Spectral Resolution

- Spectral resolution is a measure of the ability to separate nearby features in wavelength space.

$$R = \frac{\lambda}{\Delta\lambda}, \ \Delta\lambda = \text{minimum wavelength separation of two resolved features.}$$

- Delta lambda
  - often set to the full-width at half-maximum of an unresolved line
  - can be measured in the data
  - depends on data analysis
  - can be limited by diffraction, slit width, detector sampling

Spectral Linewidth

Helium

- **May expect narrow, distinct spectral lines.**
- **Physical mechanisms can broaden spectral lines.**
  - **Doppler Effect**
    - **Thermal motion**
    - **Rotation**
    - **Gas Turbulence**
  - **Collision Broadening**
  - **Magnetism**

(a)

(b)

Intensity
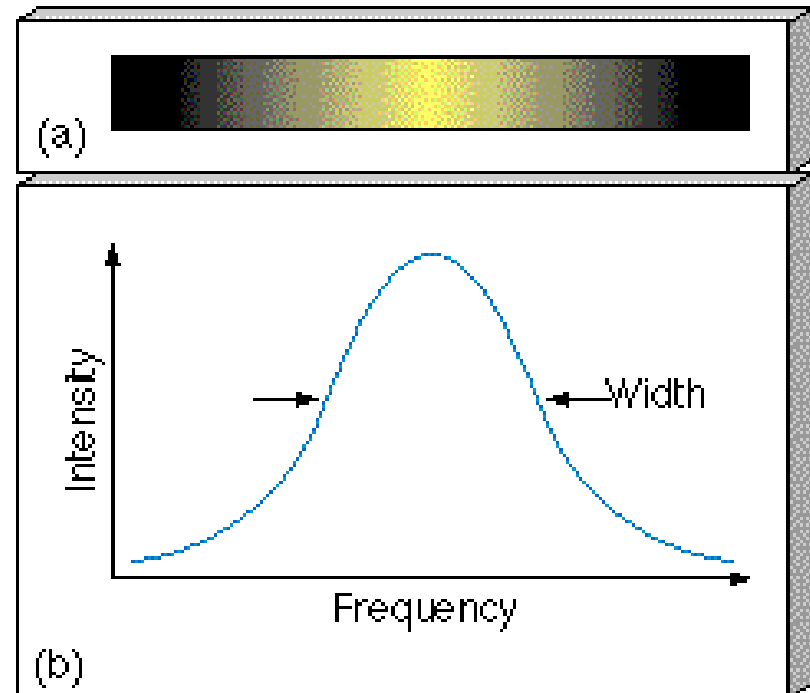
Frequency

Width

Natural Line Widths

Line broadens due
1. **Uncertainty**
2. Doppler effect
3. Pressure
4. Electric and magnetic fields

frequency

$$\Delta \gamma \Delta t \geq 1$$

Lifetime of an excited state is typically 1×10^{-8} s

$$\Delta \gamma \geq \frac{1}{10^{-8} \, s} = 5 \times 10^7 \, \frac{1}{s}$$

$$\gamma = c\lambda^{-1}$$

$$\frac{d\gamma}{d\lambda} = -1c\lambda^{-2}$$

$$\frac{d\gamma}{c\lambda^{-2}} = \left| d\lambda \right|$$

$$\frac{\Delta \gamma}{c\lambda^{-2}} = \left| \Delta\lambda \right| = \frac{\Delta \gamma \lambda^2}{c}$$

$$|\Delta\lambda| = \frac{\left(5x10^7 \, \frac{1}{s}\right)\lambda^2}{\left(3x10^8 \, \frac{m}{s}\right)\left(\frac{10^9 \, nm}{m}\right)} = \left(\frac{5x10^{-10}}{nm}\right)\lambda^2$$

Example: 253.7 nm

$$|\Delta\lambda| = \left(\frac{5x10^{-10}}{nm}\right)(253.7nm)^2 = 3.22x10^{-5} \, nm$$

Typical **natural line widths** are 10^{-5} nm

Difference of NMR with other spectroscopy

- The generation of the ground and excited NMR states requires the existence of an external magnetic field.

- NMR excited state has a life time that is on the order of 10^9 times longer than the lifetime of excited electronic states.

- According to Heisenberg Uncertainty principle, $\Delta E \Delta t \approx h/2\pi$. The longer an excited state exist, the narrower the line width.

Difference …..

- Longer lifetime also facilitates multi-dimensional spectroscopy by allowing the resonance frequency information associated with one spin to be passed to another.

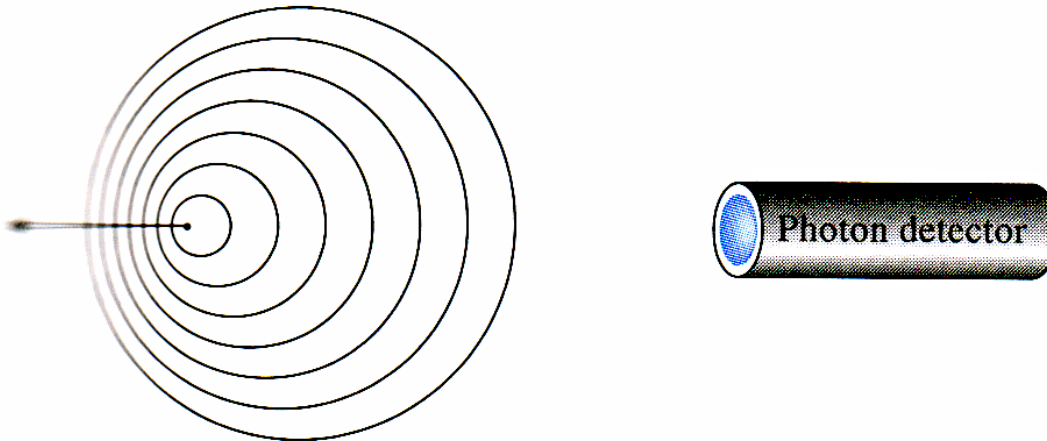- The longer life-time permits the measurement of molecular dynamics over a wide-range of time scales.

Line broadens due
1. **Uncertainty**
2. **Doppler effect**
3. Pressure
4. Electric and magnetic fields

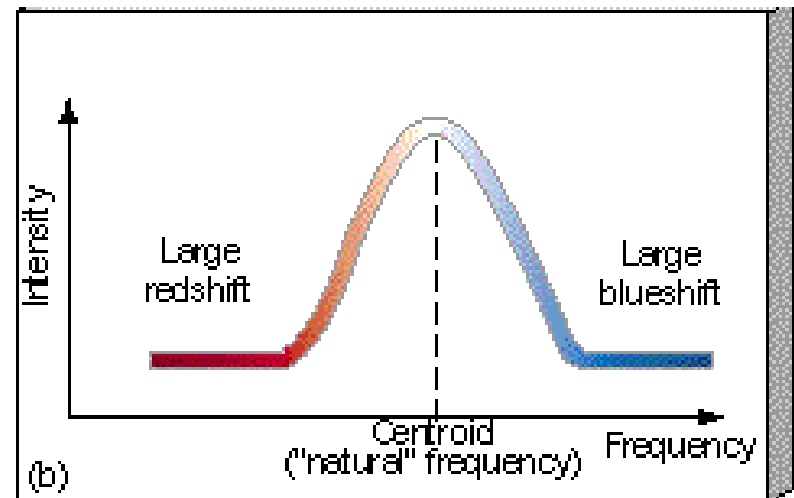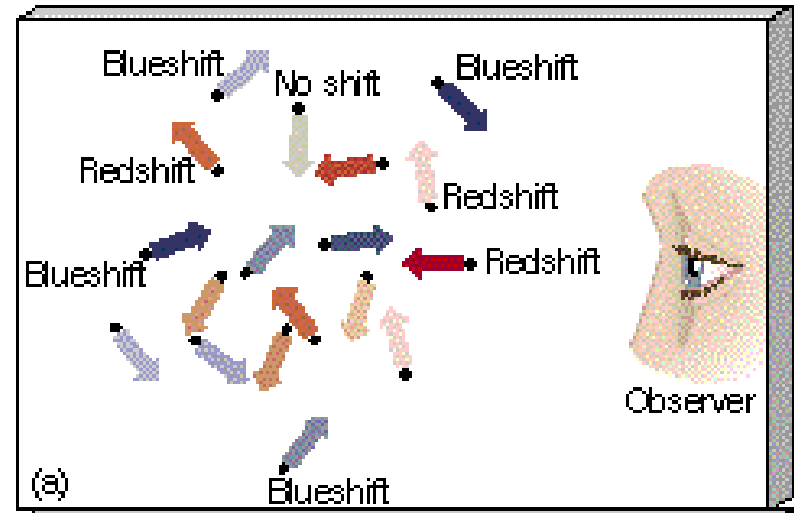$$\frac{\Delta\lambda}{\lambda_0} = \frac{v_{elocity}}{c}$$

(a)

Photon detector

Photon detector
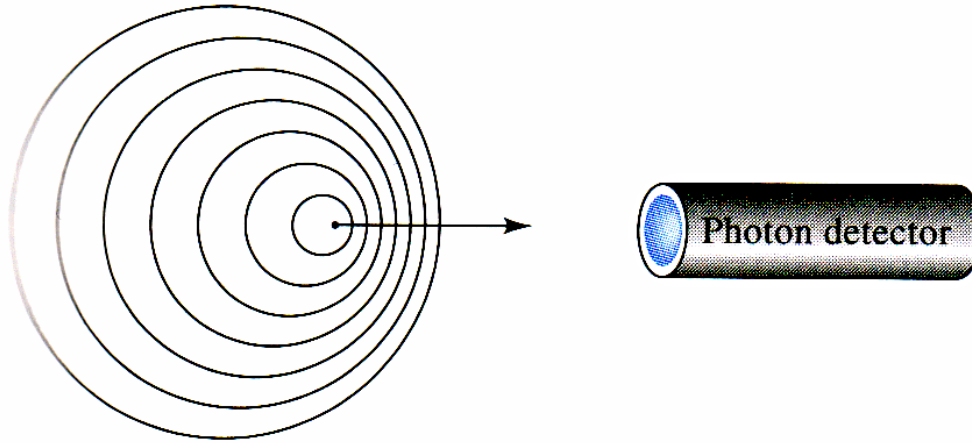
(b)

Doppler Effect:
Thermal Motion of Atoms

- **Atoms moving randomly.**

- **Redshifted, blueshifted, and unshifted emission lines created with respect to the observer.**

- **In the detector, individual redshifted and blueshifted emission lines merge with the unshifted lines to produce broadened spectral lines.**
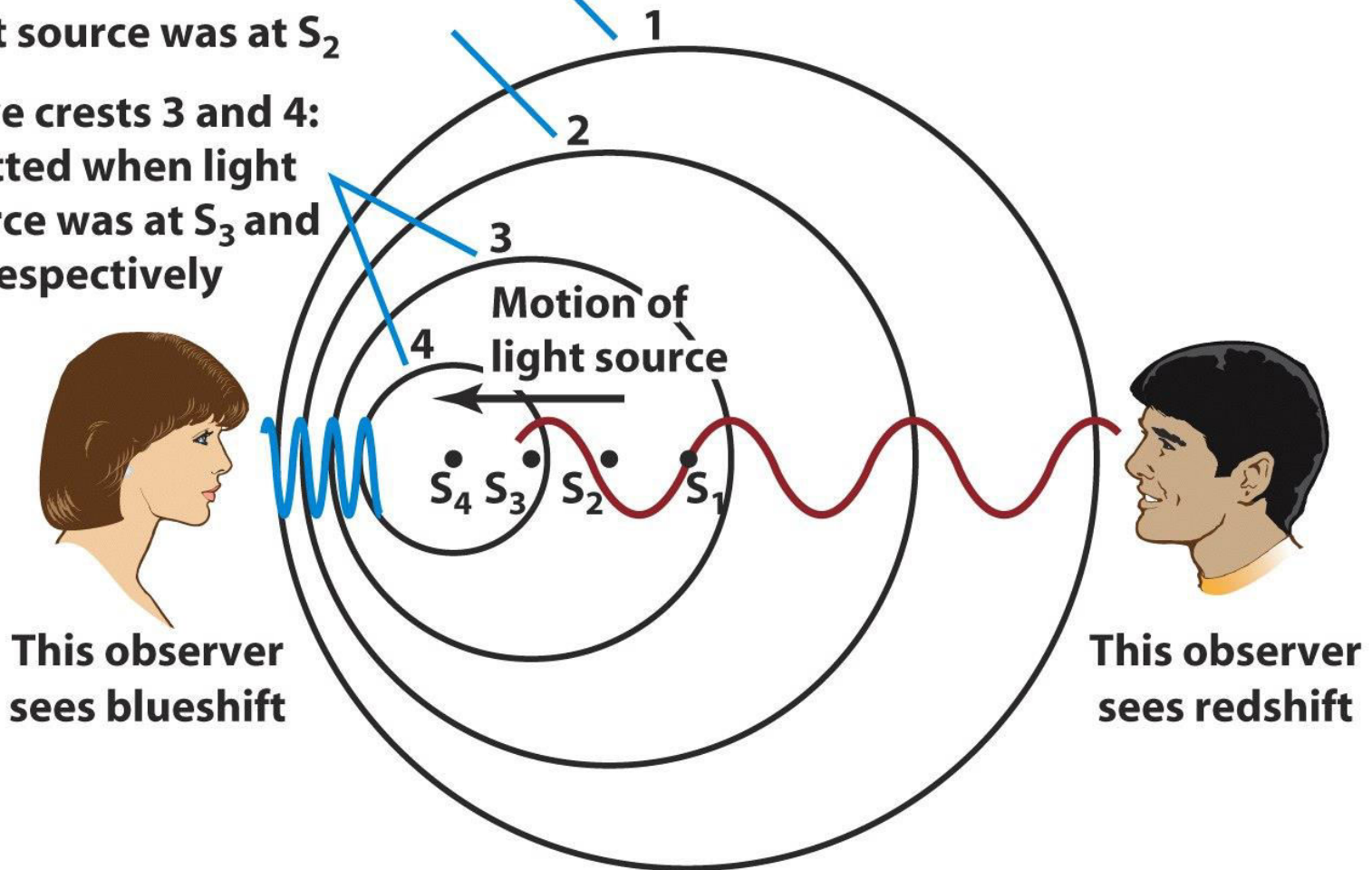
affected by the relative motion between the source and the observer

Wave crest 1: emitted when light source was at S_1

Wave crest 2: emitted when light source was at S_2

Wave crests 3 and 4: emitted when light source was at S_3 and S_4, respectively

1

2

3

4

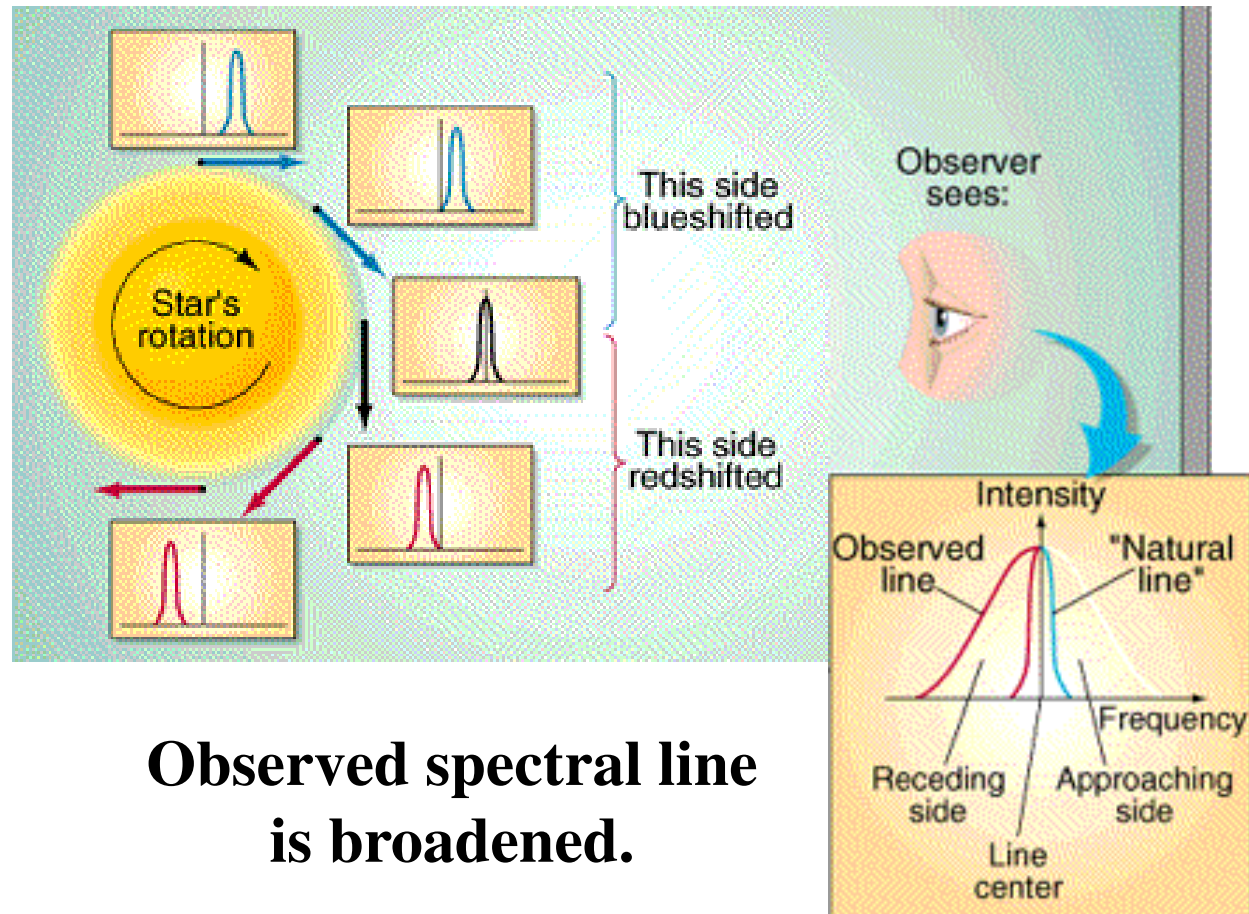Motion of light source

S_4 S_3 S_2 S_1

This observer sees blueshift

This observer sees redshift

Doppler Effect: Rotation

- **Rotation of star/gas will produce a broadening of spectral lines.**

- **Photons emitted from side *spinning toward us*, *blueshifted*.**

- **Photons emitted from side *spinning away from us*, *redshifted*.**

Observed spectral line is broadened.

Doppler Shifts

- **Red Shift**: The object is moving away from the observer
- **Blue Shift**: The object is moving towards the observer

$$\Delta\lambda/\lambda_o = v/c$$

$\Delta\lambda$ = wavelength shift

λ_o = wavelength if source is not moving

v = velocity of source

c = speed of light

Laboratory spectrum
Lines at rest wavelengths.

Object 1
Lines redshifted: Object is moving
away from us.

Object 2
Greater redshift: Object is moving
away faster than Object 1.

Object 3
Lines blueshifted: Object is
moving toward us.

Object 4
Greater blueshift: Object is moving
toward us faster than Object 3.

Doppler Shift

- The greater the velocity the greater the shift.

Line broadens due
1. **Uncertainty**
2. **Doppler effect**
3. **Pressure**
4. Electric and magnetic fields

The lifetime of a spectral event is 1×10^{-8} s

When an excited state atom is hit with another high energy atom
energy is transferred which changes the energy of the
excited state and, hence, the energy of the photon emitted.
This results in linewidth broadening.
The broadening is **Lorentzian** in shape.

$$f(\gamma) = \frac{1}{\pi} \left(\frac{\dfrac{FWHM}{2}}{\pi(\gamma - \gamma_o)^2 \left(\dfrac{FWHM}{2}\right)^2} \right)$$

We use pressure broadening
On purpose to get a large
Line width in AA for some
Forms of background
correction

FWHM = full width half maximum
γ_o is the peak "center" in frequency units

Line spectra – occur when radiating species are atomic particles which
Experience no near neighbor interactions

Line broadens due
1. **Uncertainty**
2. **Doppler effect**
3. **Pressure**
4. **Electric and magnetic fields**

Line events
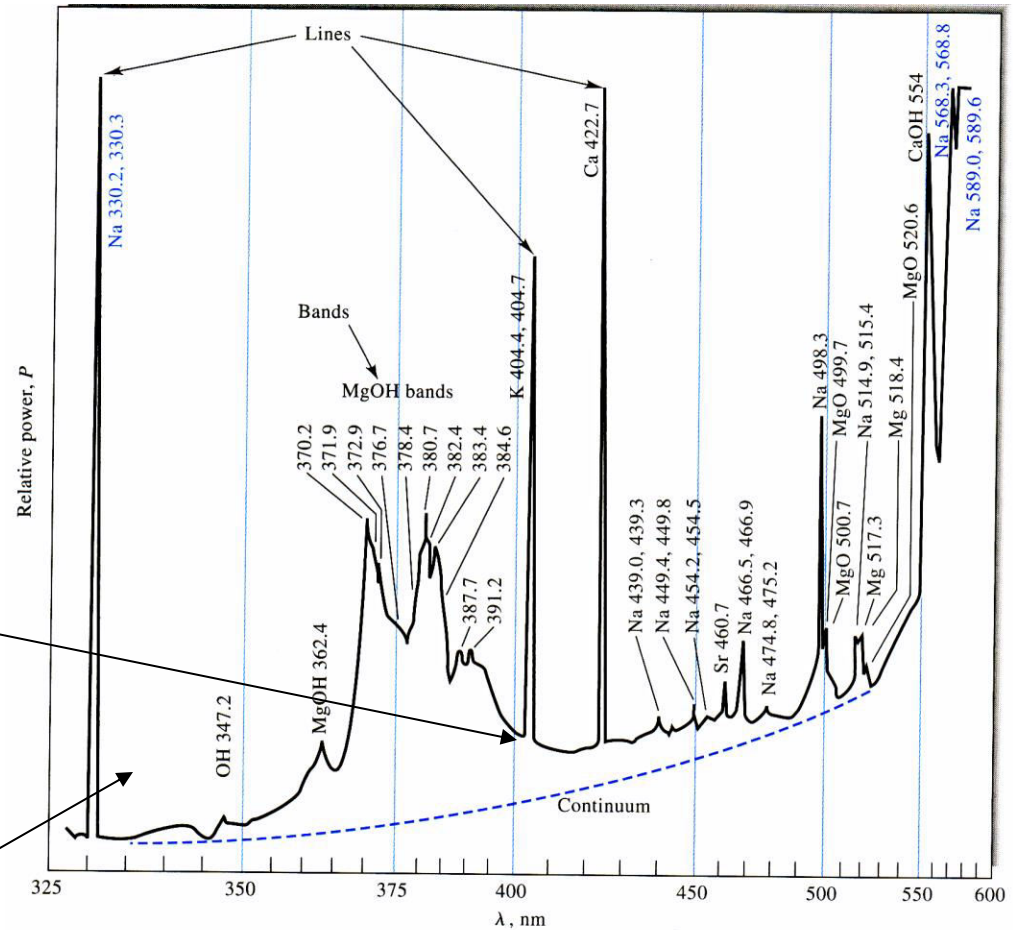Can lie on top
Of band events

FIGURE 6-19 Emission spectrum of a brine sample obtained with an oxyhydrogen flame. The spectrum consists of the superimposed line, band, and continuum spectra of the constituents of the sample. The characteristic wavelengths of the species contributing to the spectrum are listed beside each feature. (R. Hermann and C. T. J. Alkemade, *Chemical Analysis by Flame Photometry*, 2nd ed., p. 484. New York: Interscience, 1979.)

Overlapping line spectra lead to band emission

Continuum emission – an extreme example of electric and magnetic effects on broadening of multiple wavelengths

High temperature solids emit Black Body Radiation
many over lapping line and band emissions influenced by
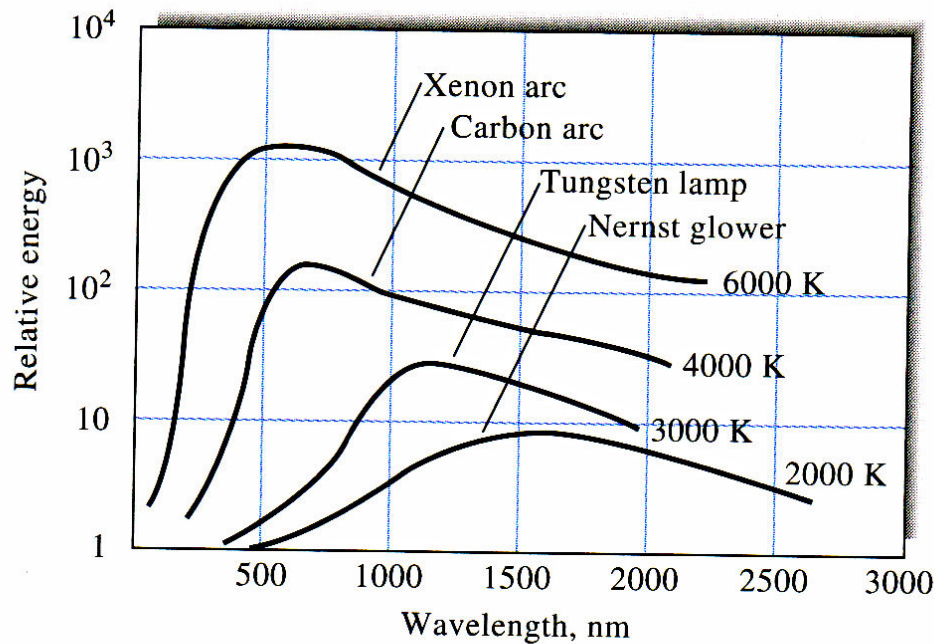near neighbors
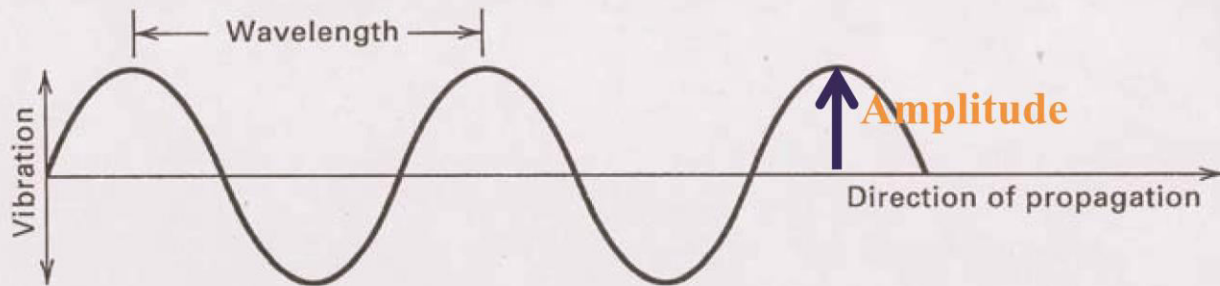

FIGURE 6-22 Blackbody radiation curves.

FIGURE 14.1 Wave motion of electromagnetic radiation.

Intensity of spectral lines

- The transition probability between the two states (selection rules)

Transition dipole moment

$$\mu_{fi} = \int \Psi_f \hat{\mu} \, \Psi_i \, d\tau = \left\langle \Psi_f \left| \hat{\mu} \right| \Psi_i \right\rangle$$

Only if this integral is non-zero, the transition is allowed

⬥ The probability for a vibrational transition to occur, i.e. the intensity of the different lines in the IR spectrum, is given by the transition dipole moment μ_{fi} between an initial vibrational state υ_i and a vibrational final state υ_f :

$$\mu_{fi} = \int \upsilon_f \, \hat{\mu} \, \upsilon_i \, d\tau = \left\langle \upsilon_f \left| \hat{\mu} \right| \upsilon_i \right\rangle$$

$$\mu(x) = \mu_0 + \left(\frac{\partial \mu}{\partial x} \right)_0 x + \frac{1}{2} \left(\frac{\partial^2 \mu}{\partial x^2} \right)_0 x^2 + \ldots$$

The electric dipole moment operator depends on the location of all electrons and nuclei, so its varies with the modification in the intermolecular distance "x". $\mu 0$ is the permanent dipole moment for the molecule in the equilibrium position Re

$$\mu_{fi} = \mu_0 \cancel{\int \upsilon_f \upsilon_i \, d\tau} + \left(\frac{\partial \mu}{\partial x}\right)_0 \int \upsilon_f \, x\upsilon_i \, d\tau + \frac{1}{2}\left(\cancel{\frac{\partial^2 \mu}{\partial x^2}}\right)_0 \int \upsilon_f \, x^2\upsilon_i \, d\tau + ...$$

$\parallel$

0

The two states υ_i and υ_f are orthogonal.

Because they are solutions of the operator H which is Hermitian

The higher terms can be neglected for small displacements of the nuclei

$$\mu_{fi} = \left(\frac{\partial \mu}{\partial x}\right)_0 \int \upsilon_f \, x \upsilon_i \, d\tau$$

First condition: $\mu_{fi} = 0$, if $\boxed{\partial \mu / \partial x = 0}$

Second condition: $\int \upsilon_f \, x \upsilon_i \, d\tau \neq 0$

In order to have a vibrational transition visible in IR spectroscopy: the electric dipole moment of the molecule must change when the atoms are displaced relative to one another. Such vibrations are " infrared active". It is valid for polyatomic molecules.

By introducing the wavefunctions of the initial state υ_i and final state υ_f , which are the solutions of the SE for an harmonic oscillator, the following selection rules is obtained:

$\boxed{\Delta \upsilon = \pm 1}$

<u>Note 1</u>: Vibrations in homonuclear diatomic molecules do not create a variation of μ ➔ not possible to study them with IR spectroscopy.

<u>Note 2</u>: A molecule without a permanent dipole moment can be studied, because what is required is a variation of μ with the displacement. This variation can start from 0.

Laporte selection Rule

- The three component of the dipole moment operator in a centrosymmetric molecule is all u.

Only allowed transitions are transitions that are accompanied by change in parity.

Population of states

$$\frac{N_{upper}}{N_{Lower}} = \exp\left(-\Delta E/kT\right)$$

Path length of the sample

Beer's Lambert Law

$$\frac{I}{I_0} = \exp\left(-\varepsilon c l\right)$$

Fourier transformation (transformation of time-domain data to frequency domain)

Two key idea

(i)   Any time-domain function can be represented by the sum of cosine waves of different frequencies and amplitude.

(ii) Cosine waves are orthogonal to each other, i.e. integral, taken between t=0 and t = ∞, of the product of any two cosine waves of different frequency is zero.
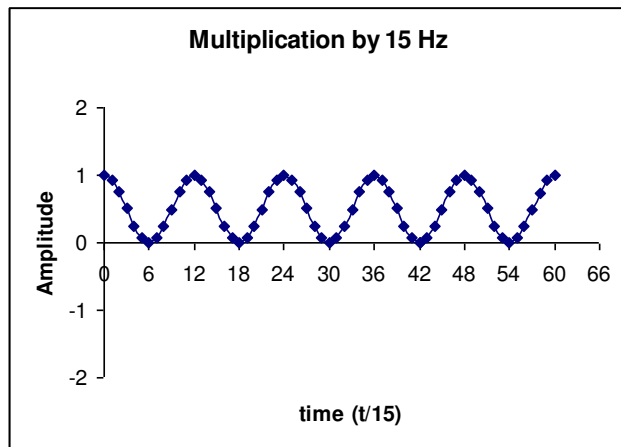
Cosine wave of 15 Hz
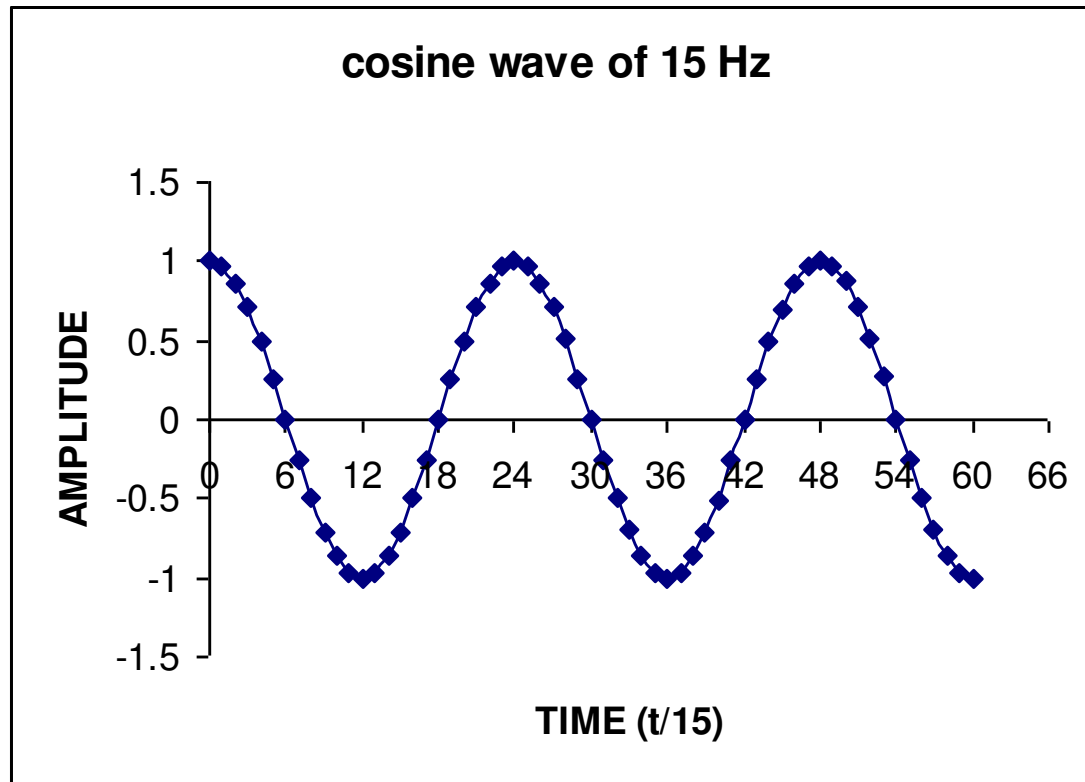
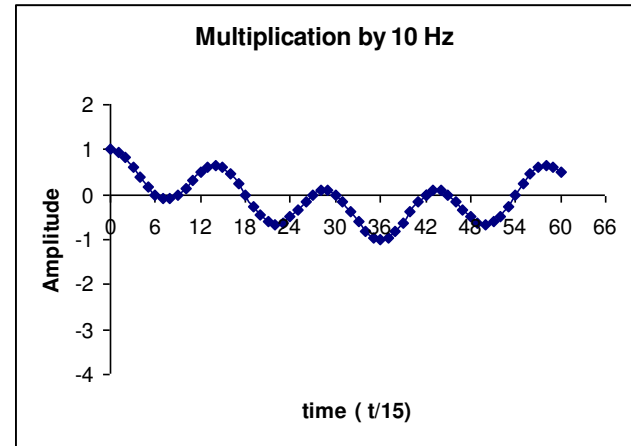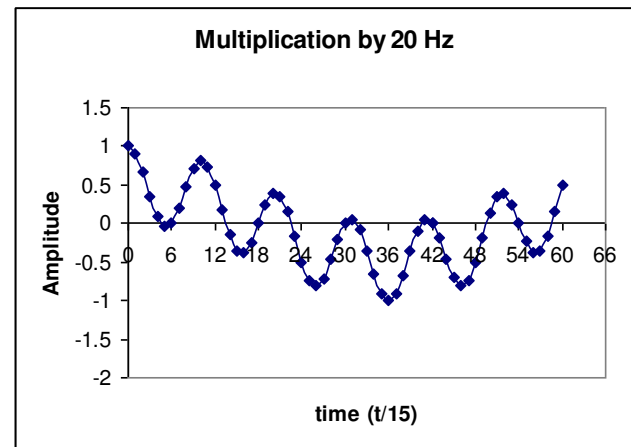# Multiplication of cosine wave of 15 Hz with cosine wave of different frequency

∑ A= - 0.97

∑ A= - 3.24

∑ A= 30.98

∑ A=-4.91