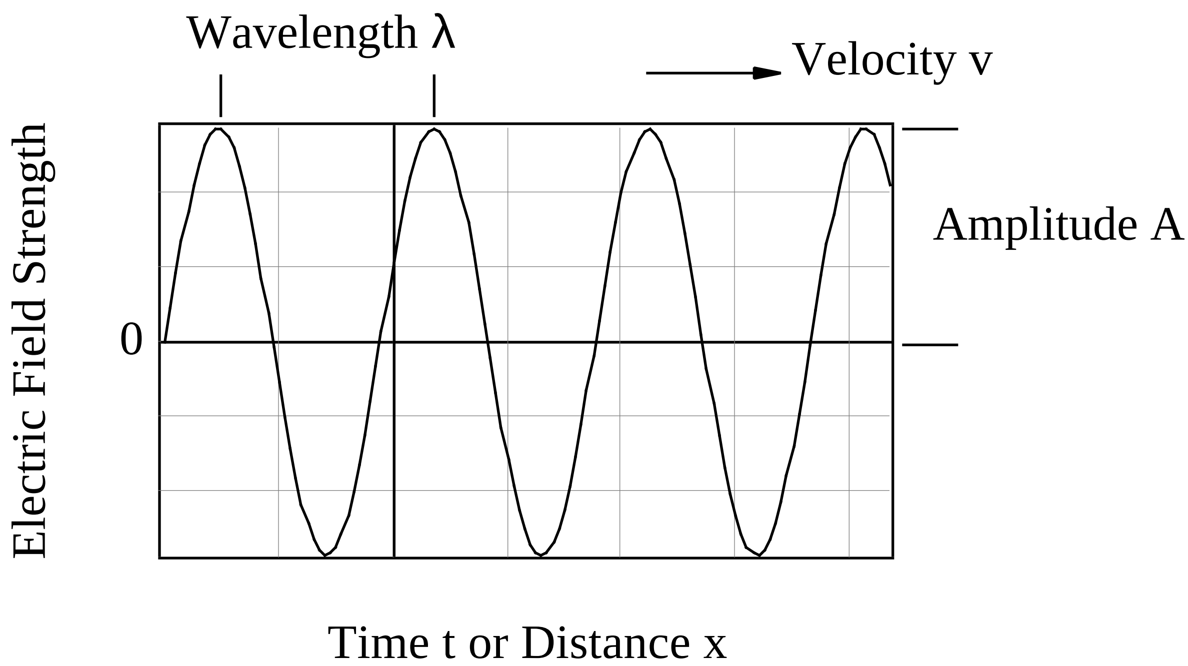
Introduction to Spectroscopy (Chapter 6)

Electromagnetic radiation (wave) description:



Period p — time for 1 λ to pass fixed point

Frequency ν — # of λ passing per s $\left(\nu = \frac{1}{p}\right)$

Wavenumber $\bar{\nu}$ — # of λ per cm $\left(\bar{\nu} = \frac{1}{\lambda}\right)$

Velocity v — Distance point on wave travels per second

$$v = \nu \lambda$$

In a vacuum: $v_{vacuum} = c$

$$= 2.99782 \text{x} 10^{8} \text{ m / s}$$

A set of waves with identical (a) freqency (b) phase are called *coherent* .

Frequency is always fixed but velocity can vary!

Waves slow down in medium (gas, liquid, solid) so $v<c$

$$v = \nu \lambda$$

Implies λ decreases in medium

Refractive index $\eta = \frac{c}{v} \geq 1.00$

Equation for Wave

$$E = A \sin(\omega t + \varphi) \quad \text{where} \quad \omega = 2\pi\nu$$

electric field	frequency
amplitude	phase
angular frequency	time

Wave description explains certain EM radiation phenomena:

- transmission
- reflection and refraction
- diffraction
- interference
- scattering
- polarization

Particle Description of Light:

Based on quantum mechanics

Energy of EM photon: $E = h\upsilon = \frac{hc}{\lambda}$

Planck's Constant=6.626x10^{-34} J·s

Postulates of QM:

1. Atoms, ions and molecules exist in discrete energy states only

   $$E_0 = \text{ground state}$$

   $$E_1, E_2, E_3 \ldots = \text{excited states}$$

   Excitation can be electronic, vibrational or rotational

   Energy levels for atoms, ions or molecules different.

   Measuring energy levels gives means of identification - spectroscopy

2. When an atom, ion or molecule changes energy state, it absorbs or emits energy equal to the energy difference

   $$\Delta E = E_1 - E_0$$

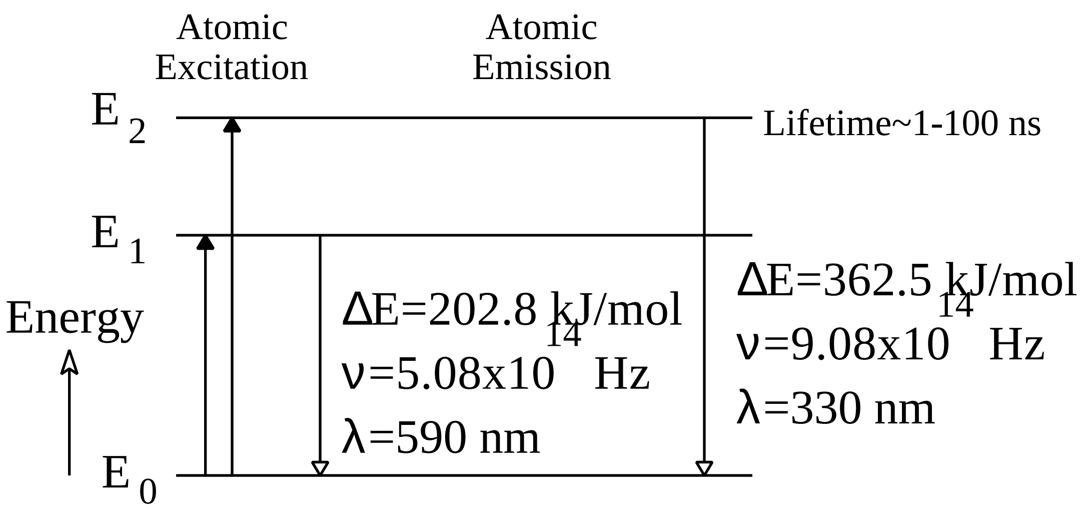
3. The wavelength or frequency of radiation absorbed or emitted during a *transition* proportional to ΔE

   $$\Delta E = h\nu = \frac{hc}{\lambda}$$

Emission Spectra

Plot of emission intensity vs. ν or λ called **emission spectrum**

Atom:

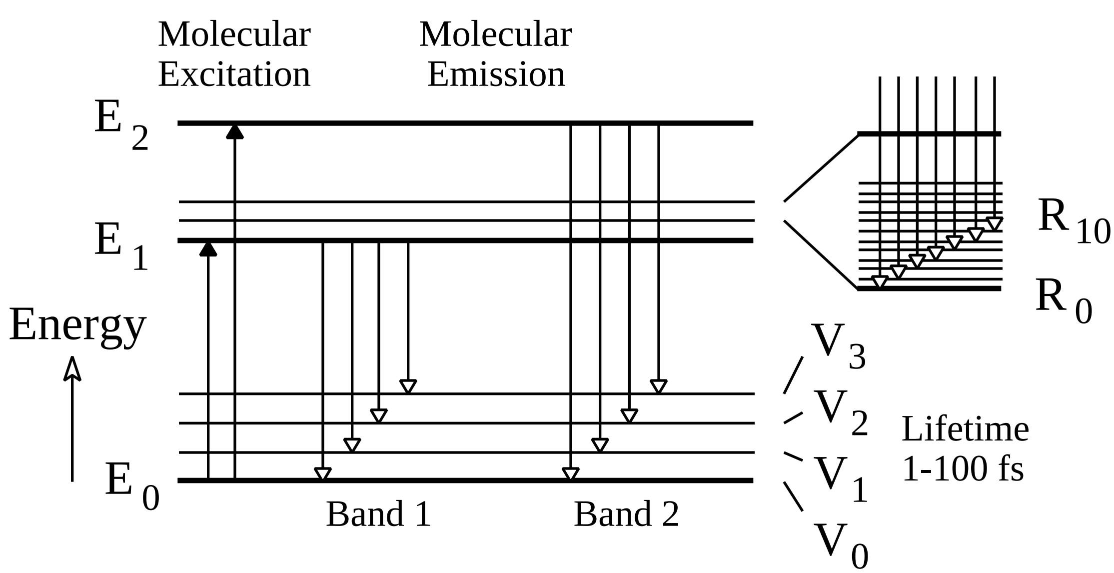


line emission spectra

Inner shell (core) electrons (1s ← 2p) - x-rays photons

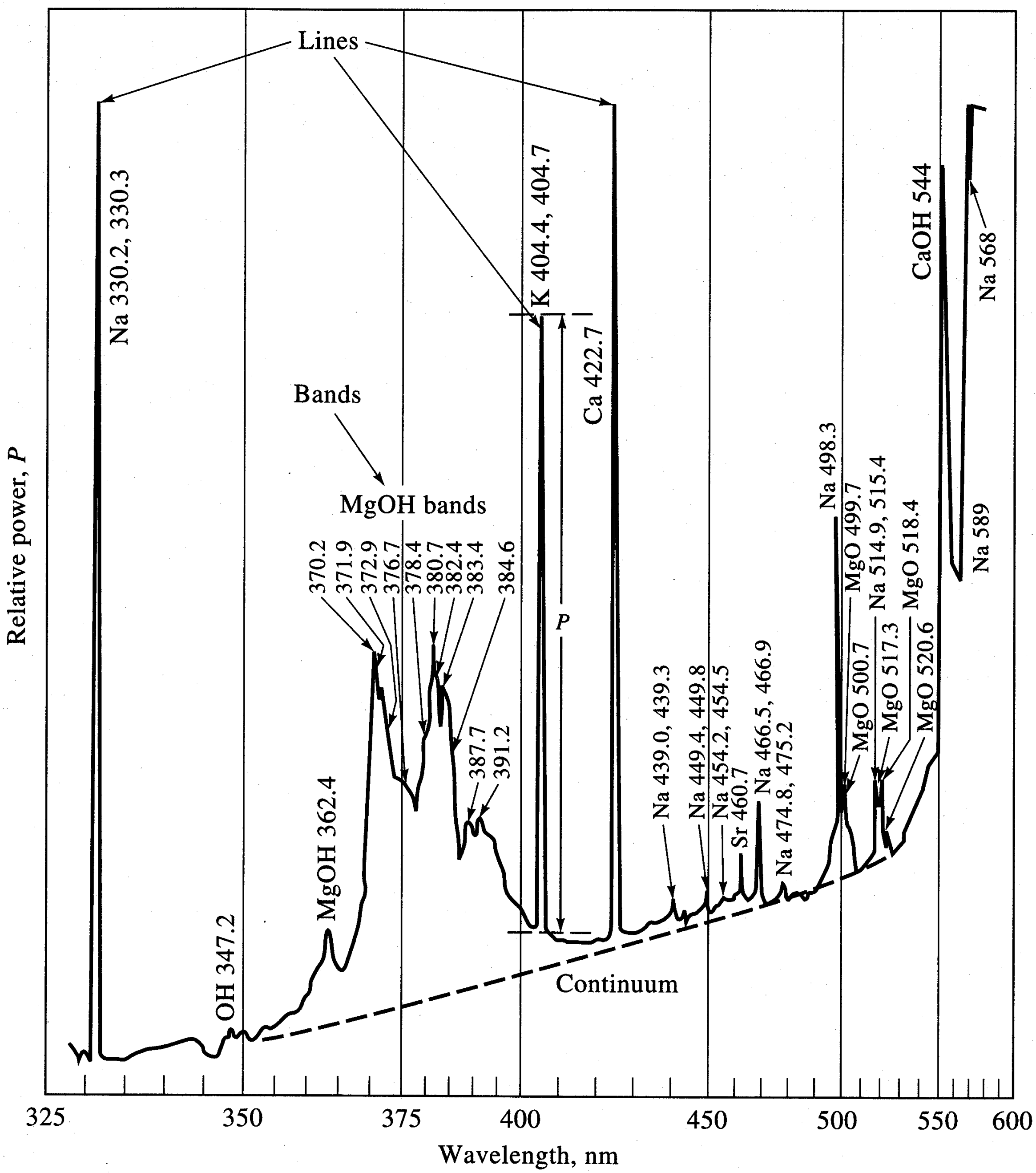
Outer shell (valence) electrons (3d ← 4p) - UV/vis photons

Molecule:



vibrational and rotational transitions - **band** emission spectra

Emission spectrum of brine (Fig. 6-15):



Ballpark Energy Level Spacings:

ΔE (Electronic) >100 MJ/mol (x-ray) to <100 kJ/mol (UV-vis)

ΔE (Vibrational) <1 to <100 kJ/mol (IR)

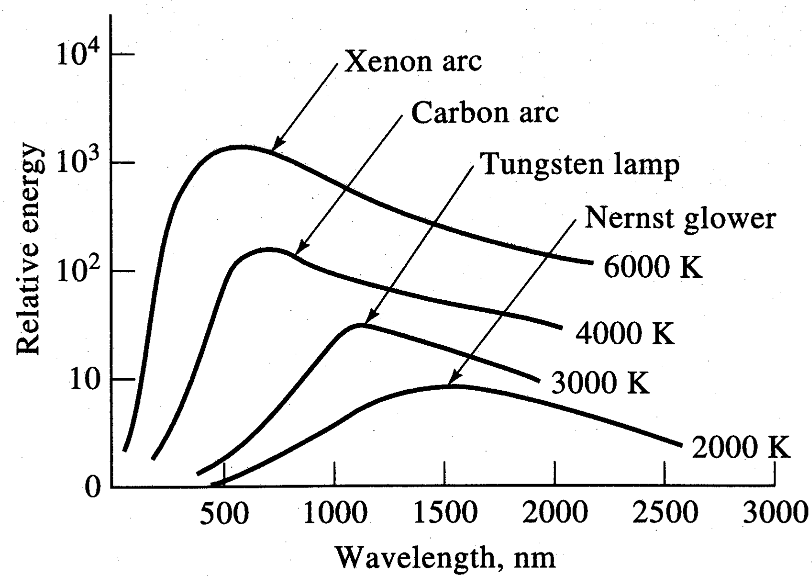
ΔE (Rotational) 10-100 J/mol (microwave)

Continuum Spectra:

Very broad band spectra in emission from solids

Produced by *blackbody* radiation - thermal excitation and relaxation of many vibrational (and rotational) levels.

Blackbody Spectrum (Fig 6-18)



Absorption Spectra

Plot of Absorbance vs. ν or λ called absorption spectrum

Just as in emisson spectra an atom, ion or molecule can only absorb radiation if energy matches separation between two energy states

Atoms:

No vibrational or rotational energy levels - sharp line spectra with few features

For example:

Na 3s → 3p 589.0, 589.6 nm (yellow)

Na 3s → 5p 285.0, 285.1 nm (UV)

Visible enough energy for valence (bonding) excitations

UV and x-ray enough energy for core (inner) excitations

Molecules:

Electronic, vibrational and rotational energy levels - broad band spectra with many features

$$\Delta E = \Delta E_{electronic} + \Delta E_{vibrational} + \Delta E_{rotational}$$

For each electronic state - many vibrational states

For each vibrational state - many rotational states

→ many features

Absorption spectra affected by

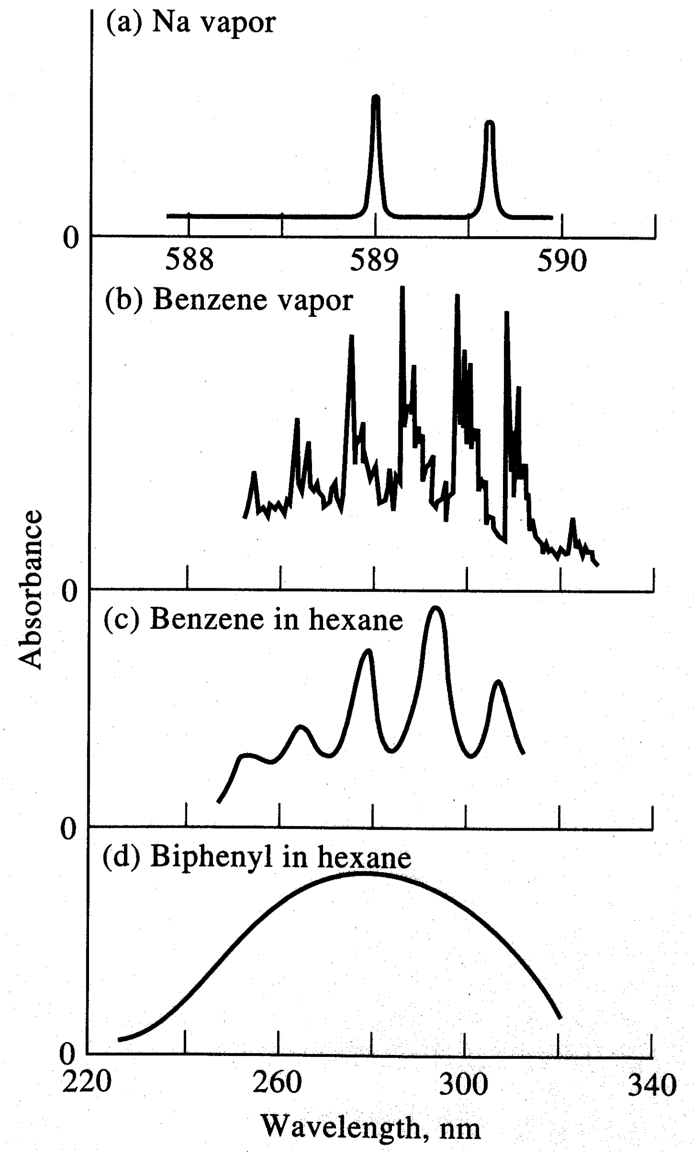
(1) number of atoms in molecule

more features

(2) solvent molecules

blurred features

Effect of Chemical State (Fig 6-19):



Relaxation Processes:

Lifetime of excited state is short (fs → ms) - relaxational processes return excited species to ground state

Nonradiative relaxation

many small collisional relaxations

tiny temperature rise of surrounding species

Radiative relaxation (emission)

fluorescence ($<10^{-5}$ s) and phosphorescence ($>10^{-5}$ s)

Resonance fluorescence

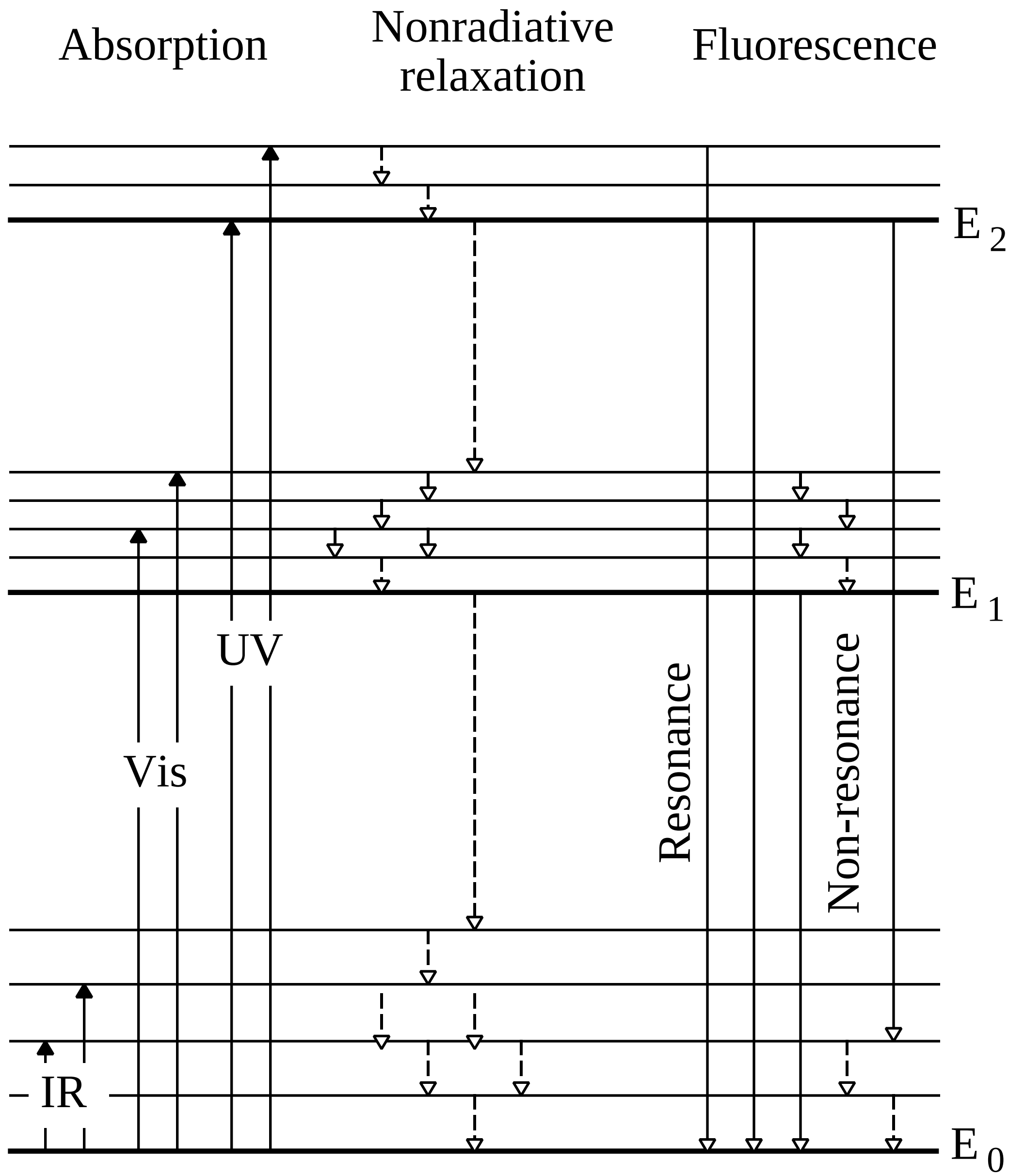
- produces emission at same energy/frequency/wavelength as absorption
- common for atoms (no V or R levels)

Non-resonance fluorescence

- produces emission at lower energy (lower frequency/longer wavelength) than absorption (Stokes shift)
- common in molecules - vibrational relaxation occurs before fluorescence

Phosphorescence

- Produced by long-lived electronic state (up to hours)



Excitation methods:

(i) EM radiation

(ii) spark/discharge/arc

(iii) particle bombardment (electrons, ions...)

(iv) chemiluminescence (exothermic chemical reaction generates excited products)