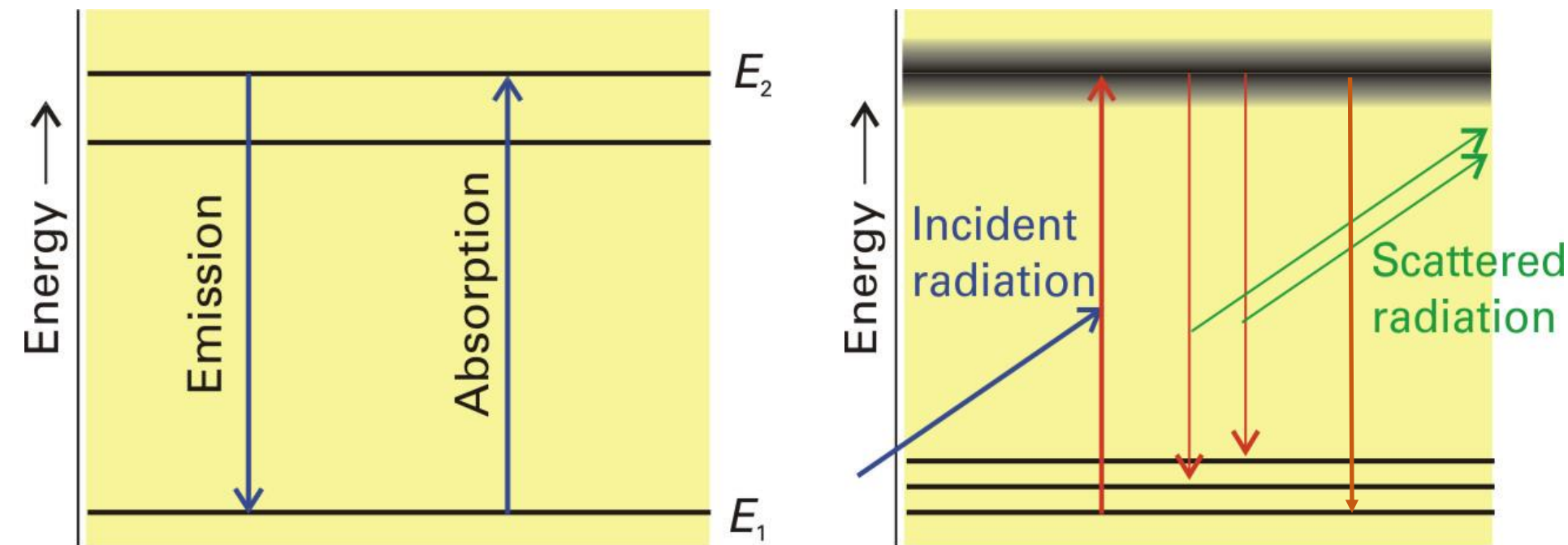# CHEM F111 : General Chemistry
Semester II: AY 2017-18
Lecture-14, 12-02-2018

Transitions induced by electric dipole are governed by transition moment integral: $R^{nm} \propto \int \Psi_n^* \, \hat{\mu} \, \Psi_m \, d\tau, \, \hat{\mu} = \sum q_i r_i$
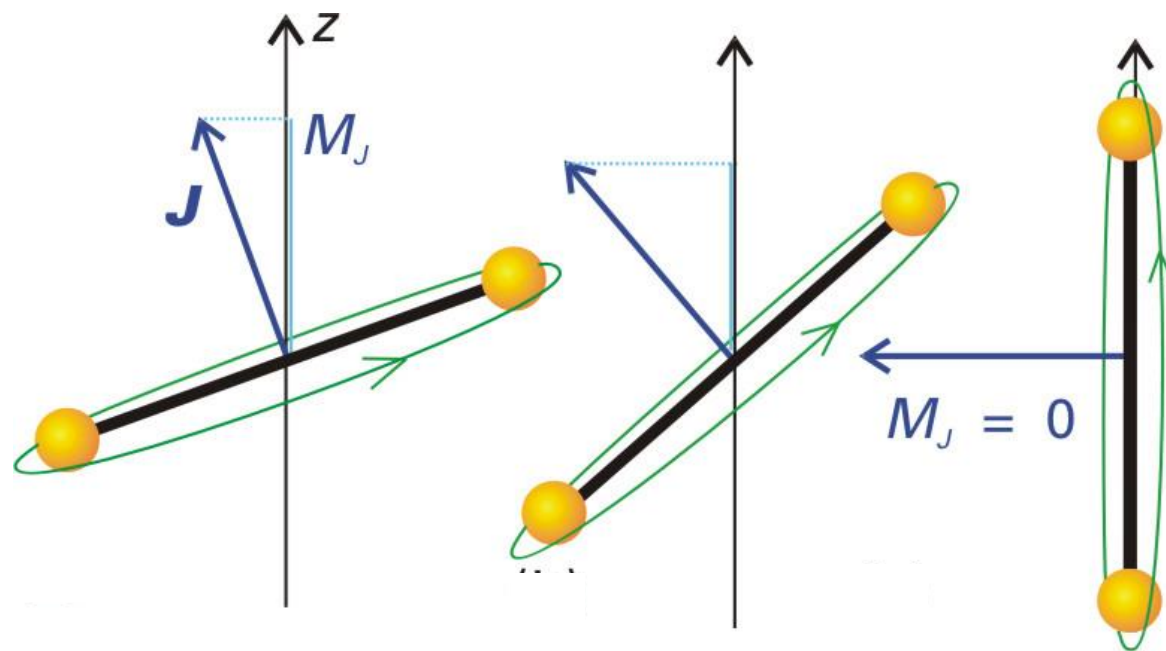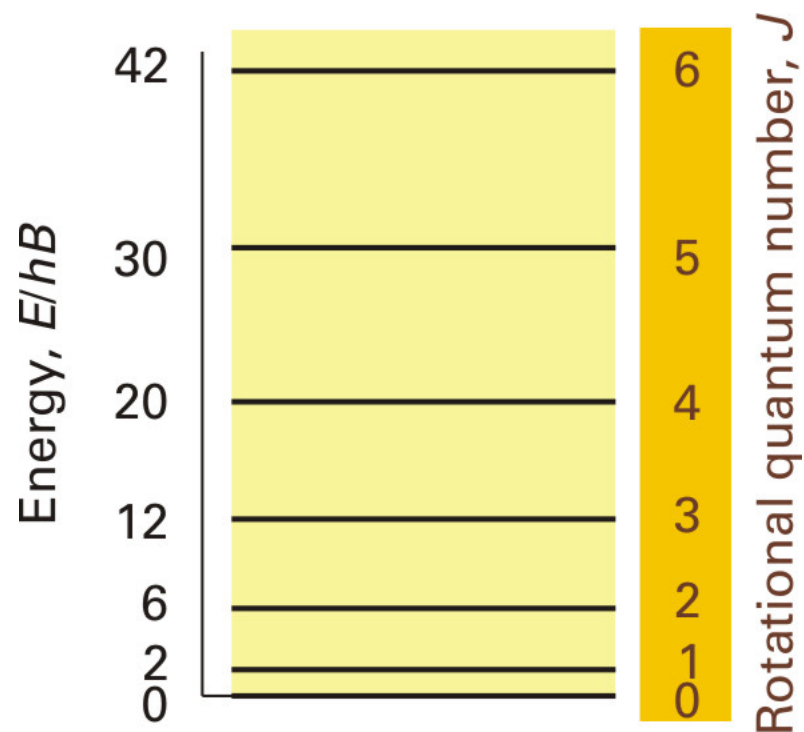
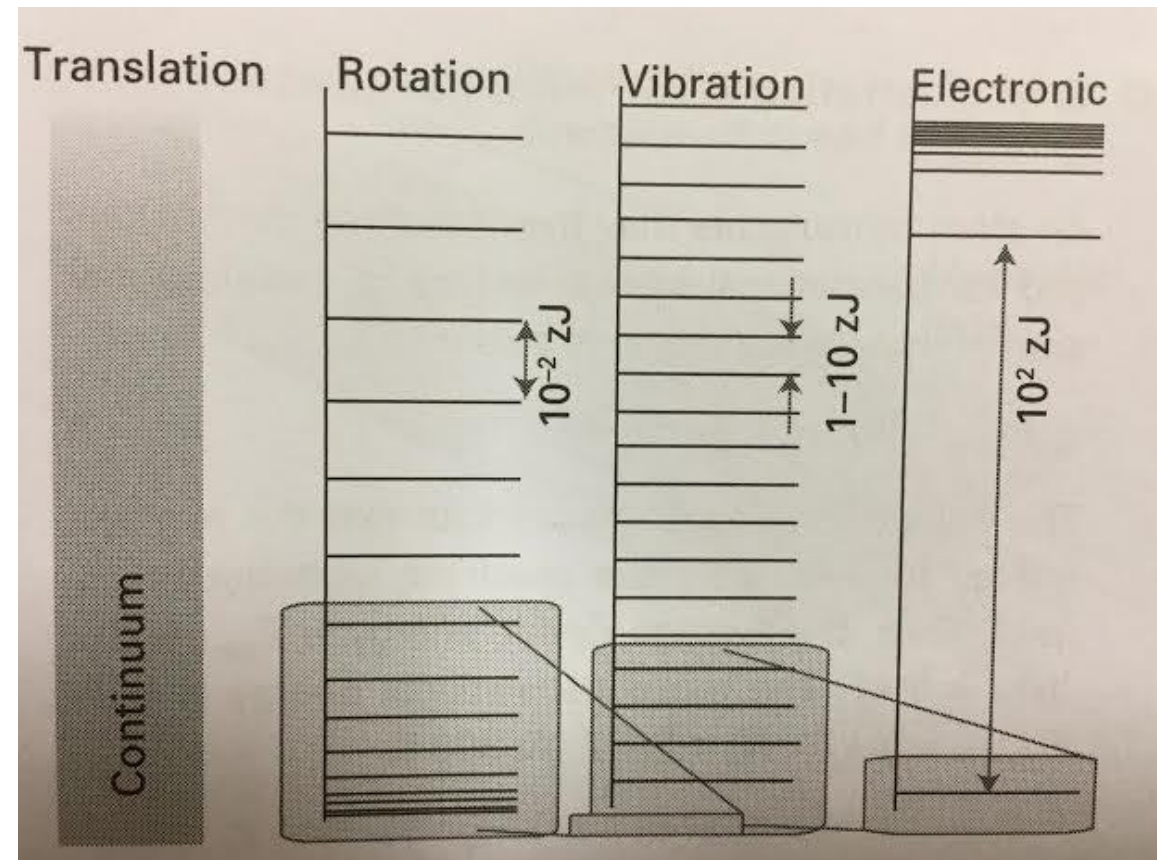Transition probability $\propto | \int \Psi_n^* \, \hat{\mu} \, \Psi_m \, d\tau |^2$

Using the energy expression for energy of a rigid rotor calculate the rotational energy levels, in Joules, for J = 0, 1, & 2 states for $^{12}C^{16}O$. Convert these energy values in cm^{-1}. Determine degeneracy for each state. Assume r_{C-O} = **1.1283** Å. # Attention: Consider unit very carefully.
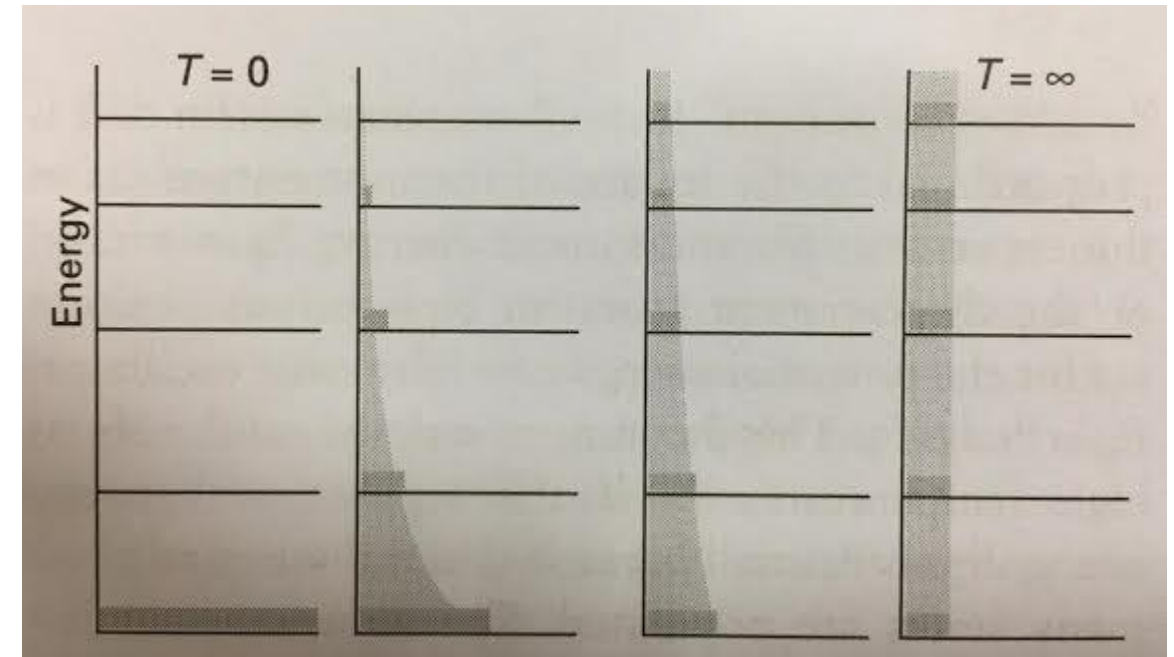
Population: Boltzmann Distribution
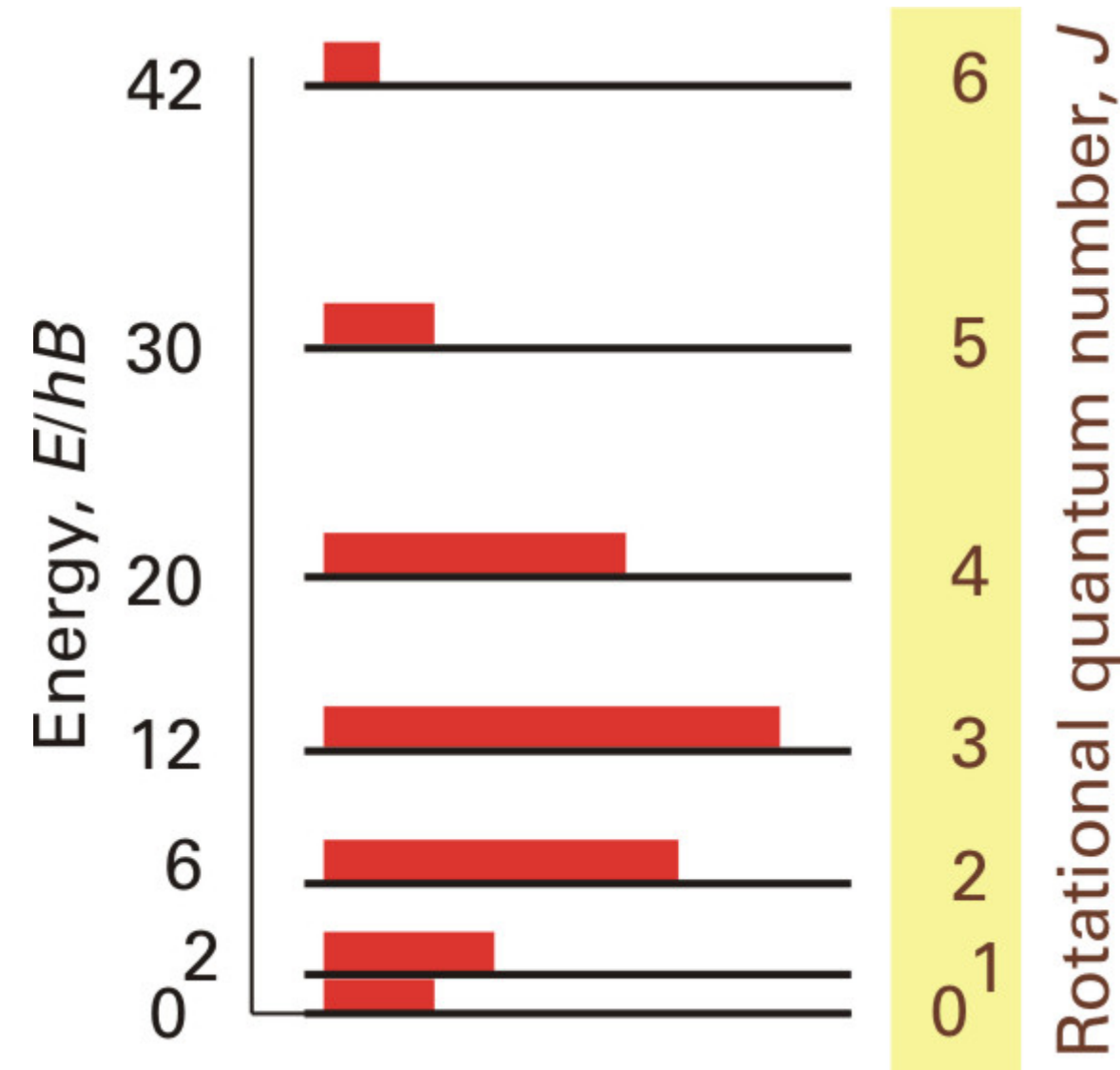

$$\frac{N_2}{N_1} = e^{-(E_2 - E_1)/kT},$$

k is Boltzmann's constant

{0.11 of Text Book}

Work out: For temperatures of 25 °C and 1000 °C, calculate the ratio of molecules in a typical excited rotational level (J =4) to that in the lowest energy level, assuming the excited level is 30 cm^{-1} above the lowest energy level.

Population of permitted rotational states

For given J: (2J+1) degenerate states.
Population using Boltzman distribution:

$$P_J = P_0 (2J + 1) e^{-hBJ(J+1)/KT}$$

Passes through a maximum at J

$$J = \left(\frac{KT}{2hB}\right)^{1/2} - 1/2$$

Population is going govern intensity of spectral transitions

Gross selection rule: Molecule must be polar.

Homonuclear diatomic molecules??

Specific selection rules:

$$\Delta J = \pm 1$$

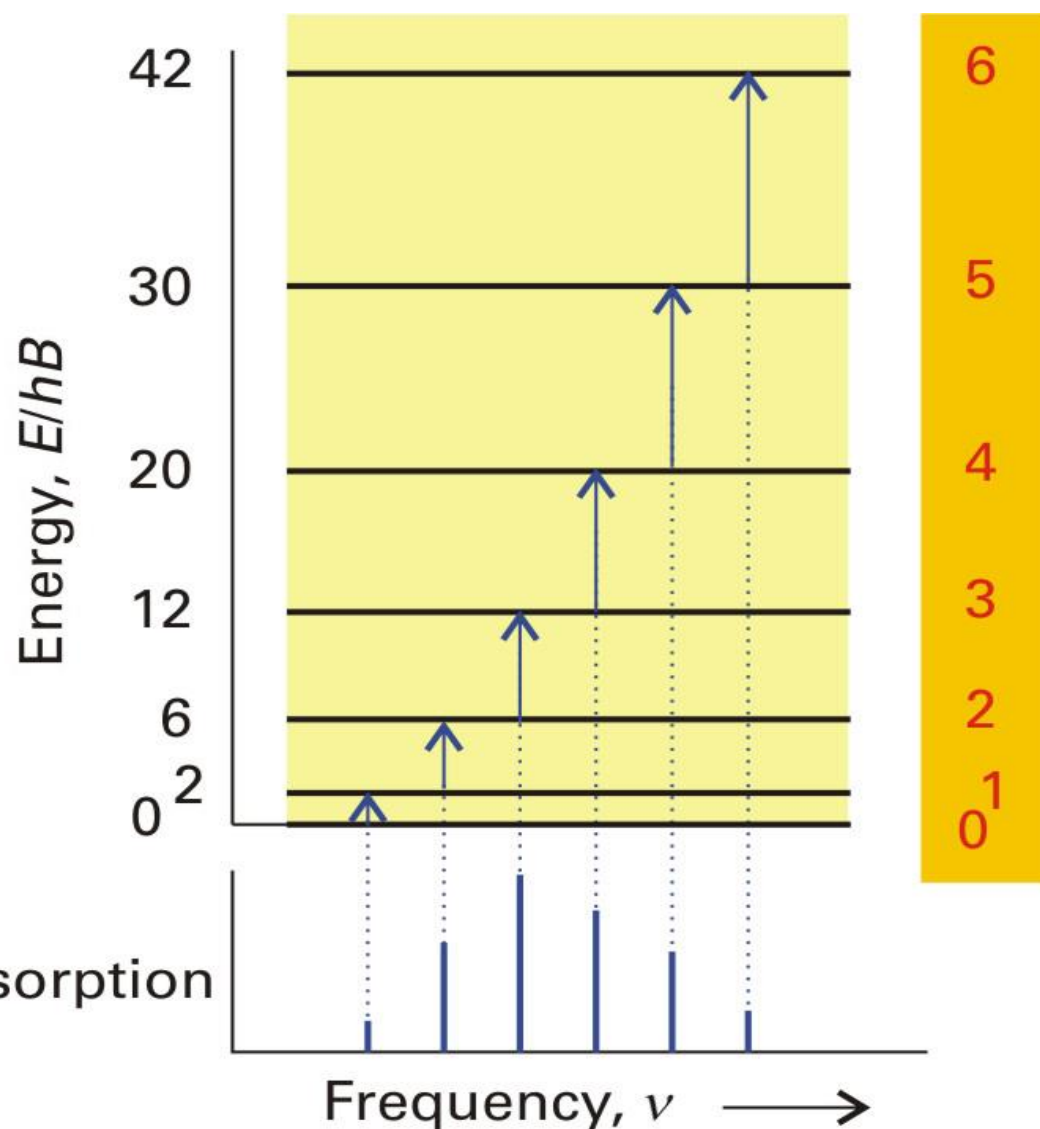**This will be complicated when we consider various molecular structure**

Pure rotational spectrum:

$$\Delta E = E_{J+1} - E_J = hB\left[(J+1)(J+2) - J(J+1)\right] = 2hB(J+1)$$

Lines of frequencies at 2B, 4B, 6B, ...

Rotational transitions – representative spectrum

First line in rotational spectrum of CO is observed at 3.84235 cm^{-1}. Calculate the bond length of CO.

Direct experimental measurement of molecular parameters/structural parameters.

Important conclusion:

Under rigid rotor approximation all the rotational energy lines are equally spaced with an energy difference of 2B cm^{-1}

First line for $^{12}C^{16}O$ = 3.84235 cm^{-1} $\Rightarrow$ B = 1.92118 cm^{-1}

First line for $^{13}C^{16}O$ = 3.67337 cm^{-1} $\Rightarrow$ B' = 1.83669 cm^{-1}
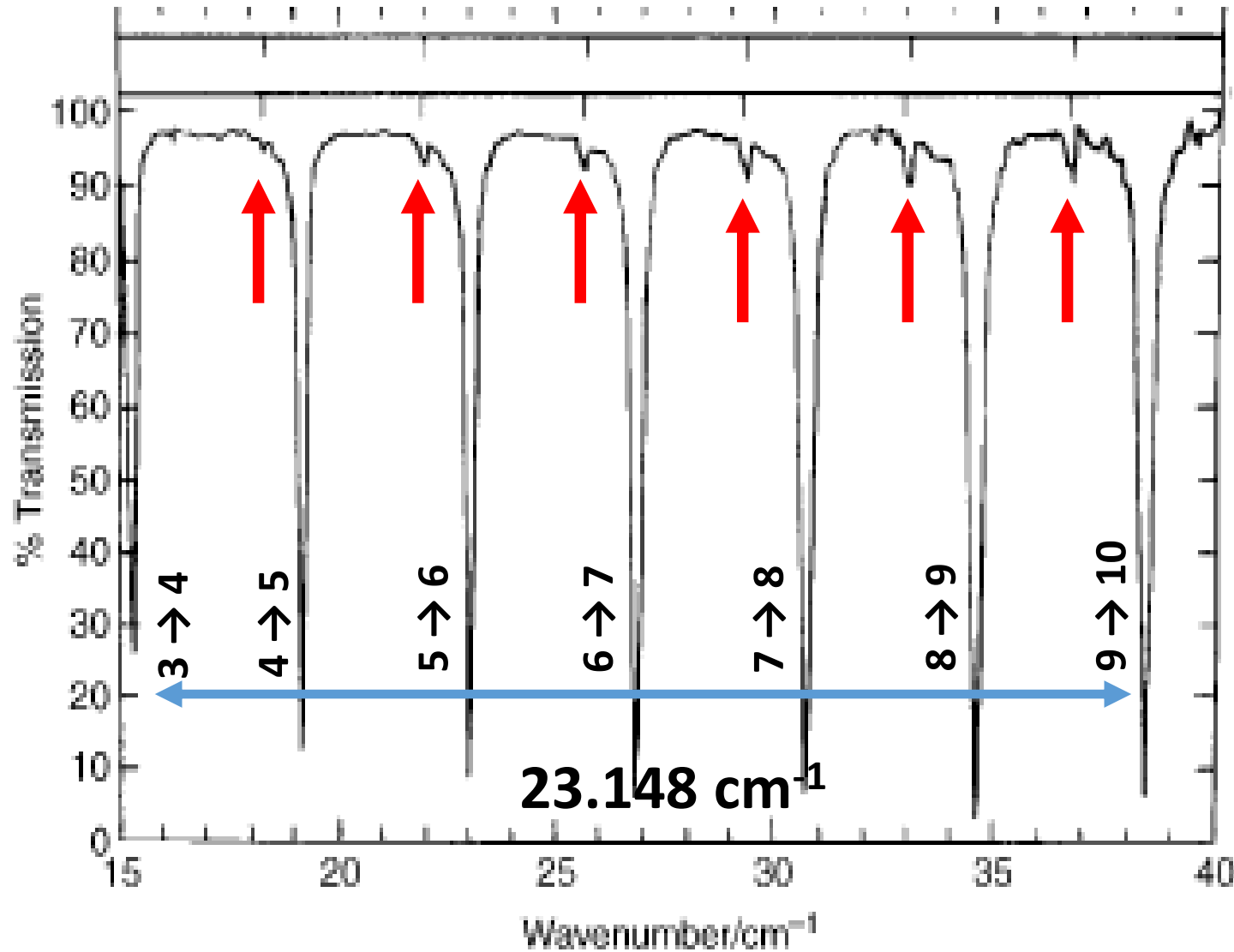
$$\frac{B}{B\prime} = \frac{h}{8\pi^2 Ic} \times \frac{8\pi^2 I'c}{h} = \frac{I\prime}{I} = \frac{\mu\prime}{\mu} = 1.046$$

Effect on rotational transitions
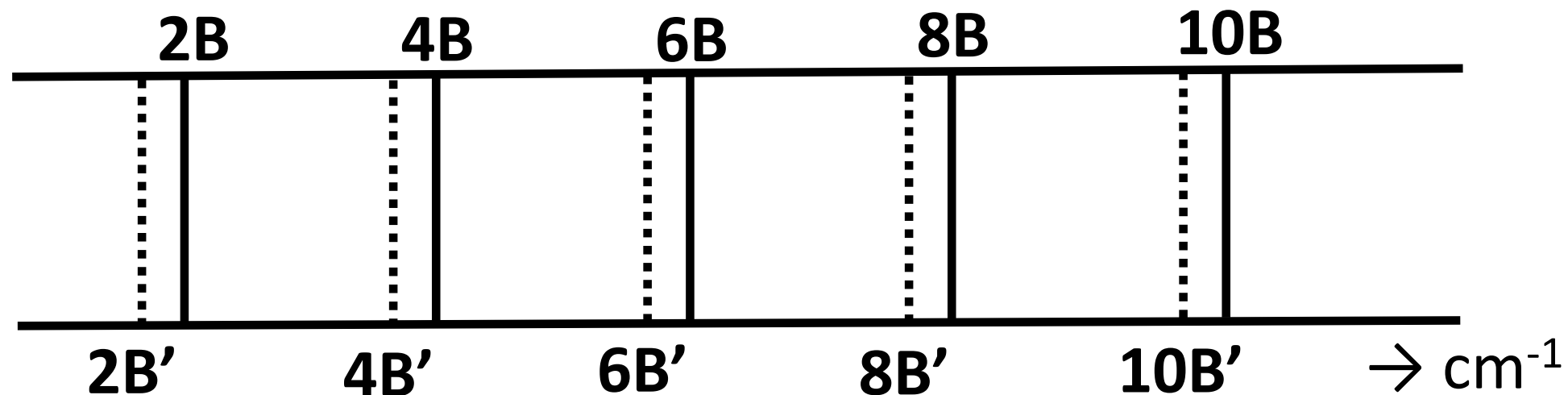
How do we interpret experimental results?

Description:

Rotationally resolved transitions of $^{12}C^{16}O$ with J'' = 3 to J'' = 9.
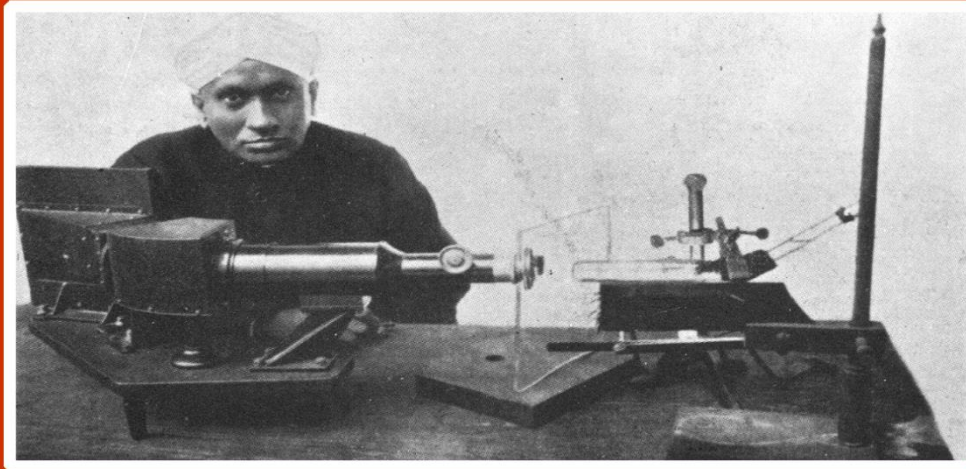
Can we estimate the bond length?

$12B = 23.148$ cm^{-1}

$B = 1.929$ cm^{-1}

With some minor extension we can even obtain the structural parameters for polyatomic molecules – may not require in this course.

Modern Spectroscopy, J. M. Hollas, Wiley

Raman Spectroscopy

Original research at IACS was started in 1907 by C. V. Raman (1888-1970), then 19 years old. Raman came to Calcutta as Assistant Auditor General of Government of India and started working at IACS beyond office hours and on holidays. He very quickly published his first paper from IACS (*Nature* 24 Oct, 1907). A. L. Sircar (son of M. L. Sircar) said in 1907 that "*Raman will be the brightest ornament of IACS.*" The initial experiments on Raman effect were done using sunlight as the light source and eye as detector. G. D. Birla provided Raman with the money to buy the spectrograph. The Raman Effect was discovered in 1928. For this discovery, Raman received the *1930 Nobel Prize in Physics*. Raman announced this discovery on 28th February, 1928. This day is celebrated as the *National Science Day* in India. It is said that Raman booked tickets to go to Stockholm 6 months in advance but cried during Nobel Prize ceremony *because there was no Indian Flag on his chair*! From 1917-33 Raman was a Palit Professor of Physics at the Calcutta University. But he carried out all his research at IACS. Raman discovered the small angle X-ray scattering in 1929.

IACS Archive

Worked at:
University of Calcutta.
Banaras Hindu University.
IISc, Bangalore.
Raman Research Institute, Bangalore.

Nobel Prize in Physics, 1930
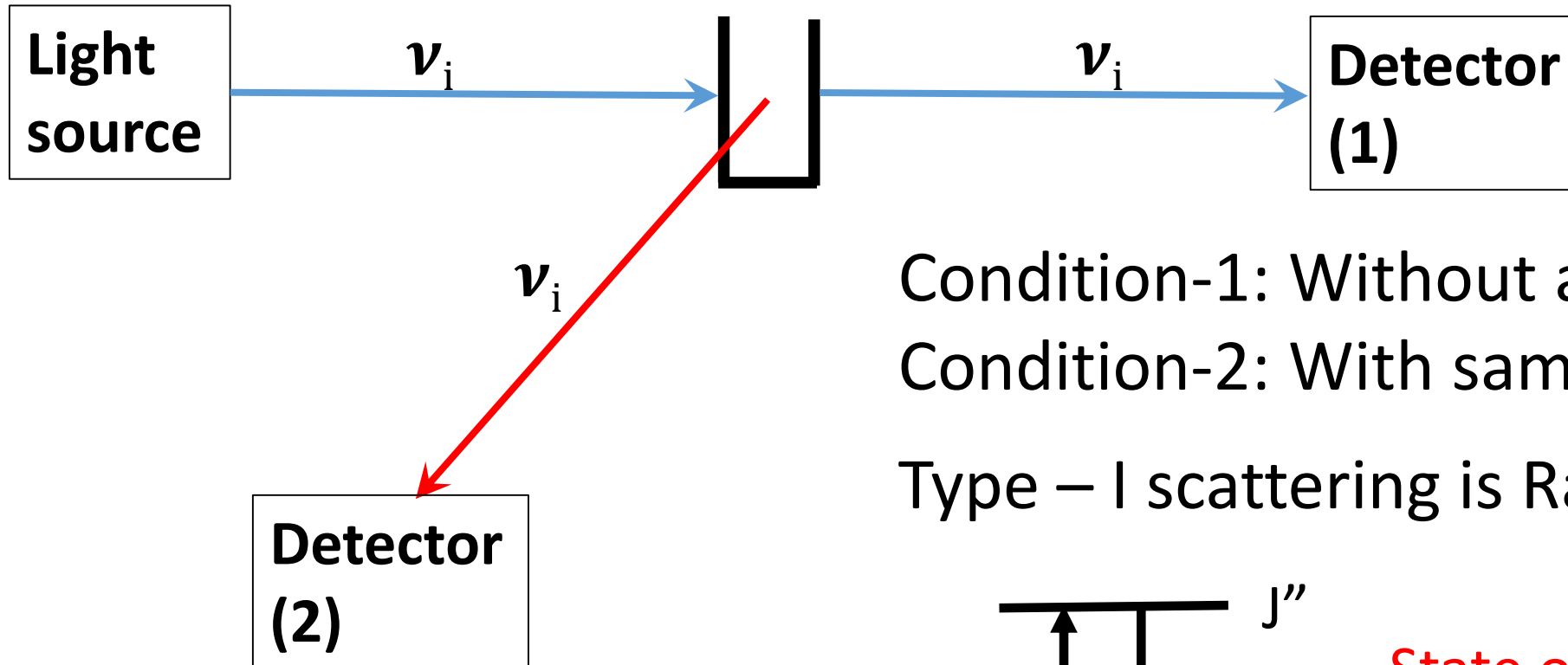
The Nobel Prize in Physics 1930 was awarded to Sir Chandrasekhara Venkata Raman *"for his work on the scattering of light and for the discovery of the effect named after him"*.
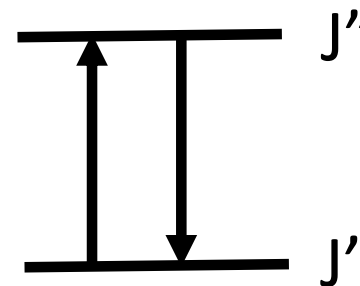
Scattering phenomenon

Type – I: Elastic scattering

Light source $\longrightarrow$ ν_i $\longrightarrow$ Detector (1)

ν_i $\longrightarrow$ Detector (2)

Condition-1: Without any sample

Condition-2: With sample

Type – I scattering is Rayleigh scattering

J"

J'

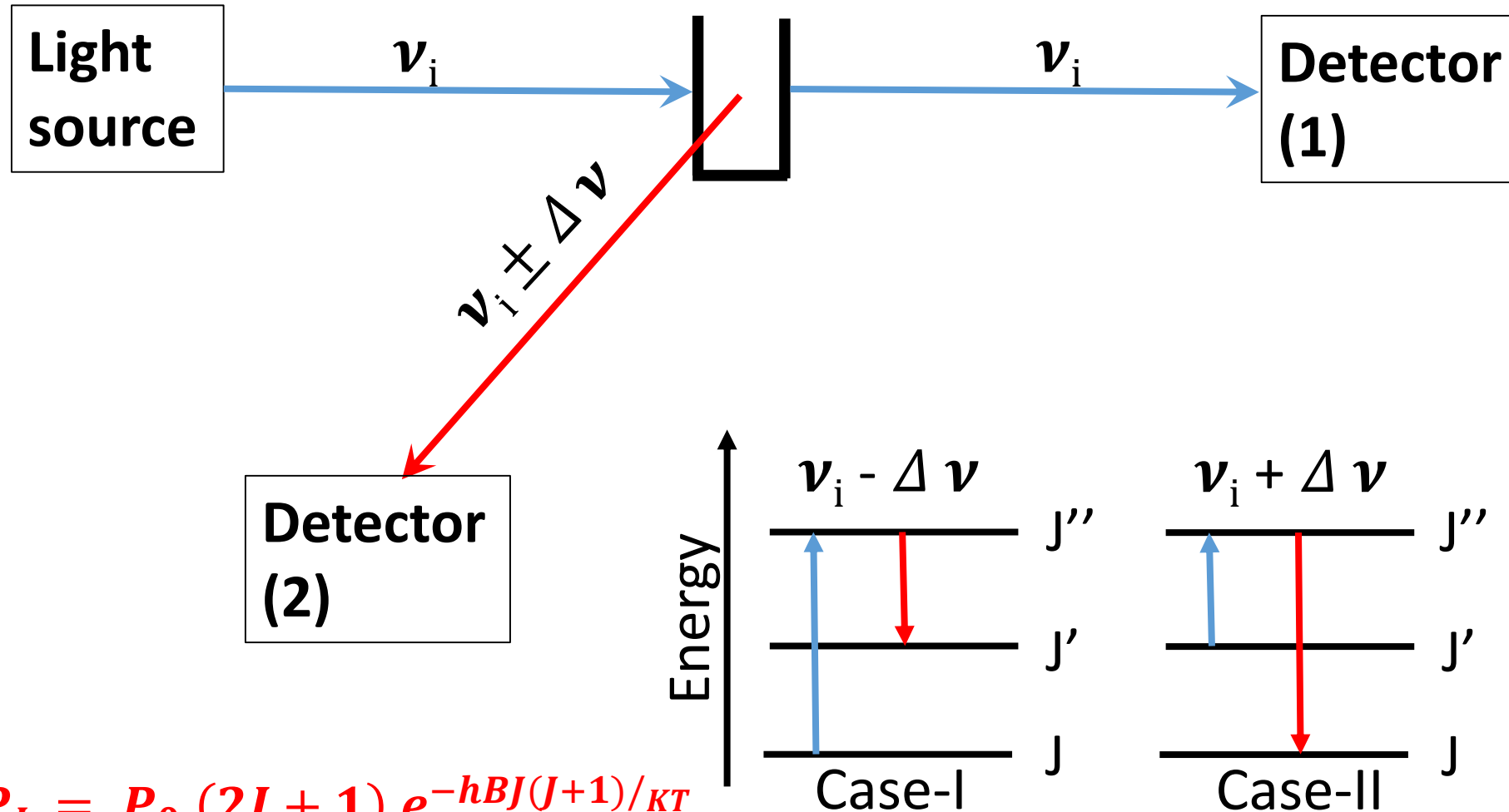State of the system remains unchanged

Scattering phenomenon

Type – II: Inelastic scattering
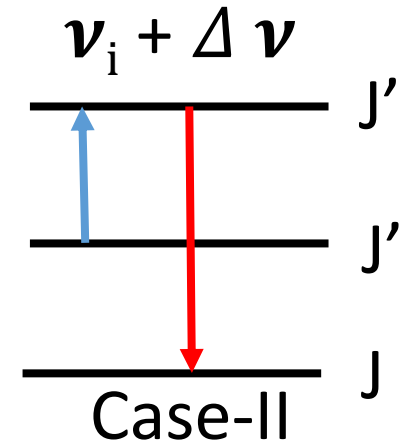
Type – II scattering is Raman scattering

Light source → ν_i → ν_i → Detector (1)

$\nu_i \pm \Delta \nu$ → Detector (2)

$\nu_i - \Delta \nu$ $\nu_i + \Delta \nu$

Energy

J''   J''
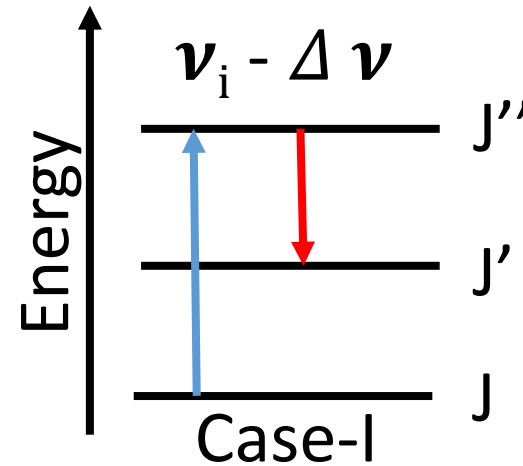
J'   J'

J   J

Case-I   Case-II

$$\frac{P_J}{P_0} = 7.8$$

$$P_J = P_0 \, (2J + 1) \, e^{-hBJ(J+1)/KT}$$

Raman Spectroscopy

Case-I: Molecule gains energy, ΔE; State changes from J to J'.

$$\nu_i - \Delta\nu \qquad \nu_i + \Delta\nu$$

Case-II: Molecule release energy, ΔE; State changes from J" to J'.

$$\nu' = \nu_i - \Delta\nu$$

$$\Rightarrow \nu_S = \nu_i - \frac{\Delta E}{h}$$

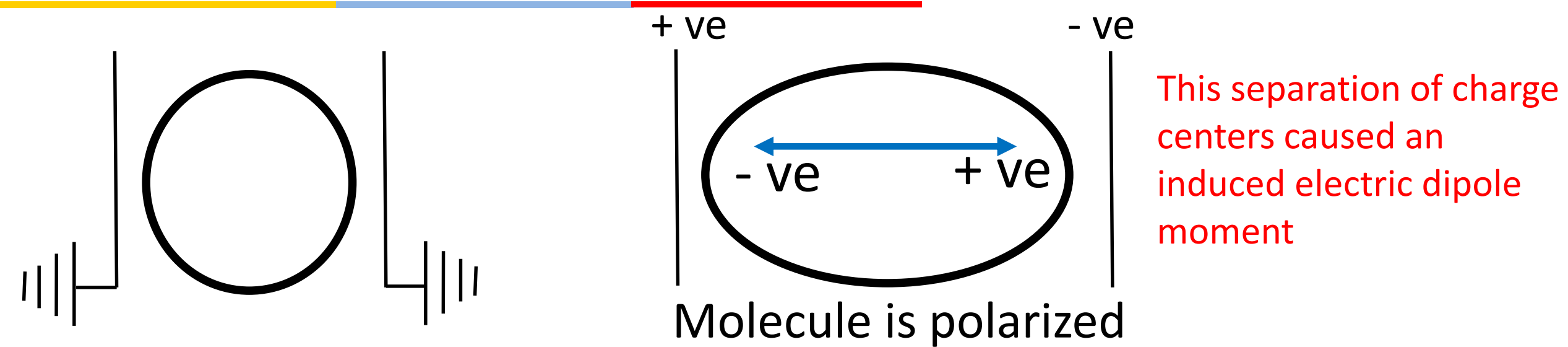Stokes' radiation

$$\nu'' = \nu_i + \Delta\nu$$

$$\Rightarrow \nu_{as} = \nu_i + \frac{\Delta E}{h}$$

Anti-Stokes' radiation

Raman Spectroscopy - explanation

+ ve   - ve

- ve   + ve

This separation of charge centers caused an induced electric dipole moment

Molecule is polarized

Polarization leads to dipole moment in the molecule – induced dipole moment

Induced dipole: $\mu = \alpha E$; $E: applied\ filed$

α is a parameter – the ease with which a molecule can be distorted - polarizability

Raman Spectroscopy – selection rule

Some internal motion of the molecule, such as, rotation and/or **vibration** must change the polarizability, i.e., $\frac{d\alpha}{dq} \neq 0$

q represents the coordinate in terms of the internal motion

If molecular rotation/vibration causes some change in molecular polarizability then those rotation/vibration must be Raman Active

Conditions imposed on rotation model we have used:
Molecules must be non-rigid and hence polarizable

Pure rotational Raman Spectroscopy

Polarizability: Bonds must be non-rigid.

For practical purposes (limited resolution) we may not obtain any information about the distortion of the molecules.

Thus, we can start with $E_J = BJ(J+1)\ cm^{-1}$, $J = 0, 1, 2, \ldots$

Selection rule: $\Delta J = 0\ or\ \pm 2$ only (Rotational Raman)

$\Delta J = 0 \Rightarrow$ Trivial transition, represents Rayleigh scattering.
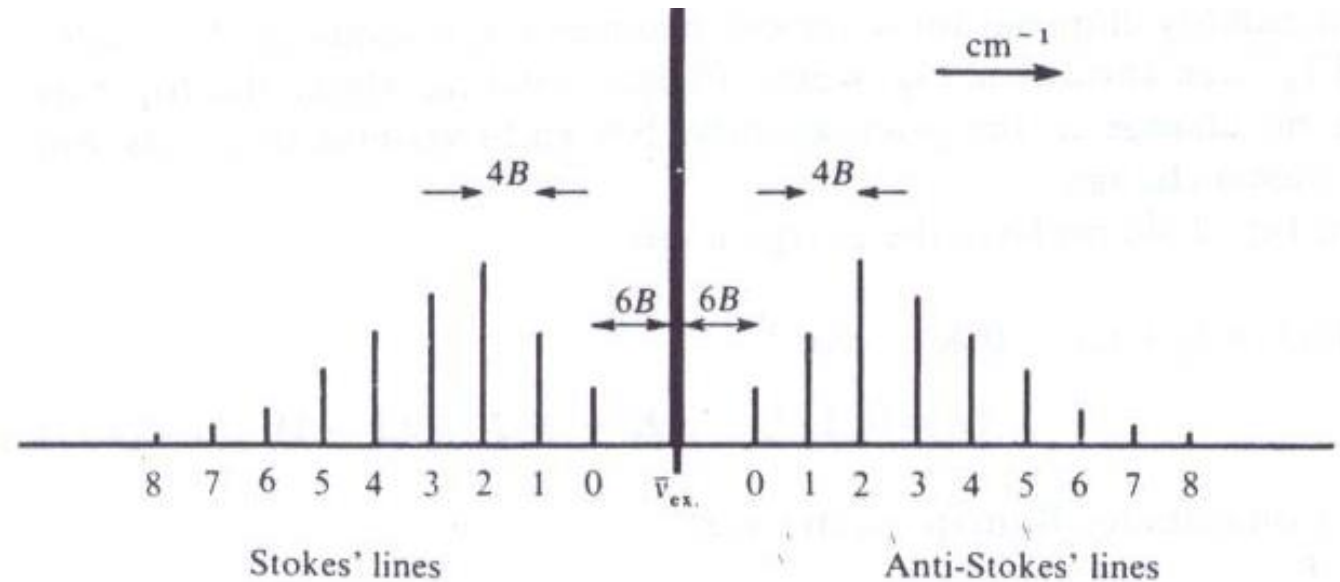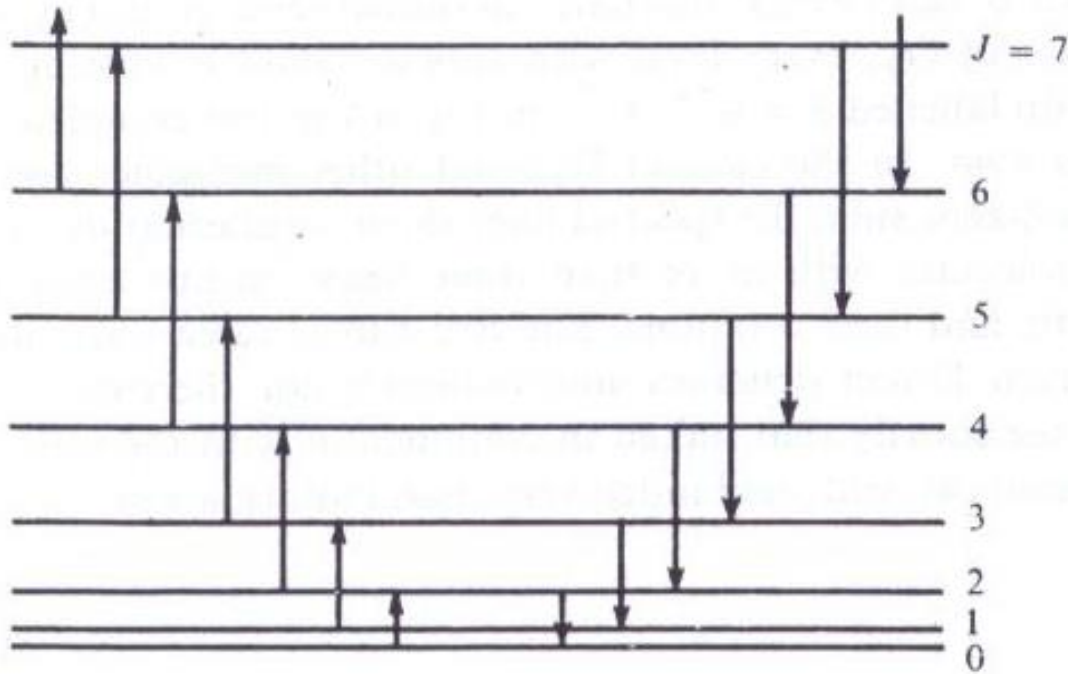
$$\Delta E_s = E_{J+2} - E_J = B(4J+6)\ cm^{-1}$$

$$\Delta E_{as} = E_J - E_{J+2} = -B(4J+6)\ cm^{-1}$$

Pure rotational Raman Spectroscopy

$$\Delta \bar{v}_s = \bar{v}_{ex} - B(4J + 6) \ cm^{-1}$$

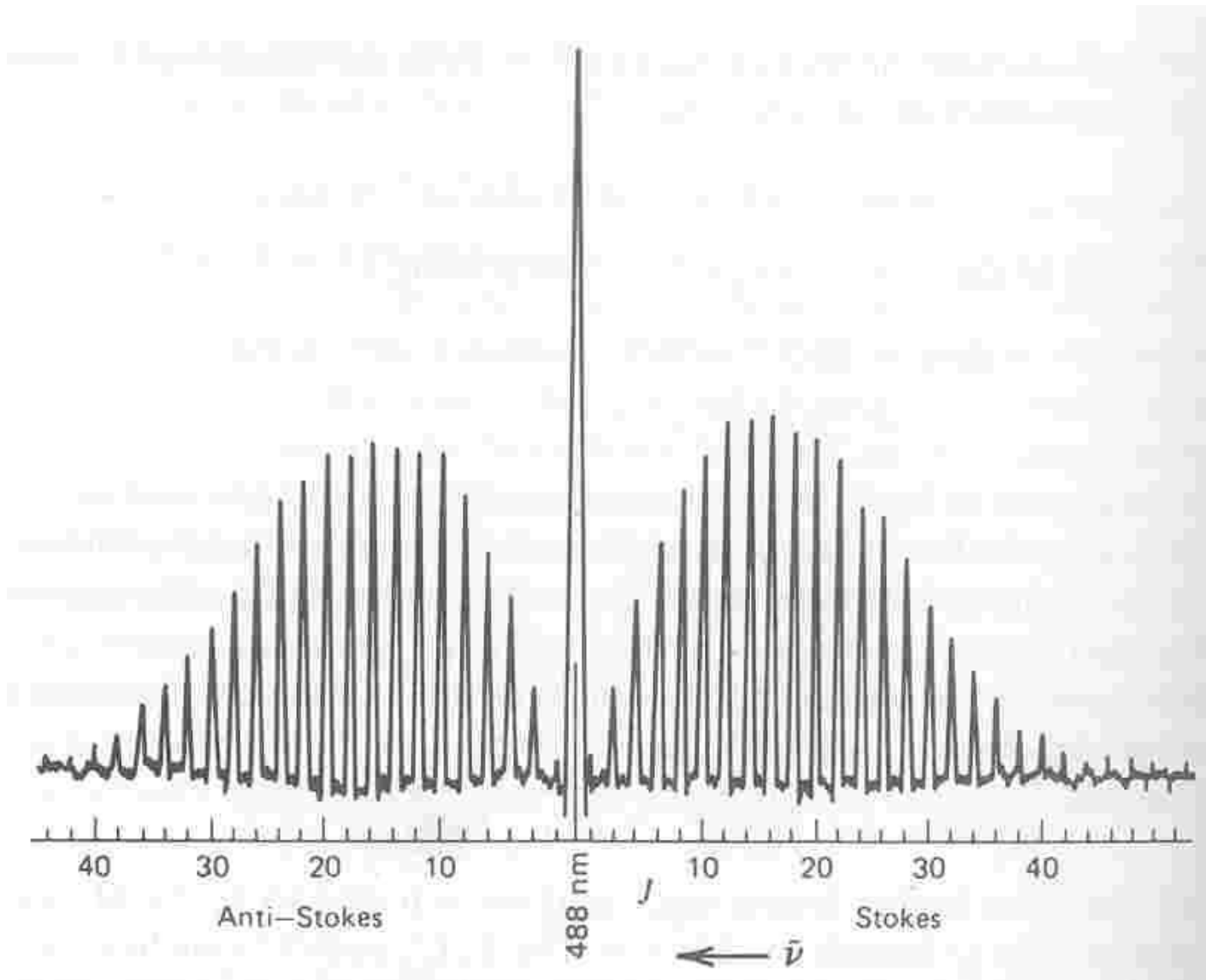$$\Delta \bar{v}_{as} = \bar{v}_{ex} + B(4J + 6) \ cm^{-1}$$

Intensity of Stoke's and anti-Stoke's lines?

Rotational Raman spectrum of CO$_2$

Homonuclear diatomics:
- H$_2$, O$_2$, N$_2$: Rotationally inactive
- Active in rotational Raman
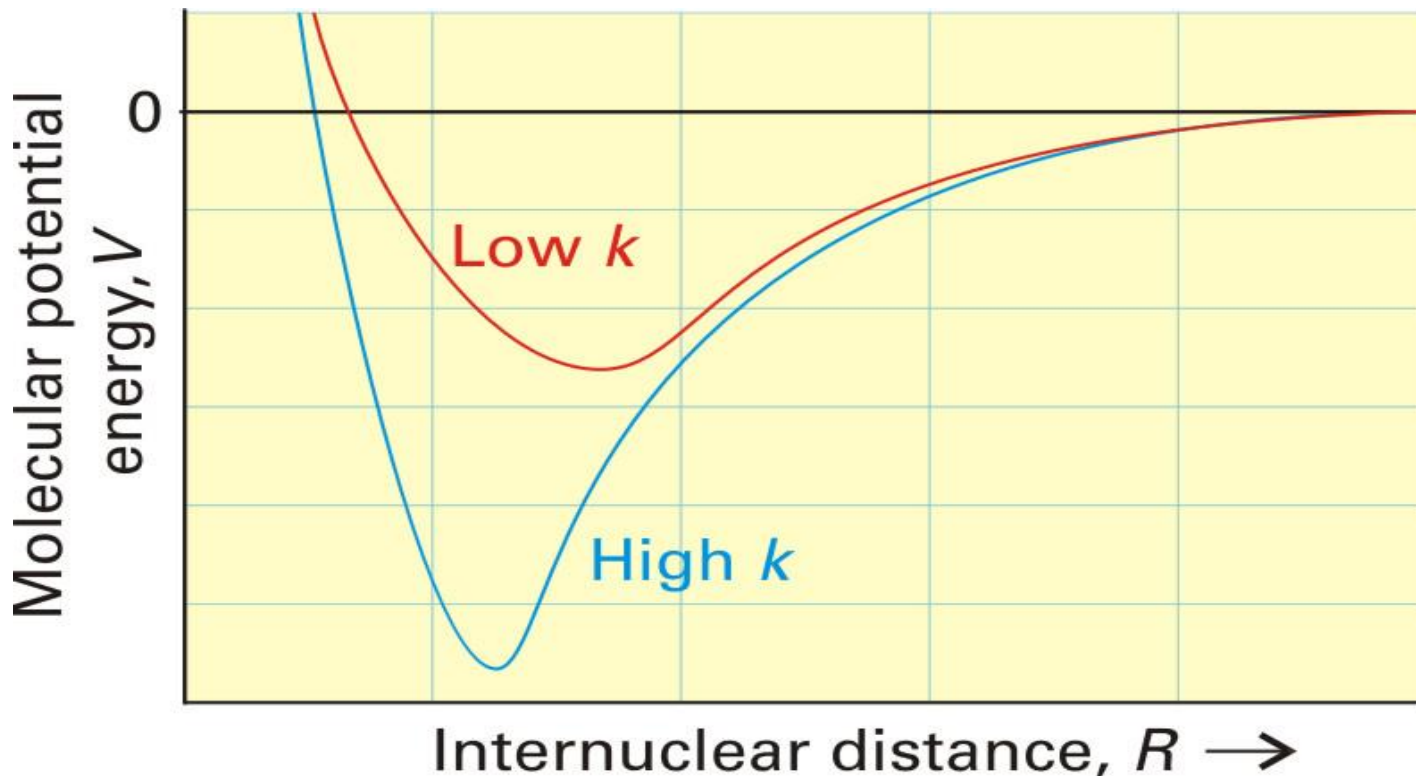- Raman spectroscopy provide information about the structure
- How?

Vibrational spectroscopy

Diatomic molecule: A-B $\quad V = \dfrac{1}{2} k x^2 = \dfrac{1}{2} k (R - R_e)^2$

K: force constant with dimension N m^{-1}

In the harmonic approximation:

$$E_v = \left(v + \frac{1}{2}\right) h\nu; \ \ v = 0, 1, 2, \ldots$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}; \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

In terms of wave number:

$$E_v = \left(v + \frac{1}{2}\right) hc\bar{\nu}, \ v = 0, 1, 2, \ldots$$