2301 Bonding and Spectroscopy

Classical Mechanics

Developed by Sir Issac Newton in the 17th century. It is suitable for explaining the motion of all known objects at the time.

The key equations of motion are

- Kinetic Energy = $\frac{1}{2} mv^2 = KE$
- Momentum = $mv = p$
- Total Energy = $KE + Potential Energy (PE)$
  
  $= \frac{1}{2} mv^2 + V$
  $= p^2/2m + V$

Wave Mechanics

The classical description of light was that it behaved as an ELECTROMAGNETIC WAVE which obeyed MAXWELL'S (1864) equations of wave theory in which the energy of the system could have any value.

$\nu (s^{-1}) = c/\lambda$

velocity 'c'
The number of waves per unit length = $1/\lambda = \nu$

usually given units of cm$^{-1}$ and called 'wavenumbers'

**DUAL NATURE OF LIGHT**

As more experiments were performed in the early 1900s a number of these were found to be at variance with the predictions of classical physics.

The most celebrated would be the BLACK BODY RADIATOR which classically predicted an ever-increasing output of energy on heating of a metal block. Experiment showed that this was not the case.

The classical approach assumed the energy of light could take any value.

But in 1900 PLANCK found that he could get agreement between theory and experiment if he assumed that only *certain* energies were allowed,

namely \[ E = n \hbar \nu \]  
where \( \hbar = 6.626 \times 10^{-34} \text{ Js} \) 
and is called Planck's Constant

The notion was that a ray of light could be thought of as

'n' particles (which we call PHOTONS) each having

\[
\text{Energy} = \hbar \nu
\]

but \( n = c/\lambda \)

and \( 1/\lambda = \nu \)
So we can write that

\[
\text{ENERGY (joules)} = h\nu = \frac{hc}{\lambda} = \frac{hc}{\nu}.
\]

For a particular frequency this is the **smallest** unit of energy possible.

The PARTICLE nature of light was reinforced by Einstein (1905) when he used Planck’s equation to explain the observations of the PHOTOELECTRIC EFFECT.

i.e. light shining on a metal surface in a vacuum can cause electrons to be ejected from the surface

\[
\text{Kinetic Energy of emitted electron = } h\nu - \phi
\]

where \( \phi \) is the work function of the metal surface

Einstein also suggested that light could transfer energy in the same way as particles do, thus PHOTONS which always travel at the velocity of light \( (c) \) must have an equivalent mass.

Hence he predicted \( \text{Energy} = mc^2 \)

but note that a **Photon** has **ZERO** rest mass
A further experiment by COMPTON in 1923 showed that when light strikes electrons it is scattered by them and at the same time the frequency of the light is changed.

Again, this could only be explained if light was behaving as a particle and momentum was being conserved in the scattering process.

It was quite clear at this stage that light could behave either as a

\[ \text{wave} \rightarrow \text{diffraction} \]

or as a

\[ \text{particle} \rightarrow \text{Photoelectric effect/ Compton effect} \]

(WITH mass)

WAVE NATURE OF PARTICLES

In the same year (1923) de Broglie (in his PhD thesis) postulated that ALL matter or particles must have some wave like characteristics and that the wavelength of these waves would be given by

\[ \lambda = \frac{h}{p} = \frac{h}{mv} = \frac{h}{\sqrt{2mE}} \]

since \( p = mv \) and \( E = \frac{1}{2}mv^2 \) \( \therefore p = \sqrt{2mE} \)

This was a bold postulate and the experimental proof that particles behave like waves was not forthcoming until 1927 when DAVISSON & GERMER showed that electrons impinging on a nickel crystal surface exhibited diffraction in the same way that BRAGG (1913) had observed the diffraction of X-Rays (photons) from a metal.
This is the Bragg equation where 'n' is an integer (0,1,2,3 etc)

**Test Question 1:** What is the momentum and energy of a photon with wavelength 1 \(\mu\)m?

\[
\lambda = 1 \times 10^{-6} \text{ m} \\
\rho = \frac{h}{\lambda} = \frac{6.626 \times 10^{-34}}{1 \times 10^{-6}} = 6.6 \times 10^{-28} \text{ kg m s}^{-1} \text{ or Ns}
\]

check units: \(\text{Js/m} = \text{kg m}^2 \text{s}^{-2} \text{s/m} = \text{kg m s}^{-1}\)

also \(\text{N} = \text{Jm}^{-1} = \text{kg m s}^{-2}\)

\[
E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 2.99 \times 10^8}{1 \times 10^{-6}} = 1.98 \times 10^{-19} \text{ J}
\]

**Test Question 2:** What is the momentum and energy of a methane molecule moving at 500 ms\(^{-1}\)?

Methane CH\(_4\)

\[
\text{MW} = 16 \quad \text{Mass of a molecule} = \frac{16 \times 10^{-3}}{6.022 \times 10^{23}} = 2.66 \times 10^{-26} \text{ kg}
\]

\[
\rho = \text{mv} = 2.66 \times 10^{-26} \times 500 = 1.33 \times 10^{-23} \text{ kg m s}^{-1} \text{ (Ns)}
\]

\[
E = \frac{1}{2} \text{mv}^2 = \frac{1}{2} \times 2.66 \times 10^{-26} \times 500^2 = 3.32 \times 10^{-21} \text{ J}
\]

another example over the page
Test Question 3: He-Ne laser ($\lambda = 632.8$ nm)

a) Note the wavelength and region of the spectrum

632.8 nm is in the red region of the electromagnetic spectrum and is in the visible region.

b) Calculate $\nu$ and $\nu = \frac{c}{\lambda} = \frac{2.99 \times 10^8}{632.8 \times 10^{-9}} = 4.7 \times 10^{14}$ s$^{-1}$

units are $\text{ms}^{-1} / \text{m} = \text{s}^{-1}$

$\nu = \frac{1}{\lambda} = 1/632.8 \times 10^{-9} \times 100 \text{ cm} = 15802 \text{ cm}^{-1}$

c) The laser is specified as producing a power of 2 mW (= energy of 2 mJ per second). How many photons per second are emitted?

$2 \text{ mW} = 2 \text{ mJs}^{-1} = 2 \times 10^{-3} \text{ Js}^{-1}$

$E = n \ h \nu$

$\therefore \ n = \frac{E}{h \nu} = \text{number of photons}$

$n = \frac{2 \times 10^{-3}}{6.626 \times 10^{-34} \times 4.7 \times 10^{14}} = 6.4 \times 10^{15} \text{ photons s}^{-1}$

check units

$\text{Js}^{-1} / \text{Js s}^{-1} = \text{s}^{-1}$

The Schrodinger Equation
De Broglie's suggestion that particles could exhibit a wave character led Schrodinger in 1926 to propose a new description of the atom in terms of waves rather than particles.

Schrodinger realised that the standing waves associated with vibrating strings and other objects were mathematically expressable by equations in which sets of integers necessarily and naturally appeared.

The classical concept of localised particles was abandoned and replaced with the idea that the position of a particle is distributed like the amplitude of a wave.

The concept of WAVE FUNCTION was introduced to replace classical concepts of trajectory.

Schrodinger proposed an equation which when solved gives the wave function of a system.

His equation is an inspired postulate.

ie. it can not be proved like F=ma

For a free particle to move in [1] dimension the equation is
\[
- \frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x) \Psi(x) = E \Psi(x)
\]

where

\[\Psi(x)\] is the wave function for [1]

\[V(x)\] is the potential energy of the particle at point \(x\)

\[E\] is the total energy (kinetic + potential)

\[\hbar\] is \(h/2\pi\)

This equation is often written as

\[\hat{H} \Psi(x) = E \Psi(x)\]

where \(\hat{H}\) is called the HAMILTONIAN OPERATOR and is

\[\hat{H} = \left[ - \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right]\]

Although the equation is a postulate its form can be readily justified as suitable.

Consider the case of a particle free to move in zero potential field.

\[V(x) = 0\]

thus the equation becomes

\[- \frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} = E(x)\]

this is a standard diff. equation whose solution is

\[\Psi(x) = e^{ikx} = \cos(kx) + i \sin(kx)\]

where \(k = \sqrt{\frac{2mE}{\hbar^2}}\)

since \(V(x)=0\) and \(E = p^2/2m = \text{kinetic energy}\)

we see that

\[p = k\hbar\]

Also \(\cos(kx)\) is a wave with wavelength \(\lambda = 2\pi/k\)
thus \[ k = \frac{2\pi}{\lambda} \]

and from above \[ p = k \hbar = \frac{2\pi}{\lambda} \cdot \hbar = \frac{h}{\lambda} \]

ie. \( p = \frac{h}{\lambda} \) which is just the de Broglie relationship which is proven experimentally.

**INTERPRETATION OF \( \Psi \)**

Based on a suggestion made by BORN (1926) using an analogy with wave theory of optics in which the square of the amplitude of an electromagnetic wave is interpreted as the intensity of the light.

Thus wavefunction \( \langle \Psi \rangle \) is the probability amplitude and \( \Psi^2 \) is the probability density.

[Strictly speaking we should use \( \Psi^* \Psi \) dx if \( \Psi \) is complex so that the probability is real
\[ (A+iB)(A-iB) = A^2 + B^2 \text{ since } i^2 = -1 \]

Thus \( \Psi^2(x) \) dx is the probability of finding the particle in the infinitesimally small region dx.

But over all space the probability must be 1

Thus

\[ \int_{-\infty}^{\infty} \Psi^*(x)\Psi(x)dx = 1 \]

Wave functions satisfying this condition are said to be NORMALIZED

This condition puts stringent requirements on the wavefunction and not all solutions of the Schrodinger equation will satisfy.

Thus not all energies will satisfy

**THIS LEADS TO QUANTIZATION OF THE ENERGY**

Furthermore, \( \Psi \) must be single valued.
The derivative $d\Psi/dx$ must be continuous. $\Psi$ can not be zero.

$\delta^2\Psi/\delta^2x$ must be well defined since Schrodinger eqn. is a $2^{nd}$ order differential equation.

We are now in a position to apply the equation to several problems provided we know the nature of the potential energy. We can then deduce the allowed values of the total energy.

The Schrodinger equation can be solved exactly for the following systems:

1. PARTICLE IN A [1] BOX – useful starting point for electronic transitions
2. HYDROGEN ATOM – leads to our notion of atomic orbitals
3. RIGID ROTOR – model for a rotating molecule
4. HARMONIC OSCILLATOR – model for a vibrating diatomic molecule

Let's start with a particle in a [1] box. Although it is only a hypothetical system it can be applied to real molecules and shows
how quantization of energy arises from the imposition of boundary conditions to atomic particles.

\[ V = \infty \quad V = \infty \]

inside the box \( V(x) = 0 \)

ie potential energy = 0

Between the walls we effectively have a free moving particle not influenced by any potential.

\( x=0 \quad x=L \)

We have already seen the solution for such a particle, \( V(x)=0 \)

\[- \frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} = E(x)\]

one solution is

\[ \Psi = e^{ikx} \quad \text{where} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \]

the general solution to this equation is

\[ \Psi = Ae^{ikx} + Be^{-ikx} \quad \text{and since} \quad \sin x = \frac{1}{2i}(e^{ix} - e^{-ix}) \quad \text{and} \quad \cos x = \frac{1}{2}(e^{ix} + e^{-ix}) \]

this can written as

\[ \Psi = A'\sin kx + B'\cos kx \quad \text{where} \quad k = \sqrt{\frac{2mE}{\hbar^2}} \]

Outside the box we have a potential energy to consider, \( V(x)=\infty \)

\[- \frac{\hbar^2}{2m} \frac{d^2\Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)\]

This can be rearranged to read

\[ \frac{d^2\Psi}{dx^2} = \frac{2m}{\hbar^2} (V - E)\Psi \]
In this particular model \( V(x) = \infty \) outside the box

Consequently if \( \Psi \neq 0 \) then \( \frac{d^2\Psi}{dx^2} = \infty \)

But the constraints that we placed on \( \Psi \) earlier were that it must be continuous, it must not be infinite and the second derivative must be well defined.

Thus the area outside the box does not present an acceptable solution since the second derivative is not well defined if it is infinite.

Therefore the alternative is that \( \Psi = 0 \) outside the box

This makes sense since \( \Psi^*\Psi = 0 \) which means the probability of finding the particle outside the box is zero.

Next we will consider what happens when we place further restrictions on the wavefunction inside the box.

**BOUNDARY CONDITIONS**

Because \( \Psi \) must be continuous then \( \Psi = 0 \) at the walls.

\[
\begin{align*}
\text{at } x=0 & \quad \Psi = A \sin kx + B \cos kx = 0 \quad \text{and} \\
\text{at } x=L & \quad \Psi = A \sin kx + B \cos kx = 0 \\
\text{at } x=0 & \quad 0 = A \sin 0 + B \cos 0 = 0 \\
& \quad 0 + B = 0 \quad \text{since } \cos 0 = 1 \\
& \quad \therefore B = 0 \\
\text{at } x=L & \quad \Psi = A \sin kL + 0 \quad \text{since } B \cos kL = 0 \\
\text{if } kL = 0 & \quad \text{then } \Psi = 0 \text{ everywhere which is unacceptable} \\
& \quad \therefore kL = n\pi \quad \text{where } n = 1, 2, 3 \text{ etc} \\
\text{hence } & \quad k = \frac{n\pi}{L} \text{ is a necessary condition for } \Psi \text{ to be acceptable}
\end{align*}
\]
This solution we call an EIGEN FUNCTION

\[ \Psi = A \sin \frac{n\pi x}{L} \]

since

\[ k = \sqrt{\frac{2mE}{\hbar^2}} \text{ then } E = \frac{k^2 \hbar^2}{2m} \text{ and } k = \frac{n\pi}{L} \text{ and } \hbar = \frac{h}{2\pi} \]

thus we get

\[ E = \frac{n^2 \hbar^2}{8mL^2} \]

these are called EIGEN VALUES where \( n = 1,2,3 \) etc

We still need to establish the value of A in the wave function.

NORMALIZATION

Each good wavefunction must satisfy the normalization condition that

\[ \int_{-\infty}^{\infty} \Psi \Psi^* dx = 1 \]

This integral can be broken into regions inside & outside the box

\[ \int = \int_{-\infty}^{0} + \int_{0}^{L} + \int_{L}^{\infty} \]

because \( \Psi = 0 \) outside the box

\[ \int_{0}^{L} \Psi \Psi^* dx = 1 \]

Thus

\[ \int_{0}^{L} A^2 \sin^2 \frac{n\pi x}{L} dx = 1 = A^2 \int_{0}^{L} \sin^2 \frac{n\pi x}{L} dx \]

using the standard integral

\[ \int \sin^2 ax \, dx = \frac{x}{2} - \frac{\sin 2ax}{4a} \]
we get that
	herefore we have the eigen function and the eigen values

\[ \Psi = A \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L} \]

\[ E = \frac{n^2 \hbar^2}{8mL^2} \]

for a particle in a [1] box.

Consider the form of the wavefunctions. When plotted they are similar to standing waves in a string of length L.

Each function has \((n-1)\) nodes

The greater the number of nodes the higher the energy

The zero point energy is the lowest possible energy which is

\[ E = \frac{\hbar^2}{8mL^2} \]

HEISENBERG’S UNCERTAINTY PRINCIPLE

Where is the particle inside the box? The momentum of the particle is well defined since

\[ p = \frac{2k\pi}{\hbar} \]  
but the position is not well defined

To define position the wavefunction must peak at that point.

This can only be achieved by the superposition of many waves of differing momenta.
Thus a **well defined position** can only be achieved at the **expense** of the knowledge of the **momentum**.

Heisenberg quantified this uncertainty by

\[ \Delta p \Delta x \geq \frac{\hbar}{4\pi} \quad \text{or} \quad \Delta E \Delta t \geq \frac{\hbar}{4\pi} \]

**Example:** Momentum of a dust particle weighing \(10^{-6}\) g whose position is known to \(10^{-3}\) mm.

\[ \Delta p = \frac{\hbar}{4\pi} \Delta x = \frac{6.626 \times 10^{-34}}{4\pi} \times 10^{-6} = 5.3 \times 10^{-29} \text{ kgms}^{-1} \]

\[ \Delta v = \Delta p/m = 5.3 \times 10^{-29}/10^{-9} = 5.3 \times 10^{-20} \text{ ms}^{-1} \] (ie stationary)

**CORRESPONDENCE PRINCIPLE**

As particles become bigger or the box becomes longer so the energy levels become more closely spaced

\[ \Delta E = E_{n+1} - E_n = [(n+1)^2 - n^2] \frac{\hbar^2}{8mL^2} = (2n+1) \frac{\hbar^2}{8mL^2} \]

Thus particles of **large mass** moving over **long distances** have energy levels so close as to be **continuous**. e.g. tennis ball etc

Particles for which \(8mL^2 \gg n^2\hbar^2\) \(\Delta E \rightarrow 0\)

and so **energies** are no longer **apparently** quantized. This is the case for macroscopic systems where the energy is continuous and classical mechanics becomes valid.

This is an example of the **Correspondence Principle**.

**ORTHOGONALITY of EIGENFUNCTIONS**

If any two wavefunctions are exact solutions of the S.E. then they are orthogonal

\[ \int_0^L \Psi_n \Psi_m dx = 0 \quad \text{where} \quad n \neq m \]

pictorially
area (+) = area (-)

\[ \hat{J} = 0 \]

the number of quantum numbers = number of dimensions

e.g. \[ E = \frac{\hbar^2}{8m} \sum \left[ \frac{n_1^2}{L_1^2} + \frac{n_2^2}{L_2^2} + \frac{n_3^2}{L_3^2} \right] \]

for a box of 3 sides \( L_1, L_2, L_3 \) in length

need a quantum number per dimension.

cf. \( n, l \) and \( m_l \) for the hydrogen atom

**Example problem:** \( \text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2 \) hexatriene

take C-C = 0.154 nm and C=C = 0.135 nm

Box length = \( 3 \times 0.135 + 2 \times 0.154 = 0.713 \text{ nm} \)

\[ E_n = n^2 \left( \frac{6.626 \times 10^{-34}}{8 \times 9.1 \times 10^{-31} \times (0.713 \times 10^{-9})^2} \right) \]

\[ = n^2 (1.19 \times 10^{-19}) \text{ J} \]

\[ = n^2 X \text{ where } X = 1.19 \times 10^{-19} \text{ J} \]

6 electrons to be accommodated in 3 levels, since 6 carbon atoms

Example of spectra using this model

Note how the bigger the box becomes the lower the energy of the transition becomes.
This model was used by Kodak to design dye with longer conjugated chains so that they would be red sensitive dyes. Finding a dye that would absorb red light was a hurdle to the initial production of colour film.

Lets now consider how one can measure the degree of absorption of light by these compounds.

Note how they all absorb different amounts of light.

The intensity of absorption is measured by the ratio of the light intensity striking the sample ($I_0$) to the light intensity transmitted by the sample ($I$)

This is quantified by the Beer-Lambert Law which states that for most concentration ranges (except extremely high concentrations)

$$\frac{I}{I_0} = 10^{-\varepsilon cl} \quad \text{or} \quad \text{Absorbance} = \log \frac{I_0}{I} = \varepsilon cl$$

where $\varepsilon = \text{molar extinction coefficient} \ (\text{cm}^{-1}\text{mol}^{-1}\text{L})$

$\varepsilon = \text{concentration of the solution} \ (\text{mol} \ \text{L}^{-1})$

$I = \text{path length of the cell} \ (\text{cm})$

Most experimental spectra are recorded as Absorbance versus wavelength

But since absorbance is a function of concentration and path length then it would be better to have a quantity which measures the intensity of a transition but is independent of path length and concentration.

This quantity is called the OSCILLATOR STRENGTH of the transition and is given the symbol $f$

This is defined by the expression

$$f = 4.33 \times 10^{-9} \int \varepsilon(\nu) \ d\nu$$

where the integral is the area under the spectral curve of $\varepsilon$ versus $\text{cm}^{-1}$. 
The constant out the front represents the inverse of the intensity of an idealised transition of one electron between two harmonic oscillator states

Consequently, a fully allowed transition should have an oscillator strength of

\[ f = 1 \]

whereas a forbidden transition made allowed possibly through a vibrational motion will have an

\[ f = 1.0 \times 10^{-3} \]

The intensity of a transition gives us some idea as to what type of electron is involved in the energy change and so helps with the identification of the molecule.

Note the difference between

\[ \text{ABSORBANCE} = \varepsilon \text{cl} \]

and

\[ \text{TRANSMITTANCE} = \frac{l}{l_0} \text{ and } \% \text{ Transmission} = \frac{l}{l_0} \times 100 \]

\[ \text{ABSORBANCE} = \log \frac{l_0}{l} \]

Beer-Lambert law is useful for measuring the concentration of air pollutants once the molar extinction coefficient of the pollutant is known.

**THE RIGID ROTOR as a model for a ROTATING MOLECULE**

and **THE HARMONIC OSCILLATOR as a model for a VIBRATING MOLECULE**

Another situation in which an exact solution of the Schrodinger equation can be found is the model of a rigid rotor which is initially a sound model for a rotating diatomic molecule.

Why do we want to be concerned with rotating molecules?

Molecules store energy and the way they do it is by absorbing rotational energy, vibrational energy, electronic energy and kinetic energy.
Spectroscopy allows us to explore the energy levels available for rotational, vibrational and electronic energy so it is important that we have a good understanding of how these levels arise.

The other situation for which an exact solution for the Schrödinger equation can be found is the HARMONIC OSCILLATOR.

This is the simplest possible model of a vibrating diatomic molecule.

**Two atoms connected by a Hooke's law spring (bond)**

Note: the particle in a box referred to electrons which hold a bond together

\[
\begin{align*}
\text{The potential energy } &= V(x) \\
&= \frac{1}{2} kx^2 \\
\text{where } x &= (r - r_e)
\end{align*}
\]

The S.E. for this system is

\[
-\frac{\hbar^2}{2m} \frac{d^2 \Psi}{dx^2} + \frac{1}{2} kx^2 \Psi = E \Psi
\]

but \(m_1\) and \(m_2\) may not always be the same so we use the REDUCED MASS (\(\mu\)) where

\[
\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} = \frac{m_1 + m_2}{m_1 m_2} \text{ or } \mu = \frac{m_1 m_2}{m_1 + m_2}
\]

The form of the potential energy is

if we make the following variable changes for ease of solution of the equation

\[
y = \frac{x}{\alpha} \quad \text{and} \quad \epsilon = \frac{2E}{\hbar \omega} \quad \text{where}
\]

\[
\alpha = \left(\frac{\hbar^2}{\mu k}\right)^{\frac{1}{2}} \quad \text{and} \quad \omega = \sqrt{\frac{k}{\mu}}
\]

The equation now takes the form

\[
\frac{d^2 \Psi}{dy^2} + (\epsilon - y^2) \Psi = 0
\]
This is HERMITE’S Equation with well known solutions

The ENERGY solutions are

\[ E(v) \text{ Joules} = (v + \frac{1}{2}) \hbar \nu \]

where \( \nu = \frac{1}{2} \pi \sqrt{k/\mu} \)

and \( v = 0, 1, 2, 3 \) etc

divide both sides by \( \hbar c \) lets us work in wavenumbers \( \text{cm}^{-1} \)

\[ G(v) \text{ cm}^{-1} = (v + \frac{1}{2}) \omega \]

where \( \omega \) is vibrational freq. in \( \text{cm}^{-1} \)

**IMPORTANT POINTS**

1. energy levels are equally spaced by \( \hbar \nu \) or \( \omega \)
2. the ZERO POINT energy is \( E_0 = \frac{1}{2} \hbar \nu \) or \( \frac{1}{2} \omega \)
3. the stronger the bond (higher \( k \)) the higher the frequency

\[ \omega \text{ (C-C)} = 700-1250 \text{ cm}^{-1} \]

\[ \omega \text{ (C=C)} = 1600-1700 \text{ cm}^{-1} \]

\[ \omega = \frac{1}{2} \pi c \sqrt{k/\mu} \]

4. heavier mass means lower frequency

\[ \omega \text{ (H-H)} = 4155 \text{ cm}^{-1} \]

\[ \omega \text{ (H-Cl)} = 2990 \text{ cm}^{-1} \]

let us now look at the form of the wavefunctions for this model

**WAVEFUNCTIONS**

The eigen functions for this S.E. look complicated but they are a standard mathematical form known as HERMITE POLYNOMIALS.

\[ \Psi_v = N_v H_v(y) e^{-\frac{y^2}{2}} \]

where \( N_v = \) normalization constant and \( H_v(y) \)

\[ \int_{-\infty}^{\infty} H_v H_{v'} e^{-\frac{y^2}{2}} dy = 0 \]  

\[ \int_0^\infty H_v y^{v-1} dy = \sqrt{\pi} \frac{\Gamma(v+1)}{\Gamma^2(v/2)} \]

\[ \frac{\Gamma}{2^{v-1} \sqrt{\pi}} \]

i.e. they are ORTHOGONAL.
which means that

\[ \Psi_v = N_v e^{-\frac{r^2}{2}} \]

which is a simple Gaussian shaped curve

**NOTE:**

1. This is totally *non-classical*. The highest probability is finding the molecule at \( r_e \) rather than at the turning points.

2. As \( v \to \infty \) the probability of finding the atoms of the molecule approaches the classical limit since the maxima of the wavefunctions tends towards the classical turning points. This is the CORRESPONDENCE PRINCIPLE again.

3. The ends of \( \Psi \) extend beyond the classical turning points meaning that there is a low but finite probability of finding the atoms beyond the turning points.

In reality a molecule only behaves as an harmonic oscillator at very low vibrational quantum numbers. Since atoms can not get too close without repulsion and the bond can not be stretched too far without breaking.

The potential energy used to describe this situation was put forward by MORSE and takes the form

\[ V(r) = D_e \left[ 1 - e^{-\beta(r-r_e)} \right]^2 \]

where \( V(r), D_e \) and \( w_e \) are in units of cm\(^{-1}\) and

\[ \beta = \omega_e \sqrt{\frac{2\pi^2 c \mu}{hD_e}} = 1.2177 \times 10^7 \omega_e \sqrt{\frac{\mu}{D_e}} \]

where \( \mu \) = atomic mass units, \((r - r_e)\) in cm\(^{-1}\)

- \( c = 2.998 \times 10^{10} \) cms\(^{-1}\)
- \( h = 6.626 \times 10^{-34} \) Js
When this form of the potential energy is substituted into the S.E. we get the following expression for the allowed energy levels.

\[ E(v) \text{ Joules} = (v + \frac{1}{2})\hbar \nu_e - (v + \frac{1}{2})^2 \hbar \nu_e x_e + (v + \frac{1}{2})^3 \hbar \nu_e y_e + \text{etc} \]

or expressed in cm\(^{-1}\) rather than joules

\[ G(v) \text{ cm}^{-1} = (v + \frac{1}{2})\omega_e - (v + \frac{1}{2})^2 \omega_e x_e + \ldots \ldots \]

The subscript 'e' stands for equilibrium. \(\omega_e\) or \(\nu_e\) are the frequencies of an infinitesimal displacement around this equilibrium position.

\(\omega_e x_e\) is usually referred to as the ANHARMONICITY CONSTANT

points to note:

- we usually round off the expression for the energy levels at the second term
- the energy levels of this model are not equally spaced but become closer together as energy increases and converge to a continuum of levels at the dissociation limit
- for \(r<r_e\) the curve is steeper than for a harmonic oscillator since the atoms of a real molecule begin to repel each other as they get closer
- for \(r>r_e\) the curve is shallower than the harmonic curve and ultimately has an asymptote at large \(r\) which represents the molecule dissociating into its individual atoms

\[ AB \rightarrow A + B \]

At dissociation the difference between successive energy levels is effectively zero.

\[ \Delta G(v) = 0 = G(v+1) - G(v) = (v+1.5)\omega_e - (V+1.5)^2 \omega_e x_e - [(v+0.5)\omega_e - (v+0.5)^2 \omega_e x_e] \]

\[ = \omega_e - 2(v+1)\omega_e x_e \]
since \( v \) is large at the dissociation limit we can ignore the 1

thus \( \nu_D = \omega_e/2\omega_e x_e \)

hence \( D_e = \omega_e \nu_D - \omega_e x_e \nu_D^2 \)

substitution yields

\[
D_e = \frac{\omega_e^2}{4\omega_e x_e}
\]

Note that this is the energy from the bottom of the potential well to the dissociation limit.

The dissociation energy that one would normally observe experimentally would be \( D_0 \) which is from the first vibrational level to the dissociation limit.

This is because a vibrating molecule can never be lower in energy than its zero point energy level (\( v=0 \))

hence the relationship between the two dissociation energies is

\[
D_e = D_0 + \text{zero point energy}
\]

\[
= D_0 + [0.5\omega_e - 0.25\omega_e x_e]
\]
VIBRATIONAL SPECTROSCOPY explored with IR spectroscopy

- a molecule can only absorb or emit light with energy corresponding to the difference between two energy levels.
  
  i.e. quantized energy levels

- light is an oscillating electric vector and it can only interact with other oscillating dipoles.

  \[
  \begin{align*}
  \text{H} & \text{— Cl} \\
  \text{H} & \text{— Cl} \quad \text{H} & \text{— H} \\
  \text{this would interact with IR radiation} & \text{no oscillating dipole} \\
  \text{no interaction} & \text{no interaction}
  \end{align*}
  \]

- solutions to the S.E. are such that there are restrictions placed on which transitions can take place. These are known as selection rules.

  Harmonic oscillator \( \Delta v = \pm 1 \)

  Anharmonic oscillator \( \Delta v = \pm 1, \pm 2, \pm 3 \) etc

We have different names for these types of transitions

**Fundamental** transition excites a molecule from its ZPE level into the \( v=1 \) level. This transition arise from the most populated level \( (v=0) \) and is usually the most intense transition in the spectrum.

**Overtone** transition excites a molecule from the highly populated \( v=0 \) level to \( v=2 \). It does not obey the Harmonic selection rule since \( \Delta v=2 \).

**Hot Band** transition arises from an excited vibrational level, eg. \( v=1 \rightarrow v=2 \). Because these excited vibrational states are not highly populated at normal temperatures they are usually weak.

Their intensity depends on the temperature of the sample.
SPECTRAL INTENSITY

For an harmonic oscillator we said that $\Delta v=1$ transitions are stronger than $\Delta v>1$.

Several factors influence how strongly a molecule will absorb light at different wavelengths.

The two most influential factors are

**BOLTZMANN FACTOR**  **LINESTRENGTH**

*Boltzmann population* defines the number of molecules that will be in a state with energy $E$ due to the thermal motions of the molecules at temperature $T$.

The function is given by

$$N(E) \propto e^{-\frac{E}{kT}}$$

At higher temperatures more higher energy levels will be populated.

Note: This is why most reactions are faster at higher temperatures.

Between any two levels $A$ and $B$ separated by $\Delta E$ we can write

$$\frac{N_A}{N_B} = e^{-\Delta E/kT}$$

where $\Delta E$ in cm$^{-1}$ and $k = 0.695$ cm$^{-1}$ K$^{-1}$ molecule$^{-1}$

**Linestrength** A quantative description of the factors affecting linestrength is beyond this course but we can consider two criteria qualitatively

- the size of the oscillating dipole will affect the strength of the absorption
consider the three polar molecules

\[ \text{HCl} > \text{HBr} > \text{HI} \]
dipole moments are 1.04 0.78 0.44 Debye

The absorption intensity goes in the same order as their dipole moments. Although they are permanent dipoles they are still oscillating when the molecule is vibrating.

• the other influence is the quantum mechanical selection rules which affect the intensity of absorption.

For molecules behaving close to HARMONIC

\[ v=0 \rightarrow v=1 \quad >>> \quad v=0 \rightarrow v=2 \]

For ANHARMONIC type molecules: HCl is anharmonic in its ZPE

the transition intensity falls by roughly a factor of 10 for every increase in $\Delta v$.

<table>
<thead>
<tr>
<th>relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v=0 \rightarrow v=1$</td>
</tr>
<tr>
<td>$v=0 \rightarrow v=2$</td>
</tr>
<tr>
<td>$v=0 \rightarrow v=3$</td>
</tr>
</tbody>
</table>

we can therefore write an expression for the intensity of a transition as

\[ I(E'' \rightarrow E') = C \times N(E'') = C \times e^{-E''/kT} \]

Constant C includes the factors discussed above and the exponential term is the population of the state from which the transition originates
PHYSICAL PROPERTIES from VIBRATIONAL SPECTRA

The objective of spectroscopy is to make measurements of fundamental chemical properties. Spectroscopy allows to do this on a molecular level and subsequently gives us the ammunition to calculate macromolecular thermodynamic properties of these molecules. It also allows us to identify molecules in the atmosphere using infrared spectroscopy.

Vibrational spectra → $\omega$ → $k$ (force constant of bonds)
→ $\omega_e$, $\omega_e \chi_e$ (anharmonicity)
→ $D_e$, $D_0$ (dissociation energies)

Consider the following example

**CH radicals are important intermediates in the combustion of hydrocarbons. CH radicals absorb strongly at 2734 cm$^{-1}$ and weakly at 5340 cm$^{-1}$.**

Calculate:

i) the equilibrium vib. freq., $\omega_e$, in cm$^{-1}$
ii) the anharmonicity constant, $\omega_e \chi_e$
iii) the force constant, $k$
iv) the dissociation energy, $D_e$ and $D_0$

Note that the overtone 5340 (0→2) is not exactly 2 x 2734 (0→1) because the molecule is anharmonic

$G(v) = (v+0.5)\omega_e - (v+0.5)^2 \omega_e \chi_e$

$G(1) - G(0) = 2734 = (1.5\omega_e - 2.25\omega_e \chi_e) - (0.5\omega_e - 0.25\omega_e \chi_e)$

$2734 = \omega_e - 2\omega_e \chi_e$ \hspace{1cm} eqn.1

$G(2) - G(0) = 5340 = (2.5\omega_e - 6.25\omega_e \chi_e) - (0.5\omega_e - 0.25\omega_e \chi_e)$

$5340 = 2\omega_e - 6\omega_e \chi_e$ \hspace{1cm} eqn.2

Multiply eqn 1 x 2 and subtract eqn 2

$\omega_e \chi_e = 64$ cm$^{-1}$

Substitute $\omega_e$ into eqn 1 to get $\omega_e = 2862$ cm$^{-1}$

The molecule is very anharmonic even at v=0
The value of \(k\) is given by

\[\omega_e = \frac{1}{2\pi c} \sqrt{k/\mu}\]

thus

\[k = 4 \pi^2 c^2 \mu \omega_e^2\]

\[= 4 \pi^2 (2.998 \times 10^{10})^2 \times (\frac{12/13 \times 10^{-3}}{6.022 \times 10^{23}}) \times 2862^2\]

\[= 446 \text{ kg s}^{-2}\]

\[= 446 \text{ N m}^{-1}\]

The value of \(D_e\) and \(D_0\) given by

\[D_e = \frac{\omega_e^2}{4} \omega_e x_e = 2862^2/4 \times 64 = 31996 \text{ cm}^{-1}\]

\[D_0 = D_e - G(0) = 31996 - [0.5 \times 2862 - 0.25 \times 64]\]

\[= 30581 \text{ cm}^{-1}\]

The experimentally observed \(D_0\) is 27760 cm\(^{-1}\)

The difference is due to the fact that we have neglected the terms in \(\omega_e y_e\) and \(\omega_e z_e\)

**Example**  Show that for HCl at 300K we are justified in neglecting the v=1 \(\rightarrow\) v=2 transition in comparison to the v=0 \(\rightarrow\) v=1 transition whose energy = 2885 cm\(^{-1}\) and assume C is approximately the same for these transitions.

\[I (v=0) \propto N (v=0)\]

\[I (v=1) \propto N (v=1)\]

\[I (v) = Ce^{-E/kT} = Ce^{-G(v)/kT}\]

If we just use the Harmonic limit

\[G(0) = 0.5 \omega_e = 1442.5 \text{ cm}^{-1}\]

\[G(1) = 1.5 \omega_e = 4327.5 \text{ cm}^{-1}\]

thus

\[I(0) = C e^{-1442.5/0.695\times300} = C \times 0.0010\]
\[ I(1) = C e^{\frac{4327.5}{0.695 \times 300}} = C \times 9.7 \times 10^{-10} \]

therefore \[ \frac{I(1)}{I(0)} = \frac{9.7 \times 10^{-10}}{1.0 \times 10^{-3}} = 9.7 \times 10^{-7} \]

i.e. the \( v=1 \) to \( v=2 \) transition is \( 10^{-6} \) times weaker than the \( v=0 \) to \( v=1 \) transition

An alternative approach is to just say what is the population of level \( v=1 \) compared to level \( v=0 \) since the intensity of the transition is going to depend on the number of molecules in the lower state from which the transition arises

this will be given by

\[ \frac{N_1}{N_0} = e^{-\frac{\Delta E}{kT}} = e^{\frac{-2885}{0.695 \times 300}} = 9.7 \times 10^{-7} \]

which is the same as above.
POLYATOMIC VIBRATIONS

Degrees of Freedom

All particles have three degrees of freedom (i.e. motion along the x, y, z directions)

A molecule with N atoms will therefore have 3N total degrees of freedom.

But remember that

3 of these are translational which involves the motion of the whole molecule in the x, y or z direction

3 of these are rotational which involves rotation of the whole molecule about its centre of mass around either of the x, y or z axes.

Thus the vibrations must be 3N-6 for a non linear molecule

For a linear molecule the rotation about the internuclear axis has no measurable angular momentum and so a linear molecule has only 2 rotational degrees of freedom

Hence 3N-5 vibrational degrees of freedom

Triatomic Molecules

Let us consider molecules with more than 2 atoms

Triatomic molecules can be either linear: CO₂, OCS, N₂O
BENT: H₂O, NO₂, O₃

If we follow our rules above then
the LINEAR molecules will have 4 different vibrations and BENT molecules will have 3 different vibrations

Examples are CO$_2$ and SO$_2$

The strength of absorption of infrared radiation depends on the same factors that you have been told about for diatomic molecules,

namely;

the size of the oscillating dipole (note the symmetric stretch of CO$_2$ is not IR active but the rest are)

selection rule is $\Delta V = 1 > \Delta V = 2$ etc

Boltzmann population of the absorbing level

This brings us to how we should label the various transitions to these vibrational levels
NOMENCLATURE

Because we are now dealing with molecules that have more than one mode of vibration we will observe more than one band in the infrared spectrum.

NOTE: in the case of CO₂ where two vibrational frequencies are degenerate we only observe one line in the infrared spectrum corresponding to these two vibrations (667 cm⁻¹).

We therefore need a way of distinguishing which vibration we are referring to.

To do this we use subscripts on the frequencies ν, wavenumbers ω, quantum numbers V.

e.g. SO₂  1 = Symmetric stretch
      2 = Bend motion (which is symmetric)
      3 = Asymmetric stretch

Thus ν₁, ω₁ and V₁ all refer to the symmetric stretch of SO₂.

As was the case with diatomic molecules, various transitions are also possible in triatomic molecules.

e.g.  
(0,0,0) → (0,0,1)

is a fundamental transition involving ν₃.

These transitions will be the strongest transitions in the molecule.

(0,0,0) → (1,0,0)

is a fundamental in ν₁.
(0,0,0) $\rightarrow$ (0,2,0) will be an overtone involving $\nu_2$

Overtone bands will be weak

(0,0,1) $\rightarrow$ (0,0,2) will be a HOT BAND involving $\nu_3$

The intensity of these bands will depend on the temperature since temperature will control the population of level $v=1$

Because the molecule has more than one vibrational frequency we have a new type of transition that can occur.

**COMBINATION BAND** (0,0,0) $\rightarrow$ (0,1,1)

This transition involves the combination of one quantum of $\nu_2$ plus one quantum of $\nu_3$ and will occur at a frequency of $(\nu_2 + \nu_3)$ in the infrared spectrum

The molecule oscillates with two vibrations simultaneously

The intensity will be similar to that of an overtone band

Examples of these features can be seen in the following spectra except that hot bands are not often observed in most spectra.
POLYATOMIC MOLECULES

This leads us to discuss molecules which have more than 3 atoms.

- As N increases so does the number of vibrations \((3N-6)\) or \((3N-5)\)

- Once the number of atoms increases the vibrations can no longer be written down by inspection but instead we need to calculate them

- For example, Benzene has 12 atoms and therefore will have \((3N-6) = 30\) vibrations

- The infrared spectrum very quickly becomes quite complicated

However, each molecule has its own distinct IR spectrum and the region that contains the main skeletal vibrations of the molecule is termed the FINGER PRINT region of the spectrum and covers the region \(700-1400\ \text{cm}^{-1}\)

![Chemical structures](image.png)

whereas the peripheral groups in the molecule have distinctive vibrational frequencies which vary from group to group and are very much independent of where in the molecule they are attached.

These are called GROUP FREQUENCIES and usually fall outside the skeletal region and may be higher or lower in frequency but they are quite characteristic of the group’s presence in the molecule.

The FINGER PRINT region of the infrared spectrum can be used to identify large organic molecules by establishing a known library of such compounds.
GROUP FREQUENCIES

On the other hand, we find that group frequencies are usually almost independent of the structure of the molecule as a whole and, with a few exceptions, fall in the regions well above and well below that of the skeletal modes.

There are far more comprehensive tables of these frequencies but a reasonable selection is provided in the following table.

Notice that vibrations of light atoms in terminal groups e.g. -CH₃, -OH, -CN, -CO are of high frequency, while those of heavy atoms e.g. -CCI, -CBr are low frequency

<table>
<thead>
<tr>
<th>Group</th>
<th>Approximate Frequency (cm⁻¹)</th>
<th>Group</th>
<th>Approximate Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH</td>
<td>3600</td>
<td>&gt;C=O</td>
<td>1750–1600</td>
</tr>
<tr>
<td>-NH₂</td>
<td>3400</td>
<td>&gt;C=C&lt;</td>
<td>1650</td>
</tr>
<tr>
<td>≡CH</td>
<td>3300</td>
<td>&gt;C=N&lt;</td>
<td>1600</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt;C=C&lt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3060</td>
<td>&gt;C=N&lt;</td>
<td>1200–1000</td>
</tr>
<tr>
<td>≡CH₂</td>
<td>3030</td>
<td>&gt;C=S</td>
<td>1100</td>
</tr>
<tr>
<td>-CH₃</td>
<td>2970 (asym. stretch)</td>
<td>&gt;C=F</td>
<td>1050</td>
</tr>
<tr>
<td></td>
<td>2870 (sym. stretch)</td>
<td>&gt;C=Cl</td>
<td>725</td>
</tr>
<tr>
<td></td>
<td>1460 (asym. deform.)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1375 (sym. deform.)</td>
<td>&gt;C=Br</td>
<td>650</td>
</tr>
<tr>
<td>-CH₂</td>
<td>2930 (asym. stretch)</td>
<td>&gt;C—I</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>2860 (sym. stretch)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1470 (deformation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-SH</td>
<td>2580</td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡N≡N</td>
<td>2250</td>
<td></td>
<td></td>
</tr>
<tr>
<td>≡N≡C</td>
<td>2220</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Their frequencies and consequently their spectra are highly characteristic of the group and can therefore be used for analysis.
A change of physical state may cause a shift in frequency particularly if the molecule is rather polar

In general the more condensed phase has a lower frequency

\[ \nu_{\text{gas}} > \nu_{\text{liquid}} \approx \nu_{\text{solution}} > \nu_{\text{solid}} \]

Thus in the relatively polar molecule like HCl there is a shift of 100 cm\(^{-1}\)
in going from vapour to liquid and a further decrease of 20 cm\(^{-1}\)
on solidification

The form of the spectrum can change quite markedly in going from solution to vapour. In smaller molecules the rotational envelope of the vibrational bands is partially resolved in the vapour and the bands become far sharper in the absence of solute/solute and solute/solvent interactions.

This can be clearly seen in the spectra of methyl iodide in liquid and vapour.

As well as the difference in the sharpness of the spectrum one can see that there is a little shift in the frequency of some bands suggesting that the molecule does possess a very large dipole moment.
\[ \text{CH}_3\text{I} = 5.4 \times 10^{-30} \text{ C m} \quad \text{c.f.} \quad \text{HCl} = 3.6 \times 10^{-30} \text{ C m} \]

but the rotational structure makes it difficult to pin point the actual origin of each band system

Note the presence of \textit{overtone} and \textit{combination} bands in this spectrum.

While we are talking about methyl iodide spectrum it is worthwhile to look at \textbf{the form of the vibrations} for this molecule.

The molecule has \(3N-6 = 9\) vibrations of which we can see all but one \((\nu_3)\) in the spectrum but it is possible to see \(2\nu_3\) weakly.

The form of the individual vibrational motions must be got by calculation using

what is known as a \textbf{NORMAL CO-ORDINATE ANALYSIS}
Note that only 6 bands appear in the spectrum although there are 9 in total.
This is because 3 vibrations are doubly degenerate and so only 1 band appears for each pair of vibrations.

**ROTATIONAL SPECTRA**

We have just been talking about rotational effects on vibrational spectra. We should now spend some time looking at how molecules can store rotational energy.

In the same way that we started with a harmonic oscillator model of a vibrating molecule and then moved to a more realistic model so also can we start with what we call a RIGID ROTOR as a model of a rotating molecule.
The classical energy of rotation is

\[ E_{\text{rotational}} = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2 \]

where \( I_i \) is the moment of inertia about the \( i^{\text{th}} \) axis

\( \omega_i \) is the angular velocity of rotation about \( i^{\text{th}} \) axis in (radians s\(^{-1}\))

For a diatomic molecule

\[ I = I_x = I_y = m_1 r_1^2 + m_2 r_2^2 \]

\[ I_z = 0 \]

Taking moments about the centre of mass gives

\[ m_1 r_1 = m_2 r_2 \quad r_1 = \frac{m_2 r_2}{m_1} \] and add

\[ m_2 r_1/m_1 \] to both sides

\[ \text{gives } r_1 = \frac{m_2 R}{(m_1+m_2)} \]

\[ r_1 = \frac{m_2 R}{(m_1+m_2)} \] and \( r_2 = \frac{m_1 R}{(m_1+m_2)} \)

therefore \( I = m_1 m_2 R^2/(m_1+m_2) = \mu R^2 \)

where \( \mu \) is the REDUCED MASS of the molecule

Such a rotational motion has no potential energy and \( V=0 \)

The S.E. is now solved as a three dimensional equation with zero potential energy which has solutions identical to the hydrogen atom minus the redial part of the wavefunction.

The most important part are the allowed energy levels for this system which turn out to be

\[ E_{\text{rot}} = J(J+1) \frac{\hbar^2}{8\pi^2} \mu R^2 \]

where \( J \) is the rotational quantum number with values 0,1,2,3 etc

The big difference now is that each rotational energy level is \( 2J+1 \) fold degenerate where vibrational levels are generally non-degenerate.
When considering the spectroscopy of rotating molecules it is more convenient to work in cm\(^{-1}\).

Thus \(E_{\text{rot}} \, (\text{cm}^{-1}) = BJ(J+1)\) where \(B \, (\text{cm}^{-1}) = \frac{\hbar}{8\pi^2 c I}\)

and \(I = \frac{\mu R^2}{\hbar}\)

Each level is \(2J+1\) fold degenerate

<table>
<thead>
<tr>
<th>Q.No.</th>
<th>Energy</th>
<th>Relative population</th>
</tr>
</thead>
<tbody>
<tr>
<td>J=3</td>
<td>12B</td>
<td>7e^{-12B/kT}</td>
</tr>
<tr>
<td>J=2</td>
<td>6B</td>
<td>5e^{-6B/kT}</td>
</tr>
<tr>
<td>J=1</td>
<td>2B</td>
<td>3e^{-2B/kT}</td>
</tr>
<tr>
<td>J=0</td>
<td>0</td>
<td>1 = 1e^{-0/kT}</td>
</tr>
</tbody>
</table>

Points to note:

- The value of \(B\) is generally fractions of a wavenumber. HCl is possibly largest at around 10 cm\(^{-1}\).
- \(J=0\) is a permitted state and represents a molecule NOT rotating. This does not violate the uncertainty principle.
- Selection rule is \(\Delta J = \pm 1\) absorbing is +1 emission is −1
- molecule must possess a PERMANENT DIPOLE MOMENT
- transitions will occur in the MICROWAVE region of the electromagnetic spectrum

On the basis of the selection rules we can show what an idealised absorption spectrum should look like
Note that the line spacing in the spectrum for a Rigid Rotor is 2B.

This means that if we record the microwave spectrum of a compound the experiment line spacing will be 2B which in turn enables us to calculate I, the moment of inertia, and subsequently a very precise value of R.

It is important to note that rotational levels are generally very well thermally populated since the separation between them is generally less than a few wavenumbers and at room temperature, 300K, the value for

\[ kT = 0.695 \times 300 = 208.5 \text{ cm}^{-1} \]

For a molecule like HCl for which B=10.44 cm\(^{-1}\) the J=4 level has an energy of 20B = 208.8 cm\(^{-1}\).

Thus the Boltzmann population of this level would be

\[ N_{J=4}/N_{J=0} = 2J+1 e^{-20B/kT} = 9 e^{-208.8/208.5} = 9 \times 0.37 = 3.3 \]

It is important not to forget the degeneracy of the rotational levels.
Should appreciate that the RIGID ROTOR model is an approximation.

A real molecule when rapidly rotating experiences a centrifugal stretching effect. The moment of inertia increases slightly and the energy levels are somewhat closer than shown in the above model.

The energy levels, when corrected for this effect, are given by

\[ E_{\text{rot}} = B(J+1) - DJ(J+1)^2 \]

where \( D = \frac{4B^3}{\omega_e^2} \) = centrifugal distortion constant which is always much smaller than \( B \). (for HCl, \( D = 0.0005 \text{ cm}^{-1} \)).

**VIBRATION – ROTATION SPECTRA**

The energy used to excite the vibrational spectrum of a molecule is always considerably larger than that necessary to excite a rotational change.

eg. Vibrations \( \approx 1000-2000 \text{ cm}^{-1} \)  Rotations \( \approx 0.01-10 \text{ cm}^{-1} \)

Consequently, when a change in vibrational energy occurs due to the absorption of a photon there will be a simultaneous change in the rotational energy levels as well.
For a diatomic molecule the rotational selection rule is still
\[ \Delta J = \pm 1 \]
\[ \Delta J = 0 \] is forbidden in diatomic molecules but becomes allowed for other types of molecules.

Thus the diatomic molecule always changes its rotational state when it changes its vibrational state.

In the case of a harmonic oscillator \( B' = B'' \) since the mean value of \( r \) is the same for each vibrational level.

But for an anharmonic oscillator we usually find that \( B' < B'' \) since
\[ B \ (\text{cm}^{-1}) = \frac{h}{8\pi^2 c \mu r^2} \]
and generally the molecule stretches slightly as it is vibrationally excited with the result that \( r_e' > r_e'' \)

This means that for a real molecule the R branch lines get closer together while at the same time the P branch lines get slightly further apart.

Nevertheless, it is possible to readily obtain the values of \( r_e' \) and \( r_e'' \) from a real spectrum by taking note of where transitions start and finish.

We normally label the transitions as either P or R with the lower J level as the label.
P(J") or R(J")

ie P(1) is transition from J"=1 to J'=0 since ΔJ = -1

and R(1) is transition from J"=1 to J'=2 since ΔJ = +1

a true spectrum of HCl is shown in the following diagram. Note the absence of the Q branch.

the energy of the first 4 transitions in each branch is given below

<table>
<thead>
<tr>
<th>Energy</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>2963.1</td>
<td>R(3)</td>
</tr>
<tr>
<td>2944.9</td>
<td>R(2)</td>
</tr>
<tr>
<td>2925.9</td>
<td>R(1)</td>
</tr>
<tr>
<td>2906.1</td>
<td>R(0)</td>
</tr>
<tr>
<td>2865.0</td>
<td>P(1)</td>
</tr>
<tr>
<td>2843.5</td>
<td>P(2)</td>
</tr>
<tr>
<td>2821.5</td>
<td>P(3)</td>
</tr>
<tr>
<td>2798.9</td>
<td>P(4)</td>
</tr>
</tbody>
</table>

To calculate the value of B" we need to choose two transitions that have the same upper state but differing lower states. eg P(2) and R(0). The difference between them is 6B'

$$6B" = 2906.1 - 2843.5 = 62.60 \text{ cm}^{-1}$$  thus $$B" = 10.43 \text{ cm}^{-1}$$
Similarly to calculate the value of $B'$ we need to choose two transitions that have the same lower state but different upper states. eg $P(1)$ and $R(1)$ the difference being $6B'$.

$$6B' = 2925.9 - 2865.0 = 60.90 \text{ cm}^{-1} \quad \text{thus } B' = 10.15 \text{ cm}^{-1}$$

In order to calculate the internuclear distance we use the equation for $B$

$$B (\text{cm}^{-1}) = \frac{h}{8\pi^2 c \mu r^2}$$

therefore

$$r = \sqrt{\frac{h}{8\pi^2 c \mu B}}$$

$$r_e' = \sqrt{(6.626\times10^{-34}/8\times9.87\times2.988\times10^{10}\times10.15\times1.614\times10^{-27})}$$

$$= 0.1309 \text{ nm}$$

$$r_e'' = \sqrt{(6.626\times10^{-34}/8\times9.87\times2.988\times10^{10}\times10.43\times1.614\times10^{-27})}$$

$$= 0.1292 \text{ nm}$$

Thus we see that the molecule has stretched by about 0.002 nm in going from the ground to the first excited vibrational level.
Another useful diagnostic tool is RAMAN spectroscopy which complements Infrared spectroscopy.

Remember that we said earlier that a molecule can only absorb IR radiation if during the period of its vibration the molecule has an oscillating dipole moment.

What about a molecule like $\text{H}_2$? It does not have a dipole moment and yet we can get its vibrational frequency. How?

We use Raman spectroscopy.

For a vibration to be Raman active the molecule must have a changing polarisability. Hard to visualise.

Even though $\text{H}_2$ does not have a dipole or a changing dipole its polarisability changes, that is the charge distribution around the molecule changes as it vibrates.

When this occurs the molecule is able to scatter light which is usually in the visible region of the electromagnetic spectrum and during the interaction of the photon with the molecule a quantum of vibrational energy is either absorbed or emitted by the molecule.

In the infrared absorption process the excited $v=1$ state has a finite lifetime of about $10^{-14}$ s but in the RAMAN SCATTERING case it is an instantaneous collision of a molecule and a photon.
Since most collisions are non-productive, the scattered photon remains unchanged in energy and the so-called RAYLEIGH scattered light is the most intense line.

The Raman scattered light is about 1000 times less intense than the Rayleigh scattered light and is shifted to lower energy by an amount equal to the energy of a molecular vibration.

$$h\nu_{\text{in}} - h\nu_{\text{out}} = \text{energy of a vibration}$$

ALL TOTALLY SYMMETRIC VIBRATIONS ARE RAMAN ACTIVE

hence the totally symmetric vibration of $H_2$ would be Raman active but not infrared active.

It is also possible that the molecule is already in an excited vibrational state when the photon hits it.

When this is the case, the molecule can either do nothing in which case the emitted photon is just Rayleigh scattered or else the molecule can lose its vibrational excitation and return to the ground state.

In this case, the emitted Raman photon is higher in energy than the exciting photon by an amount equal to the vibrational frequency of the molecule.

This line is known as anti-Stokes radiation.

Needless to say, it is weaker again than the Stokes scattering since the original population of the vibrational state is temperature dependent by virtue of the Boltzmann factor.