Chapter 2
Interaction of Electromagnetic Radiation (EMR) with Matter

Course Code: SSCP 4473

Course Name: Spectroscopy & Materials Analysis

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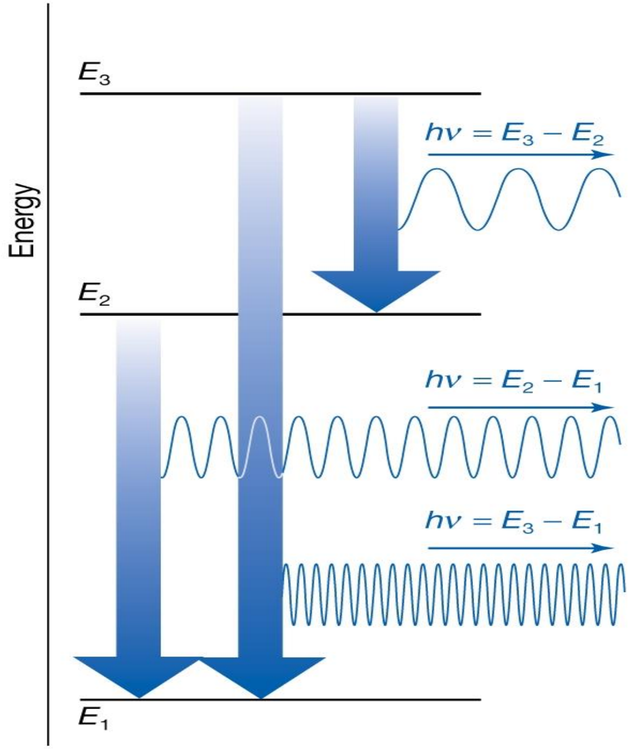
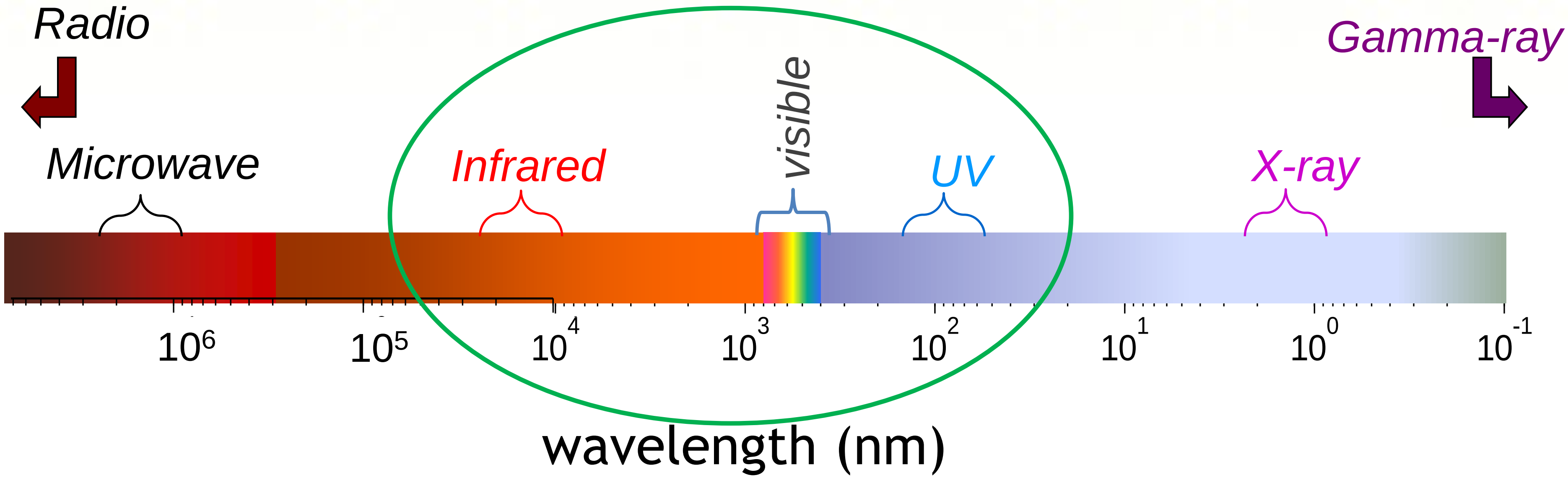
Outline

- ✓ Light Matter Interaction
- ✓ Broadening
- ✓ Radiation Laws
- ✓ Absorption & Emission
- ✓ Polarization
- ✓ Luminescence
- ✓ Scattering
- ✓ Transition Probabilities
- ✓ Selection Rules



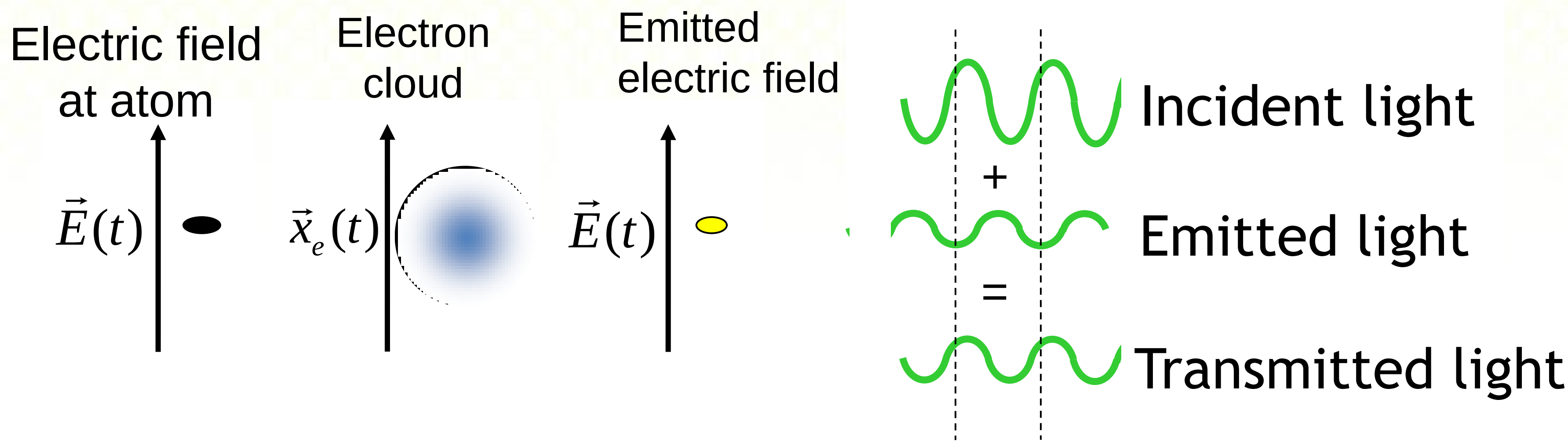
The Electromagnetic Spectrum



The transition wavelengths are a bit arbitrary…

Interaction of EMR & Matter

External EMR excites atoms, which then emit more light following



On **resonance** (the light frequency is the same as that of the atom)

The relative phase of the incident and re-emitted radiation is vital. For ~180° out of phase destructive interference occurs, where the radiation gets attenuated called absorption.
For ~ ±90° out of phase: the speed of light changes called refraction.

Nature of Electromagnetic Radiation

- Its Nature and Properties: Dual Nature

  - Wave properties: $c\ (m/s) = \lambda\nu$
  - Particle Properties: $m = 0$, $E = h\nu$, $p = E/c = h\nu/c = h/\lambda$
    Planck constant $h \approx 6.63 \times 10^{-34}$ J s

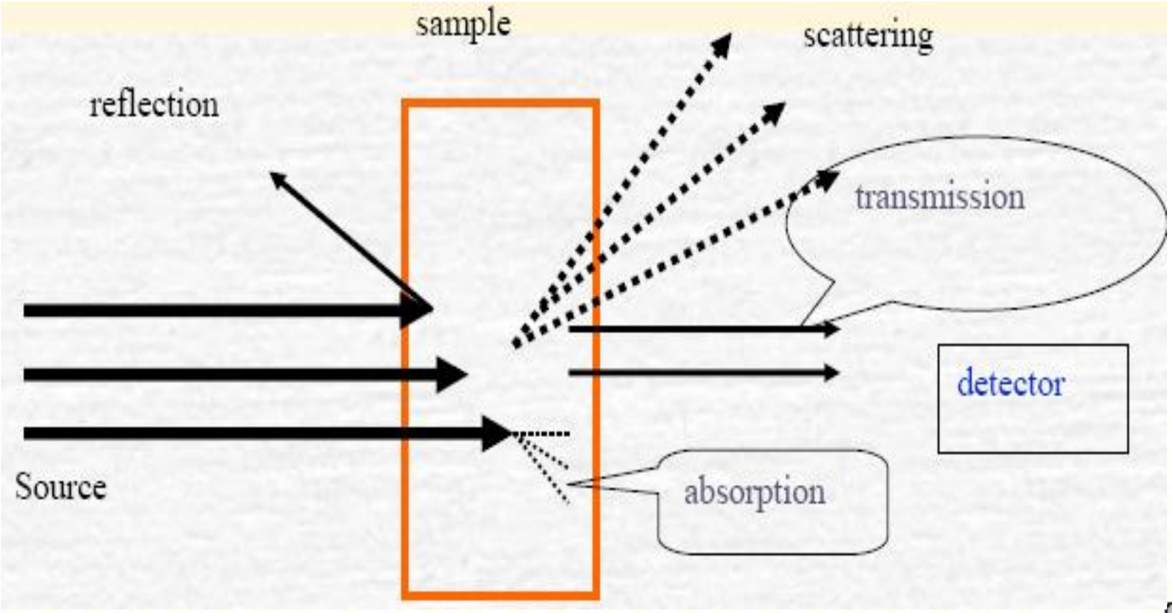
  - Photons = Neutral
    - *cannot steadily lose E as they penetrate matter*
    - *can travel some distance* ***d*** *before interacting with any atom*
  - Photon can be absorbed - and it disappears,
  - Photon can scatter, changing its direction with or without E-loss
  - Photons are Bosons and obey B-E statistics
  - Photon number is not conserved
  - Chemical potential for photon is ZERO
  - Photons are zero mass and spin one particle

"Light is, in short, the most refined form of matter."

Louis de Broglie

Radiation Matter Interaction

Spectroscopy uses the absorption, emission, or scattering phenomena of EMR by matter to qualitatively or quantitatively determine the matter or physical processes. The matter can be atoms, molecules, atomic or molecular ions, or solids. The interaction of radiation with matter can cause redirection of the radiation and/or transitions between their quantized energy levels.



Three Main Light Matter Interaction

Three main processes of EMR interaction with matter

Absorption:

- Converts radiative energy into internal energy.

Emission:

- Converts internal energy into radiative energy.

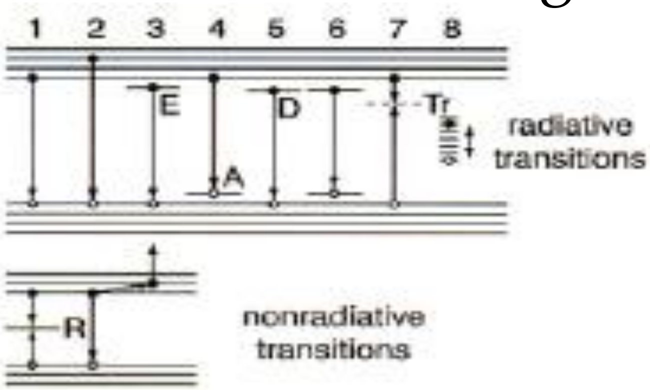
Scattering:

- Radiative energy is first absorbed and then radiated.

No interaction at all called ***transmission***

Luminescence

- Luminescence is the inverse process of absorption
- Consequence of radiative recombination of excited electrons
- Compete with nonradiative recombination processes
- PL (photoluminescence): non-equilibrium obtained by photons
- EL (electroluminescence): non-equilibrium obtained by electrons
- Important for Laser, LED, and other light emitting devices



Interaction of Photons with Matter

1. Photons are indirectly ionising radiation
2. They interact with matter via **5** processes:

- Photoelectric Effect
- Elastic Scattering
- Compton Scattering
- Pair Production
- Photonuclear Reactions

In addition, there are two processes with very small energy transfer:

- Thomson (elastic) scattering on a 'free' electron, redirection of low energy photon without change in energy
- Raleigh (coherent) scattering results from combined (coherent) action of an atom as a whole.

Coherent & Incoherent Scattering

For nonrandom phases field amplitudes are added: Coherent

$$E_{total} = E_1 + E_2 + \ldots + E_n$$

$$I_{total} = \underbrace{I_1 + I_2 + \ldots + I_N}_{} + \underbrace{c\varepsilon \operatorname{Re}\left\{E_1 E_2^* + E_1 E_3^* + \ldots + E_{N-1} E_N^*\right\}}_{}$$

I_1, I_2, … I_n are the irradiances of the various wavelets (positive and real numbers)

E_i E_j^* are cross terms with phase factors $\exp[i(\theta_i - \theta_j)]$, wher θ's are non random and don't cancel ach other

For random phases are random irradiances (intensity) are added: Incoherent

$$I_{total} = I_1 + I_2 + \ldots + I_n$$

Scattering in Different Media

Elastic scattering

- No exchange of internal energy of the medium with the radiated field
- No change of frequency of incident wave upon scattering

Inelastic scattering

- Involves exchange of internal energy of the medium with that of the radiated field.

Three Main Scattering Processes

- Light that is scattered at the same wavelength as the incoming light is called **Rayleigh** scattering - Elastic scattering dominates.

- Light that is scattered in transparent solids due to vibrations **(phonons)** is called **Brillouin** scattering. Brillouin scattering is typically shifted by 0.1 to 1 cm^{-1} from the incident light.

- Light that is scattered due to vibrations in molecules or optical phonons in solids is called **Raman** scattering. Raman scattered light is shifted by as much as 4000 cm^{-1} from the incident light. 1 part in 10^8 is inelastically scattered.

Rayleigh Scattering

- This occurs when driving frequency is less than the natural frequency of the oscillator (blue color of sky and use of RGY colors in signals).

- The cross section is given as:

$$\sigma_n^{ray} = \frac{1}{6\pi}\left(\frac{\omega}{c}\right)^4 \left(\frac{e^2}{m_e \varepsilon_o \omega_o^2}\right)^2$$

Spectral Features

✓ **Position of line /bands:**

- Determined by spacing of the energy levels

✓ **Intensity of spectral lines:**

- Determined by transition probability (selection rules)
- Population of states
- Path length of sample

$$N_f / N_i = e^{-\Delta E / kT}$$

$$\log(I_o / I) = \varepsilon cl = A$$

✓ **Width of spectral lines:**

- Collision broadening (molecular interactions)
- Doppler broadening (gases)
- Uncertainty principle

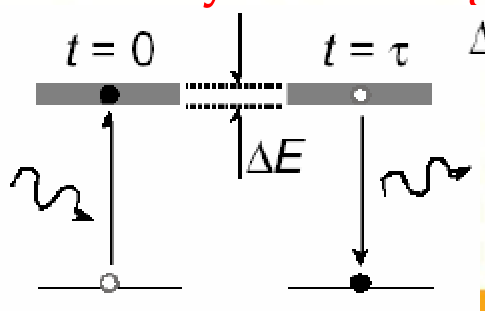
$$\delta E x \delta t \approx \frac{h}{2\pi} \approx 10^{-34}\ Js$$

$$\delta\nu = \frac{\delta E}{h} \approx \frac{h}{2\pi h\,\delta t} \approx \frac{1}{2\pi\delta t}$$

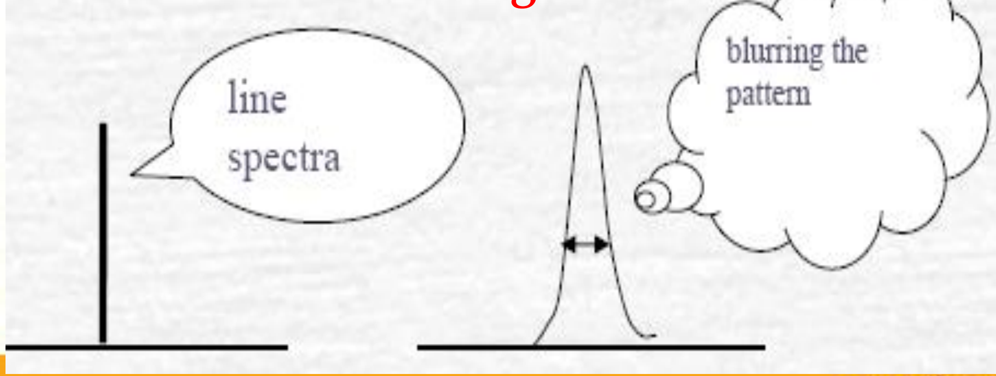
✓ **Shape of lines / bands:**

Uncertainty broadening

$\Delta E\ \Delta t \approx \hbar$

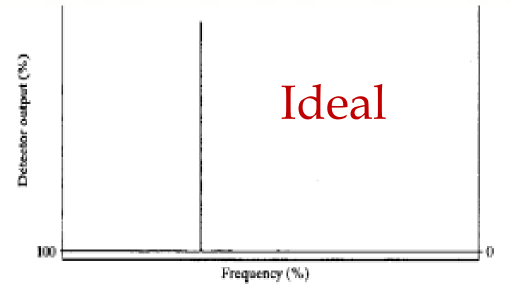


Broadening



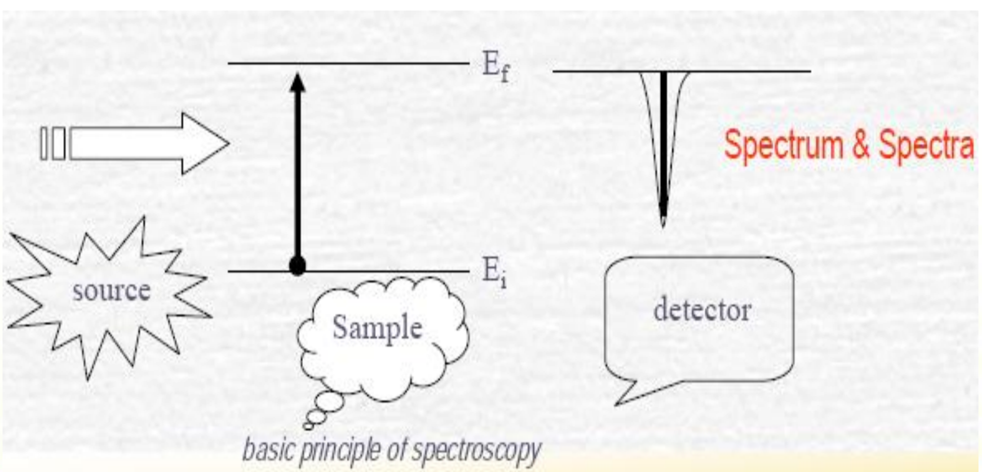
Spectral Line & Line-shapes

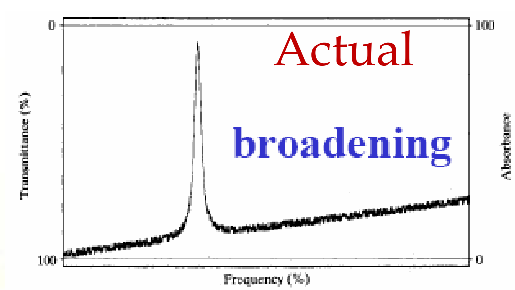
- Atoms and molecules prefer to be in their ground state.
- Excited species spontaneously emit radiation and relax back into their ground states.
- Emission spectrum: plot of the relative power (intensity) of the emitted radiation as a function of the wavelength or frequency of the radiation.
- Theoretically one must gets a **line spectra**



Three types of absorption/emission spectra:

- o Sharp lines of finite widths
- o Aggregations (series) of lines called bands
- o Spectral continuum extending over a broad range of wavelengths





Sources of Line Broadening

Natural Broadening

$$\Delta E \Delta t \approx \frac{h}{2\pi} \qquad \Delta t \approx \frac{h}{2\pi . h \Delta \nu} \approx \frac{1}{2\pi \Delta \nu}$$

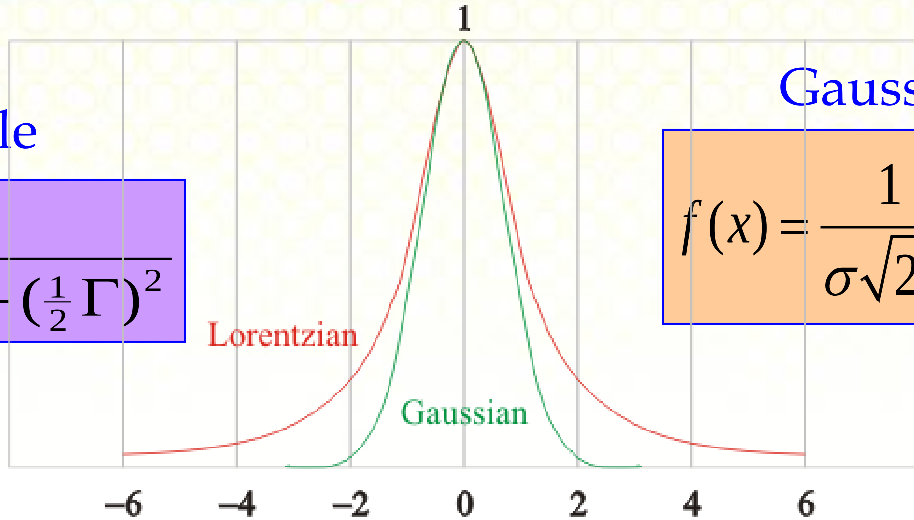
Pressure Broadening

$$\alpha_L \approx \alpha_L (STP) \frac{n \mathrm{v}_{rel}}{n_L \mathrm{v}_{rel} (STP)} = \alpha_L (STP) \frac{n\sqrt{T}}{n_L \sqrt{T_0}}$$

Doppler Broadening

$$\nu' = \nu + \frac{\mathrm{v} \cos\theta}{\lambda} = \nu + \frac{\nu\, \mathrm{v} \cos\theta}{c} = \nu (1 + \frac{\mathrm{v}}{c} \cos\theta)$$

Broadening Profile



Lorentzian profile

$$L(x) = \frac{1}{\pi}\frac{\frac{1}{2}\Gamma}{(x-x_0)^2 + (\frac{1}{2}\Gamma)^2}$$

Gaussian profile

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right)$$

Doppler profile

$$\alpha_D = \mathrm{v}_0 \nu_0 / c$$

$$\sigma_n(\nu) = S\,\Phi_D(\nu) = \frac{S}{\sqrt{\pi\alpha_D}}\exp\left[-(\nu-\nu_0)^2/\alpha_D^2\right]$$

Fano profile

$$\frac{\left(\frac{q\Gamma_{res}}{2} + E - E_{res}\right)^2}{\left(\frac{\Gamma_{res}}{2}\right)^2 + (E - E_{res})^2}$$

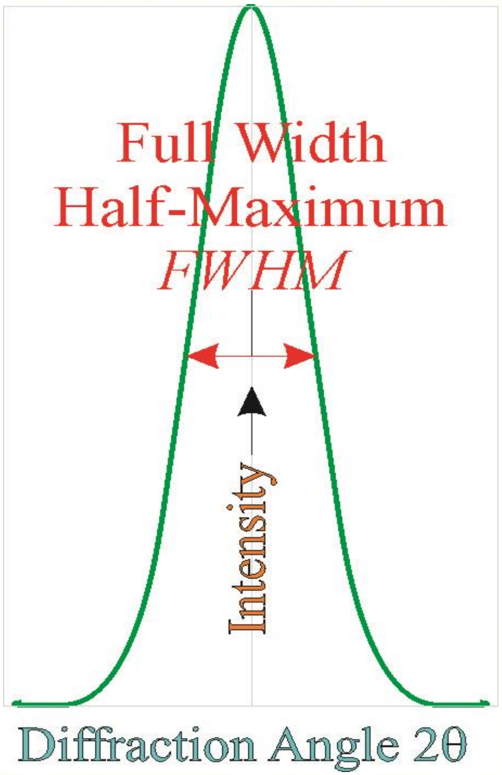
Combined Lorentz and Doppler: Voigt profile

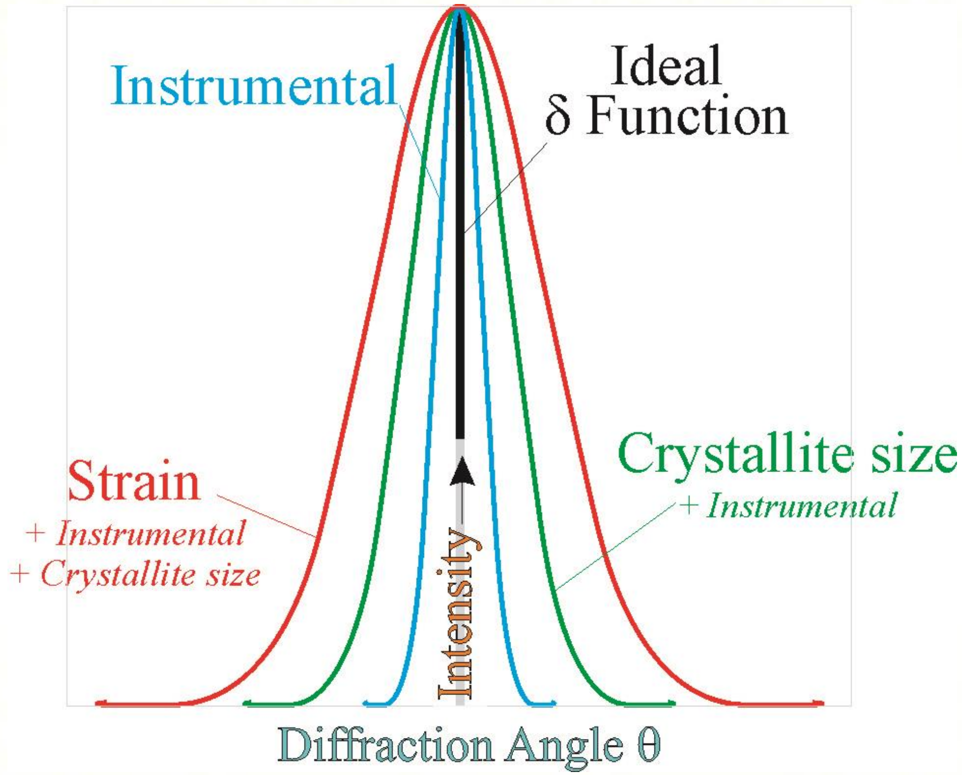
$$\sigma_n(\nu) = S\,\frac{a}{\pi^{3/2}\alpha_D}\int_{-\infty}^{+\infty}\frac{dy\,\exp(-y^2)}{(\mathrm{v}-y)^2 + a^2}$$

$$a = \alpha_L / \alpha_D = dampingratio$$

$$\mathrm{v} = (\nu - \nu_0)/\alpha_D$$

The diffraction peak we see is a result of various broadening 'mechanisms'





Absorption

- Energy selectivity is its outstanding characteristic.
- Energy attenuation due to absorption is dominant in near IR and thermal IR spectral ranges.
- Absobed radiative enegy in IR regions causes excitation of lattice vibrations, molecular vibrational states, and intermolecular vibrations.
- Absorbed radiative energy in UV and shorter wavelength leads to photodissociation and photoionisation.

Absorption in solids

- Conductors have a small gap between the energy bands and are higly absorbing and reflecting in visible and IR.
- Insulators have a bigger energy gap between the bands,so they are absorbing in UV
- Insulators are more or less transparent in visible and IR.
- Selective absorption is responsible nearlly for all color of objects in the environment

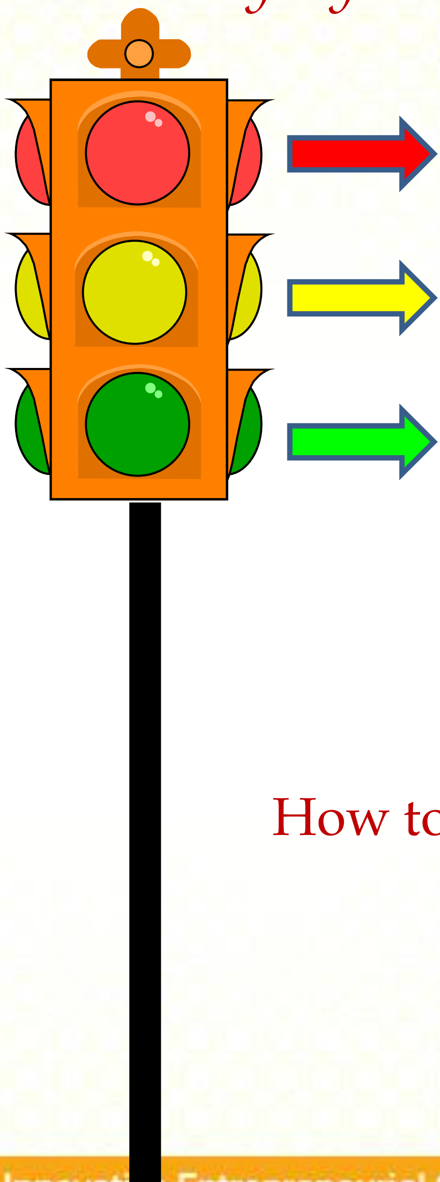
Emission

Emission: A transition from a excited level to a lower (ground) level with transfer of energy from the emitter to the radiation field. If no radiation is emitted during transition it is called **nonradiative** decay.

- Atoms, molecules, or solids that are excited to high energy levels decay to lower levels by emitting radiation (emission or luminescence).
- Atoms excited using high-temperature energy source this light emission is commonly called atomic or optical emission.
- Atoms excited via light it is called atomic fluorescence. For molecules it is called **fluorescence** if the transition is between states of the same spin and **phosphorescence** if the transition occurs between states of different spin.
- The **emission intensity** of an emitting substance is linearly proportional to analytic concentration at low concentrations

Selection Rules

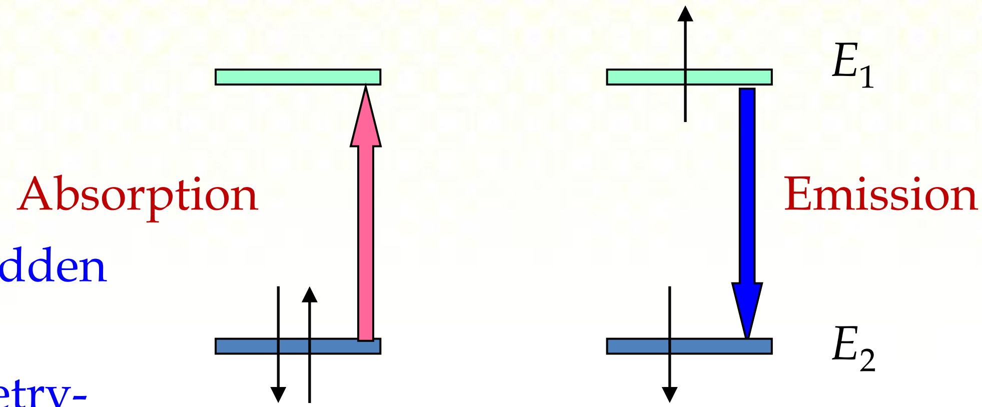
Decided by Symmetry, Spin, Parity and other Quantum numbers



Spin-forbidden

Symmetry-forbidden

Spin and Symmetry-allowed



Oscillator strength:

$f = f(\text{symmetry}) \times f(\text{spin}) \times f(\text{FC})$

How to Separate out Electronic Co-ordinates from Nuclear Co-ordinates? *Born-Openheimer approximation*

Selection Rules

Pauli Exclusion Principle

$\vec{L_1} + \vec{L_2} = \vec{L}$

$\vec{2} + \vec{2} = 0,1,2,3,4$

$\vec{S_1} + \vec{S_2} = \vec{S}$

$\vec{1/2} + \vec{1/2} = 0,1$

$\vec{J} = \vec{L} + \vec{S} = 0,1,2,3,4$

These identical electrons must produce an antisymmetric wavefunction.

$$\Psi = \Psi_{spin}\Psi_{orbital}$$

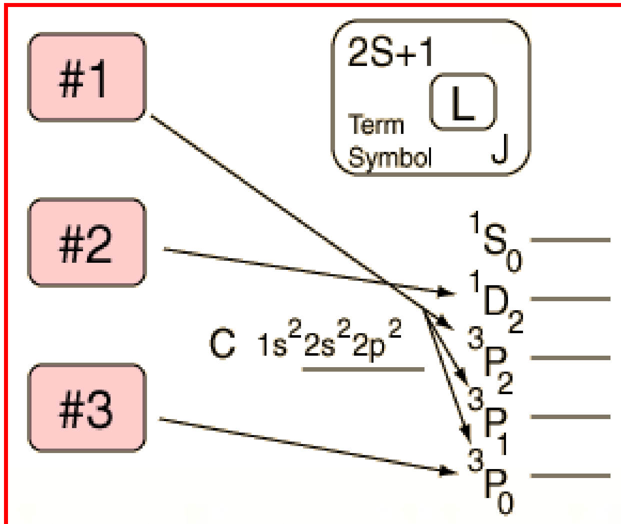
Since S=1 represents a symmetric spin state, it must couple with antisymmetric orbital states L=1 and L=3

"sharp"	*s*	$\ell = 0$
"principal"	*p*	$\ell = 1$
"diffuse"	*d*	$\ell = 2$
"fundamental"	*f*	$\ell = 3$

For example, if n=2, ℓ=1, the state is designated 2p

		n=1	n=2	n=3	n=4
s -- sharp	ℓ =0	1s	2s	3s	4s
p -- principal	ℓ =1		2p	3p	4p
d -- diffuse	ℓ =2			3d	4d
f -- fundamental	ℓ =3				4f
g	ℓ =4	beyond this point, the notation just follows the alphabet			
h	ℓ =5				
...					

Hund's Rules



$^{2S+1}L_J$ Term Symbol

$J_1 = L_1 + S_1$

$J_2 = L_2 + S_2$

...

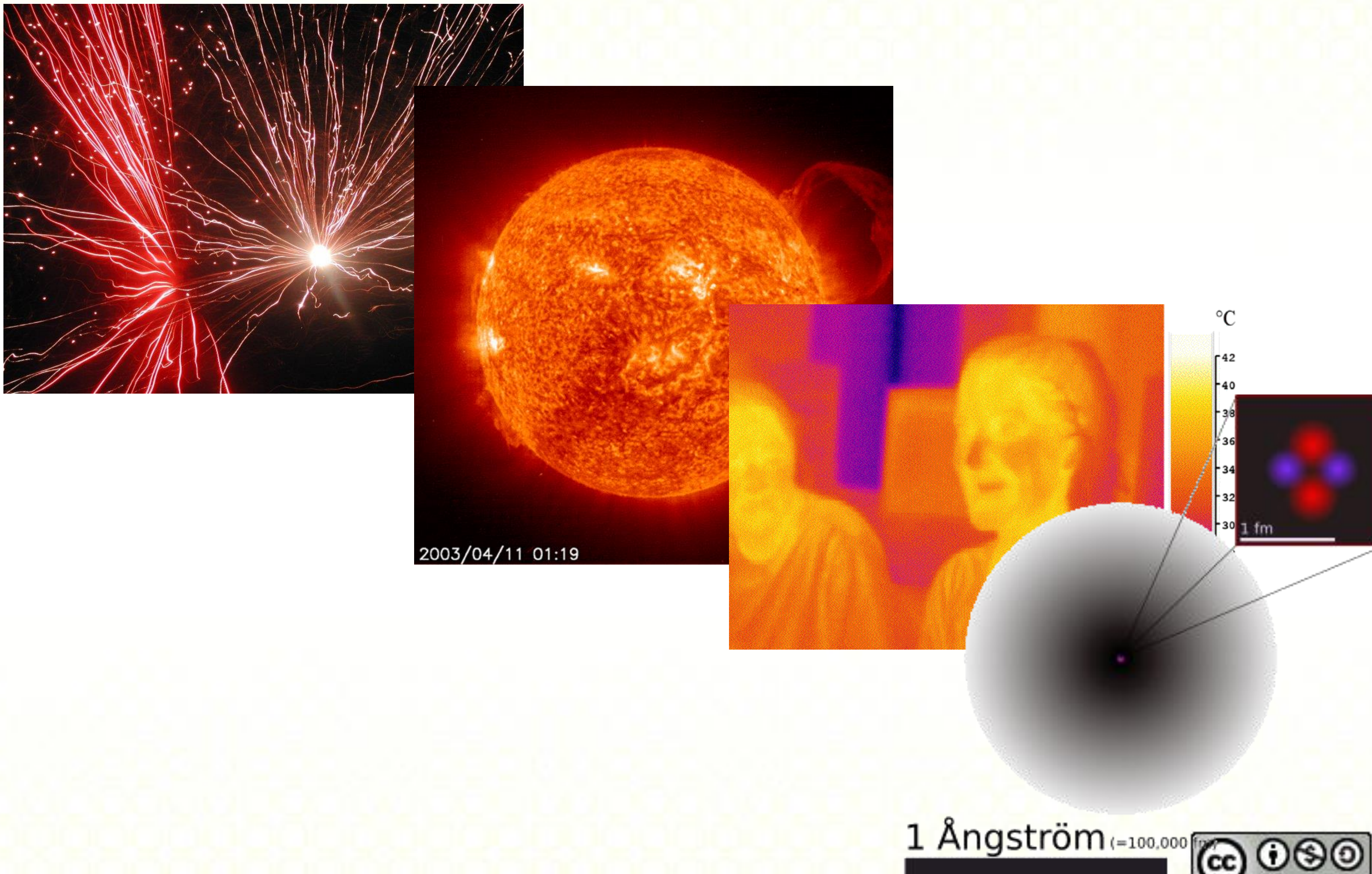
$J = \sum_i J_i$

$L^2 = \ell(\ell+1)\hbar^2$

$\ell(\ell+1)$ *where* $\ell = 0,1,2,3,\ldots n-1$

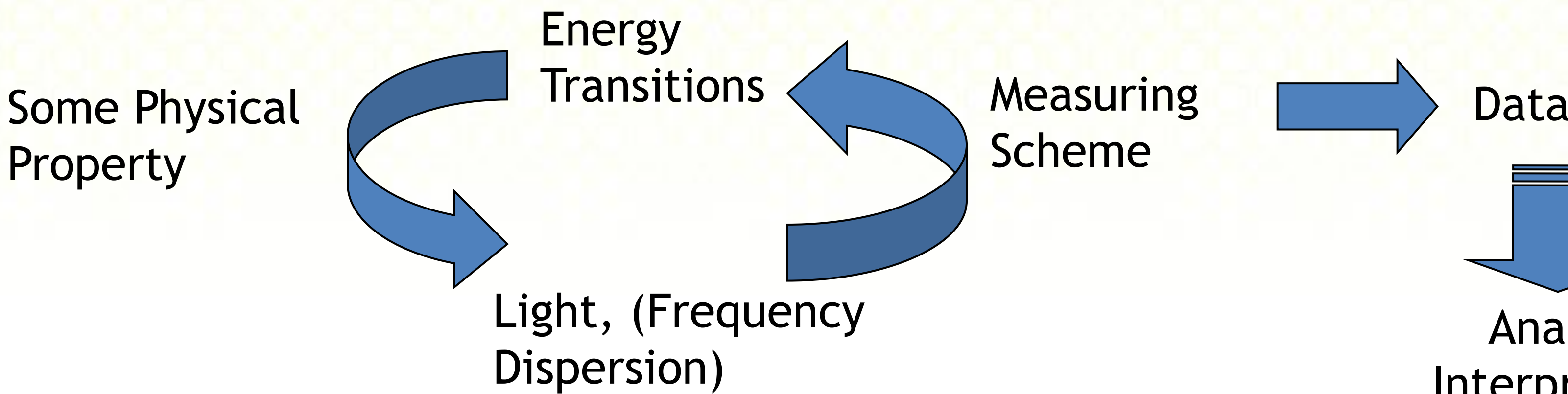
The term symbol selection rules are: **ΔS=0, ΔL=0,±1, Δl=±1, ΔJ=0,±1**

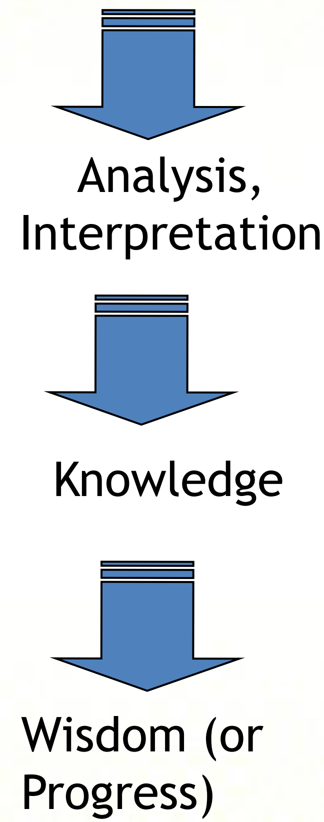
What Causes Emission?



Absorption

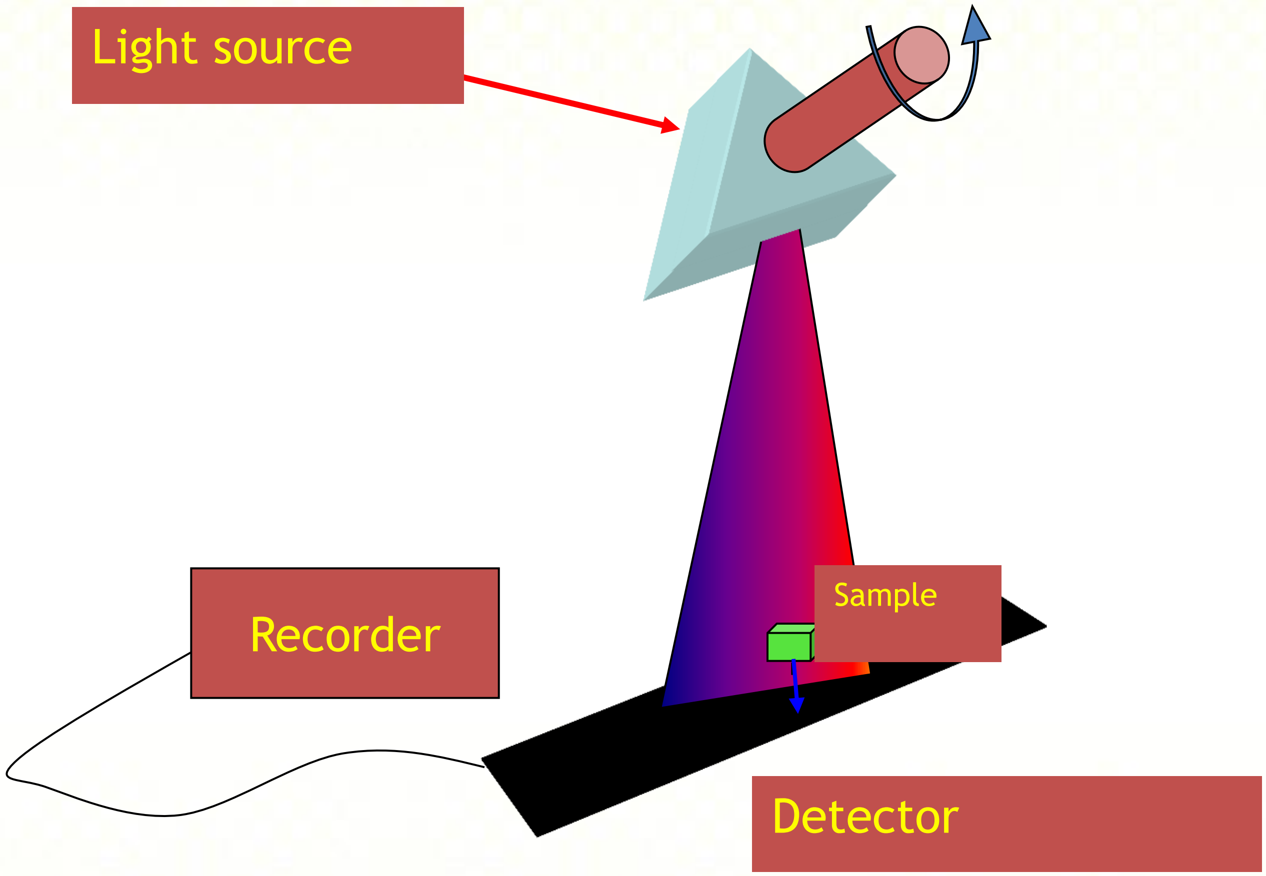
Features in Common for all Spectroscopy





A key for us here is, we use instruments to ***Disperse*** energy across a scale appropriate to a chemical property

Typical Spectrometer



Conclusion

- The colour spectrum of an object is a complex result of its surface properties, its transmission properties, and its emission properties, all of which contribute to the mixing of wavelengths in the light leaving the surface of the object after interacting with the material.

- The perceived colour is further conditioned by the nature of the ambient illumination, and by the colour properties of other objects nearby, and via other characteristics of the perceiving eye and brain.

- Colour is the visual effect that is caused by the spectral composition of the light emitted, transmitted, or reflected by objects. It depends on the nature of light, materials and the viewing angle.

Processes that affects the propagation of electromagnetic radiation are:

Absorption
Emission
Reflection
Scattering
Transmission
Refraction
Diffraction
Dispersion

Thanks