The God Quasiparticle:
The Plasmon and Infrared spectroscopy of proteins
Boston University
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Thanks to Prof Sid Redner

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Outline

Vibrational Infrared Spectroscopy

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 Mixon², NSF]
IR spectra are “fingerprints” of biomolecules.

Jeff Shattuck, L Chieffo Water (2008)
Infrared radiation

ca1800, **Willam Herschel** discovered 'infrared' radiation.
What is a Plasmon?
"The God Quasi-Particle"

\[ \omega_p^2 = \frac{N e^2}{\varepsilon_0 m} \]
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”
EELS (Electron energy loss spectroscopy)
Numbers for The God Quasi-Particle

The Plasmon

\[ \omega_P^2 = \frac{Ne^2}{\varepsilon_0 m} \]

defines the "Plasma Frequency"

1) Copper metal at room temperature:
\[ N \approx 9 \times 10^{29} \text{ m}^{-3} \Rightarrow \omega_P \approx 8.7 \text{ eV} \text{ or } 2.1 \text{ PHz} \text{ or } \]
\[ ... \text{ "70660 cm}^{-1}" \text{ or } \lambda_P = 120 \text{ nm} \]

2) Seawater (~ 0.6 M salt):
\[ \omega_P = 5 \times 10^{12} \text{ s}^{-1} \text{ ["THz"]} \]

3) Earth's Ionosphere:
\[ N \approx 10^{10} - 10^{12} \text{ m}^{-3} \Rightarrow \omega_P \approx 1 - 10 \text{ MHz} \Rightarrow \lambda_P = 1 \text{ km} \]
The Plasmon is a Macroscopic Quantum Phenomenon

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 – Evanesence in both media

Total Internal Reflection

- Critical angle
- “Evanescent” wave does not propagate in air

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

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

(a)

(b)

Energy (eV)

Expanded to see rotational energy levels

Expanded to see vibrational energy levels

Electronic levels

Vibrational levels

Rotational levels

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**Vibrational spectroscopy: CO$_2$**

A Dipole Moment = charge imbalance in the molecule

**Infrared spectroscopy**

**Raman spectroscopy: a polarizability**
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, Rubens, and Snow, 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 and by Ångstrom. Ångstrom 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.

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, oxyhaemoglobin, potassium alum, ammonium alum, and ammonium-iron alum.
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

\[ I = I_0 e^{-\alpha L} \equiv I_0 \times 10^{-\varepsilon CL} \]

\[ \Rightarrow \varepsilon = \frac{1}{2.303} \sigma N_A \]

“Beer’s Law”

C concentration in mM (milliMoles per litre)
Cross-sections: Free electron

\[ E = mc^2 \]

\[ E = \frac{e^2}{4\pi\varepsilon_0 r_e} \Rightarrow r_e = \frac{e^2}{4\pi\varepsilon_0 mc^2} = 2.82 \times 10^{-13} \text{ cm} \]

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

1 barn = \(1 \times 10^{-24}\) cm\(^2\)

Bohr: “Form factor”
QM result

\[ \sigma_a = \frac{8\pi}{3} r_e^2 |f(\omega)|^2 \]

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

Critical mass:

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

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What can we learn from IR spectroscopy?

- **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

G. Herzberg
Cross-sections: Near Resonance

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

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

An enormous range in values....

<table>
<thead>
<tr>
<th>Process</th>
<th>Crosssection (cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman</td>
<td>$10^{-31}$</td>
</tr>
<tr>
<td>IR absorption</td>
<td>$10^{-18}$-$10^{-21}$</td>
</tr>
<tr>
<td>Single molecule fl</td>
<td>$10^{-13}$</td>
</tr>
<tr>
<td>Neutrino reaction</td>
<td>$10^{-43}$</td>
</tr>
</tbody>
</table>
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)

Martin & Holman (LBNL)
Atherosclerotic plaque imaging between 5 and microns in wavelength

Optical microscope

Polarizing microscope

SNIM $\lambda = 6.05 \mu m$

$1650 \text{ cm}^{-1}$

(Amide I)

SNIM $\lambda = 5.75 \mu m$

$1735 \text{ cm}^{-1}$

(Lipid C=O)

Jeung et al
First Mid-infrared images of single living cells

Increased contrast at the lipid absorption wavelength \(~ 1750\text{cm}^{-1}\). 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 $\sim$ magnetic dipole

Transmitted Power falls like $\sim r^{-6}$

$$\eta_B = \frac{64(kr)^4}{27\pi^2}$$

Surface Plasmon

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

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

Jackson, Chapter 9. Bethe (corrected by Beukamp); Genet, Ebbesen Nature (2007) review
Surface Plasmon explains why Bethe’s calculation was wrong for real metals

Amazing:

Plasmon assisted transport of entangled photons

Surface Plasmons can give rise to extraordinary phenomena (Raman, IR…)
History: Enhancement of IR absorption by metal

Why Physicists talking Chemistry is inherently dangerous

Hartstein, Kirtley & Tsang, PRL (1980)

Problem: Not nitrobenzoic acid.
Vacuum pump oil!

Plasmon Enhancement confirmed by many groups

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)

Surface enhanced infrared absorption (SEIRA) alkanethiol
Surface plasmon at IR region with nanostructures: Mid-IR EOT of rectangular coaxial nanoaperture array

Phase matching condition

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

\[ n_{SPP} = \frac{\beta c}{\omega} \quad \lambda_{SPP} (n, m) = \frac{n_{SPP}a_0}{\sqrt{n^2 + m^2}} \]

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

CaF2 Substrate → PMMA Resist → E-Beam Write

Lift-Off → Au Deposition → Develop

Plasmonic Arrays
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 $\text{CH}_2 \sim 3 \times 10^5$

Still higher enhancements are possible but distort the spectra
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
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