Spectroscopy: Optical and Electronic

Spectroscopy is the use of light, sound or particle emission to study matter. It originated through the study of visible light dispersed, according to its wavelength, by a prism. Later, the concept was expanded greatly to comprise any interaction with radiative energy as a function of its wavelength or frequency.

The data that is obtained from spectroscopy is called a spectrum. A spectrum can be used to obtain information about the specimen's energy states, its atomic or molecular arrangements, and related processes.

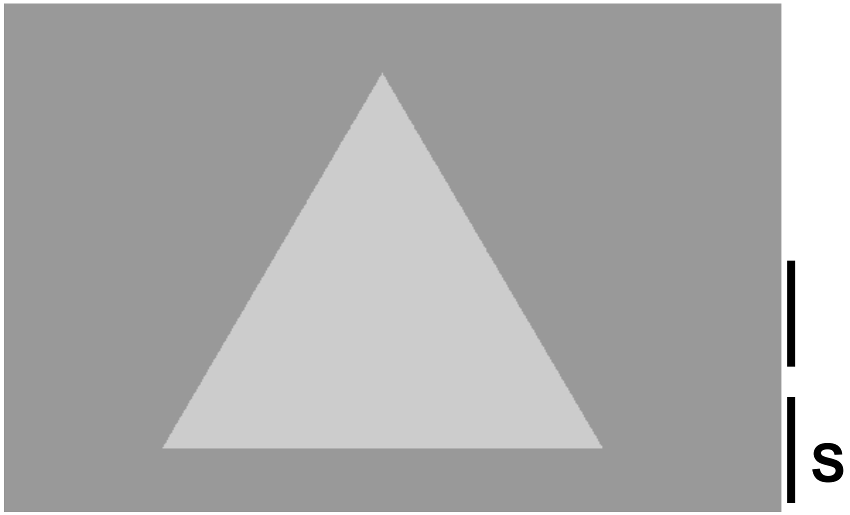
Nature of the interaction between radiation and material

Types of spectroscopy can be distinguished by the nature of the interaction between the probing radiation and the material.

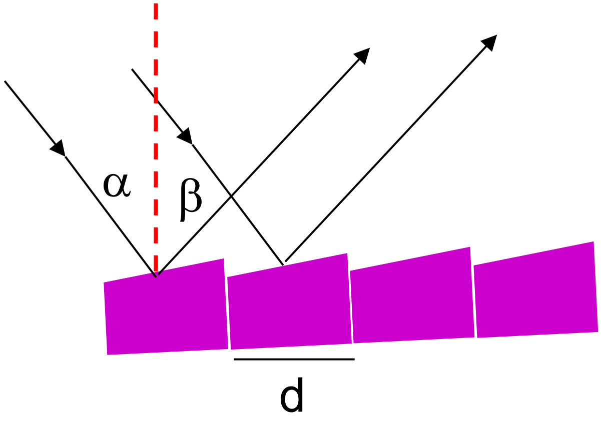
- Elastic Scattering: incident radiation reflected or transmitted by a material without energy loss.
- Inelastic Scattering: involving an exchange of energy between the radiation and the matter that shifts the wavelength of the scattered radiation.
- Refraction: the ability of a medium to impede or slow the transmittance of energy.
- Absorption: measuring the fraction of incident energy transmitted through the material.
- Emission: radiative energy released by the material.
- Resonance: radiative energy couples two quantum states of the material in a coherent interaction.

Spectroscopy originates from the dispersion of light through a prism.

Prism

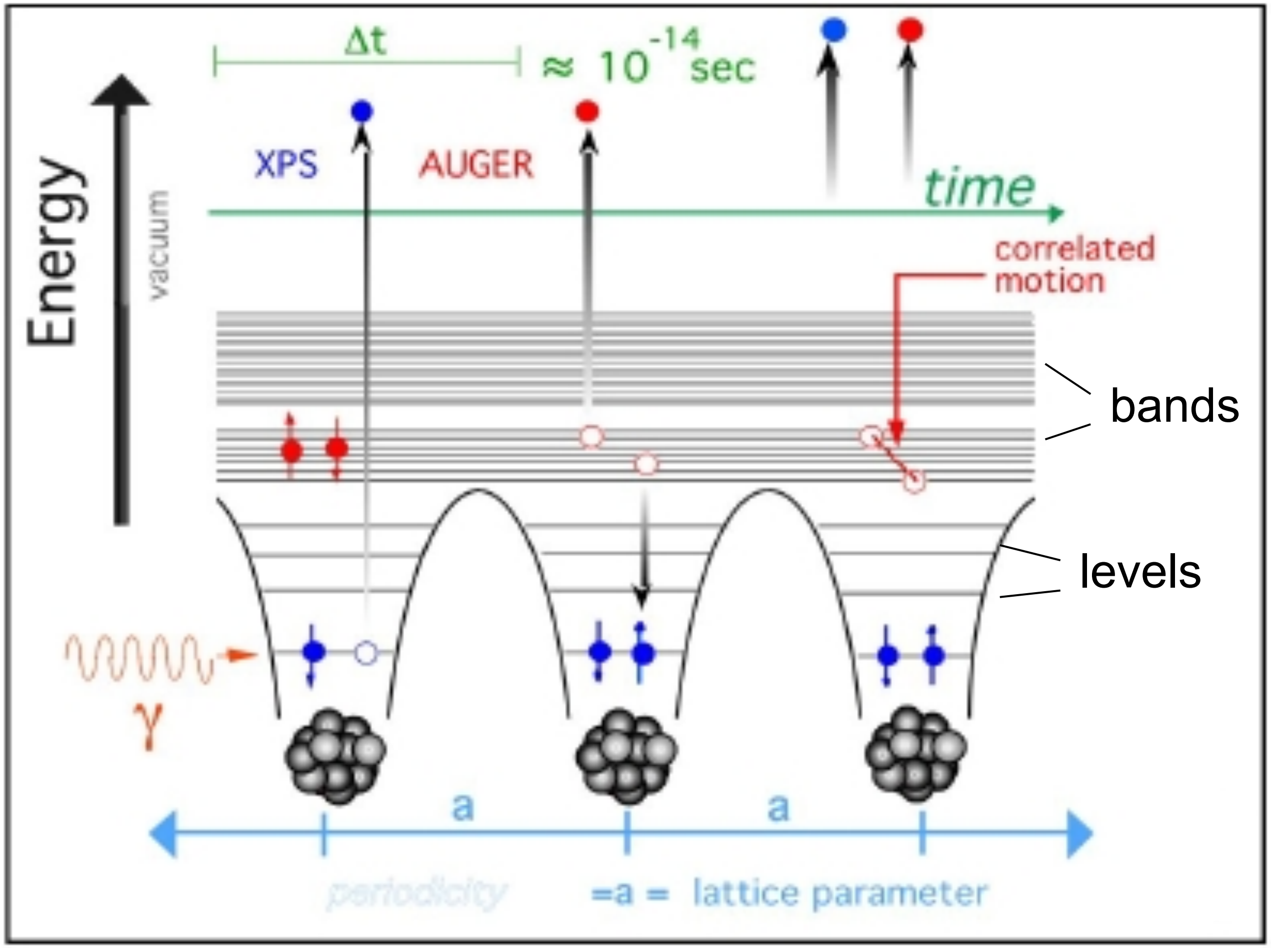


Grating



$$\Delta s = d\,(\sin\alpha - \sin\beta) = m\lambda$$

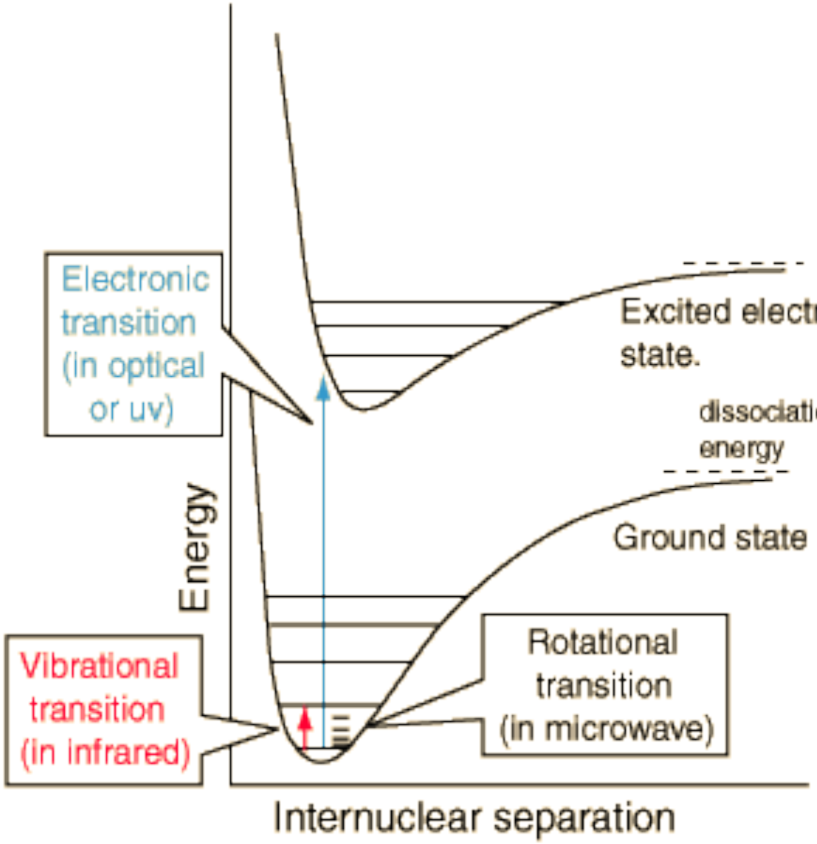
Energy levels and bands

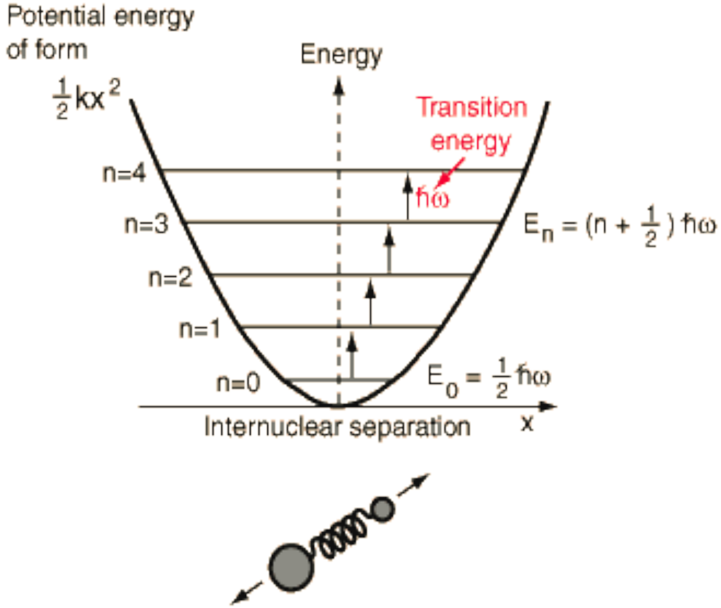


Electronic and vibrational levels

Born-Oppenheimer Approximation

$$\psi_{\text{molecule}}(\vec{r}_i,\vec{R}_j) = \psi_{\text{electrons}}(\vec{r}_i,\vec{R}_j)\,\psi_{\text{nuclei}}(\vec{R}_j)$$





x=0 represents the equilibrium separation between the nuclei.

Transition between two quantum states

Fermi's golden rule

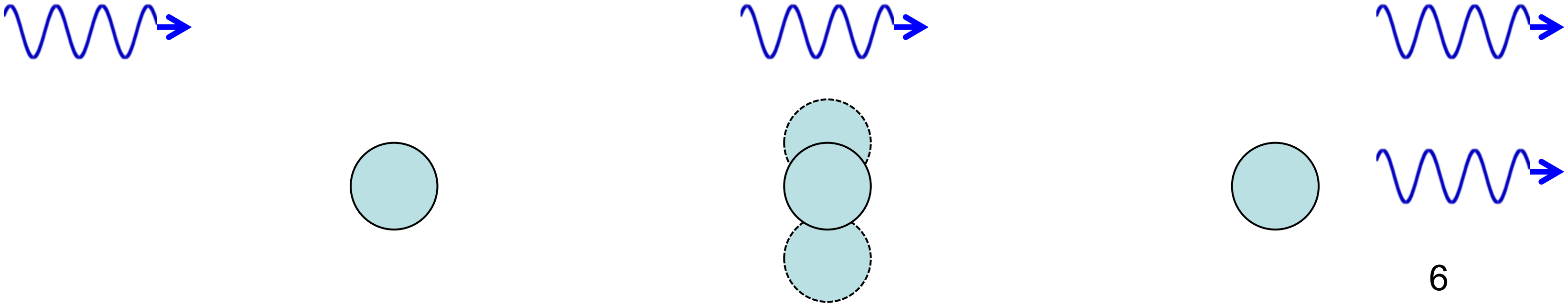
Transition rate:

$$T_{i\rightarrow f} = \frac{2\pi}{\hbar}\left|\langle f|H'|i\rangle\right|^2 \rho,$$

Transition probability

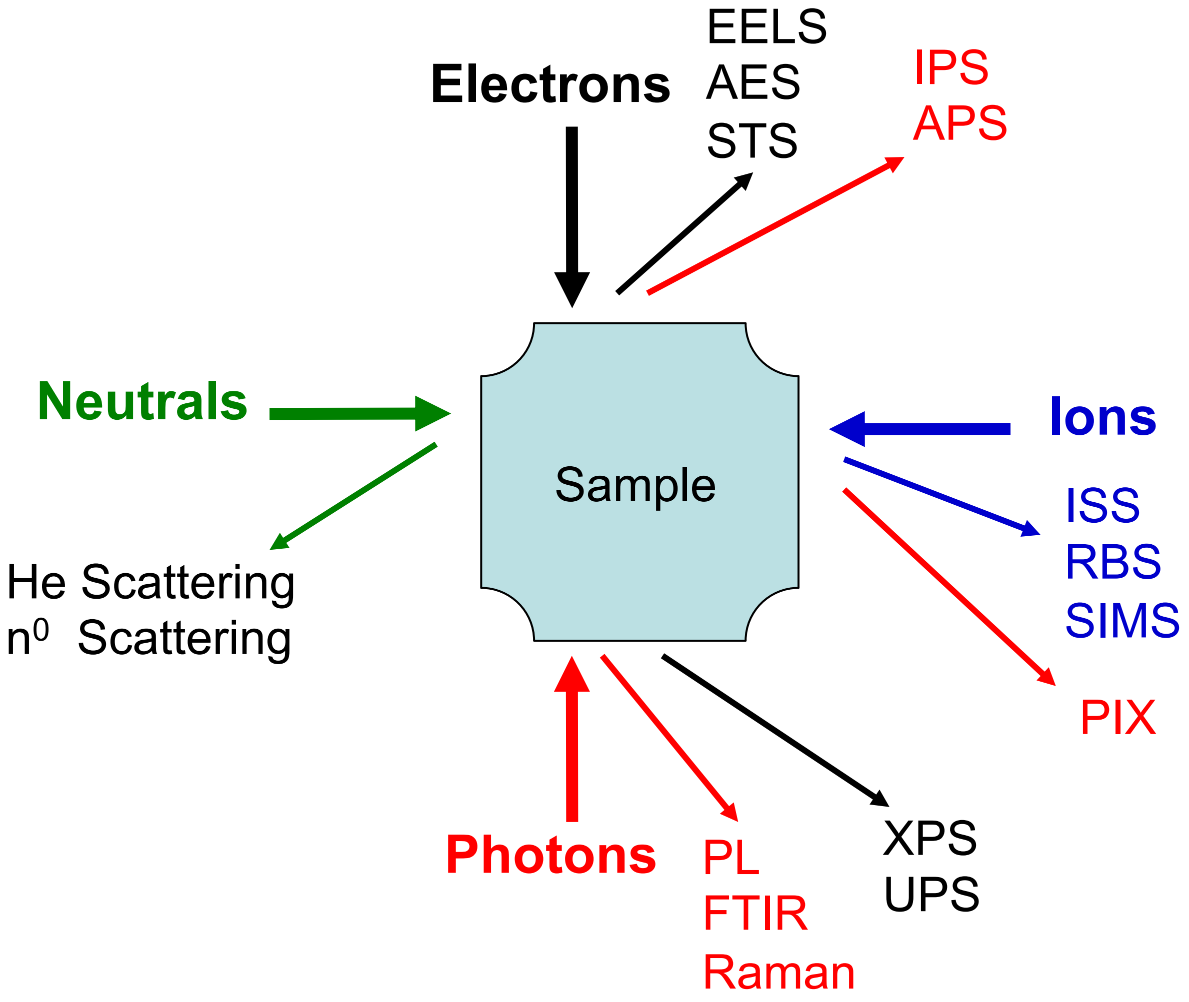
Density of final states

Transition probability is determined by the wavefunction overlapping of initial and final states, and dictated by the selection rules reflecting the nature of interaction *H'*.



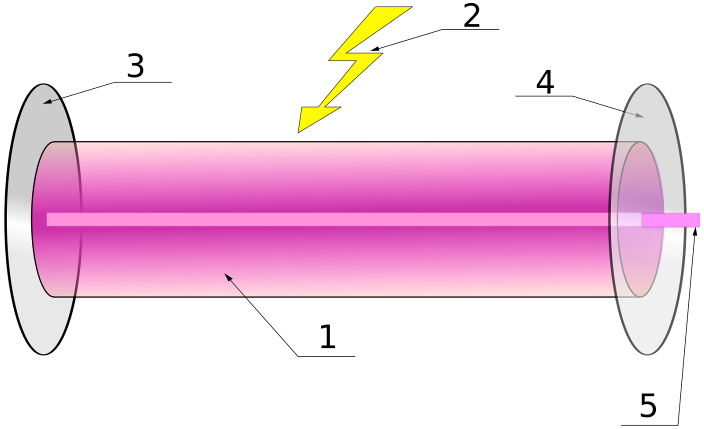
Various spectroscopic methods

Spectroscopy is the use of light, sound or particle emission to study matter.

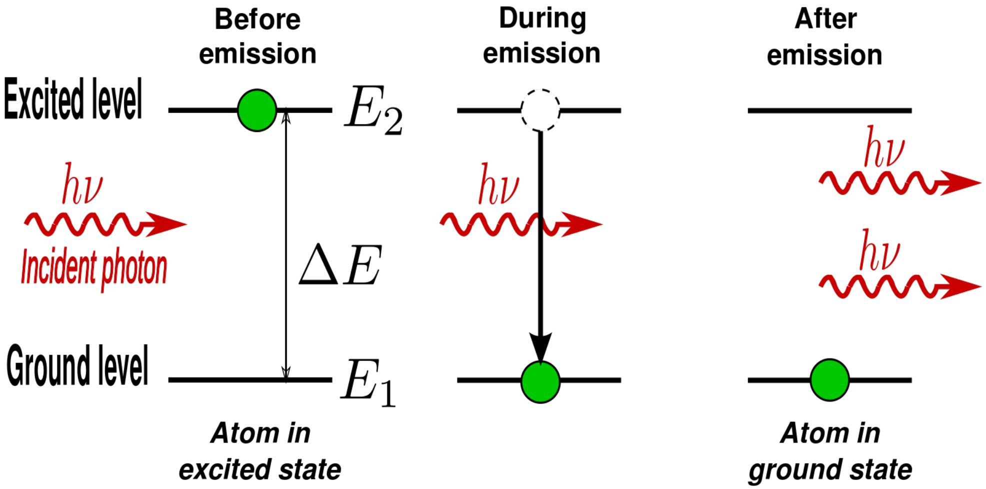


Laser

The term "laser" originated as an acronym for "light amplification by stimulated emission of radiation”.



1. Gain medium
2. Laser pumping energy
3. High reflector
4. Output coupler
5. Laser beam



$$E_2 - E_1 = \Delta E = h\nu$$

Types of Lasers

Lasers are commonly designated by the type of lasing material employed, which can be a solid, gas, liquid or semiconductor.

Solid-state lasers have lasing material distributed in a solid matrix (such as the ruby or neodymium:yttrium-aluminum garnet "Yag" lasers). The neodymium-Yag laser emits infrared light at 1,064 nm.

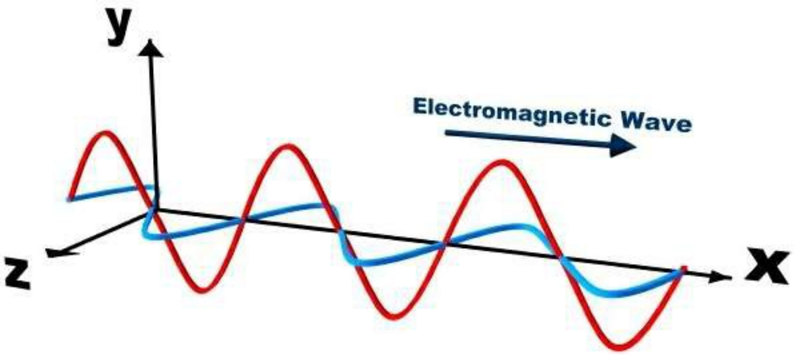
Gas lasers (helium and helium-neon, HeNe, are the most common gas lasers) have a primary output of visible red light. CO_2 lasers emit energy in the far-infrared, and are used for cutting hard materials.

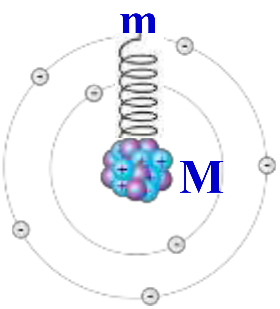
Excimer lasers use reactive gases, such as chlorine and fluorine, mixed with inert gases such as argon, krypton or xenon. When electrically stimulated, a pseudo molecule (dimer) is produced. When lased, the dimer produces light in the ultraviolet range.

Dye lasers use complex organic dyes, such as rhodamine 6G, in liquid solution or suspension as lasing media. They are tunable over a broad range of wavelengths.

Semiconductor lasers, sometimes called diode lasers, are not solid-state lasers. These electronic devices are generally very small and use low power. They may be built into larger arrays, such as the writing source in some laser printers or CD players.

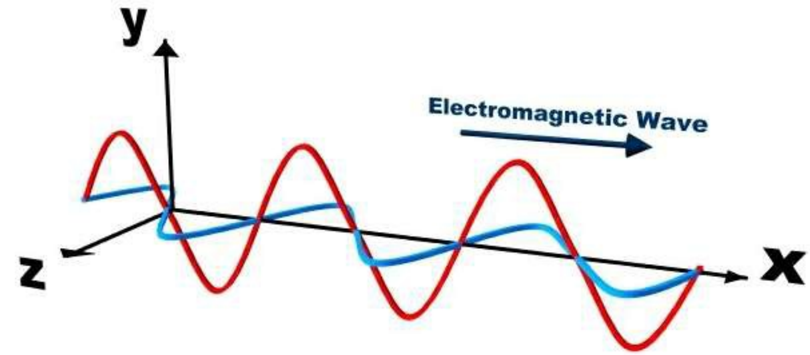
Interaction of Electron and E Field

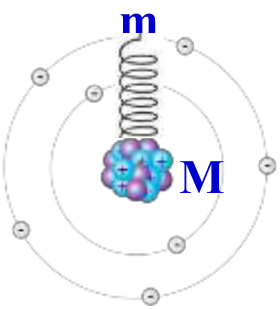


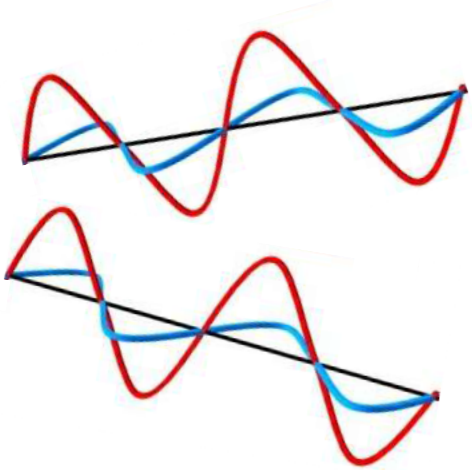


- Electrons response to the E field.
- Electrons □ Polarizability □ Susceptibility □ Dielectric function □ Refraction index.
- Resonance will result in absorption and dispersion

Re-emission and Resonance

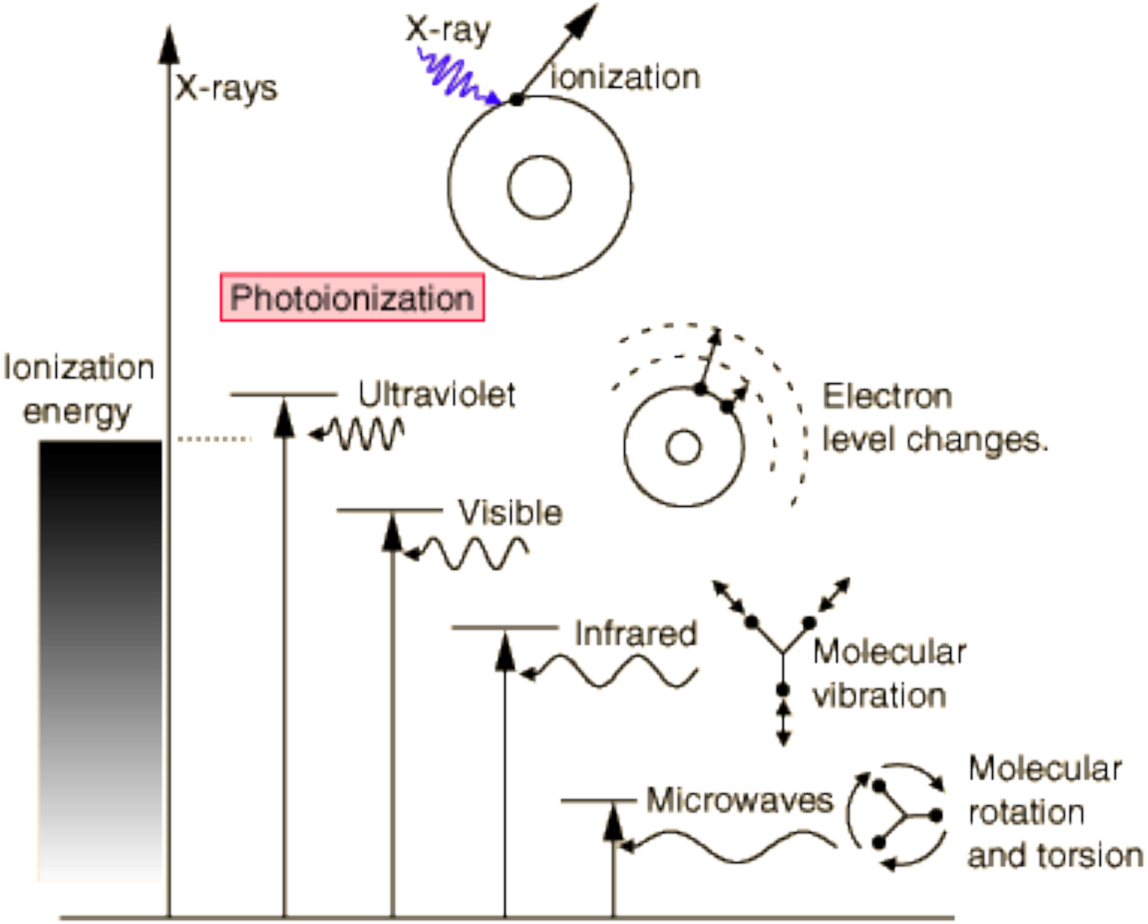




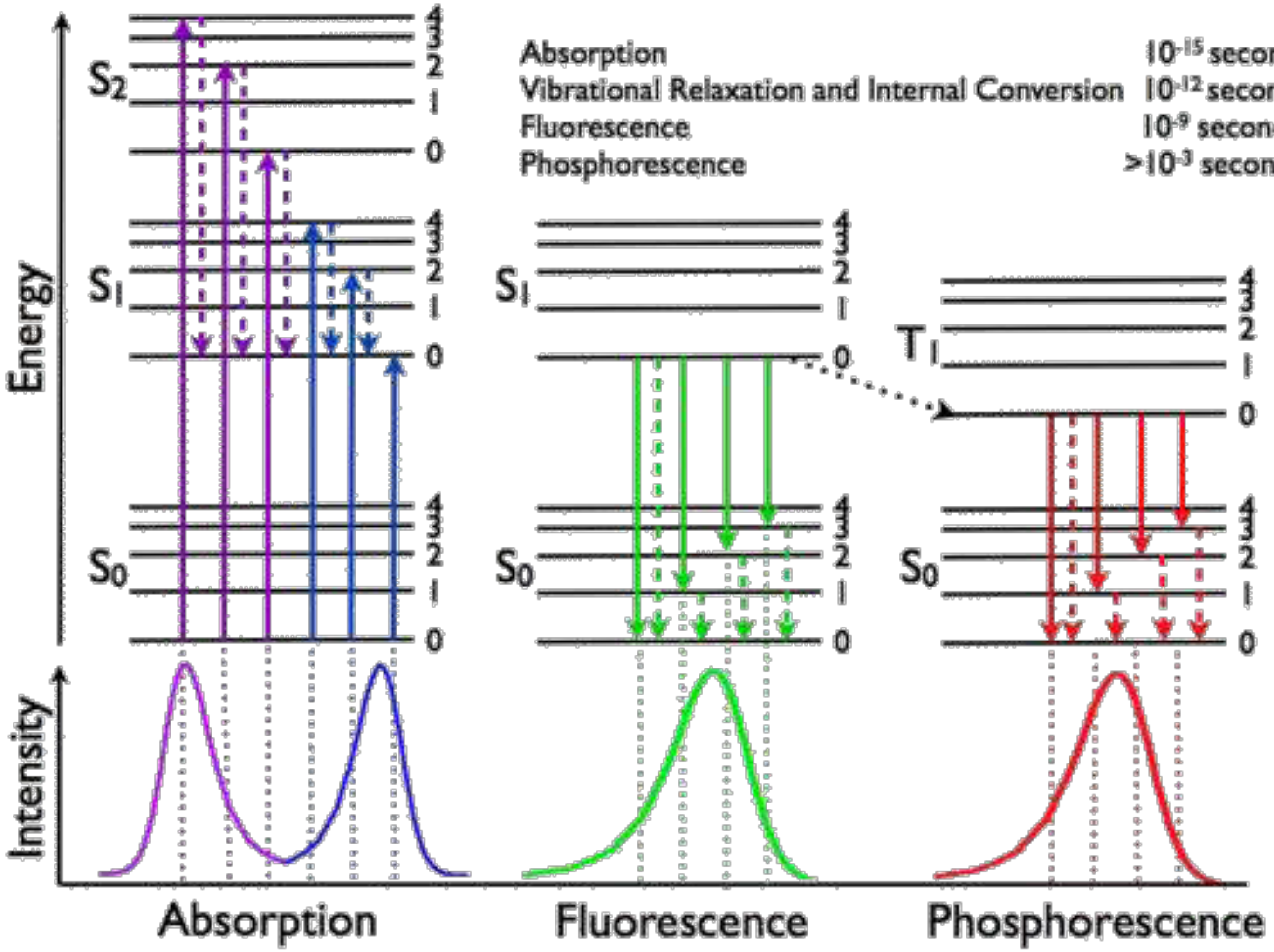


- Nonresonance $\xrightarrow{\text{1 -10 fs}}$ re-emission **(scattering)**
- Resonance : absorption $\xrightarrow[\text{0.1 -100 ns}]{}$ re-emission **(photoluminescence)**

Resonance

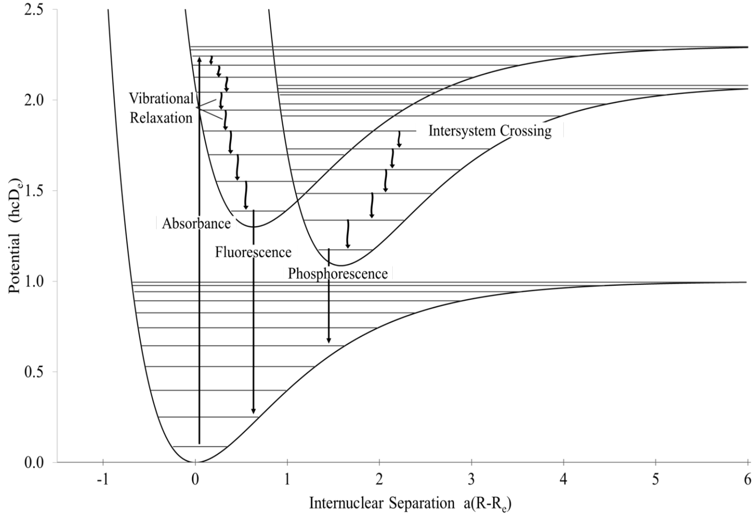

X-ray
ionization
X-rays
Photoionization
Ionization energy
Ultraviolet
Electron level changes.
Visible
Infrared
Molecular vibration
Microwaves
Molecular rotation and torsion

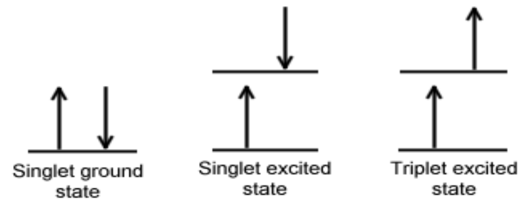
Energy Diagram

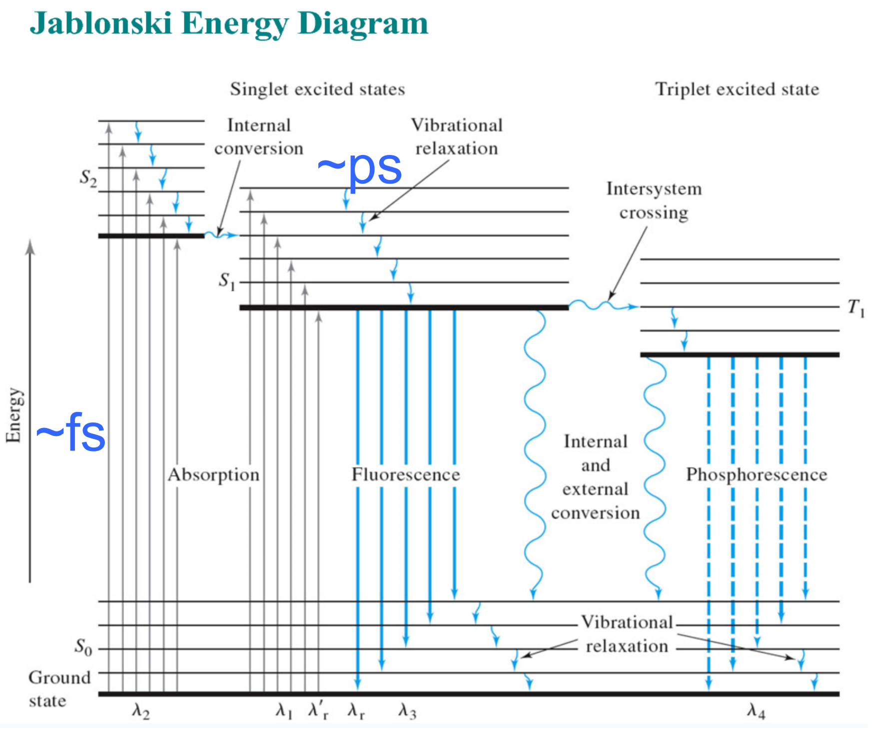


Fluorescence Spectroscopy

Fluorescence spectroscopy, usually using ultraviolet light analyzes fluorescence from a sample. The beam of light excites the electrons in molecules of certain compounds and causes them to emit light; typically, but not necessarily, visible light.







~ps

~fs

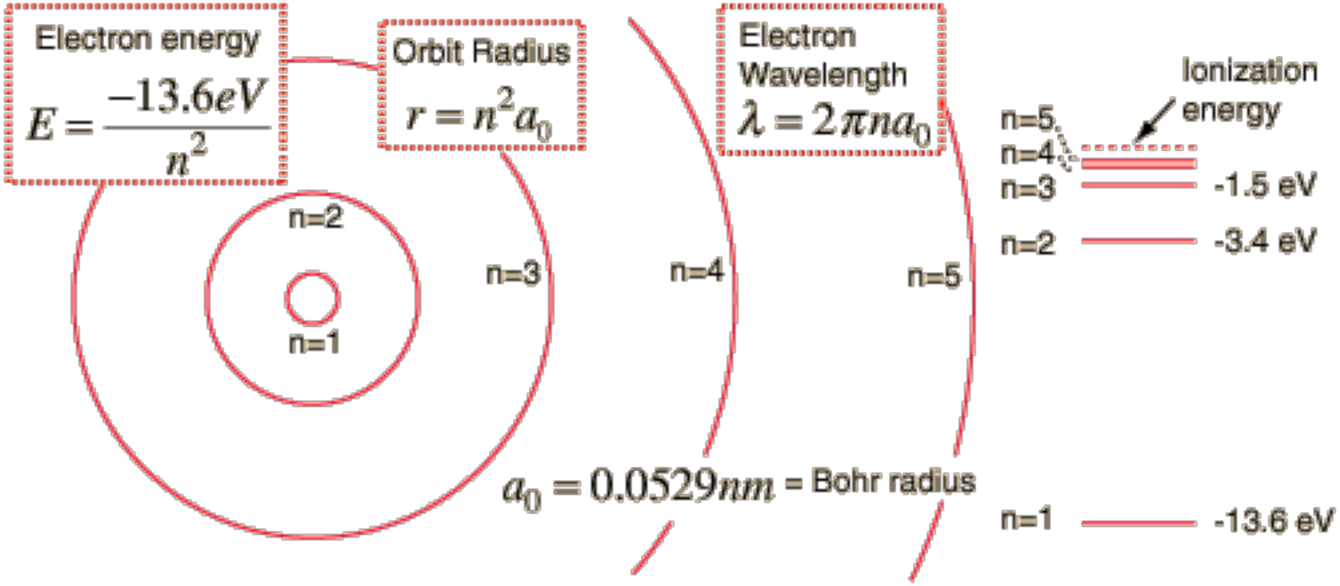
~ns

~ms

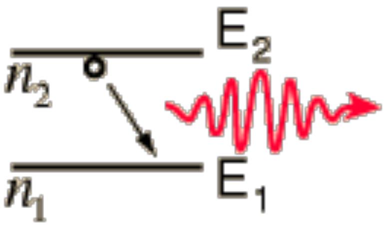
Bohr model of hydrogen atom

$$E = -\frac{Z^2 m e^4}{8 n^2 h^2 \varepsilon_0^2} = \frac{-13.6 Z^2}{n^2} eV \qquad r = \frac{n^2 h^2 \varepsilon_0}{Z \pi m e^2} = \frac{n^2 a_0}{Z}$$

$$a_0 = 0.0529 nm = Bohr\ \ radius$$



Electron Transitions



A downward transition
involves emission of
a photon of energy:

$$E_{photon} = h\upsilon = E_2 - E_1$$

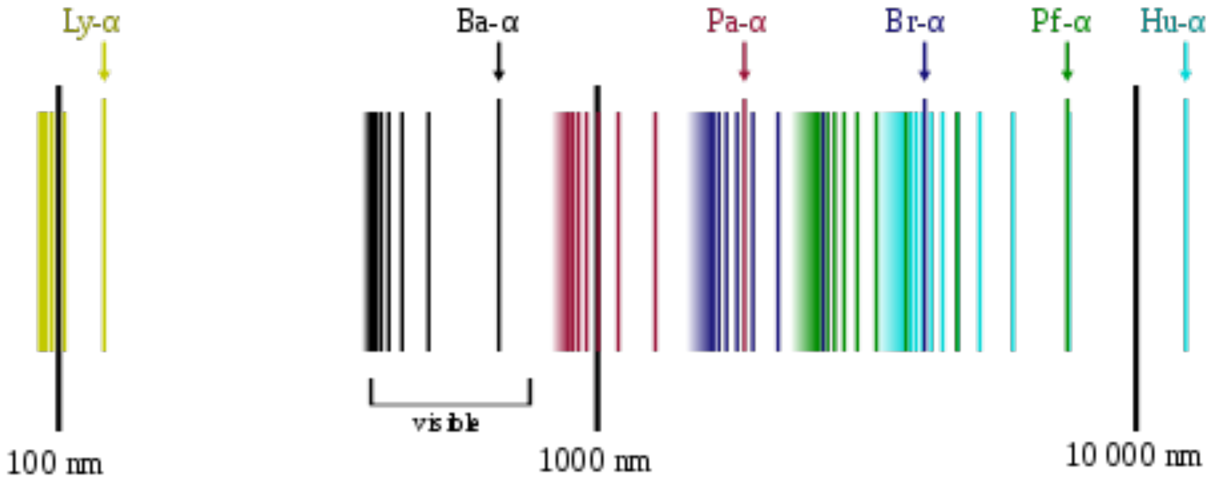
Given the expression for the energies of the hydrogen electron states:

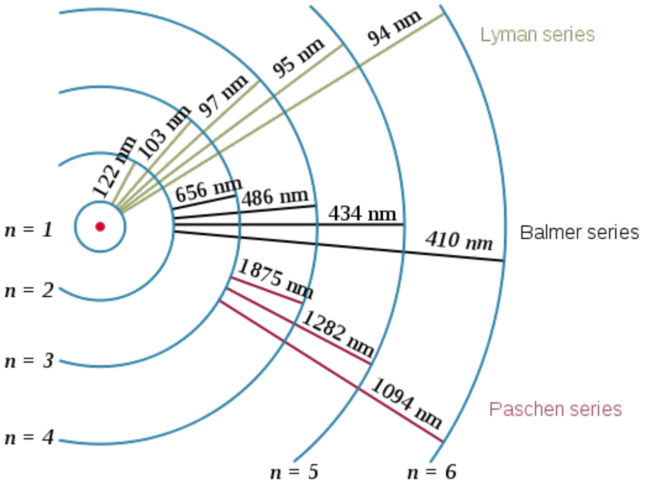
$$h\upsilon = \frac{2\pi^2 m e^4}{h^2}\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right] = -13.6\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right]\text{eV}$$

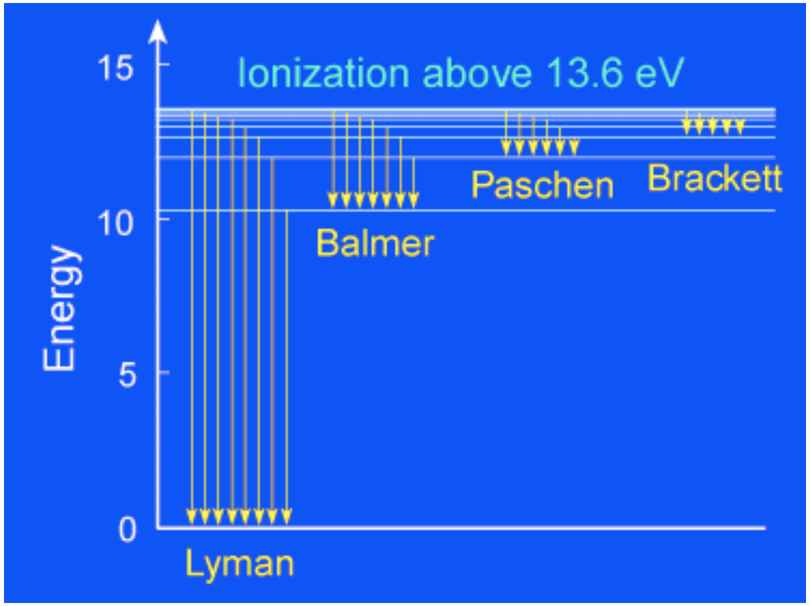
Fermi's golden rule is a way to calculate the transition rate (probability of transition per unit time) between two eigenstates

$$T_{i\rightarrow f} = \frac{2\pi}{\hbar}\left|\langle f|H'|i\rangle\right|^2\rho,$$

Absorption spectra of atomic hydrogen





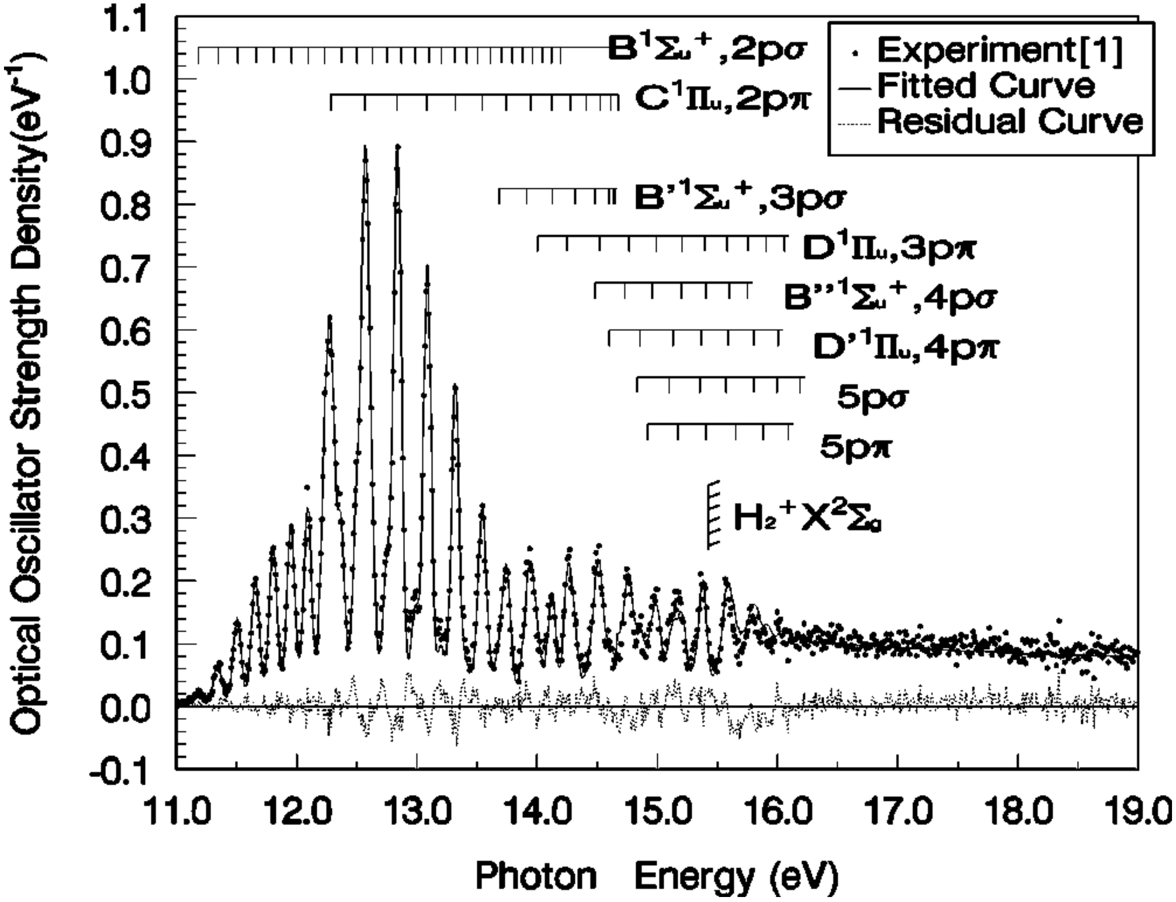


Infrared Spectroscopy

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately 14000–4000 cm^{-1} (0.8–2.5 μm wavelength) can excite harmonic vibrations. The mid-infrared, approximately 4000–400 cm^{-1} (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately 400–10 cm^{-1} (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy.

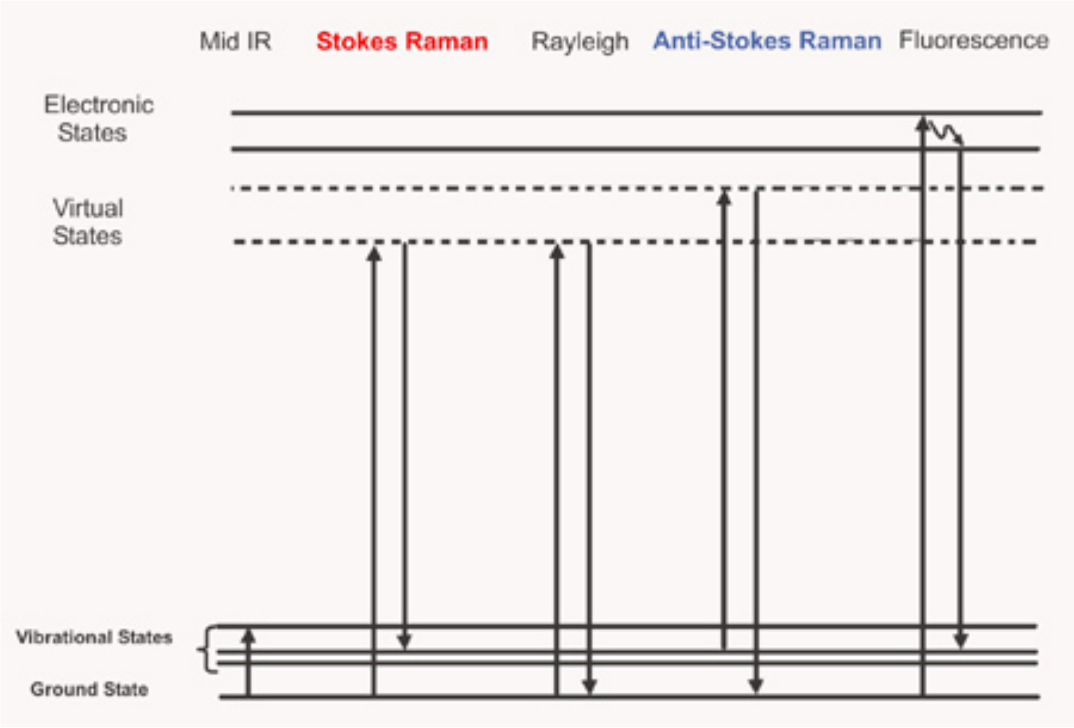
Absorption spectra of molecular hydrogen

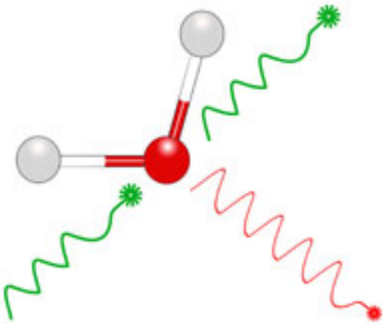


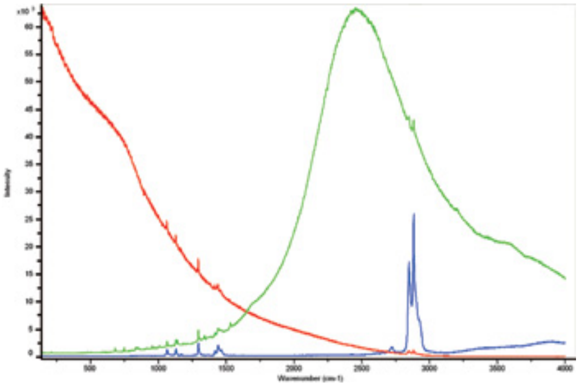
Zhi Ping Zhong et al., Phys. Rev. A **60**, 236 (1999)

Raman Spectroscopy

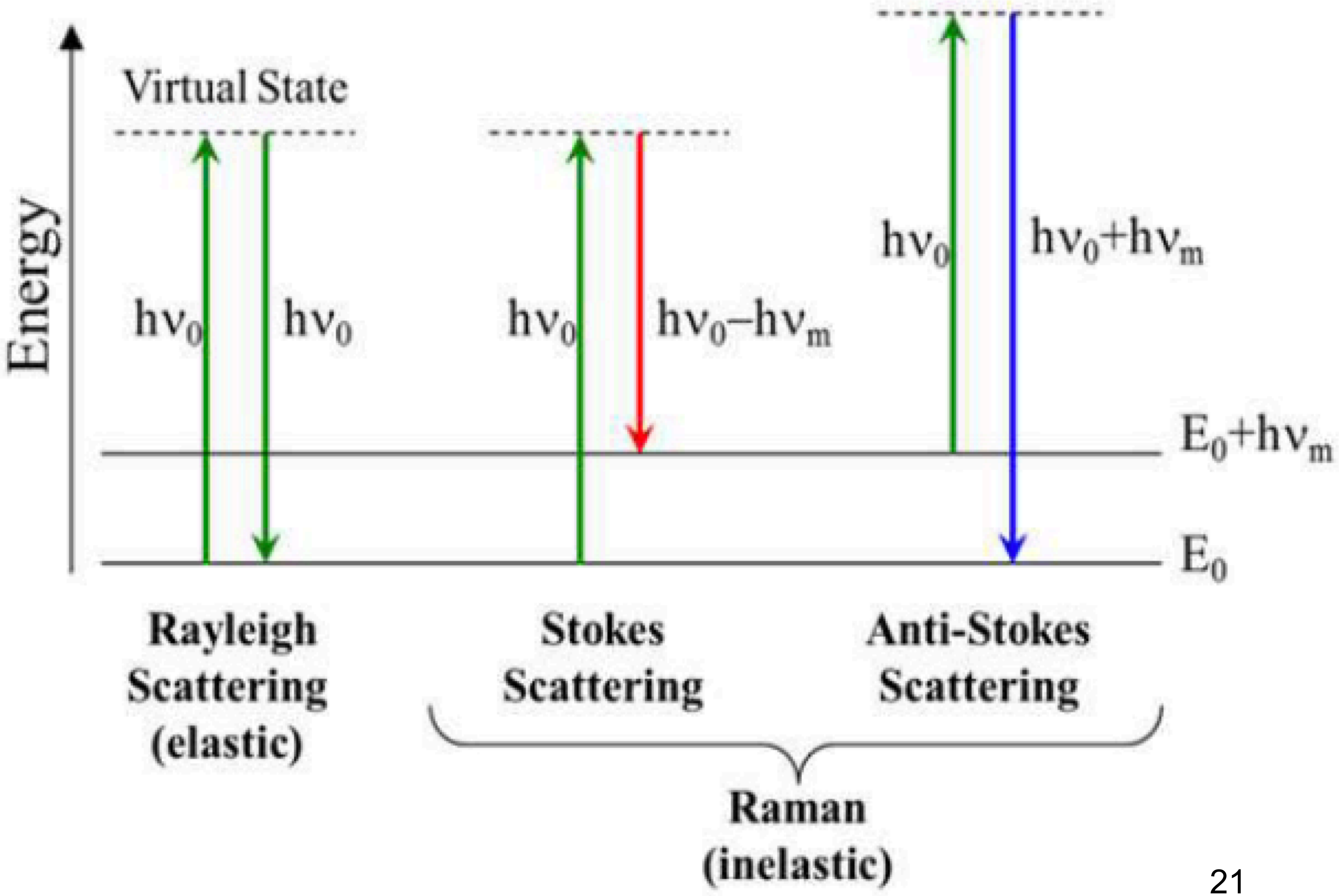
Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a system. Raman spectroscopy is commonly used in chemistry to provide a fingerprint by which molecules can be identified.

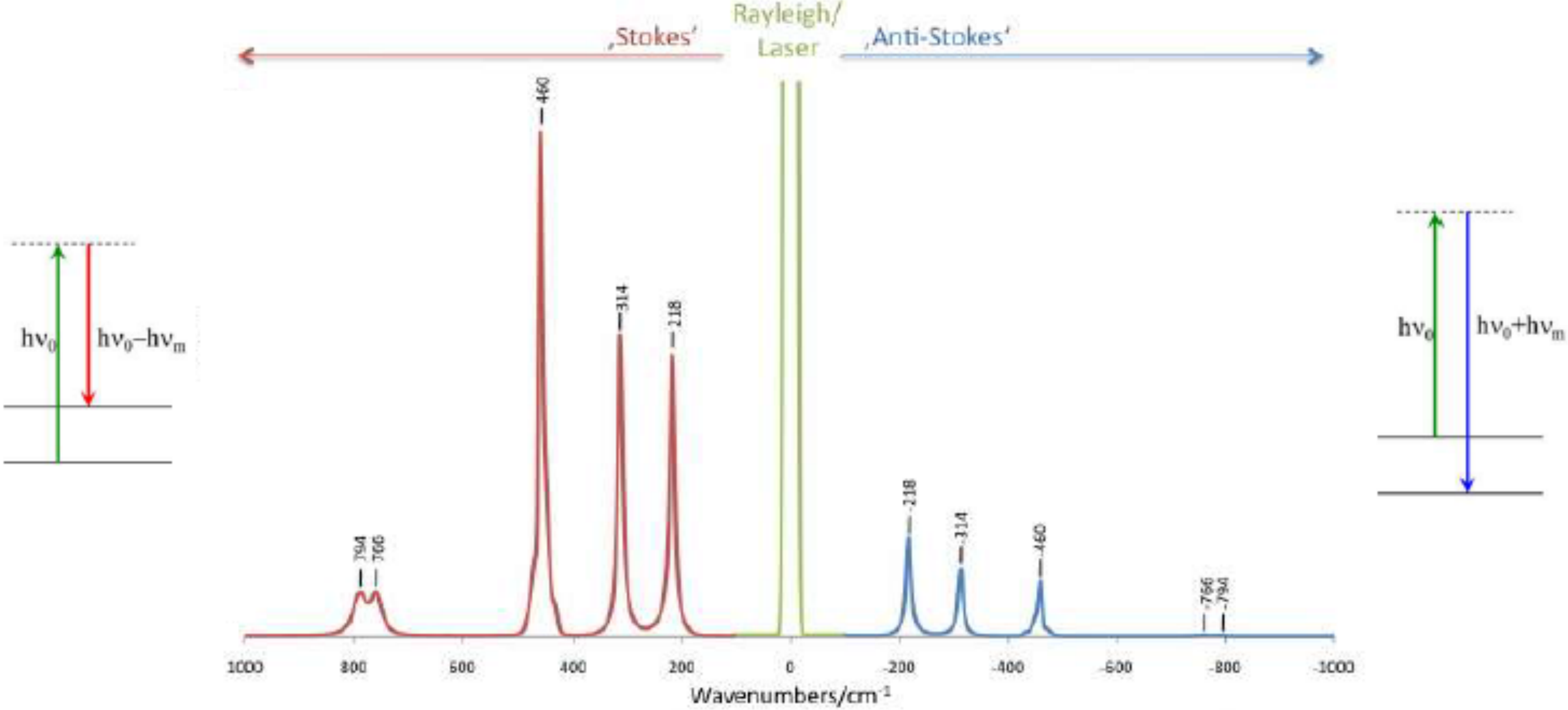






Raman and Rayleigh Scattering




‚Stokes'
Rayleigh/
Laser
‚Anti-Stokes'
794
766
460
314
218
-218
-314
-460
-766
-794
1000
800
600
400
200
0
-200
-400
-600
-800
-1000
Wavenumbers/cm-1
hν0
hν0–hνm
hν0
hν0+hνm

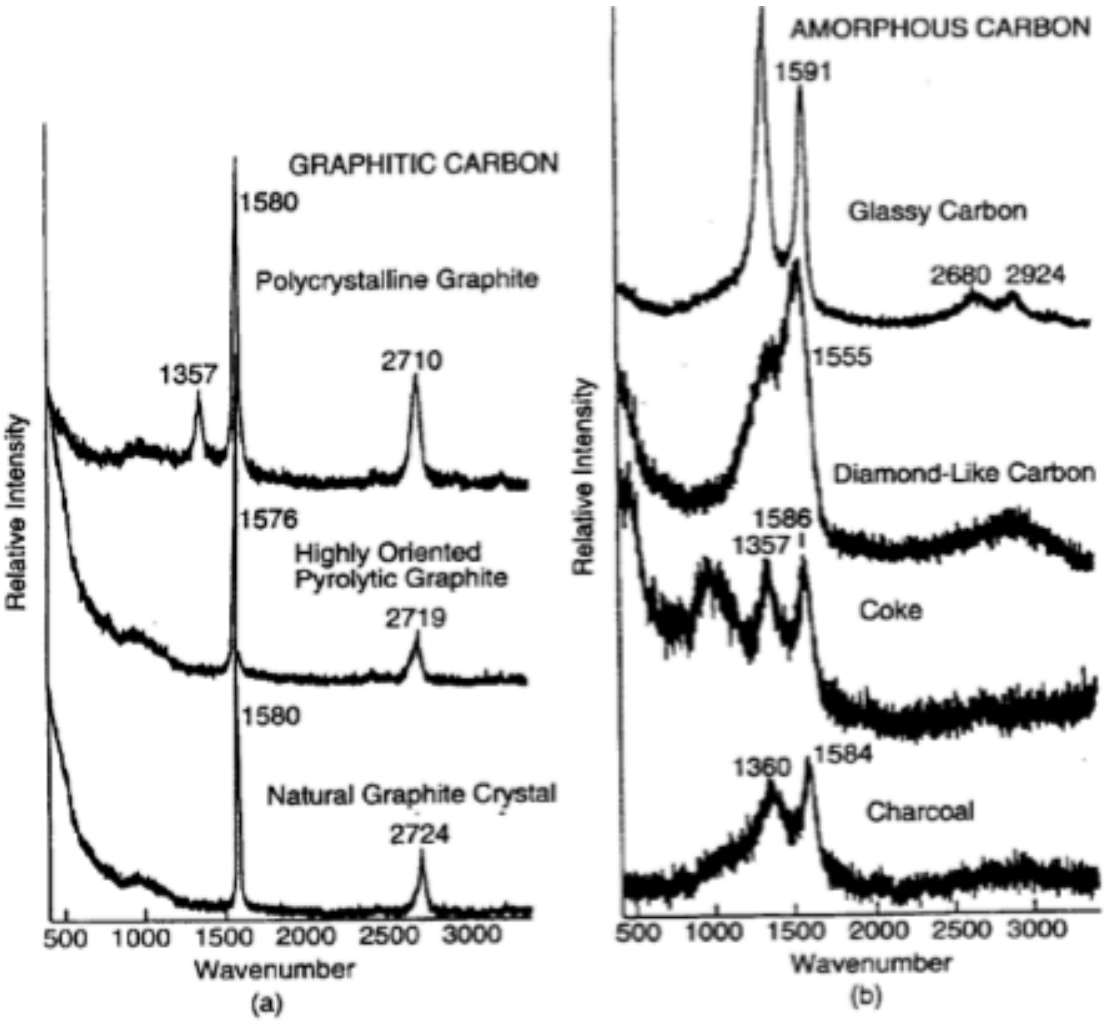
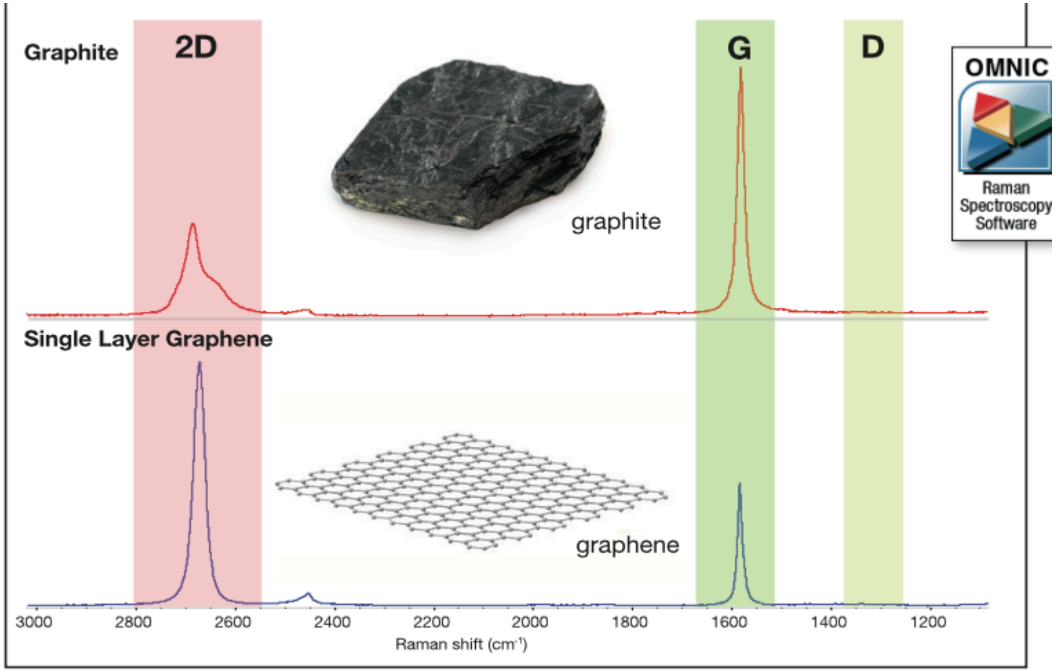
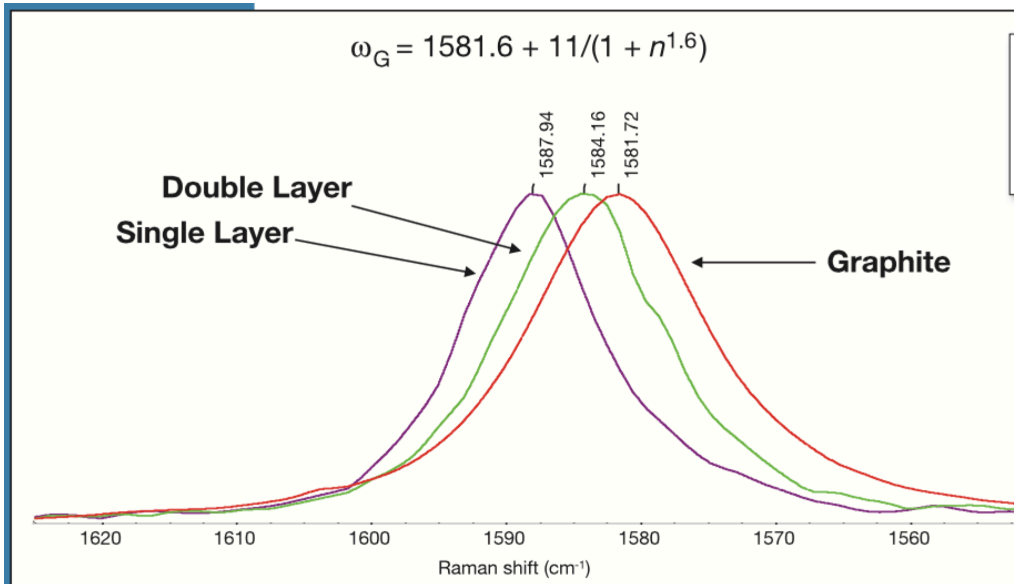


Figure 8.19. Raman spectra of (a) crystalline graphites and (b) noncrystalline, mainly graphitic, carbons. The *D* band appears near 1355 cm^{-1} and the *G* band, near 1580 cm^{-1}. [From D. S. Knight and W. B. White, *J. Mater. Sci.* **4**, 385 (1989).]





$$\omega_G = 1581.6 + 11/(1 + n^{1.6})$$

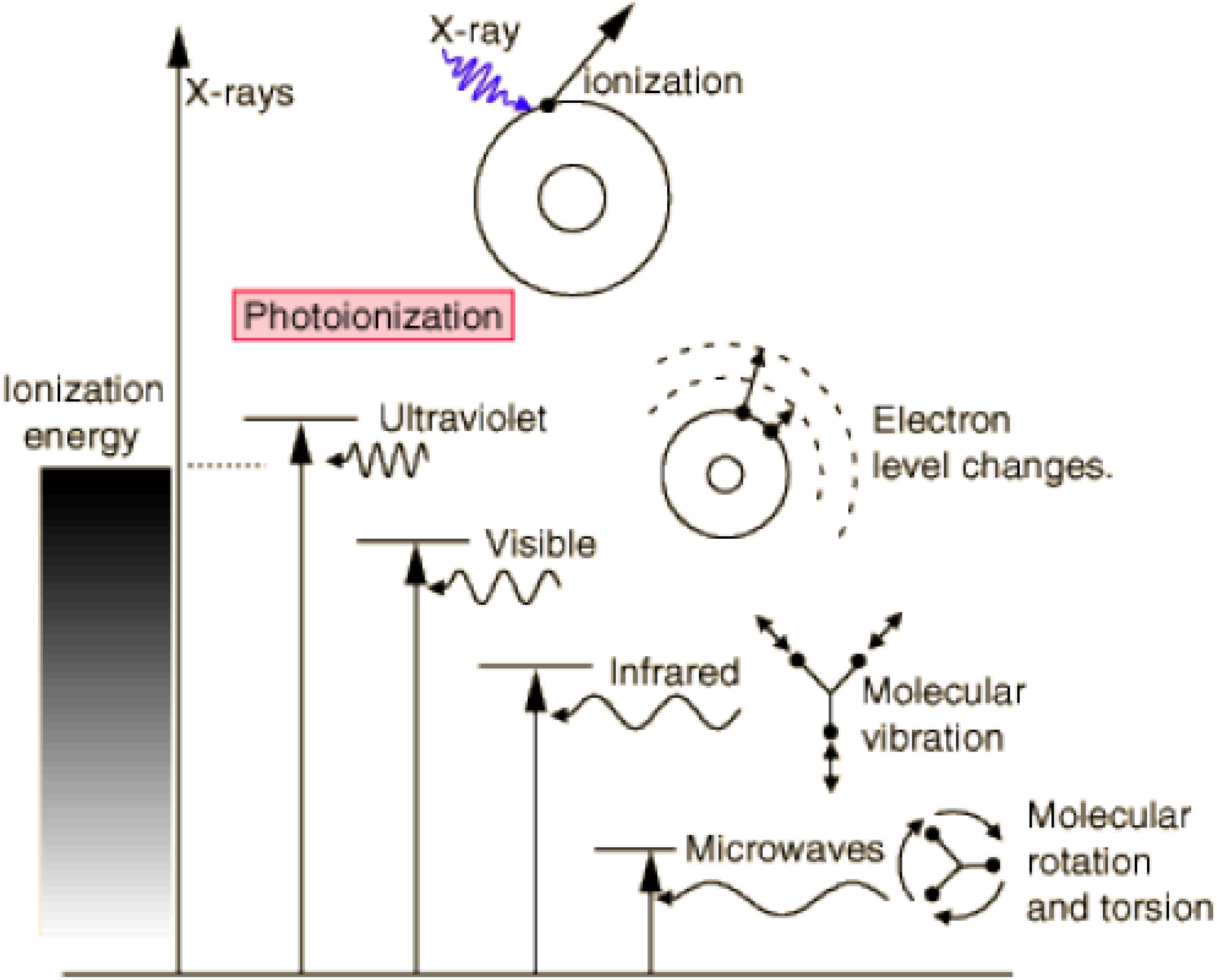
Wang, Hui; Cao, Xuewei; Feng, Min; and Lan, Guoxian
J. Raman Spectrosc. **2009**, *40*, 1791-1796

Spectroscopy at nanometer scale

1. Spectroscopy vs. Microscopy

1. Physics and Chemistry of nanomaterials

Resonance

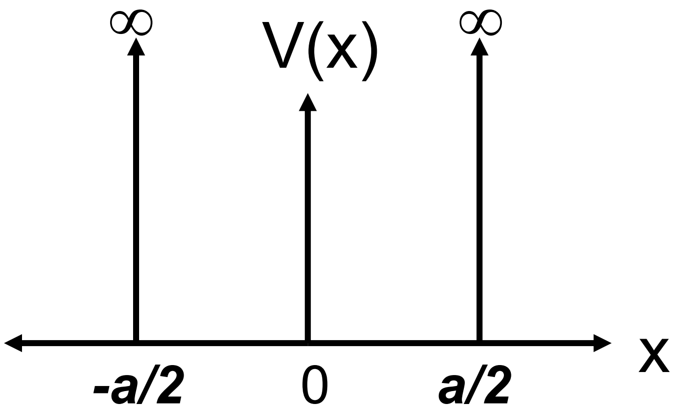

X-rays
X-ray
ionization
Photoionization
Ionization energy
Ultraviolet
Electron level changes.
Visible
Infrared
Molecular vibration
Microwaves
Molecular rotation and torsion

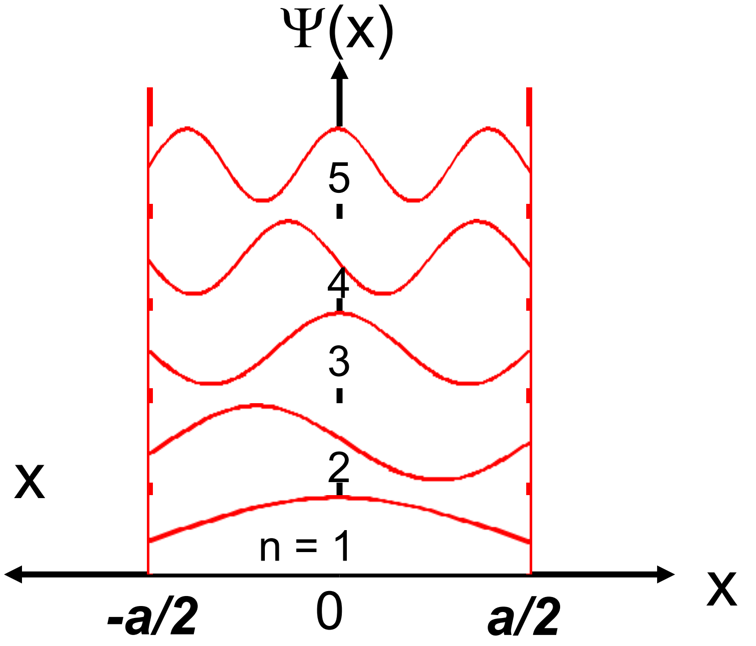
Microscopy is the science of investigating small objects that are too small for the naked eye. The microscopic study involves revelation of the structure and morphology of the matter under investigation.

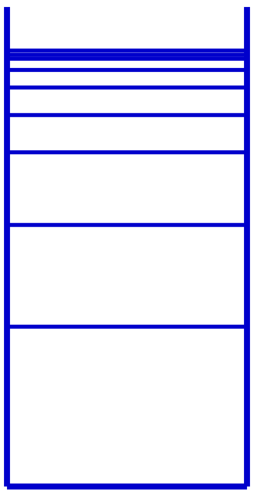
Spectroscopy is the study of the interaction between matter and radiated energy. With the mechanism of "resonance", the characteristic nature of the matter can be probed.

Both microscopic and spectroscopic techniques are essential for nanoscience research.

One dimensional size effect







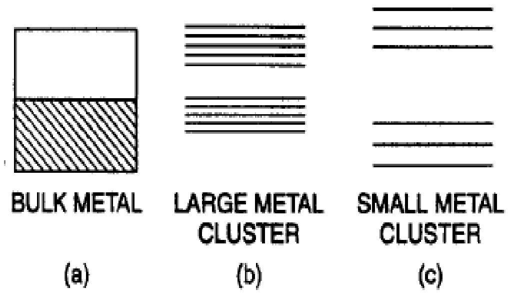
Atomic Levels

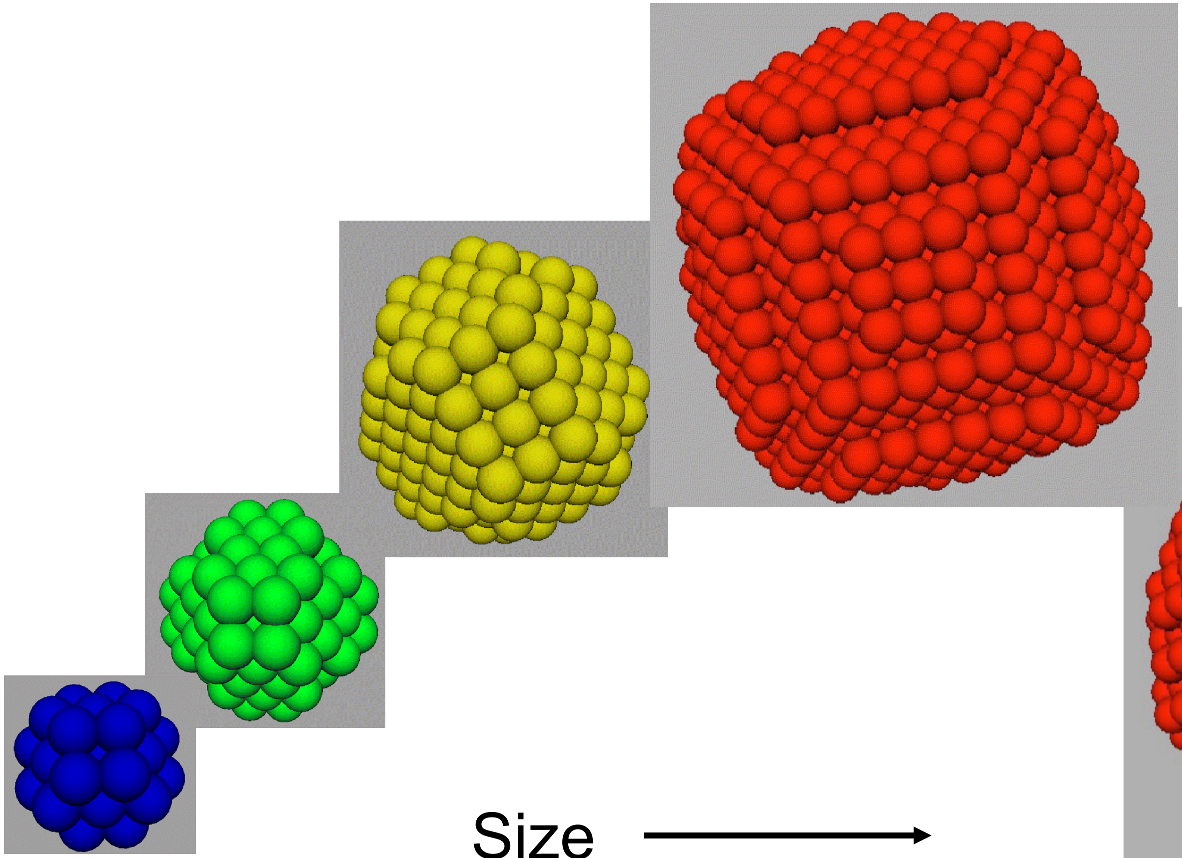
$$\Psi(x) = \begin{cases} \sin(n\pi x/a),\ n \text{ even} \\ \cos(n\pi x/a),\ n \text{ odd} \end{cases}$$

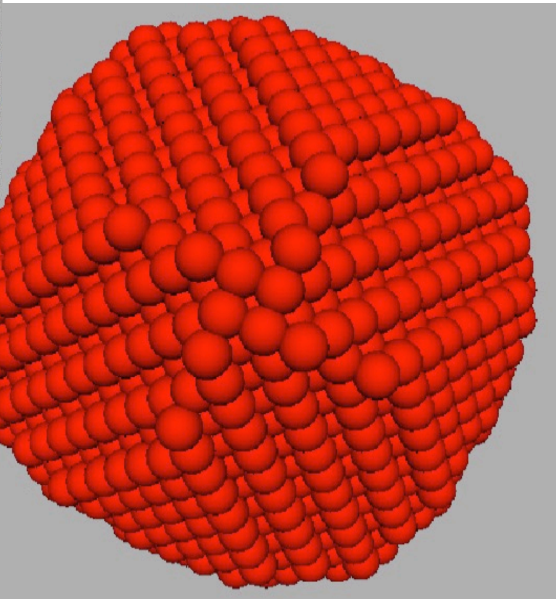
$$E = n^2\pi^2\hbar^2/2ma^2,\ n = 1,2,3\ldots$$

Size effect

CHANGE IN VALENCE ENERGY BAND LEVELS WITH SIZE

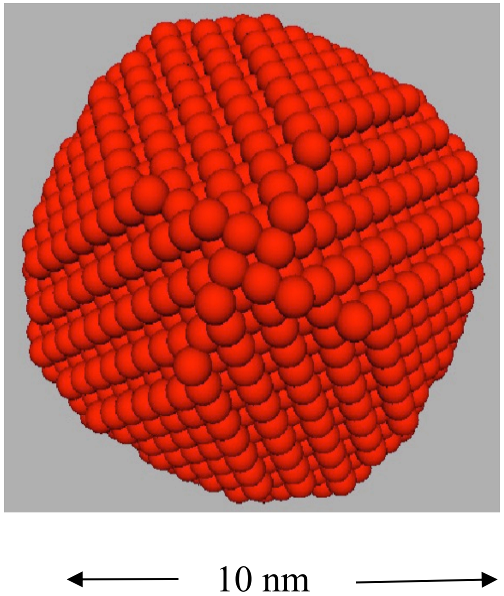






Size →

Au nanoparticle as an example



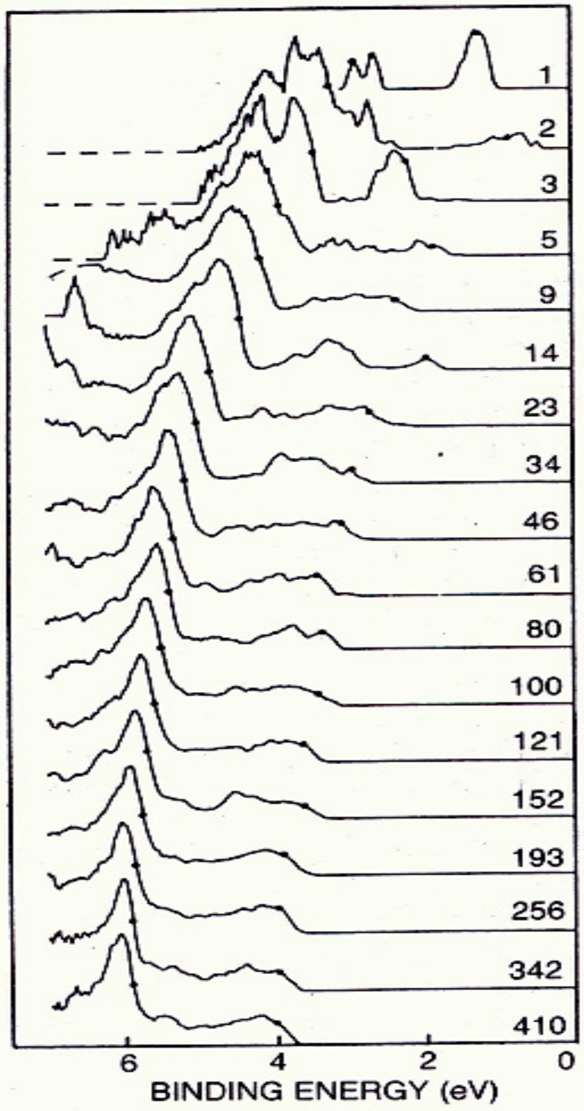
$$E_F = (\hbar^2/2m)\,(3\pi^2 n)^{2/3}$$

$$g(E_F) = (3/2)\,(n/E_F)$$

$$\delta = 2/[g(E_F)V] = (4/3)\,(E_F/N)$$

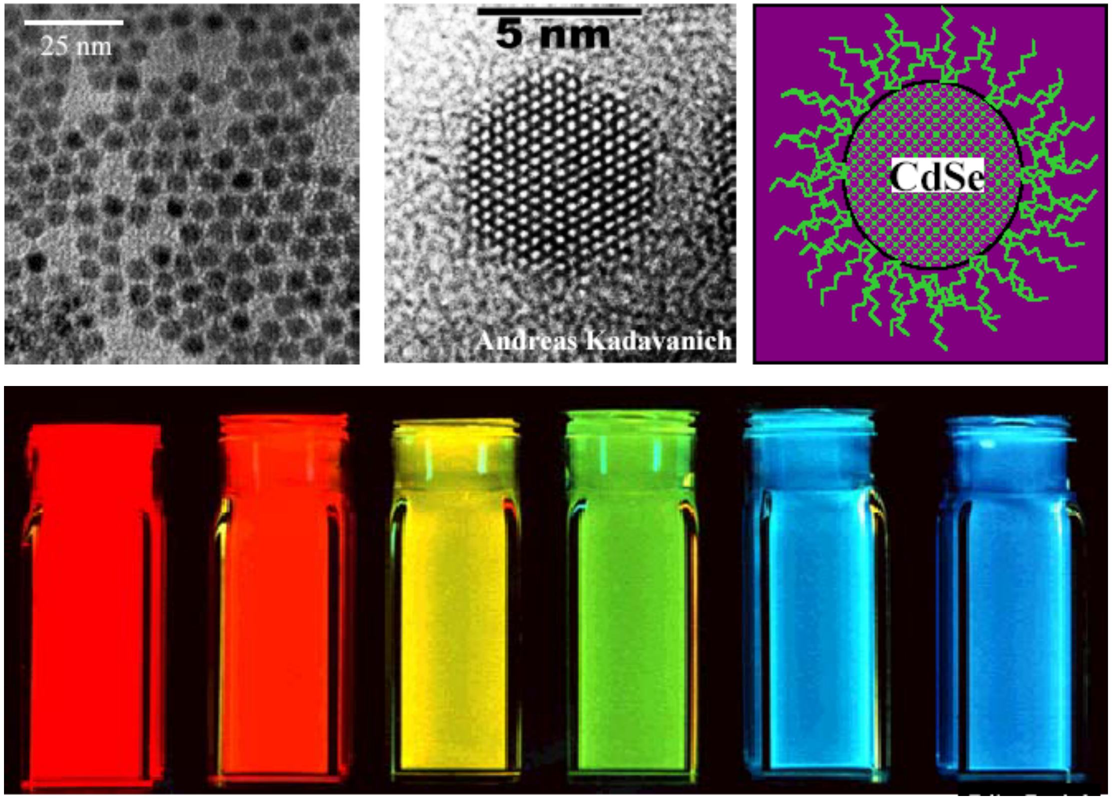
Number of valence electrons (N) contained in the particles is roughly 40,000. Assume the Fermi energy (E_F) is about 7 eV for Au, then

$$\delta \sim 0.22 \text{ meV} \sim 2.5 \text{ K}$$

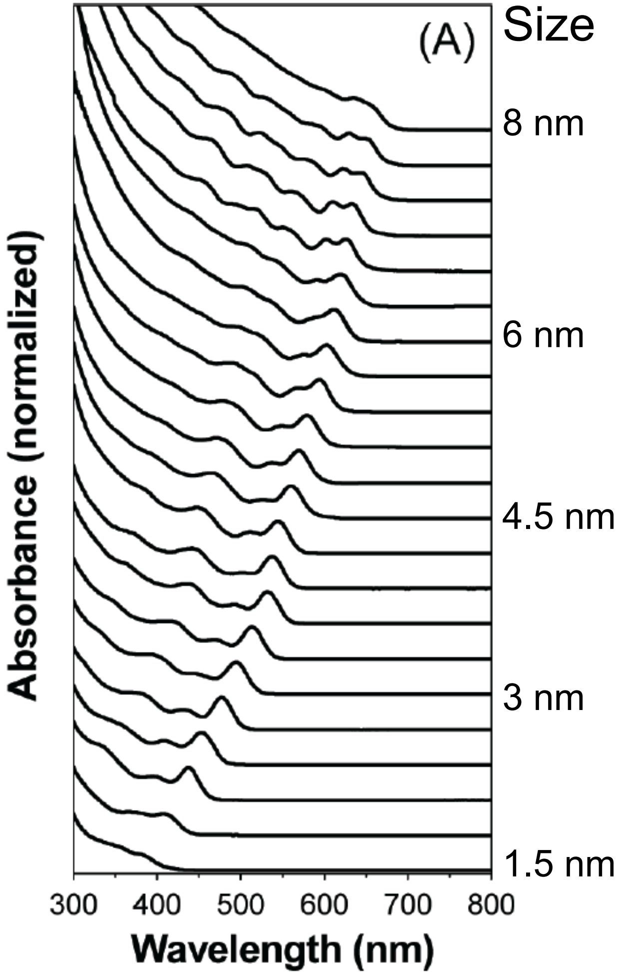


Ultraviolet photoemission spectra of ionized copper clusters Cu_N^- ranging in size from N of 1 to 410 show the energy distribution versus binding energy of photoemitted electrons. These photoemission patterns show the evolution of the 3d band of Cu as a function of cluster size. As the cluster size increases, the electron affinity approaches the value of the bulk metal work function. (Adapted from ref. 10.) **Figure 5**

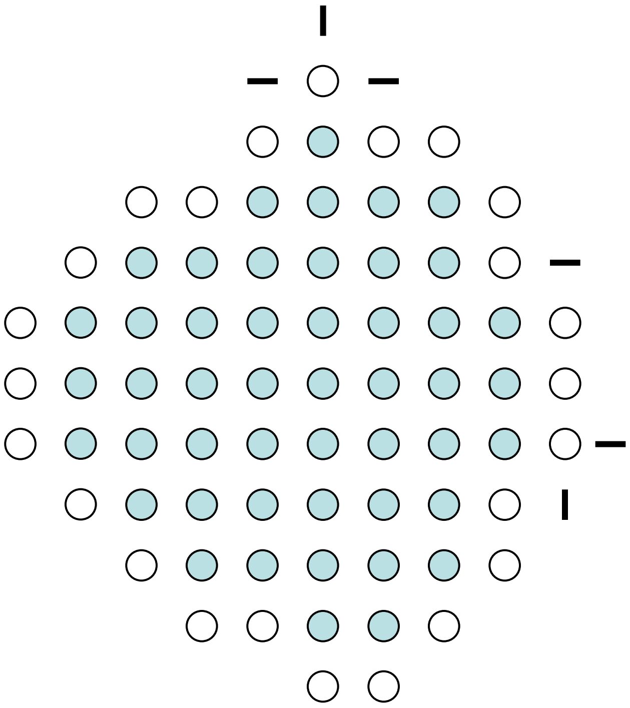
Semiconductor quantum dots



(Reproduced from Quantum Dot Co.)



Optical properties of nanoparticles (in the infrared range)



(1) Broad-band absorption:
Due mainly to the increased normal modes at the surface.

(2) Blue shift:
Due mainly to the bond shortening resulted from surface tension or phonon confinement.

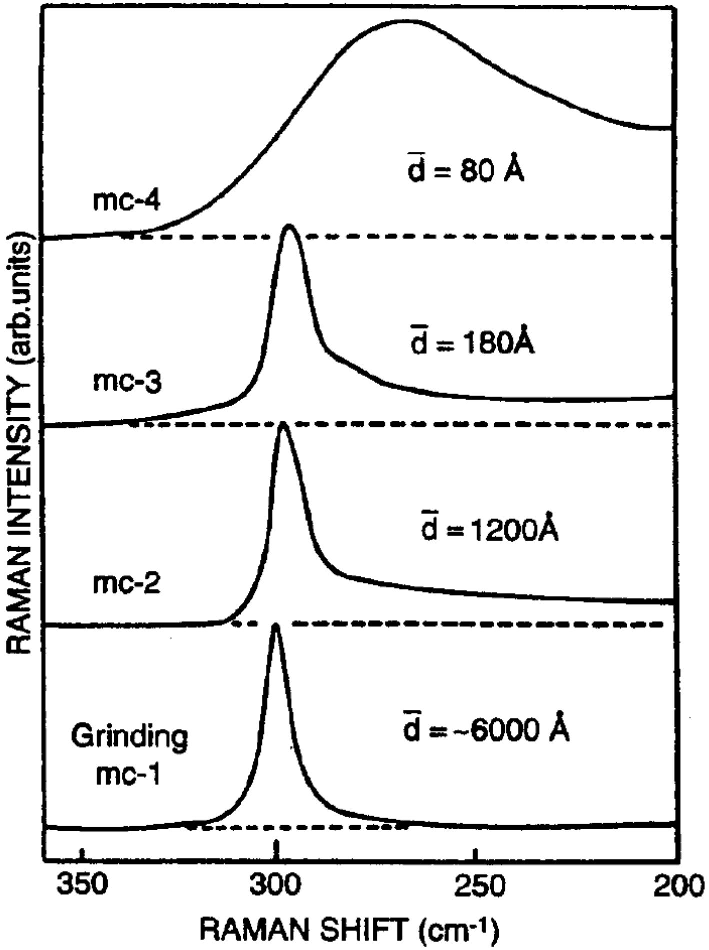
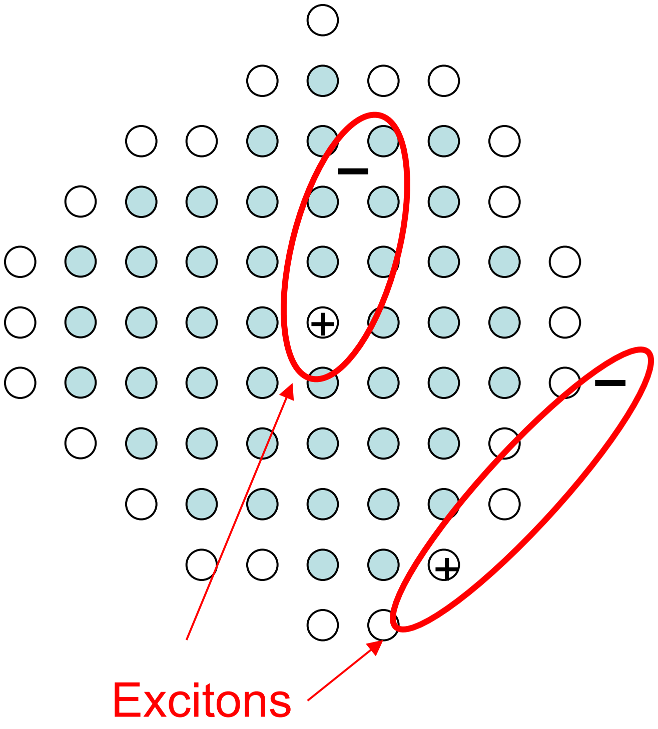


Figure 8.11. Raman spectra of Ge nanocrystallites produced by gas condensation showing the broadening and shift to lower wavenumbers as the particle size decreases. The lowest spectrum was obtained from ground bulk germanium. [From S. Hayashi, M. Ito, and H. Kanamori, *Solid State Commun.* **44**, 75 (1982).]

Optical properties of nanoparticles (in the visible light range)



(1) Blue shift:
Due mainly to the energy-gap widening because of the size effect.

(2) Red shift:
Bond shortening resulted from surface tension causes more overlap between neighboring electron wavefunctions. Valence bands will be broadened and the gap becomes narrower.

(3) Enhanced exciton absorption:
Due mainly to the increased probability of exciton formation because of the confining effect.

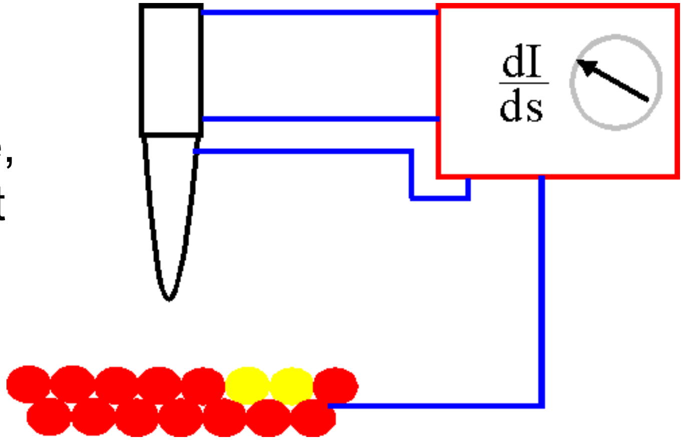
Scanning Tunneling Spectroscopy

1. Barrier Height Imaging

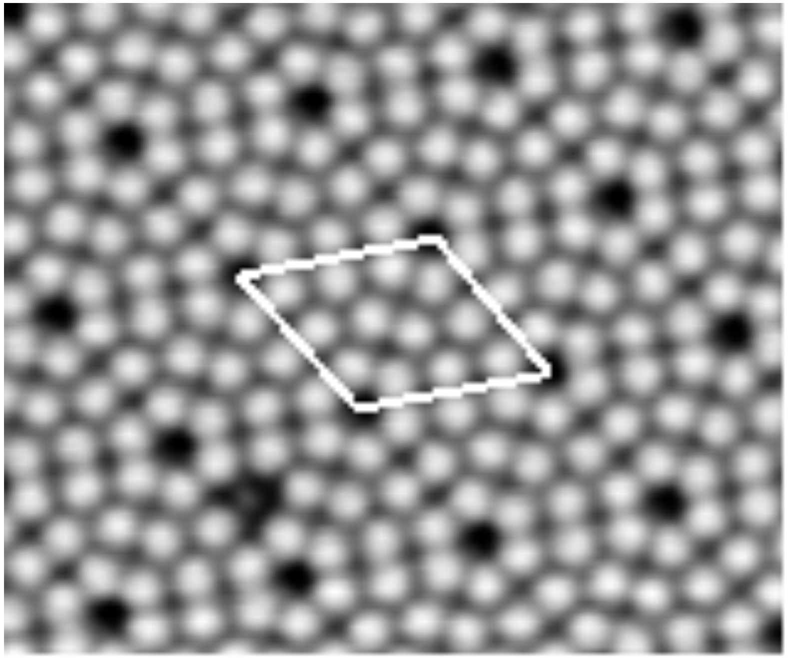
Up to now homogeneous surfaces were considered. If there is an inhomogeneous compound in the surface the work function will be inhomogeneous as well. This alters the local barrier height. Differentiation of tunneling current yields

$$\frac{d(\ln I)}{ds} \propto \sqrt{\Phi}$$

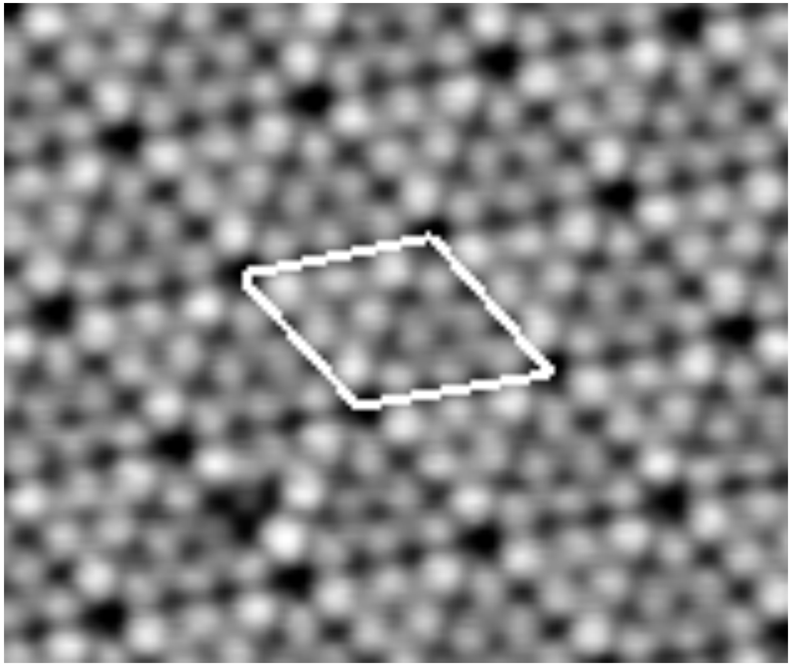
Thus the work function can directly be measured by varying the tip-sample distance, which can be done by modulating the current with the feedback turned on.



STM Images of Si(111)-(7×7)



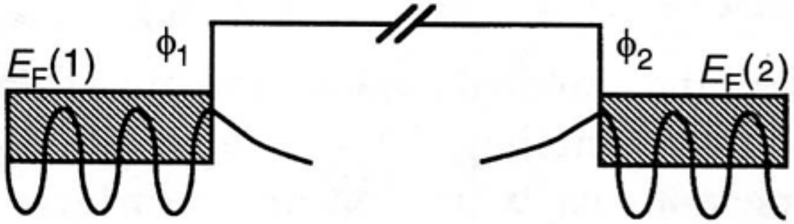
Empty-state image



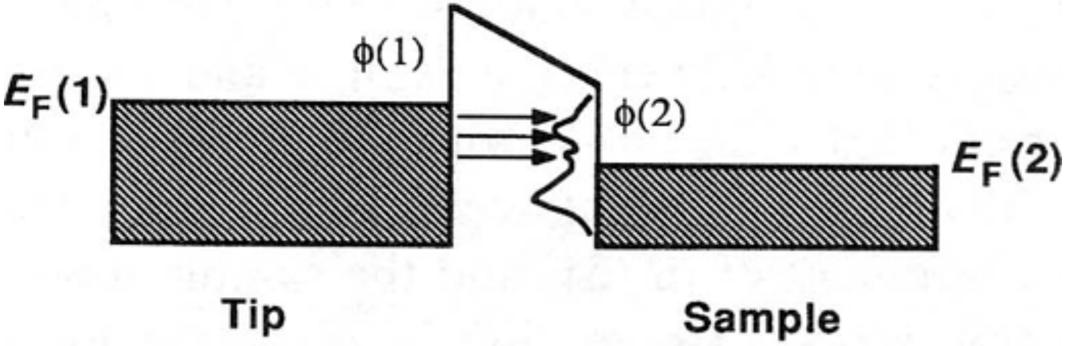
Filled-state image

Electronic Structures at Surfaces

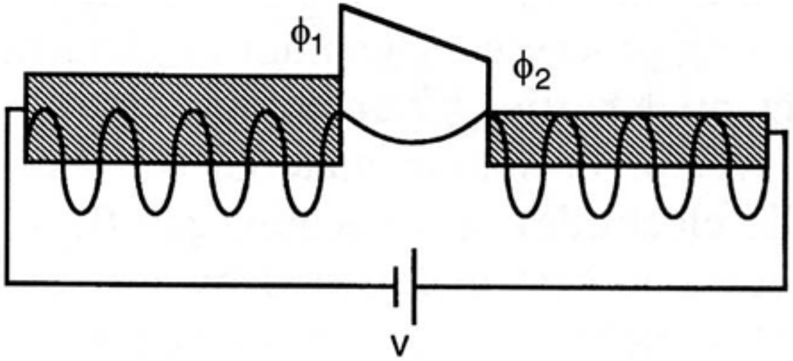
Not Tunneling



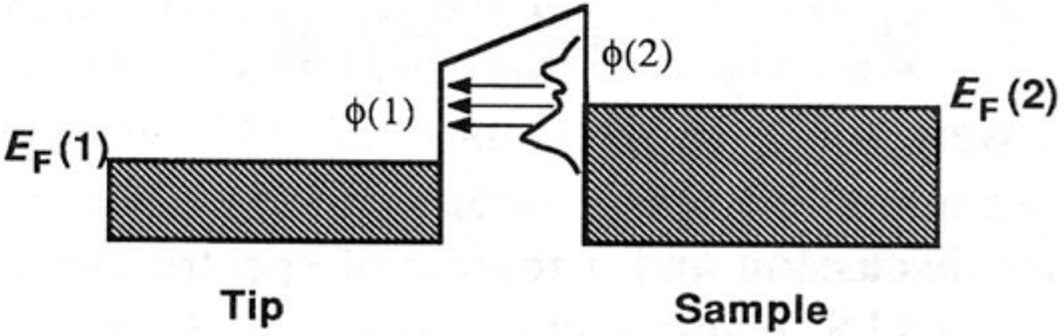
Empty-State Imaging



Tunneling



Filled-State Imaging



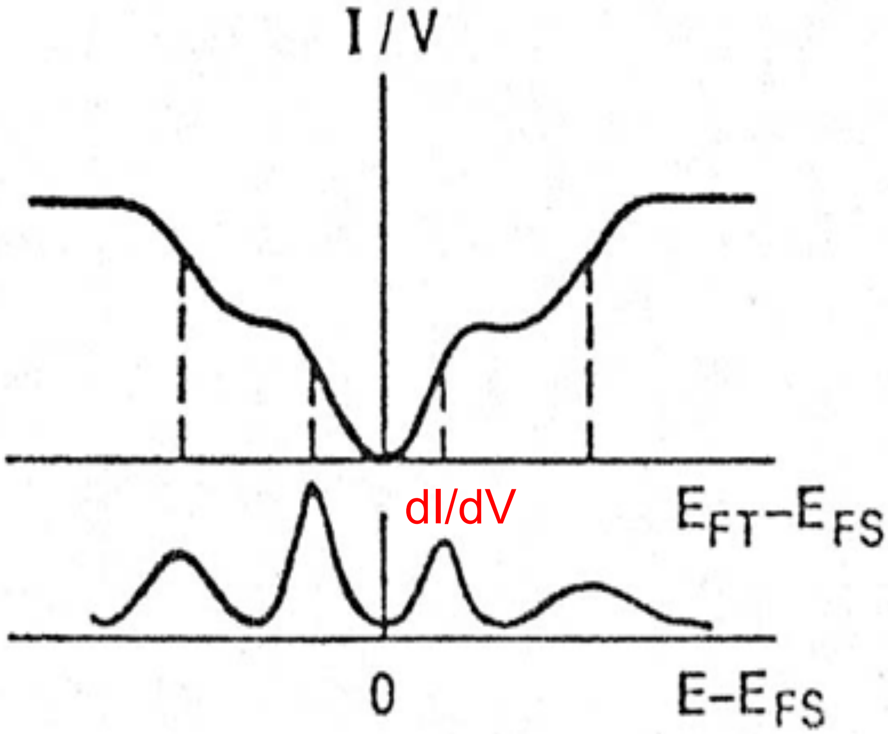
2. dI/dV imaging

If the matrix element and the density of states of the tip is nearly constant, the tunneling current can be estimated to

$$I \propto \int_0^{eV} \rho_{sa}\left(E_F - eV + \varepsilon\right) d\varepsilon$$

Differentiation yields the density of state

$$\frac{dI}{dV} \propto \rho_{sa}\left(E_F - eV\right)$$

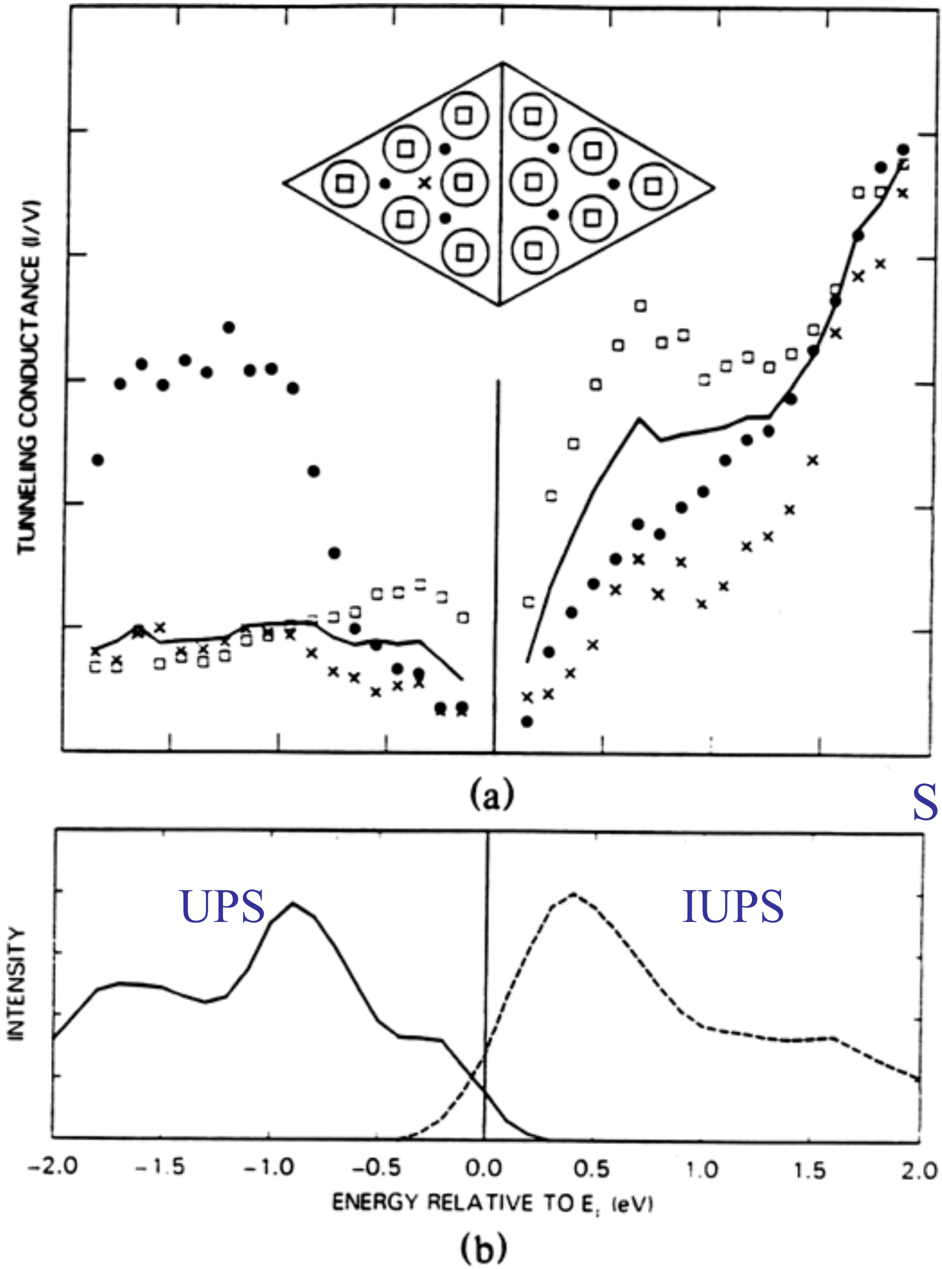


Density of state (DOS)

The mapping of surface density of states can be deduced by

- Modulation of the bias voltage (dI/dV imaging): The tip is scanned in the constant current mode to give a constant distance to the sample. A dither voltage of ~1k Hz is added to the bias voltage while the feedback loop remains active. A lock-in technique is employed to obtain the current change at the dither frequency.
- Current-Imaging Tunneling Spectroscopy (CITS): The tip is scanned in the constant current mode to give a constant distance to the sample. At each point the feedback loop is disabled and a current-voltage curve (I-V curve) is recorded.

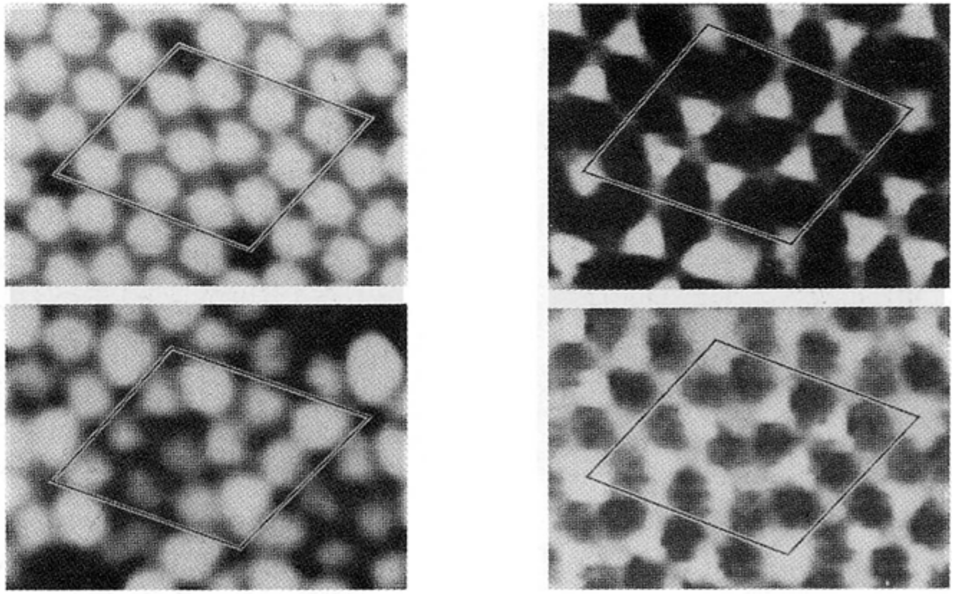
STS of Si(111)-(7x7)

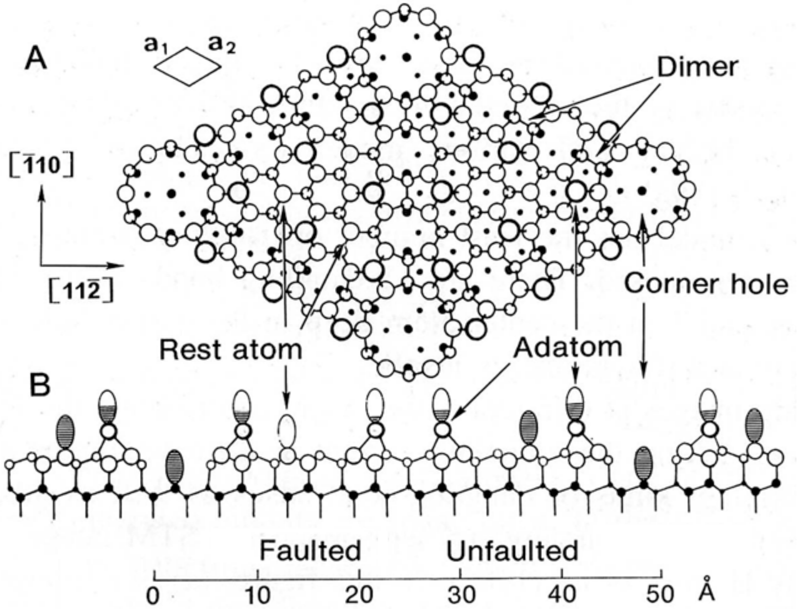


Science **234**, 304 (1986).

STS of Si(111)-(7x7)

topograph



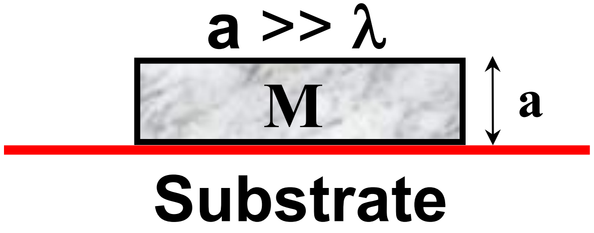


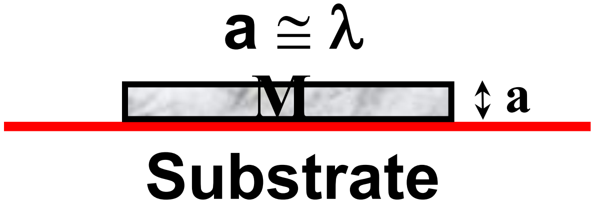
1. Science **234**, 304-309 (1986).
2. Phys. Rev. Lett. **56**, 1972-1975 (1986).

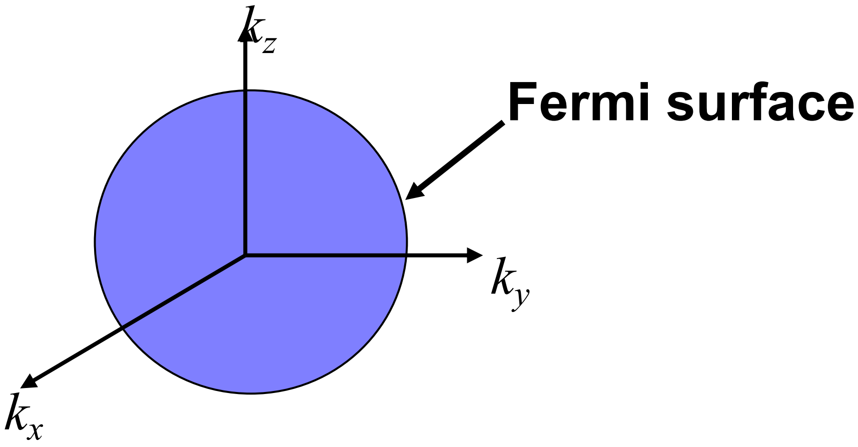
Quantum size effect

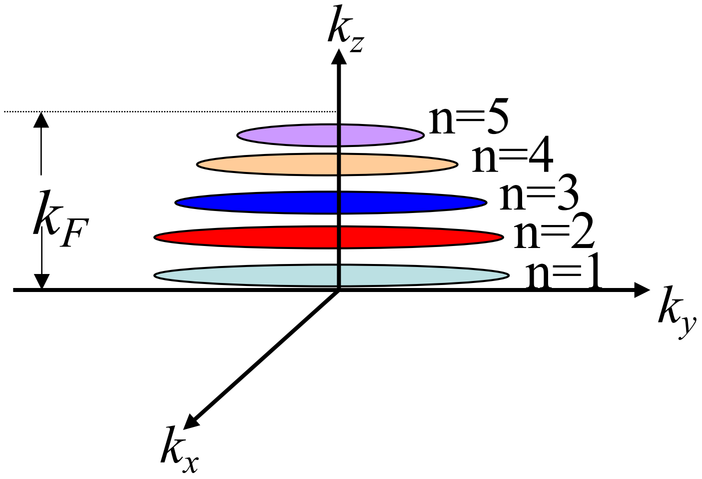
λ = de Broglie wavelength of electron

a = thickness of metal film

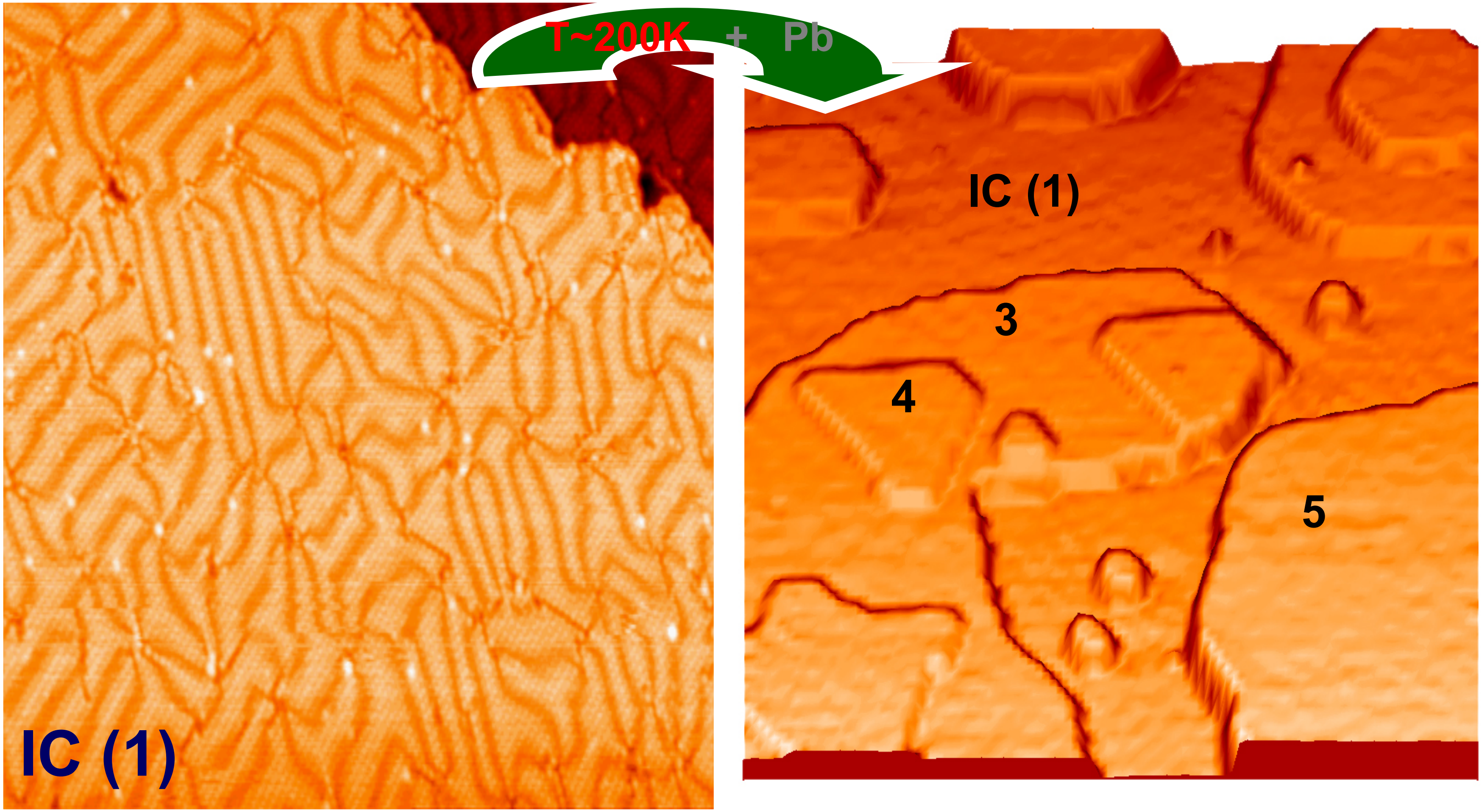




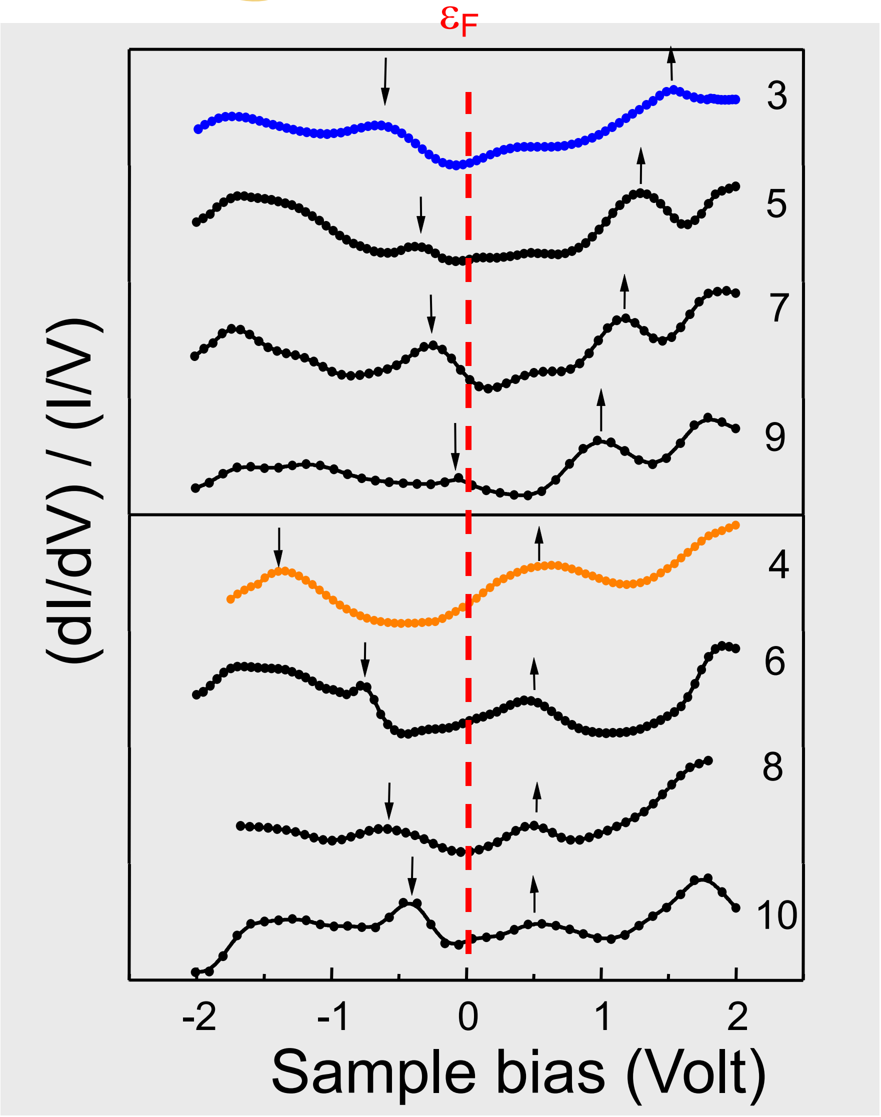


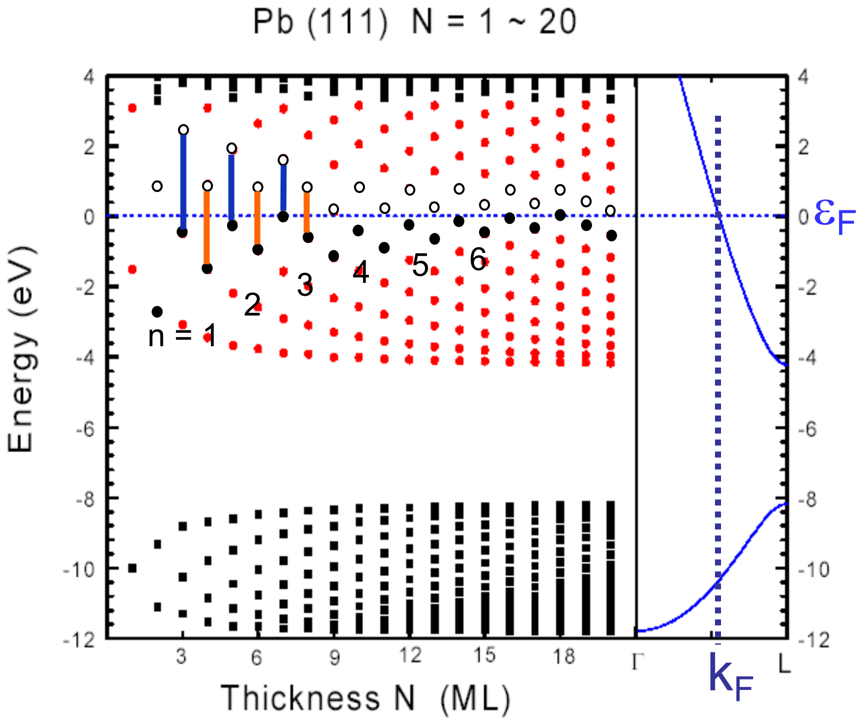


Pb islands on the IC Pb/Si(111)



Spectra for Pb Films





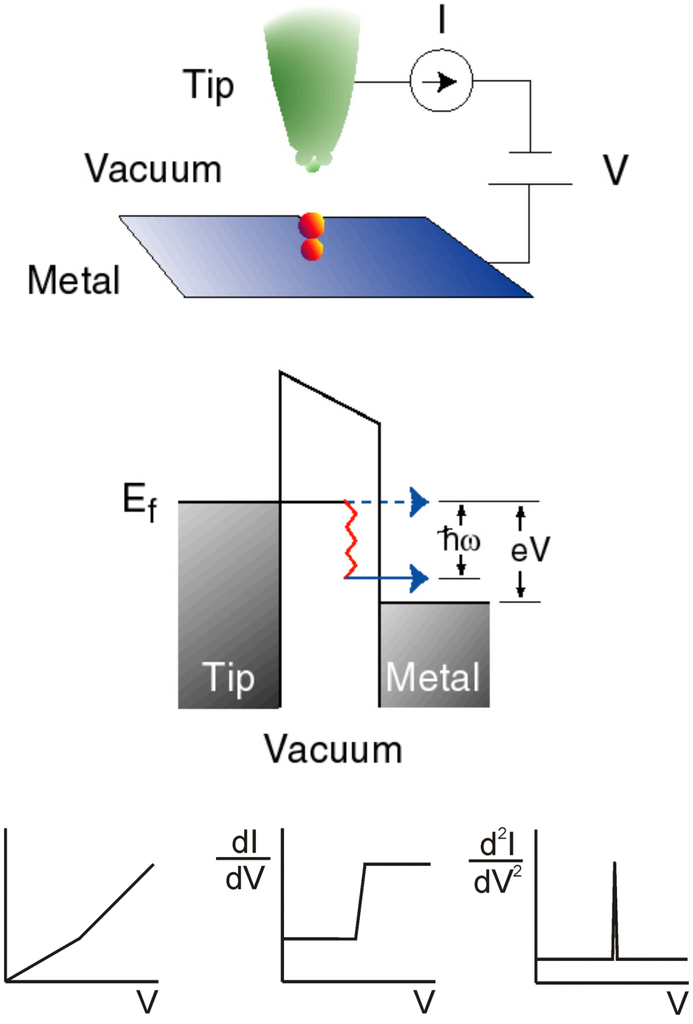
C.M. Wei and M.Y. Chou

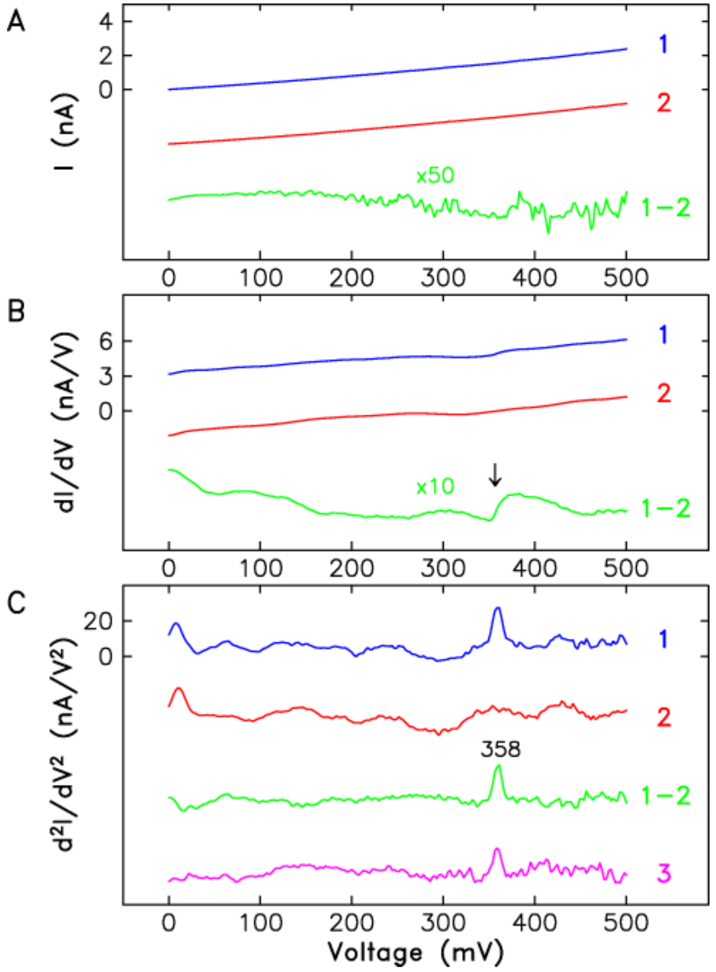
$d_0 = 2.85$ Å $\quad \lambda_F = 3.94$ Å

$2d_0 \approx 3(\lambda_F/2)$

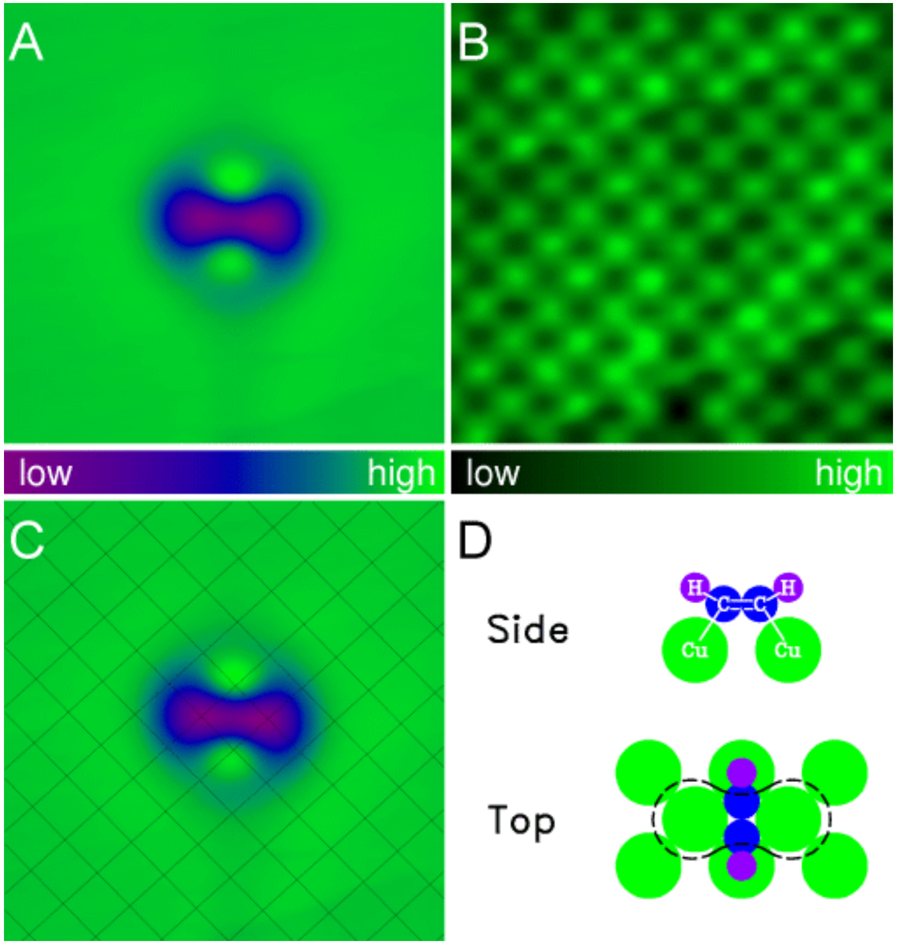
Inelastic Tunneling

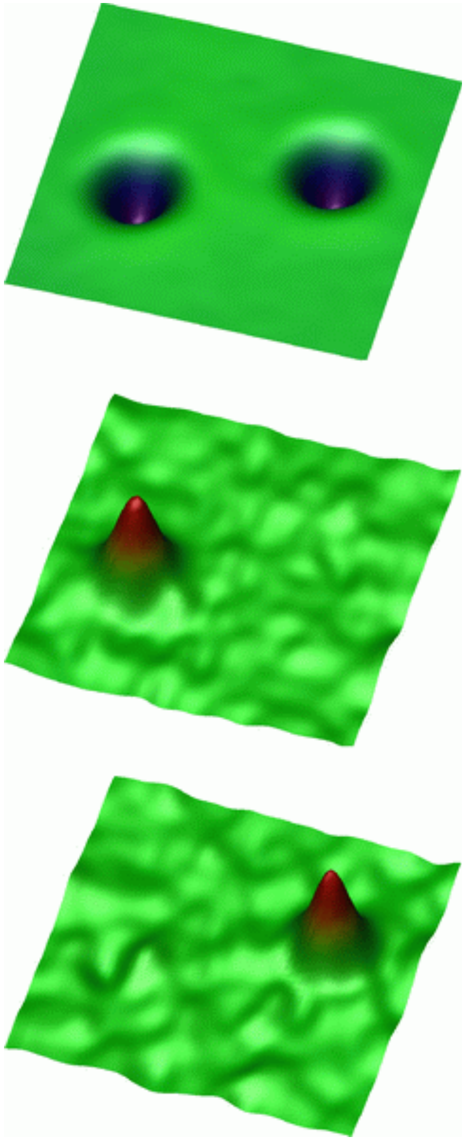
Elastic vs. Inelastic Tunneling





Single Molecule Vibrational Spectroscopy and Microscopy





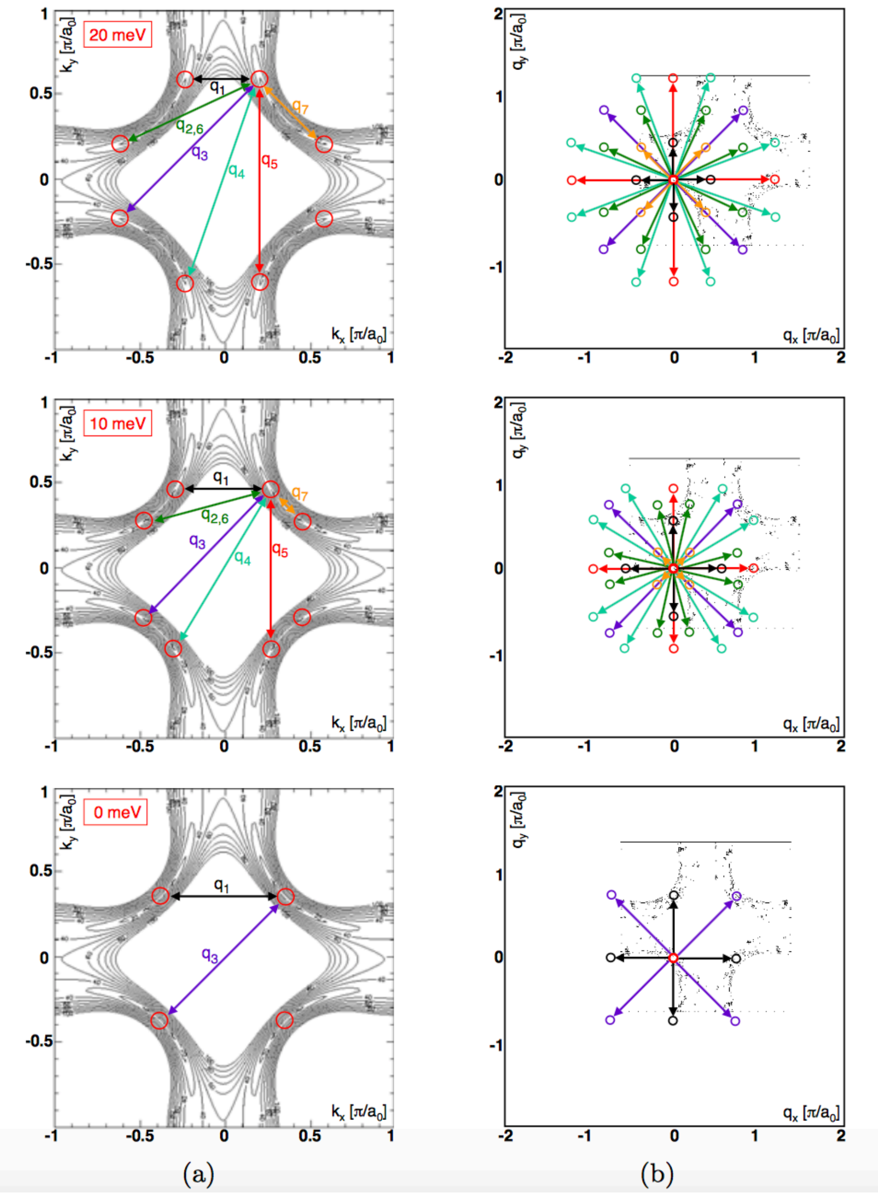
B.C. Stipe, M.A. Rezaei, and W. Ho,
Science **280**, 1732-1735 (1998).

Quasiparticle Interference (QPI)

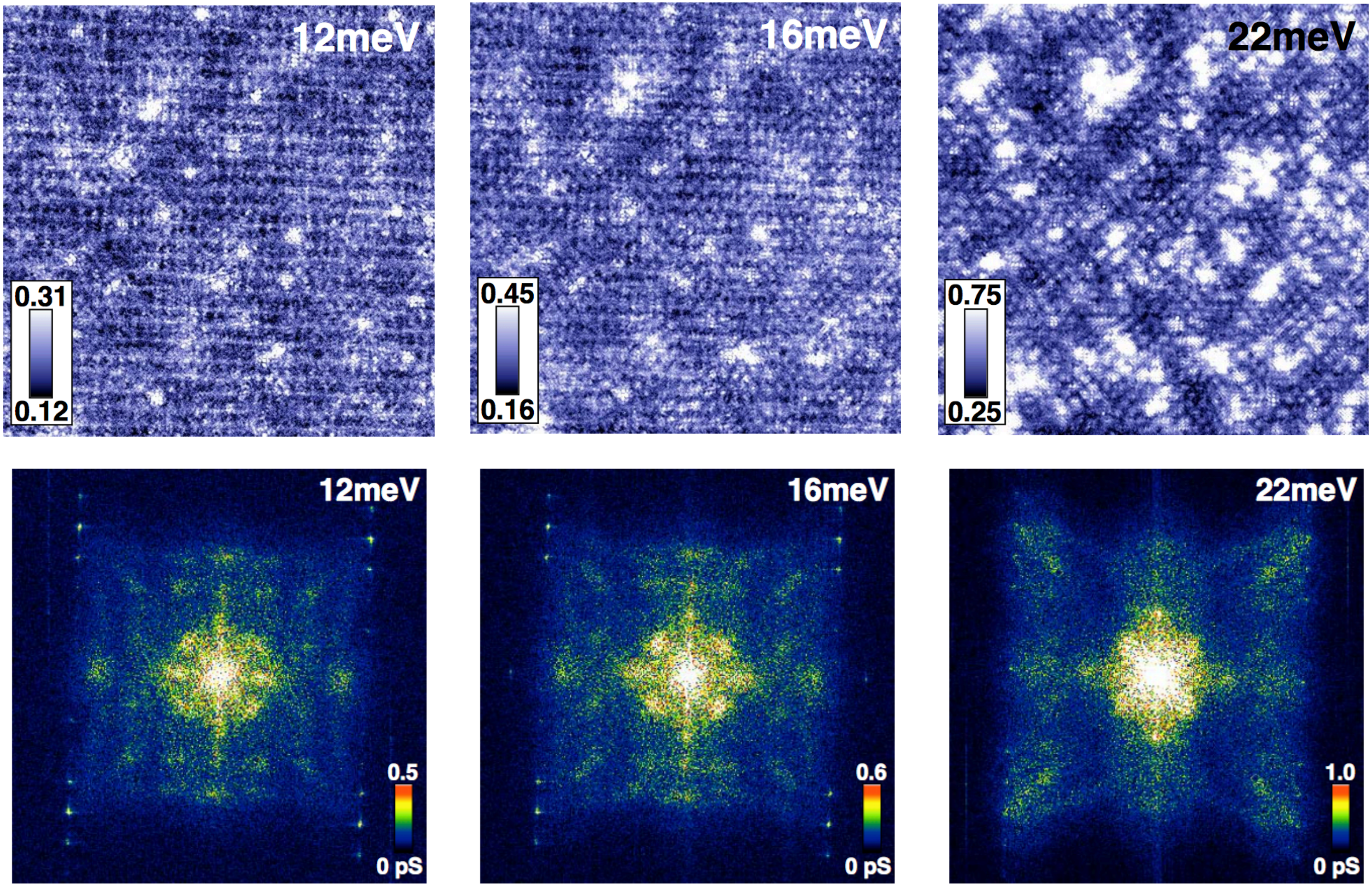
In an ideal metal, the Landau quasiparticle eigenstates are Bloch wavefunctions characterized by wavevector **k** and energy ε. Their dispersion relation, $\varepsilon(\mathbf{k})$, can be measured by real space imaging techniques, such as scanning tunneling microscopy (STM). This is because the local density of states LDOS (E) spectrum at a single location **r** is related to the **k**-space eigenstates $\Psi_{\mathbf{k}}(\mathbf{r})$ by

$$\mathrm{LDOS}\,(E\,,\,\mathbf{r}) \propto |\,\Psi_{\mathbf{k}}(\,\mathbf{r}\,)\,|^2\,\delta\,(\,E-\varepsilon\,(\,\mathbf{k}\,)\,)$$

Sources of disorder such as impurities or crystal defects cause elastic scattering which mixes eigenstates of different **k** but the same $\varepsilon(\mathbf{k})$. In other words, elastic scattering mixes states that are located on the same quasiparticle contour of constant energy (CCE) in **k**-space. When scattering mixes states $\mathbf{k_1}$ and $\mathbf{k_2}$, the result is a standing wave in the quasiparticle wavefunction $\Psi_{\mathbf{k}}$ of wavevector $\mathbf{q} = (\mathbf{k_1}-\mathbf{k_2})/2$. Since LDOS is proportional to the norm of the quasiparticle wavefunction $|\Psi_{\mathbf{k}}|^2$, the LDOS will contain an interference pattern with wavevector $\mathbf{q} = \mathbf{k_1}-\mathbf{k_2}$, or wavelength $\lambda = 2\pi/q$.



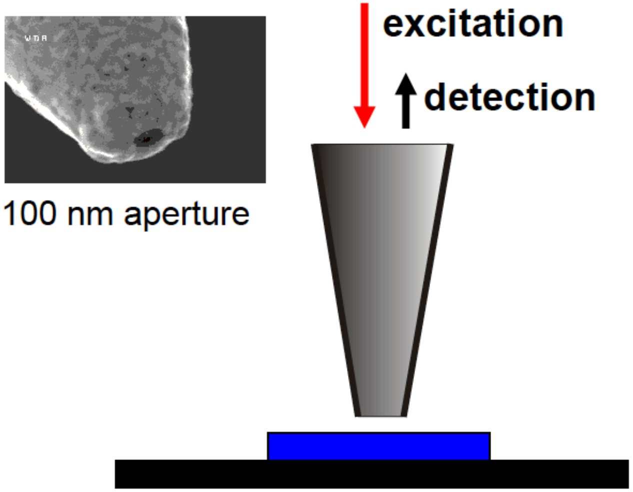
(a) (b)



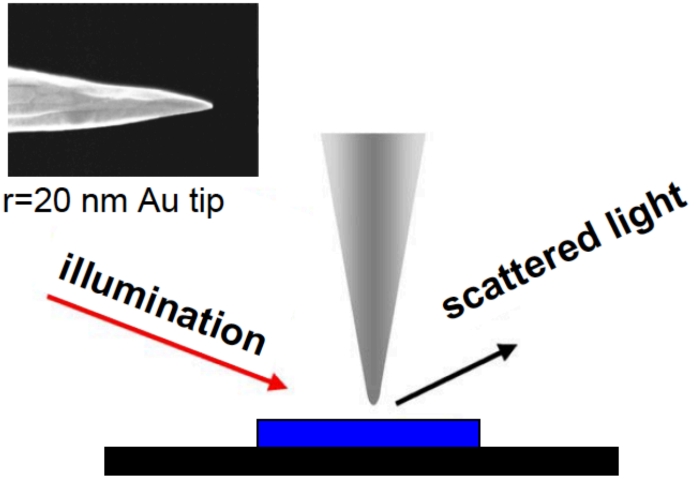
(a) 12 meV |FT(DOS)| (b) 16 meV |FT(DOS)| (c) 22 meV |FT(DOS)|

Optical methods with sub-wavelength spatial resolution

Aperture near-field probes



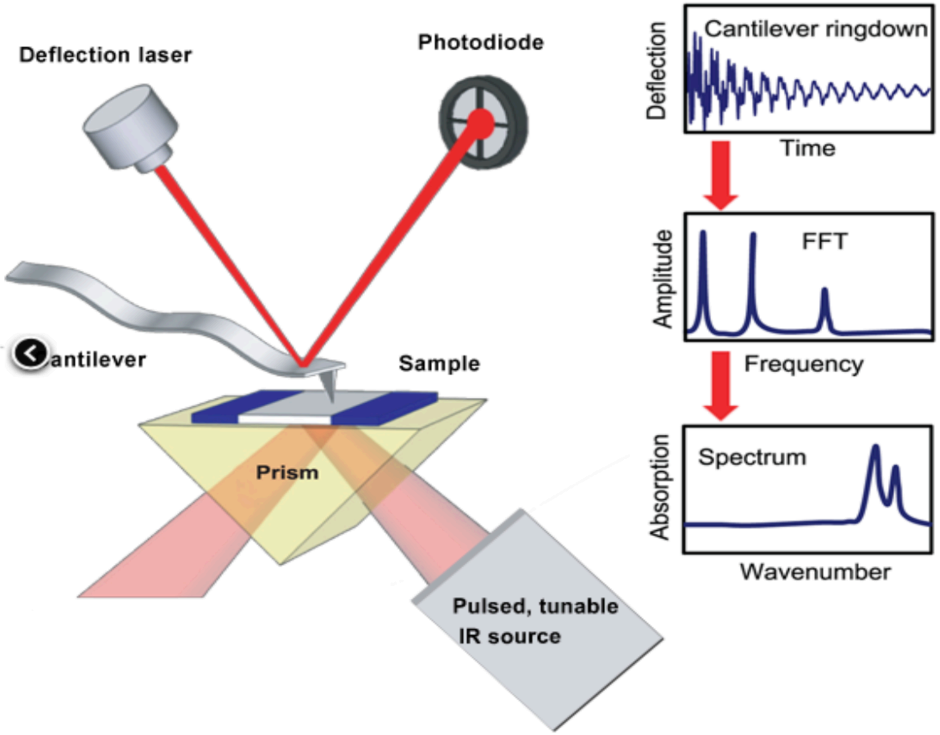
Apertureless scattering



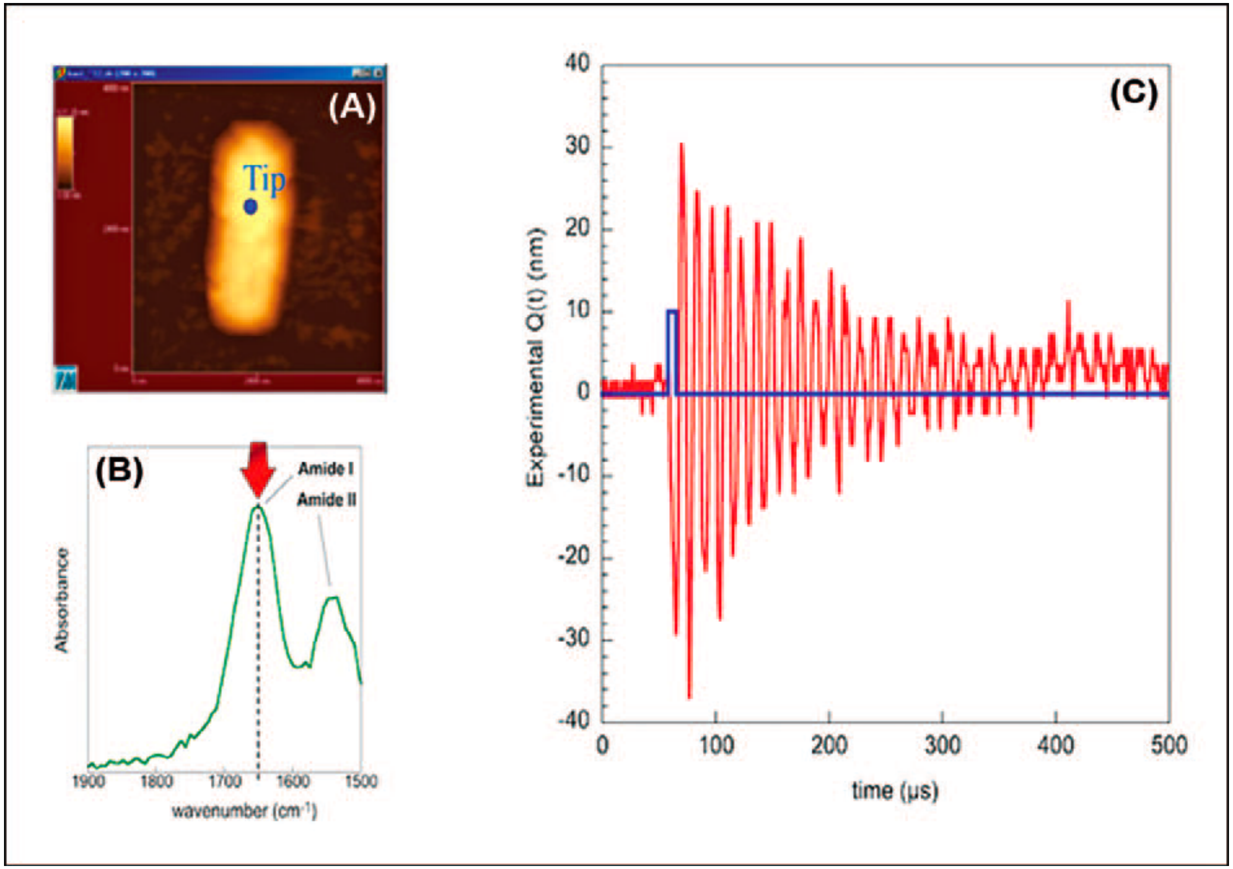
	Aperture near-field probes	Apertureless scattering
Spatial resolution	**100 nm**	**10 nm**
Time resolution	**100 fs - cw**	**10 fs - cw**
Spectral resolution (cw)	**30 µeV**	**several meV**
Sample temperatures	**10 - 300 K**	**300 K**

Recent development: AFM-IR system

AFM-IR can perform IR spectroscopic chemical identification with sub-100 nm spatial resolution



Scheme of the AFM–IR setup. The AFM cantilever ring-down amplitude plotted as a function of laser excitation wavelength produces the IR spectrum.



(a) AFM topography picture of the bacterium; the position of the tip is indicated in blue. (b) FT–IR spectrum; the bacterium absorption spectrum is drawn in green, and the wavenumber of the CLIO laser is indicated by the red arrow. (c) Oscillations recorded by the four-quadrant detector (in red) as function of time superposed on the CLIO pulse laser (blue).

Alexandre Dazzi et al., APPLIED SPECTROSCOPY OA 66, 1365 (2012)

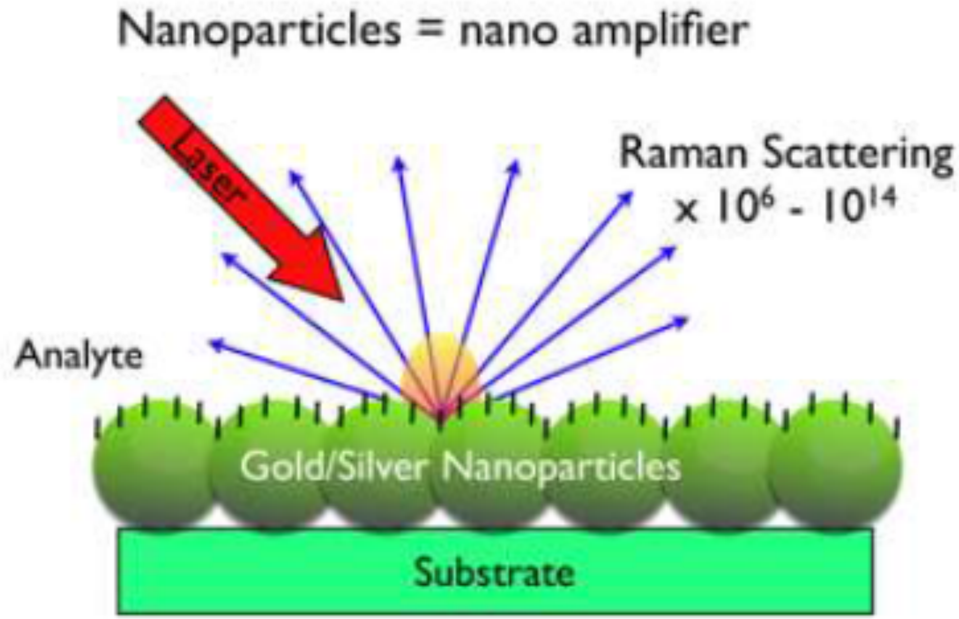
Surface-enhanced Raman spectroscopy (SERS)

SERS is a surface-sensitive technique that enhances Raman scattering by molecules adsorbed on rough metal surfaces or by nanostructures such as plasmonic-magnetic silica nanotubes. The enhancement factor (EF) can be as much as 10^{10} to 10^{11}, which means the technique may detect single molecules.

The electromagnetic theory proposes the excitation of localized surface plasmons ($EF \alpha E^4$), while the chemical theory proposes the formation of charge-transfer complexes. The chemical theory applies only for species that have formed a chemical bond with the surface, and the electromagnetic theory of enhancement can be applied regardless of the molecule being studied.

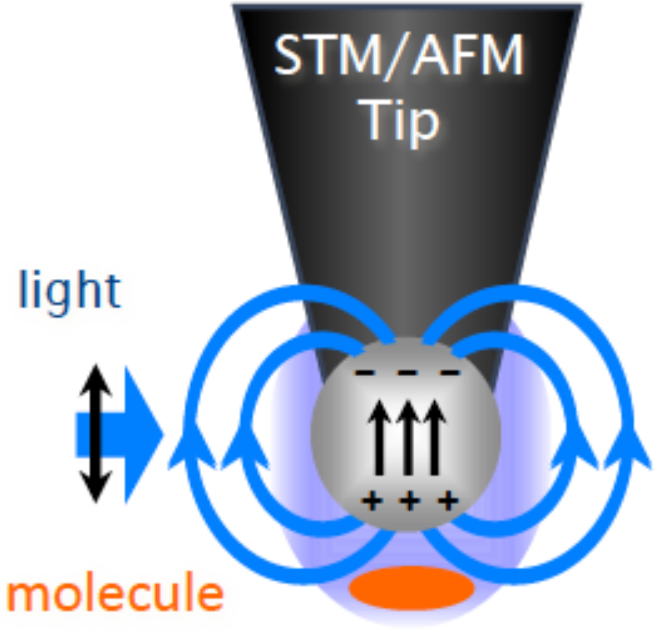
SERS

Surface Enhanced Raman Scattering



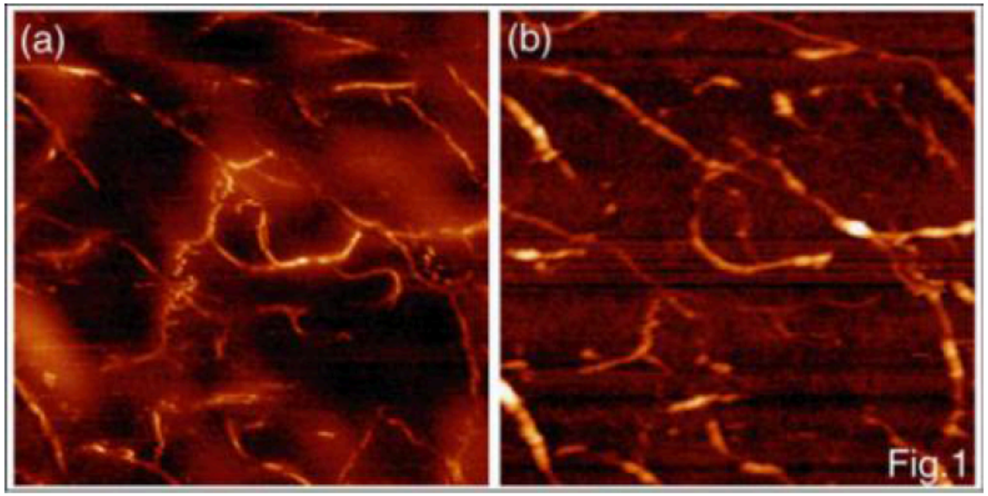
- SERS is a surface sensitive technique.
- Huge enhancement on rough metal surfaces.
- The enhancement factor can be as much as $10^{14} – 10^{15}$.
- High sensitivity possibly for single molecule detection.

Tip Enhancement

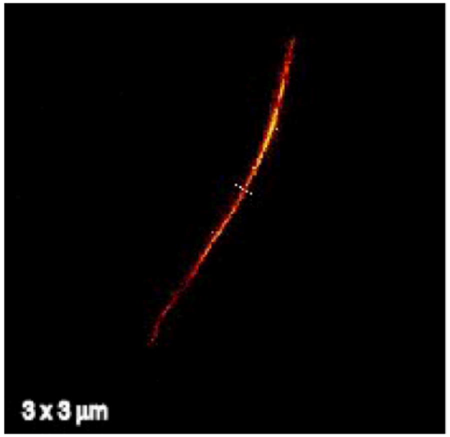


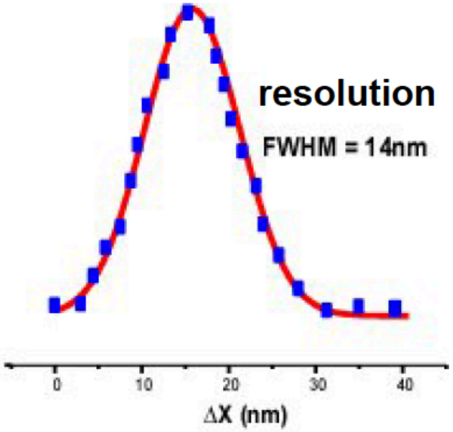
- LSP results in enhancement of EM field.
- Similar to surface enhanced Raman scattering (SERS)
- Provides location dependent tip enhanced Raman spectrum.

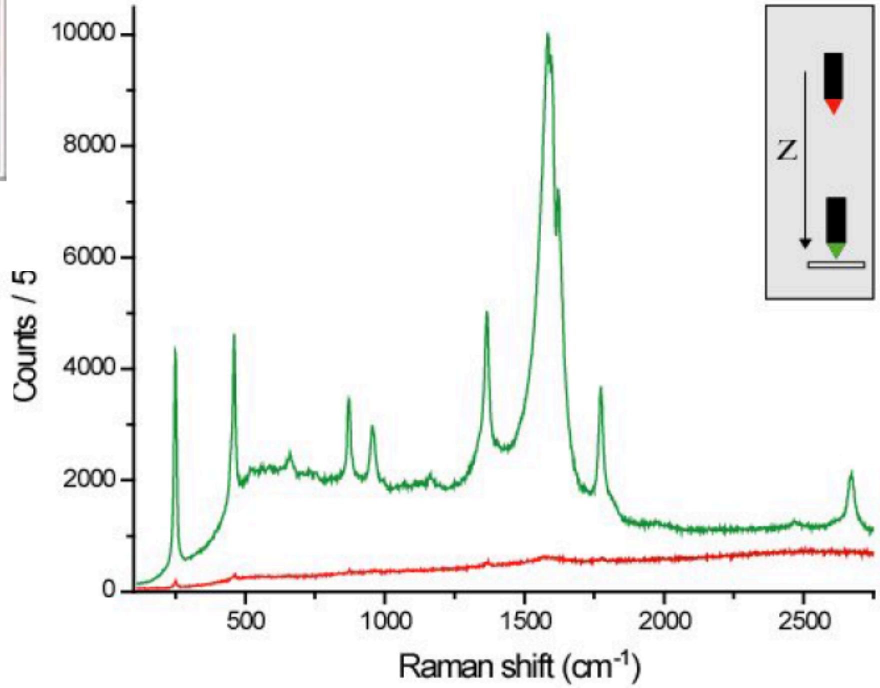
Tip-enhanced Raman spectroscopy



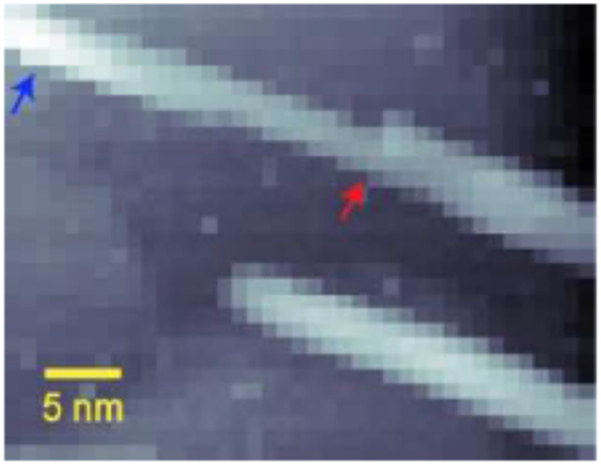
Topography **1594 cm^{-1} vibration**



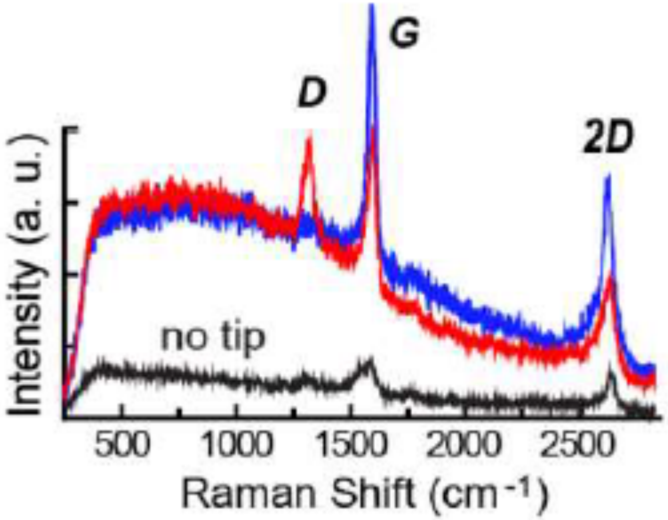




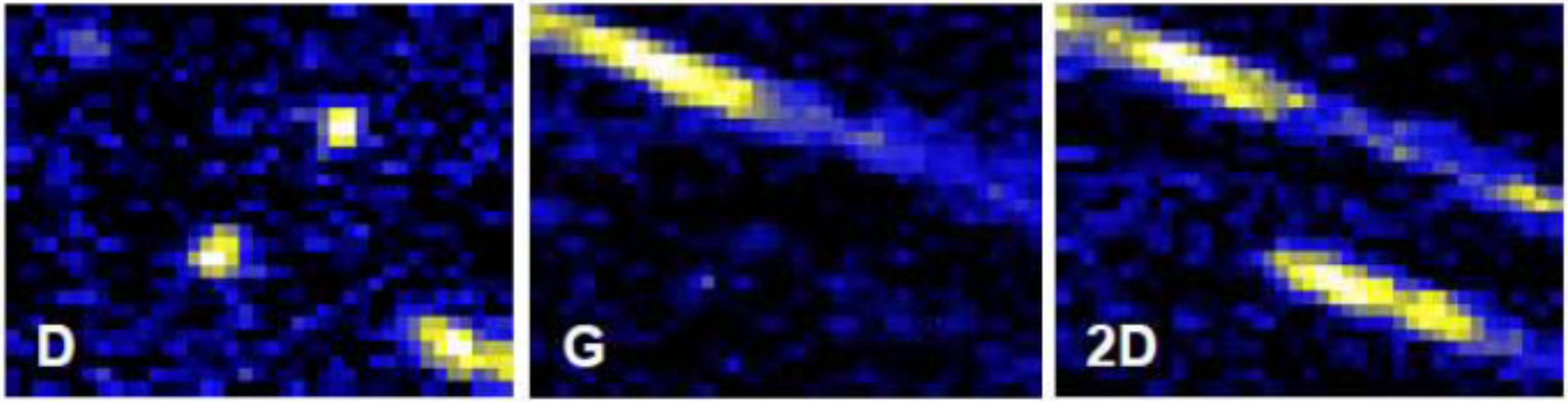
STM TERS Imaging of CNT



40 x30 px

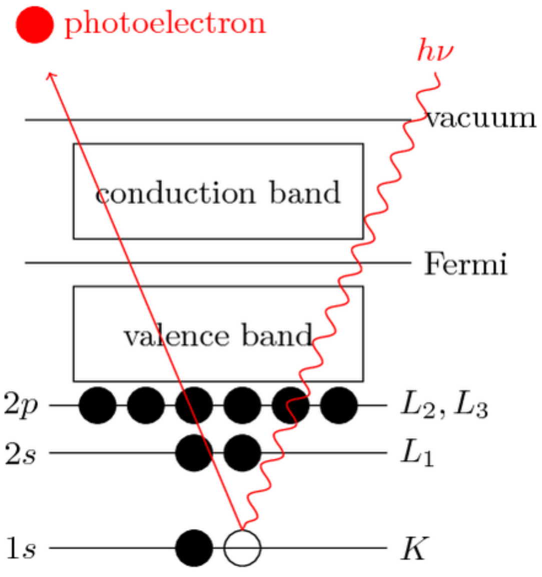


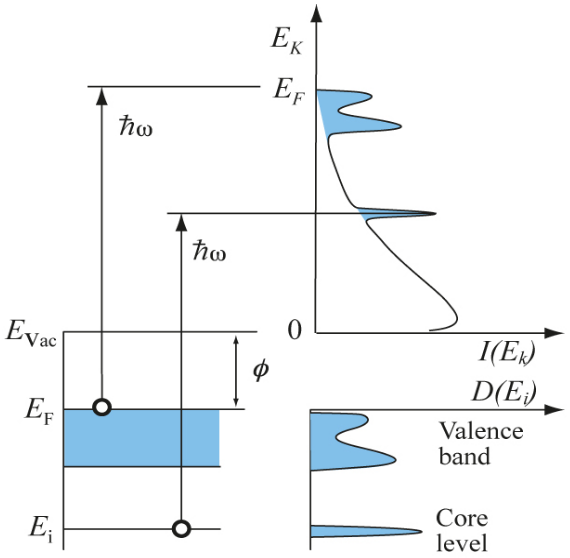
Simultaneous STM and Raman imaging.

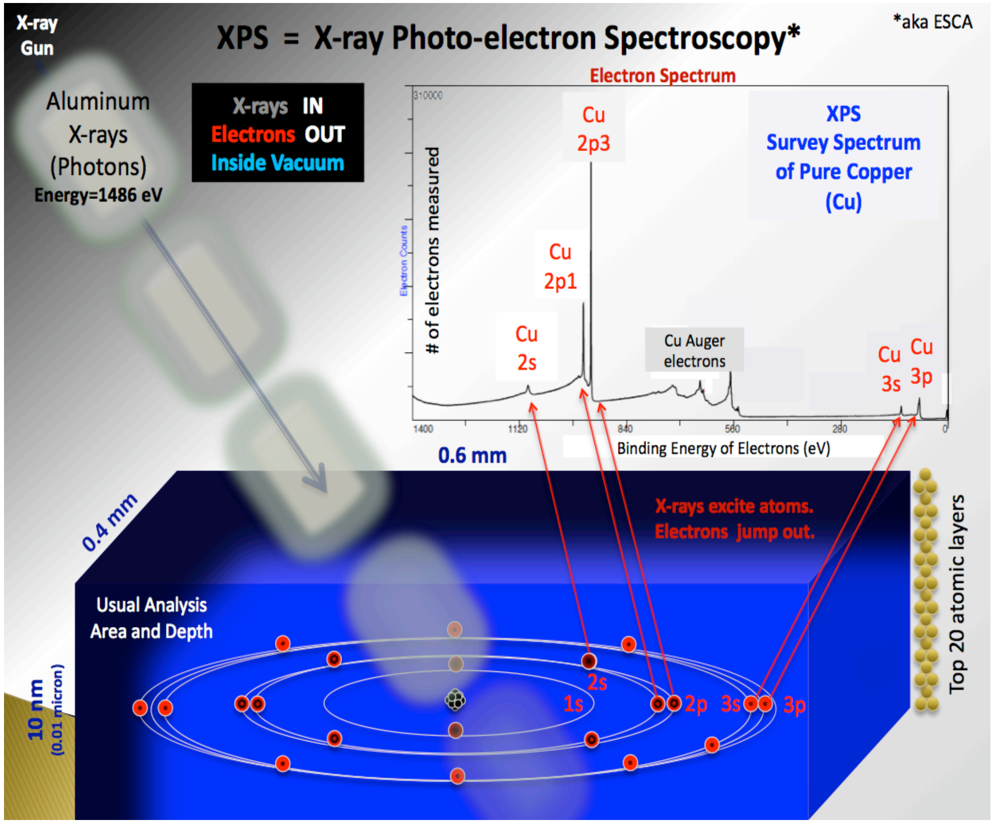


C. Chen, N. Hayazawa, and S. Kawata, Nature Comm. 5, 3312 (2014)

X-ray Photoelectron Spectroscopy (XPS)

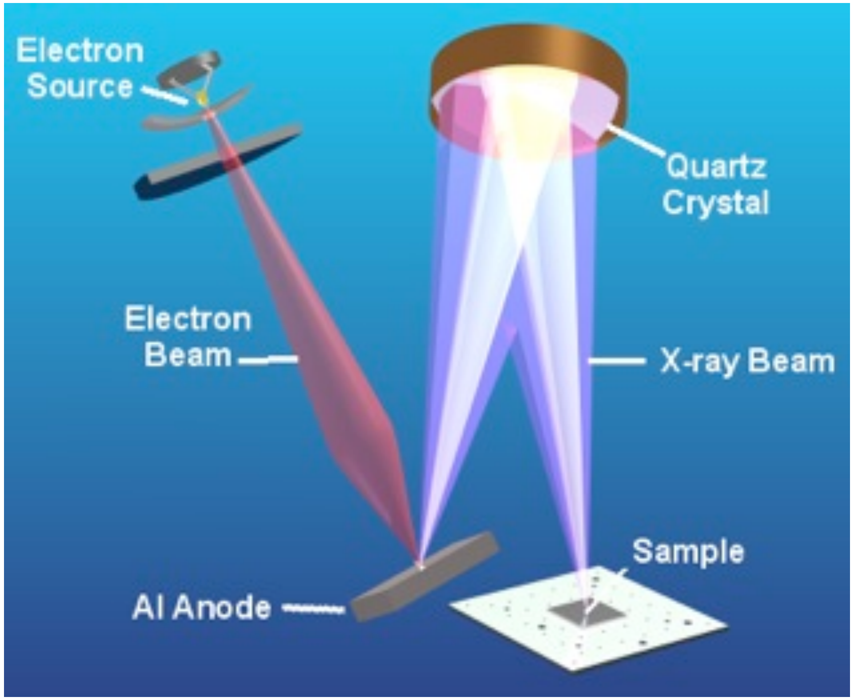


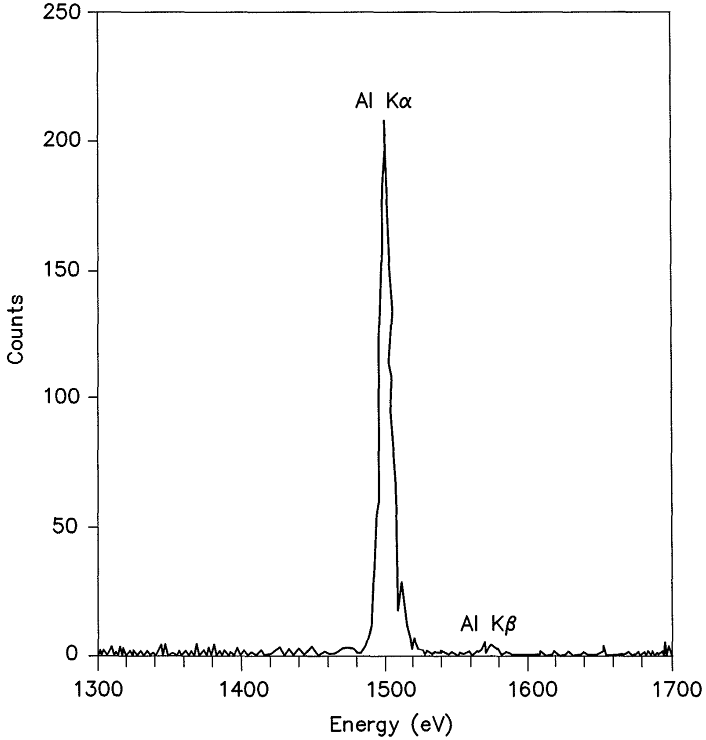




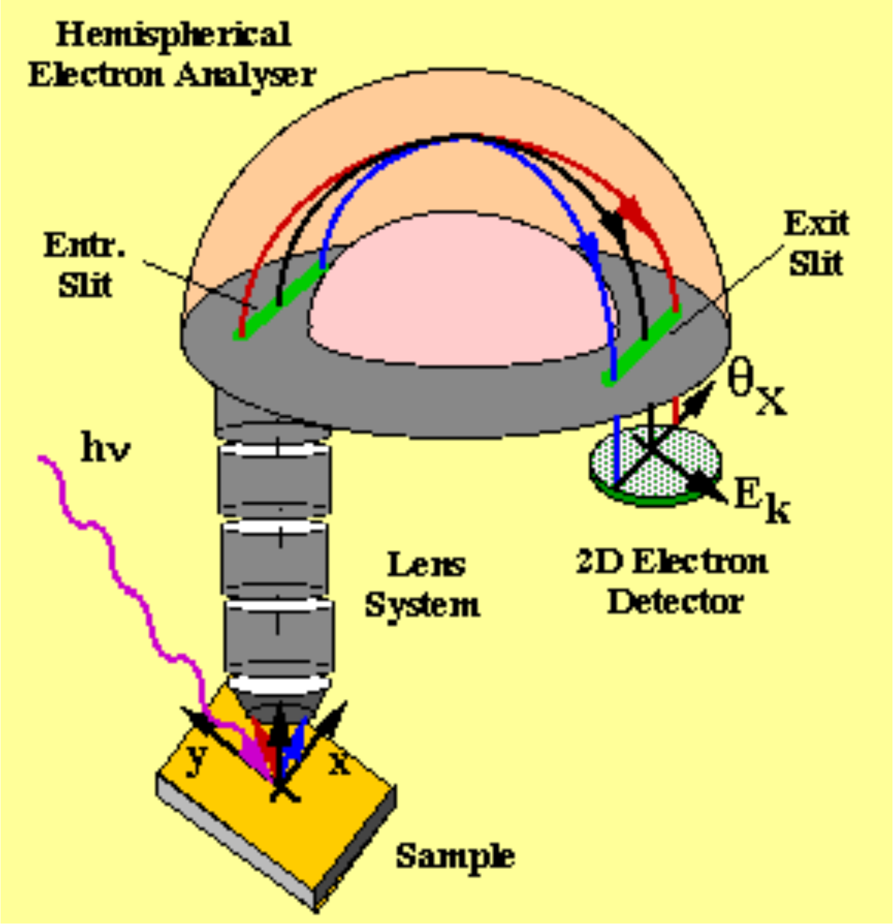
$$E_i = E_{h\nu} - (E_k + \phi)$$

X-ray source


Electron Source
Quartz Crystal
Electron Beam
X-ray Beam
Sample
Al Anode


Al Kα
Al Kβ
Counts
250
200
150
100
50
0
1300
1400
1500
1600
1700
Energy (eV)

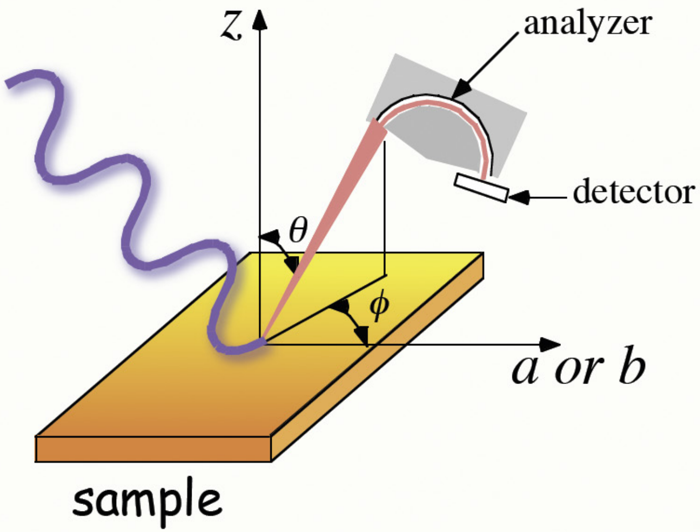
Concentric Hemispherical Analyzer (CHA)



$\Delta E/E_0 = s/R_0$

s: mean slit width; R_0: mean radius

Angle-resolved photoemission spectroscopy (ARPES)



We need:

binding energy - E_b

initial momentum - k^i

$$E_b = E - h\nu + W$$

$$k^i_{||} = k^f_{||} = \sqrt{2mE/\hbar^2}\,\sin\theta$$

$$k^i_{\perp} = k^f_{\perp} - G = \sqrt{2mE/\hbar^2}\,\cos\theta - G$$