Light, Metal and Molecules

Thomas W. Ebbesen

Institut Universitaire de France
ISIS, University of Strasbourg and CNRS
France

ISIS: C. Genet, E. Devaux, J. Hutchison, T. Schwartz, A.Cuche, Y. Godoretsky
A. Canaguier-Durand, J. George, B. Stein, J. Yi, S. Wang, G. Schnoerel

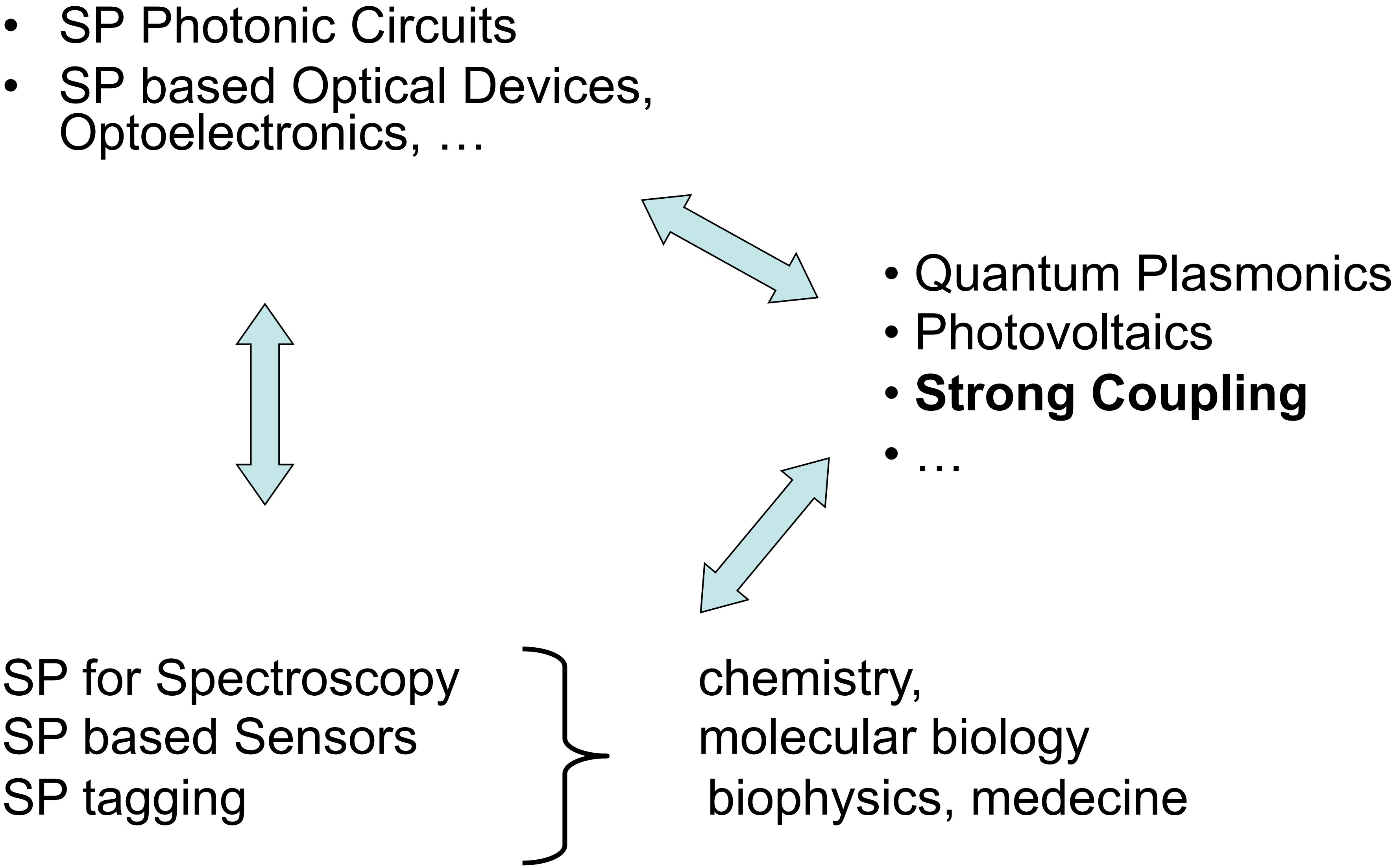
FRC
International Center for
Frontier Research in Chemistry

IUF

Light– Metal Interactions

- Surface Plasmons -

Current trends in SP:



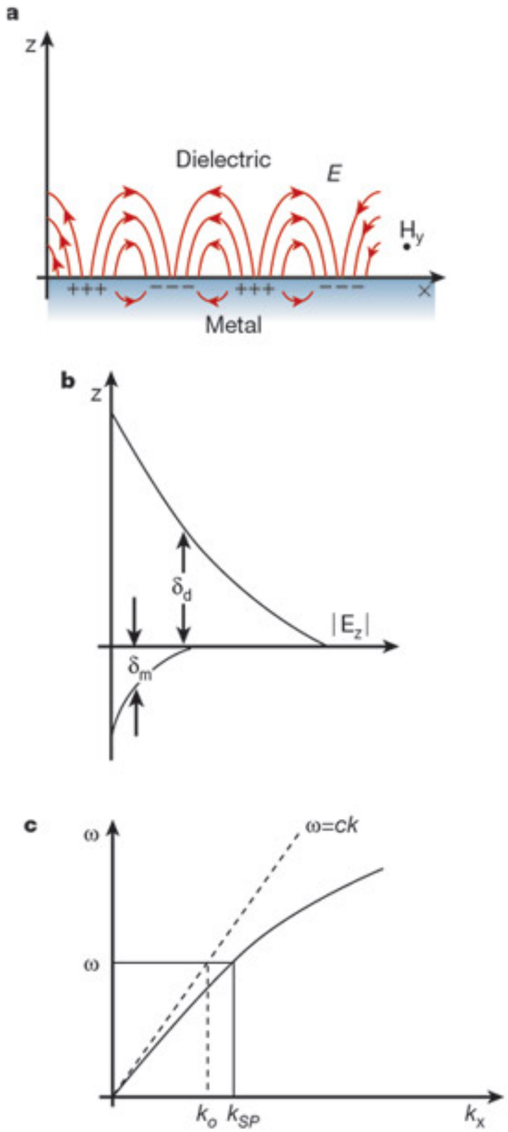
- SP Photonic Circuits
- SP based Optical Devices, Optoelectronics, …

- Quantum Plasmonics
- Photovoltaics
- **Strong Coupling**
- …

SP for Spectroscopy
SP based Sensors
SP tagging

chemistry,
molecular biology
biophysics, medecine

Surface Plasmons



- SPs allow concentration of EM energy in a subwavelength space

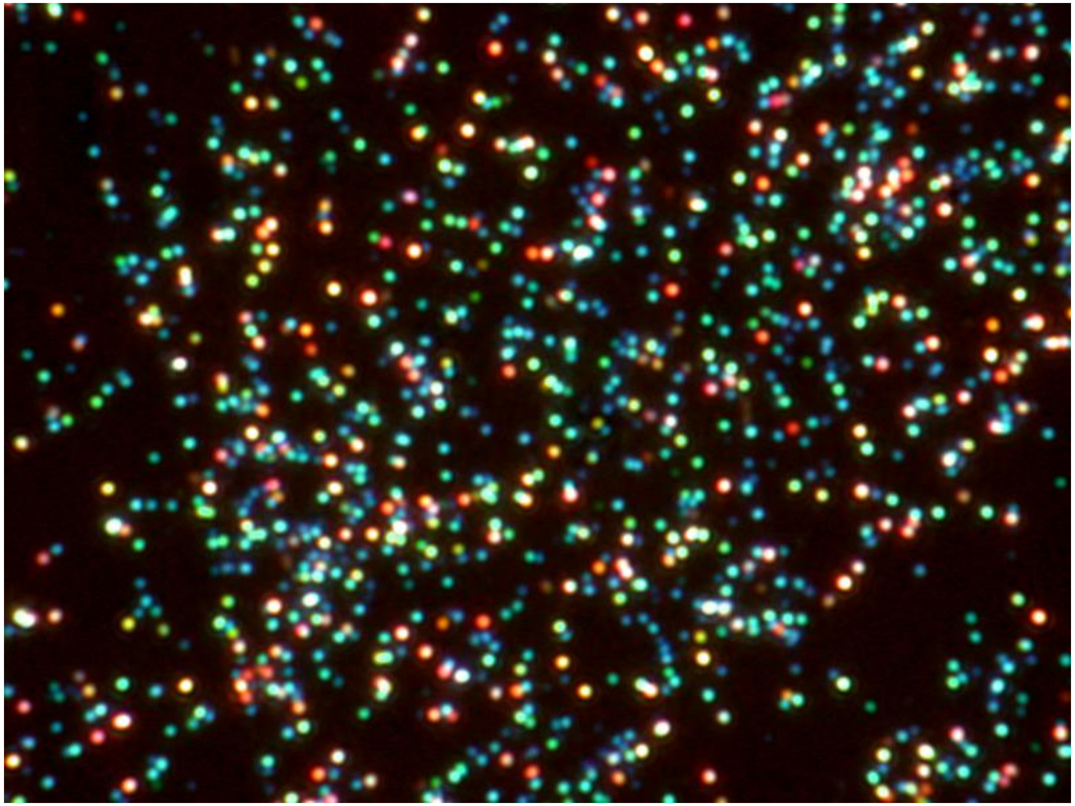
-SP properties can be tailored by controlling the metal structure at the nanometer scale

-Metals and therefore the associated SPs are durable.

-SP come in different flavors

W.L. Barnes, A. Dereux and T.W. Ebbesen, Nature 424, 16-22 (2003)

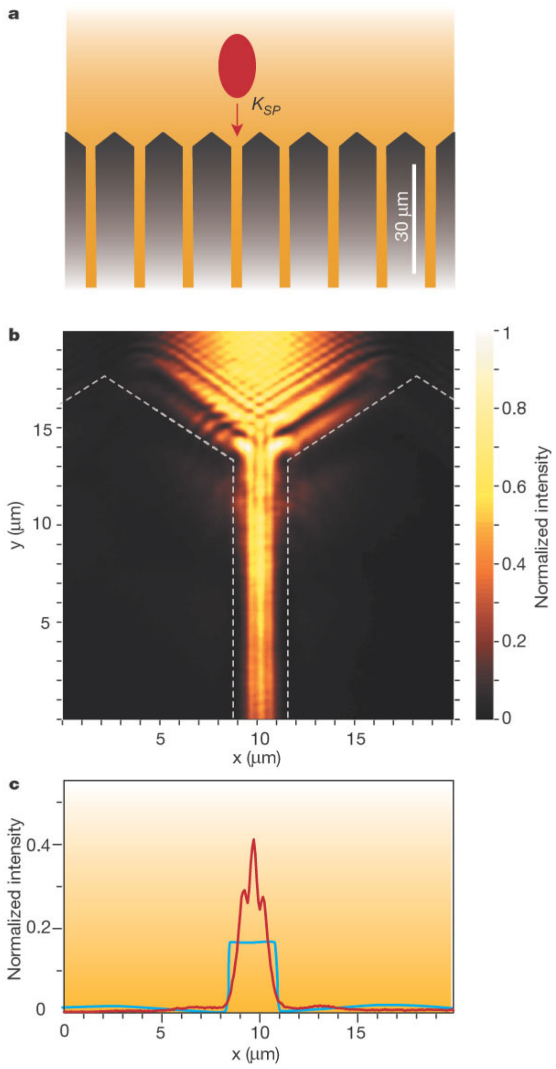
Localized Surface Plasmons



Dark field images of Ag particles

Image courtesy of M. Kall, Chalmers University

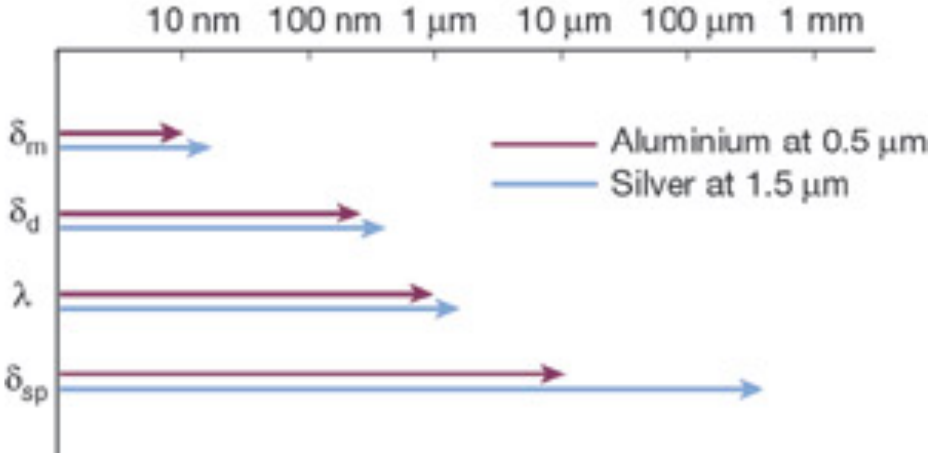
Propagating Surface Plasmon Polaritons:



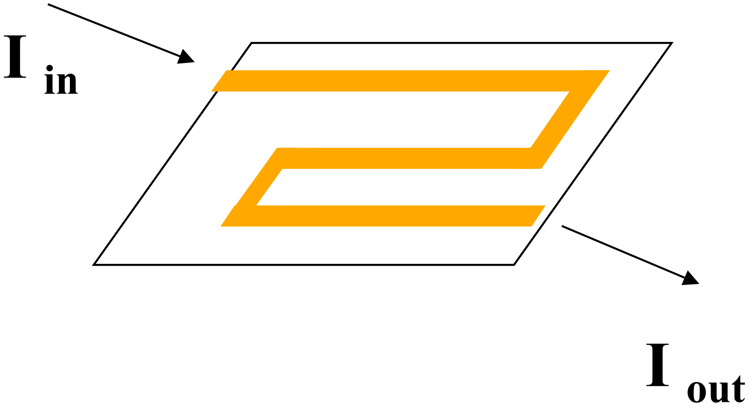
Dereux, Weeber et al, Dijon

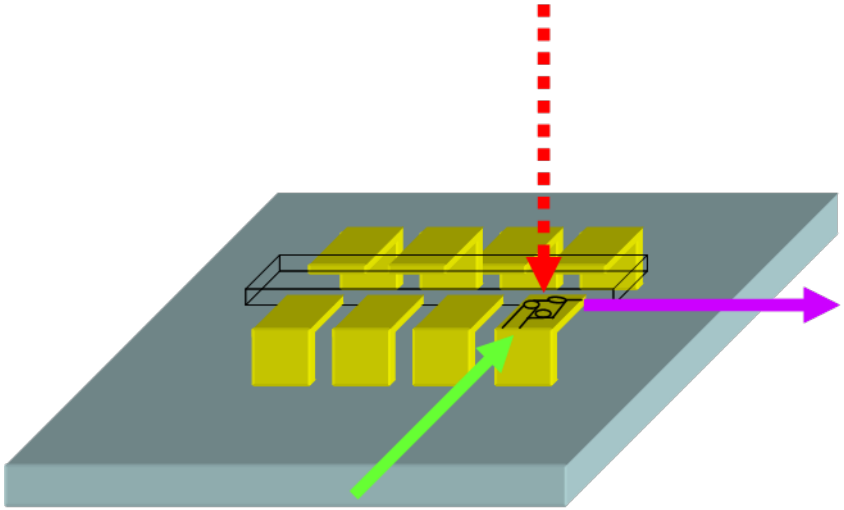
SP propagation length on a flat metal surface:

$$\delta_{\mathrm{SP}} = \frac{1}{2k''_{\mathrm{SP}}} = \frac{c}{\omega}\left(\frac{\varepsilon'_{\mathrm{m}} + \varepsilon_{\mathrm{d}}}{\varepsilon'_{\mathrm{m}}\varepsilon_{\mathrm{d}}}\right)^{\frac{3}{2}} \frac{\left(\varepsilon'_{\mathrm{m}}\right)^{2}}{\varepsilon''_{\mathrm{m}}}$$



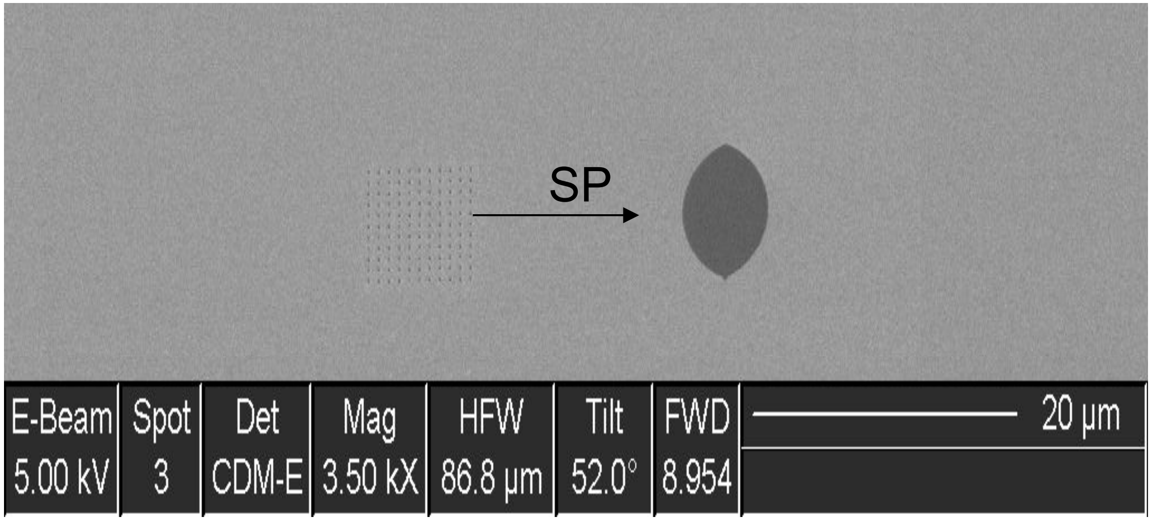
The SP Photonic Circuit

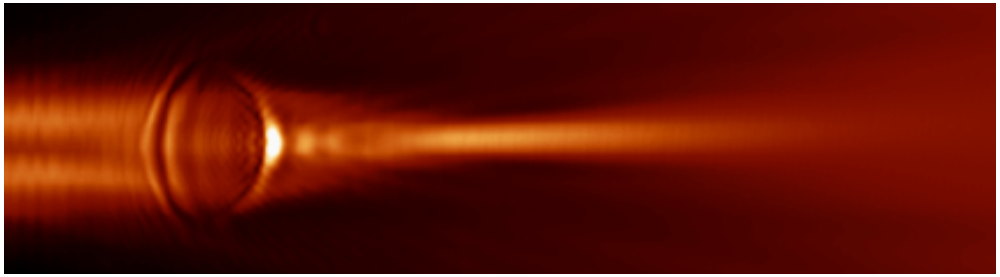




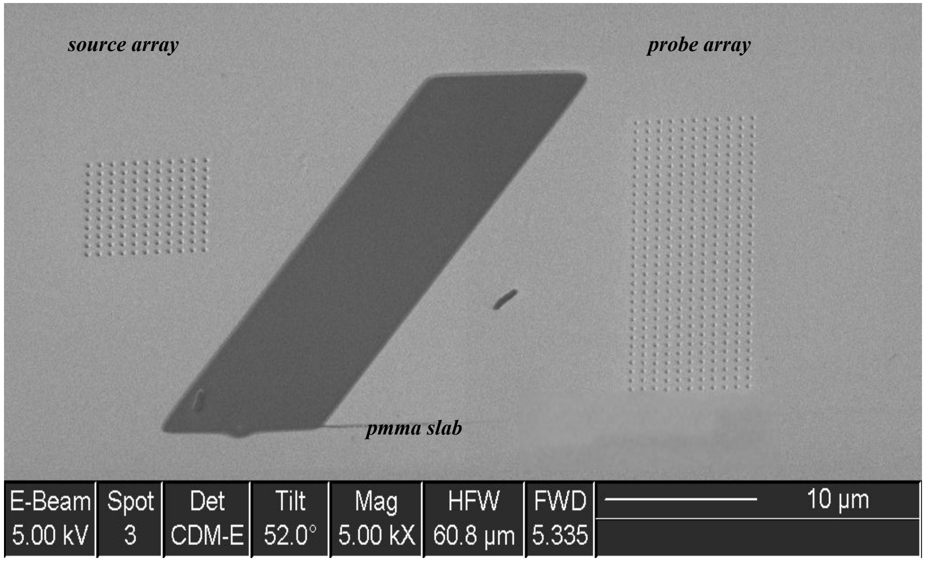
- SP launchers
- Optical elements and devices for SPs
- SP decouplers and detectors

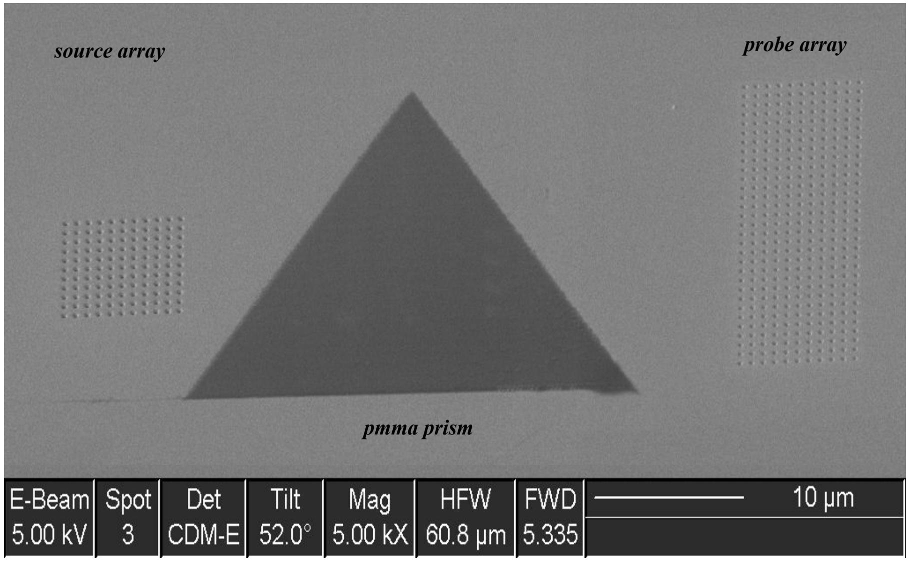
Diffractive lens for SPs

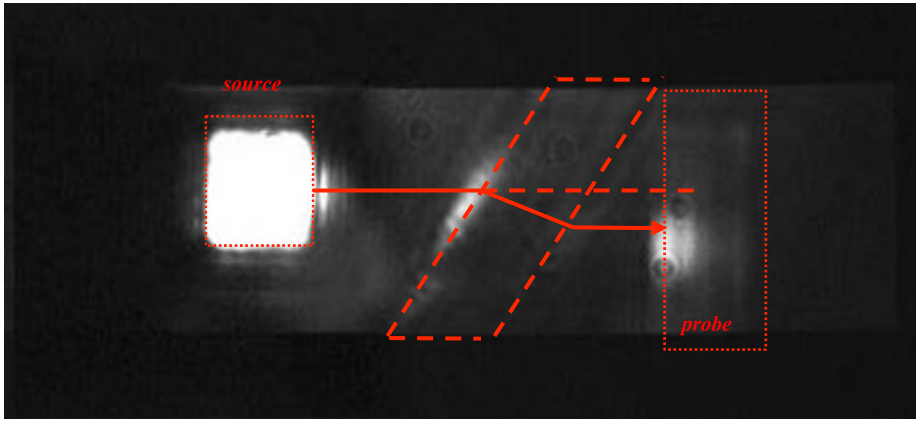


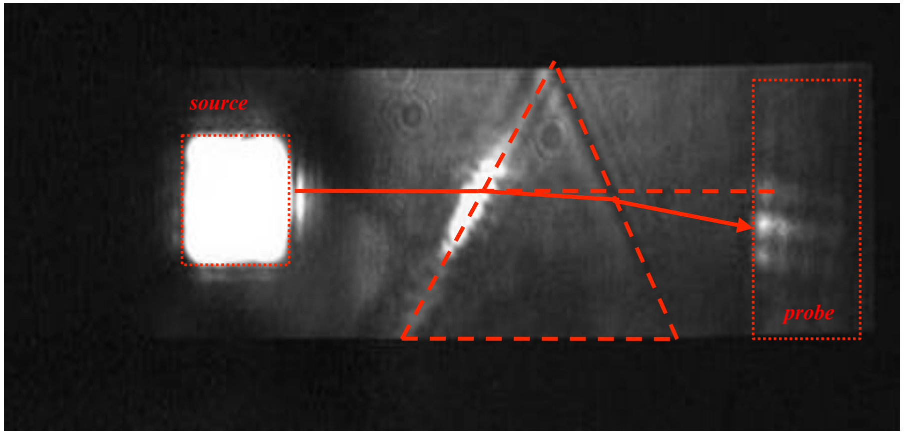


Far-field characterization of 2D optical elements









Issues:

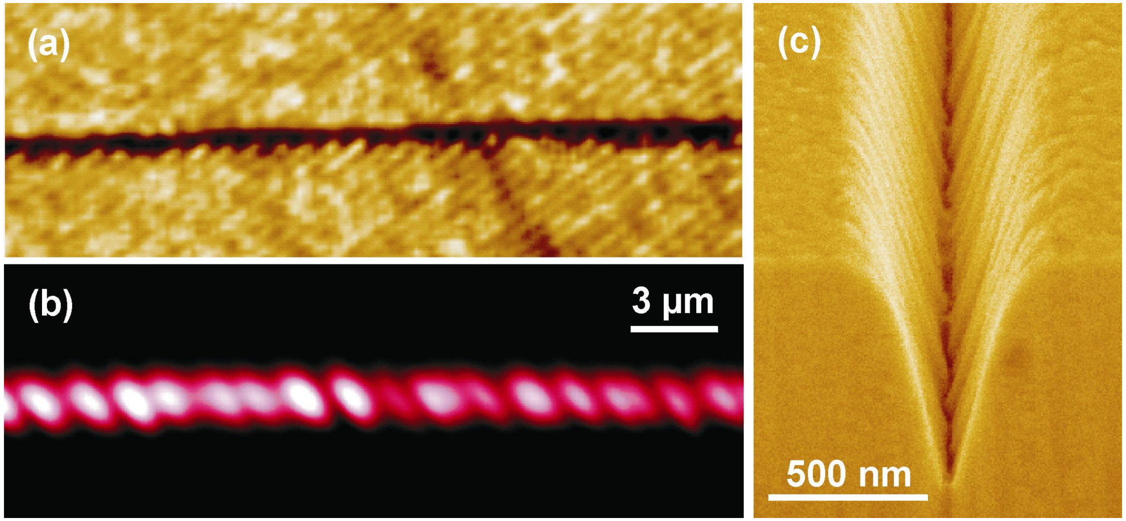
-Impedance mismatch

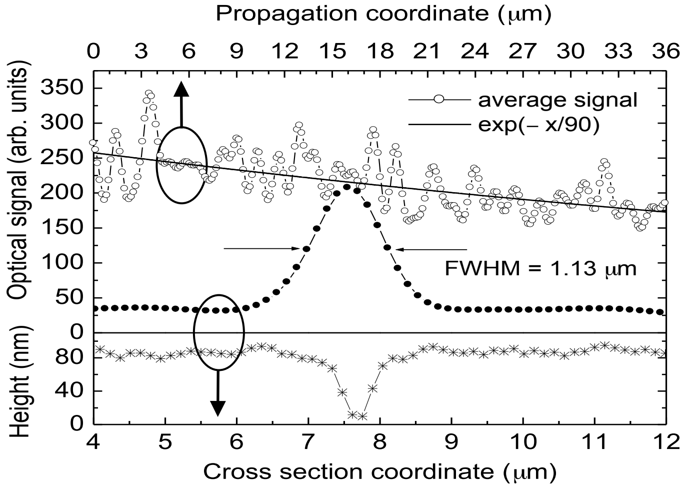
-Coupling and decoupling

- Propagation length versus confinement

Channel Plasmon Polariton:

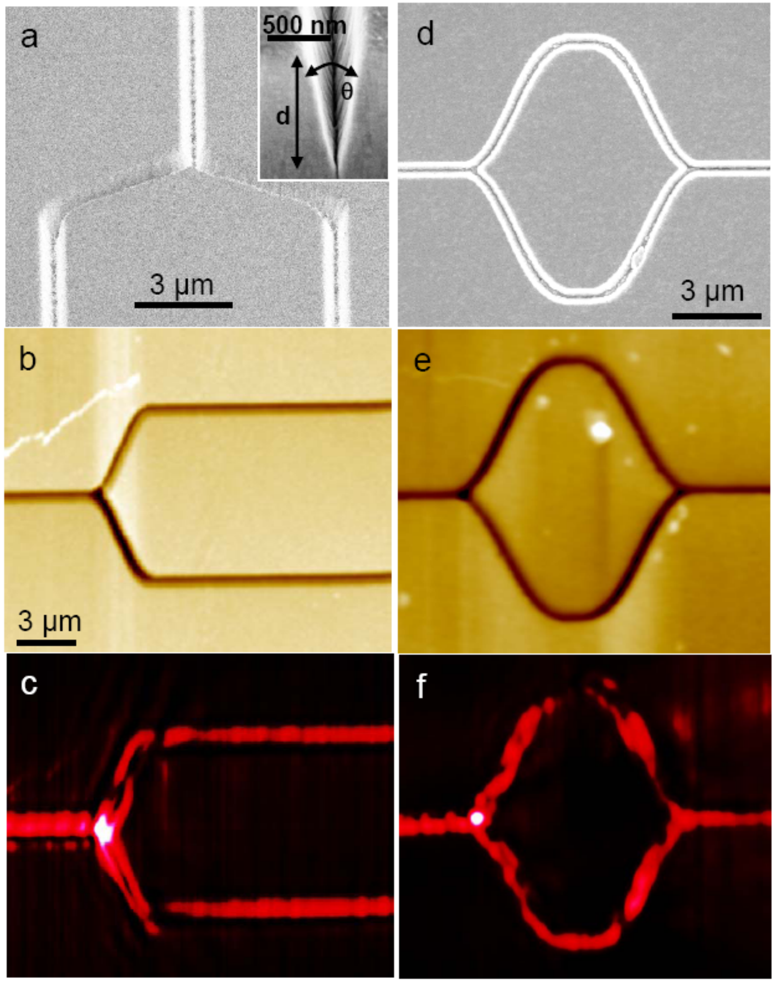
Low loss plasmon mode confined to a groove in the metal





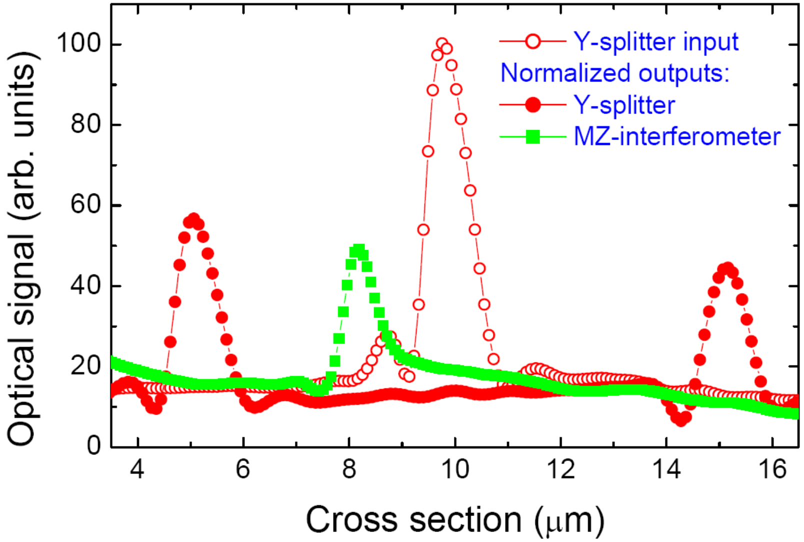
Bozlevonyi et al, PRL 2005

SP propagating in Grooves: Channel Plasmon Polaritons



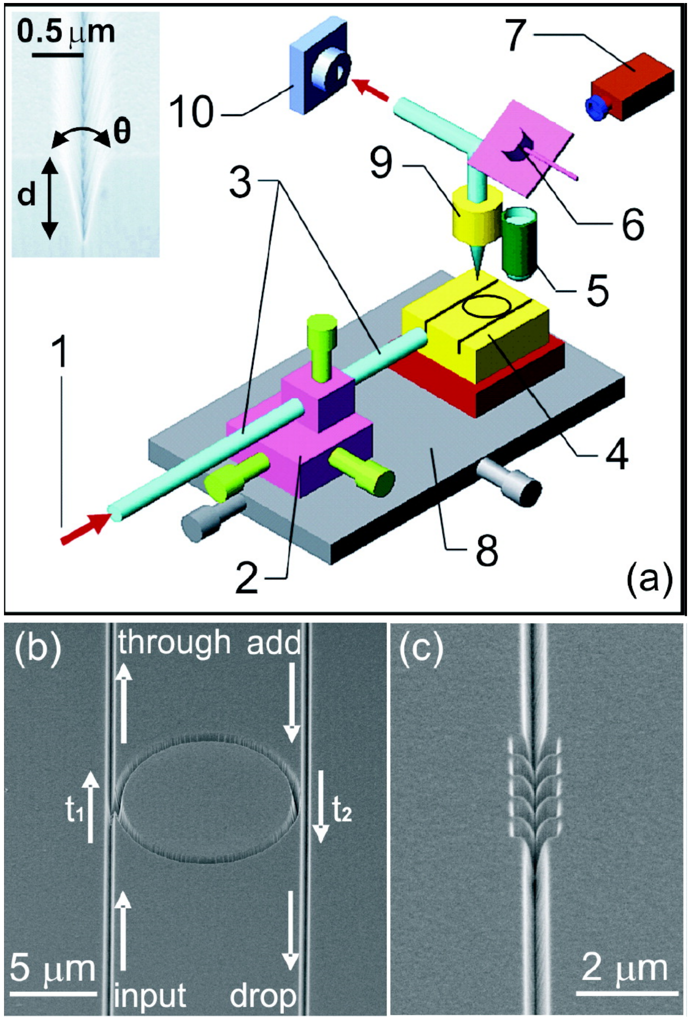
Y-splitter MZ interferometer

High confinement, low losses

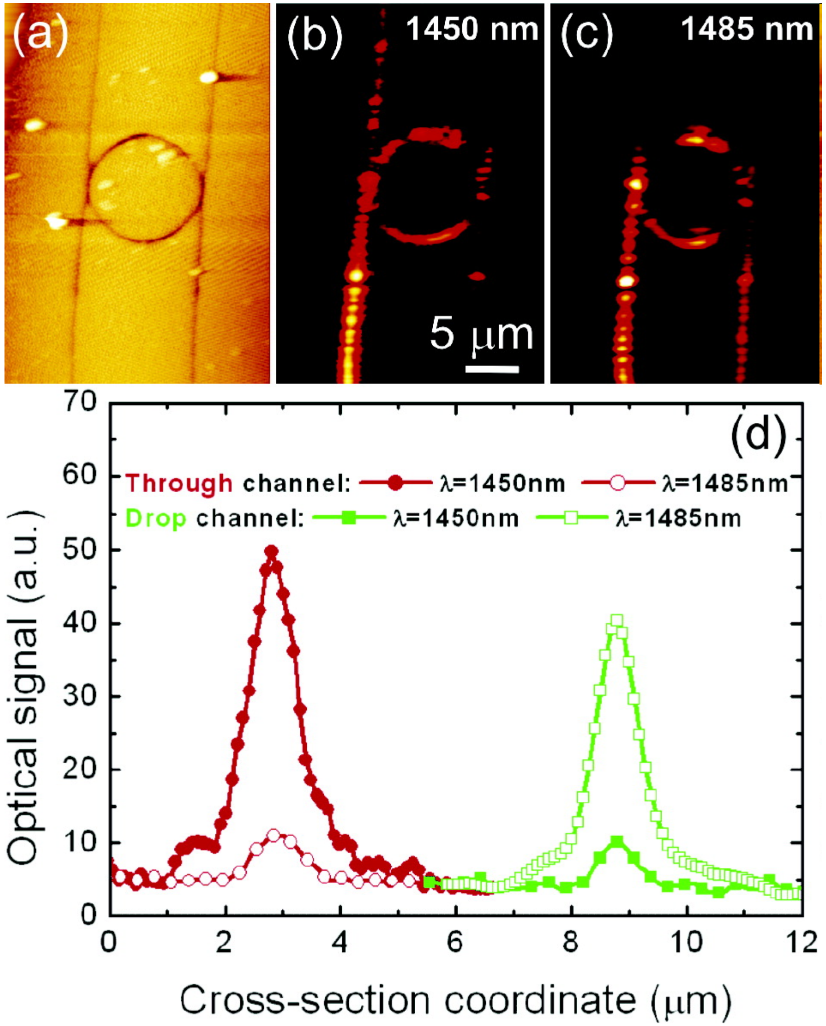


PRL 2005, Nature 2006

Wavelength selective Devices:



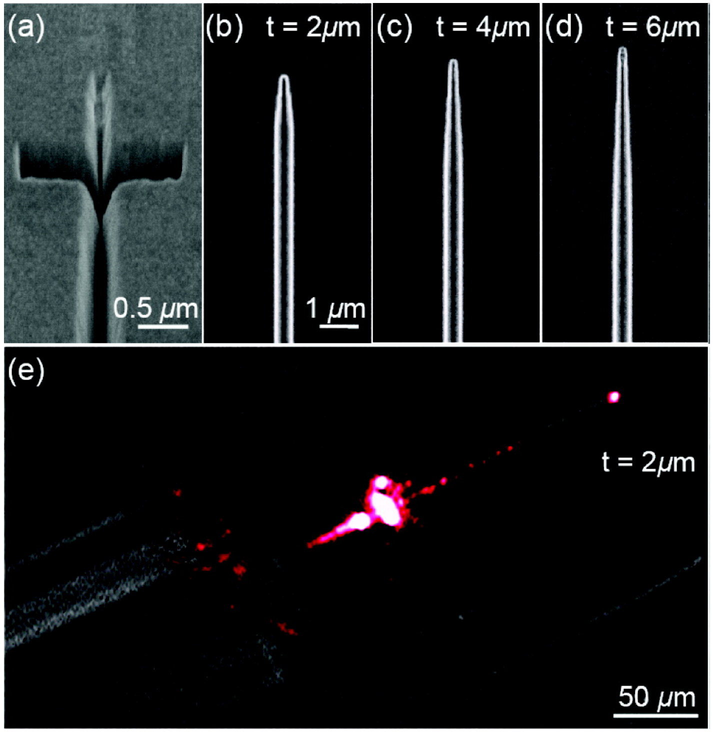
Add-drop multiplexer Bragg grating filter

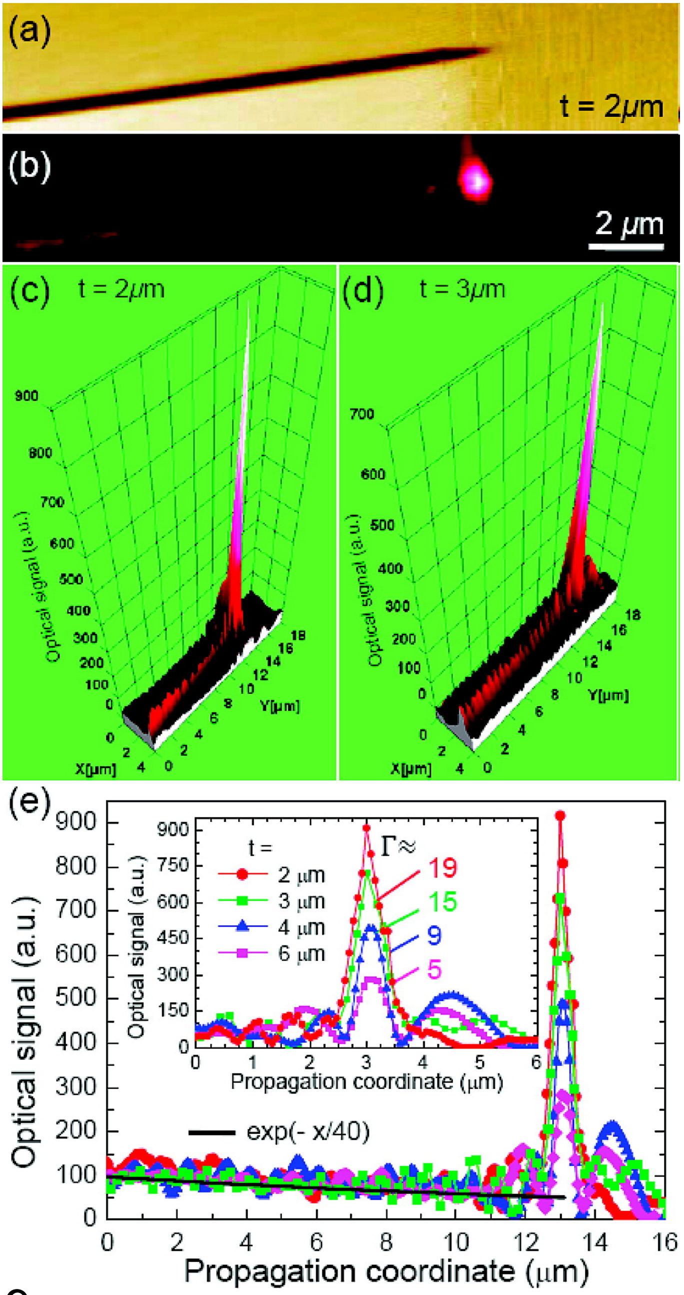


Nano Lett. 2007

Nanofocusing with CPP

with tapered grooves (width and depth)

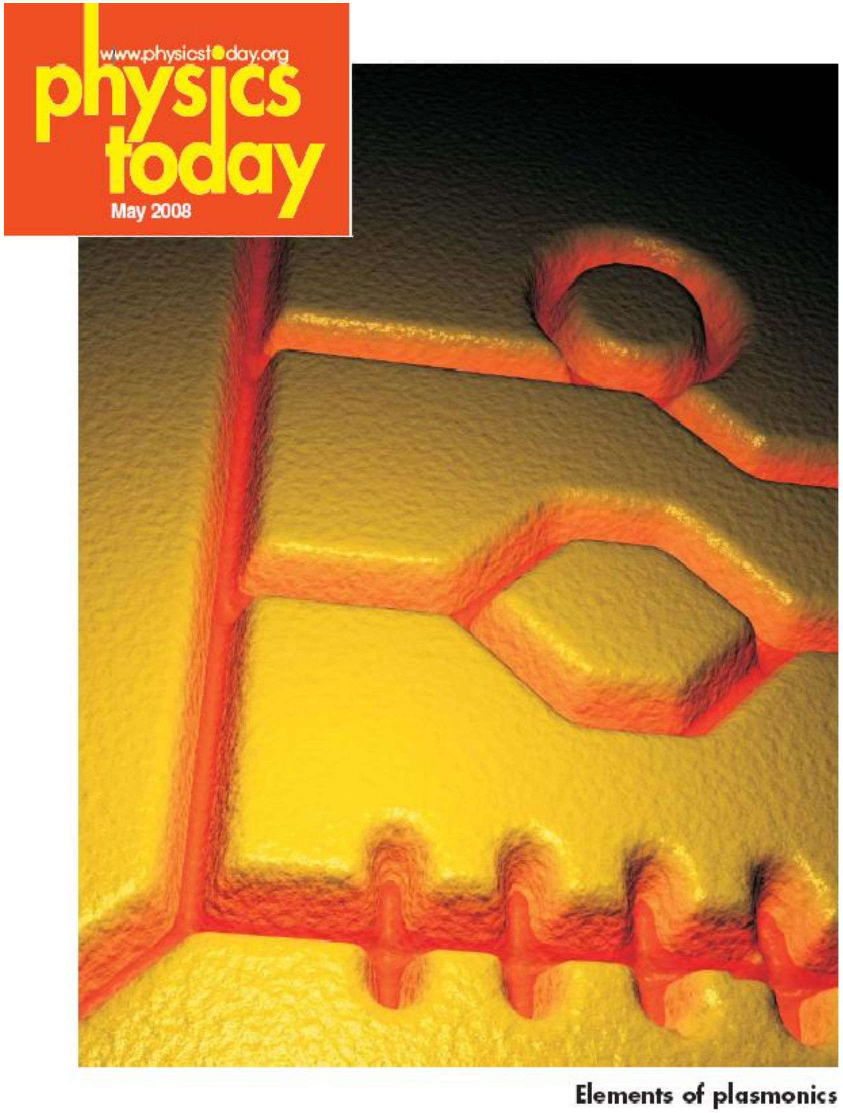




Field enhancements:

Experiments ~ 90
Theory ~ 1000

Nano Lett. 2009

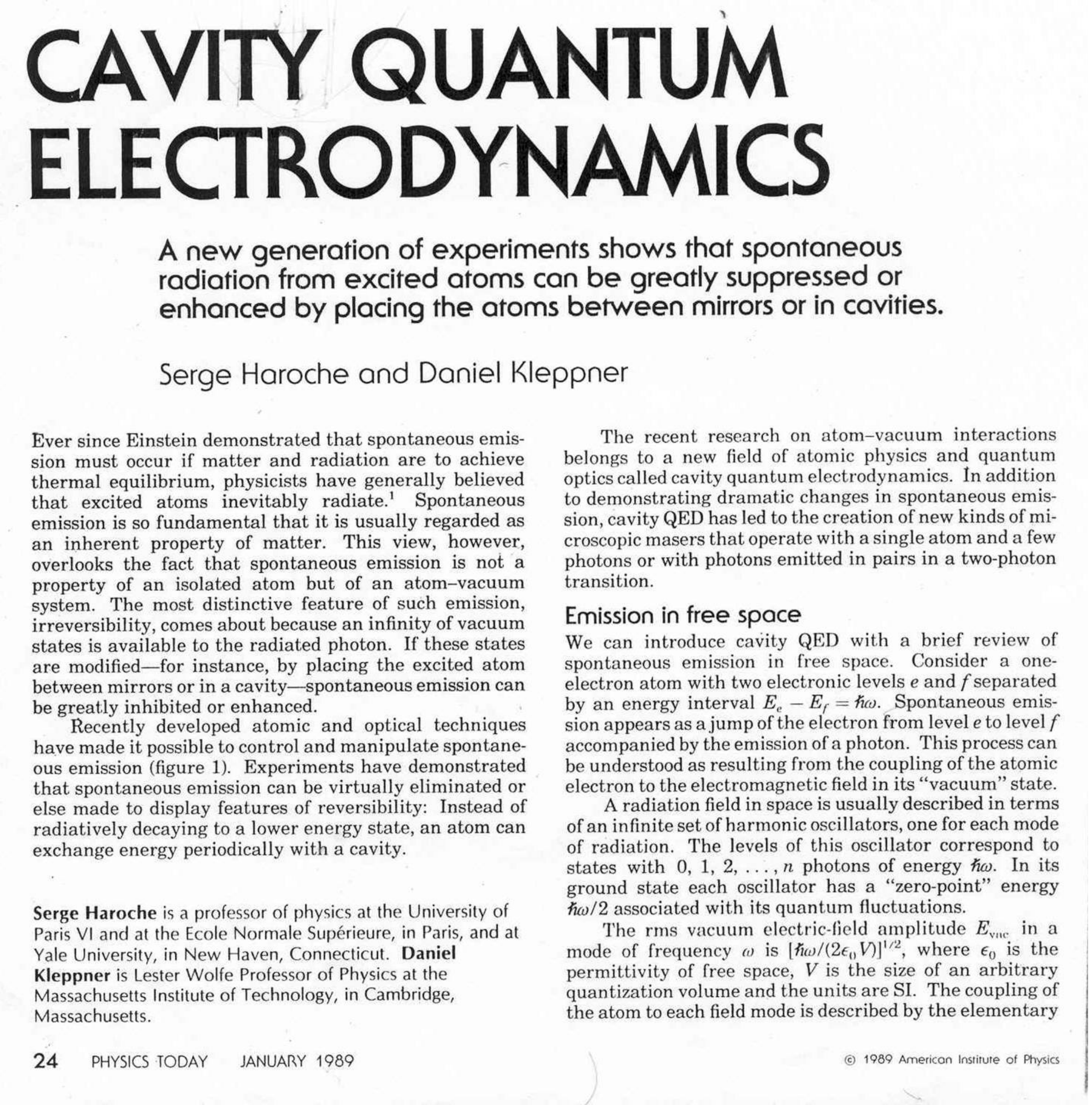


www.physicstoday.org
physics today
May 2008

Elements of plasmonics

Surface Plasmon Circuitry, Physics Today, May 2008

NEC 1989



CAVITY QUANTUM ELECTRODYNAMICS

A new generation of experiments shows that spontaneous radiation from excited atoms can be greatly suppressed or enhanced by placing the atoms between mirrors or in cavities.

Serge Haroche and Daniel Kleppner

Ever since Einstein demonstrated that spontaneous emission must occur if matter and radiation are to achieve thermal equilibrium, physicists have generally believed that excited atoms inevitably radiate.[1] Spontaneous emission is so fundamental that it is usually regarded as an inherent property of matter. This view, however, overlooks the fact that spontaneous emission is not a property of an isolated atom but of an atom–vacuum system. The most distinctive feature of such emission, irreversibility, comes about because an infinity of vacuum states is available to the radiated photon. If these states are modified—for instance, by placing the excited atom between mirrors or in a cavity—spontaneous emission can be greatly inhibited or enhanced.

Recently developed atomic and optical techniques have made it possible to control and manipulate spontaneous emission (figure 1). Experiments have demonstrated that spontaneous emission can be virtually eliminated or else made to display features of reversibility: Instead of radiatively decaying to a lower energy state, an atom can exchange energy periodically with a cavity.

Serge Haroche is a professor of physics at the University of Paris VI and at the Ecole Normale Supérieure, in Paris, and at Yale University, in New Haven, Connecticut. **Daniel Kleppner** is Lester Wolfe Professor of Physics at the Massachusetts Institute of Technology, in Cambridge, Massachusetts.

The recent research on atom–vacuum interactions belongs to a new field of atomic physics and quantum optics called cavity quantum electrodynamics. In addition to demonstrating dramatic changes in spontaneous emission, cavity QED has led to the creation of new kinds of microscopic masers that operate with a single atom and a few photons or with photons emitted in pairs in a two-photon transition.

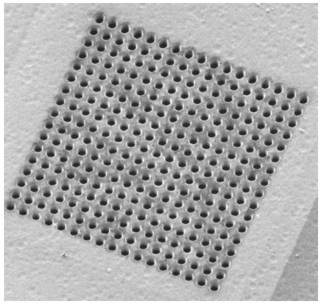
Emission in free space

We can introduce cavity QED with a brief review of spontaneous emission in free space. Consider a one-electron atom with two electronic levels e and f separated by an energy interval $E_e - E_f = \hbar\omega$. Spontaneous emission appears as a jump of the electron from level e to level f accompanied by the emission of a photon. This process can be understood as resulting from the coupling of the atomic electron to the electromagnetic field in its "vacuum" state.

A radiation field in space is usually described in terms of an infinite set of harmonic oscillators, one for each mode of radiation. The levels of this oscillator correspond to states with 0, 1, 2, . . . , n photons of energy $\hbar\omega$. In its ground state each oscillator has a "zero-point" energy $\hbar\omega/2$ associated with its quantum fluctuations.

The rms vacuum electric-field amplitude E_{vac} in a mode of frequency ω is $[\hbar\omega/(2\epsilon_0 V)]^{1/2}$, where ϵ_0 is the permittivity of free space, V is the size of an arbitrary quantization volume and the units are SI. The coupling of the atom to each field mode is described by the elementary

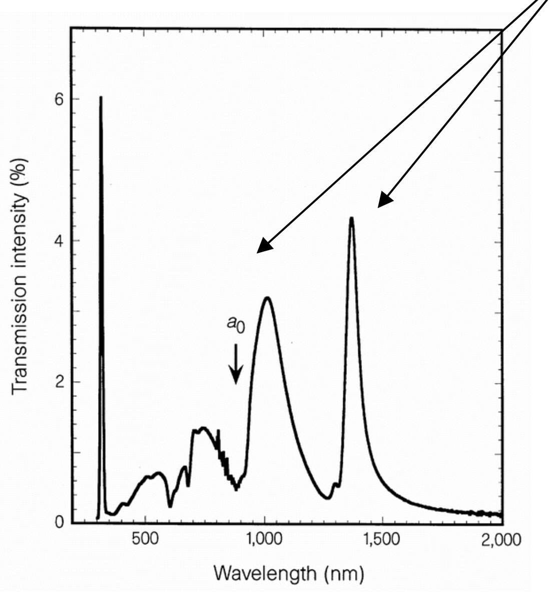
Extraordinary Transmission through Sub-Wavelength Holes

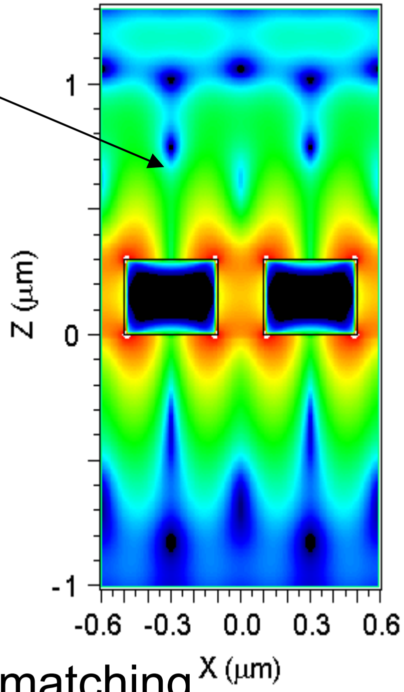


NEC 1989-1998

Surface Plasmon modes :

(standing waves matching the periodic structure)



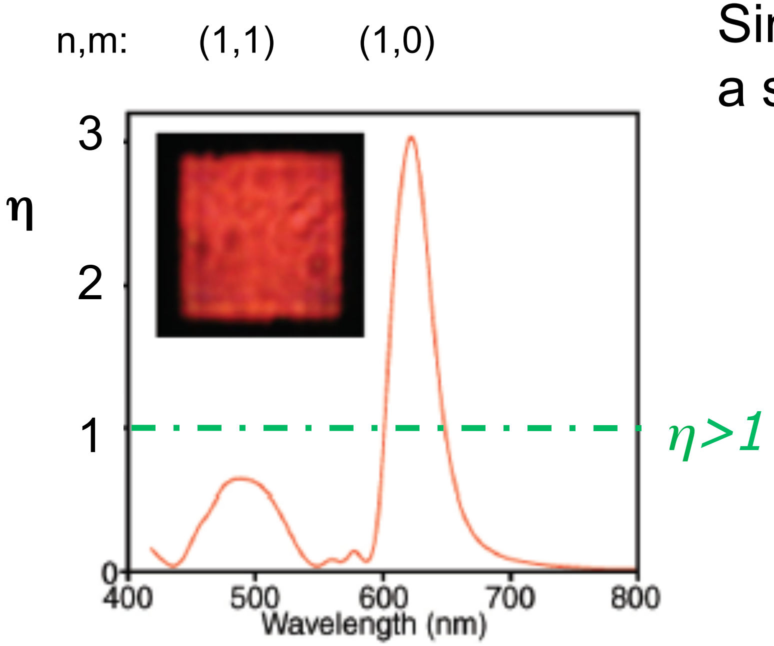


- Periodic structures provides momentum matching

- Weak Tunneling probability (λ > 2 x diameter) compensated by high surface plasmon EM fields

Nature 1998

SP-assisted extraordinary transmission



filling factor 13%

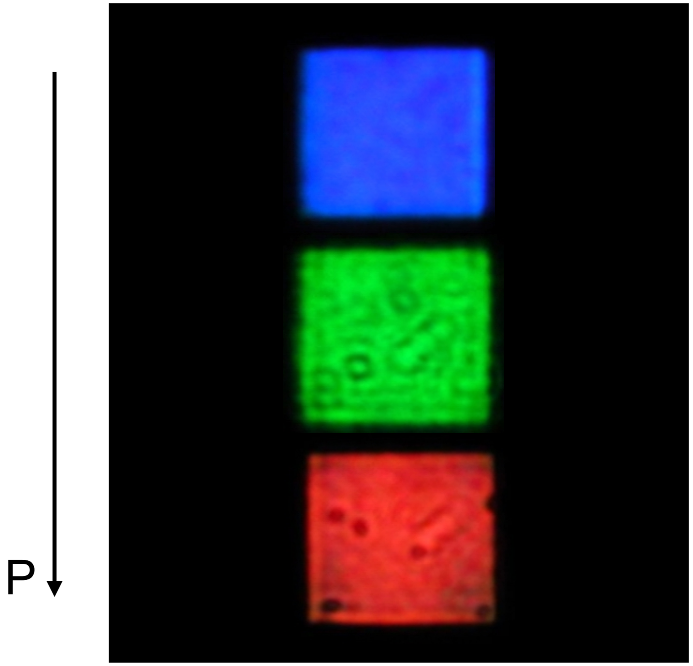
Simplest description, SP resonances occur in a square array lattices of holes at:

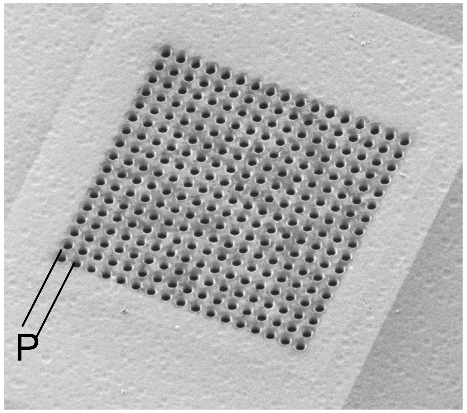
$$\lambda_{SP} = \frac{P}{\sqrt{n^2+m^2}}\sqrt{\frac{\varepsilon_{metal}\varepsilon_{substrate}}{\varepsilon_{metal}+\varepsilon_{substrate}}}$$

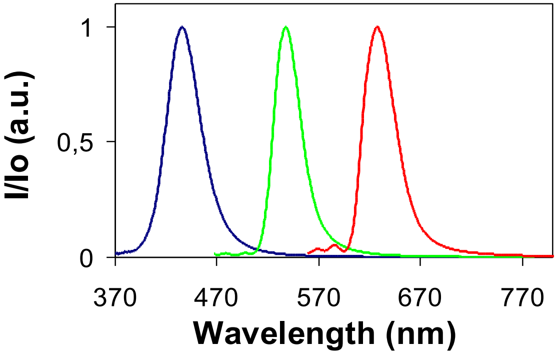
Many factors influence the modes involved and therefore spectrum….

Ag suspended film: thickness 300nm, period 540 nm, hole diameter 220 nm

Resonances can be controlled with the symmetry of the arrays and the periodicity (P) of holes:

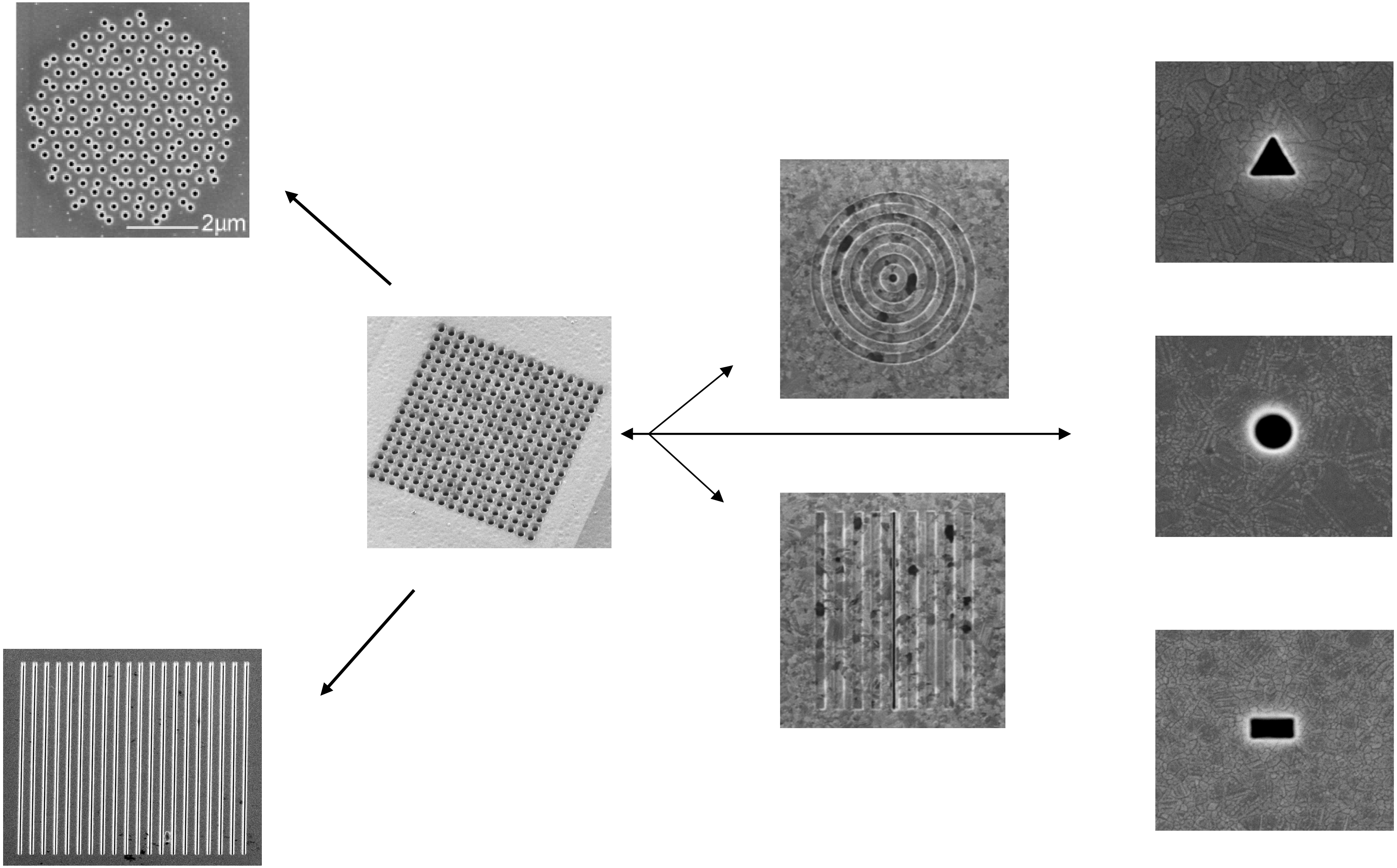






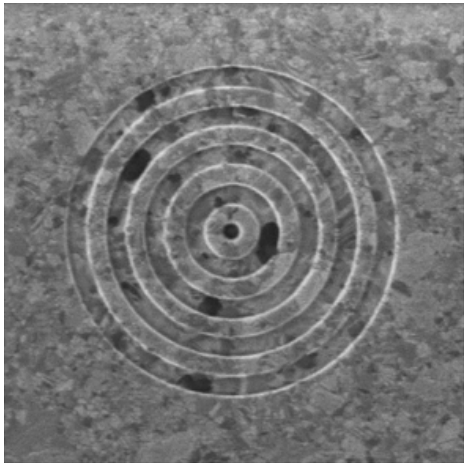
Other important factors: hole shape, dielectric properties of metal, coupling between interfaces, etc.

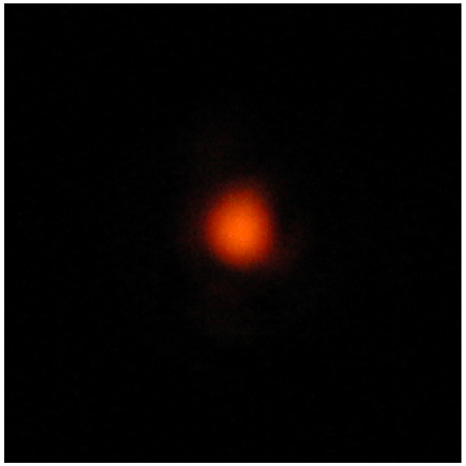
Extraordinary Transmission thru Apertures

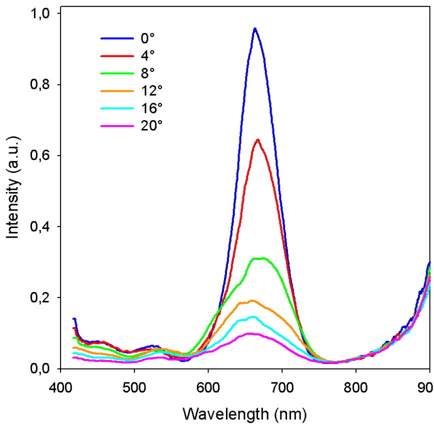


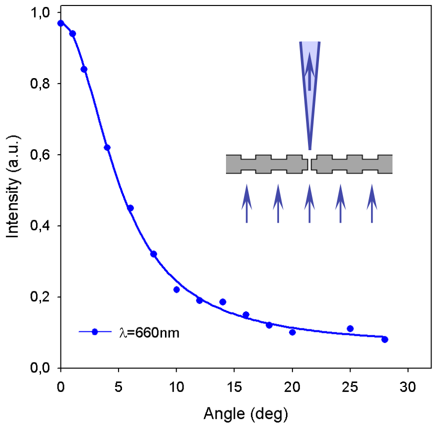
Reviews: Genet and Ebbesen, Nature 2007
Garcia-Vidal et al, RMP 2010

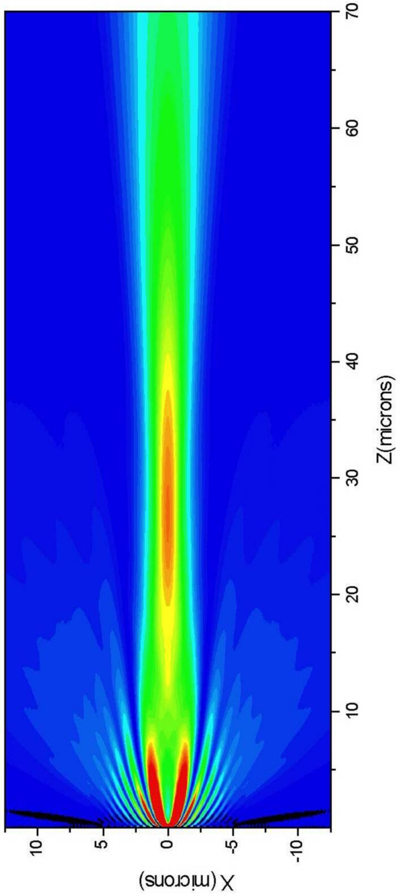
Beaming light from a subwavelength aperture: Diffraction control







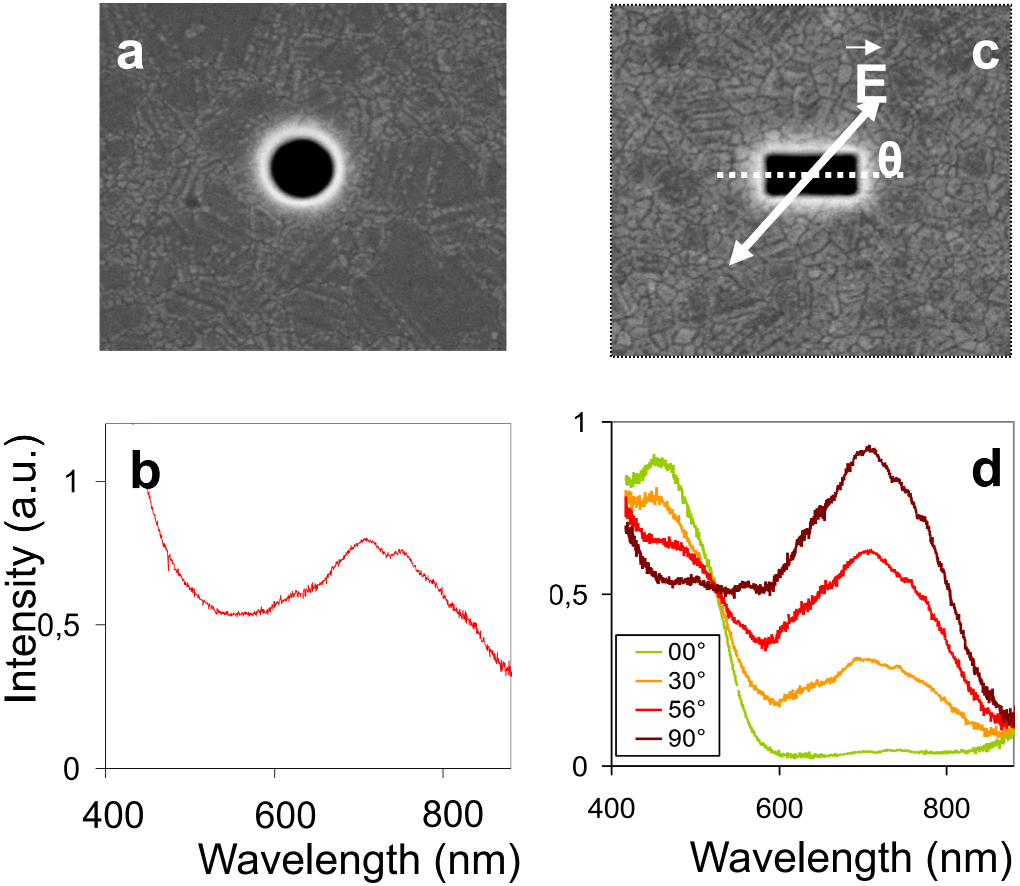




Science (2002)
PRL (2003)

Single holes have LSP resonances like metal nanoparticles:

Consequences for **Transmission** and **Diffraction**



Degiron et al, Optics Com. 239, 61 (2004)

Diffraction of Single Subwavelength Holes

PRL, in press

Implications of EOT

Applications:

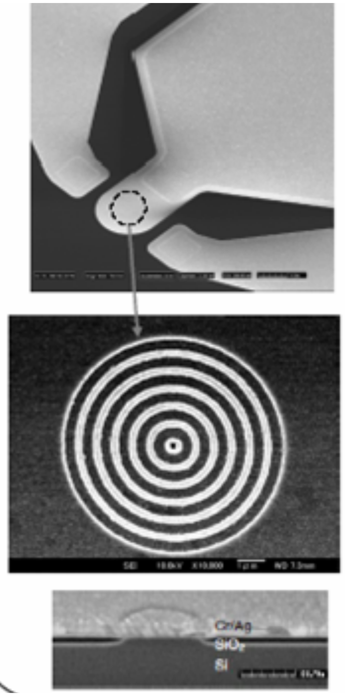
- **Filters**
- **Bright subwavelength sources for**
  - **high density storage**
  - **scientific instruments**
- **Spectroscopy and Sensors**
- **Subwavelength lithography**
- **Optical switches**
- **Enhancement of non-linear phenomena and devices**
- **BEC**
- **Quantum entanglement**
- **Spectral and Polarimetric Imaging**
- **Optical Devices: photodectectors, LEDs, lasers, etc.**
- **Metal – Molecule interactions: strong coupling…**

Transposition to other waves: surface phonon polaritons, atom matter waves, acoustics…

Combinations of arrays or aperture structures: negative refraction, polarization effects, etc.

Photon Sorting with SP

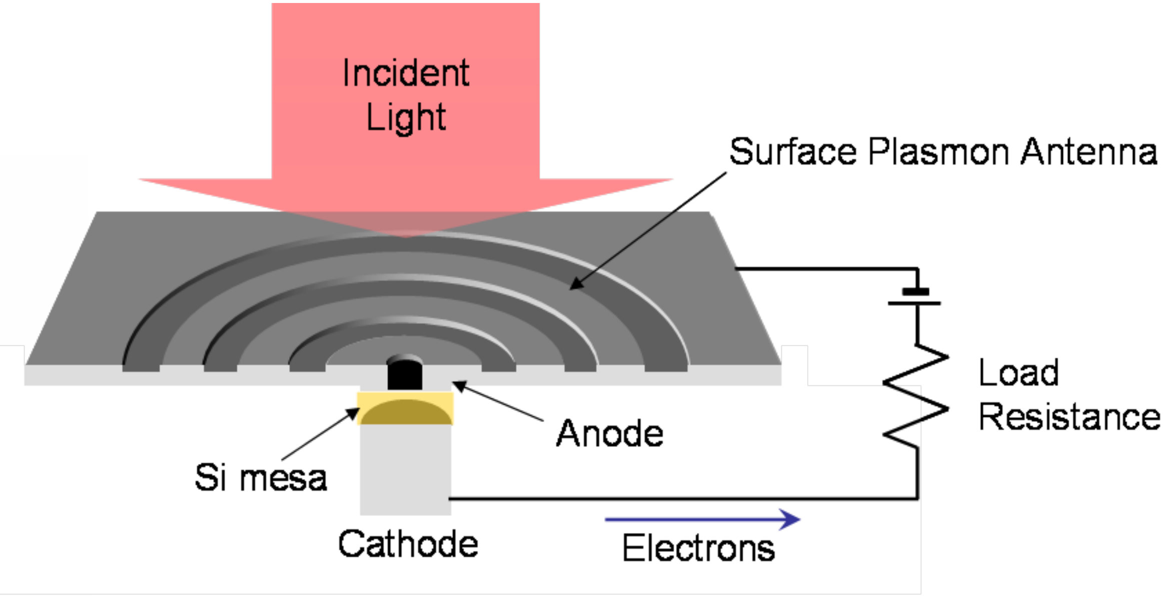
Ultrafast and Small Surface Plasmon based Photodetectors: by NEC



Electrodes
For Si
nanophotodio

SP Antenna
Sub-wavelength aperture
and corrugated rings on
Ag film

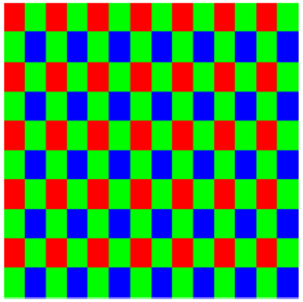
Ag Film on Si mesa
Before Ag etching



Jap. J. Appl. Phys., **44**, L364 (2005). Tsutomu ISHI et al.

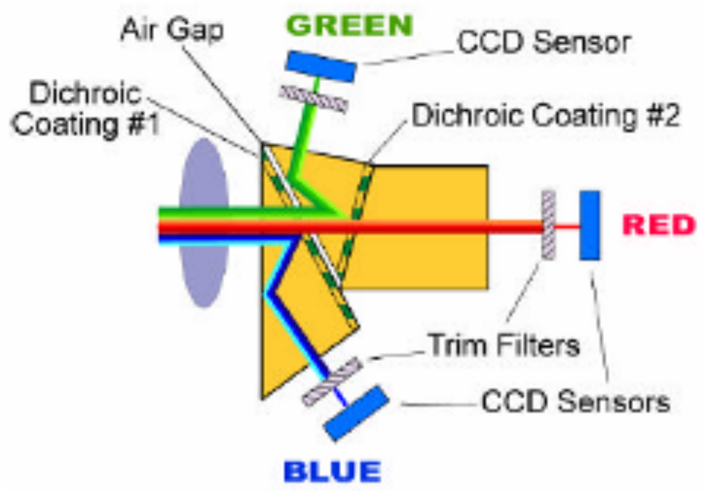
Spectral imaging

- Color Filter Array (Bayer mosaic)



- most popular
- low pixel resolution: interpolation algorithms
- color-artefacts in the resulting image

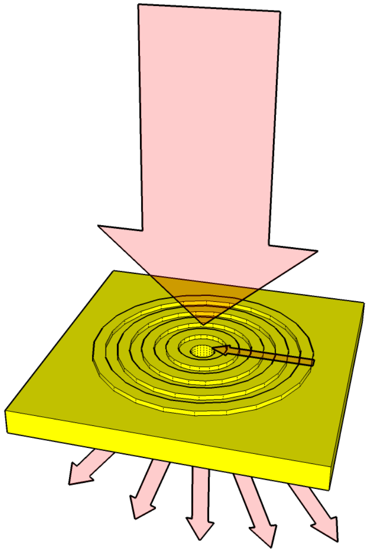
- 3-chips

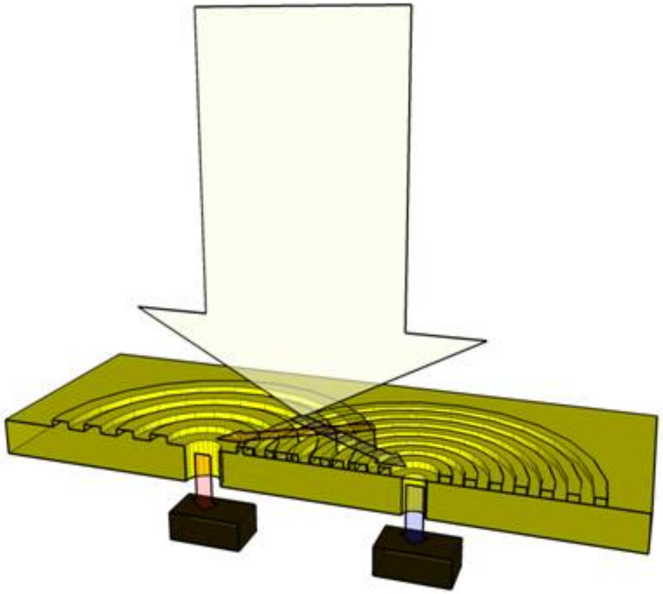


- redirect the full image frame on each detector
- simultaneous color captures
- expensive

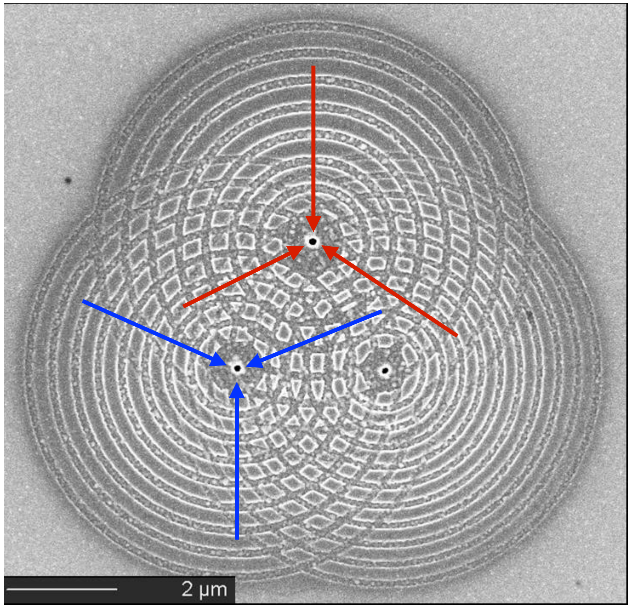
Photon Sorting with SPs

- photons are sorted out on different detector elements depending on wavelengths

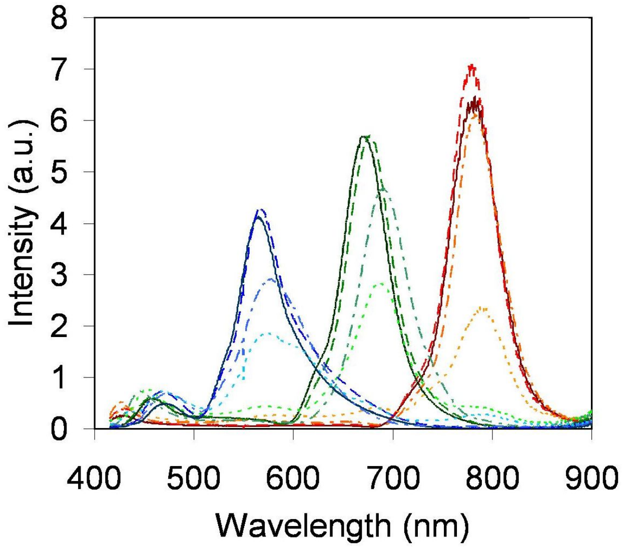


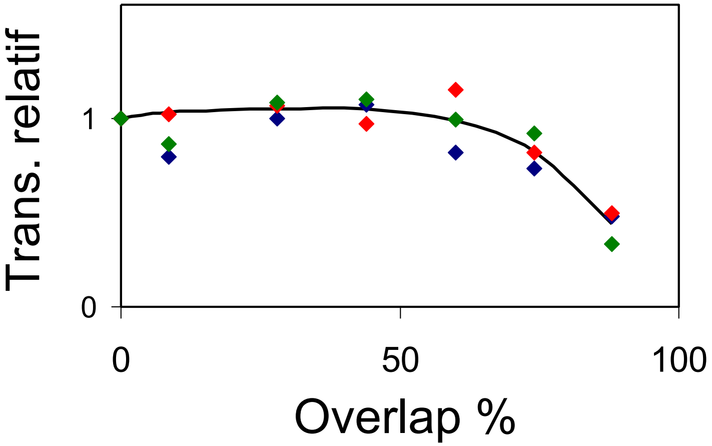


Extracting light from the same area



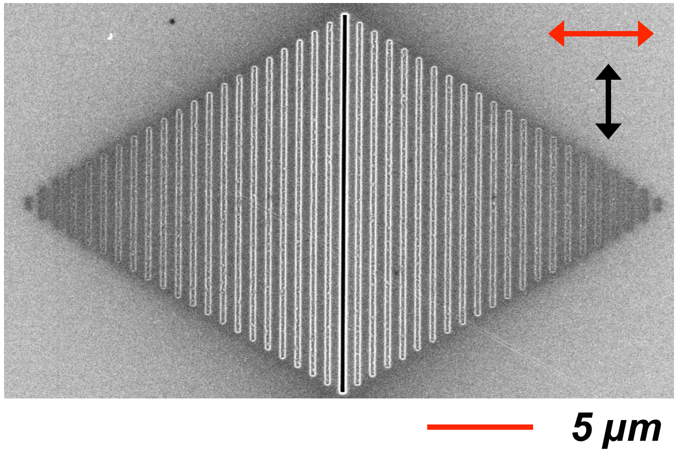
Overlap 77%
(inter-hole distance 4μm)



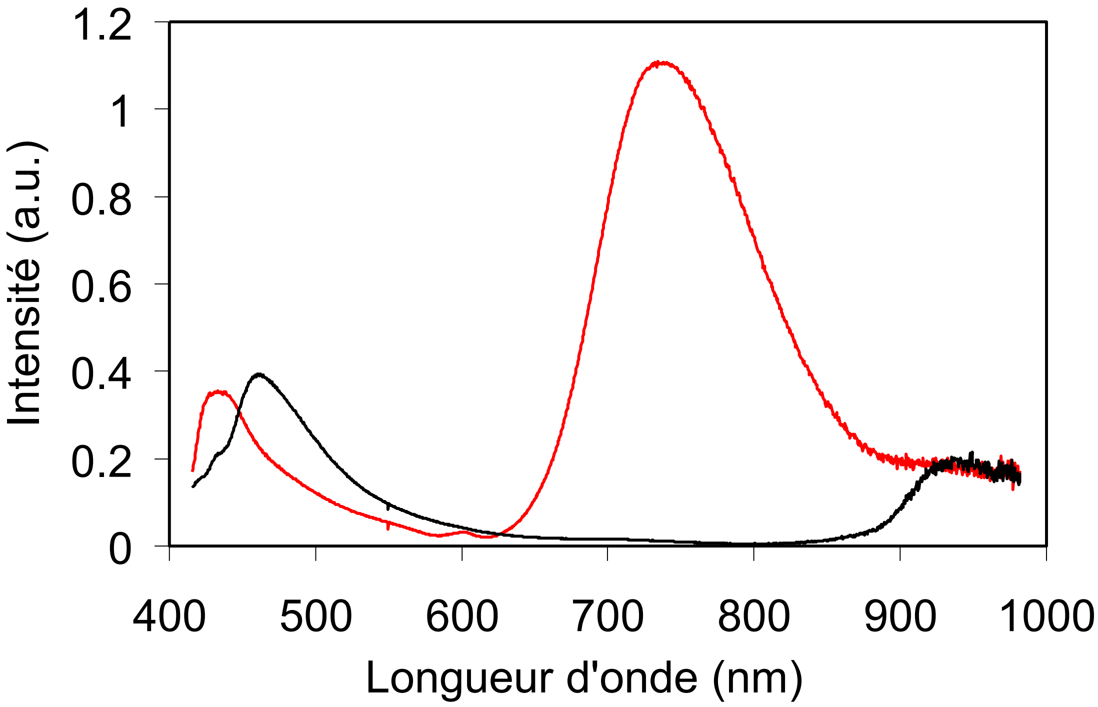


Laux et al, Nature Photonics 2008

Slit and grooves as polarization sensitive element



Extinction factor~*1:100*

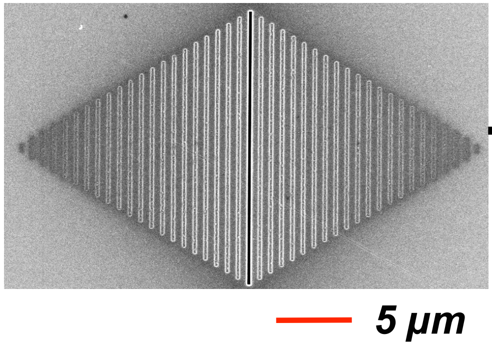


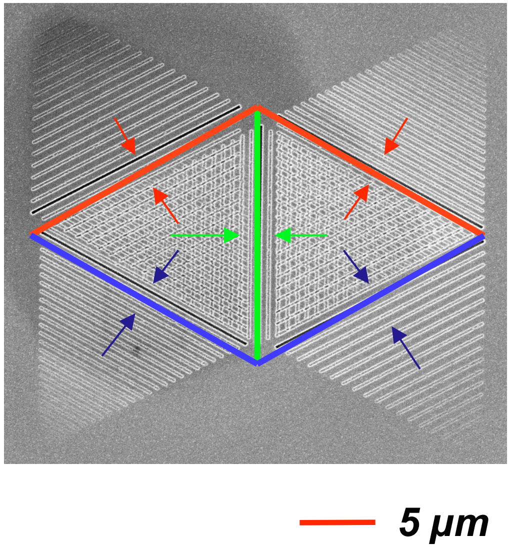
Slit width: 175nm

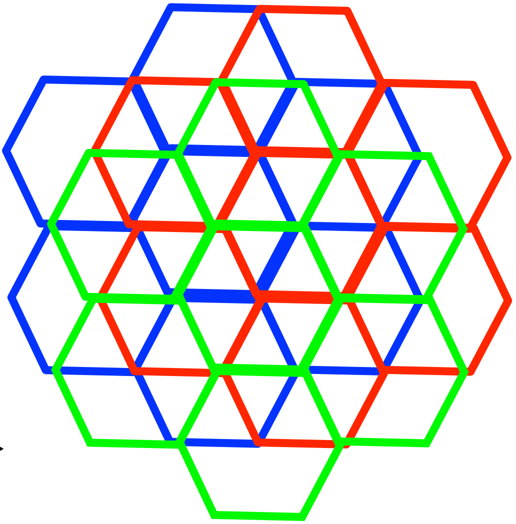
Groove period: 600nm

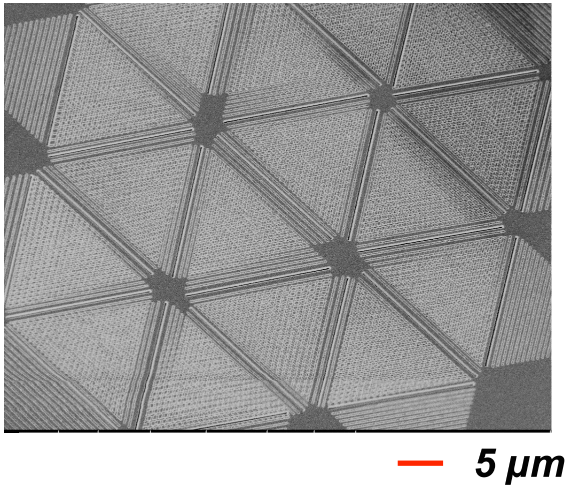
Laux et al*, Nat. Photon. 2, 161-164 (2008)*

Slit/groove array





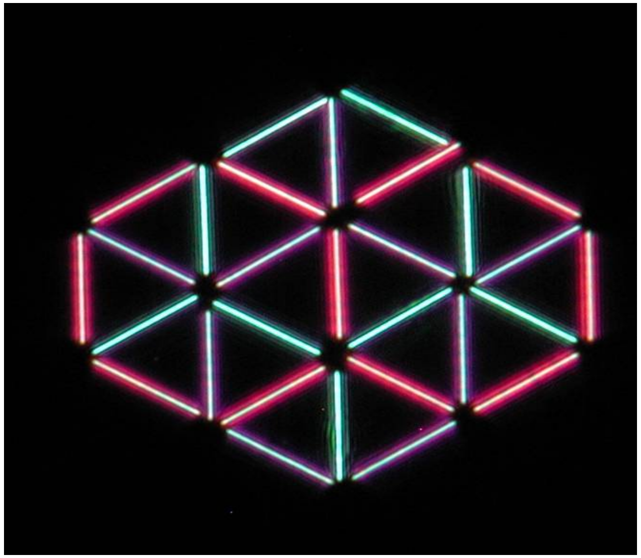


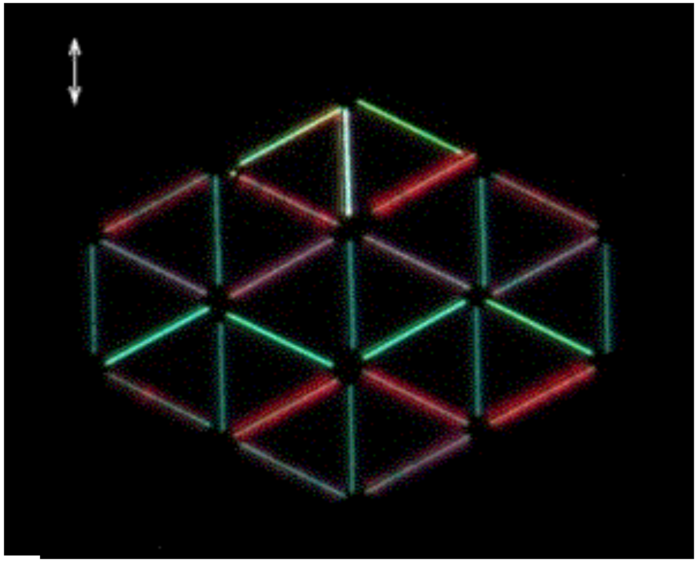


SP photon sorting with polarization sensitivity

Non polarized light

Polarized light





Absolute transmission efficiency for whole device is ca. 10% before optimization.

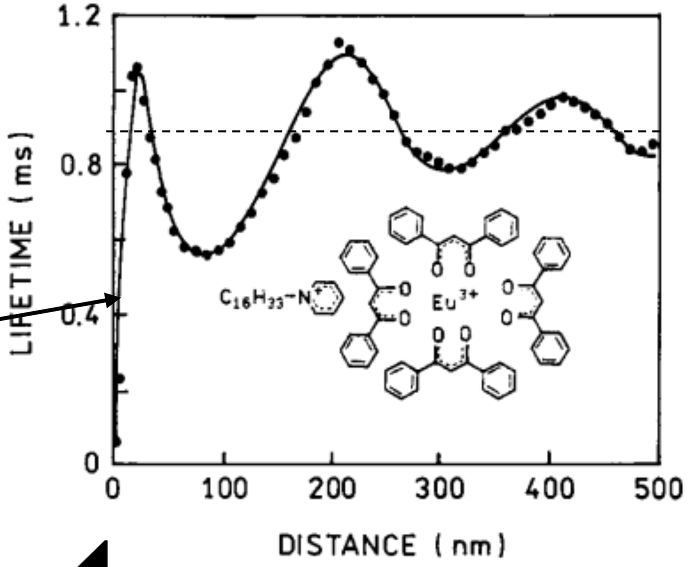
Slit 15µm x 175nm

Ag film thickness 360nm

Laux et al, Nature Photonics 2008

Light - Molecule – Metal Interactions

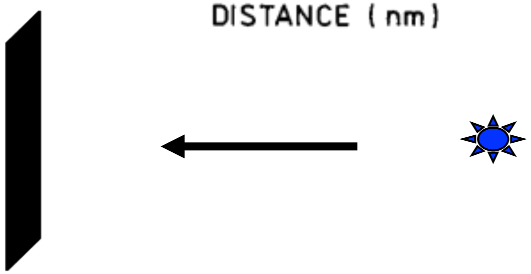
Fluorescence near a metal surface:



“natural lifetime”:

Energy transfer to
vacuum states

Quenching
(energy transfer
to metal)



Metal

Fluorescent Molecule

Lifetime of Eu^{3+} ions near Ag mirror as a function of the separation between the Eu^{3+} ions and the mirror (LB deposition with a transparent spacer)

K.H. Drexhage, *Progress in Optics XII*. North-Holland, Amsterdam,1974

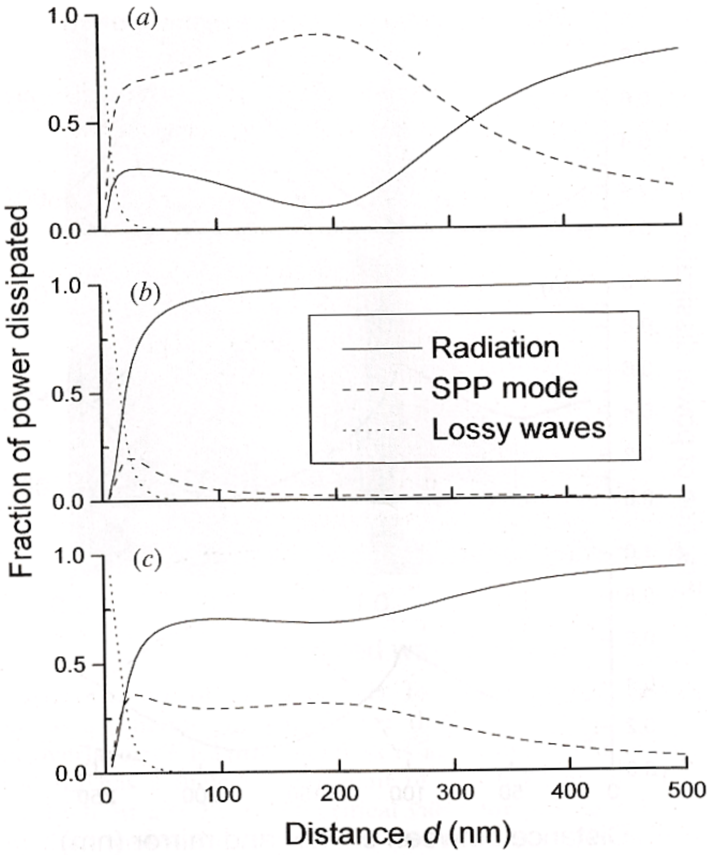
S.Haroche and D. Kleppner, Physics Today p.24 (1989)

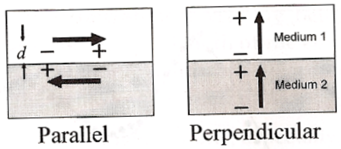
The interaction depends not only on the metal—emitter distance but also on the dipole orientation, choice of metal, structure of the metal, etc

Parallel

Perpendicular

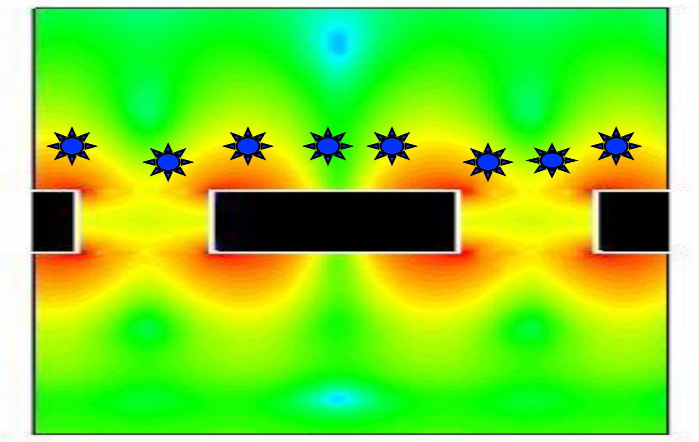
Isotropic:





Barnes, J. Mod. Optics 45, 661-699 (1998)

Molecule-SP interactions



Weak Coupling:

→ *Effects of SP on molecular photophysics:*

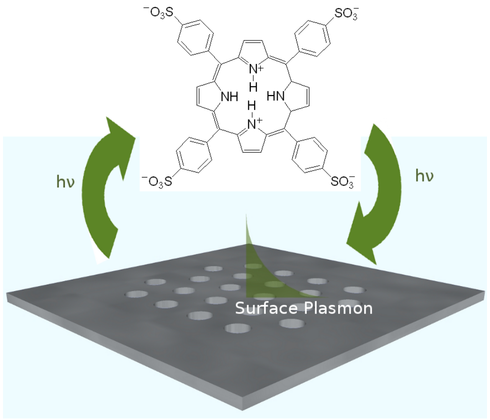
- increases the probability of molecular excitation or absorption efficiency, e.g. enhanced photochemistry
- changes the probability of emission (radiative rate)

→ *Effects of Molecules on SP:*

- refractive index at absorption bands
- additional damping and decoupling channels

Strong Coupling:

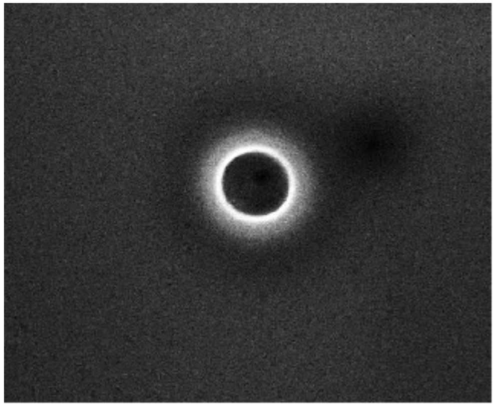
→ Hybrid Molecule – SP states

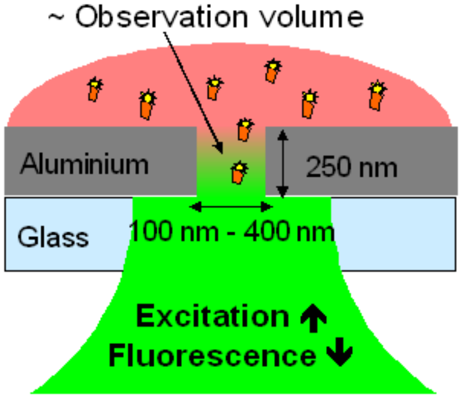


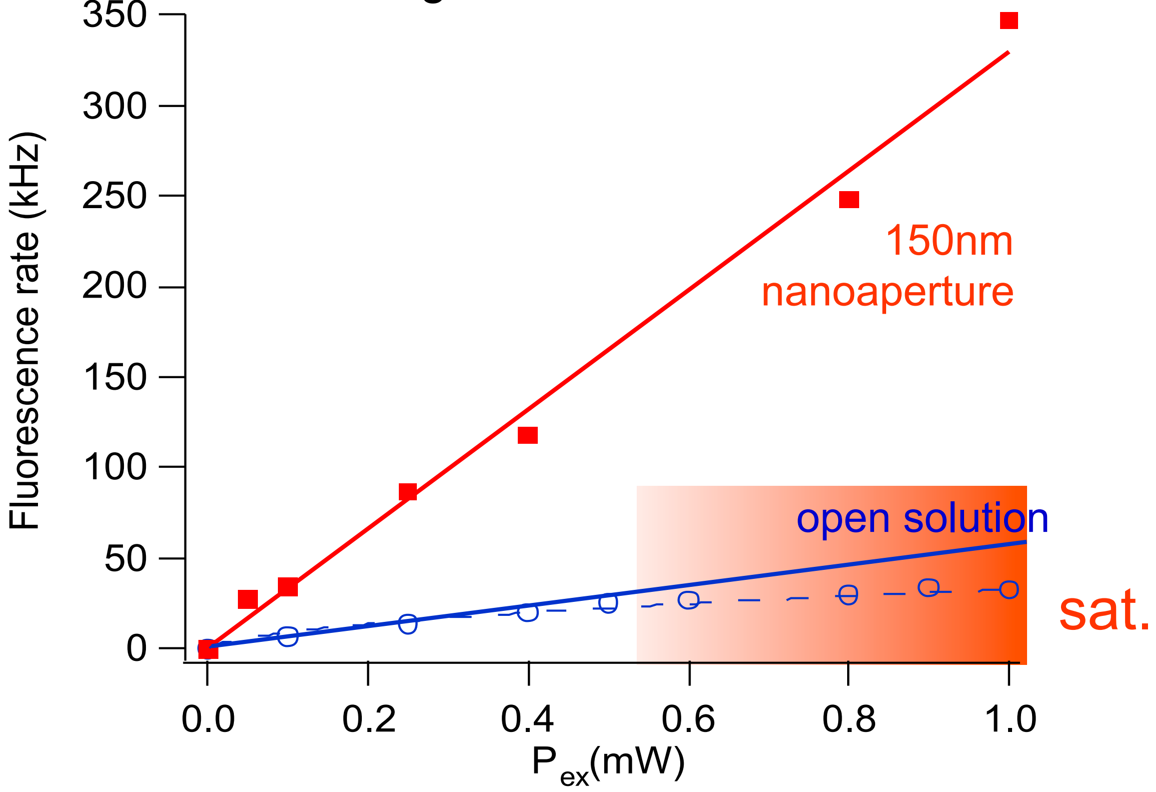
Weak Coupling Regime

Fluorescence Correlation Spectroscopy in a single hole:

Advantages: Higher signal, 1000 times smaller volume so 1000 times higher concentrations can be investigated.



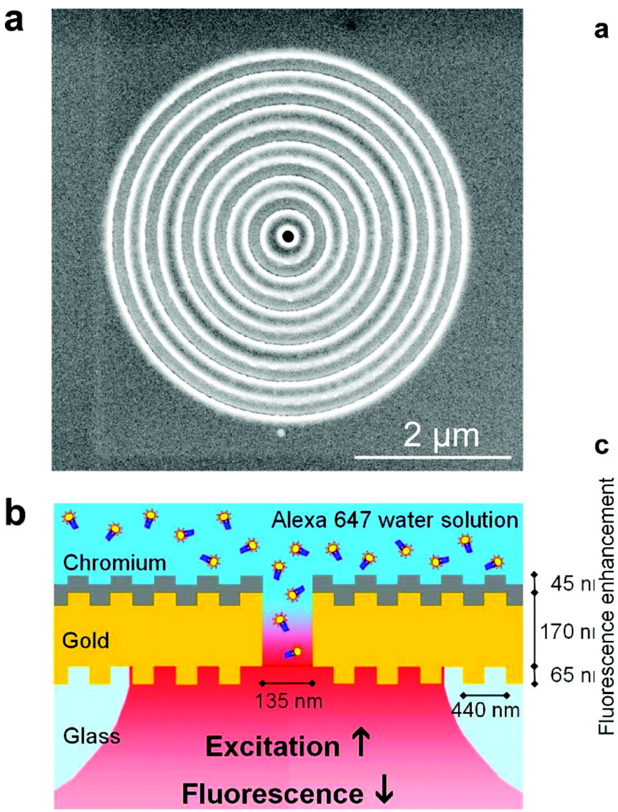


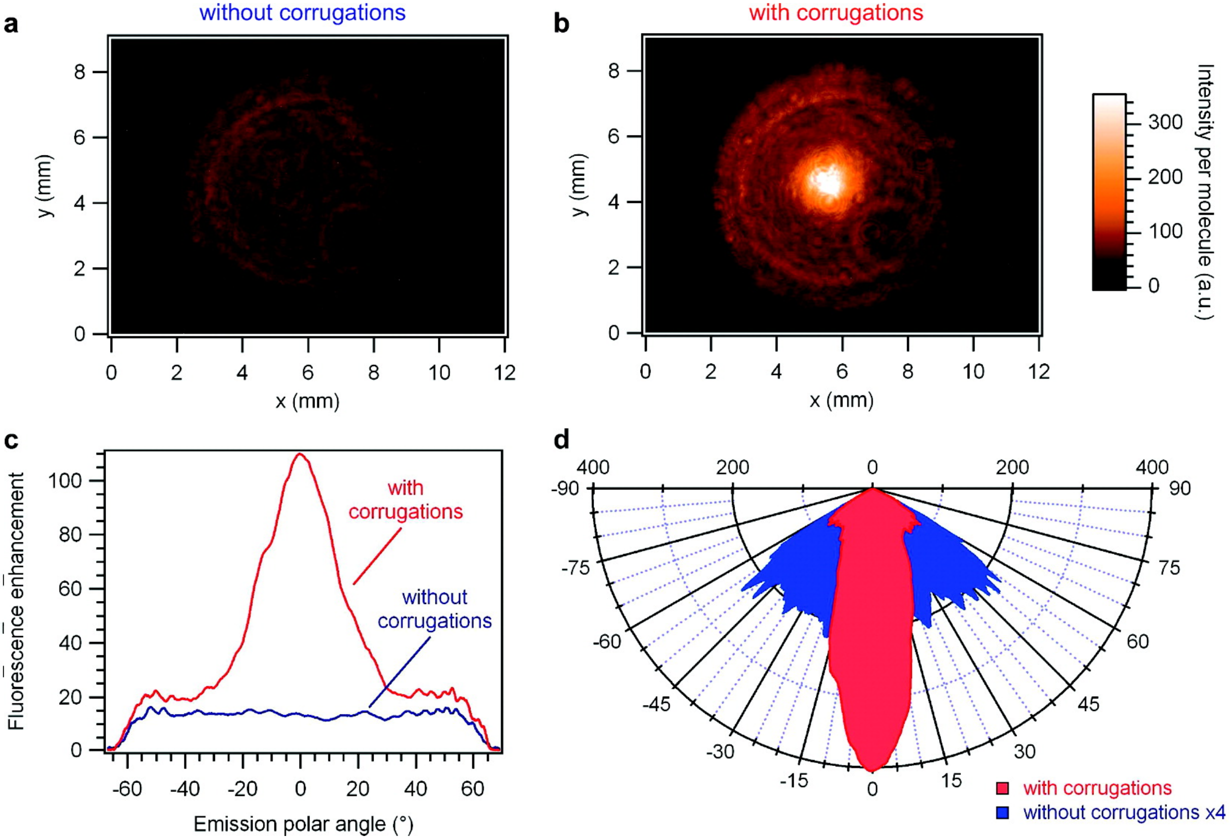


Levene et al, *Science* **299,** 682 (2003)

Cavity mode

Rignault et al , PRL 2005
SP modes...





With Institut Fresnel

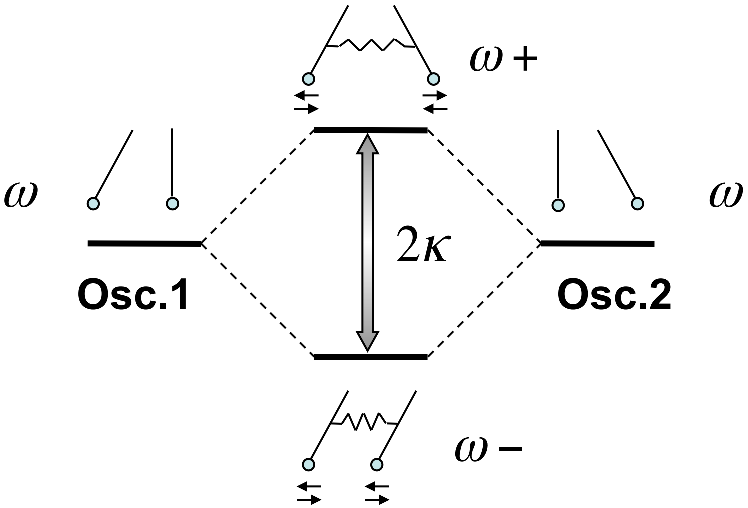
Enhanced absorption, enhanced emission and beaming to detector

Aouani et al, Nano Letters 11, 637-644 (2011)

Strong Coupling Regime

Coupled Classical Oscillators

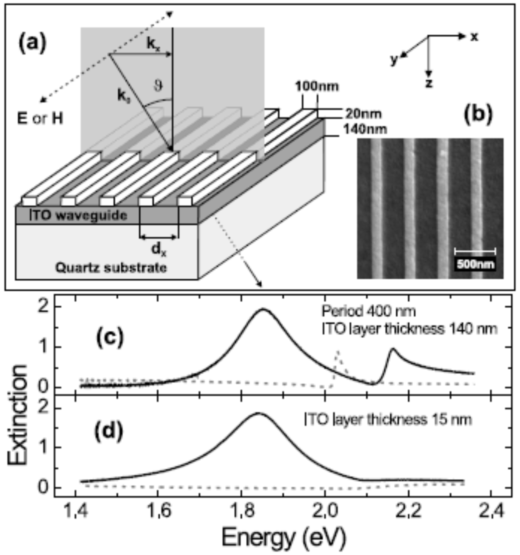
Coupling two oscillators causes an energy splitting into two levels

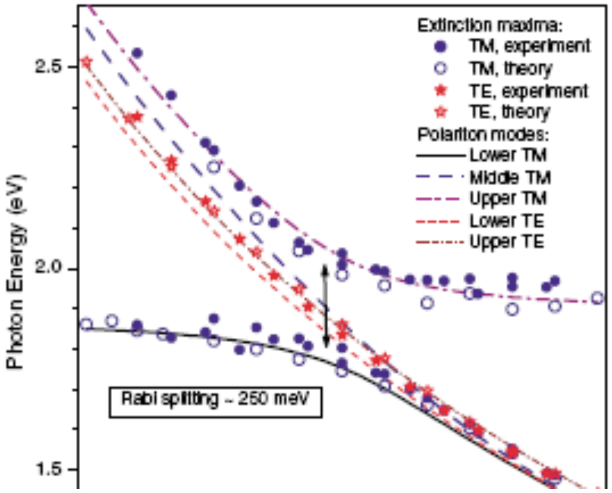


κ coupling constant, reflects energy exchange

For a finite dissipation rate Γ the oscillators are strongly coupled if κ > Γ

Strong coupling
between waveguide mode and surface plasmon mode

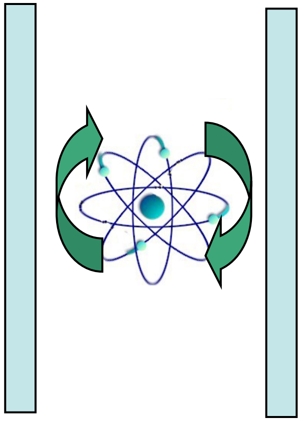




- Normal modes and avoided crossing in the dispersion diagrams

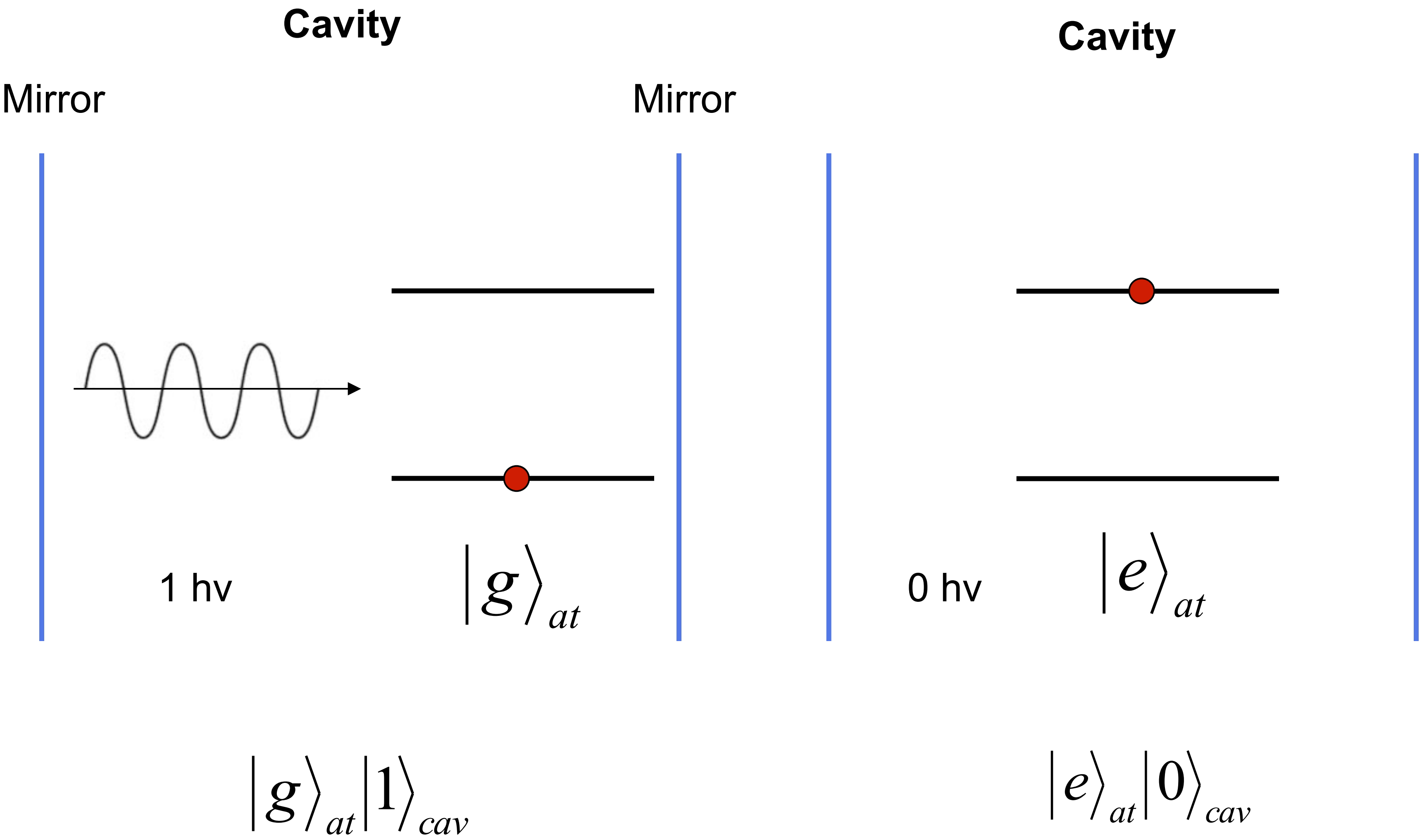
Christ et al., PRL (2003)

Strong Light – Matter Interactions



Coupling an electronic transition and an optical mode

Coupling an electronic transition and a cavity resonance



Cavity

Mirror

Mirror

1 hv

$|g\rangle_{at}$

$|g\rangle_{at}|1\rangle_{cav}$

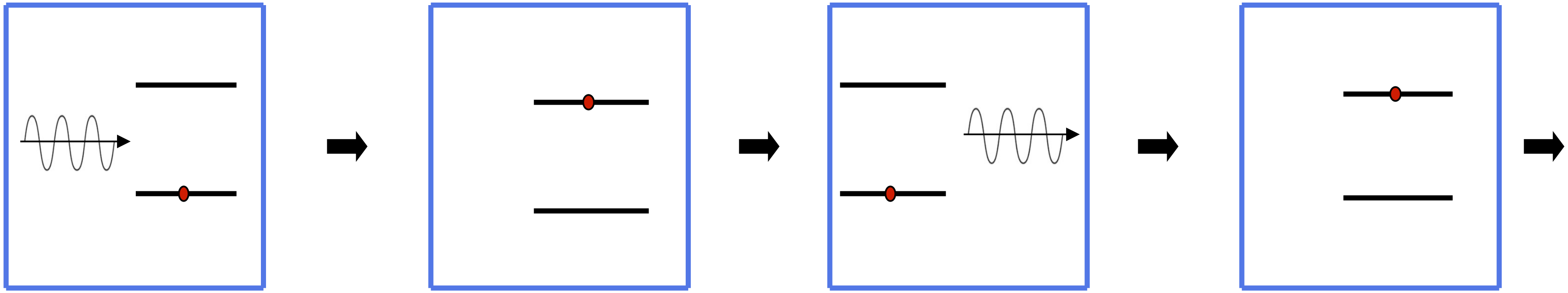
Cavity

0 hv

$|e\rangle_{at}$

$|e\rangle_{at}|0\rangle_{cav}$

Exchange of photon between cavity and electronic transition: Rabi Oscillations

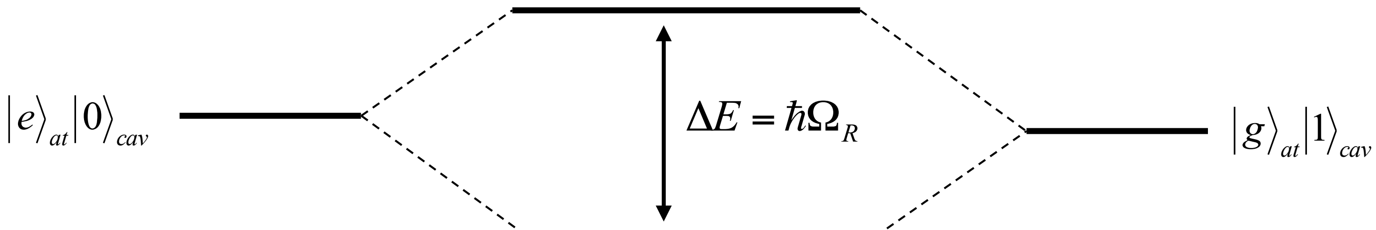


The exchange of photon is faster than dissipation

The Cavity + Atom forms a new System with its own eigen states

The eigen states of the cavity system in which the photon mode interacts resonantly with a transition are the mixed symmetric and anti-symmetric states:

$$|+\rangle = C_{11}|e\rangle_{at}|0\rangle_{cav} + C_{12}|g\rangle_{at}|1\rangle_{cav}$$



with

$$|-\rangle = C_{22}|e\rangle_{at}|0\rangle_{cav} - C_{21}|g\rangle_{at}|1\rangle_{cav}$$

At resonance: $$\Delta E = E_+ - E_- = \hbar\Omega_R = \sqrt{4V_n^2 - (\Gamma_c - \Gamma_e)^2}$$

$\hbar\Omega_R$ is the Rabi splitting

Γ_c Dissipation of the cavity

$$2V_n = 2E_0 \cdot d = 2d\sqrt{\frac{\hbar\omega}{2\varepsilon_0 V}} \times \sqrt{n_{ph} + 1}$$

Transition dipole

Photon E-field

Γ_e Dissipation of the excited state i.e. non-radiative lifetime

(JC Two state model)

Short and Quick History of Cavity Strong Coupling

1980's: Atom-Cavity systems (Haroche, Kimble,…) – Ω_R~10-100MHz / 1meV

1990's: Excitons in Semiconductors (Weisbuch, Nishioka, Arakawa…)
Bulk, Quantum Wells, dots, etc. – Ω_R~ 1-100meV
Intersubband transitions Ω_R~ 10-100 meV

Control of light-matter interaction in the single-quanta level, polariton condensation (Deveaud-Plédran, …), threshold-less lasing, …

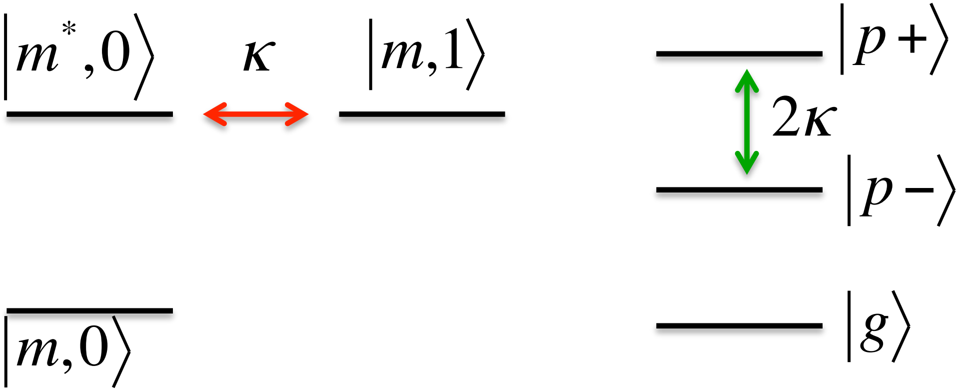
Lidzey *et al.*, Nature **395** (1998):
Strong coupling with dye molecules Ω_R~ 200meV

Motivation - High transition dipole moment

Can we use molecules to take strong coupling into new directions?

Can we use strong coupling to take molecules and materials into new directions?

Strong coupling with N molecules



$$\hbar\Omega_R = 2d \cdot E = 2d\sqrt{\frac{\hbar\omega_C}{2\varepsilon_0 v}}$$

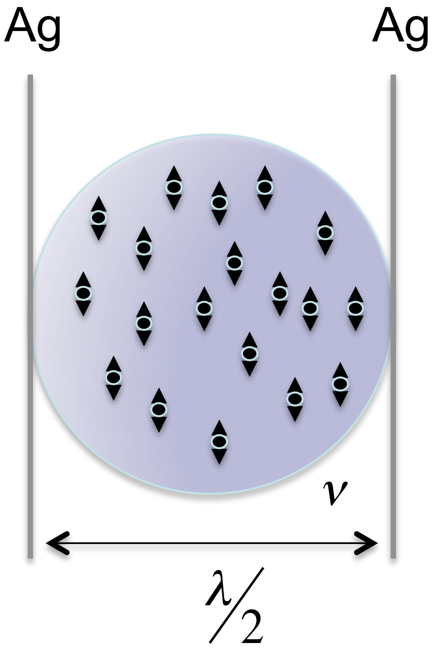
Coupling collectively to N molecules, the Dicke state:

$$|G,1\rangle = (|g,g,\ldots g\rangle)|1\rangle$$

$$|D,0\rangle = \frac{1}{\sqrt{N}}\left(\sum_{j=1}^{N}|g,\ldots,e_j,\ldots g\rangle\right)|0\rangle$$

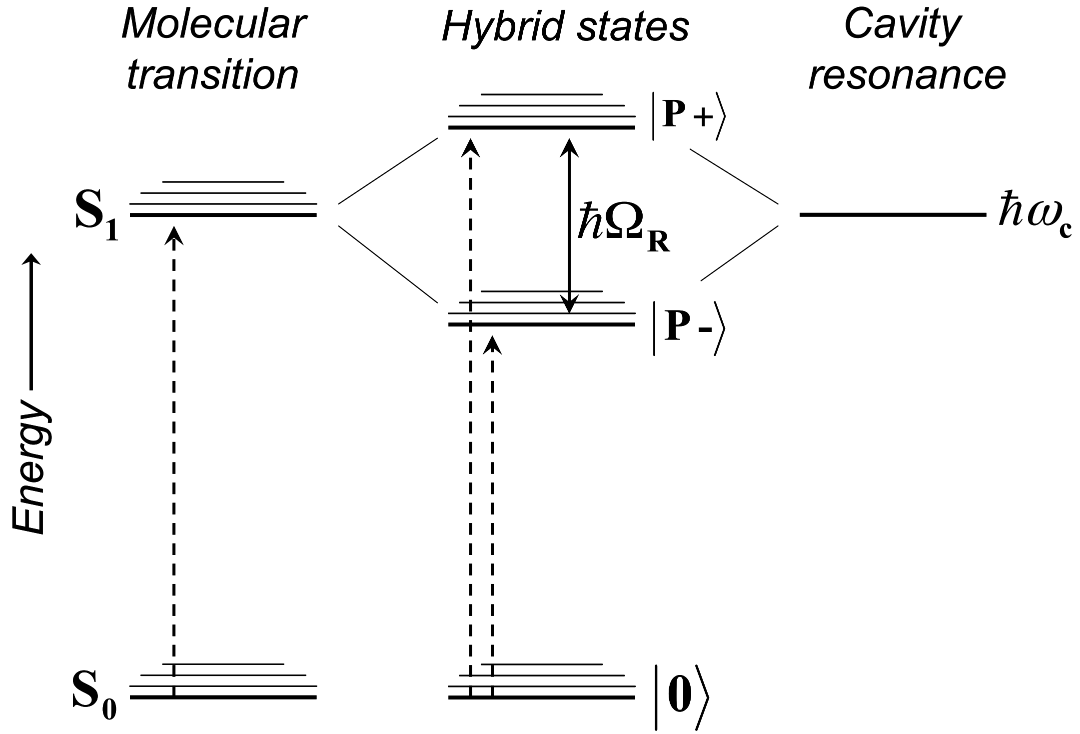
$$\hbar\Omega_R^N = 2\left\langle D\middle|\hat{d}\middle|G\right\rangle\sqrt{\frac{\hbar\omega_C}{2\varepsilon_0 v}} = \underline{\sqrt{N}\hbar\Omega_R}$$

The Dicke State: A collective state



N dipoles (molecules) in the mode volume v

Average distance between molecules much smaller than λ



> What are the properties of $|P+\rangle$ and $|P-\rangle$?

The hybrid states are known as Polaritonic, when populated form quasi – Bosonic particles

➢How do they influence the physical chemistry or chemistry of molecules? the properties of materials? And can it advance the physics?

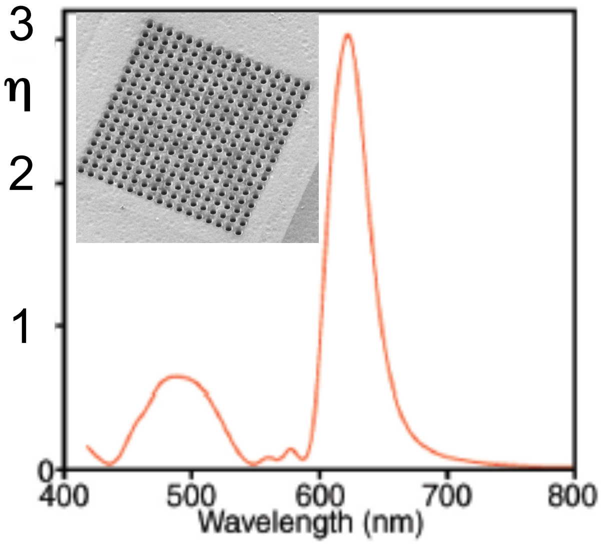
Strong Coupling Regime

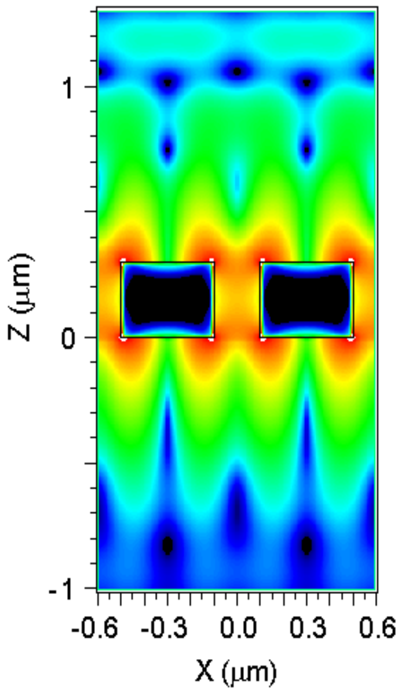
Using Nano-Cavities or Surface Plasmons

- High transition dipole moments of molecules can compensate for low Q factor cavities

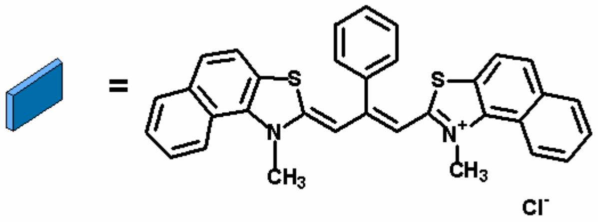
-Surface plasmon resonances are strong enough to act as poor cavities Q ~ 10 and they have low mode volumes

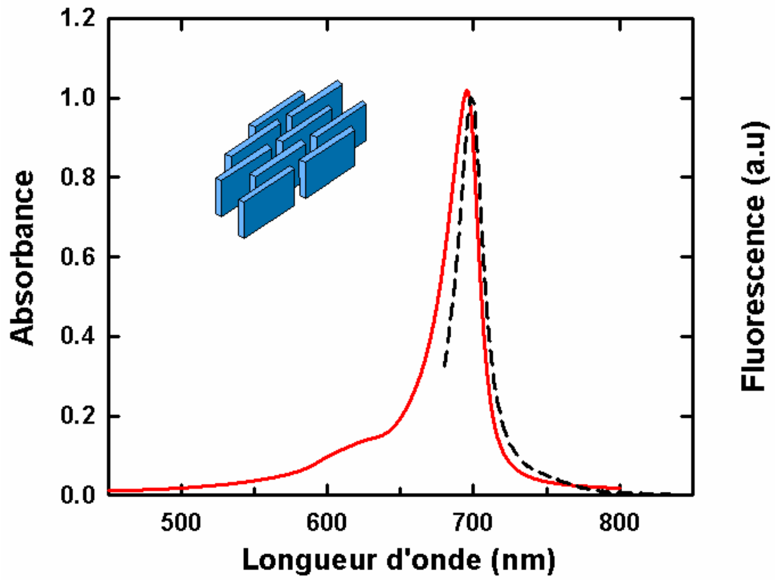
SP on hole arrays + J-Aggregate Molecules



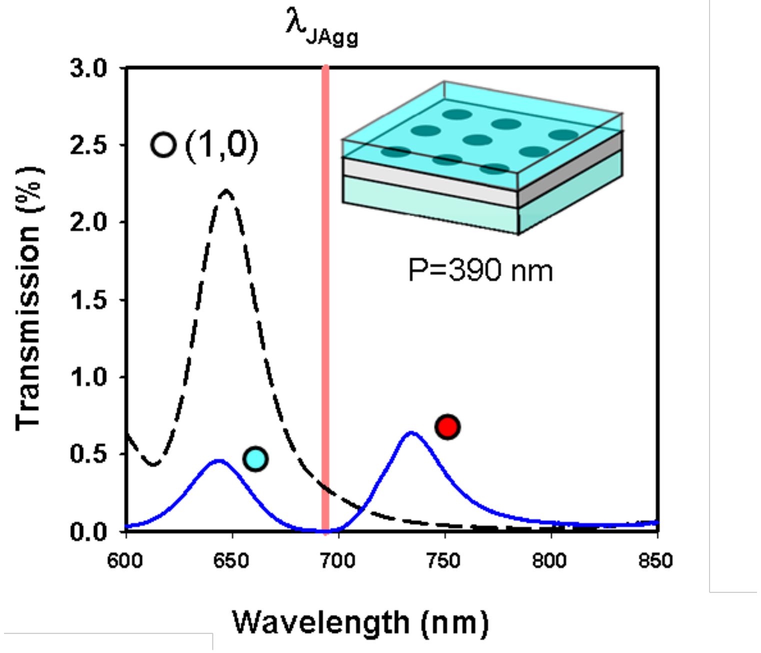


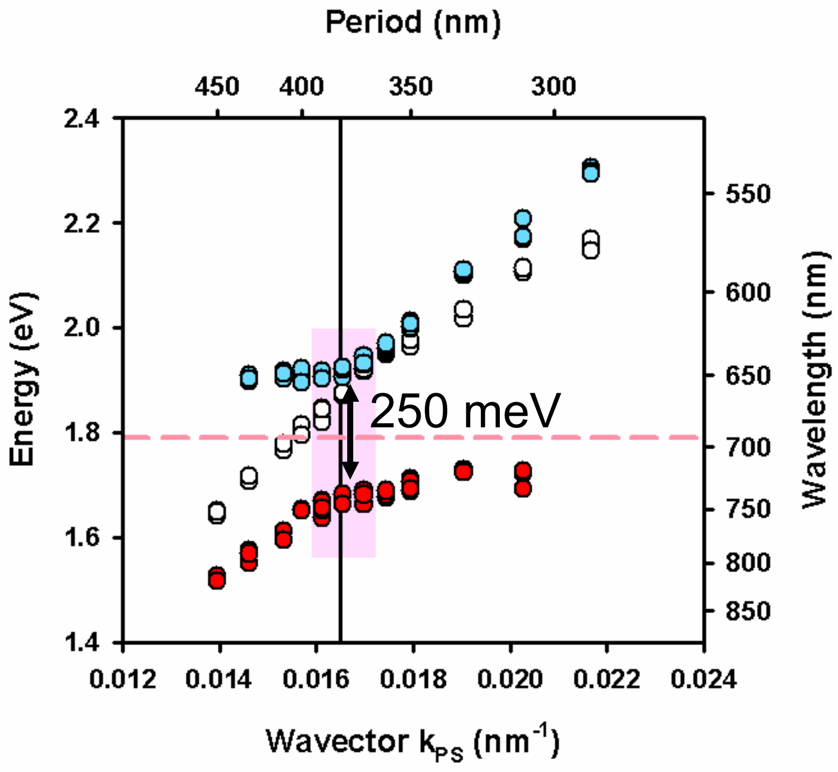
- Strong oscillator strength ($\varepsilon \sim 10^5\,M^{-1}cm^{-1}$)
- Sharp resonance (FWHM<30 nm)





Strong coupling between Hole Array SP modes and J-aggregate molecules





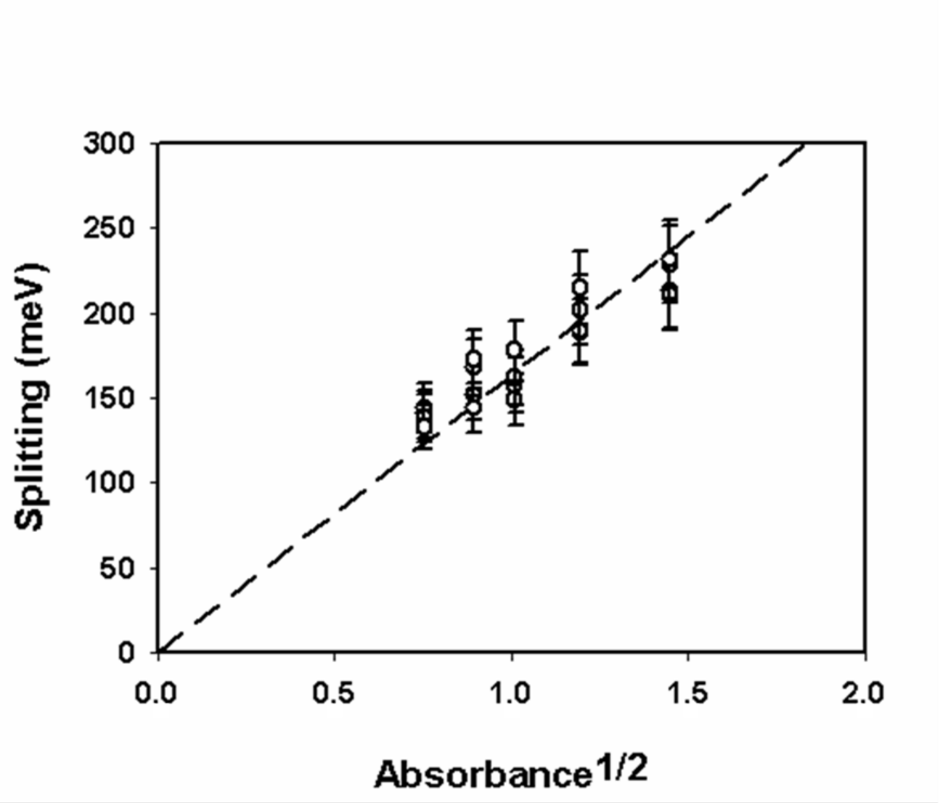
- - - Covered with PVA only

— Covered with PVA doped with J-aggregate

Photophysical properties of Molecule are changed: new possibilities

Dintinger et al., *Phys. Rev. B* **71**, 035424 (2005)

Effect of molecule concentration



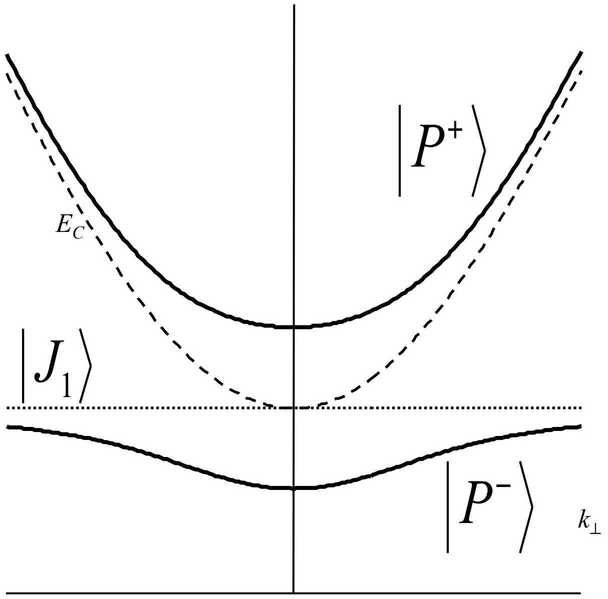
$$\hbar\Omega_R \propto \sqrt{\frac{N}{v}} \propto \sqrt{[M]}$$

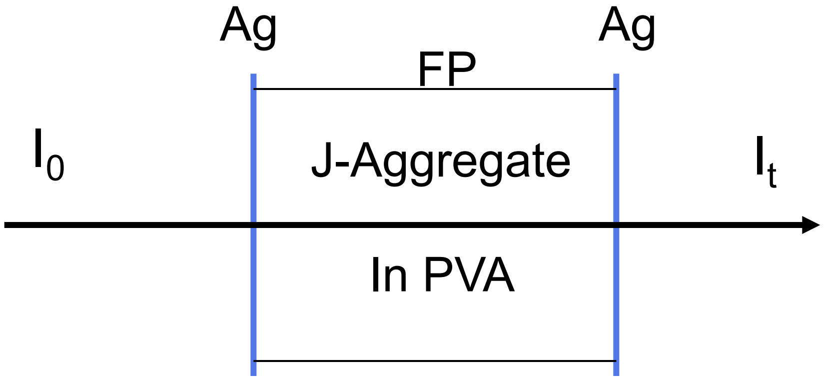
- Rabi splitting is proportionnal to the square root of the chromophore density as expected

- 10^4 ~10^5 molecules in the mode volume

Dintinger et al., *Phys. Rev. B* **71**, 035424 (2005)

J-aggregates (molecules) – Fabry Perot Cavity Strong Coupling




Ag

Ag

FP

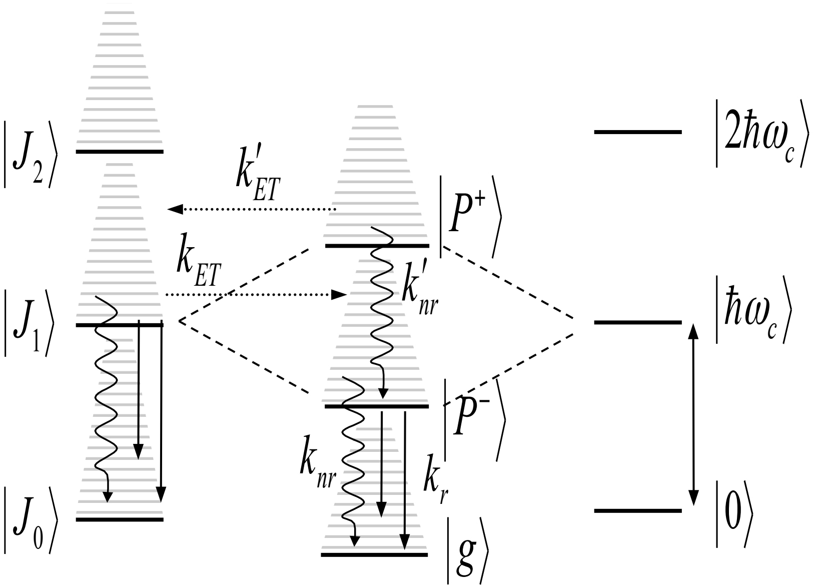
I_0

J-Aggregate

I_t

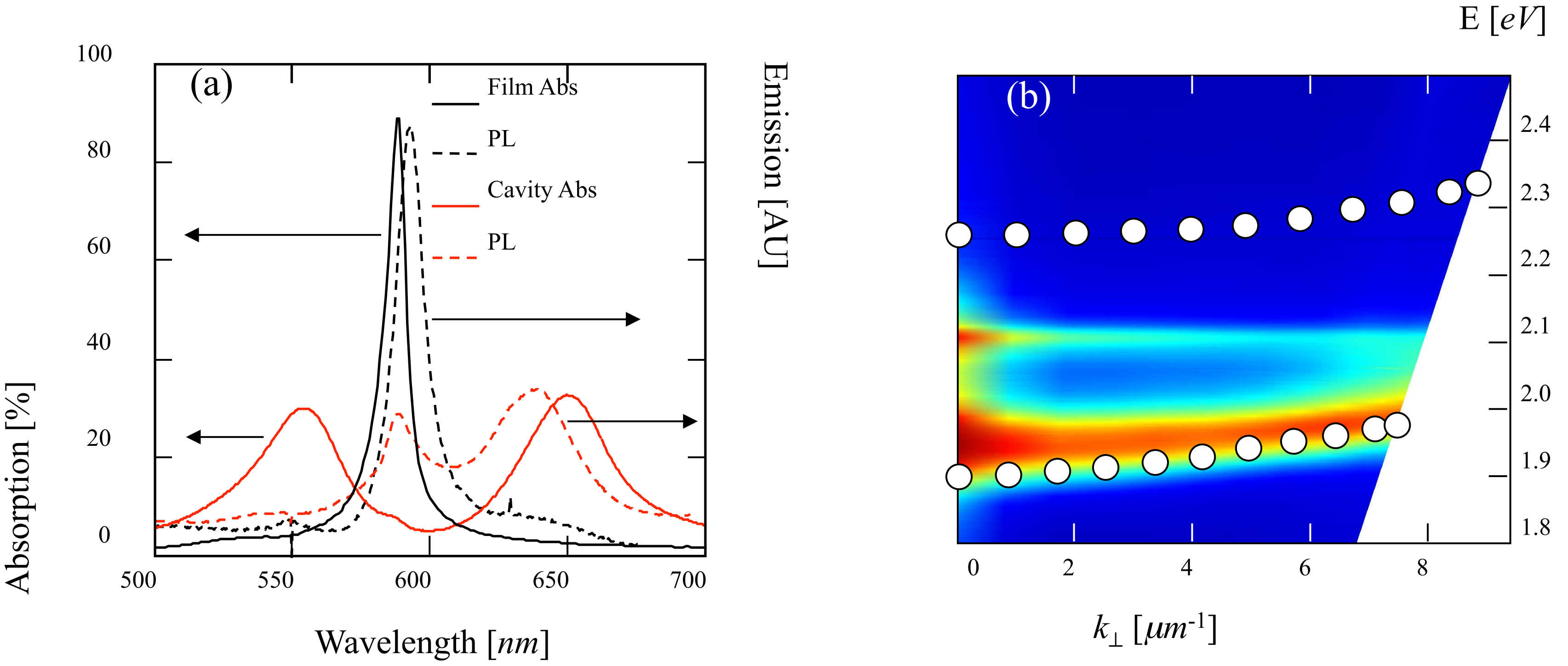
In PVA

Jablonski diagram



Mapping the internal dynamics

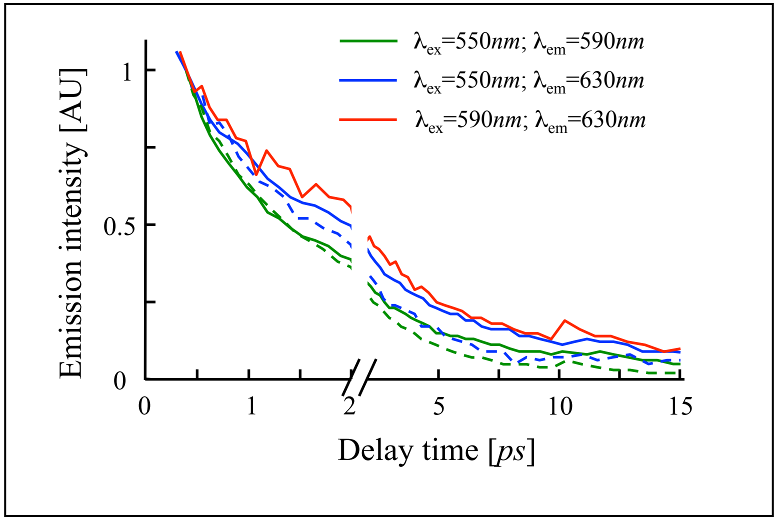
Fluorescence of strongly coupled TDBC J-aggregate - Cavity system



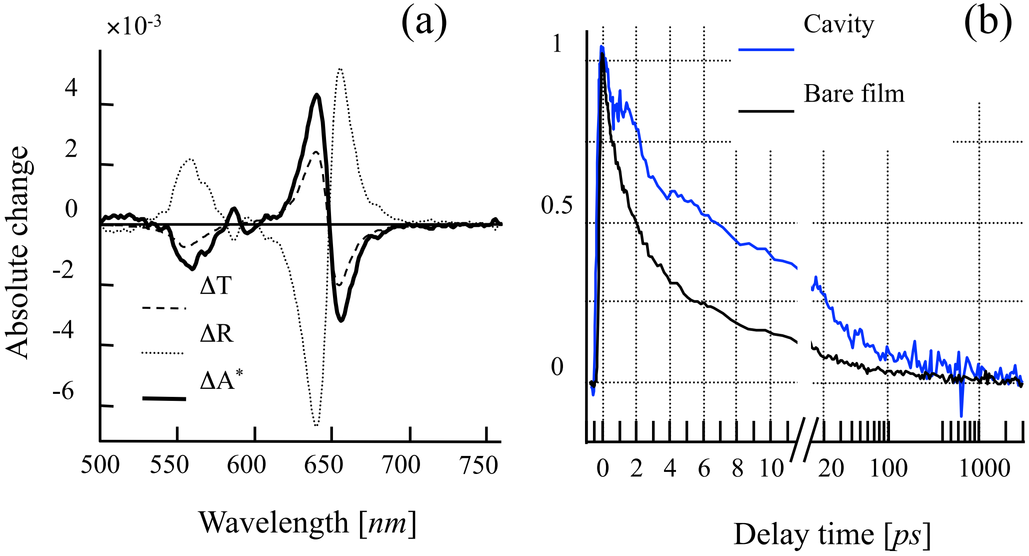
Collective State: Emission is coherent over the extent of the mode (see Aberra Guebrou, Bellesa et al, PRL 2012)

Decay of the Lowest Polariton $\left|P-\right\rangle$

Fluorescence

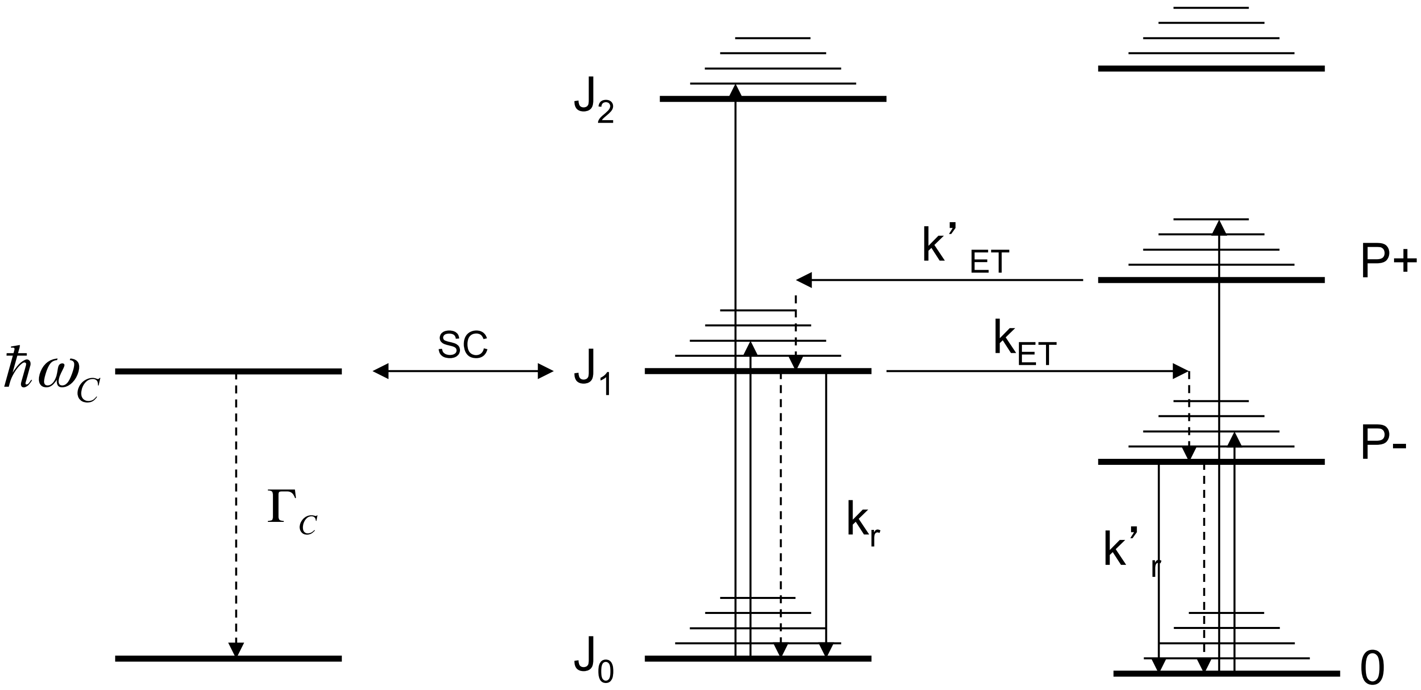


Transient Absorbance (150fs)



$$\tau_{P_-} > \tau_{J1} >> \frac{1}{\Gamma_C}$$

Cavity + Molecules = Hybrid System



$$\tau_{P-} > \tau_{J1} >> \frac{1}{\Gamma_C}$$

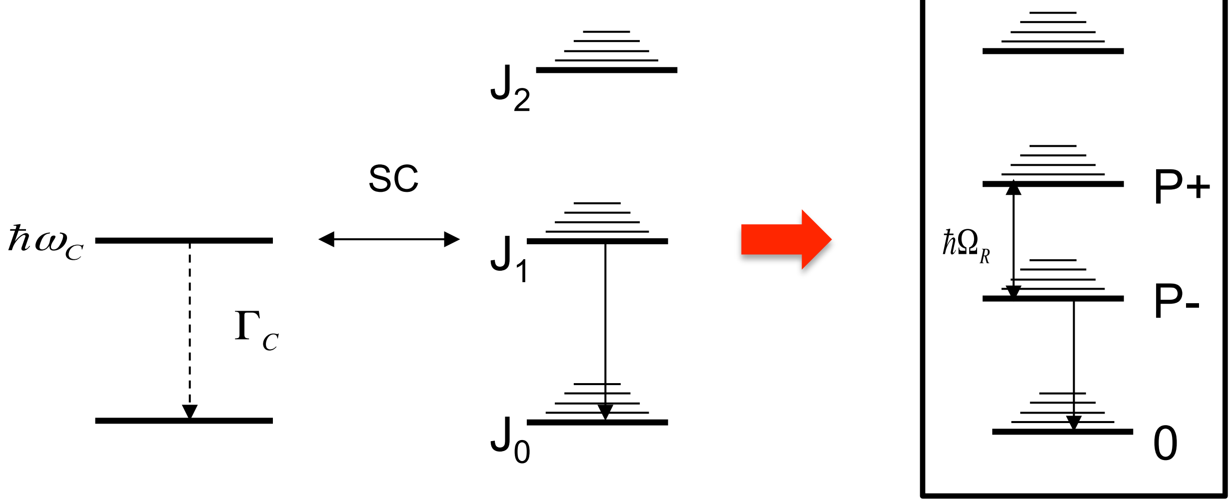
4ps, 1ps and 25 fs

Strong Coupling without Light….

- The observed coupling involves Vacuum (Electromagnetic) Fields
- No light is necessary…Just « Harvest » the Vacuum Field!

$$\hbar\Omega_R = 2d \cdot E = \sqrt{\frac{\hbar\omega_C}{2\varepsilon_0 \nu}} \times \sqrt{n_{ph} + 1}$$

Vacuum field

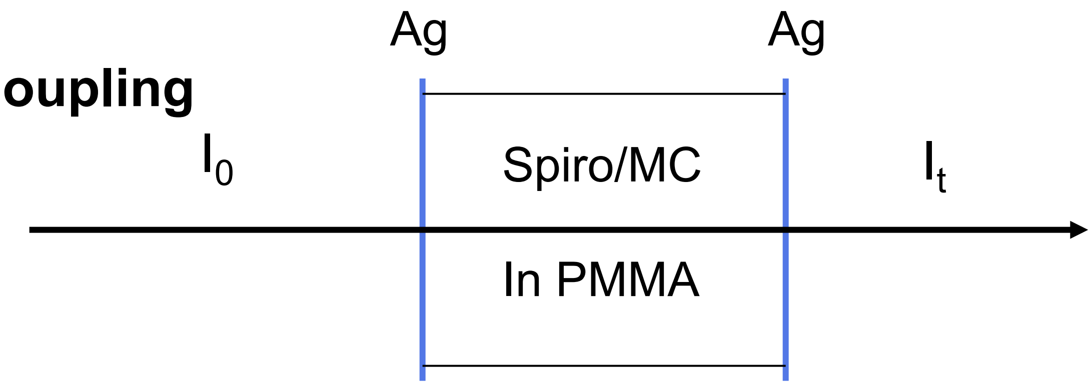


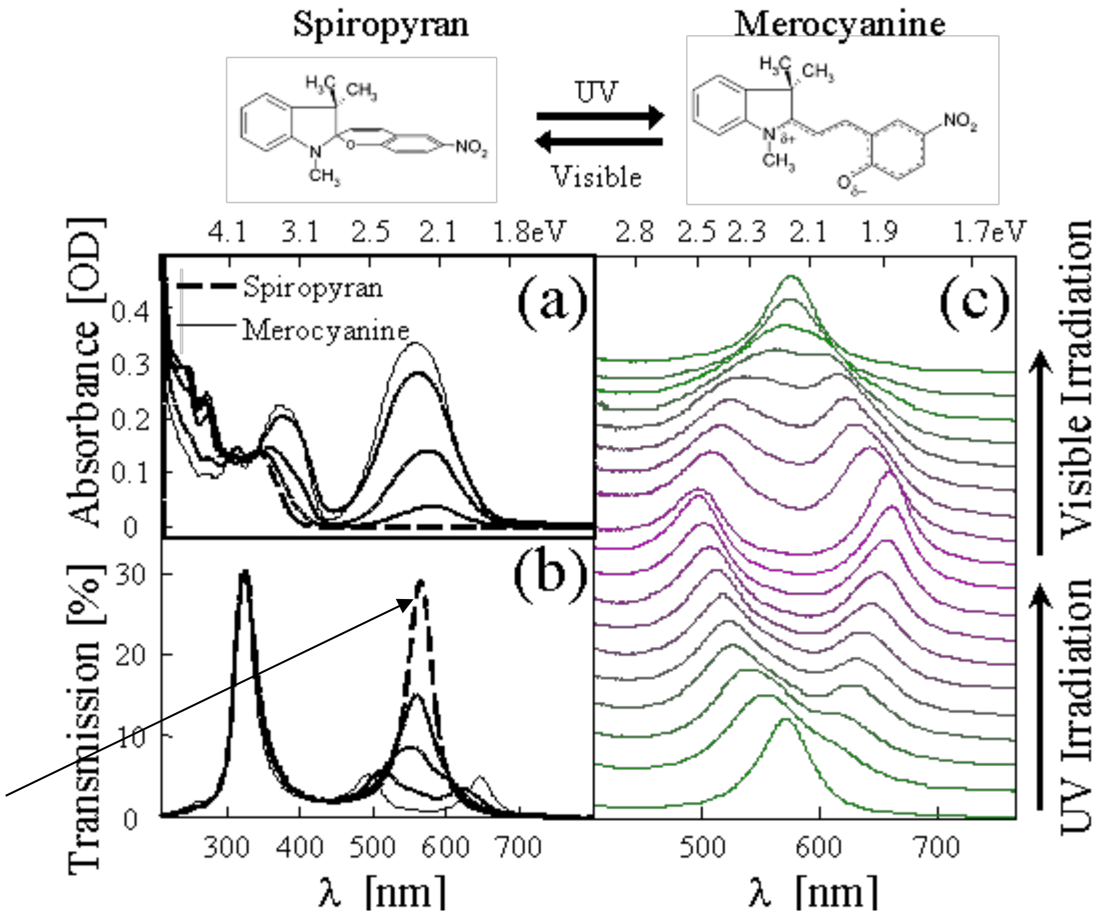
$$\tfrac{1}{2}\hbar\Omega_R >> kT$$

Fundamental configuration:

Material dressed by the Vacuum field

Reversible Ultra-Strong Coupling in a Metal Cavity:



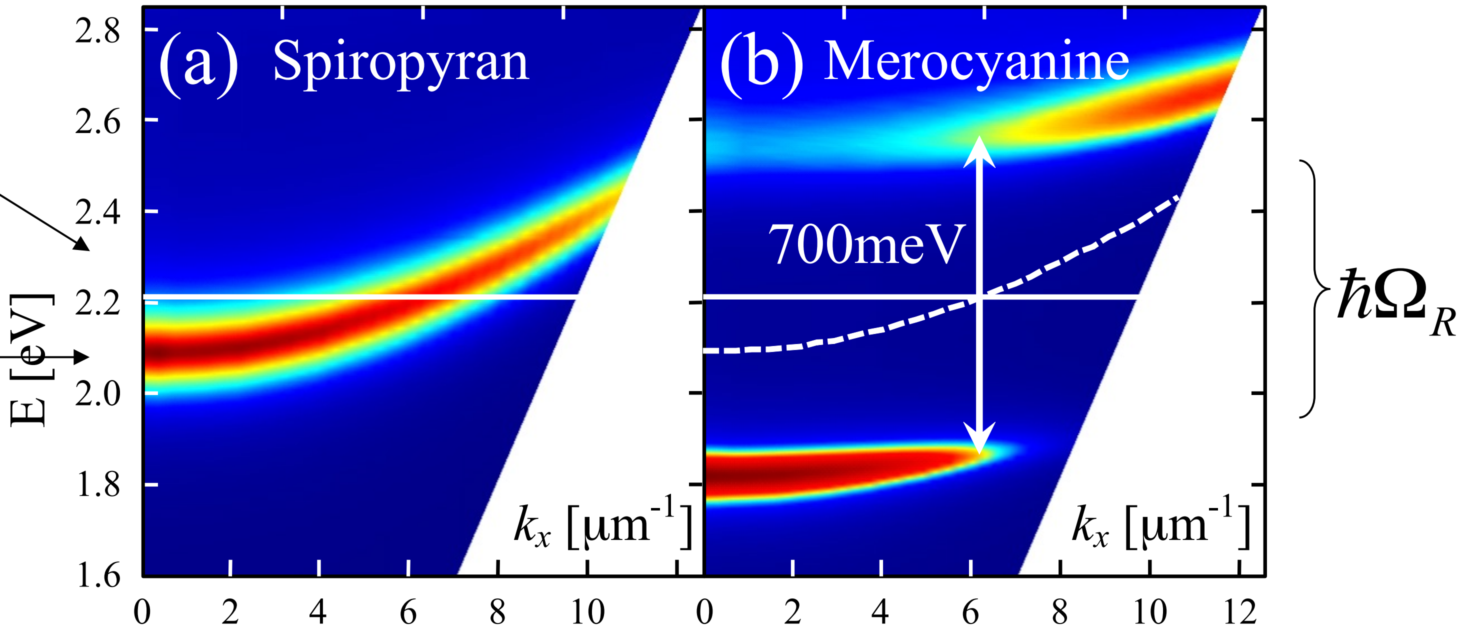


Fabry-Perot Mode of empty cavity

Dispersion Curves of Cavity

MC peak

Fabry-Perot
cavity mode



Rabi Splitting: 1/3 of transition energy

Schwartz et al, PRL 106, 196405 (2011)

Cavity Strong Coupling:

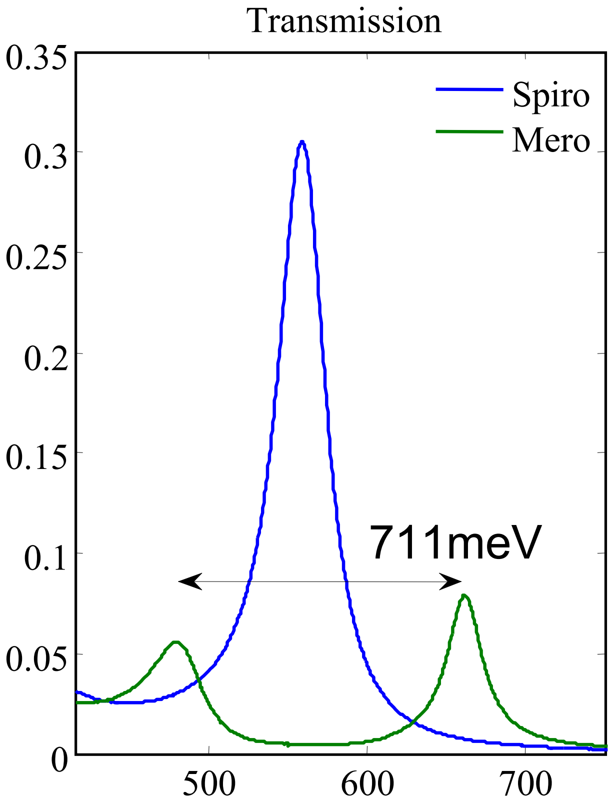
Transmission vs Absorbance Measurement

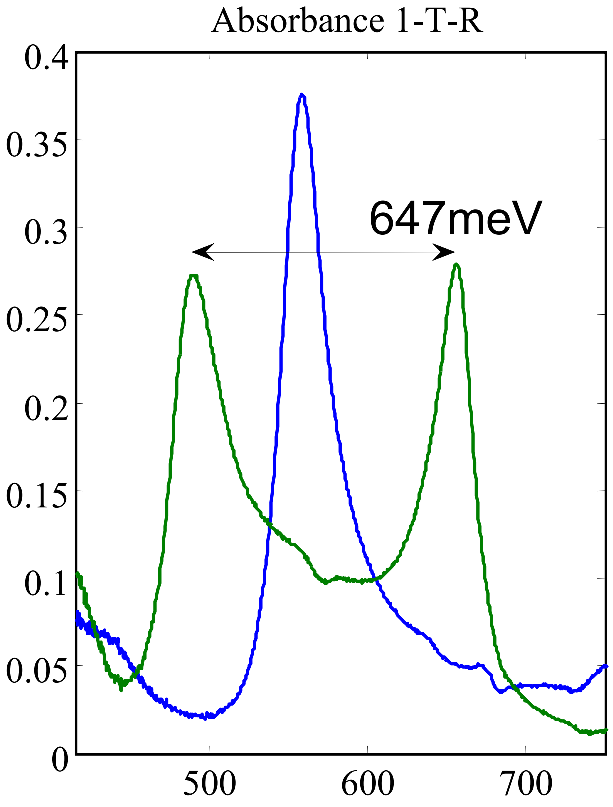
A world record….

And at room temperature

Splitting:

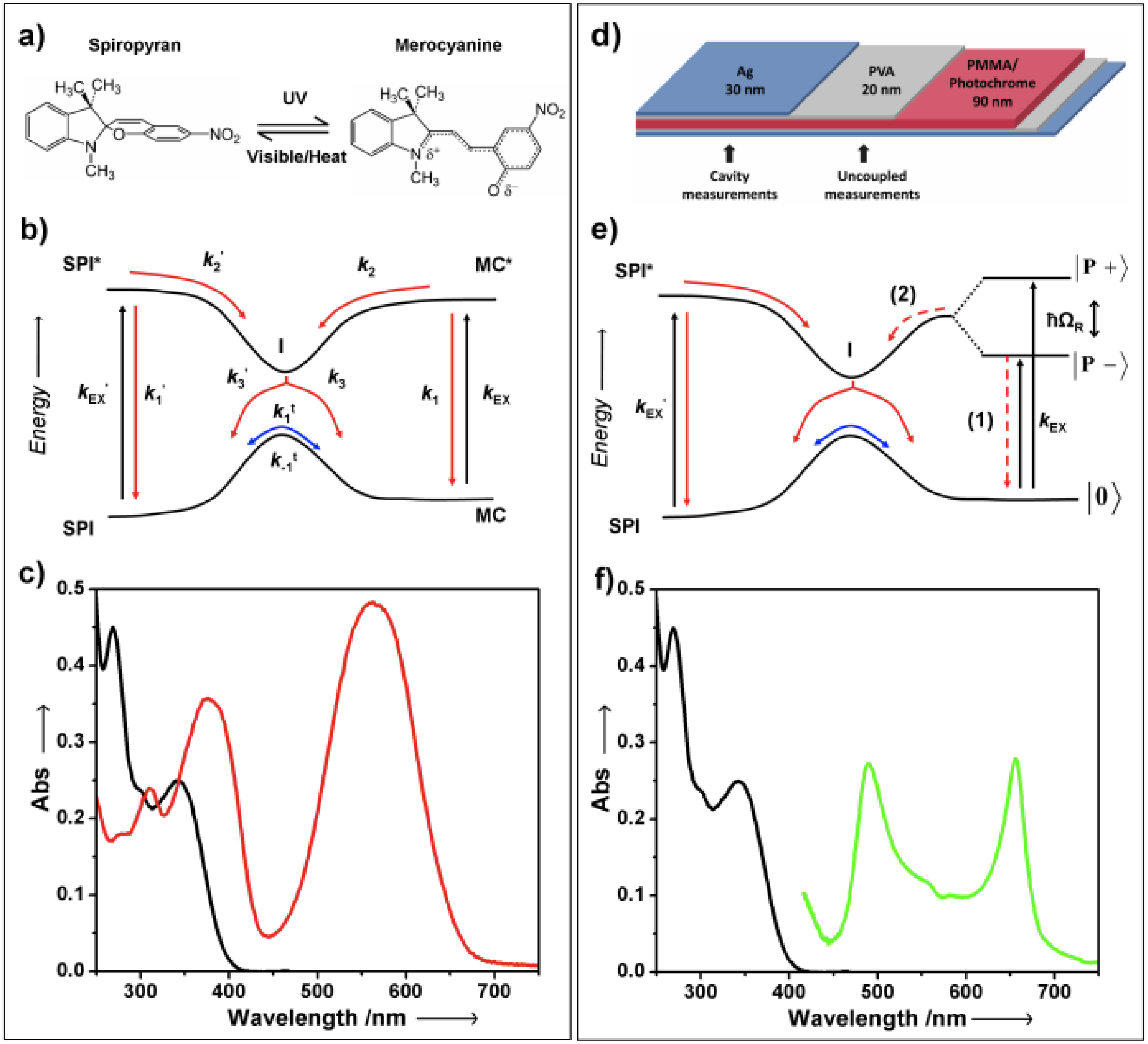
T > R > A or E





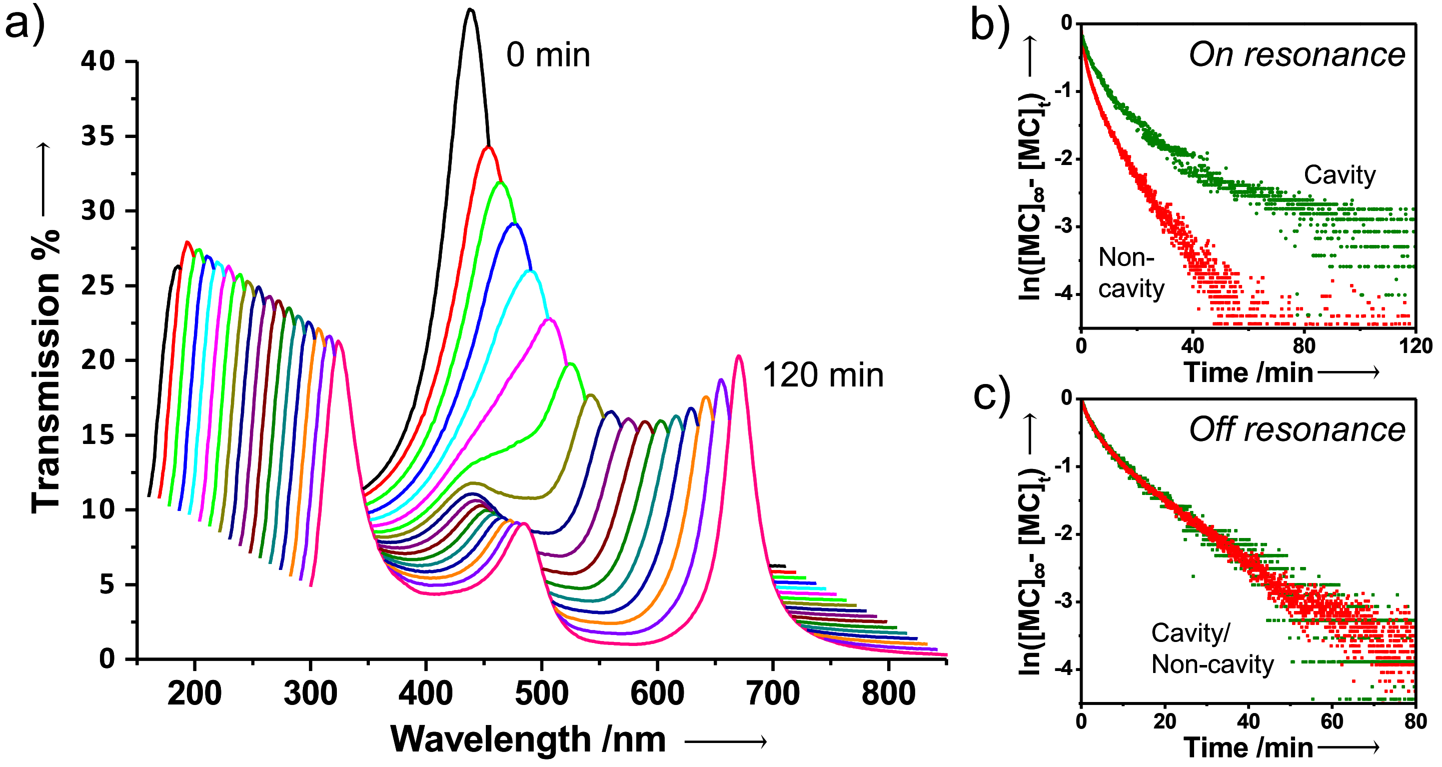
Rabi Oscillations: 7 fs
Dissipation rate of cavity: 25 fs
Dissipation of Excited state (non-rad lifetime): > 10 ps

Chemistry of Coupled Systems



Hutchison et al, Angew. Chem. 2012

Chemical Kinetics in the Coupled Regime



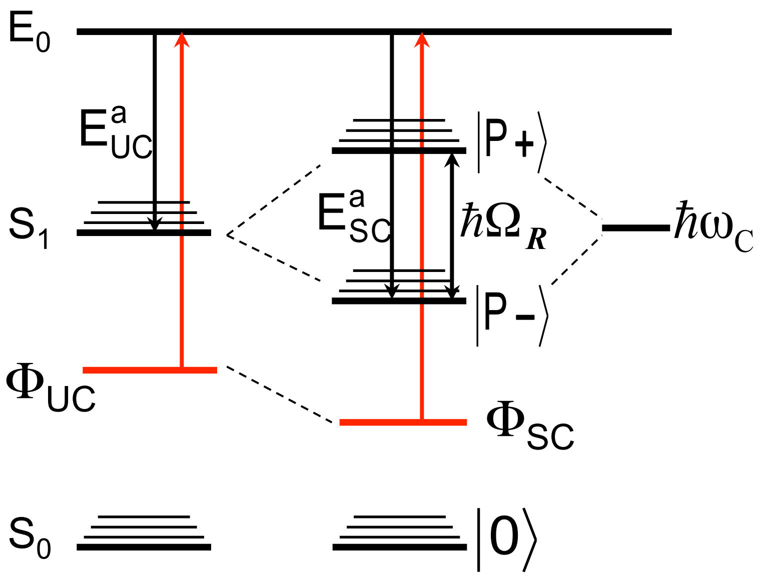
Rate decreases
MC yield increases

$$\frac{\mathrm{d[MC]}}{\mathrm{dt}} = -\mathrm{k}_{\mathrm{obs}}[\mathrm{MC}] + \mathrm{b}$$

$$k_{obs} = \left(\frac{k'_3}{k_3 + k'_3} \frac{k_2}{k_1 + k_2} + \frac{k_3}{k_3 + k'_3} \frac{k'_2}{k'_1 + k'_2} \right) k_{ex}$$ and $$b = \frac{k_3}{k_3 + k'_3} \frac{k'_2}{k'_1 + k'_2} k_{ex}[SPI]_0$$

Hutchison et al, Angew. Chem. 2012

Strong coupling effect on Material Properties

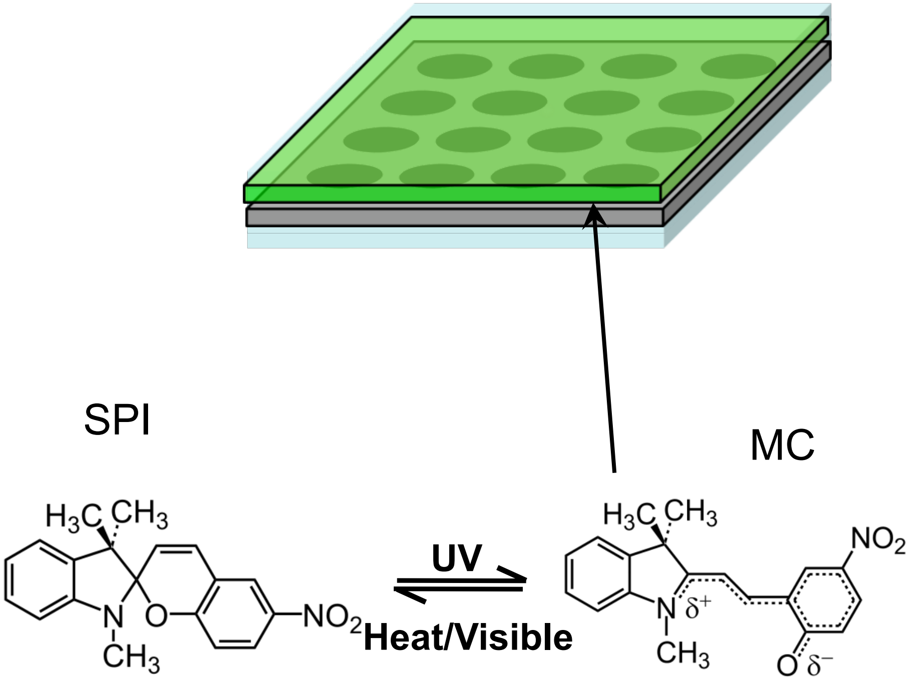


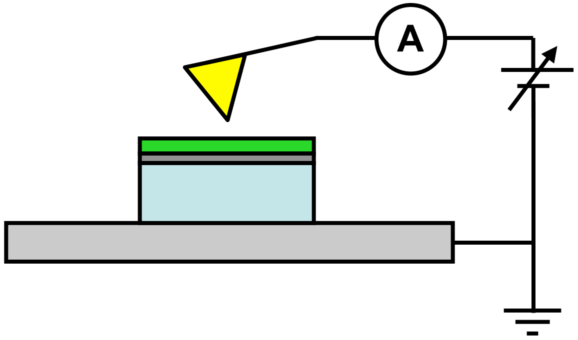
Tuning the Work function Φ by strong coupling with the Vacuum field

In collaboration with P. Samori, A. Liscio, V. Palermo

The Work function is measured with a Kelvin Probe

(in the dark, no contact)





Kelvin Probe Force Microscope

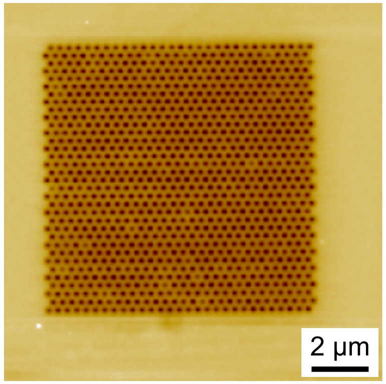
Measures change in capacitance

In collaboration with P. Samori, A. Liscio, V. Palermo

Strong coupling induced change in Work function on hole arrays

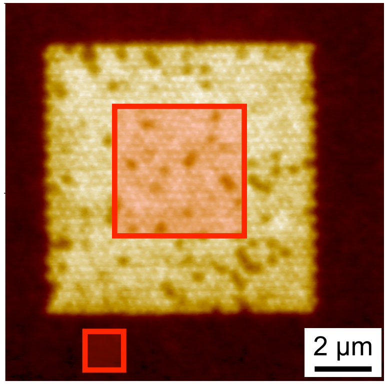
Topography

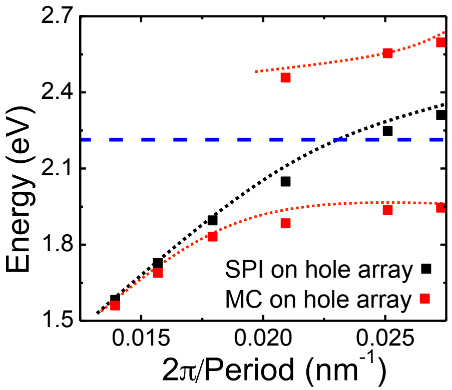
Z range = 100 nm



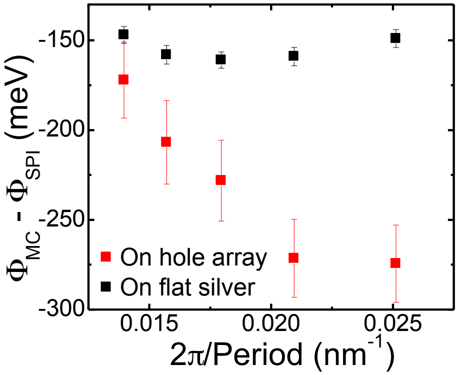
Potential

Z range = 200 meV

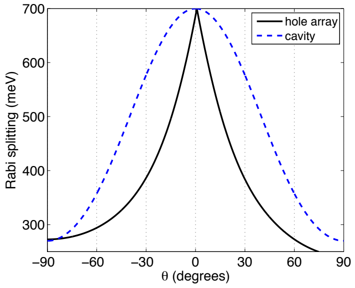




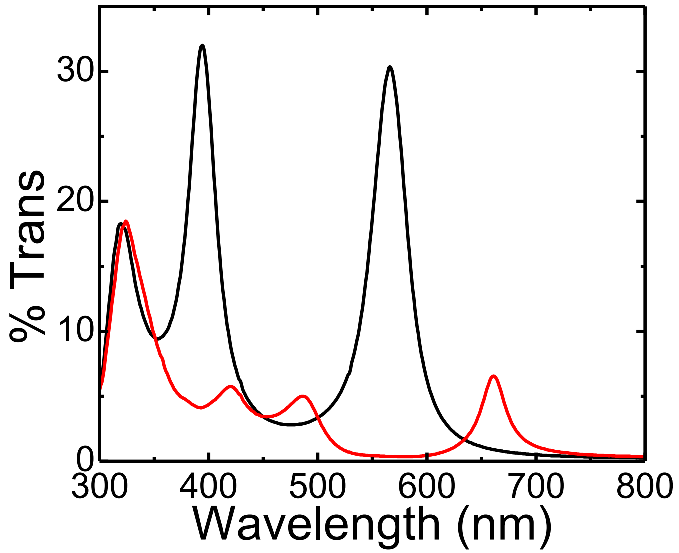
$$\hbar\Omega_R \cong 650 meV$$

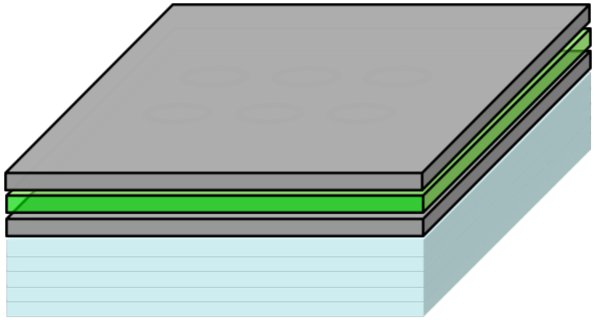


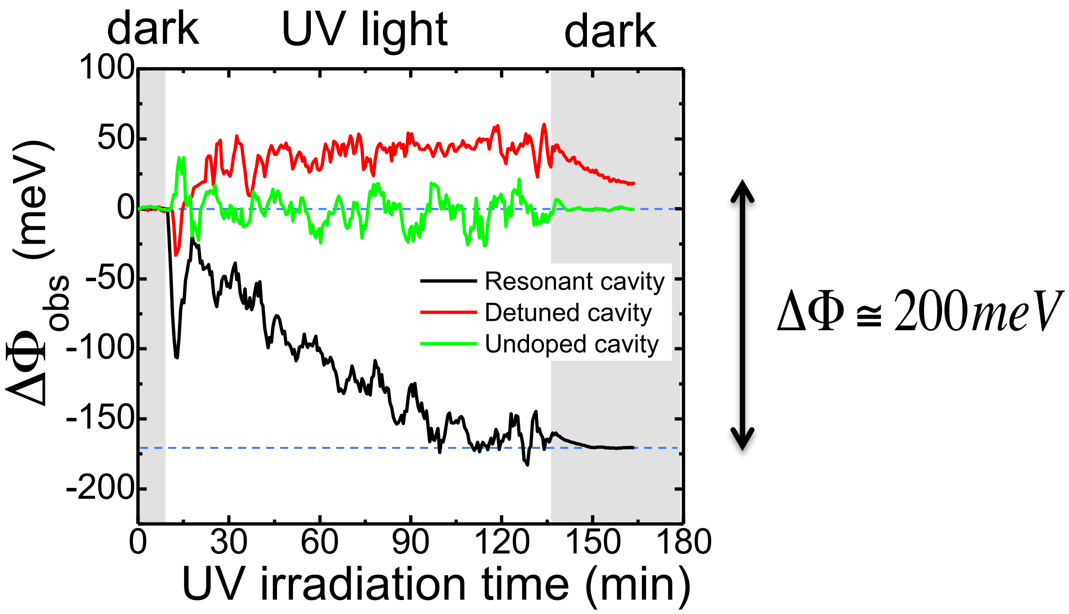
$$\Delta\Phi \cong 120 meV$$

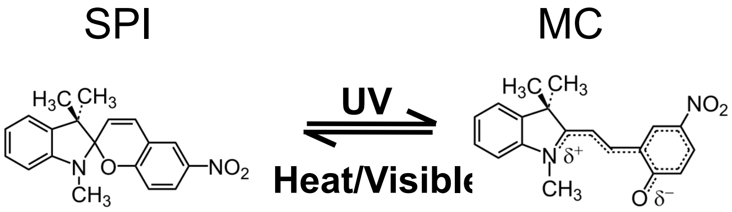


Strong coupling induced change in Work function measured for a Fabry-Perot cavity:

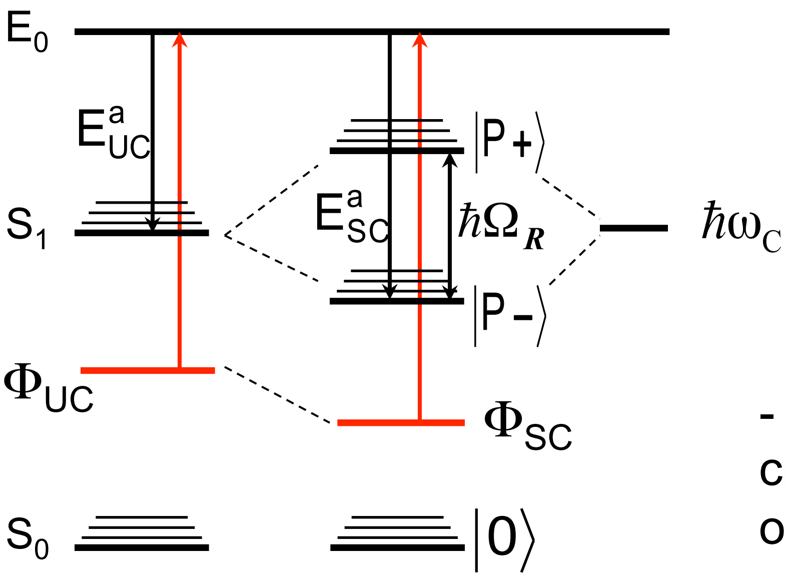








Tuning the Work function Φ by strong coupling with the Vacuum field



- Tuning the work function is critical for devices, specially organic devices such as OLEDs, etc.

- The work function becomes angle sensitive when dressed by the vacuum field, opening new possibilities for device design.

Consequences for Molecular and Material Sciences:

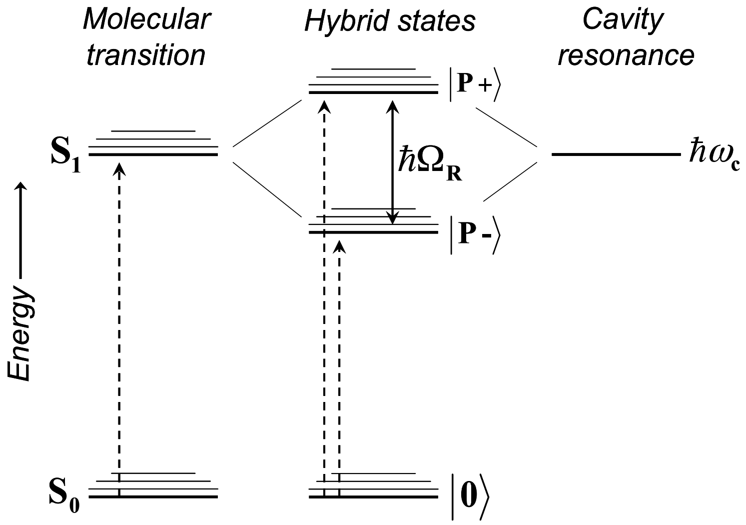
- New tool to modify the rate and yields of chemical reactions…

- New tool to tailor the material properties: work function, etc …

- **The coupled states are collective states…**

- **The molecules or material are dressed by the vacuum field**

- New theoretical considerations? QED Chemistry?



Looking for post-doc to work on strong coupling…

Current Funding:

French Ministry of Higher Education and Research
CNRS
ERC Advanced Grant