Linear and nonlinear response of plasmonic systems by TDDFT

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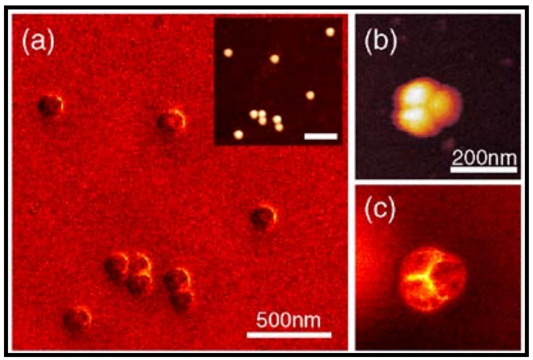
NanoSaclay
Laboratoire d'Excellence
en Nanosciences et Nanotechnologies

Motivation

- Coupling metallic nanoparticles : amplified field enhancement, Fano-like interferences

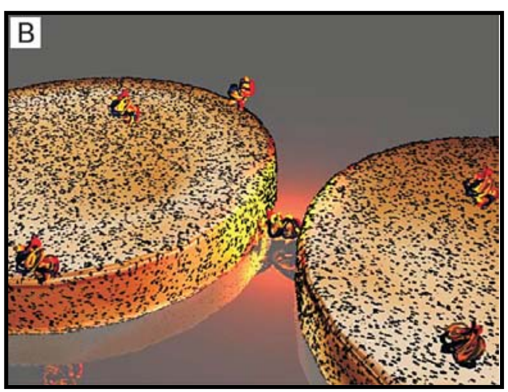
Optical frequency mixing

Danckwerts and Novotny,
Phys. Rev. Lett. 98, 026104 (2007)



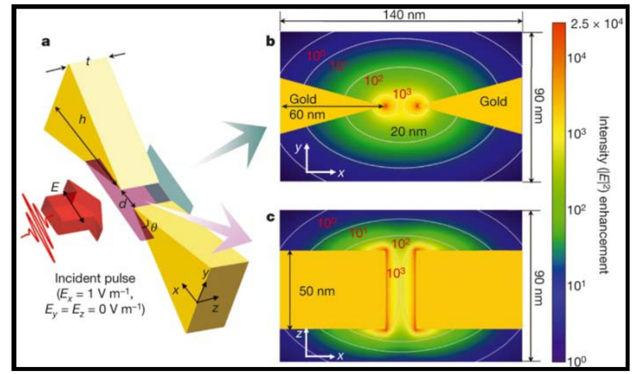
Single-molecule sensing

Aćimović et al, *ACS Nano* 3 (2009)



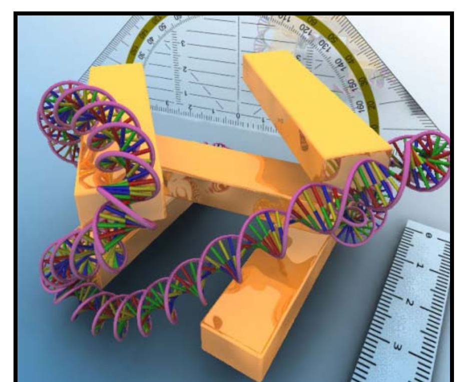
High harmonic generation

Kim et al, Nature 453, 757-760 (2008)



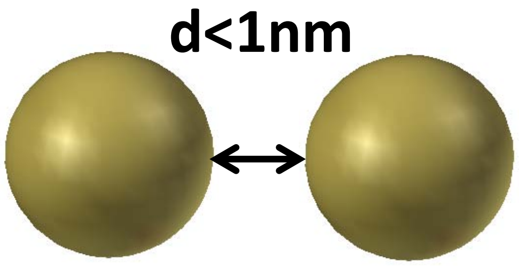
Three-Dimensional Plasmon Rulers

Liu et al, Science 332, 1407 (2011)



Motivation

- Optical response of plasmonic nanoparticles separated by **sub-nanometer** gaps : **quantum effects** become important



  ⇨ non-local dynamical screening

  ⇨ electron tunneling across the junction

  ⇨ strong field ionization

Quantum treatment

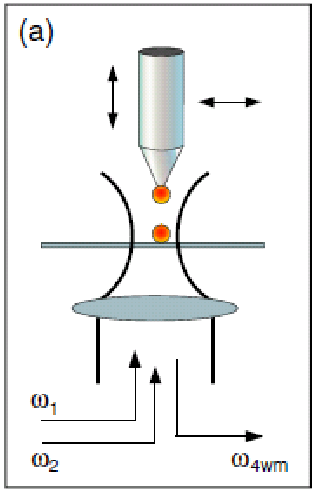
- Experimental probe of the optical response in the quantum regime

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

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

Plasmonic nanoparticles close to the touching point

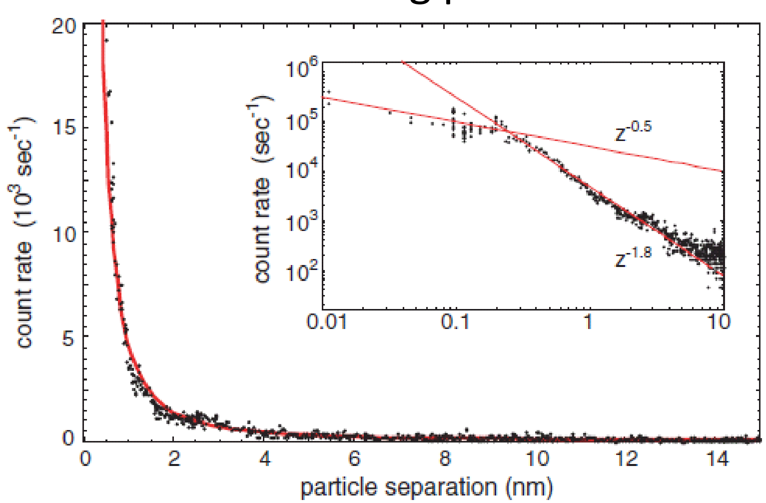
- novel plasmonic modes due to charge transfer



Experiment

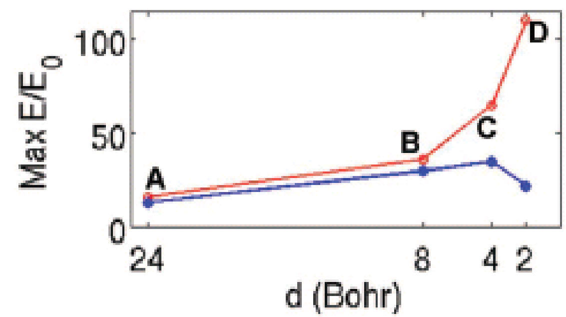
Danckwerts and Novotny
PRL 98, 026104 (2007)

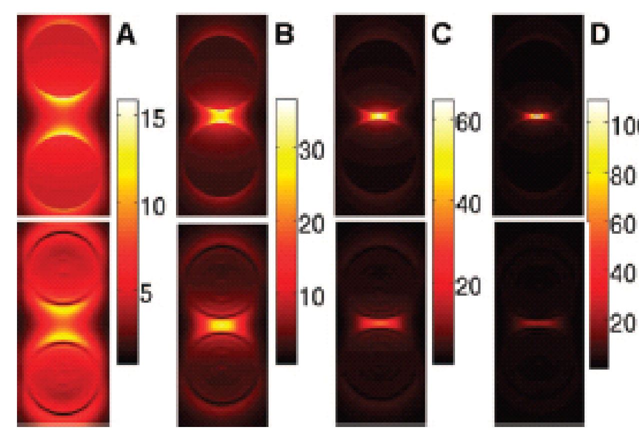
4w mixing photon count



Theory TDDFT

Zuloaga, Prodan, Nordlander
Nano Letters 9, 887 (2009)





Quantum modelling of plasmonic systems

Time dependent density functional theory

- Quantum description of metallic nanoparticles (NP) from electronic states
- Dynamics of the system under a time-dependent external field
- Real time TDDFT : **linear** and **nonlinear** (strong field) reponse
- Jellium model

  ⇨ metallic NPs containing a few 1000's of atoms

  ⇨ well-defined plasmonic modes

Quantum modelling of plasmonic systems

Time dependent density functional theory

- TDSE for the Kohn-Sham orbitals : $$i\frac{\partial \psi_j(t)}{\partial t} = H\left[n(t)\right]\psi_j(t)$$

- Potential is a function of the electronic density $$H\left[n(t)\right] = T + V\left[n(t)\right]$$ $$T = -\frac{1}{2}\nabla^2$$ $$V\left[n(t)\right] = V_H\left[n(t)\right] + V_{XC}\left[n(t)\right] + V_{ext}(t)$$

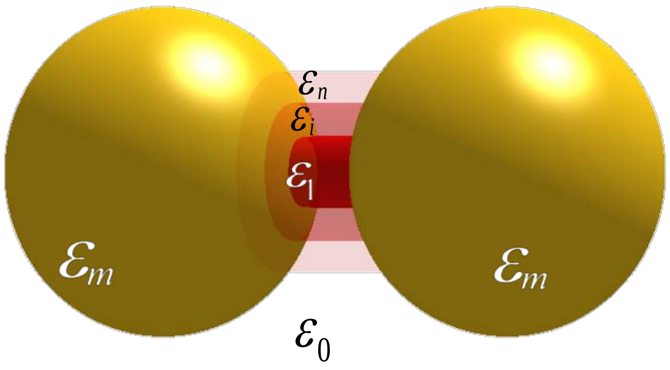
- Electronic density (spin restricted) $$n(t) = \sum_{j\,occ} \left|\psi_j(t)\right|^2$$

- Short-time propagation $$\Psi_j(t + d\,t) = e^{-i\,H\,dt}\,\Psi_j(t)$$

Quantum modelling of plasmonic systems

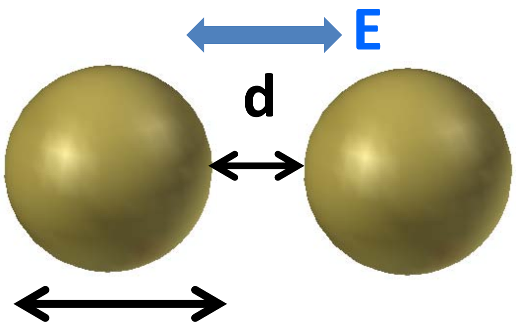
- Large plasmonic systems separated by sub-nm gaps : multi-scale problem

Quantum corrected model (QCM)

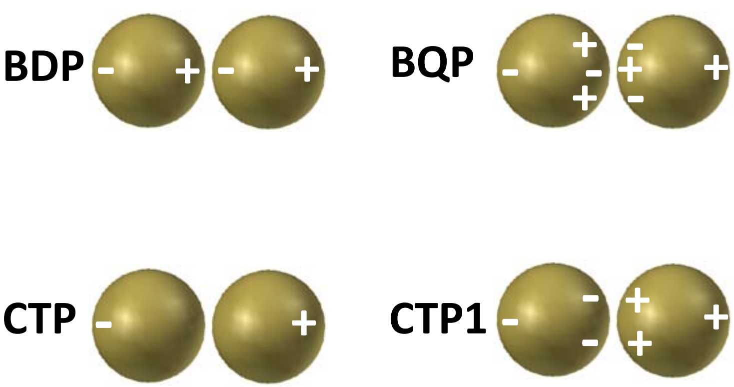


R. Esteban, A.G.Borisov, P. Nordlander, J. Aizpurua
Nature Communications DOI: 10.1038/ncomms1806

Plasmonic NP dimer : linear response

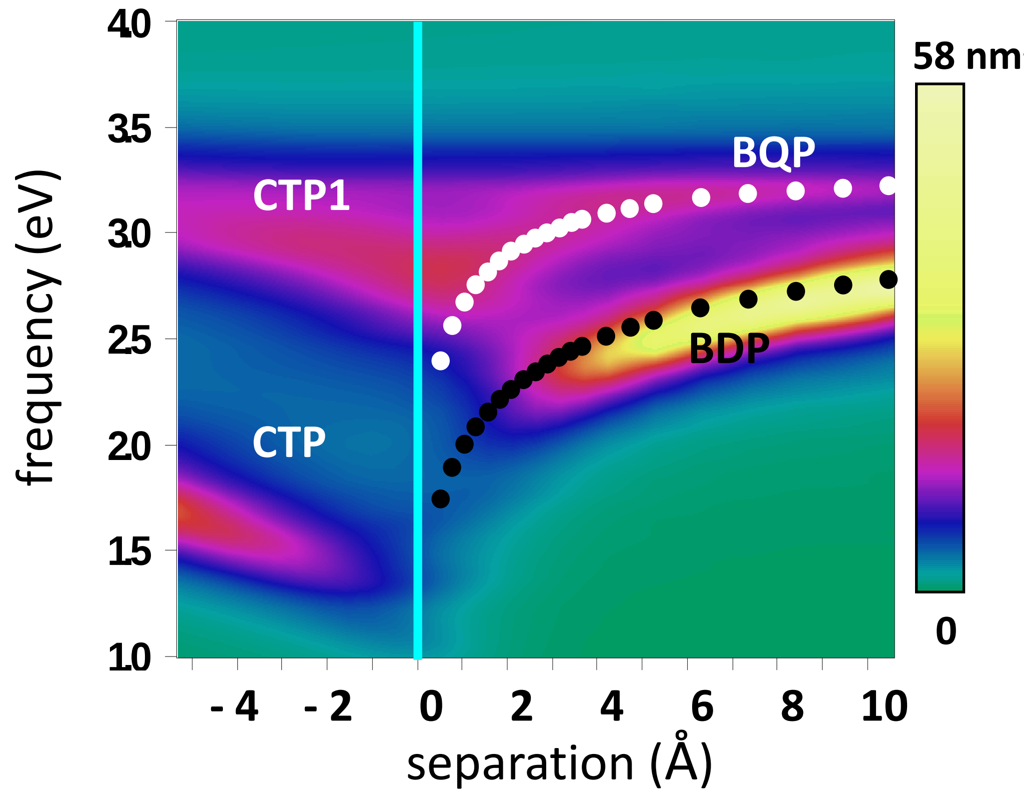


D=4nm Na nanoparticles

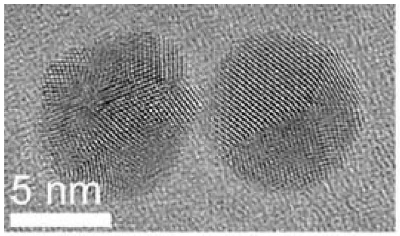


Absorption cross-section

$$\Sigma_{abs}(\omega) = \frac{4\pi\omega}{c} Im\left\{\alpha(\omega)\right\}$$



Plasmonic NP dimer : linear response

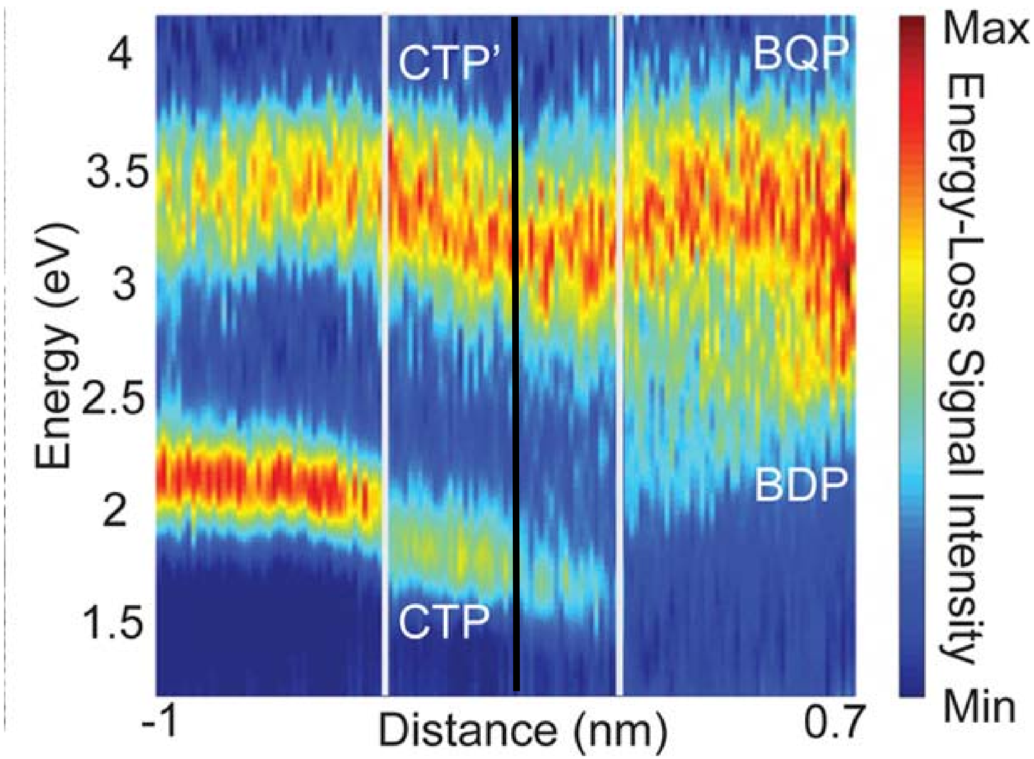


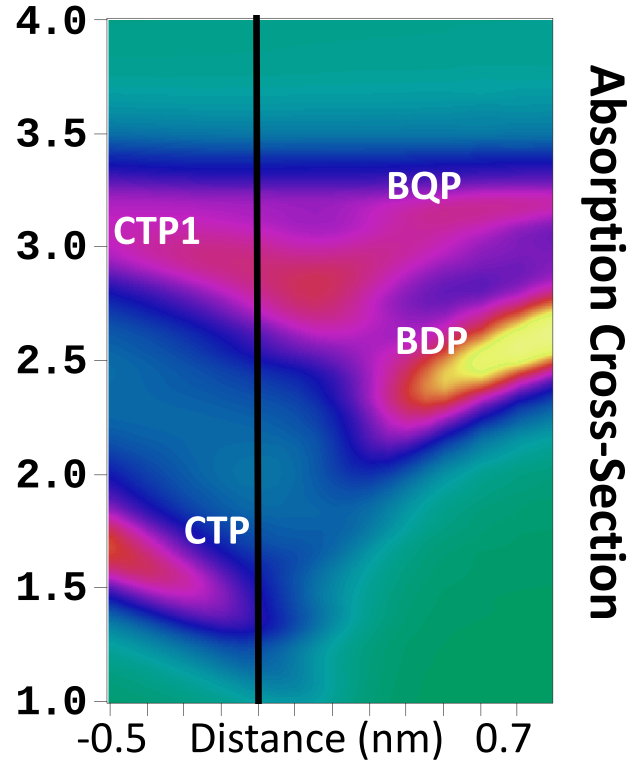
Experiment

D=9 nm
Ag nanoparticles

Theory TDDFT

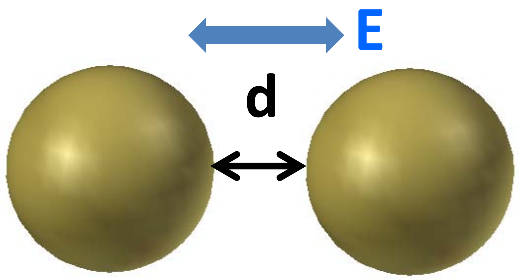
D=4 nm
Na nanoparticles



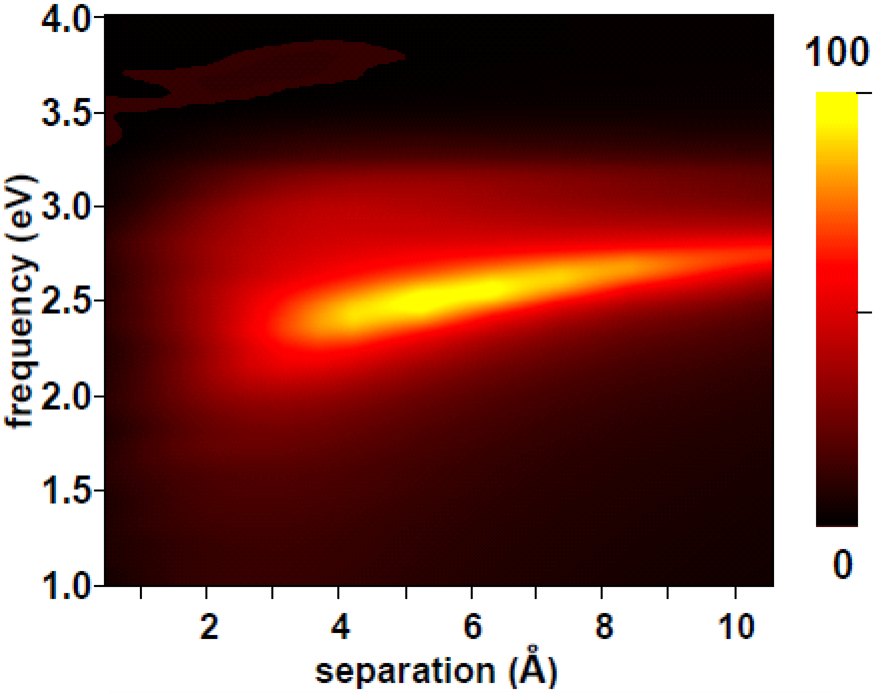


J.A. Scholl, A. García-Etxarri, A.L. Koh, and J.A. Dionne, *Nano Lett.* 13 , 564 (2013).

Plasmonic NP dimer : linear response

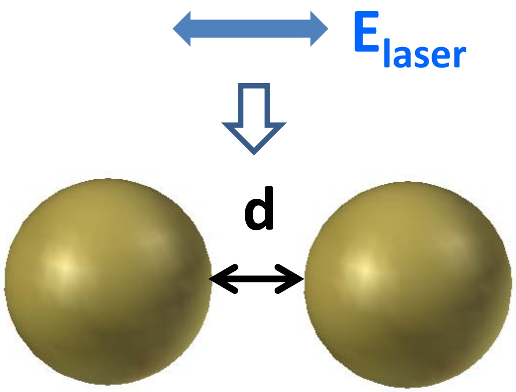


Field enhancement in the middle of the gap
$|E_{local} / E_{inc}|$



see also Zuolaga et. al, Nano Lett. 9, 887, (2009)

Plasmonic NP dimer : nonlinear response



- laser field resonant with the BDP (bonding dipolar plasmon)

$$\mathbf{E}_{laser}(t) = \mathbf{E}_0 \exp\left[-\frac{(t-t_0)^2}{\tau^2}\right]\cos(\Omega t)$$

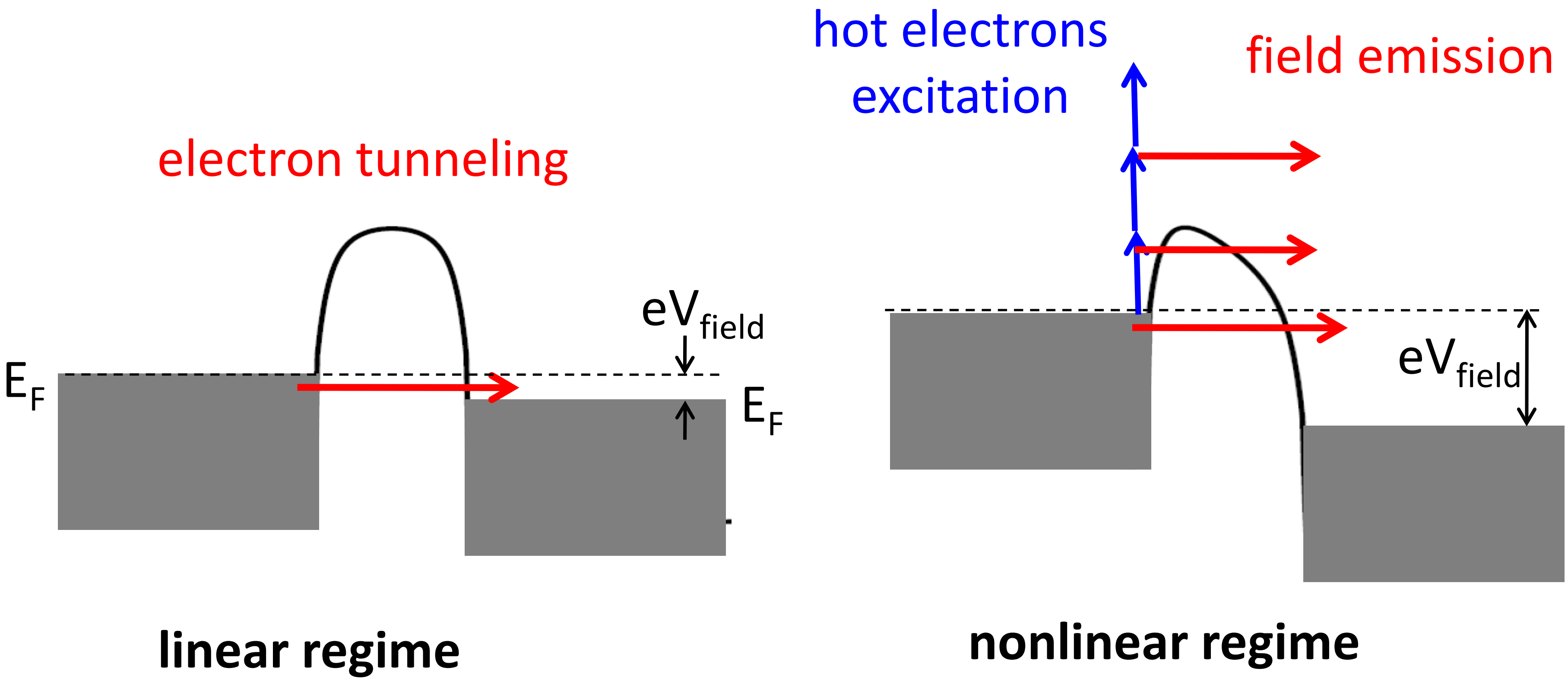
- pulse duration : $2\tau = 5.8\,fs$
- laser integrated power varied from

$\mathcal{P} = 10^6 W/cm^2$ to $\mathcal{P} = 10^{12} W/cm^2$

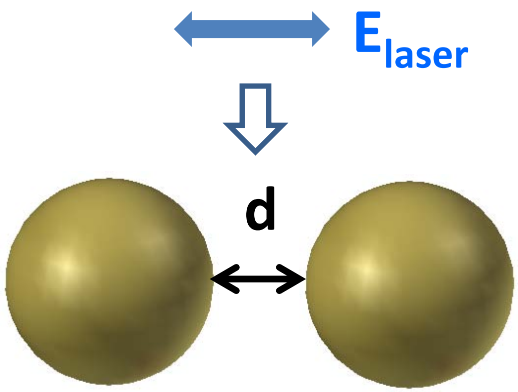
$E_{peak} = 5.5\times 10^6 V/m$ $E_{peak} = 5.5\times 10^9 V/m$

D.C.Marinica, A.K.Kazansky, P.Nordlander, J.Aizpurua, A.G.Borisov, *Nano Lett.* 12 (2012) 1333

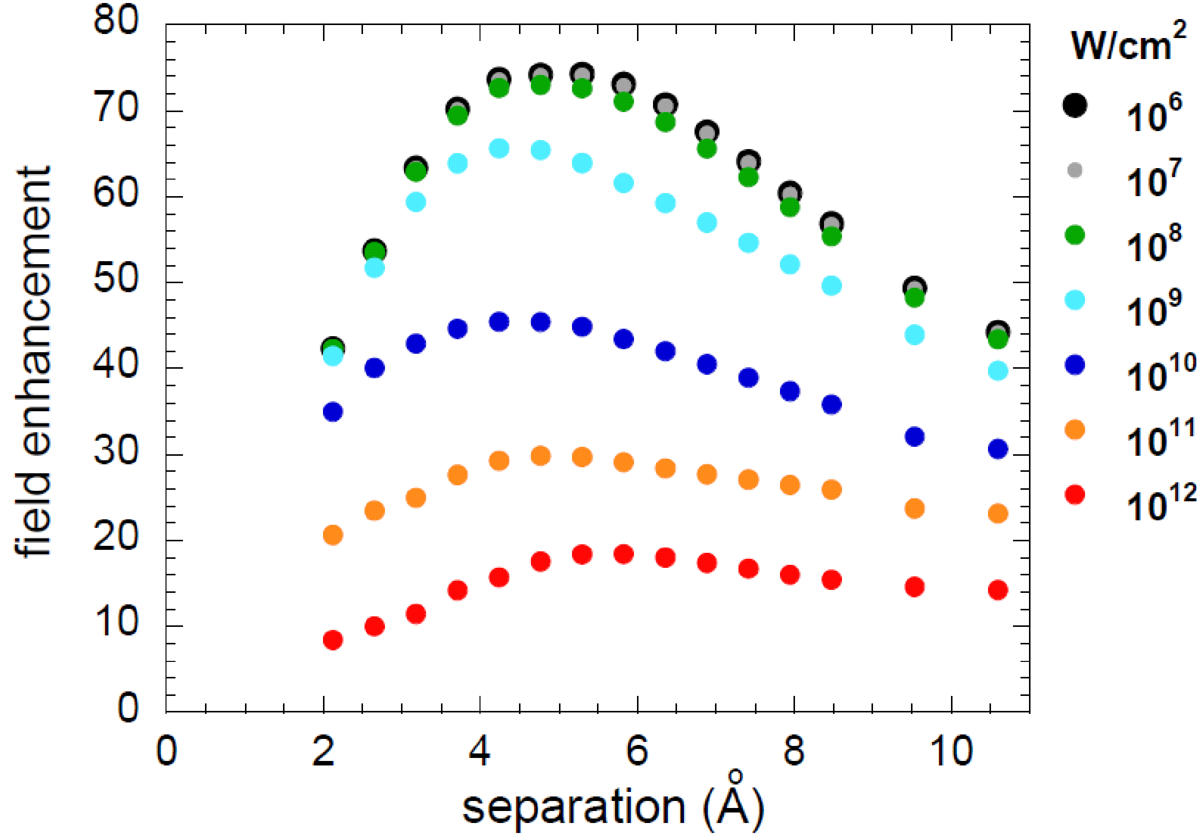
Adiabatic view of laser-assisted electron transfer mechanisms



Plasmonic NP dimer : nonlinear response



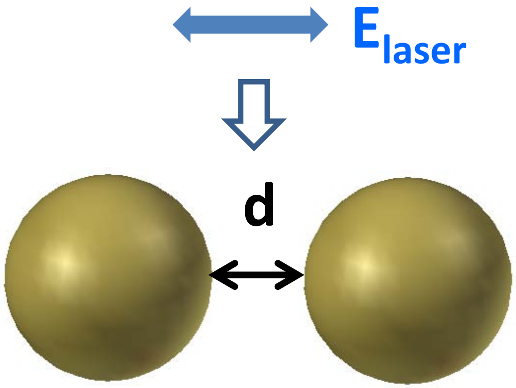
Field enhancement
in the middle of the gap



Nonlinear regime :

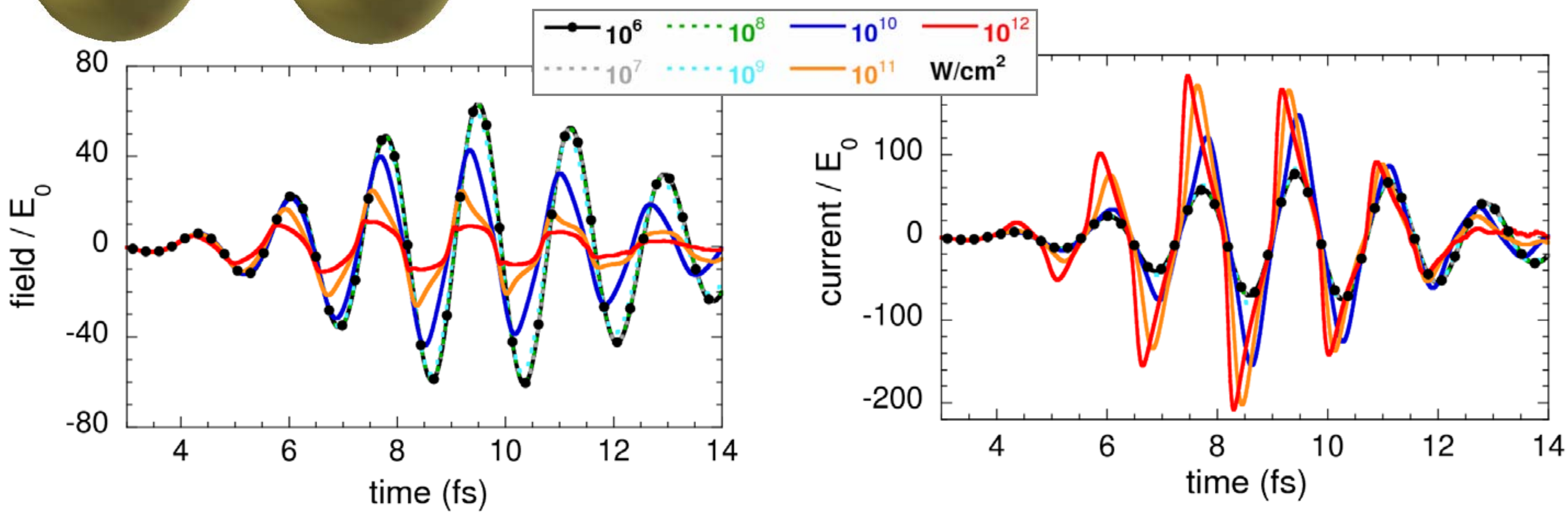
- strong reduction of the field enhancement
- for all the separation distances !!

Plasmonic NP dimer : nonlinear response



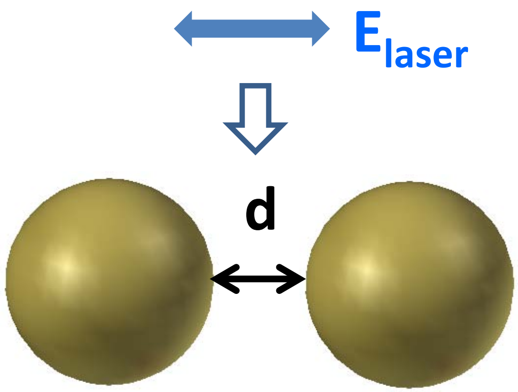
Time evolution of the Induced currents and fields

d=0.3 nm



- increase of the induced current correlated with the reduction of the field enhancement

Plasmonic NP dimer : nonlinear response



Time evolution of the induced currents and fields

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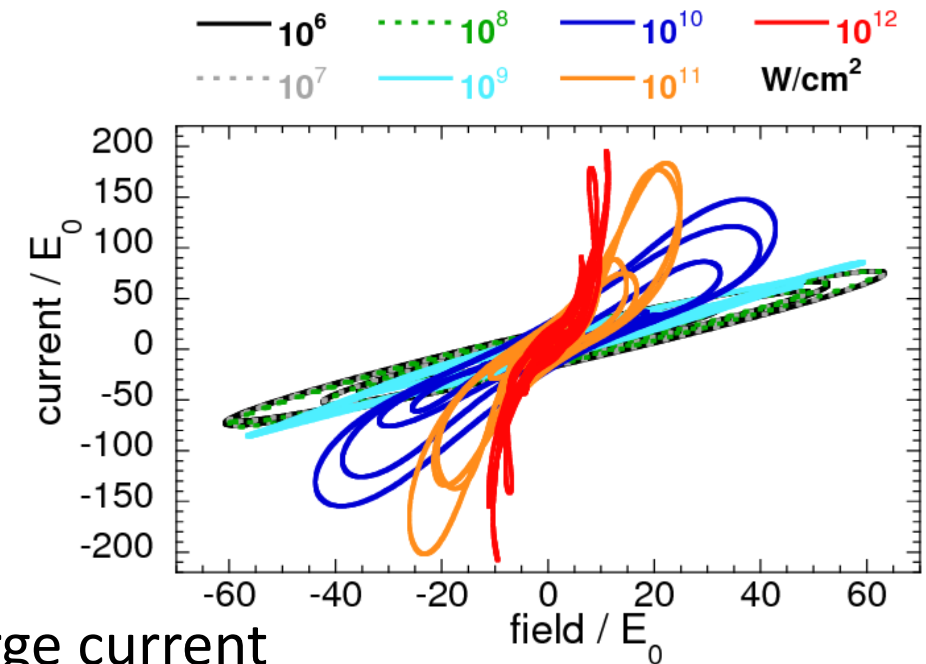
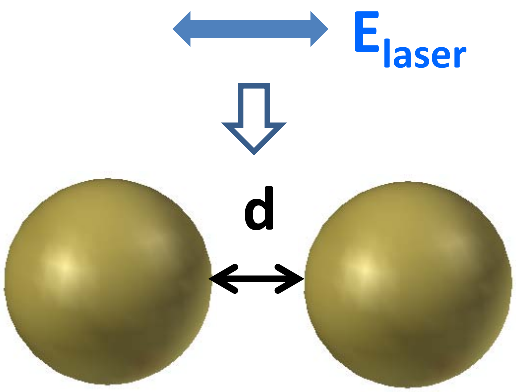


- low power : $I(t) = \sigma E(t)$
  resistive junction
- moderate power : $I(t) \approx \sigma E(t)$
  increased conductivity
- high power : nonlinear discharge current

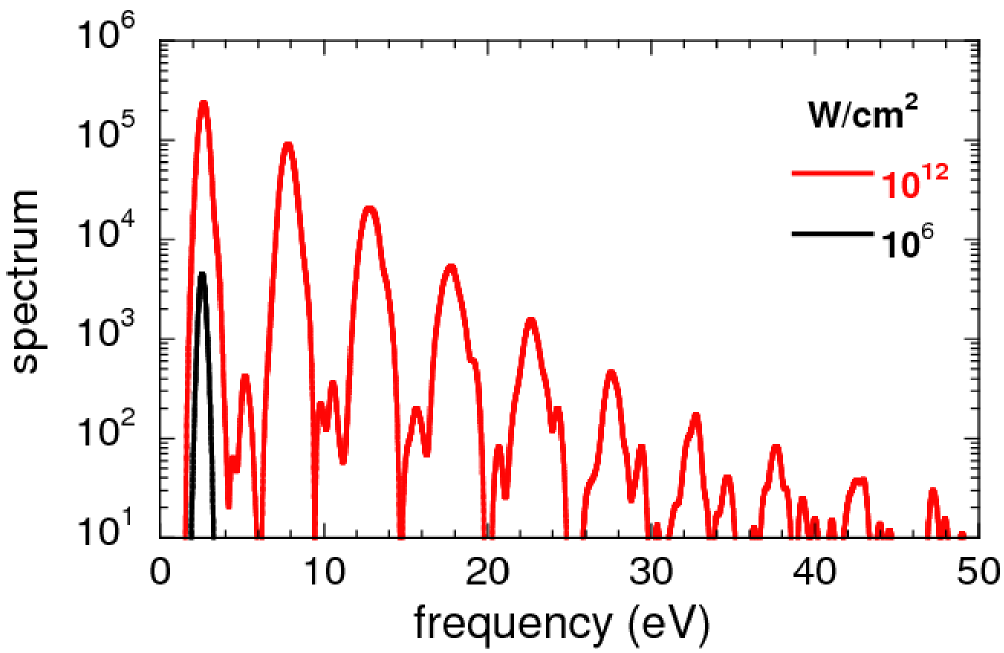
- tunable gap conductivity by the external field

Plasmonic NP dimer : nonlinear response



Spectrum of the tunneling current $\omega^2 \, |I(\omega)|^2$

d=0.3 nm

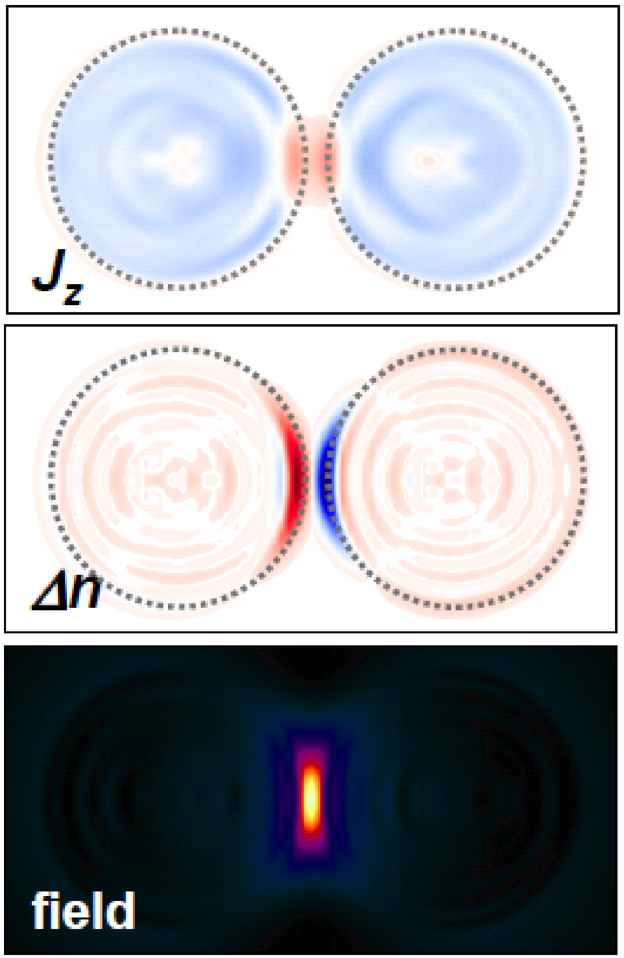


- generation oh high harmonic currents through the junction
- nonlinear effect due exclusively to the charge transfer between NPs

Plasmonic NP dimer : nonlinear response

d=0.5nm

$\mathcal{P} = 10^6\ \mathrm{W/cm^2}$

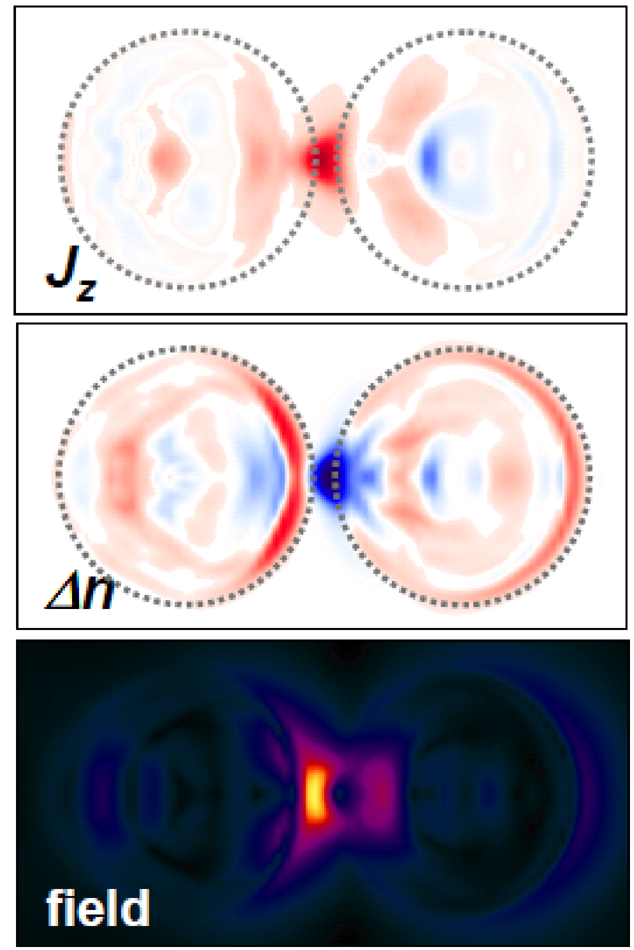


Induced current

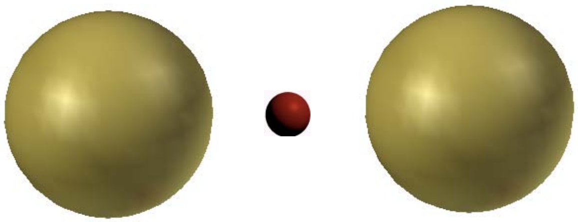
Induced density

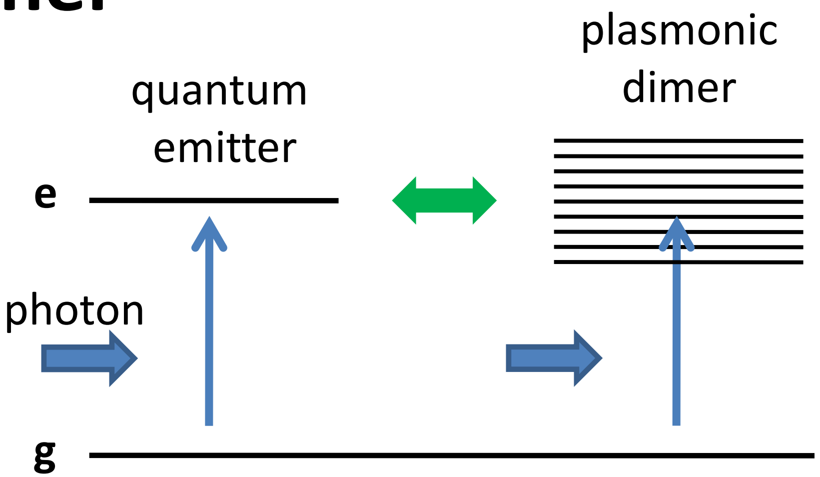
Induced field

$\mathcal{P} = 10^{12}\ \mathrm{W/cm^2}$



Quantum emitter coupled to a plasmonic dimer





Quantum plexcitonics

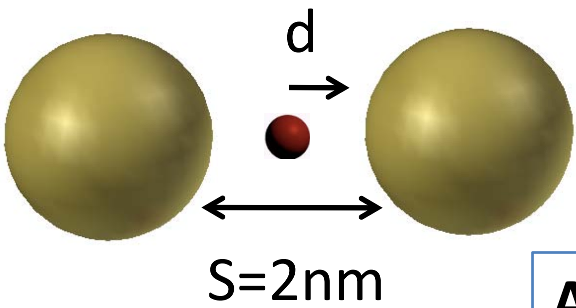
A.Manjavacas, F.J.Garcia de Abajo, P.Nordlander *Nano Lett.* 11 (2011) 2323

- near field strong coupling between the quantum emitter and the plasmonic dimer

- linear optical response modification due to the decay of the emitter excited state by charge transfer through the metallic NPs

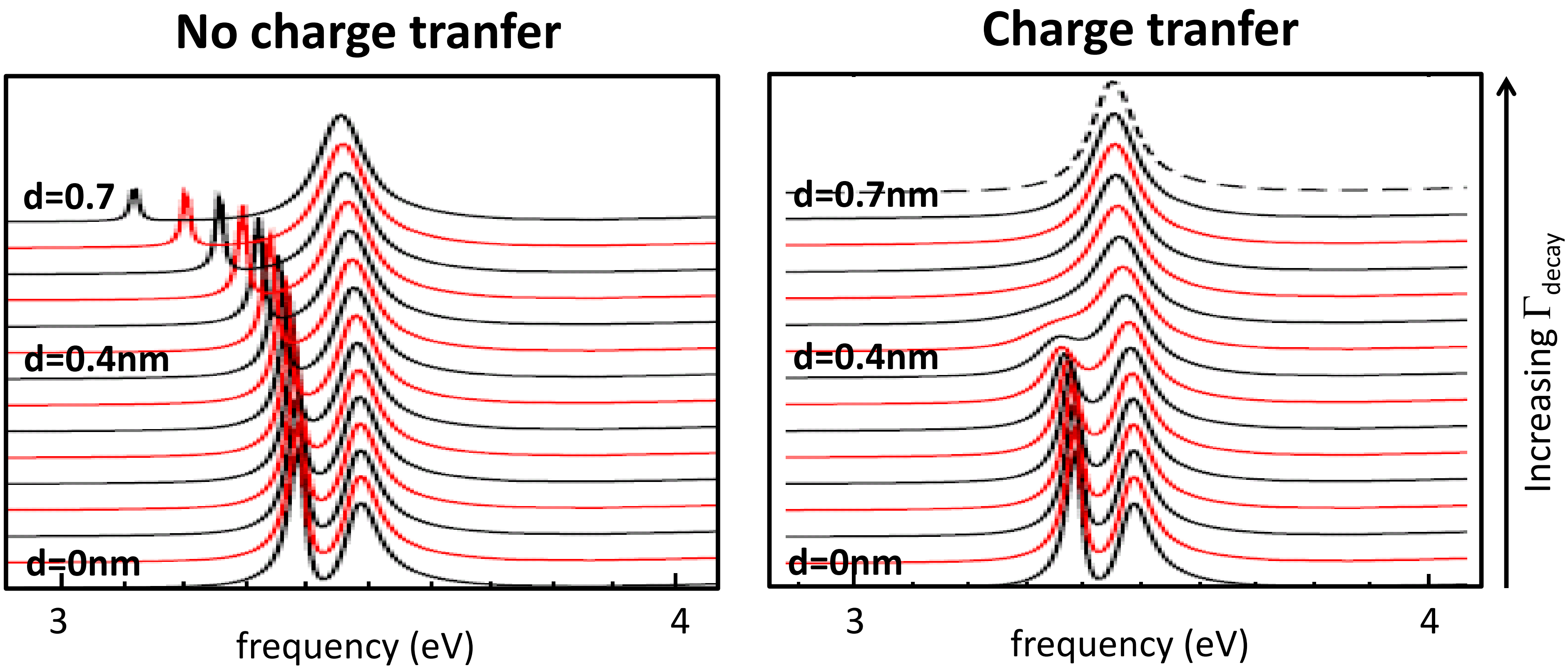
- charge transfer decay width from quantum calculations of alkali atoms on metallic surfaces

Quantum emitter coupled to a plasmonic dimer



- quantum emitter : Na atom
- plasmonic dimer : Ag nanoparticles
- transition frequency resonant with the BDP

Absorption cross section



Conclusions

- Fully quantum mechanically treatment of sub-nm gap plasmonic dimer

- For moderate and strong laser pulses, excitation of conduction electrons in the NPs and plasmonic field enhancement in the junction drive the system into the **field emission regime**

- The main effects obtained for very small NPs can be generalized to larger systems : the **tunneling** phenomena that cause non-linear effects depend on the local electron potential barrier separating the NPs and on the field in the junction

- Linear optical response of a quantum emitter coupled to a plasmonic dimer : charge tranfer effects

Collaborators

Andrey Borisov

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and Donostia International Physics Center – DIPC, Spain

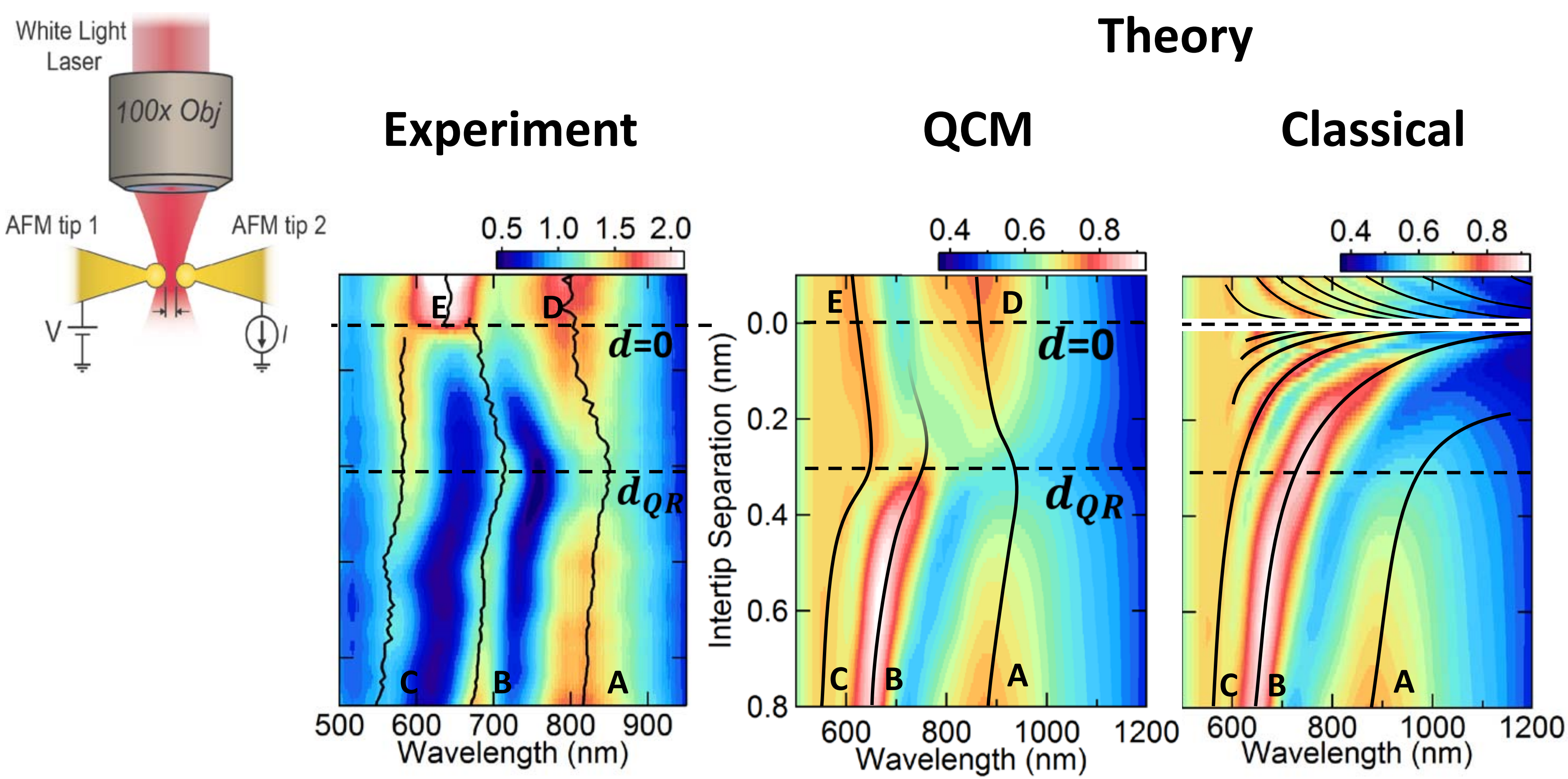
Peter Nordlander

Laboratory for Nanophotonics, Rice University

Andrey Kazansky

Donostia International Physics Center – DIPC, Spain

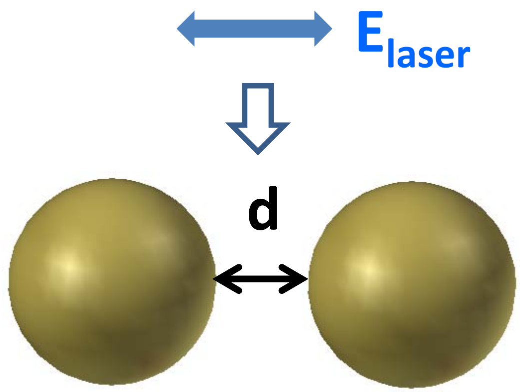
Optical response in the tunneling regime



- charge tranfer plasmons dominate for d < 0.35nm

K.J.Savage, M.H.Hawkeye, R.Esteban, A.G.Borisov, J.Aizpurua, J.J.Baumberg, *Nature* 491 (2012)

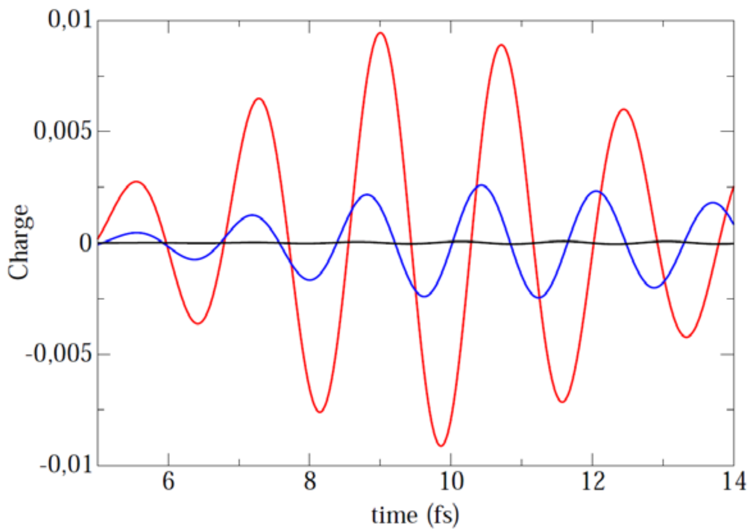
Plasmonic NP dimer : nonlinear response



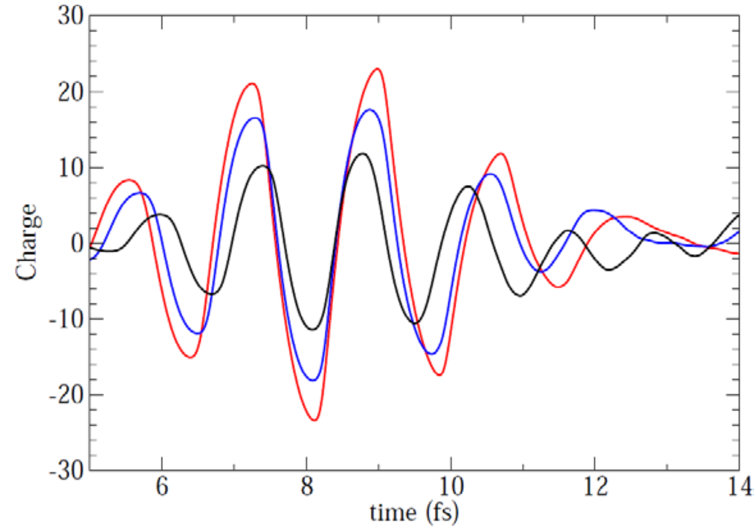
Induced charge transfer between the NPs

d=0.3nm
d=0.5nm
d=1nm

$\mathcal{P} = 10^6 W/cm^2$



$\mathcal{P} = 10^{12} W/cm^2$



- nonlinear regime : NPs « connected » even for 1nm gap junctions