

Vibrational-Rotational Spectroscopy

Recommended Reading:

Banwell and McCash Section 3.2, 3.3

Atkins Section 16.12

Harmonic oscillator vibrations have the exact selection rule:

$$\Delta v = \pm 1$$

and the energy spacing is constant, the same for all energy levels:

$$\Delta \tilde{\nu} = G(v+1) - G(v) = \tilde{\nu}$$

This would give rise to very boring spectra, since the lines for all possible vibrational transitions would lie at the same energy (or wavenumber of frequency)

This does not occur for two reasons

1) No molecule is a perfect Harmonic Oscillator; as discussed before we must use an anharmonic potential as a better representation of the true molecular potential (e.g. Morse potential)

$$\Delta \tilde{\nu}_{n \rightarrow n+1} = G(n+1) - G(n) = \tilde{\nu}_0 - 2\tilde{\nu}_0 \chi_e (n+1)$$

so transitions shift to lower energy as n increases

2) Absorption or Emission of light **MUST** be accompanied by a change in angular momentum of the molecule because of the gain/loss of the photon's angular momentum.

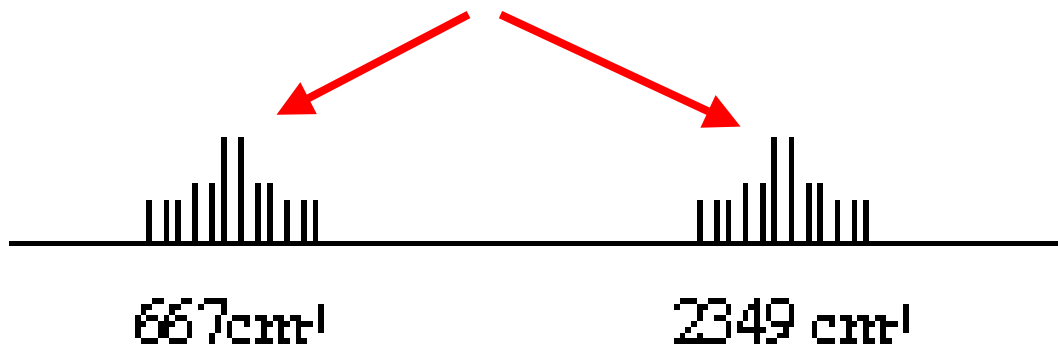
All vibrational spectra **MUST** be **Vibration-Rotation Spectra** and the rotational component for the transition must obey the usual rotational selection rule $\Delta J = \pm 1$.

IR spectrum of CO₂ In Solution: Low resolution, see two absorption bands



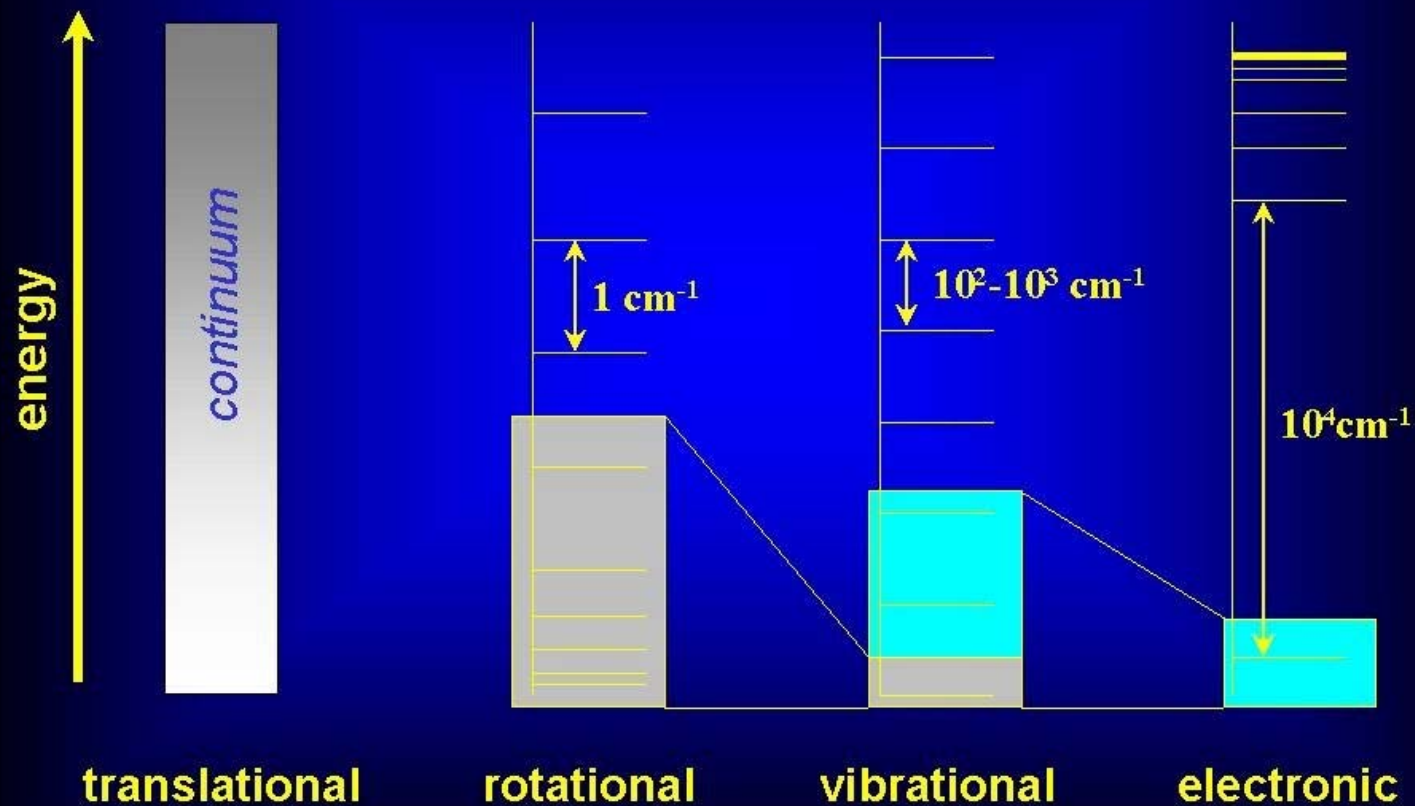
In Gas Phase: High resolution

Rotational fine structure



Relative energies of transitions

energy level separations



$$E_{\text{rot}} < E_{\text{vib}} < E_{\text{el}}$$

The Born-Oppenheimer Approximation

Typical **rotational energies** for a diatomic molecule are of the order of **1 to 10 cm⁻¹**, while the separation of the **vibrational energy levels** are typically **1000 to 5000 cm⁻¹**.

Since the energies of the two motions are so different we can assume, as a first approximation, that the rotational and vibrational motions of the diatomic molecule are independent of each other.

This is an example of the **Born-Oppenheimer approximation**, and is equivalent to assuming that the combined rotational-vibrational energy of the molecule is simply the sum of the separate energies.

$$E_{\text{total}} = E_{\text{rot}} + E_{\text{vib}} \text{ Joules} \quad \text{or} \quad \varepsilon_{\text{total}} = \varepsilon_{\text{rot}} + \varepsilon_{\text{vib}} \text{ cm}^{-1}$$

We have already derived expressions for the rotational and vibrational energies of the molecule

$$\varepsilon_{\text{rot}} = F(J) = BJ(J+1) + DJ^2(J+1)^2$$

and

$$\varepsilon_{\text{vib}} = G(n) = \left(n + \frac{1}{2}\right) \tilde{\nu} - \left(n + \frac{1}{2}\right)^2 \chi_e \tilde{\nu}$$

The Born-Oppenheimer Approximation

Another way to understand the Born-Oppenheimer Approx is to consider typical times involved in rotational and vibrational motions.

Rotational Motion:

Rotational Constants B are of the order of $1 - 100 \text{ cm}^{-1}$.

Taking $B = 1.0 \text{ cm}^{-1}$ gives

$I = 2.8 \times 10^{-47} \text{ kg.m}^2$ and $E(J = 1) = 3.97 \times 10^{-23} \text{ J}$.

Since $E = \frac{1}{2} I \omega^2$ this gives $\omega = 1.7 \times 10^{12} \text{ rad.s}^{-1} = 2.7 \times 10^{11} \text{ rot.s}^{-1}$.

Vibrational Motion:

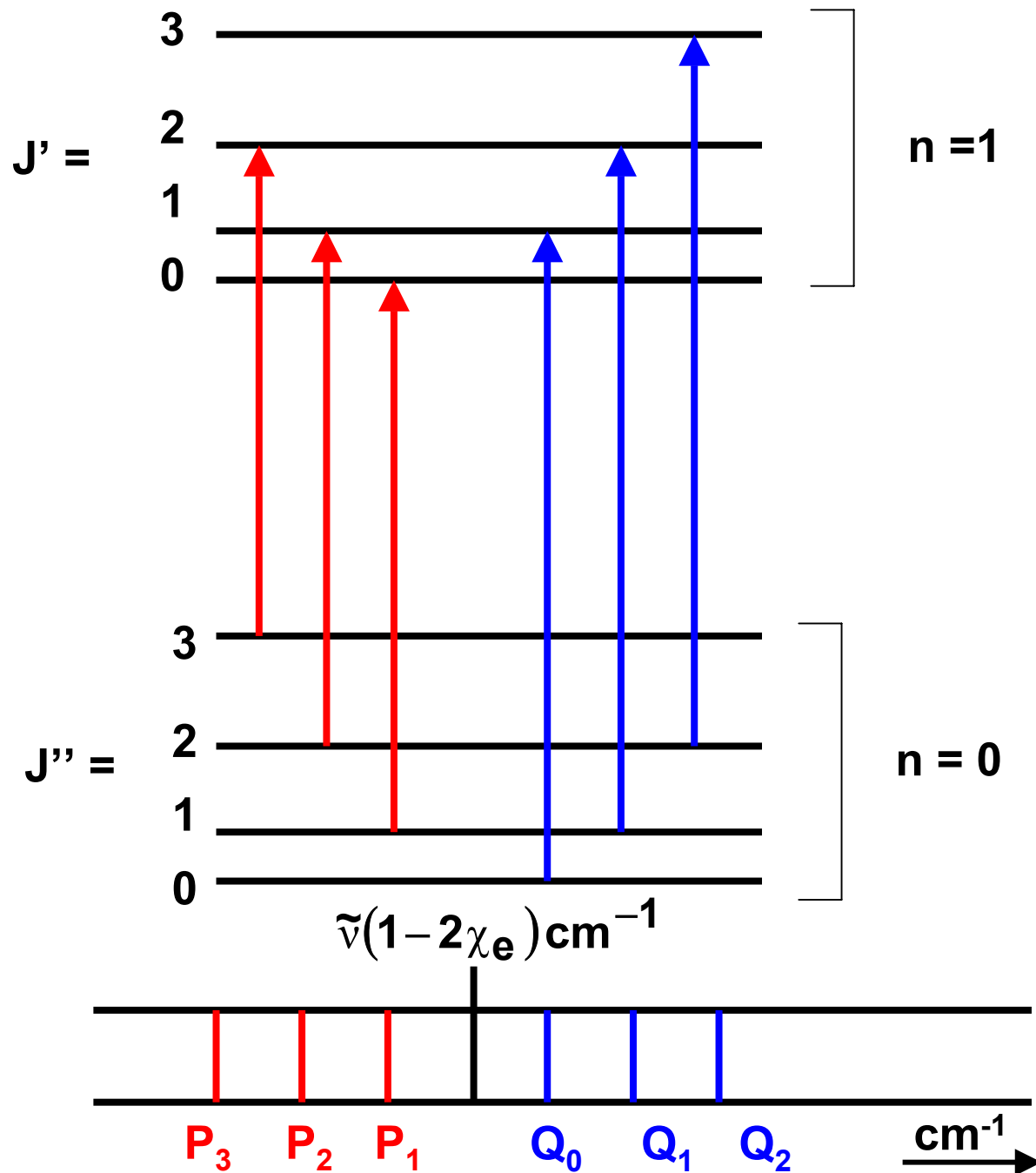
Vibrational energies are typically $500 - 5000 \text{ cm}^{-1}$. Taking 2000 cm^{-1} gives a vibrational frequency of $6.0 \times 10^{13} \text{ s}^{-1}$.

This shows that the rotational and vibrational motions take place on significantly different time scales, (the above example shows 222 vibrations occurring during a single rotation of the molecule).

So it is a good approximation to assume that these motions are decoupled and, to a first approximation, do not influence each other.

Energy level diagram of a diatomic molecule showing the $n = 0$ and $n = 1$ vibrational energy levels and associated rotational states.

Note this diagram is not to scale. - The vibrational states are typically $500 - 5000 \text{ cm}^{-1}$ apart while the rotational levels have typical separations of $1 - 100 \text{ cm}^{-1}$



Spectral Branches

The appearance of the vibration-rotation spectrum of a diatomic molecule can then be discussed in terms of the combined

vibration rotation term $S(n, J)$.

$$S(n, J) = G(n) + F(J)$$

If we ignore the centrifugal distortion then

$$S(n, J) = \left(n + \frac{1}{2}\right) \tilde{\nu} - \left(n + \frac{1}{2}\right)^2 \chi_e \tilde{\nu} + BJ(J+1)$$

vib. term + anharm term + rot. term

When a vibrational transition occurs $n \rightarrow n+1$ it must be accompanied by a change in the rotational state in order to conserve angular momentum so $J \rightarrow J \pm 1$ (Note that in some cases $\Delta J = 0$ is allowed)

The transitions then fall into three groups called **branches** of the spectrum. Designating the rotational quantum numbers in the $n = 0$ state as J'' and in the $n = 1$ state as J' then an analytical expression for the spectrum may be obtained by applying the selection rules to the energy levels. Considering the $n = 0$ to $n = 1$ transition:

$$\Delta \varepsilon_{J,v} = \varepsilon_{J',n=1} - \varepsilon_{J'',n=0} = \tilde{\nu}(1 - 2\chi_e) + B(J' - J'')(J' + J'' + 1) \text{ cm}^{-1}$$

P and R Spectral Branches

We now have **three** cases to consider $\Delta J = -1$, $\Delta J = +1$ and $\Delta J = 0$ which can occur in some molecules.

Case 1: P Branch, $\Delta J = -1$ that is $J'' = J' + 1$ or $J' - J'' = -1$; hence

$$\Delta \varepsilon_{J,n} = \tilde{\nu}(1 - 2\chi_e) - B(J' + 1) \text{ cm}^{-1} \quad J' = 0, 1, 2, K$$

This corresponds to a vibrational transition in which the rotational energy of the molecule decreases by one unit of angular momentum \Rightarrow spectral lines at $\tilde{\nu} - 2B$, $\tilde{\nu} - 4B$, $K \text{ cm}^{-1}$ with an intensity distribution reflecting (1) the population of the rotational levels and (2) the magnitude of the $J \rightarrow J-1$ transition moment

Case 2: R Branch, $\Delta J = +1$ that is $J' = J'' + 1$ or $J' - J'' = +1$; hence

$$\Delta \varepsilon_{J,n} = \tilde{\nu}(1 - 2\chi_e) + B(J'' + 1) \text{ cm}^{-1} \quad J'' = 0, 1, 2, K$$

This corresponds to a vibrational transition in which the rotational energy of the molecule decreases by one unit of angular momentum \Rightarrow spectral lines at $\tilde{\nu}(1 - 2\chi_e) + 2B$, $\tilde{\nu}(1 - 2\chi_e) + 4B$, $K \text{ cm}^{-1}$ again, with an intensity distribution reflecting (1) the population of the rotational levels and (2) the magnitude of the $J \rightarrow J+1$ transition moment.

These two expressions may be combined into a single expression

$$\Delta \varepsilon_{J,n} = \tilde{\nu}_{\text{spect}} = \tilde{\nu}(1 - 2\chi_e) + 2Bm \text{ cm}^{-1} \quad m = \pm 1, \pm 2, \pm 3, K$$

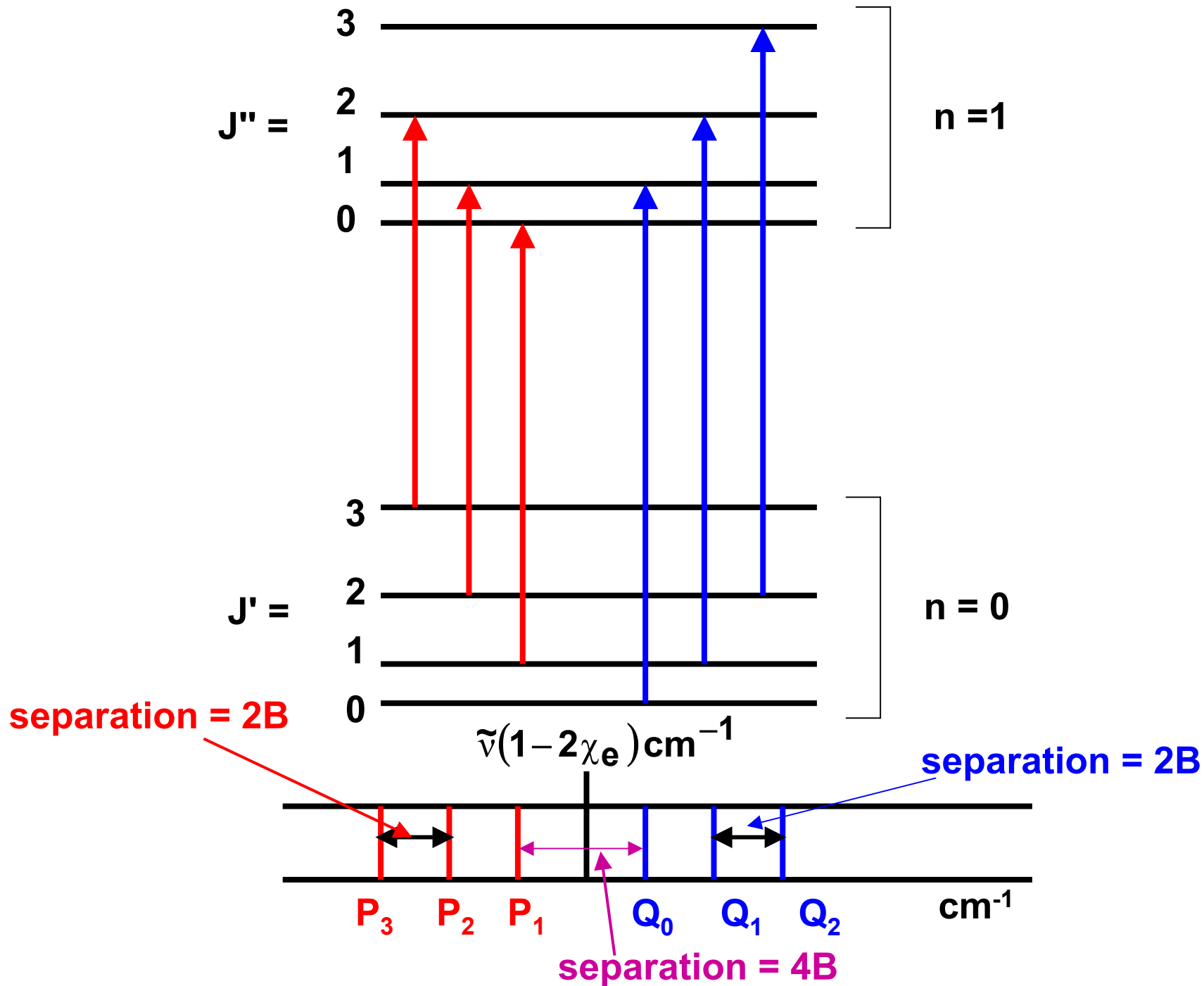
where positive values of m correspond to $\Delta J = +1$ transitions while negative values of m correspond to $\Delta J = -1$ transitions.

Case 3: Q Branch, $\Delta J = 0$ that is $J'' = J'$ or $J' - J'' = 0$; hence

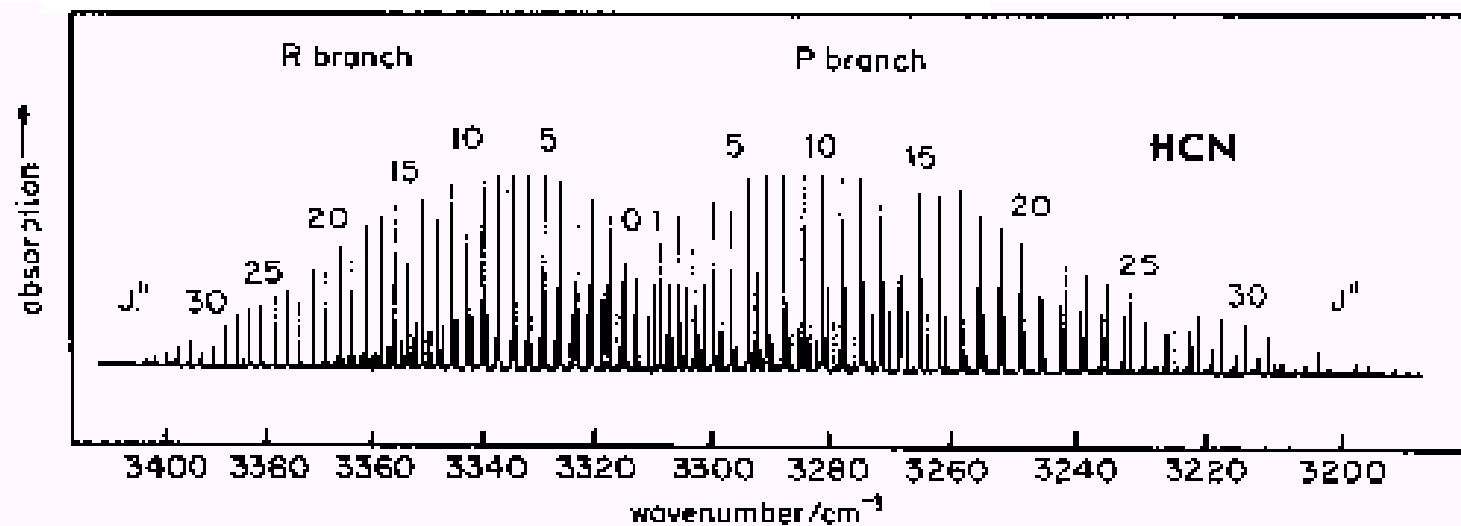
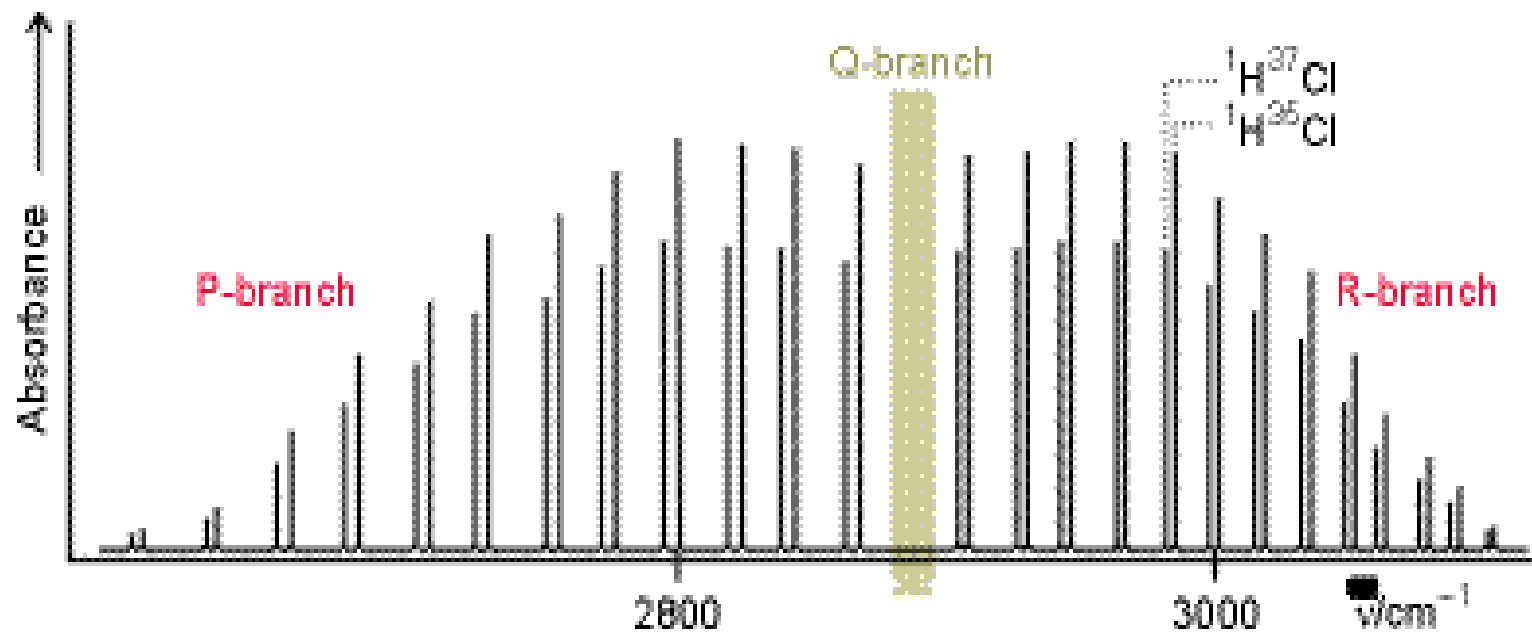
$$\Delta \varepsilon_{J,n} = \tilde{\nu}(1 - 2\chi_e) \text{ cm}^{-1}$$

The frequency $\nu_0 = \tilde{\nu}(1 - 2\chi_e)$ is the band origin or band centre

The Q-branch is usually not observed in diatomic molecules.

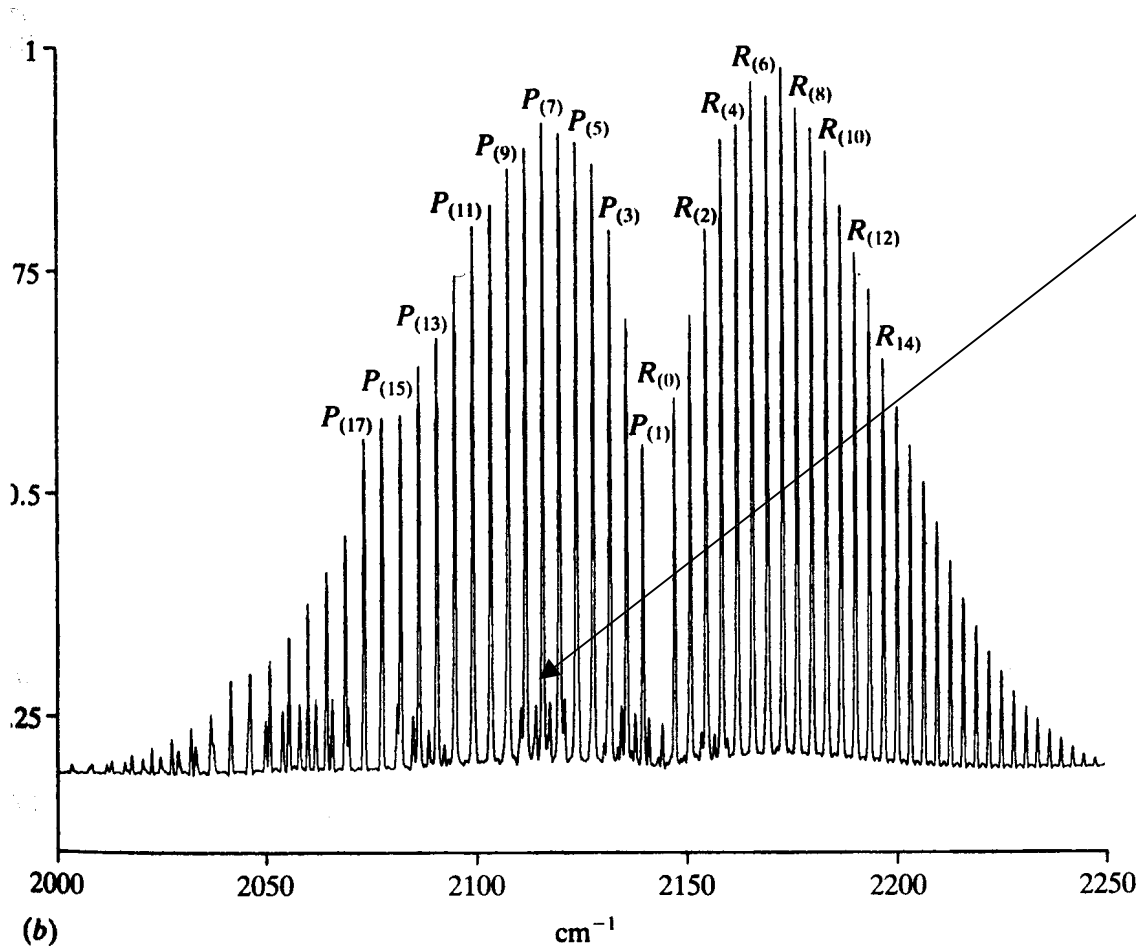


Vibration Rotation Spectra



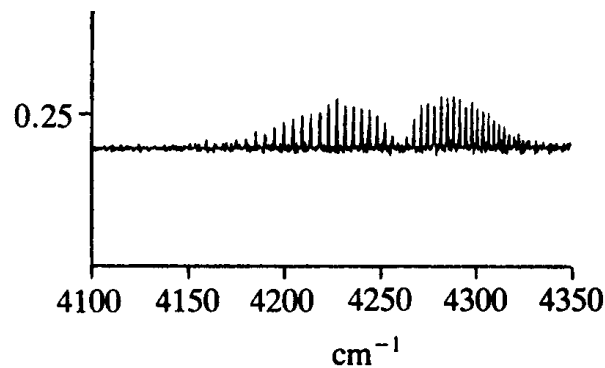
Vibration Rotation Spectrum of CO

Fundamental transition $\Delta n = 1$.

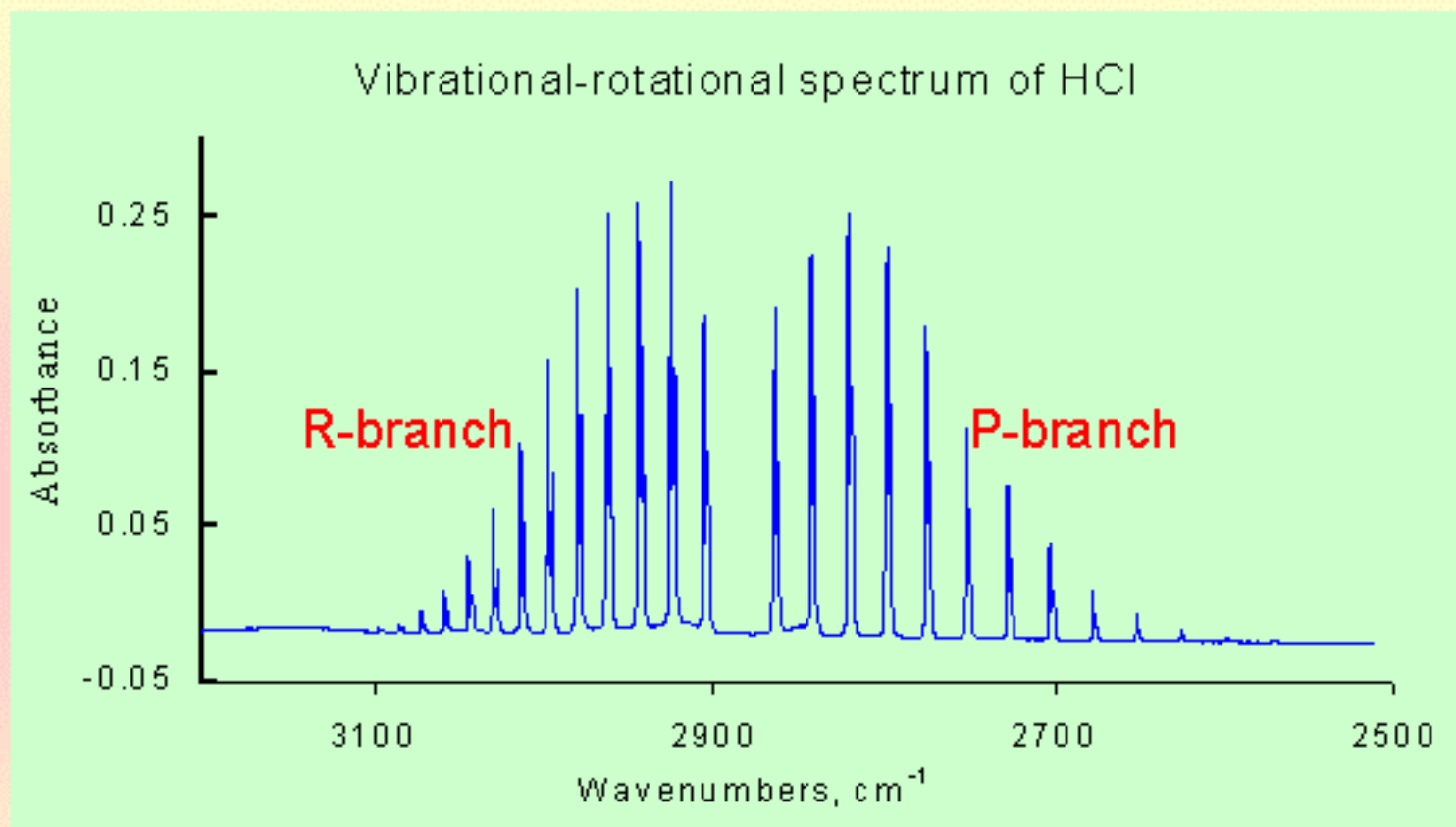


Note second band, centred at 2100 cm^{-1} due to the 1% of ^{13}CO .

First overtone $\Delta n = 2$.



Rotational Structure of the Fundamental Band



Note: Intensity of the lines follows the same pattern as for pure rotational spectra. Maximum population is observed at

$$J_{max} \approx \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

Vibration Rotation Spectrum of CO

Recall from Rotation Spectroscopy that the maximum population level occurs at a J value of

$$\sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$$

And since $m = J+1$ we see that at the maxima in the P and R branches

$$m = \pm \sqrt{\frac{kT}{2Bhc}} + \frac{1}{2}$$

The maximum intensity values are at

$$\tilde{\nu}_{\text{max.int}} = \tilde{\nu}(1-2\chi_e) \pm 2B \left(\sqrt{\frac{kT}{2Bhc}} + \frac{1}{2} \right)$$

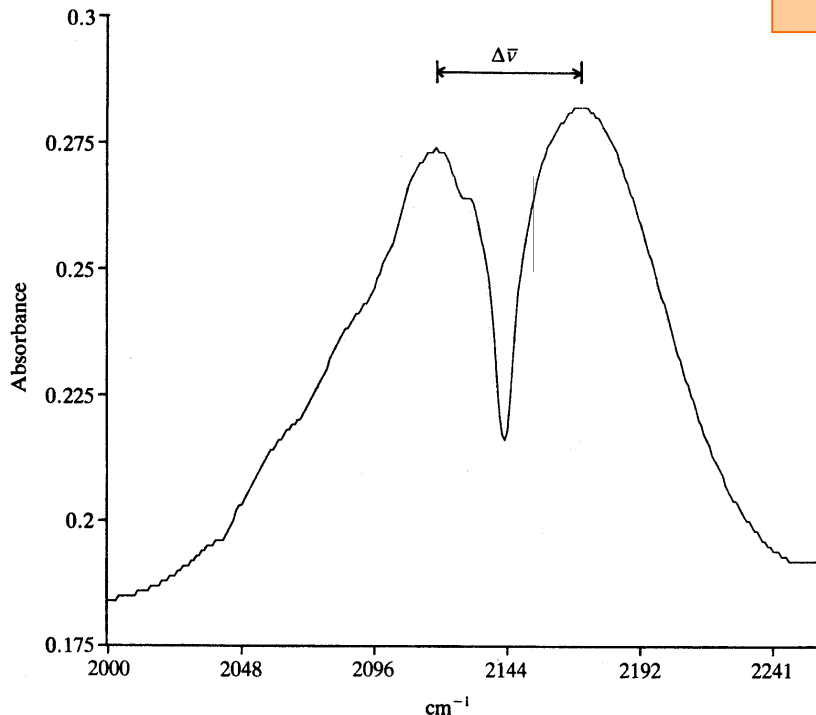
The separation between the maxima is:

$$\Delta\tilde{\nu} = \sqrt{\frac{8kTB}{hc}} + 2B$$

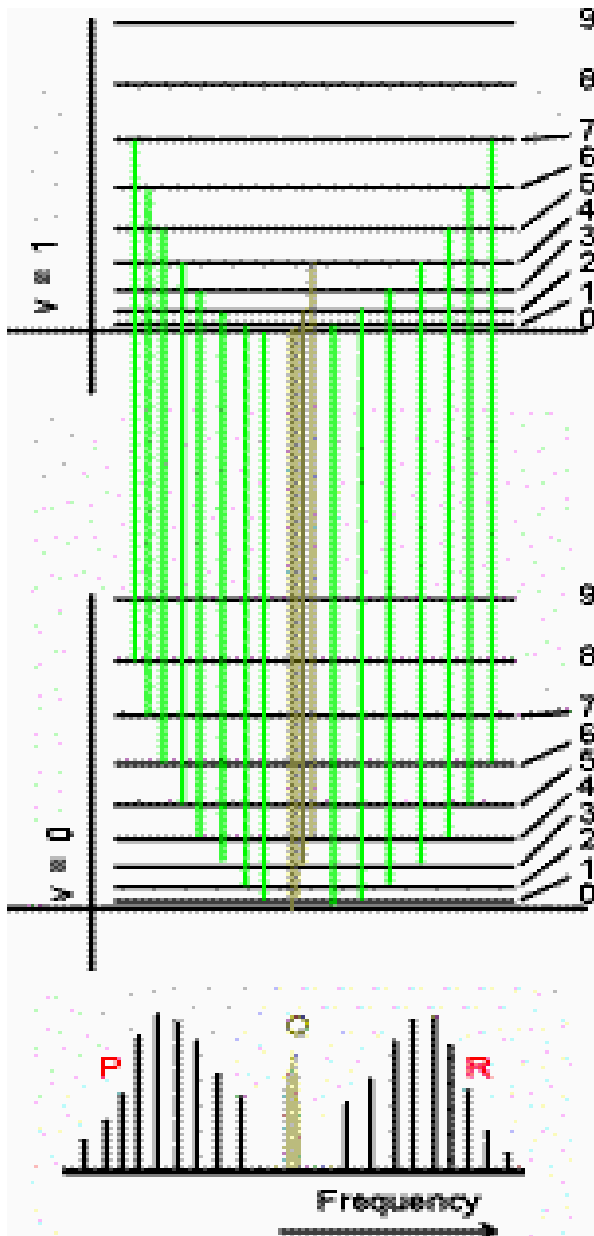
or since B is small compared with $\Delta\tilde{\nu}$ we can write

$$\Delta\tilde{\nu} = \sqrt{\frac{8kTB}{hc}} \Rightarrow B = \frac{hc(\Delta\tilde{\nu})^2}{8kT} \text{ cm}^{-1}$$

→ Can estimate rotational constant B from the vibrational spectrum.



Combination Differences



In general the rotational constant B_1 of a vibrationally excited state is slightly smaller than the rotational constant of the ground vibrational state B_0 , because the vibration causes a more extended bond in the upper state. As a result, in the anharmonic oscillator:

- (i) the Q band, if it exists, consists of a series of closely spaced lines
- (ii) the lines of the R branch converge slightly as J increases and
- (iii) those of the P branch diverge.

We can quantify this as follows:

The ground vibrational state $n = 0$, has a rotational constant B_0 and therefore its term values are

$$S(0, J) = \frac{\tilde{\nu}}{2} - \frac{\chi_e \tilde{\nu}}{4} + B_0 J(J+1)$$

The first excited vibrational state $n = 1$, has a rotational constant B_1 and its terms are

$$S(1, J) = \frac{3\tilde{\nu}}{2} - \frac{9\chi_e \tilde{\nu}}{4} + B_1 J(J+1)$$

The P-branch of the fundamental vibration now becomes

$$\tilde{\nu}_P(J) = S(1, J-1) - S(0, J) = \tilde{\nu}(1 - 2\chi_e) - (B_1 + B_0)J + (B_1 - B_0)J^2$$

Note that since B_0 is always greater than B_1 the last term will always be negative, showing that lines in the P-branch diverge as J increases.

Similarly, the R-branch of the fundamental vibration is

$$\tilde{\nu}_R(J) = S(1, J+1) - S(0, J) = \tilde{\nu}(1 - 2\chi_e) + (B_1 + B_0)(J+1) + (B_1 - B_0)(J+1)^2$$

Again because the last term is always negative, the lines in the R-branch will tend to converge as J increases

In molecules where the Q-branch exists, we find

$$\tilde{\nu}_Q(J) = S(1, J) - S(0, J) = \tilde{\nu}(1 - 2\chi_e) + (B_1 + B_0)J(J+1)$$

We can determine the rotational constants individually using the method of **Combination Differences**. A technique widely used in all branches of spectroscopy to determine information about a particular state.

It involves setting up expressions for the difference in wavenumbers of transitions to a common state.

From diagram we see that the transitions

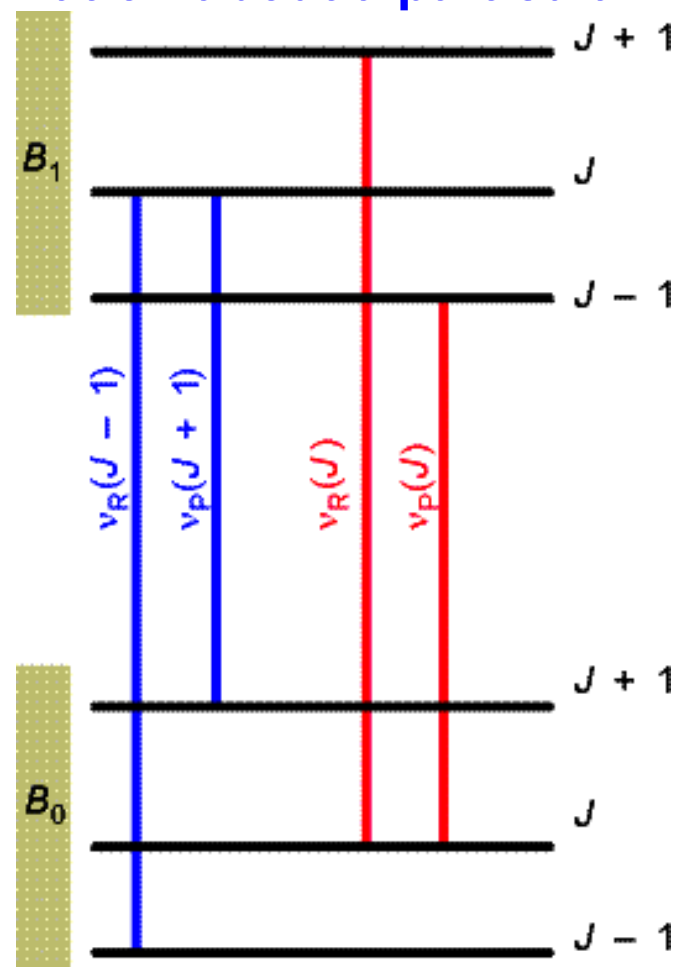
$$\tilde{\nu}_R(J-1)$$

and

$$\tilde{\nu}_P(J+1)$$

have a common upper state and from the above equations we see that

$$\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1) = 4B_0 \left(J + \frac{1}{2} \right)$$



Therefore a plot of the combination difference

$$\tilde{\nu}_R(J-1) - \tilde{\nu}_P(J+1) \quad \text{against} \quad J+1/2$$

should be a straight line of slope $4B_0$, so the rotational constant of the $n=0$ state can be determined. Any deviation from a straight line can be attributed to centrifugal distortion so it can also be investigated.

Similarly, we can look at transitions originating from a common ground state. For example

$$\tilde{\nu}_R(J)$$

and

$$\tilde{\nu}_P(J)$$

have a common lower state, their combination difference gives

$$\tilde{\nu}_R(J) - \tilde{\nu}_P(J) = 4B_1 \left(J + \frac{1}{2} \right)$$

A plot of this combination difference against $(J+1/2)$ gives a straight line of slope $4B_1$, so the rotational constant of the $n=1$ vibrational state can be determined.

When applied to the vib-rot spectra of $^1\text{H}^{35}\text{Cl}$ this technique gives $B_0 = 10.440 \text{ cm}^{-1}$ and $B_1 = 10.136 \text{ cm}^{-1}$.

