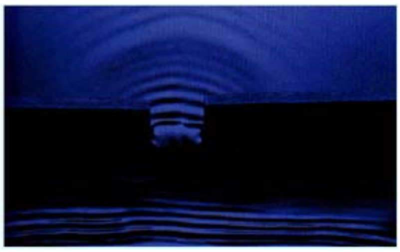
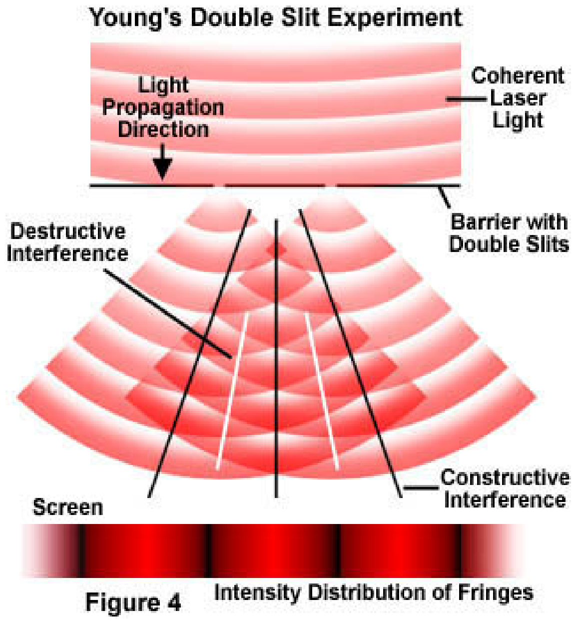
Diffraction of Radiation

- A process in which a parallel beam of radiation is bent as it passes by a sharp barrier or through a narrow opening.

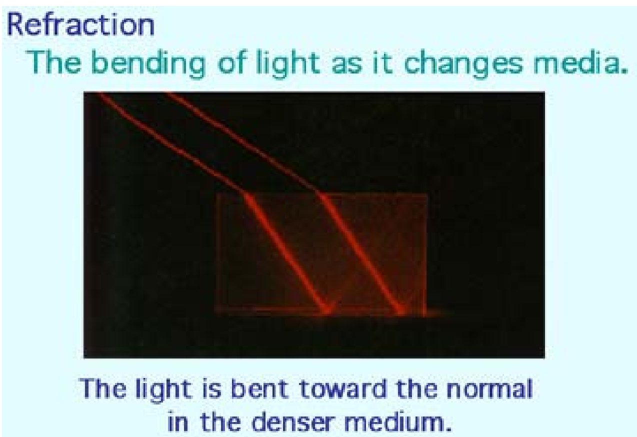


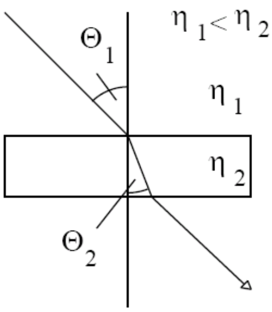


Where crest meets crest or trough meets trough, we have constructive interference. Crest plus trough cause destructive interference
– Constructive makes bright bands, destructive makes dark bands
(ex ; grating)

Refraction

– As a consequence of a difference in velocity of the radiation in the two media (ex ; prism)





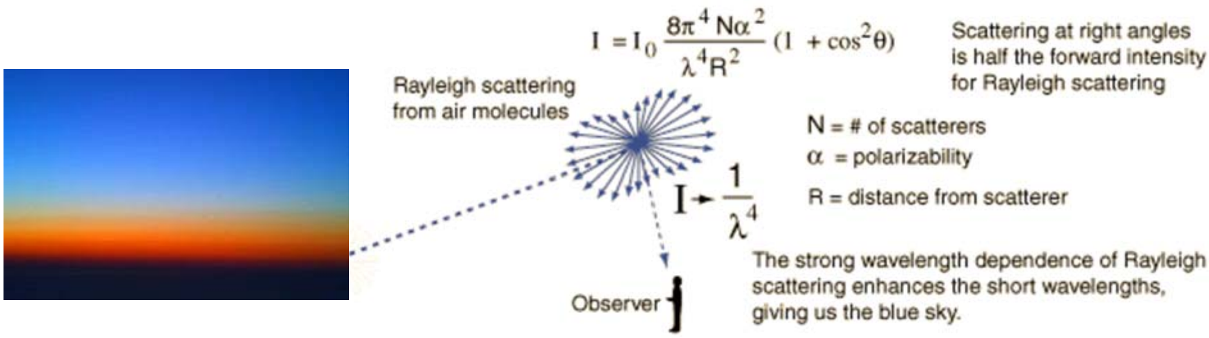
$$\frac{\sin\Theta_2}{\sin\Theta_1} = \frac{\eta_1}{\eta_2} = \frac{v_2}{v_1} = \frac{\upsilon_2 \cdot \lambda_2}{\upsilon_1 \cdot \lambda_1}$$

velocity

Snell's Law

Scattering

- 물질 투과 시 물질의 입자에서 모든 방향으로 복사선이 재방출되는 현상
- Rayleigh scattering
  - Particles smaller than the wavelength of the radiation
  - Intensity = $(\lambda)^{-4}$(particle sizes) $(\alpha)^2$



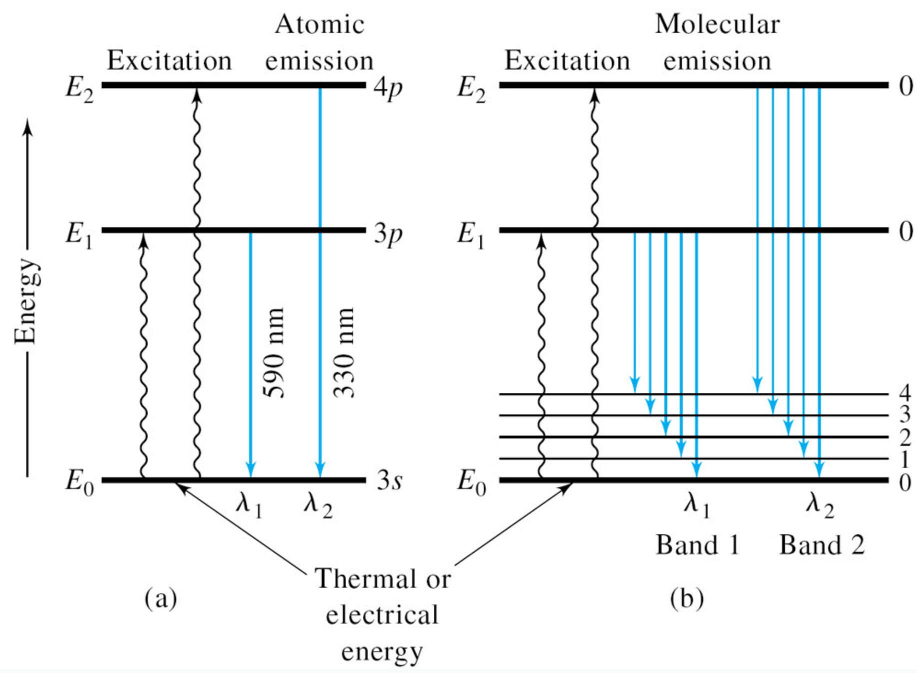
- Raman scattering
  - Frequency changes

Absorption Spectra

- Plot of Absorbance vs. ν or λ
  - Is called absorption spectrum
- Just as in emission spectra in atom,
  - ion or molecule can absorb radiation if energy matches separation between two energy states

Emission Spectra

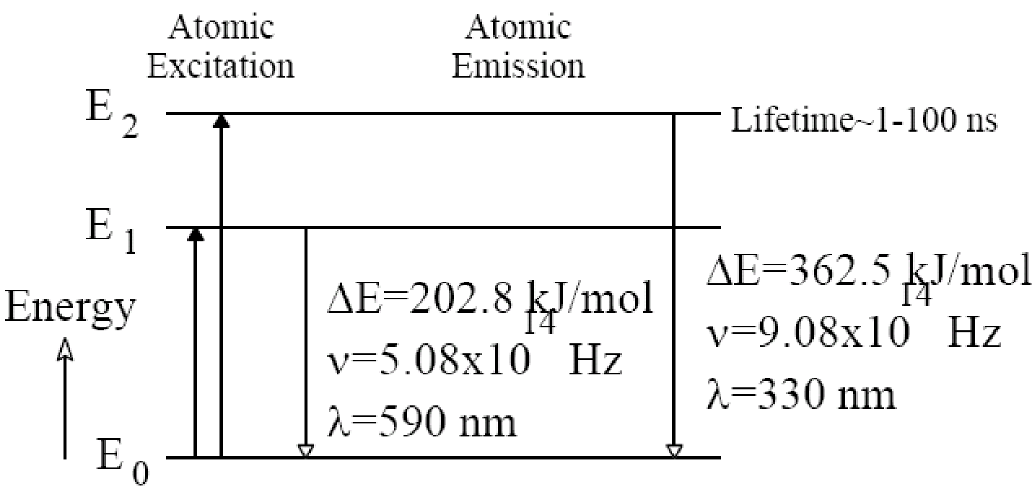
- Plot of emission intensity vs. ν or λ
- How to excite particles
  - Electron or sub-particle collision (X-ray)
  - Spark, flame, or heat (UV, VIS, IR)
  - EMW (for fluorescence)
  - Exothermic reaction (for chemiluminscence)



Energy-level diagrams for (a) a sodium atom showing the source of a line spectrum and (b) a simple molecule showing the source of a band spectrum.

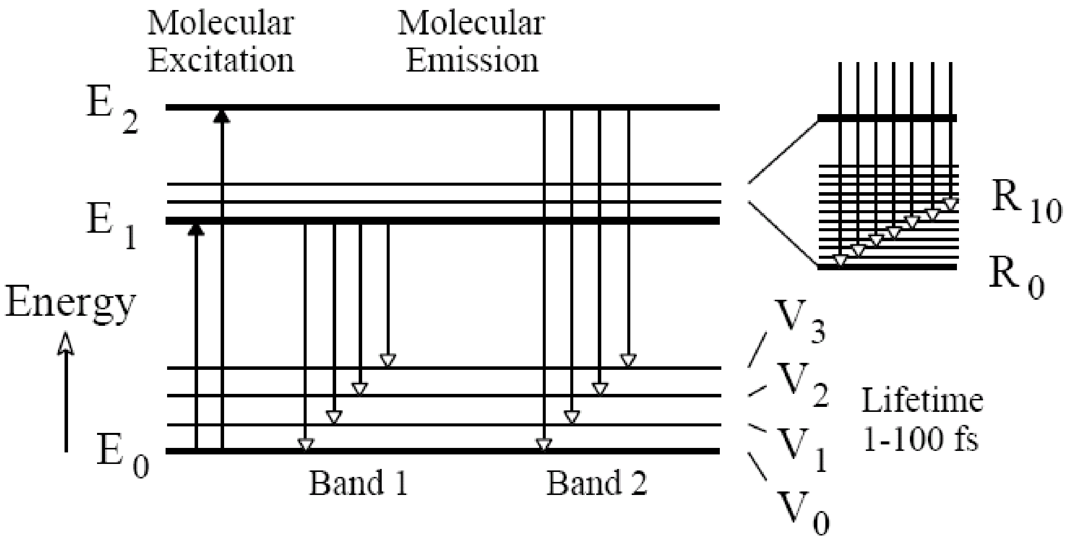
Line spectrum

- Usually Atomic Transition
- linewidth 약 1/10000 Å
- 흥분, 들뜸, 여기 – (1–10 ns 후) – 방출



Band spectra

- Small molecules or radicals
- Fast vibrational relaxation (1–10 fs)
- From Electronic excited but vibrationaly relaxed states



Relaxation Process

- Why?
  - Lifetime of excited state is short (fs to ms)
  - relaxational processes

- Process Types

Nonradiative relaxation

- return excited species to ground state by many small collisional relaxations
- Results – tiny temperature rise of surrounding species

Radiative Relaxation

- Excited by EMW, relaxed at lower energy with EMW
- Monitored at 90° of excitation light
- Example : Fluorescence from a series of organic semiconductor materials

Fluorescence (FL) and phosphorescence (PL)

- 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)
  - Selection rule forbidden process (triplet to singlet)

TABLE 6-2 Major Classes of Spectrochemical Methods

Class	Radiant Power Measured	Concentration Relationship	Type of Methods
Emission	Emitted, P_e	$P_e = kc$	Atomic emission
Luminescence	Luminescent, P_l	$P_l = kc$	Atomic and molecular fluorescence, phosphorescence, and chemiluminescence
Scattering	Scattered, P_{sc}	$P_{sc} = kc$	Raman scattering, turbidimetry, and particle sizing
Absorption	Incident, P_0, and transmitted, P	$-\log \frac{P}{P_0} = kc$	Atomic and molecular absorption