

## Continuing Vibration - Rotation Spectra

For a fundamental V-R band of a molecule ( $n=1$ ), lines are at

$$hc\bar{\nu} = hc\omega + 2hcB [J+1, -J] \quad \begin{array}{l} \text{can't} \\ \text{have} \\ \Delta J = -1 \end{array}$$

The line strength can be determined from our previous expression if we use approp. matrix elements and use  $hc\bar{\nu}_0$  (average energy of the transition) instead of  $hc\bar{\nu} = 2E_0(J+1) = 2Bhc(J+1)$ .

$$S \propto hc\bar{\nu} \frac{J[+1]}{2J+1} \left( 1 - \exp\left[-\frac{hc\bar{\nu}}{kT}\right] \right) \times (2J+1) \exp\left[-\frac{E_0 J(J+1)}{kT}\right]$$

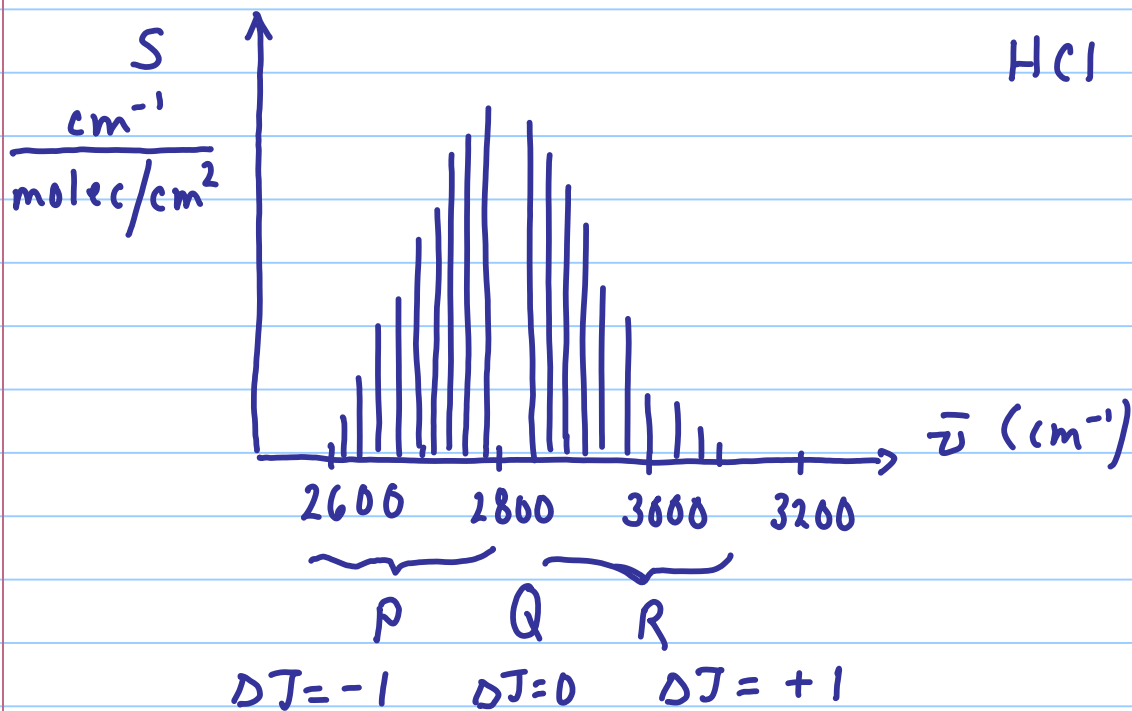
For a vibrational transition,  $hc\bar{\nu} \gg kT$ :

$$S \propto hc\bar{\nu} \frac{J[+1]}{2J+1} \left( \frac{E_0(2J+1)}{kT} \right) \exp\left[-\frac{E_0 J(J+1)}{kT}\right]$$

energy per transition
transition probability
lower state population

This expression gives quite accurate description of a vibration-rotation system.

Note: The maximum in line strength shifts with  $T \rightarrow$  can be used to measure planetary temperatures. Measure spectrum, find the peaks, then calculate the radiating  $T$ .



Three branches of IR spectrum.

P       $\Delta J = -1$

Q       $\Delta J = 0$        $\rightarrow$  not present for diatomic molecules

R       $\Delta J = +1$

Energy, frequency, wavenumber increase with  $P \rightarrow Q \rightarrow R$ .

If Q branch existed, all lines of any  $J$  would

be superimposed on each other.

## Next Level of Approximation for Diatomic Molecules.

Close examination of an HCl vibration-rotation spectrum shows several unpredicted features:

- doubling of some of the lines
- unequal spacing of lines of increasing  $J$

Reason for unequal spacing:

The "other terms" in our equation for the energy of a diatomic molecule are as follows:

$$\text{In cm}^{-1}: \frac{E}{hc} = W_v \left(v + \frac{1}{2}\right) + B J(J+1) - D_c J^2(J+1)^2 - x_e W_v \left(v + \frac{1}{2}\right)^2 - \alpha_e \left(v + \frac{1}{2}\right) J(J+1) + \text{other terms}$$

where

$-D_c J^2(J+1)^2$  is the centrifugal term which implies that as the molecule rotates faster, the bond stretches and the moment of inertia increases.

Considering only the rotational spectrum with this new term, the line spacing becomes

$$2B(J+1) - 4D_e(J+1)^2$$

so

rotational lines become more closely spaced as  $J$  increases.

For the vibration-rotation spectrum, the energy difference is:

$$\begin{aligned} \bar{\nu} = & \omega_v \Delta v + 2B[J+1, -J] \\ & - 4D_e[(J+1)^3, -J^3] \\ & - \alpha_c \omega_v \Delta v (1 + 2v + \Delta v) \\ & - \alpha_c [(J+1)(\Delta v J + 2(v + \Delta v + 1/2), \\ & \quad J(\Delta v J - 2(v + \Delta v + 1/2) + 2\Delta v)] \end{aligned}$$

First terms  $\Rightarrow \Delta J = +1$  (R branch)

Second terms  $\Rightarrow \Delta J = -1$  (P branch)

Let's simplify for the fundamental band where  $v = 0$  and  $\Delta v = 1$ :

$$\begin{aligned} \bar{\nu} = & \omega_v + 2B[J+1, -J] \\ & - 4D_e[(J+1)^3, -J^3] \\ & - 2\alpha_c \omega_v \\ & - \alpha_c [(J+1)(J+3), J(J-1)] \end{aligned}$$

alter line spacing within the band

alters the position of the band

In general:

- first term (centrifugal) alters line spacing with all bands
- ~~second~~<sup>third</sup> term alters line spacing from band to band
- ~~third~~<sub>second</sub> term alters central position of the bands.



## Band Nomenclature

Names of bands are associated with the vibrational quantum number  $v$ .

### fundamental bands

occur when lower value is  $v=0$  and  $v$  increases by 1 ( $v=0$  is the ground state)

### overtone bands

occur when lower value is  $v=0$  and  $v$  increases by more than 1

e.g. First overtone  $v=0 \rightarrow v=2$

### hot bands

occur when lower value of  $v$  is non-zero.

Absorption in these bands depends on the finite population of the lower state, so they tend to be weak bands and strongly dependent

on temperature because the population of the lower state follows Boltzmann's Formula  $\exp\left[-\frac{\Delta E}{kT}\right]$ .

hot overtone bands occur when lower state of  $v$  is non-zero and  $v$  increases by more than 1 (not common and weak)

isotope bands

All bands are really isotope bands, but usually one isotopic molecule dominates the spectrum, and so the bands of the weaker isotopes are called isotope bands.

The rotational line spacing and the band position both depend on the isotope so each isotope has distinct bands.

Look at table of HCl lines from HITRAN.

Polyatomic Molecules

→ more complicated vibration-rotation spectra because molecules can vibrate in several modes and rotate on more than one axis.

However, some polyatomic molecules have spectra resembling that of a diatomic molecules except that  $\Delta J=0$  transition is allowed, resulting in a Q branch.

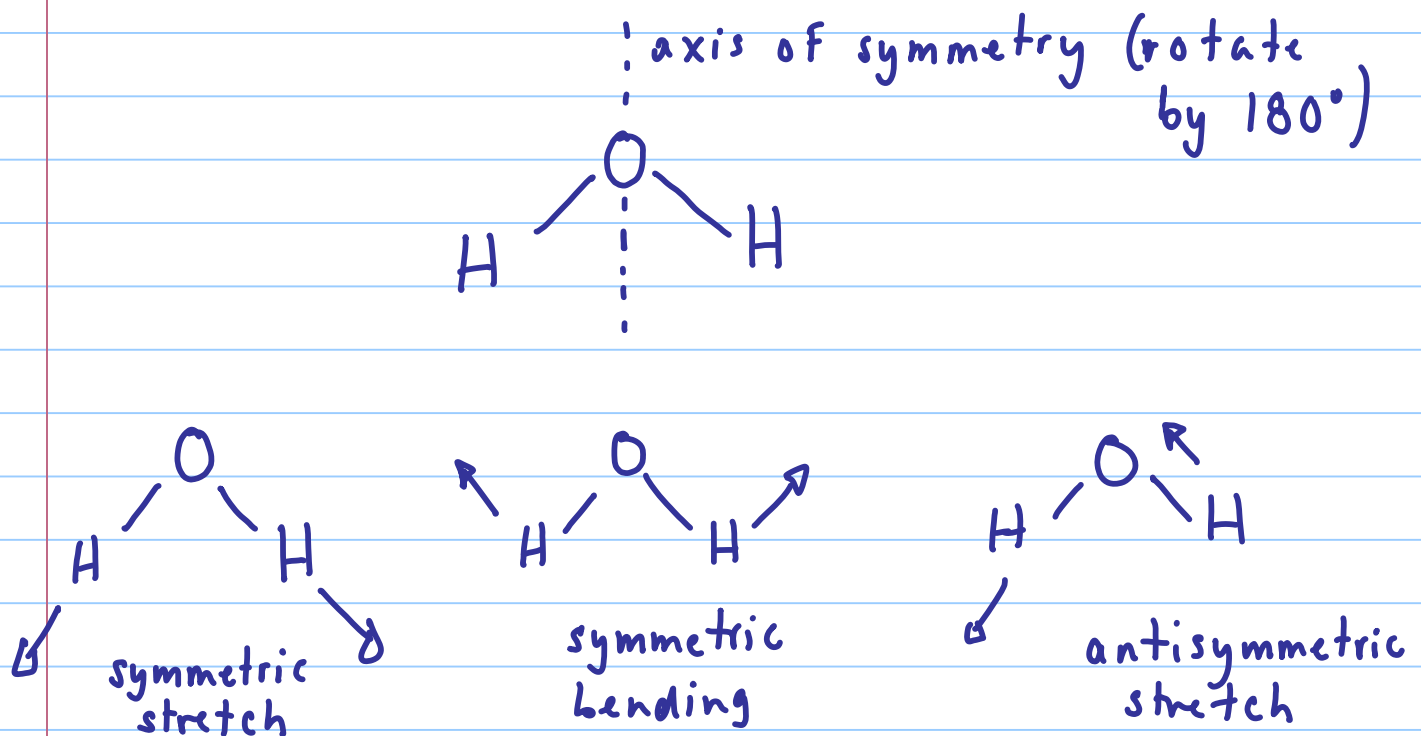
Two most common atmospheric molecules with vibration-rotation spectra are  $\text{H}_2\text{O}$  and  $\text{CO}_2$ .

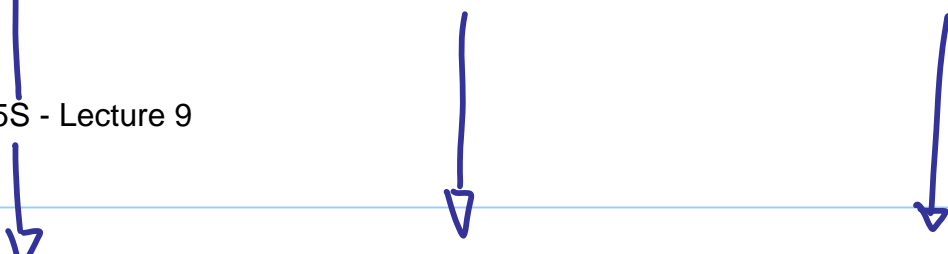
→ both have fundamental bands in the IR

e.g.  $\text{H}_2\text{O}$  @  $6.3 \mu\text{m}$   
 $\text{CO}_2$  @  $15 \mu\text{m}$

→ also have several overtone and combination bands

Three fundamental vibrations of  $\text{H}_2\text{O}$





$\nu_1$   
3615.7  $\text{cm}^{-1}$

$\nu_2$   
1595.0  $\text{cm}^{-1}$

$\nu_3$   
3755.8  $\text{cm}^{-1}$

These three vibrational motions are called the normal modes of vibration

→ motion in which the atoms move in phase and with the same frequency.

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## Width and Shape of Spectral Lines

Before considering the calculation of energy transfer in the atmosphere, we need to consider how the shape of a spectral line differs from the delta function assumed thus far.

The natural (very narrow) shape of a line is broadened by two processes:

- ① Doppler shifts
- ② collisions

## Line Shape Function

Because the strength of a transition is unchanged while the transition is spread



out over a small region of the spectrum, these two effects are separated

$$k_{\bar{\nu}} = S f_{\bar{\nu}} \quad \text{Sometimes written as}$$

$$k_{\bar{\nu}} = S f(\bar{\nu} - \bar{\nu}_0)$$

where

$k_{\bar{\nu}}$  = absorption coefficient

$S$  = line strength

$f_{\bar{\nu}}$  = lineshape function that contains all the frequency ( $\bar{\nu}$ ) dependence

In addition, the line strength is fixed for a given transition, so the total  $S f_{\bar{\nu}}$  over all  $\bar{\nu}$  must equal  $S$ :

$$\int_0^{\infty} f_{\bar{\nu}} d\bar{\nu} = 1 \quad \text{from} \quad \int_0^{\infty} S f_{\bar{\nu}} d\bar{\nu} = S$$

i.e. the lineshape function is normalized.

## Doppler Broadening

The non-relativistic Doppler shift of a molecule travelling along our line-of-sight with velocity  $V$

$$\bar{\nu} = \bar{\nu}_0 \left( 1 \pm \frac{V}{c} \right) \quad \therefore V = \frac{c}{\bar{\nu}_0} (\bar{\nu} - \bar{\nu}_0)$$

where  $\bar{\nu}_0$  = wavenumber of absorbed or emitted photon.

→ applies for reasonable atmospheric velocities  
 $\sim 300$  m/sec.

When considering large numbers of molecules, we must consider the probability of a molecule having velocity between  $V$  and  $V + dV$ .  
 → probability is given by the Boltzmann distribution

$$p(v) dV = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mV^2}{2kT}\right)$$

where

$m =$  molecular mass

Substitute  $V = c/\bar{\nu}_0 (\bar{\nu} - \bar{\nu}_0)$  to relate the number of molecules to the wavenumber:

$$f_{\bar{\nu}} \propto \exp\left(-\frac{mc^2(\bar{\nu} - \bar{\nu}_0)^2}{2kT\bar{\nu}_0^2}\right)$$

where the constants have been dropped because  $f_{\bar{\nu}}$  will be normalized.

Define line width parameter:  $\alpha_D = \frac{\bar{\nu}_0}{c} \sqrt{\frac{2kT}{m}}$

Then

$$f_{\bar{\nu}} \propto \exp\left[-\left(\frac{\bar{\nu} - \bar{\nu}_0}{\alpha_D}\right)^2\right]$$

Now normalize  $\int_0^{\infty} f_{\bar{z}} d\bar{z} = 1$  to get

$$f_{\bar{z}}^D = \frac{1}{\alpha_D \sqrt{\pi}} \exp \left[ - \left( \frac{\bar{z} - \bar{z}_0}{\alpha_D} \right)^2 \right] \text{ Doppler lineshape}$$

Note that the Doppler half-width is not  $\alpha_D$ !  
It is  $\alpha_D \sqrt{\ln 2}$ .

The Doppler "line width" is usually taken to be  $\alpha_D$  rather than the actual HWHM.