

$$I(\mu)_{el}^2 \approx |\mu_{el}|^2 \underbrace{|\langle v' | v'' \rangle|^2}_{q_{v'v''}}$$

$q_{v'v''}$ French-Condor factor

Orthornormality does not pertain here; the vibrational functions have different Re. Rather, the intensities depend on the square of the overlap integral, which in turn depends on the relationships between Re' & Re'' .

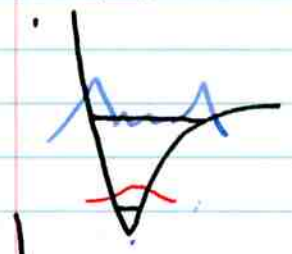
Case (i) $Re' \sim Re''$ "diagonal FC factors" (near orthornormality)



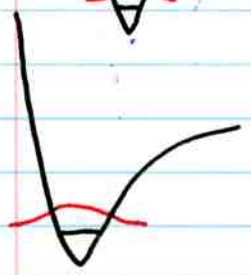
$\Delta v = 0$ strongest transitions



Case (ii) $Re' > Re''$ (common)



$\Delta v \neq 0$ stronger; max. overlap between $v''=0$ & $v' > 0$.
The larger the $Re' - Re''$ difference, the larger the preferred v' .



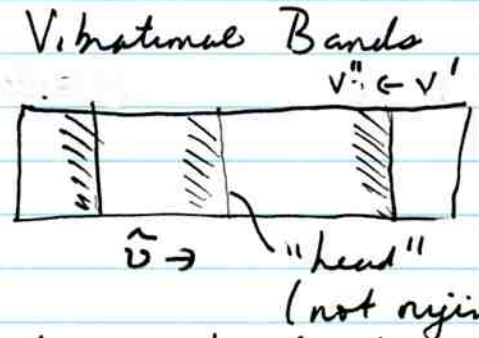
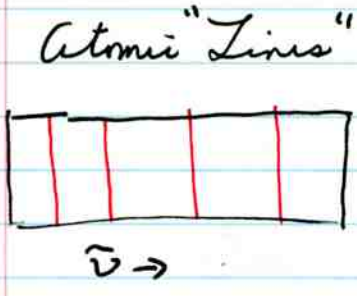
Vibrational Bands $A \leftarrow X$

Let's first neglect rotation.

$$\tilde{\nu}(v', v'') = \underbrace{(\tilde{T}_{e'} - \tilde{T}_{e''})}_{\text{Constant}} + \tilde{G}_{v'} - \tilde{G}_{v''} \quad (\text{cm}^{-1})$$

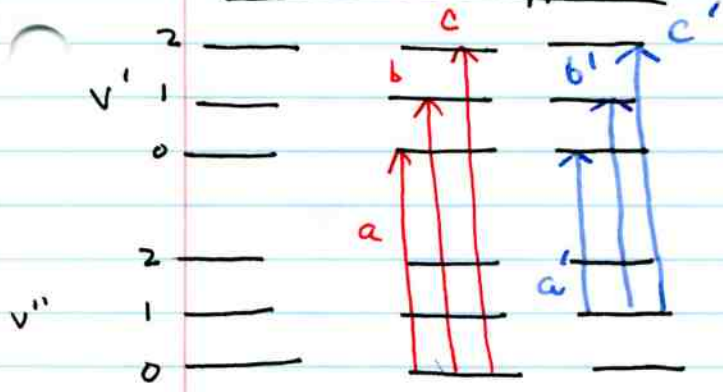
At low resolution, a vibrational "band" is seen, in which rotational structure is unresolved.

Photographic Plates



Dooland's Table: tabulation of bands by $v' v''$ to aid assignments.

Combination Differences Δ (Vibrational Spacings)



$\Delta''_{1,0} = a - a', b - b', c - c'$
 must be equal if assignments correct.

$\Delta'_{1,0} = b - a, b' - a'$

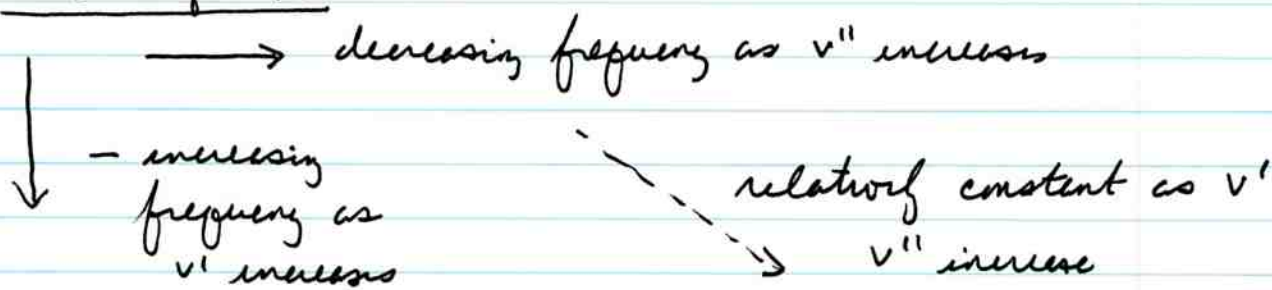
Example: $A^2\Pi - X^2\Sigma^+$ ($\tilde{\nu}$ in cm^{-1})

See pp 151-153 of text for full table

$v' \backslash v''$	0	$\Delta''_{1,0}$	1	$\Delta''_{2,1}$
0	9,150.63	2047.3	7103.36	
$\Delta'_{1,0}$	1786.6		1785.4	
1	10,937.25	2048.4	8888.8	
$\Delta'_{2,1}$	1761.5		1768.01	
2	12,698.73	2041.9?	10656.81?	1761.2
		2048.7	should be same?	$\rightarrow 10650.0?$

(approx. w/o rotational assignments - use heads)

Features of Table



(illustrate with energy levels)

Note: entries can be limited by Franck-Condon factors and, in absorption, by thermal considerations (only low v'' populated - see CN example)

The combination differences (vibrational spacings) should decrease with increasing vibrational quantum number.

$$\Delta'_{1,0} = \tilde{G}'_1 - \tilde{G}'_0 = \tilde{\omega}'_e - 2\tilde{\omega}'_e x'_e$$

$$(\Delta'_{v'+1,v} = \tilde{G}'_{v'+1} - \tilde{G}'_v = \tilde{\omega}'_e - 2\tilde{\omega}'_e x'_e (v'+1))$$

$$\Delta'_{2,1} = \tilde{\omega}'_e - 4\tilde{\omega}'_e x'_e$$

$$\Delta'_{1,0} - \Delta'_{2,1} = 2\tilde{\omega}'_e x'_e = 25.1 \text{ cm}^{-1} \quad \text{for CN}$$

$$\tilde{\omega}'_e x'_e = 12.55 \text{ cm}^{-1} \Rightarrow \tilde{\omega}'_e = 1812 \text{ cm}^{-1}$$

ROTATIONAL "FINE" STRUCTURE (${}^1\Sigma$)

$$\Delta J = J' - J'' = 0, \pm 1 \quad (\text{R, P branches})$$

"Q" branch exists unless $\Omega = 0$ in both states

$$\tilde{F}_v(J) = \tilde{B}_v J(J+1) - \tilde{D}_v J^2(J+1)^2 + \dots$$

$$\tilde{B}_v = \tilde{B}_e - \tilde{\alpha}_e (v+1/2) + \dots \quad \tilde{D}_v = \tilde{D}_e - \tilde{\beta}_e (v+1/2) + \dots$$

ignoring distortion:

a) Q branch

$$\begin{aligned}
 \tilde{\nu}_Q(J) &= \tilde{\nu}_0 + (\tilde{B}_{v'} - \tilde{B}_{v''}) J(J+1) \\
 J \leftarrow J & \quad \text{"band region"} \quad \tilde{\nu}(v', v'') \\
 &= \tilde{\nu}_0 + (\tilde{B}_{v'} - \tilde{B}_{v''}) J + (\tilde{B}_{v'} - \tilde{B}_{v''}) J^2
 \end{aligned}$$

Normally $R_e' > R_e'' \Rightarrow \tilde{B}_{e'} < \tilde{B}_{e''} \Rightarrow \tilde{B}_{v'} < \tilde{B}_{v''}$

$\therefore \tilde{\nu}_Q(J)$ decreases with increasing J .

b) P branch

$$\begin{aligned}
 \tilde{\nu}_P(J) &= \tilde{\nu}_0 + \tilde{B}_{v'}(J-1)J - \tilde{B}_{v''} J(J+1) \\
 J-1 \leftarrow J & \\
 J \geq 1 & \\
 &= \tilde{\nu}_0 - \underbrace{(\tilde{B}_{v'} + \tilde{B}_{v''})J}_{\text{negative}} + \underbrace{(\tilde{B}_{v'} - \tilde{B}_{v''})J^2}_{\text{usually small + negative until large } J}
 \end{aligned}$$

$J+1 \leftarrow J$ c) R branch

$$\begin{aligned}
 \tilde{\nu}_R(J) &= \tilde{\nu}_0 + \tilde{B}_{v'}(J+1)(J+2) - \tilde{B}_{v''} J(J+1) \\
 J \geq 0 & \\
 &= \tilde{\nu}_0 + \underbrace{(\tilde{B}_{v'} + \tilde{B}_{v''})(J+1)}_{\text{positive}} + (\tilde{B}_{v'} - \tilde{B}_{v''})(J+1)^2
 \end{aligned}$$

(see vibrational spectrum)

