# Rotational Spectroscopy

**Microwave Spectroscopy**

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# Facts about rotational spetroscopy

- Free rotation in gas phase
- Quantized rotational energy states
- Pure rotation spectra occur in the microwave region of the spectrum (~1 - 200 $cm^{-1}$)
- molecule must possess a permanent electric dipole moment  Thus, CO, NO, and HCl will all exhibit rotational spectra but S2 or H2 will not.

# Rigid Rotor Model

bodies

that do not distort under the stress of rotation

# Types of Rigid Rotors

Linear Molecule

$$I_B = I_C, I_A = 0$$

Spherical Rotor (Top)

Spherical rotors have three equal principal moments of inertia.

$$I_a = I_b = I_c$$

# Symmetric Rotor (Top)

Symmetric rotors have two equal principal moments of inertia and one that is different. Two cases exist for symmetric rotors.

- Prolate tops

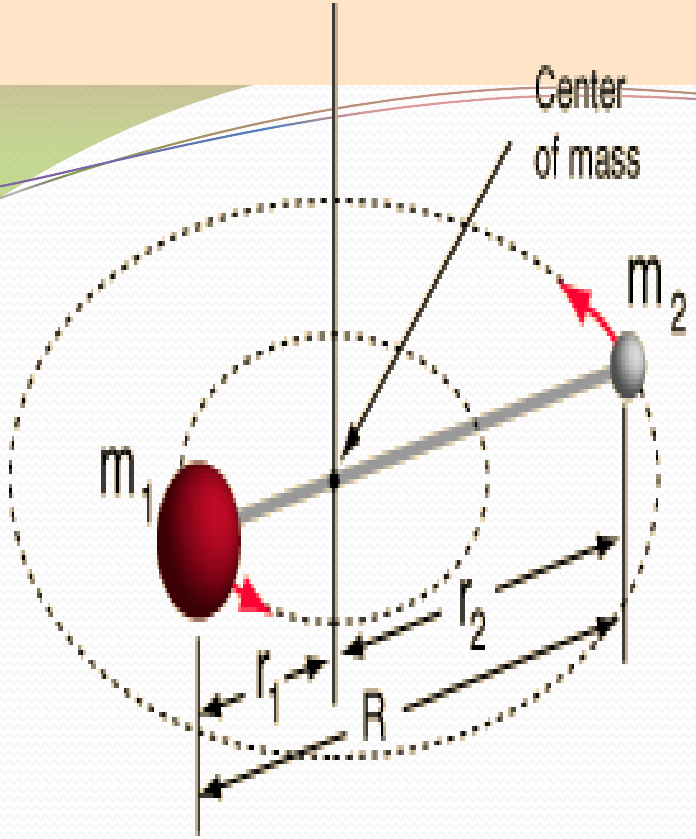
In a prolate top, the c axis and b axis moments of inertia are equal, that is,

$I_c = I_b > I_a$

- *Oblate top*

In an **oblate top, the a axis and b axis moments of inertia are equal, that is, Ic > Ib = Ia**

# Rigid Rotor Model of a Diatomic Molecule




The bond distance: $R = r_1 + r_2$

The center of mass has a physical property,

$$r_1 m_1 = r_2 m_2 \qquad 1.$$

The moment of inertia:

$$I = m_1 r_1^2 + m_1 r_2^2 \qquad 2.$$

The radial distances from masscenter can be given by bond length

$$r_1 = \frac{m_2 R}{m_1 + m_2} \qquad r_2 = \frac{m_1 R}{m_1 + m_2} \qquad 3.$$

Substituting $r_1$ and $r_2$ into Equation 2. we get for $\boldsymbol{I}$

$$\mathbf{I} = \frac{m_1 m_2}{m_1 + m_2}\mathbf{R}^2$$

Introducing reduced mass, $\mu$

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \qquad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\mathbf{I} = \mu \cdot \mathbf{R}^2$$

$$E = \frac{I_a \omega_a^2}{2} + \frac{I_b \omega_b^2}{2} + \frac{I_c \omega_c^2}{2} \qquad 2.$$

Equation 2. can be transformed

$$E = \frac{I_a^2 \omega_a^2}{2I_a} + \frac{I_b^2 \omega_b^2}{2I_b} + \frac{I_c^2 \omega_c^2}{2I_c}$$

to substitute angular momentum, *J*.

$$E = \frac{J_a^2}{2I_a} + \frac{J_b^2}{2I_b} + \frac{J_c^2}{2I_c}$$

Classical theory Expression of Energy

# Schrödinger equation

$$E\Psi = \hat{H}\Psi$$

but quantum theory requires that a molecule may only possess energies given by equation

$$E_{rot}(J) = J(J+1)\cdot\frac{h^2}{4\pi^2\cdot 2I} = J(J+1)\cdot\frac{h^2}{8\pi^2\cdot I}$$ joules

where J is the rotation quantum number J= 0, 1, 2, 3,...;

$$\varepsilon_J = \frac{E_J}{hc} = \frac{h}{8\pi^2 Ic} J(J+1)\ \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots)$$

$$\varepsilon_J = BJ(J+1)\ \text{cm}^{-1} \qquad (J = 0, 1, 2, \ldots)$$

where $B$, the *rotational constant*, is given by $B = \frac{h}{8\pi^2 I_B c}\ \text{cm}^{-1}$

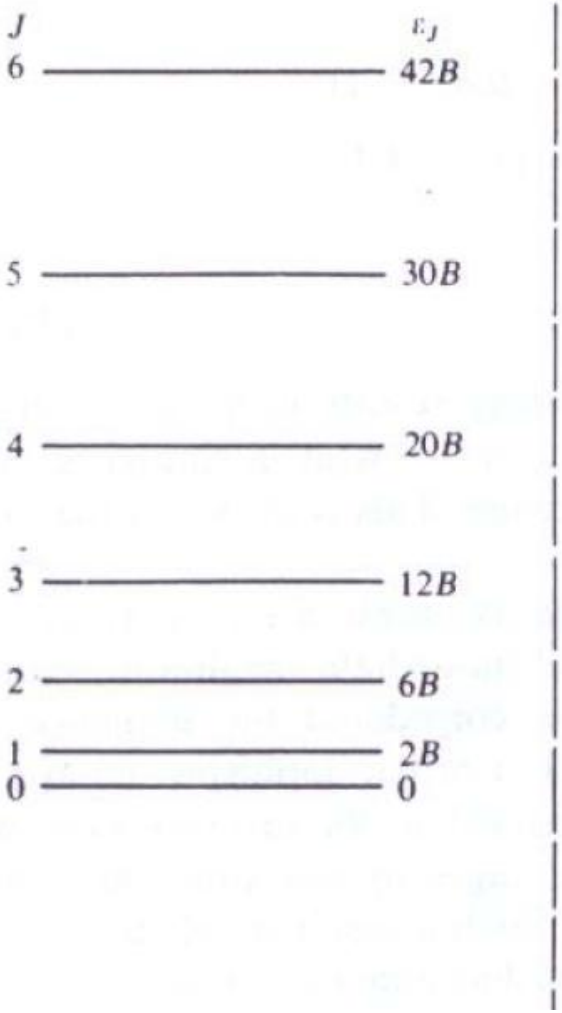
$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2 = \mu r_0^2$$

# Rotational Spectra of Rigid Diatomic molecule

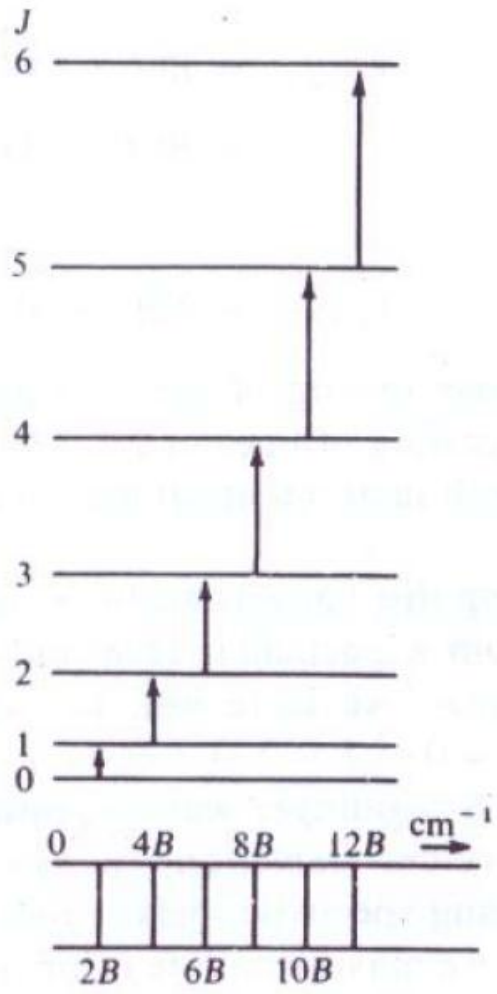
**For rigid rotor, J → J + 1,**

$$\bar{\nu}_{J \to J+1} = 2B(J+1)\ \text{cm}^{-1}$$

Selection rule: $\Delta J = \pm 1$




The allowed rotational energy levels of a rigid diatomic molecule




Allowed transitions between the energy levels of a rigid diatomic molecule and the spectrum

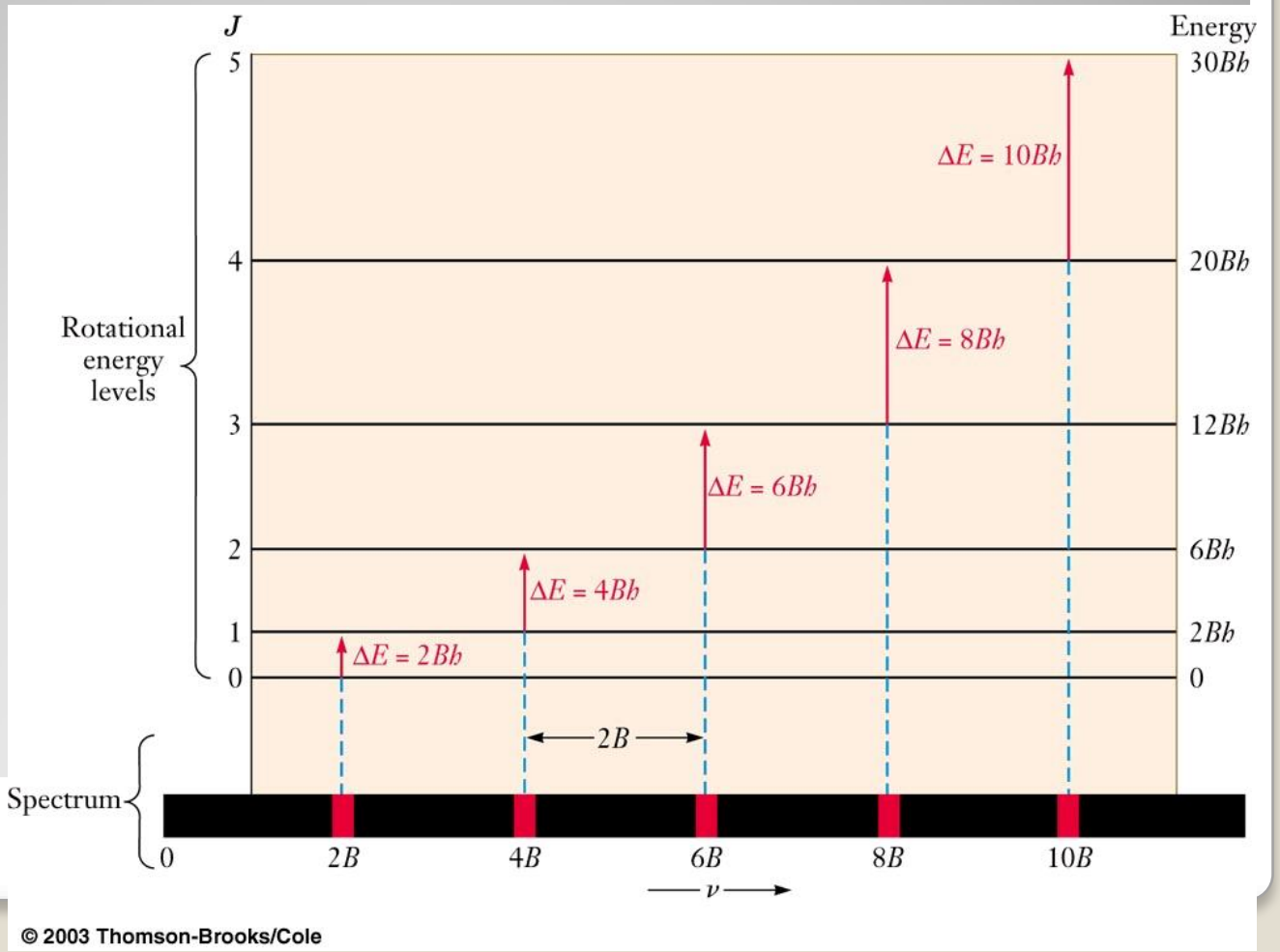
# Rotational Spectra of Rigid Rotor

**Selection Rule**: Apart from **Specific rule, $\Delta J = \pm 1$,** Gross rule- the molecule should have a **permanent electric dipole moment, $\mu$ .** Thus, **homonuclear diatomic molecules do not have a pure rotational spectrum. Heteronuclear diatomic molecules do have rotational spectra.**

$$\Delta j = \pm 1$$

$$\Delta j = +1 \ (absorption)$$

$$\Delta j = -1 \ (emission)$$

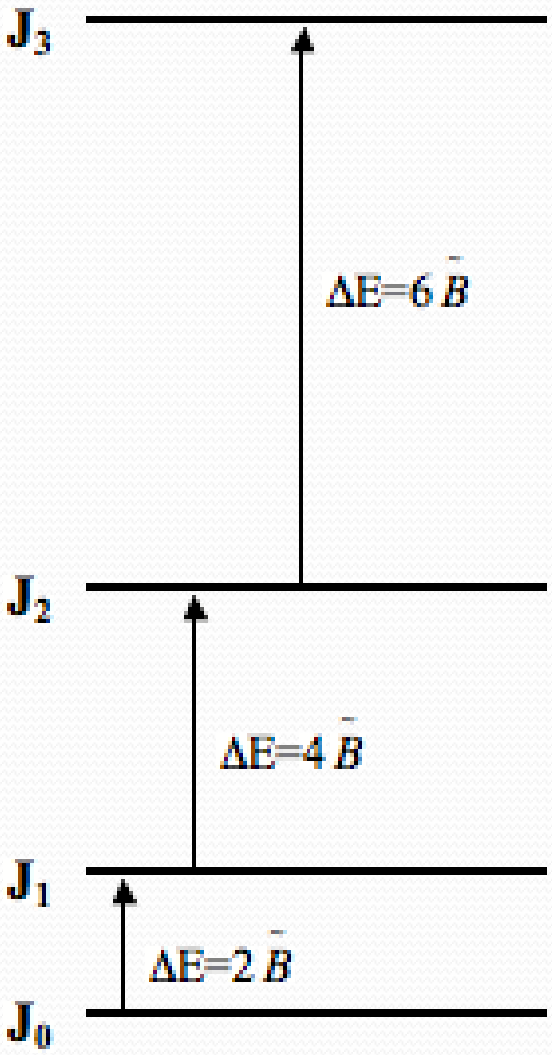


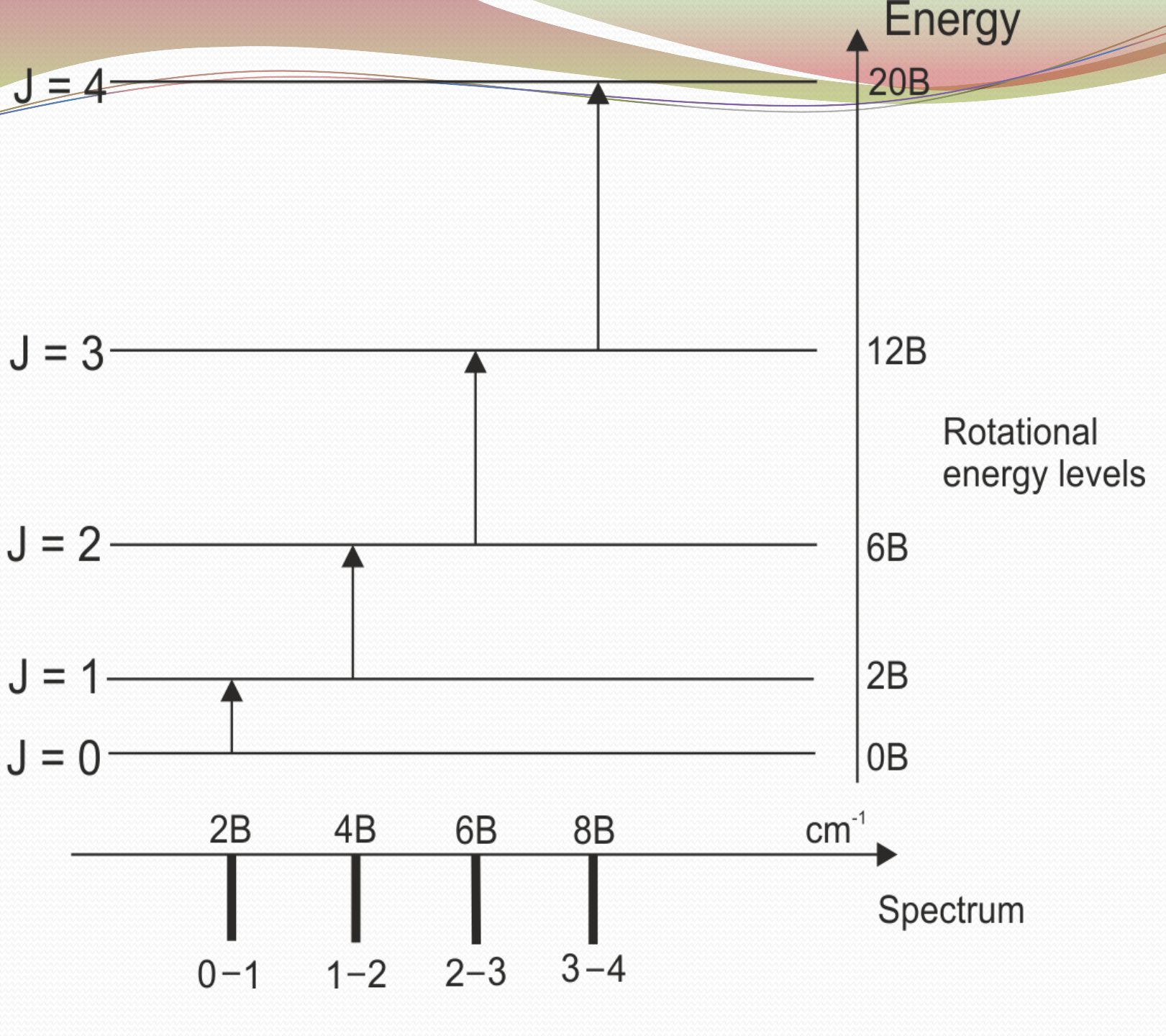
# Rotational energy levels allowed for a rigid diatomic molecule

# Selection Rule

- pure rotation spectrum obeys the selection rule $\Delta J = \pm 1$

# Rotational Energy Levels




Energy
J = 4
20B
J = 3
12B
Rotational
energy levels
J = 2
6B
J = 1
2B
J = 0
0B
2B
4B
6B
8B
cm-1
Spectrum
0−1
1−2
2−3
3−4