Optical Spectroscopy in Nanoscience
奈米科學的光譜檢測

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Outline

Dr. Juen-Kai Wang, CCMS & IAMS

- Introduction
- Optical microscopy
- Semiconductor quantum dots
- Single-molecule spectroscopy
- Raman scattering
- Plasmon resonance in nanostructures
- SERS and nano-scaled Raman spectroscopy

Reference

Dr. Juen-Kai Wang, CCMS & IAMS

- Characterization of Nanophase Materials, edited by Z. L. Wang (Wiley-VCH, Weinheim, 2000), Chap. 7 and 9.
- Single-Molecule Optical Detection, Imaging and Spectroscopy, edited by T. Basche, W. E. Moerner, M. Orrit and U. P. Wild (Wiley-VCH, Weinheim, 1997).
- Handbook of Raman Spectroscopy: from the Research Laboratory to the Process Line, edited by I. R. Lewis, G. Howell and M. Edwards (Marcel Dekker, New York, 2001).

Optical spectro-microscopy setup

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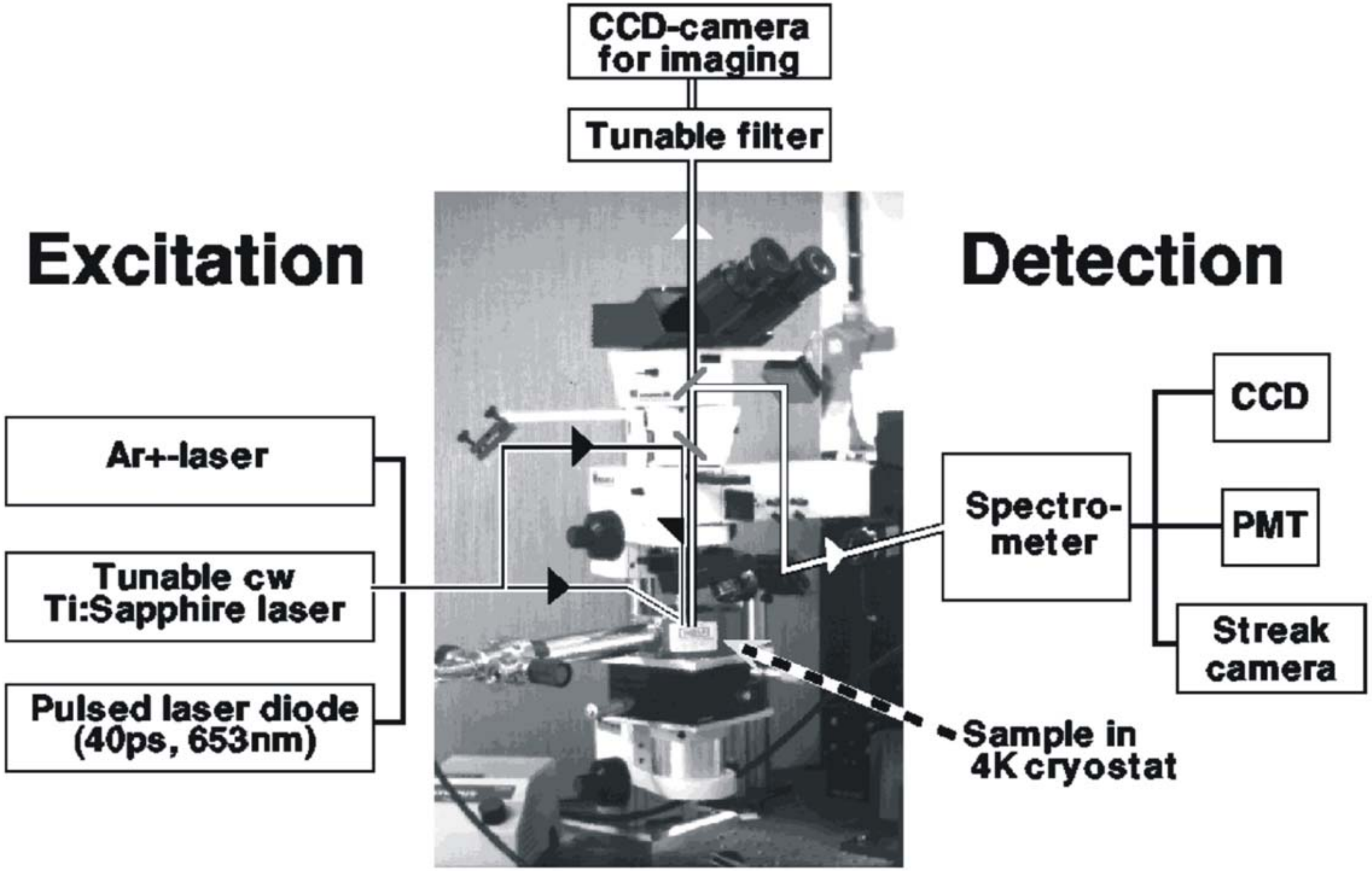

A. Gustafsson et al., J. Appl. Phys. **84**, 1715 (1998).

Optical microscopy

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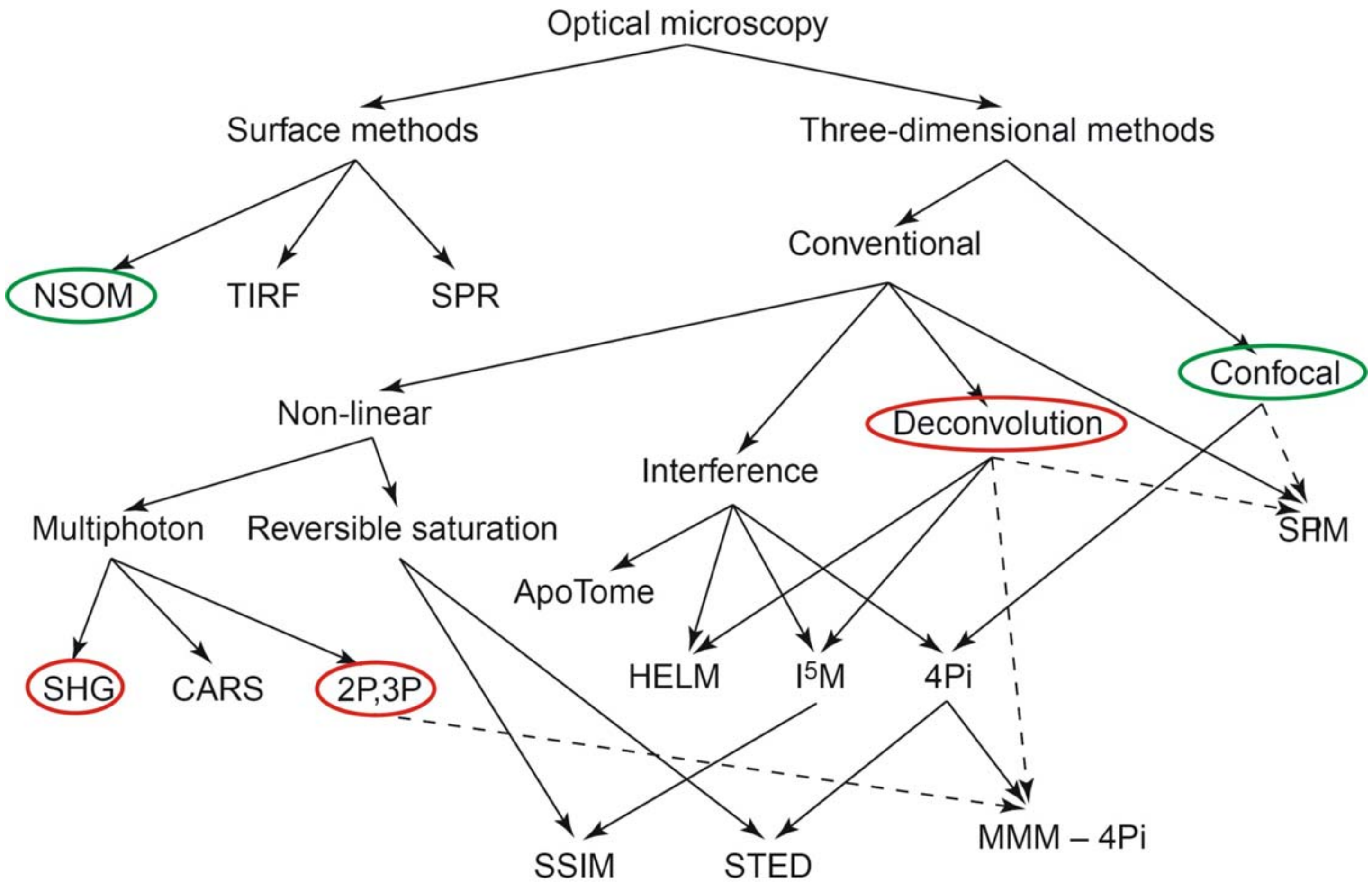
- Rayleigh criteria:
  - $d_{x,y} = 0.61\lambda/NA$
  - $d_z = 2\lambda/NA^2$



Y. Garini et al., Curr. Opin. Biotech. **16**, 1 (2005).

Confocal microscopy

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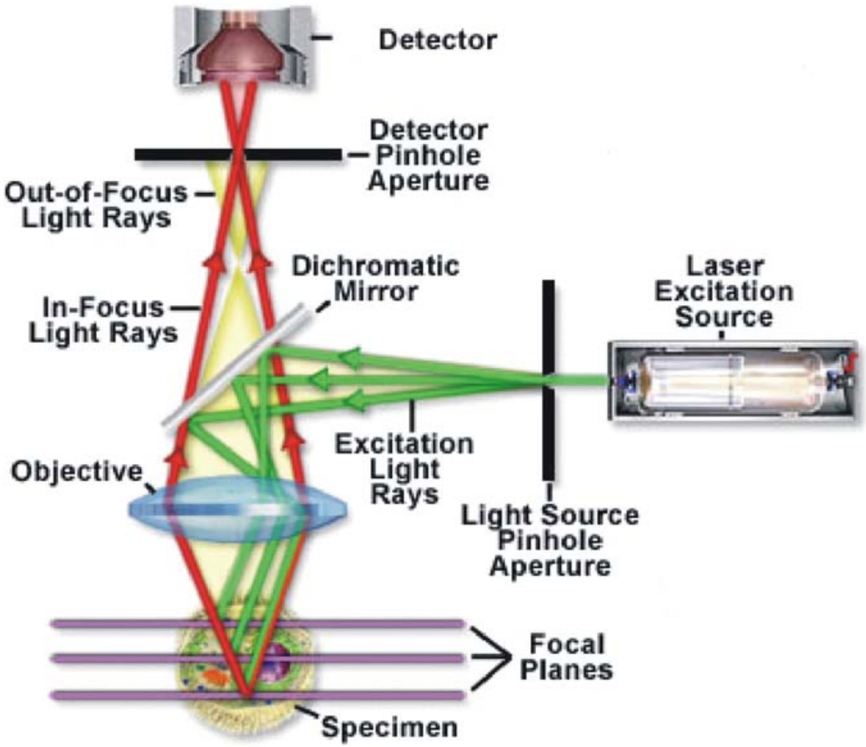

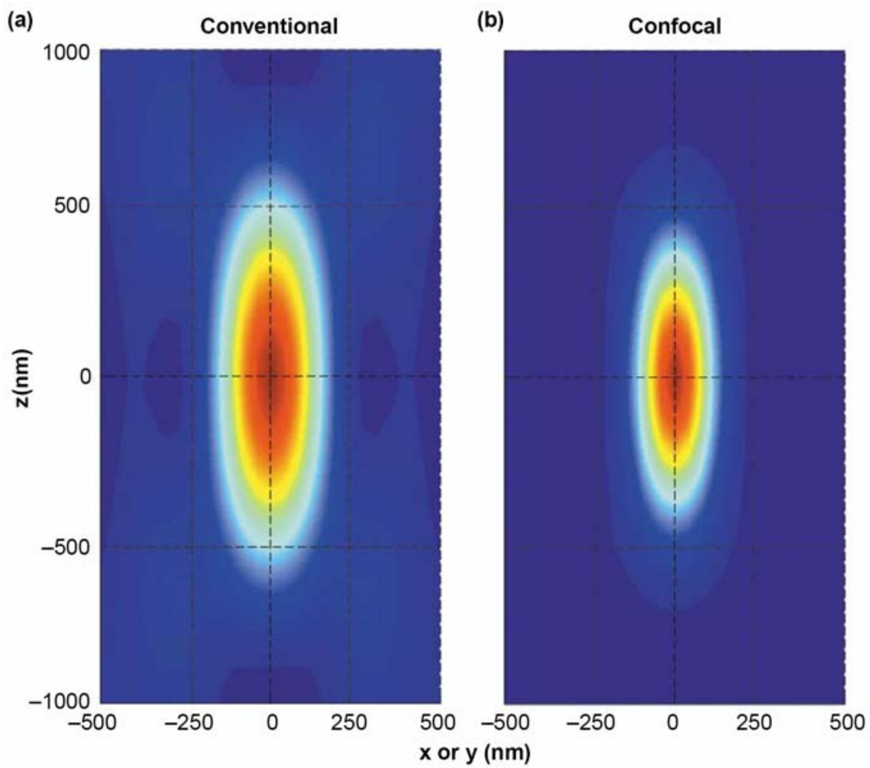

Linear optics *vs.* nonlinear optics

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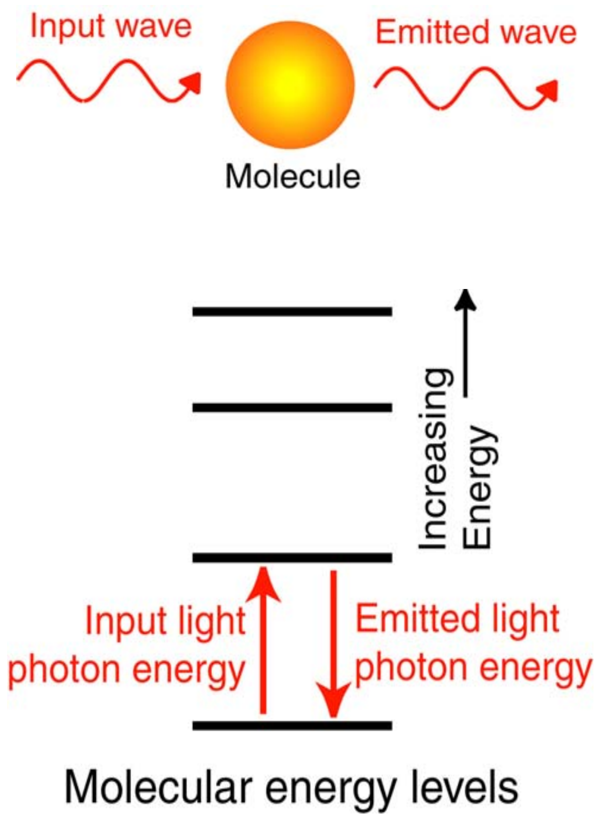
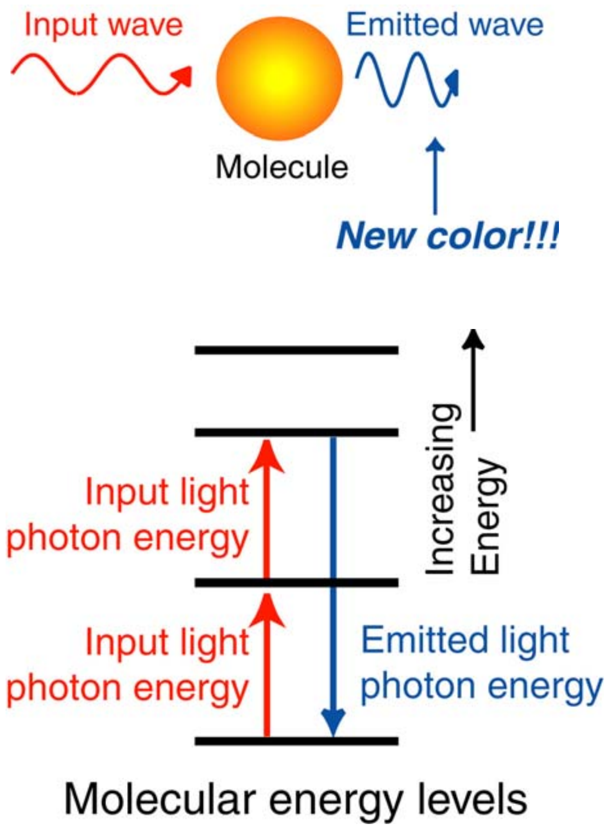
Linear optics



Nonlinear optics



Multiphoton fluorescence microscopy

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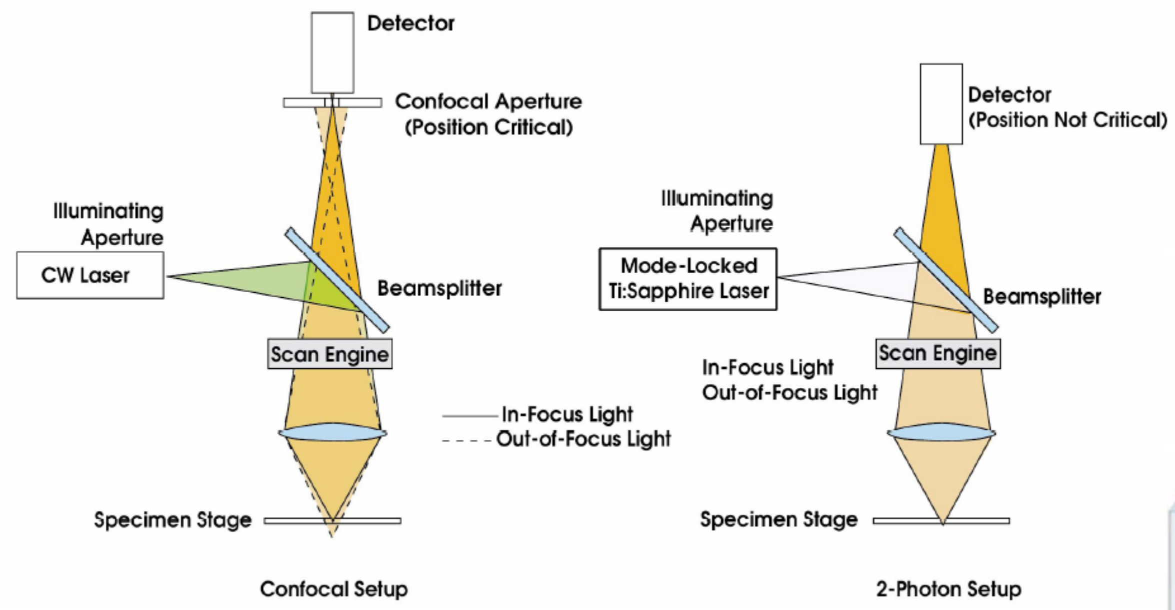

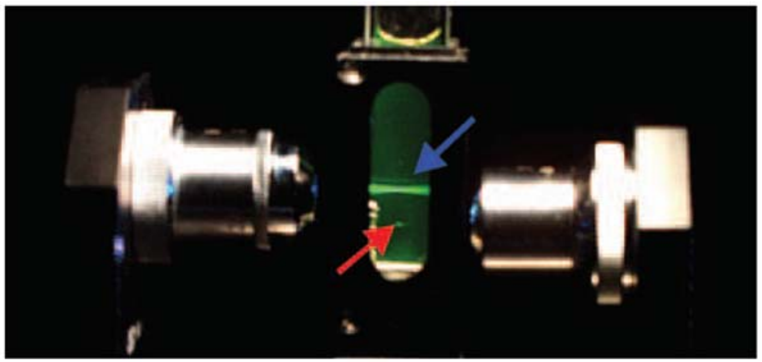

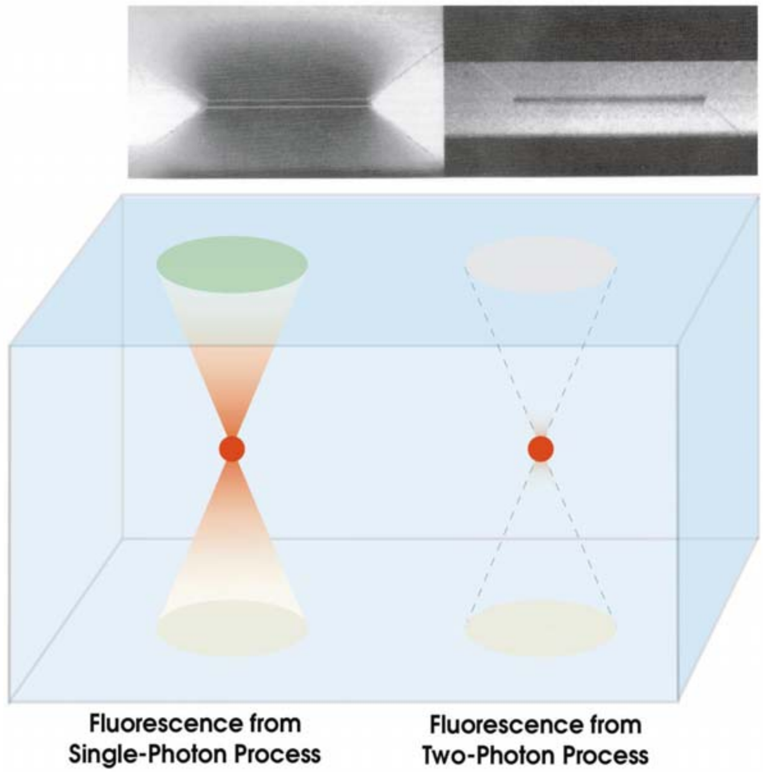

Harmonic-generation microscopy

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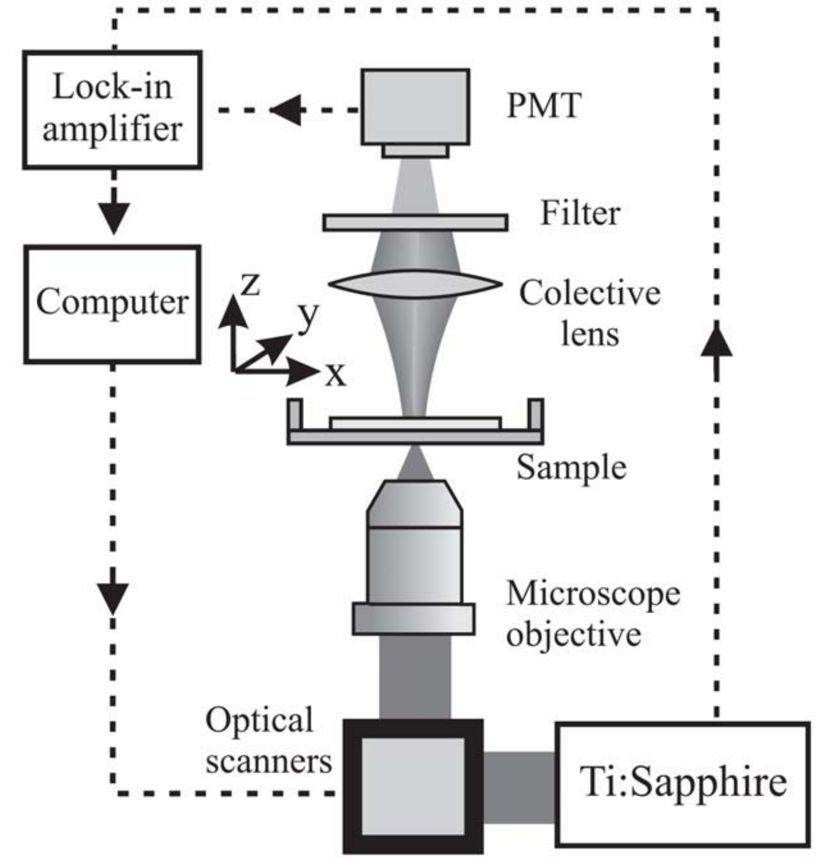
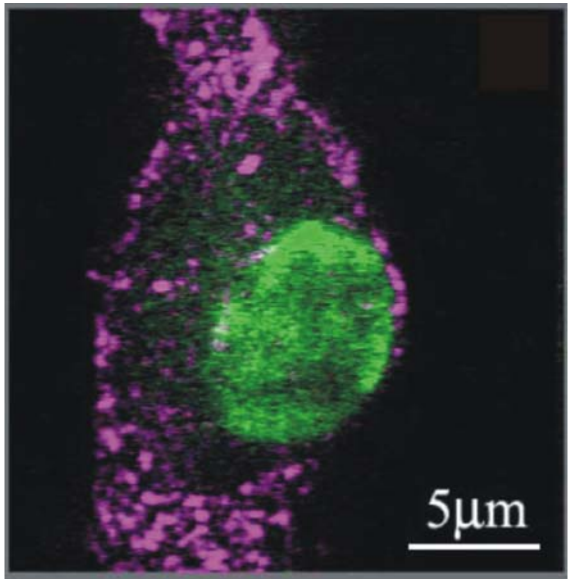


- It can be combined with multiphoton fluorescence microscopy easily.
- Forward and backward detection.
- It requires no fluorescent specie.
- It is reflected to structure-related optical properties.
- More sensitive detection.
- Depth probing!



Scanning Near-field Optical Microscopy (SNOM)

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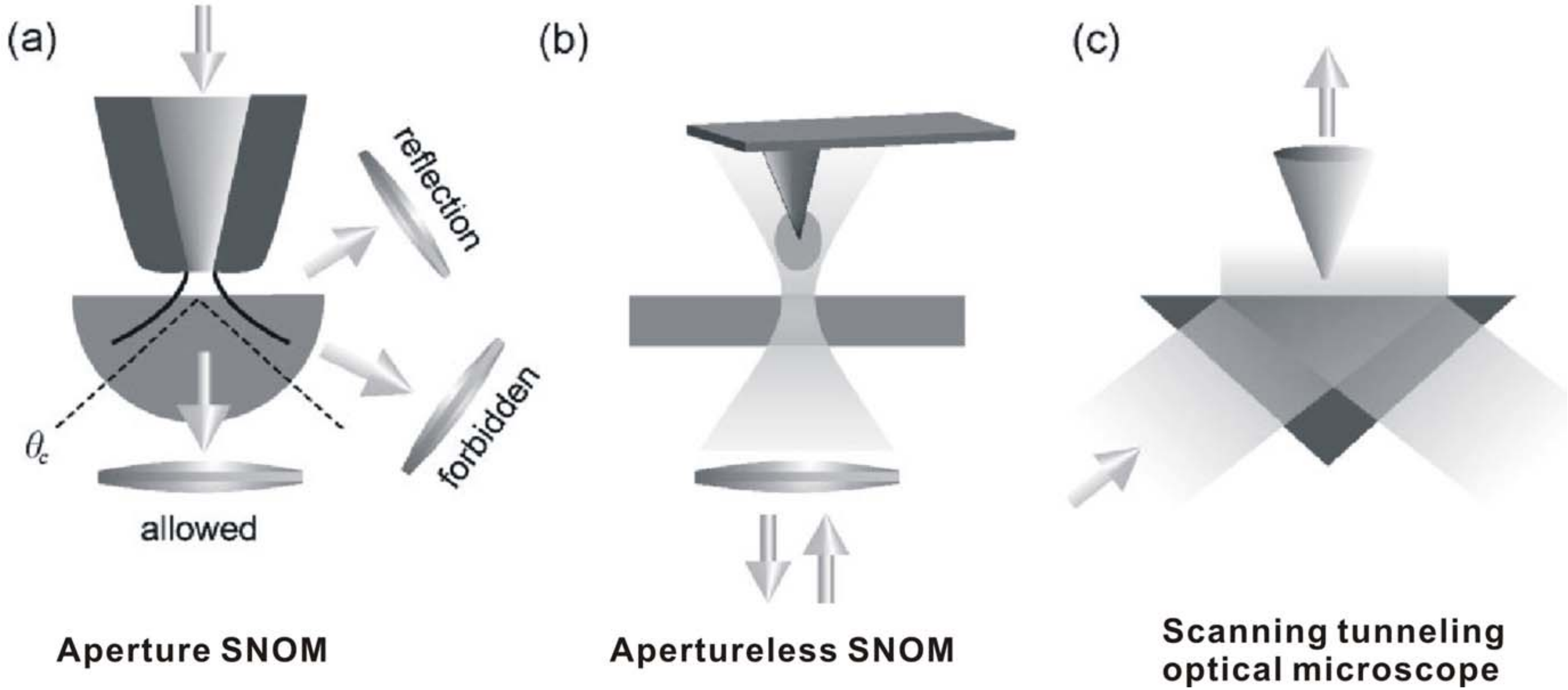

B. Hecht et al., J. Chem. Phys. ***112****, 7761 (2000).*

SNOM setup

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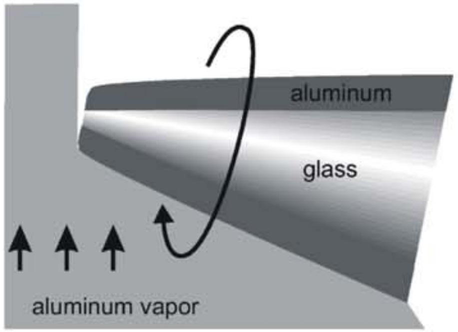

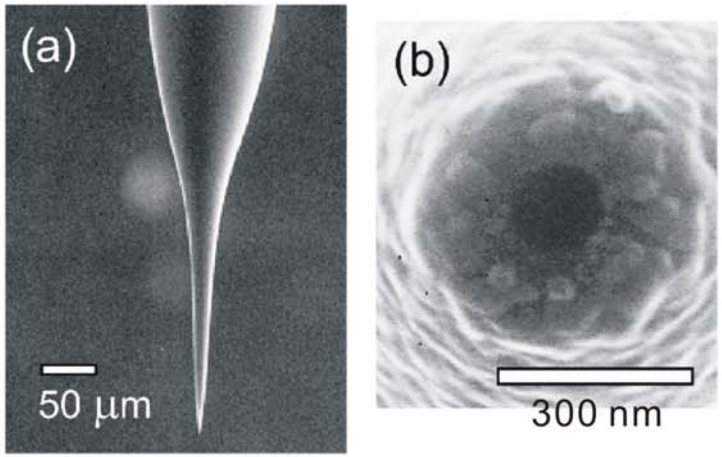

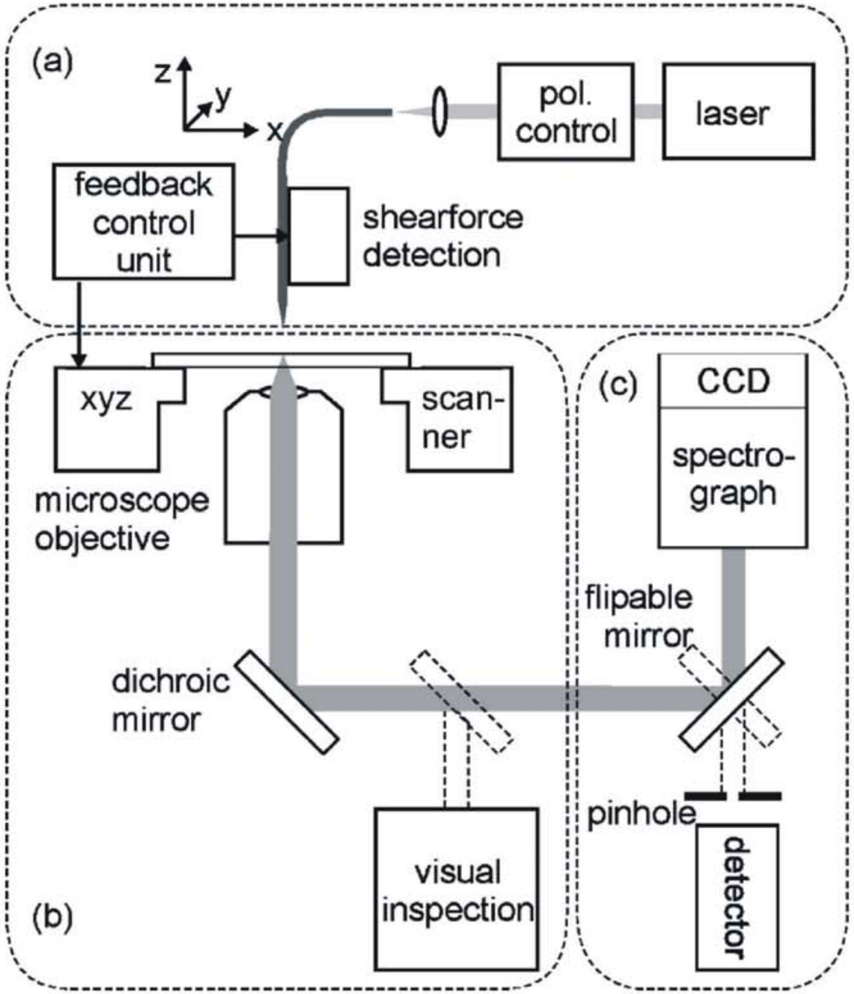

Quantization in nanostructures

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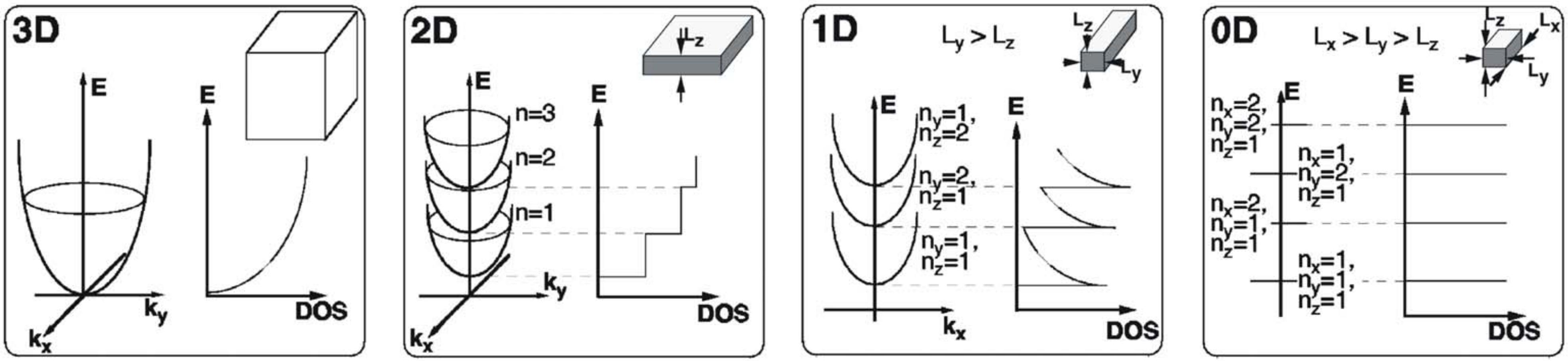

Absorption and emission in nanostructures

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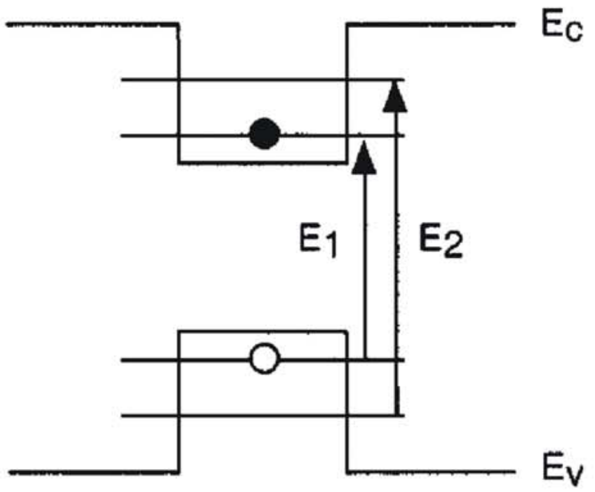

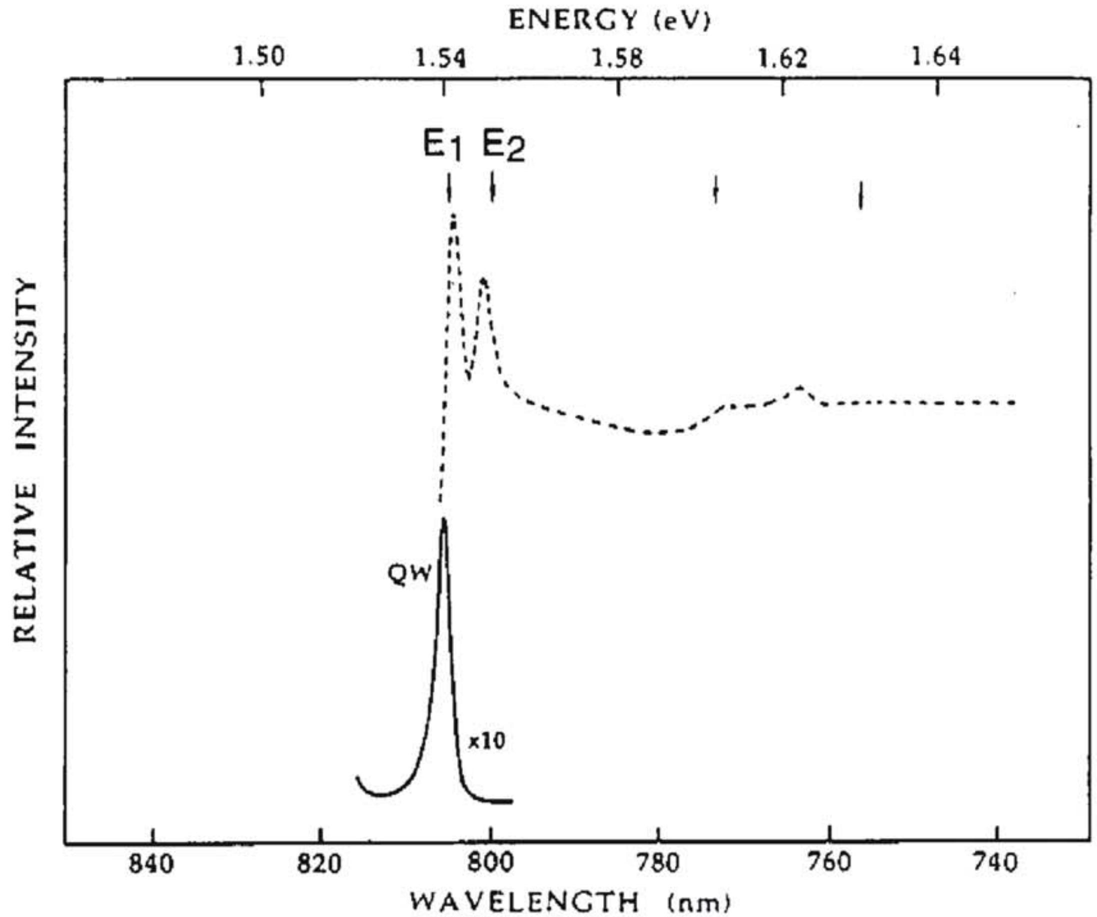

Colloidal semiconductor nanocrystals

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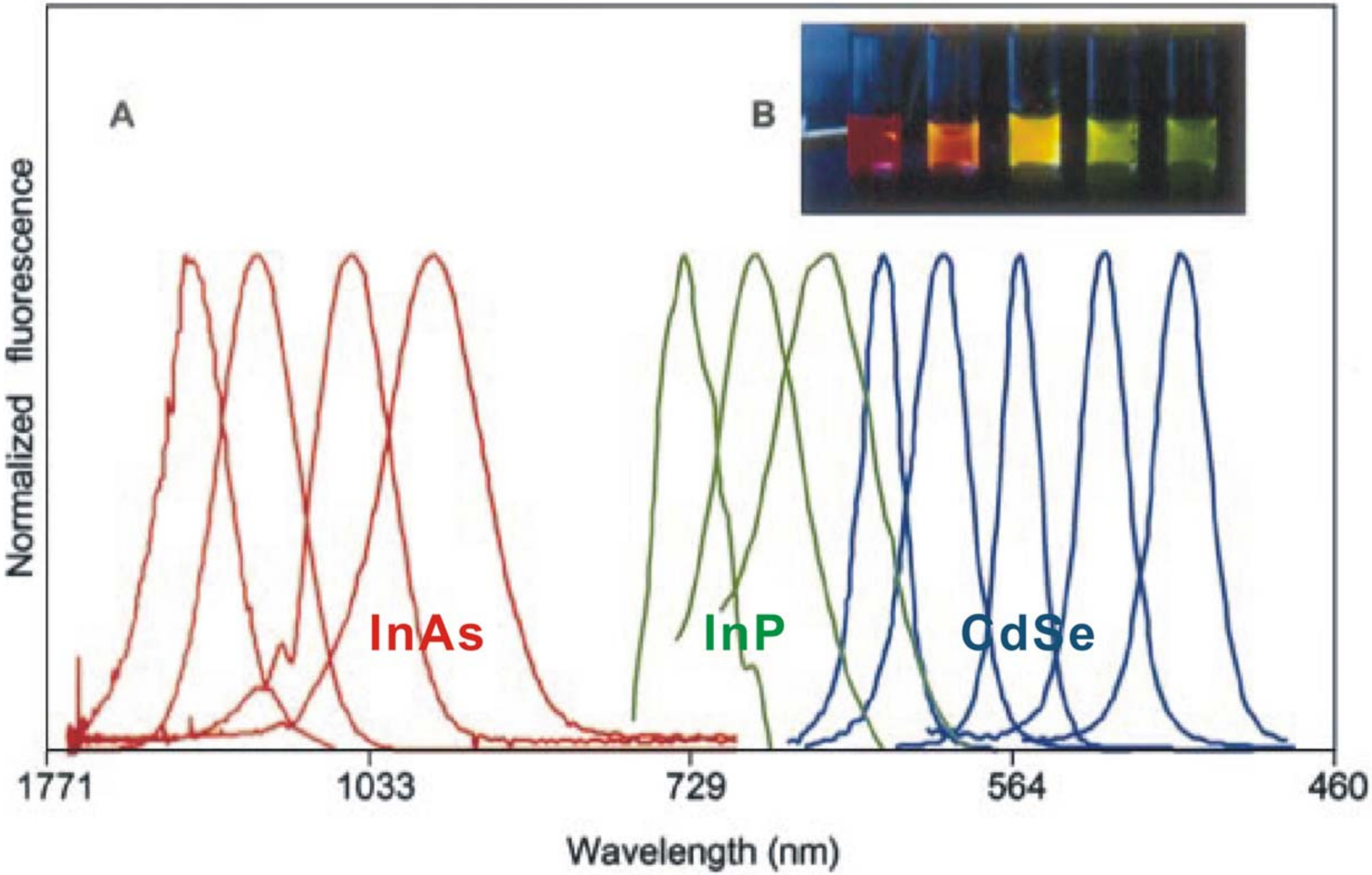

M. Bruchez Jr. et al., Science **281**, 2013 (1998).

Colloidal PbSe nanocrystals

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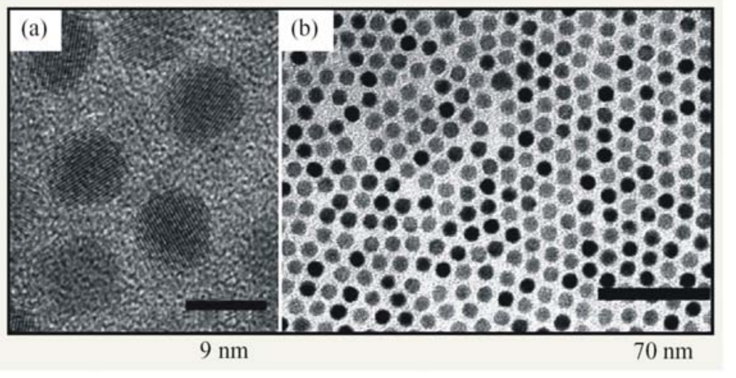

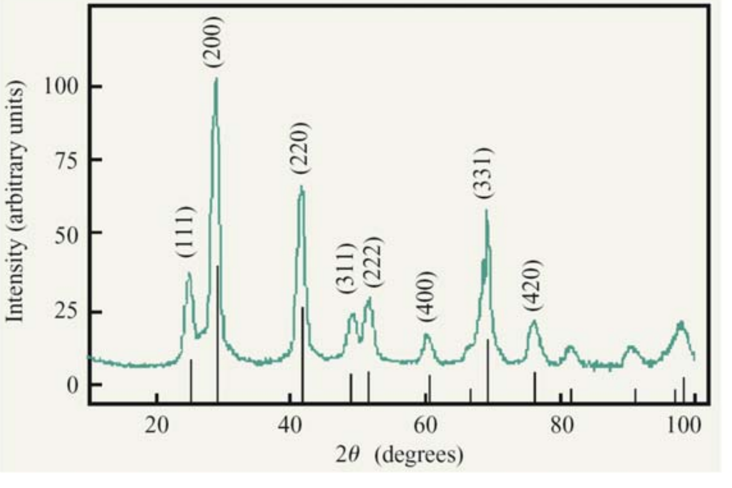

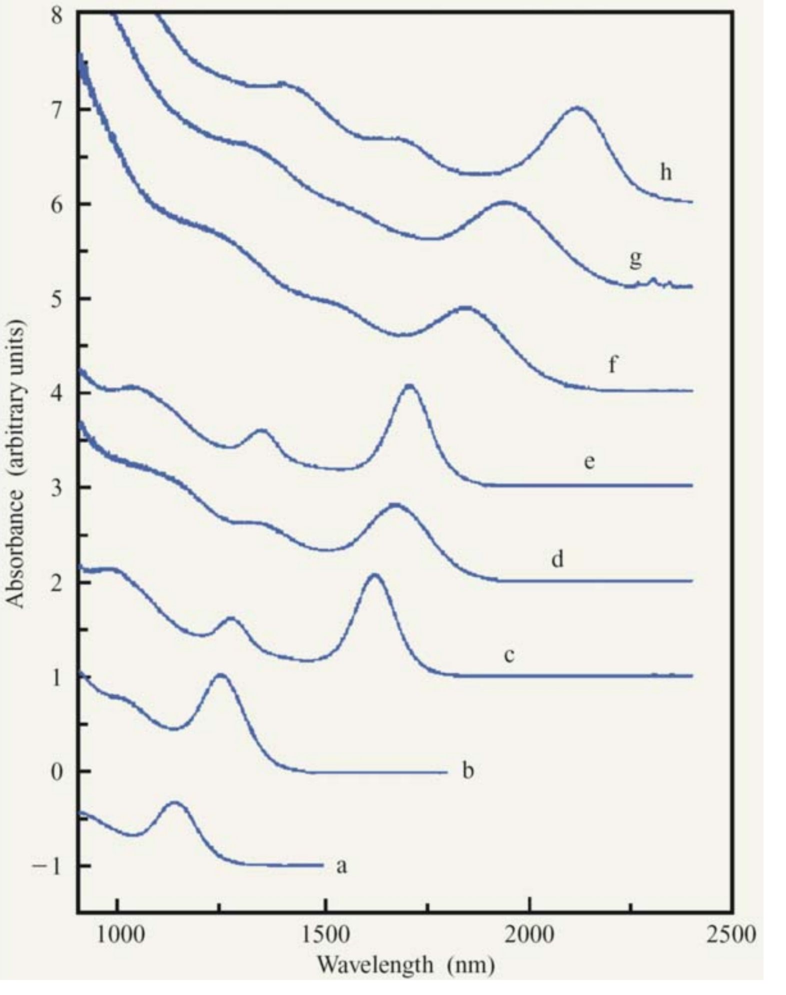

C. B. Murray et al., *IBM J. Rev. Dev.* ***45***, *47 (2001).*

Single nanocrystal spectroscopy of CdSe

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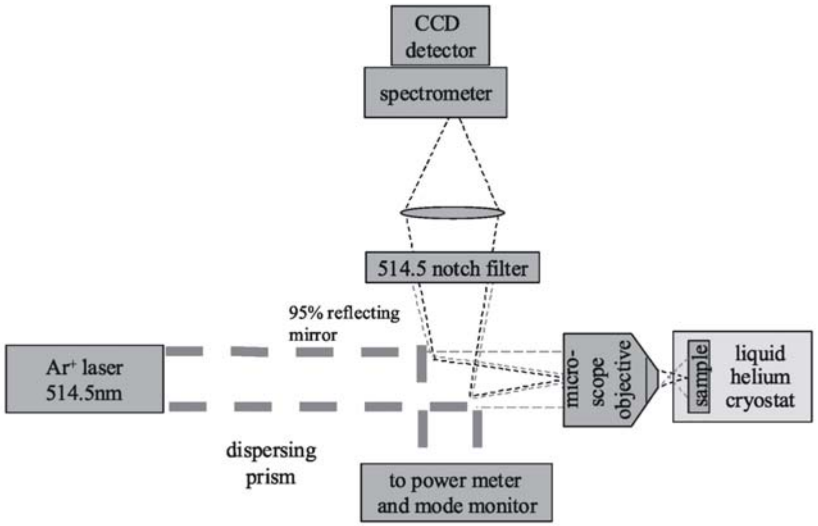

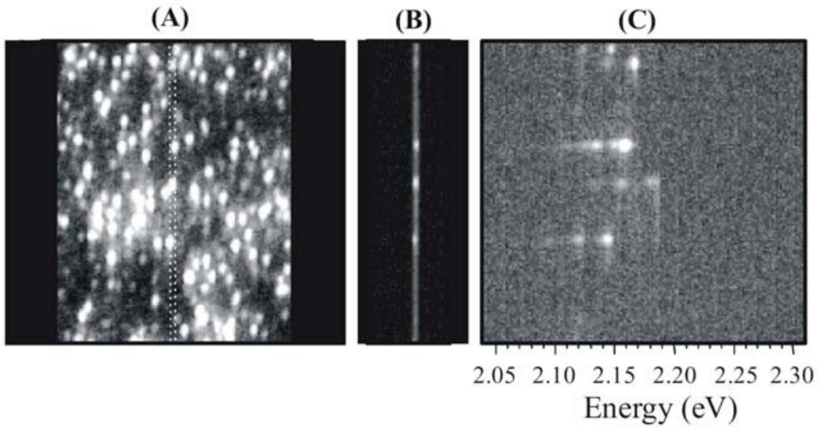

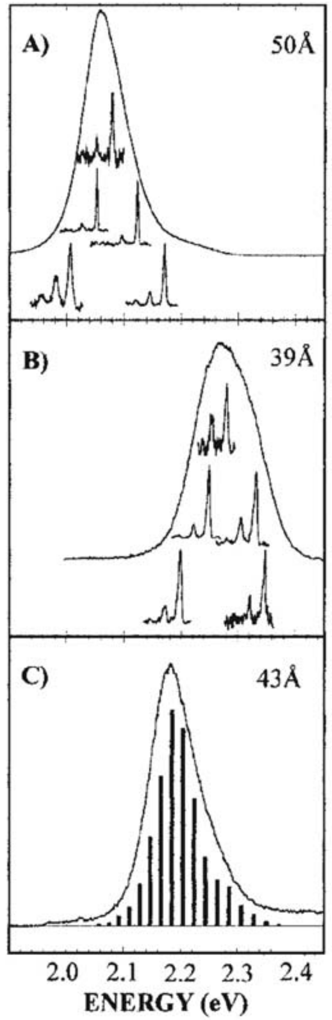

S. A. Empedocles, R. Neuhauser, K. Shimizu and M. G. Bawendi, Adv. Mater. ***11****, 1243 (1999).*

Ensemble emission spectra of CdSe nanocrystals

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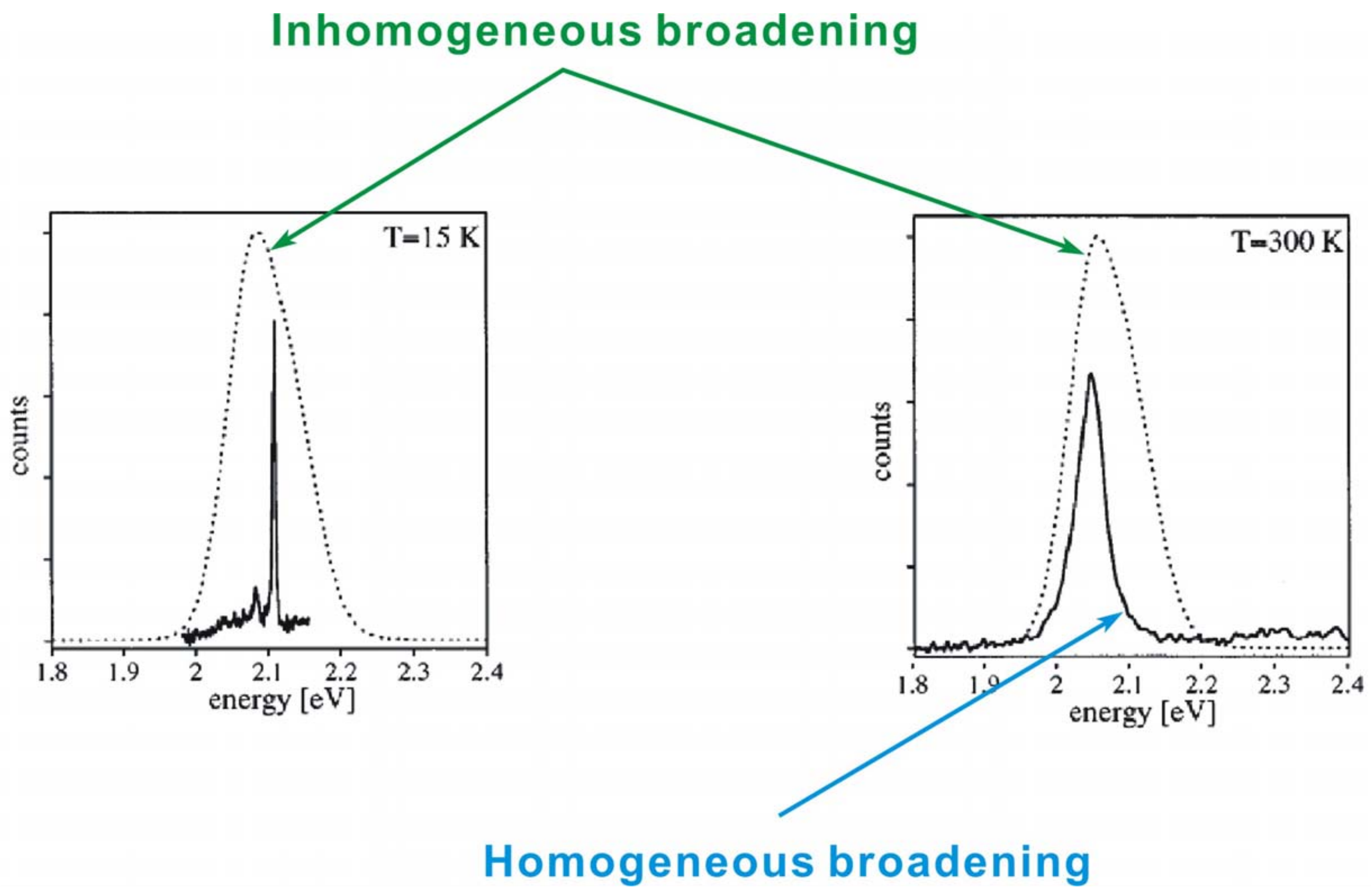

ZnO nanolasers

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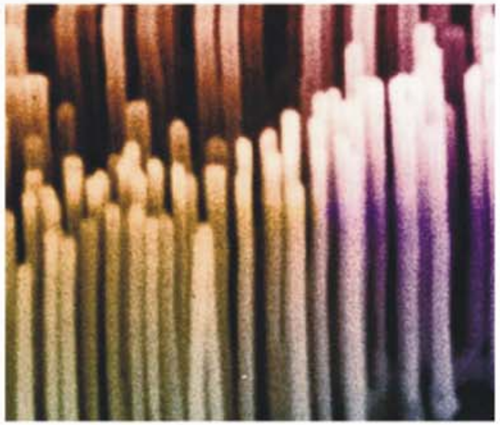

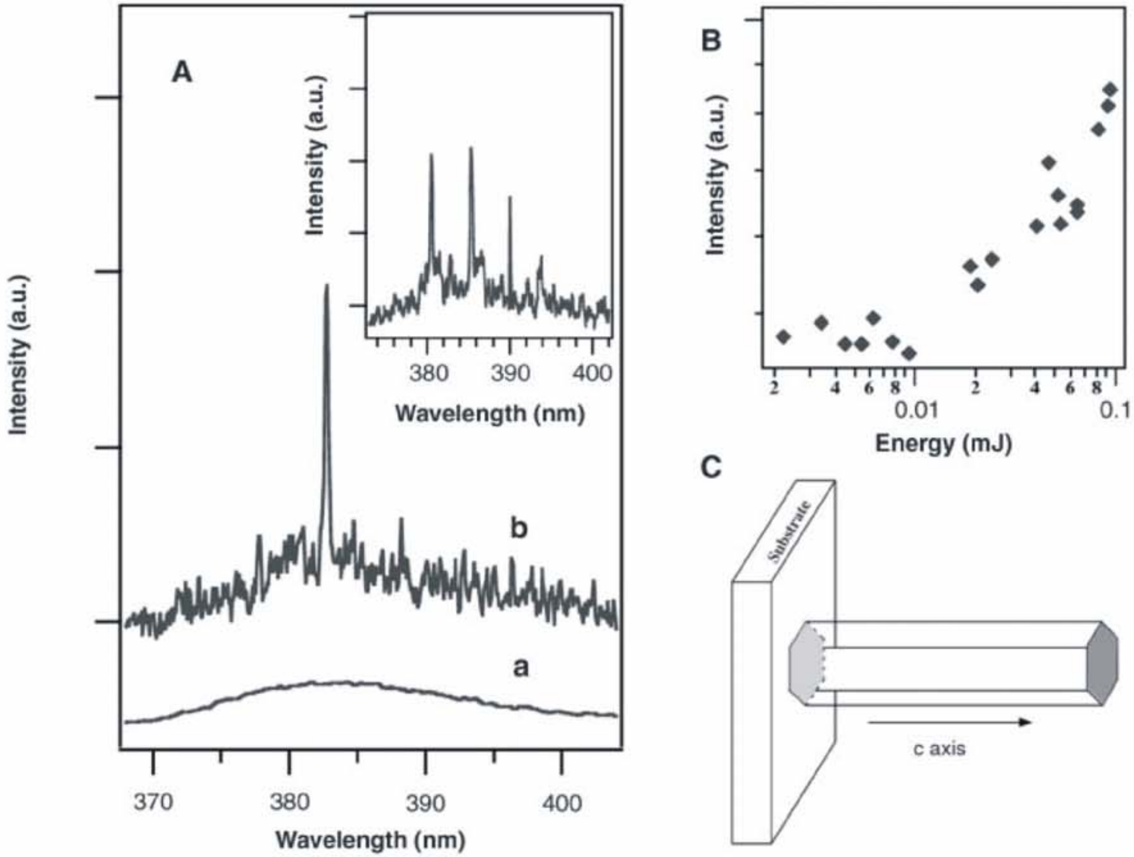

*M. H. Huang et al., Science **292**, 1897 (2001).*

Single GaN nanowire lasers

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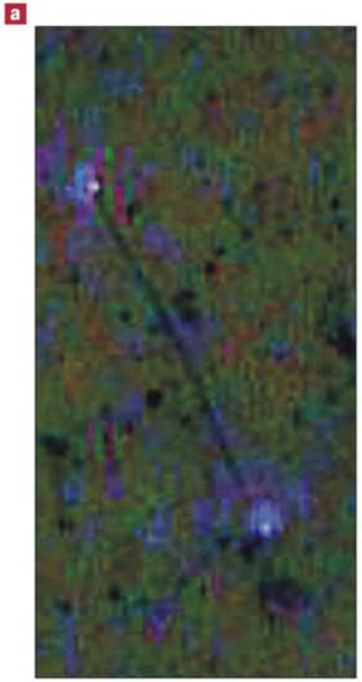

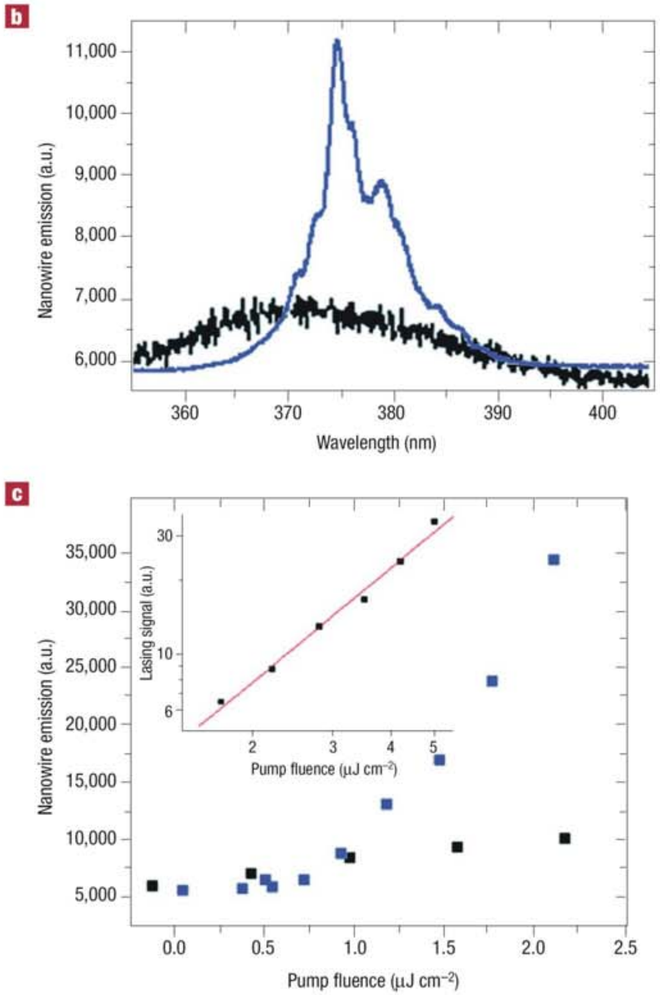

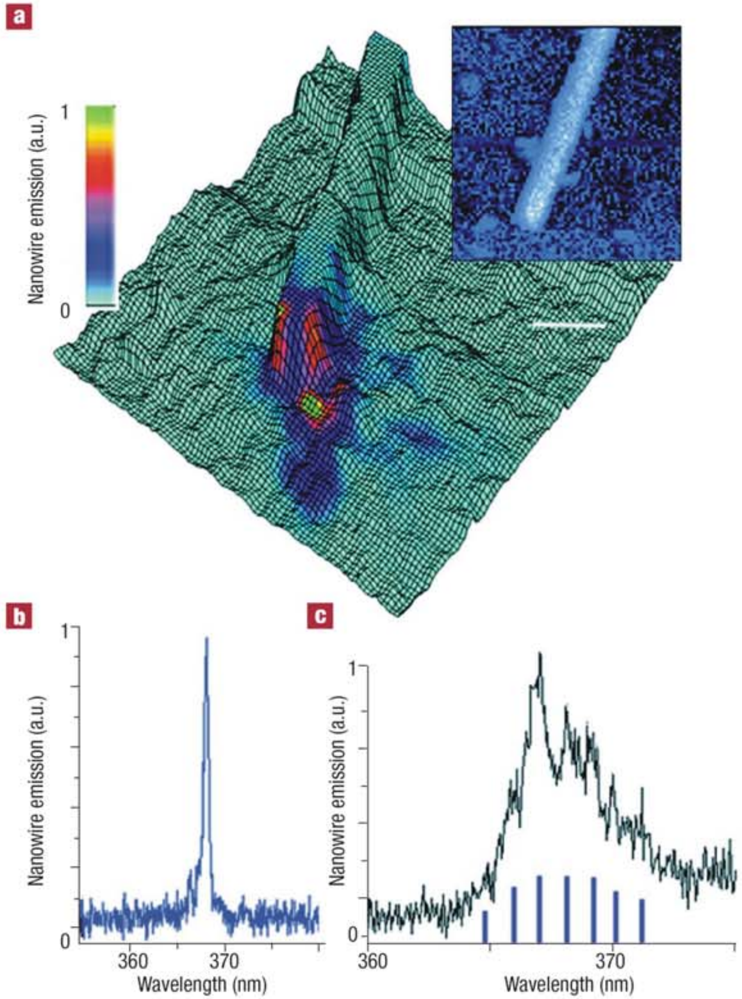

*J. C. Johnson et al., Nature Materials **1**, 106 (2002).*

Applications of nanocrystals in bio-imaging

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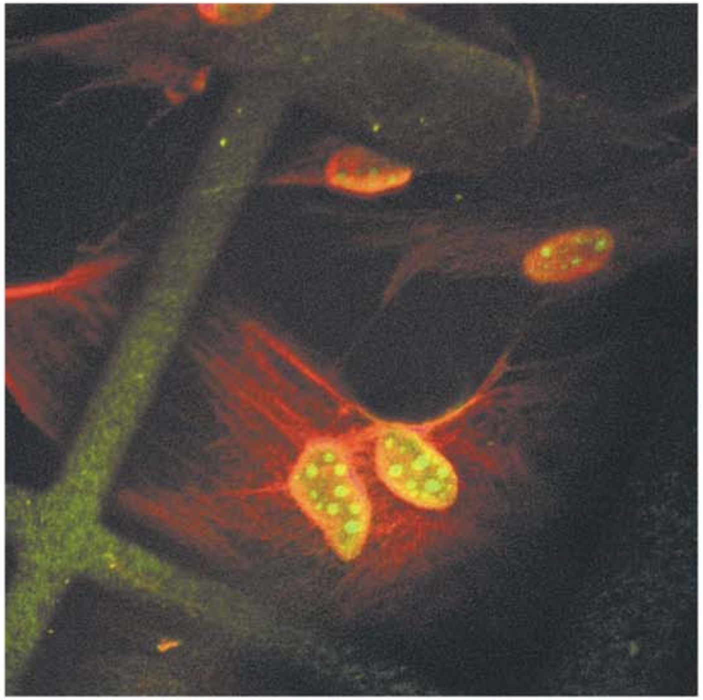
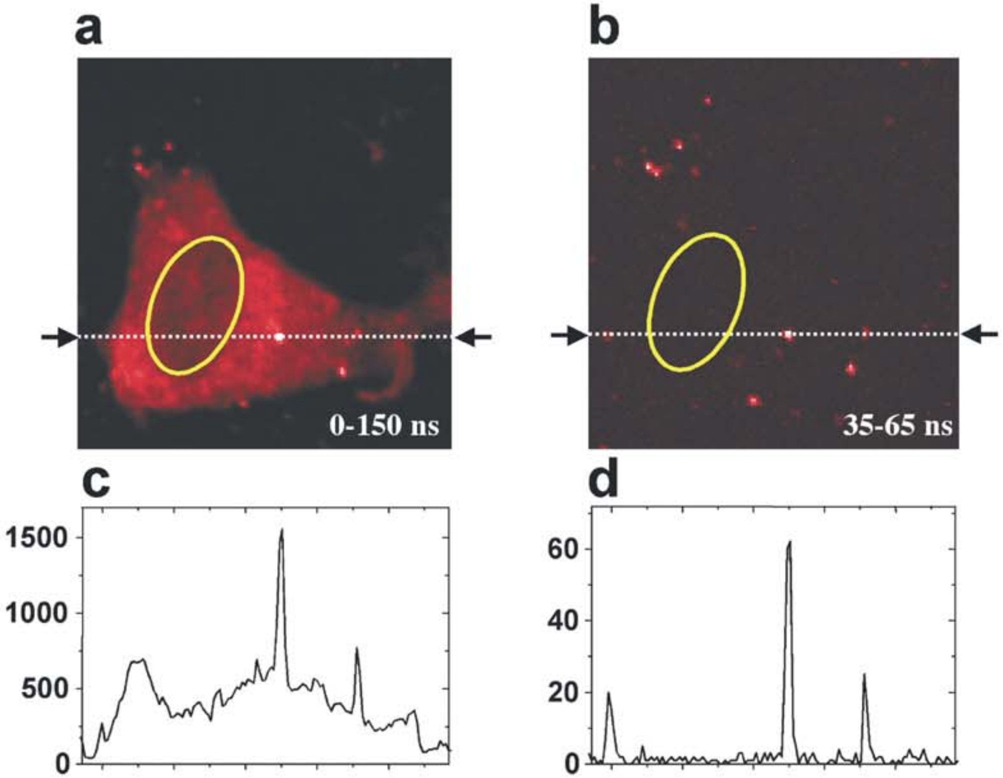
Bio-labeling with nanocrstyals



Time-gated imaging



X. Michalet et al., Single Mol. ***2****, 261 (2001).*

PL spectroscopy of single GaAs QD's

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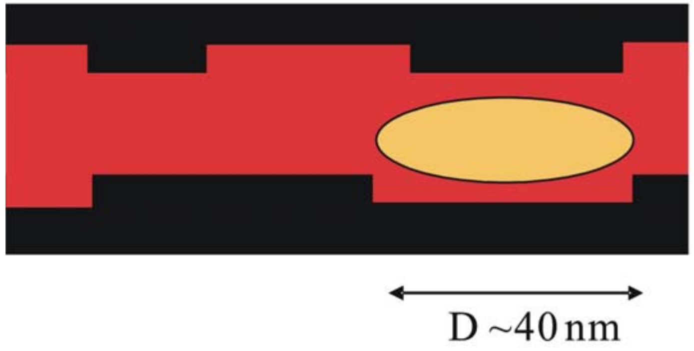
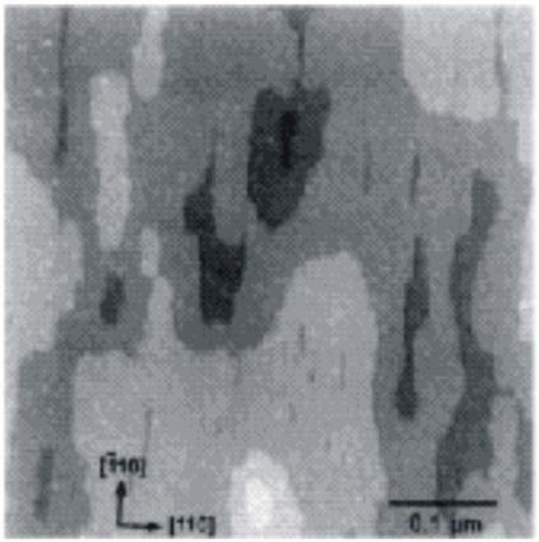
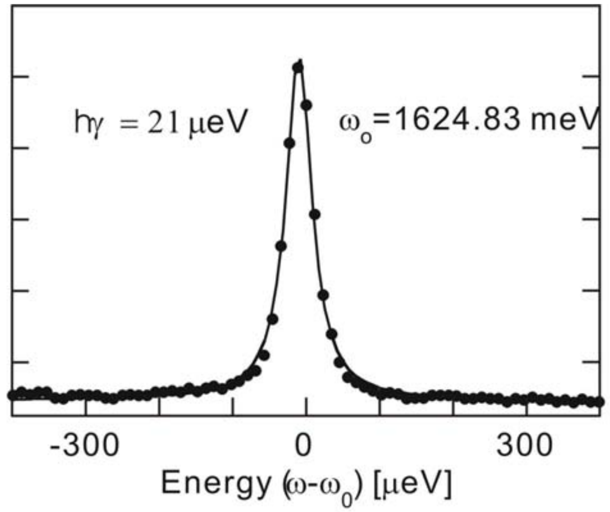
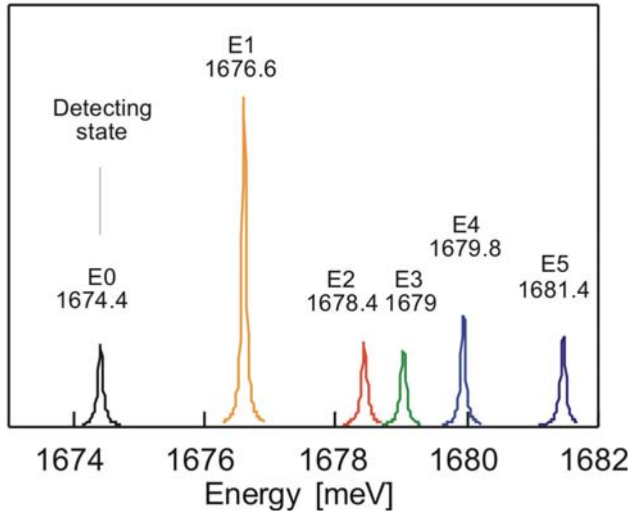


STM image







D. Gammon and D. G. Steel, Physics Today Vol. ***35****, No. 10, 36 (2002).*

Microscopic techniques used in SMS

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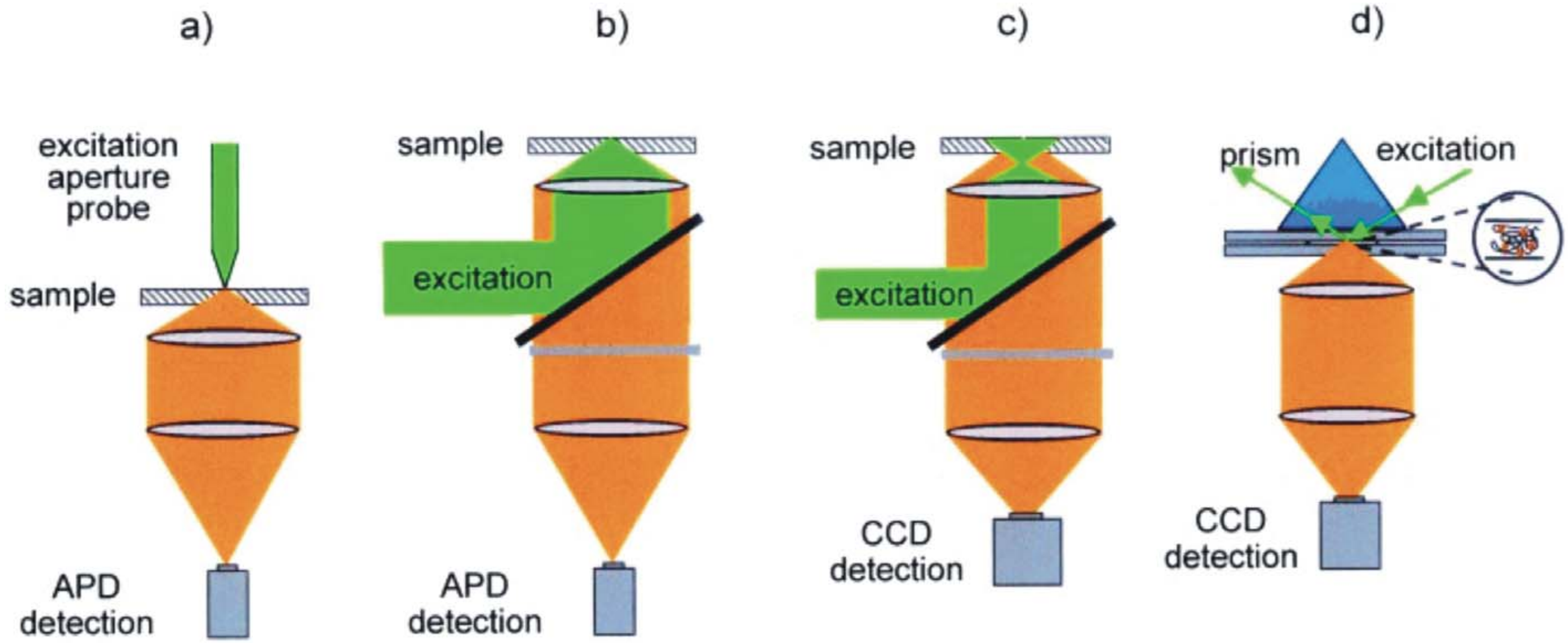

Near-field microscopy **Confocal microscopy** **Wide-field microscopy** **Total internal reflection microscopy**

Why single-molecule spectroscopy?

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- **Measurements on single molecules in a sample differ because their environments are different, or in the case large and complex molecules such as proteins, because they present a number of different conformations.**

- **Single-molecule studies show dynamical fluctuations (time-resolved changes in molecular properties), particularly when dealing with kinetic experiments of complex systems, like proteins. By looking at a single molecule, we select only one state or one formation at a given time.**

- **A single molecule can serve as a nano-probe to its local environment and local external perturbations (such as pressure, electric and magnetic fields).**

Applications of SMS

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- **Local nonuniform distribution**
- **Local dynamics**
- **Photophysics and photochemistry**
- **Diffusional motions**
- **Comformational motions of macromolecules**
- **Chemical activitivies**

Single molecule imaging

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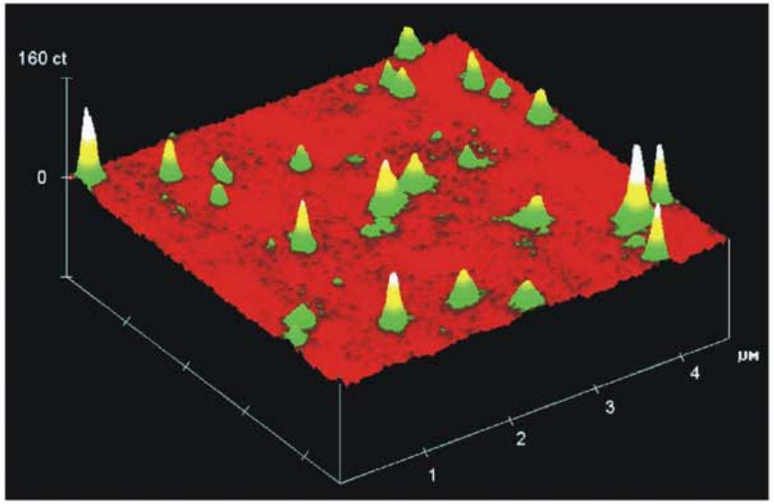
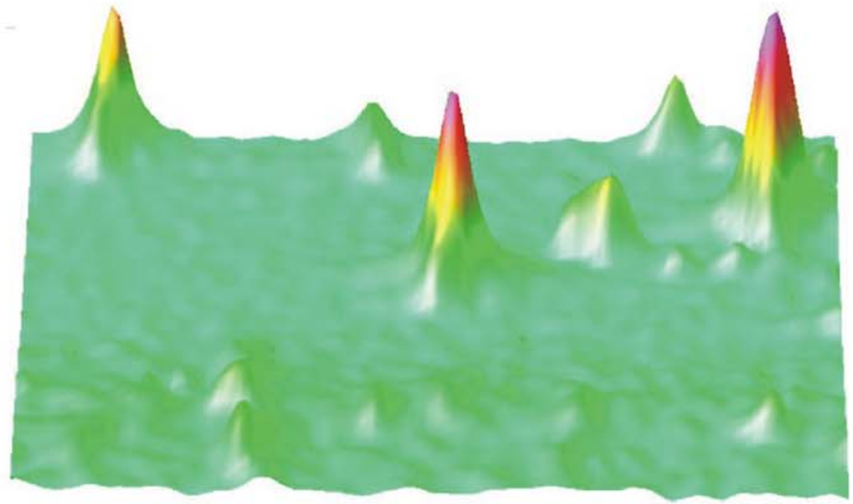


Oxanine 720 dispersed on a PMMA film



Hybrid space-frequency image of pentacene in a p-terphenyl crystal

*W. E. Moerner and M. Orrit, Science **283**, 1670 (1999).*

Single molecule spectroscopy

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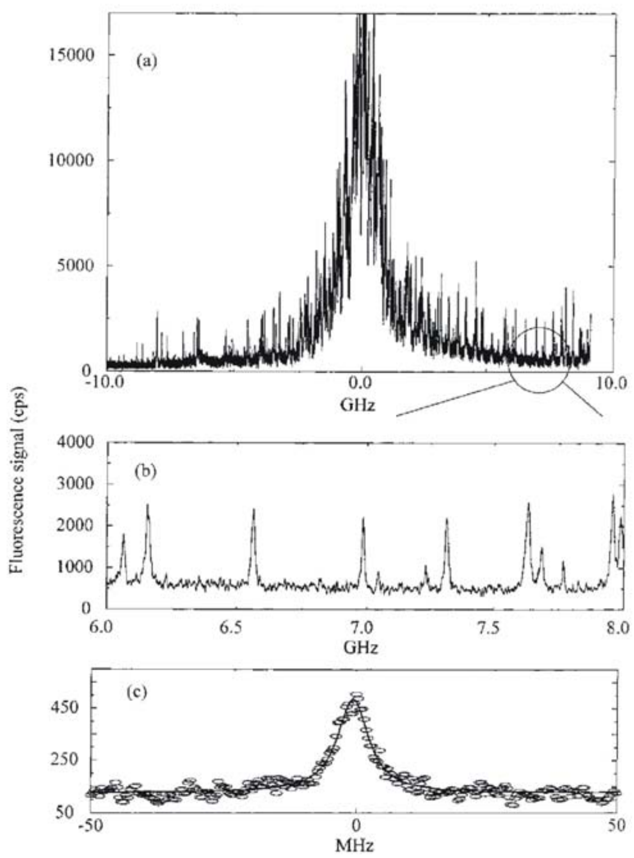
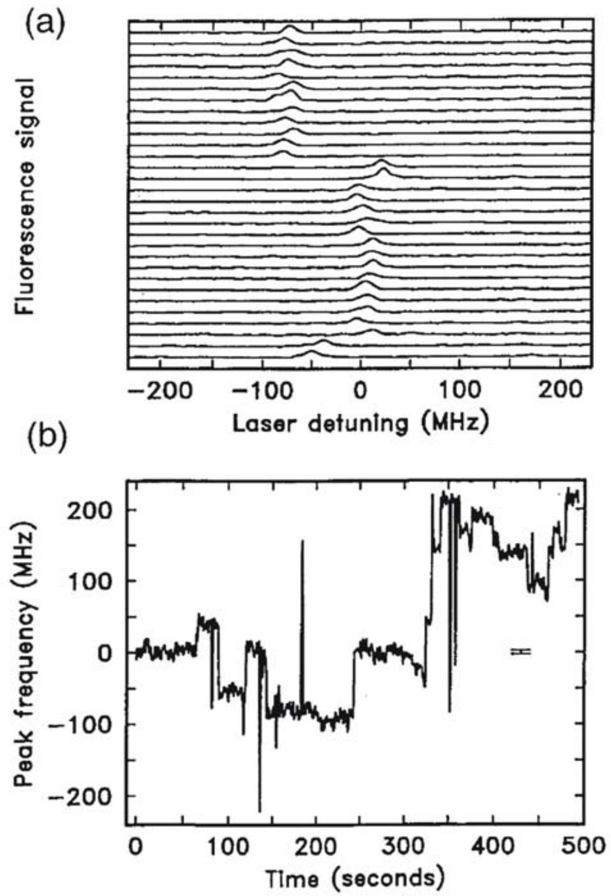


Spectral dilution



Spectral diffusion

W. E. Moerner, J. Phys. Chem. B ***106****, 910 (2002).*

Single-biomolecule study schemes

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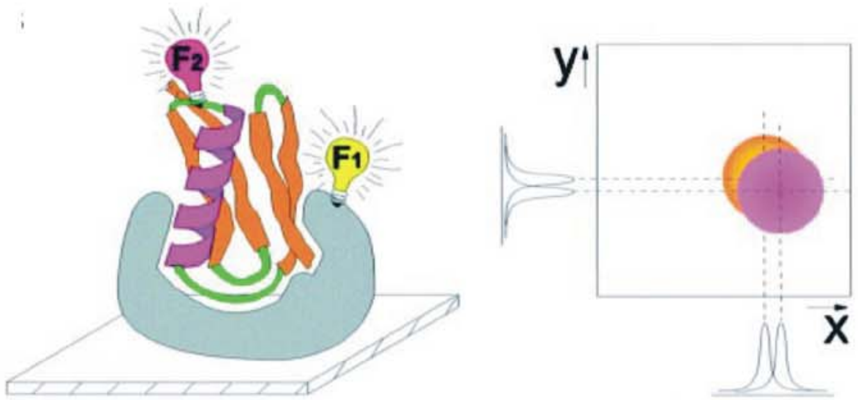
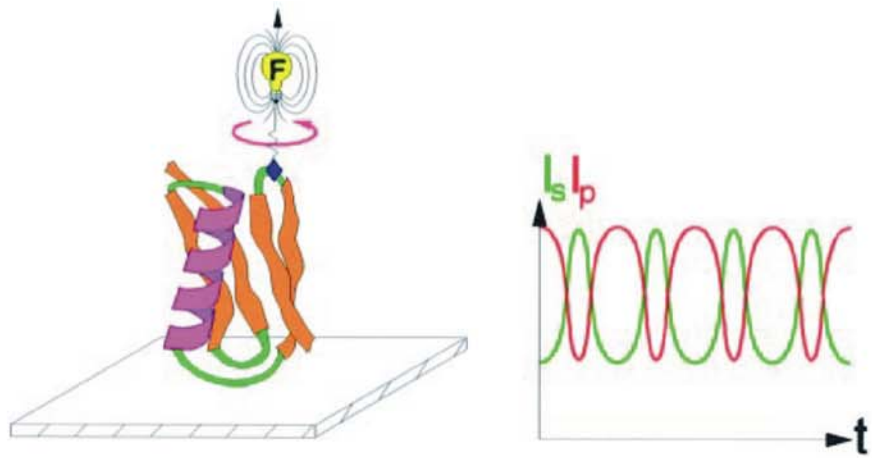
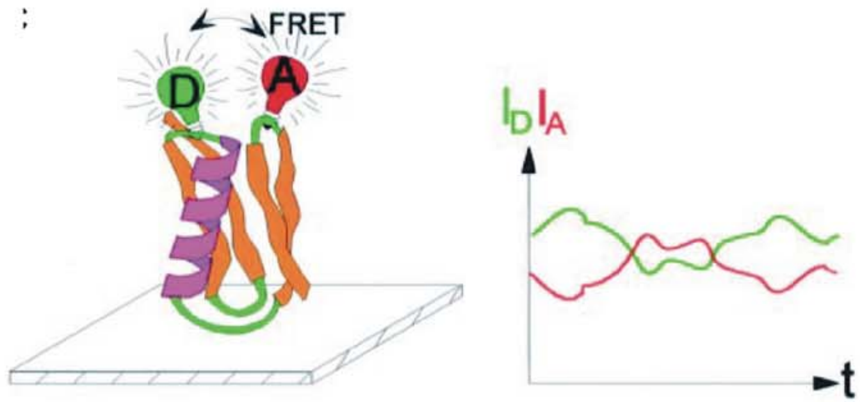


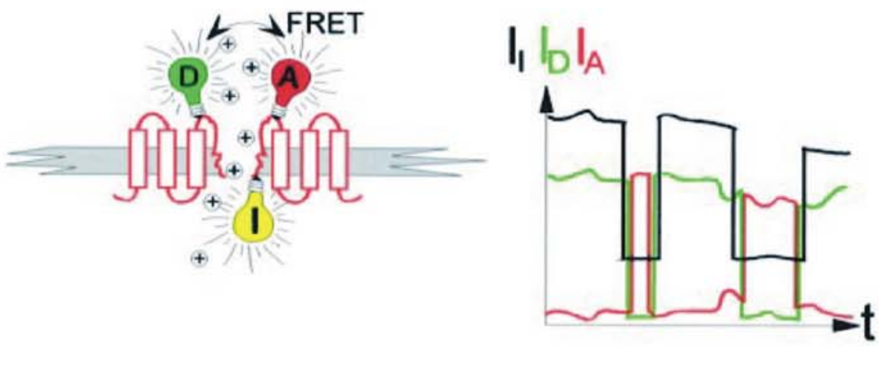
Colocation of two macromolecules



Orientational motion by polarization detection



Conformation change by FRET



Conformation change and ion channeling

S. Weiss, *Science* **283**, 1676 (1999).

C. V. Raman and his instrument

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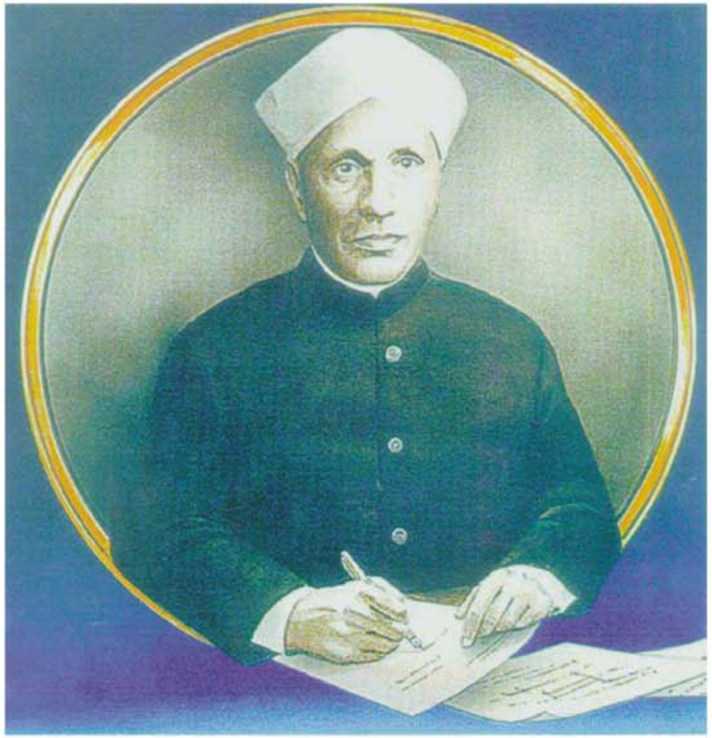

Sir C. V. Raman

Raman's spectrograph

Raman spectrum of CCl_4 by C. V. Raman

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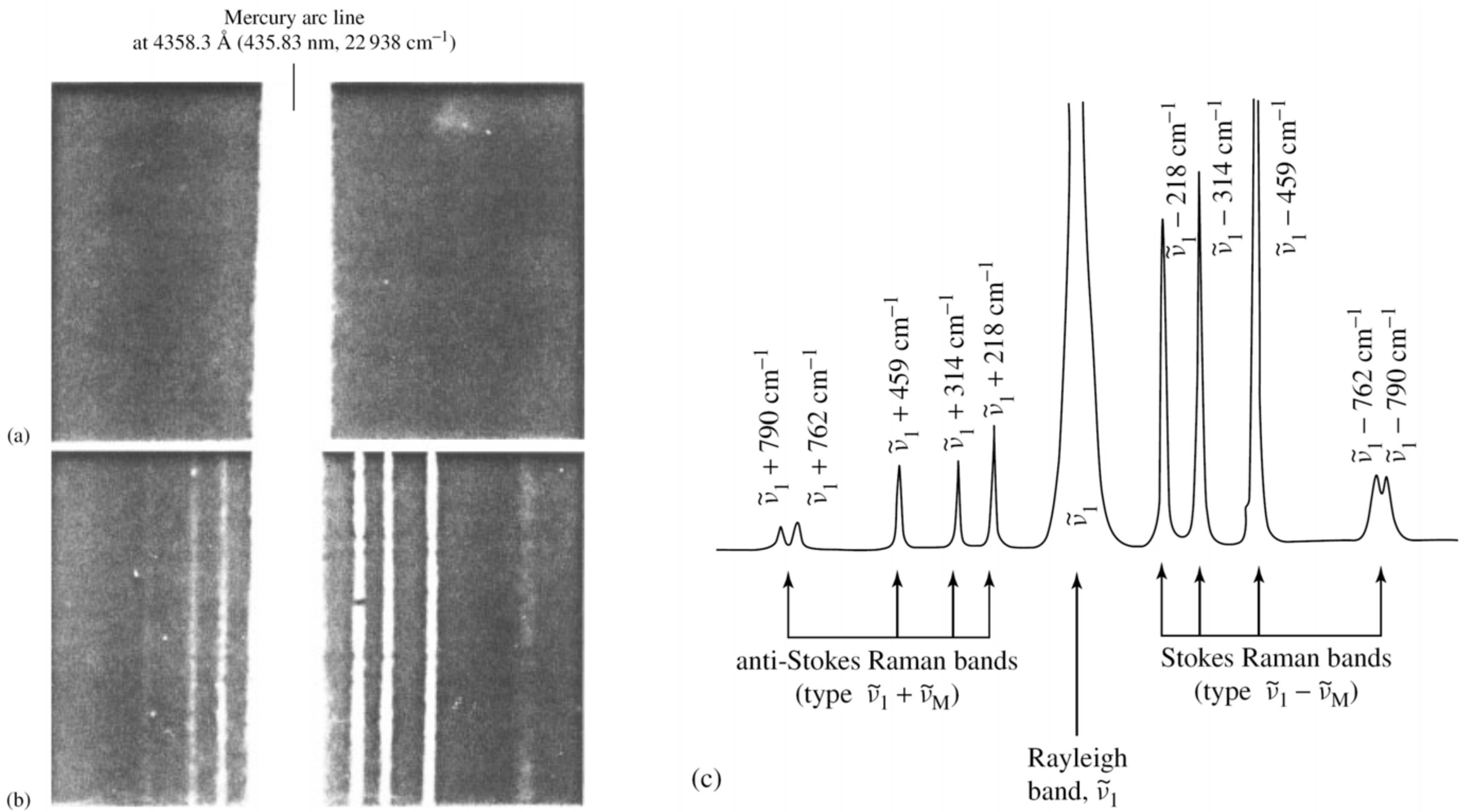

Raman scattering

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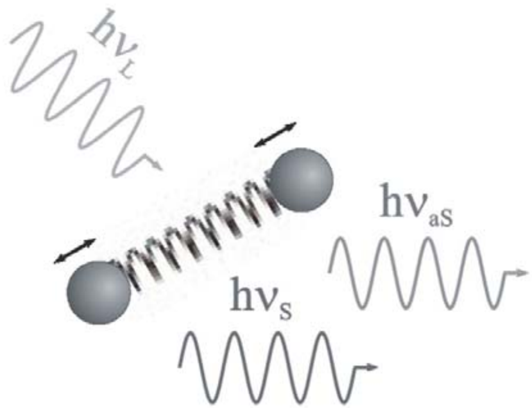
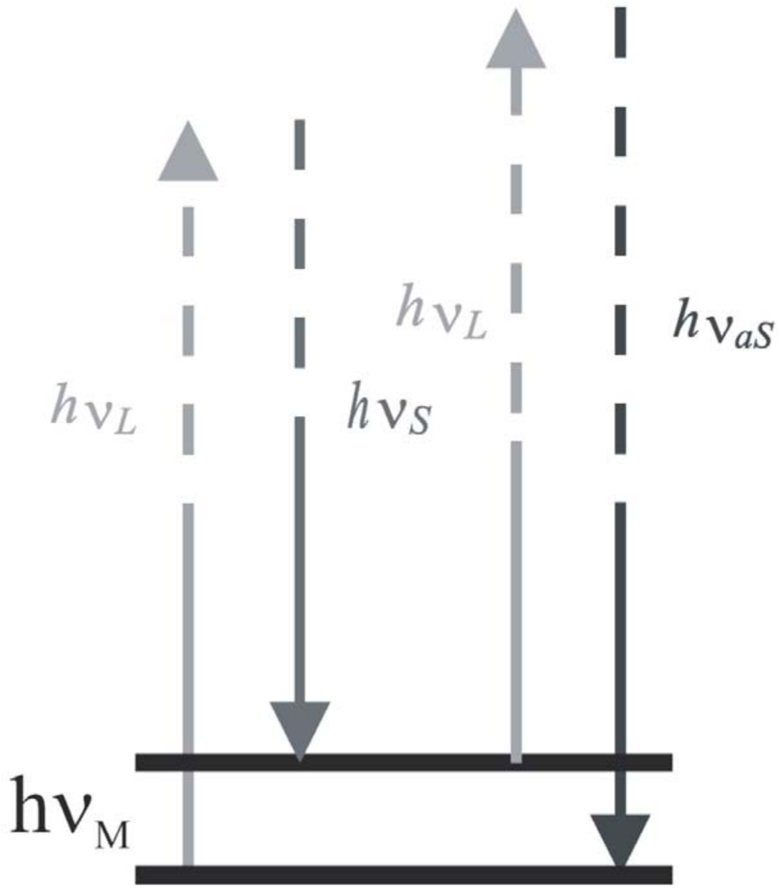


$$\nu_{aS} = \nu_L + \nu_M$$

$$\nu_S = \nu_L - \nu_M$$



Comparison of IR and Raman spectroscopy

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	Near-IR	Mid-IR	Raman
Spectral range (cm^{-1})	13,300–3300	4000–400	4000–50
Analysis of:			
Gases	No	Yes	Yes
Liquids	Yes	Yes	Yes
Solids	Yes	Yes	Yes
Aqueous systems	Difficult	Very difficult	Yes
Macroscopic samples	Yes	Yes	Yes
Microscopic samples	No	Yes	Yes
Signal	Strong	Strong	Weak
Sampling	Easy	Difficult	Easy
Through glass windows	Yes	No	Yes
In situ	No	No	Yes
Quantitative	Yes	Difficult	Yes
Noninvasive	Yes	No	Yes
Fiber optic interfacing	Yes	No	Yes
Information content	Low. Limited to O–H, N–H, and C–H vibrations	High	High
Reaction monitoring and modeling	Requires chemometrics	Yes	Yes

Commercial Raman instruments

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LabRam HR, Jobin Yvon

T64000, Jobin Yvon

CPM 2000, WITec

InVia Raman microscope, Renishaw

Raman Rnx 1, Kaiser Optical Systems

Raman setup

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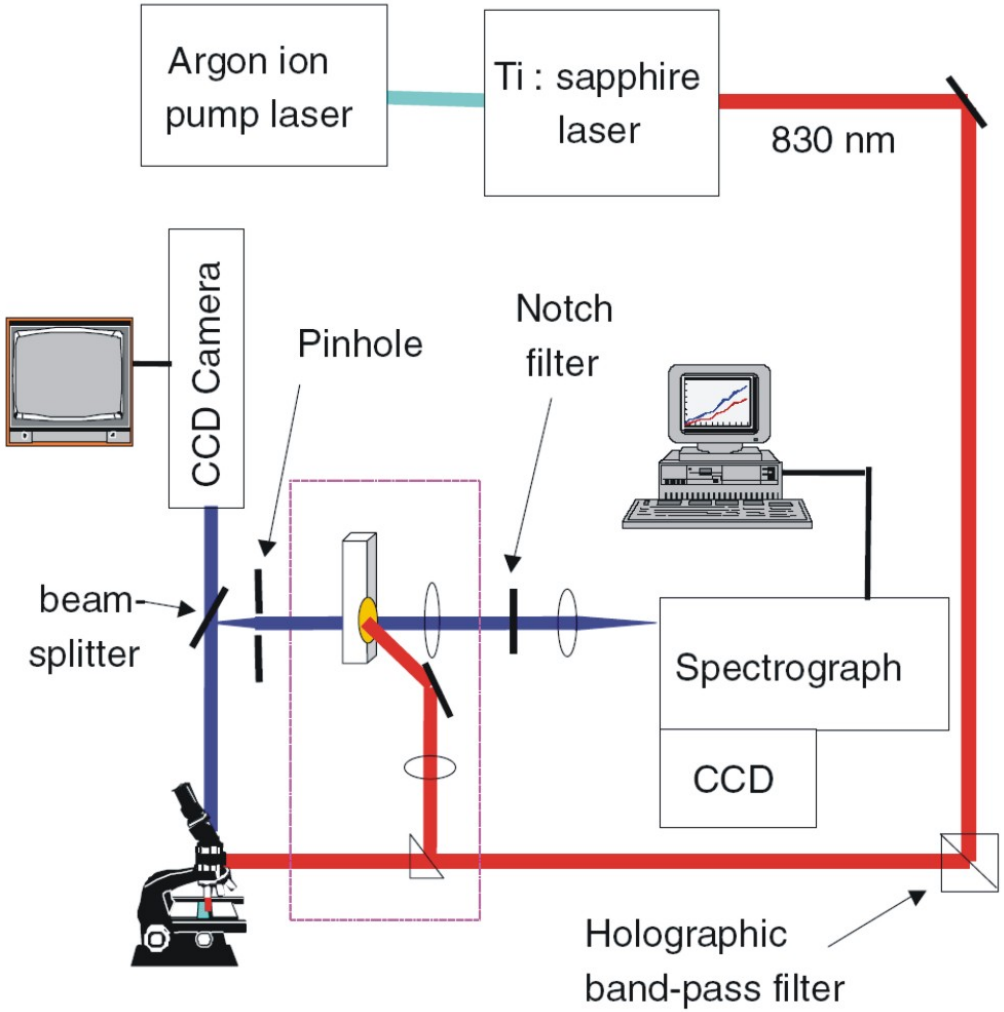

Excitation wavelength considerations-I

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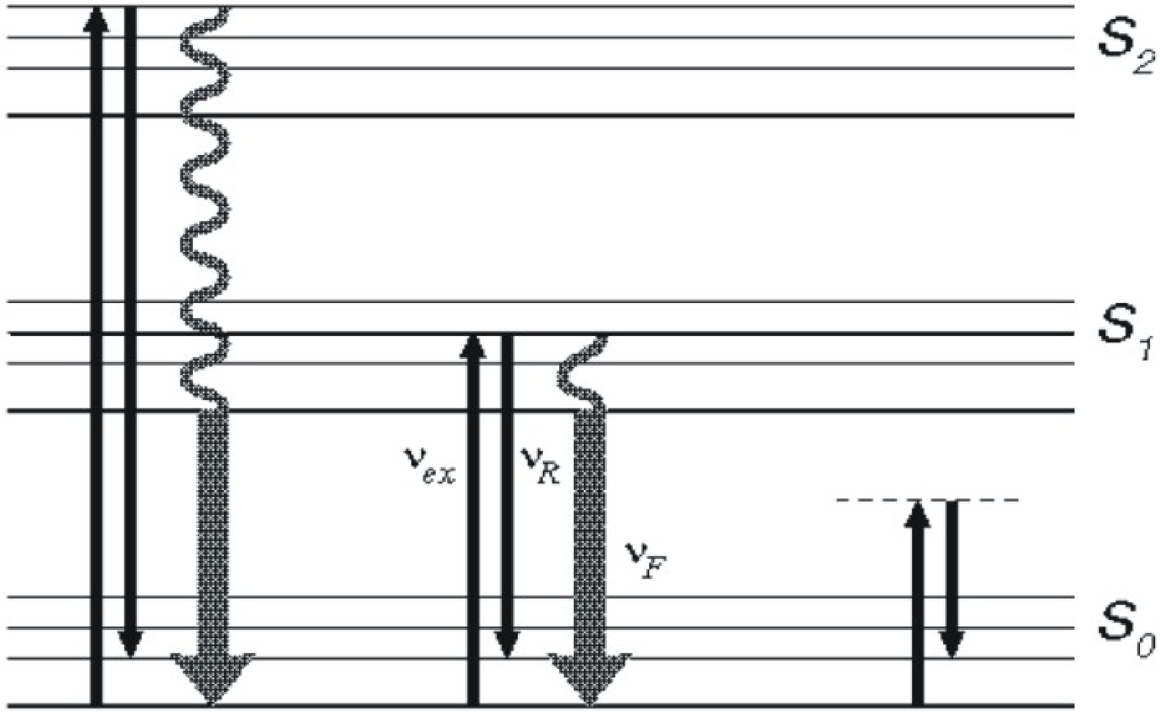

UV Resonant Excitation
< 300 nm

Visible Excitation
300-700 nm
(Fluorescence)

Near IR Excitation
> 700 nm

Excitation wavelength considerations-II

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	λ_{exc} > 800 nm (NIR excitation)	400 nm < λ_{exc} < 800 nm (visible excitation)	λ_{exc} < 400 nm (UV excitation)
Raman cross section	Small	Medium	Large
Probing depth	Long	Medium	Small
Resonant Raman	No	Yes	Yes
Fluorescence background	No	Some	Significant
Spatial resolution	Low	Medium	High
Detection sensitivity	Low	Medium	High

Confocal Raman microscopy

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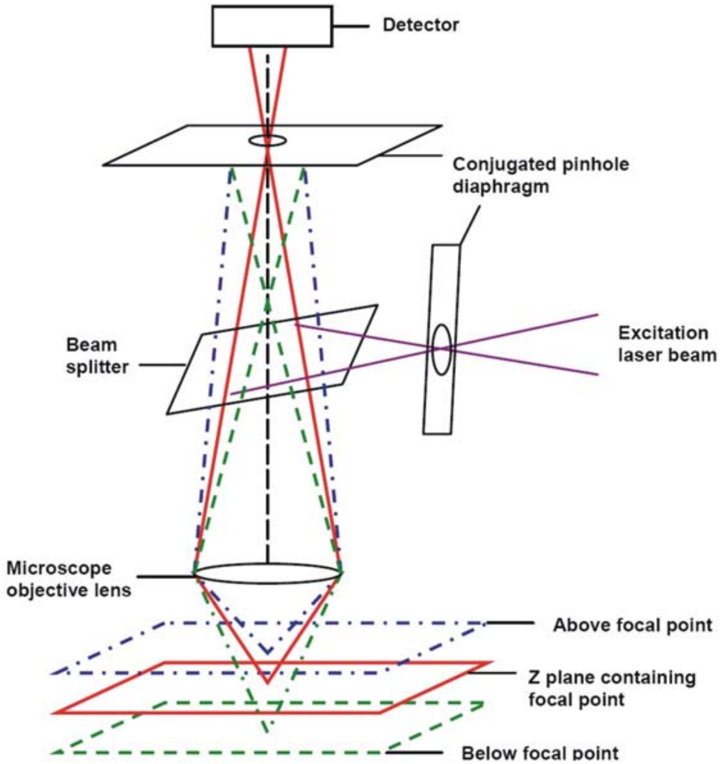

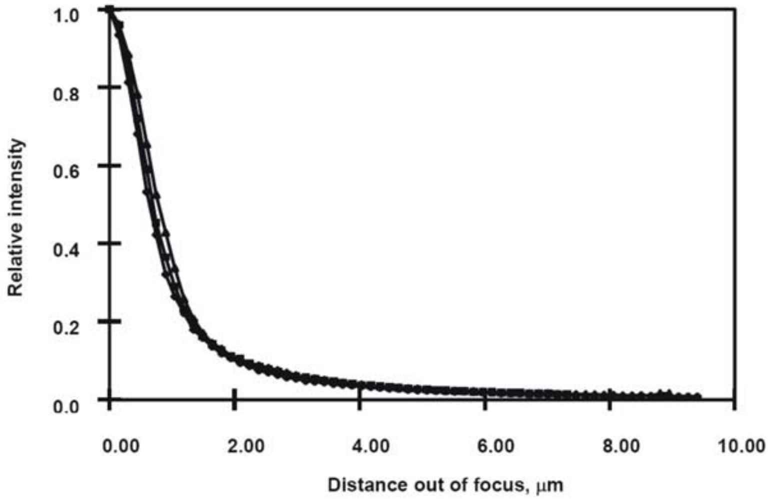

Micro Raman of CNT under local strain

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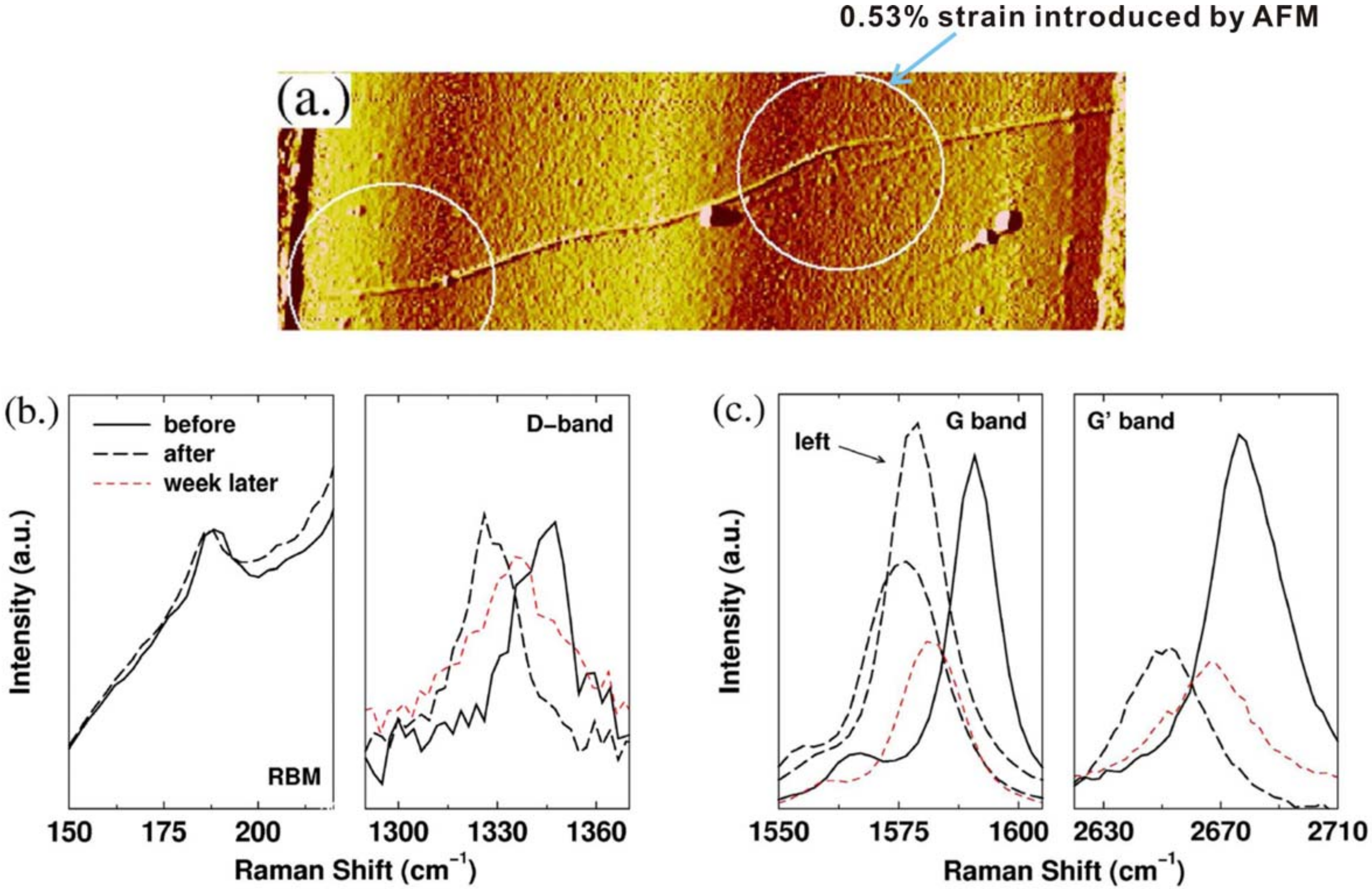

S. B. Cronion et al., Phys. Rev. Lett. ***93****, 167401 (2004).*

Micro Raman studies of graphite edges

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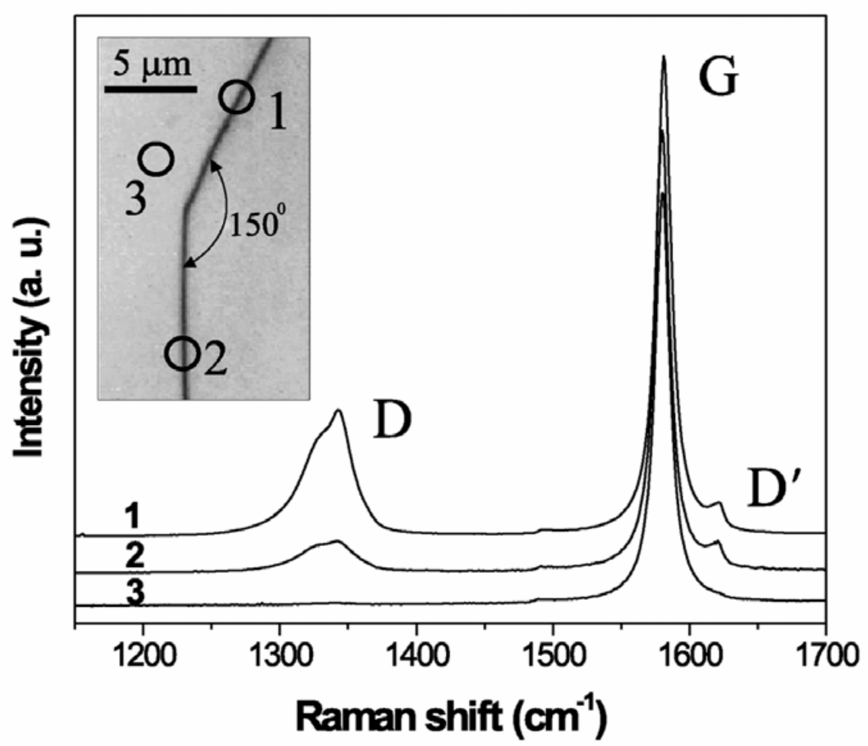
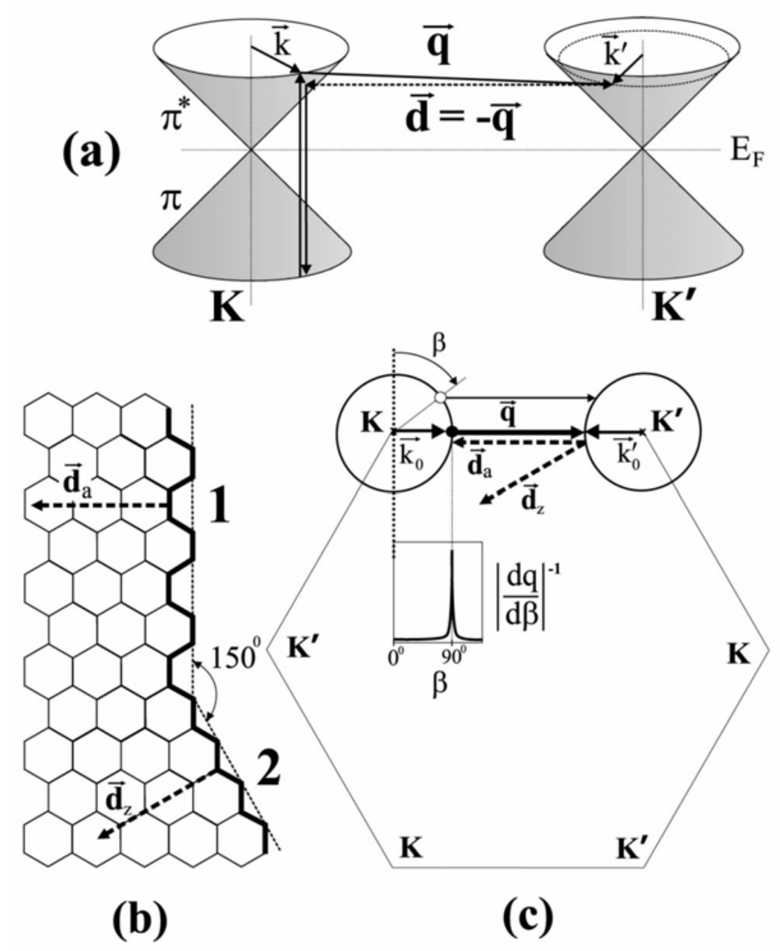
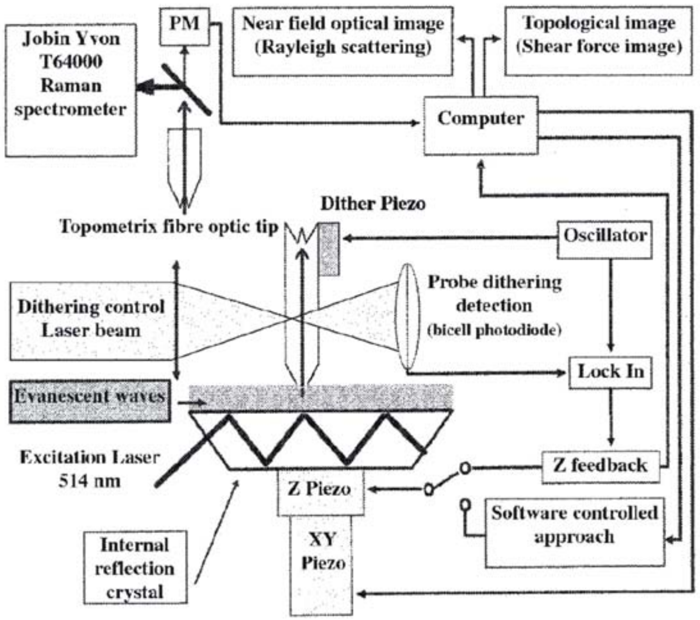


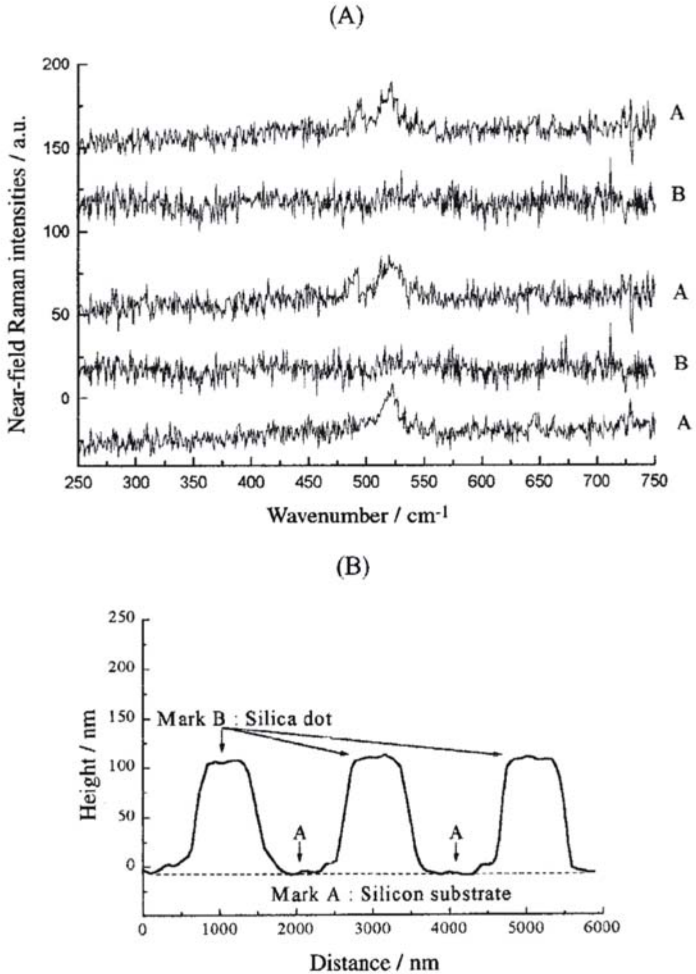


L. G. Cancado et al., *Phys. Rev. Lett.* ***93***, *247401 (2004).*

Near-field Raman spectroscopy

Dr. Juen-Kai Wang, CCMS & IAMS





J. Grausen et al., J. Raman Spectrosc. ***30****, 833 (1999).*

Lycurgus Cup in Roman times

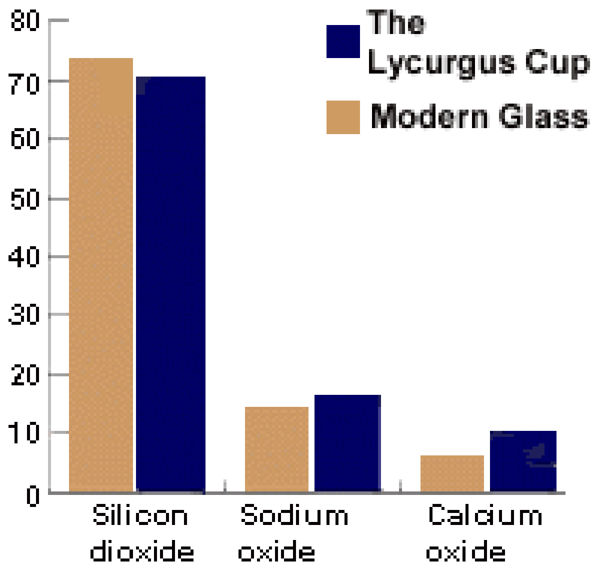
Dr. Juen-Kai Wang, CCMS & IAMS

The glass appears green in daylight (reflected light), but red when the light is transmitted from the inside of the vessel.

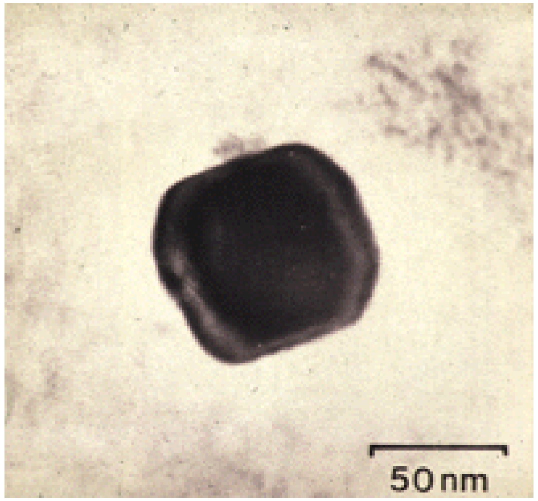
The Lycurgus Cup, Roman (4th century AD), British Museum
*F. E. Wagner et al., Nature **407**, 691 (2000).*

Mysterious red color in Lycurgus Cup

Dr. Juen-Kai Wang, CCMS & IAMS



The same composition as modern glass



X-ray analysis:
70% Ag + 30% Au

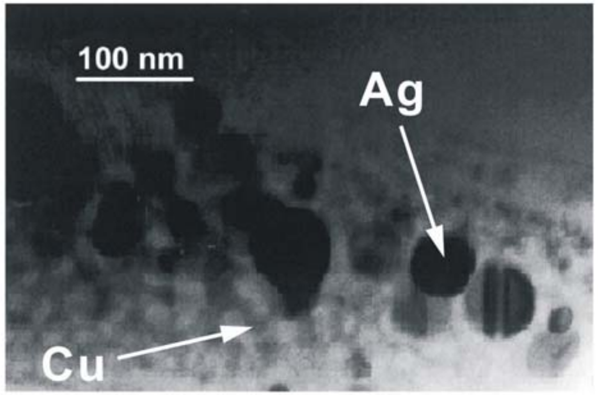
These Ag-Au nanoparticles (~300 ppm) scatter the light, rather in the same way that fine particles in the atmosphere cause a 'red sky at night' effect. They cause the color effects shown by the Cup.

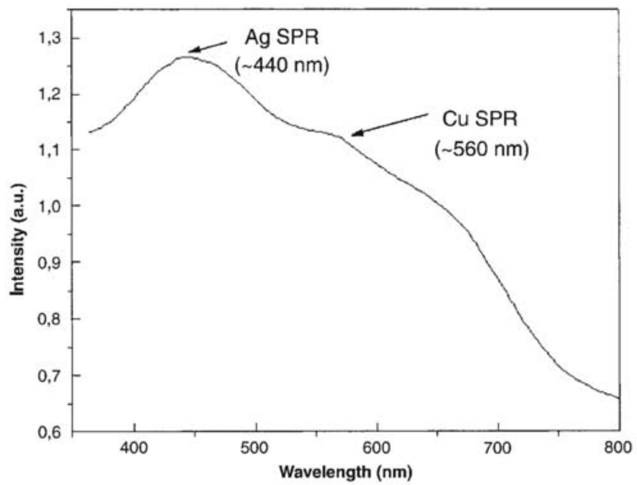
The Lycurgus Cup, Roman (4th century AD), British Museum (www.thebritishmuseum.ac.uk)

Ag and Cu nanoparticles in gold Lustre

Dr. Juen-Kai Wang, CCMS & IAMS

Majolica dish
lustred by Mastro Giorgio Andreoli
(16th century AD)





Museo Civico-Palazzo dei Consoli, Gubbio *(www.comune.gubbio.pg.it/musei/palconsoli2.htm)*
G. Padeletti and P. Fermo, Appl. Phys. A ***76****, 515 (2003).*
S. Padovani et al., J. Appl. Phys. ***93****, 10058 (2003).*

Stained glasses

Dr. Juen-Kai Wang, CCMS & IAMS

Reynard the Fox
early 15-th century, *Holy Cross Church*

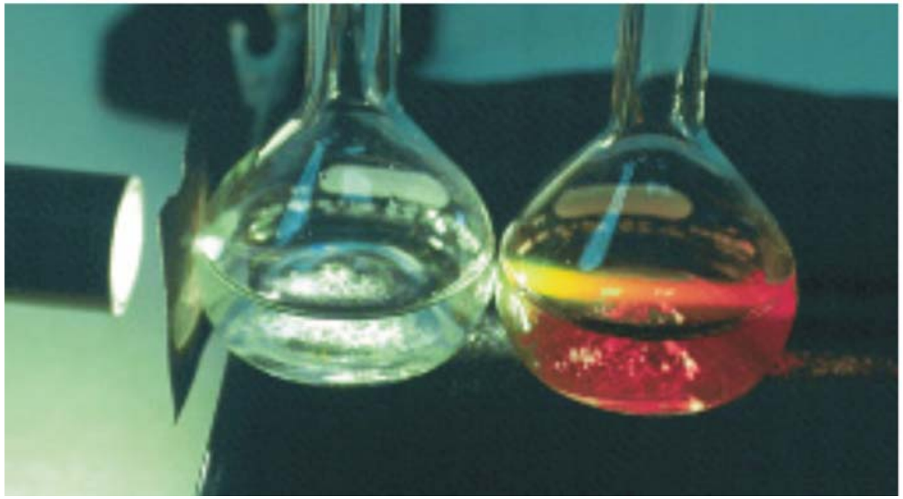
The Ascent of Elijah
c.1863, *Trinity Methodist Church*

The Stained Glass Museum *(www.stainedglassmuseum.org)*

Faraday's works on Au nanoparticles

Dr. Juen-Kai Wang, CCMS & IAMS

Faraday-Tyndall Effect



A solution of gold chloride **Gold colloids**

Faraday's slides
Prepared in 1856, in conjunction with Faraday's research on finely-divided gold
(The Royal Institution of Great Britain)

*M. Faraday, Philos. Trans. R. Soc. London **147**, 145 (1857).*
R. D. Tweney, Department of Psychology, Bowling Green State University, USA (personal.bgsu.edu/_tweney)

Scattering by a metal sphere

Dr. Juen-Kai Wang, CCMS & IAMS

Induced dipole by the applied field

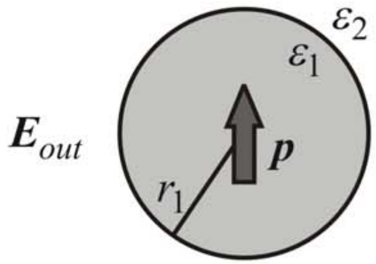
$$\boldsymbol{E}_{out} = E_0\boldsymbol{e}_z + \boxed{\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}\frac{r_1^3}{r^3}E_0\left(2\cos\theta\,\boldsymbol{e}_r+\sin\boldsymbol{e}_\theta\right)}$$

$$\Downarrow$$

$$\boldsymbol{p} = \varepsilon_2\alpha E_0$$

$$\boxed{\alpha = 4\pi r_1^3\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}}$$

Effective dipole inside the sphere



Near-field radiation power from $\boldsymbol{p}(t)$ (near-field scattering cross section)

$$C_{sca}(r) = \int_0^{2\pi}d\theta\int_0^{\pi}d\phi\left|\boldsymbol{E}\right|^2 r^2\sin\theta = \frac{\alpha^2}{6\pi}\left(\frac{3}{r^4}+\frac{k^2}{r^2}+k^4\right)$$

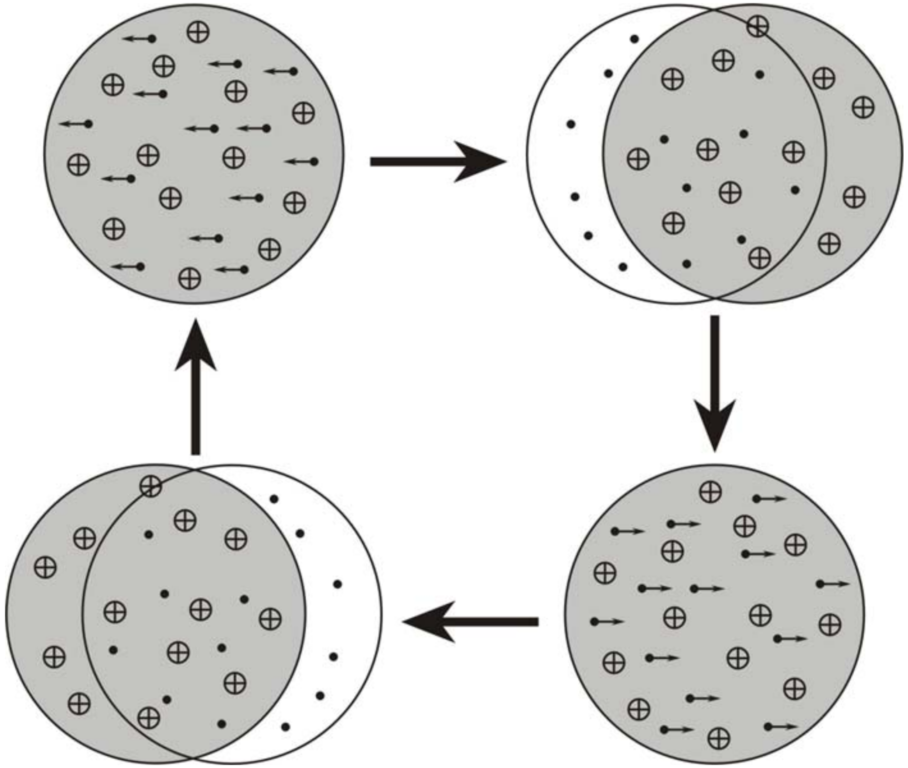
$\boldsymbol{E}$: the near-field electric field by $\boldsymbol{p}(t)$

$$\boxed{C_{sca}^{NF} = C_{sca}(r) = \frac{\alpha^2}{6\pi}\left(\frac{3}{r_1^4}+\frac{k^2}{r_1^2}+k^4\right)}$$

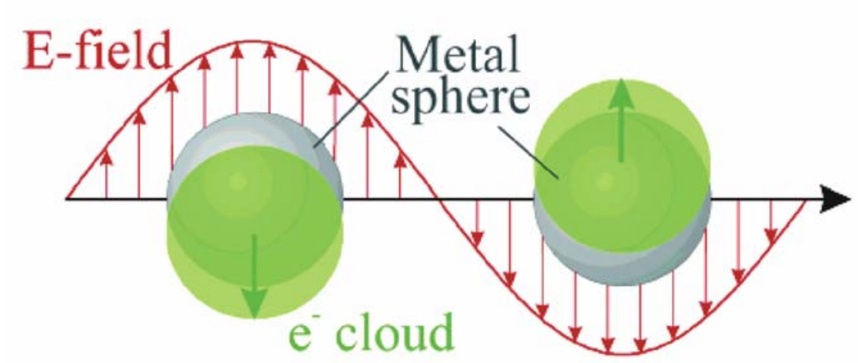
*G. Mie, Ann. Phys. (N.Y.) **25**, 377 (1908).*

Electron collective motion in metal clusters

Dr. Juen-Kai Wang, CCMS & IAMS



Coherent oscillatory motion

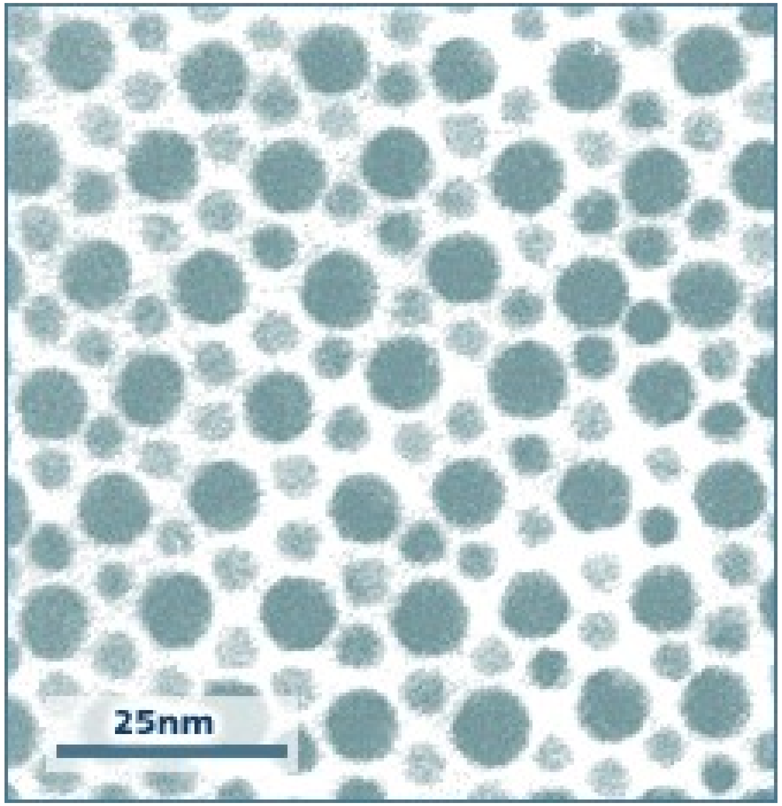


Resonant excitation

Au nanospheres

Dr. Juen-Kai Wang, CCMS & IAMS

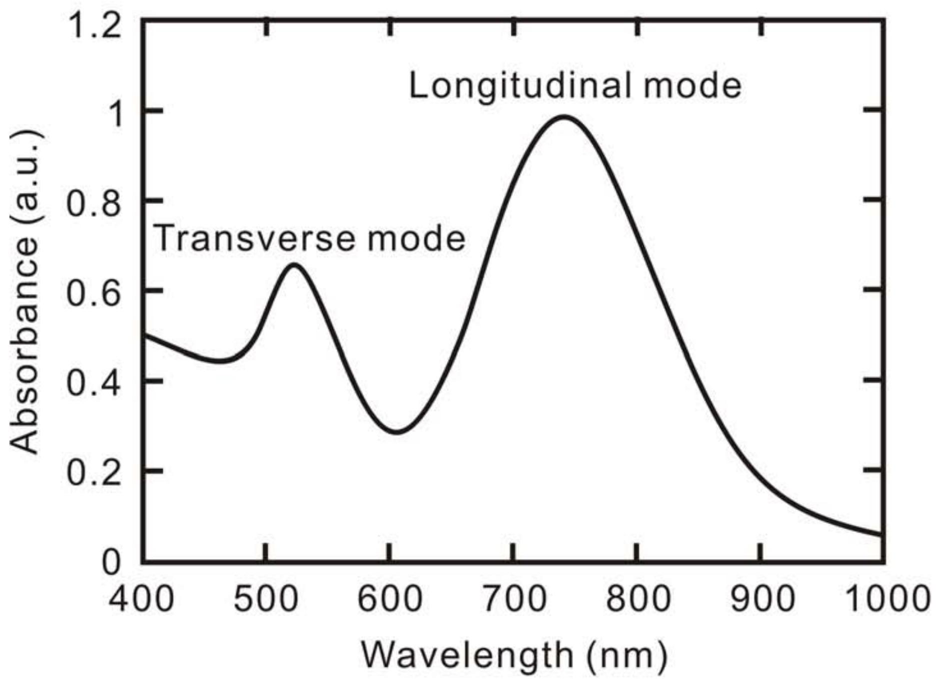
1.4 nm **6 nm** **agglomerated**

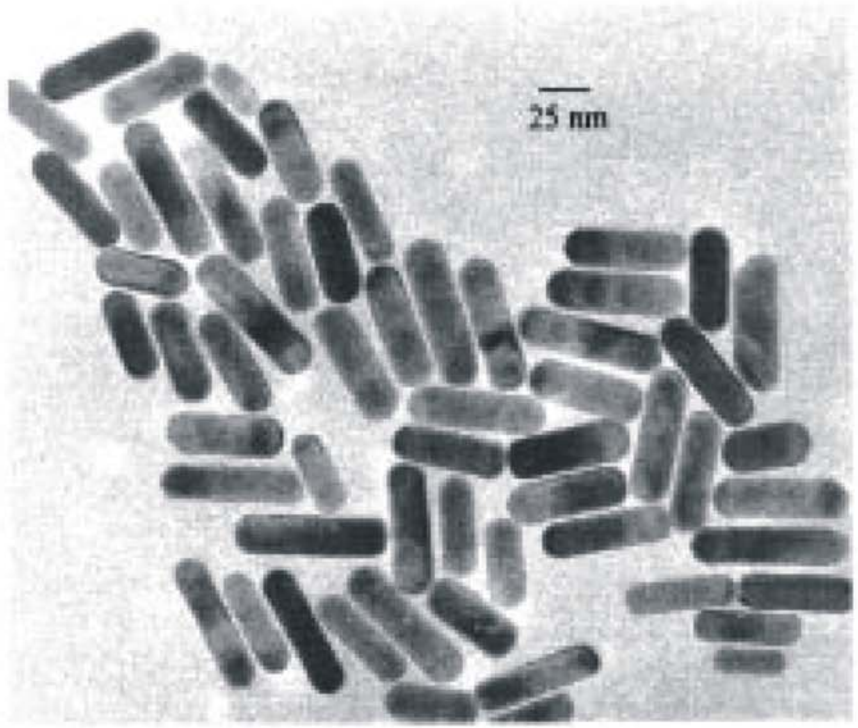


*C. J. Kiely, J. Fink, M. Brust, D. Bethell and D. J. Schiffrin, Nature **444**, 396 (1998)*

Au nanorods

Dr. Juen-Kai Wang, CCMS & IAMS

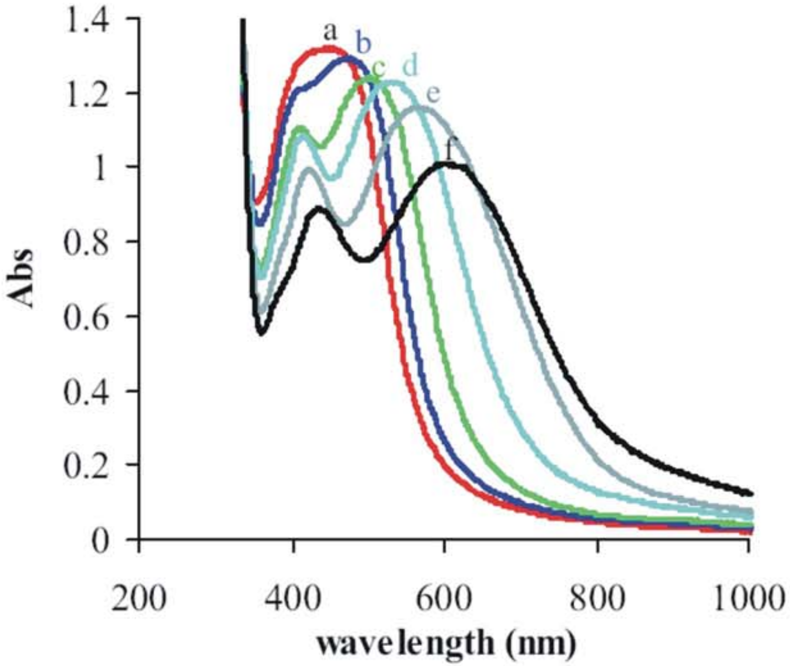




S. Link, M. B. Mohamed and M. A. El-Sayed, J. Phys. Chem. B ***103****, 3073 (1999).*

Ag nanorods

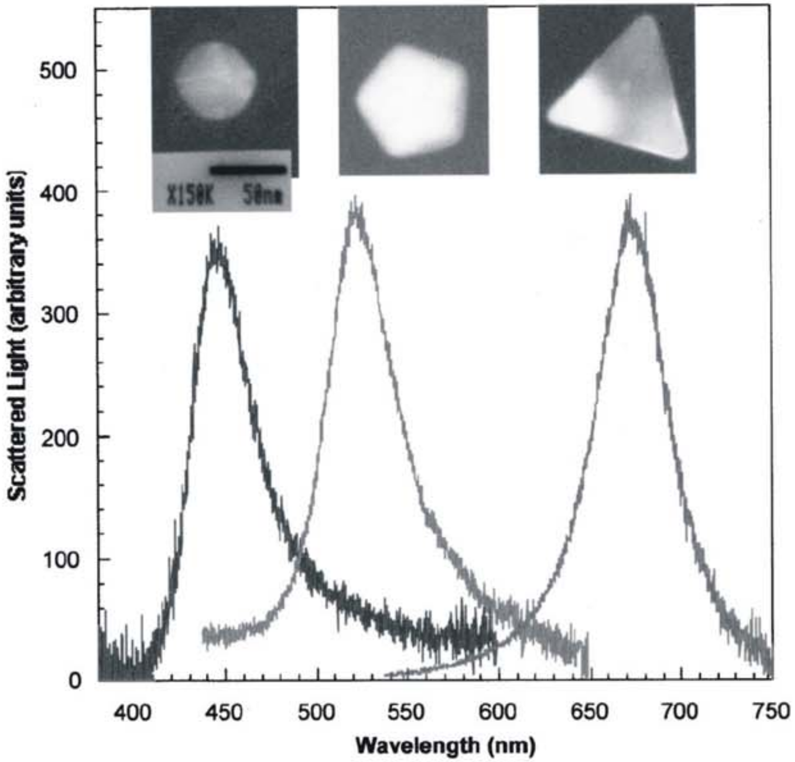
Dr. Juen-Kai Wang, CCMS & IAMS

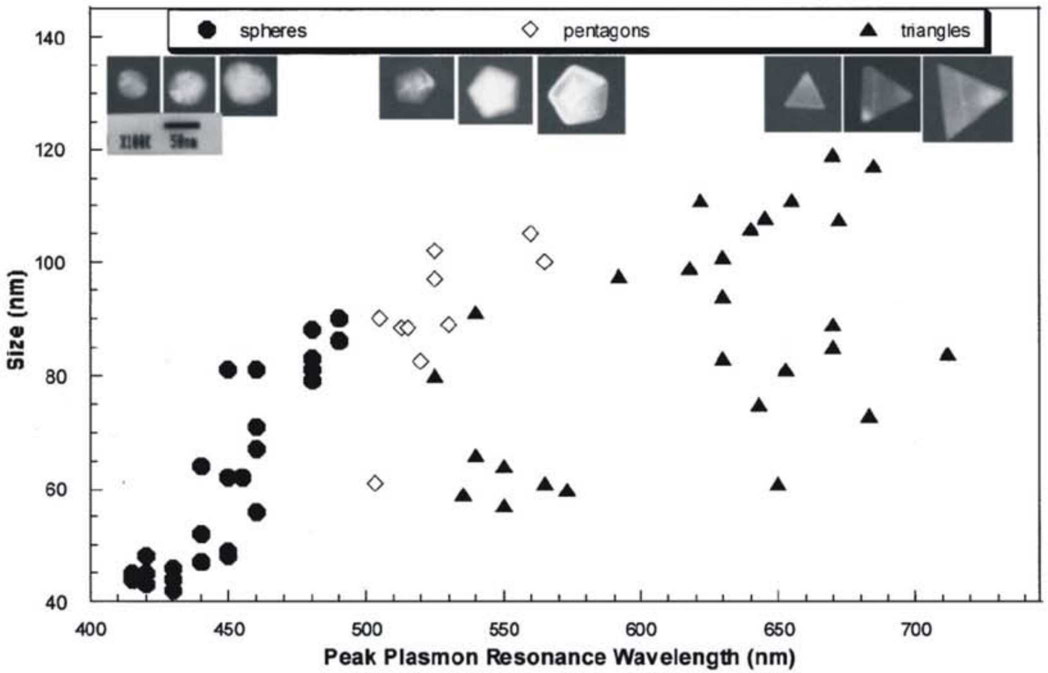


C. J. Murphy and N. R. Jana, *Adv. Mater.* **14**, 80 (2002)

Shape-dependent plasmons

Dr. Juen-Kai Wang, CCMS & IAMS

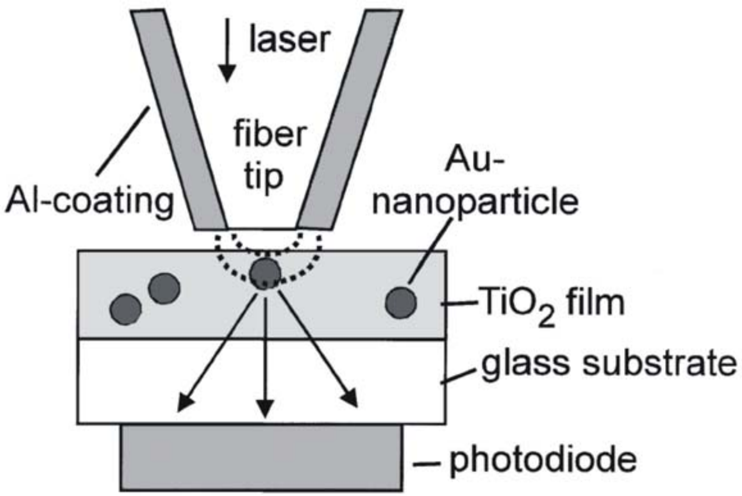


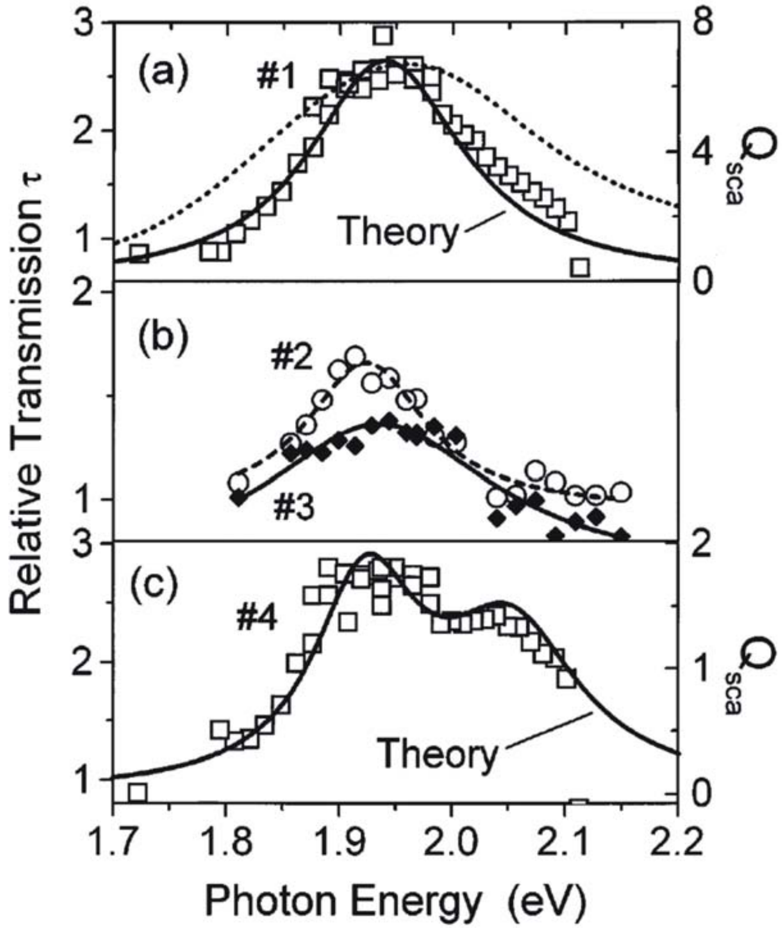


J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz, J. Chem. Phys. ***116****, 6755 (2002).*

SPR in single metallic nanoparticles

Dr. Juen-Kai Wang, CCMS & IAMS

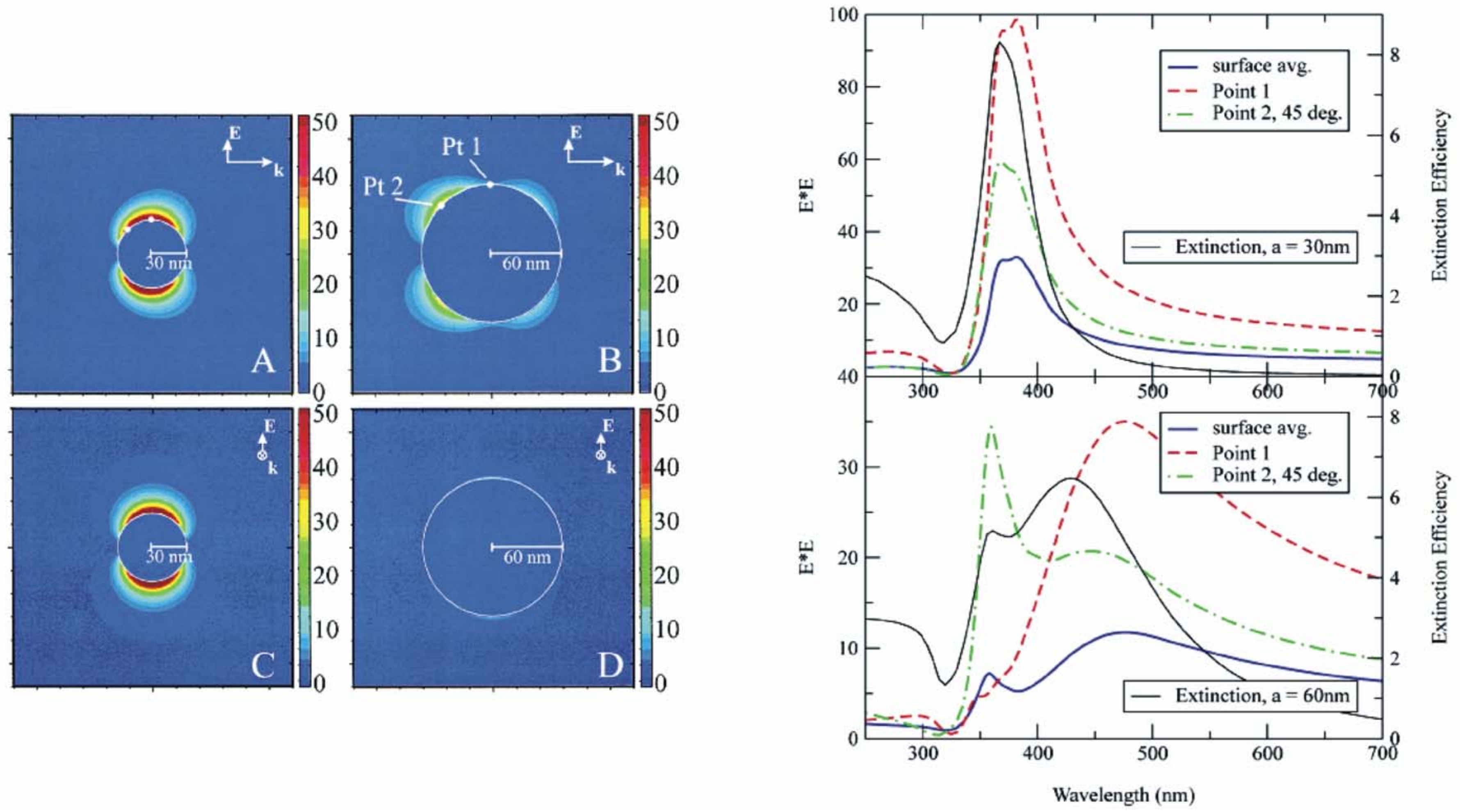




T. Klar, M. Perner, S. Grosse, G. von Plessen, W. Spirkl and J. Feldman, Phys. Rev. Lett. ***80****, 4249 (1998).*

Simulations of Ag nanoparticles

Dr. Juen-Kai Wang, CCMS & IAMS

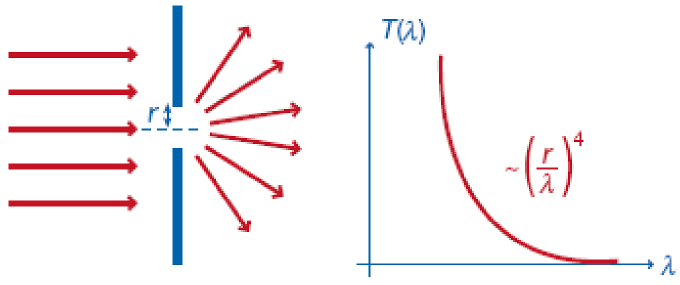


K. Lance Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, J. Phys. Chem. B ***107****, 668 (2003).*

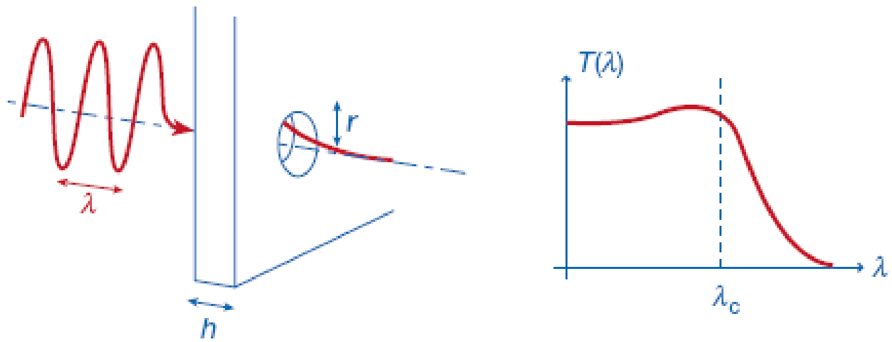
Spectroscopy of single holes

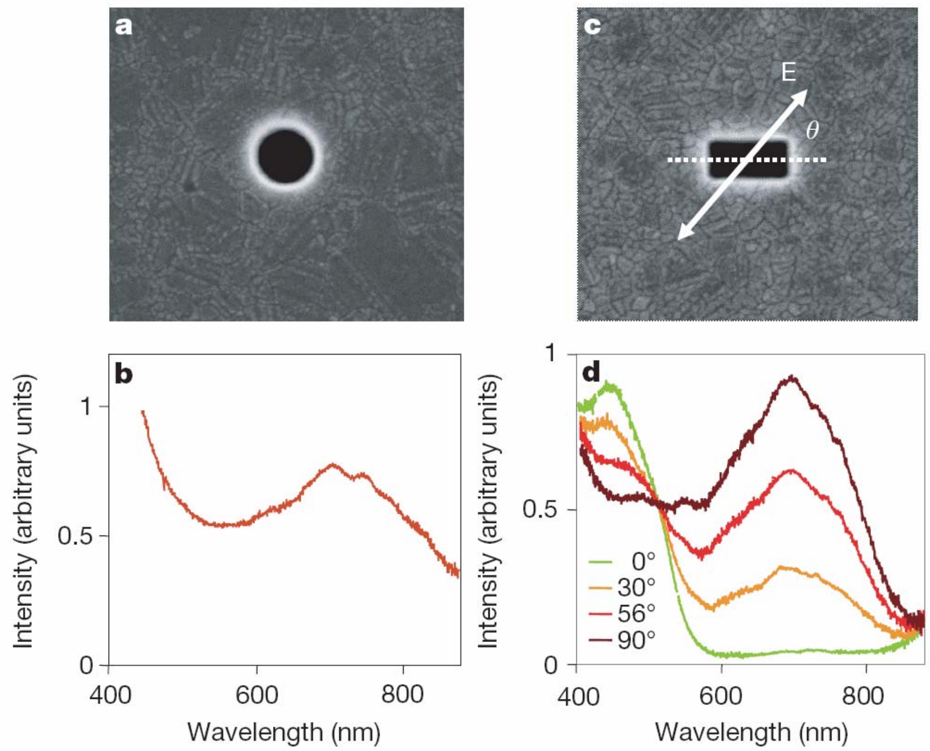
Dr. Juen-Kai Wang, CCMS & IAMS

Bethe's theory



Light through a cylindrical waveguide

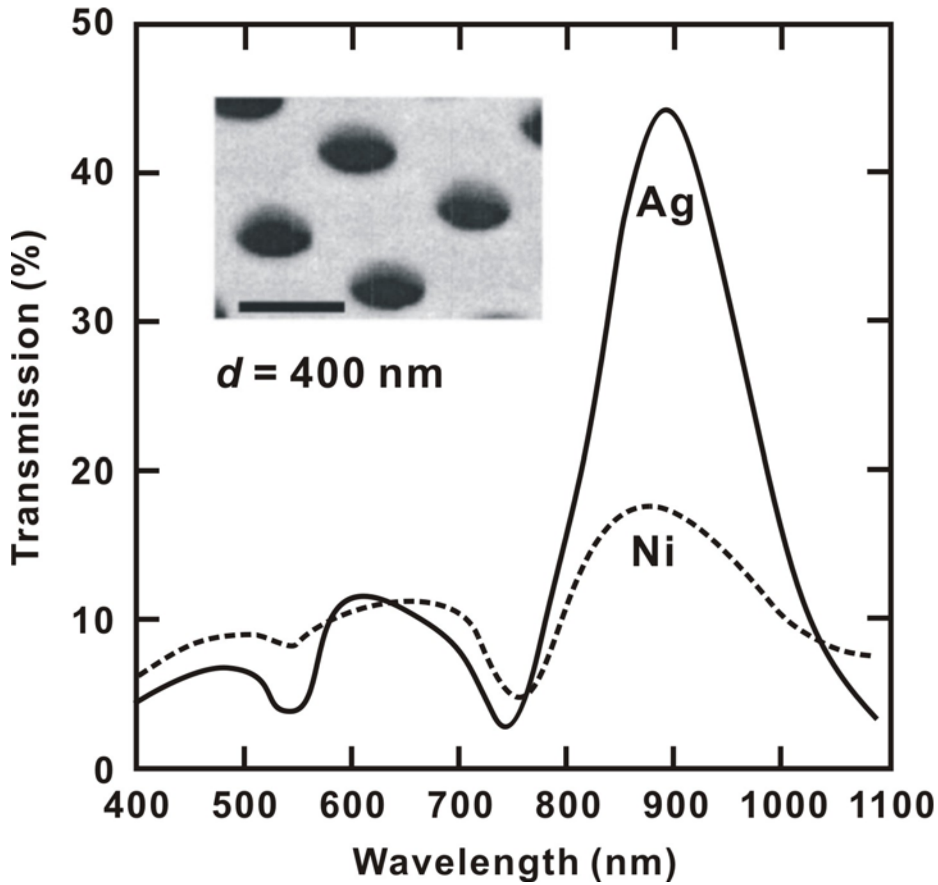




T. W. Ebbesen, Nature ***445****, 39 (2007)*

Subwavelength hole array

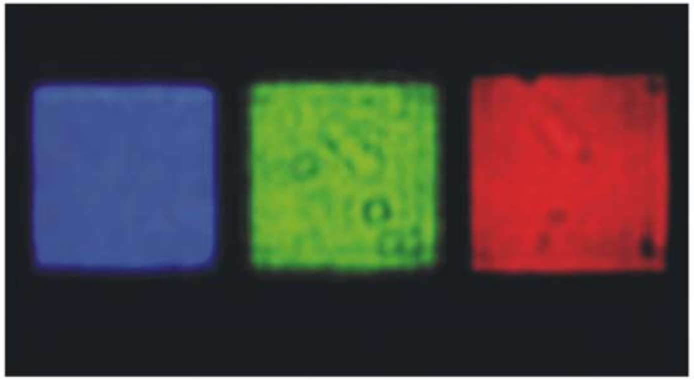
Dr. Juen-Kai Wang, CCMS & IAMS

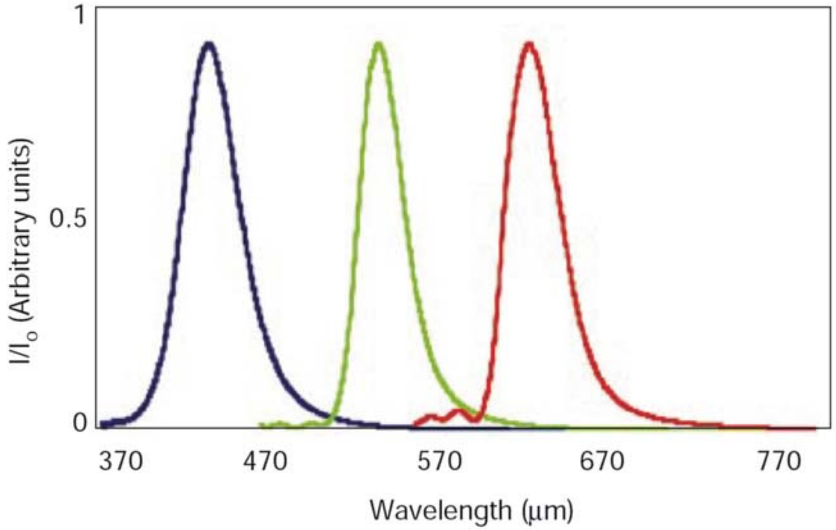


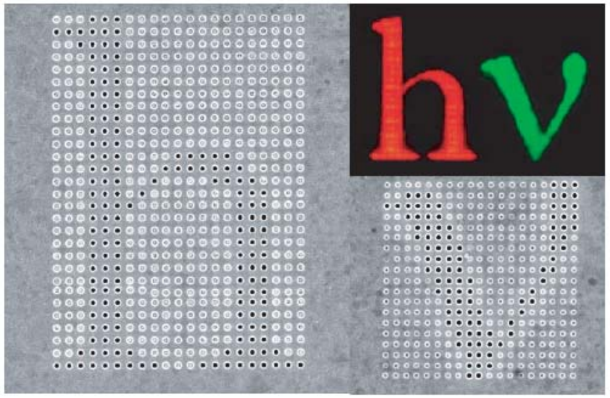
D. E. Grupp et al., Appl. Phys. Lett. ***77****, 1569 (2000)*
L. Martin-Moreno et al., Phys. Rev. Lett. ***86****, 1114 (2001).*

Spectroscopy of nanohole patterns

Dr. Juen-Kai Wang, CCMS & IAMS





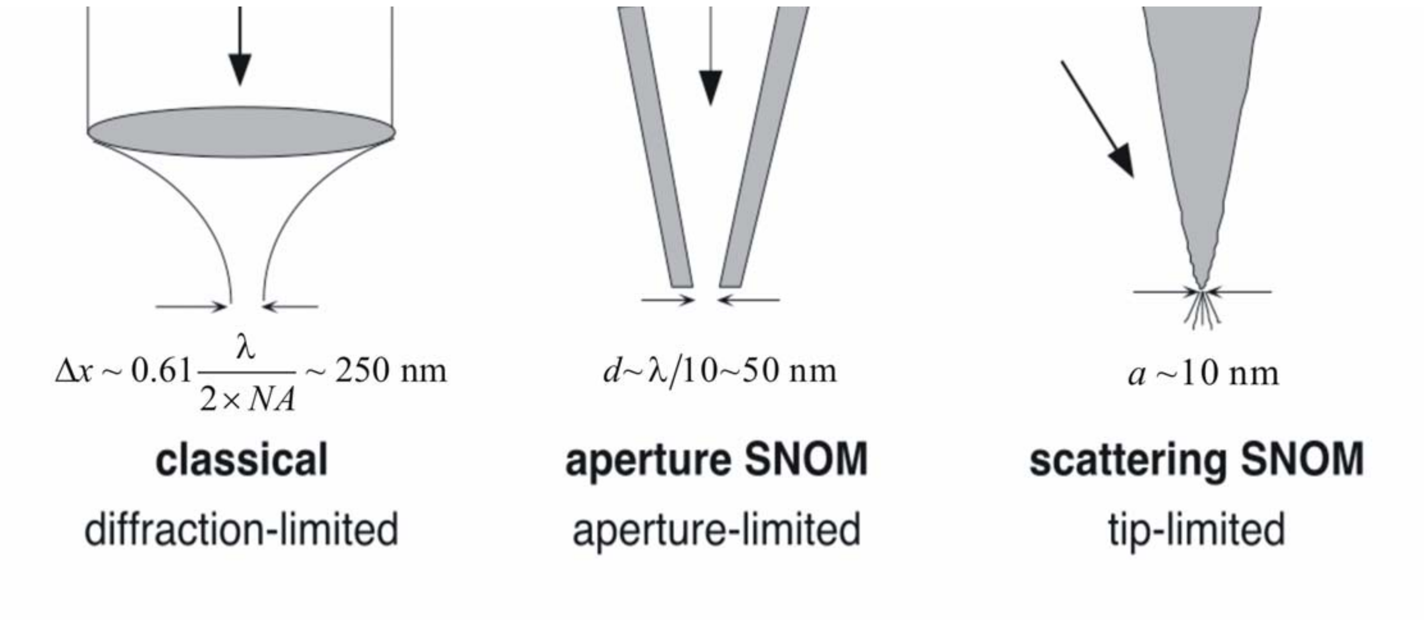


W. L. Bames, A. Dereux, and T. W. Ebbesen, Nature ***424****, 824 (2003); T. W. Ebbesen, Nature* ***445****, 39 (2007)*

Comparison of optical microscopes

Dr. Juen-Kai Wang, CCMS & IAMS

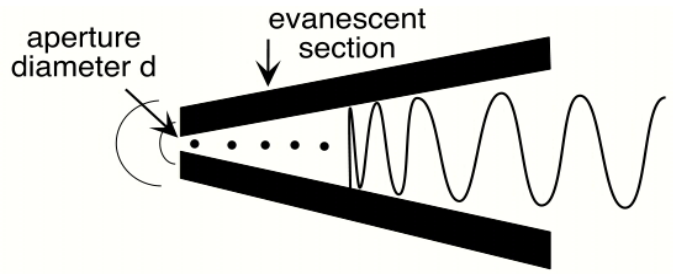
- Performing optical spectroscopy in nanometer scales is one of the critical steps in the development of nanoscience and nanotechnology.
- Taking advantage of localized enhanced field generated by plasmon, optical signal generated in nanometer scale can be observed macroscopically.
- New physics involving light-matter interaction in nanometer scales need to be developed.

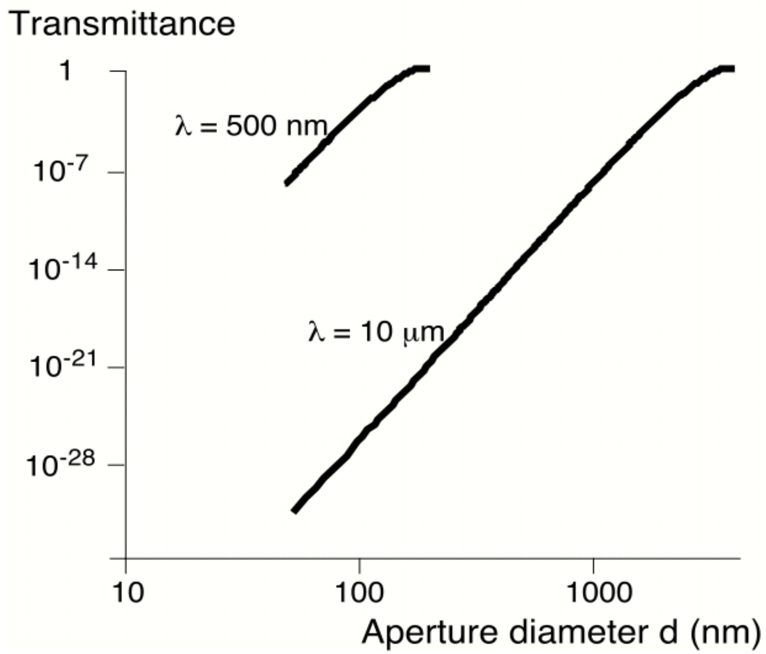


Limits of aperture-type SNOM

Dr. Juen-Kai Wang, CCMS & IAMS

- **Low optical throughput**
- **Spatial resolution: >50 nm**
- **Wavelength dependent throughput**



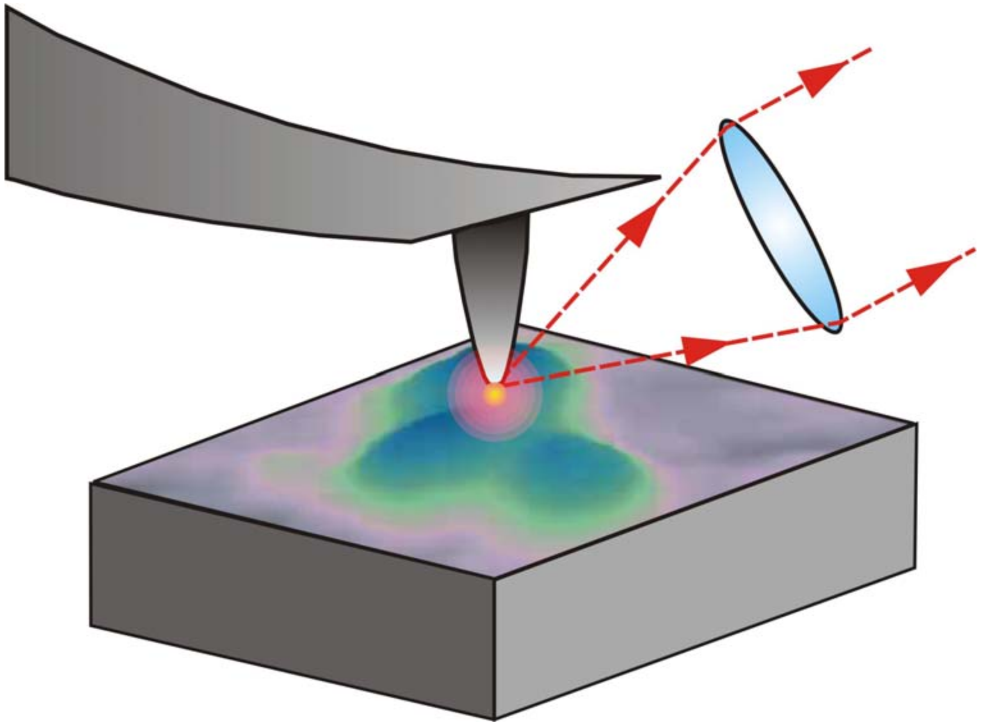


Reproduced from Dr. Keilmann

Tip-enhanced optical spectroscopy

Dr. Juen-Kai Wang, CCMS & IAMS

- **Scattering-SNOM**
  - collecting elastic scattering signal
- **Tip-enhanced spectroscopy**
  - collecting inelastic scattering signal (Raman or fluorescence)

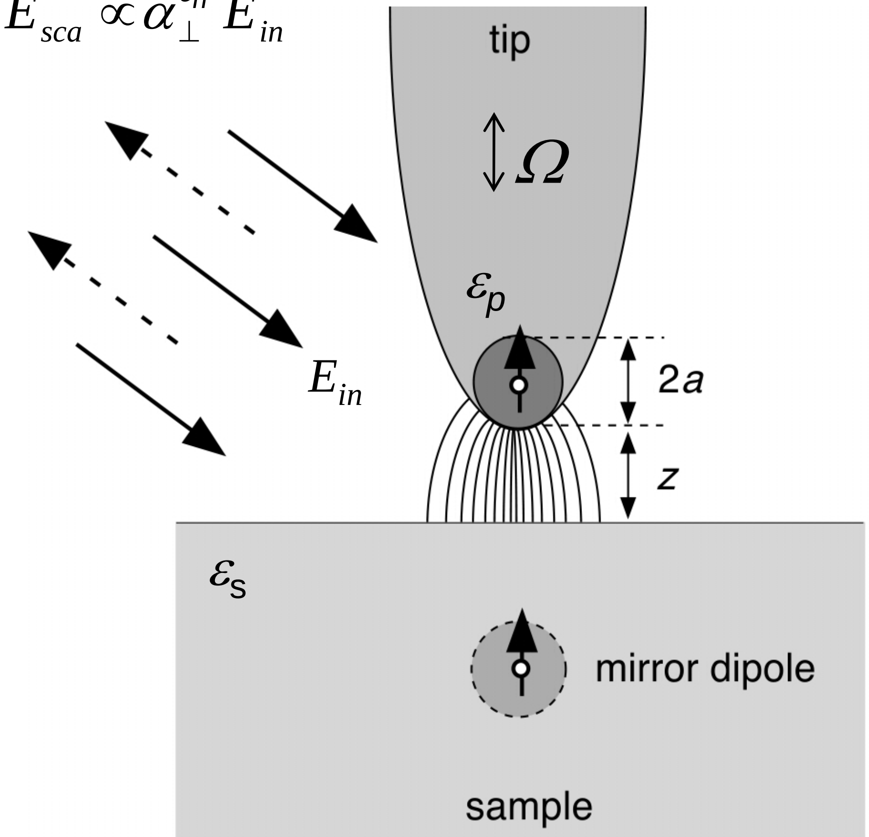


Model of tip-sample near-field interaction

Dr. Juen-Kai Wang, CCMS & IAMS

Far-field scattering:

$$E_{sca} \propto \alpha_{\perp}^{eff} E_{in}$$



Polarizability of the tip: $\alpha = 4\pi a^3 \dfrac{(\varepsilon_p - 1)}{(\varepsilon_p + 2)}$

Effective polarizability of tip and sample:

$$\alpha_{\perp}^{eff} = \frac{\alpha(1+\beta)}{1 - \dfrac{\alpha\beta}{16\pi(z+a)^3}}$$

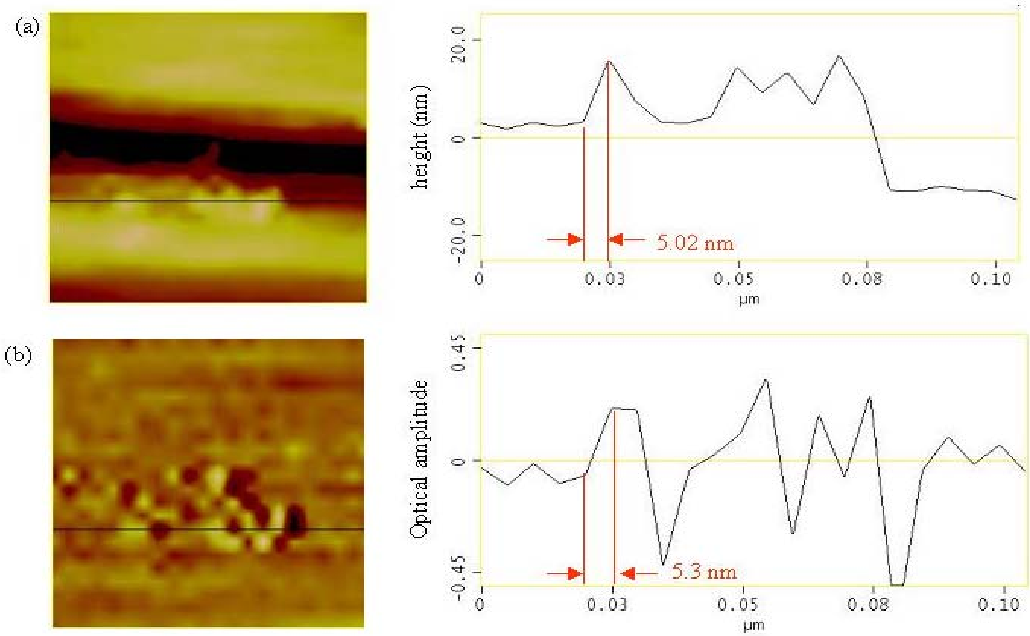
$$\beta = \frac{1-\varepsilon_s}{1+\varepsilon_s}$$

Reproduced from Dr. Keilmann

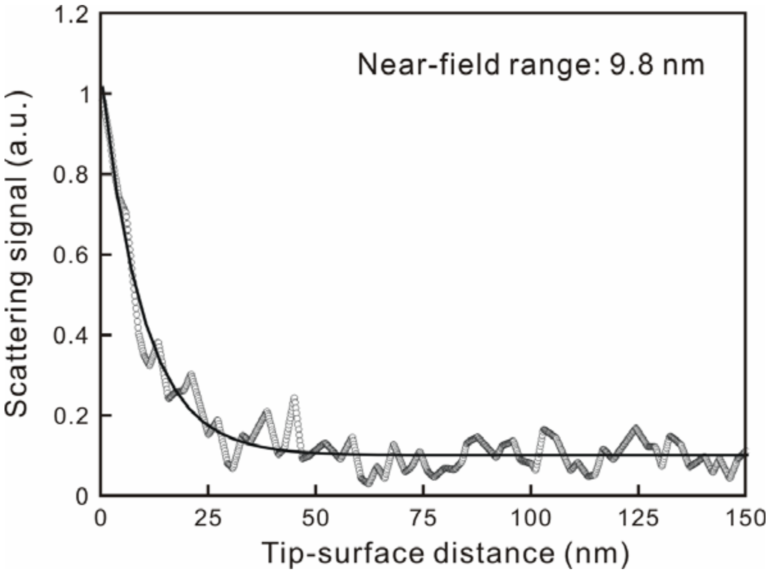
Spatial resolution

Dr. Juen-Kai Wang, CCMS & IAMS

AFM image



s-SNOM image



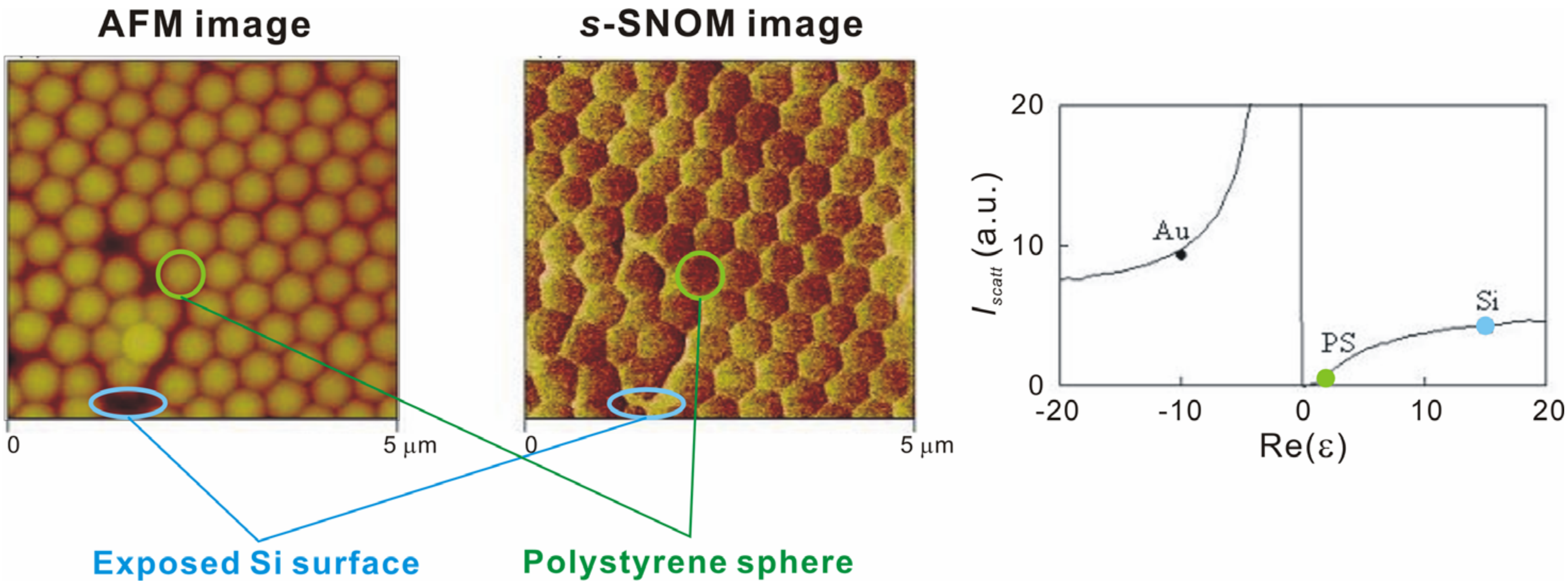
Lateral resolution: 5 nm

Vertical resolution: 10 nm

Material contrast

Dr. Juen-Kai Wang, CCMS & IAMS

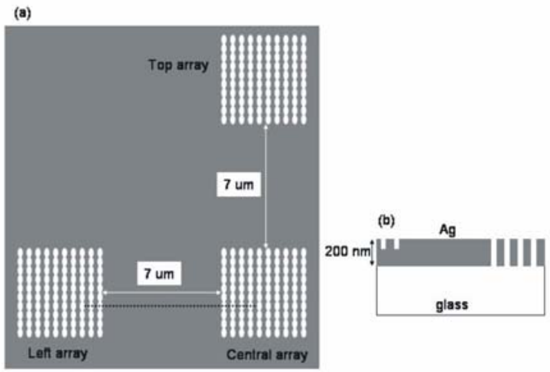
Polystyrene sphere on Si(111)



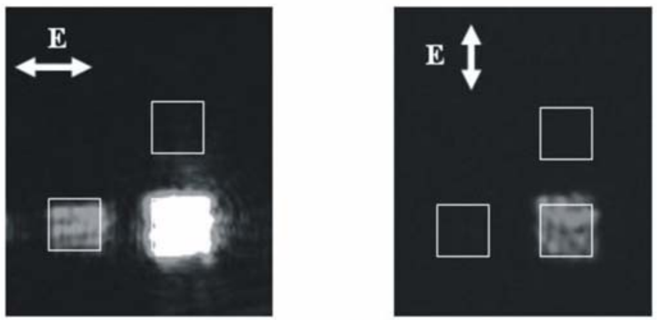
- **Detection limit of Δn: 0.02**

Near-field observation of ellipical hole arrays

Dr. Juen-Kai Wang. CCMS & IAMS



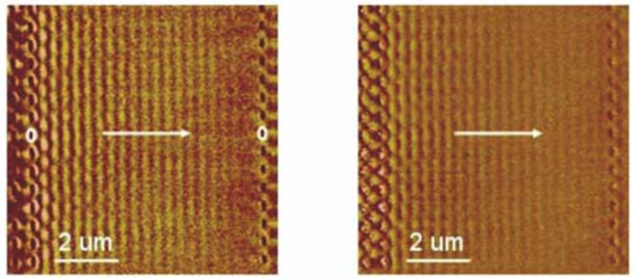
Far-field transmission images



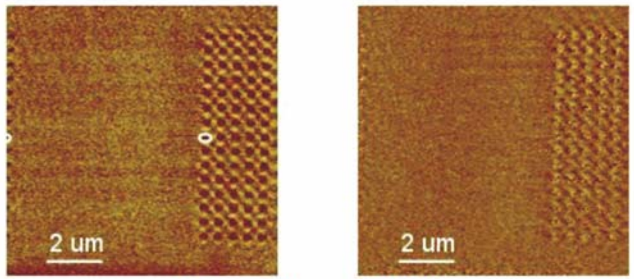
TM-mode excitation TE-mode excitation

Near-field images

I ϕ



TM-mode excitation

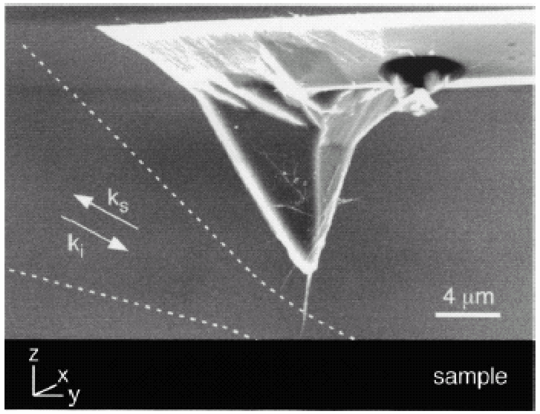


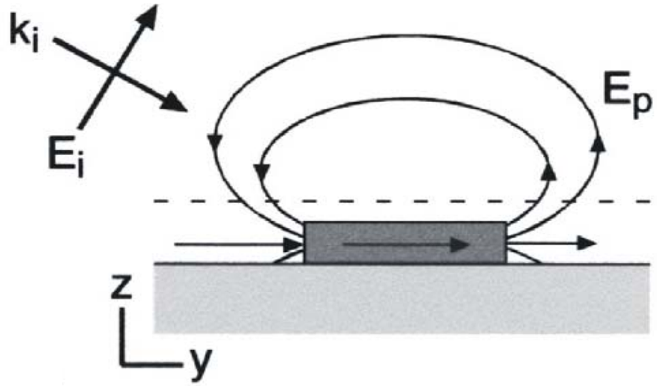
TE-mode excitation

- A TM-mode excitation gives an enhanced transmission image and also produces an emission image at an adjacent pattern.
- Clear surface plasmon only exits in TM-mode excitation and prominent dipole field oscillation emerges at each elliptical hole. This confirms that the surface plasmon is the superposition of local plasmon of holes.

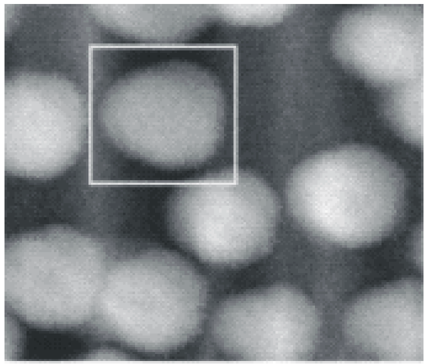
Apertureless SNOM with single CNT

Dr. Juen-Kai Wang, CCMS & IAMS

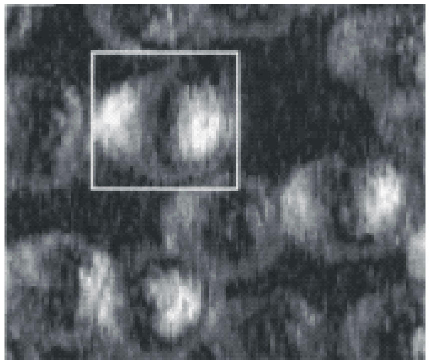




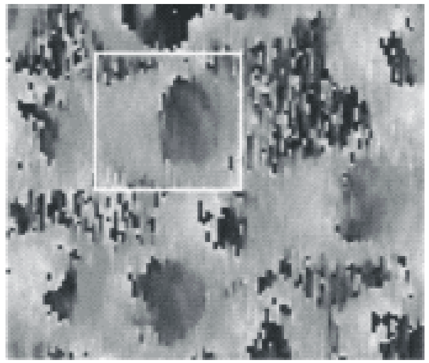
AFM image



Amplitude image



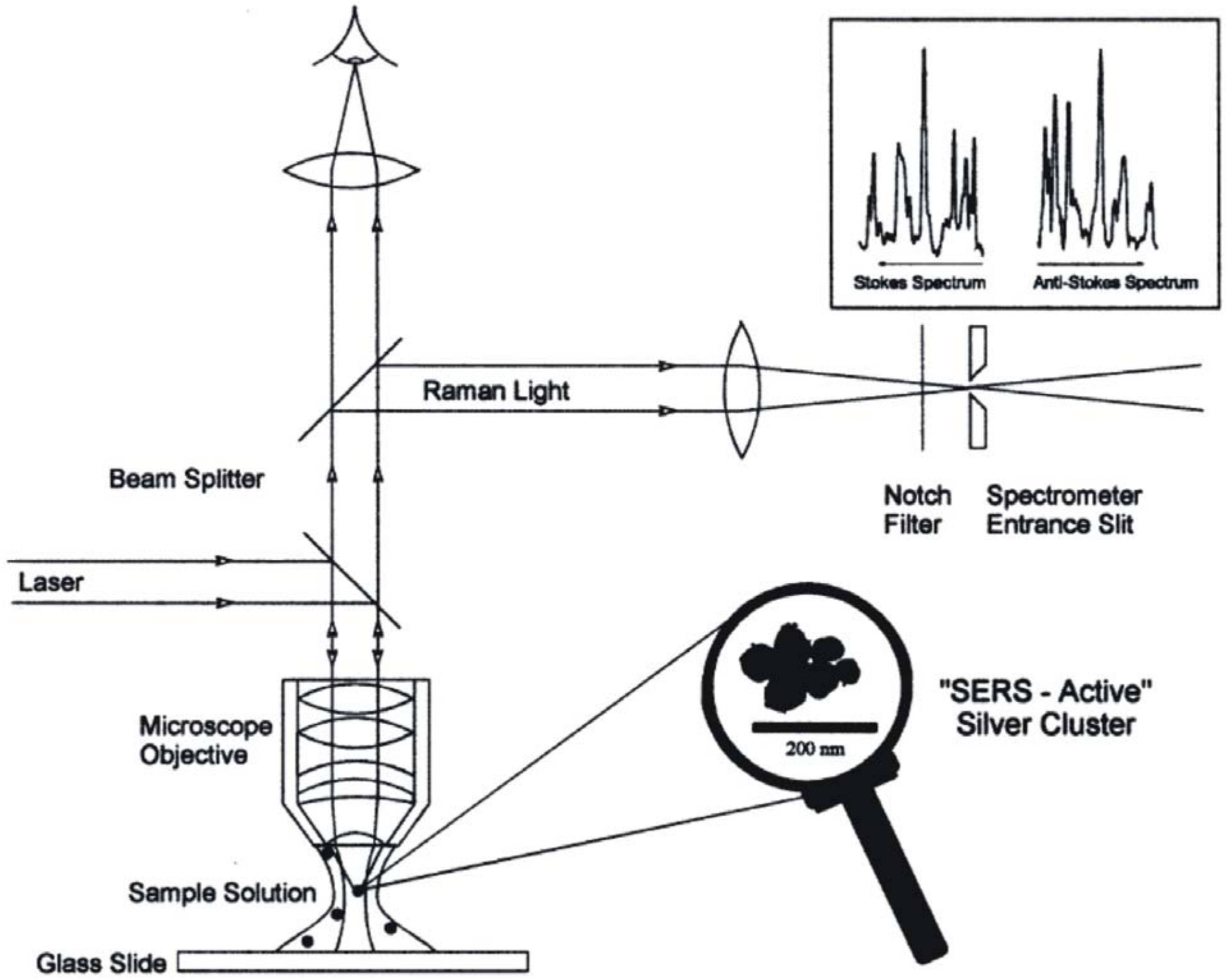
Phase image



R. Hillenbrand et al., Appl. Phys. Lett. ***83****, 368 (2003).*

SERS setup

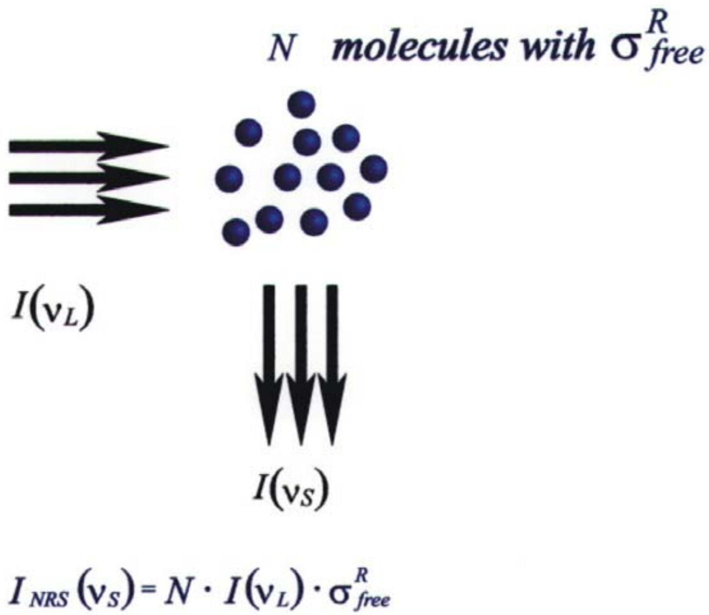
Dr. Juen-Kai Wang, CCMS & IAMS



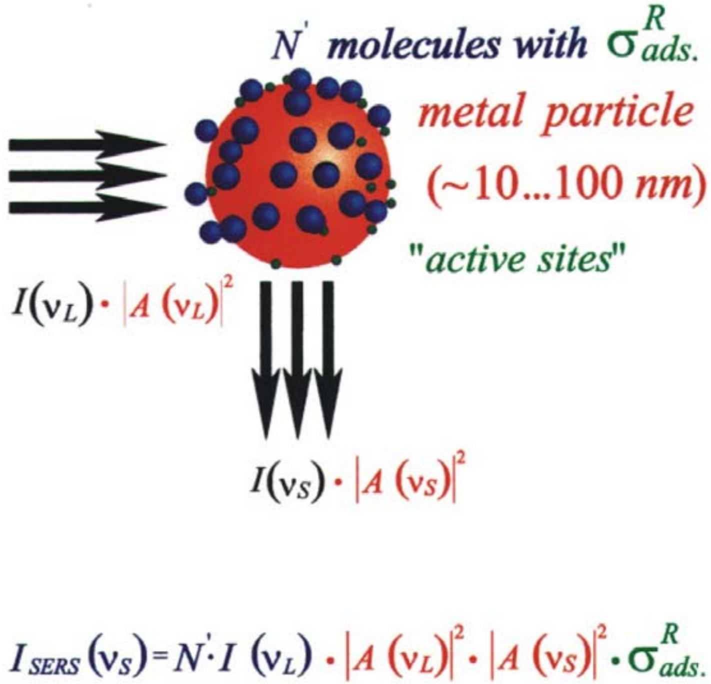
K. Kneipp et al., *Bioimaging* ***6***, *104 (1998).*

Comparison between Raman and SERS

Dr. Juen-Kai Wang, CCMS & IAMS



Unenhanced Raman scattering



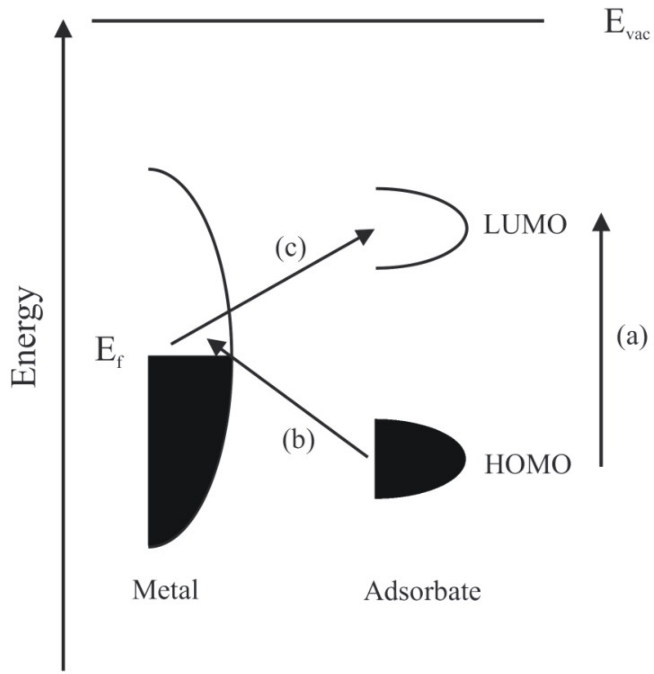
SERS

K. Kneipp et al., *Bioimaging* **6**, 104 (1998).

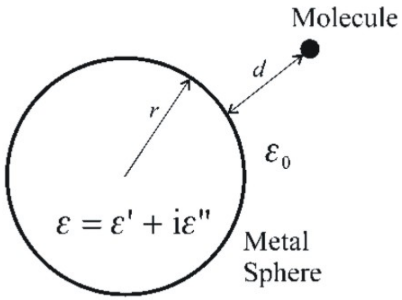
Chemical and EM field enhancement

Dr. Juen-Kai Wang, CCMS & IAMS

Chemical enhancement



Electromagnetic field enhancement



$$E_M = E_0 + E_{sp}$$

E_{sp}: field of a point dipole in the center of the sphere

$$\frac{r}{\lambda} \leq 0.05$$

$$E_{sp} = r^3 \frac{\varepsilon - \varepsilon_0}{\varepsilon + 2\varepsilon_0} E_0 \frac{1}{(r+d)^3}$$

$$A(\nu) = \frac{E_M(\nu)}{E_0(\nu)}$$

$$G_{em}(\nu_s) = \left| A(\nu_L) \right|^2 \bullet \left| A(\nu_S) \right|^2$$

$$G_{em}(\nu_S) \sim \left| \frac{\varepsilon(\nu_L) - \varepsilon_0}{\varepsilon(\nu_L) + 2\varepsilon_0} \right|^2 \bullet \left| \frac{\varepsilon(\nu_S) - \varepsilon_0}{\varepsilon(\nu_S) + 2\varepsilon_0} \right|^2 \bullet \left(\frac{r}{r+d} \right)^{12}$$

SERS of living cells with Au nanoparticles-II

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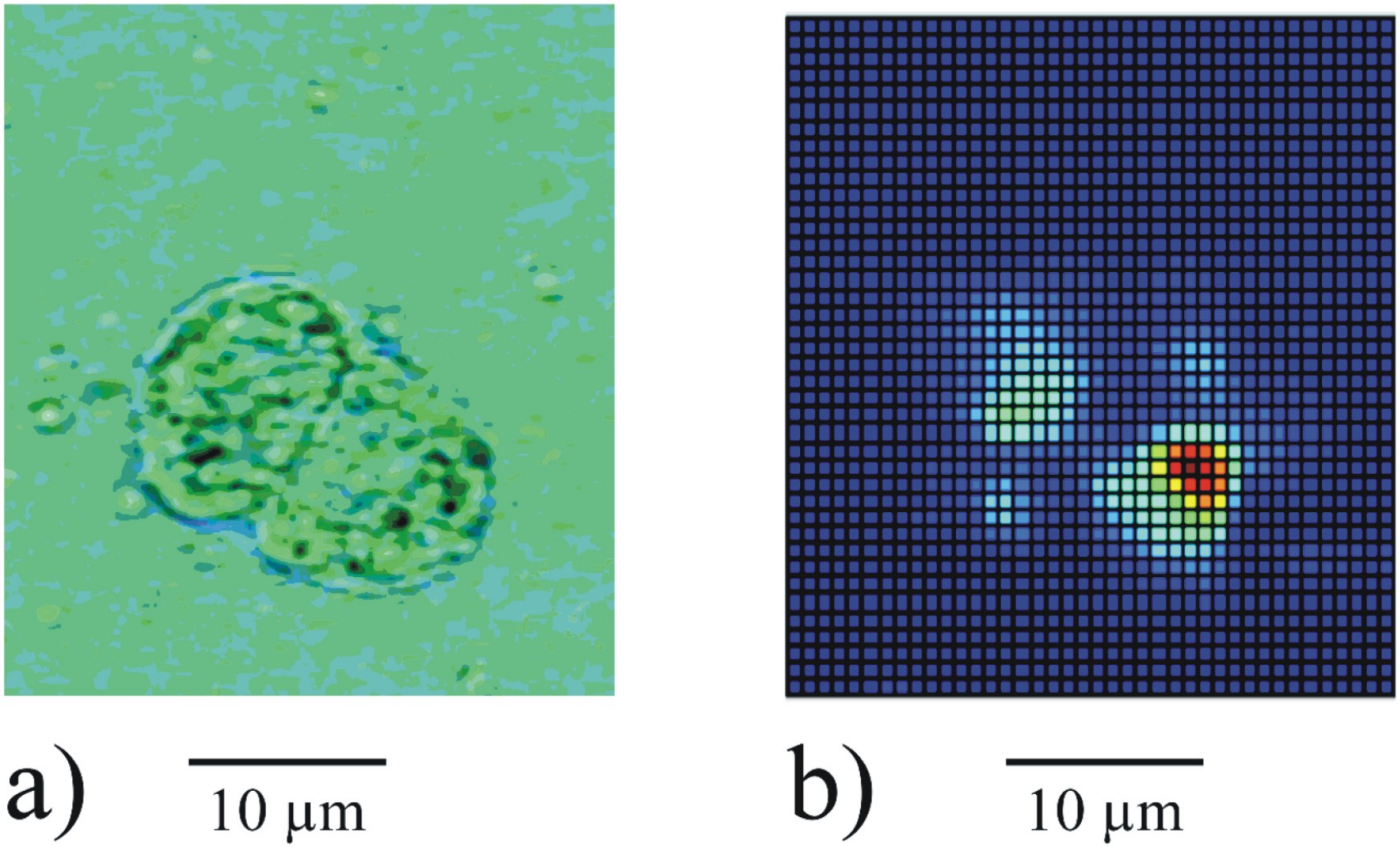

K. Kneipp et al., *Appl. Spectrosc.* **56**, 150 (2002).

Single-molecule Raman spectroscopy (SMRS)

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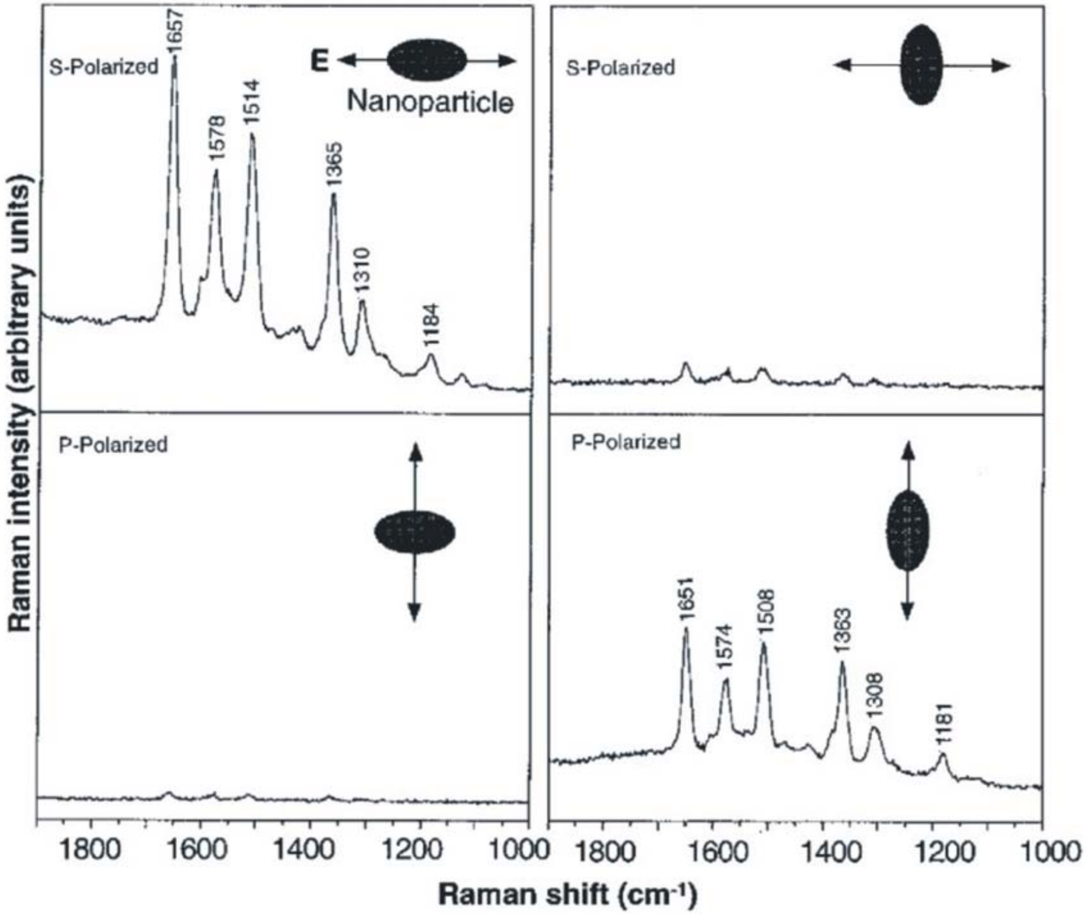
Polarized single molecule Raman spectra of dye-to-colloidal particles



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Plasmon-enhanced Raman detection of DNA and RNA

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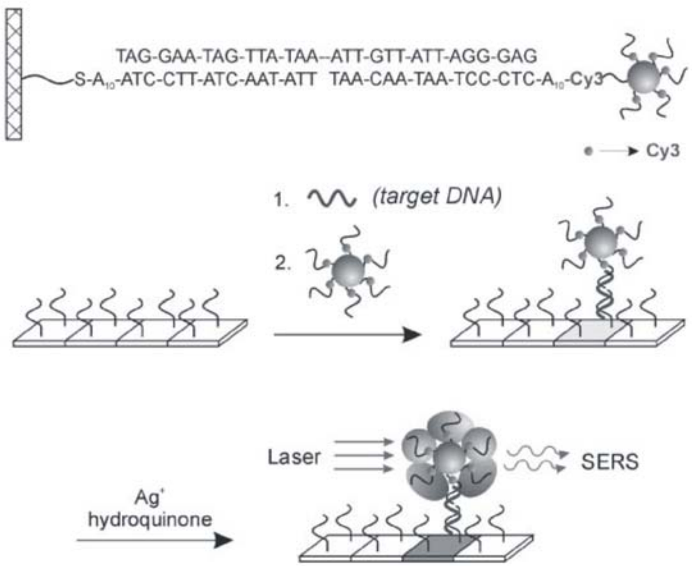

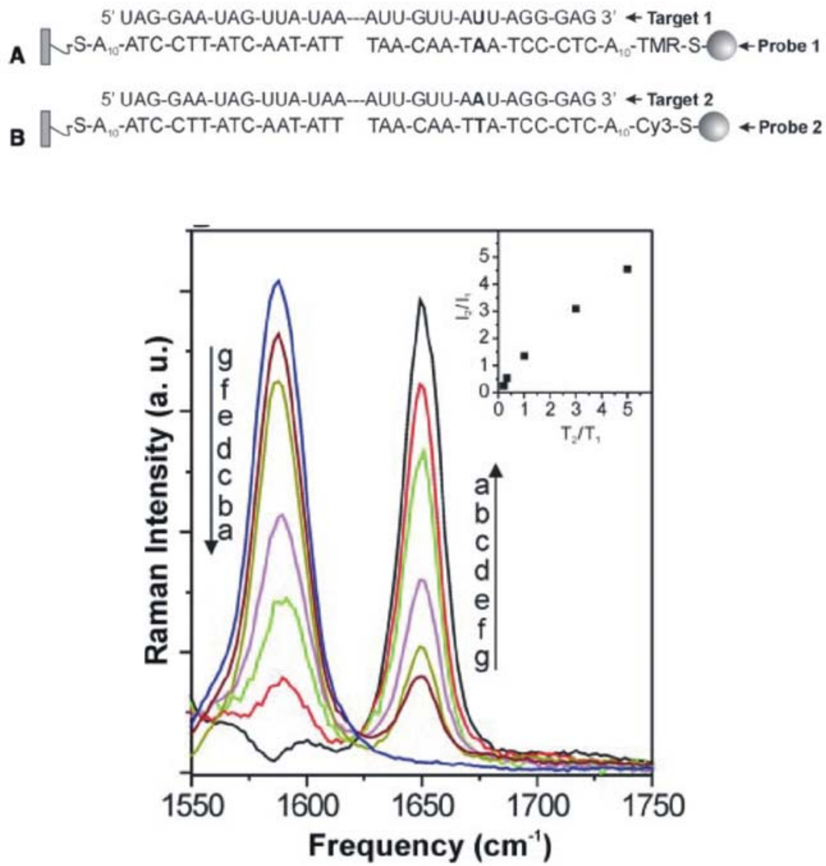

*Y. C. Cao, R. Jin and C. A. Mirkin, Science **297**, 1536 (2002).*

Near-field fluorescence spectroscopy

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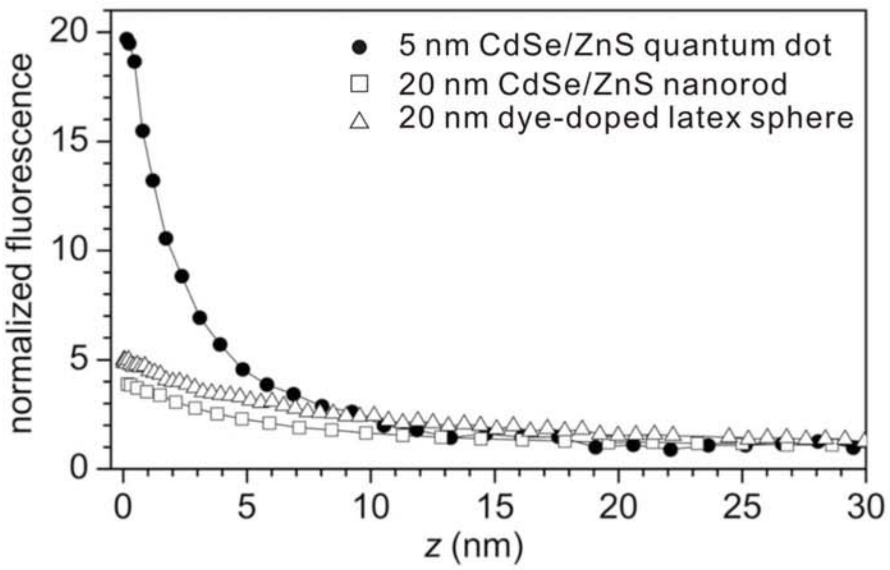
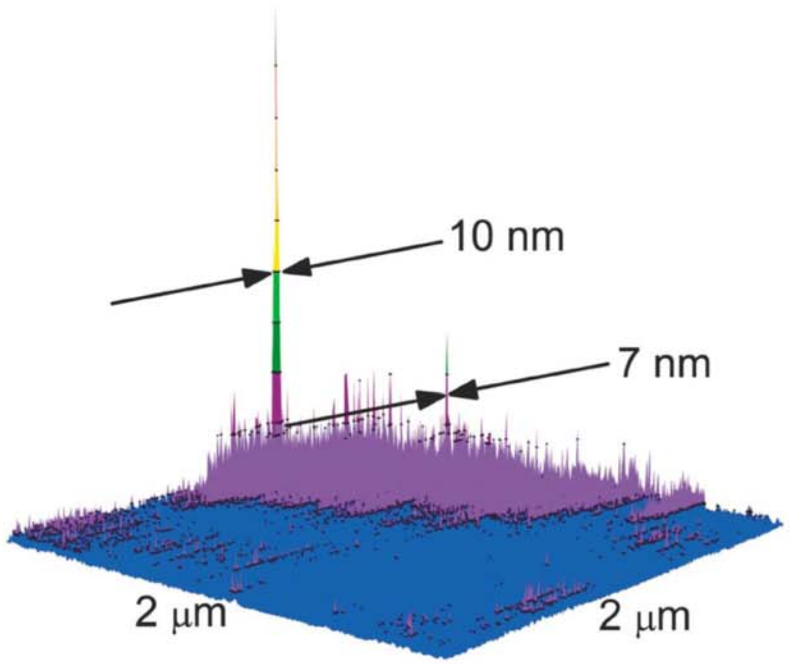


Fluorescence enhancement near a silicon tip



Tip-enhanced fluorescence image of quantum dots

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Near-field Raman spectroscopy of CNT

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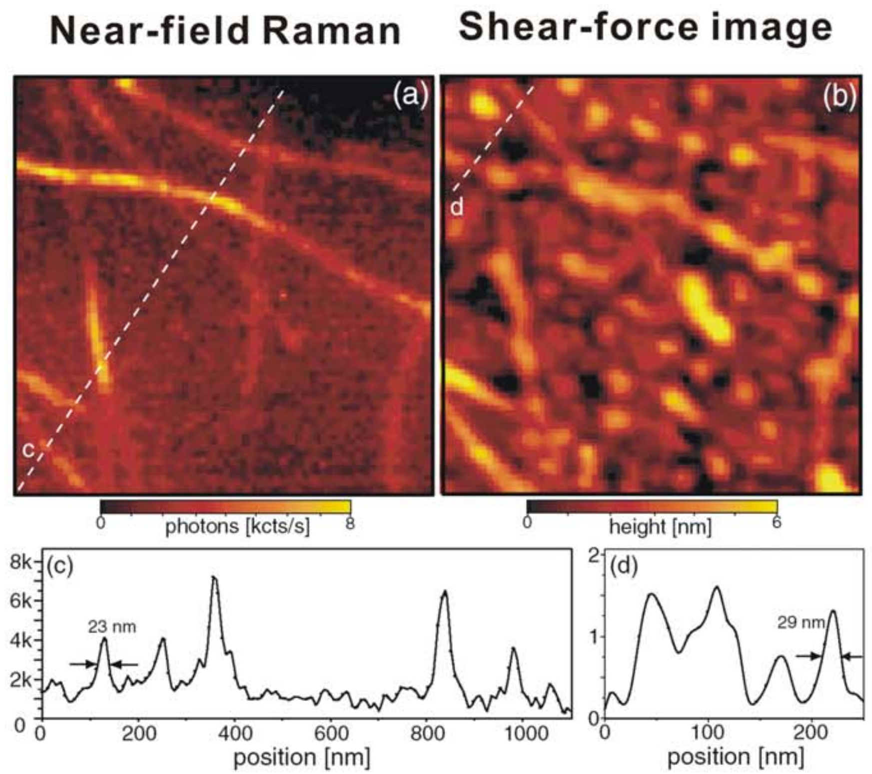

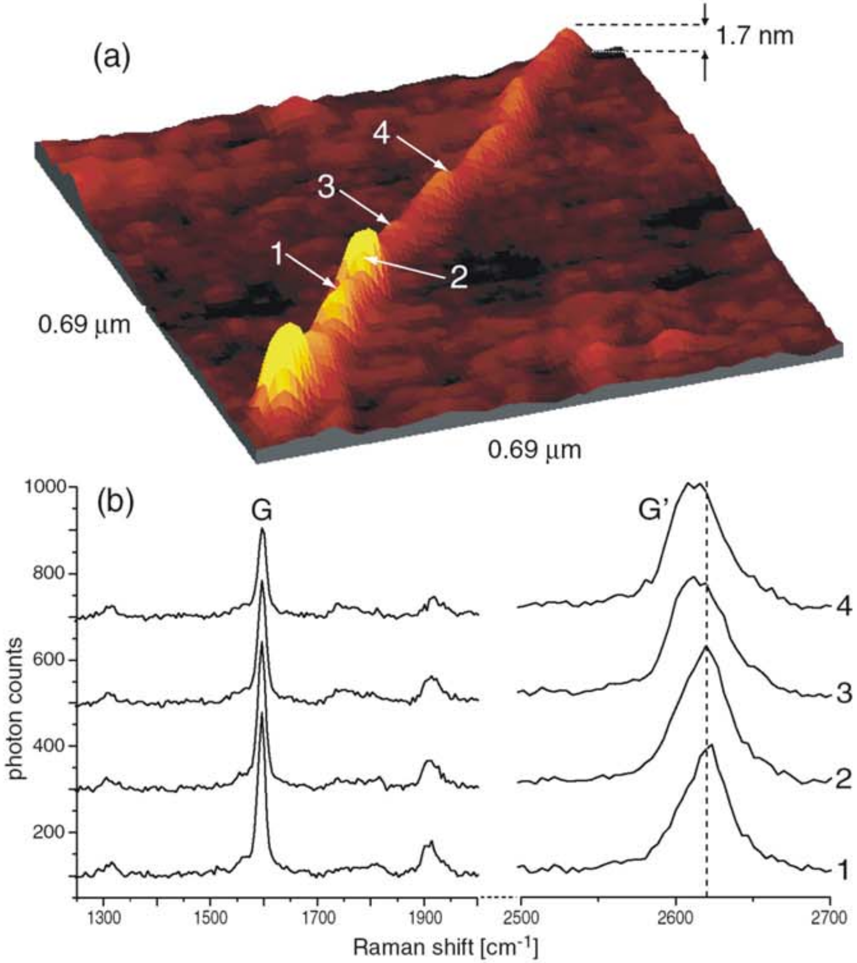

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