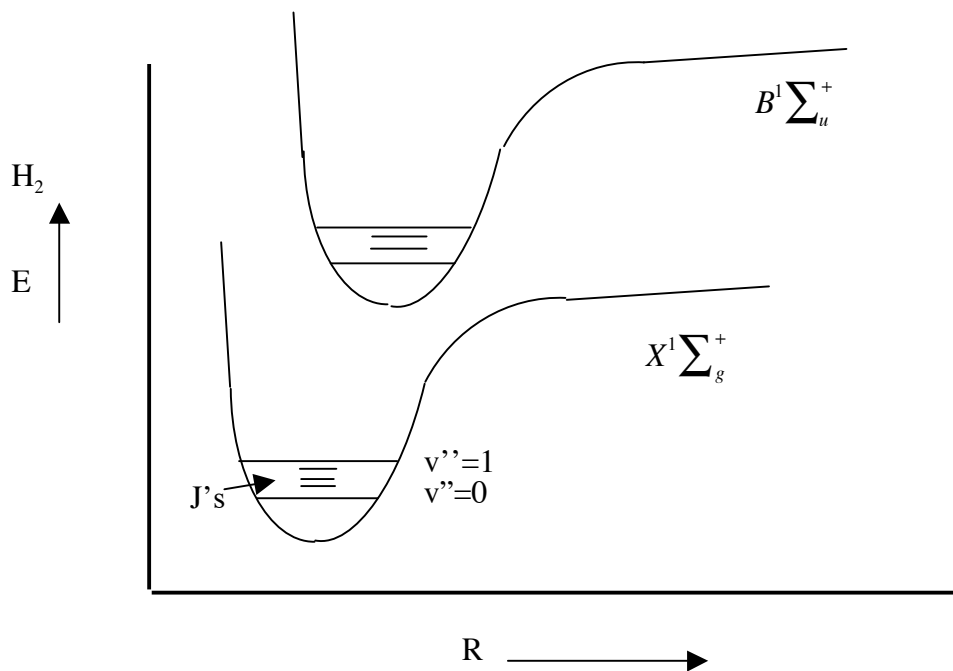


Ch. 5 - MOLECULAR SPECTROSCOPY



Rotational, Vibrational, and Electronic Transitions

Rigid Rotors

$$\frac{E_{rot}}{hc} [cm^{-1}] = B J(J+1)$$

where

J=rotational quantum #

B=rotational constant for that electronic/vibrational state

(In real cases, also need to correct for *stretching*)

For rotational transitions, need a permanent dipole (H_2 has none) and the transition rule is:

$$\Delta J = \pm 1$$

Traditionally, the upper level is labeled J' and the lower level J'' .

This leads to an emitted spectrum with wavenumbers $\tilde{\nu}_{J',J''} = BJ'(J'+1) - BJ''(J''+1)$ for a constant value of B for both levels (not always the case). But if $J' = J''+1$, for example, we get

$$\tilde{\nu}_{J',J''} = B(J'+1)(J''+2) - BJ''(J''+1) = 2B(J'+1)$$

leading to a series of lines separated by 2B:

$$\begin{array}{cccccccc} J' & 0 & 1 & 2 & 3 & \dots & \overbrace{\quad}^{2B} & | & | \\ \tilde{\nu} & 2B & 4B & 6B & 8B & \dots & & \tilde{\nu} \rightarrow & \end{array}$$

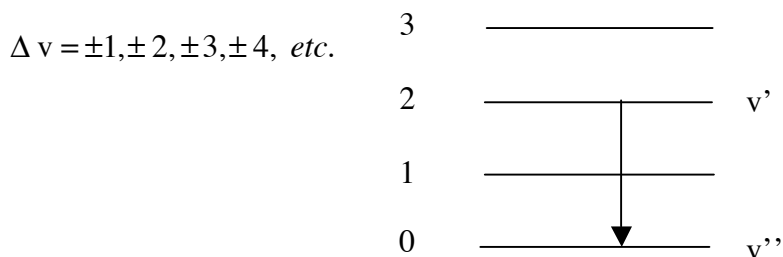
Example: CO B=1.98 cm⁻¹

| J' | J'' | $\tilde{\nu}(cm^{-1})$ | $\lambda(cm)$ |
|----|-----|------------------------|---------------|
| 1 | 0 | 3.96 | 0.252 |
| 2 | 1 | 7.92 | 0.126 |
| 3 | 2 | 11.88 | 0.0843 |

Vibrational

$$\frac{E_{vib}}{hc} = \omega(v + \frac{1}{2}) \text{ harmonic oscillator}$$

$$\left[= \omega_e(v + \frac{1}{2}) - \omega_e X_e(v + \frac{1}{2})^2 + \omega_e Y_e(v + \frac{1}{2})^3 + \dots \right] \text{ anharmonic oscillator}$$



Example: CO

$$\omega_e = 2170 \text{ cm}^{-1}$$

$$\omega_e X_e = 13.5 \text{ cm}^{-1}$$

$$\omega_e Y_e = 0.031 \text{ cm}^{-1}$$

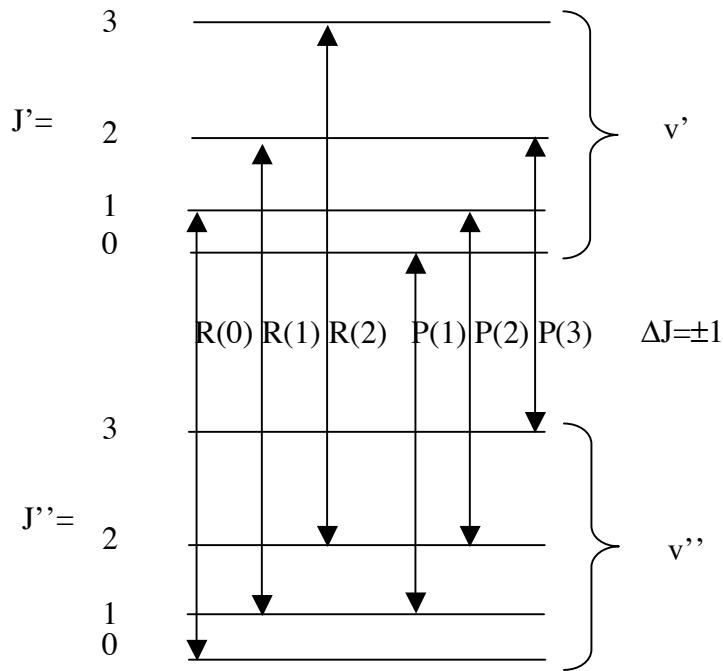
Combined Vibrational-Rotational

$$\frac{E_{vib} + E_{rot}}{hc} = \omega_e \left(v + \frac{1}{2} \right) - \omega_e X_e \left(v + \frac{1}{2} \right)^2 + \omega_e Y_e \left(v + \frac{1}{2} \right)^3 + B_v J(J+1) - D_v J^2(J+1)^2$$

where $B_v = B_e - \alpha_e \left(v + \frac{1}{2} \right)$

$D_v = D_e - \beta_e \left(v + \frac{1}{2} \right)$

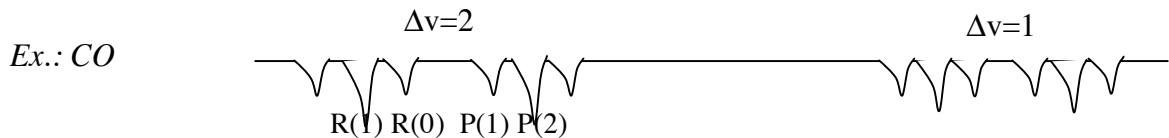
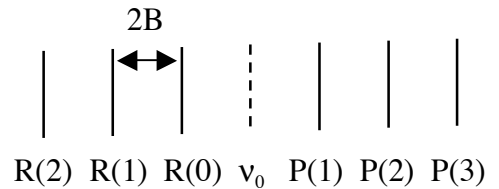
etc.



| | | |
|-------------|-----------------|-----------------|
| | R branch | P branch |
| | $J' - J'' = +1$ | $J' - J'' = -1$ |
| Designation | R(J'') | P(J'') |

R $\tilde{\nu}_R = \nu_0 + 2B_{v'} + (3B_{v'} - B_{v''})J' + (B_{v'} - B_{v''})J'^2$
 $J' = 0, 1, 2, 3, \dots$

P $\tilde{\nu}_P = \nu_0 - (B_{v'} + B_{v''})J' + (B_{v'} - B_{v''})J'^2$
 $J' = 1, 2, 3, 4, \dots$



Electronic Transitions

$$\tilde{\nu} = [\text{electronic term}] + [\text{vibrational term}] + [\text{rotational term}]$$

Selection Rules"

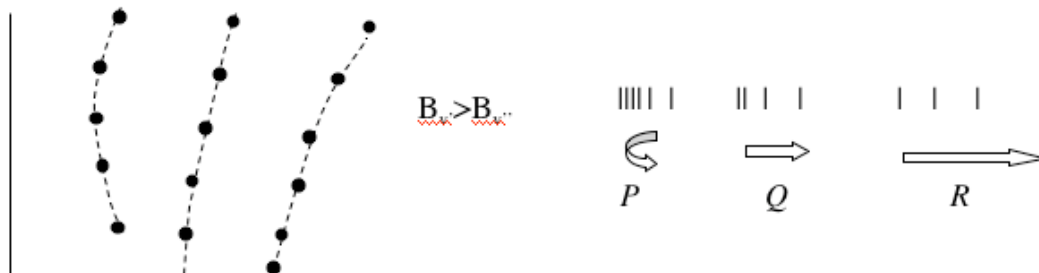
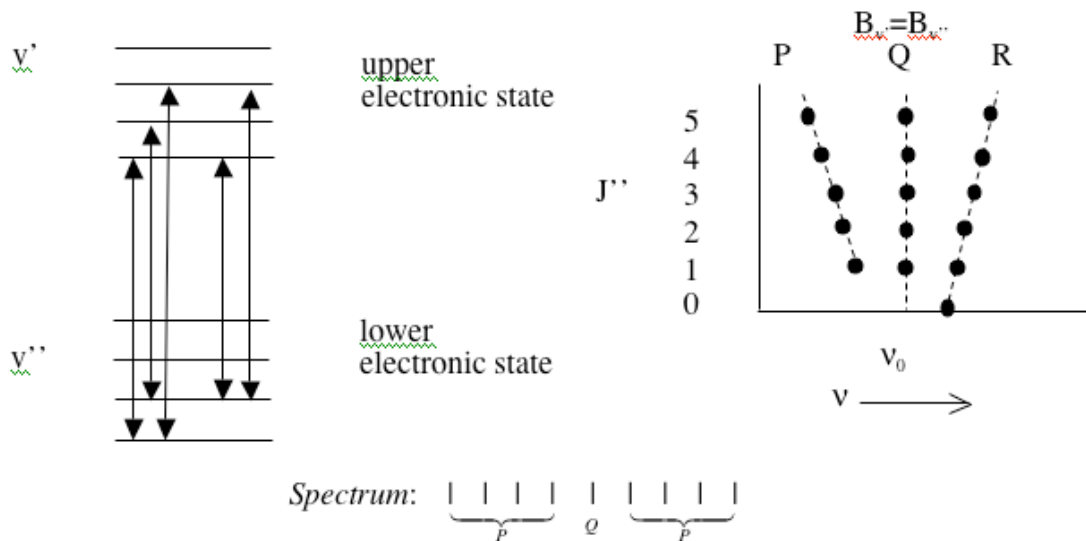
electronic \rightarrow only to same spins (usually)

vibrational $\rightarrow \Delta v = 0, \pm 1, \pm 2, \pm 3, \text{etc.}$

rotational $\rightarrow \Delta J = 0, \pm 1$ except $0 \leftrightarrow 0$

↑
Note! Not possible for $\Sigma \leftrightarrow \Sigma$

$\Delta J = 0 \Rightarrow Q\text{-branch}$



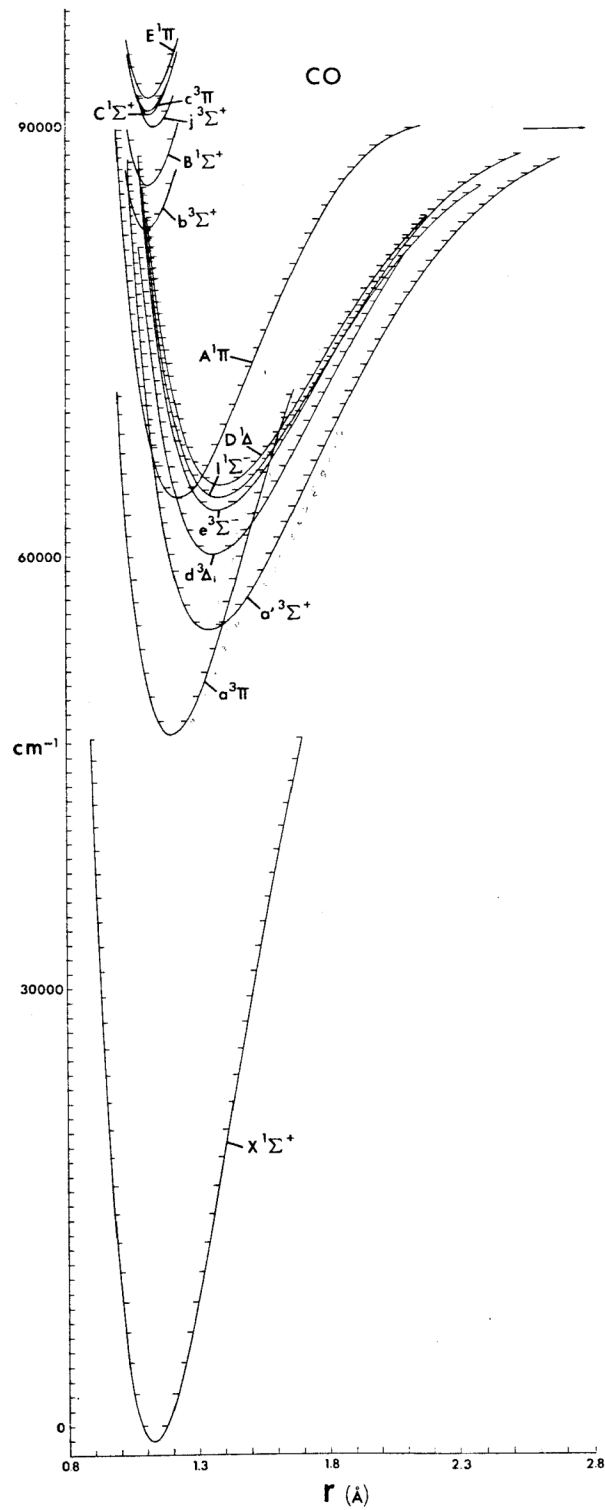


FIGURE 3. Potential energy curves for the observed states of CO below 11.77 eV.

The arrow indicates the dissociation energy of CO. The dash marks on the potential curves indicate the vibrational levels.