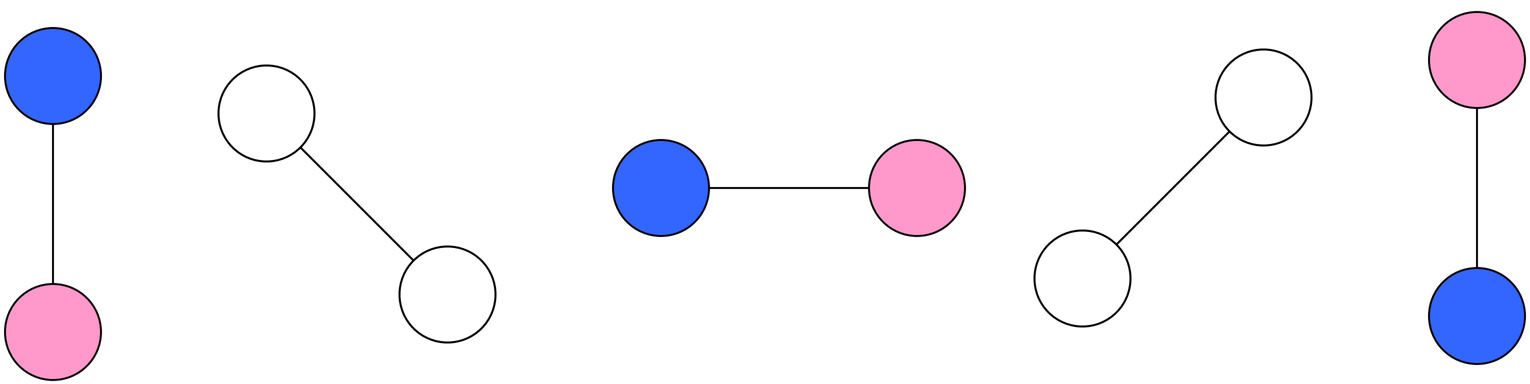
Interaction with radiation

The choice of cos(θ) means that we consider z-polarized microwave light. In general we could consider x- or y-polarized as well.

x sin(θ)cos(ϕ)
y sin(θ)sin(ϕ)
z cos(θ)

$$\mu_0 = \mu_X i + \mu_Y j + \mu_Z k$$

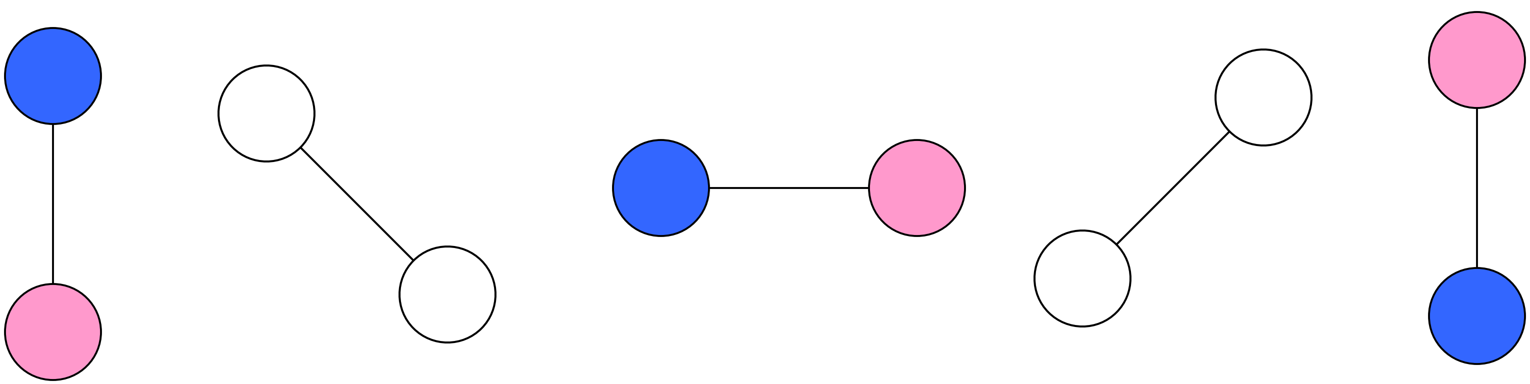
$$\mu_0 = \mu_0 \left(\sin\theta\cos\phi i + \sin\theta\sin\phi j + \cos\theta k \right)$$



Interaction with radiation

For example, if an oscillating electromagnetic field enters as $E_0\cos(\omega t)\cos(\theta)$ such that $\hbar\omega$ is equal to a rotational energy level difference, the interaction of the electric field with the transition moment is

$$M_{rot} = E_0\, \mu_0 \int_0^{2\pi}\int_0^{\pi} Y^*_{J+1,M} \cos(\theta) Y_{JM} \sin(\theta)\, d\theta\, d\phi$$



Rotational Transitions

- Treat the electromagnetic wave as having a polarization along x, y, or z.

$$E_x = Esin\theta cos\phi \; , E_y = Esin\theta sin\phi \; , E_z = Ecos\theta$$

$$\int_0^\pi cos^2\theta sin\theta d\theta = \int_{-1}^{1} x^2 dx = \left[\frac{x^3}{3}\right]_{-1}^{1} = \frac{1}{3} - \frac{-1}{3} = \frac{2}{3}$$

- The transition integral is not zero in this case since the z-polarized transition is matched to the p_z rotational orbital.

Pure rotational spectra

- A pure rotational spectrum is obtained by microwave absorption.

- The range in wavenumbers is from 0-200 cm^{-1}.

- Rotational selection rules dictate that the change in quantum number must be

$$\Delta J = \pm 1$$

- A molecule must possess a ground state dipole moment in order to have a pure rotational spectrum.

The rotational constant

The spacing of rotational levels in spectra is given by $\Delta E = E_{J+1} - E_J$ according to the selection rule

$$\Delta E = B[(J+1)(J+2) - J(J+1)] = 2B(J+1)$$

The line spacing is proportional to the rotational constant B

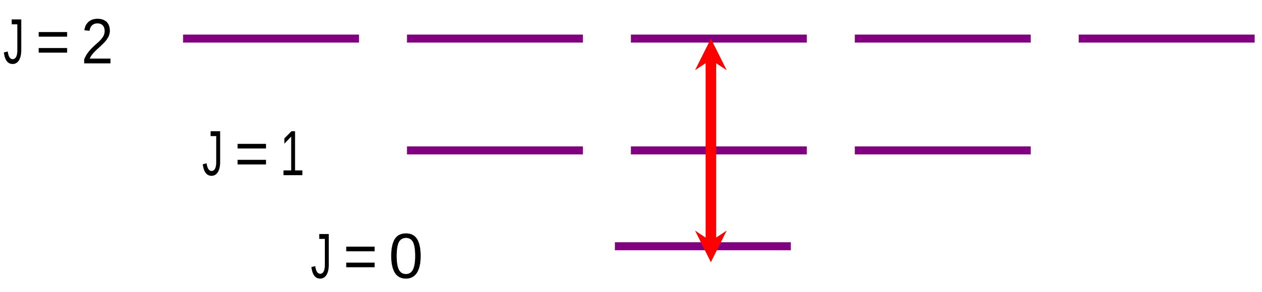
$$\frac{\hbar^2}{2I} = B$$

In units of wavenumbers (cm^{-1}) this is:

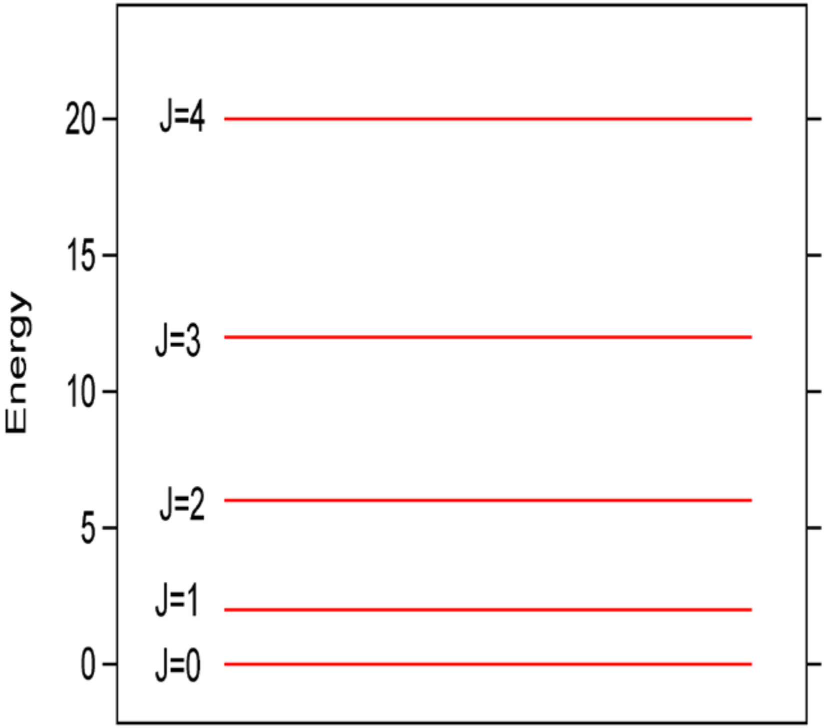
$$\frac{\hbar^2}{2I} = hc\tilde{B}\,,\; \tilde{B} = \frac{\hbar}{4\pi cI} = \frac{h}{8\pi^2 cI} = \frac{h}{8\pi^2 c\mu R^2}$$

Rotational Transitions

- Electromagnetic radiation can interact with a molecule to change the rotational state.
- Typical rotational transitions occur in the microwave region of the electromagnetic spectrum.
- There is a selection rule that states that the quantum number can change only by + or - 1 for an allowed rotational transition ($\Delta J = \pm 1$).



Energy level spacing



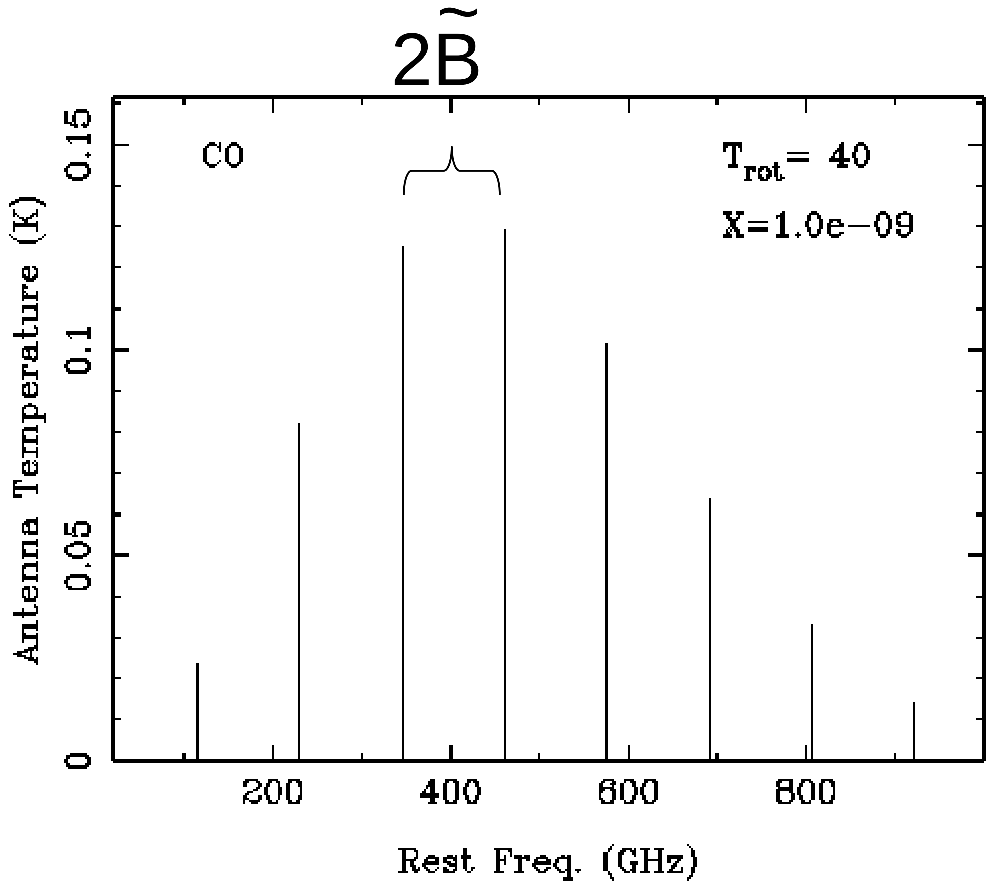
Energy levels

$$E_J = \frac{\hbar^2}{2I} J(J+1)$$

Energy Differences
of $\Delta J = \pm 1$

$$E_{J+1} - E_J = \frac{\hbar^2}{2I} 2(J+1)$$

A pure rotational spectrum



$$\nu = c\tilde{\nu}$$

$$\tilde{\nu} = \frac{\nu}{c}$$

A pure rotational spectrum is observed in the microwave range of electromagnetic spectrum.

Key Points

- The vibrational energy levels are given by:

$$E = \frac{\hbar^2}{2I} J(J+1)$$

The energy levels have a degeneracy of 2J + 1

- The wave functions are the spherical harmonics. Transition energies are given by:

$$\Delta E = B[(J+1)(J+2) - J(J+1)] = 2B(J+1)$$

- B is the rotational constant
- Rotational spectra consist of a series lines separated by 2B.