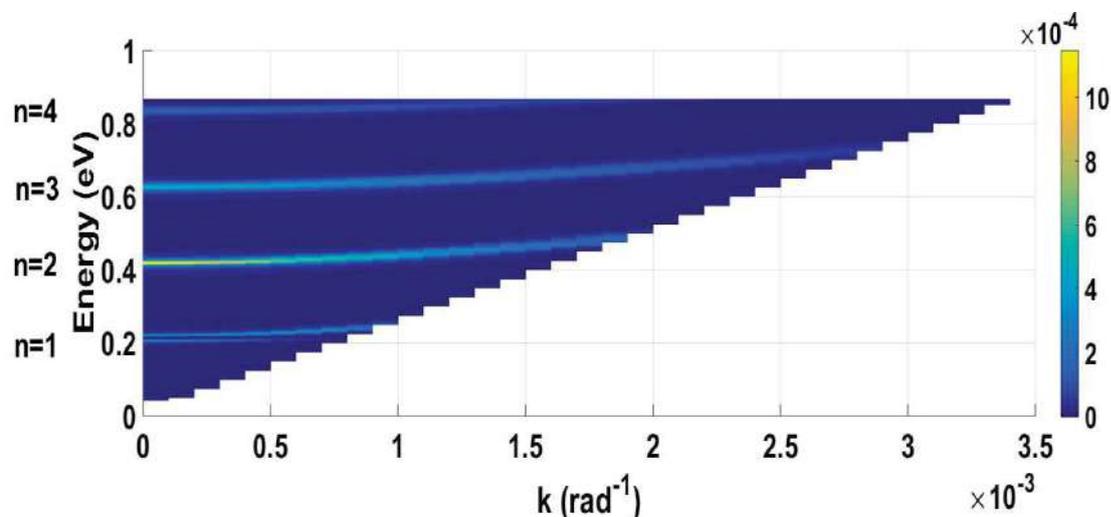


Figure 1: FTIR transmission results in the form of a dispersion curve, showing strong coupling between molecular vibration (PMMA) and the Fabry-Perot cavity mode at $\sim 0.2\text{eV}$

[1] Long J. P. and Simpkins B. S., ACS Photonics (2015) **2** 130

[2] Shalabney A. et al. Nature Communications (2015) **6** 5981

[3] Galego J., Garcia-Viadal F. J. and Feist, J. Phys Rev X (2015) **5** 041022

Controlling the quantum state of molecular vibrations in resonant Surface-Enhanced Raman Scattering

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The recent description of off-resonance Surface-Enhanced Raman Spectroscopy (SERS) within the framework of cavity quantum electrodynamics (QED) indicates that a plasmonic cavity interacting with the vibrational levels of a molecule can be understood as a molecular optomechanical system [1,2]. We extend this description to resonant SERS (see Figure), and establish an analogy with analogue hybrid optomechanical systems [3]. We find important coherent effects in SERS that arise from the interaction between the resonant Raman scattering and the resonant fluorescence. Notably, this interaction leads to a particular signature in the experimentally observable plasmon emission spectra. We further show that the resulting vibrational pumping could offer the possibility to optically manipulate the quantum states of molecular vibrations, providing applications, for example, in single molecule chemistry and quantum nanooptics.

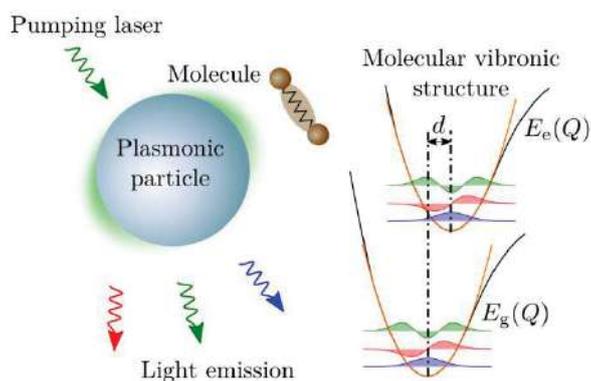


Figure: Schematics of the studied model. A coherent monochromatic laser illuminates a plasmonic particle that is coupled to a molecule. The molecule is modeled as a two level system with additional vibrational states.

[1] P. Roelli, C. Galland et al., *Nat. Nano.* 11, 164-169 (2015)

[2] M. K. Schmidt, R. Esteban et al., *ACS Nano* 10(6), 6291-6298 (2016)

[3] T. Ramos, V. Sudhir et al., *Phys. Rev. Lett.* 110(19), 193602 (2013)

Growth and Characterization of Organic Nanocrystals for Nanophotonic Applications

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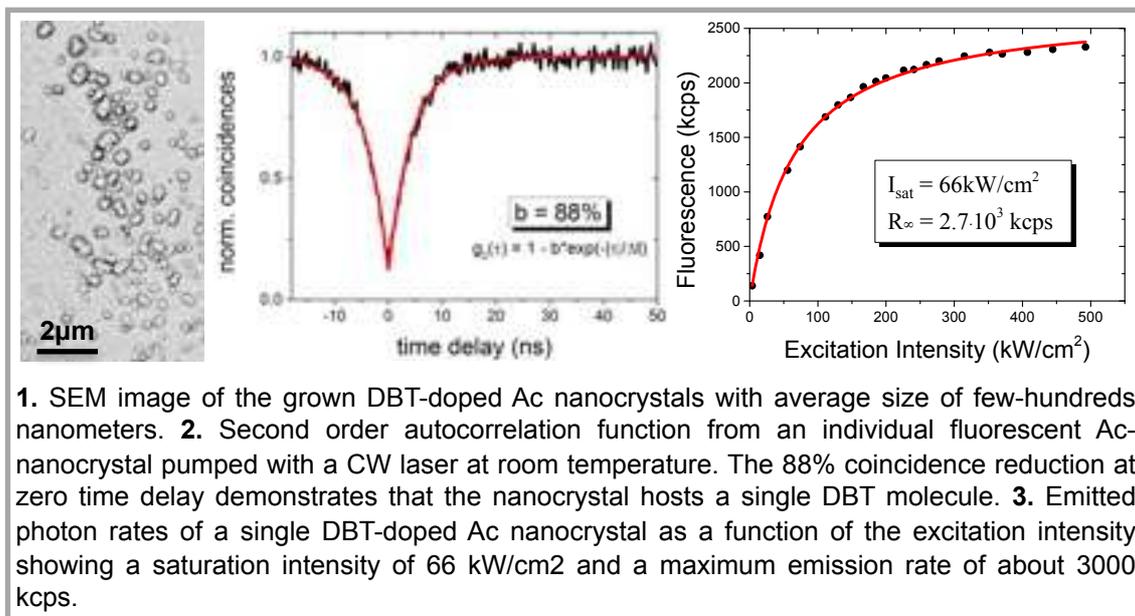
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Dibenzoterrylene (DBT) molecules embedded in Anthracene (Ac) crystals combines a bright and stable emission in the near-infrared, both at room and low temperature, with a narrow lifetime-limited emission (~ 40 MHz) around 785 nm at cryogenic temperature [1]. To date, DBT:Ac system has been successfully integrated in nanophotonics layered structures thanks to the 50 nm-thickness of Ac spin-coated crystals, covering several hundreds μm^2 of the substrate [2]. However, to fully exploit this molecule-based solid state system as a single photon source to e.g. deliver photons into a nearby waveguide, precise positioning method and/or controllable size of the emitter is indeed desirable.

In this work we present a novel technique to fabricate DBT-doped anthracence crystals with average size of few-hundreds nanometers and controllable DBT concentration. Preliminary investigations demonstrate that the optical properties of the bulky DBT:Ac system at room temperature are preserved.



1. SEM image of the grown DBT-doped Ac nanocrystals with average size of few-hundreds nanometers. **2.** Second order autocorrelation function from an individual fluorescent Ac-nanocrystal pumped with a CW laser at room temperature. The 88% coincidence reduction at zero time delay demonstrates that the nanocrystal hosts a single DBT molecule. **3.** Emitted photon rates of a single DBT-doped Ac nanocrystal as a function of the excitation intensity showing a saturation intensity of 66 kW/cm^2 and a maximum emission rate of about 3000 kcps.

[1] J. B. Trebbia et al., Opt. Express, 23986–23991 (2009).

[2] C. Toninelli et al., Opt. Express 18, 6577–6582 (2010)

Optomechanics of Raman scattering from molecules in plasmonic cavities

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Substrate Enhanced Raman Scattering (SERS) is a fundamental spectroscopic technique that allows us to access the rich vibrational structure of molecules. A number of recent implementations of Raman experiments [Ref 1] appear to provide results which escape the standard description of the Raman process based on the classical treatment of the electromagnetic enhancement of fields inside a plasmonic cavity [Ref 2].

To address those effects, we present a novel theoretical framework, inherited from the optomechanical community [Ref 3,4] and apply it to predict a plethora of effects which are not encompassed by the classical framework, e.g. the onset of the supra-linear dependence of the intensity of Stokes and anti-Stokes emission on the power of the incident illumination and the anomalous dependence on the detuning between the incident laser and the resonance of the plasmonic cavity.

Furthermore, we show that such systems can serve as the implementations of optomechanical Hamiltonian in the largely unexplored regime of THz mechanical frequencies, low-Q cavities and large single-photon couplings.

Finally, we provide a complete numerical characterization of the two-photon frequency-resolved spectra of light emitted from the SERS cavity. We analyze the rich landscape of correlations, and identify regimes of strong bunching and anti-bunching of the scattered light [Ref 5].

[Ref 1] R. Zhang, et al., Nature 498, 82 (2013).

[Ref 2] H. Xu, et al., Phys. Rev. Lett. 93, 243002 (2004).

[Ref 3] P. Roelli, et al., Nat. Nano. 11, 164 (2016).

[Ref 4] M.K. Schmidt, et al., ACS Nano 10, 6291 (2016).

[Ref 5] M.K. Schmidt, et al., in preparation.

Ground State Chemical Reactivity under Vibrational Coupling to the Vacuum Field

Anoop Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Chervy, X. Zhong, E. Devaux, C. Genet, J. Hutchison and T.W. Ebbesen

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The ground state deprotection reaction of a simple alkynyl silane is studied under vibrational strong coupling to the zero-point fluctuations, or vacuum electromagnetic field, of a resonant IR microfluidic cavity. It is found that the reaction rate is slowed by a factor of up to 5.5, when the reactant's Si-C vibrational stretching modes are strongly coupled, and the relative change in the reaction rate under strong coupling depends on Rabi splitting energy. Product analysis by GC-MS confirms the kinetic results. Temperature dependence shows that the activation enthalpy and entropy change significantly, suggesting that the transition state is modified from an associative to a dissociative type. These findings show that vibrational strong coupling provides a new powerful tool for modifying and controlling chemical landscapes, and for understanding reaction mechanisms, among other things¹

[1] A. Thomas, J. George, A. Shalabney, M. Dryzhakov, S. J. Varma, J. Moran, T. Chervy, X. Zhong, E. Devaux, C. Genet, J. Hutchison and T.W. Ebbesen, *Angew. Chem. Int. Ed.*, Accepted (2016)

Plasmon-enhanced fluorescence near nonlocal metallic nanospheres

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Spontaneous emission and fluorescence of organic molecules are known to strongly depend on the local electromagnetic environment. Plasmonic nanoparticles are widely explored as templates for controlling light-matter interactions, and can be tailored to optimize the fluorescence rate (γ_{em}) of a dipole emitter. Here we explore the importance of hitherto disregarded nonclassical effects in the description of emitter-plasmon hybrids, focusing on the roles of metal nonlocal optical response and size-dependent plasmon damping [1]. Comparison between the common local response approximation (LRA) and the generalized nonlocal optical response (GNOR) theory [2] shows that a significant decrease in fluorescence enhancement is obtained for emitters close to small metallic nanospheres or thin metallic nanoshells, while the optimum emitter position is also affected. In this respect, our recent work introduces the study of emitter-plasmon coupling (in the weak-coupling limit) as a sensitive test for the validity of state-of-the-art nonclassical models. For the regime of strong emitter-plasmon coupling, we anticipate an analogously wide importance of a description beyond classical electrodynamics, particularly once electron spill-out and tunneling are also fully considered.

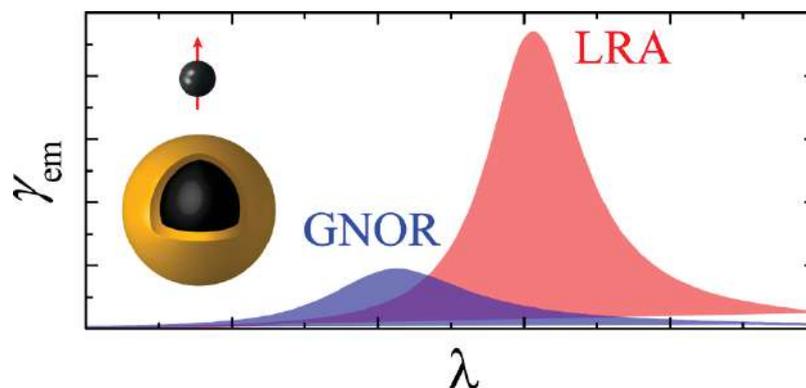


Figure 1. Schematic representation of the fluorescence (γ_{em}) differences calculated within the local (LRA, red curve) or the generalized nonlocal (GNOR, blue curve) approach, for an emitter near a thin gold nanoshell.

[1] C. Tserkezis, N. Stefanou et al., *Nanoscale* 8, DOI: 10.1039/C6NR06393D (2016)

[2] N. A. Mortensen, S. Raza et al., *Nature Commun.* 5, 3809 (2014)

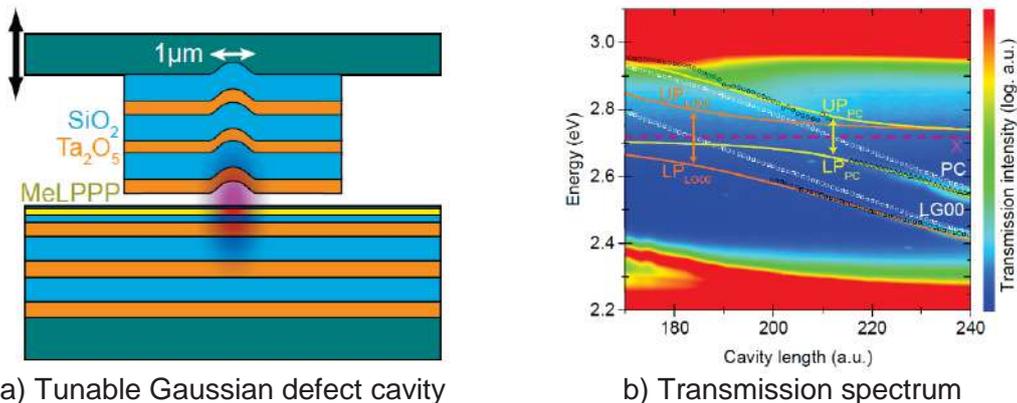
Tunable coupled Gaussian defect microcavities supporting zero-dimensional polaritons in a π -conjugated polymer at room-temperature

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We demonstrate tunable Gaussian defect microcavities (Fig. 1 a) which provide lateral confinement of light supporting zero-dimensional organic exciton-polaritons at room temperature¹. We show real space and k-space images of both confined and planar cavity modes. Furthermore, by detuning the cavity length we show strong light-matter interaction between ladder-type conjugated polymer² and individual modes of a vertical microcavity having a Rabi splitting between two polariton branches of $2g = 166$ meV (Fig. 1 b). To demonstrate two coupled Gaussian defect microcavities we place an additional Gaussian defect nearby and create a photonic molecule with tunnel coupling strength of up to $2J = 50$ meV.



a) Tunable Gaussian defect cavity
 b) Transmission spectrum
 Fig. 1. Scheme of tunable microcavity (a) and transmission spectrum (b) showing the splitting of the localized LG00 mode and the planar cavity (PC) mode into lower (LP) and upper (UP) polariton branches when the cavity length is tuned.

To establish such microcavities various manufacturing techniques are required. Here, we present the fabrication steps of such cavities using magnetron sputtering, Focused Ion Beam (FIB) milling, patterning using Atomic Force Microscope (AFM) and optical lithography. Additionally, we discuss distinct challenges such as 0.7 nm RMS surface roughness and material imperfections that have to be overcome in order to achieve strong light-matter interaction.

In conclusion, we have shown tunable wavelength-scaled coupled Gaussian defect optical microcavities supporting zero-dimensional exciton-polaritons at room temperature. This platform enables the creation of potential landscapes for polariton simulators.

[1] D. Urbonas, T. Stöferle et al., ACS Photonics DOI:10.1021/acsp Photonics.6b00334

[2] U. Scherf, A. Bohnen et al., Makromol. Chem. 193, 1127-1133 (1992)

Vibrational strong coupling of proteins

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Vibrational strong coupling (VSC) of molecular materials involves the hybridization of a vibrational transition to a photonics cavity mode.[Ref 1, 2] It offers the prospect of modification of the ground state reactivity of selected chemical functionalities within a complex molecule.[Ref 3] In principle, VSC should be applicable to biomolecules such as proteins given these are also organic species. However to date, VSC has only been demonstrated on solid polymer thin films and pure organic liquids in cavities. Such conditions are not compatible with any physiologically relevant studies of proteins.[Ref 4, 5] Proteins may undergo structural and functional changes at high concentrations, including an increased tendency to aggregate. Here, we demonstrate the VSC of poly-*L*-glutamic acid and bovine serum albumin in solution via backbone and side chain vibrational modes with Fabry-Pérot cavity. The onset of the strong coupling is confirmed by observed dispersion anti-crossings, vacuum Rabi splittings larger than the cavity and bare vibration linewidths, and square root concentration dependence. We confirm that BSA adopts a near-native fold by 1D and 2D TOCSY NMR spectroscopy under the conditions used in our measurements. These results open up many possibilities of employing VSC for studies of structure and function of proteins such as elucidating the role of vibrational dynamics in enzyme catalysis or expanding the capabilities of H/D exchange methods for protein folding experiments.

[Ref 1] J. George, A. Shalabney et al., *J. Phys. Chem. Lett.*, page 1027-1031 (2015)

[Ref 2] A. Shalabney, J. George et al., *Nat. Commun.*, page 1-6 (2015)

[Ref 3] A. Thomas, J. George et al., *Angew. Chem. Intl. Ed.*, accepted (2016)

[Ref 4] A. Miklos, M. Sarkar et al., *J. Amer. Chem. Soc.*, page 7116-7121 (2011)

[Ref 5] J. Guo, N. Harn et al., *Biochem.*, page 8686-8696 (2006)

[Ref 6] R. Vergauwe, J. George et al., submitted

Coupling single molecules to a microcavity with ultrasmall mode volume

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We report on the realization of a scannable, tunable and broadband microcavity with a mode volume as small as $0.8\lambda^3$. As depicted in Fig. 1a, the cavity consists of a planar distributed Bragg reflector (DBR) and a micromirror with a radius of curvature of 2-5 μm fabricated with focused ion-beam milling and coated with silver [1]. By integrating an organic matrix in this microcavity system at liquid helium temperature, we are able to couple individual molecules to the single mode of the cavity. Figure 1b shows an example of the inhomogeneous spectra recorded in the cavity [2]. We describe the current results and future prospects of our experimental approach for modifying the radiative properties of solid-state quantum emitters and for achieving coupling among them.

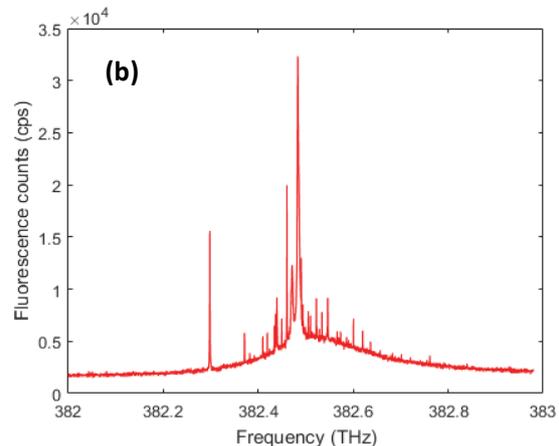
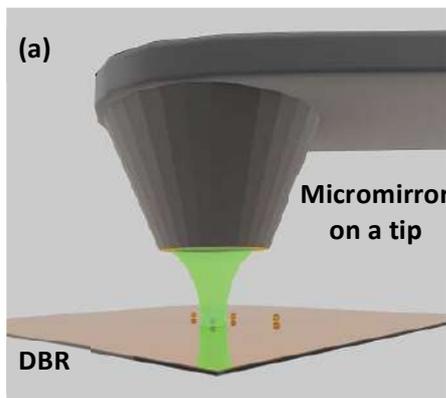


Figure 1. (a) Schematics of the cavity geometry. (b) Fluorescence excitation spectrum across the inhomogeneous broadening of the molecules. Changes in the molecular linewidth and the background level indicate the cavity enhancement.

[1] H. Kelkar, et al., *Phys. Rev. Appl.* **4**, 054010 (2015).

[2] D. Wang, et al., *in preparation*.

Quantum Yield of Polariton Emission from Hybrid Light-Matter States

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The efficiency of light-matter strong coupling is tuned by precisely varying the spatial position of a thin layer of cyanine dye J-aggregates in Fabry–Perot microcavities, and their photophysical properties are determined. Placing the layer at the cavity field maximum affords an interaction energy (Rabi splitting) of 503 meV, a 62% increase over that observed if the aggregates are simply spread evenly through the cavity, placing the system in the ultrastrong coupling regime. The fluorescence quantum yield (QY) of the lowest polaritonic state P–integrated over k-space is found to be $\sim 10^{-2}$. The same value can be deduced from the 1.4 ps lifetime of P– measured by femtosecond transient absorption spectroscopy and the calculated radiative decay rate constant. Thus, the polariton decay is dominated by nonradiative processes, in contrast with what might be expected from the small effective mass of the polaritons. Subsequently, photophysics of other high QY emitters strongly coupled with open plasmonic structures were investigated, which will be presented in this poster. These findings provide a deeper understanding of hybrid light-molecule states and have implications for the modification of molecular and material properties by strong coupling.

[1] S. Wang et al., J. Phys. Chem. Lett., 5, 1433(2014)

[2] J. George et al., Faraday Discuss., 178, 281(2015)

[3] X. Zhong et al., Angew. Chem. 124, 1624(2016)

[4] M., Ramezani et al., arXiv:1606.06866, (2016)

Strong Light-Matter Interactions Detected via Rabi Splitting in Photoluminescence

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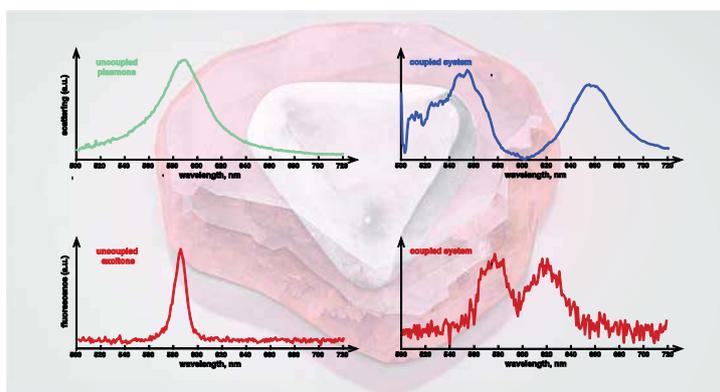
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Strong light-matter interactions at the nanoscale is an interesting topic for numerous reasons, including realization of future quantum optics and quantum plasmonics. Recent published works have demonstrated single-particle strong coupling by studying scattering from plasmonic nanoparticles together with dye molecules [1, 2]. This has opened up new promising routes towards future single photon non-linearities, which is a vital component in quantum optics [3]. However, these works lack signatures of spectral hybridization in photoluminescence (PL), which is yet another important sign of strong coupling dynamics.

Here we demonstrate Rabi splitting not only in scattering, but also in photoluminescence from single core-shell structures comprised by Ag nanoprisms embedded in J-aggregated TDBC. To our knowledge, this is the first time Rabi splitting in PL is experimentally observed on a single particle level, and hence our findings give further support for dynamics within a deep strong coupling regime.



[1] G. Zengin, M. Wersäll et al., *Physical Review Letters*, 114, 157401 (2015)

[2] G. Zengin, G. Johansson et al., *Scientific Reports*, 3:3074 (2013)

[3] M. S. Tame, K. R. McEnery et al., *Nature Physics*, Vol 9 (2013)

Spatial control of the coherent interaction between a single molecule and a plasmonic nanocavity

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Yun Jie Yu², Li Zhang², Ruben Esteban¹, Zhen Chao
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An excitation in a single molecule can be regarded as an ideal exciton with two energy levels, while a localized plasmon can serve as a local optical cavity to probe and interact with the excitons. Thus a system composed by a single molecule and a plasmonic nanocavity would be a good candidate for the studies of coherent coupling in the hybrid systems. In our previous studies, the plasmonic nanocavity formed by a tip-substrate configuration has been applied to enhance the Raman signals of a single molecule [1], and retrieve the information of dipole-dipole coupling at sub-molecular level [2], but the intrinsic properties of the coherent coupling between the single molecule and plasmon have not been studied yet.

In this work, we use the zinc phthalocyanine (ZnPc) molecule as quantum emitter, and the tip-substrate nanocavity in the scanning tunneling microscope (STM) to generate a localized plasmonic field for the study of coherent coupling between the plasmon and a single molecule at the sub-nanometer scale. If there is no molecule under the STM tip, an emission spectrum of the nanocavity plasmon is observed. However, if the STM tip is placed in the proximity of the molecule, a spectral evolution from a pure plasmon peak to a Fano lineshape is observed, which can be attributed to the coherent coupling between the molecular transition and the plasmonic resonance. The Fano lineshape, as well as the corresponding coupling strength, can be controlled precisely by varying the lateral distance between the STM tip and the molecule, due to the ultra-confined plasmonic field of the nanocavity. All these results can provide a better understanding of the exciton-plasmon coupling at a sub-nanometer level, as well as enable further applications in molecular sensing, optical modulation, and quantum information processing.

[1] R. Zhang*, Y. Zhang*, Z. C. Dong, S. Jiang, C. Zhang, L. G. Chen, L. Zhang, Y. Liao, J. Aizpurua, Y. Luo, J. L. Yang, and J. G. Hou, *Nature* 498, 82-86 (2013).

[2] Yang Zhang*, Y. Luo*, Yao Zhang*, Y. J. Yu, Y. M. Kuang, L. Zhang, Q. S. Meng, Y. Luo, J. L. Yang, Z. C. Dong, and J. G. Hou, *Nature* 531, 623-627 (2016).

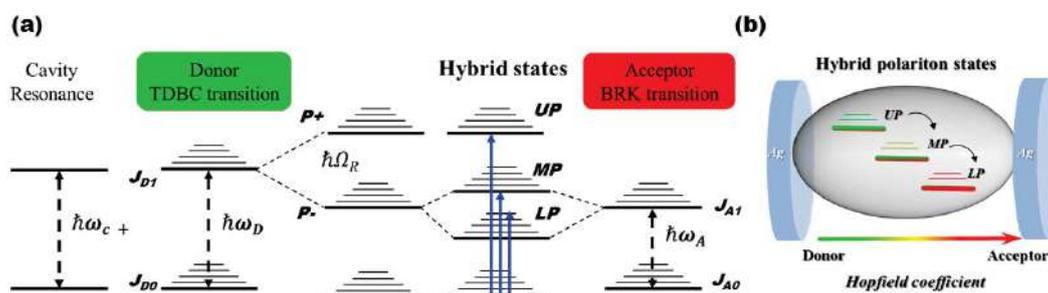
Non-Radiative Energy Transfer via Hybrid Light-Matter States

Xiaolan Zhong*, Thibault Chervy, Shaojun Wang, Jino George, Anoop Thomas, James A. Hutchison, Eloïse Devaux, Cyriaque Genet, and Thomas W. Ebbesen

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When an exciton transition and a resonant optical mode exchange energy faster than any competing dissipation process, it can lead to light-matter strong coupling. This brings about interesting properties possessed by neither the original exciton nor the optical mode and leads to new possibilities such as enhanced conductivity of organic semiconductors. In this case, the enhancement stems from the delocalized nature of the hybrid states over the spatial extent of the optical mode which is also expected to affect energy transport according to recent theoretical studies [1, 2]. In this context, it is interesting to consider how such hybrid states would affect energy transfer between donor and acceptor molecules [3, 4]. Strong coupling could provide an alternate effective path for energy transfer in analogy with chemically bridged donors and acceptors where the linker mediates the interactions by an effective overlap between the wave functions of both the donor and the acceptor. In the strong coupling case, it is the polaritonic states which are by construction either donor or acceptor-like that mediates the interactions in the system due to their delocalized nature. We present direct evidence of enhanced non-radiative energy transfer between two J-aggregated cyanine dyes strongly coupled to the vacuum field of a cavity. Excitation spectroscopy and femtosecond pump-probe measurements show that the energy transfer is highly efficient when both the donor and acceptor form light-matter hybrid states with the vacuum field.



(a) Schematic representation of strong coupling (b) Schematic diagram of different donor and acceptor content (Hopfield coefficient)

- [1] J. Feist et al., Phys. Rev. Lett. 114, 196402 (2015).
- [2] J. Schachenmayer et al., Phys. Rev. Lett. 114, 196403 (2015).
- [3] X. Zhong et al, Angew. Chem. Int. Ed. 55, 6202-6206 (2016).
- [4] X. Zhong et al, (prepared)

Practical Information

Venue

Donostia - San Sebastián is located in the northeast of the Spanish Basque Country: 110 km from Bilbao, 500 km from Madrid, and 800 km from Paris. It is a charming medium-size city set in a picturesque countryside, on the edge of the Biscay Gulf and surrounded by mountains. A city of deep-rooted international tourist tradition dating back to the 19th century, San Sebastián offers quite a few tourist attractions, a varied choice of hotels and one of the most creative gastronomies in the world.

Further information on the city and the region can be found at:
<http://www.sansebastianturismo.com>
<http://tourism.euskadi.net/>

The scientific meetings will be held in the unique environment of the Miramar Palace that overlooks San Sebastián's Bay. Its rooms are home to the University of the Basque Country Summer Courses. See map with the location of Miramar Palace at the end of this booklet.



Access to the conference rooms of the symposia

The symposia will take place in the Palace Miramar. We recommend entering the building through the eastern side entrance, even though other entries are also available. Please check here the air-view of the palace:



Transportation

The airport of San Sebastián is around 20 kilometers from the city. The Bilbao Airport is often the most convenient alternative, with frequent buses (<http://www.pesa.net/pesa/en/horarios>, destination Loiu for the airport and “Donostia” or “San Sebastian” for the city). The ticket from the airport can be bought in the bus, but the ticket to the airport has to be bought before boarding the bus. Notice that the bus station to the Bilbao Airport has recently changed position and can appear incorrectly in maps. The new station is situated next to the Atocha train station (<http://www.estaciondonostia.com>), in Federico García Lorca 1 Pasealekua. Another possibility is the airport of Biarritz (in France) but communication by public transport can be difficult. You can find more information in <http://www.sansebastianturismo.com/en/come/how-to-get-here>

Meals

Lunch breaks

Lunch is included in the symposia fee for the three days of the conference (October 19th, 20th and 21st). Lunch will be served at the conference venue

Conference Dinner

All participants to the conference are invited to the conference dinner that will take place on Thursday in the Sidreria “Petritegi” (<https://www.petritegi.com/en>), a typical basque cider-place (included in the registration fee).

A bus will be ready for the trip to the restaurant on Thursday evening. The bus will depart Thursday, the 20th, at 8.00 p.m from the Alfonso XIII Plaza, near the conference venue and close to church Parroquia la Antigua, (see indication in the map). If you miss the bus, the address of the restaurant is Petritegi Bidea, 20115 Astigarraga, Gipuzkoa (Outside the city)

We notice that there is a fixed menu for the dinner consisting in:

- Salt cod omelette
- Fried salt cod with peppers
- 1 bone-in ribeye steak (weighing 700g) for 2 people
- Dessert (cheese, quince jelly, walnuts, almond ‘tiles’ and ‘cigarettes’)
- Txiri (Cider) and bread

For those that informed us that they are vegetarian, the alternative menu is

- Salad (lettuce, tomato and onion)
- Vegetable Omelet (onion and pepper) or cheese
- Tofu hamburger with pepper and onion
- Dessert (cheese, quince jelly, walnuts, almond ‘tiles’ and ‘cigarettes’)
- Txiri (Cider) and bread

Relevant spots with their address

Main Bus Station: Federico García Lorca Pasealekua 1, Donostia-San Sebastián

Conference Venue: Palacio Miramar, Mirakontxa Pasealekua, 48, Donostia-San Sebastián

Conference Dinner (outside the city) Sidreria “Petritegi”, Petritegi Bidea, 20115 Astigarraga, Gipuzkoa

Bus pick-up for the conference dinner: Alfonso XIII Plaza, Donostia-San Sebastián

Hotel La Galeria: Kristina Infantaren Kalea, 3, Donostia-San Sebastián

Hotel Barceló Costa Vasca: Pio Baroja Pasealekua, 15, Donostia-San Sebastián

Colegio Mayor Olarain: Ondarreeta Pasealekua, 24, Donostia-San Sebastián

Hotel NH Aránzazu: Calle Vitoria 5, Donostia-San Sebastián (Gasteiz Kalea 5, Donostia-San Sebastián)

Hotel San Sebastian: Zumalakarregi Hiribidea, 20, Donostia-San Sebastián

Acknowledgment

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DONOSTIA SAN SEBASTIÁN

- Parking souterrain / Underground parking
- Parking de dissuasion / Overflow parking lot
- Arrêt des bus groupes / Bus stop groups
- Parking conventionnel / Conventional park
- Police / Police
- L'Espace DSS2016 Space 2016 European Capital of Culture
- Caspian Estampation de la Culture 2016

- Bus Touristique / Tourist Bus
- Train Touristique / Tourist Train
- Bicyclette / Bicycle
- Station services / Tourist stations
- Douches / Showers
- Hôtel / Hospital
- Train station / Arrêt train
- Bus Station / Gare bus

- Eglise San Vicente / San Vicente Church
- Place de la Constitución / Constitución Square
- Eglise Santa Maria / Santa Maria Church
- Construcción de la Plaza / Construction of the Plaza
- Caserío de los Angeles / English Consulate
- Maison de la Média / Maison of the Media
- Hôtel de Villa / Town Hall
- Conseil Régional / County Council
- Théâtre Victoria Eugenia / Victoria Eugenia Theatre
- Catedral Buen Pastor / Buen Pastor Cathedral
- "El Pinar del Viento" (Edificio Chillida) / The Pines of the Wind, sculpture / Wind tower, sculpture
- Funiculaire / Funicular
- Palais de Congrès Kursaal / Kursaal Conference Centre
- "La Phénix de la Paix" / Aida The House of Peace
- La Colonia de la Paix, sculpture / Dove of Peace, sculpture
- Musée San Telmo / San Telmo Museum
- Musée Naval / Naval Museum
- Aquarium
- Centre International de Culture Contemporaine / International Centre for Contemporary Culture
- Real Sociedad football club, Musée / Museum
- Etnelak Musée de la Science / Science Museum
- Musée Chillida-Leku (temporairement fermé) / Chillida-Leku Museum (temporarily closed)
- Musée du Cinéma Reola / Reola Cinema Museum
- Parc Ugaitz / Ugaitz Park
- Palais de la Paix / Peace Palace and Park
- Parc Cristina-Enea / Cristina-Enea Park
- Centre de Ressources Environnementales / Environmental Resources Centre
- Parc Aiete / Aiete Park
- "Ciudad San Sebastián", Promenade en mer / Tourist Boat
- Balneario-nareite a l'île (Séjour en été) / Balneario to the island (only in summer)
- Centre "Thalasso-sport La Peña" / Thalasso-sport La Peña
- Casino Kursaal / Kursaal Casino
- Kales Mithelak, Centre Culturel / Cultural Centre
- Donostia Arena 2016-Hondre / Ice rink
- Centre Sportif / Sport Centre
- Anetia terrain de football / Anetia soccer field
- Royal Club de Tennis / Royal Tennis Club
- Mont Igeldo (Parc d'Attractions) / Mont Igeldo (Amusement Park)
- Mont Igeldo (Parc d'Attractions) / Mont Igeldo (Amusement Park)
- Théâtre / Theatre
- Funiculaire / Funicular
- Fourrière / Car Pound
- "Eusko Tren" (TPO) Gare / Station
- "REWE" Gare du Train / Train Station
- Gare Routière / Bus Station
- 112 - 761, Emergences / Urgences 112

MONUMENTS • MONUMENTS

MUSEES • MUSEUMS

PARCS • PARKS

LOISIR • LEISURE

INFO UTILE

USERRA INFO

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