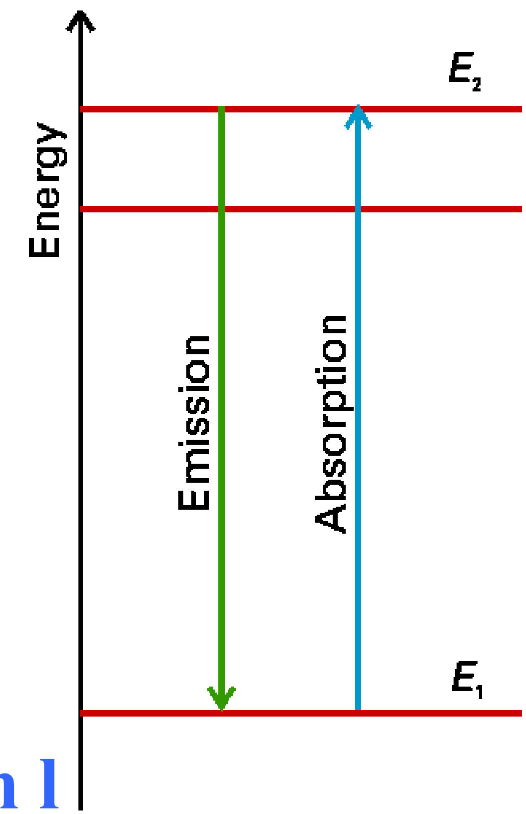
The intensity of spectral lines depends on:

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



- population of states

$$\frac{N_{\text{upper}}}{N_{\text{lower}}} = \exp(-\Delta E/kT)$$

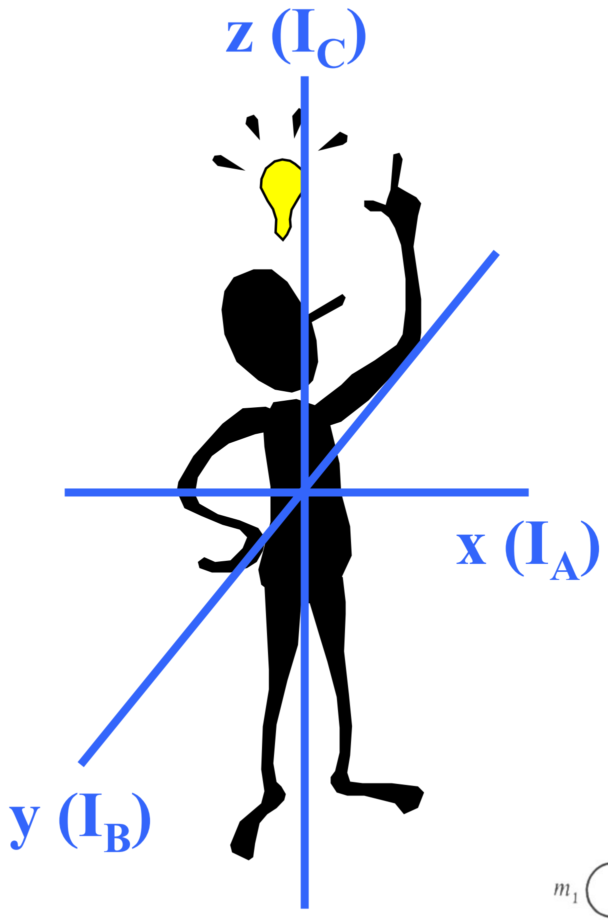
Boltzmann constant

- in absorption, the sample path length l and concentration c (Beer-Lambert law)

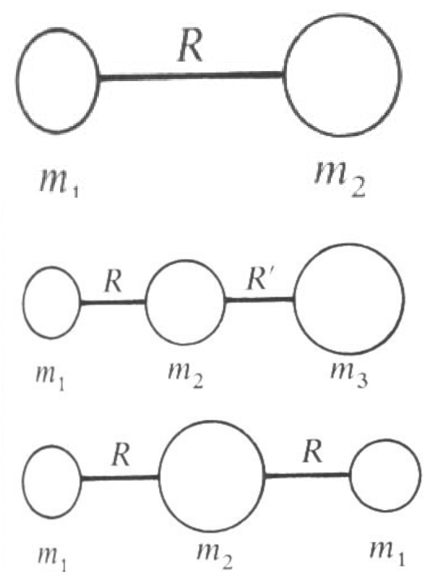
$$\frac{I}{I_0} = \exp(-\varepsilon c l)$$

extinction coefficient

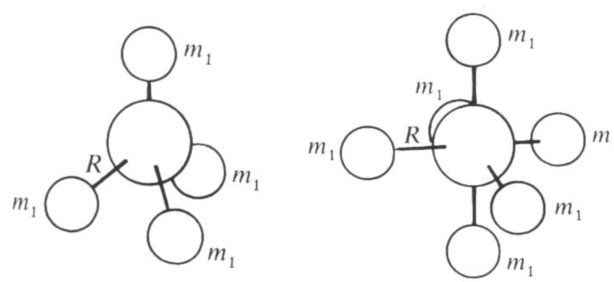
Rotational spectroscopy: The rotation of molecules



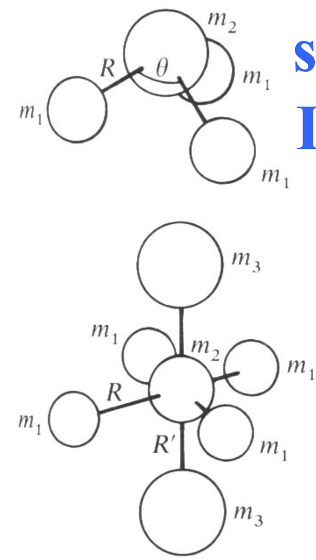
Rotor in 3-D



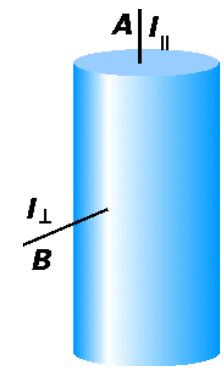
linear: $I_A=0; I_B=I_C$

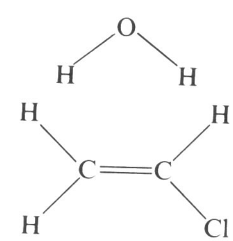


spherical: $I_A=I_B=I_C \neq 0$



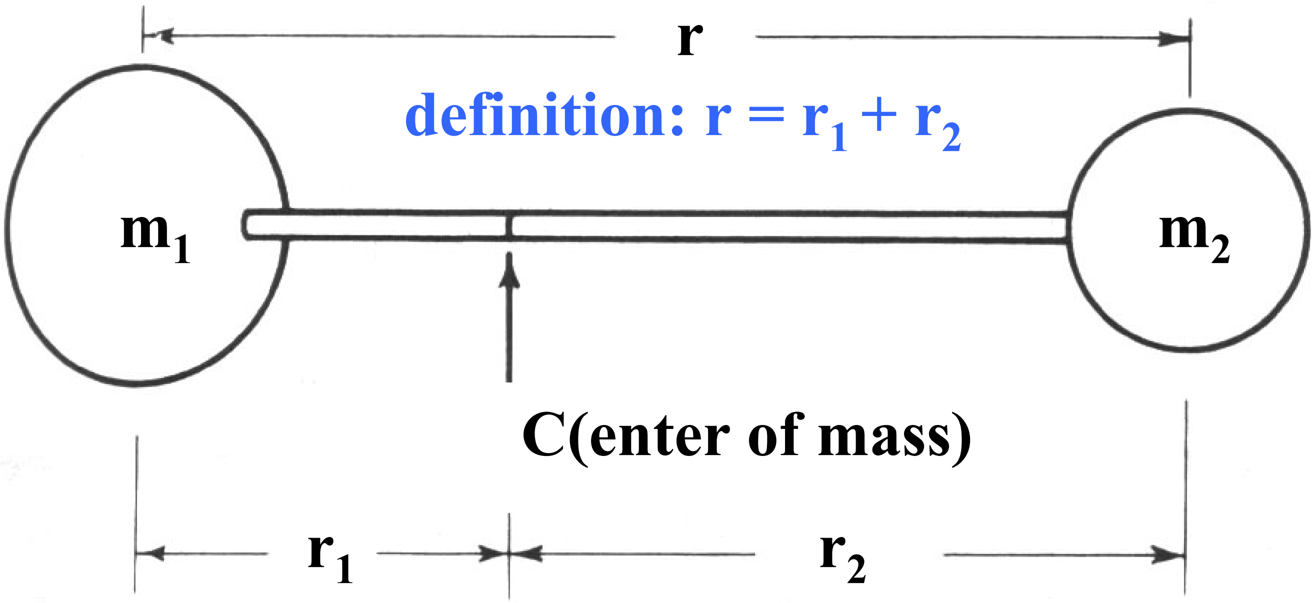
symmetric: $I_A=I_B \neq I_C \neq 0$





asymmetric: $I_A \neq I_B \neq I_C \neq 0$

The moment of inertia for a diatomic (linear) rigid rotor



definition: $r = r_1 + r_2$

Balancing equation: $m_1 r_1 = m_2 r_2$

Moment of inertia:
$I = m_1 r_1^2 + m_2 r_2^2$

$$\Rightarrow \quad I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

μ = reduced mass

Solution of the Schrödinger equation for the rigid diatomic rotor

$$-\frac{h^2}{2\mu}\nabla^2\Psi = E\Psi$$

$$\nabla^2 = \frac{d^2}{dx^2}+\frac{d^2}{dy^2}+\frac{d^2}{dz^2}$$

(No potential, only kinetic energy)

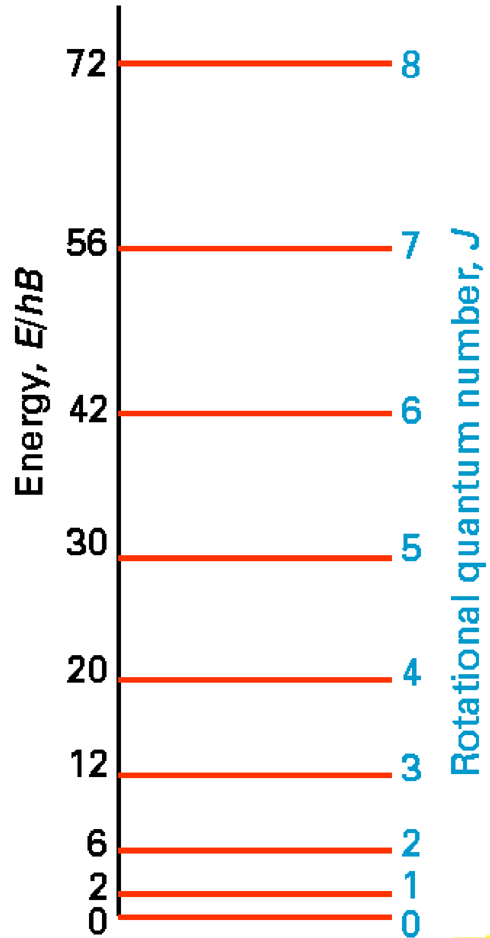
$\Rightarrow$ $\mathbf{E_J = hBJ(J+1)}$;

rot. quantum number J = 0,1,2,...

$$B = \frac{\hbar}{4\pi I} \quad \text{[Hz]}$$

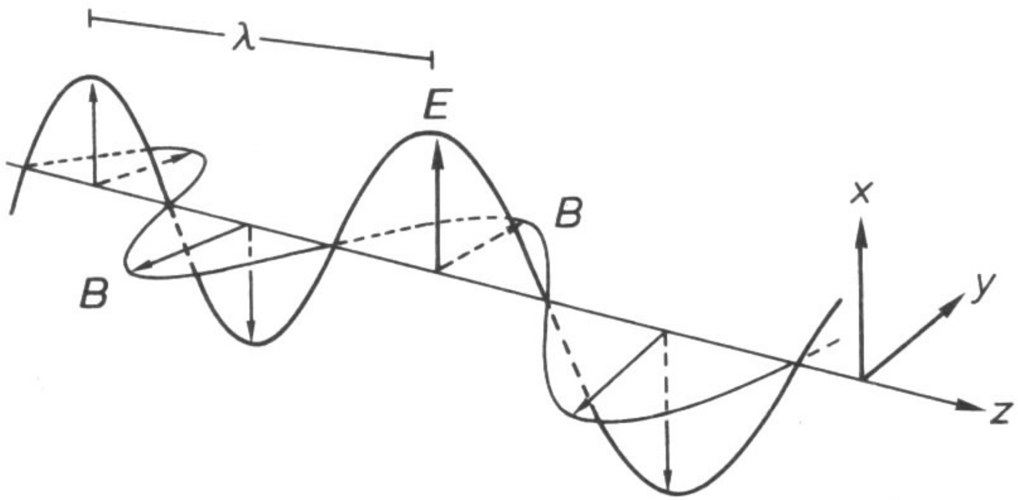
$\Rightarrow$ $\mathbf{E_{J+1} - E_J = 2hB(J+1)}$

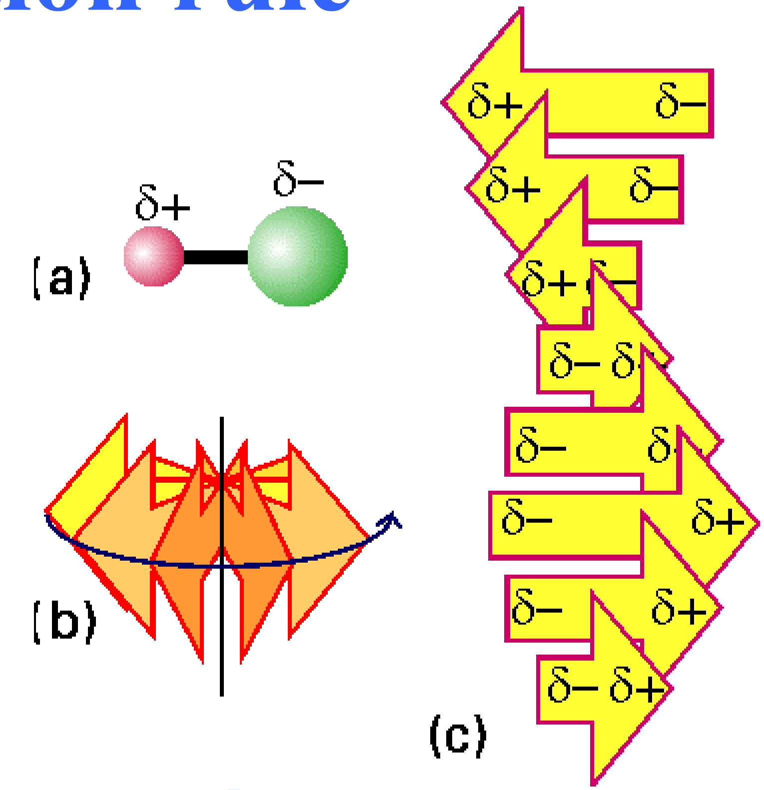
$\Rightarrow$ **microwave spectroscopy (GHz range)**



Selection rules for the diatomic rotor: 1. Gross selection rule

Light is a transversal electromagnetic wave





a polar rotor appears to have an oscillating electric dipole

⇒ a molecule must be polar to be able to interact with light

Selection rules for the diatomic rotor: 2. Specific selection rule

rotational quantum number J = 0,1,2,…
describes the angular momentum of a molecule
(just like electronic orbital quantum number l=0,1,2,...)

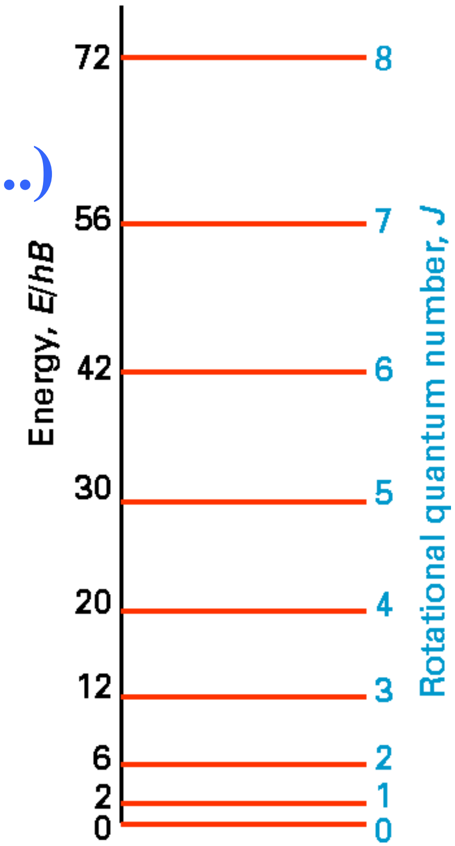
and

light behaves as a particle: photons
have a spin of 1, i.e., an angular
momentum of one unit

and

the total angular momentum upon
absorption or emission of a photon has to
be preserved

$$\Rightarrow \Delta J = \pm 1$$



Okay, I know you are dying for it: Schrödinger also can explain the $\Delta J = \pm 1$ selection rule

Transition dipole moment

$$\mu_{fi} = \int \Psi_f \mu \Psi_i d\tau$$

final state (Ψ_f), **initial state** (Ψ_i)

$\Rightarrow$ only if this integral is nonzero, the transition is allowed (for $\Delta J = \pm 1$) ; if it is zero, the transition is forbidden

The angular momentum

$$E = \frac{1}{2} I\omega^2$$ rotational frequency

classical rotational energy

$$P = I\omega \quad \Rightarrow \quad P = \sqrt{2EI}$$

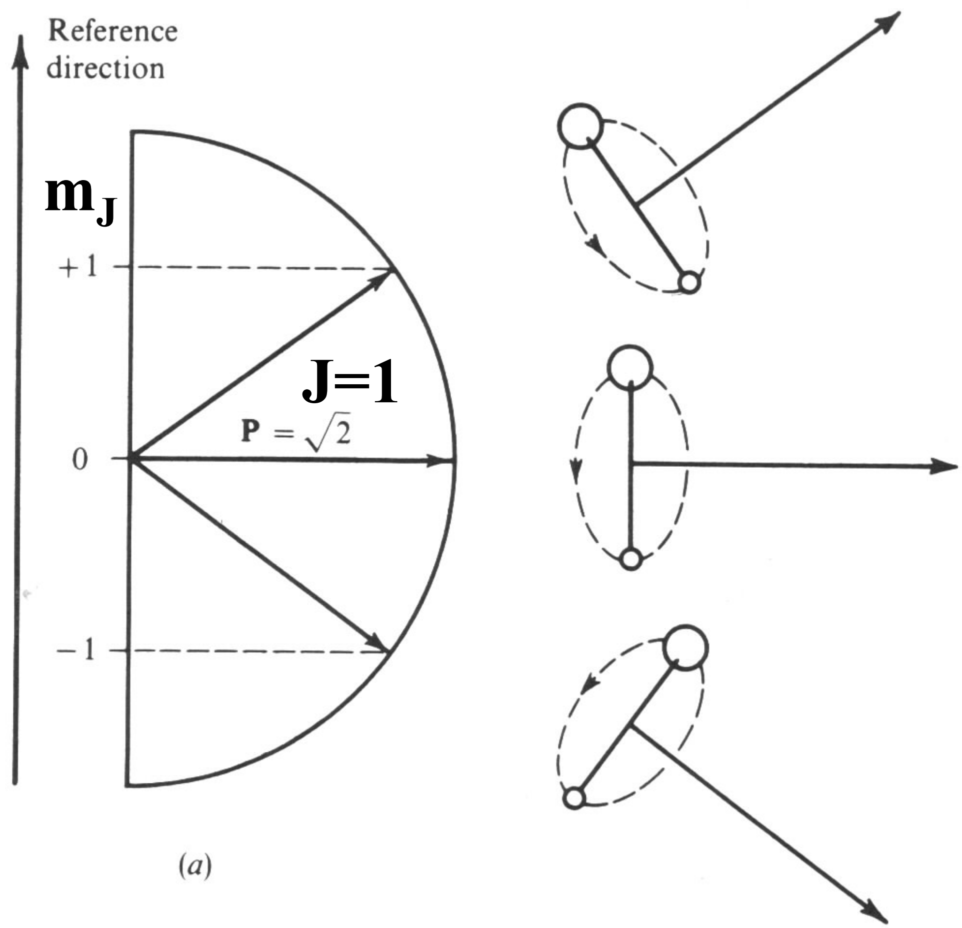
classical angular momentum

and $$E_J = hBJ(J+1)$$

with $$B = \frac{\hbar}{4\pi I}$$

$$\Rightarrow \quad P = \sqrt{J(J+1)}\hbar$$

But P is a vector, i.e., has magnitude and direction



(a)