

Ro-vibrational Transitions

ASTR
300B

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

$$\psi \sim H_n(r) e^{-r^2/2}$$

Hermite polynomials

$$E_v = \hbar \omega_0 (v + \frac{1}{2})$$

vibrational quantum number

$$\omega_0 = \sqrt{\frac{k}{\mu}} \leftarrow \begin{array}{l} \text{spring constant} \\ \text{reduced mass} \end{array} = 2\pi \nu_0$$

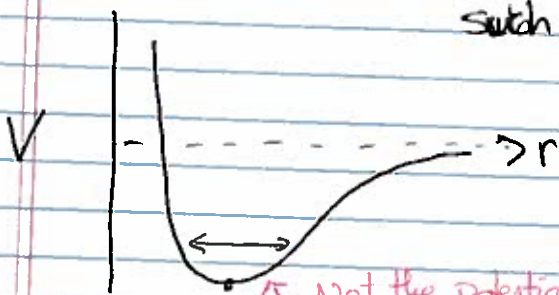
the fundamental frequency

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

$$\Delta v = \pm 1 \quad \text{IF vibration induces time varying electric dipole.}$$

* BUT *

Real molecular potentials have "anharmonicity". This makes it such that larger Δv are electric dipole allowed.



Not the potential well of a perfect harmonic oscillator

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

$\Delta v \geq 2$ called overtones and usually weaker.

NOTATION

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

<u>ΔJ</u>	<u>Notation</u>	<u>MEANS</u>
+ 2	O (J_e)	O branch $J_{e-2}' \rightarrow J_e$
+ 1	P (J_e)	P branch $J_{e-1}' \rightarrow J_e$
0	Q (J_e)	Q branch $J_e' \rightarrow J_e$
- 1	R (J_e)	R branch $J_{e+1}' \rightarrow J_e$
- 2	S (J_e)	S branch $J_{e+2}' \rightarrow J_e$
⋮	⋮	⋮

$V_u \rightarrow V_e$ 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!

Fundamental frequency : ν_0 corresponds to $\lambda_0 \sim 4.6 \mu\text{m}$ in mid-IR

Note $E_u(\nu=1) \sim 3100 \text{ K}$!

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

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

EXAMPLE 2 : H_2

vibration induces variation in electric quadrupole - so don't expect electric dipole transitions!

Electric

Quadrupole selection rules : $\Delta J = 0, \pm 2 \Rightarrow$ observe Q, Q and S branches!

ν_0 corresponds to $\lambda_0 \sim 2.1 \mu m$ in near-IR

EXAMPLE 3 : CO_2

No permanent electric dipole moment, so we have to figure out if vibration induces a time varying μ_e ?

3 types of vibration that CO_2 can undergo :



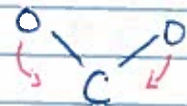
Symmetric Stretch

NO Ro-vibrational transitions!



Asymmetric Stretch

$\nu_0 \Rightarrow \lambda_0 \sim 4.3 \mu m$



Bending Mode

Yes! $\Delta J = \pm 1$ allowed

Yes!

Also - when μ_e change is \perp to molecular axis, $\Delta J = 0$ also electric dipole allowed. So get Q branch here too!

$\nu_0 \Rightarrow \lambda_0 \sim 15 \mu m$

\uparrow
 $E_u \sim 1000 K$

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 $V_u \rightarrow V_e$ $J_u \rightarrow J_e$ ro-vibrational transition

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

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

$$\begin{aligned} \nu_R &= \nu_0 + B_u (J_e + 1)(J_e + 2) - B_e J_e^2 - B_e J_e \\ &= \nu_0 + B_u J_e^2 + 3B_u J_e + 2B_u - B_e J_e^2 - B_e J_e \end{aligned}$$

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

↑ Notice that signs are different. ↑ I want this to be +. Think about why...

↑ At high J_e , the $- \propto J_e^2$ term will dominate and ν_R will head back toward ν_0 .

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

$$\begin{aligned} \nu_P &= \nu_0 + B_u (J_e - 1)(J_e) - B_e J_e^2 - B_e J_e \\ &= \nu_0 + B_u J_e^2 - B_u J_e - B_e J_e^2 - B_e J_e \end{aligned}$$

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

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.