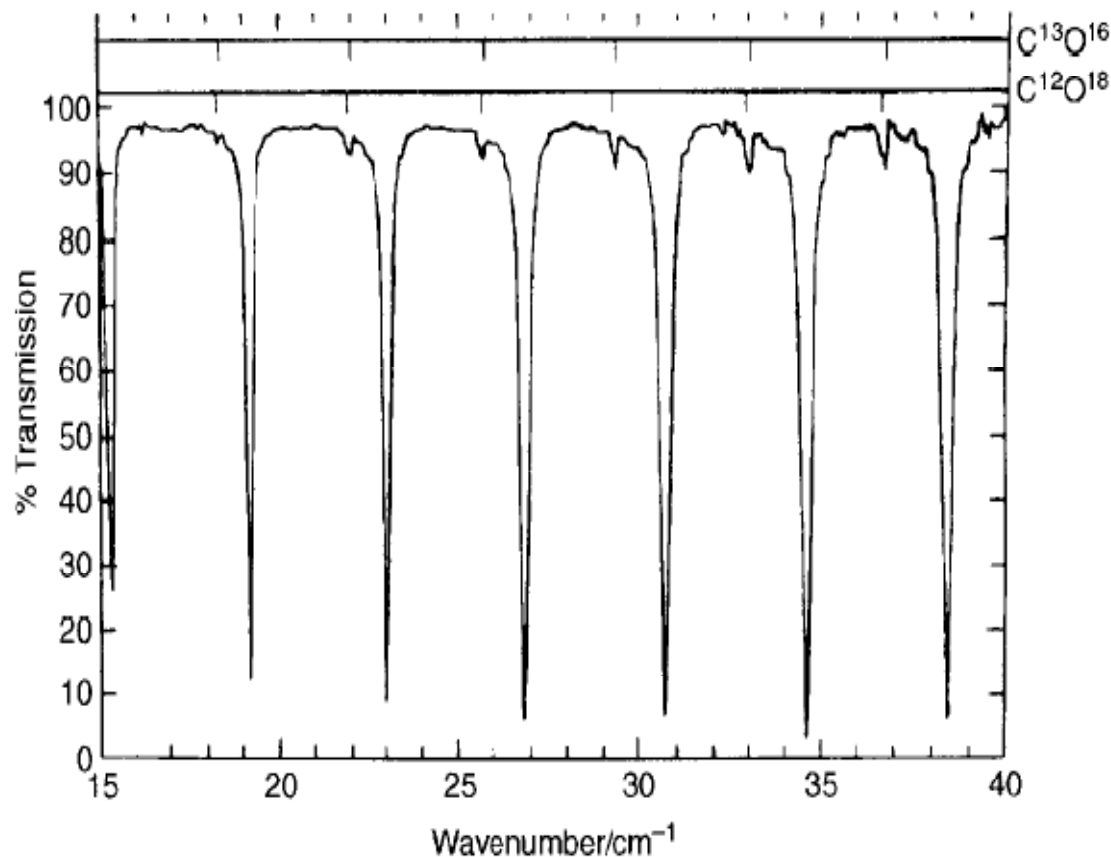


# Line positions



CHEM 5161  
09 Sept 2008

# Rigid rotor (linear molecules)

- Eigenstates

$$E_r = \frac{h^2}{8\pi^2 I} J(J + 1)$$

- $I = \mu r^2$  [kg] moment of inertia

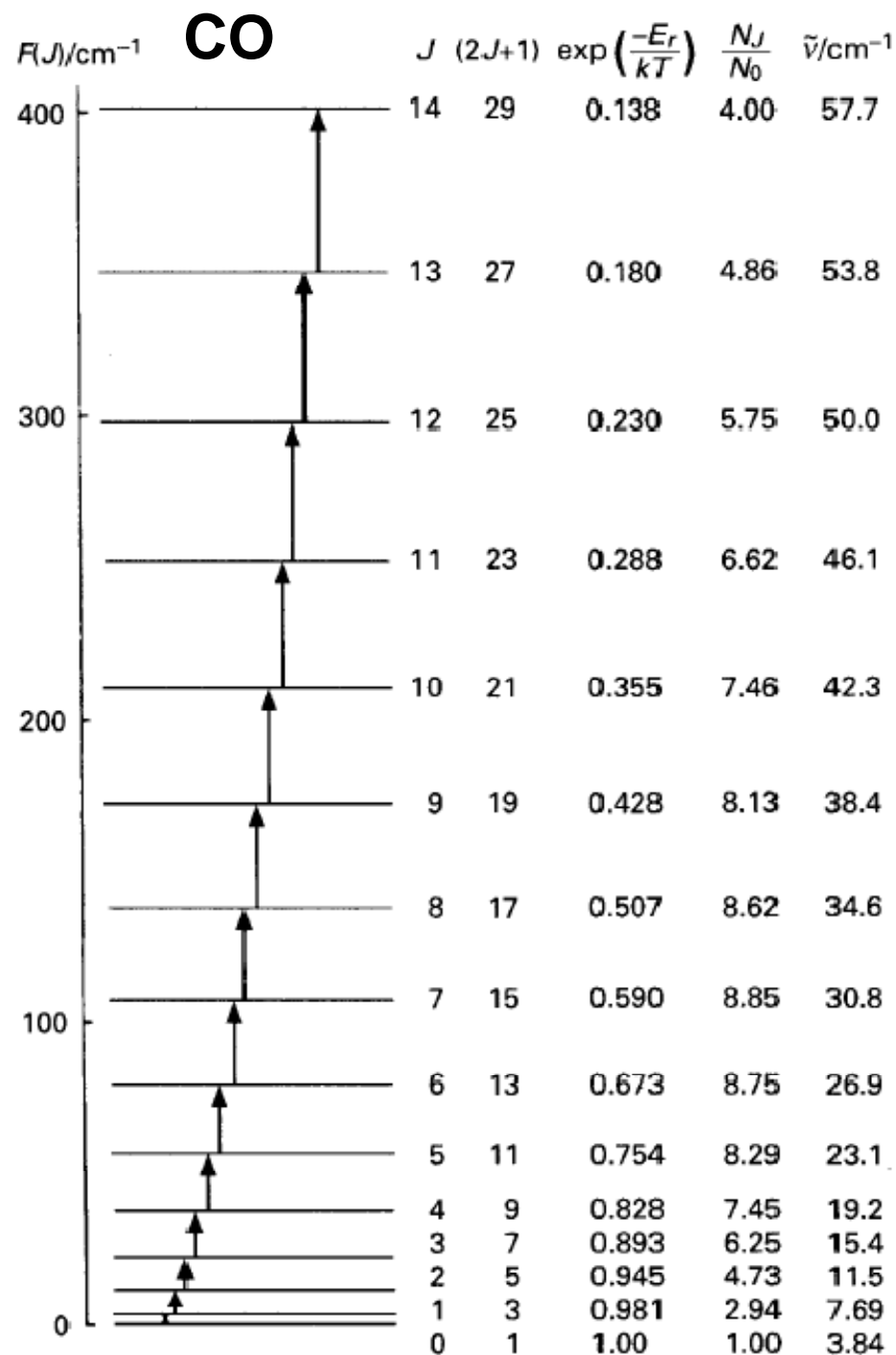
- $B = \frac{h}{8\pi^2 c I}$  [cm<sup>-1</sup>]  
rotational constant

- $J_{\max} = \left( \frac{kT}{2hcB} \right)^{1/2} - \frac{1}{2}$

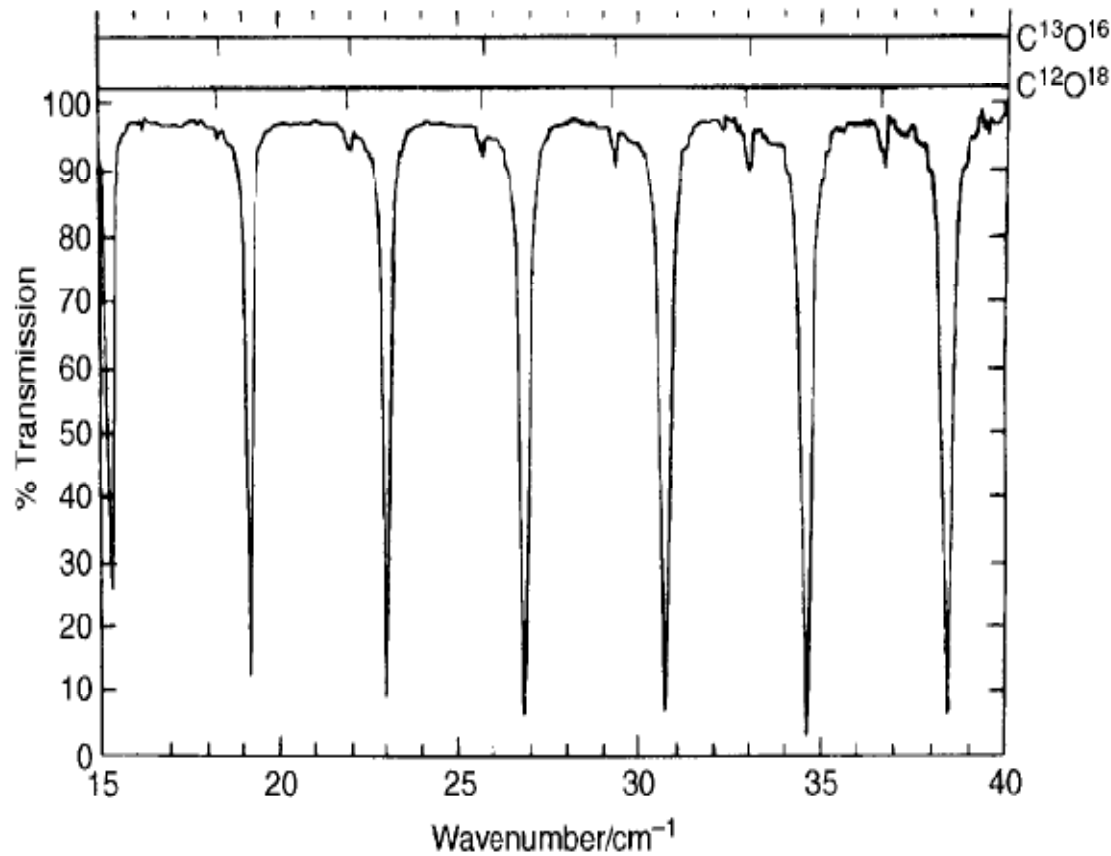
- Selection rules

IR:  $\Delta J = \pm 1$   
 $\Delta M_j = 0, \pm 1$

Raman:  $\Delta J = 0, \pm 2$



From the below measurement, determine the average separation of rotational transitions in  $^{12}\text{C}^{16}\text{O}$ , and hence estimate the bond length.



# Centrifugal distortion

- Term values

$$F(J) = B J (J+1) - D J^2 (J + 1)^2$$

- Frequency spacing

$$F(J+1) - F(J) = 2B(J+1) - 4D(J+1)^3$$

- $D$  [ $\text{cm}^{-1}$ ]: centrifugal distortion constant

$$D = 4B^3/\omega^2 \text{ (harmonic approximation of vibrations)}$$

- $B$  (and  $D$ ) vibration dependence

$$B_v = B_e - \alpha(v+1/2)$$

$\alpha$  [ $\text{cm}^{-1}$ ]: vibration-rotation interaction constant

# Stark Effect

- Space quantization of rotational angular momentum leads to  $(2J + 1)$  degenerate energy levels
- In presence of an electric field this degeneracy is removed.
- Additional energy term:
  - $\mu$ : electric dipole moment
  - $M_j^2$ : energy is independent of  $M_j$
- Application: quantification of dipole moments

$$E_{\mathcal{E}} = \frac{\mu^2 \mathcal{E}^2 [J(J+1) - 3M_j^2]}{2hBJ(J+1)(2J-1)(2J+3)}$$

# Harmonic oscillator

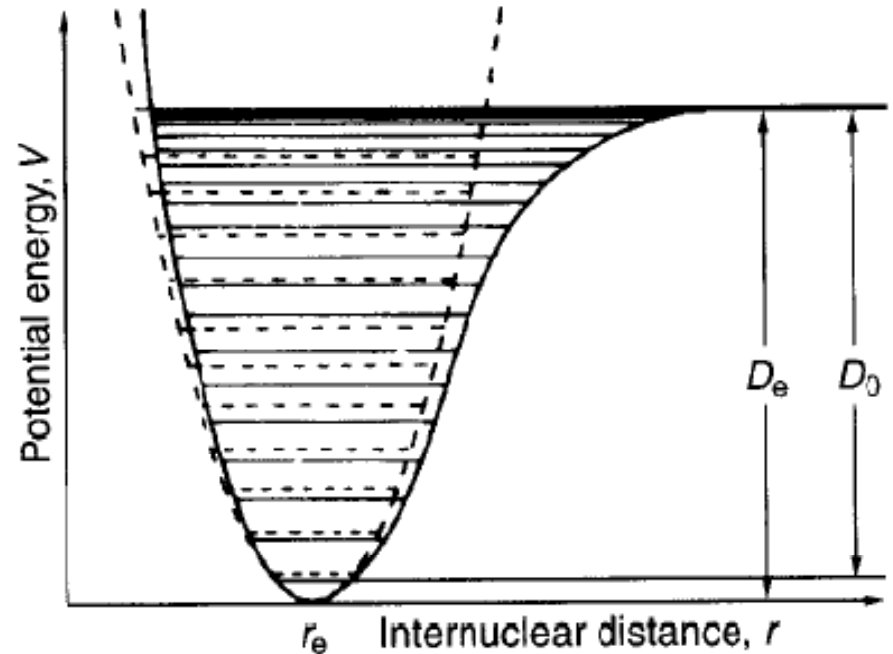
- Eigenstates  $E_v = hv(v + \frac{1}{2})$
- Dissociation Energy  $D_e \approx \left( \frac{\omega_e^2}{4\omega_e x_e} \right)$
- $\omega$  [ $\text{cm}^{-1}$ ]: vibration wavenumber
- Selection rules  
IR:  $\Delta v=1, \Delta J = 0, \pm 1$   
Raman:  $\Delta v=1, \Delta J = 0, \pm 2$   $\Delta J = 0, \pm 2$

# Anharmonicity

- Modifies the selection rule of IR and Raman to:  
 $\Delta v = \pm 1, \pm 2, \pm 3 \dots$
- Vibrational overtones
- Additional Energy term:

$$G(v) = \omega_e (v + 1/2) - \omega_e x_e (v + 1/2)^2 + \omega_e y_e (v + 1/2)^3 + \dots$$

- $\omega_e$  is the vibrational wavenumber [ $\text{cm}^{-1}$ ]
- $\omega_e x_e, \omega_e y_e$  are anharmonic constants



From the following separations of vibrational levels in the ground electronic state of CO, obtain values of  $\omega_e$ ,  $\omega_e X_e$  and also an approximate value for the dissociation energy

$v'-v''$	1-0	2-1	3-2	4-3	5-4	6-5
$[G(v+1) - G(v)]/\text{cm}^{-1}$	2143.1	2116.1	2088.9	2061.3	2033.5	2005.5