Ro-vibrational Transitions

When transitions happen between 2 vibrational states of a molecule, the rotational state can also change — these are "ro-vibrational" transitions.

For a harmonic oscillator potential the solutions to Schrodinger's Equations are

$$\psi \sim H_n(r) \, e^{-r^2/2} \qquad\qquad E_v = \hbar \omega_0 \left(v + \tfrac{1}{2}\right)$$

Hermite polynomials

vibrational quantum number

$$\omega_0 = \sqrt{\frac{k}{\mu}} \quad \leftarrow \text{spring constant} \atop \leftarrow \text{reduced mass} \qquad = 2\pi \nu_0$$
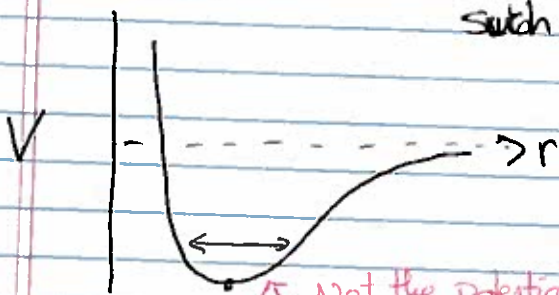
the fundamental frequency

If the molecular potential energy were a perfect harmonic oscillator, the selection rules for v would be

$$\Delta v = \pm 1 \qquad \text{If vibration induces time varying electric dipole}$$

⚡ **BUT** ⚡ Real molecular potentials have "anharmicity". This makes it such that larger Δv are <u>electric</u> dipole <u>allowed</u>.

V |- - - - - - - - -> r

↖ Not the potential well of a perfect harmonic oscillator

$$\Delta v \geq 1 \text{ allowed}$$

$$\Delta v \geq 2 \text{ called overtones/} \text{ and usually weaker}$$

NOTATION

CONSIDER a transition from $V_u \to V_e$. Depending on how J, the rotational angular momentum, changes, we have different "branches"

ΔJ	Notation		MEANS
$\vdots$	$\vdots$		
$+2$	$O(J_e)$	O branch	$J'_{e-2} \to J_e$
$+1$	$P(J_e)$	P branch	$J'_{e-1} \to J_e$
0	$Q(J_e)$	Q branch	$J'_e \to J_e$
-1	$R(J_e)$	R branch	$J'_{e+1} \to J_e$
-2	$S(J_e)$	S branch	$J'_{e+2} \to J_e$
$\vdots$	$\vdots$		

$V_u \to V_e$ with corresponding change in J

EXAMPLE 1 : CO   vibration changes μ_e so there are "IR active" ro-vib. transitions

Electric dipole selection rules for rotations:
- $\Delta J = \pm 1$ = we should observe strong P and R branch transitions

$\Delta J = 0$ forbidden $\Rightarrow$ No Q branch in gas phase

** IN solid state (ICES!) there are no rotations so Q branch is a strong band!

Note $E_u(v=1) \sim 3100\,K$!

Fundamental frequency: γ_0 corresponds to $\lambda_0 \sim 4.6\mu m$ in mid-IR

Overtone $v = 2-0$ close to $\lambda_{2-0} \sim 2.3\mu m$ in near-IR

"Hotbands" are any transitions between $V_u, V_e \neq 0$.

Bandheads

Because the R branch and P branch transitions have different sign w.r.t. J, it causes R branch lines to "pile up" and form a bandhead:

CONSIDER $\quad V_u \to V_e \quad\quad J_u \to J_e \quad$ ro-vibrational transition

$$\nu_{rovib} = \nu_0 + B_u J_u(J_u+1) - B_e J_e(J_e+1)$$

R branch $\quad J_u = J_e + 1 \quad\quad \Delta J = -1$

$$\nu_R = \nu_0 + B_u(J_e+1)(J_e+2) - B_e J_e^2 - B_e J_e$$

$$= \nu_0 + B_u J_e^2 + 3B_u J_e + 2B_u - B_e J_e^2 - B_e J_e$$

$$= \nu_0 \oplus (3B_u - B_e) J_e \ominus (B_e - B_u) J_e^2 + 2B_u$$

I want this to be +. Think about why...

Notice that signs are different. At high J_e, the $-\alpha J_e^2$ term will dominate and ν_R will head back toward ν_0

P branch $\quad J_u = J_e - 1 \quad\quad \Delta J = +1$

$$\nu_P = \nu_0 + B_u(J_e-1)(J_e) - B_e J_e^2 - B_e J_e$$

$$= \nu_0 + B_u J_e^2 - B_u J_e - B_e J_e^2 - B_e J_e$$

$$= \nu_0 \ominus (B_u + B_e) J_e \ominus (B_e - B_u) J_e^2$$

Notice these terms same sign! So P branch does NOT reverse in frequency at high J_e.

Bandhead is formed by R branch high J lines piling up.