Vibrational-Rotational Spectroscopy

Vibrational-Rotational Spectrum of Heteronuclear Diatomic

Absorption of mid-infrared light ($\sim$300-4000 cm^{-1}):

- Molecules can change vibrational and rotational states

- Typically at room temperature, only ground vibrational state populated but several rotational levels may be populated.

- Treating as harmonic oscillator and rigid rotor: subject to selection rules
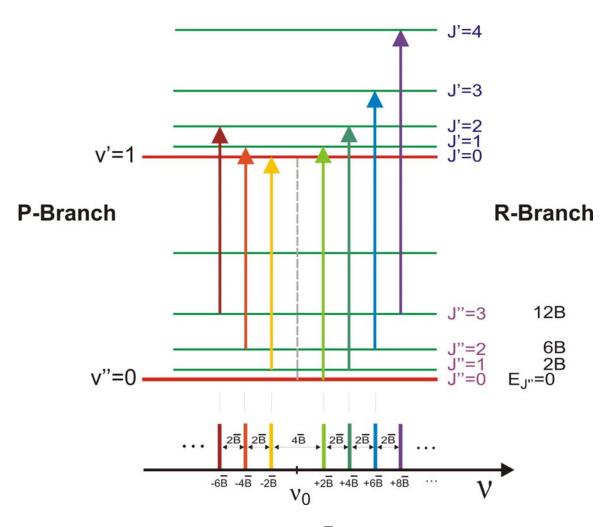
$$\Delta v = \pm 1 \text{ and } \Delta J = \pm 1$$

$$E_{field} = \Delta E_{vib} + \Delta E_{rot}$$

$$\hbar\omega = E_f - E_i \quad = \quad E(v', J') - E(v'', J'')$$

$$\bar{v} = \frac{\omega}{2\pi c} = \left[\bar{v}_0\left(v' + \tfrac{1}{2}\right) + \bar{B}J'(J'+1)\right] - \left[\bar{v}_0\left(v'' + \tfrac{1}{2}\right) + \bar{B}J''(J''+1)\right]$$

At room temperature, typically v''=0 and $\Delta v = +1$:

$$\bar{v} = \bar{v}_0 + \bar{B}\left[J'(J'+1) - J''(J''+1)\right]$$

Now, since higher lying rotational levels can be populated, we can have:

$\Delta J = +1$	$J' = J'' + 1$	$\bar{v} = \bar{v}_0 + 2\bar{B}(J''+1)$	$R - branch$
$\Delta J = -1$	$J' = J'' - 1$	$\bar{v} = \bar{v}_0 - 2\bar{B}J''$	$P - branch$

By measuring absorption splittings, we can get $\overline{B}$. From that, the bond length!

In polyatomics, we can also have a Q branch, where $\Delta J = 0$ and all transitions lie at $\overline{v} = \overline{v}_0$. This transition is allowed for perpendicular bands: $\partial \mu / \partial q \perp$ to molecular symmetry axis.

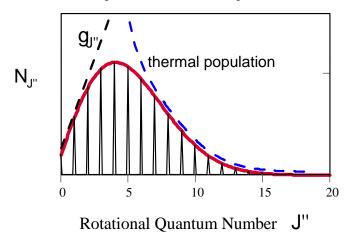## *Intensity of Vibrational-Rotational Transitions*

There is generally no thermal population in upper (final) state (v',J') so intensity should scale as population of lower J state (J").
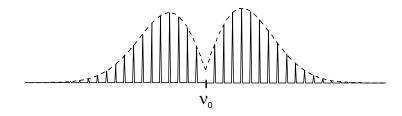
$$\Delta N = N(v', J') - N(v'', J'') \approx N(J'')$$

$$N(J'') \propto g(J'') \exp(-E_{J''} / kT)$$
$$= (2J'' + 1) \exp(-hc\overline{B}J''(J'' + 1) / kT)$$

Rotational Populations at Room Temperature for $B = 5$ cm^{-1}
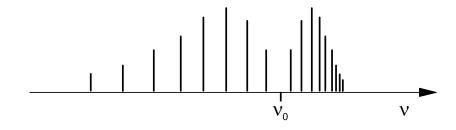

Rotational Quantum Number J''

So, the vibrational-rotational spectrum should look like equally spaced lines about ν_0
with sidebands peaked at J''>0.

- Overall amplitude from vibrational transition dipole moment
- Relative amplitude of rotational lines from rotational populations

In reality, what we observe in spectra is a bit different.

Vibration and rotation aren't really independent!

Two effects:

1) **Vibration-Rotation Coupling:**
    For a diatomic: As the molecule vibrates more, bond stretches
    $\rightarrow$ I changes $\rightarrow$ $\bar{B}$ dependent on v.

$$\bar{B} = \bar{B}_e - \alpha_e \left(v + \tfrac{1}{2}\right)$$

Vibrational-rotational coupling constant!

2) **Centrifugal distortion:** As a molecule spins faster, the bond is pulled apart
    $\rightarrow$ I larger $\rightarrow$ $\bar{B}$ dependent on J
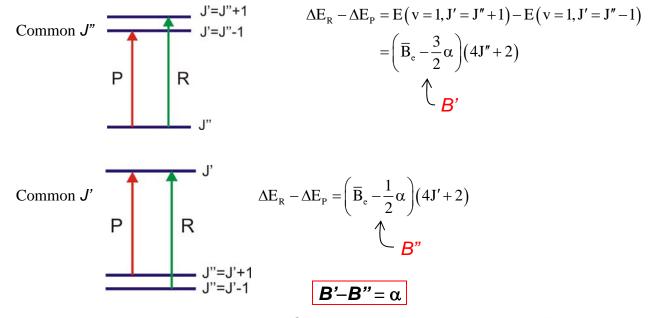
$$\bar{B} = \bar{B}_e - D_e J(J+1)$$

Centrifugal distortion term

So the energy of a rotational-vibrational state is:

$$\frac{E}{hc} = \bar{v}_0 \left(v + \tfrac{1}{2}\right) + \bar{B}_e J(J+1) - \alpha_e \left(v + \tfrac{1}{2}\right) J(J+1) - D_e \left[J(J+1)\right]^2$$

Analysis in lab:
    Combination differences – Measure $\Delta\Delta E$ for two transitions with common state

$$\Delta E_R - \Delta E_P = E(v=1, J'=J''+1) - E(v=1, J'=J''-1)$$

$$= \left(\bar{B}_e - \frac{3}{2}\alpha\right)(4J'' + 2)$$

B'

$$\Delta E_R - \Delta E_P = \left(\bar{B}_e - \frac{1}{2}\alpha\right)(4J' + 2)$$

B''

$$\boxed{B' - B'' = \alpha}$$

Vibrations of Polyatomic Molecules – Normal Modes

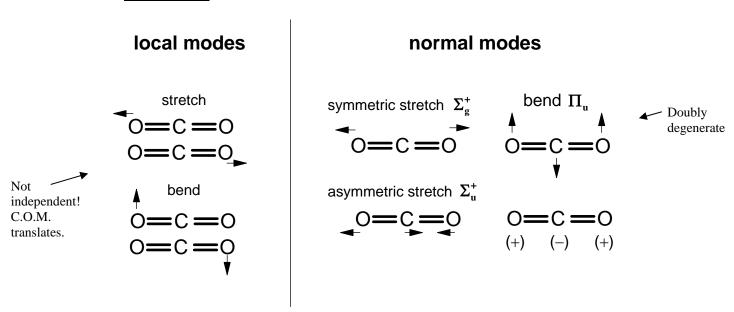- Remember that most of the nuclear degrees of freedom are the vibrations! $3n-6$ nonlinear
  $3n-5$ linear

C.O.M.
fixed

- It was clear what this motion was for diatomic (only one!).

- For a polyatomic, we often like to think in terms of the stretching or bending of a bond. — This "local mode" picture isn't always the best for spectroscopy.

- The local modes aren't generally independent of others! The motion of one usually influences others.
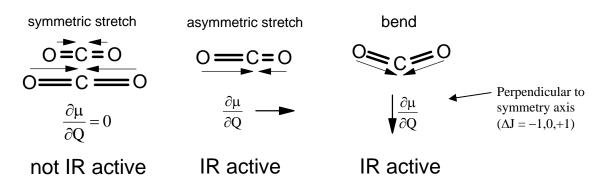
EXAMPLE: CO_2 linear: $3n-5 = 4$ normal modes of vib.

local modes   ## normal modes

stretch

Not
independent!
C.O.M.
translates.

bend

symmetric stretch Σ_g^+ bend Π_u

— Doubly degenerate

asymmetric stretch Σ_u^+

$(+)$ $(-)$ $(+)$

Molecules with linear symmetry: Σ : motion axially symmetric
Π : motion breaks axial symmetry
g/u : maintain/break center of symmetry

Which normal modes are IR active?

symmetric stretch   asymmetric stretch   bend

Perpendicular to
symmetry axis
$(\Delta J = -1,0,+1)$

$$\frac{\partial\mu}{\partial Q} = 0$$ $$\frac{\partial\mu}{\partial Q} \longrightarrow$$ $$\frac{\partial\mu}{\partial Q} \downarrow$$

not IR active   IR active   IR active