Nanoparticle Technology

Lecture 08: Nanomaterials Characterization I

Lecture 08: table of contents

Introduction to Spectroscopy

Characterization methods

Nanomaterial characterization methods

Structural characterization

- X-ray diffraction
- Small angle X-ray scattering
- Electron microscope
  - Scanning electron microscope
  - Transmission electron microscope
- Scanning probe microscope
  - Scanning tunneling microscope
  - Atomic force microscope
- Gas physical and chemical adsorption

Chemical characterization

- Optical spectroscopy
  - UV-visible spectroscopy
  - FT-IR spectroscopy
  - Raman spectroscopy
- Electron spectroscopy
  - Energy dispersive spectroscopy
  - Electron probe micro analyser
  - Electron energy loss spectroscopy
  - Auger electron spectroscopy
  - X-ray photoelectron spectroscopy

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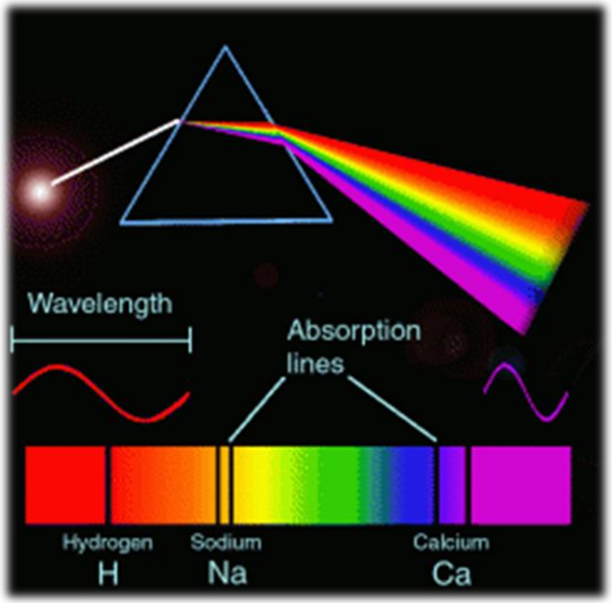
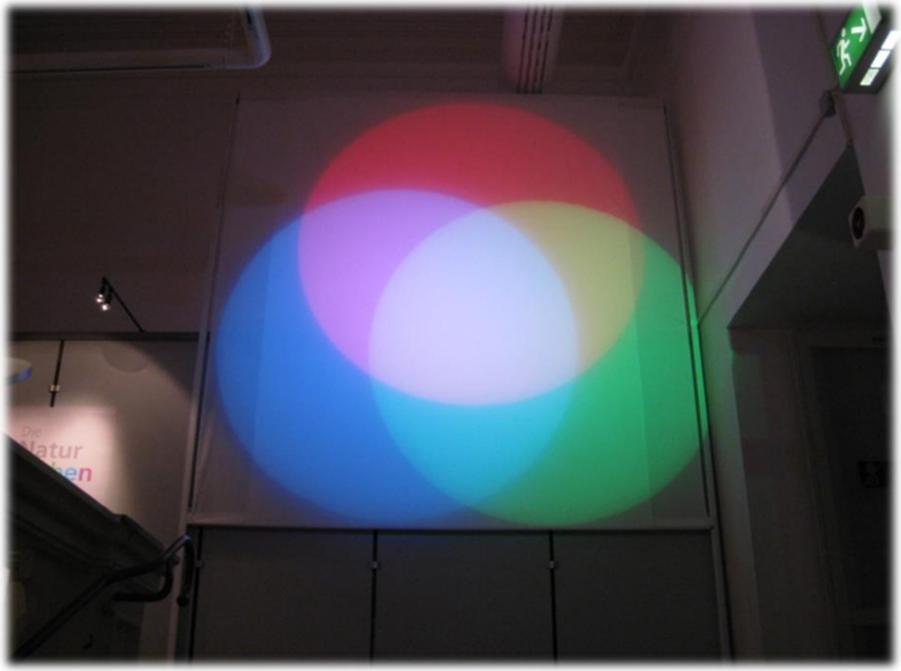
Spectroscopy

Spectroscopy is the study of the interaction between matter and electromagnetic radiation.



History of spectroscopy

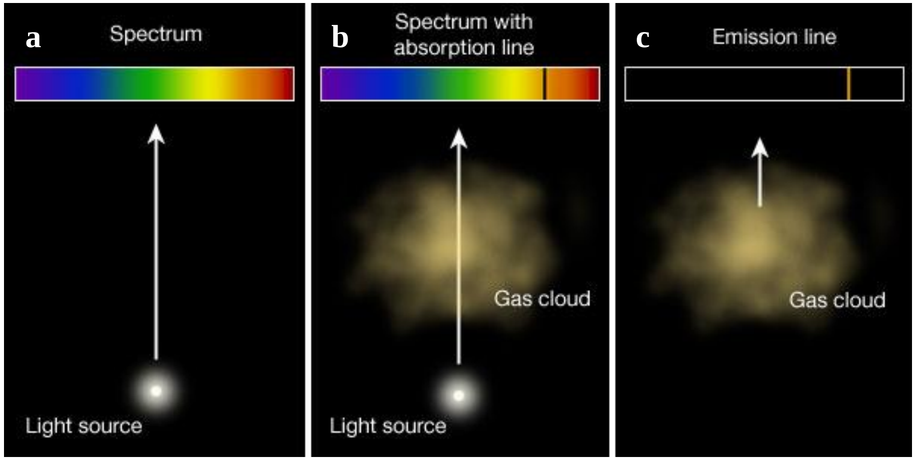
Sir Issac Newton (1643 ~ 1727)



- Advances in optics, specifically prisms, enabled systematic observations of the solar spectrum.
- Isaac Newton first applied the word spectrum to describe the rainbow of colors that combine to form white light.

History of spectroscopy

Joseph von Fraunhofer (1787 ~ 1826)

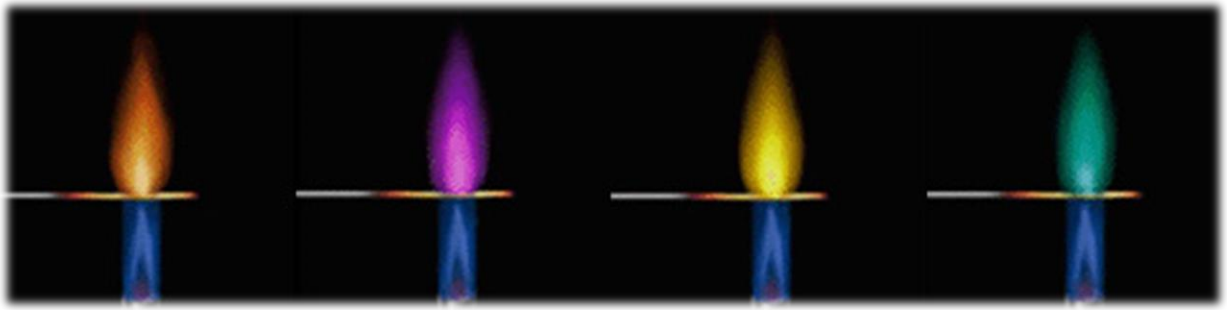


Fraunhofer lines

a. Solids, fluids and high-pressure gases emit a continuous spectrum.
b. When the light passes through a low-density cold gas, specific colors of light are absorbed.
c. A low-density hot gas emits a line spectrum.

History of spectroscopy

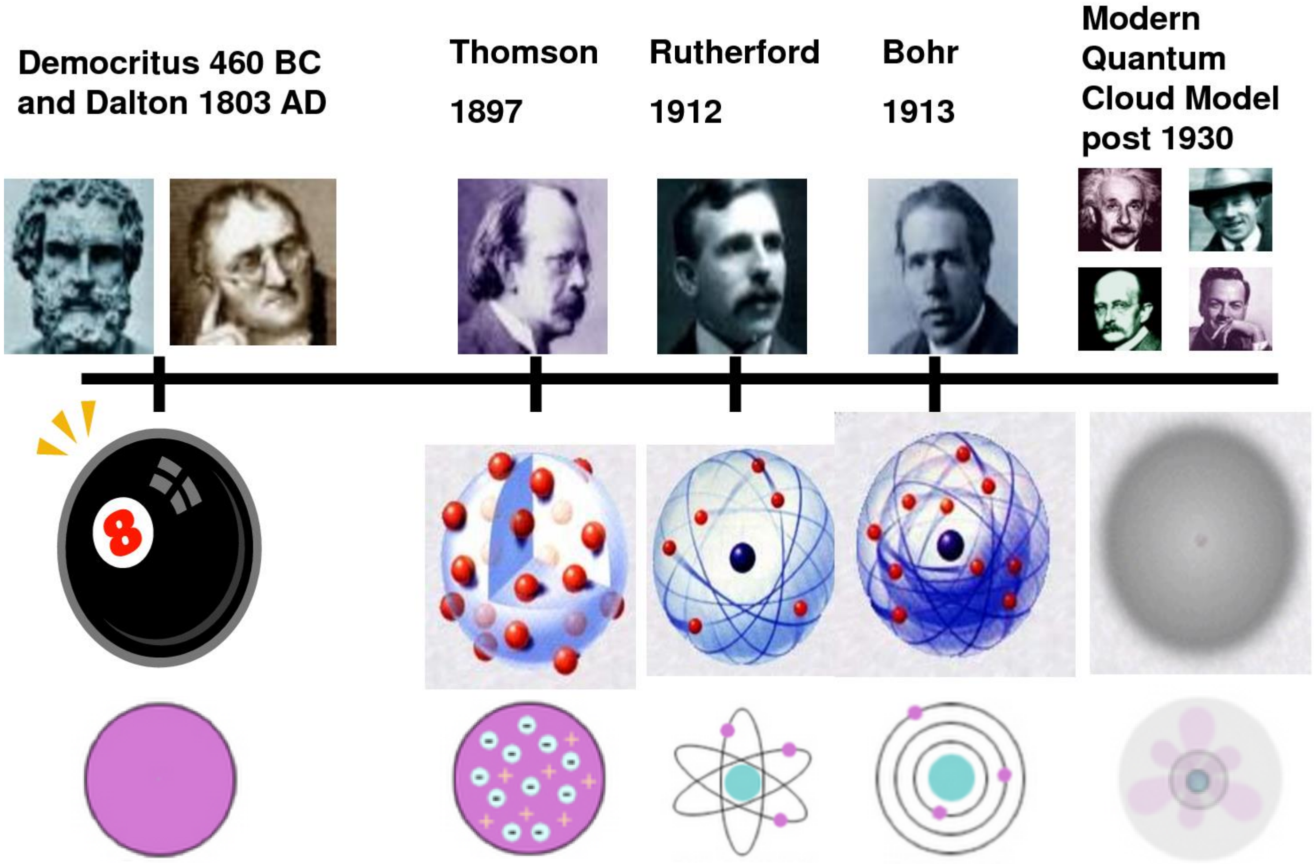
Gustav Robert Kirchhoff (1824 ~ 1887)



Calcium (Ca) Kalium (K) Natrium (Na) Copper (Cu)

- A flame test is an analytic procedure used in chemistry to detect the presence of certain elements.
- Based on each element's characteristic, different emission spectrum is shown.
- The color of flames in general also depends on temperature.

Atom models: historical time line



Democritus 460 BC and Dalton 1803 AD

Thomson

1897

Rutherford

1912

Bohr

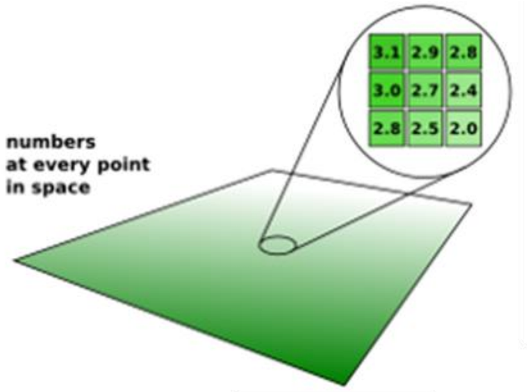
1913

Modern Quantum Cloud Model post 1930

Classical mechanics vs. Quantum mechanics

Classical mechanics

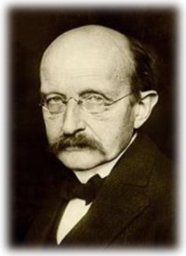
Issac Newton

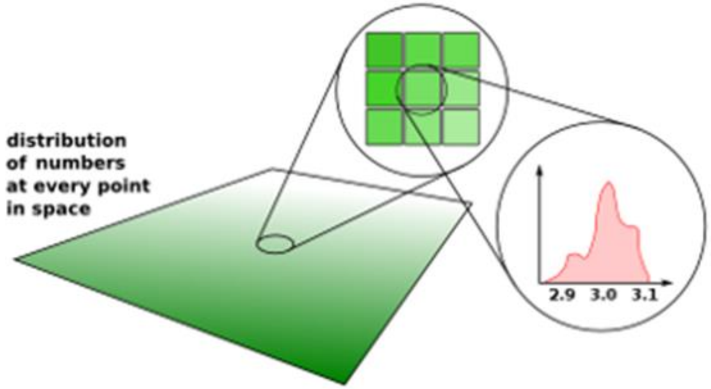


3.1	2.9	2.8
3.0	2.7	2.4
2.8	2.5	2.0

Quantum mechanics

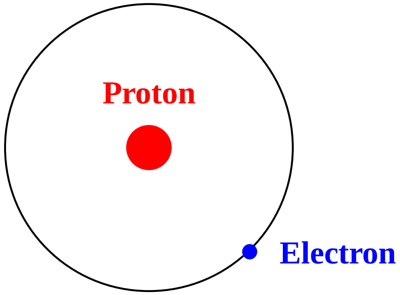
Max Planck

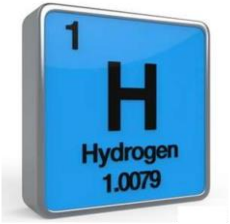




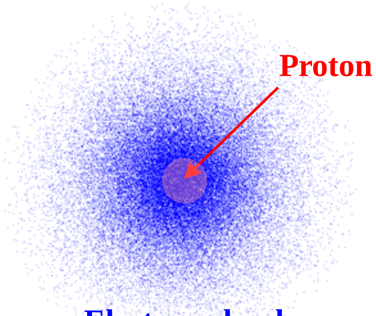
Quantum mechanics: electron cloud

Classical mechanics

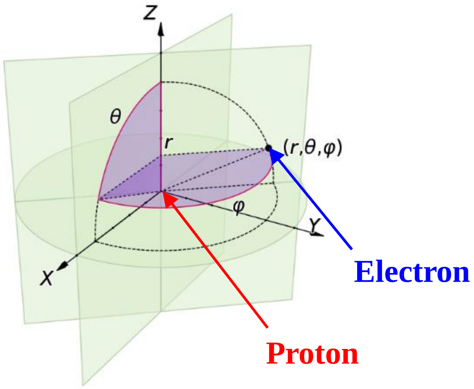




Quantum mechanics



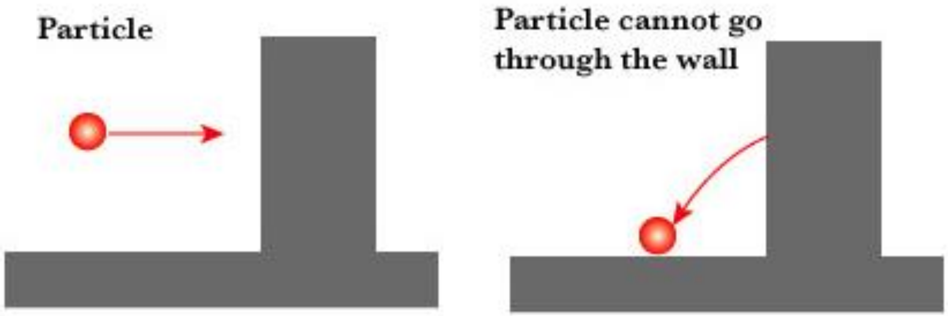
Electron cloud (probability)



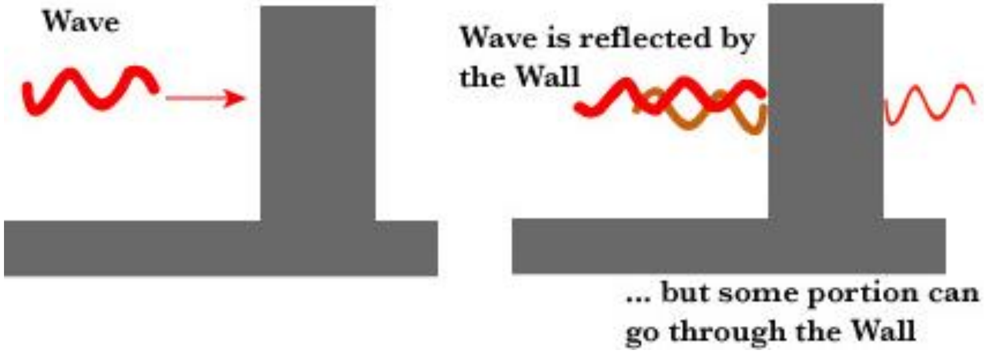
Wave function $\psi(r,\theta,\phi)=\frac{1}{4}\left(\frac{1}{2\pi a_0^5}\right)^{1/2} re^{-r/2a_0}\sin\theta\cos\phi$

Quantum mechanics: tunnel effect

Classical mechanics



Quantum mechanics



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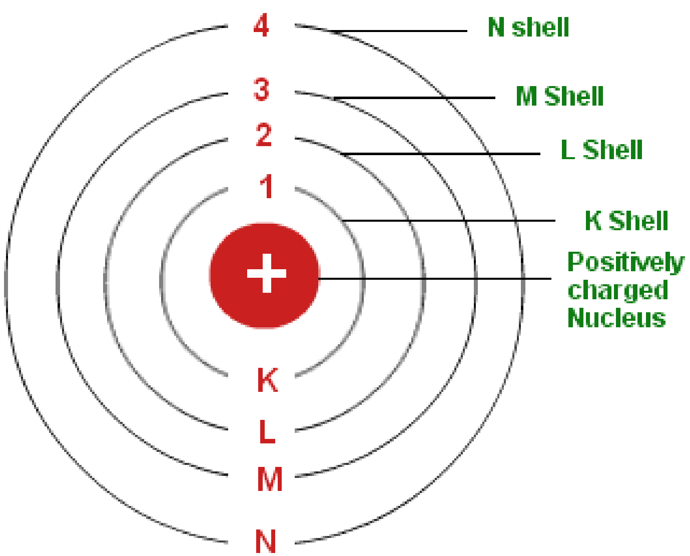
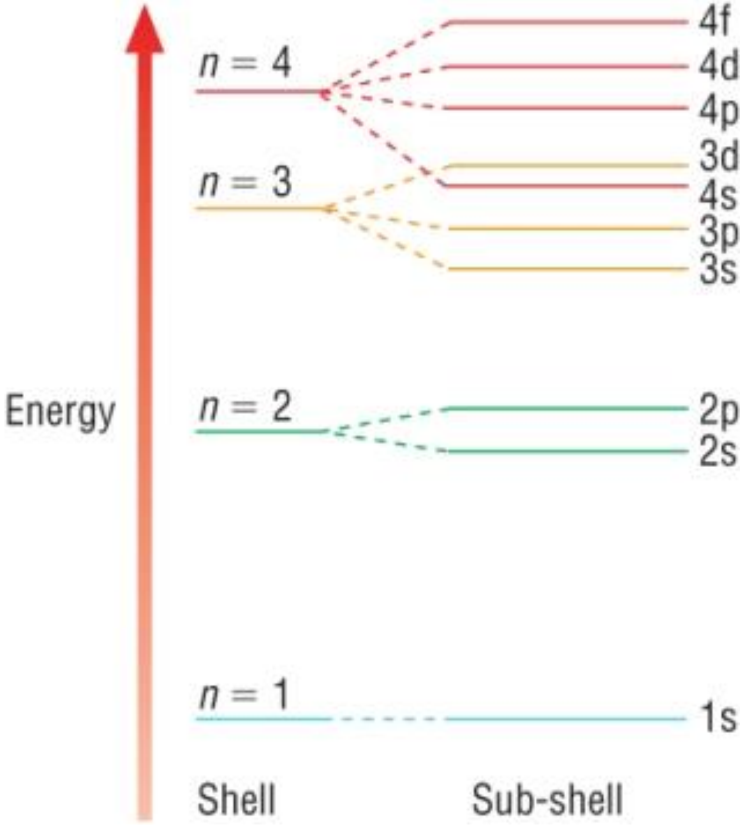
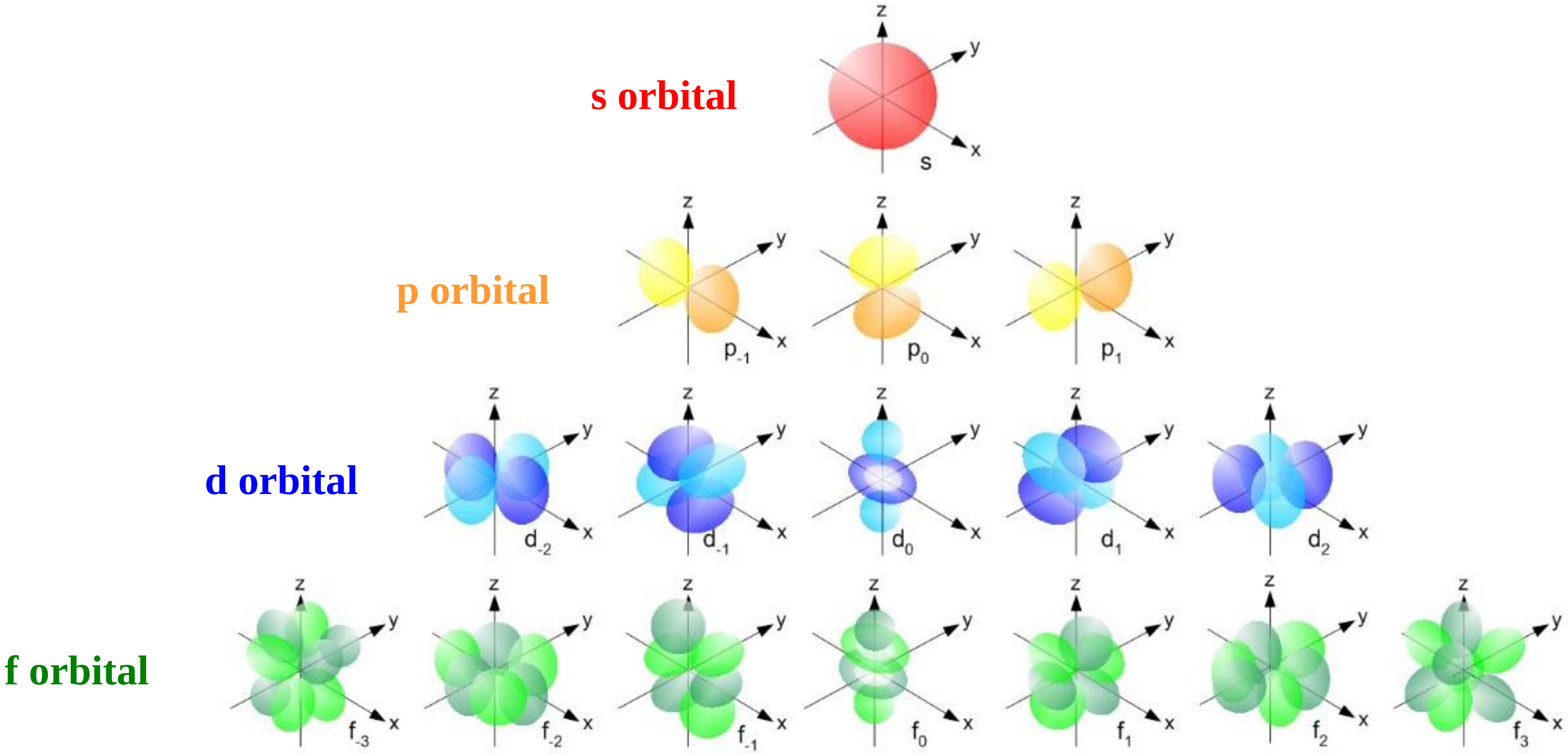
Energy level of atoms





Orbitals of atoms



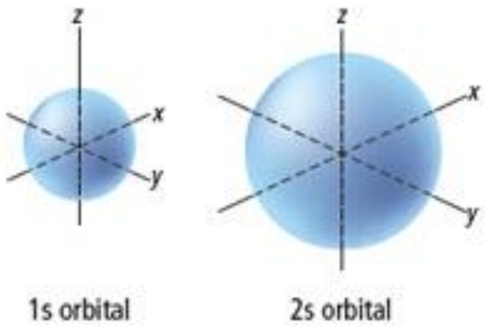
s orbital

p orbital

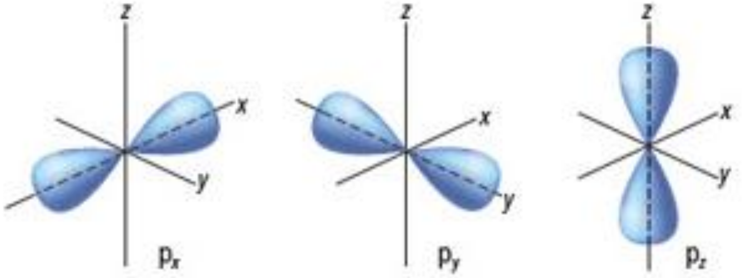
d orbital

f orbital

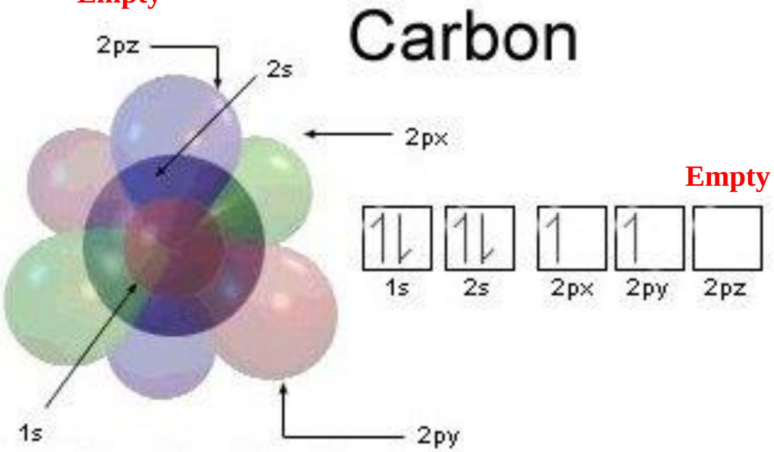
Example: carbon orbital



All s orbitals are spherical, and their size increases with increasing principal quantum number.



The three p orbitals are dumbshell-shaped and are oriented along the three perpendicular *x*, *y*, and *z* axes.



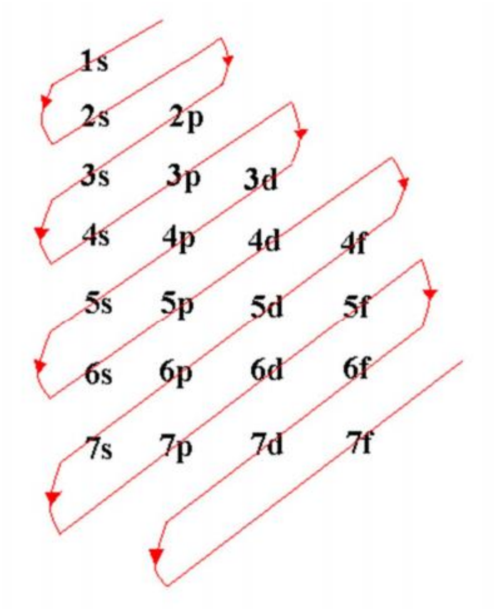
Empty

Empty

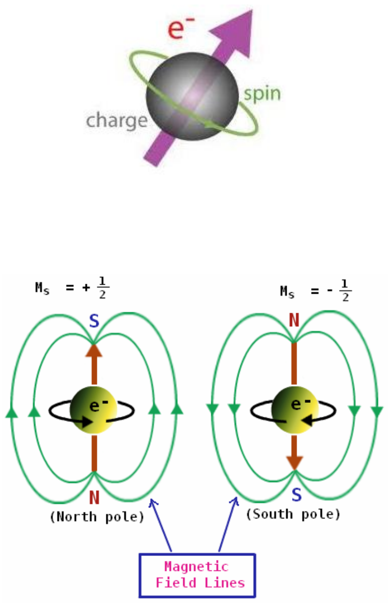
Three principles for electron configuration

Electron configuration in orbitals

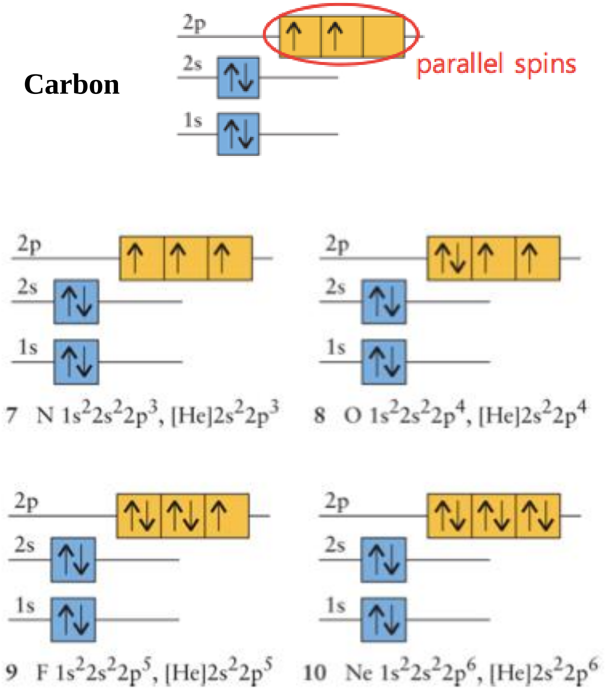
1. Building-up principle



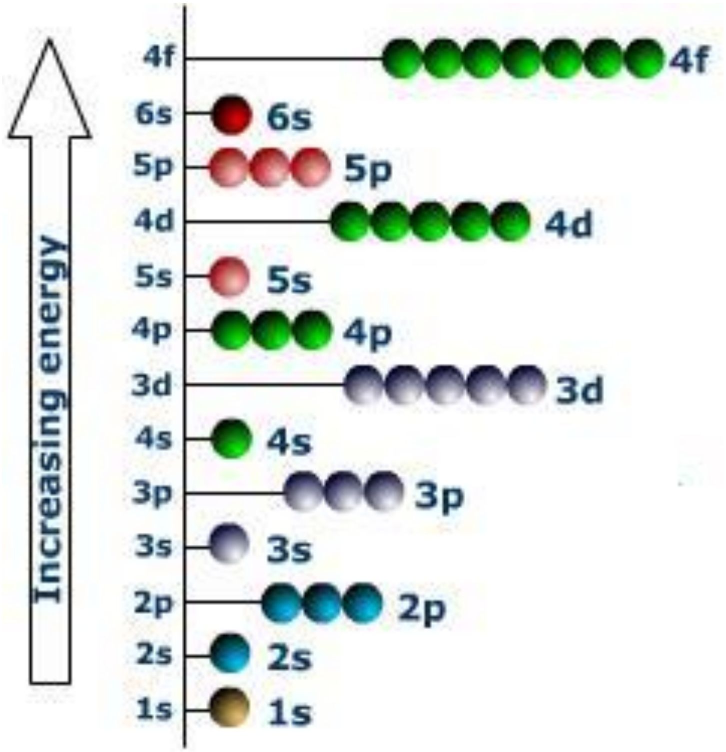
2. Pauli exclusion principle



3. Hund's rule



Electron configuration diagrams



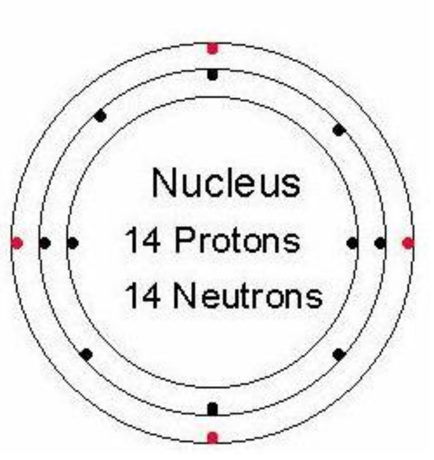
			1s	2s	2px	2py	2pz
Lithium,	Li	$1s^2 2s^1$	↑↓	↑			
Beryllium,	Be	$1s^2 2s^2$	↑↓	↑↓			
Boron,	B	$1s^2 2s^2 2p^1$	↑↓	↑↓	↑		
Carbon,	C	$1s^2 2s^2 2p^2$	↑↓	↑↓	↑	↑	
Nitrogen,	N	$1s^2 2s^2 2p^3$	↑↓	↑↓	↑	↑	↑
Oxygen,	O	$1s^2 2s^2 2p^4$	↑↓	↑↓	↑↓	↑	↑
Fluorine,	F	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑↓	↑↓	↑
Neon,	Ne	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓	↑↓	↑↓

Examples: silicon and copper

Elemental property with electron configuration

Silicon (Si)

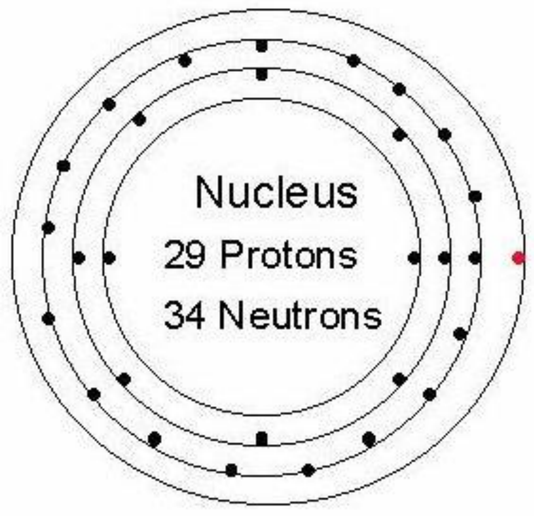
$1s^2 2s^2 2p^6 3s^2 3p^2$



- Si has 14 electrons in 3 shells
- The valence shell has 4 electrons.
- Half-full valence shell gives semiconductor property

Copper (Cu)

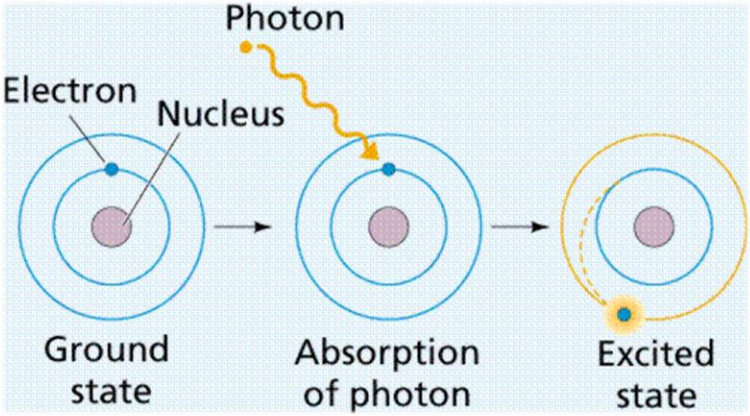
$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$



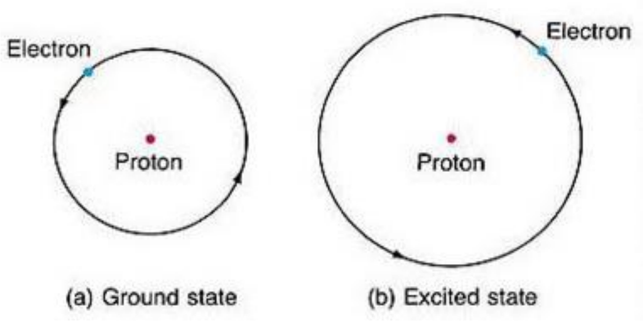
- Cu has 29 electrons in 4 shells
- The valence shell has 1 electrons.
- Single valence electron makes copper a good conductor.

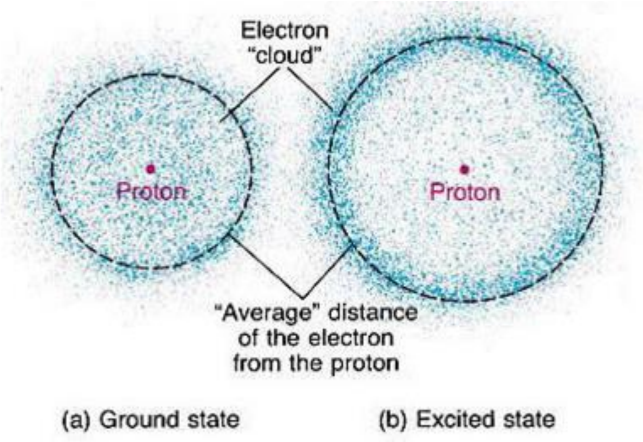
Excited state of electron

Hydrogen atom



Early concept

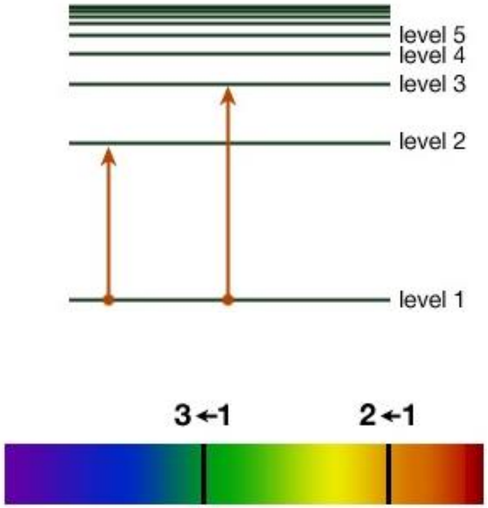


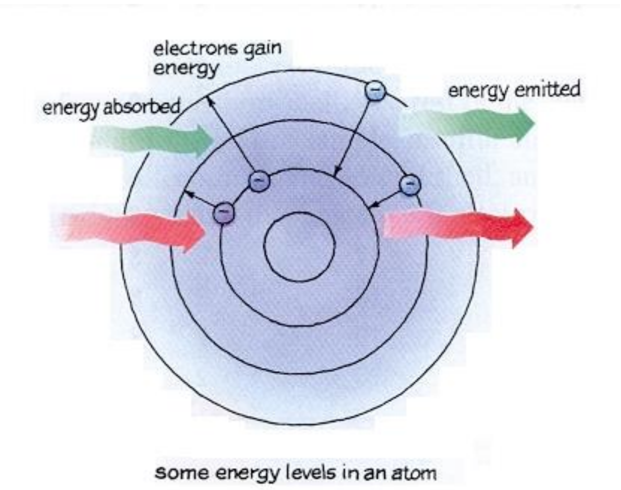


Modern concept

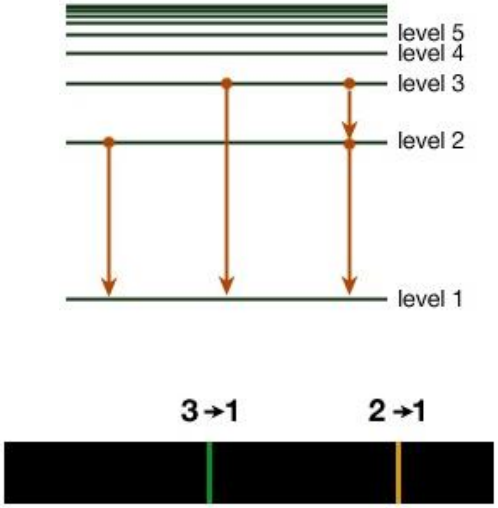
Absorption and emission

Absorption





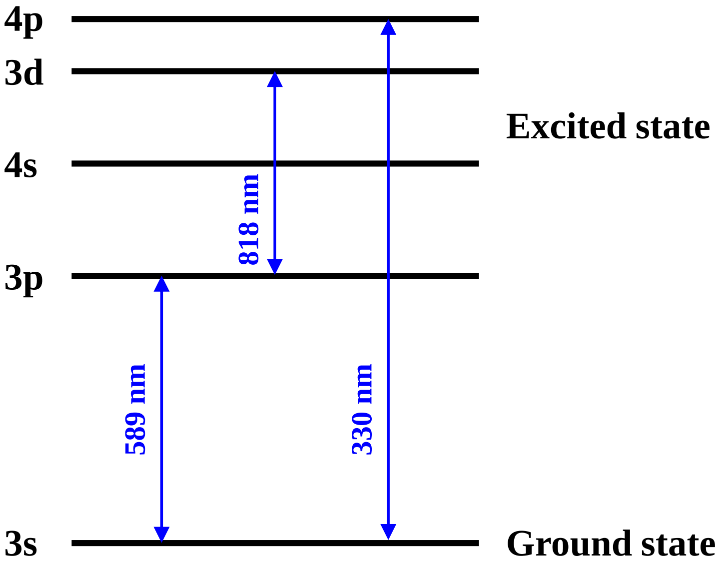
Emission



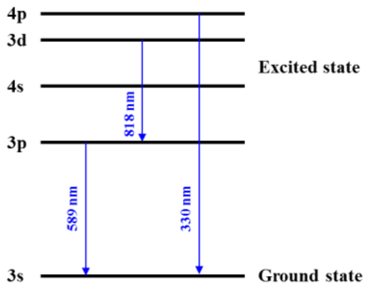
Example of spectrums: atom

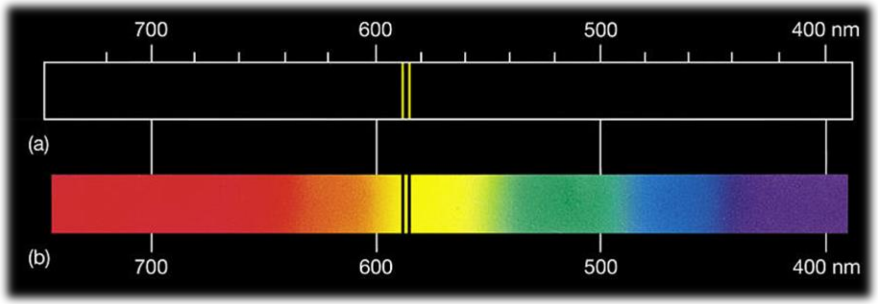
Natrium (Na)

$1s^2 2s^2 2p^6 3s^1$

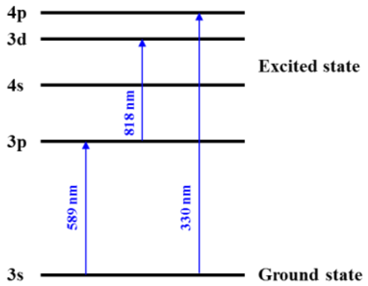


Emission spectrum





Absorption spectrum



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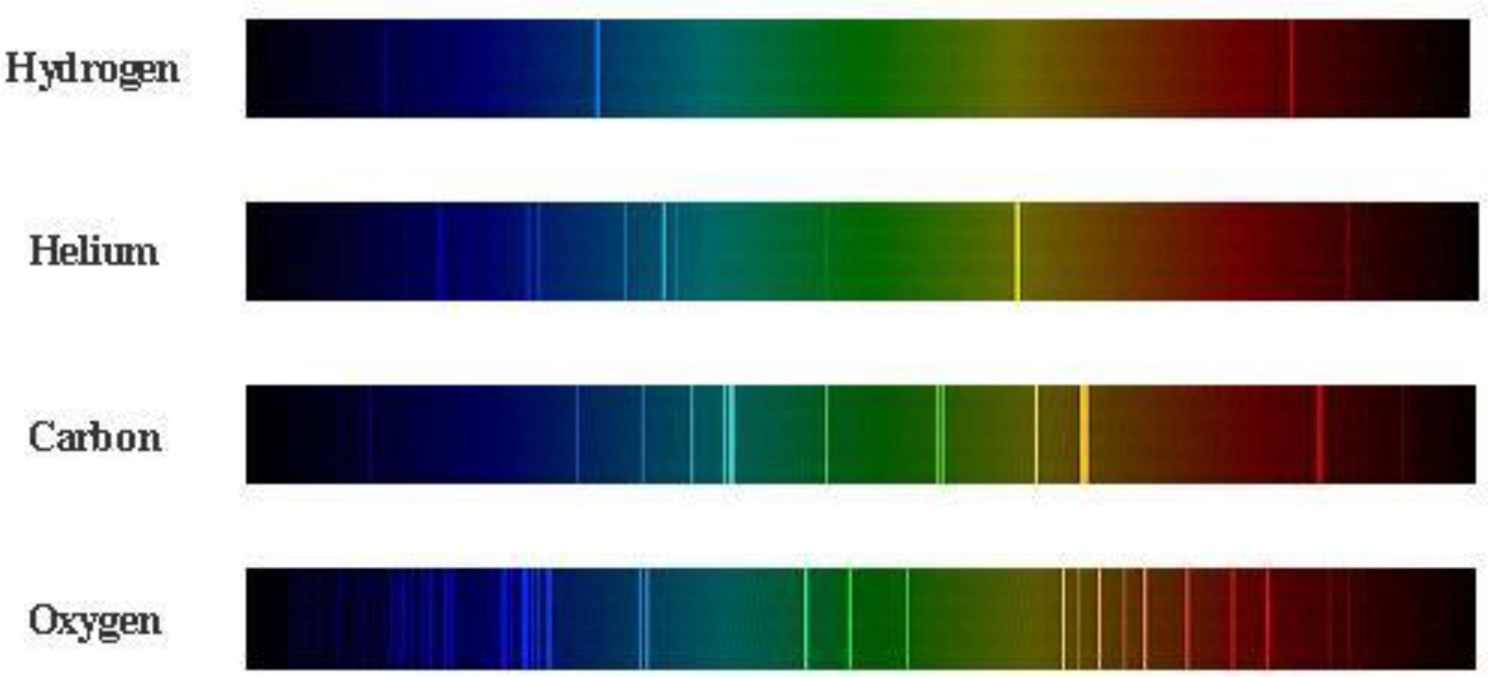
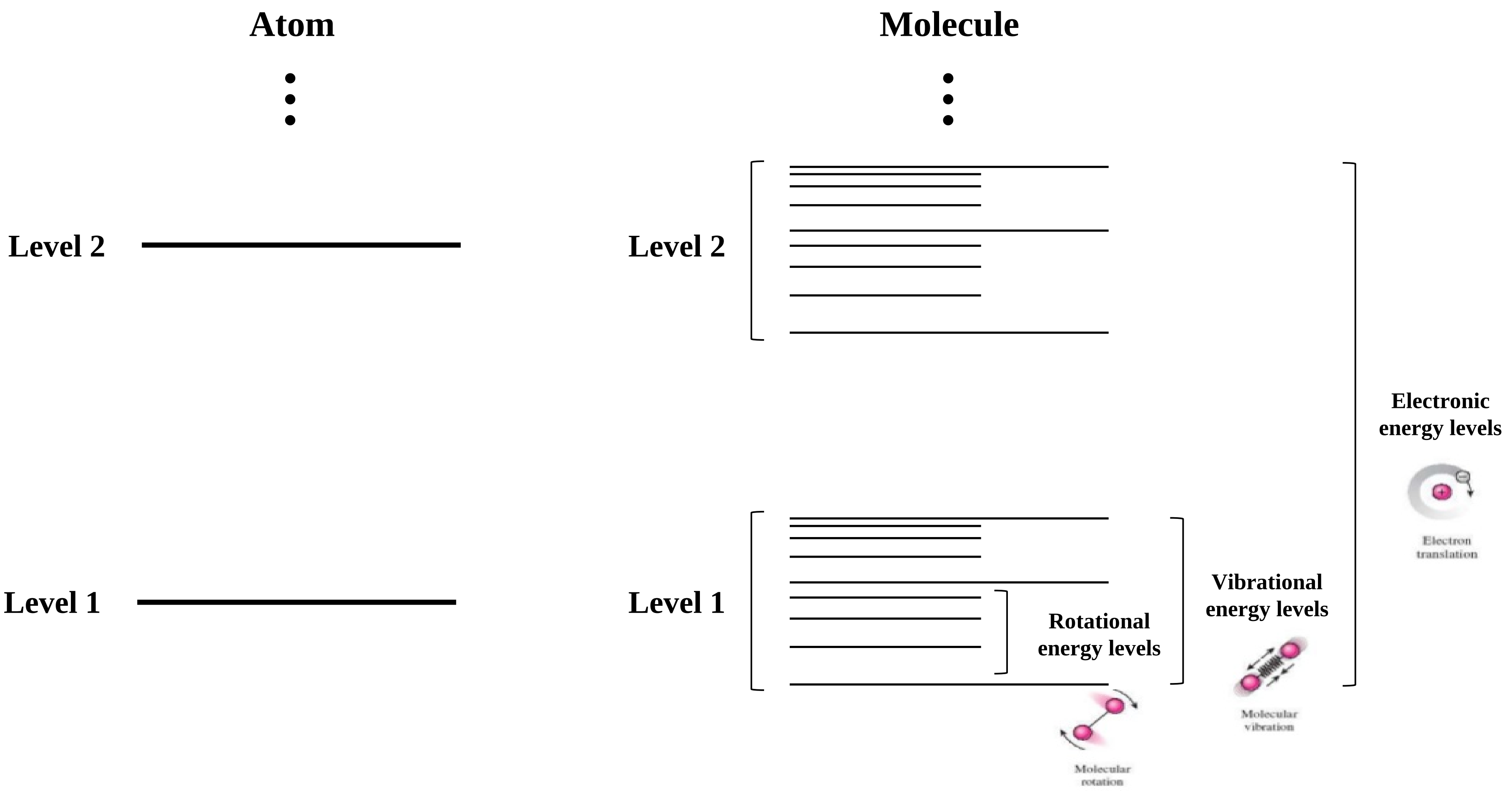
Example of spectrums: atom



Energy levels: atom vs. molecule



Atom

Molecule

Level 2

Level 1

Level 2

Level 1

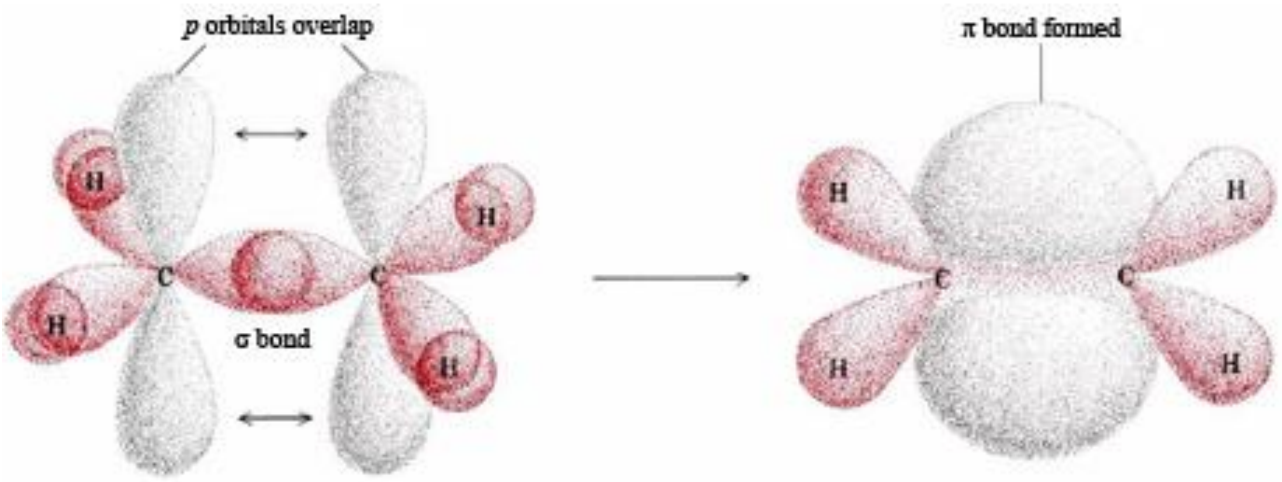
Rotational energy levels

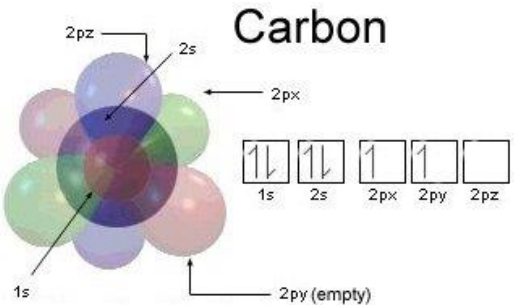
Vibrational energy levels

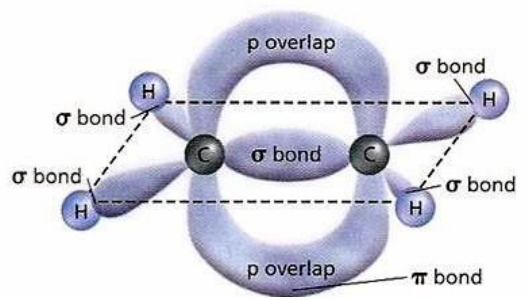
Electronic energy levels

Electronic energy levels: molecule

Molecular orbital (MO) of ethene

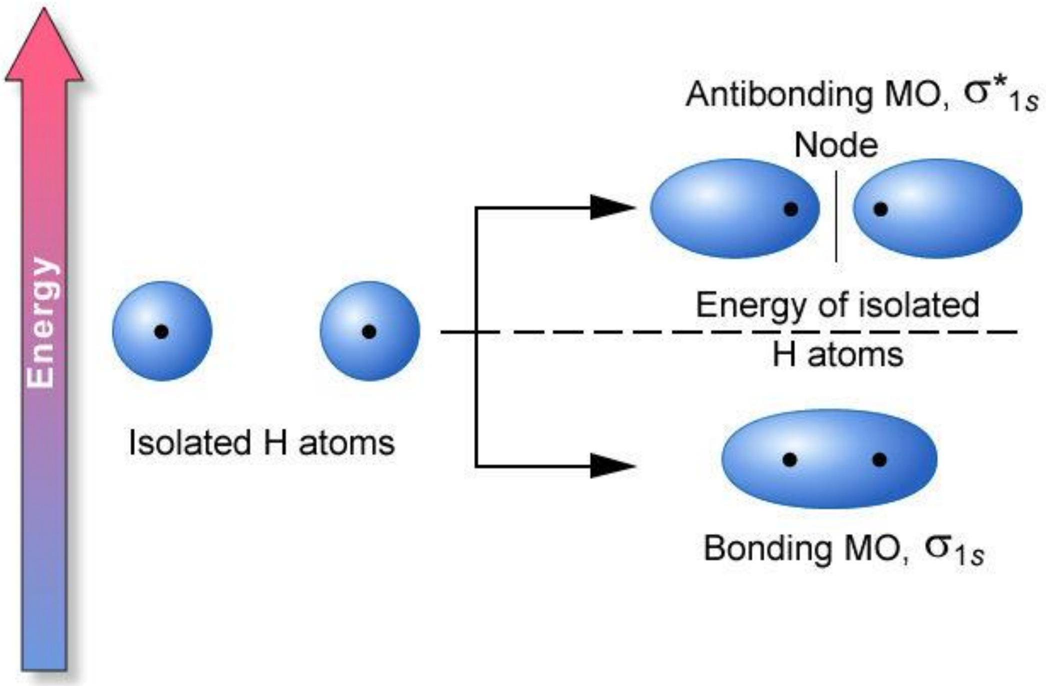






Electronic energy levels: molecule

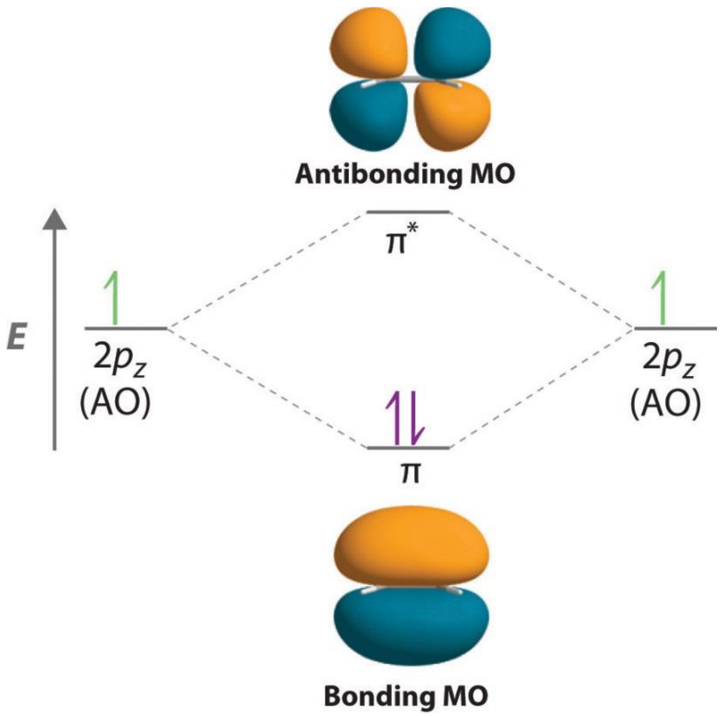
Molecular orbital (MO) of s orbitals

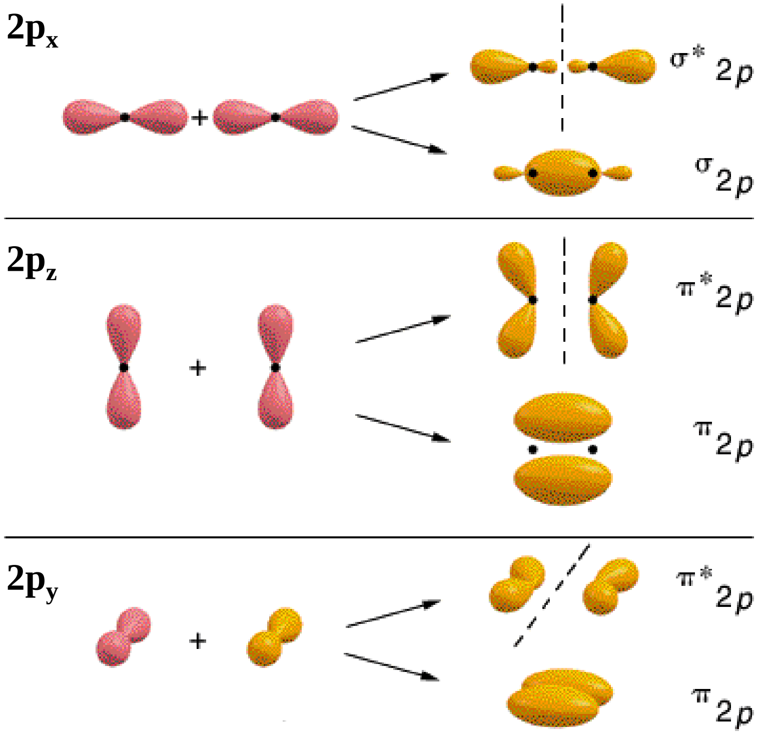


$$H + H \rightarrow H_2$$

Electronic energy levels: molecule

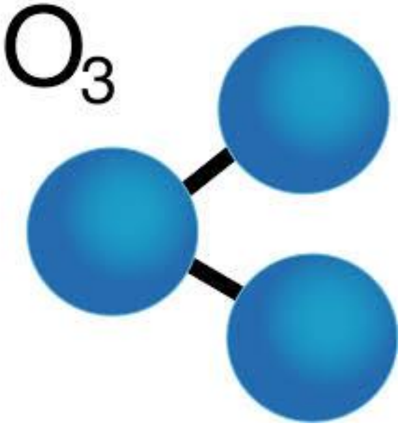
Molecular orbital (MO) of p orbitals

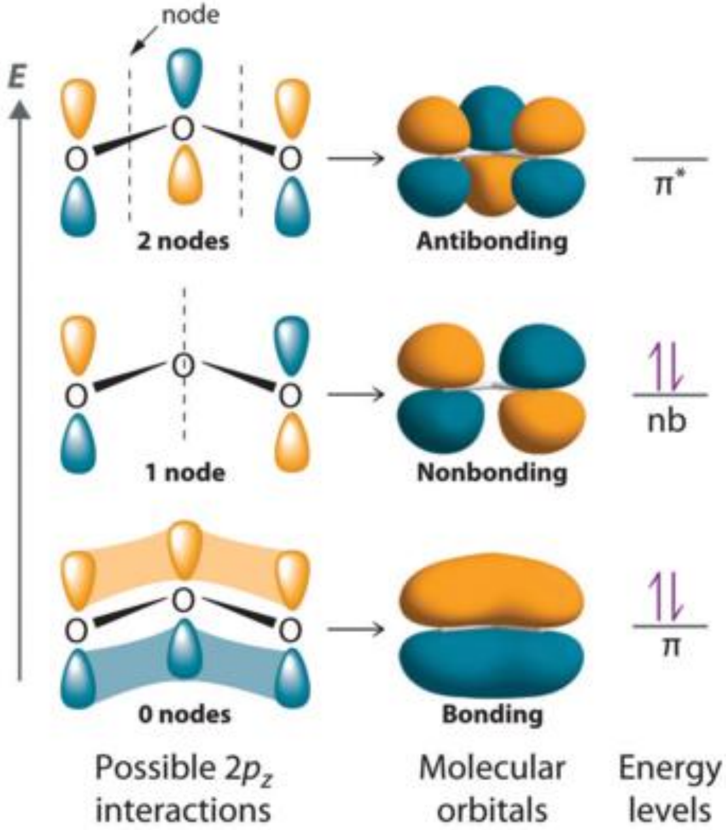




Electronic energy levels: molecule

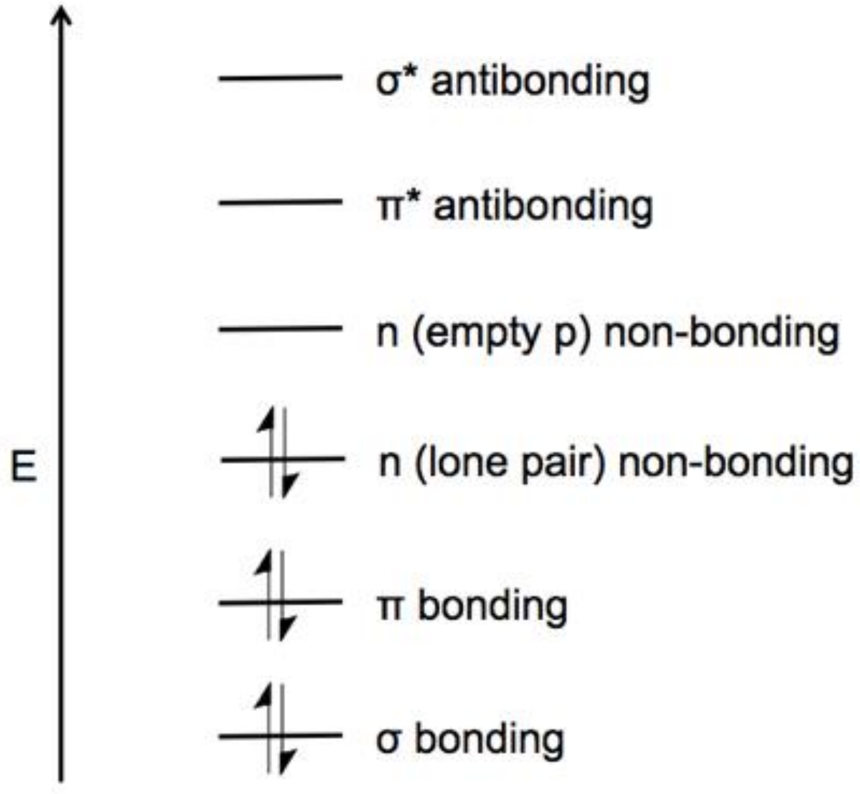
Molecular orbital (MO) of p orbitals





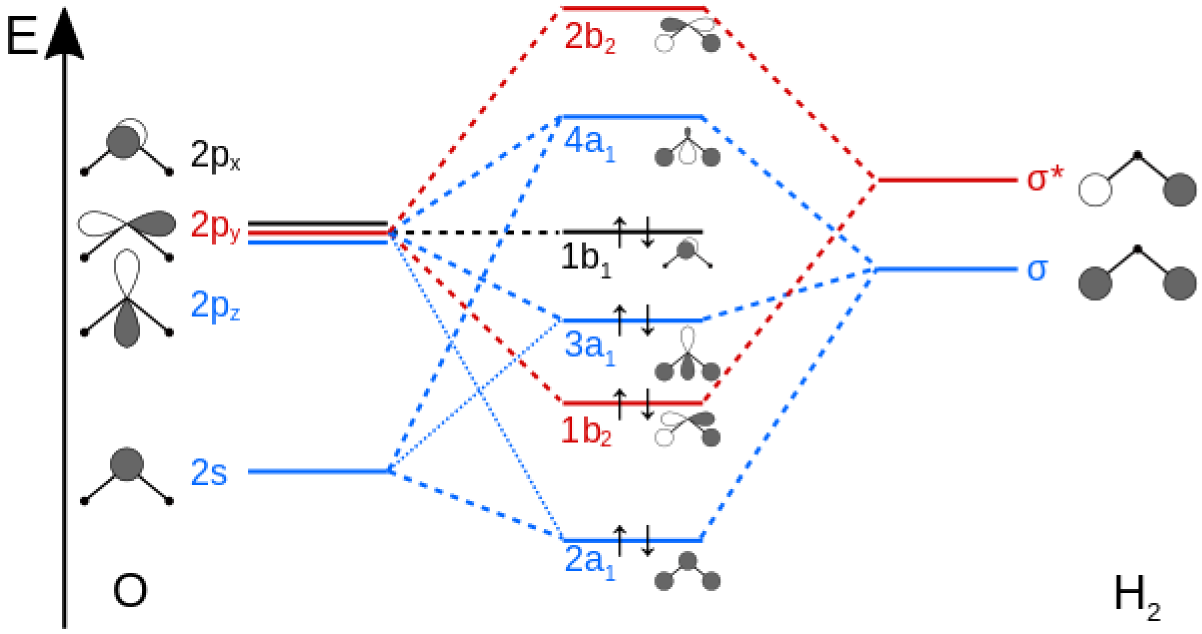
Electronic energy levels: molecule

Bonding, antibonding, nonbonding in molecular orbital (MO)



Electronic energy levels: molecule (example)

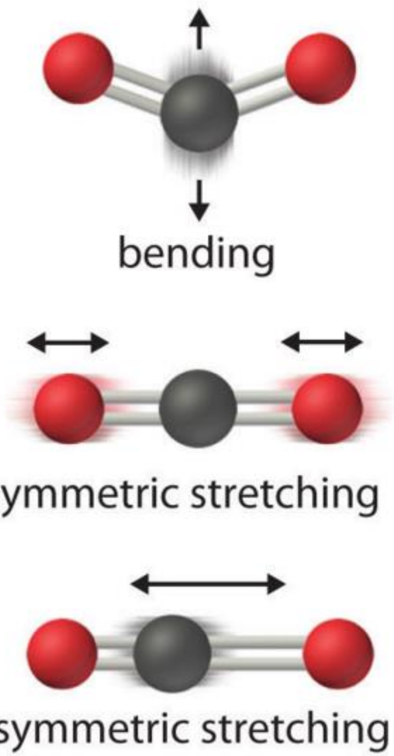
Atomic orbital (AO) of oxygen + Molecular orbital (MO) of hydrogen = water (H_2O)

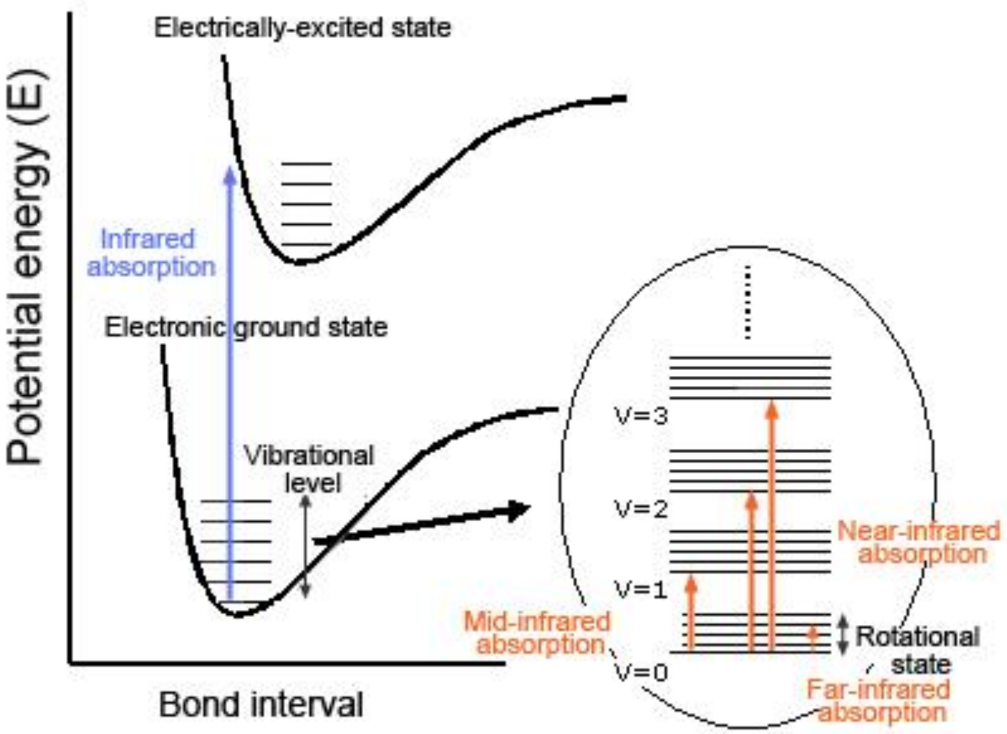


- $2a_1$ MO: oxygen 2s AO + hydrogen σ MO
- $1b_2$ MO: oxygen $2p_y$ AO + hydrogen σ^* MO
- $3a_1$ MO: oxygen $2p_z$ AO + hydrogen σ MO
- $1b_1$ (nonbonding MO): oxygen 2px AO

Vibrational energy levels: molecule

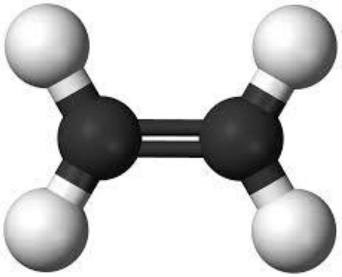
Vibrational motions

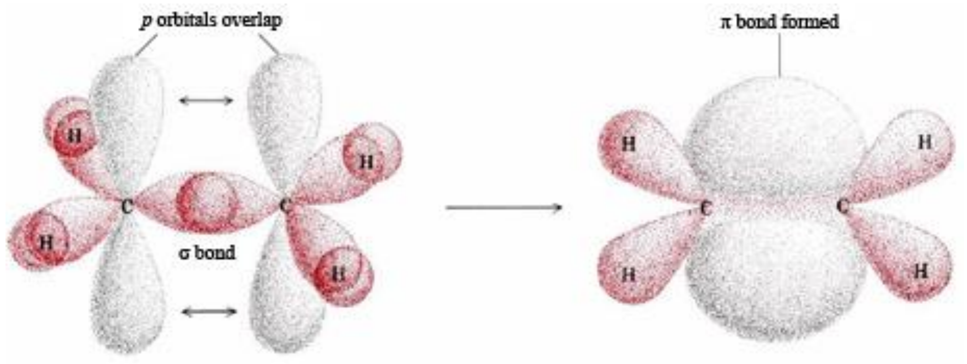




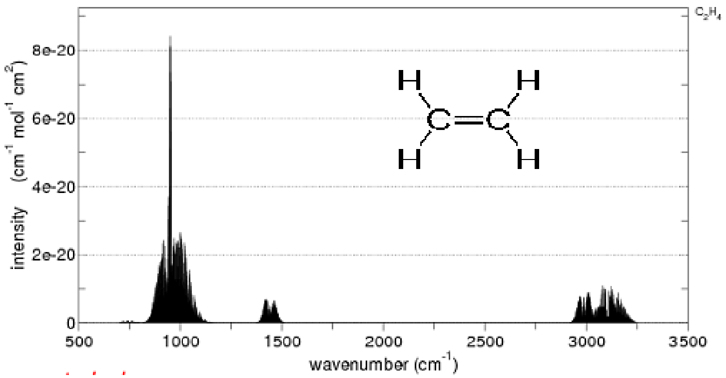
Example of spectrums: molecule

Ethene (C_2H_4)

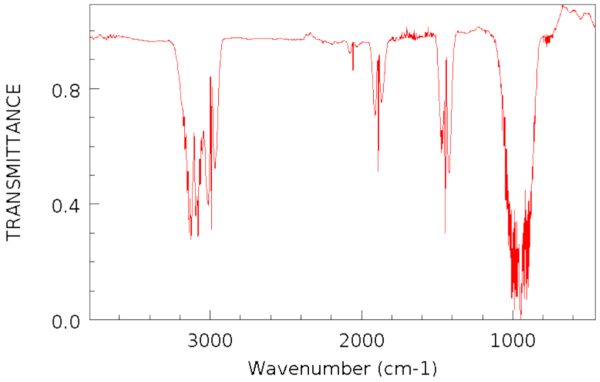




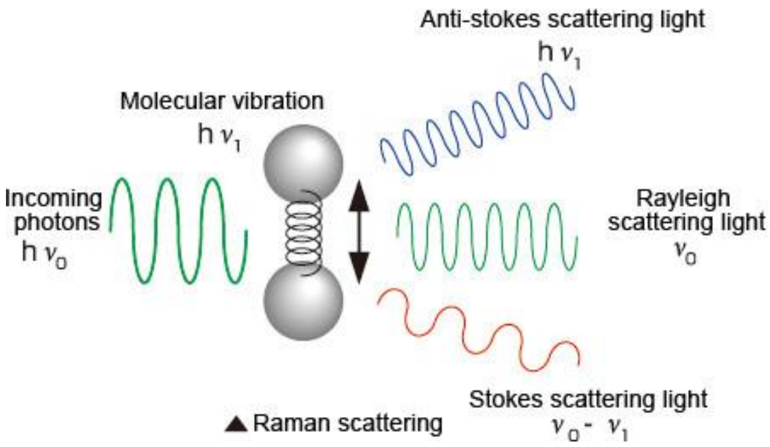
Theoretical spectrum of C_2H_4



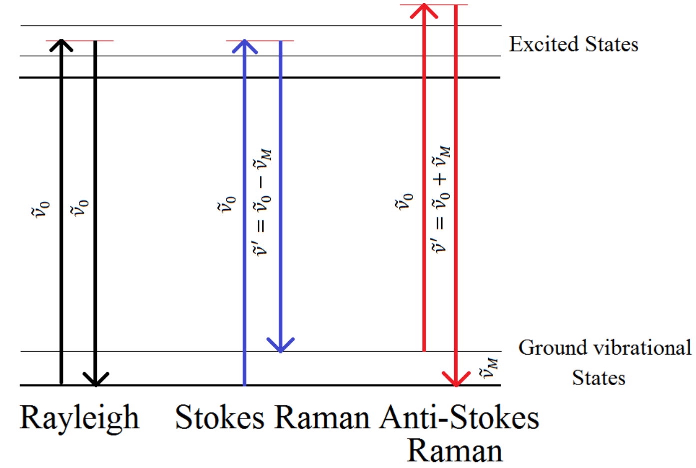
Experimental spectrum of C_2H_4

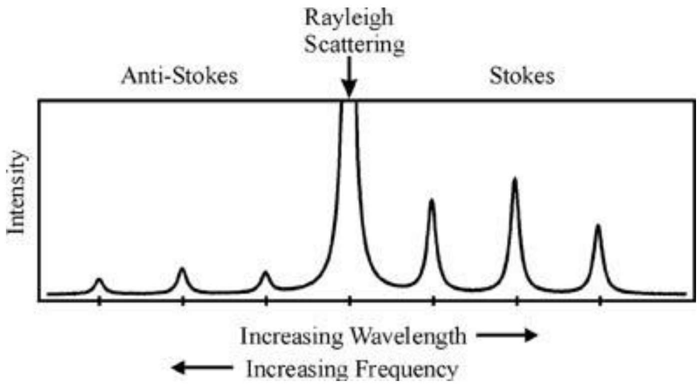


Example of spectrums: molecule



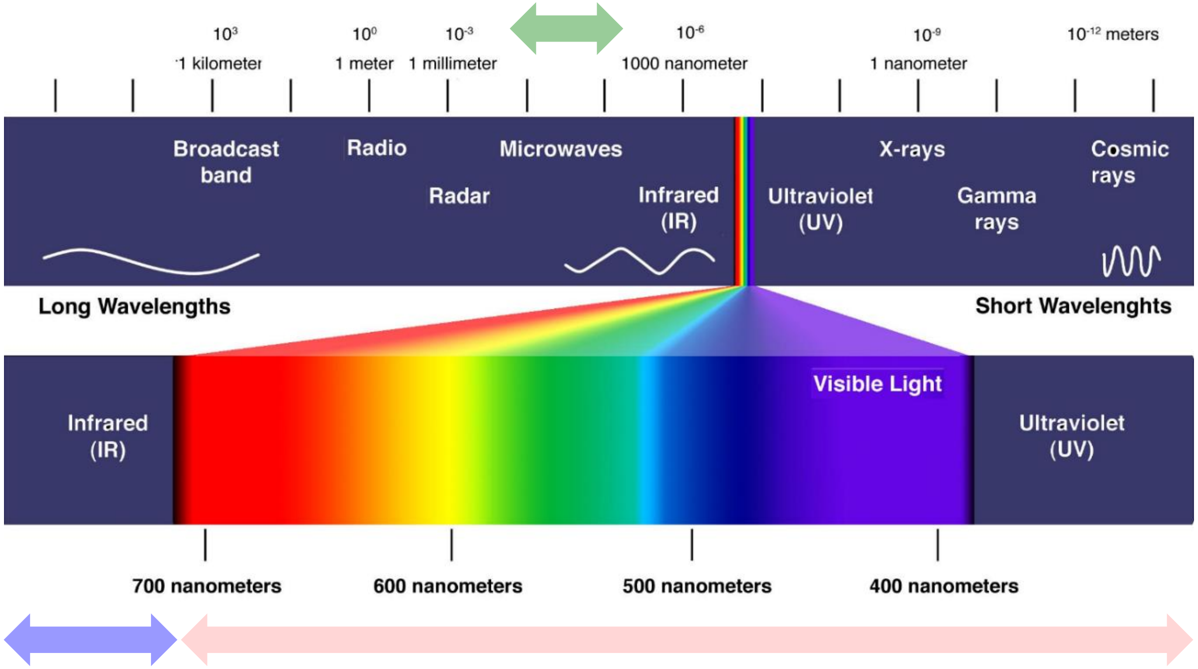
▲Raman scattering





Classification of spectroscopy

Molecular rotation
Microwave spectroscopy



Molecular vibration
IR spectroscopy
Raman spectroscopy

Molecular dissociation
UV-vis spectroscopy

Ultraviolet-visible Spectroscopy

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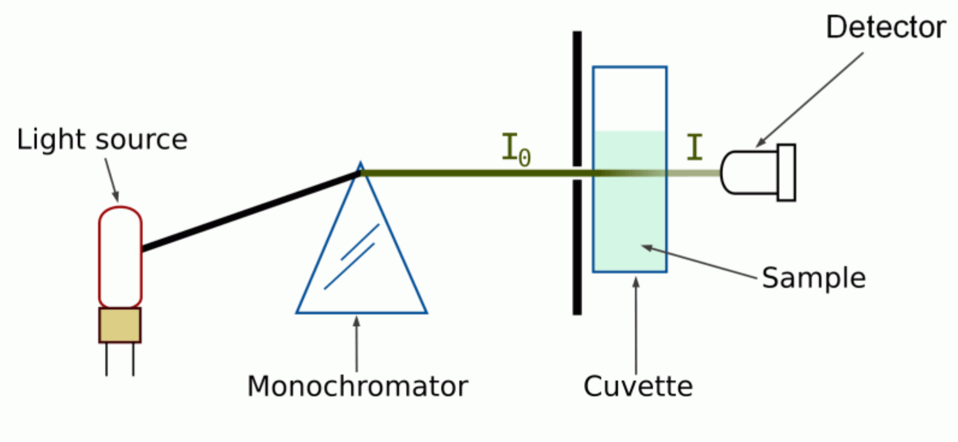
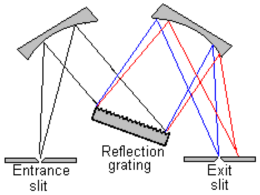
Instrument diagram and image



Monochromator
(wavelength selector)



1. Light sources

- UV source: deuterium (D_2) lamp emit radiation in the range of 160 ~ 375 nm.
- Visible source: tungsten (W) filament lamp is commonly employed in the range of 350 ~ 2500 nm.

2. Monochromator (wavelength selector): prism and grating

3. Cuvette

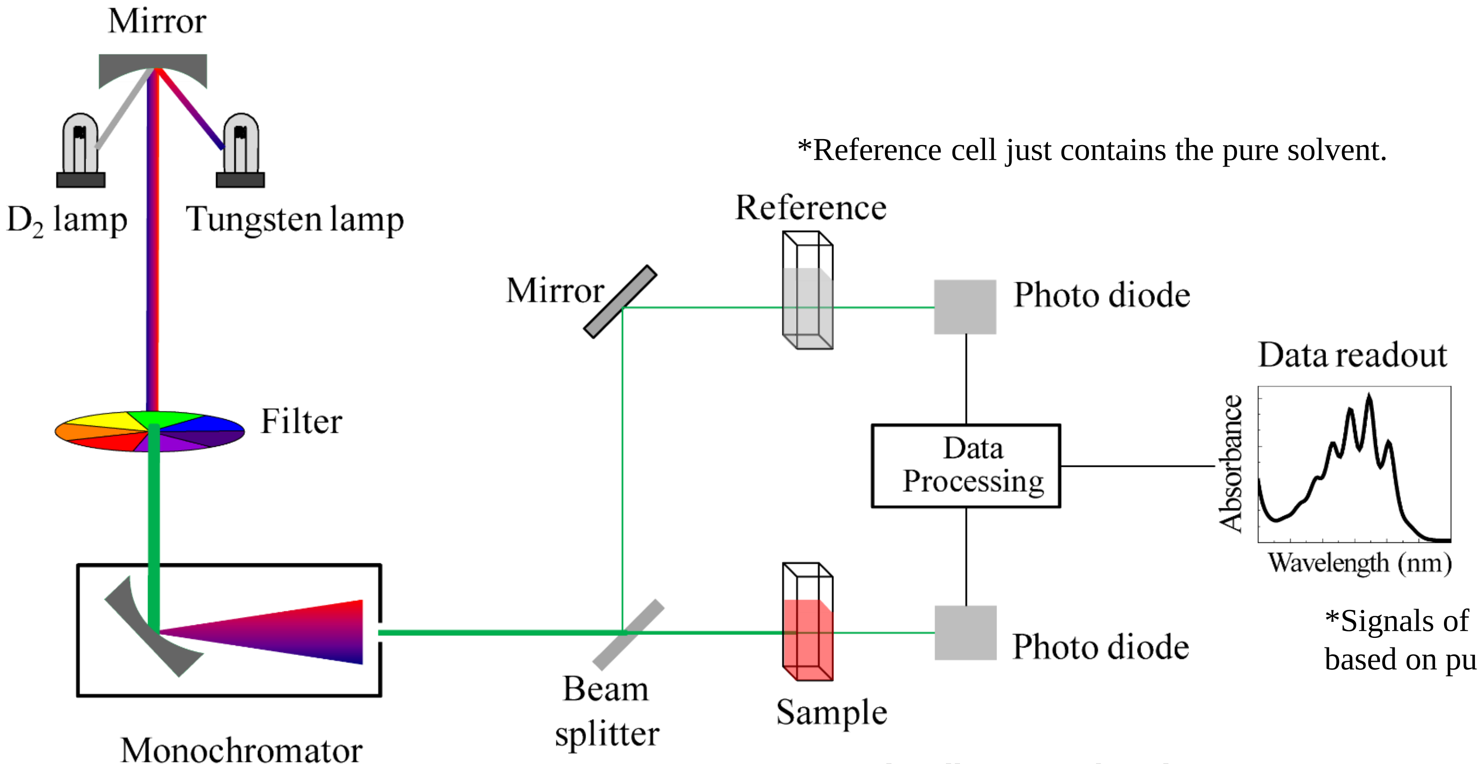
- The containers for sample and reference solution must be transparent to the radiation which will pass through them (quartz or fused silica).

4. Detector

- The photomultiplier tube is a commonly used detector in UV-Vis spectroscopy.

Instrument diagram

Double beam spectrometer

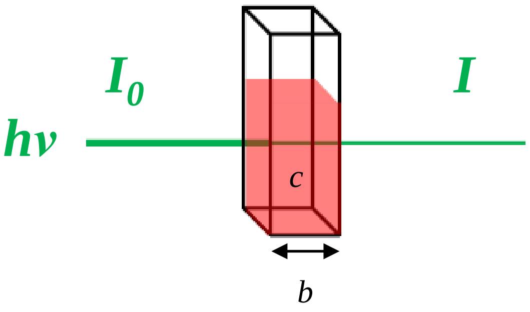


*Reference cell just contains the pure solvent.

*Sample cell contains the solution.

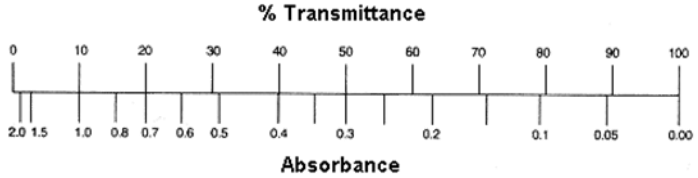
*Signals of solution based on pure solvent

Transmittance and absorbance (Beer-Lambert law)



Transmittance (T): $T = I / I_0$

Absorbance (A): $A = \log_{10} I_0 / I = \log_{10} 1 / T$

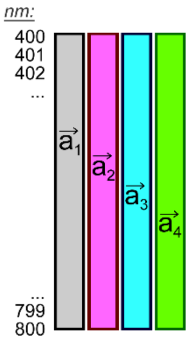


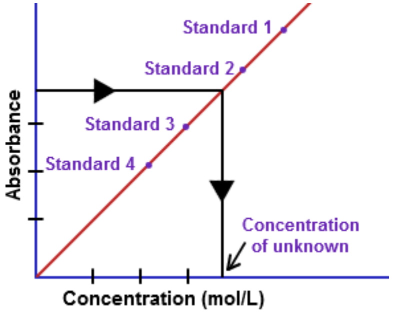
Beer-Lambert law

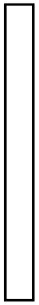
$$A = \log_{10} I_0 / I = \varepsilon bc$$

ε: molar absorbtivity (L/mol·cm)
b: path length of the sample (cm)
c: concentration of compound in solution (mol/L)

Standard samples

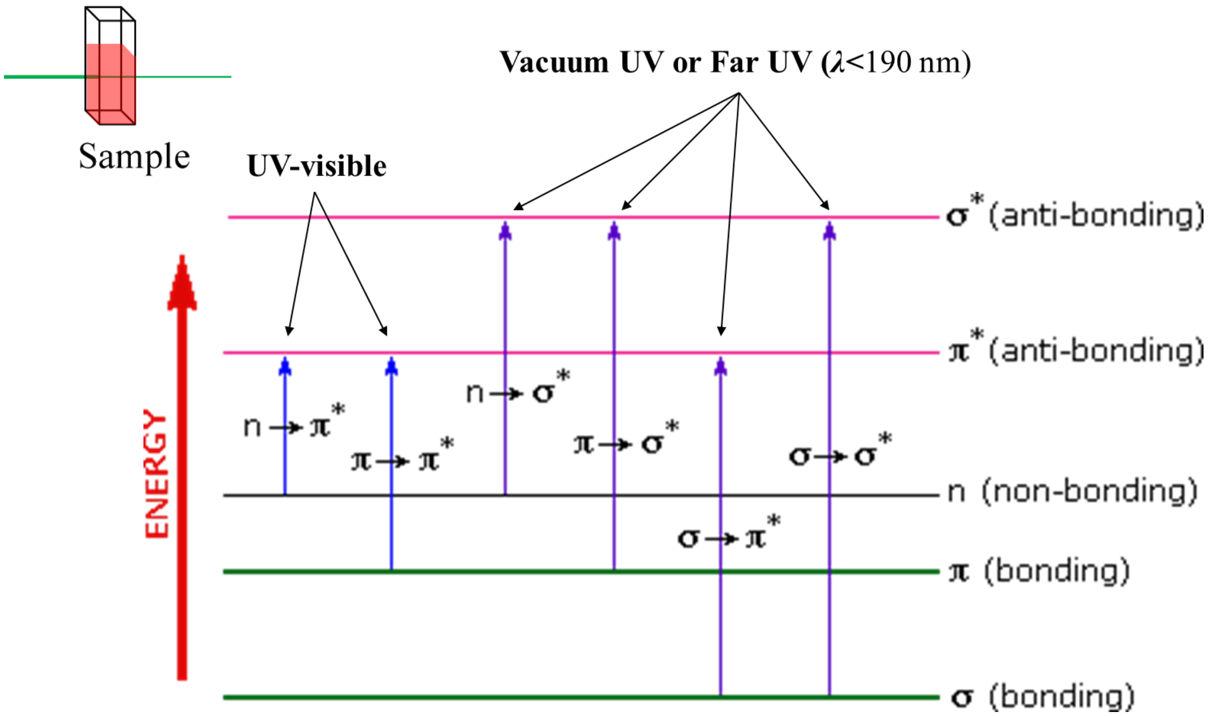


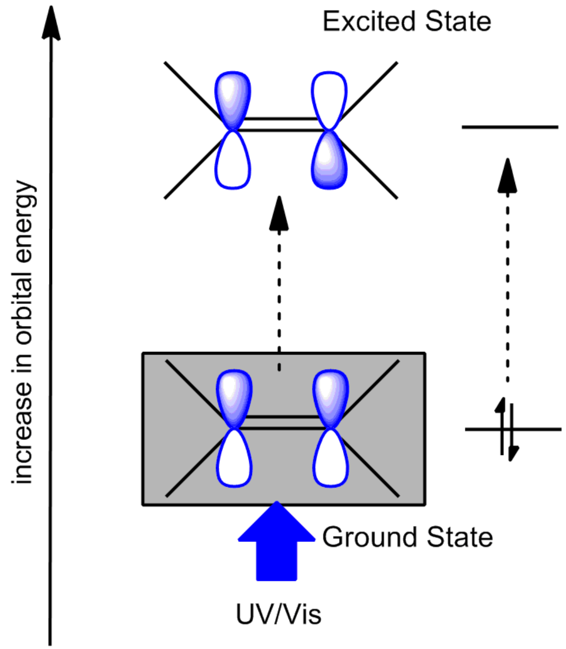




Unknown sample

Electron transitions of molecular energy level





Wavelength

Visible: 400 ~ 750 nm

Ultraviolet (UV): 200 ~ 400 nm

Vacuum UV or Far UV: ~ 200 nm

Electron transitions of molecular energy level

σ → σ* transitions

1. An electron in a bonding s orbital is excited to the corresponding antibonding.
2. The required energies to these transitions are very large.
3. Methane shows an absorbance maximum at 125 nm which is not seen in typical UV-visible spectra.

n → σ* transitions

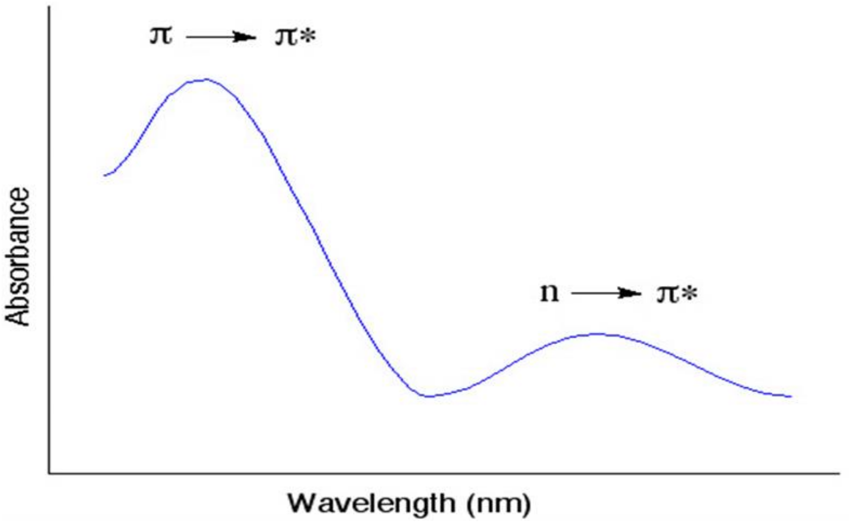
1. Saturated compounds containing atoms with lone pairs (nonbonding) are capable for these transitions.
2. These transitions usually need less energy than σ → σ* transitions.
3. They can be initiated by light whose wavelength is in the range of 150 ~ 250 nm.

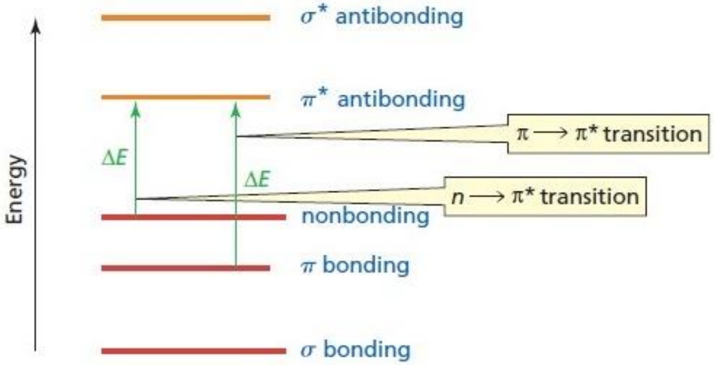
n → π* transitions and π → π* transitions

1. Most absorption spectroscopy of organic compounds is based on these transitions.
2. These transitions are belong to an experimentally convenient region of the wavelength (200 ~ 700 nm).
3. These transitions need an unsaturated group in the molecule to provide the π electrons.

UV-visible spectroscopy analysis

Typical absorbance spectra of carbonyl group



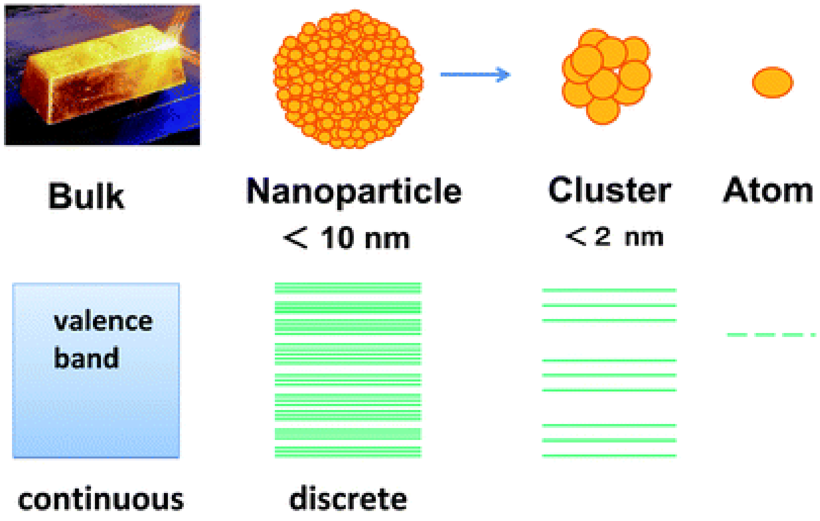


Functional group	λ_{max} (nm) strong $\pi \rightarrow \pi^*$	 weak $n \rightarrow \pi^*$
C=O	166	280
C=C–C=O	240	320
C=C–C=C–C=O	270	350

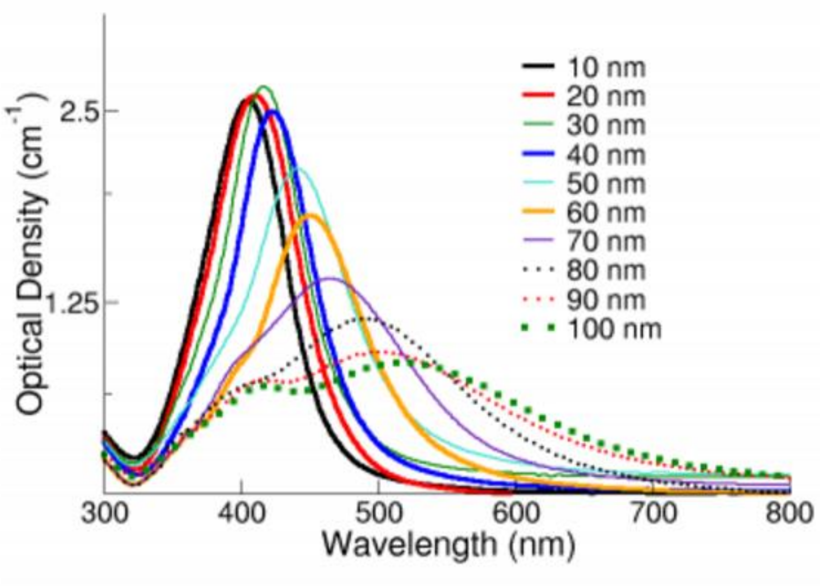
Nanoparticle Technology

UV-visible spectroscopy analysis in nanotechnology

Energy levels
(dimension dependency)



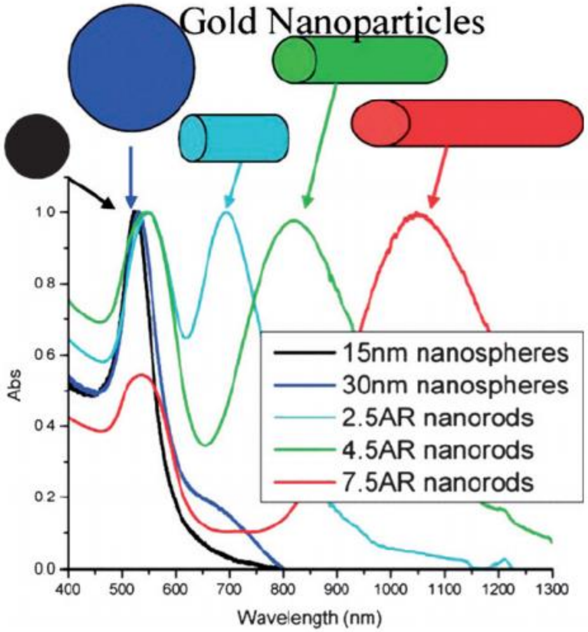
UV-visible spectrum
(size dependent on Ag nanoparticles)



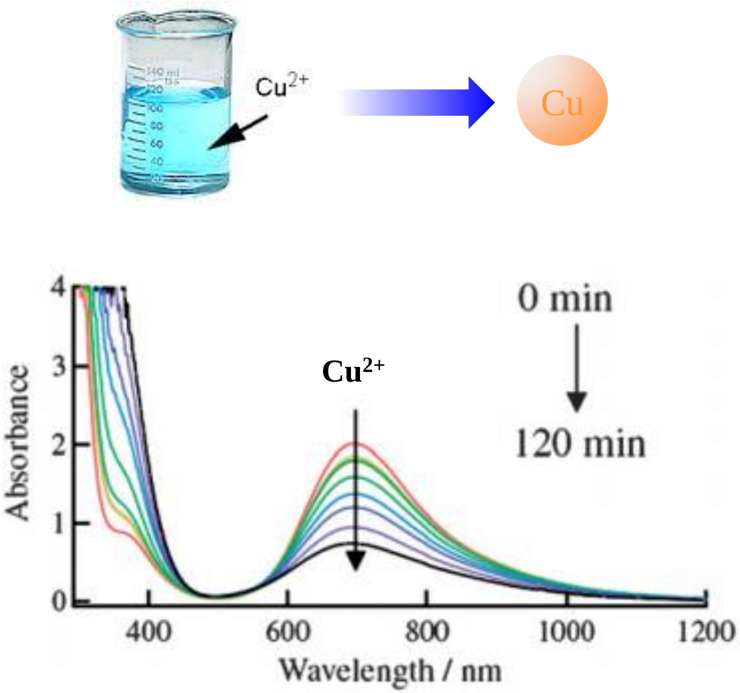
Nanoparticle Technology

UV-visible spectroscopy analysis in nanotechnology

UV-visible spectrum
(shape dependent on Au nanomaterials)



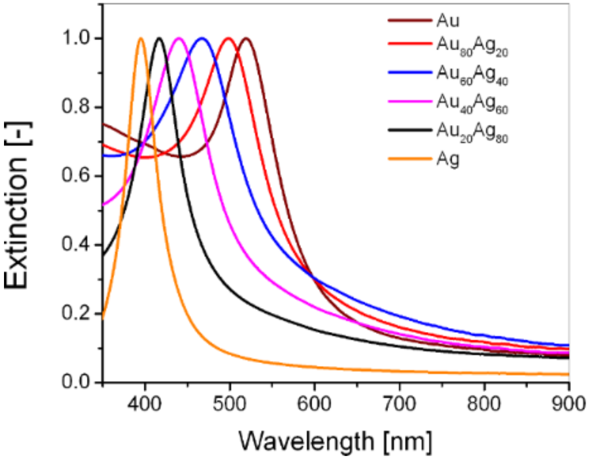
UV-visible spectrum
(time dependent on Cu^{2+} reduction)

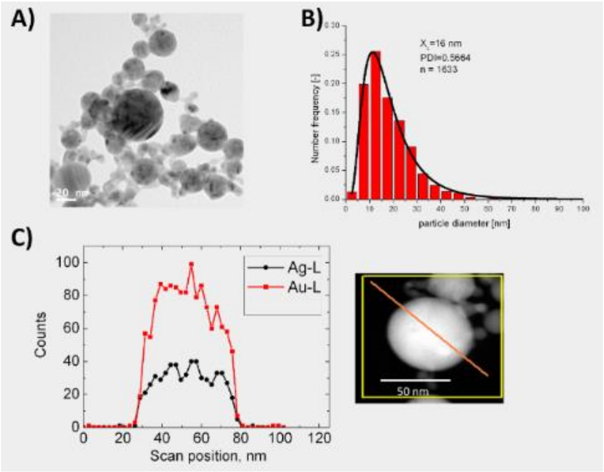


Nanoparticle Technology

UV-visible spectroscopy analysis in nanotechnology

Compositional analysis on AuAg alloy nanoparticles



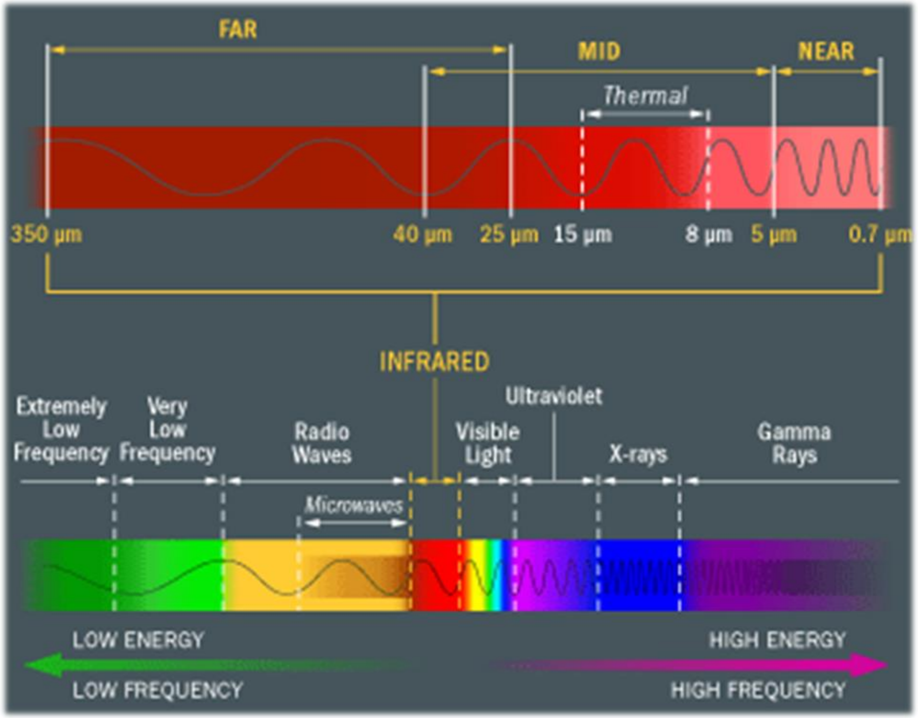


Infrared Spectroscopy

Nanoparticle Technology

What is infrared (IR)?

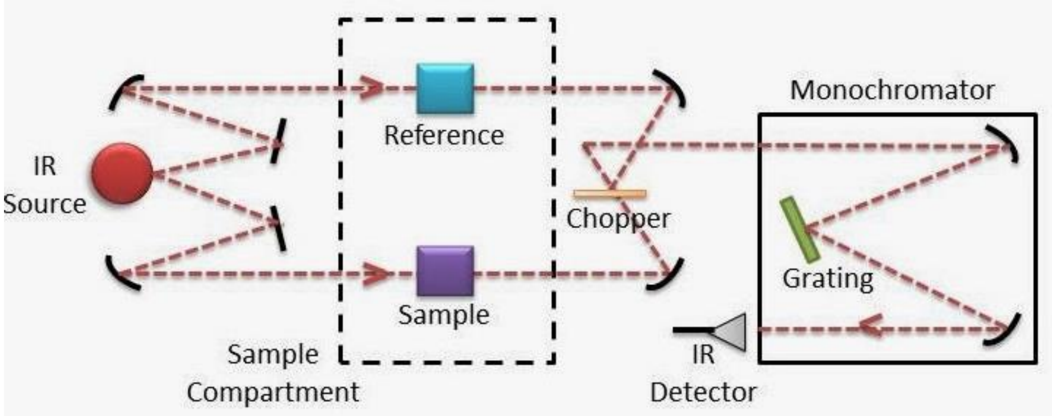
Classification of IR spectrum depending on wavelength



Wavelength range (λ)

- Near-IR (NIR): (0.7 ~ 1) to 5 µm
- Middle-IR (MIR): 5 to (25 ~ 40) µm
- Far-IR (FIR): (25 ~ 40) to (200 ~ 350) µm

Instrument diagram and image



1. Light source

- Infrared (IR) source: Nernst lamp (ZrO_2, CeO_2, THO_2) or Globar lame (SiC)

2. Sample

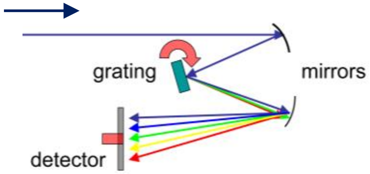
- Powder samples are generally used in IR spectroscopy.

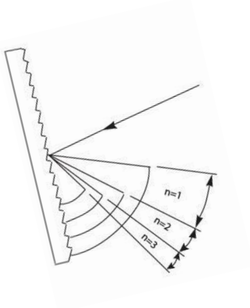
3. Monochromator (wavelength selector)

- Prism: NaCl (670 ~ 4000 cm^{-1}), KBr (250 ~ 670 cm^{-1}), LiF (2000 ~ 10000 cm^{-1})
- Blazed grating: a special type of diffraction grating

4. Detector

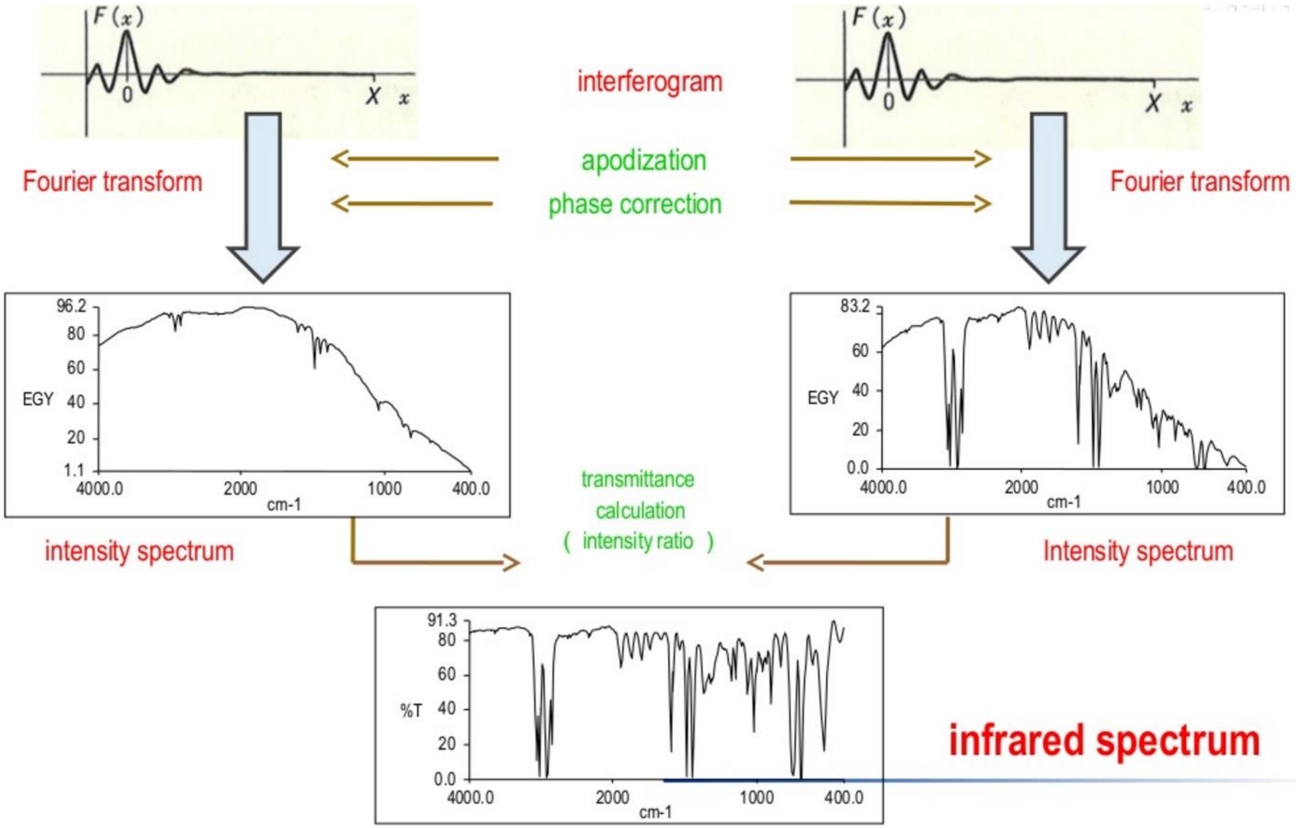
- Thermocouple, pyroelectric (triglycine sulfate) and photoconductive (PbS, CdTe, InSb) detectors are commonly used in IR spectroscopy.





Signal processing (Fourier Transform)

Reference **Sample**

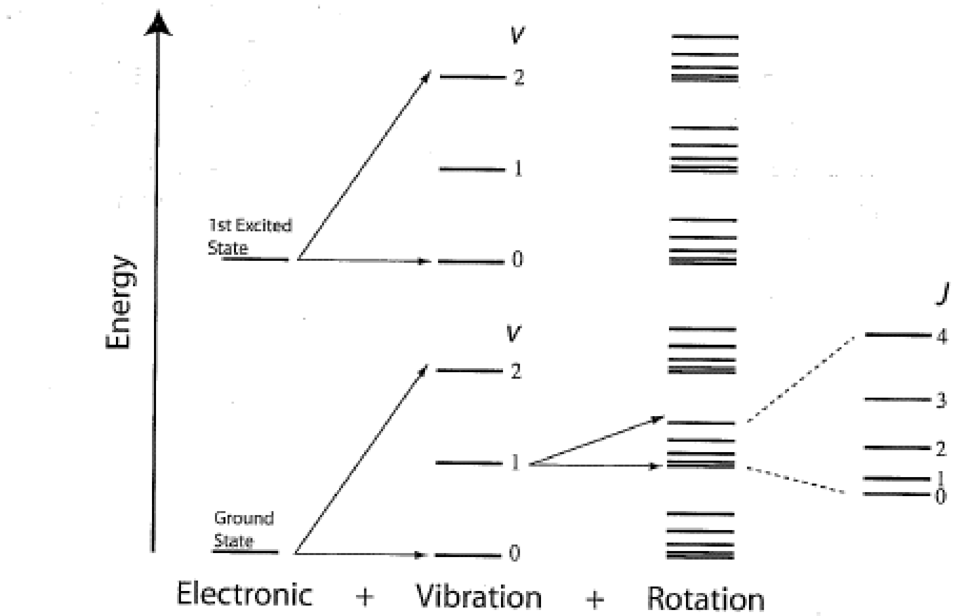


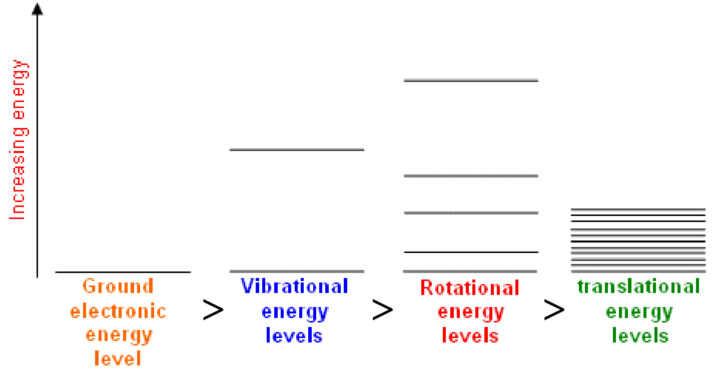
[http://www.slideshare.net/muttaqinpapasafira/principles-of-ftir]

Molecular energy

Molecular energy

$$E = E_{electronic} + E_{vibration} + E_{rotation} + E_{transition}$$





Electronic

Electron moving between electron shells

Vibrational

Stretching and compressing of the bond lengths and bond angles

Rotational

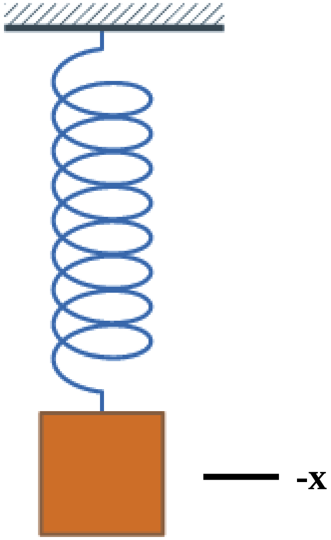
spinning around

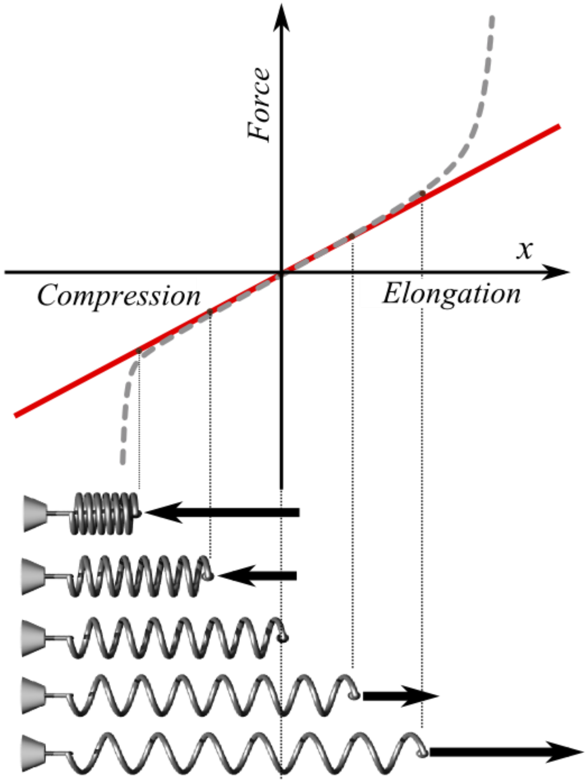
Translational

moving of the whole particle from one place to another

Hooke’s law

Robert Hooke (1635 ~ 1703)





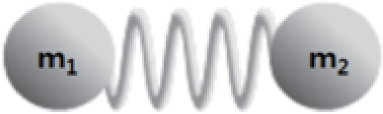
Hooke’s law

$$F = -kx$$

F: forces needed to extend or compress a spring
k: spring constant
x: distance

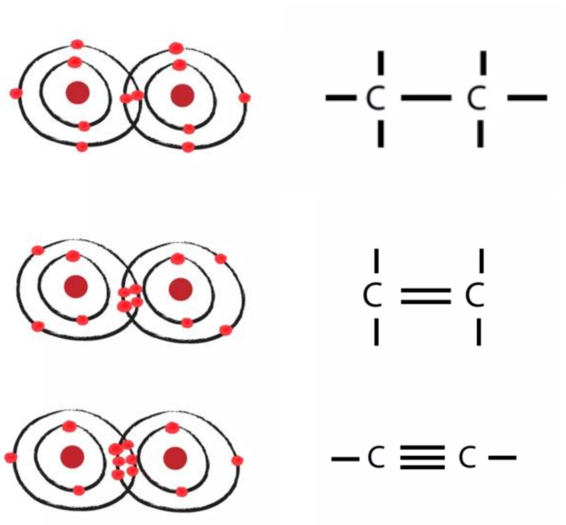
Molecular vibration (Hooke's law)

If the molecular vibration is harmonic oscillator…



$$\nu = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

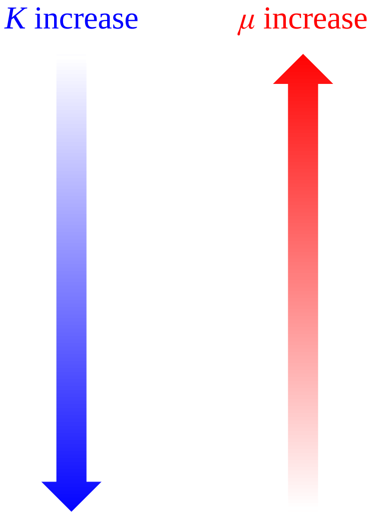
ν: frequency (cm^{-1})
c: light velocity (3×10^{10} cm/s)
K: force constant (dyne/cm)
m: atomic mass
μ: reduced mass of atoms, $m_1 \cdot m_2 / (m_1 + m_2)$



Single bond
($1200\ cm^{-1}$)

Double bond
($1650\ cm^{-1}$)

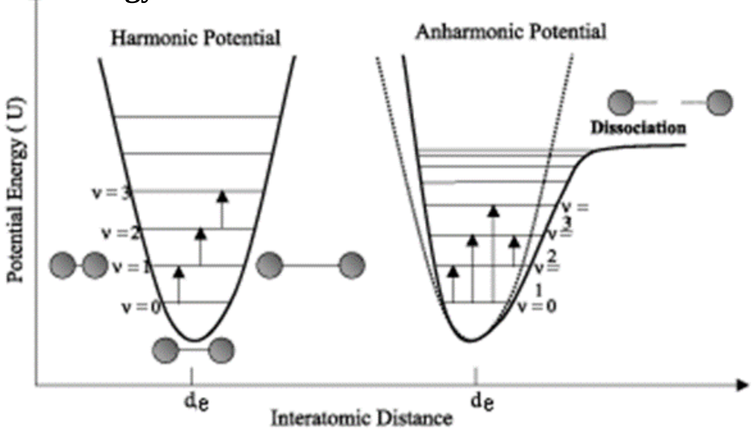
Triple bond
($2150\ cm^{-1}$)



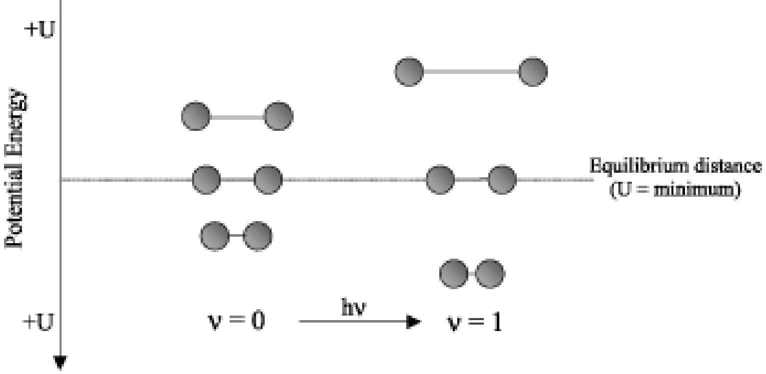
C – Cl	($750\ cm^{-1}$)
C – O	($1100\ cm^{-1}$)
C – C	($1200\ cm^{-1}$)
C – D	($2206\ cm^{-1}$)
C – H	($3000\ cm^{-1}$)

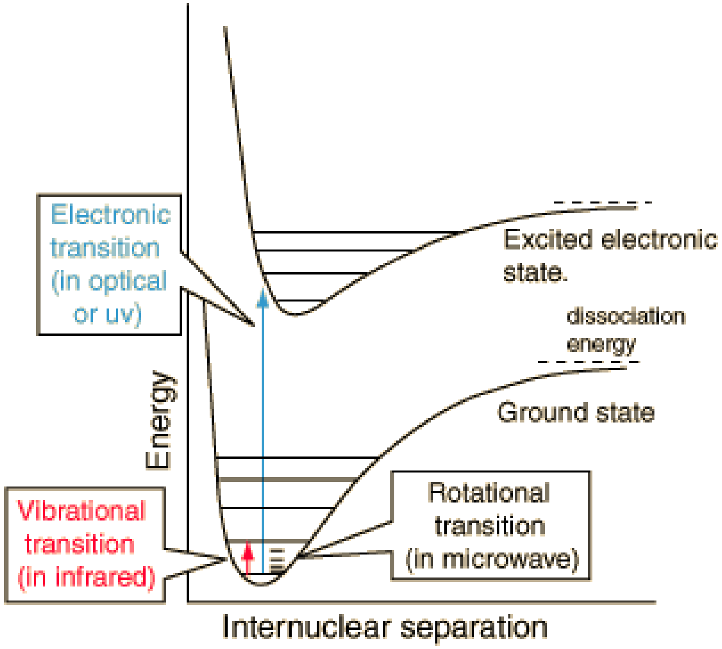
Molecular vibration (energy levels)

Energy levels of molecule with dissociation



Vibrational transition

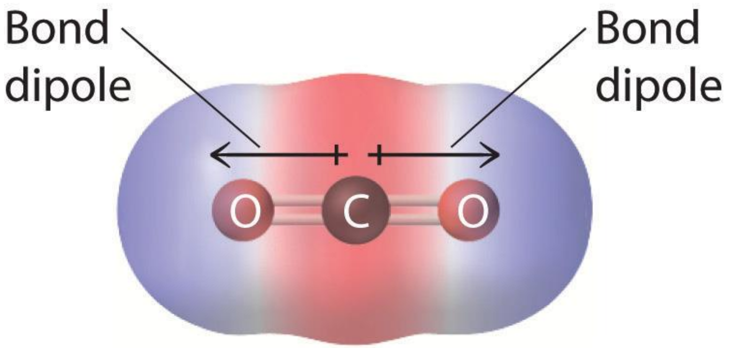




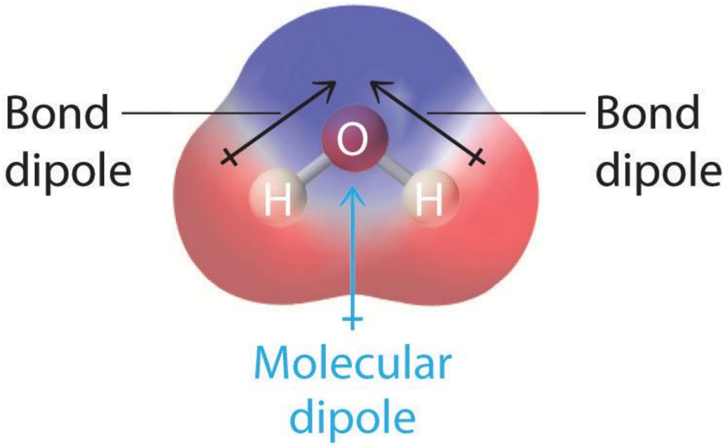
Molecular vibration (example)

Net dipole moment

Carbon dioxide (CO_2)



Water (H_2O)



Net dipole moment = 0

IR inactive

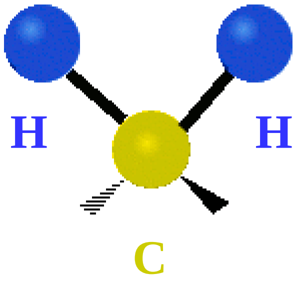
Net dipole moment ≠ 0

IR active

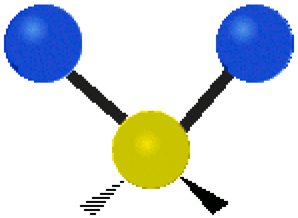
Molecular vibration (example)

Example: vibrations of methylene group (-CH_2-)

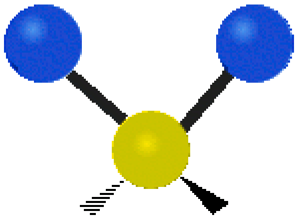
Symmetric Stretching



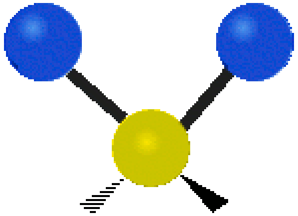
Asymmetric Stretching



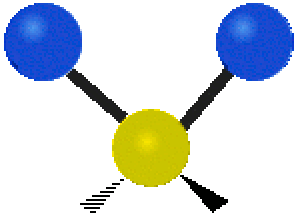
Scissoring (bending)



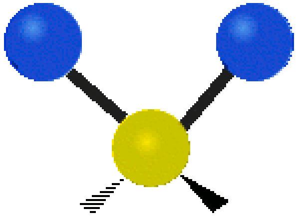
Rocking



Wagging



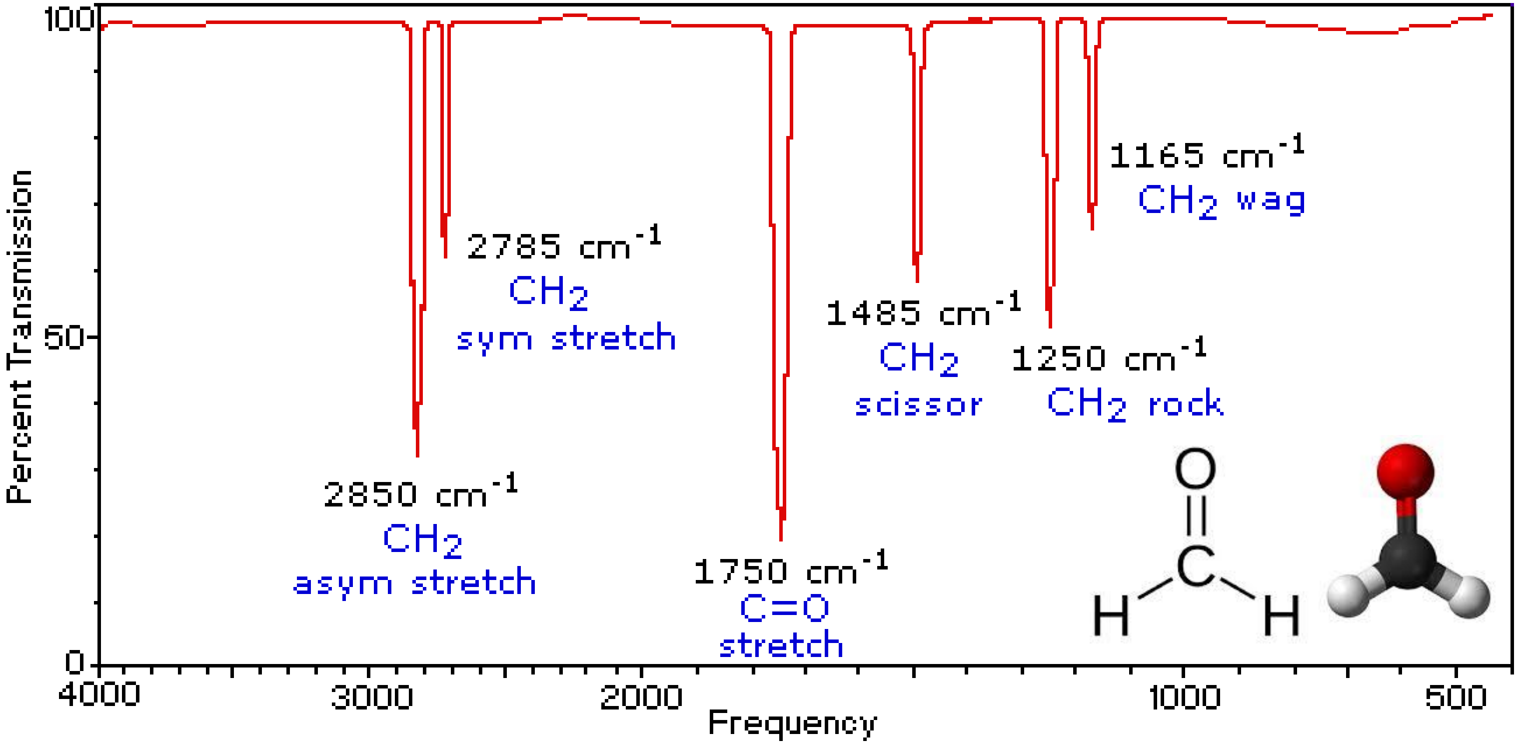
Twisting



[https://en.wikipedia.org/wiki/Molecular_vibration]

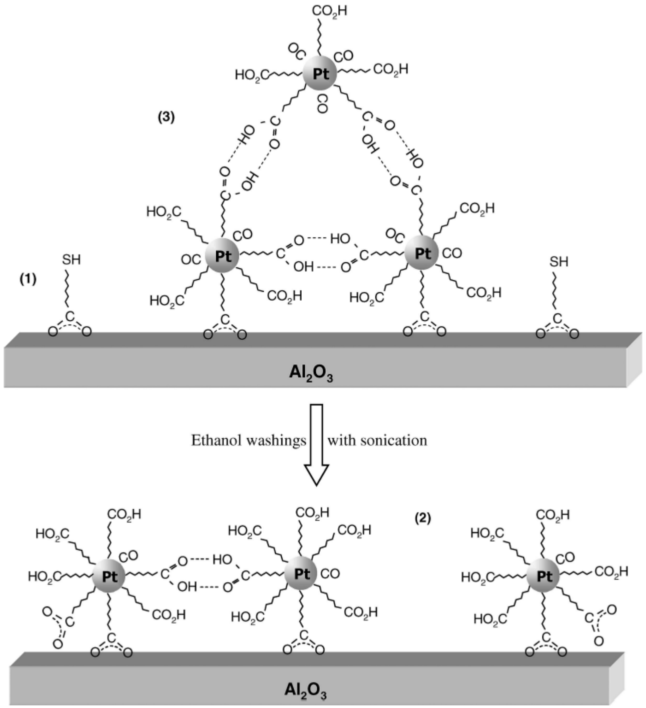
Molecular vibration (example)

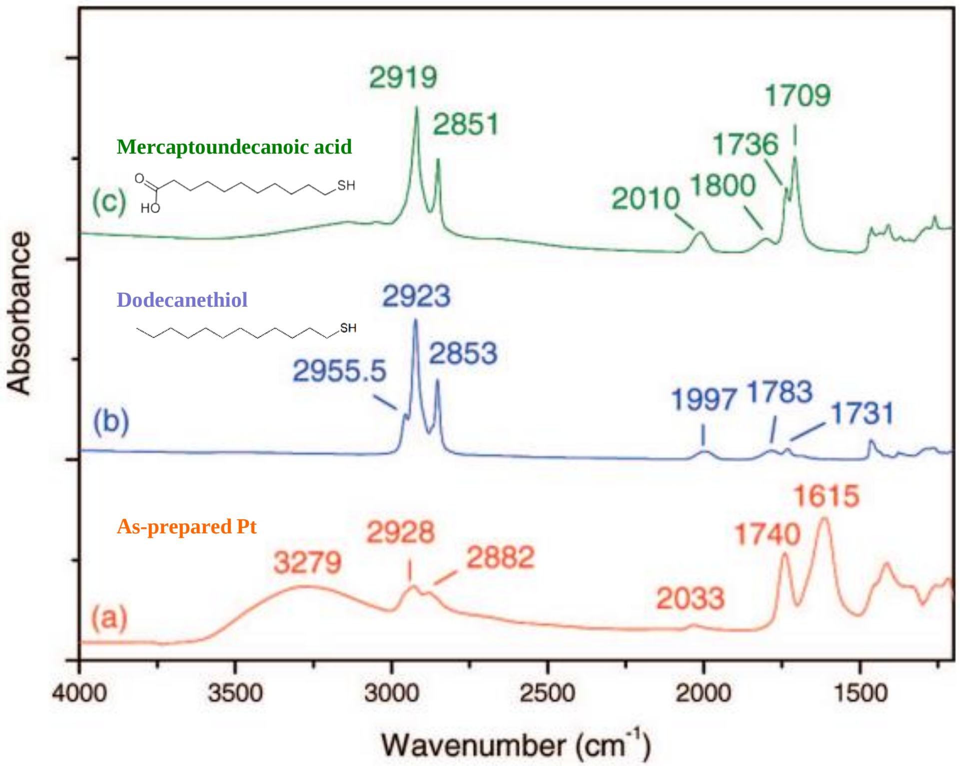
Example: Fourier transform-infrared (FT-IR) spectrum of formaldehyde



FT-IR spectroscopy analysis in nanotechnology

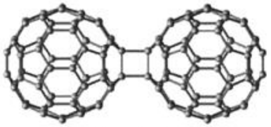
Evidence for the existence of functionalized groups on Pt nanoparticle



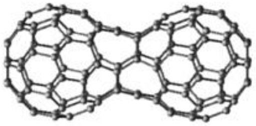


FT-IR spectroscopy analysis in nanotechnology

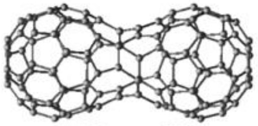
Evidence for the existence of C_{120} structures



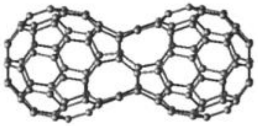
(a) Dumb-bell



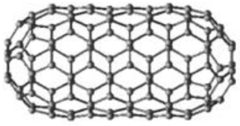
(b) Peanuts P55



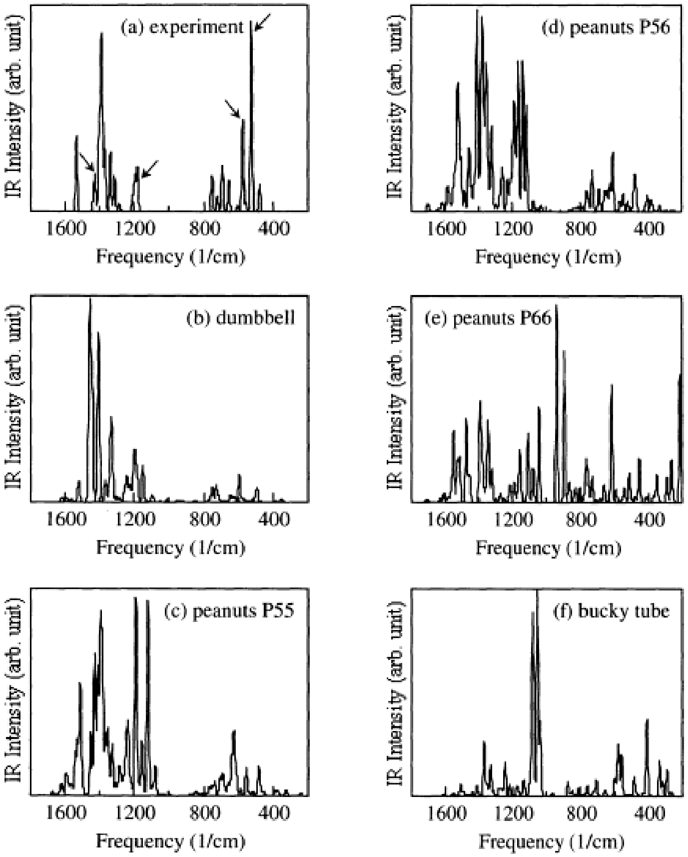
(c) Peanuts P56



(d) Peanuts P66

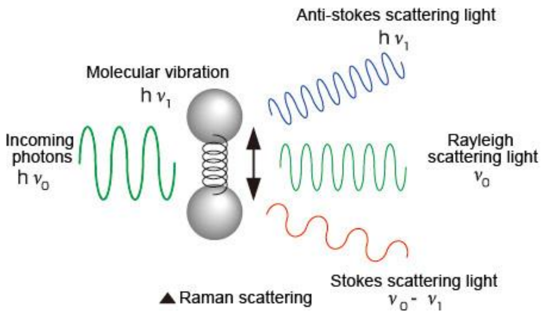


(e) Tube



Raman Spectroscopy

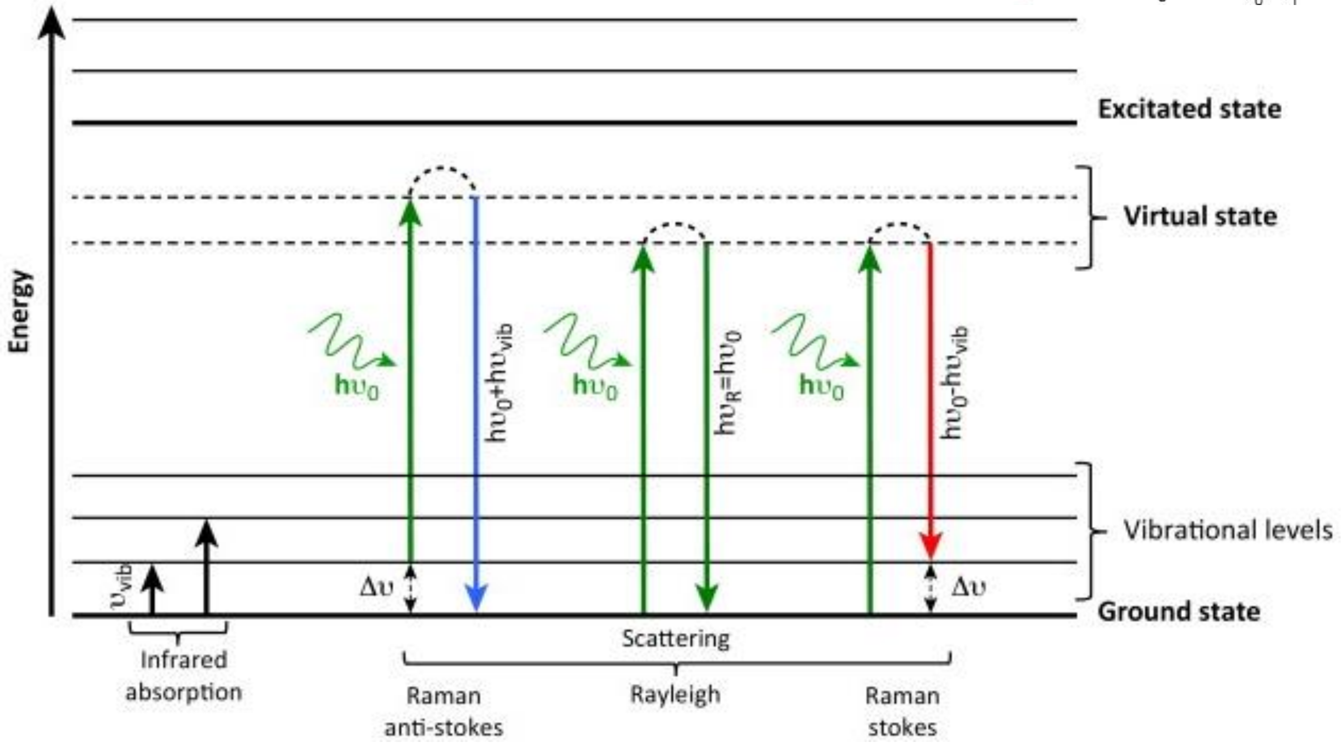
Raman scattering



Rayleigh and Raman stokes/anti-stokes scattering

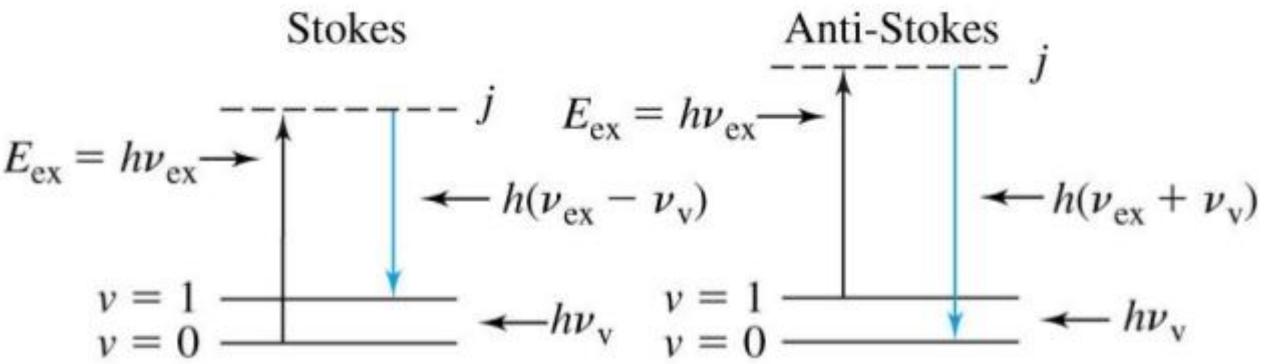
Sir Raman
(1888 ~ 1970)

Lord Rayleigh
(1842 ~ 1919)



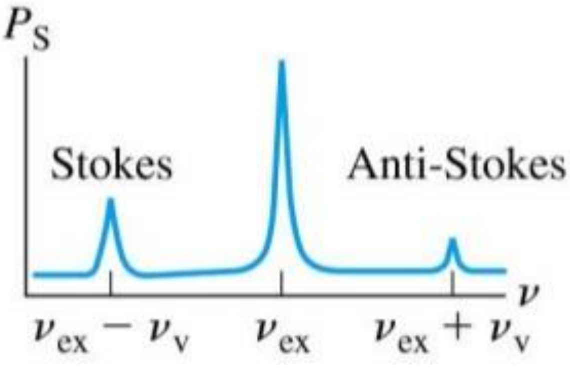
Raman scattering

Rayleigh and Raman stokes/anti-stokes scattering



Stokes lines are those in which the photon has lost energy to the molecule.

ν_{ex} - ν_v



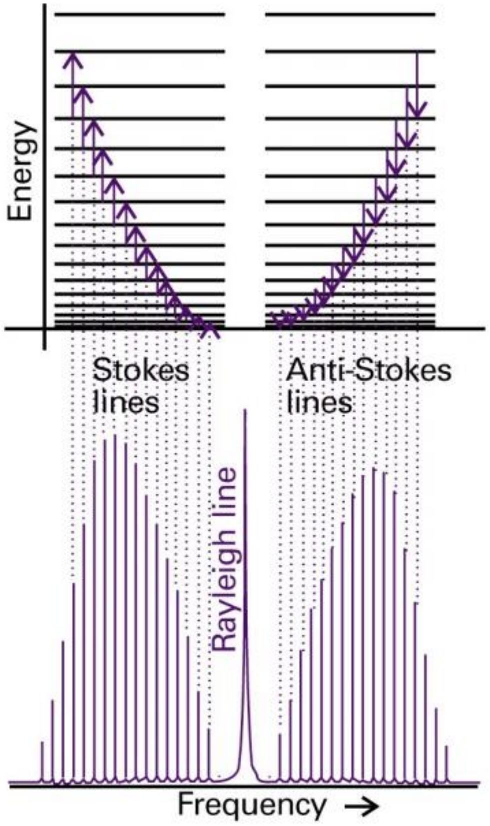
Anti-Stokes lines are those in which the photon has gained energy from the molecule.

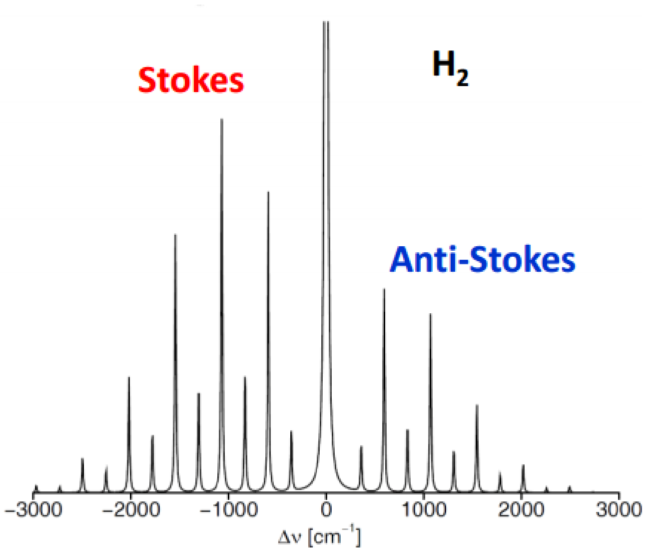
$\nu_{ex} + \nu_v$

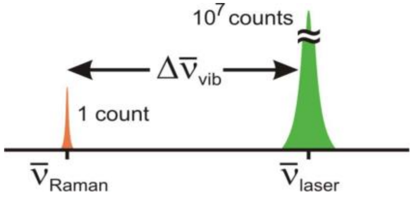
The strongest scattering is Rayleigh scattering.

Raman scattering

Rayleigh and Raman stokes/anti-stokes scattering

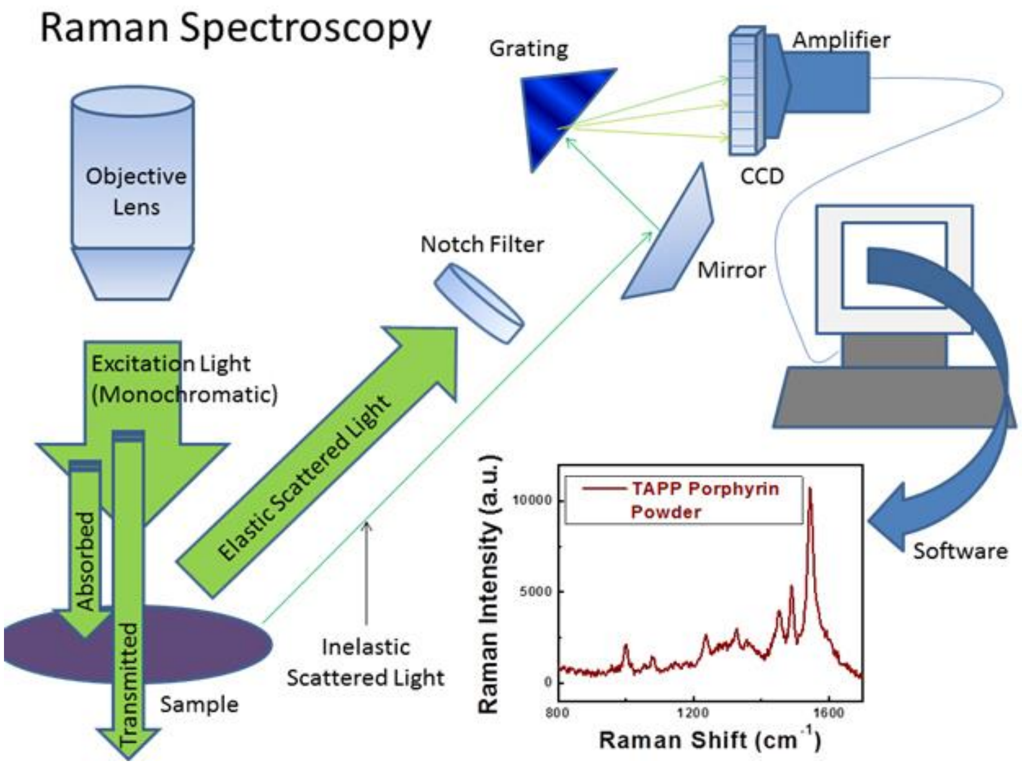






Raman scattering intensity
: 1 in 10^7 photons is scattered inelastically.

Instrument diagram and image

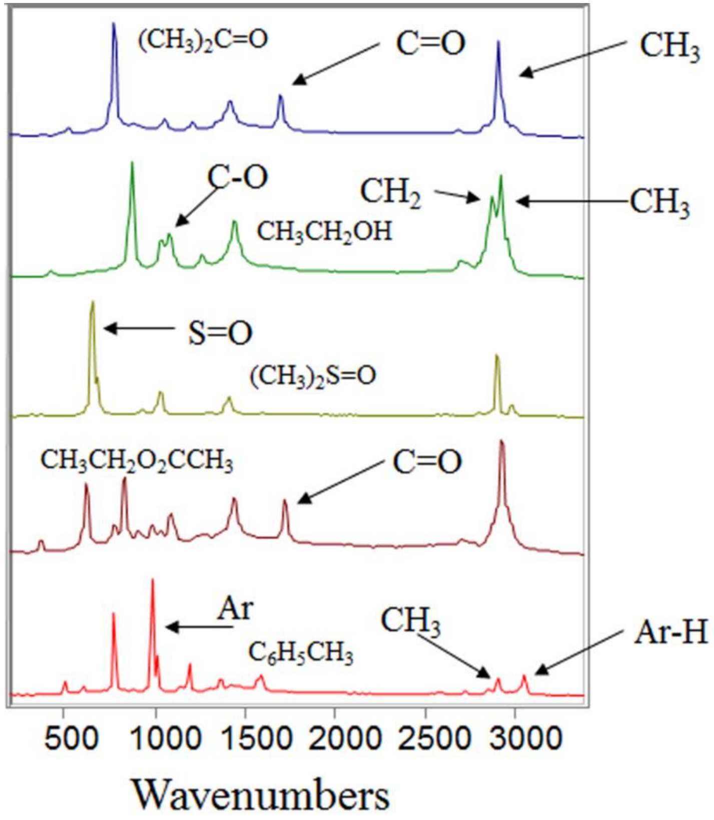


Light source
500 ~ 700 nm laser

Elastic scattered light
:Rayleigh scattering

Inelastic scattered light
:Raman stokes/anti-stokes scattering

Raman spectrums (example)



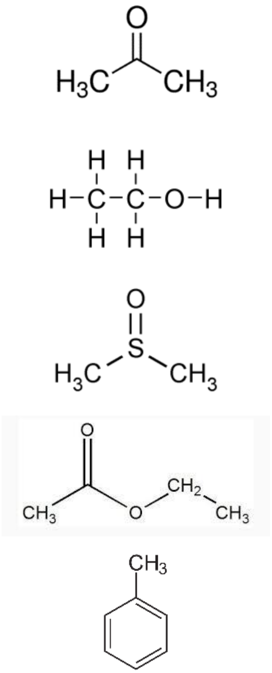
Acetone

Ethanol

Dimethyl sulfoxide

Ethyl acetate

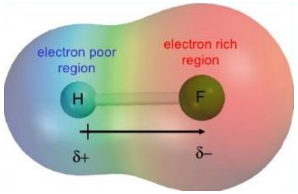
Toluene



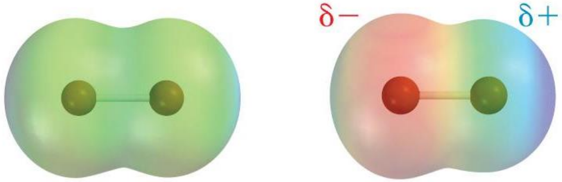
FT-IR spectroscopy vs. Raman spectroscopy

FT-IR spectroscopy (dipole moment)

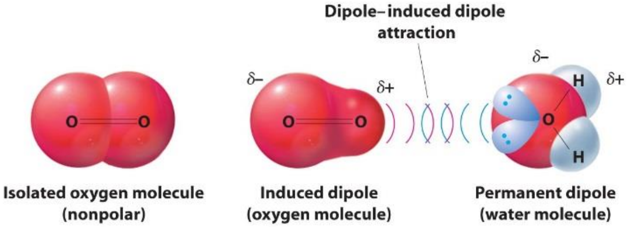
Permanent dipoles (AB: HF)



Instantaneous dipoles (A_2: Br_2)



Induced dipoles (O_2 by H_2O)

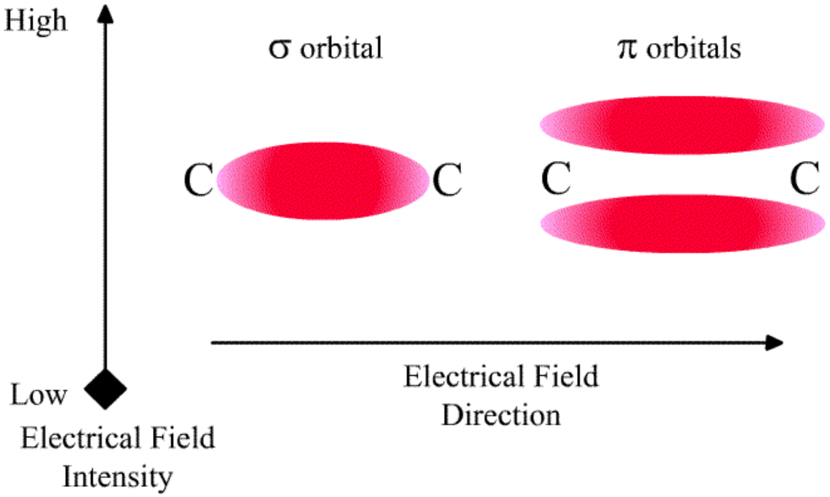


Raman spectroscopy (polarzability)

$$p = \alpha E$$

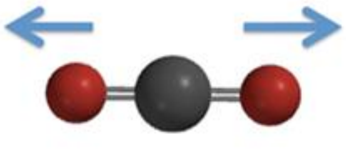
p: induced dipole moment
α: polarizability (C·m^2/V)
E: electric field

Polarizability is the ability for a molecule to be polarized.



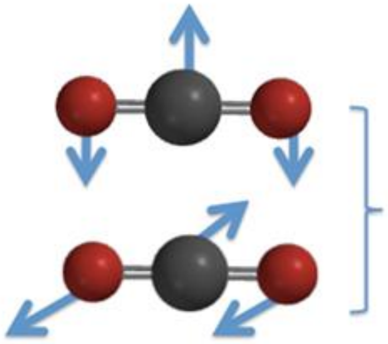
FT-IR spectroscopy vs. Raman spectroscopy

Vibrational modes of CO_2



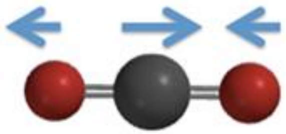
Symmetric C-O stretching

Raman: active (change in polarizability)
IR: inactive (no change in dipole moment)



Bending

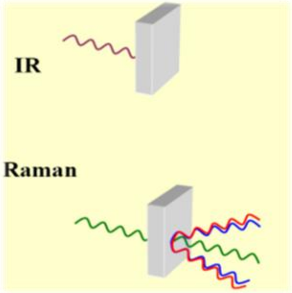
Raman: inactive (no change in polarizability)
IR: active (change in dipole moment)



Asymmetric C-O stretching

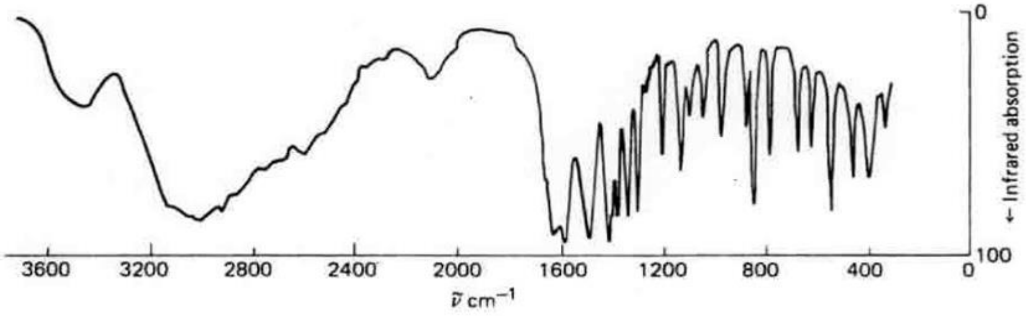
Raman: inactive (no change in polarizability)
IR: active (change in dipole moment)

FT-IR spectroscopy vs. Raman spectroscopy

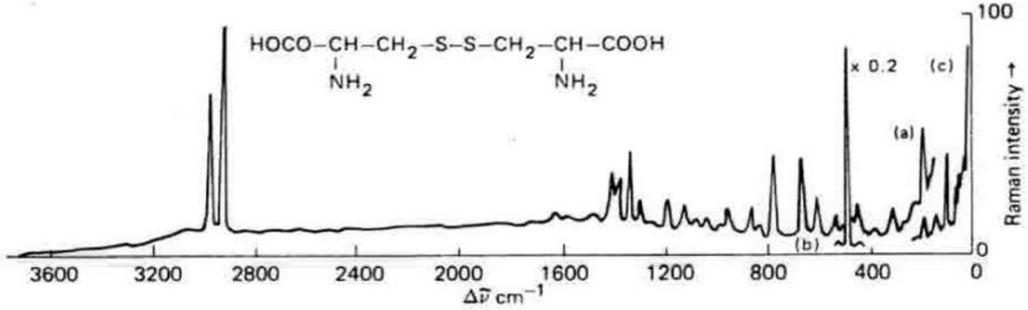


Spectrum comparison

FT-IR spectrum



Raman spectrum



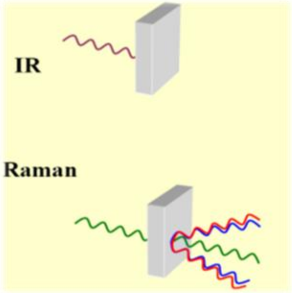
In 3000 cm^{-1} region
FT-IR: NH_3^+ vibration
Raman: CH and CH_2 stretching

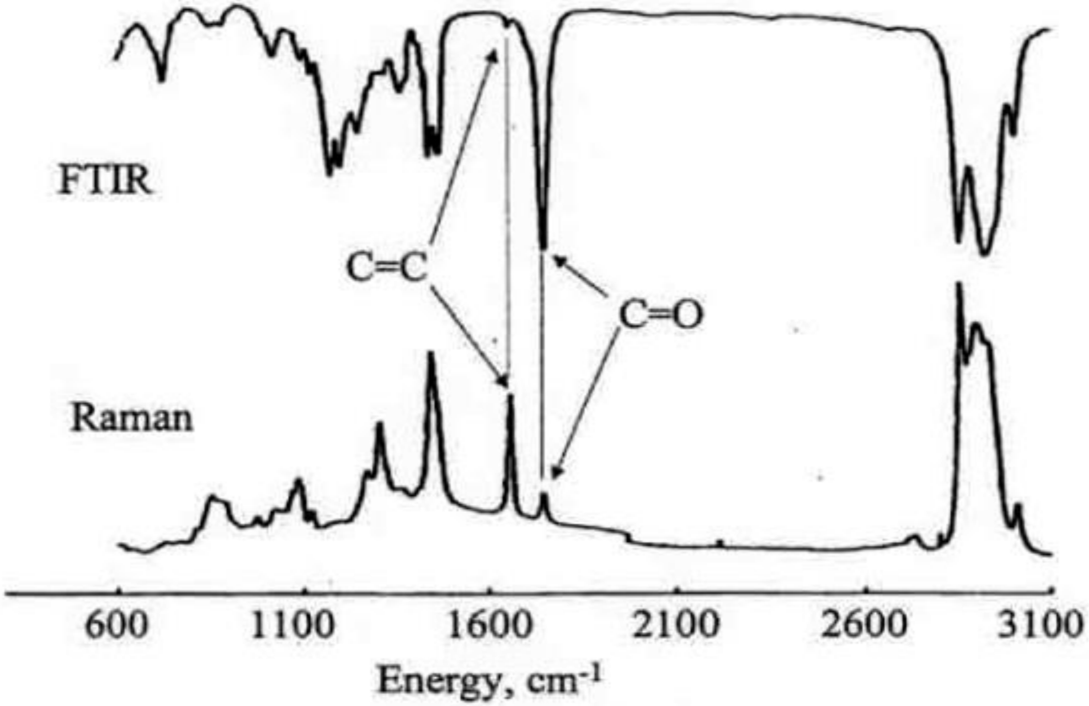
In 1600 cm^{-1} region
FT-IR: NH_3^+ deformation
Carboxylate asymmetric vibration
Raman: very weak signal

In 410 cm^{-1} region
FT-IR: weak signal
Raman: -S-S- stretching

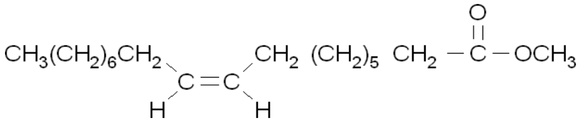
FT-IR spectroscopy vs. Raman spectroscopy

Spectrum comparison



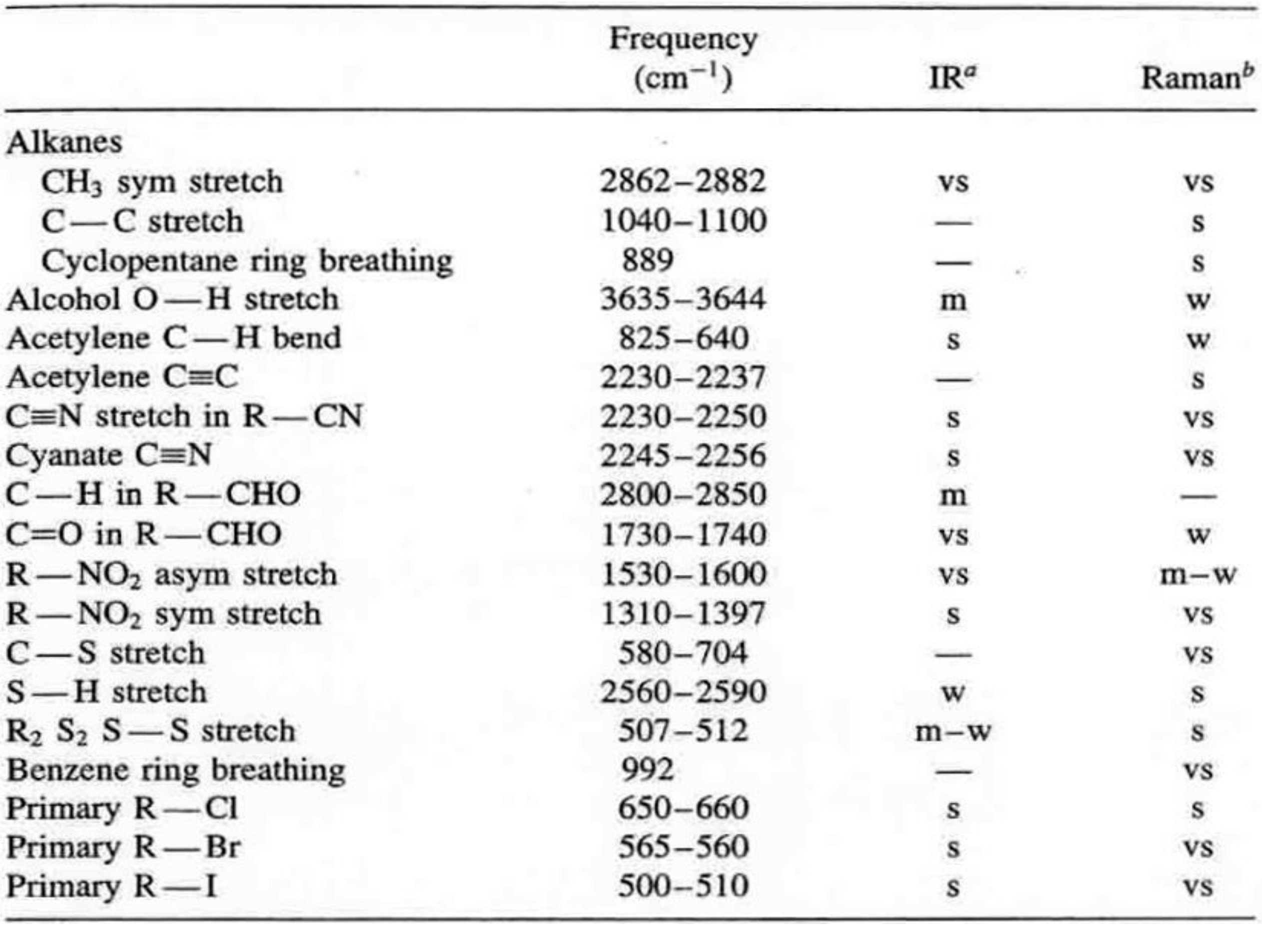


Oleic acid methyl ester



$CH_3(CH_2)_6CH_2-\underset{H}{C}=\underset{H}{C}-CH_2\ (CH_2)_5\ CH_2-\overset{O}{\overset{||}{C}}-OCH_3$

FT-IR spectroscopy vs. Raman spectroscopy



	Frequency (cm^{-1})	IR[a]	Raman[b]
Alkanes			
CH_3 sym stretch	2862–2882	vs	vs
C—C stretch	1040–1100	—	s
Cyclopentane ring breathing	889	—	s
Alcohol O—H stretch	3635–3644	m	w
Acetylene C—H bend	825–640	s	w
Acetylene C≡C	2230–2237	—	s
C≡N stretch in R—CN	2230–2250	s	vs
Cyanate C≡N	2245–2256	s	vs
C—H in R—CHO	2800–2850	m	—
C=O in R—CHO	1730–1740	vs	w
R—NO_2 asym stretch	1530–1600	vs	m–w
R—NO_2 sym stretch	1310–1397	s	vs
C—S stretch	580–704	—	vs
S—H stretch	2560–2590	w	s
R_2 S_2 S—S stretch	507–512	m–w	s
Benzene ring breathing	992	—	vs
Primary R—Cl	650–660	s	s
Primary R—Br	565–560	s	vs
Primary R—I	500–510	s	vs

vs = very strong
s = strong
m = medium
w = weak
dash = absent

FT-IR spectroscopy vs. Raman spectroscopy

FT-IR spectroscopy

Advantages

- Simple instrumentation
- Fast measurement
- Available for low concentrated samples

Disadvantages

- High priced detector
- Dissolution problem with aqueous solutions

Raman spectroscopy

Advantages

- Well-suited for aqueous solutions
- No sample preparation necessary
- Bands below 400 cm^{-1} are measurable.

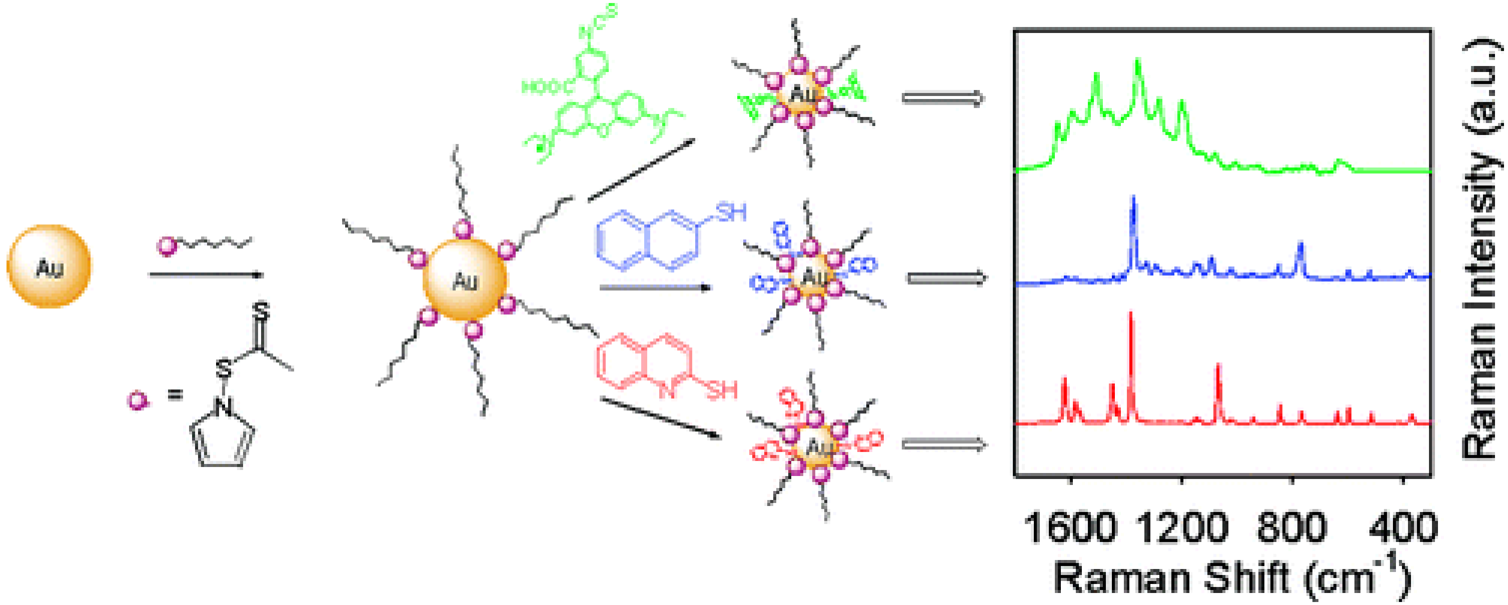
Disadvantages

- Strong laser is required.
- Lower sensitivity because scattering effect is weaker.
- Fluorescence of sample may overlap with the signal

Nanoparticle Technology

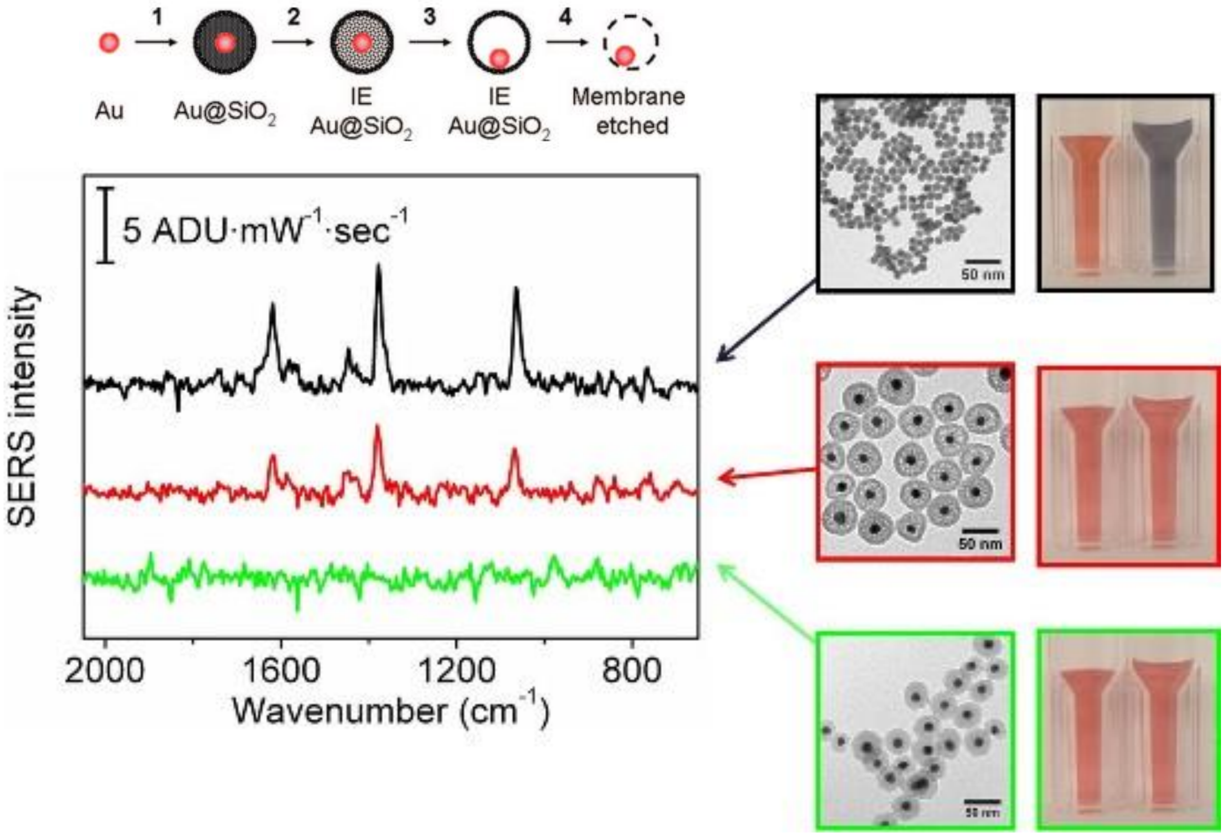
Raman spectroscopy analysis in nanotechnology

Functional polymers on Au nanoparticles



Raman spectroscopy analysis in nanotechnology

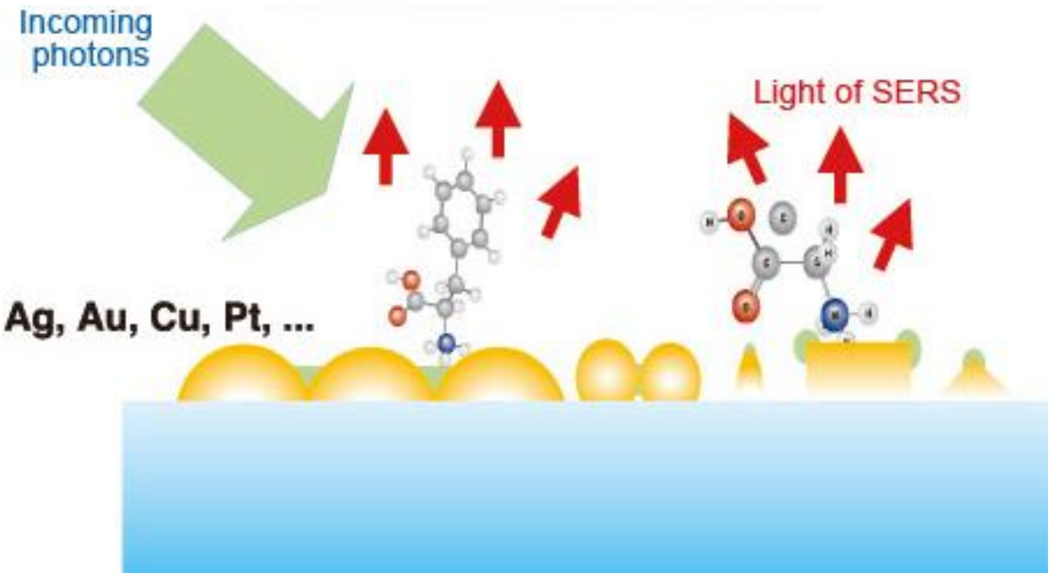
Internally etched (IE) Au@SiO_2 core-shell nanoparticles

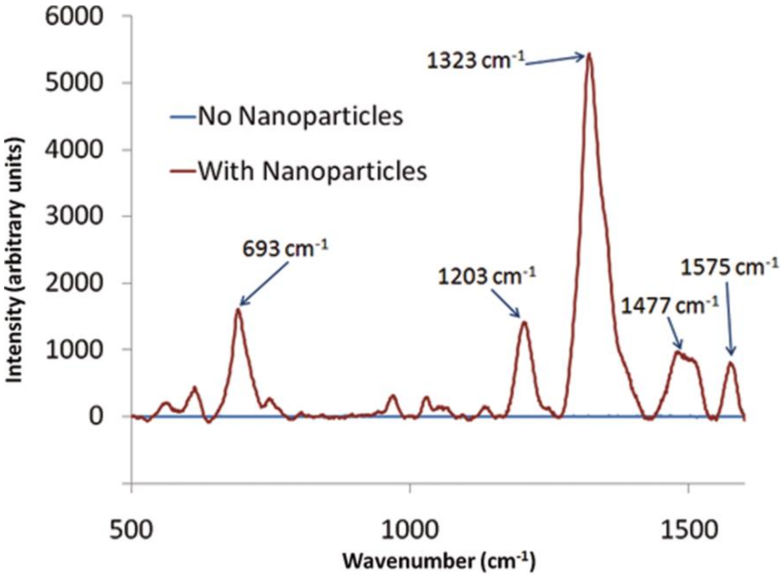


Nanoparticle Technology

Raman spectroscopy analysis in nanotechnology

Conceptual diagram of surface enhanced Raman spectroscopy (SERS)





Raman spectroscopy analysis in nanotechnology

Phosphoric acid adsorption on Au surface