Vibrational-Rotational Spectroscopy

Vibrational-Rotational Spectrum of Heteronuclear Diatomic

Absorption of mid-infrared light (~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

$$\Delta v = \pm 1 \text{ and } \Delta J = \pm 1$$

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

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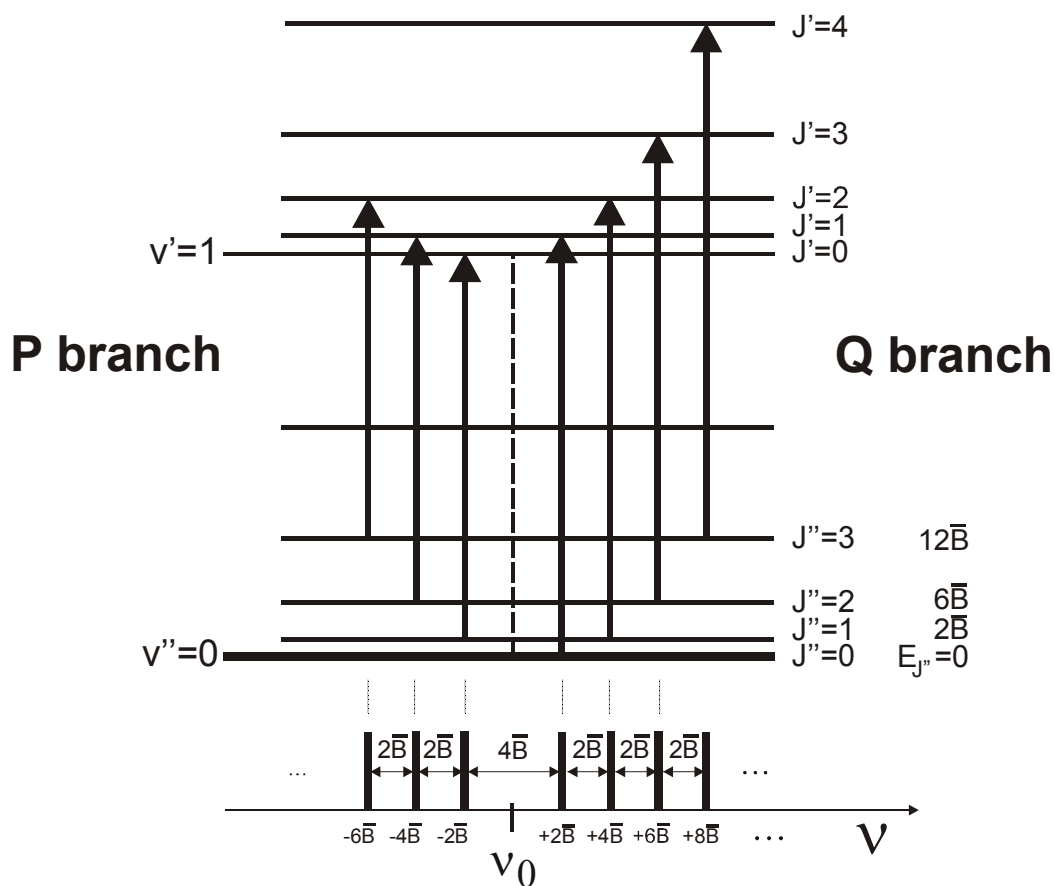
$$\bar{v} = \frac{\omega}{2\pi c} = \left[\bar{v}_0 \left(v' + \tfrac{1}{2} \right) + \bar{B}J'\left(J'+1\right) \right] - \left[\bar{v}_0 \left(v'' + \tfrac{1}{2} \right) + \bar{B}J''\left(J''+1\right) \right]$$

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

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

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

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

$$\Delta J = -1 \qquad J' = J''-1 \qquad \bar{v} = \bar{v}_0 - 2\bar{B}J'' \qquad P-branch$$

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.
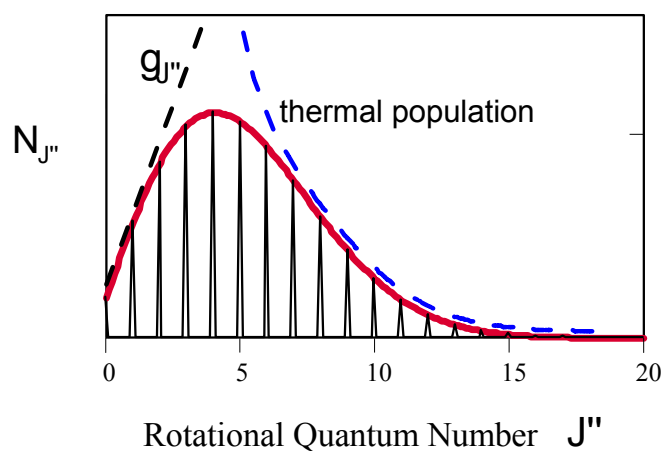
## *Intensity of Vibrational-Rotational Transitions*

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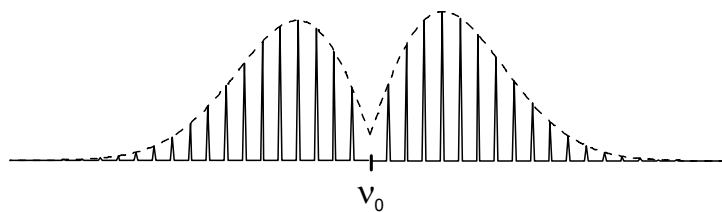
$$\Delta N = N(v', J') - N(v'', J'') \approx N(J'')$$

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

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

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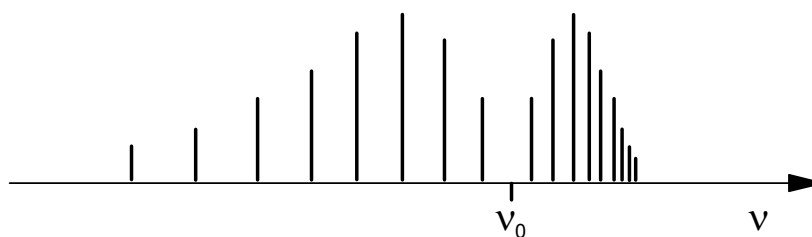
So, the vibrational-rotational spectrum should look like equally spaced lines about ν_0
with sidebands peaked at J''>0.

- 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

$$\bar{B} = \bar{B}_e - D_e J\left(J + 1\right)$$

   Centrifugal distortion term
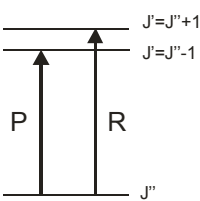
So the energy of a rotational-vibrational state is:

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

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

Common J"

P   R

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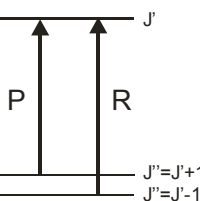
$$\Delta E_R - \Delta E_P = E\left(v = 1, J' = J'' + 1\right) - E\left(v = 1, J' = J'' - 1\right)$$

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

B'

Common J'

P   R

J'
$J'' = J'+1$
$J'' = J'-1$

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

B"

B'–B" = α

Vibrations of Polyatomic Molecules – Normal Modes
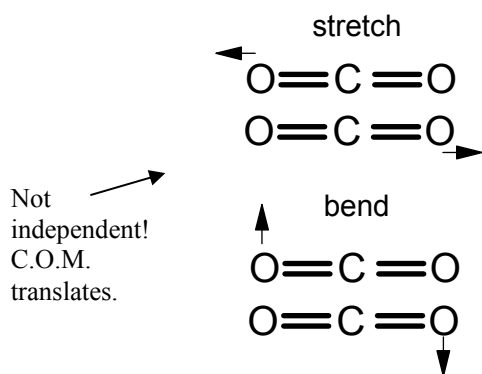
- Remember that most of the nuclear degrees of freedom are the vibrations!

  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.
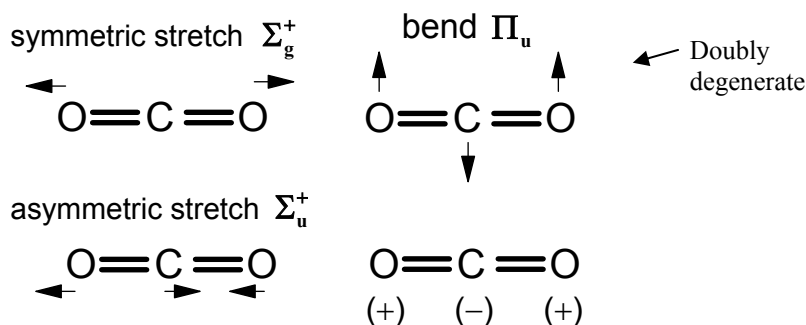
EXAMPLE: CO_2 linear: 3n−5 = 4 normal modes of vib.

local modes   normal modes

stretch

O$=$C$=$O

O$=$C$=$O

Not independent!
C.O.M. translates.

bend

O$=$C$=$O

O$=$C$=$O

symmetric stretch Σ_g^+

O$=$C$=$O

asymmetric stretch Σ_u^+

O$=$C$=$O

bend Π_u

O$=$C$=$O

O$=$C$=$O
(+)   (−)   (+)

Doubly degenerate
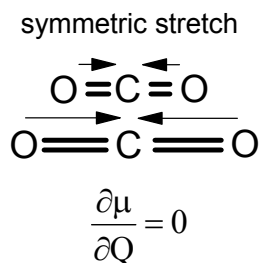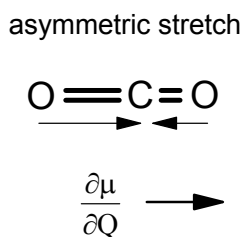
Molecules with linear symmetry: Σ : motion axially symmetric
Π : motion breaks axial symmetry
g/u : maintain/break center of symmetry
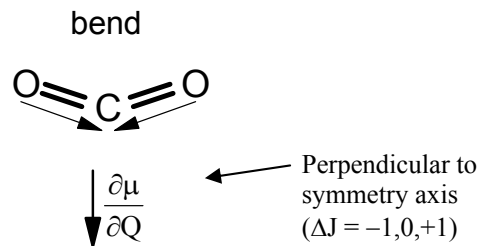
Which normal modes are IR active?

symmetric stretch   asymmetric stretch   bend

O$=$C$=$O

O$=$C$=$O

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

O$=$C$=$O

$$\frac{\partial \mu}{\partial Q} \longrightarrow$$

O$=$C$=$O

$$\frac{\partial \mu}{\partial Q}$$

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

not IR active   IR active   IR active