The God Quasiparticle: The Plasmon and Infrared spectroscopy of proteins

Boston University

PY482, May 2, 2013

Ronen Adato, Alp Artar, Alket Mertiri, Hatice Altug, M. K. Hong

Thanks to Prof Sid Redner

Shyam Erramilli [“Shaam”]
Physics, Biomed Eng, Materials Sci & Eng, Photonics Center

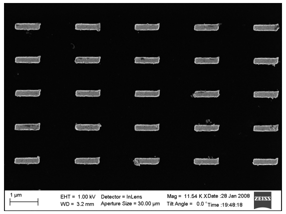
College and Graduate School of Arts and Sciences Physics Department

chemistry at Boston University

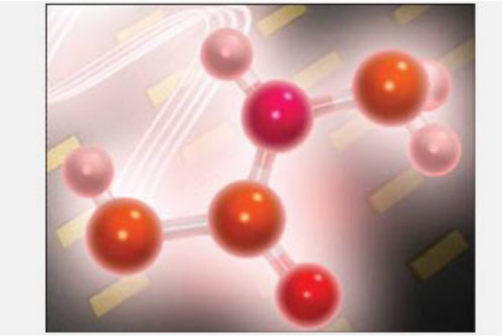
The Boston University photonics center

NSF

Outline



Vibrational Infrared Spectrscopy



Plasmon the “God Quasiparticle”

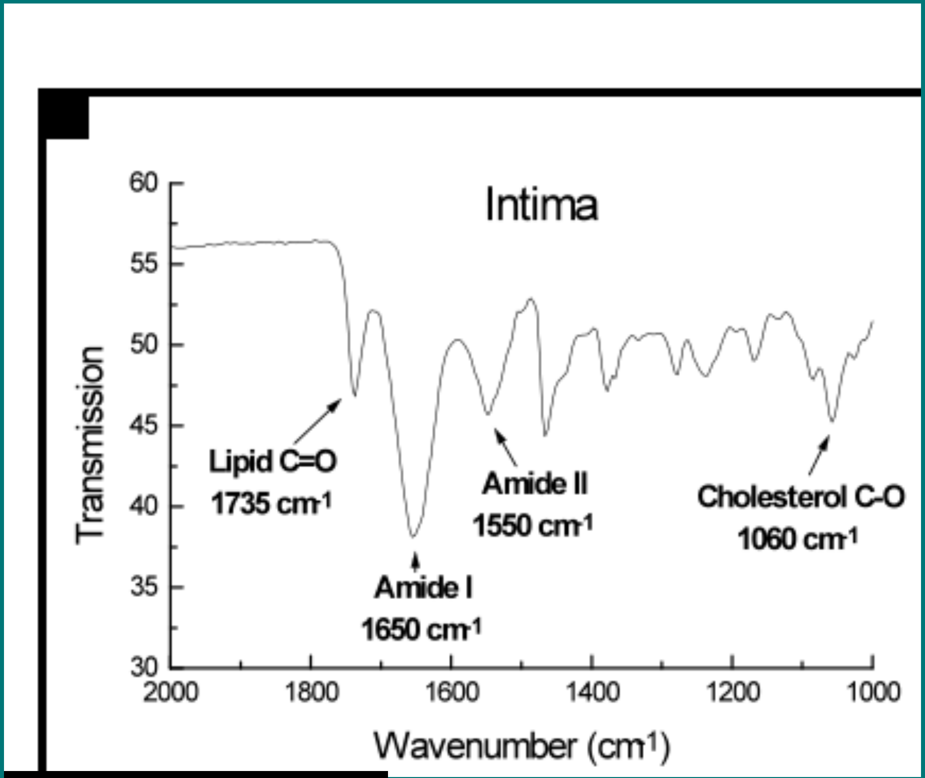
- Surface Enhanced Infrared Absorption (SEIRA)
- Extraordinary Optical Transmission (EOT)

• Nanoplasmonic metamaterials to enhance the amide I absorption band in proteins

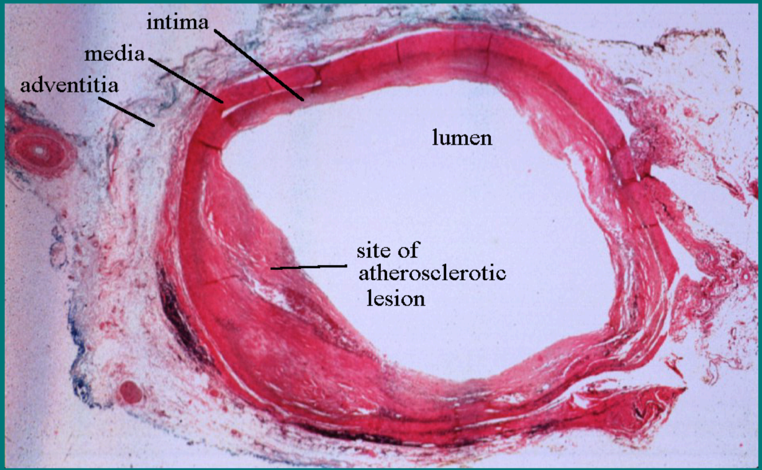
• Zeptomole protein study

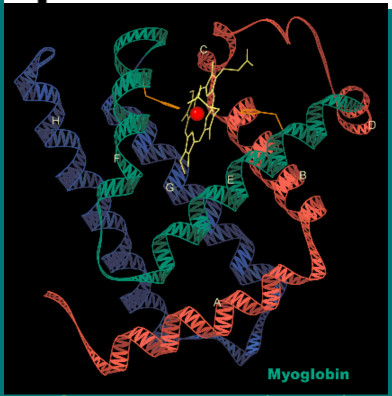
NSF Press release 09-207 [Altug, Credit: Bobby Mixon, NSF]

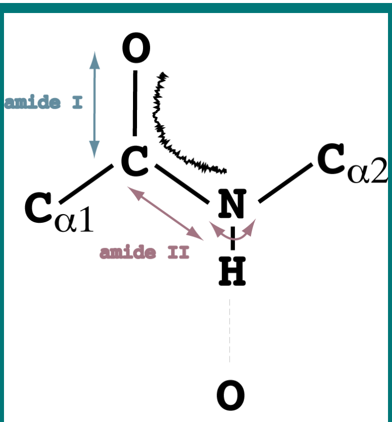
IR spectra are "fingerprints" of biomolecules

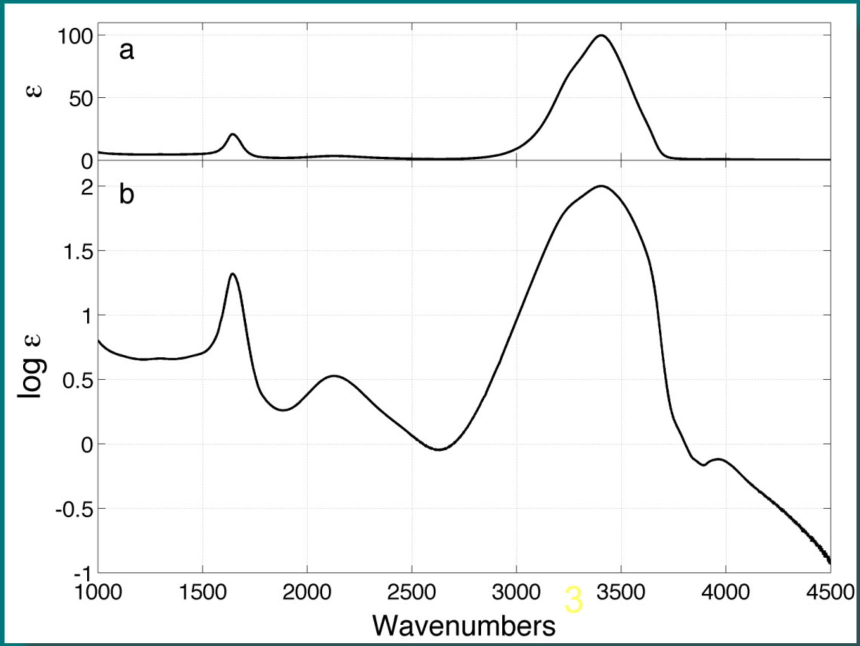


ATHEROSCLEROSIS
("hardening of the arteries")





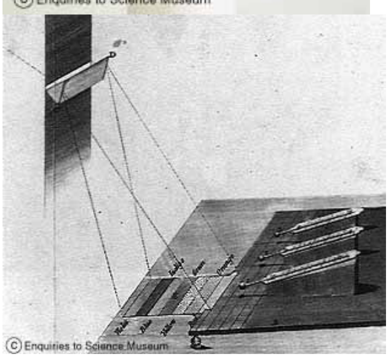


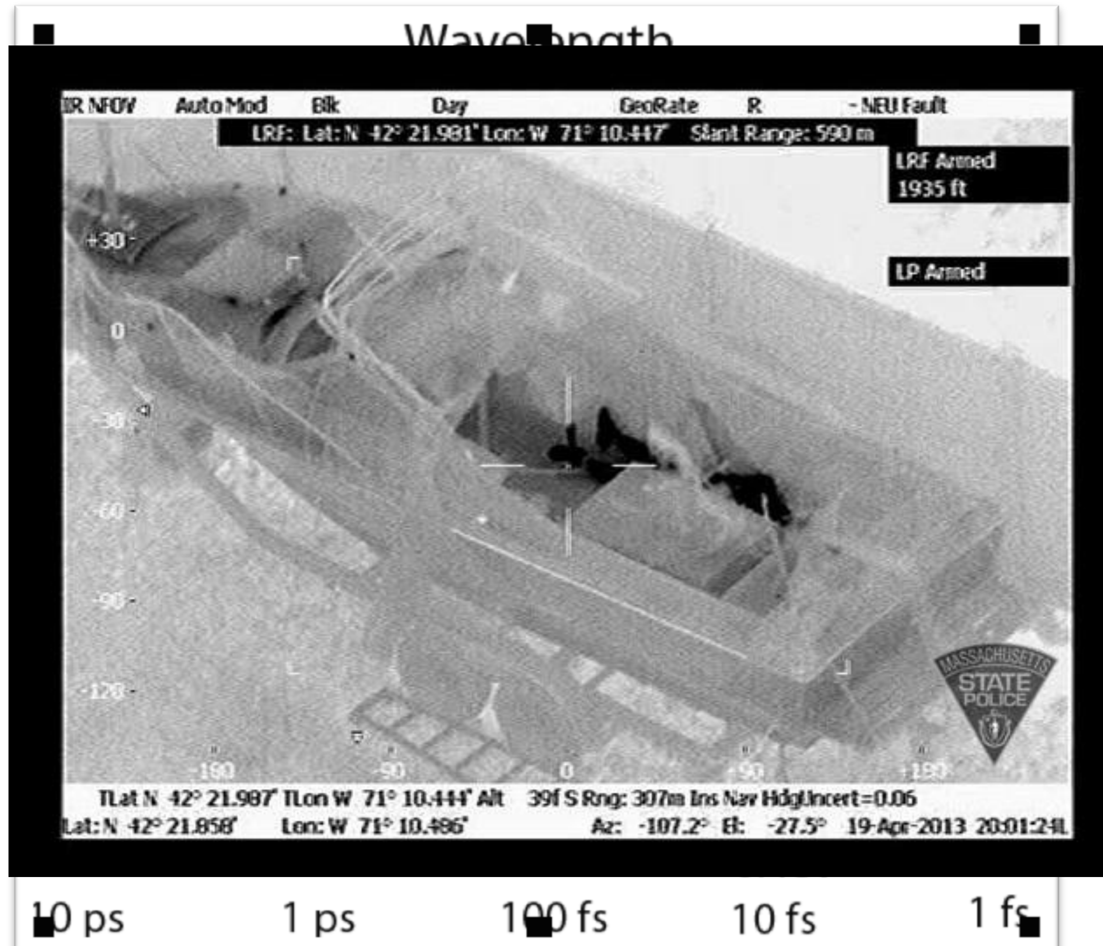


A. G. Jeung et al (1997)
M. K. Hong et al (1998)
Jeff Shattuck, L Chieffo Water (2008)

Infrared radiation

ca1800, **Willam Herschel** discovered 'infrared' radiation.





The Science Museum, UK

Mike Martin, LBNL

Prof Rick Averitt, Boston

What is a Plasmon?
“The God Quasi-Particle”

$$\omega_P^2 = \frac{Ne^2}{\varepsilon_0 m}$$ defines the "Plasma Frequency"

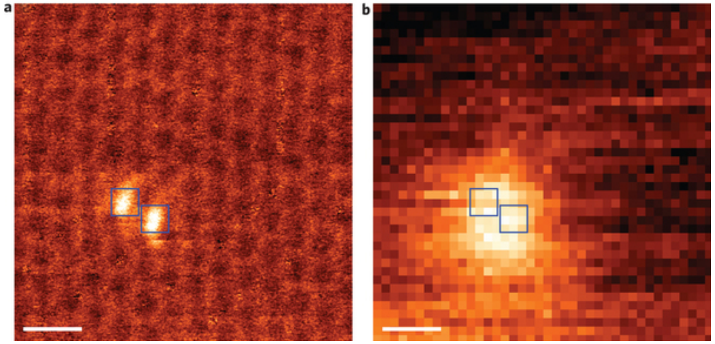
Highest frequency of response

Corresponds to a collective oscillation of ALL the electrons

The Quasi-particle "Plasmon" is extraordinarily important

"Plasmonics" is one of the hottest fields in Physics today

2-D manifestation is the "Surface Plasmon"



“Atomically localized plasmon enhancement in graphene”
Zhou et al Nature (2012)
EELS (Electron energy loss spectroscopy)

Numbers for The God Quasi-Particle

The Plasmon

$$\boxed{\omega_P^2 = \frac{Ne^2}{\varepsilon_0 m}}$$ defines the "Plasma Frequency"

1) Copper metal at room temperature:

$$N \simeq 9\times 10^{29}\,\text{m}^{-3} \Rightarrow \omega_P \doteq \text{"8.7 eV" or "2.1 PHz" or}$$

$$\ldots\ \text{"70660 cm}^{-1}\text{" or "}\lambda_P = 120\ \text{nm"}$$

2) Seawater (~ 0.6 M salt):

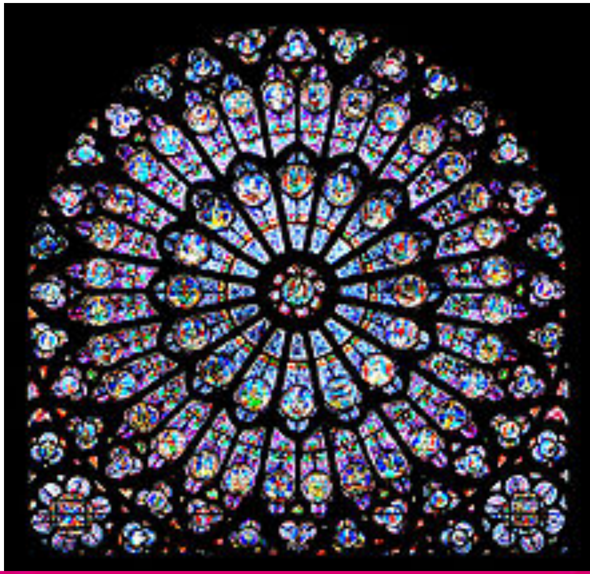
$$\omega_P = 5\times 10^{12}\,\text{s}^{-1}\ [\text{"THz"}]$$

3) Earth's Ionosphere:

$$N \simeq 10^{10} - 10^{12}\,\text{m}^{-3} \Rightarrow \omega_P \sim 1-10\ \text{MHz} \Rightarrow \lambda_P = 1\ \text{km}$$

The Plasmon is a Macroscopic Quantum Phenomenon

wikipedia



A “collective excitation” in which
ALL THE free ELECTRONS in a material behave like one collective quantum particle.

A MACROSCOPIC QUANTUM STATE

- Like flux in Superconductors
- Schrodinger’s Cat
- A famous Italian cookie

Next: Surface Plasmon

Surface Plasmon – Evanescence in both media

Total Internal Reflection

- Critical angle
- "Evanescent" wave does not propagate in air

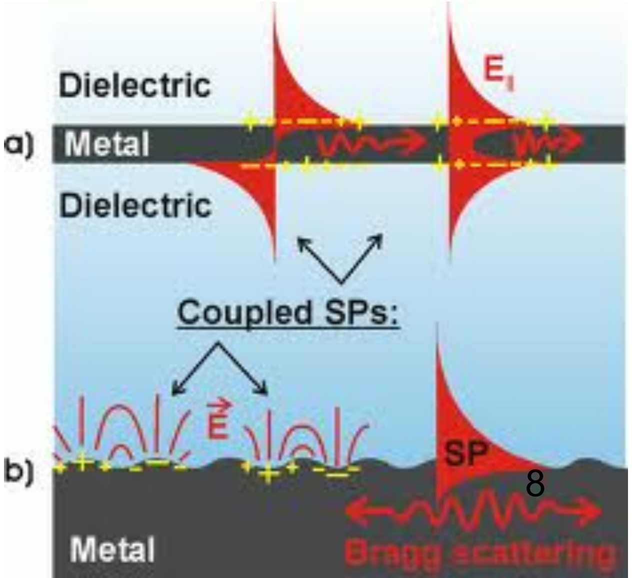
Wikipedia;
Northwestern Marks grp

Surface Plasmon

The Wave is evanescent in BOTH media

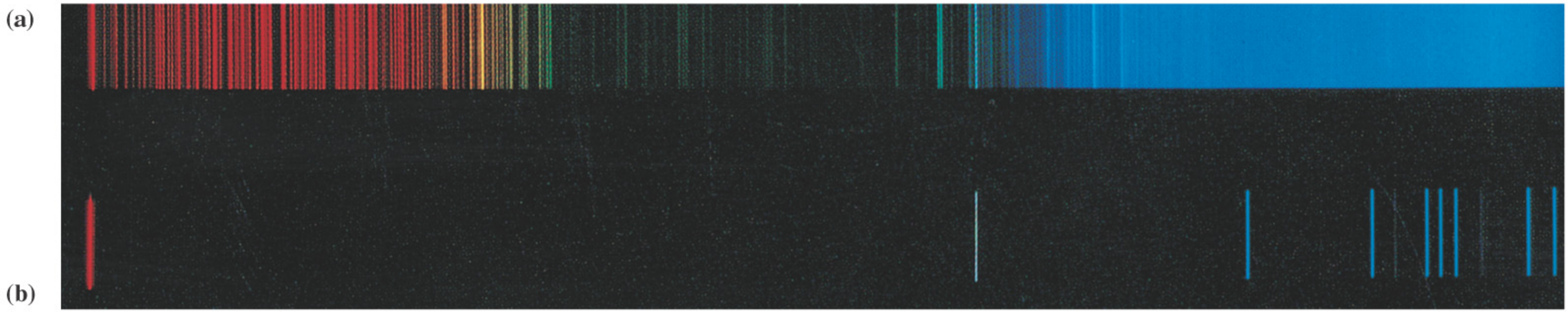
- Wave can only propagate along the surface

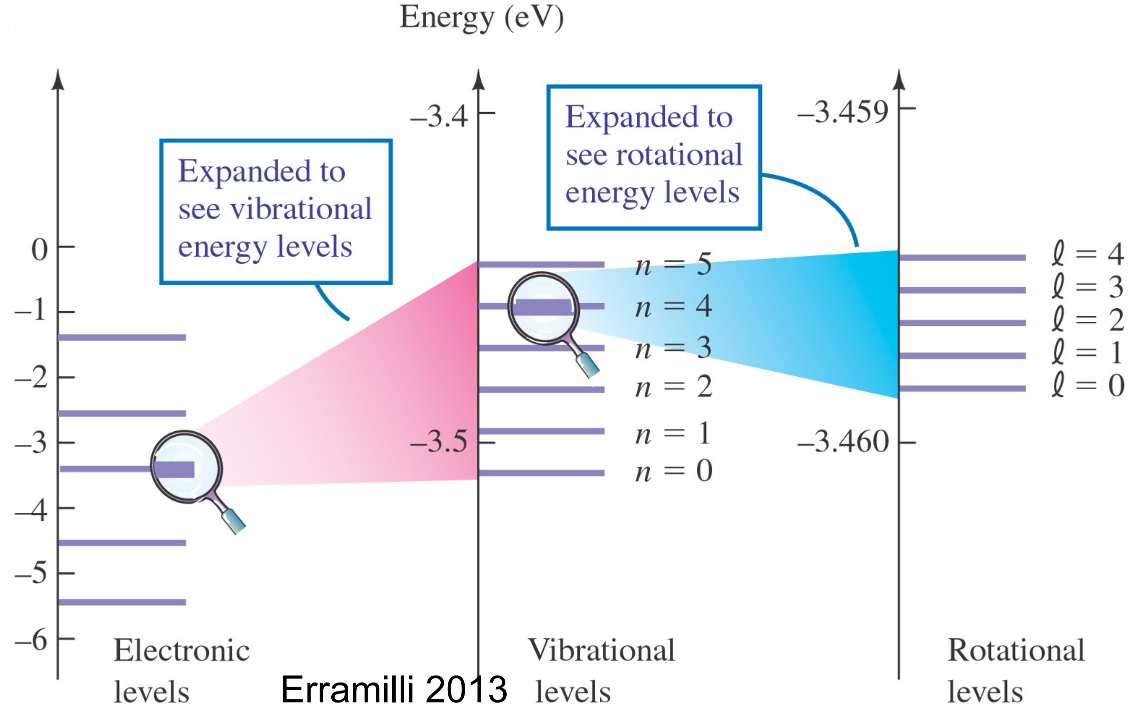
- Localized & Collective effects can enhance
- E-fields and B-fields



Erramilli 2013

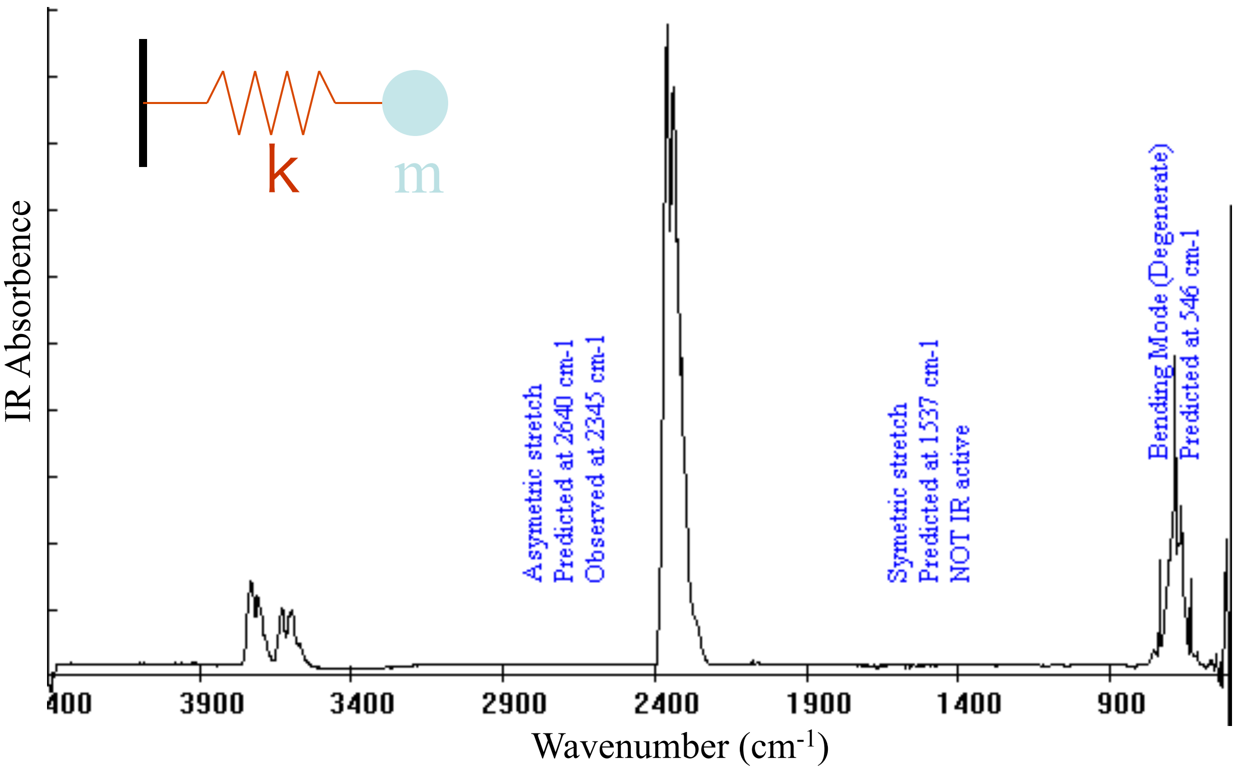
Back to IR spectroscopy Comparison of the spectra of (a) molecular hydrogen and (b) atomic hydrogen

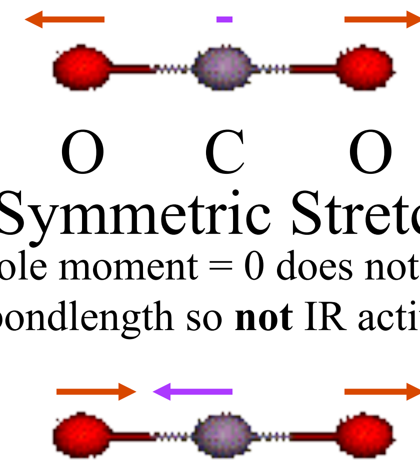




Copyright © 2005 Pearson Prentice Hall, Inc.

• Vibrational spectroscopy: CO_2





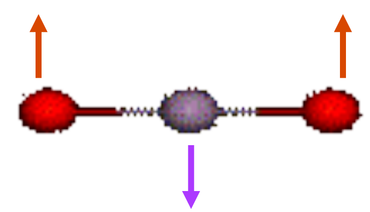
O C O

Symmetric Stretch

(Dipole moment = 0 does not change wit bondlength so **not** IR active)

Asymmetric Stretch

(Has dipole moment that depends on bondlength so IR active)



Bending Mode

(Has dipole moment so IR active)

A Dipole Moment = charge imbalance in the molecule

Infrared spectroscopy

Raman spectroscopy: a polarizability

Legacy of IR spectrosopy on Biomolecules

Volume I. *July–August, 1893.* *Number 1.*

THE

PHYSICAL REVIEW.

A STUDY OF THE TRANSMISSION SPECTRA OF CERTAIN SUBSTANCES IN THE INFRA-RED.

By Ernest F. Nichols.

WITHIN a few years the study of obscure radiation has been greatly advanced by systematic inquiry into the laws of dispersion of the infra-red rays by Langley,[1] Rubens,[2] Rubens and Snow,[3] and others. Along with this advancement has come the more extended study of absorption in this region. The absorption of atmospheric gases has been studied by Langley[1] and by Ångstrom.[4] Ångstrom[5] has made a study of the absorption of certain vapors in relation to the absorption of the same substances in the liquid state, and the absorption of a number of liquids and solids has been investigated by Rubens.[6]

In the present investigation, the object of which was to extend this line of research, the substances studied were: plate glass, hard rubber, quartz, lamp-black, cobalt glass, alcohol, chlorophyll, water, oxyhæmoglobin, potassium alum, ammonium alum, and ammonium-iron alum.

Phys Rev, Vol 1, Page 1

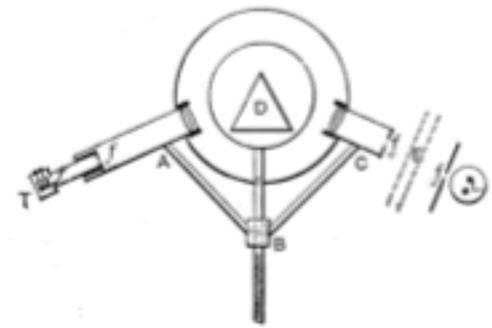
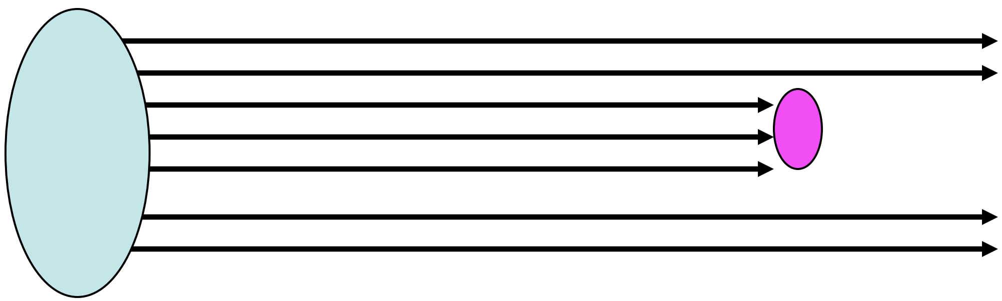


Fig. 1.

Source: Edisonian Light bulb

oxyhæmoglobin,

Cross-sections, extinction coefficient



Absorption probability
- depends on area

$$\sigma = \pi r^2$$

Cross-section is an effective "area" presented by the molecule to the incident wave

$$I = I_0 e^{-\alpha L} \equiv I_0 \times 10^{-\varepsilon C L}$$

"Beer's Law"

$$\Rightarrow \varepsilon = \frac{1}{2.303} \sigma N_A$$

C concentration in mM (milliMoles per litre)

Cross-sections: Free electron

Thomson

$$E = mc^2$$

"Classical radius of electron"

$$E = \frac{e^2}{4\pi\varepsilon_0 r_e} \Rightarrow r_e = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82\times10^{-13}\,\text{cm}$$

$$\sigma_e = \frac{8\pi}{3} r_e^{\,2} = 6.65\times10^{-25}\,\text{cm}^2$$

$$1\ \text{barn} = 1\times10^{-24}\,\text{cm}^2$$

Bohr: "Form factor"
QM result

$$\sigma_a = \frac{8\pi}{3} r_e^2 \left|f(\omega)\right|^2$$

Fast neutron fusion cross-section for ^{235}U is ~ 1.2 barns

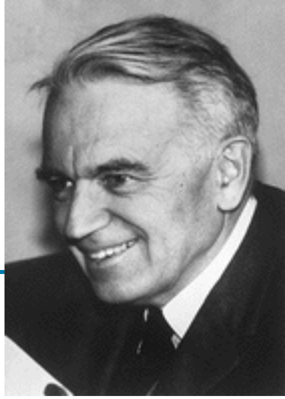
Critical mass:

$$M_c = \frac{4\pi^4}{3^{5/2}(\nu-1)^{3/2}}\left[\frac{1}{n\sigma_{fusion}}\right]^3$$

Erramilli 2013

Microsoft Clip Art; Trinity test (atomicarchive)

What can we learn from IR spectroscopy?



G. Herzberg

- **Molecules vibrate at frequencies in the IR range**
- **Chemical Analysis:**
  - Match spectra to known databases
    - Identifying an unknown compound, Forensics, etc.
  - Monitor chemical reactions *in-situ*
- **Structural ideas:**
  - Can determine what chemical groups are in a specific compound
- **Electronic Information:**
  - Measure optical conductivity
    - Determine if Metal, Insulator, Superconductor, Semiconductor
    - Band Gaps, Drude model

Cross-sections: Near Resonance

$$\sigma_e = \frac{8\pi}{3} r_e^2 = 6.65 \times 10^{-25}\,\text{cm}^2$$

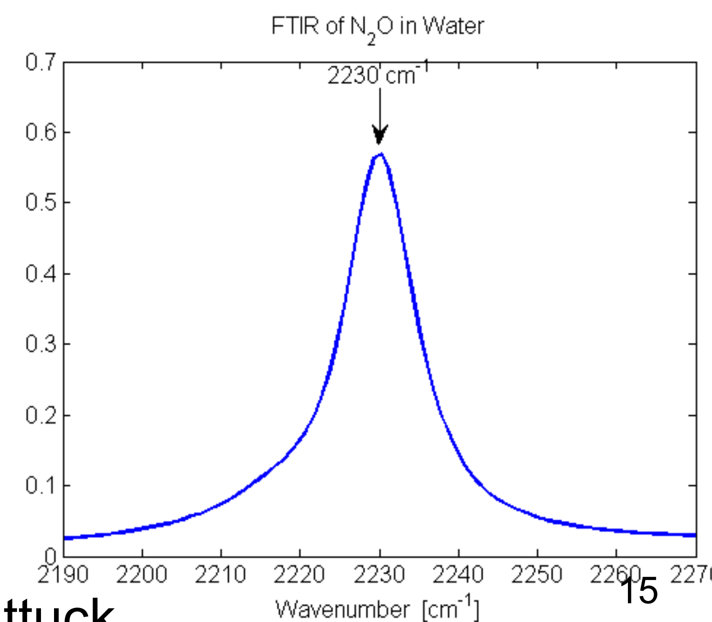
Usually sum over many resonances.

Selection rules imposed by Parity of the dipole operator

$$\sigma_a = \frac{8\pi}{3} r_e^2 \left| f(\omega) \right|^2 \Leftrightarrow f(\omega) \propto \left\langle \psi_f \middle| \mu_{ez} \middle| \psi_i \right\rangle \Leftrightarrow \sigma_a = \frac{8\pi}{3} r_e^2 \left| \frac{f_0 \omega^2}{\omega^2 - \omega_0^2 + i\gamma_0 \omega} \right|^2$$

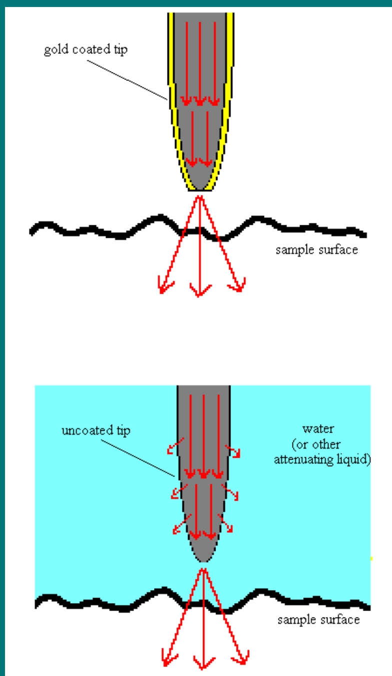
An enormous range in values….

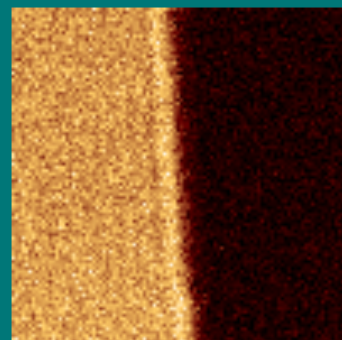
Process	Crosssection (cm^2)
Raman	10^{-31}
IR absorption	10^{-18}-10^{-21}
Single molecule fl	10^{-13}
Neutrino reaction	10^{-43}

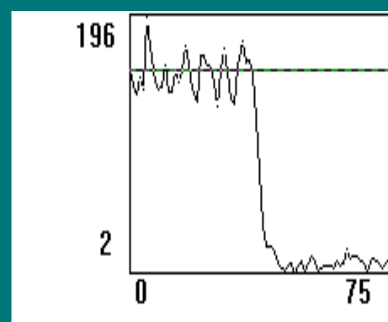


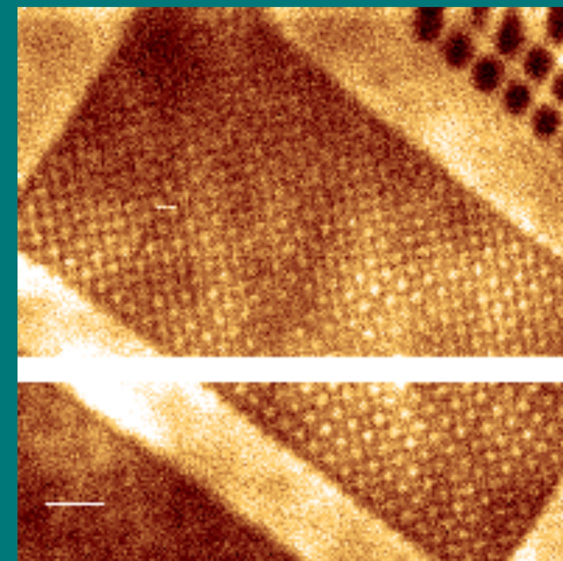
1. Imaging The first underwater mid-infrared image in history (at 6 microns) 1995

Eric Betzig; Pohl; A Levin (Cornell)







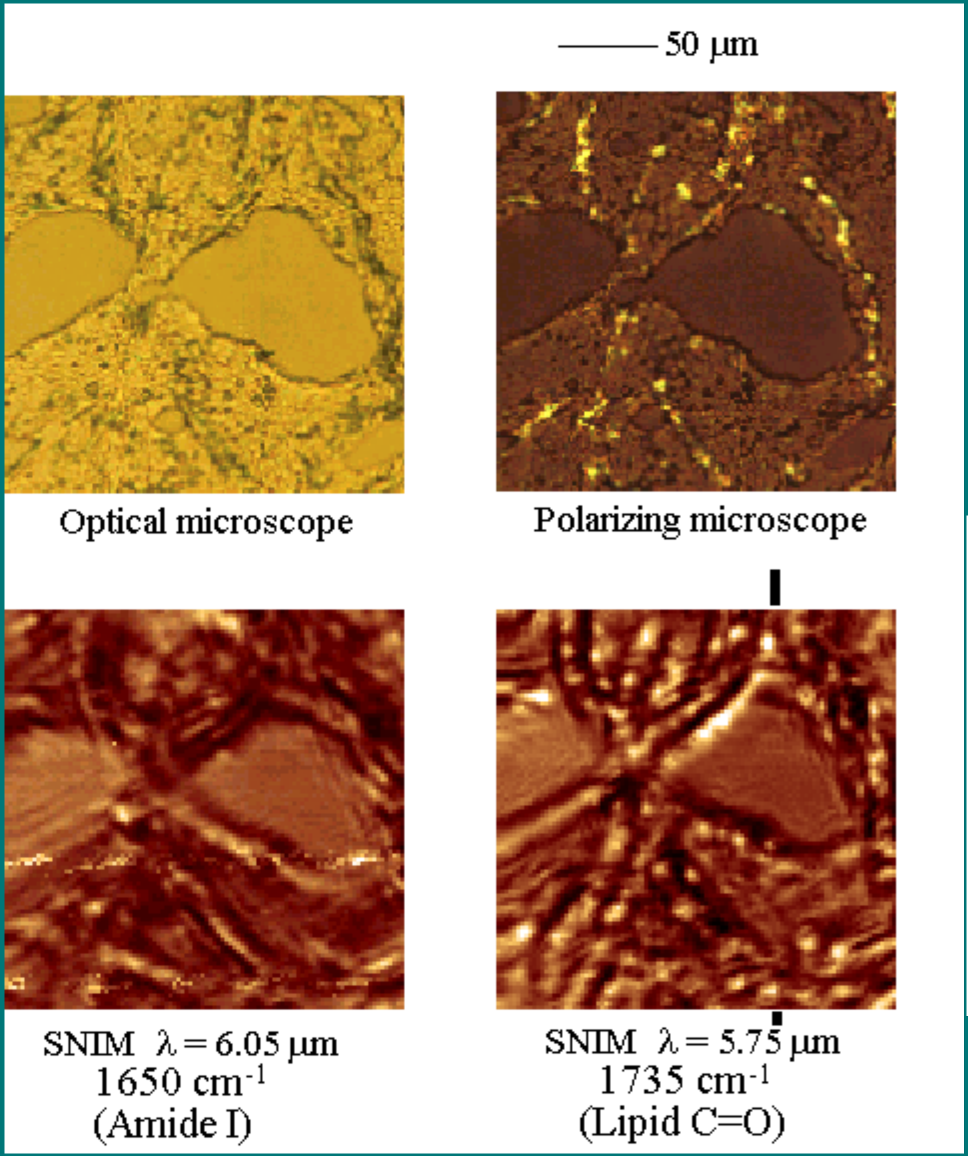


Spatial resolution < 1 μm. The very first image broke the diffraction barrier

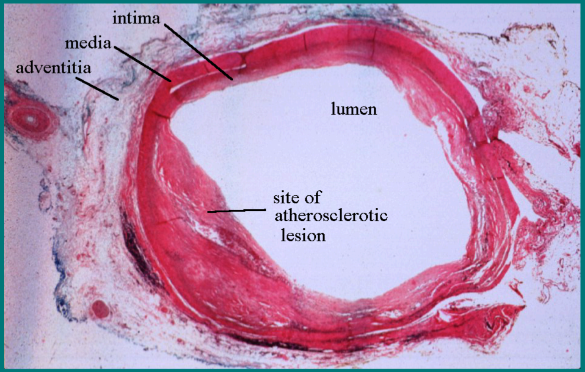
Keilman - apertureless methods
Wickramasinghe (IBM)

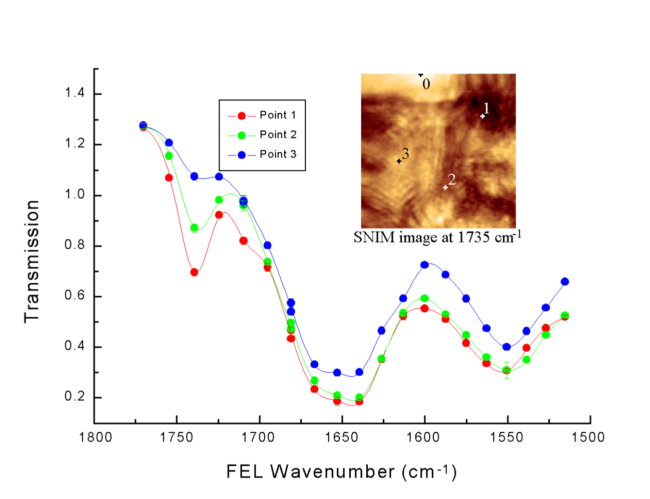
A. G. Jeung et al (1997)
M. K. Hong et al (1998)
Martin & Holman (LBNL)

Atherosclerotic plaque imaging between 5 and microns in wavelength



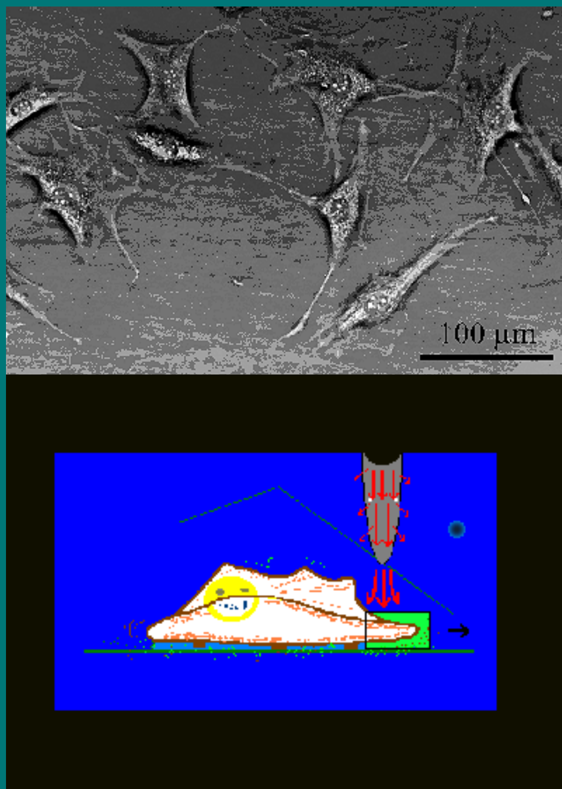
ATHEROSCLEROSIS
("hardening of the arteries")

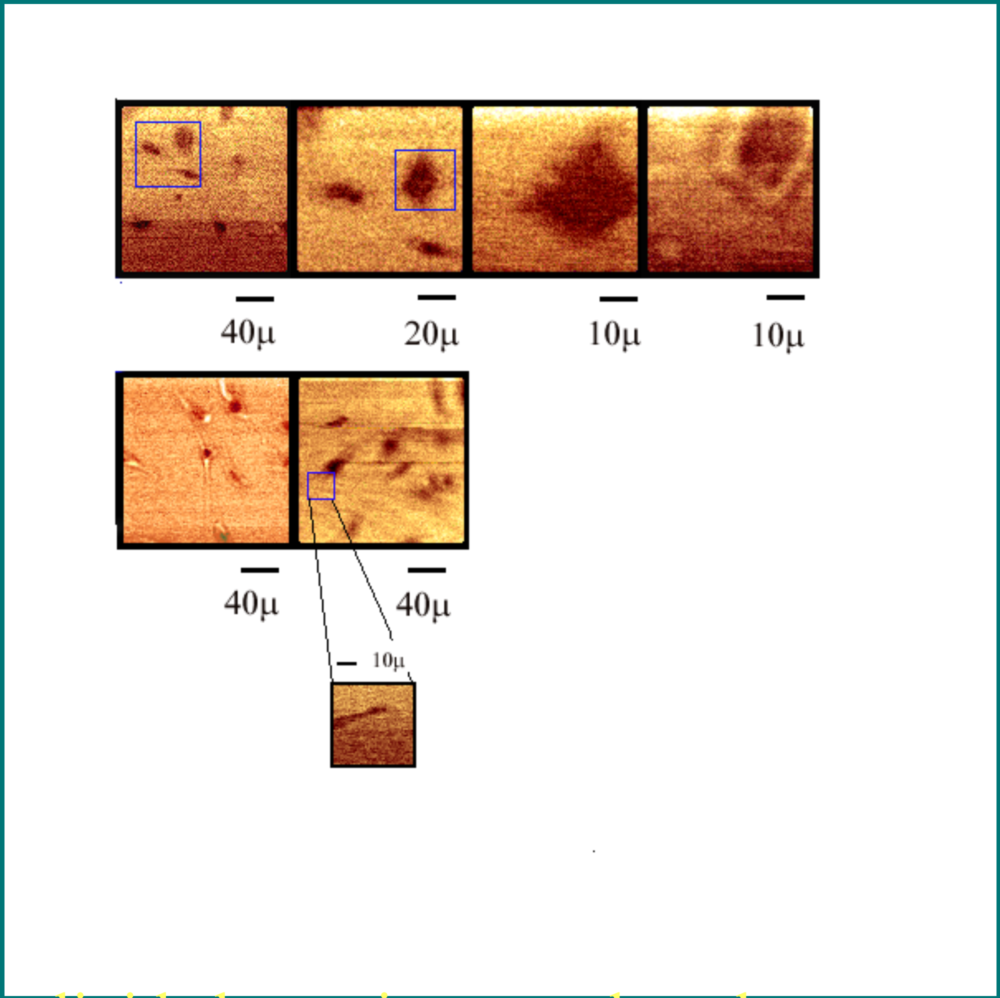




Jeung et al

First Mid-infrared images of single living cells





Increased contrast at the lipid absorption wavelength ~ 1750cm^{-1}. All images taken under water

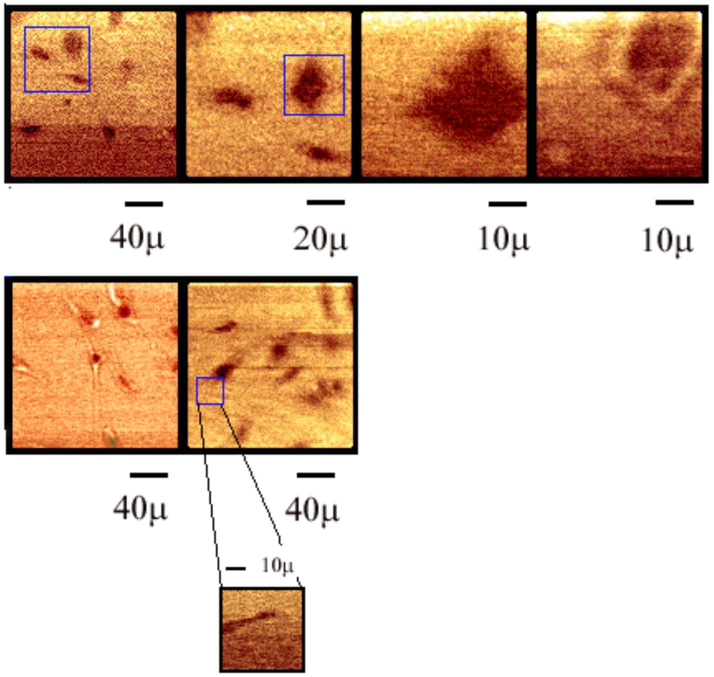
Jeung, Hong et al Nucl Instr Meth

Experimental Observation

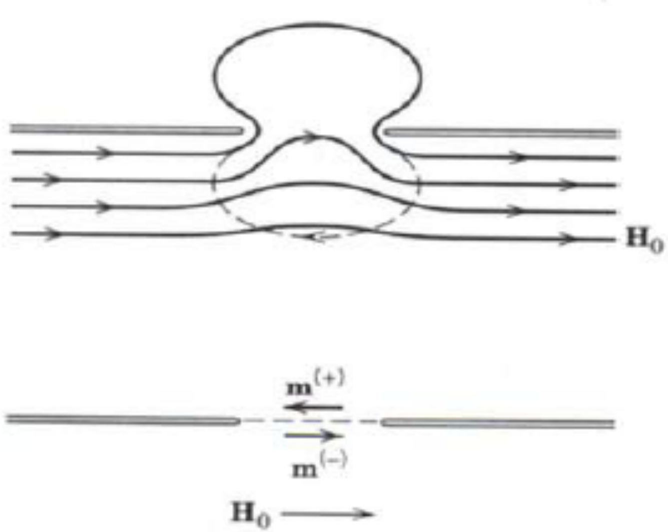
Why is the absorption from lipid molecules in the membrane so surprisingly large?
[~ 50 times larger than the lipid concentration based estimates]

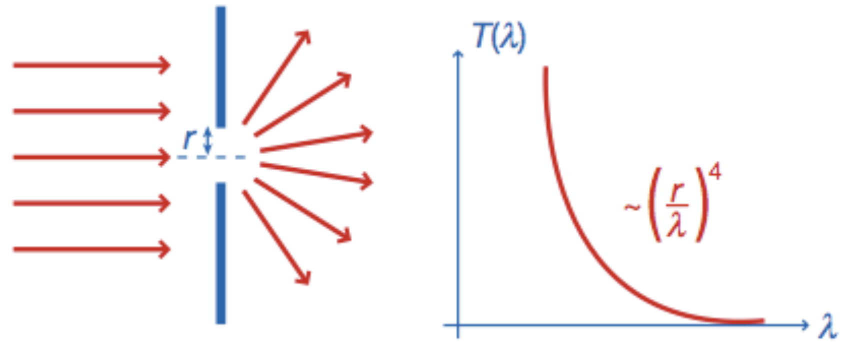
- New biology?
  (vesicle transport in the lamellopodium)
- New Physics?

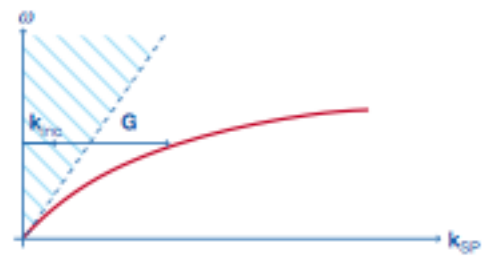
- Answer: New Physics



Discovery of Extraordinary Optical Transmission (EOT)







Bethe: Aperture is ~ magnetic dipole

Transmitted Power falls like ~ r^{-6}

$$\eta_B = 64(kr)^4/27\pi^2$$

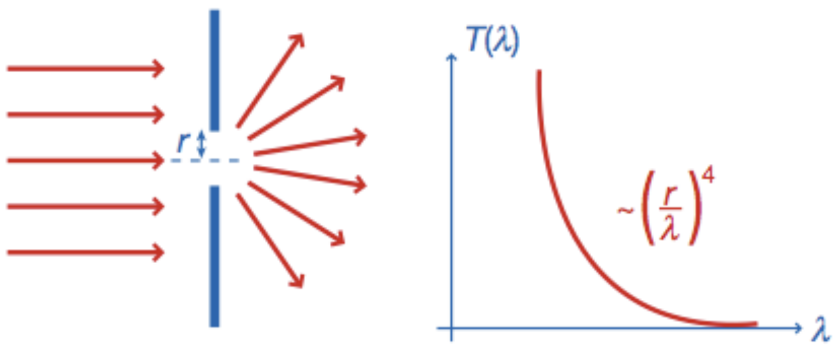
Surface Plasmon

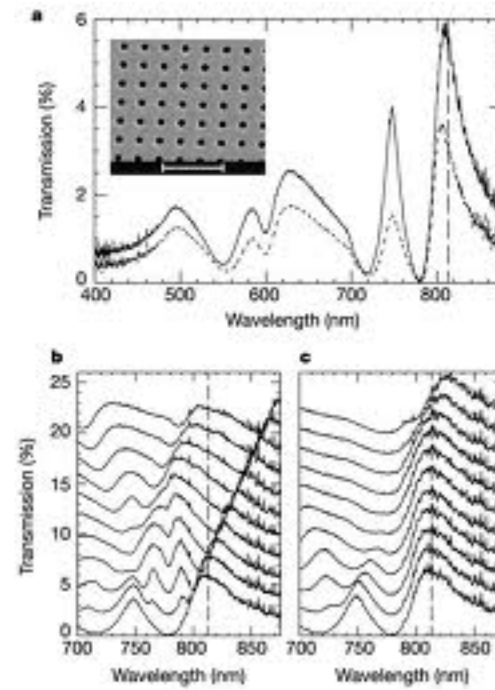
$$c^2 k_x^2 = \frac{\omega^2(\omega_P^2 - \omega^2)}{\omega_P^2 - 2\omega^2} \quad > 0 \text{ for } 0 < \omega < \frac{\omega_P}{\sqrt{2}}$$

Experiments show deviations from ideal conductor:
EOT: Transmission > 2 orders of magnitude above Bethe theory.

Jackson, Chapter 9. Bethe (corrected by Beaukamp); Genet, Ebbesen Nature (2007) review

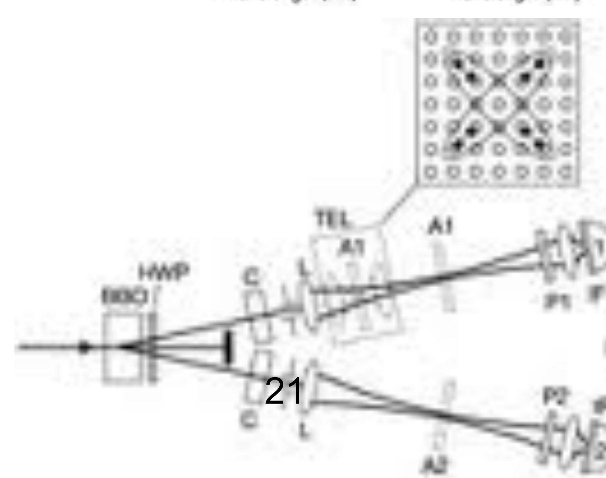
Surface Plasmon explains why Bethe's calculation was wrong for real metals





Amazing:

Plasmon assisted transport of entangled photons
Altewischer et al Nature (2002)



Surface Plasmons can give rise to extraordinary phenomena (Raman, IR…)

History: Enhancement of IR absorption by metal

Why Physicists talking Chemistry is inherently dangerous

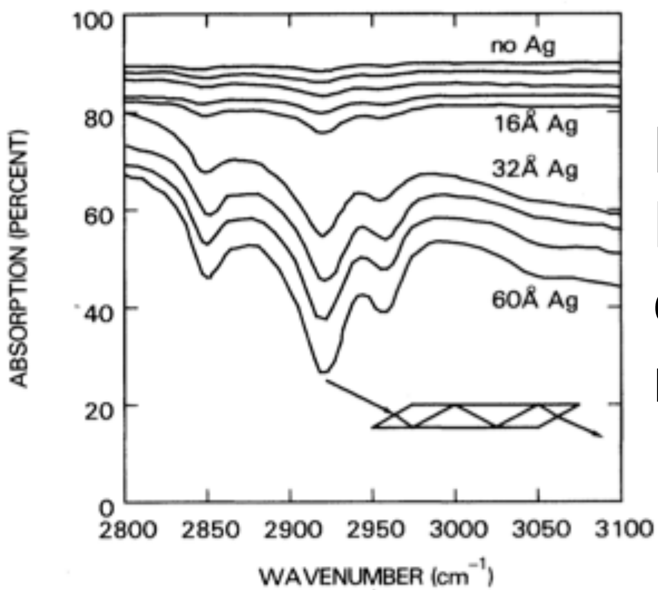
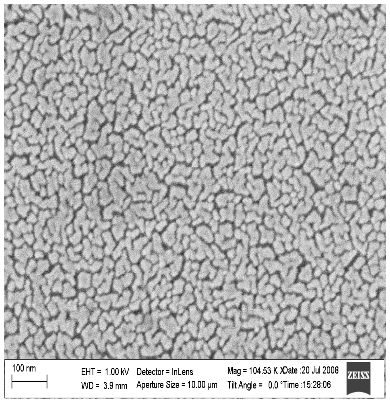
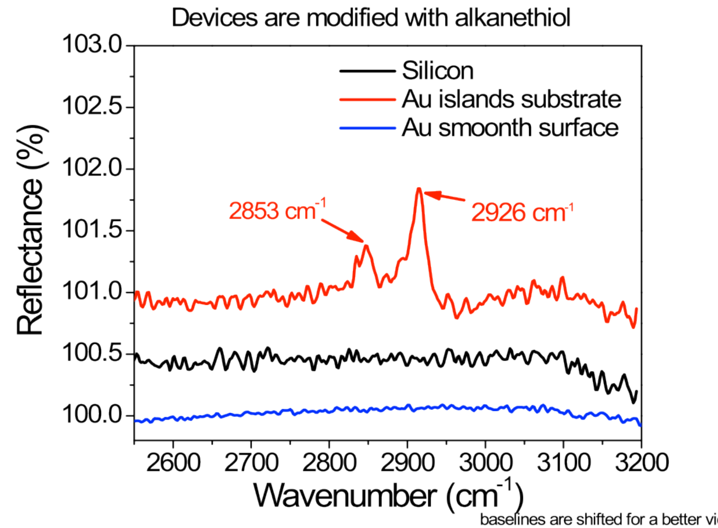


FIG. 1. Absorption of the C-H modes of a monolayer of 4-nitrobenzoic acid. The curves are for increasing

Hartstein, Kirtley & Tsang, PRL (1980)

Plasmon Enhancement confirmed by many groups

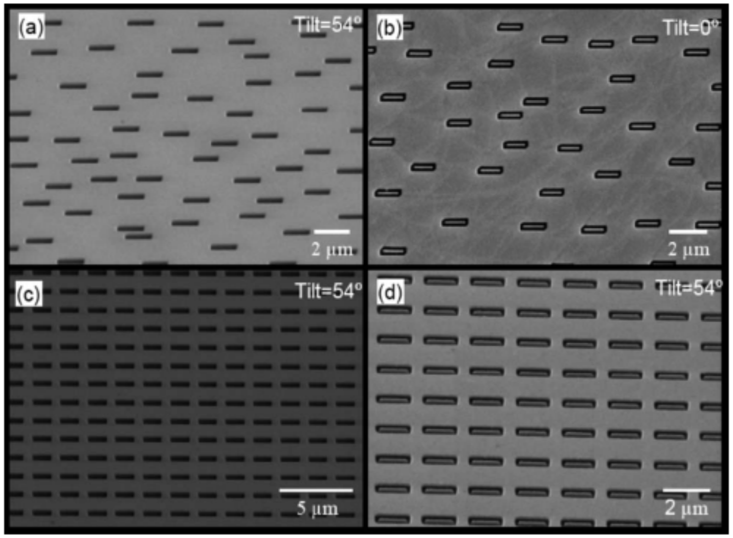


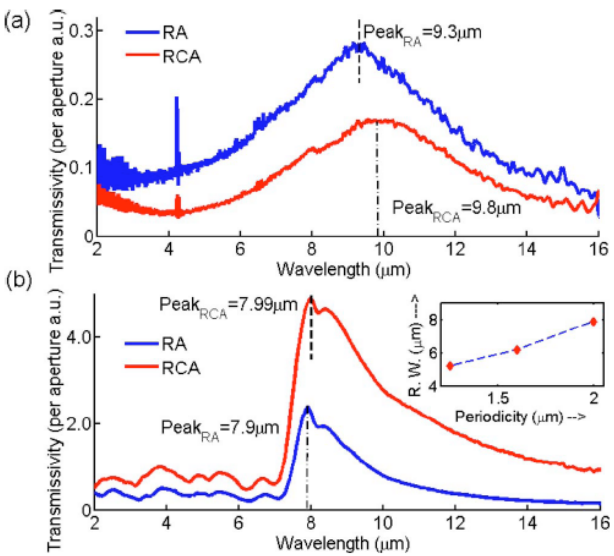


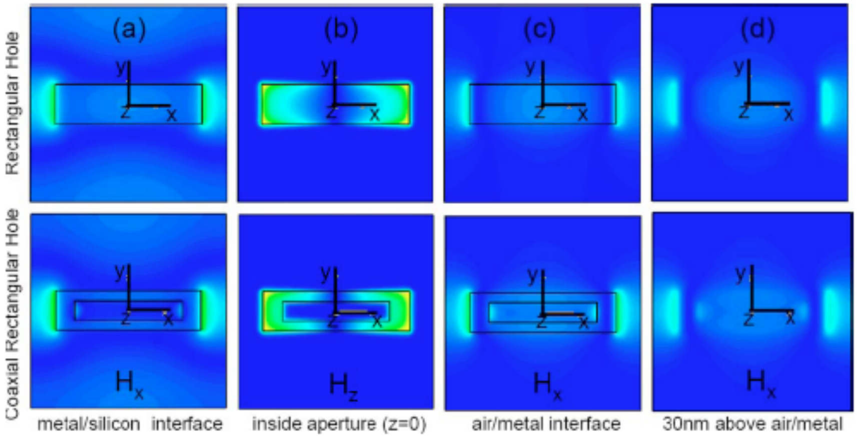
Problem: Not nitrobenzoic acid.
Vacuum pump oil!

Surface enhanced infrared absorption (SEIRA) alkanethiol

Surface plasmon at IR region with nanostructures: Mid-IR EOT of rectangular coaxial nanoaperture array







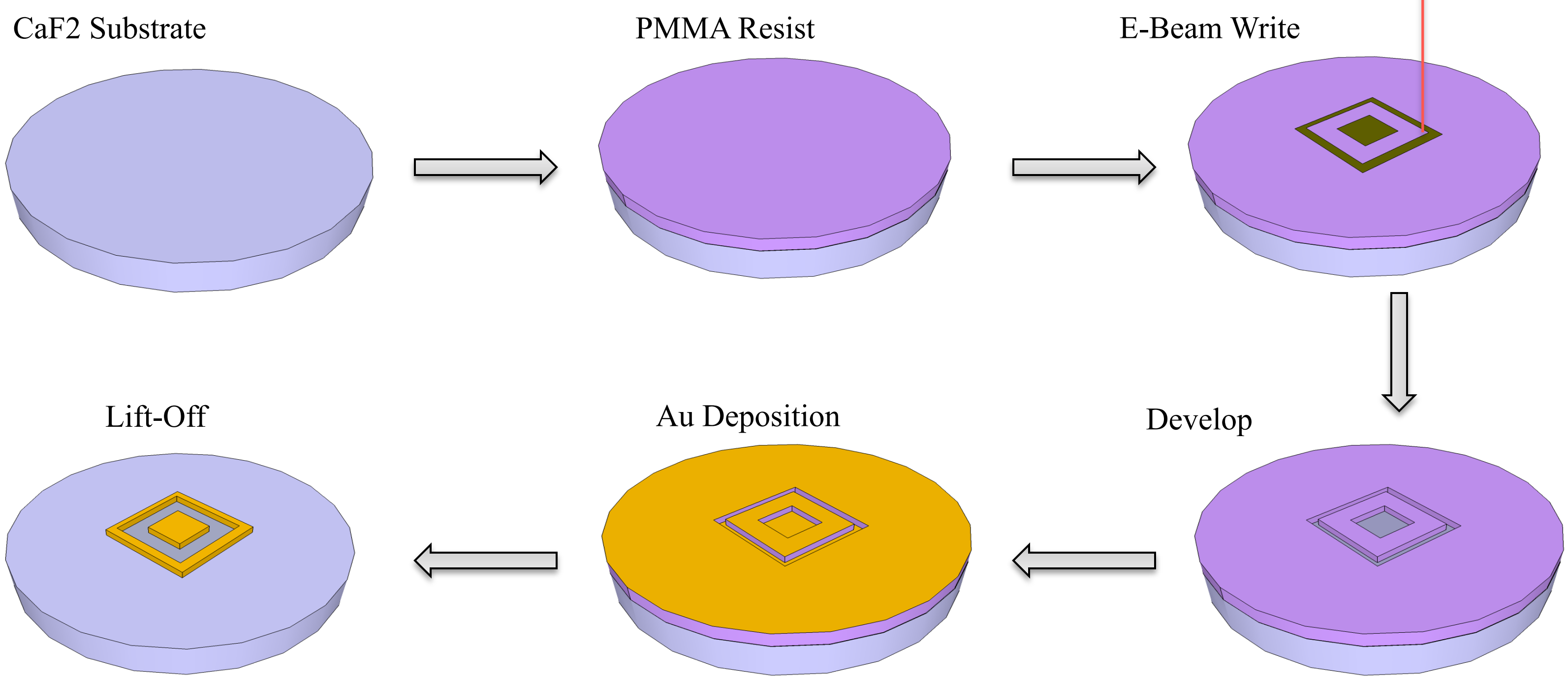
Phase matching condition

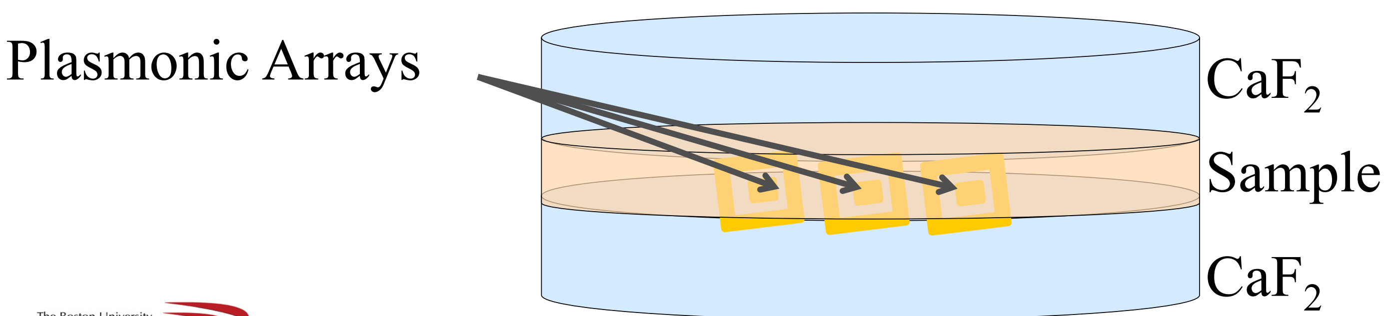
$$\beta = k_x \pm nG_x \pm mG_y = k_0 \sin\theta \pm (n+m)\frac{2\pi}{a_0}$$

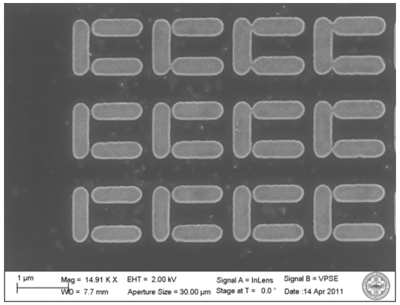
$$n_{SPP} = \beta c/\omega \qquad \lambda_{SPP}(n,m) = \frac{n_{SPP} a_0}{\sqrt{n^2+m^2}}$$

A. Yanik, R. Adato, X. Wang, S. Erramilli, M. K. Hong & H. Altug, Appl. Phys. Lett. 93, 081104 (2008)

From Paper Napkin to Plasmonic Nanoantennae: Design, simulation, e-beam lithography & IR testing: 48 hours



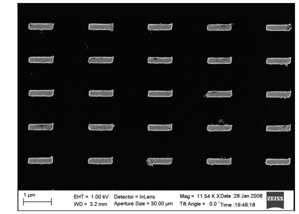


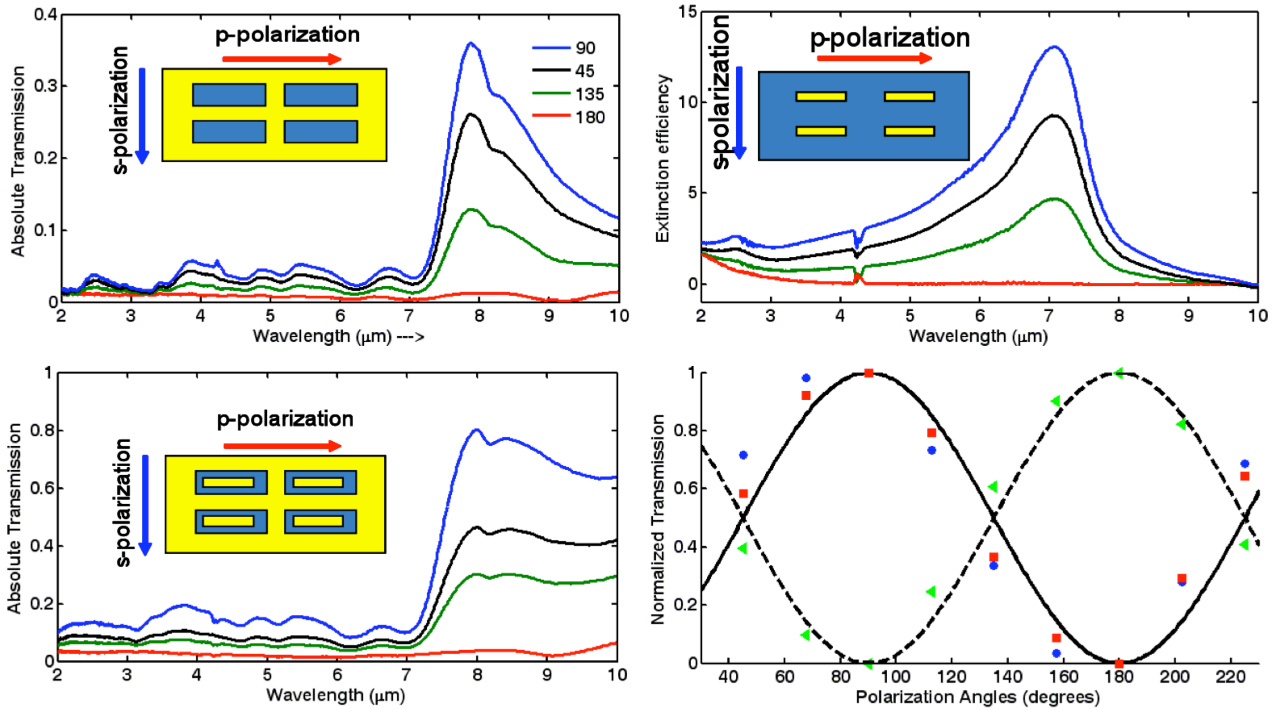


BOSTON UNIVERSITY

The Boston University photonics center

Nanorod antennae

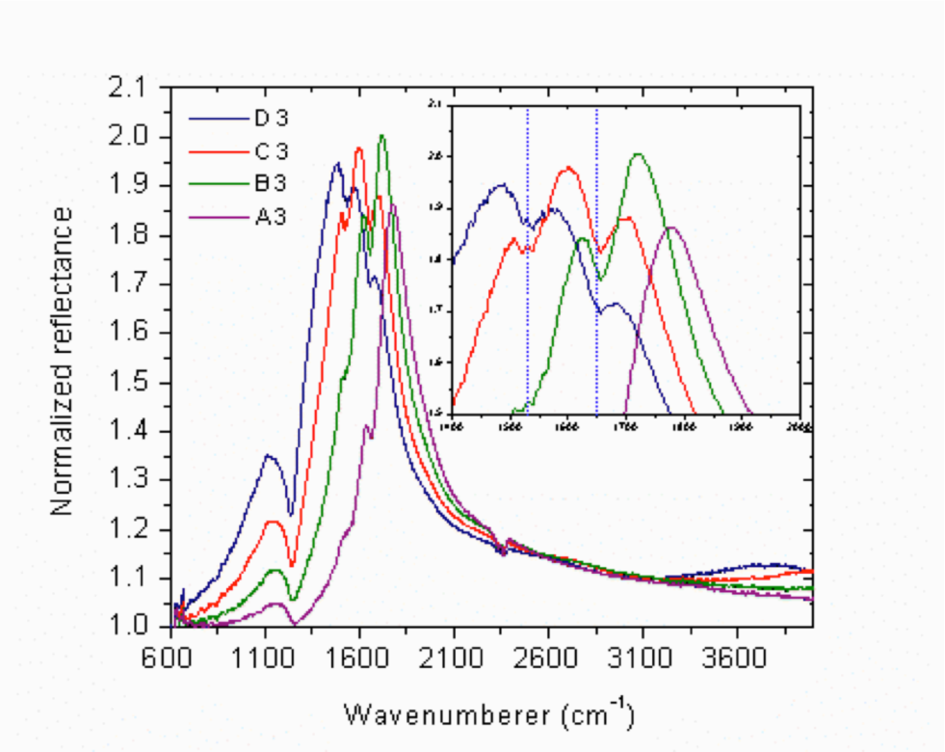


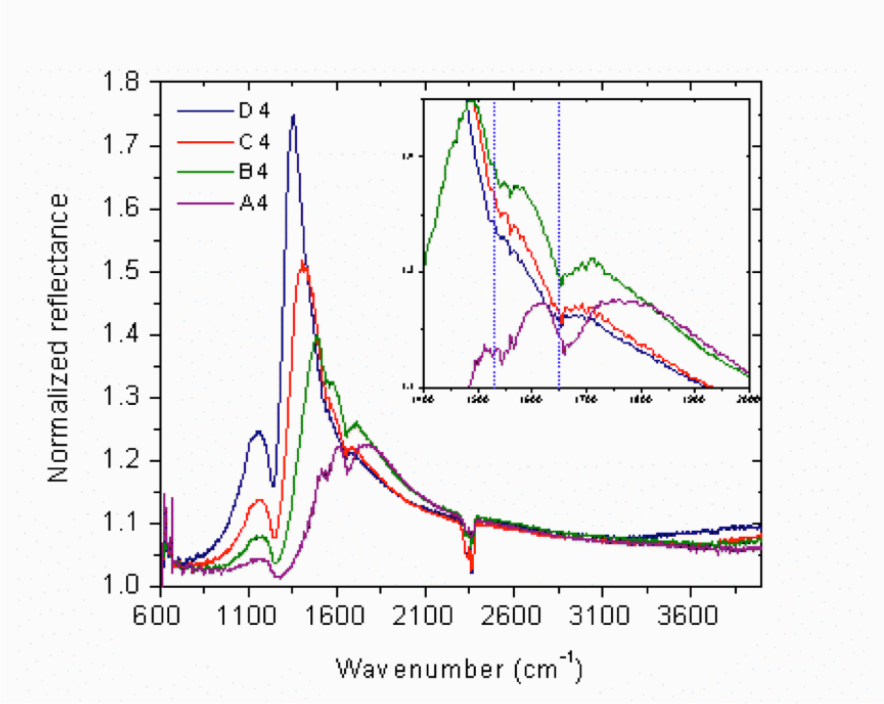


Yanik et al (2009) Polarization dependence of the EOT signal is shown for (a) rectangular and (b) coaxial nano-cavities. Extinction efficiency for Nanorod antennae is given for changing polarization angles for incident light. (d) Complementary behavior of cavities and nanorod is observed.

Response is non-local in space and non-local in time (Mukamel)

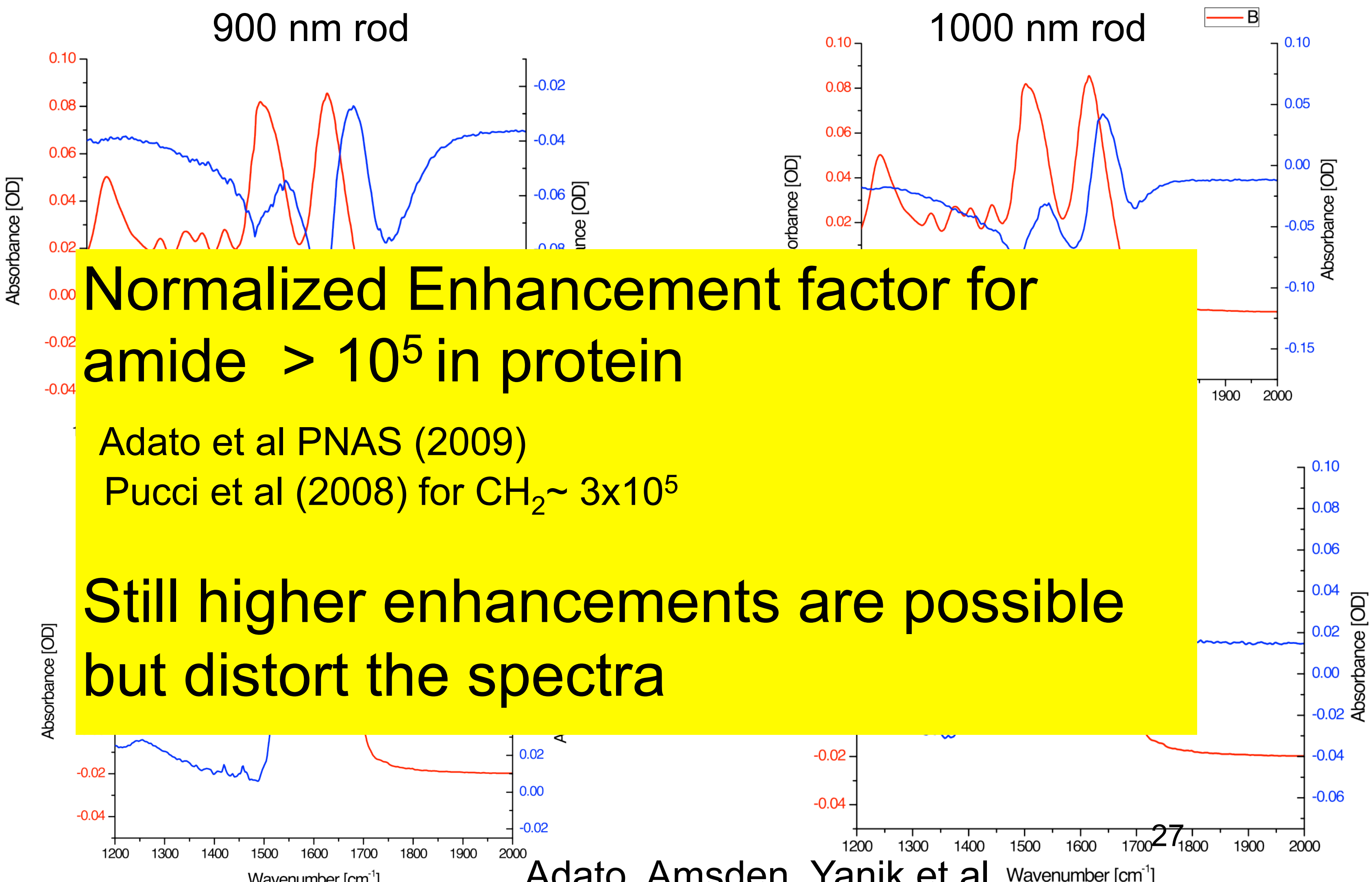
Surface enhancement of silk fibroin





Rows 3 and 4 of chip 1213c (left, right) correspond to periodicities of 1.5 and 2 μm respectively, with rods 200 nm in width. Inset: Blue lines 1530 and 1650 cm^{-1} [Adato et al; with Amsden, Kaplan, Omenetto, Tufts]

Plasmonic SEIRA silk study



Normalized Enhancement factor for amide > 10^5 in protein

Adato et al PNAS (2009)

Pucci et al (2008) for CH_2~ $3x10^5$

Still higher enhancements are possible but distort the spectra

Adato, Amsden, Yanik et al

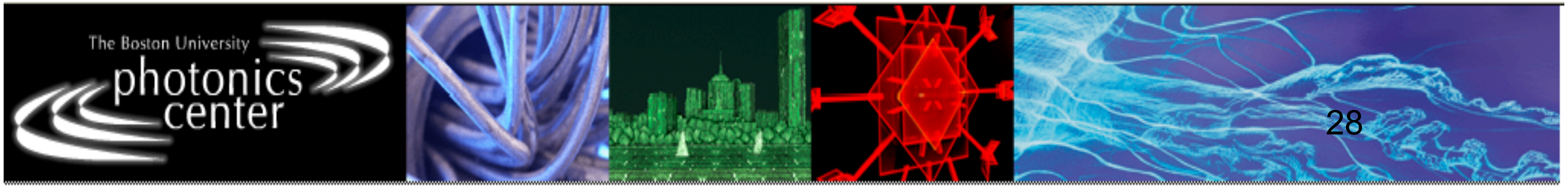
Summary: Infrared Plasmonic Metamaterials

1. Infrared spectroscopy
2. Plasmon and Metamaterials
3. Surfaced enhanced infrared absorption in single monolayer of silk fibroin

Questions/Comments:

Please contact shyam@bu.edu

BOSTON UNIVERSITY



Acknowledgements

- Jeffrey Shattuck
- Jason Amsden
- Larry Ziegler
- K. J. Rothschild

Funding provided by

- NSF, DOD

- H. Altug
- Feng Wang
- Eric Pinnick
- M. K. Hong
- A. A. Yanik
- R. Adato
- Xihua Wang

BOSTON UNIVERSITY