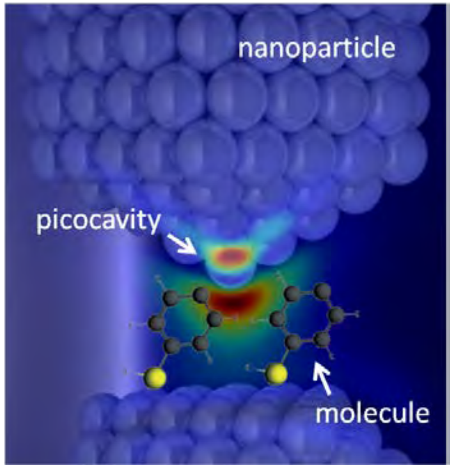
Light-matter interactions in plasmonic cavities

(Bringing nanophotonics to the atomic scale)

Javier Aizpurua

http://cfm.ehu.es/nanophotonics

Center for Materials Physics, CSIC-UPV/EHU and Donostia International Physics Center - DIPC
Donostia-San Sebastián



SPICE Workshop: Molecular electro-opto-spintronics

October 15-18, 2019, Mainz, Germany

Electromagnetic Coupling on an Atomic Scale

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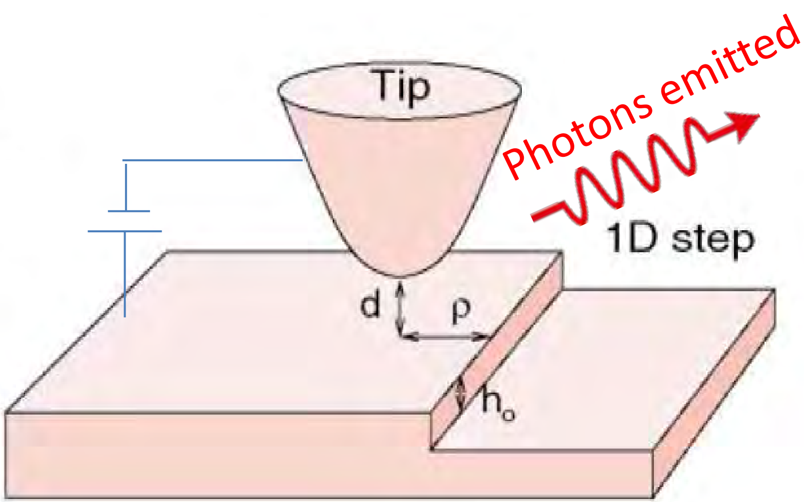
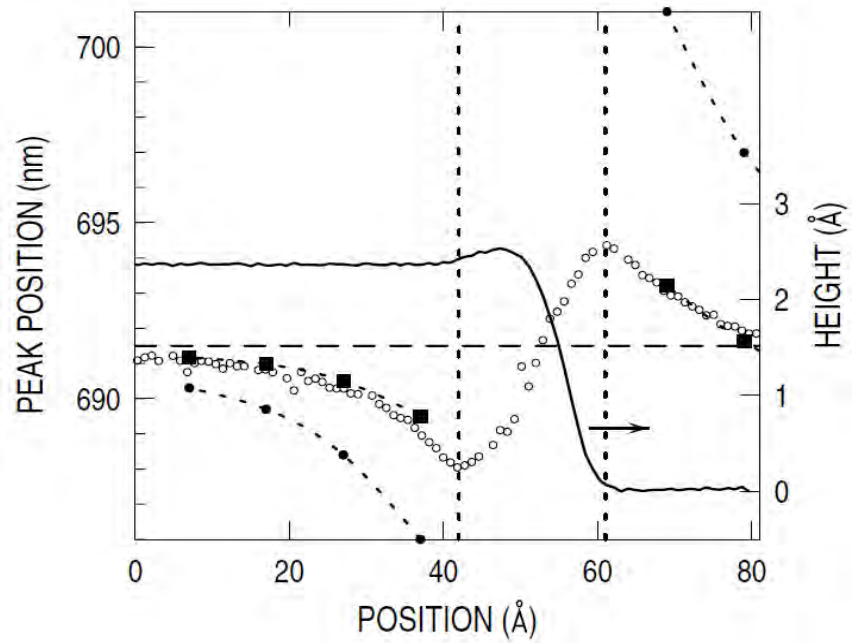
[3]University Outreach, Kristianstad University, SE-291 88 Kristianstad, Sweden
(Received 17 May 2002; published 24 September 2002)

Subatomic scale modifications of the tip-sample region cause spectral shifts of the fluorescence as demonstrated for a monatomic step

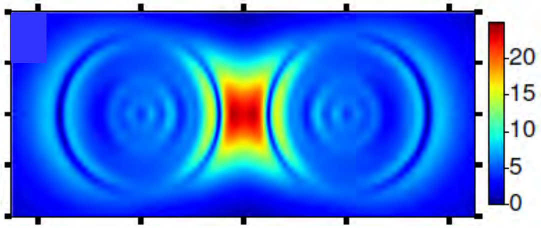




Light-matter interaction at the nanoscale

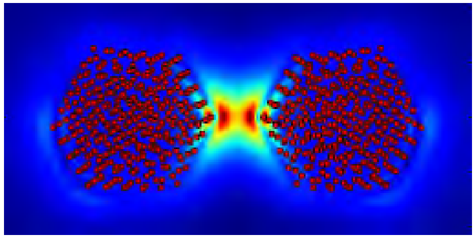
Intro to plasmonics

Plasmonic nanogap



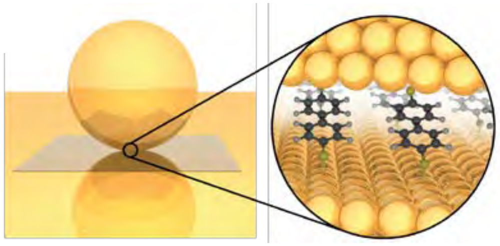
Quantum effects in nanogaps

Photoemission in nanogaps



Atomistic effects in field localization

Transport at optical frequencies



Exciton-plasmon coupling

Molecular electroluminescence in nanogaps

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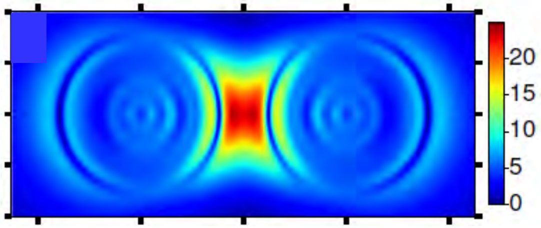
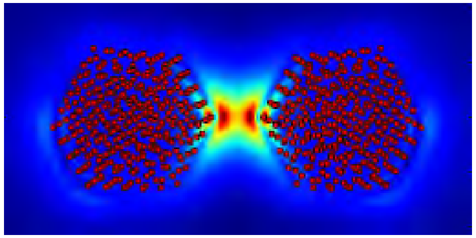
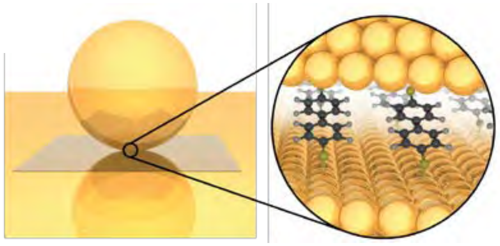
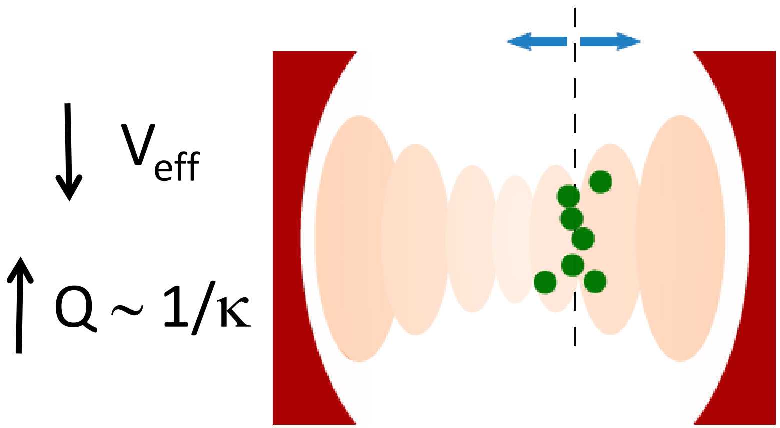




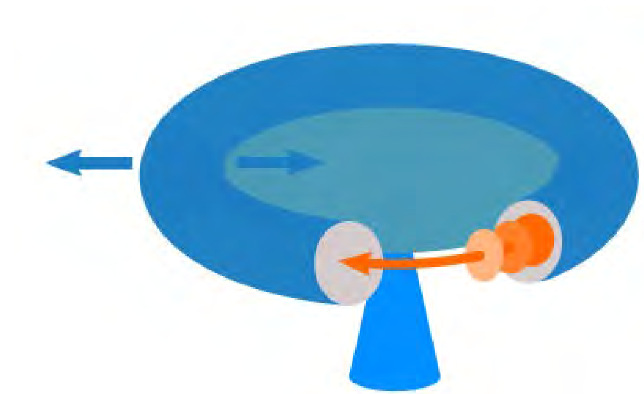


Optical cavities to enhance light-matter interaction

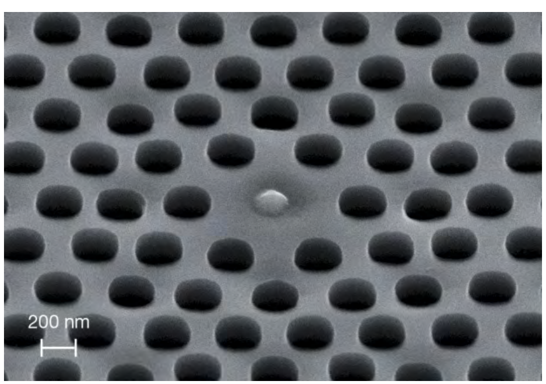
Optical mirrors



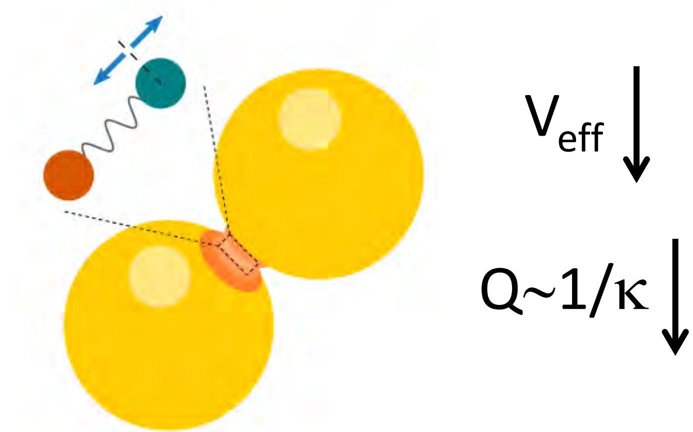
Dielectric resonator



Photonic crystals



Plasmonic cavity

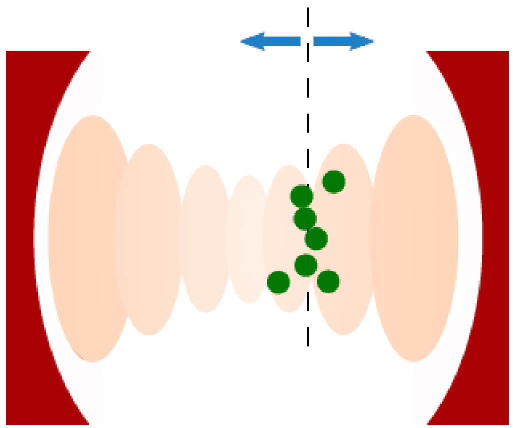


Optical cavities to enhance light-matter interaction

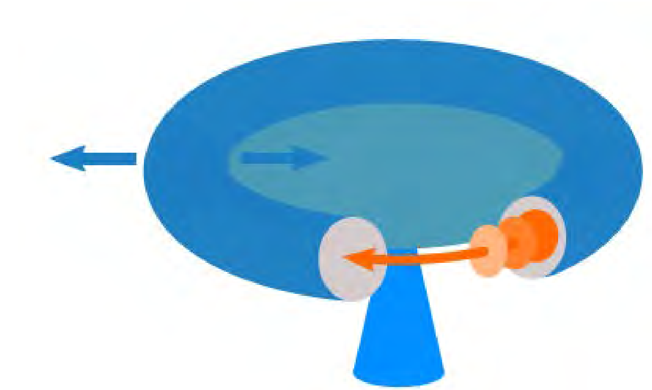
Optical mirrors

$\downarrow V_{eff}$

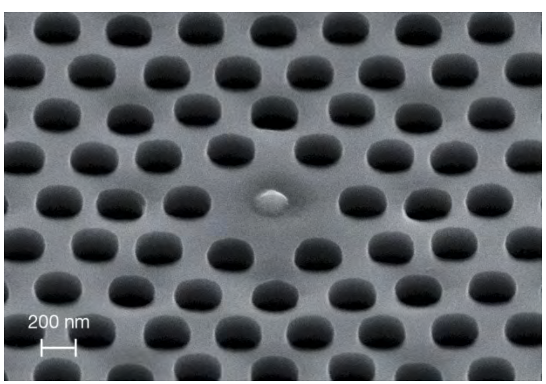
$\uparrow Q \sim 1/\kappa$



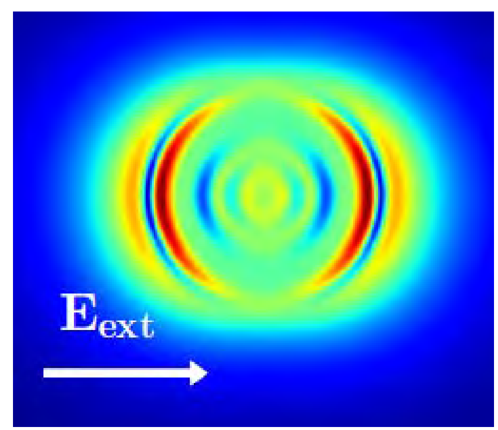
Dielectric resonator



Photonic crystals



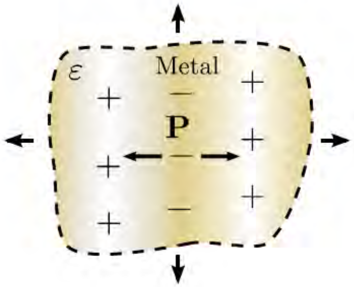
Plasmonic antenna

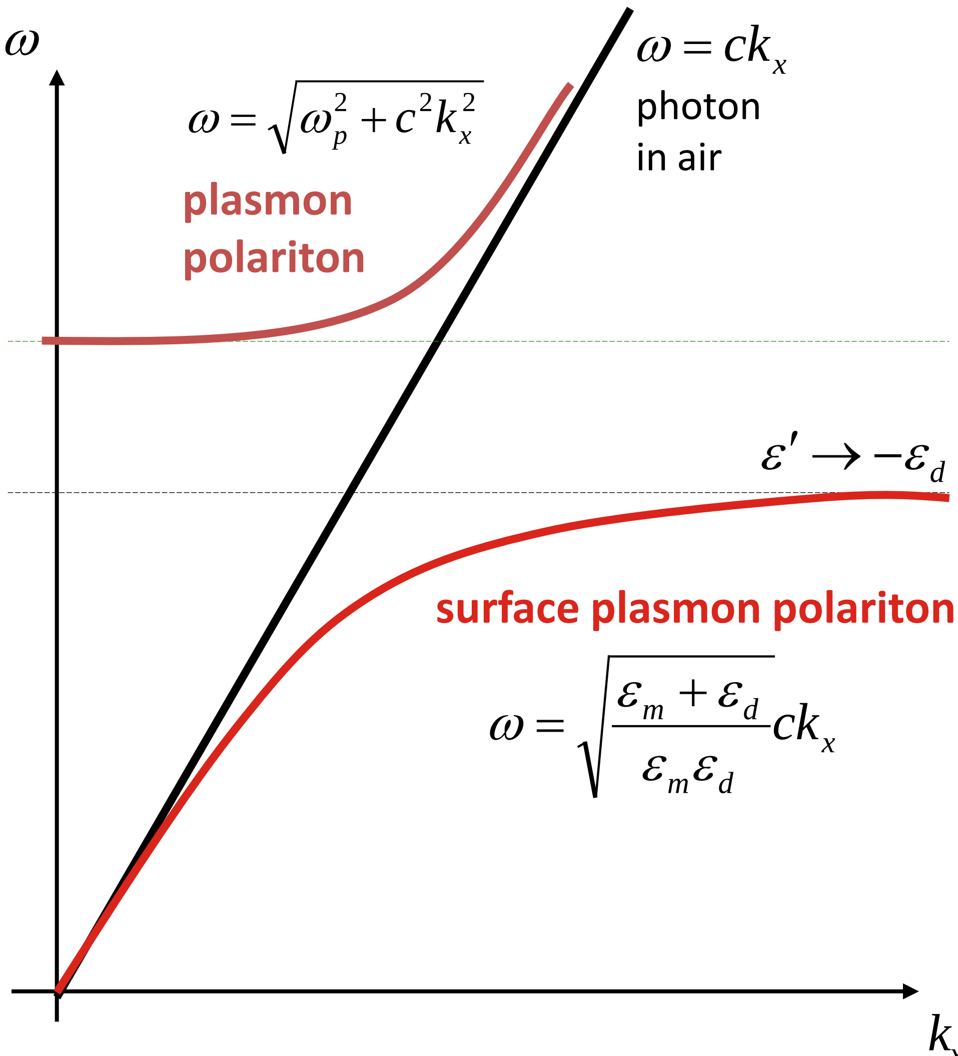


$V_{eff} \downarrow$

$Q \sim 1/\kappa \downarrow$

Bulk and Surface plasmon polaritons





ω_p

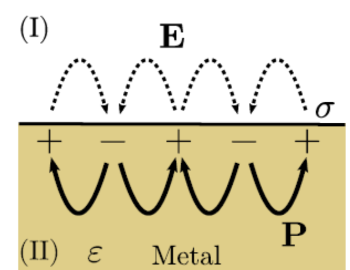
$$\omega_{SP} = \omega_p \sqrt{\frac{1}{1+\varepsilon_d}}$$

Dielectric function

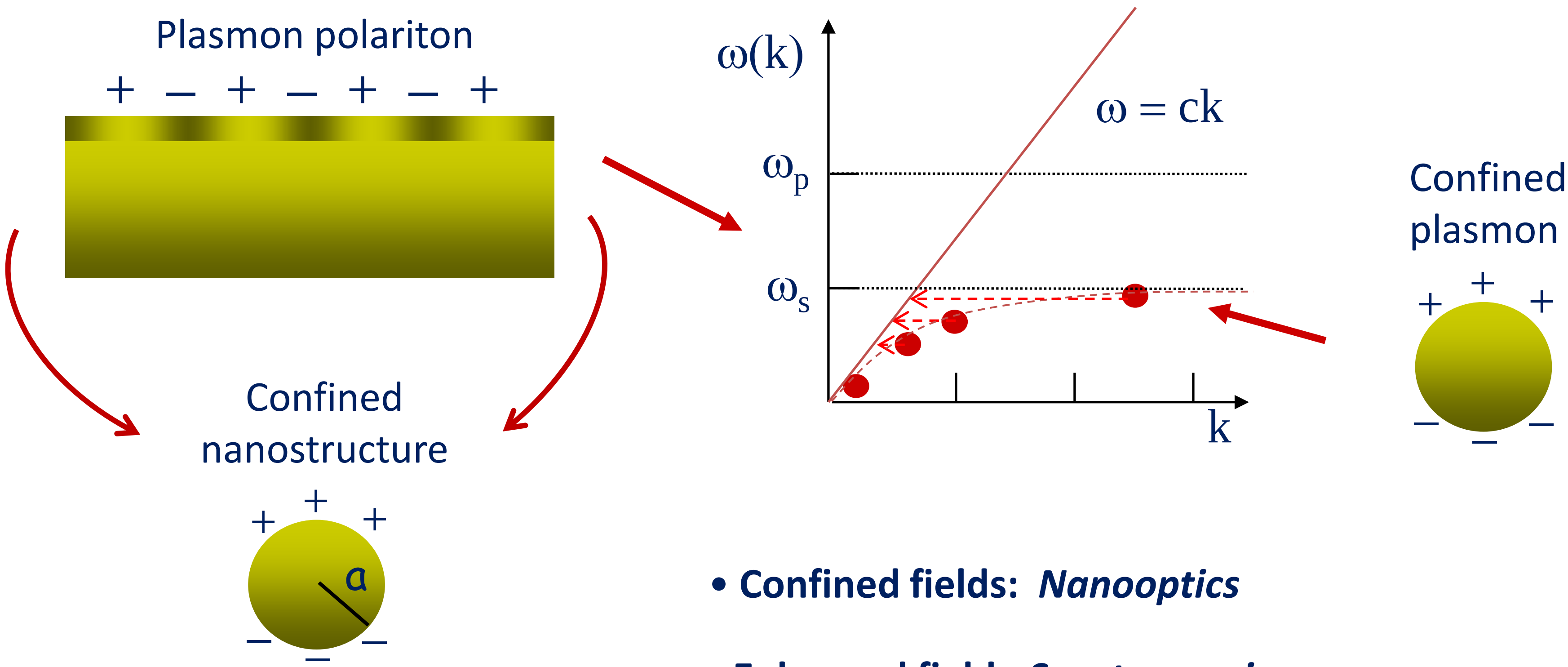
$$\varepsilon_m = 1 - \frac{\omega_p^2}{\omega^2}$$

Bulk plasmon

Surface plasmons collective oscillations of electron plasma near the surface



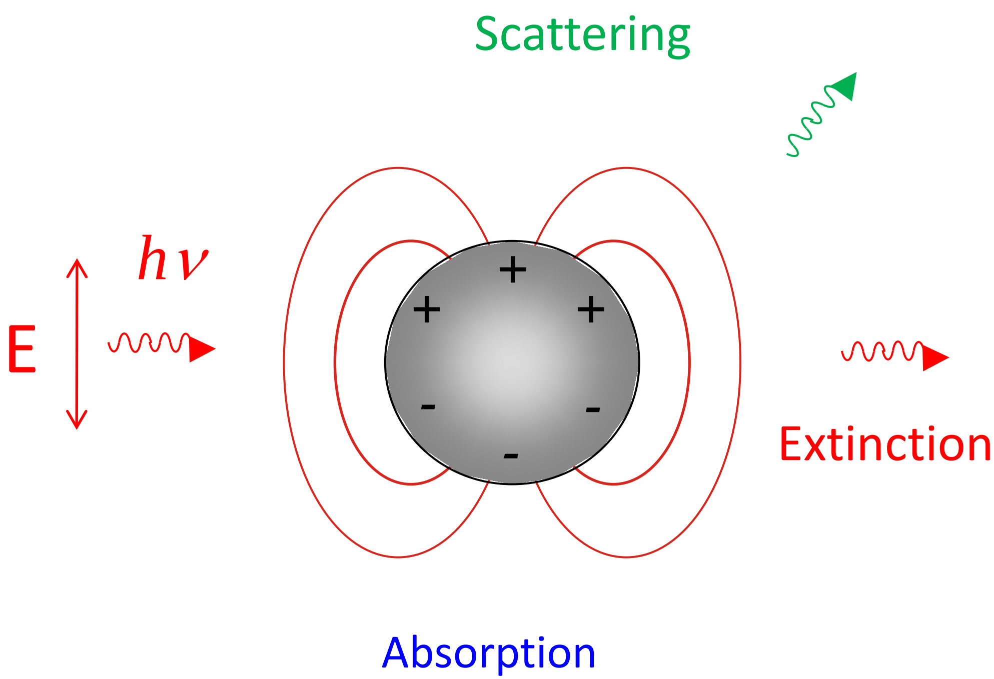
Nano-optics with localised plasmons

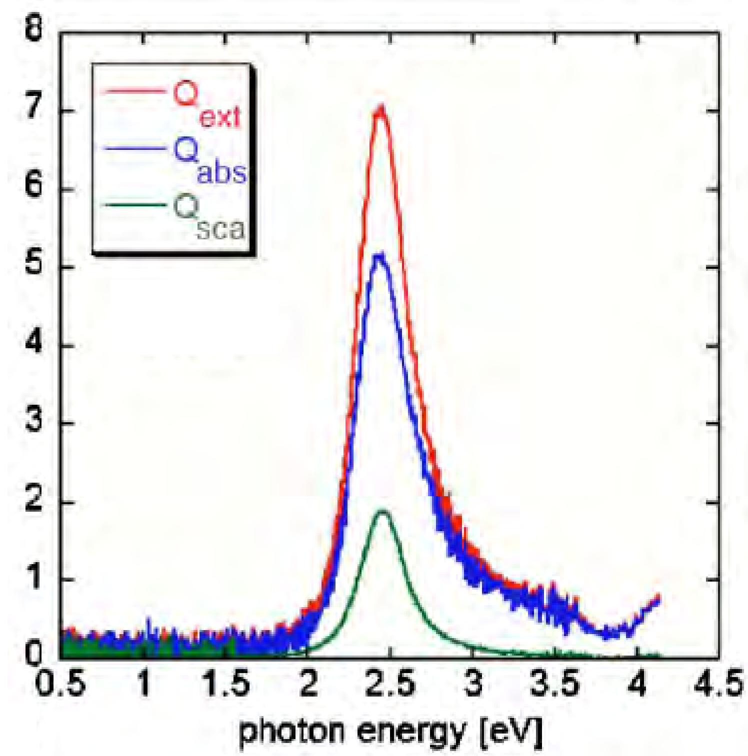


$$k \approx \frac{2\pi n}{2\pi a} \approx \frac{n}{a}$$

- **Confined fields:** ***Nanooptics***
- **Enhanced field:** ***Spectroscopies***
- **Tunability:** ***Nanogeometries: Visible → Infrared***

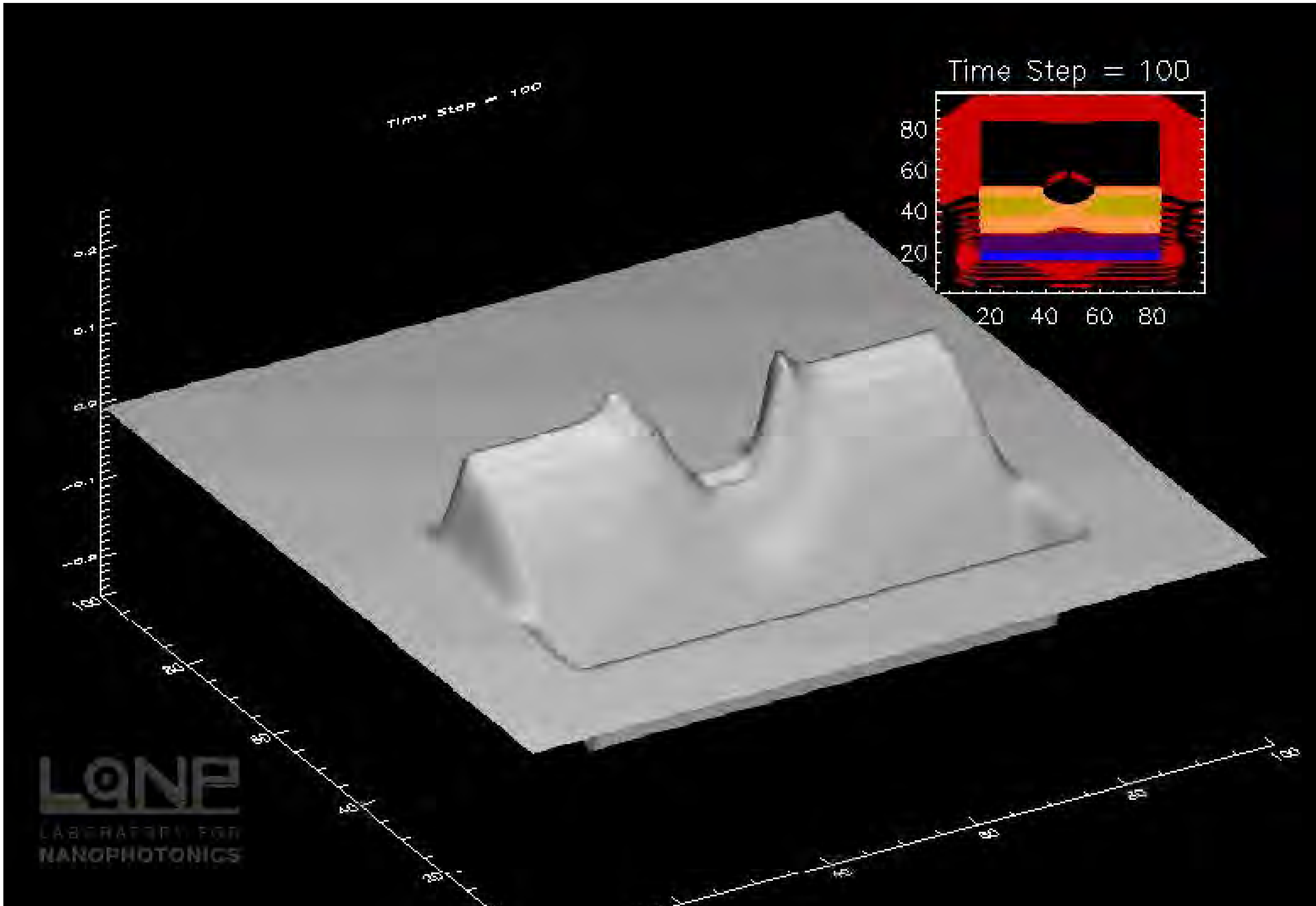
The simplest plasmonic resonator





Enhancement of absorption and emission:
Bringing effectively the far-field into the near-field

Excitation of a plasmon
in a metallic spherical nanoparticle by a pulse



Metal particle plasmons

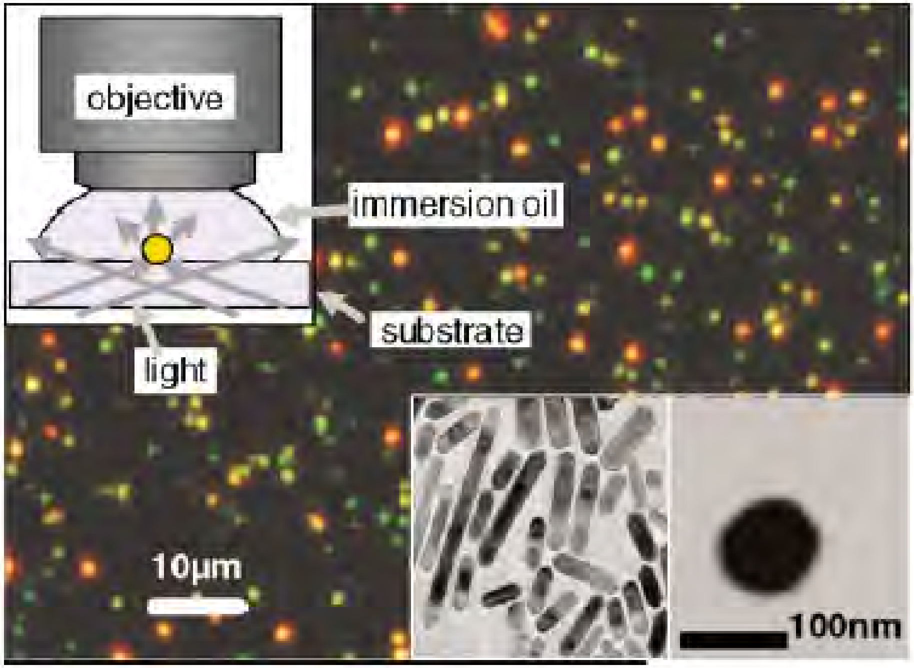
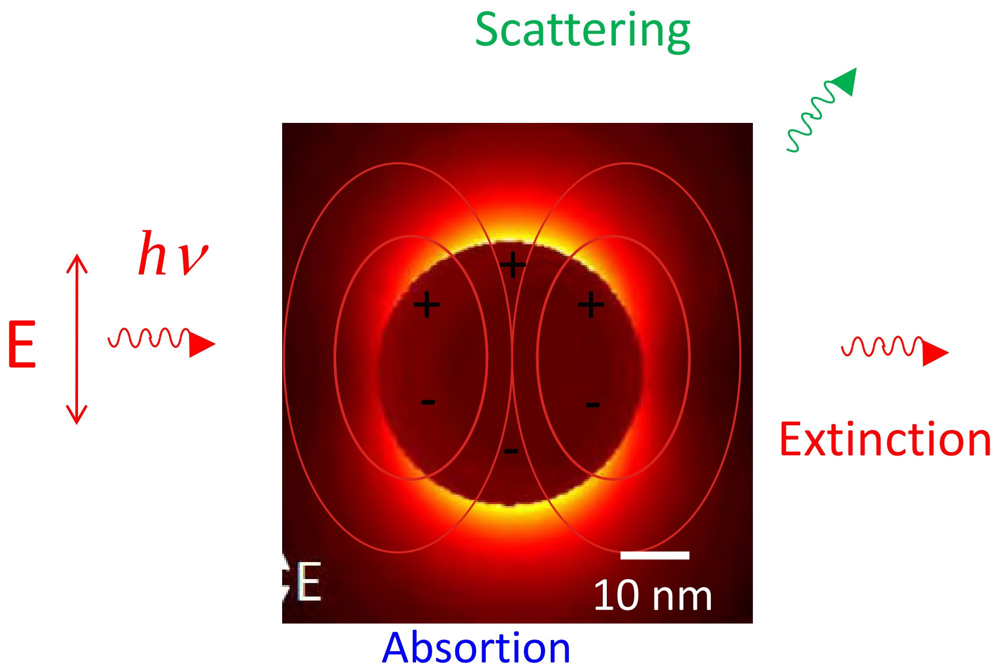
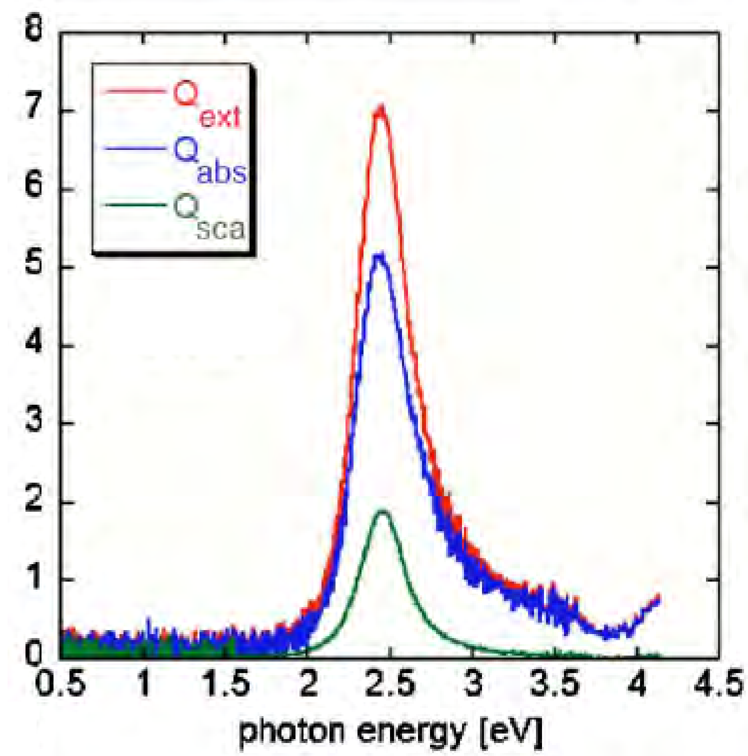


FIG. 2 (color). True color photograph of a sample of gold nanorods (red) and 60 nm nanospheres (green) in dark-field illumination (inset upper left). Bottom right: TEM images of a dense ensemble of nanorods and a single nanosphere.

- Kreibig, Vollmer, Optical properties of metal clusters, Springer1995
- Bohren, Huffmann, Absorption and scattering of light by small particles, Wiley 1983

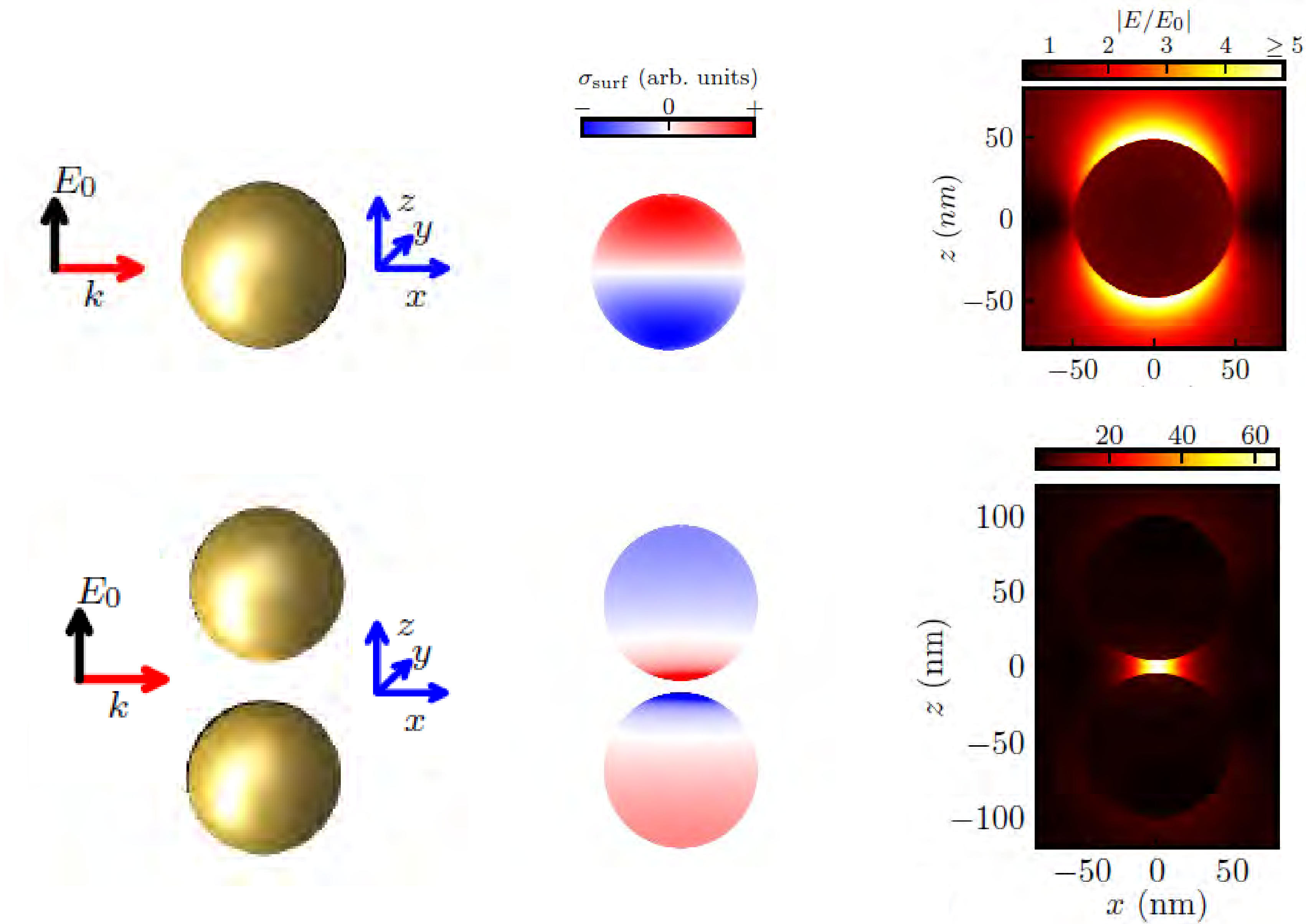
Beating the diffraction limit





Enhancement of absorption and emission:
Bringing effectively the far-field into the near-field

Plasmonic particle versus plasmonic cavity



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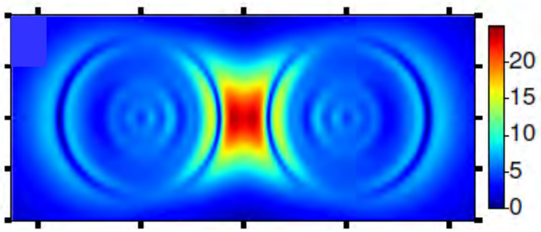
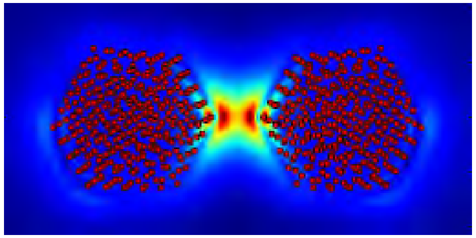


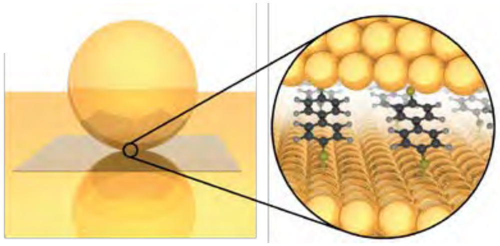
Quantum effects in nanogaps

Photoemission in nanogaps



Atomistic effects in field localization

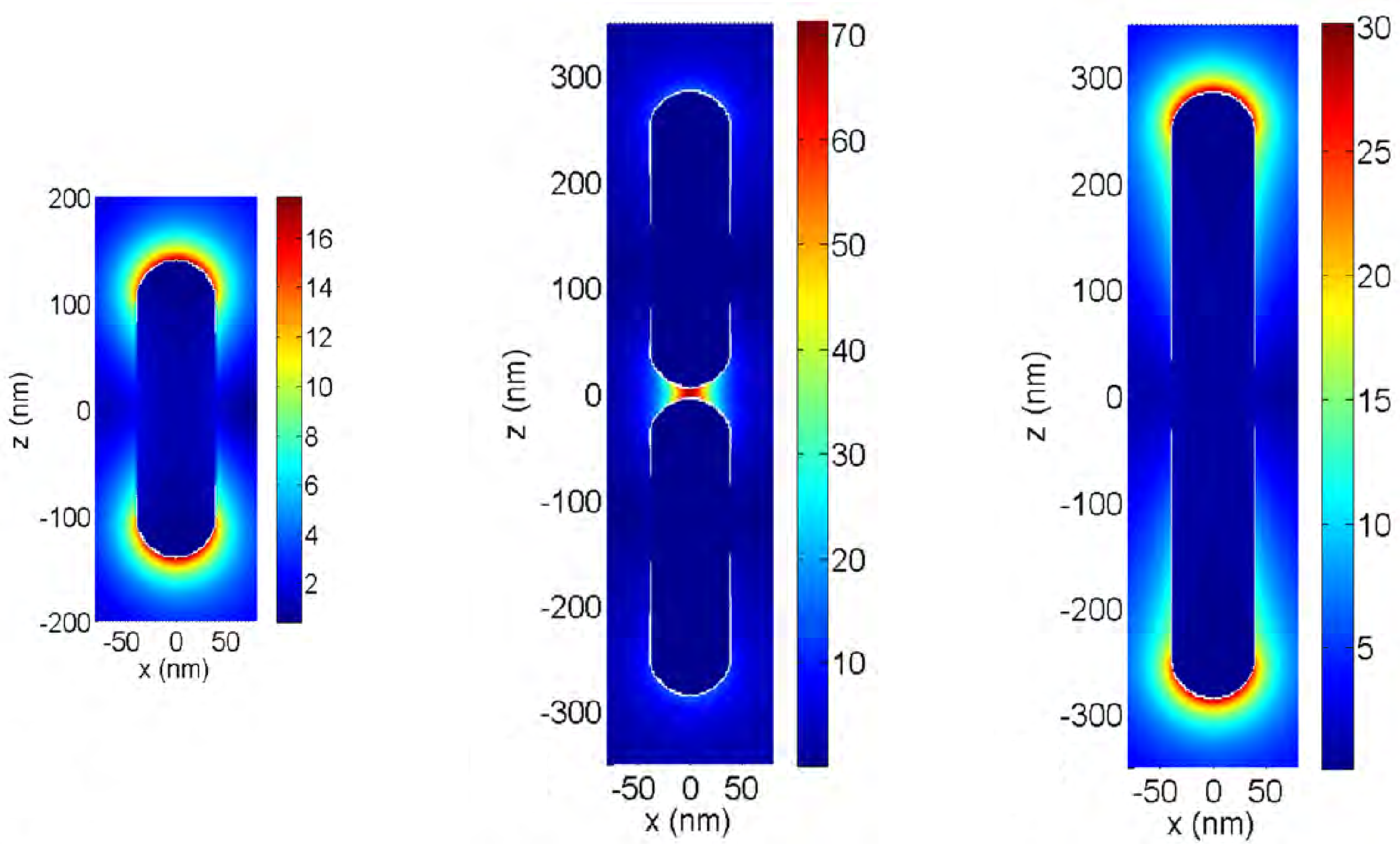
Transport at optical frequencies



Exciton-plasmon coupling

Molecular electroluminescence in nanogaps

Localization and Field-enhancement at nanogaps



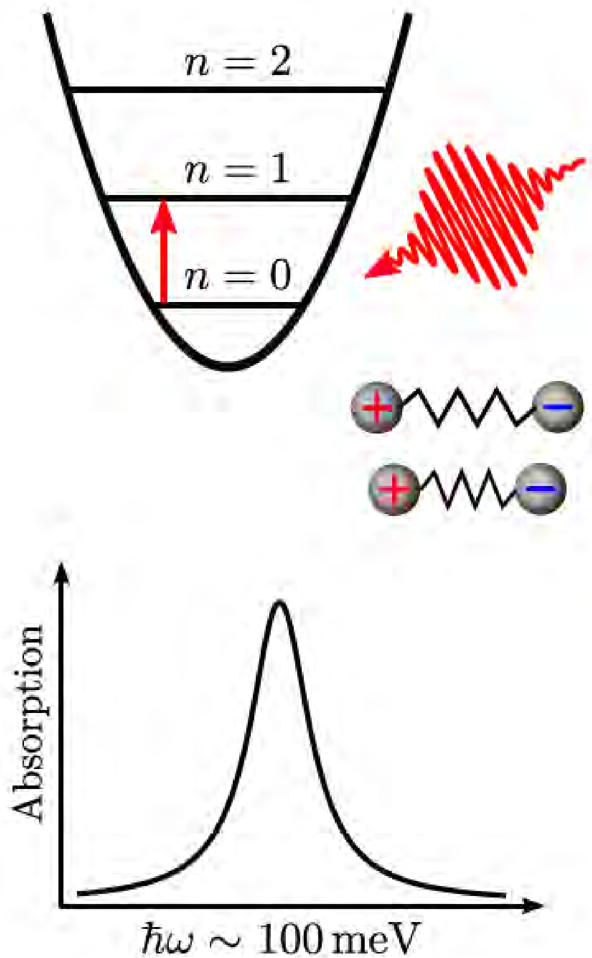
Single antenna

Gap-antenna
Bonding Dimer Plasmon

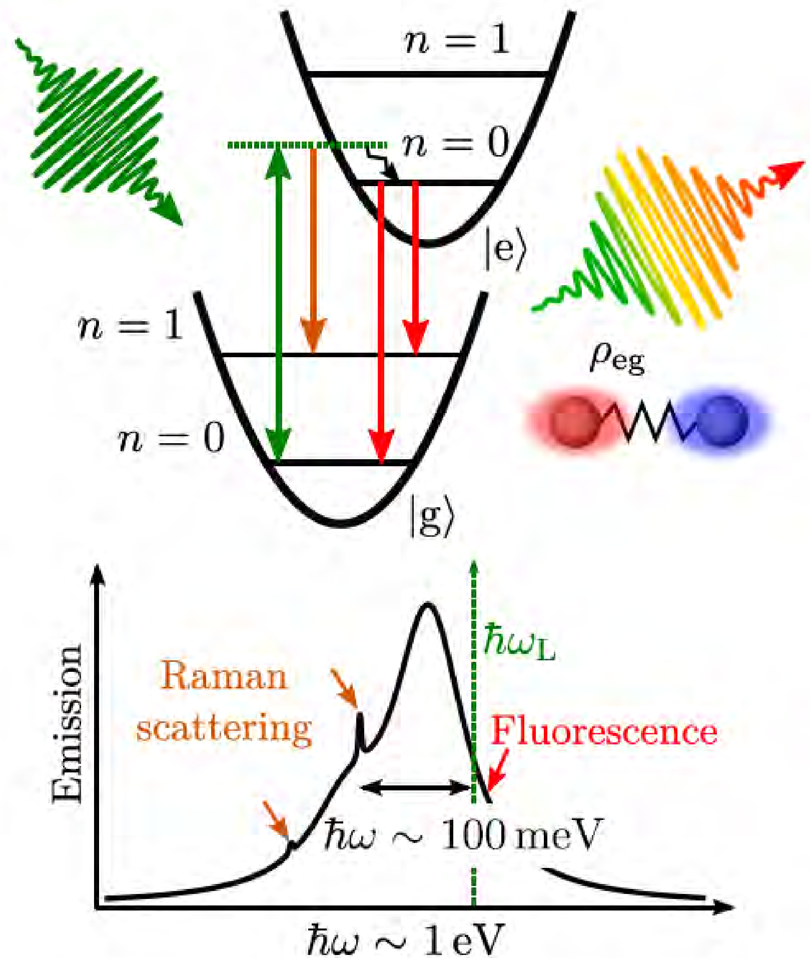
Large dipole
Charge Transfer Plasmon

Molecular spectroscopy: Excitons and vibrations

Infrared absorption

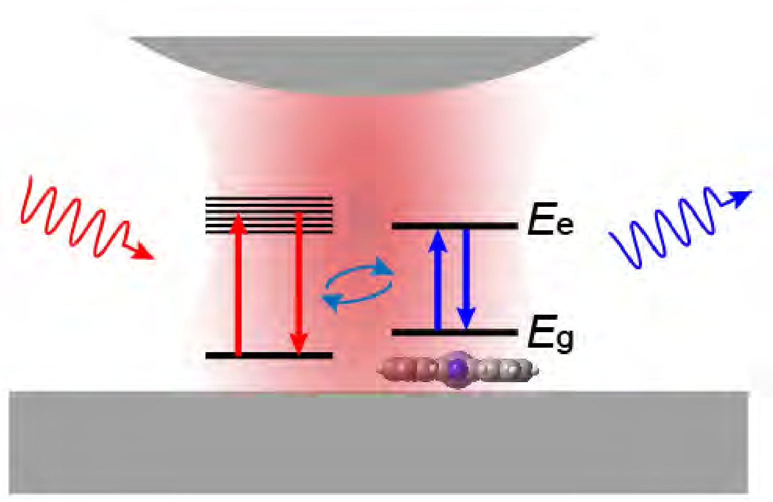


Fluorescence and Raman scattering



Coupling of cavity photons and matter excitations

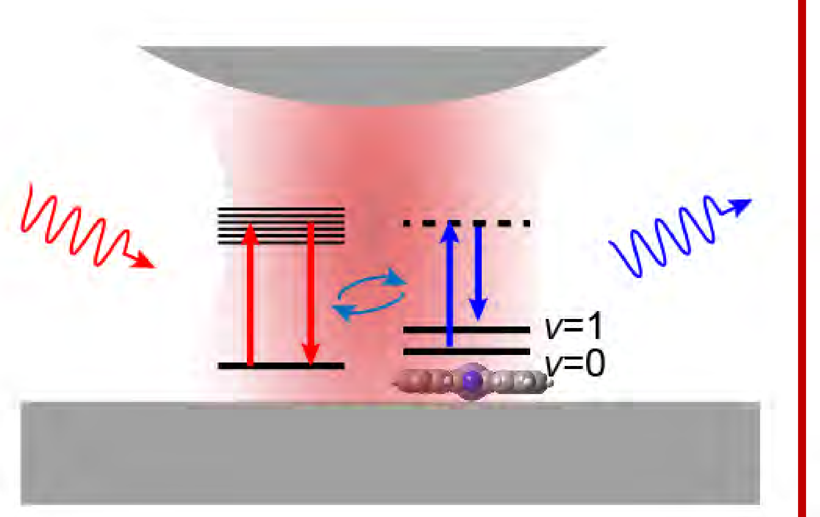
Plasmon-Exciton Coupling



Surface-enhanced

Absorption, Scattering,
Fluorescence

Plasmon-Vibration Coupling



Surface-enhanced

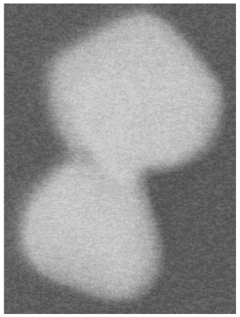
IR Absorption,
Raman Scattering

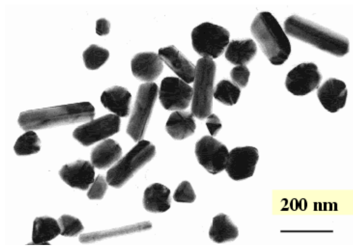
$V_{eff}\downarrow$

Plasmonic cavity assisting in spectroscopy: SERS

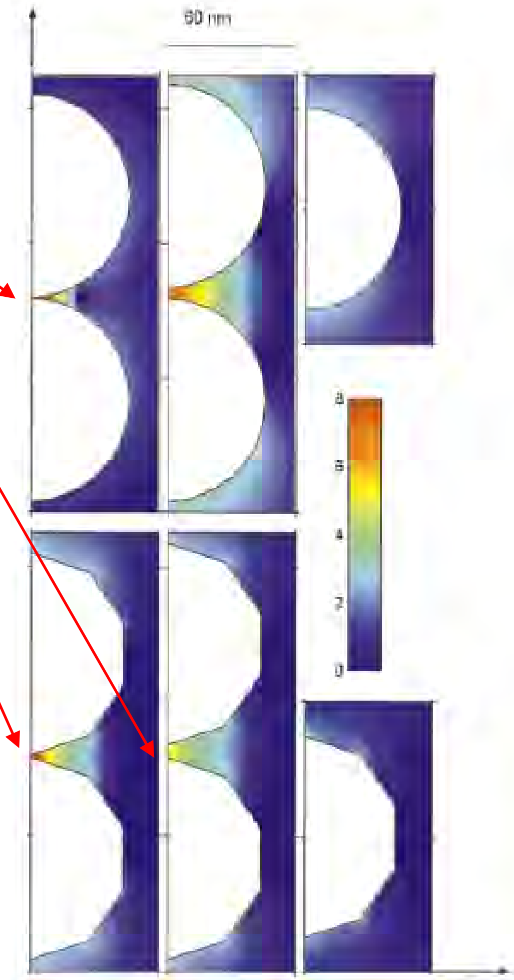
Xu et al. Phys Rev. Lett. (1999)

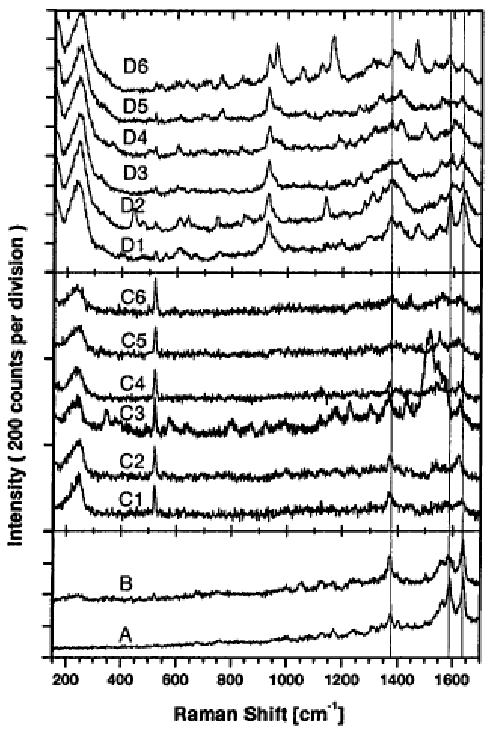
Xu et al., Phys. Rev. E. 62, 4318 (2000)





Hot sites





topography

amplitude

phase

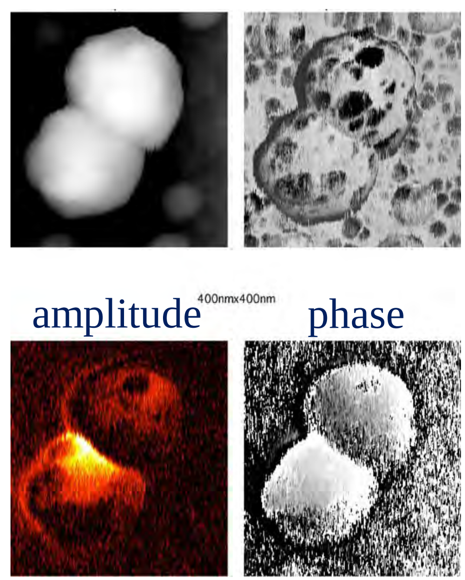
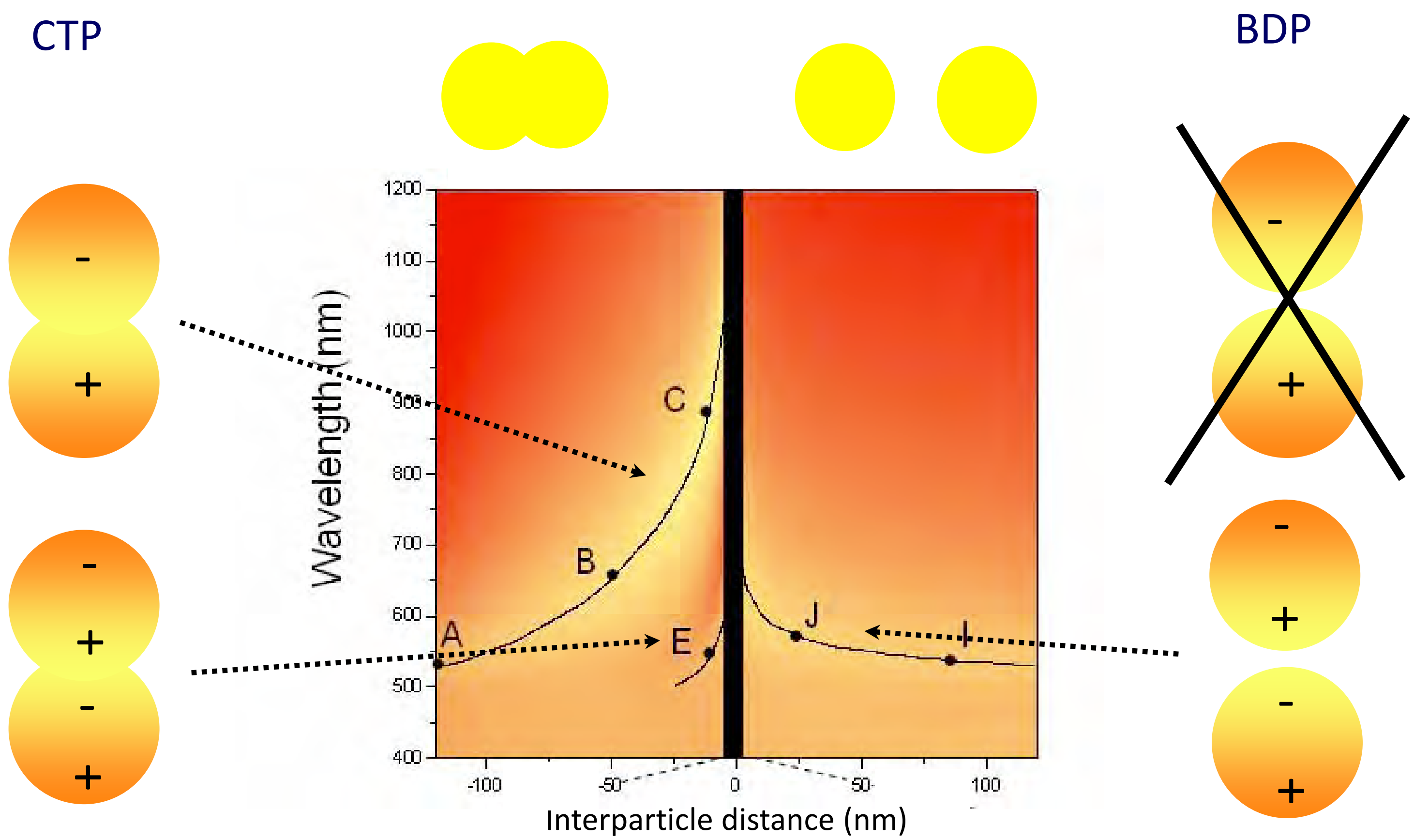


Image obtained by R. Hillenbrand,
(Max Planck, Munich)

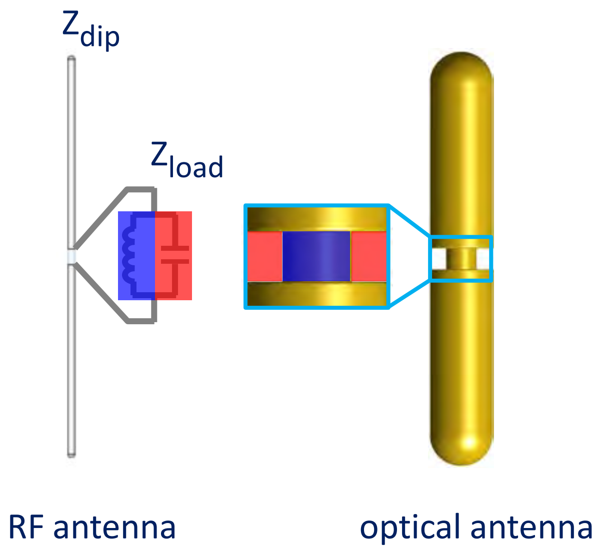
The color of gaps

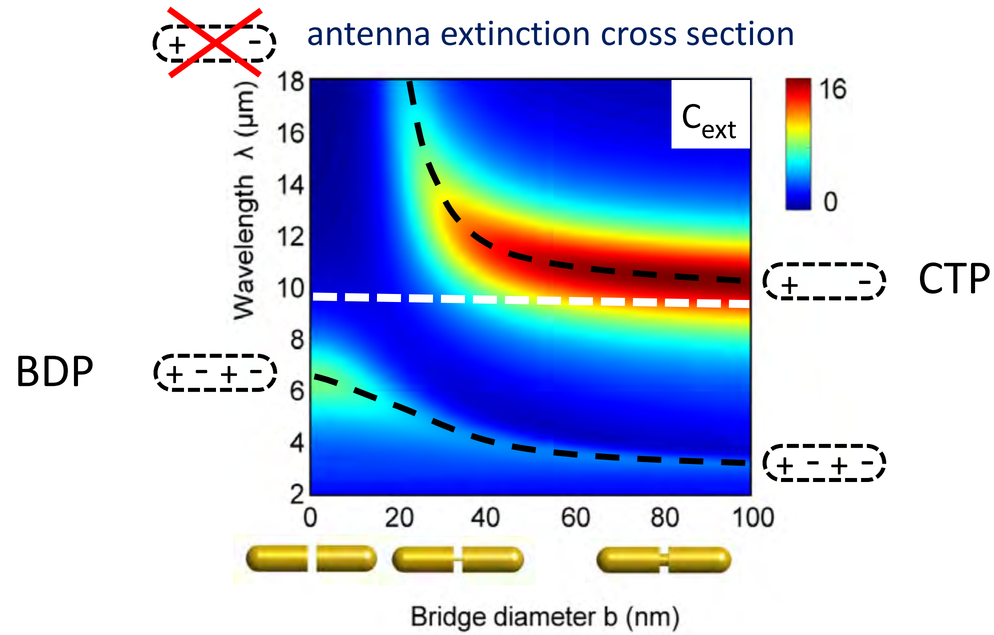


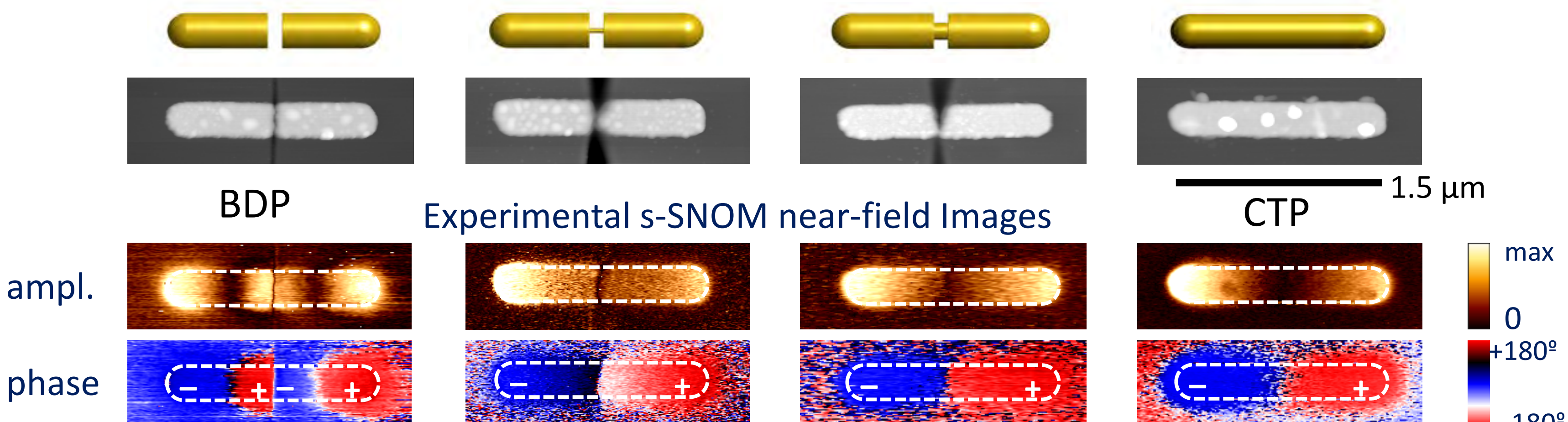
I. Romero, J. Aizpurua, G. W. Bryant and F. J. Garcia de Abajo, Optics Express 14, 9988 (2006)

Controlling antenna loading with metallic bridges

M. Schnell, A. García-Etxarri, J. Aizpurua, and R. Hillenbrand, Nature Phot. **3**, 287-291 (2009)







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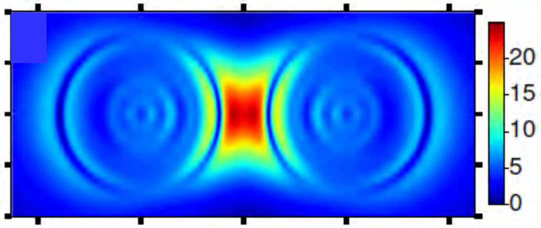
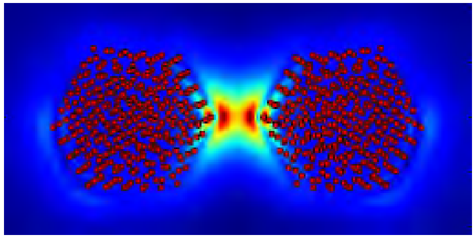
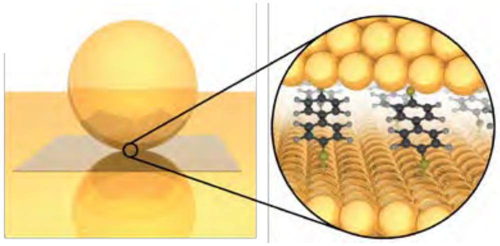
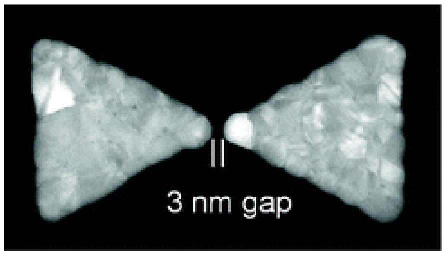




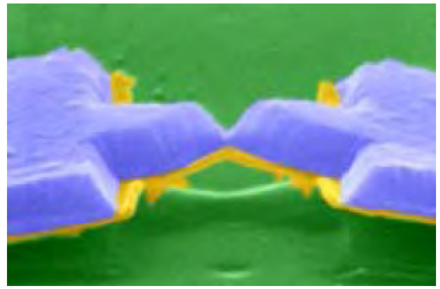


(Sub)nanometric plasmonics

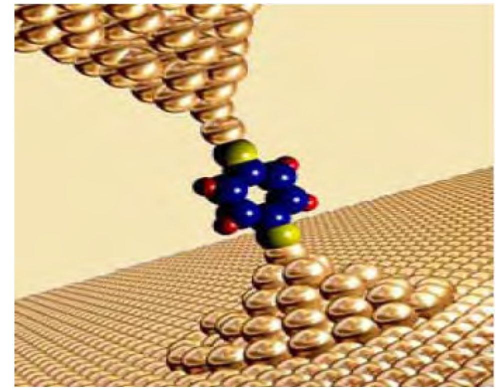
lithography



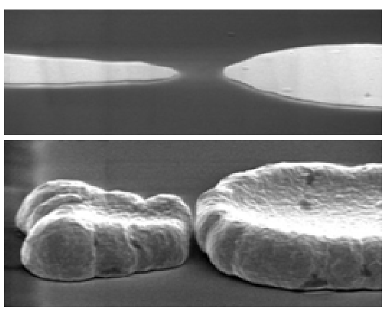
break junctions



STM

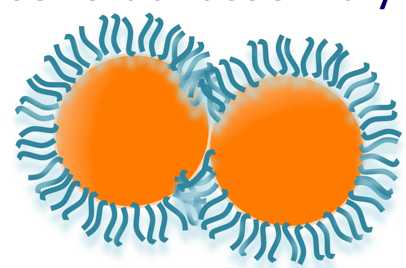


electrochemistry

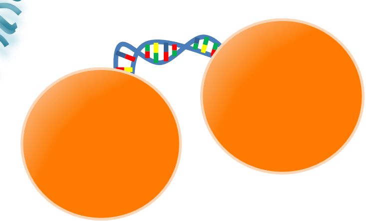


electro-migration

colloidal assembly

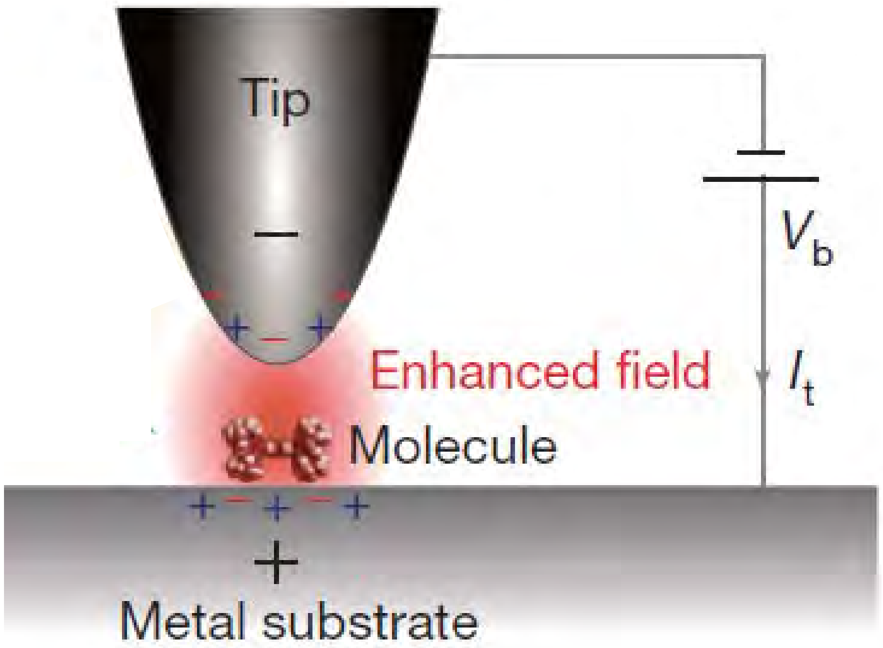


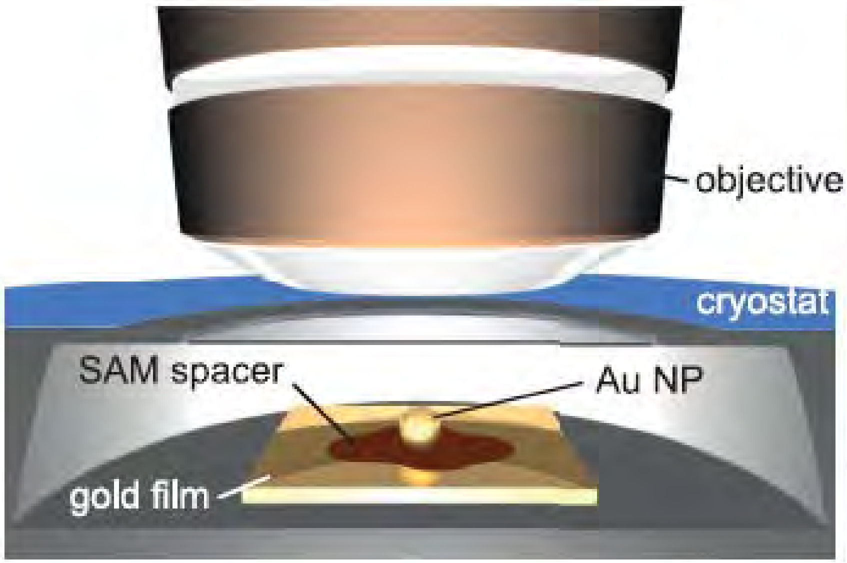
molecules



Experimental approaches provide nanometric and subnanometric gaps

Extreme plasmonic cavities



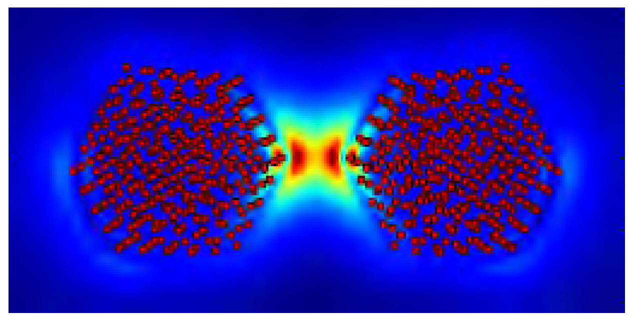


Top-down
STM ultra high-vacuum
Low temperature
(Hefei, China)

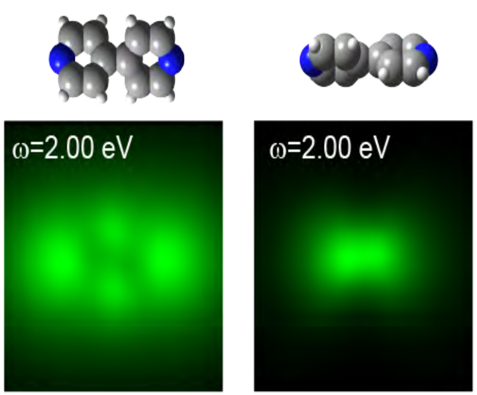
Bottom-up
Wet Chemistry
Self-assembled monolayers
(Cambridge, UK)

Nanophotonics beyond the nanoscale

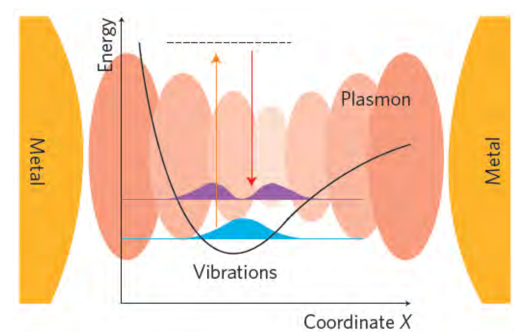
Condensed Matter Physics



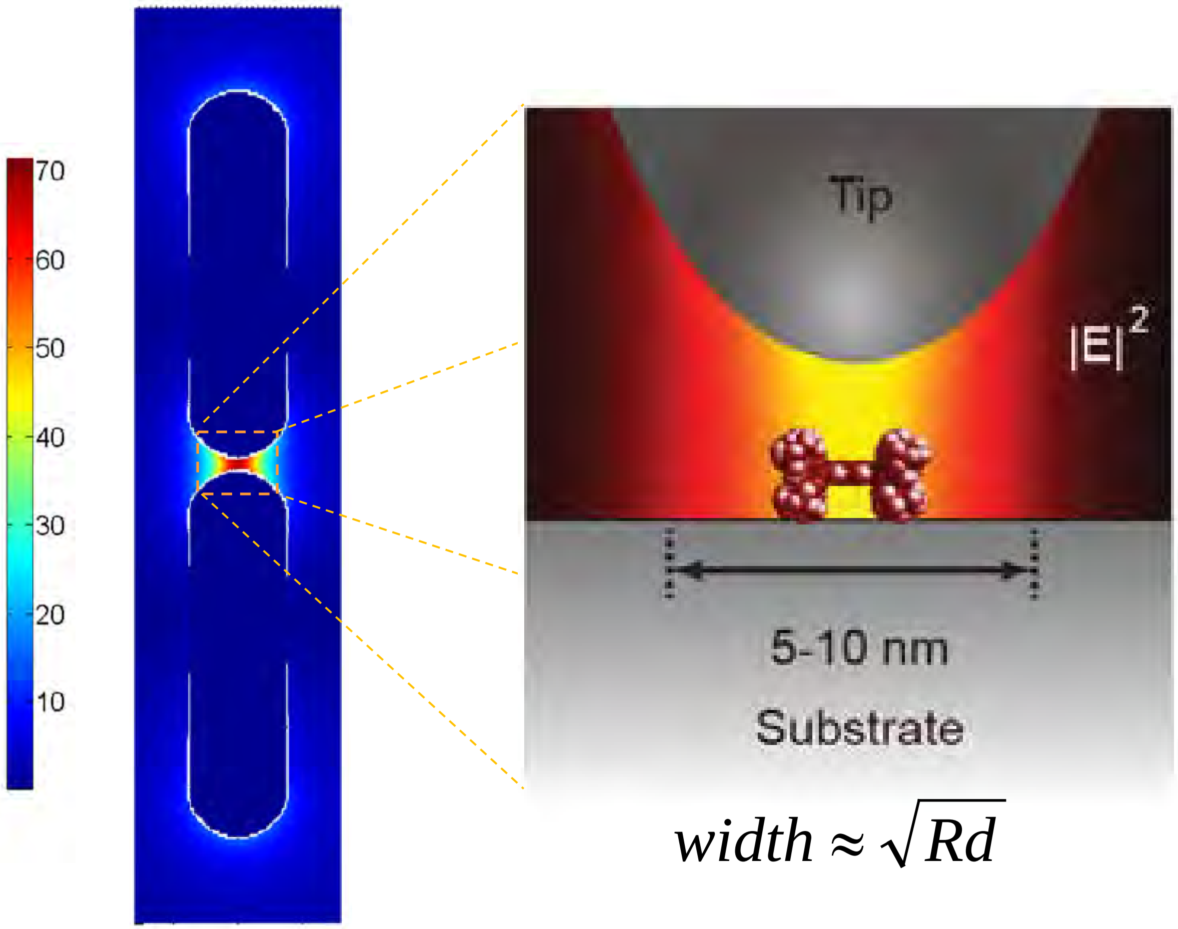
Quantum Chemistry



Cavity QED



Classical confinement of light

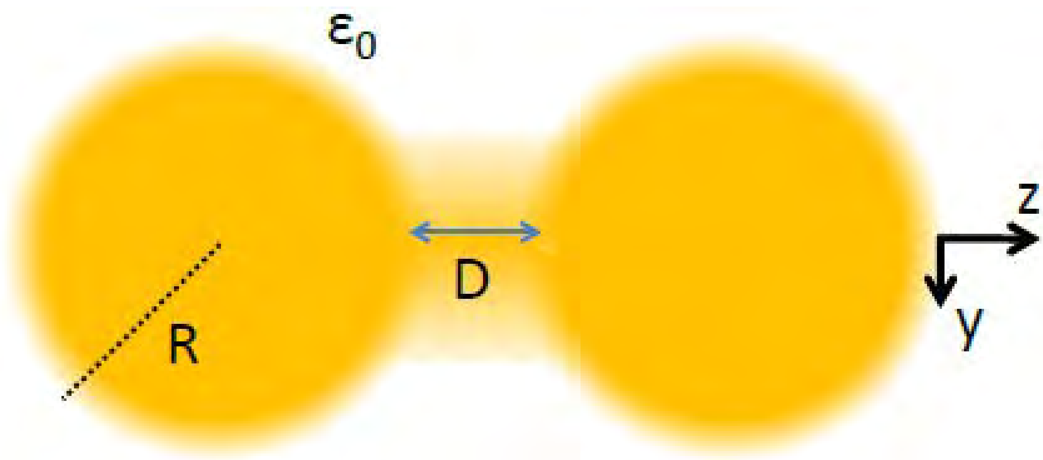


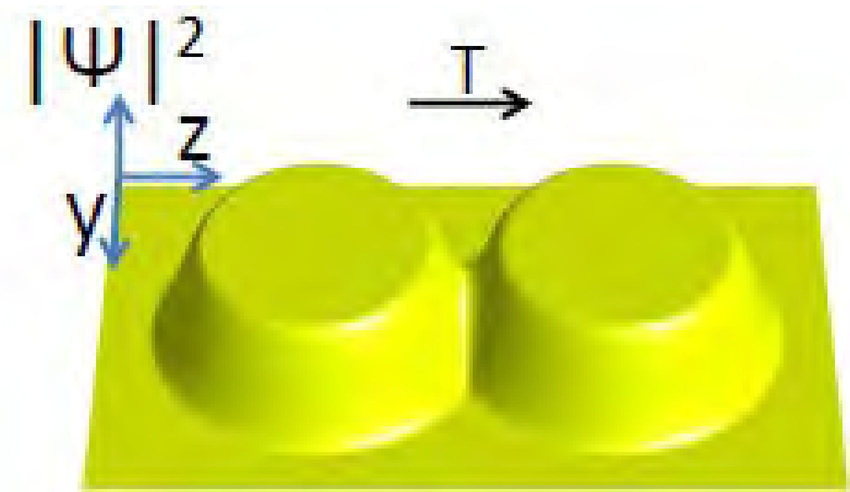
$$width \approx \sqrt{Rd}$$

Micron scale

Nanometric scale

Quantum Mechanical Model -QM-





The optical response of a matter block can be obtained by following the dynamical evolution of the electrons that compose it

Time-dependent Density Functional Theory (TDDFT).

Non-linear TDSE for Kohn-Sham Orbitals:

$$i\frac{d\,\Psi_j(t)}{d\,t} = H\left[n(t)\right]\,\Psi_j(t);$$

Potential is a function of the electronic density:

$$H = T + V\left[n(t)\right]; \quad T = -\frac{1}{2}\Delta$$

Density:

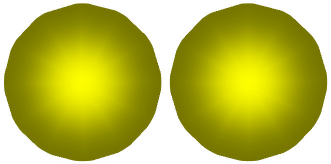
$$n(t) = 2\sum_{j=occ}\left|\Psi_j(t)\right|^2$$

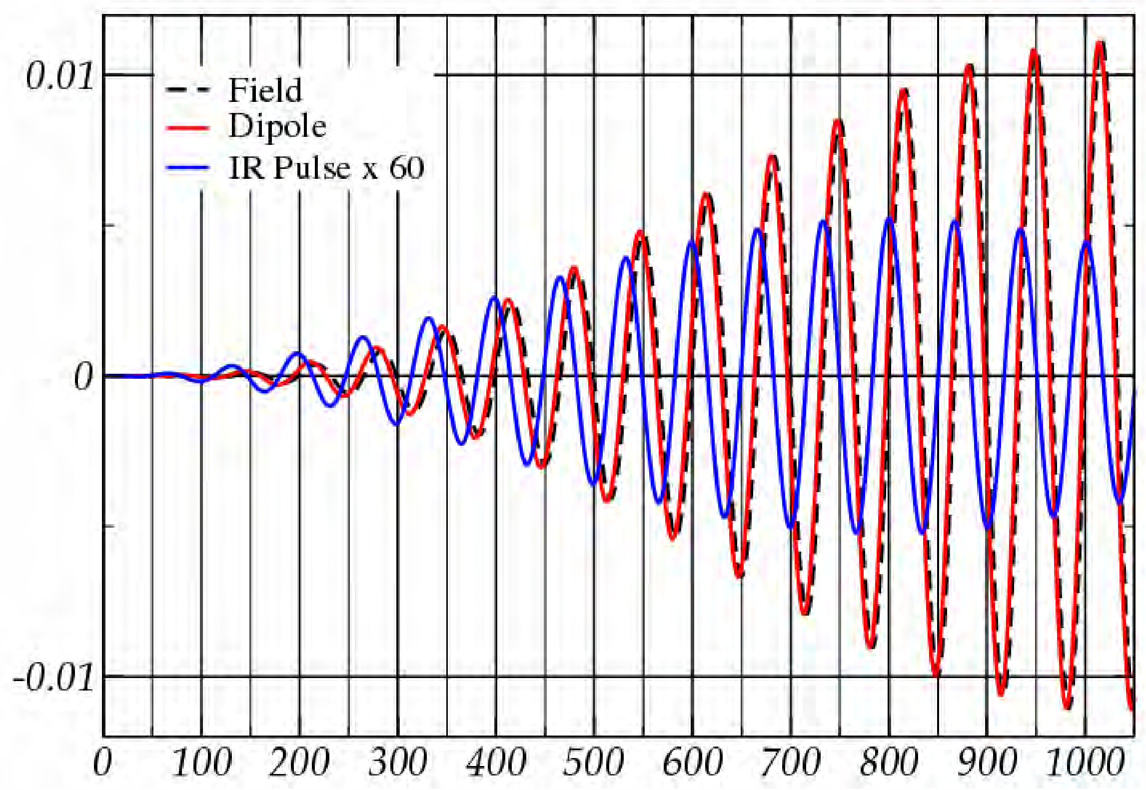
Short-step (δt) time propagation:

$$\Psi_j(t+\delta t) = e^{-i\,H(t+\delta t/2)\,t}\,\Psi_j(t)$$

Tracing the response

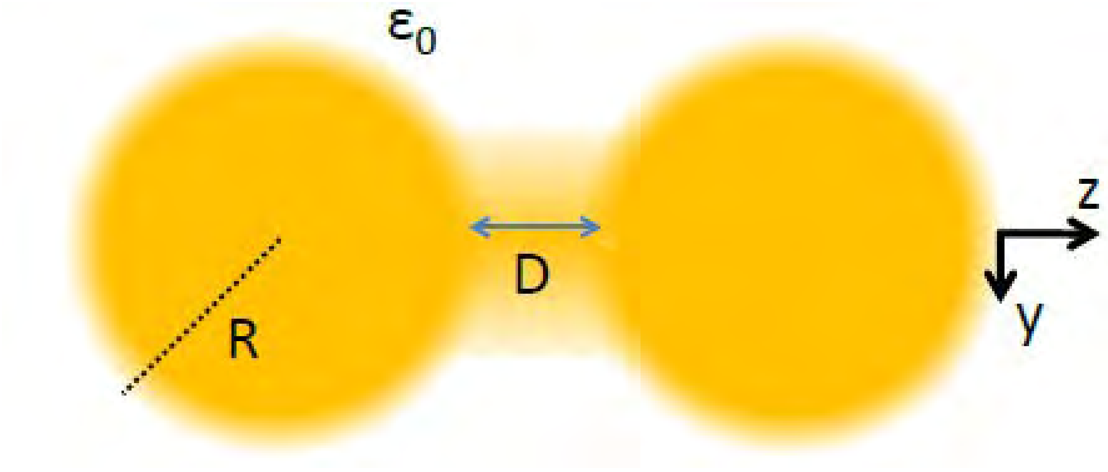
In collaboration with C. Marinica and A. Borissov, ISMO, Orsay, France





ω=2.55 eV
Dipolar
plasmon resonance

Quantum Mechanical Calculation -QM-

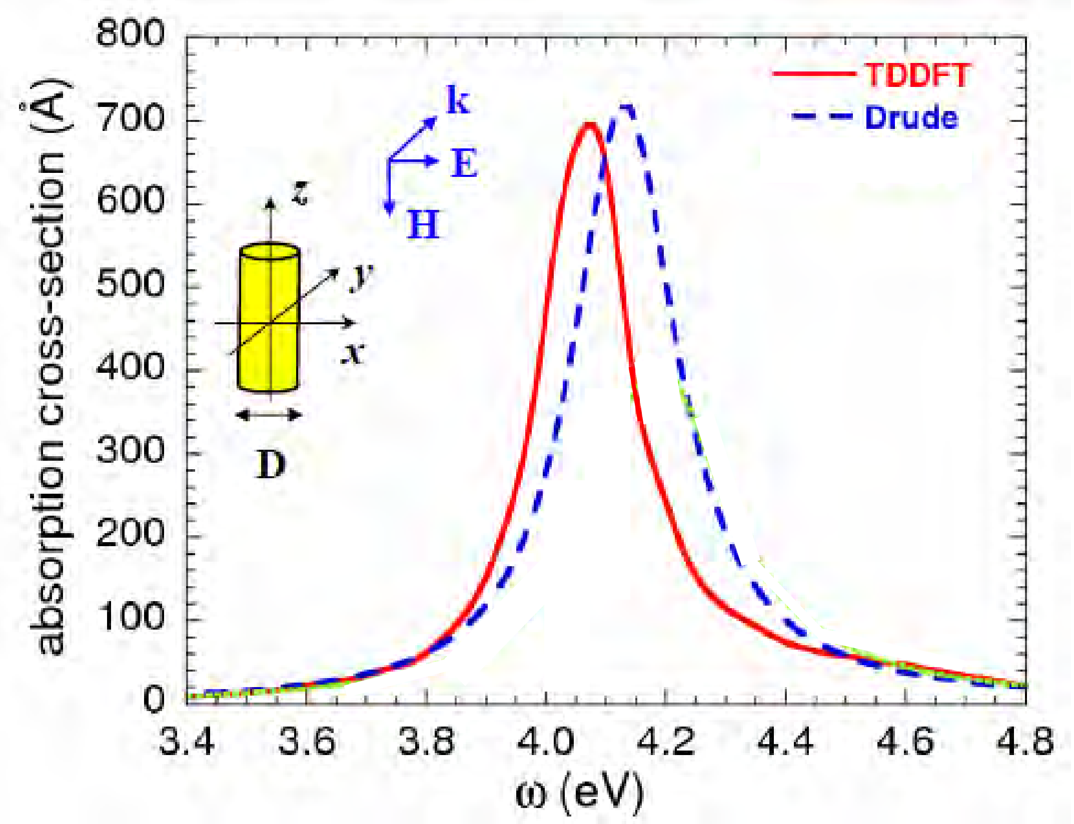


The quantum mechanical model can account for:

- (i) quantum size effect
- (ii) nonlocal interactions
- (iii) electron spill-out
- (iv) atomistic effects
- (v) electron tunneling

Quantum versus classical models

(Red shift)

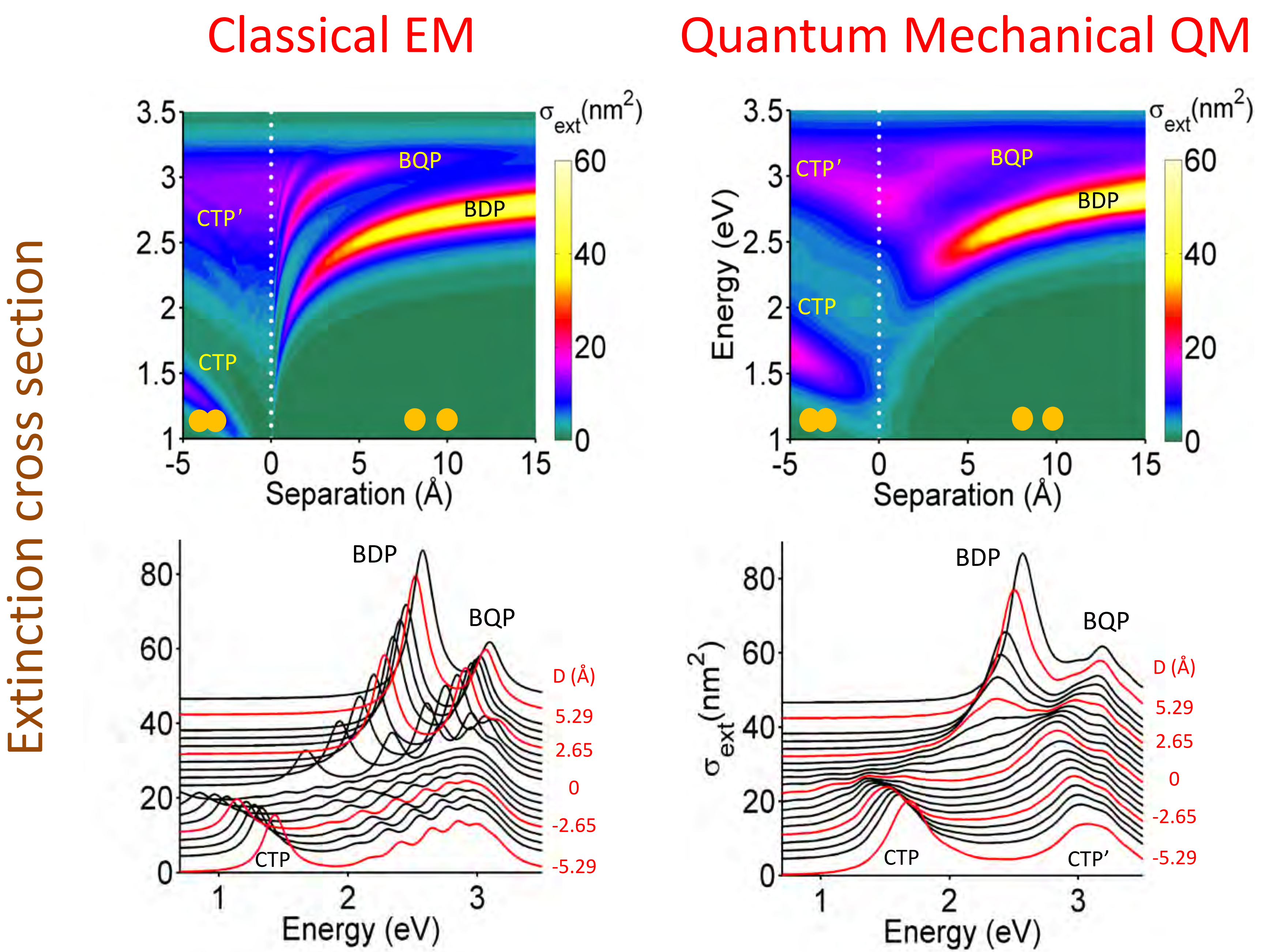


Single metallic wire of diameter D=9.8 nm

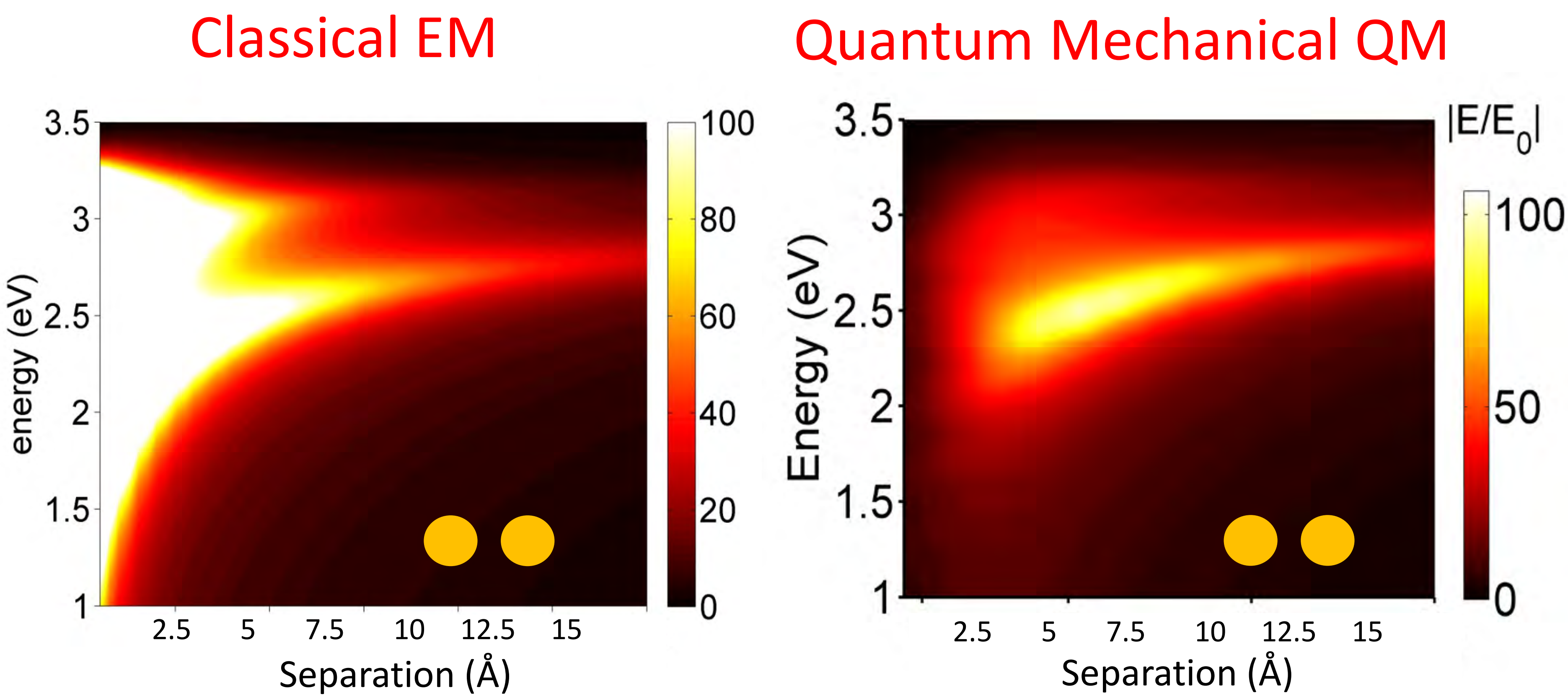
TDDFT calculation within the Jellium model

T. Teperik, P. Nordlander, J. Aizpurua, A. Borisov, Phys. Rev. Lett. 110, 263901 (2013)

Small Na dimer (particles of 2nm)

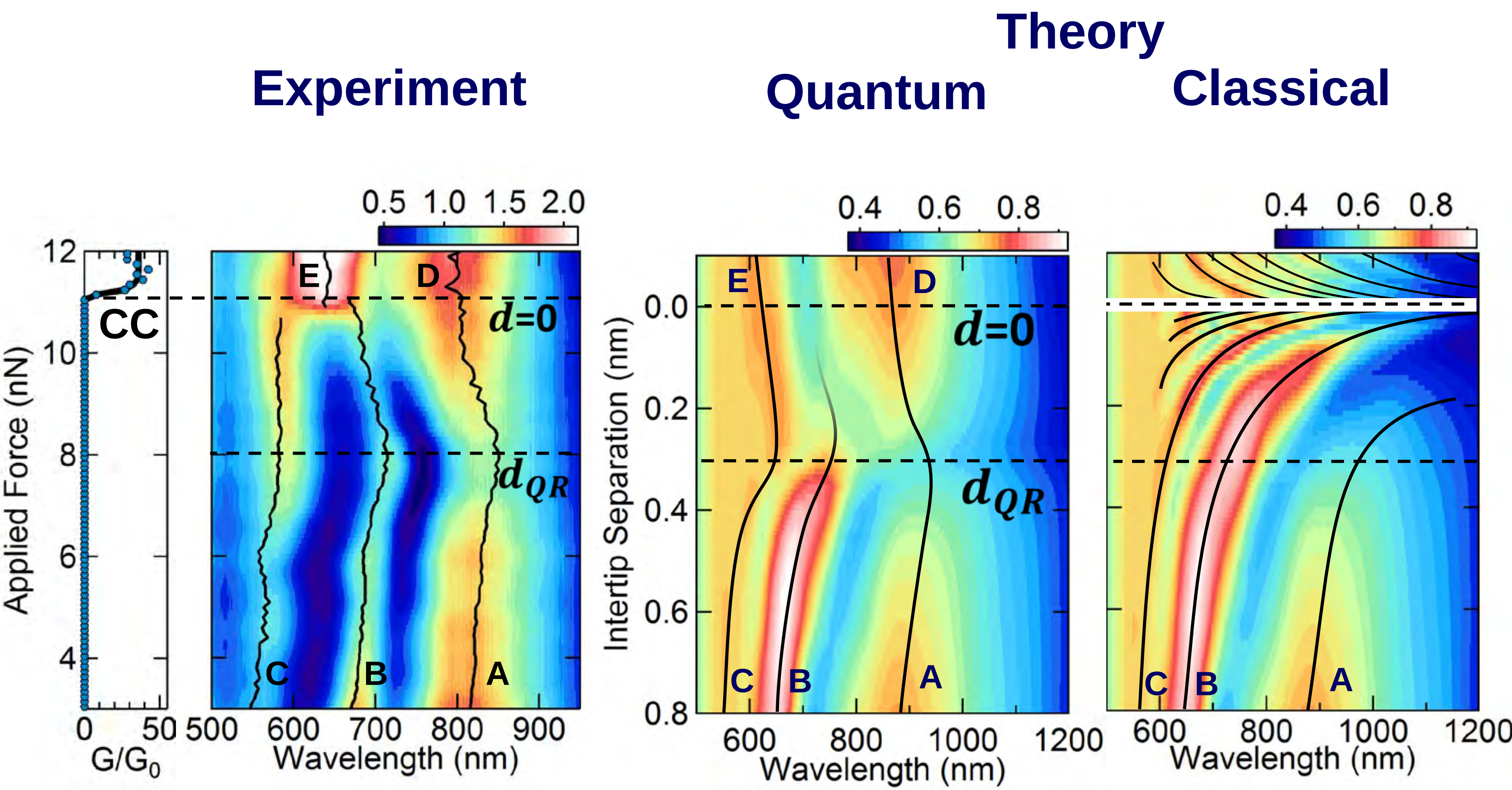


Near-Field at the gap



Rubén Esteban et al., Nature Communications 3, 825 (2012)

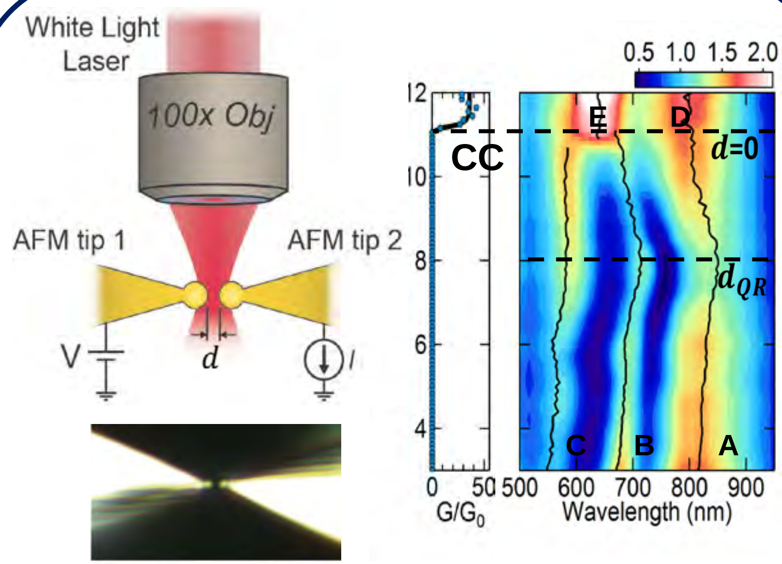
Revealing the Quantum regime in tunnelling plasmonics



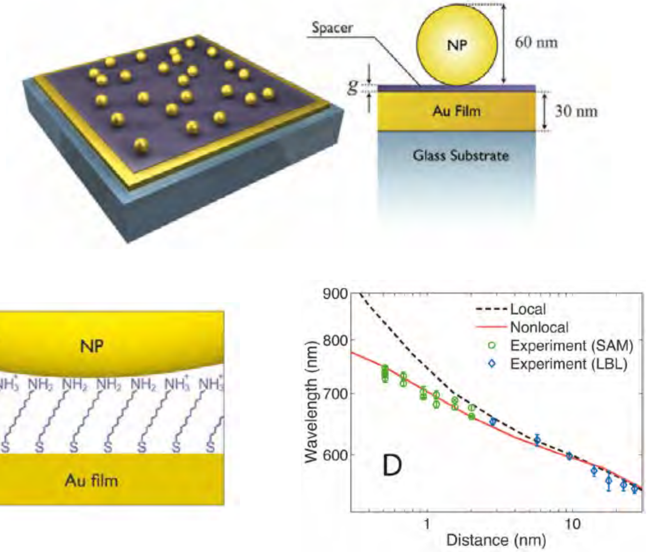
Quantum regime dominates for d_{QR}> 0.35nm

K. Savage *et al*. NATURE 491, 574 (2012)

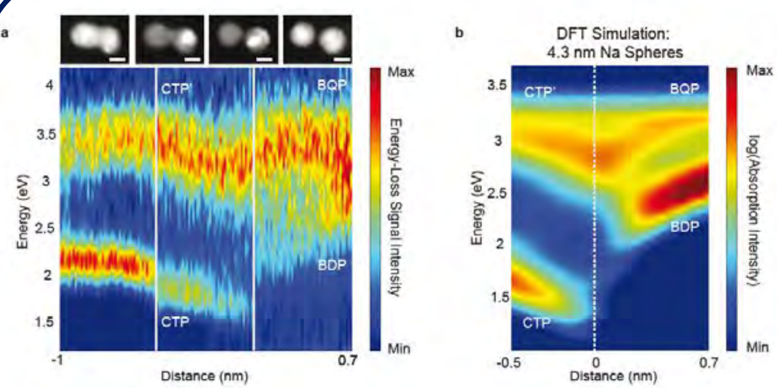
Subnanometric plasmonics



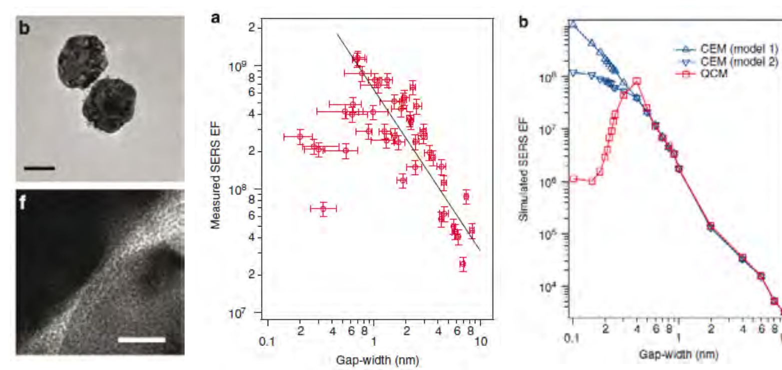
K. Savage et al., NATURE 491, 574 (2012)



C. Ciraci et al., Science 337, 1072 (2012)

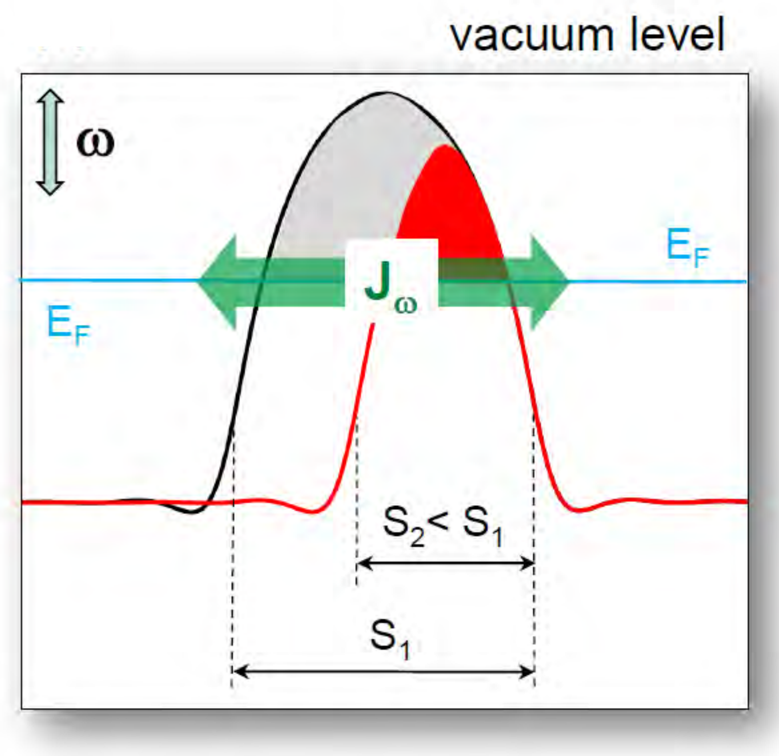


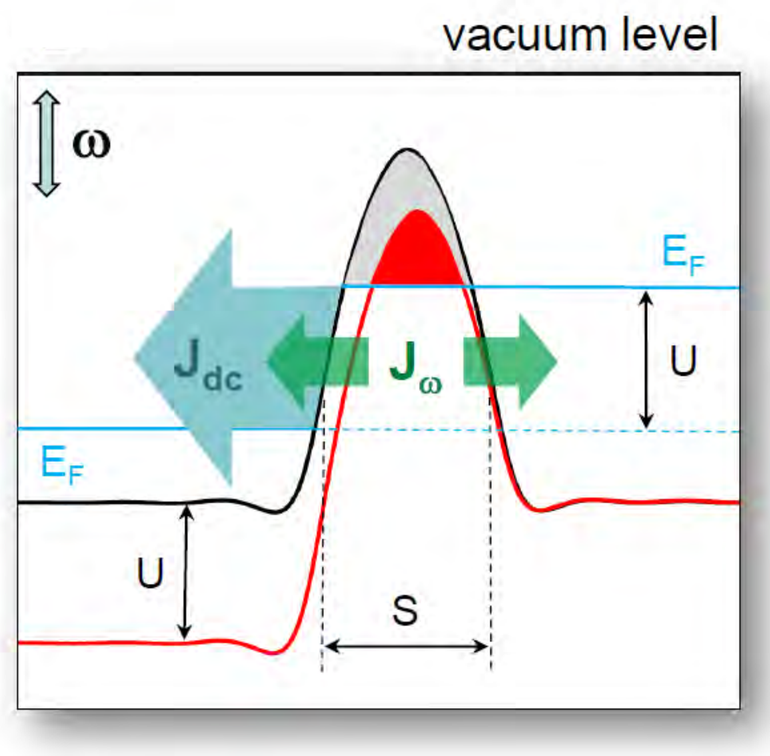
J. Scholl et al., Nano Lett. 13, 564 (2013)



W Zhu et al., Nat. Comm. 5 Sept. (2014)

Active quantum plasmonics





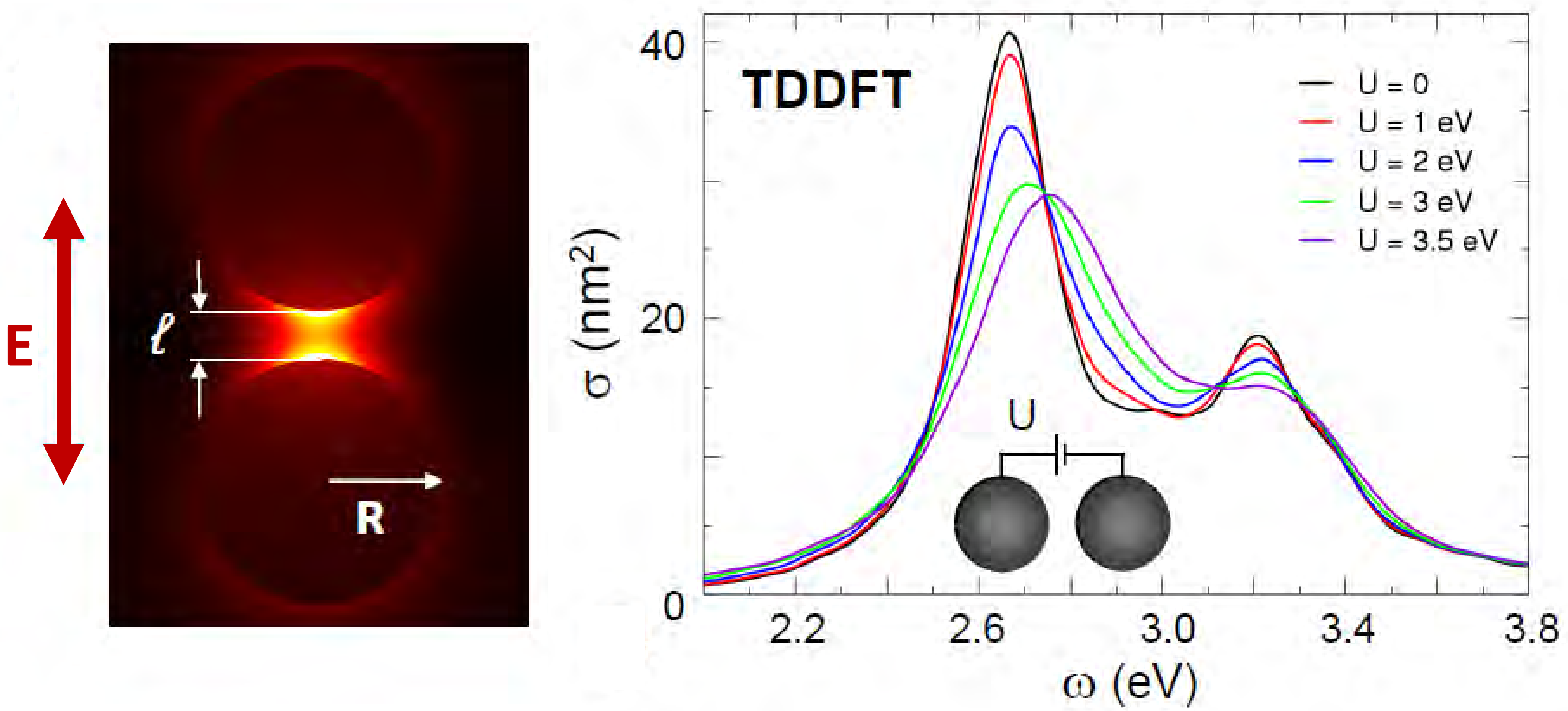
Control over separation

Control over an external bias

Rubén Esteban *et al.*,
Nature Communications **3**, 825 (2012)

C. Marinica *et al.*
Science Advances **1**, e1501095 (2015)

Active quantum plasmonics

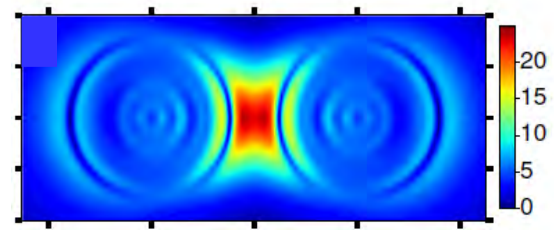


C. Marinica *et al*. Science Advances **1**, e1501095 (2015)

Light-matter interaction at the nanoscale

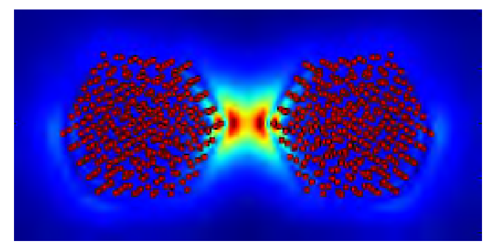
Intro to plasmonics

Plasmonic nanogap



Quantum effects in nanogaps

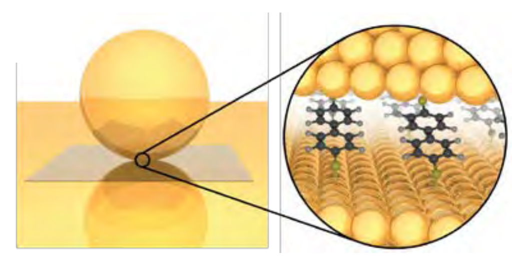
Photoemission in nanogaps



Atomistic effects in field localization

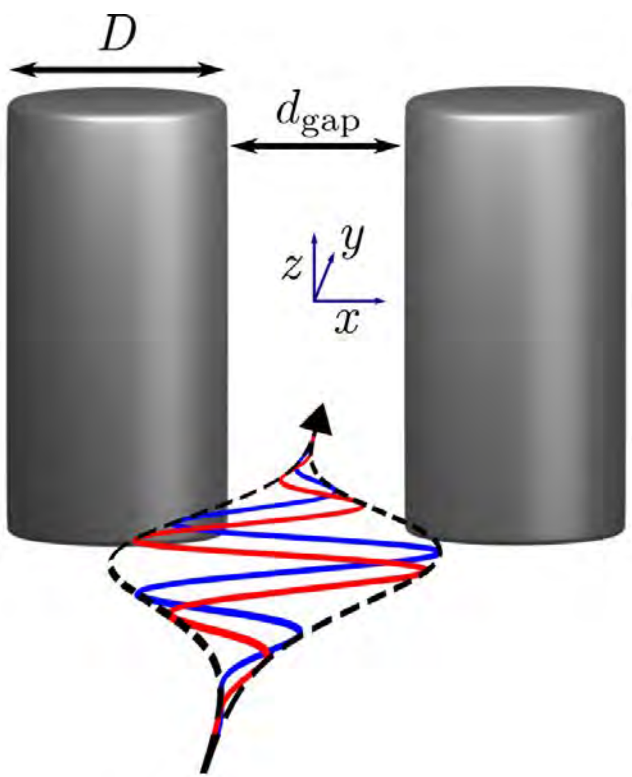
Transport at optical frequencies

Exciton-plasmon coupling



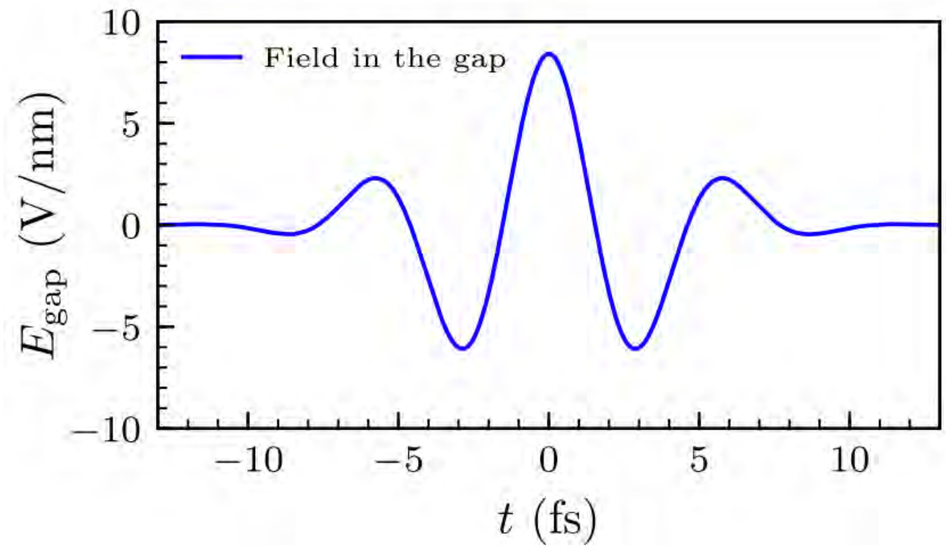
Molecular electroluminescence in nanogaps

Ultrafast photo-induced electron currents in plasmonic gaps



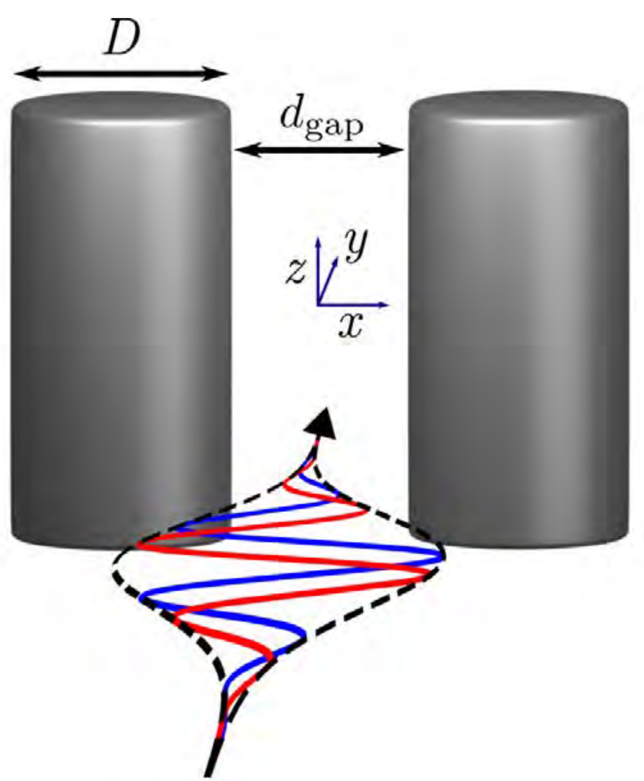
$$E(t) = \tilde{E}\cos(\omega t + \phi)e^{-t^2/\tau^2}$$

Field in the gap



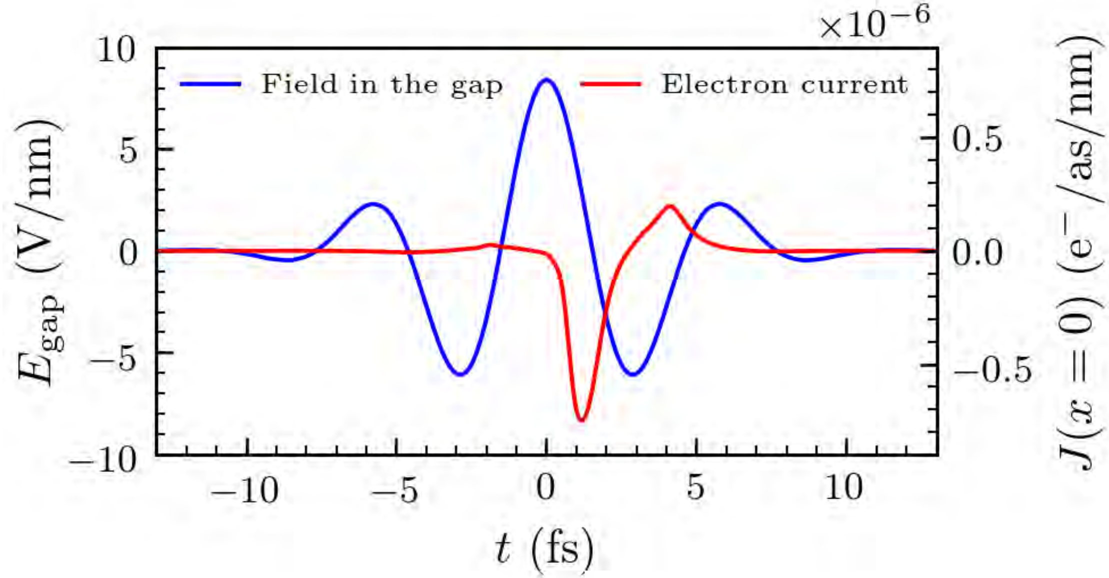
G. Aguirregabiria *et al.*
Faraday Discussions **214**, 147-157 (2019)

Ultrafast photo-induced electron currents in plasmonic gaps



$$E(t) = \tilde{E}\cos(\omega t + \phi)e^{-t^2/\tau^2}$$

Electron current



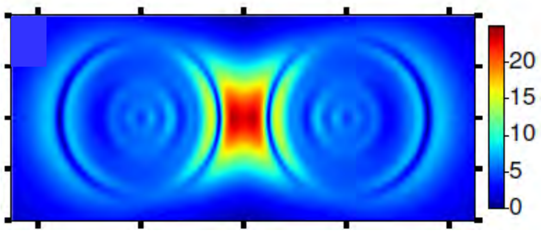
Ultrafast electron bursts follow the optical cycle

G. Aguirregabiria *et al.*
Faraday Discussions **214**, 147-157 (2019)

Light-matter interaction at the nanoscale

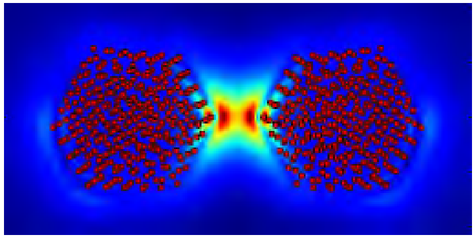
Intro to plasmonics

Plasmonic nanogap



Quantum effects in nanogaps

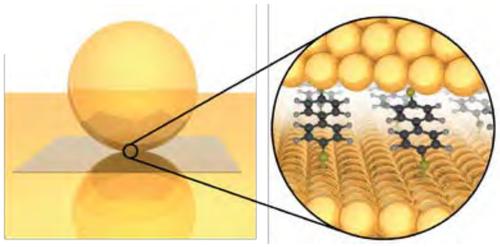
Photoemission in nanogaps



Atomistic effects in field localization

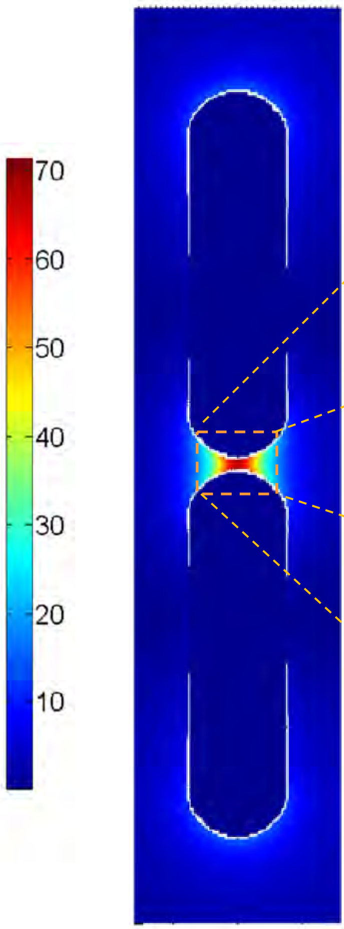
Transport at optical frequencies

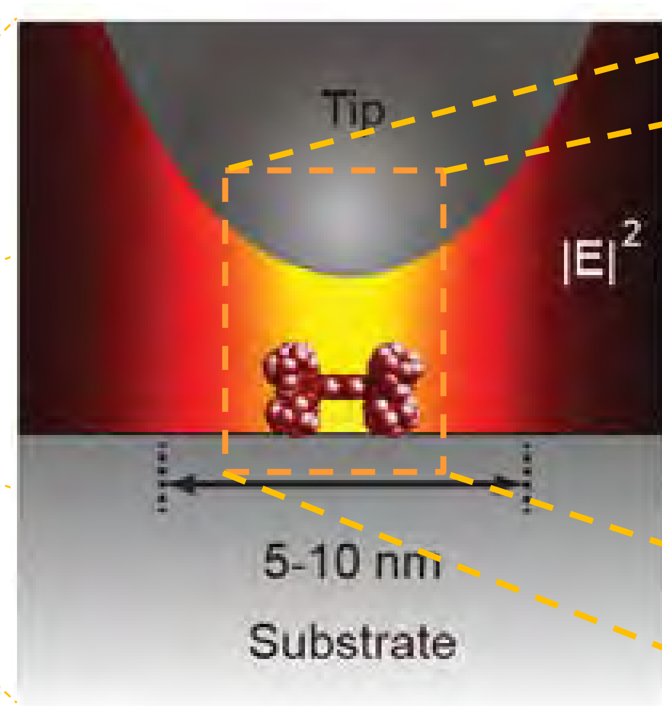
Exciton-plasmon coupling



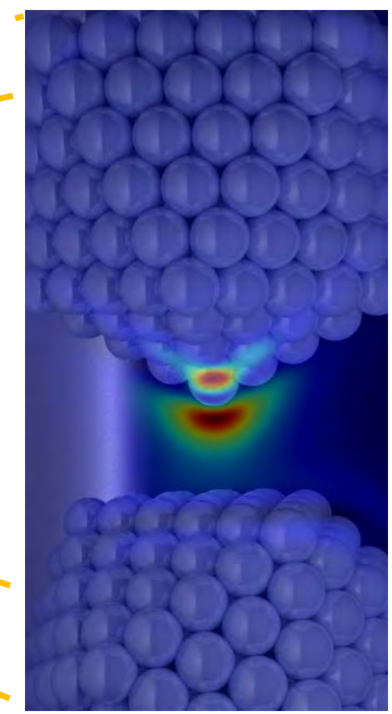
Molecular electroluminescence in nanogaps

Beyond classical plasmonic confinement





$$width \approx \sqrt{Rd}$$



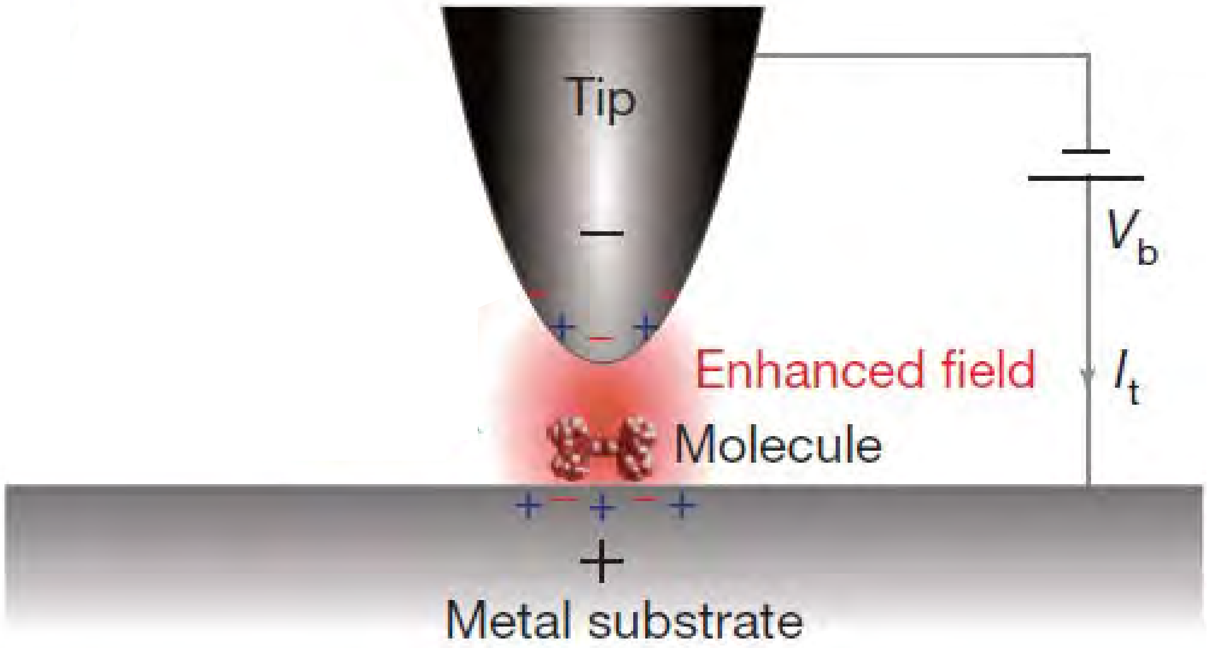
???

Micron scale

Nanometric scale

Atomic scale

Single molecule Plasmon-Enhanced Raman in a STM cavity



Top-down

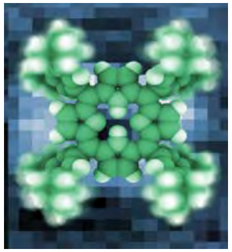
STM ultra high-vacuum

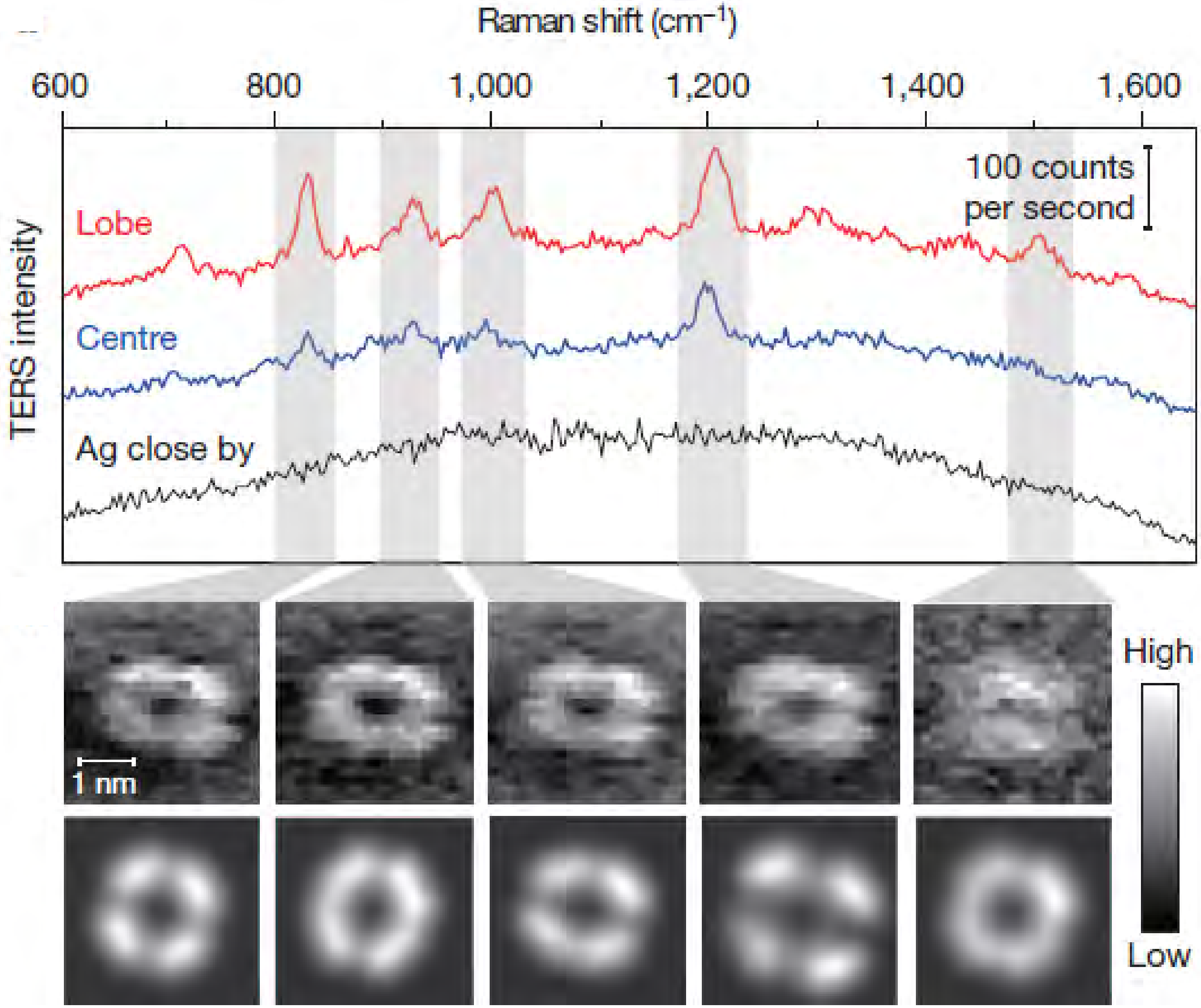
Low temperature

(Hefei, China)

R. Zhang *et al*. NATURE 598, 82-86 (2013)

Chemical mapping of a single molecule by TERS
Porfirine in an Ag cavity





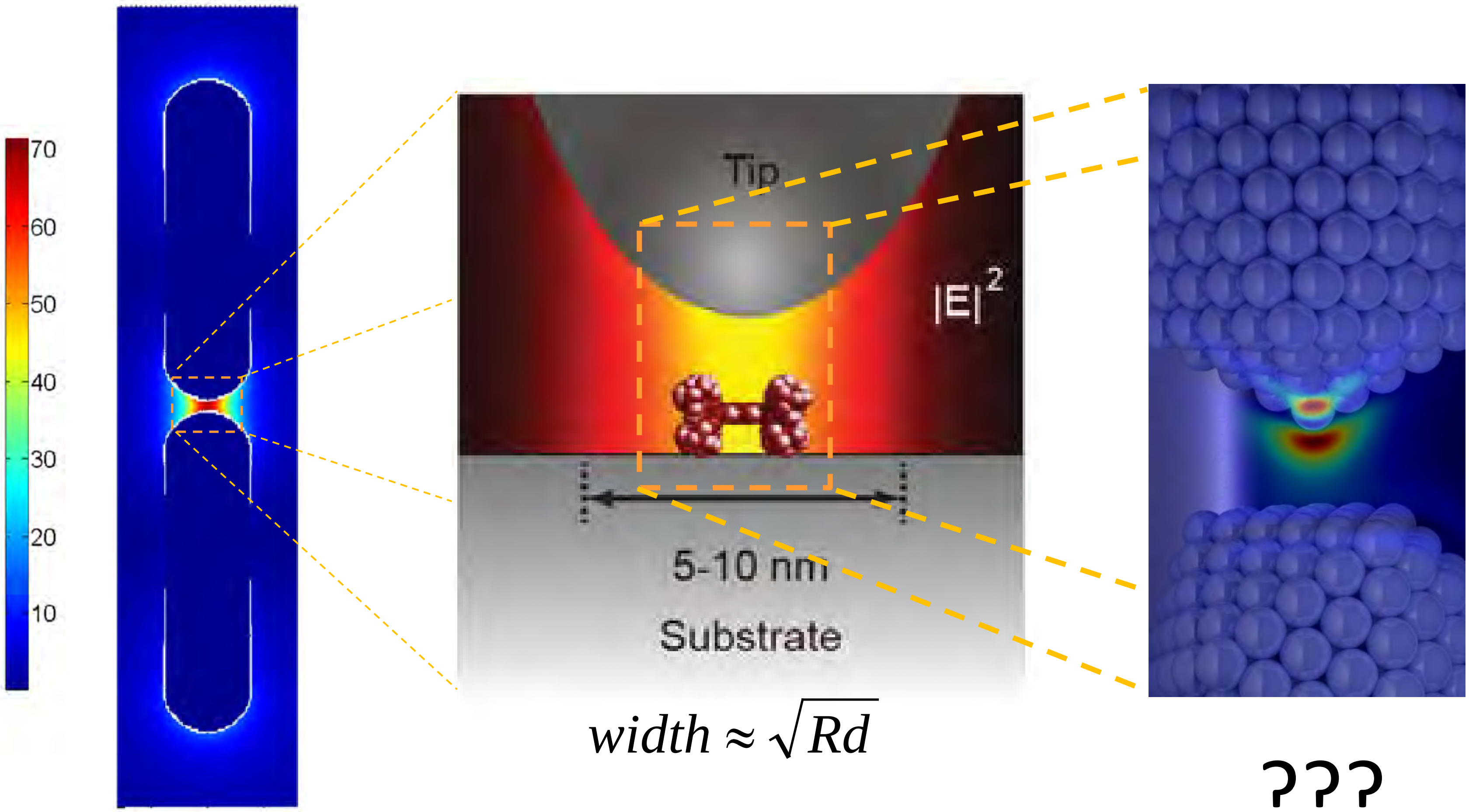
Spectral Mapping (acquired at each pixel)

Experiment

Simulation

R. Zhang *et al*. NATURE 598, 82-86 (2013)

Beyond classical plasmonic confinement



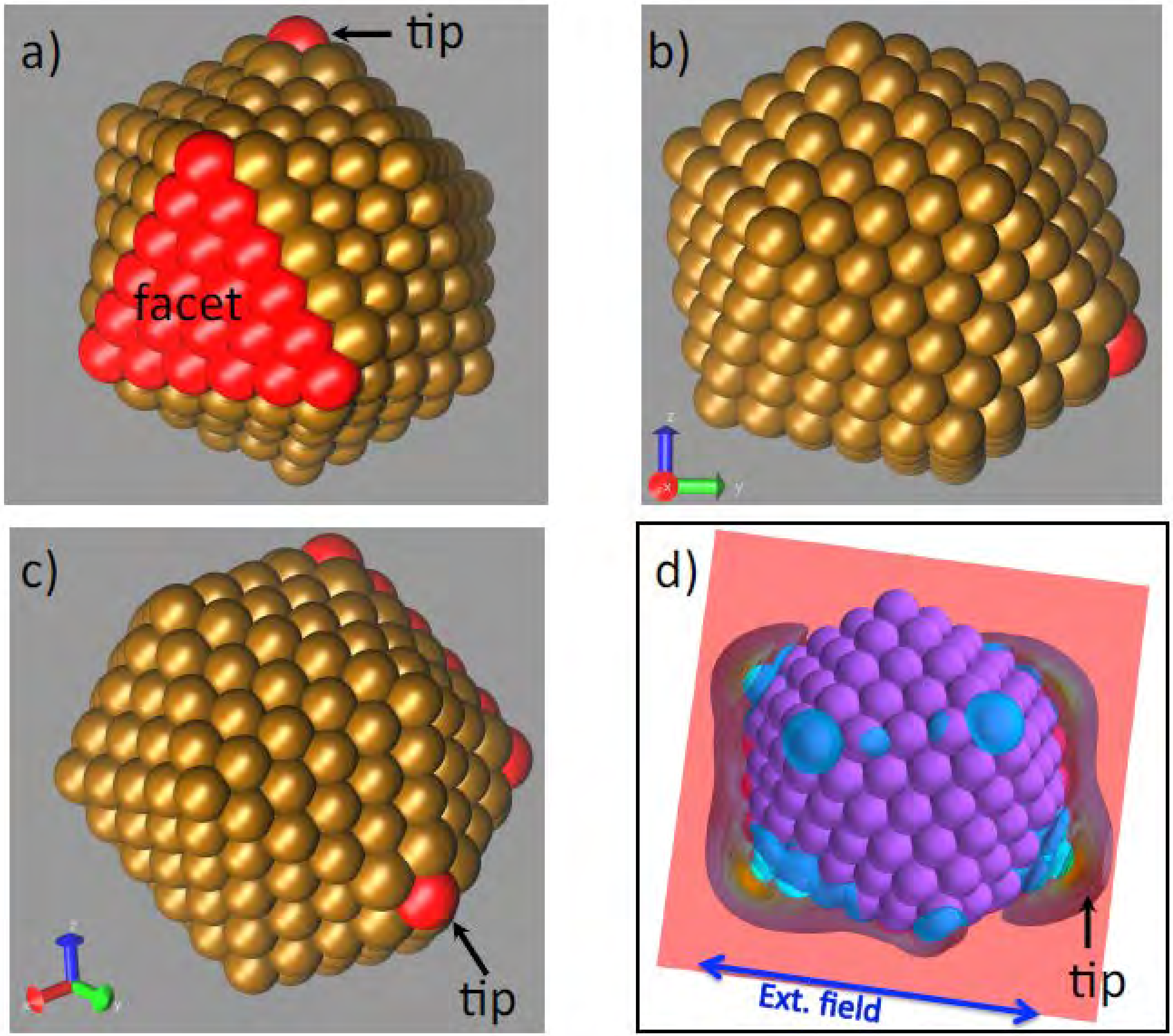
$$width \approx \sqrt{Rd}$$

???

Micron scale | **Nanometric scale** | **Atomic scale**

Atomistic structure of a nanoparticle

(TDDFT, Daniel Sánchez Portal, in San Sebastián, CFM)

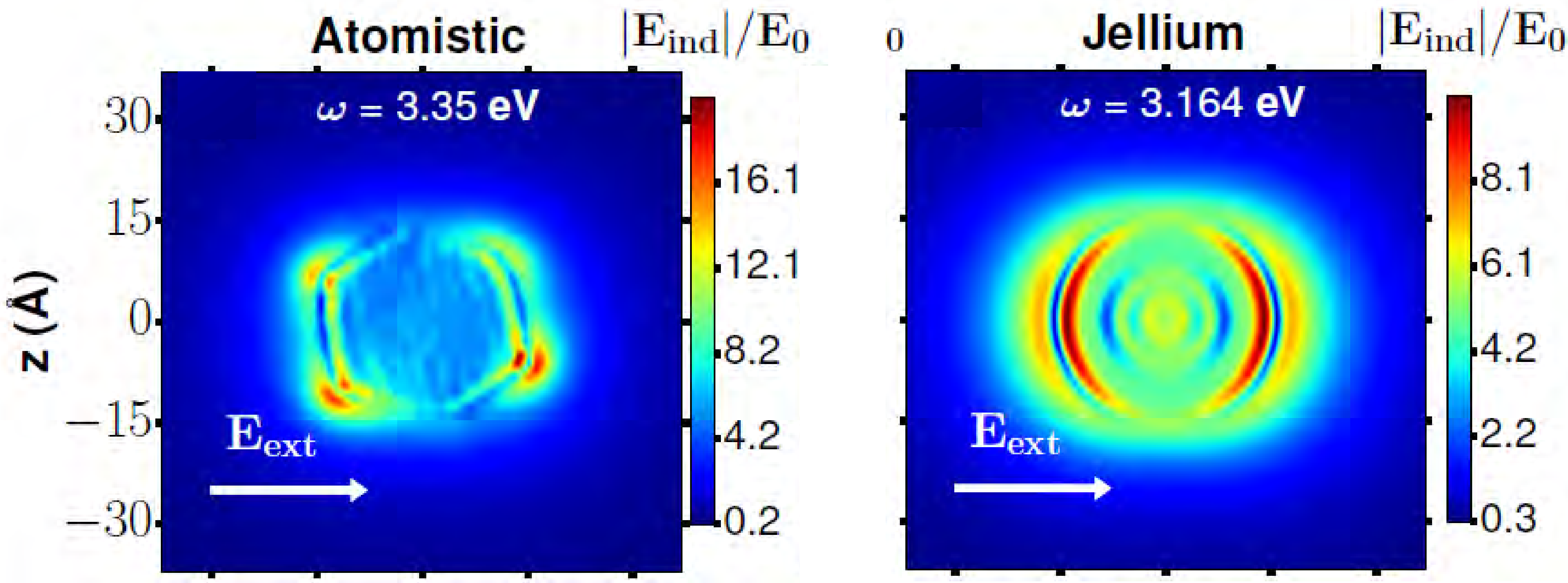


M. Barbry *et al*. Nano Lett. **15**, 3410-3419 (2015) and Supp. Inf.

Atomistic nanoplasmonics

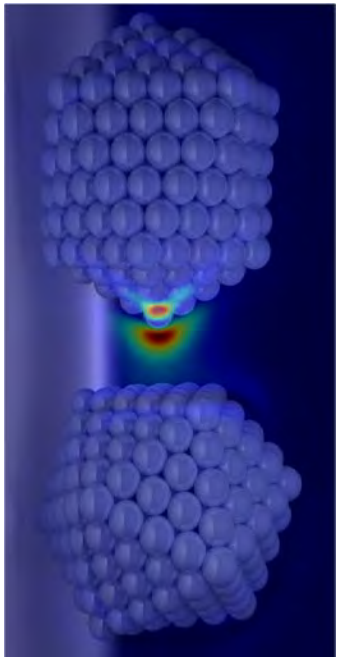
M. Barbry *et al*. Nano Lett. **15**, 3410-3419 (2015)

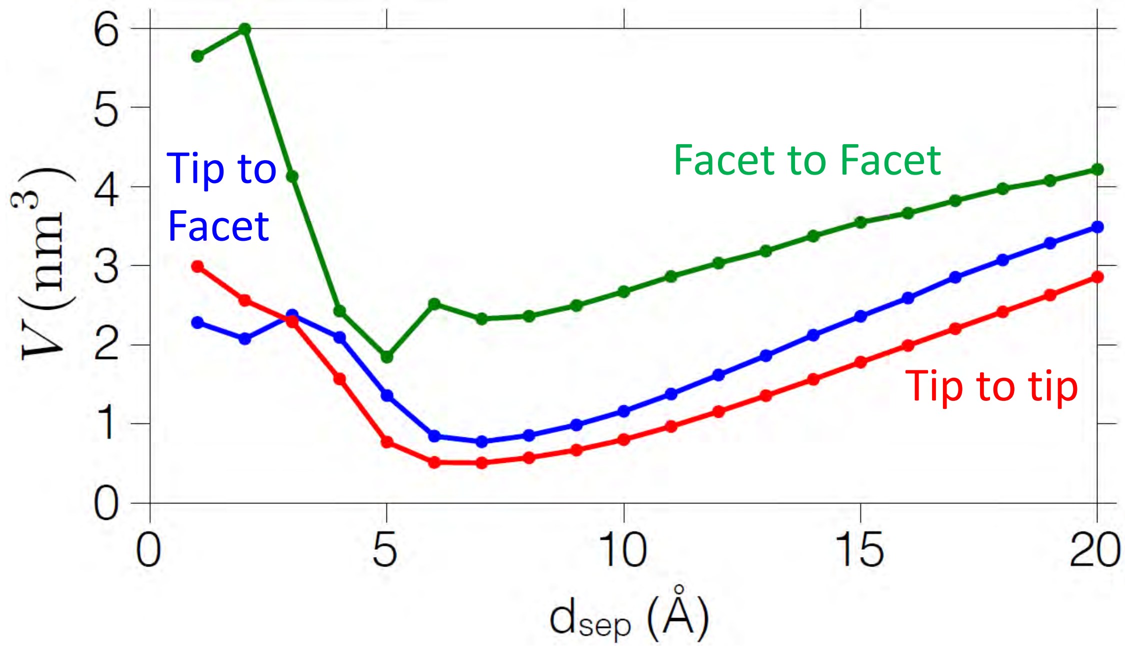
In resonance



Sub-nanometric localization of light

Effective volume < 1 nm^3 ; "picocavity"



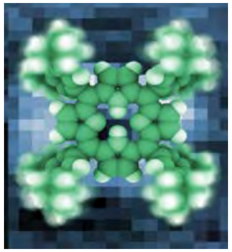


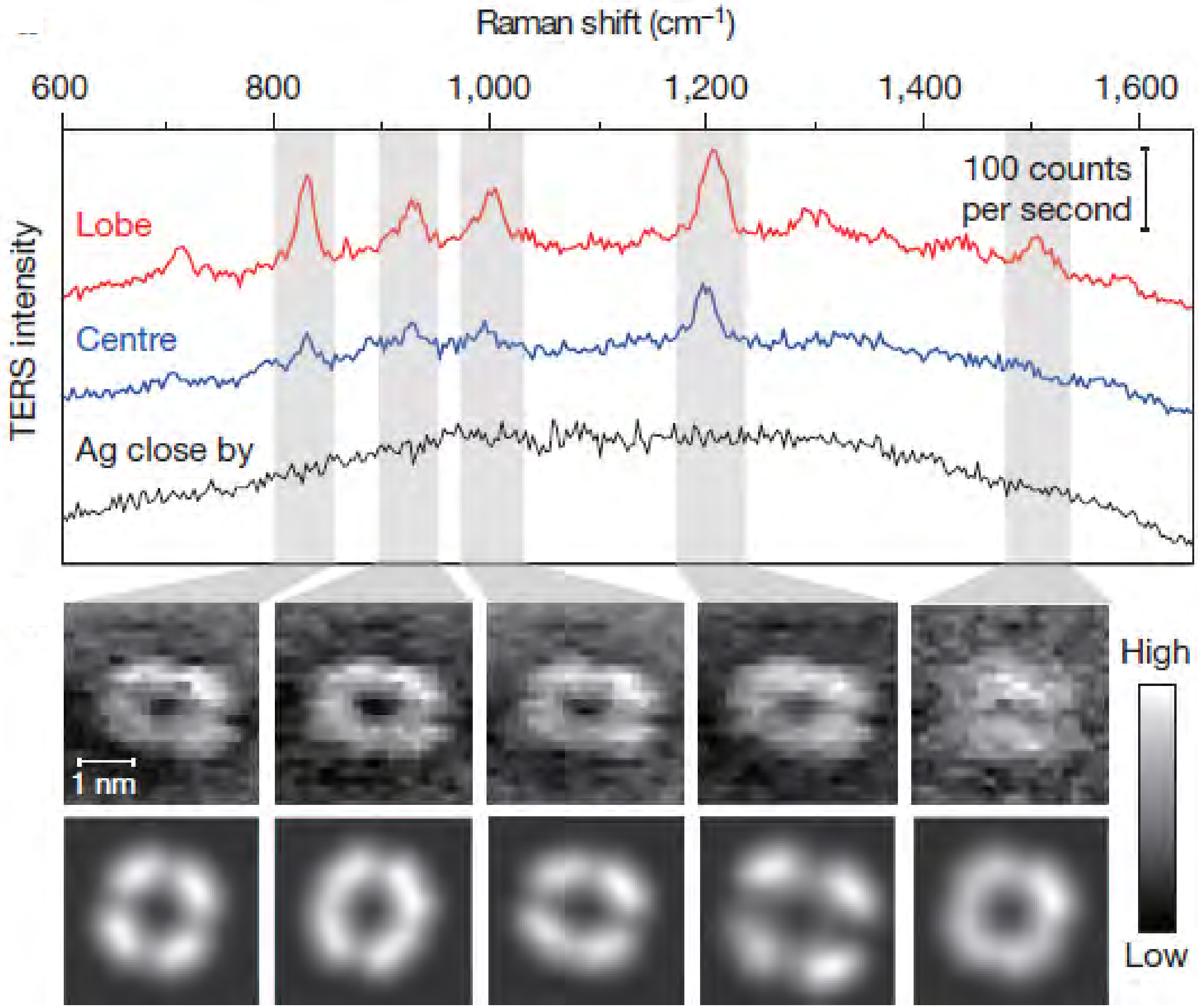
Effective Mode Volume *V*

$$\int_V \frac{|\mathbf{E}_{\mathrm{ind}}(x,y,z)|^2}{|\mathbf{E}_{\mathrm{ind}}^{\mathrm{max}}|^2} dV$$

M. Barbry *et al*. Nano Lett. **15**, 3410-3419 (2015)

Chemical mapping of a single molecule by TERS
Porfirine in an Ag cavity





Spectral Mapping (acquired at each pixel)

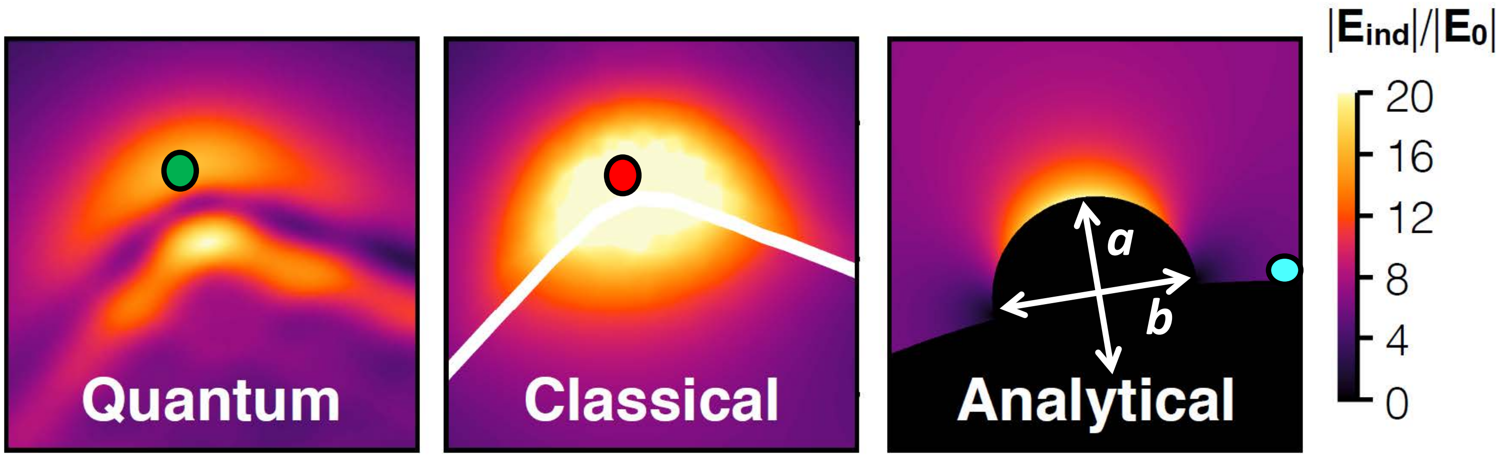
Experiment

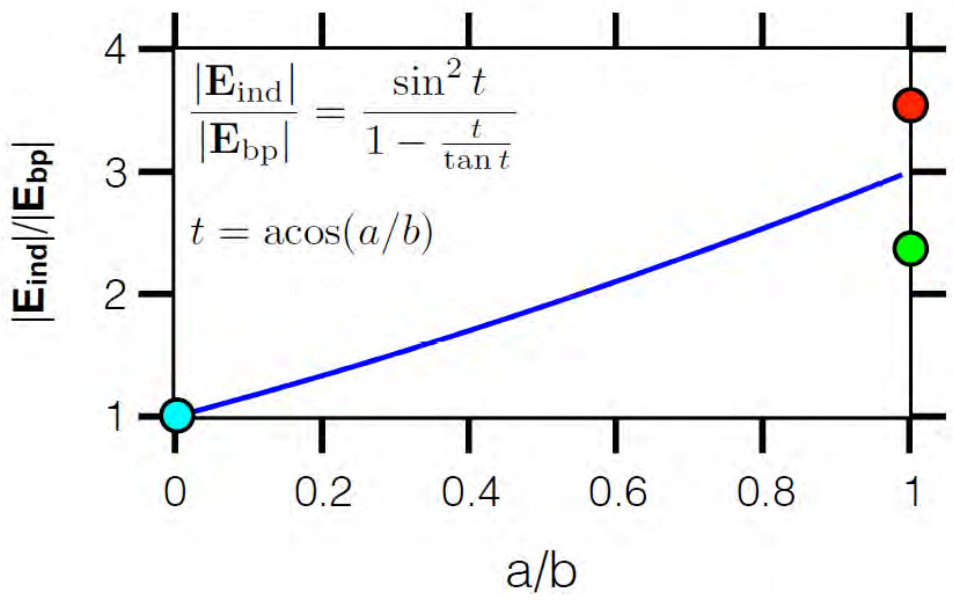
Simulation

R. Zhang *et al*. NATURE 598, 82-86 (2013)

Atomic-scale lightning rod effect: a classical view to a quantum effect

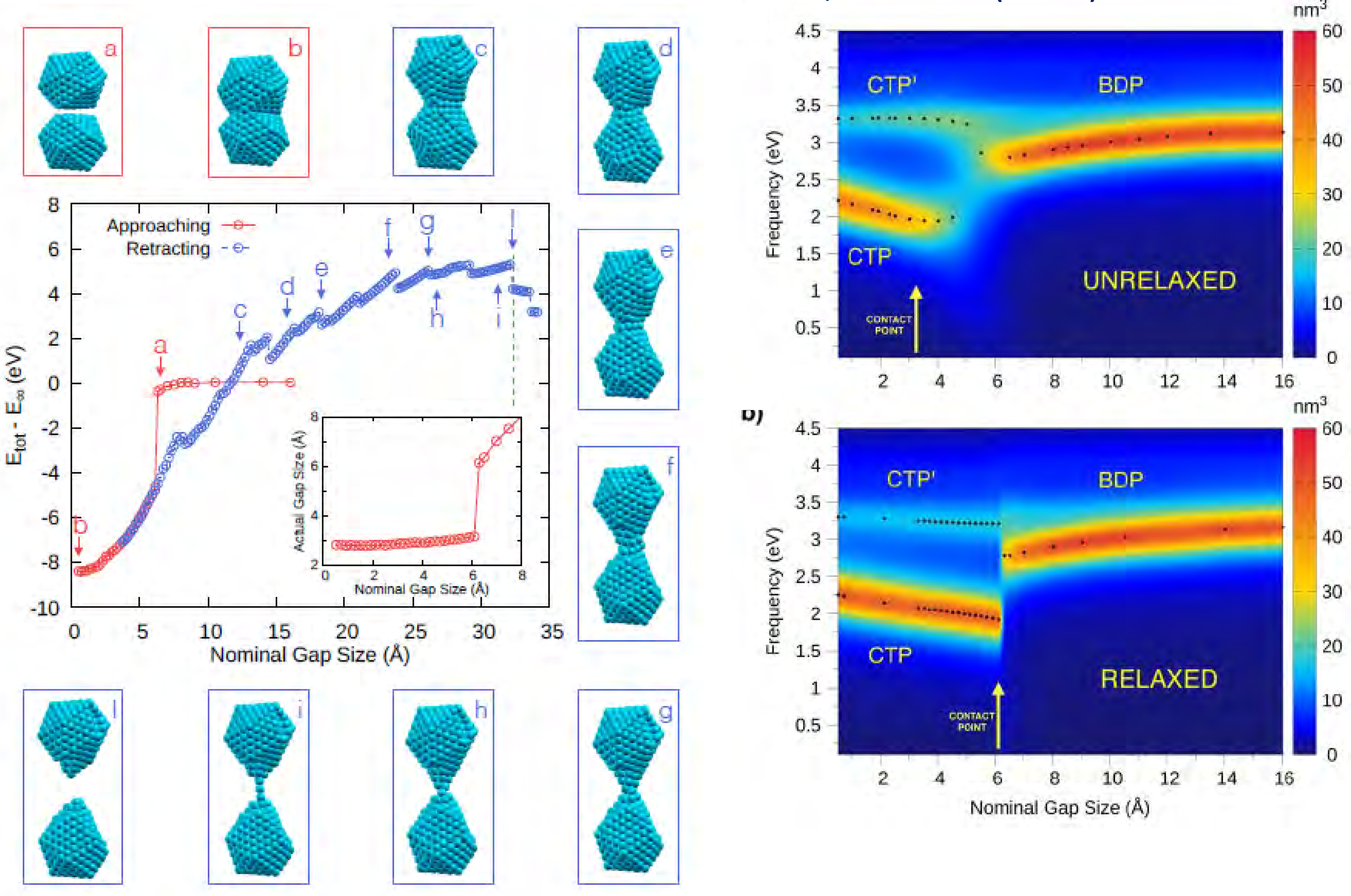
Mattin Urbieta *et al*. ACS Nano **12**, 585-595 (2018)





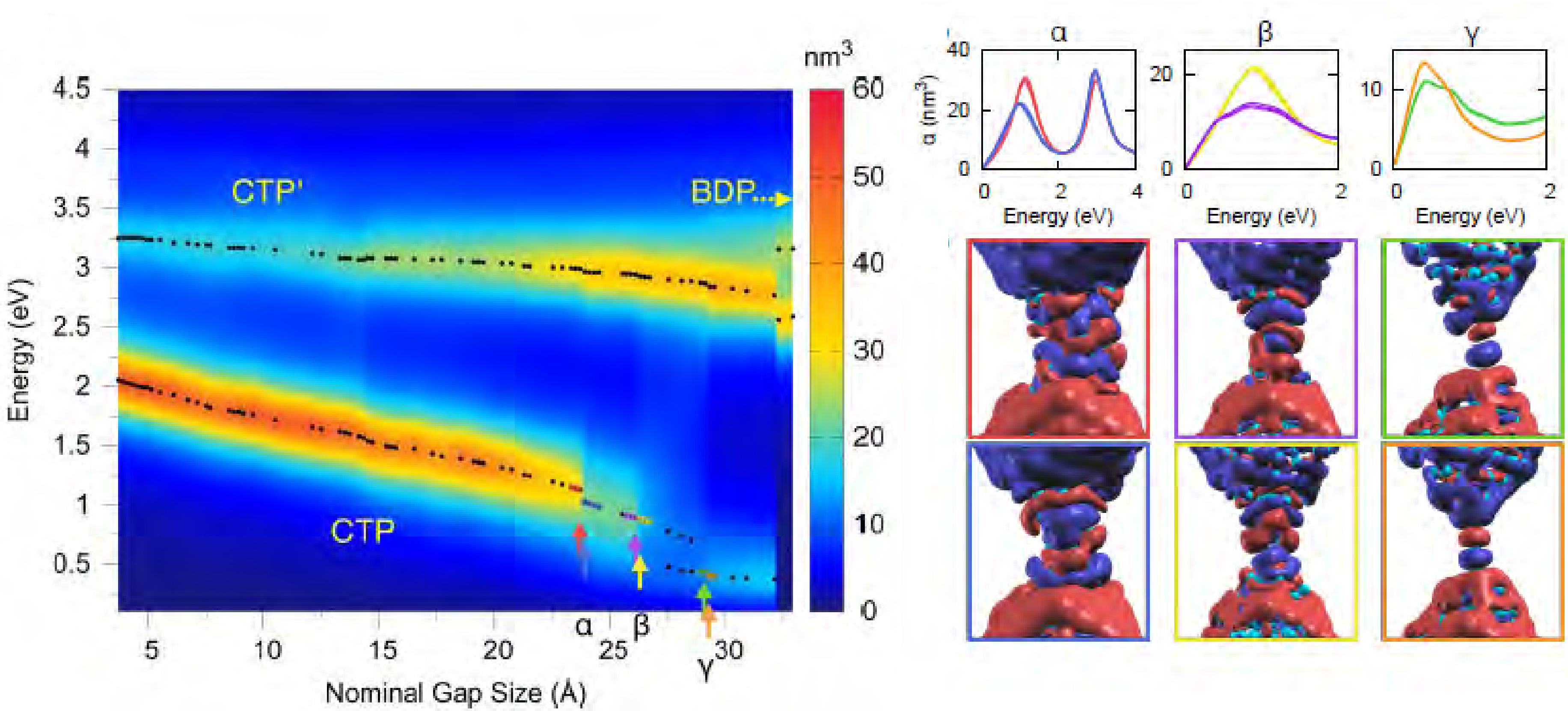
Atomic relaxation around the gap

F. Marchesin *et al*. ACS Photonics **3**, 269-277 (2016)



Single atoms can determine the optics

Optics and quantized transport are related

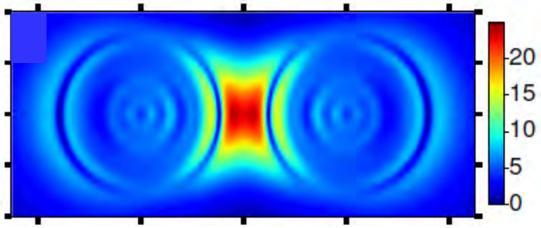


F. Marchesin *et al*. ACS Photonics **3**, 269-277 (2016)

Light-matter interaction at the nanoscale

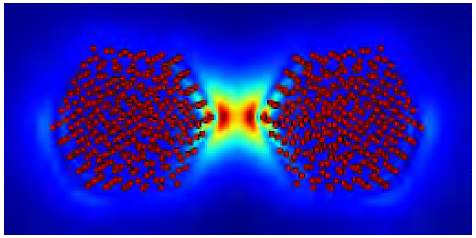
Intro to plasmonics

Plasmonic nanogap



Quantum effects in nanogaps

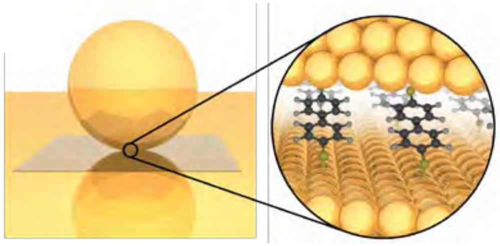
Photoemission in nanogaps



Atomistic effects in field localization

Transport at optical frequencies

Exciton-plasmon coupling

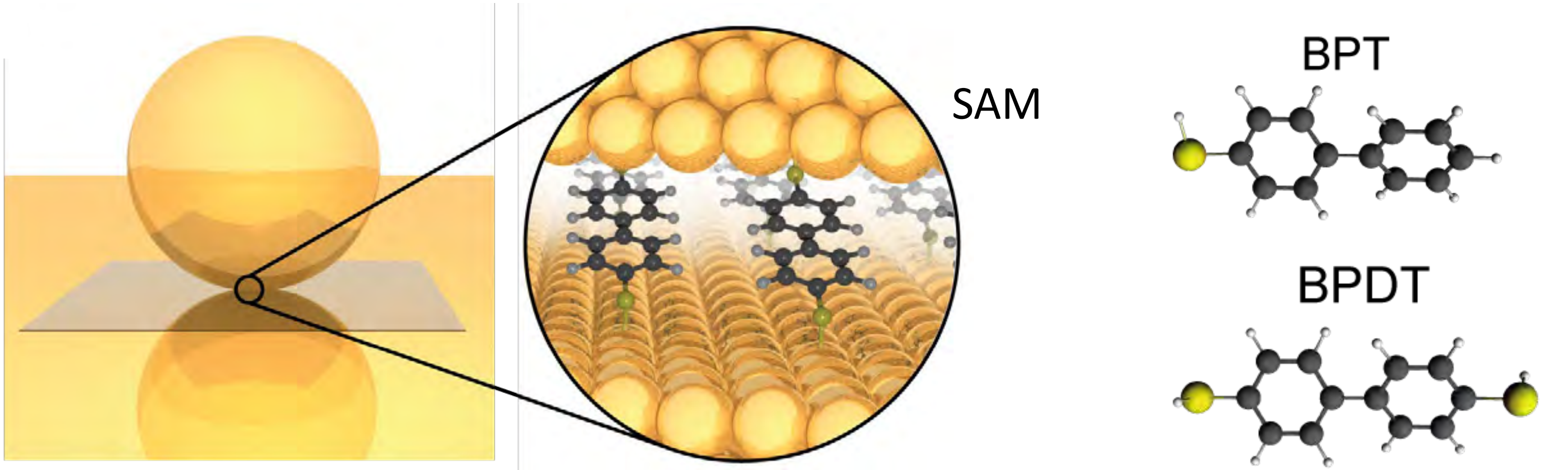


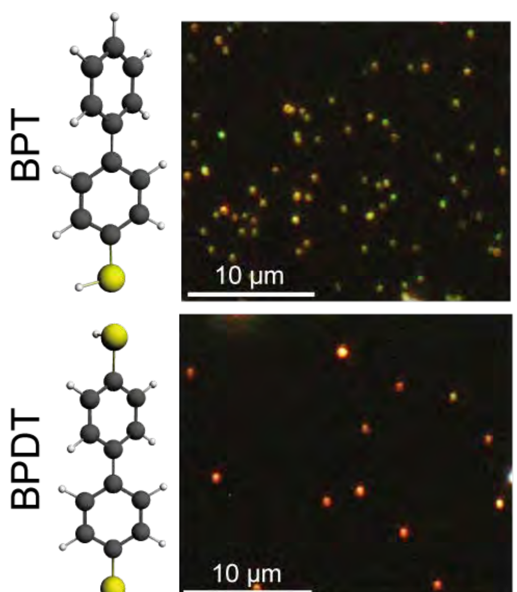
Molecular electroluminescence in nanogaps

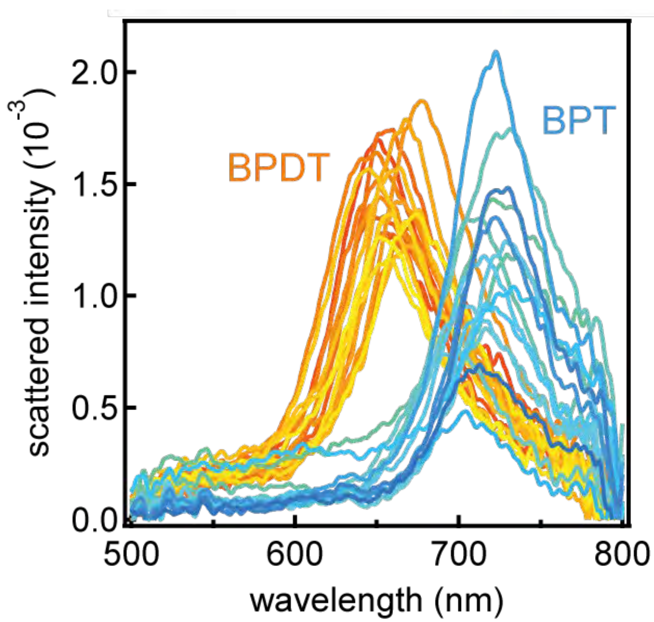
Optical spectroscopy to probe molecular transport

Optical fingerprints of high-frequency transport

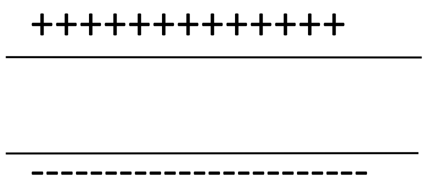
F. Benz *et al*, Nano Lett. 15, 669 (2015)



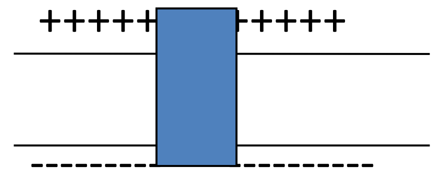




Blue shift of the Bonding Dimer Plasmon (BDP)



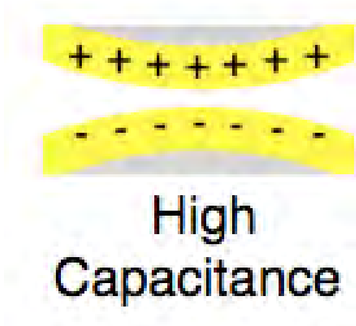
Junction area A_J



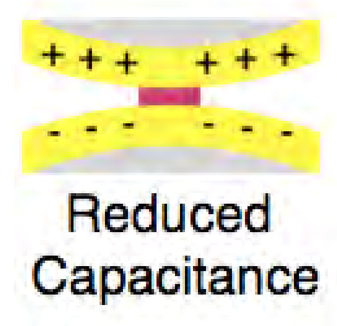
Large Coulomb attraction

Smaller Coulomb attraction as conductivity increases

BDP



SBDP

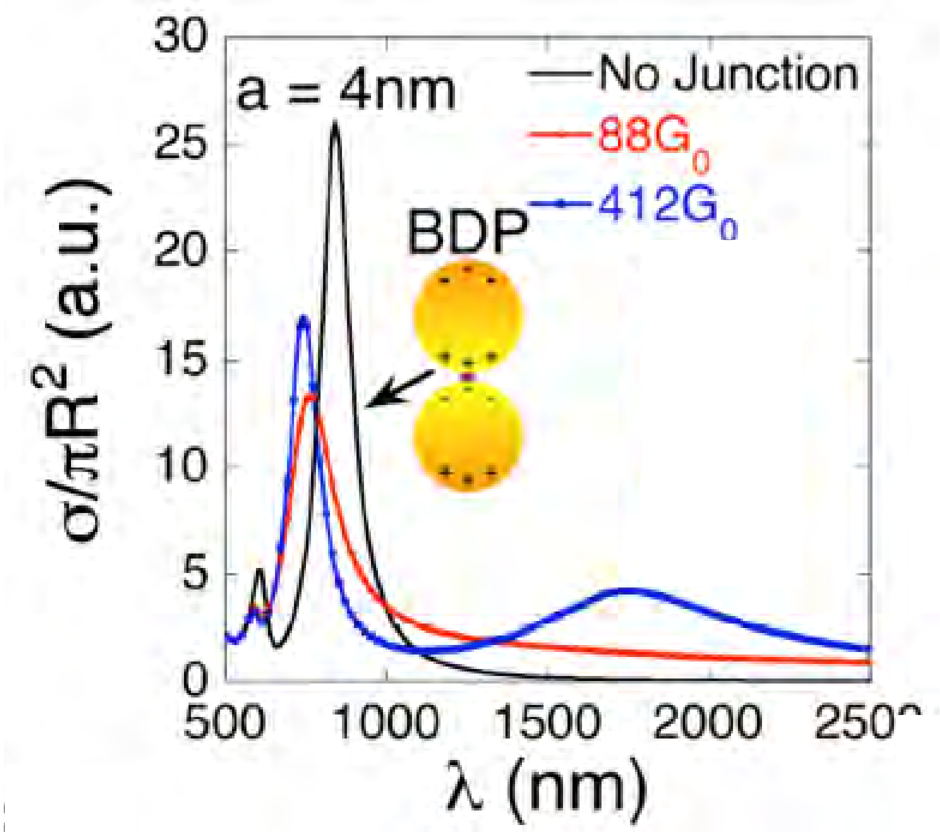


Blueshift depends on the charge screened:

$$\left|\frac{\Delta Q}{Q}\right| \alpha \left|\frac{\Delta \omega}{\omega}\right|$$

Optical signature of molecular conductance at AC

(O. Pérez-González et al. Nano Letters 10, 3090 (2010))



Conductance thresholds
trigger out optical features

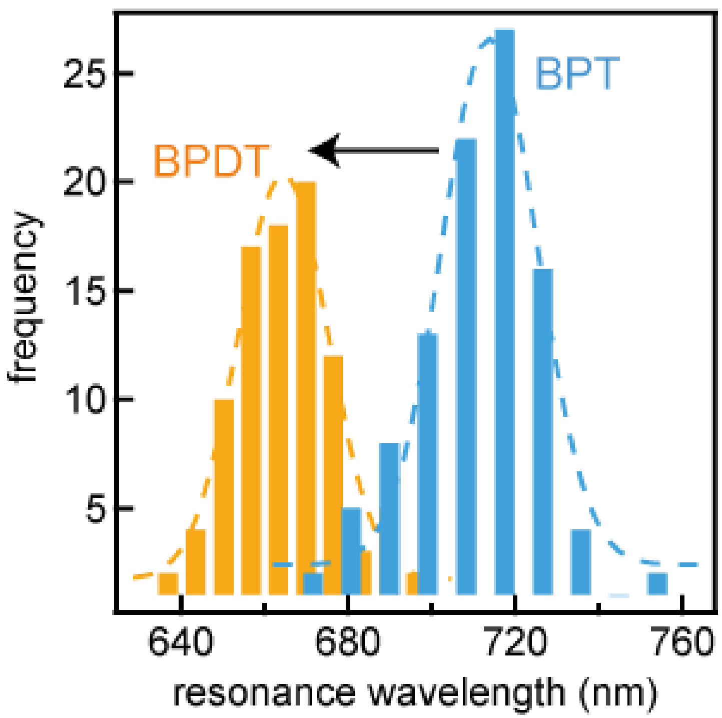
See also O. Pérez-González, N. Zabala and J. Aizpurua, N. J. Phys. 13, 083013 (2011)

Molecular-shunted plasmonic nanojunctions

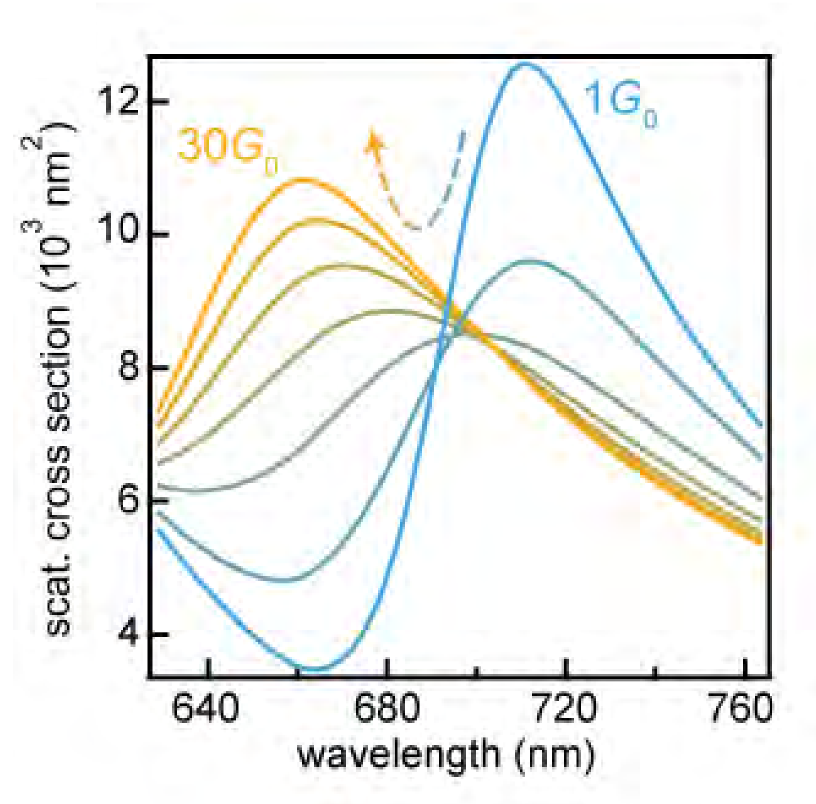
F. Benz *et al.*, Nano Lett. 15, 669 (2015)

60 nm spectral shift

Experiment

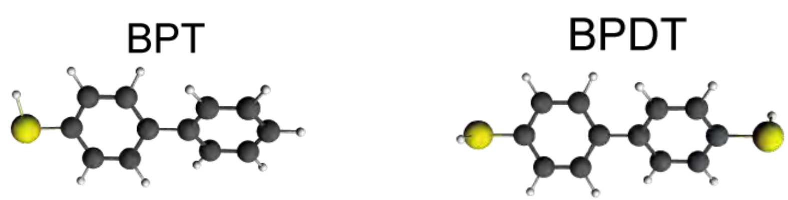


Simulation

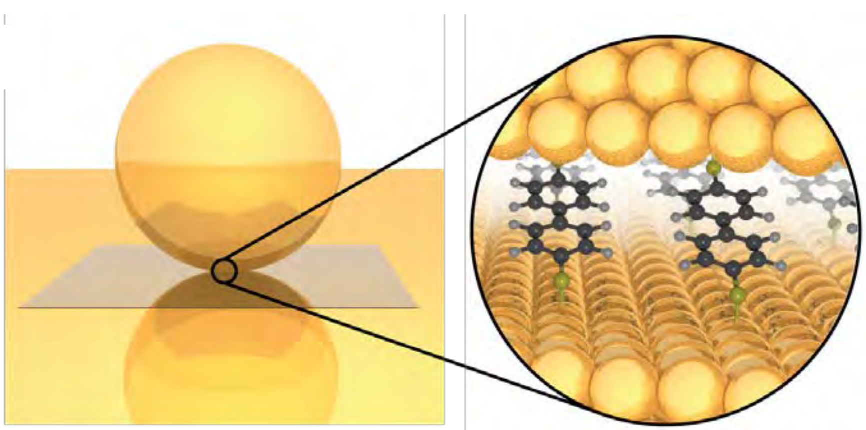


Molecular-shunted plasmonic nanojunctions

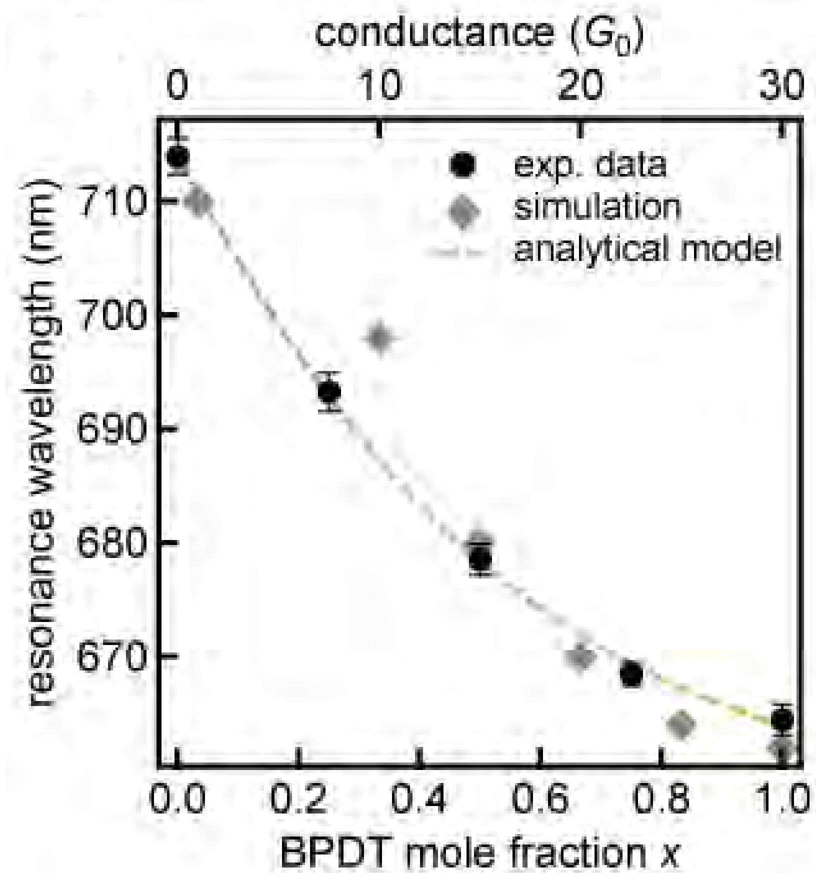
F. Benz *et al.*, Nano Lett. 15, 669 (2015)



x = fraction of BPDT molecules

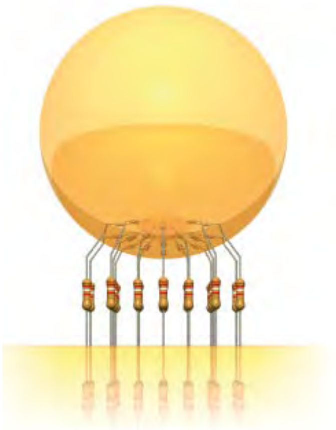


Spectral shift



Molecular-shunted plasmonic nanojunctions

F. Benz *et al.*, Nano Lett. 15, 669 (2015)

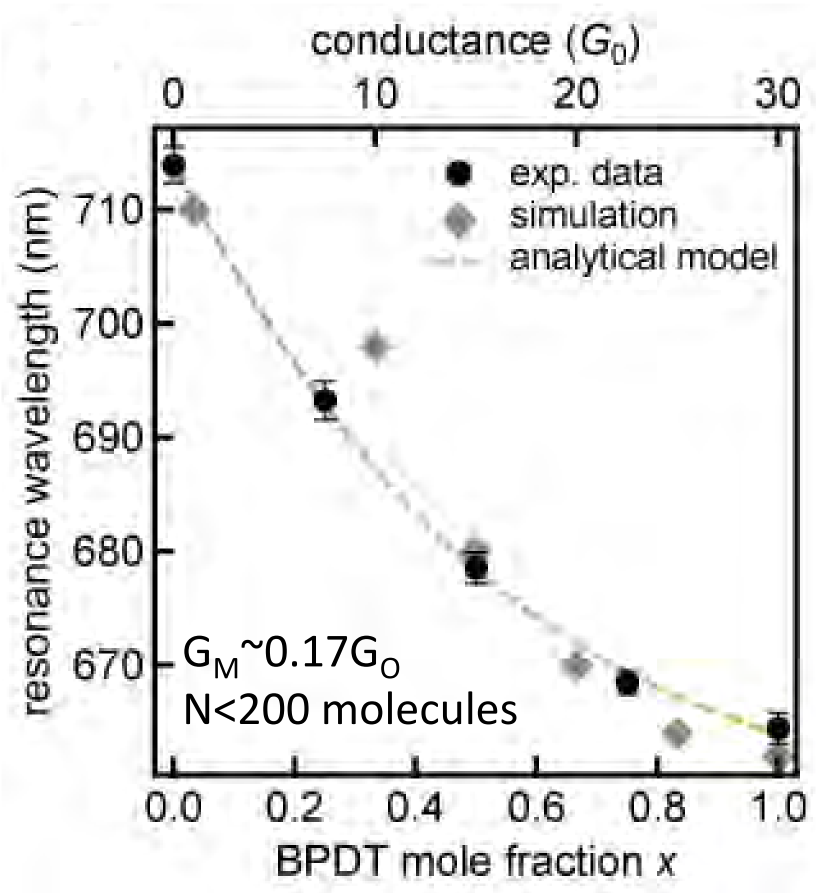


$$\left|\frac{\Delta Q}{Q}\right| = \frac{1}{|Z|C\omega} = \frac{1}{\sqrt{(RC\omega)^2+1}} \propto \frac{\Delta\omega}{\omega}$$

$$\lambda_{\mathrm{NPoM}}(G) = \frac{\lambda_{\mathrm{NPoM}}(G=0)}{1 + b/\sqrt{(\tau_{\mathrm{RC}}\omega)^2+1}}$$

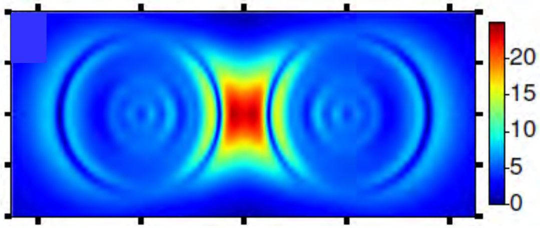
$$\tau_{\mathrm{RC}} = \frac{\varepsilon_0 n_{\mathrm{gap}}^2 A_{\mathrm{M}}}{x d G_{\mathrm{M}}}$$

Spectral shift



Light-matter interaction at the nanoscale

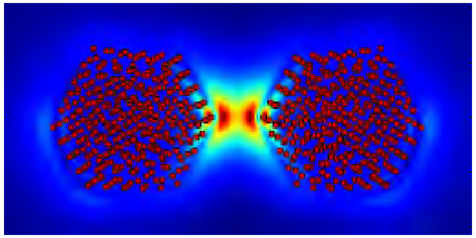
Intro to plasmonics



Plasmonic nanogap

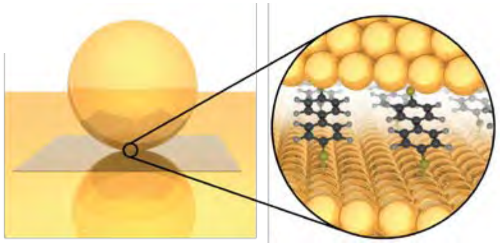
Quantum effects in nanogaps

Photoemission in nanogaps



Atomistic effects in field localization

Transport at optical frequencies

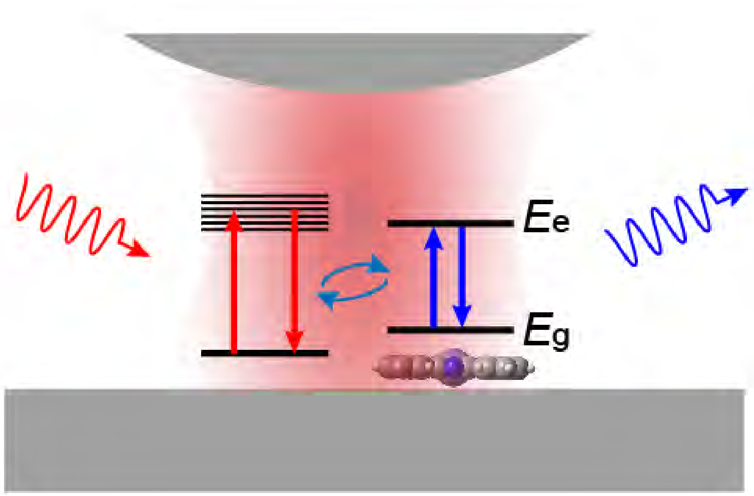


Exciton-plasmon coupling

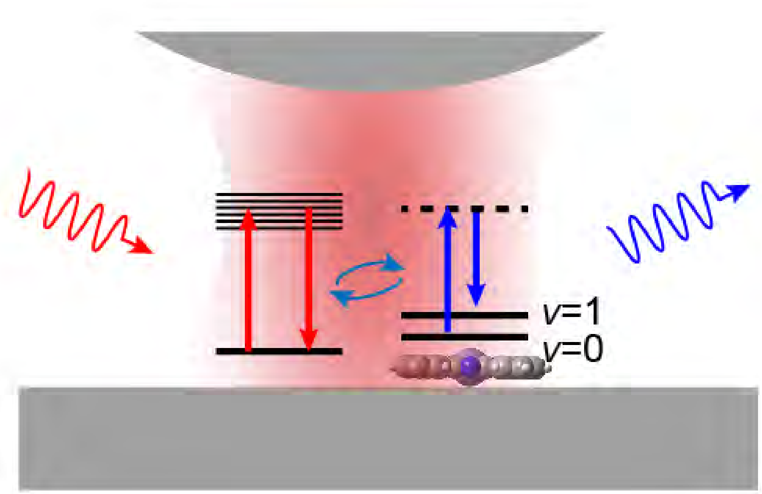
Molecular electroluminescence in nanogaps

Coupling of photons and matter excitations

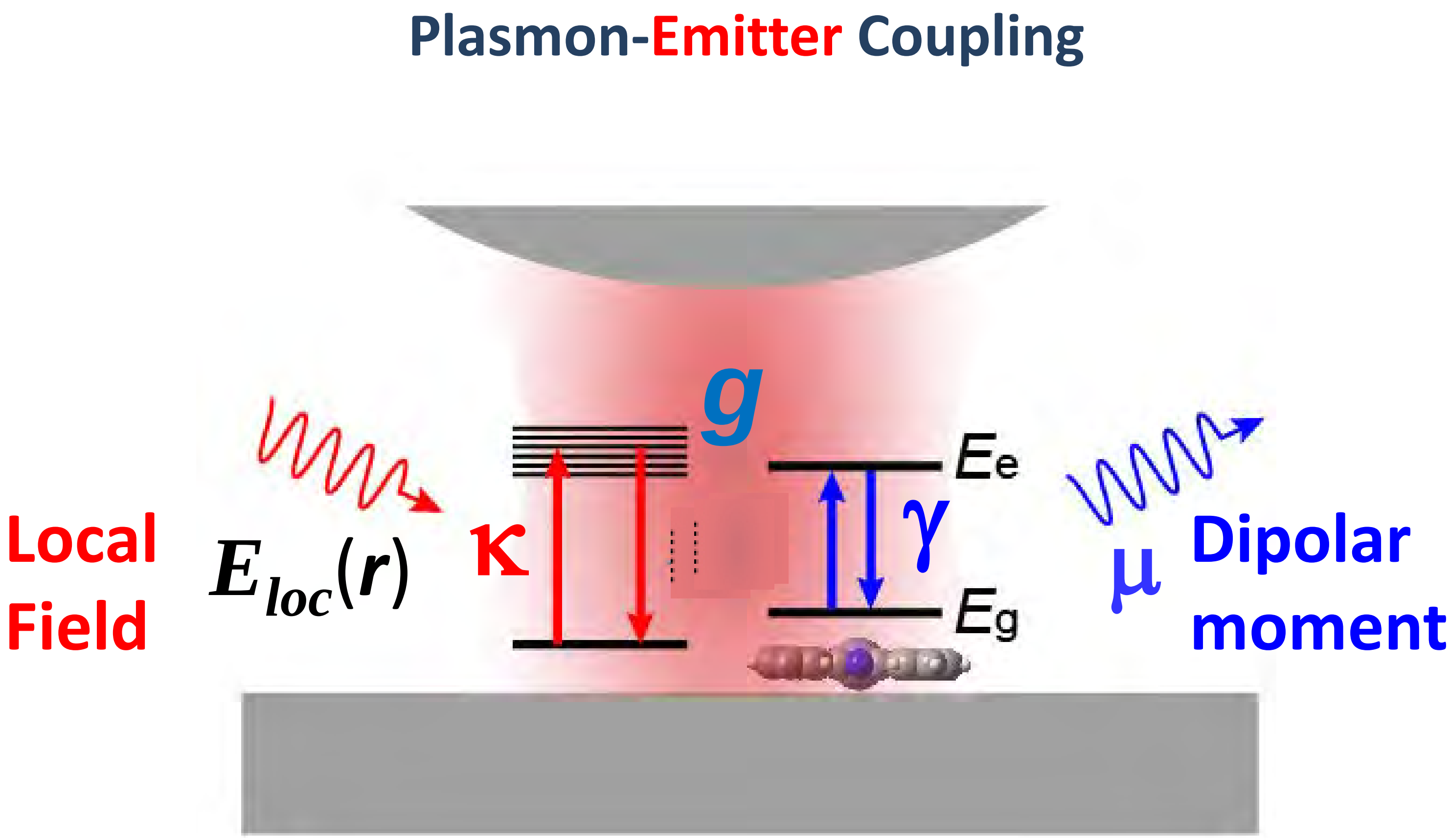
Plasmon-Emitter Coupling



Plasmon-Vibration Coupling



Coupling of photons and matter excitations



Coupling strength

$$\hbar g = -\mathbf{E} \cdot \boldsymbol{\mu}$$

Coupling of photons and matter excitations

Plasmon-Emitter Coupling

Energy

Weak Coupling

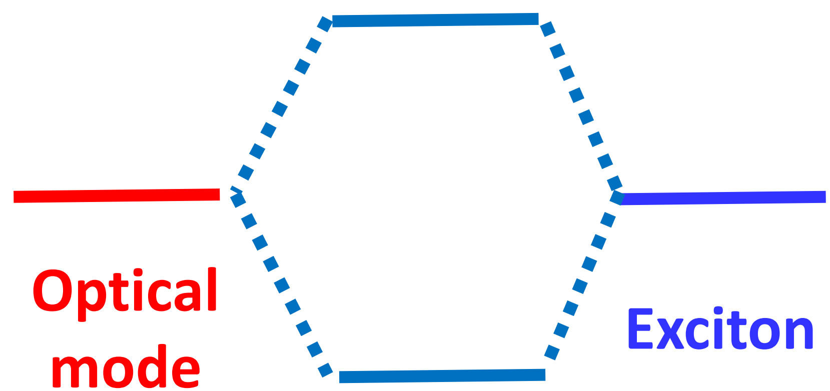
$g < \kappa, \gamma$

Cavity decay　Exciton decay

Purcell effect

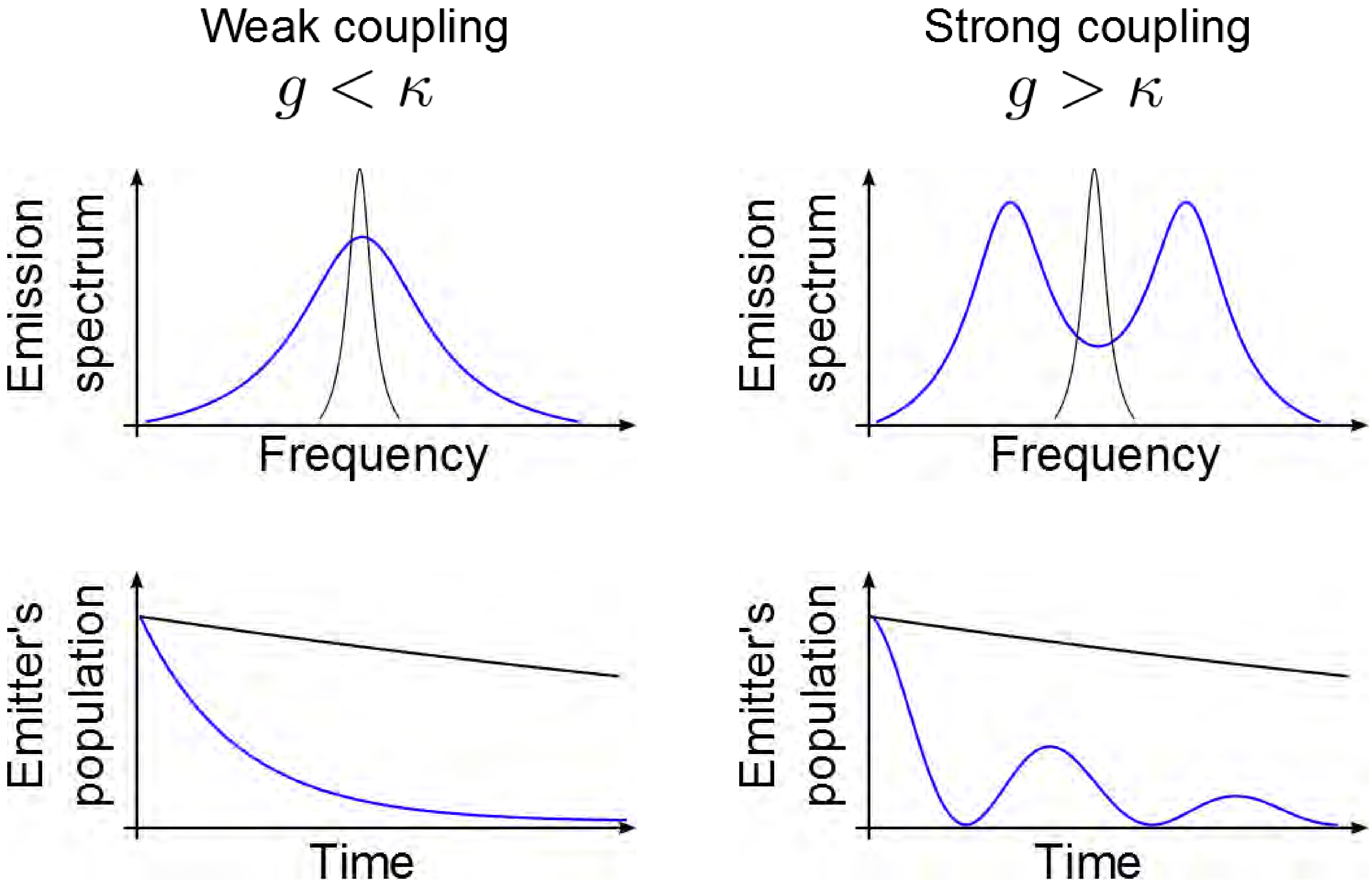
Strong Coupling

$g > \kappa, \gamma$



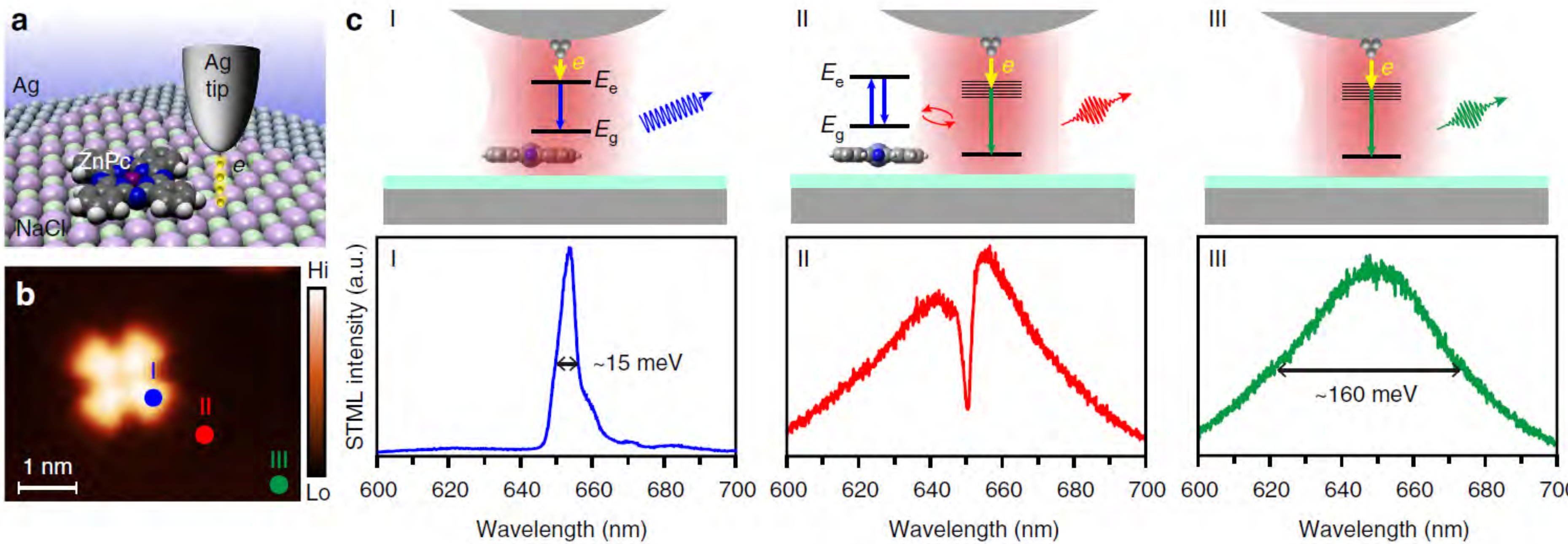
Rabi oscillation

Coupling rate g



Control of the coherent interaction between a single molecule and a plasmonic nanocavity

Weak coupling regime



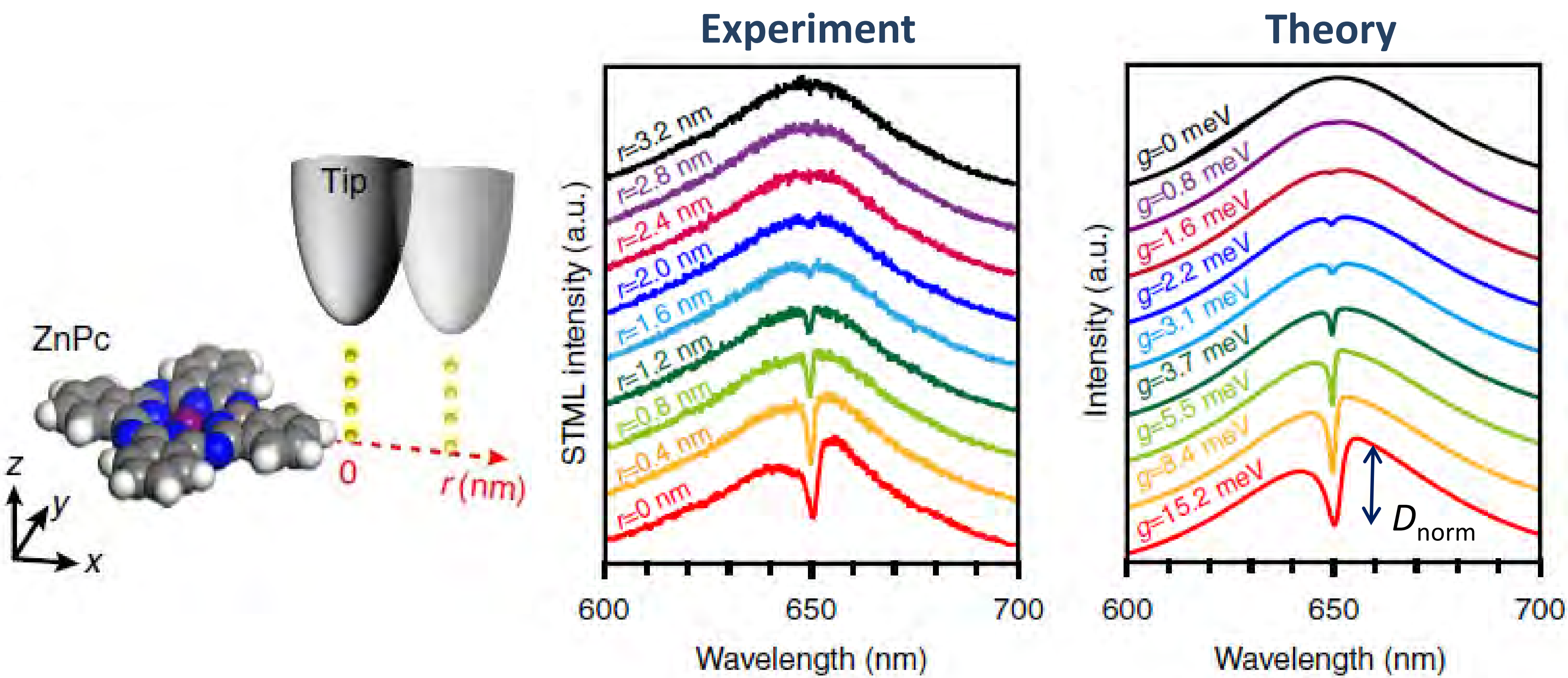
Exciton

Coupled system

Plasmonic resonator

Y. Zhang *et al*. Nature Communications. **8**, 15225 (2017)

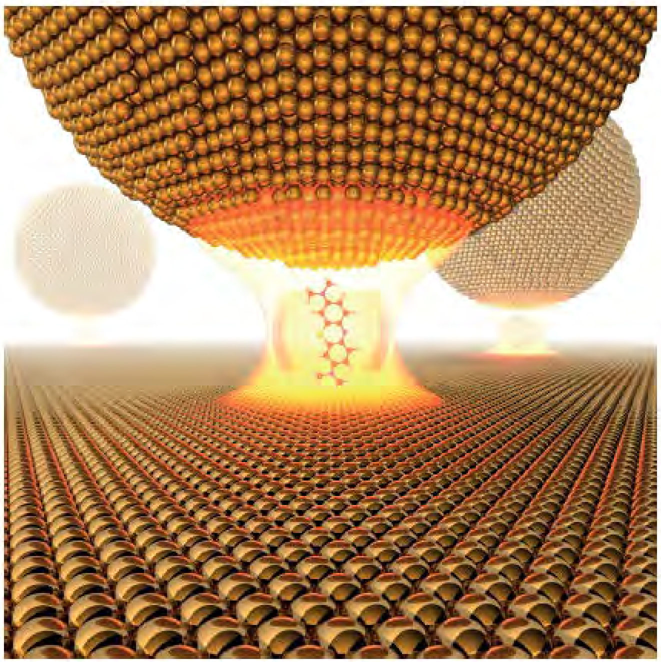
Controlling single molecule coupling in a plasmonic cavity

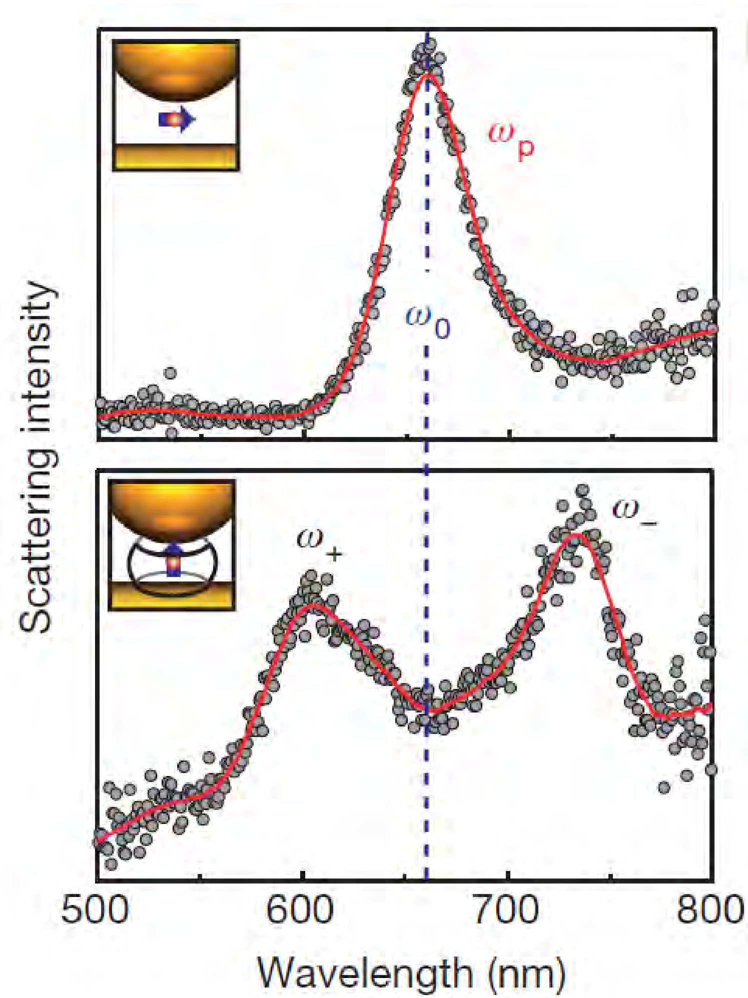


$$g \approx \left[\gamma_p \gamma'_m \left(\sqrt{1/(1-D_{norm})} - 1\right)/4\right]^{1/2}$$

Y. Zhang *et al*. Nature Communications. **8**, 15225 (2017)

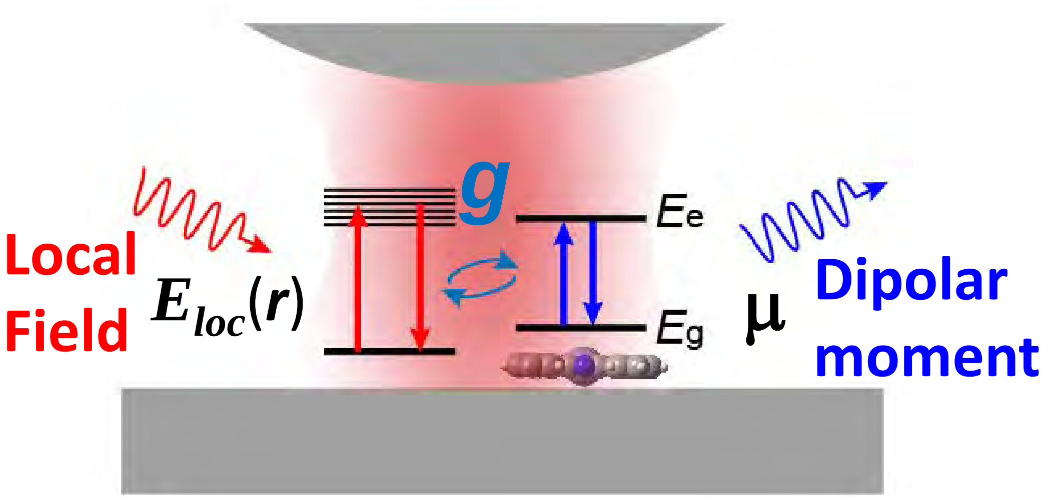
Strong coupling of a single molecule in a plasmonic cavity

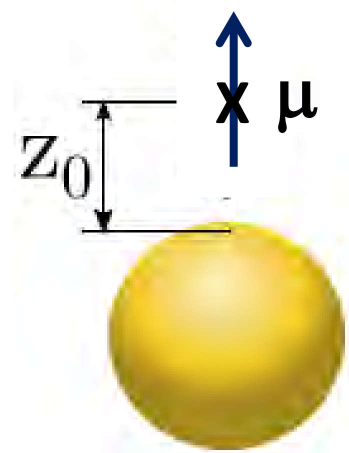




R. Chikkaraddy *et al*. Nature **535**, 127-130 (2016)

Beyond the dipole approximation
A Quantum Chemistry Aproach

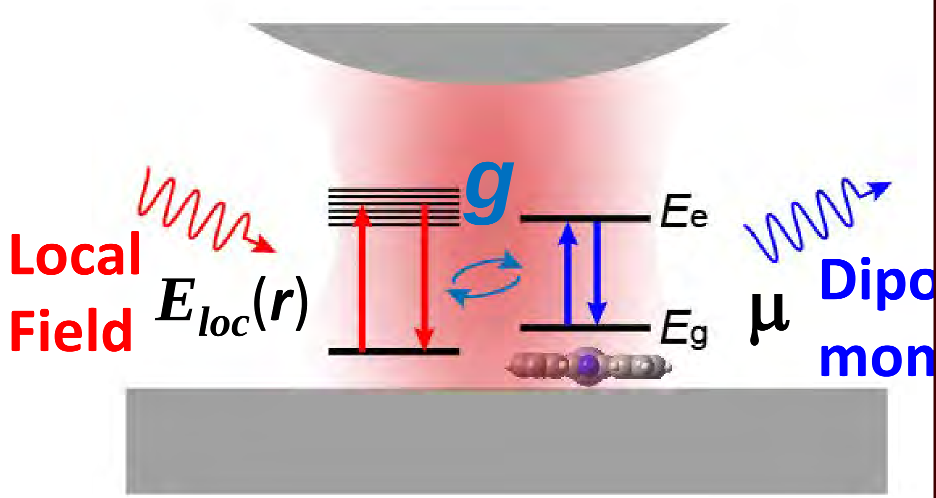


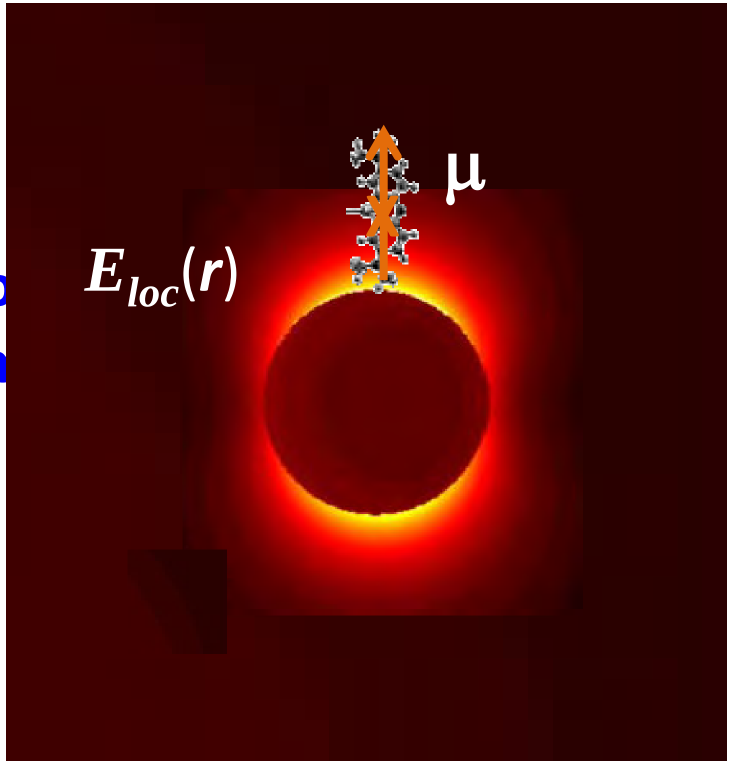


$$\hbar g = -\mathbf{E} \cdot \mu$$

Point-dipole model (PDM)

Beyond the dipole approximation
A Quantum Chemistry Aproach



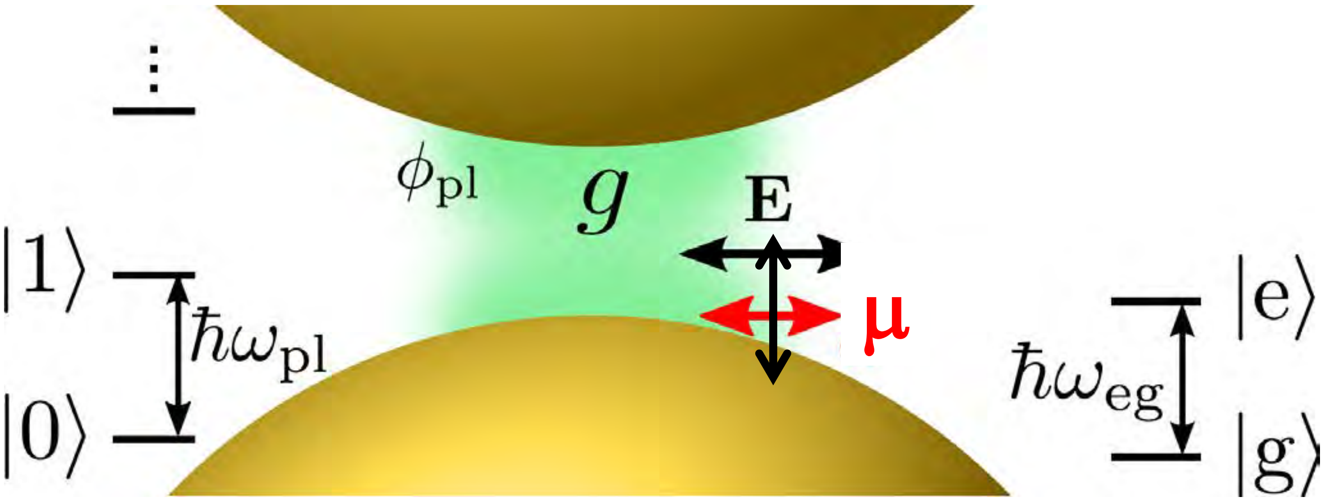


$$\hbar g = -\mathbf{E} \cdot \mu$$

Point-dipole model (PDM)

Beyond the dipole approximation

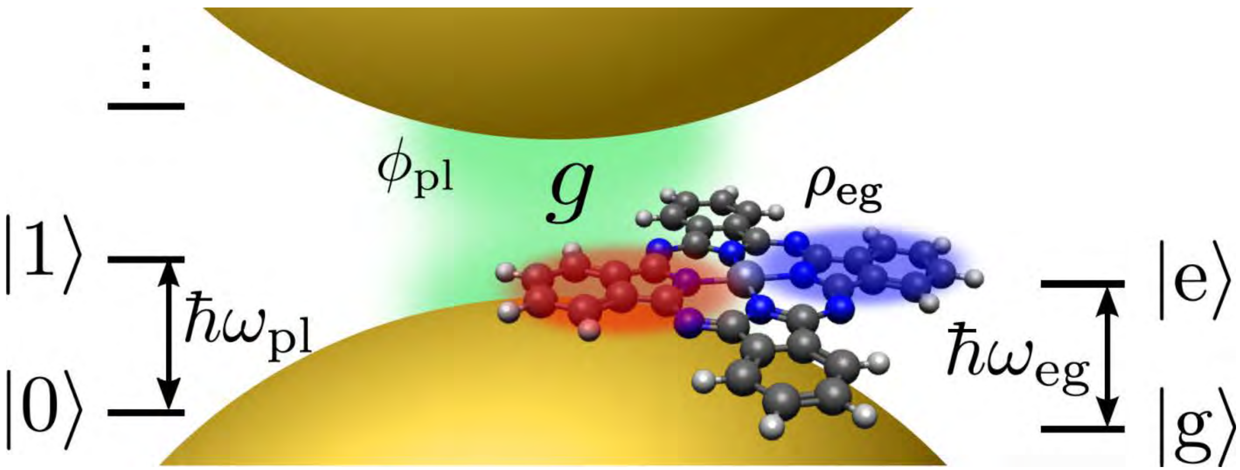
T. Neuman *et al.*, Nano Letters, **18**, 2358-2367 (2018)



$$\hbar g = -\mathbf{E} \cdot \boldsymbol{\mu}$$

Point-dipole model (PDM)

Beyond the dipole approximation
A Quantum Chemistry approach

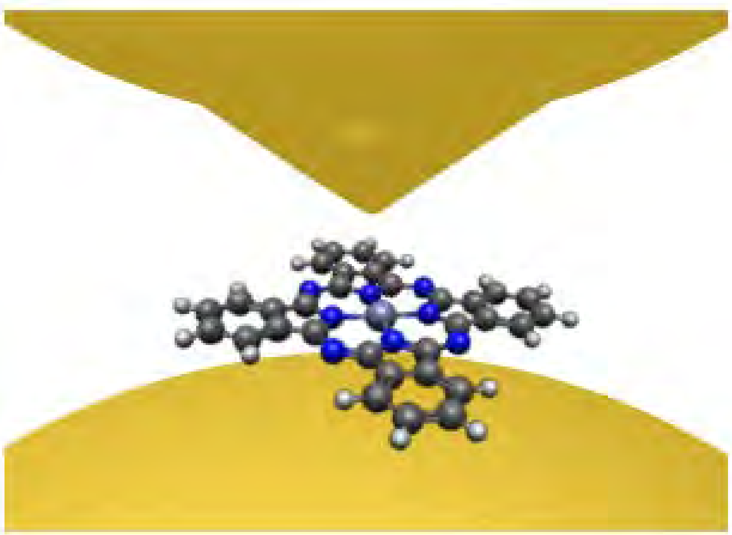


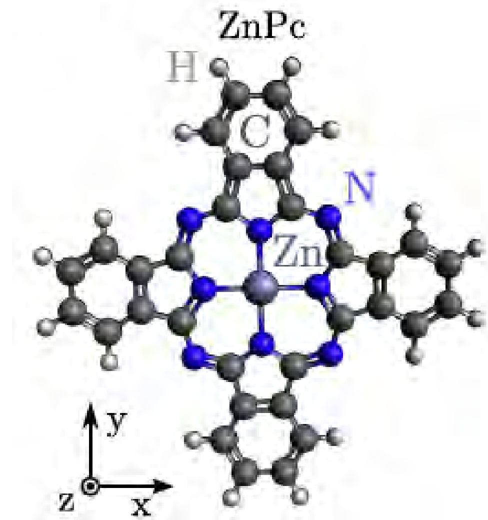
$$\hbar g = \iiint \rho_{\mathrm{eg}} \phi_{\mathrm{pl}} \mathrm{d}^3\mathbf{r}$$

Full-quantum model (FQM)

Beyond the dipole approximation
A Quantum Chemistry Aproach

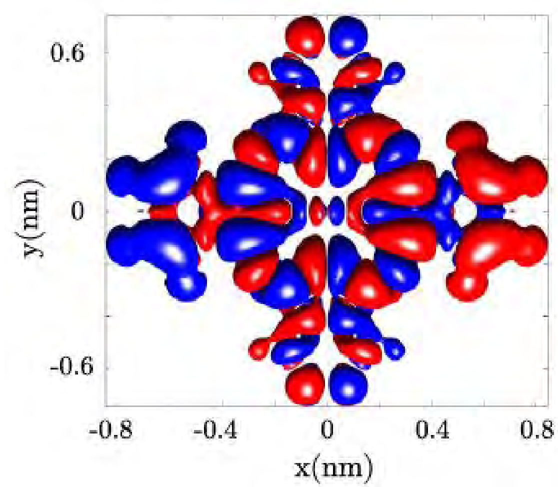
Zinc Phtalocyanine (ZnPc)





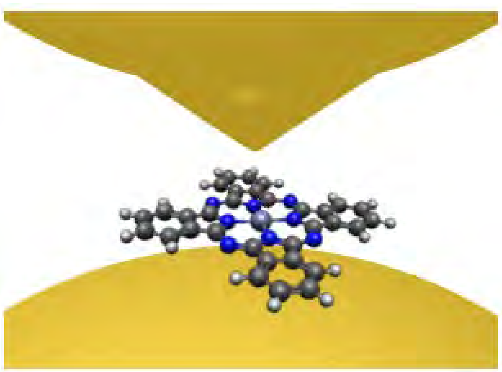
Quantum Model

Point Dipole

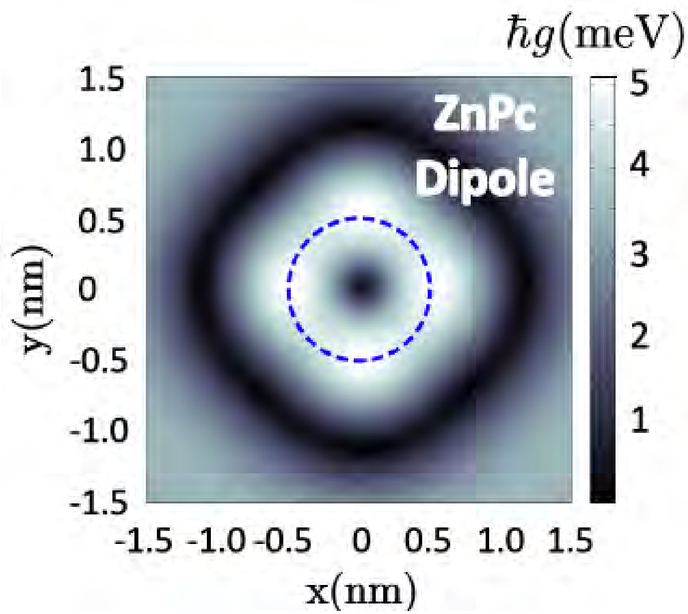


Beyond the dipole approximation
A Quantum Chemistry Aproach

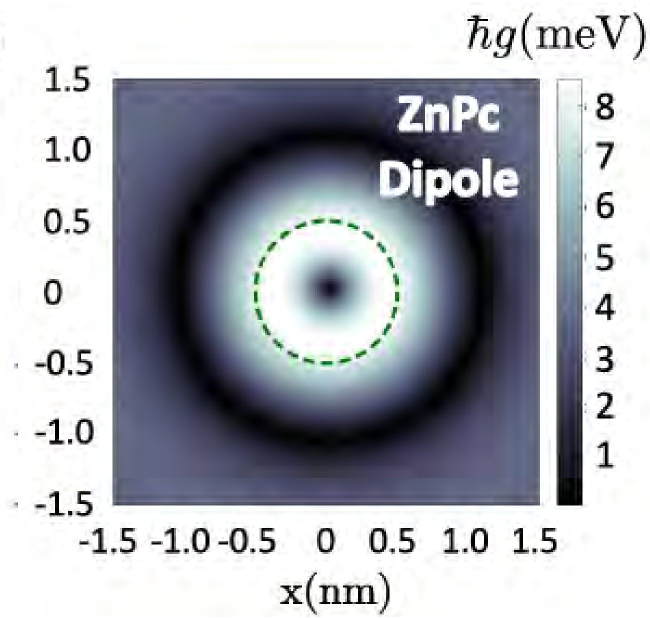
Zinc Phtalocyanine (ZnPc)



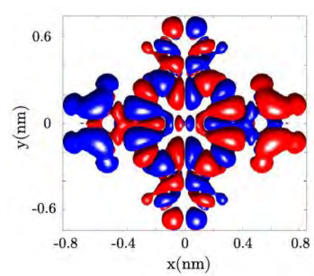
Quantum Model



Point Dipole



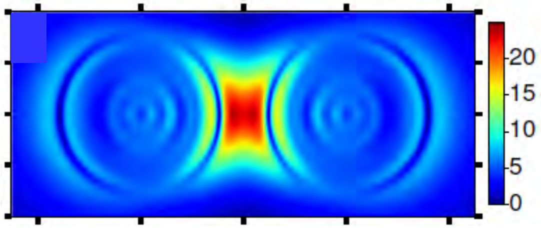
$$\hbar g = \iiint \rho_{eg} \phi_{pl} d^3\mathbf{r}$$



Light-matter interaction at the nanoscale

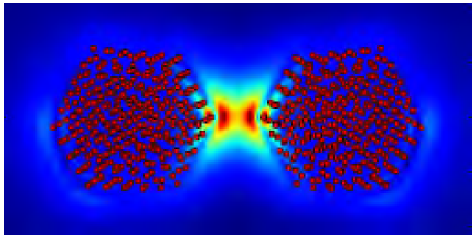
Intro to plasmonics

Plasmonic nanogap



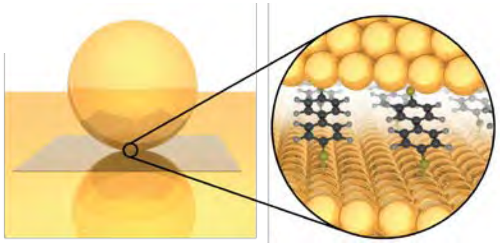
Quantum effects in nanogaps

Photoemission in nanogaps



Atomistic effects in field localization

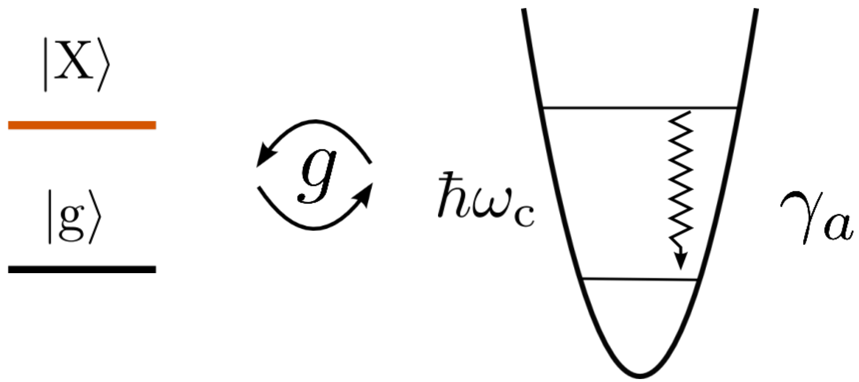
Transport at optical frequencies

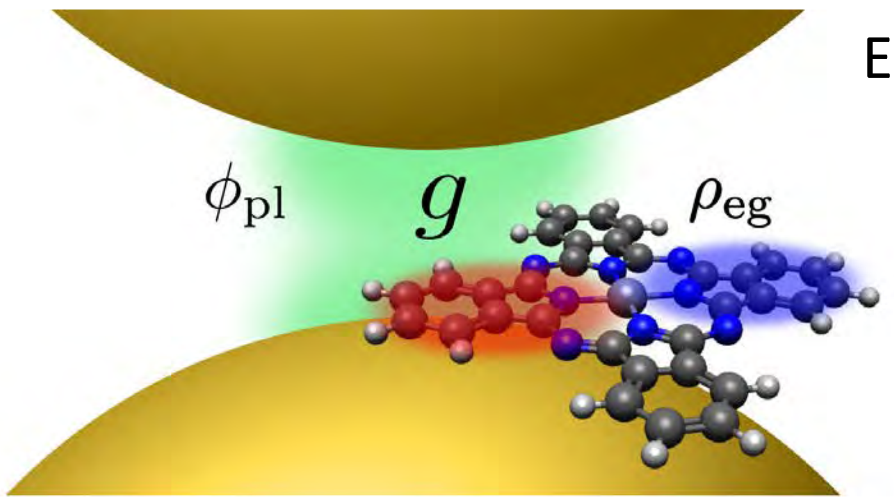


Exciton-plasmon coupling

Molecular electroluminescence in nanogaps

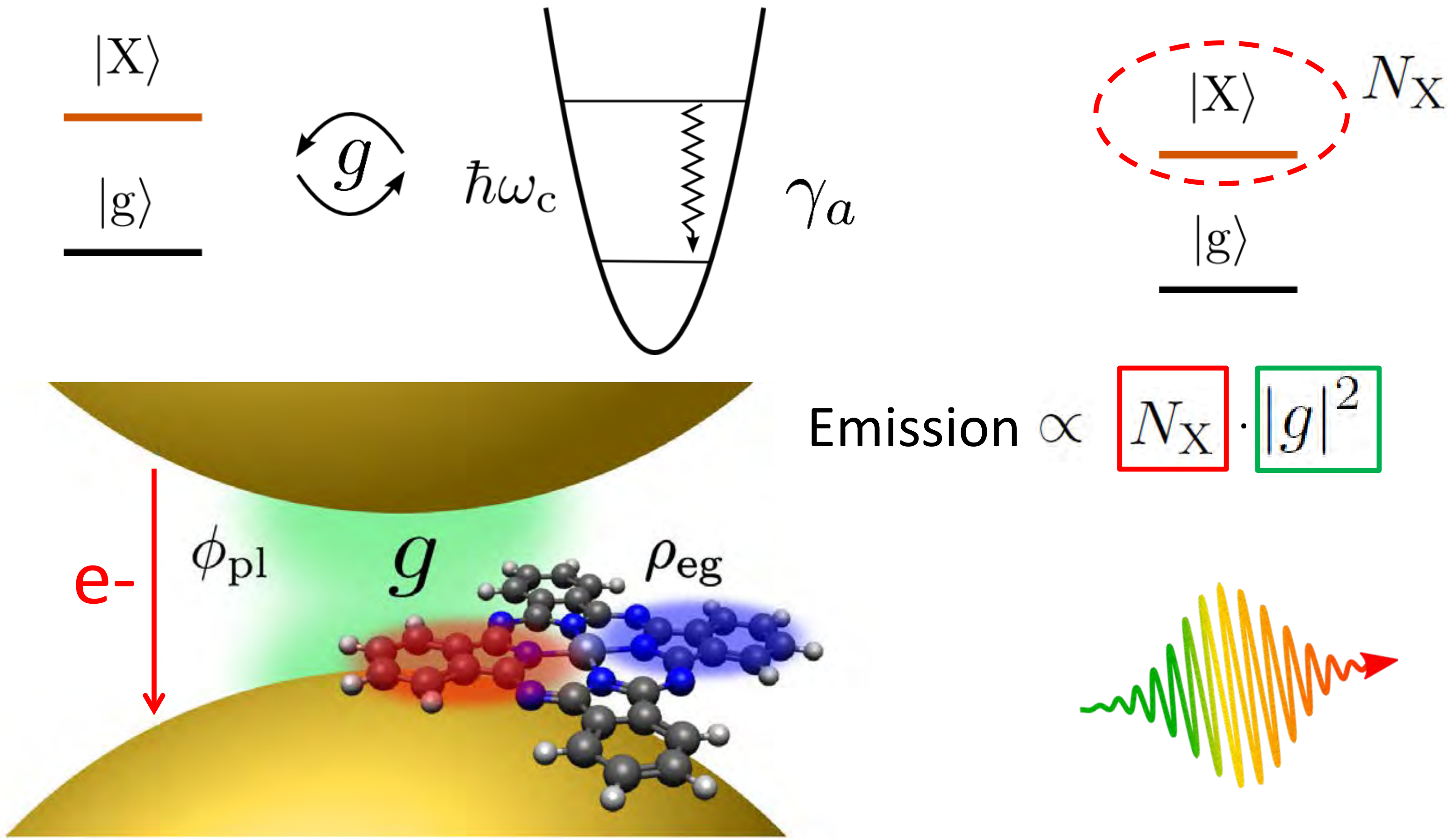
Decay of molecular excitations



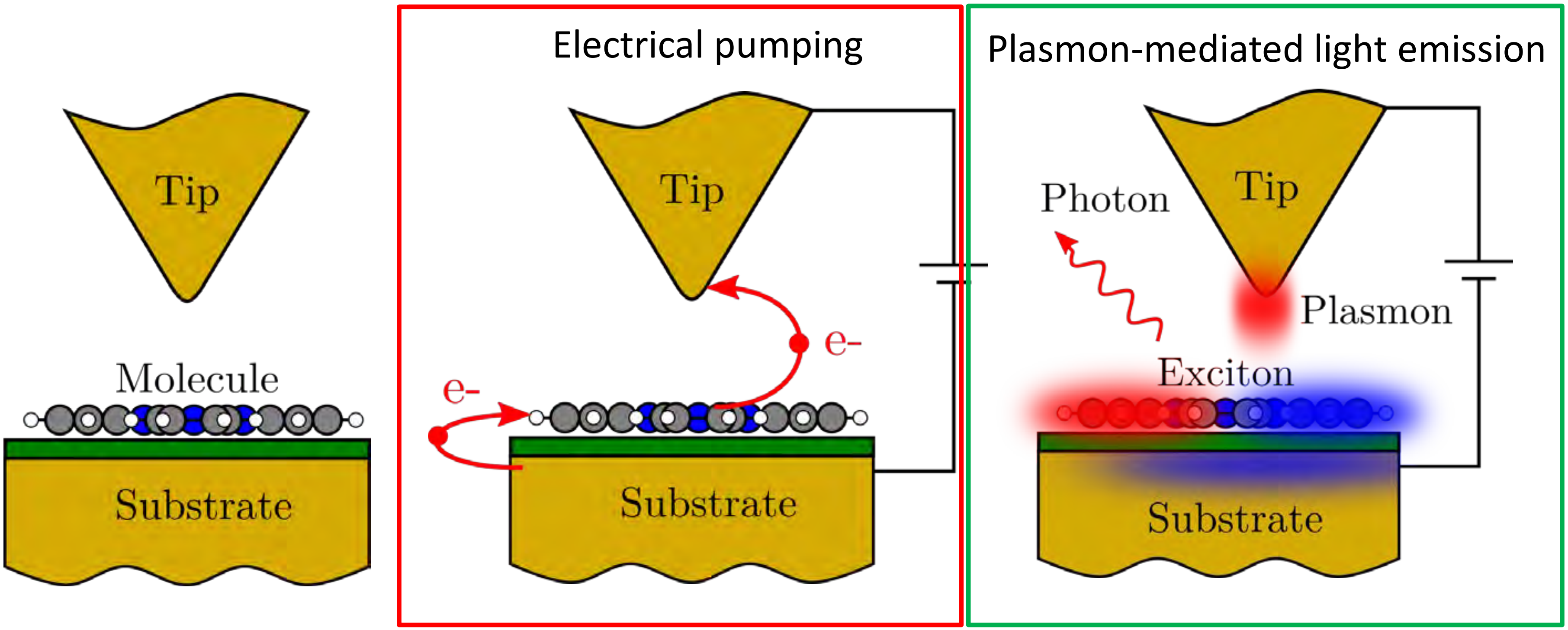


Emission $\propto |g|^2$

Decay of molecular excitations



STM-induced electroluminescence



Detected efficiency of photon generation

$$\mathscr{I}_{\mathrm{det}} \propto \eta_{\mathrm{pump}}(\mathbf{r}) \cdot \eta_{\mathrm{em}}(\mathbf{r})$$

Pumping efficiency (electron tunneling)

Emission probability

Photon emission from molecules in STM

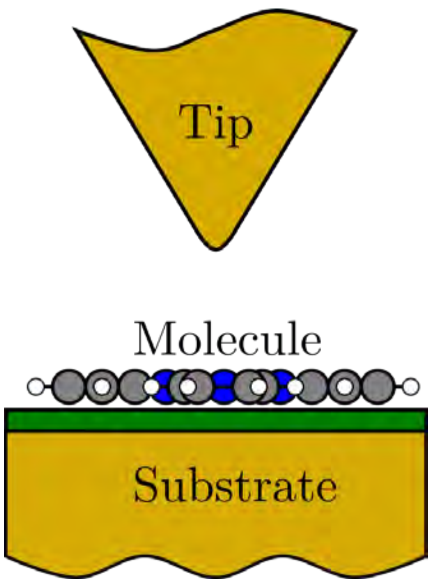
$$\mathscr{I}_{\mathrm{det}} \propto \boxed{\eta_{\mathrm{pump}}(\mathbf{r})} \cdot \boxed{\eta_{\mathrm{em}}(\mathbf{r})}$$

$$\mathscr{I}^{\mathrm{Q}}_{\mathrm{det}}(\mathbf{r}) \propto \boxed{\frac{N_{\mathrm{X}}(\mathbf{r})}{I_{\mathrm{H}}(\mathbf{r}) + I_{\mathrm{BG}}}} \cdot \boxed{|g_{\mathrm{Q}}(\mathbf{r})|^2}$$

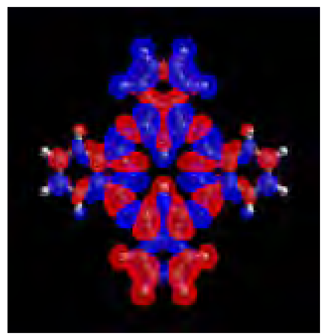
Pumping **Emission**

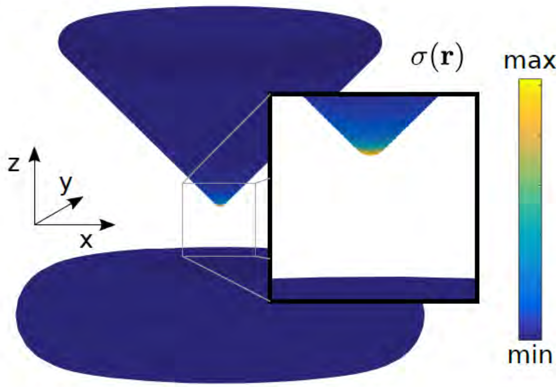
Photon emission from molecules in STM

$$|g_{\mathrm{Q}}(\mathbf{r})|^2$$

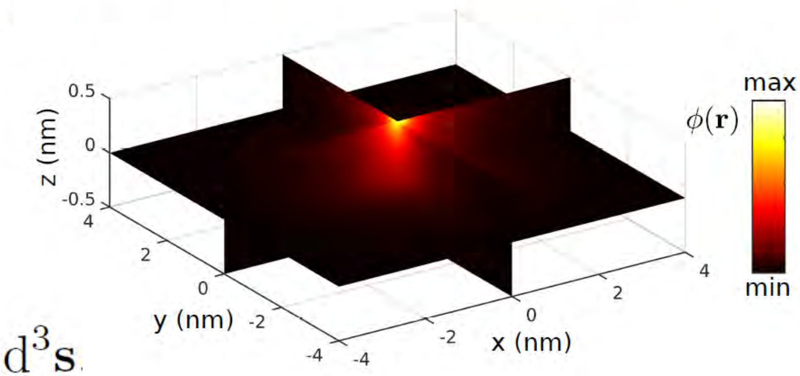


$\rho_{\mathrm{Q}}(\mathbf{s})$





Surface-charge density

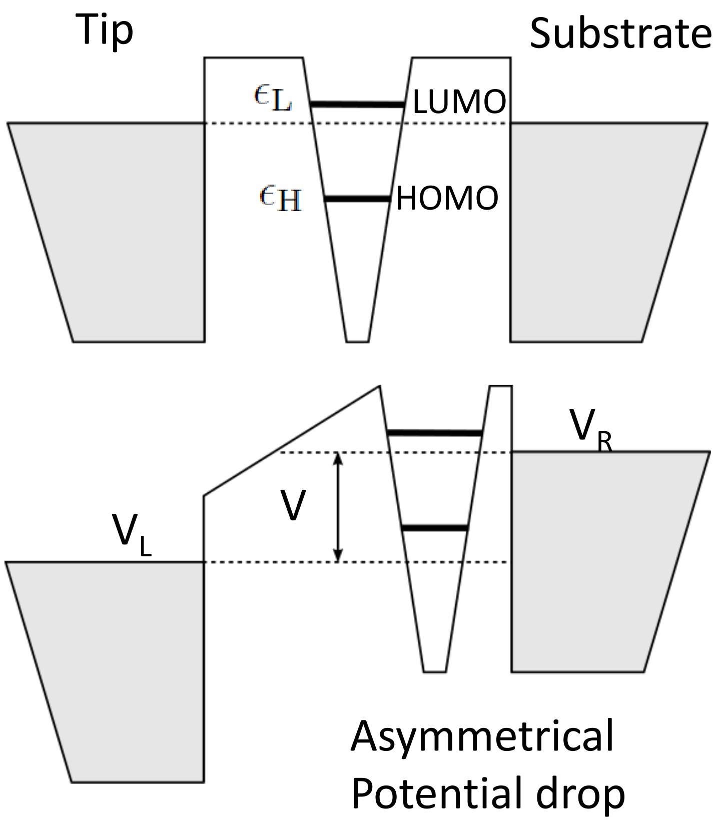


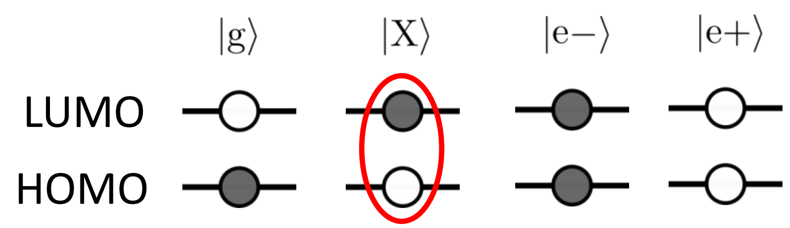
Plasmonic potential

$$g_{\mathrm{Q}}(\mathbf{r}) = \iiint \rho_{\mathrm{Q}}(\mathbf{s})\phi(\mathbf{s}-\mathbf{r})\mathrm{d}^3\mathbf{s}.$$

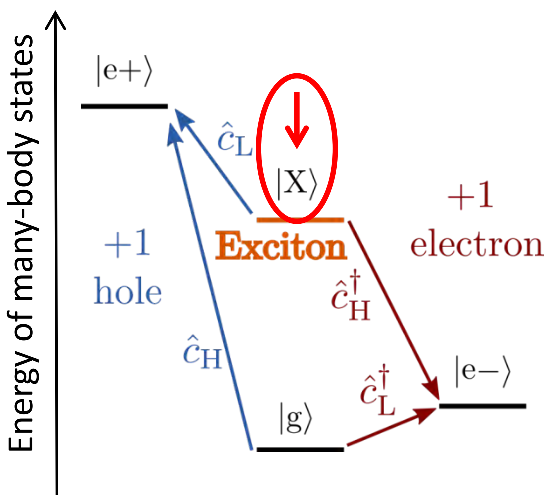
Electron tunnelling

$$N_{\mathrm{X}} \propto |\psi_{\mathrm{HOMO}}|^2$$

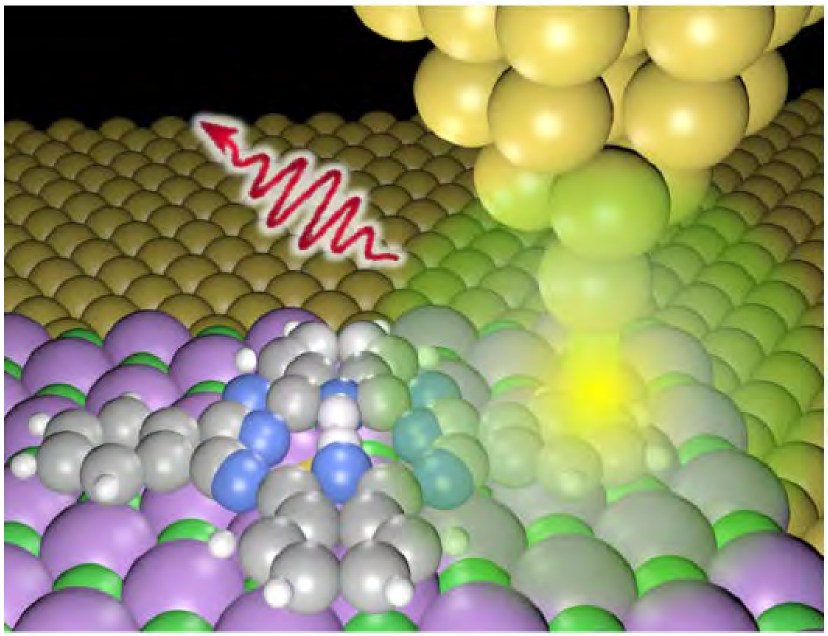


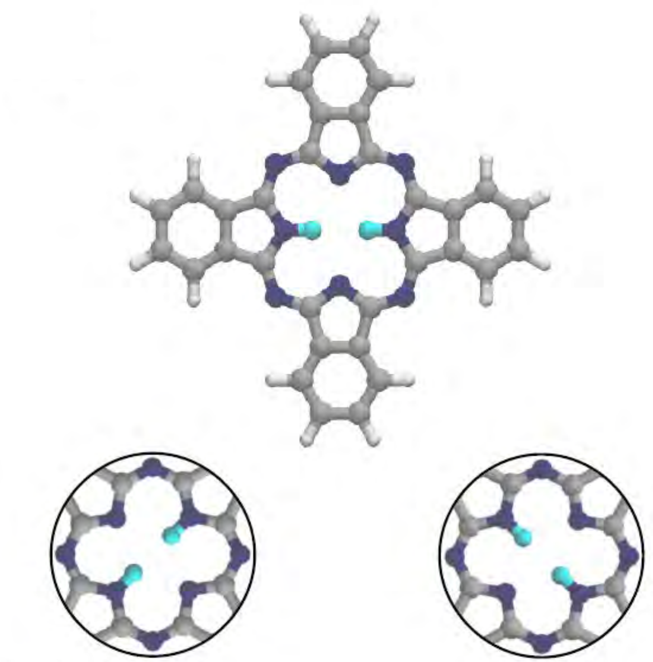


Coulomb attraction lowers exciton energy



Identifying molecular configurations with light
Tautomerization





to appear in Nat. Nanotech.; Collaboration with Guillaume Schull, Strasbourg

Collaborations

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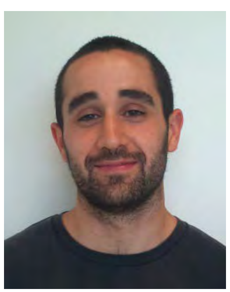
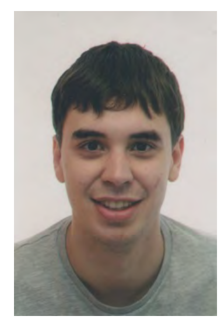


Garikoitz Aguirregabiria

Antton Babaze

Alvaro Nodar



Unai Muain

Carlos Maciel

Thank you for your attention