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Instituto de Tecnología Química

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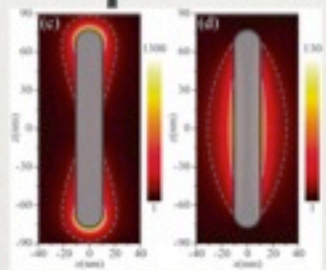
Universitat Politècnica de València

Metamaterials and magnetic light. Possibilities for forbidden photochemistry



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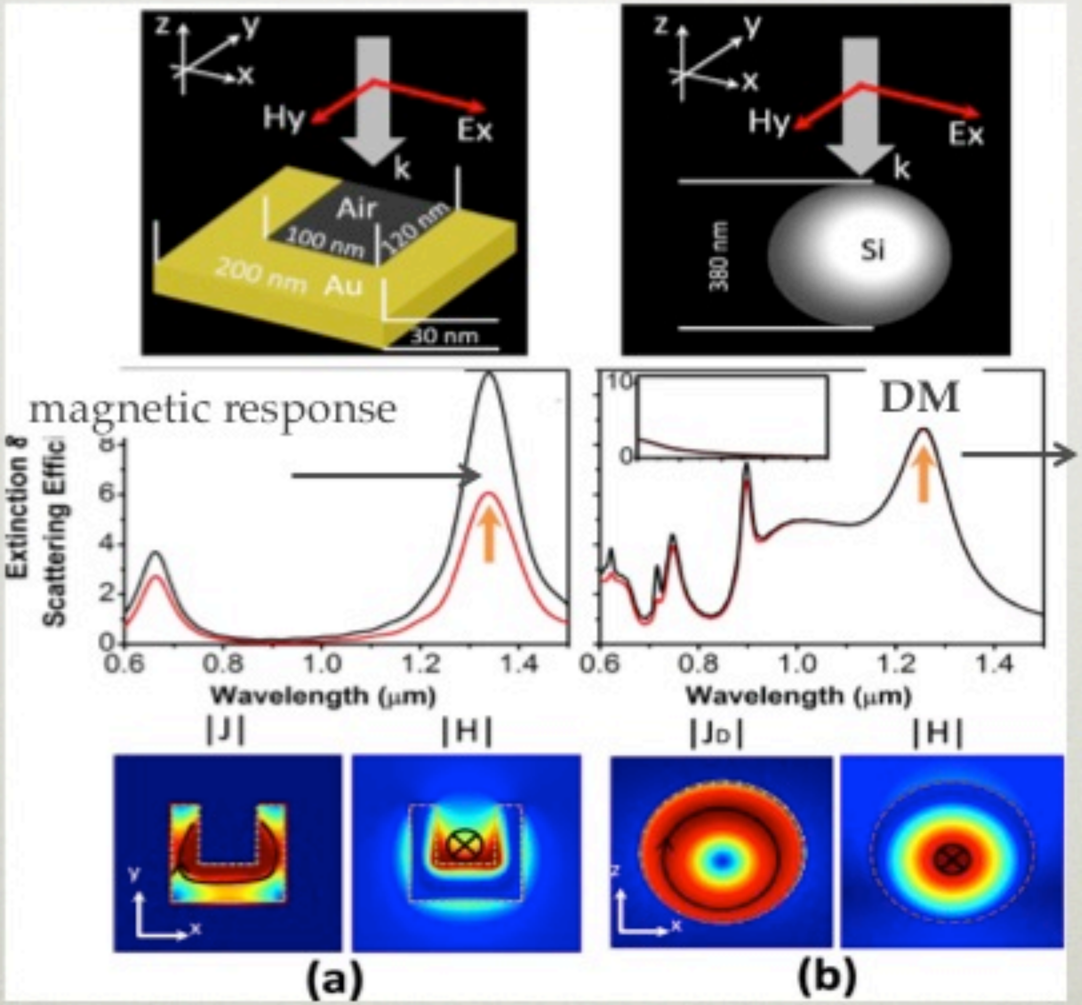
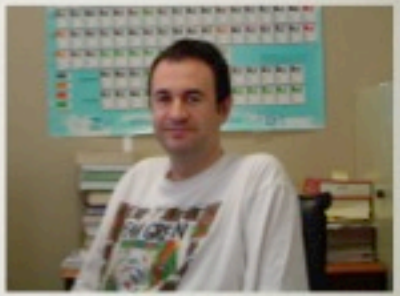
Nanolight, C. C. Benasque, March 11th-March 16th 2018

Outline

- **Introduction & Motivation**
- **Optical properties nanostructures. The magnetic response**
- **High magnetic response candidates.**
- **Forbidden optical transitions. The case of singlet oxygen**
- **Theoretical results**
- **Experiments**
- **Conclusions**

Metallic vs insulator metamaterial resonator



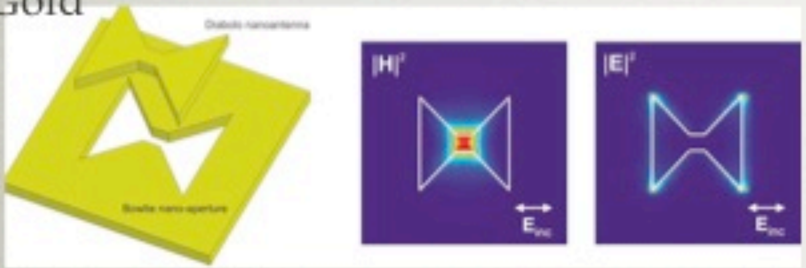


R. Fenollosa

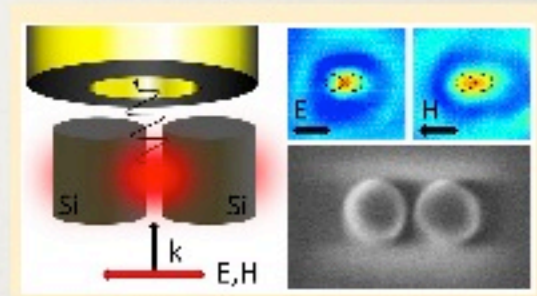
L. Shi, J. T. Harris, R. Fenollosa, I. Rodriguez, X. Lu, B. A. Korgel, and F. Meseguer
Nature Communications 4, 1904 (2013).

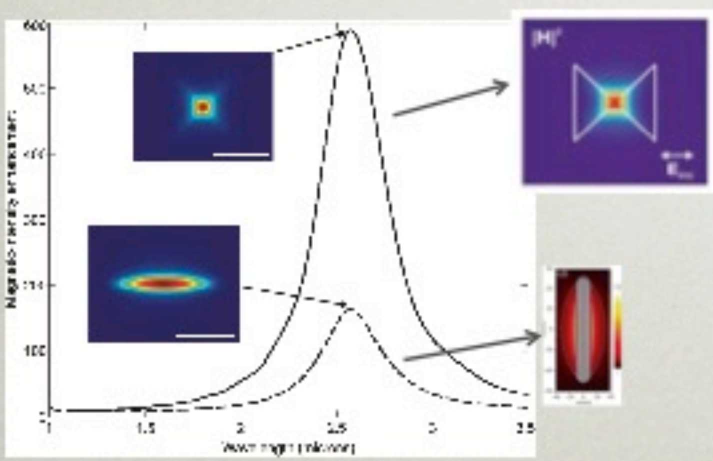
Nanoantenas for Enhancing Magnetic field

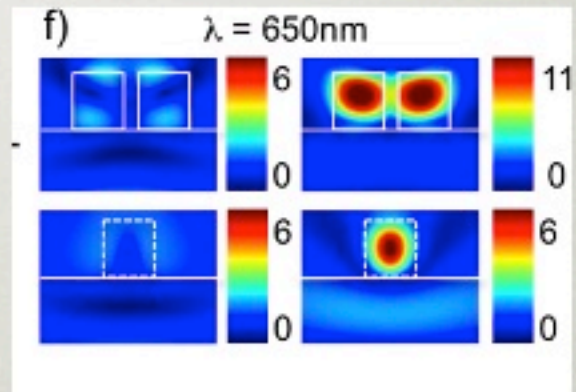
Diabolo structures (T. Grosjean / NL 2011)
Gold



Silicon dimmer (Kuznetsov NL 2015)



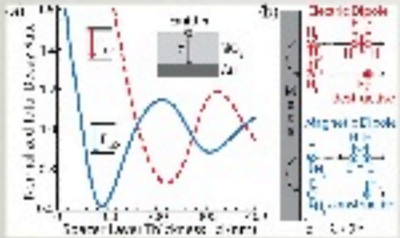


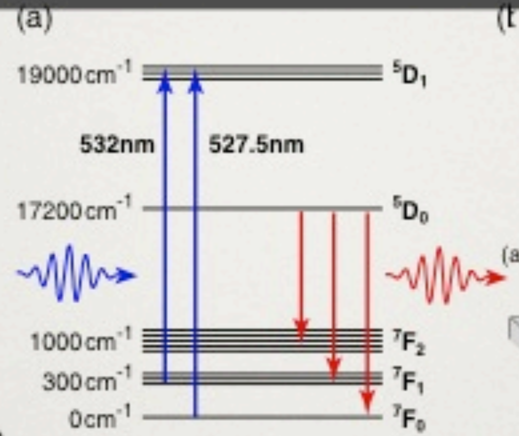


We need nanoparticles with high B in a large volume, suspended in a liquid/solid medium

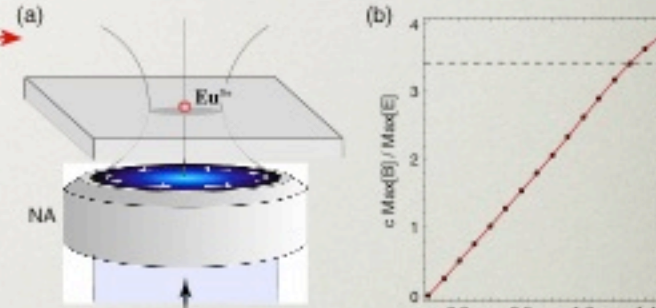
Dipole Electric (DE) vs Dipole magnetic (DM) transitions.
Enhancing **Dipole magnetic** transitions in Eu^{3+}

Gold/dielectric interface
Karaveli Opt Lett 2010

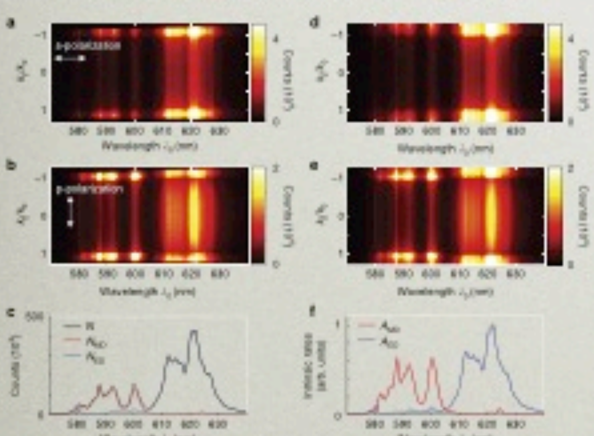




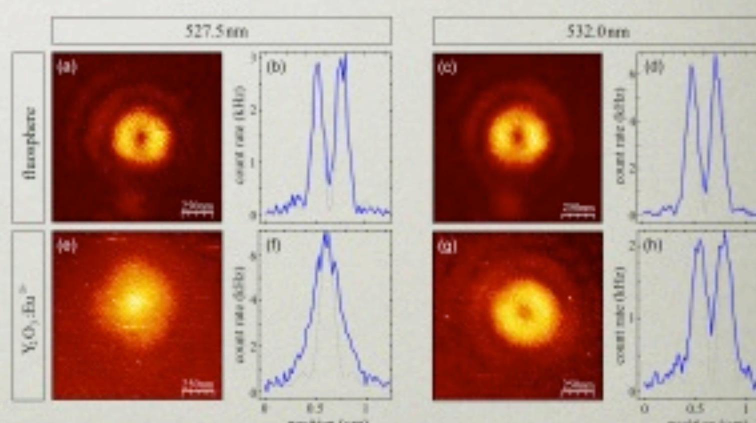
Azimutally polarized light
L. Novotny, PRL 2015



Momentum resolved emission
Back Focal plane spectroscopy
Taminiau Nat Comm 2012



DM DE



Optical transitions in Eu (also Er) Dipole Electric & Dipole Magnetic character !!

We will focus on systems with completely forbidden DE transitions!!

Forbidden Dipole Electric (DE) transitions.
The case of singlet oxygen

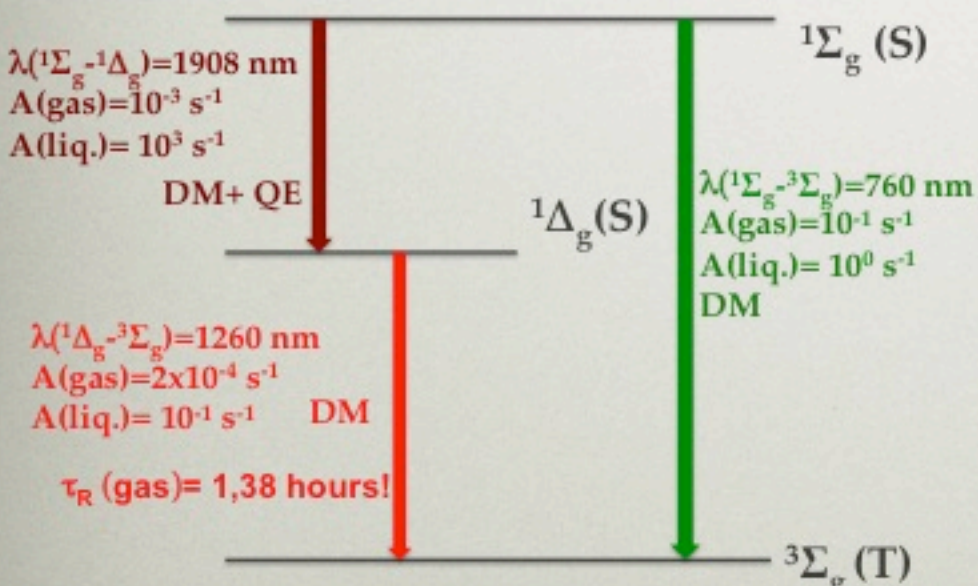
Cornerstone of life processes

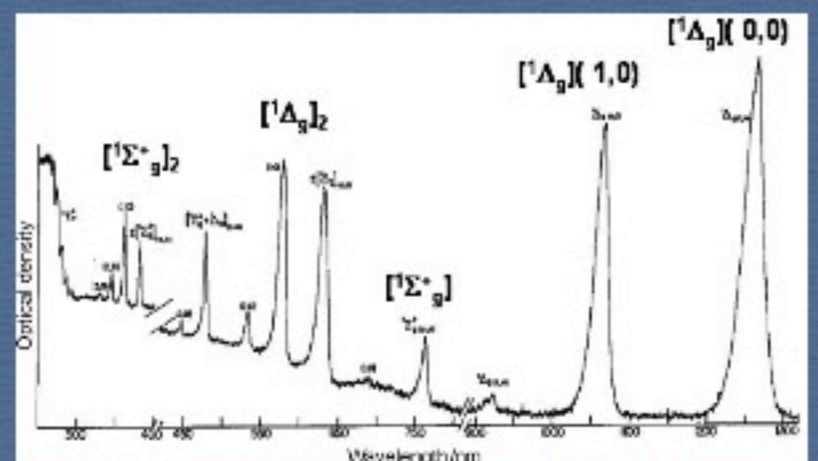
WHY OXYGEN ??

Key component in the oxidative processes of life

electronic transitions are (dipole electric) forbidden !!!!
It prevents the spontaneous photo-oxidation of living systems under sun exposure !!

Electronic transition of O_2



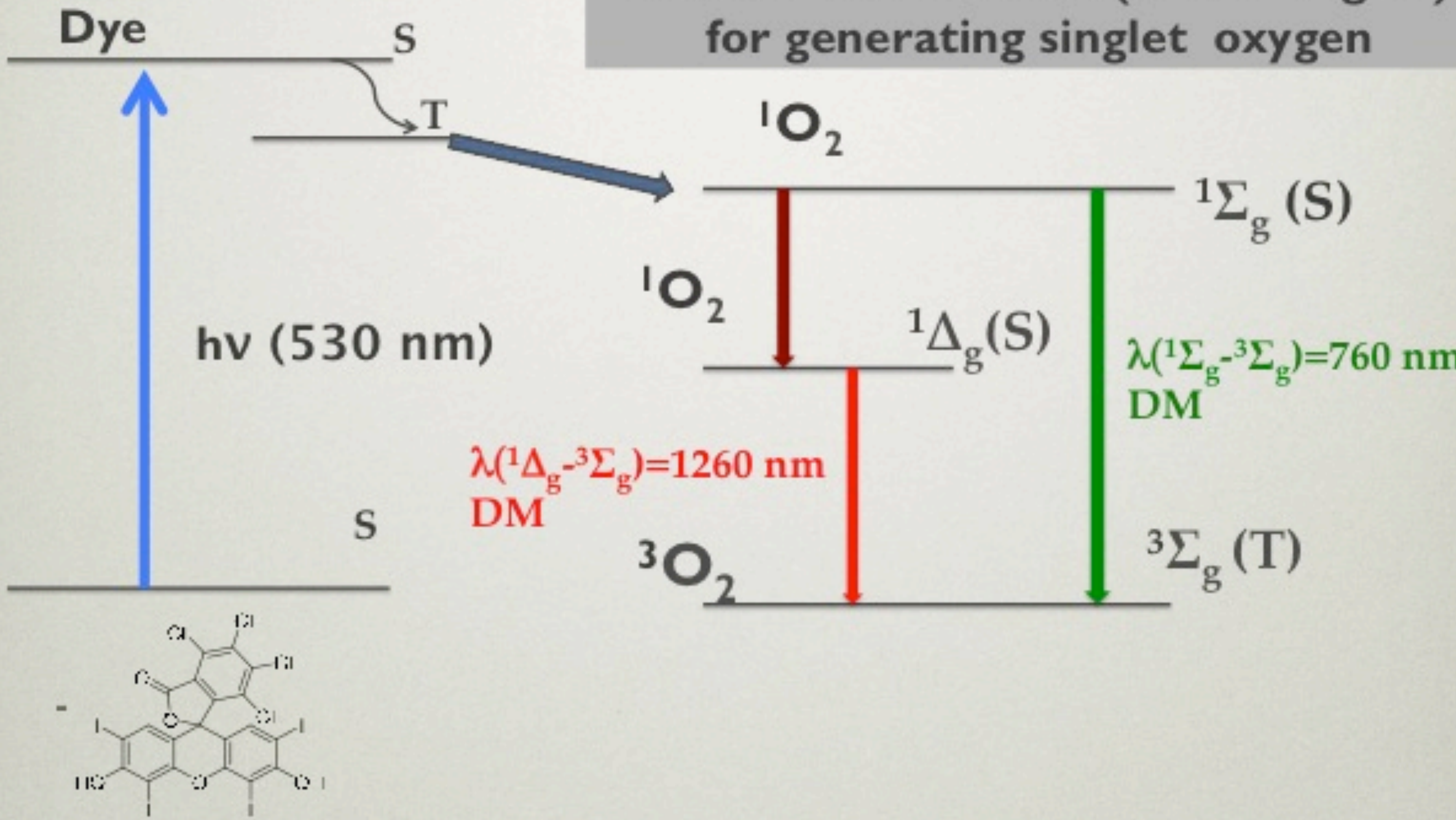


Liquid O_2 spectrum (Khalil 1978)
Sample thickness 3.5 cm !!!

Generation of singlet oxygen through high power pulsed fs lasers
Peter R. Ogilby, et al ., J. Photochem and Photobio A: Chemistry 321 297, (2016).

Photochemical activation of singlet oxygen

The use of sensitizers (Rose Bengale) for generating singlet oxygen



Dye (Rose Bengale)

C. Schweitzer and R. Schmidt, Chem. Rev., 103, 1685–1758 (2003).

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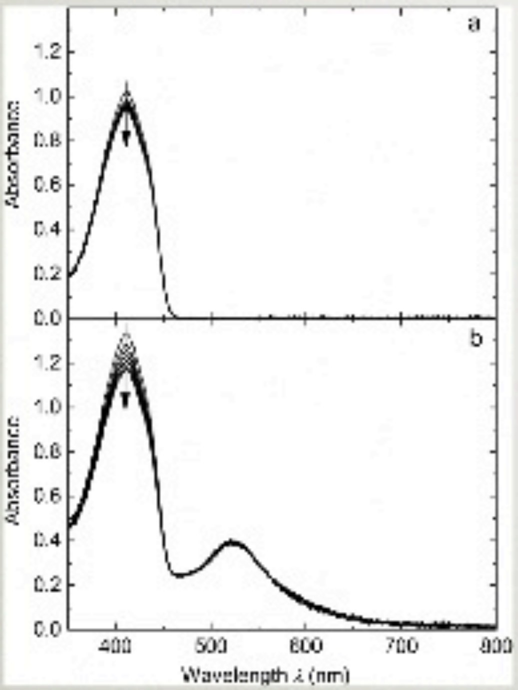
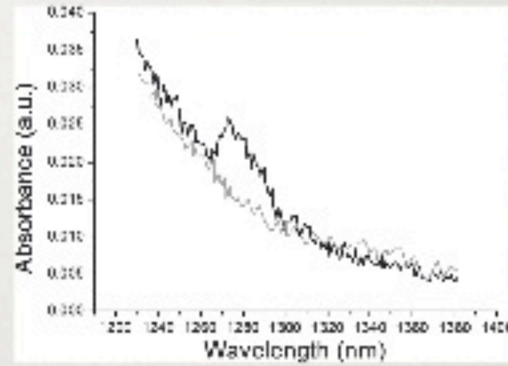
Metal NPs singlet oxygen generation

NPs mediated sensitizer Photo-bleaching,
M. Volk. J. Chem. C, 120, 10647, 2016

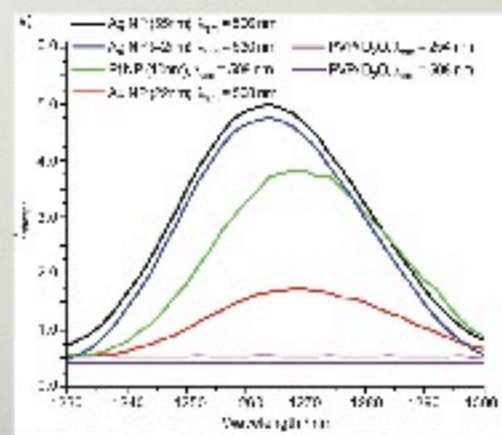


Thermal generation of singlet oxygen
Though hot electron excitation in NPs
A. N. Romanov , M. Y. Bykhovskii , Y. thermal generation
Singlet oxygen N. Rufov , Kinetics Catal. 2000

NPs mediated Absorption. Pasparakis
Small, 9, No. 24, 4130, 2013



NPs mediated PL emission, H. Wang
Ang. Chem. Int. Ed. 50, 10640, 2011



No evidences of dipole magnetic generation of singlet oxygen

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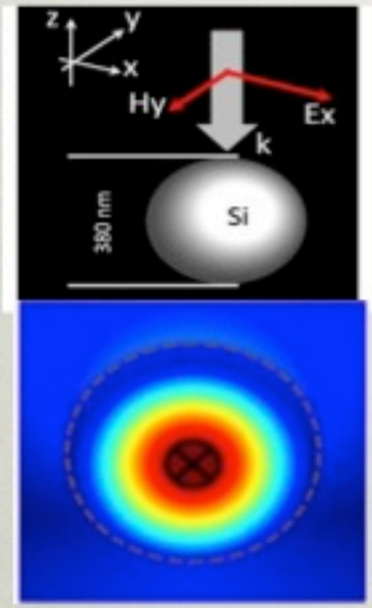
Magnetic field resonances in Metamaterials
Silicon nanocavities vs Gold nanorods

We need resonant structures with maximum B values spreading out the material !!. Two types of available systems. Silicon and gold nanoparticles

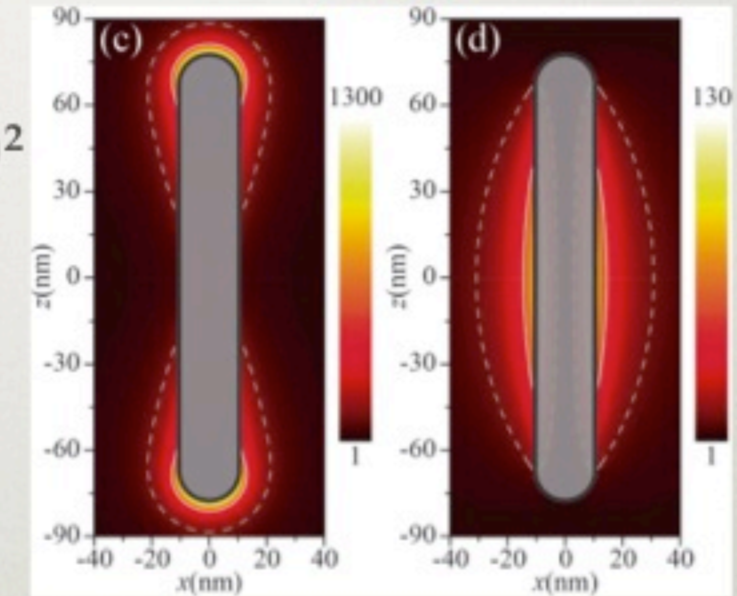
SILICON



$(B/B_0)^2$

GOLD

$(E/E_0)^2$



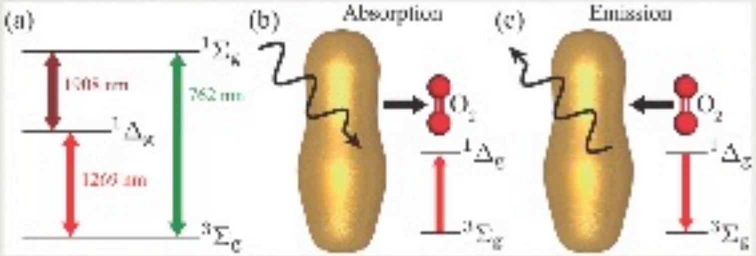
$(B/B_0)^2$

B FIELD OUTSIDE THE PARTICLE !!

GOLD NRs MUCH BETTER THAN SILICON NANOPARTICLES!!

A. Manjavacas et al, J. Mater. Chem. C, ,5, 11824-11831, (2017)

Magnetic light induced Optical transitions



$$H = -\mathbf{p}\cdot\mathbf{E} - \mathbf{m}\cdot\mathbf{B} - \mathbf{Q}:\nabla\mathbf{E} + \ldots$$

B is very small , **H=-pE. Dipolar electric approximation**

In metamaterials **B** $\neq 0$ **H=-pE - mB**

$$\boldsymbol{P_A} = \frac{\mathbf{2}\boldsymbol{\pi}}{\hbar}\left[\left[\langle \boldsymbol{f}|-\boldsymbol{pE}|\boldsymbol{i}\rangle\right]^2 + \left[\langle \boldsymbol{f}|-\boldsymbol{mB}|\boldsymbol{i}\rangle\right]^2\right]$$

$$\boldsymbol{if}\ \left[\left[\langle \boldsymbol{f}|-\boldsymbol{pE}|\boldsymbol{i}\rangle\right]^2 = \mathbf{0}\right], \boldsymbol{P_A} = \frac{\mathbf{2}\boldsymbol{\pi}}{\hbar}\left[\left[\langle \boldsymbol{f}|-\boldsymbol{mB}|\boldsymbol{i}\rangle\right]^2\right]$$

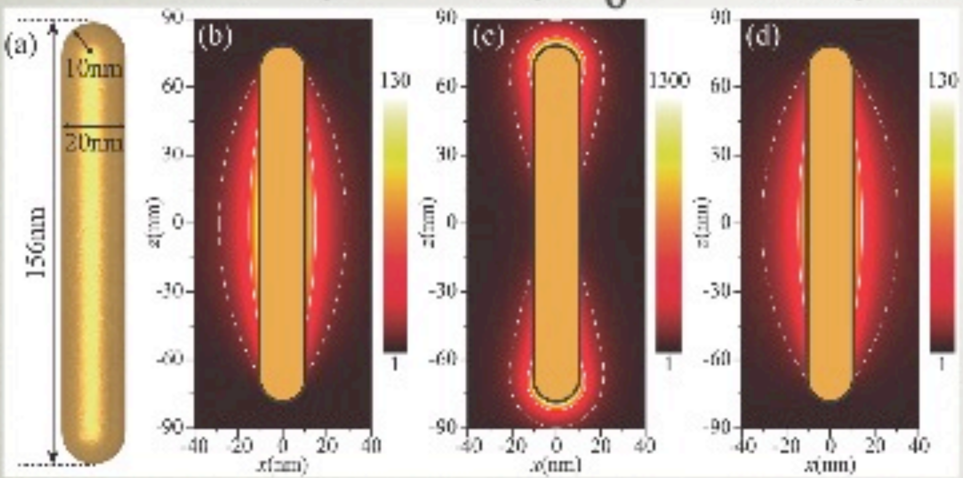
Dipolar magnetic transitions might play role

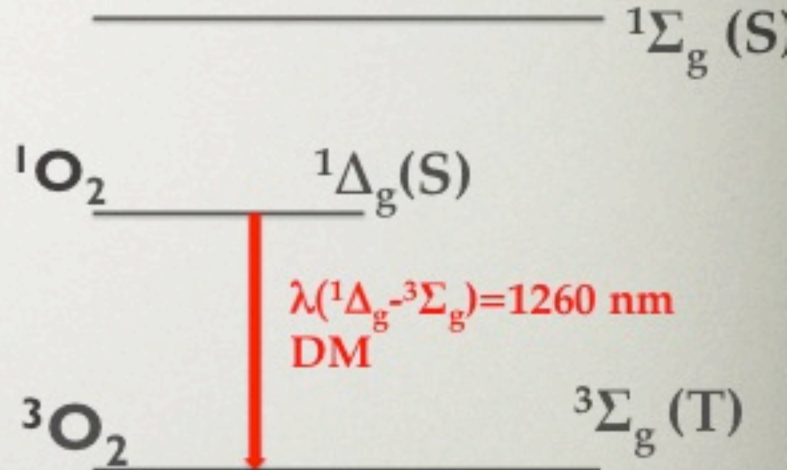
A. Manjavacas et al, J. Mater. Chem. C, 5, 11824-11831, (2017)

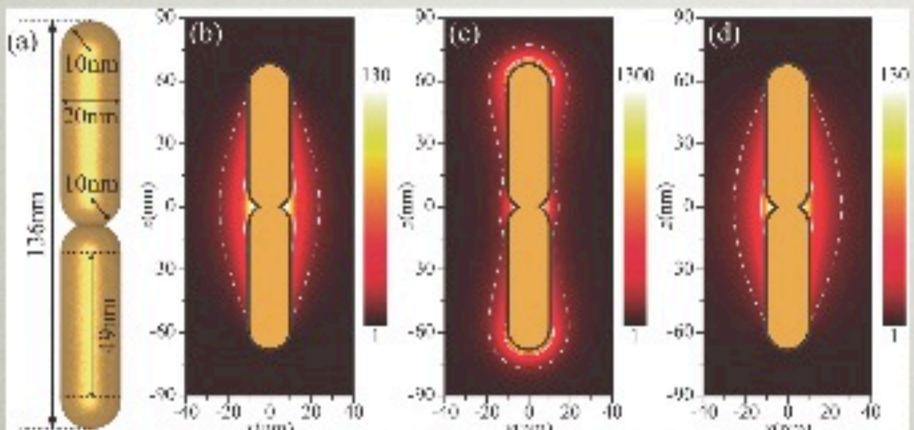
Standard and tip-to-tip welded NRs

λ= 1269 nm. =$\lambda(^1\Delta_g$-$^3\Sigma_g)$

$(B/B_0)^2$ $(E/E_0)^2$ (PL/PL_0)







Other processes

A) Quadrupolar electric transitions (J. Mod. Opt., 62, 1435, 2015

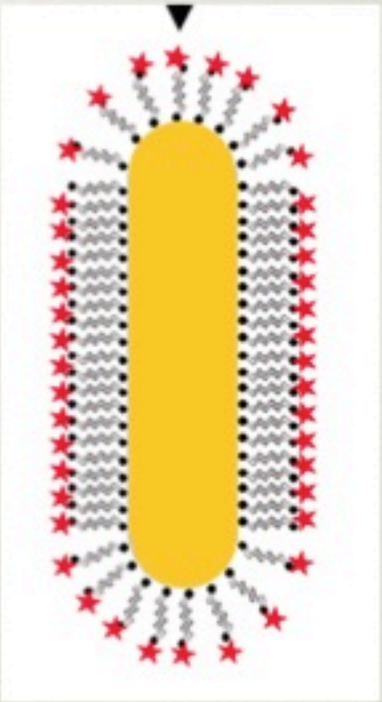
B) Hot electrons (Romanov, Kinetics Catal. 2000)

A. Manjavacas et al, J. Mater. Chem. C, 5, 11824-11831, (2017)

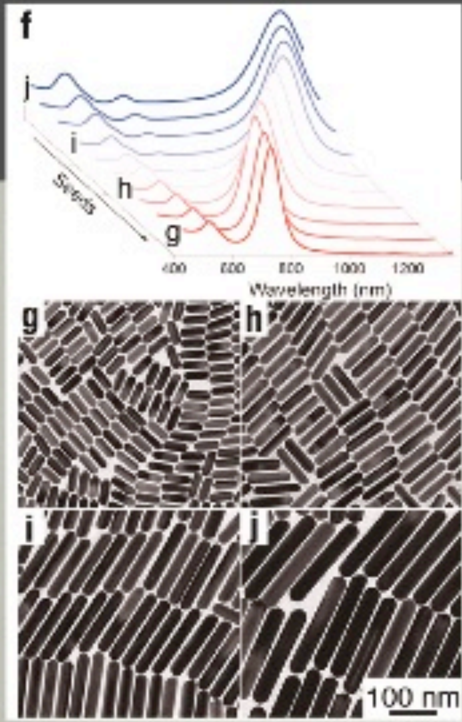
Characteristics/needs for photochemistry associated to singlet oxygen

- nanostructures with large surface area (photolithography vs synthesis)
- Large magnetic volume
- Bare particles to promote the close contact of Oxygen to the particle (trying to avoid surfactant as CTAB)
- Simple processing method
- Liquid suspensions for photochemistry process
- For cw PL and SERS substrate supported NPs might work
- High intensity light sources vs. time accumulative experiments.

CTAB + Au NRs .



L(CTAB)= 3 nm

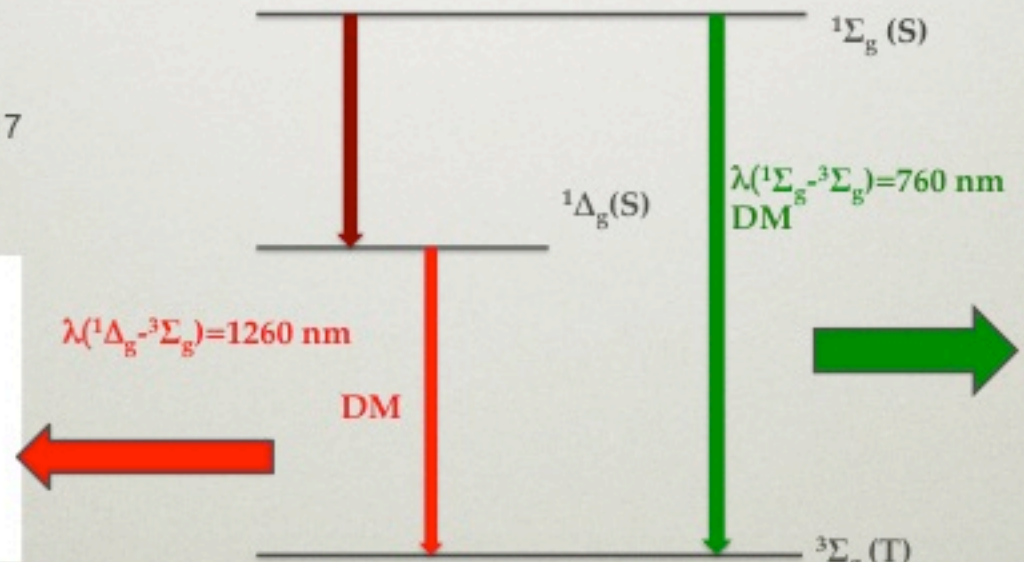


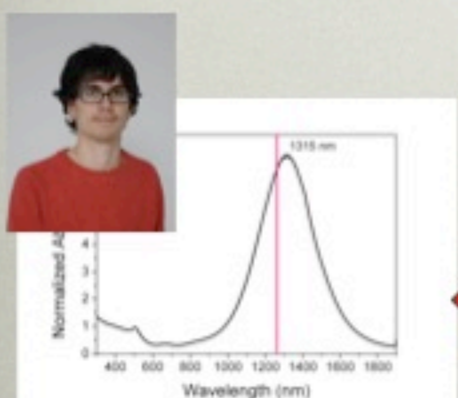
A Sanchez- Iglesias et JAQS 2017

Gold Nanorods available (Liz-Marzan's group)

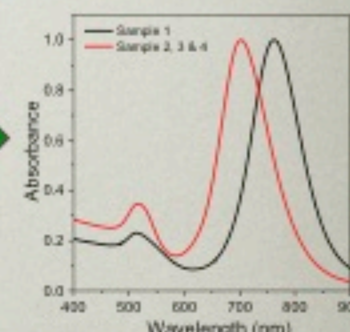
1060 nm= $\lambda(^1\Delta_g\text{-}^3\Sigma_g)$=1260 + 1 phonon O2

	L(nm)	d (nm)	λ(nm)	Transition
1	66	20	780	$\lambda(^1\Sigma_g\text{-}^3\Sigma_g)$
2	**110**	**20**	1060	$\lambda(^1\Delta_g\text{-}^3\Sigma_g)$**+ 1 phonon**
3	140	20	1300	$\lambda(^1\Delta_g\text{-}^3\Sigma_g)$





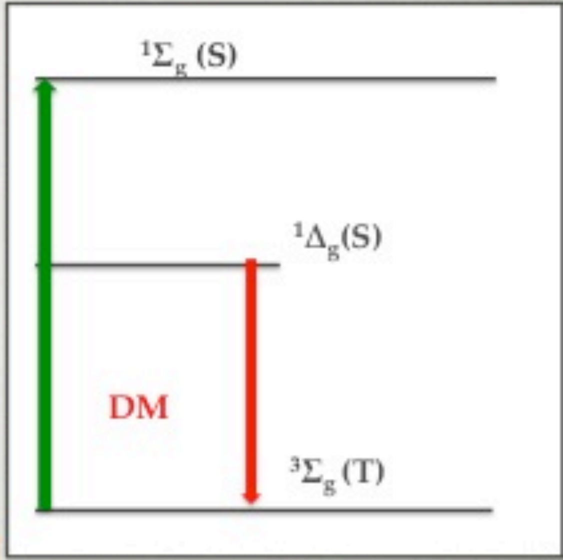
G. Gonzalez et al unpubl.



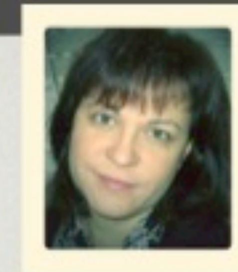
see also Liz-Marzan, et al , Nano Lett.,, 15, 8282, 2015

Potential experiments

Technique	Advantages	Drawback
Optical absorption by of Singlet oxygen sensitizers (photochemical reactions Anthracene to endoperoxide)	Time accumulative experiment Low excitation power	Not conclusive experiment
CW Photoluminescence/phosphorescence (direct measure of the de-excitation energy)	High sensivity	Very low efficiency High laser excitation power Non radiative channels in liquid suspensions
Time resolved Photoluminescence/phosphorescence (direct measure of the de-excitation rate)	High sensivity	Pulsed laser High laser excitation power Non radiative channels in liquid suspensions
Raman SERS Measure of the vibrational modes of endoperoxide component	High SERS efficiency Dual role of the excitation laser A) Photoreaction B) SERS signal of the chemical	High laser excitation power



Sample preparation and experiment



SERS equipment.

A) Renishaw micro Raman system

B) Controlled atmosphere and temperature chamber

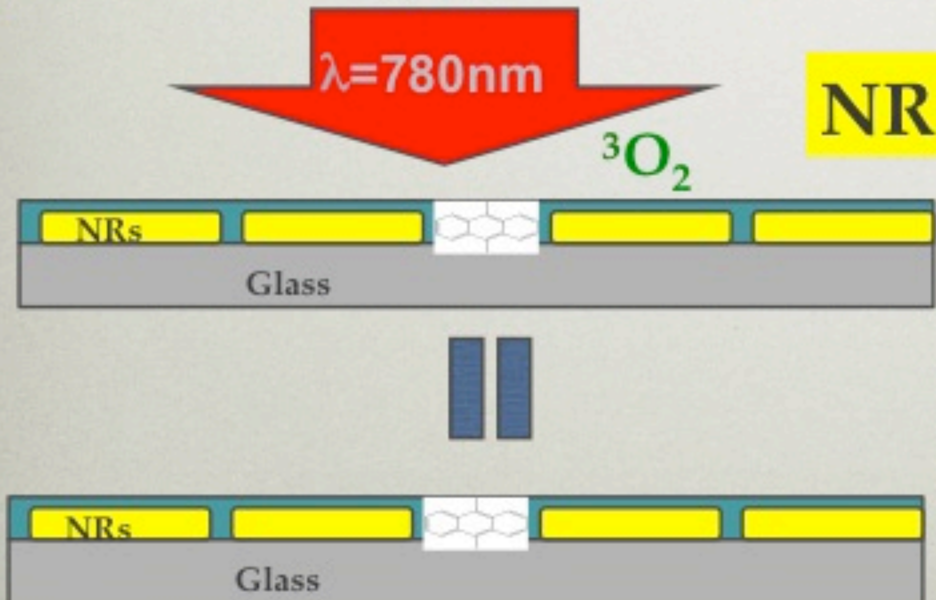
C) Laser λ=785nm plasmon resonance at singlet oxygen transition

Dual role of the excitation laser!!

Photoreaction

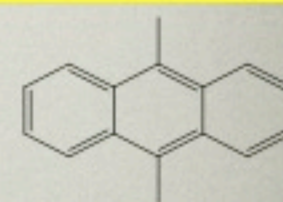
SERS signal of endoperoxide

D) The Raman fingerprint corresponds to that of the endoperoxide

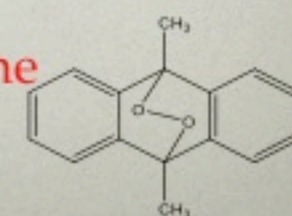


NRs supported (no CTAB)

dimethyl anthracene

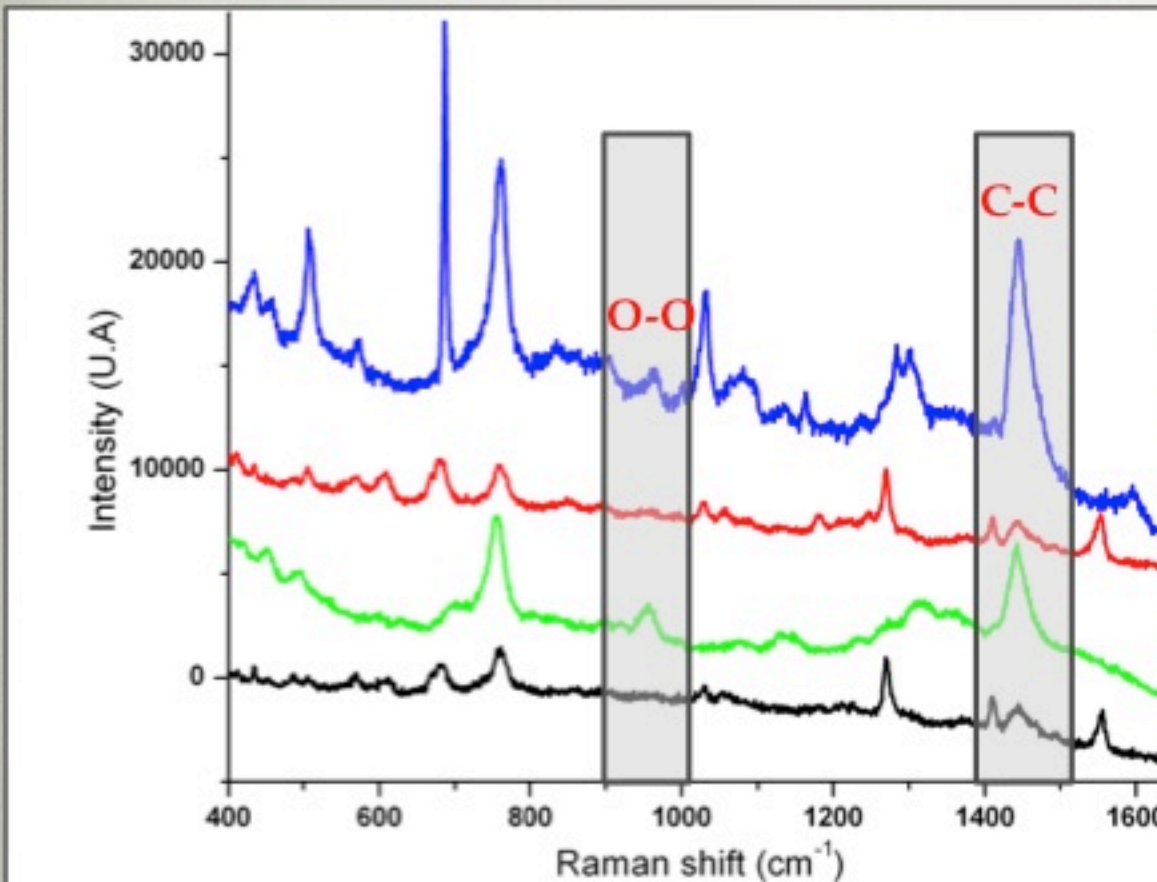


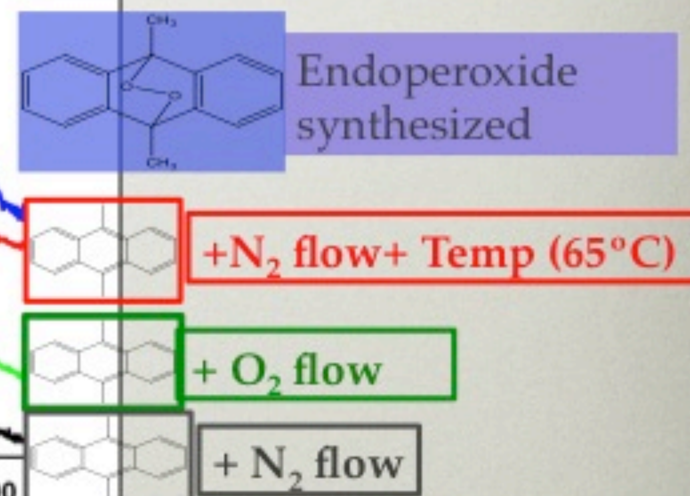
dimethyl anthracene endoperoxide



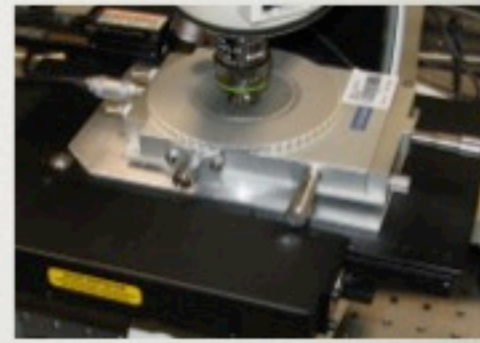
SERS spectra (λ=785 nm)

Nanorods (NRs)+ dimethyl anthracene + plasmon resonance at singlet oxygen





J. Chen et al., J. Raman Spectrosc. 46, 64, (2015)



I. Rodriguez et al., to be submitted

Conclusions

- Magnetic resonances calculación in gold NRs
- Potential application to magnetic transitions in photochemistry
- Potential experiments for singlet oxygen generation
- Detection of singlet oxygen through SERS experiments

References

A. Manjavacas et al, J. Mater. Chem. C, ,5, 11824-11831, (2017)

I. Rodriguez et al., to be submitted

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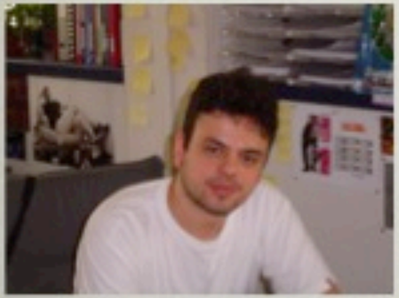

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