Vibrational Spectroscopy 1

Recommended Reading:

Banwell and McCash Chapter 3

Atkins Physical Chemistry Chapter 16

Introduction

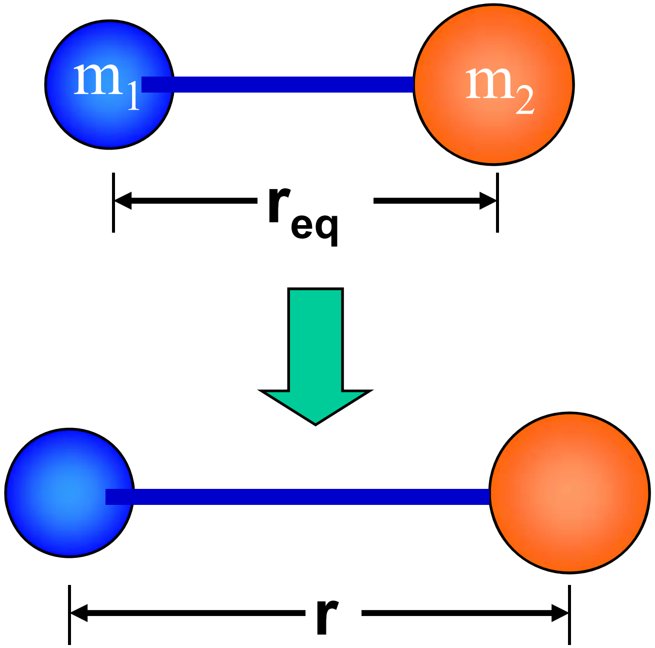
What is it? Vibrational spectroscopy detects transitions between the quantised vibrational energy levels associated with bond stretching and/or bond angle bending in molecules.

How do we do it? Transitions are observed by measuring the amount of infrared radiation that is absorbed or emitted by vibrating molecules in solid, liquid or gas phases.

Why do we do it? A knowledge of the vibrational level spacings gives us the value of the stretching (or bending) force constants which characterise the stifness of a bond, allows us to estimate the bond dissociation energy, and gives us a means of identifying characteristic functional groups of atoms within large molecules.

Vibrational Spectroscopy

Chemical bonds are not rigid, the atoms in a molecule vibrate about an equilibrium position.



The force required to stretch or compress the bond length to r is proportional to ($r-r_{eq}$)

The energy required to stretch the bond is

$$\boxed{E = \frac{1}{2}k\left(r - r_{eq}\right)^2 = \frac{1}{2}kx^2}$$

where $x = (r-r_{eq})$

k = force constant of bond, units $N.m^{-1}$

Just like a spring which obeys Hooke's Law.

Potential Energy Curve

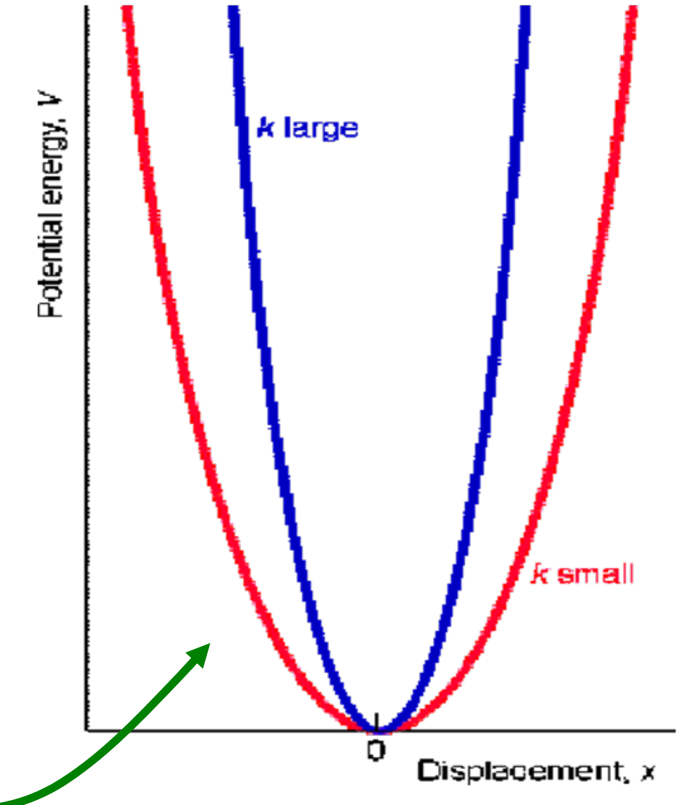
Connection between shape of potential energy curve and strength of bond k.

$$V(x) = \cancel{V(0)} + \cancel{\left(\frac{dV}{dx}\right)_0} x + \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2 + \dots$$

$$\boxed{V(x) \approx \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)_0 x^2 = \frac{1}{2}kx^2}$$

Potential energy curve is approximately parabolic and the force constant k is related to the potential by

$$\boxed{k = \left(\frac{d^2V}{dx^2}\right)_0}$$



Big $\left(\frac{d^2V}{dx^2}\right) \Rightarrow$ steep potential $\Rightarrow$ large k

Small $\left(\frac{d^2V}{dx^2}\right) \Rightarrow$ shallow potential $\Rightarrow$ small k

CO, k = 1902 Nm^{-1},
⇒ strong.

HCl, k = 516 Nm^{-1},
⇒ weak.

Quantum Approach

Schrodinger Equation for Simple Harmonic Oscillator

$$-\frac{\hbar^2}{2\mu}\frac{\partial^2\psi(x)}{\partial x^2}+\frac{1}{2}kx^2\psi(x)=E\psi(x)$$

Where μ is the effective (reduced) mass of the molecule

$$\mu=\frac{m_1m_2}{m_1+m_2}$$

From Quantum II notes we know that the wavefunctions are given by

$$\psi_n=N_nH_n(y)e^{-y^2/2}$$

where $H_n(y)$ are the Hermite Polynomials, and

$$y=\frac{x}{\alpha}$$

with

$$\alpha=\left(\frac{h^2}{4\pi^2mk}\right)^{1/4}$$

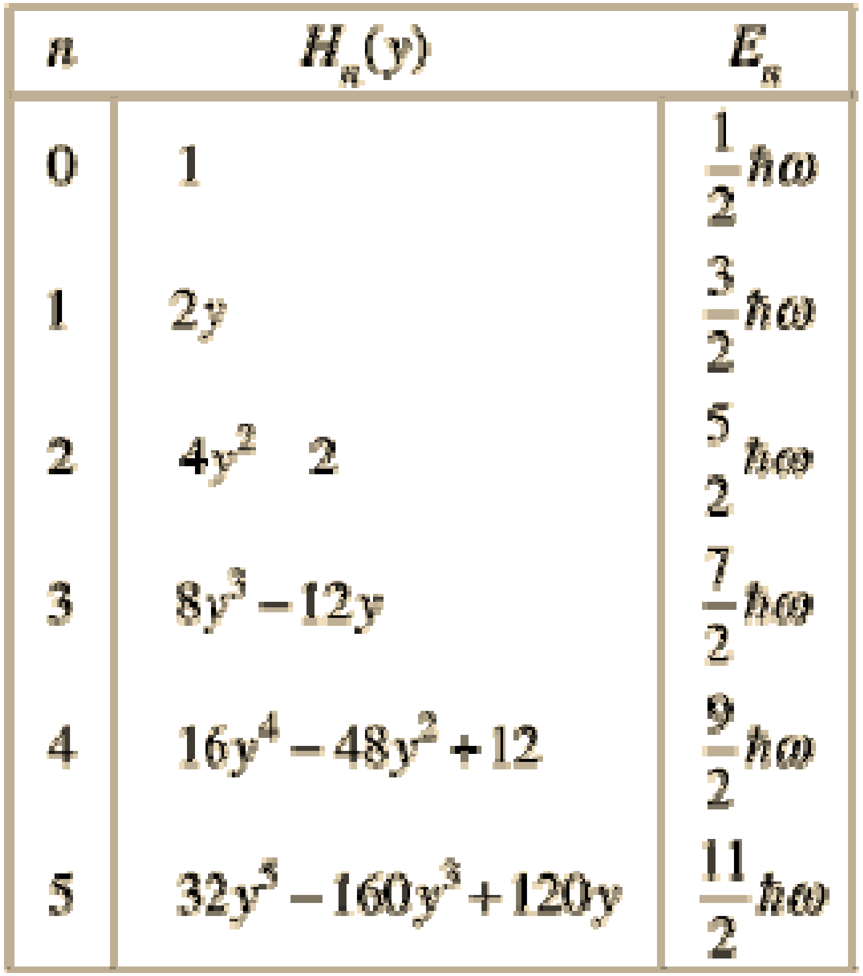
The energy levels are quantised and are given by

$$E_n=\left(n+\frac{1}{2}\right)\hbar\omega$$

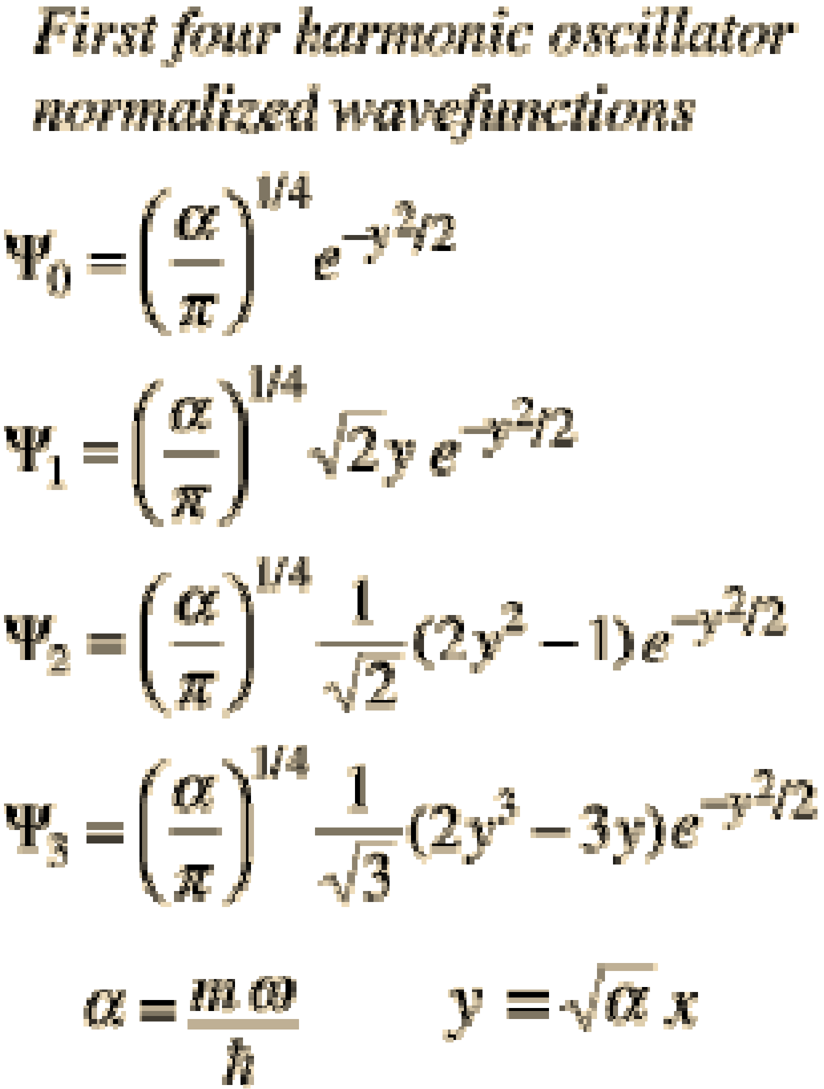
$$\omega=\sqrt{\frac{k}{\mu}}$$

where n is the vibrational quantum number, n = 0, 1, 2, 3, …

Hermite Polynomials and SHO wavefunctions



n	$H_n(y)$	E_n
0	1	$\frac{1}{2}\hbar\omega$
1	$2y$	$\frac{3}{2}\hbar\omega$
2	$4y^2 \quad 2$	$\frac{5}{2}\hbar\omega$
3	$8y^3-12y$	$\frac{7}{2}\hbar\omega$
4	$16y^4-48y^2+12$	$\frac{9}{2}\hbar\omega$
5	$32y^5-160y^3+120y$	$\frac{11}{2}\hbar\omega$



First four harmonic oscillator normalized wavefunctions

$$\Psi_0=\left(\frac{\alpha}{\pi}\right)^{1/4}e^{-y^2/2}$$

$$\Psi_1=\left(\frac{\alpha}{\pi}\right)^{1/4}\sqrt{2}y\,e^{-y^2/2}$$

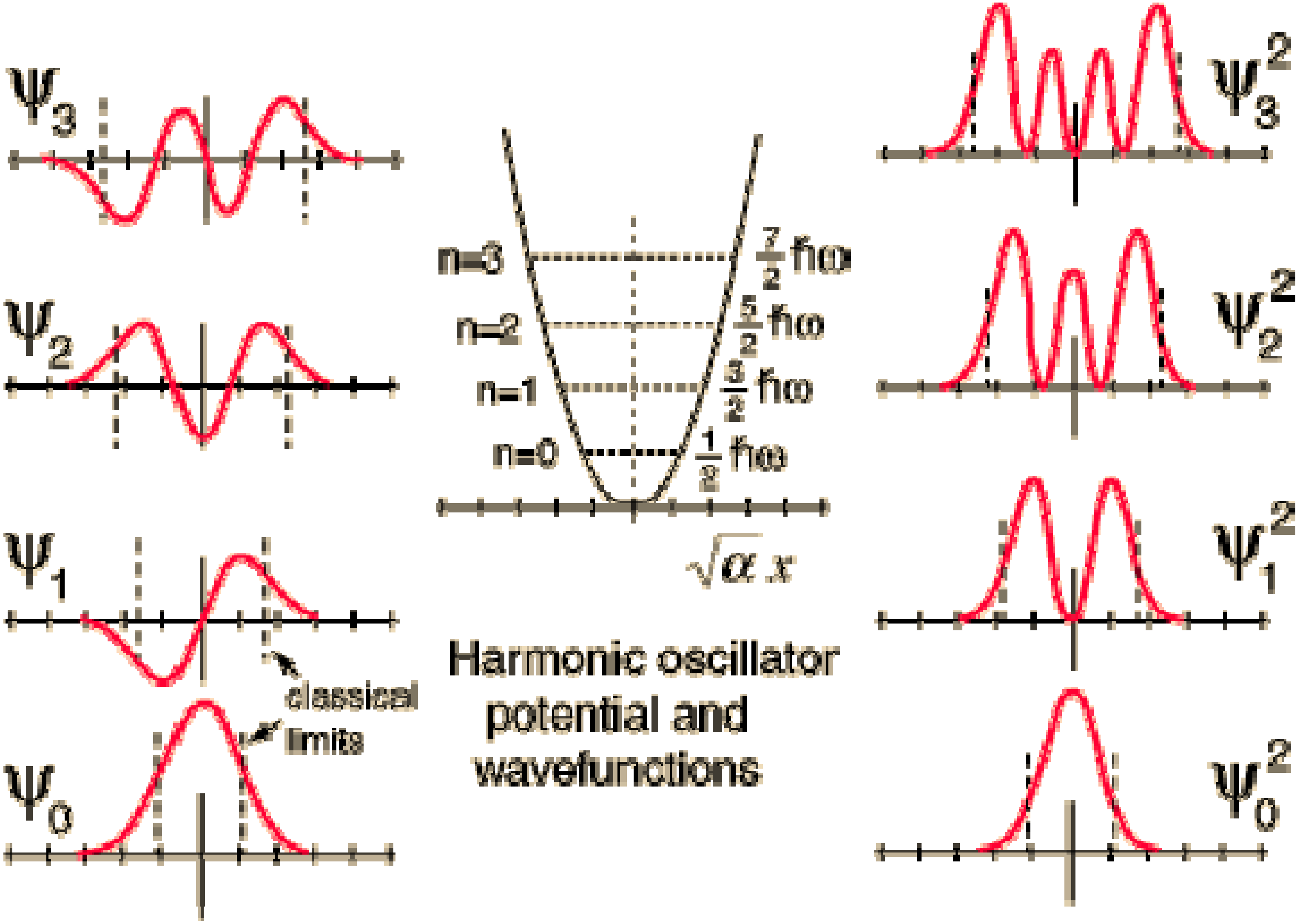
$$\Psi_2=\left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{2}}(2y^2-1)e^{-y^2/2}$$

$$\Psi_3=\left(\frac{\alpha}{\pi}\right)^{1/4}\frac{1}{\sqrt{3}}(2y^3-3y)e^{-y^2/2}$$

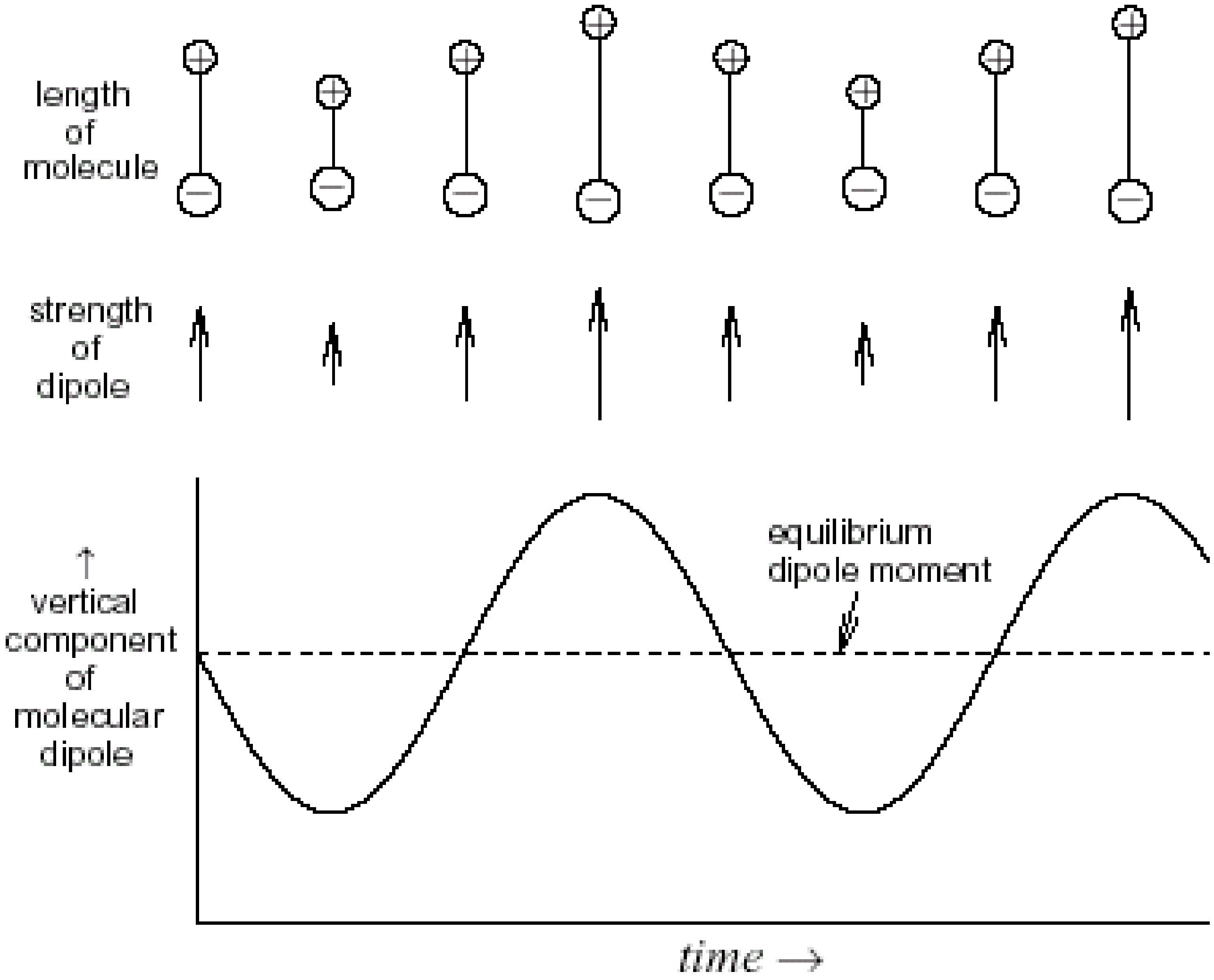
$$\alpha=\frac{m\omega}{\hbar} \qquad y\equiv\sqrt{\alpha}\,x$$

Wavefunctions

First four wavefunctions and corresponding probability distributions for the SHO potential.



Selection Rules



Dipole moment of a vibrating polar diatomic molecule which is fixed and aligned in space

Selection Rules

Molecules may interact with an electro-magnetic field through their electric dipole moments.

If they possess an oscillating dipole moment then they can absorb or emit photons.

An oscillation is infra-red active if it changes in magnitude or direction when the atoms are displaced relative to each other

Selection Rules:

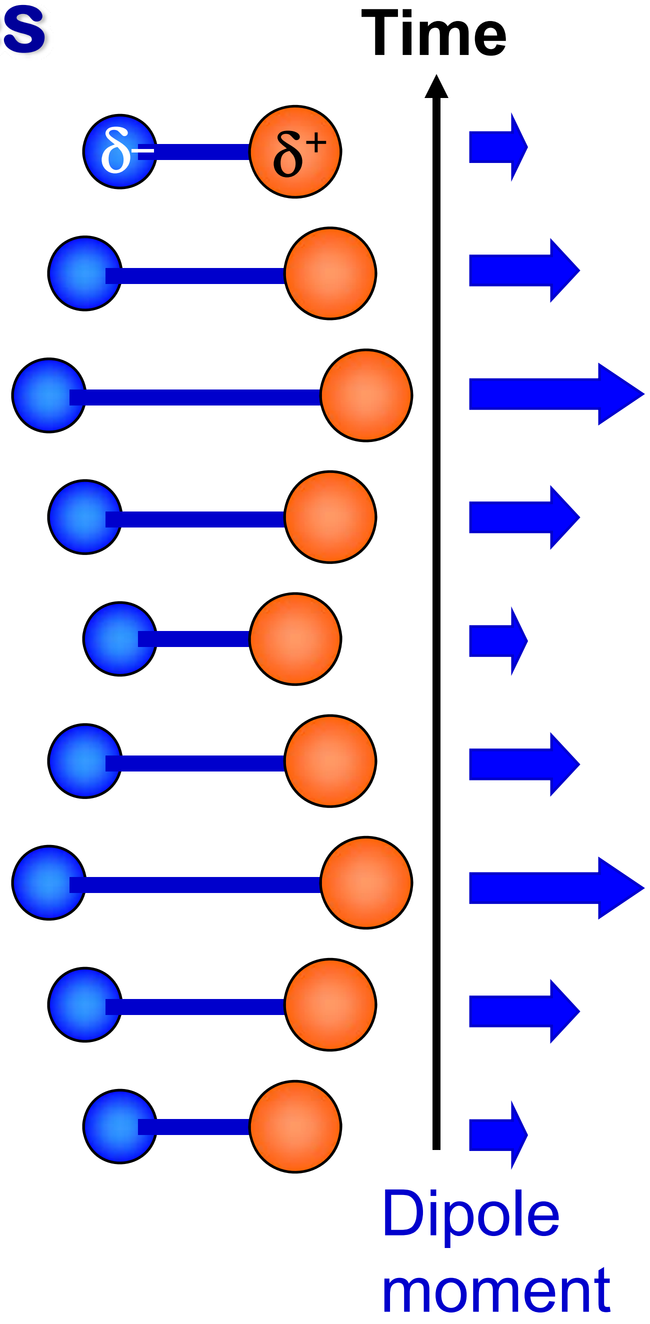
1. Dipole moment must change as molecule oscillates.

2. $\Delta n = \pm 1$ +1 ⇒ absorption of photon

-1 ⇒ emission of photon

Examples:

HCl √, HI √, H_2O √, O_2 X, H_2 X, ...



Justification for Selection Rules I

Selection Rules arise from the transition dipole moment $\langle \varphi_f | \hat{\mu} | \varphi_i \rangle$

Consider a one dimensional oscillator (e.g. diatomic molecule). The dipole moment arises from two partial charges $\pm\delta q$ separated by a distance $R = R_e + x$. Then

$$\hat{\mu} = \hat{R}\delta q = R_e \delta q + \hat{x}\delta q = \hat{\mu}_0 + \hat{x}\delta q$$

Where μ_0 is the dipole moment operator when the atoms are at their equilibrium separation. Then, assuming that the initial and final states are different ($i \neq f$),

$$\langle \varphi_f | \hat{\mu} | \varphi_i \rangle = \mu_0 \langle \varphi_f | \varphi_i \rangle + \delta q \langle \varphi_f | \hat{x} | \varphi_i \rangle$$

First term is zero because the oscillator states are orthogonal. So the transition moment is

$$\langle \varphi_f | \hat{\mu} | \varphi_i \rangle = \delta q \langle \varphi_f | \hat{x} | \varphi_i \rangle$$

and because $\delta q = \frac{d\mu}{dx}$ we can write the transition moment more generally as :

$$\langle \varphi_f | \hat{\mu} | \varphi_i \rangle = \langle \varphi_f | \hat{x} | \varphi_i \rangle \left(\frac{d\mu}{dx} \right)$$

the right hand side is zero unless there is a varying dipole moment. So there is no absorption unless the molecule has a changing dipole moment.

Justification for Selection Rules II

The specific selection rule is determined by considering the value of the matrix element

$$\boxed{\langle \varphi_f | \hat{x} | \varphi_i \rangle}$$

We write out the matrix element explicitly in terms of the Hermite polynomials and evaluate the integral

$$\boxed{\langle \varphi_f | \hat{x} | \varphi_i \rangle = \int_{-\infty}^{\infty} N_f H_f \hat{x} N_i H_i \exp\left(-y^2\right) dy = \alpha^2 \int_{-\infty}^{\infty} N_f H_f \hat{y} N_i H_i \exp\left(-y^2\right) dy}$$

To evaluate the integral we use the recursion relation

$$\boxed{yH_n = nH_{n-1} + \frac{1}{2} H_{n+1}}$$

$$H_f \longrightarrow H_{nf}$$

$$H_i \longrightarrow H_{ni}$$

This turns the matrix element to

$$\boxed{= \alpha^2 N_f N_i \left\{ n_i \int_{-\infty}^{\infty} H_{n_f} H_{n_{i-1}} \exp\left(-y^2\right) dy + \frac{1}{2} \int_{-\infty}^{\infty} H_{n_f} H_{n_{i+1}} \exp\left(-y^2\right) dy \right\}}$$

Now using the orthogonality condition

$$\int_{-\infty}^{\infty} H_{n_f} H_{n_{i+1}} \exp\left(-y^2\right) dy = \begin{cases} 0 & \text{if } n_f \neq n_i \\ \sqrt{\pi}\, 2^{n_i} n_i! & \text{if } n_f = n_i \end{cases}$$

We see that the first integral is zero unless $n_f = n_i - 1$ and the second integral is zero unless $n_f = n_i + 1$.

So the transition dipole moment is zero unless $\Delta n = \pm 1$.

A Third Selection Rule

At this point we note that there is no angular momentum associated with the radial vibrational motion of the molecule. Since angular momentum must be conserved when a photon is emitted or absorbed this implies that all vibrational transitions must be accompanied by a change in the rotational quantum number J.

So in reality all vibrational spectra are due to vibrational-rotational transitions in the molecule with a simultaneous change in the J quantum number.

We will come back to this point later!!!

Energy Levels in Harmonic Oscillator

Vibrational energy is quantised

$$\boxed{E_n = \left(n + \frac{1}{2}\right)\hbar\omega_o} \qquad \boxed{\omega_o = \sqrt{\frac{k}{\mu}}}$$

Vibrational terms of a molecule G(n) = energies of vibrational states expressed in wavenumbers.

$$\boxed{G(n) = \frac{E_n}{hc} = \left(n + \frac{1}{2}\right)\frac{\hbar\omega_o}{hc} = \left(n + \frac{1}{2}\right)\tilde{\nu}_o}$$

where

$$\boxed{\tilde{\nu}_o = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}}$$

Units: cm^{-1}

$$E_0 = \frac{1}{2}\hbar\omega_o \Rightarrow G(0) = \frac{1}{2}\tilde{\nu}_o$$

= Zero point energy

Example: $^1H^{35}Cl$ has a force constant of 519 cm^{-1}. Find its oscillation frequency ν_0.

$$\mu = \frac{1 \times 35}{1 + 35}\text{amu} = 1.61 \times 10^{-27}\text{kg}$$

$$\nu_0 = \frac{\omega_o}{2\pi} = \frac{1}{2\pi}\sqrt{\frac{516\ N.m^{-1}}{1.61 \times 10^{-27}kg}}$$

$$= 9.0 \times 10^{13} Hz$$

And therefore

$$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 m.s^{-1}}{9.0 \times 10^{13} \sec^{-1}}$$

$$= 3.3 \times 10^{-6} m$$

$$= 3.3 \mu m$$

$$\Rightarrow \tilde{\nu}_0 = 2990 cm^{-1}$$

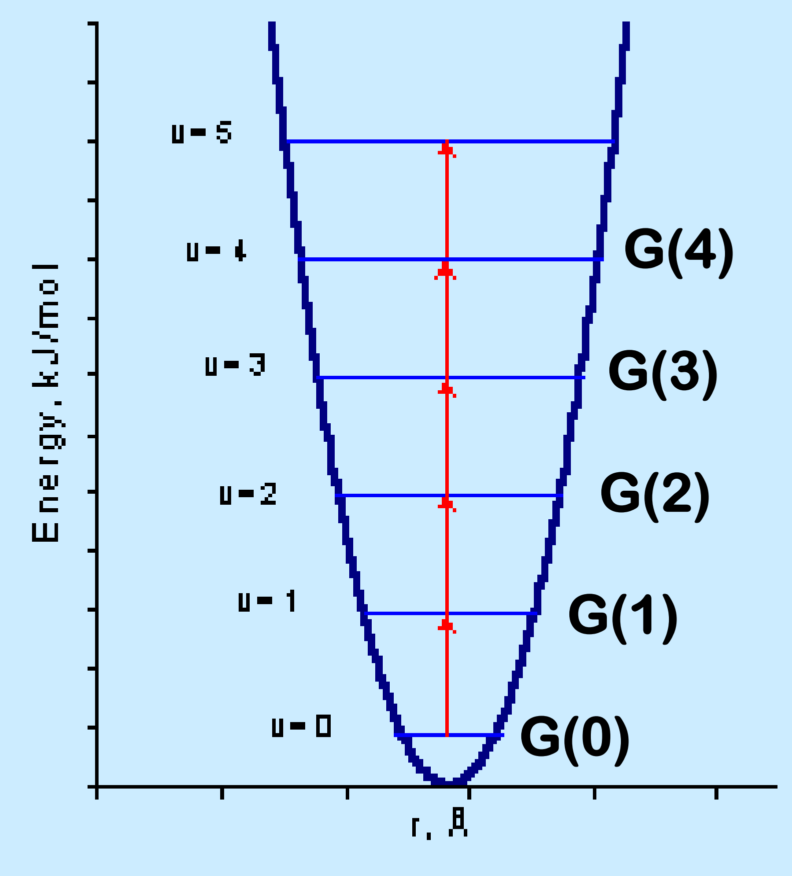
We can excite the $^1H^{35}Cl$ vibration with radiation of this wavelength ⇒ infra-red

Vibrational Spectrum (Diatomic)

From the selection rules we see that the wavenumbers of the allowed transitions are given by

$$G(n+1)-G(n)=\left[\left(n+\frac{3}{2}\right)-\left(n+\frac{1}{2}\right)\right]\tilde{\nu}_0=\tilde{\nu}_0$$

All allowed transitions occur at the same frequency $\Rightarrow$ only one line in the spectrum. Position of line depends on $\tilde{\nu}_0$ and therefore k and μ.



At room temperature kT $\approx$ 200 cm^{-1}.

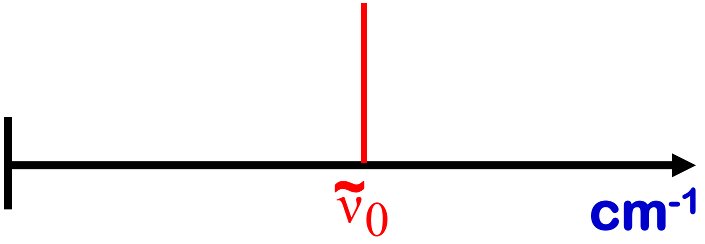
For most molecules $\tilde{\nu}_0 > 200\,\text{cm}^{-1}$

therefore at room temp only the lowest vibrational state will be occupied.

$\Rightarrow$ dominant spectral transition will be

$$n = 0 \rightarrow n = 1.$$

= Fundamental transition



Population of Energy Levels

In diatomic molecules the vibrational transitions typically have wavenumbers in the range 500 to 2000 cm^{-1} (~0.05 to ~ 0.25 eV).

The populations of the vibrational energy levels are given by the Boltzmann distribution.

$$\boxed{\frac{N_j}{N_i} = \exp\left(-\frac{\Delta E}{kT}\right)}$$

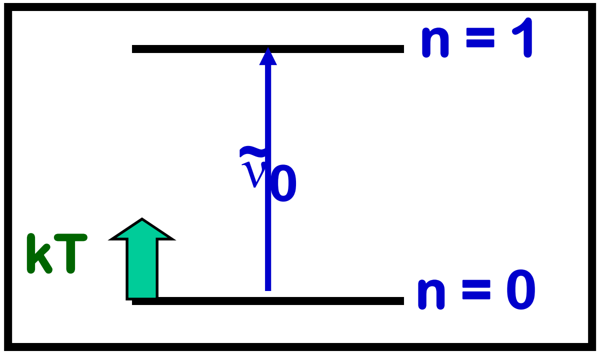
(Note that vibrational levels are non-degenerate so there is no degeneracy factor).

At room temperature (300), kT ~ 1/40 eV $\Rightarrow$ kT /hc ~200cm^{-1} this is less than the typical separation of the energy levels

So at room temperature almost all of the molecules will be in the ground (n = 0) state and the predominant transition is adsorption from the n = 0 to n = 1 state.

Example HCl

Example: $^{1}H^{35}Cl$ has a fundamental vibration at $\tilde{\nu}_0 = 2990\text{cm}^{-1}$ find the relative population of the n = 1 vibrational state at room temperature (300K) and at (5000K)



At room temperature kT/hc = 200 cm^{-1}.

At 5000K kT/hc = 3475 cm^{-1}.

From Boltzmann distribution

T = 300K

$$\frac{N_1}{N_0} = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{hc\tilde{\nu}_0}{kT}\right)$$

$$= \exp\left(-\frac{2990\text{cm}^{-1}}{200\text{cm}^{-1}}\right) = 3.2 \times 10^{-7}$$

At 300K only 3 in 10 million molecules are in the n = 1 vib. state the rest are in the ground (n = 0) state.

T = 5000 K

$$\frac{N_1}{N_0} = \exp\left(-\frac{\Delta E}{kT}\right) = \exp\left(-\frac{hc\tilde{\nu}_0}{kT}\right)$$

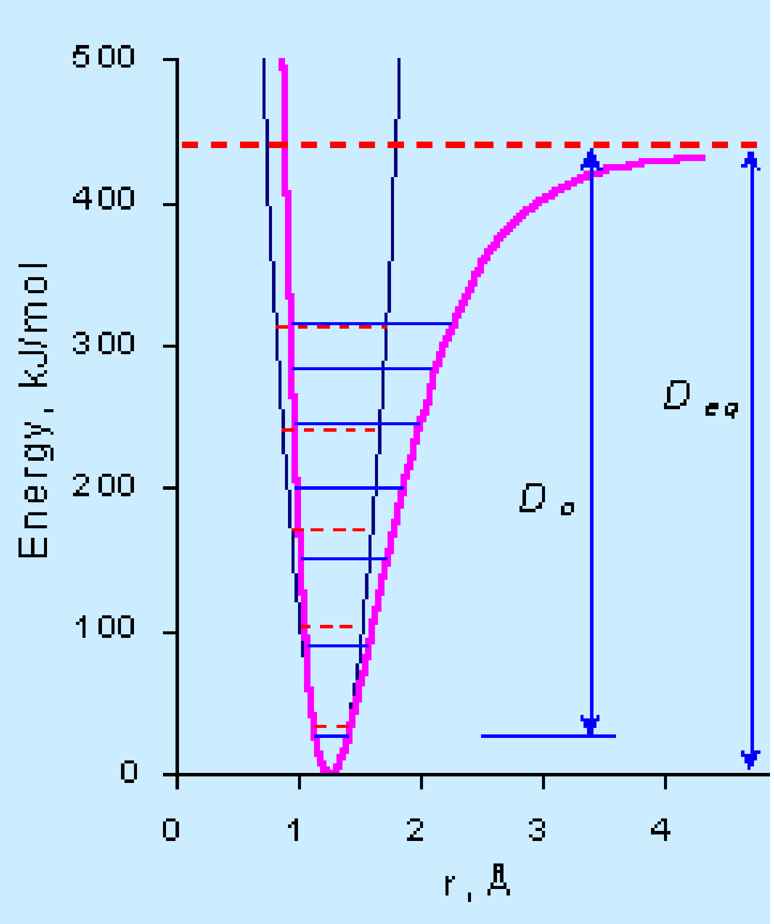
$$= \exp\left(-\frac{2990\text{cm}^{-1}}{3475\text{cm}^{-1}}\right) = 0.423$$

At 5000 K about 43 % of the molecules are in the n = 1 state.

The Anharmonic Oscillator

Real molecules do not behave like harmonic oscillators.

- **The Harmonic Oscillator does not dissociate; it can have $n = \infty$ but $(r - r_{eq}) = \infty$, does not make physical sense.**
- **In real molecules the vibrational energy levels get closer together as E increases.**



In real molecules the harmonic oscillator approximation breaks down.

Must consider additional terms in the Potential Energy.

$$V(x) = \frac{1}{2}\left(\frac{d^2V}{dx^2}\right)x^2 + \frac{1}{6}\left(\frac{d^3V}{dx^3}\right)x^3 + \ldots$$

Include Anharmonic terms in potential.

The Morse Potential

Use an empirical function that is a good representation of the true potential curve.

The Morse potential is one such function.

$$\boxed{V = hcD_{eq}\left[1 - e^{-a\left(r - r_{eq}\right)}\right]^2}$$

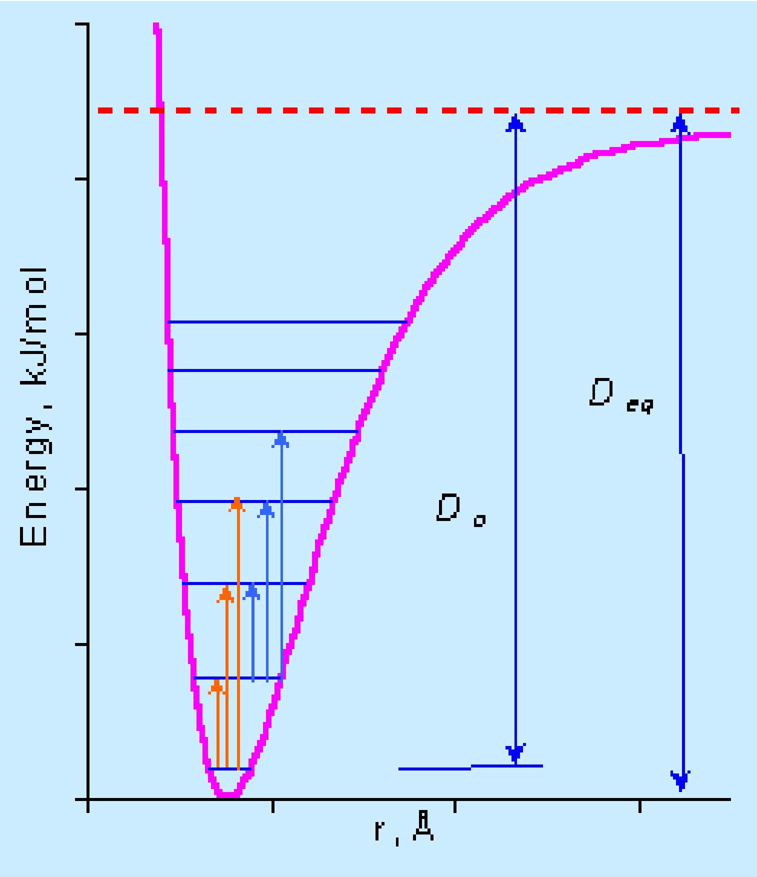
Where $a = \left(\dfrac{\mu\omega^2}{2hcD_{eq}}\right)^{1/2} = \left(\dfrac{\mu\nu^2}{8\pi^2 hcD_{eq}}\right)^{1/2}$

D_{eq} is the depth of the Morse potential

Note that the Dissociation Energy D_0 is given by

$$\boxed{D_0 = D_{eq} - \frac{\hbar\omega}{2} = D_{eq} - \frac{hc\tilde{\nu}}{2}}$$

Units of D_0 and D_{eq} are energy, J or eV



Note energy levels get closer together as n increases

The Morse Potential

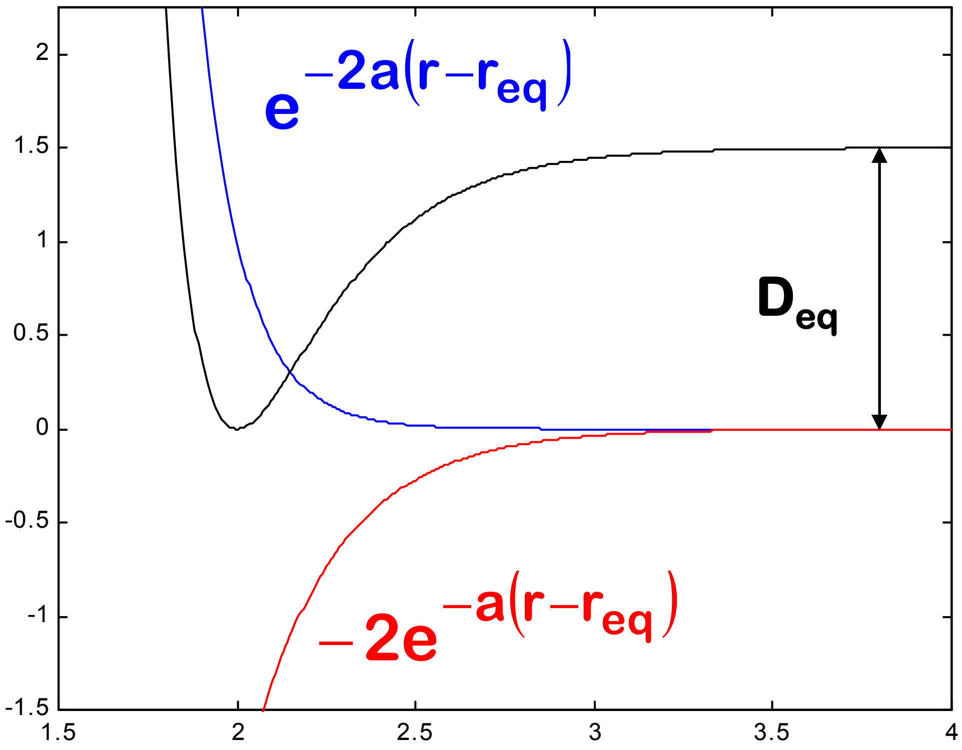
A way of seeing the physics behind the Morse potential is to expand it

$$\frac{V}{hc} = D_{eq}\left[1-e^{-a\left(r-r_{eq}\right)}\right]^2 = D_{eq}\left[e^{-2a\left(r-r_{eq}\right)} - 2e^{-a\left(r-r_{eq}\right)} + 1\right]$$

Short range repulsion term

long range attraction term

asymptote



The Morse Potential

Using the fact that

$$e^{-x} = 1 + \sum_{n=1}^{\infty}\left(\frac{(-x)^{n}}{n!}\right) = 1 - x + \frac{x^{2}}{2} - \frac{x^{3}}{6} + \frac{x^{4}}{24} + \ldots.$$

expanding the exponential term in the Morse potential and collecting terms gives

$$\frac{V(r)}{hc} \approx D_{eq}\left\{\left[a\left(r-r_{eq}\right)\right]^{2} - \left[a\left(r-r_{eq}\right)\right]^{3} + \frac{7}{12}\left[a\left(r-r_{eq}\right)\right]^{4} + \ldots\right\}$$

For the Harmonic Oscillator potential $V(r) = 1/2k(r-r_{eq})^{2.}$ So we note that for small values of $|r-r_{eq}|$, the cubic and higher terms will be small, the first term will dominate and we return to the harmonic oscillator with

$$\frac{V(r)}{hc} \approx D_{eq}\left\{\left[a\left(r-r_{eq}\right)\right]^{2}\right\}$$

Put rhs = ½ $k_{Morse}x^{2} \longrightarrow \boxed{k_{Morse} \approx 2D_{eq}a^{2}}$

Morse potential = Harmonic Oscillator potential with cubic and higher anharmonic terms added to make the shape more realistic.

The Morse Potential

We can solve the Schrodinger equation with the Morse potential to find the allowed energy levels (eigenvalues). Difficult but can be done analytically.

Energy levels given by

$$\boxed{E_n = \left(n+\frac{1}{2}\right)\hbar\omega_o \underbrace{- \left(n+\frac{1}{2}\right)^2 \chi_e \hbar\omega_o}_{\text{Anharmonic correction}}}$$

with $\boxed{\omega_o = \sqrt{\frac{k}{\mu}}}$

The vibrational terms are given by

$$\boxed{\begin{aligned} G(n) = \frac{E_n}{hc} &= \left(n+\frac{1}{2}\right)\tilde{\nu}_o - \left(n+\frac{1}{2}\right)^2 \chi_e \tilde{\nu}_o \\ &= \tilde{\nu}_o\left[1-\chi_e\left(n+\frac{1}{2}\right)\right]\left(n+\frac{1}{2}\right) \end{aligned}}$$

χ_e the **Anharmonicity constant,** depends on molecule, small correction factor ≈ 0.01

$$\boxed{\chi_e = \frac{\tilde{\nu}_0}{4D_{eq}} = \frac{a^2\hbar}{2\mu\omega_0}}$$

The number of vibrational states is now finite, $n = 0,1,2,\ldots.\ n_{max}$.
Above n_{max} the molecule dissociates (breaks apart)

Selection Rules for Anharmonic Oscillator

Selection Rules:

1. Dipole moment must change as molecule oscillates.
2. $\Delta n = \pm 1, \pm 2, \pm 3, \ldots$ all transitions allowed but only the $\Delta n = \pm 1$ transition is strong.
3. Conservation of angular momentum, so really we have vibrational-rotational transitions.

Fundamental Transition

$$\boxed{\tilde{\nu}_{n=0\rightarrow n=1} = G(1) - G(0) = \tilde{\nu}_0\left(1-2\chi_e\right)}$$

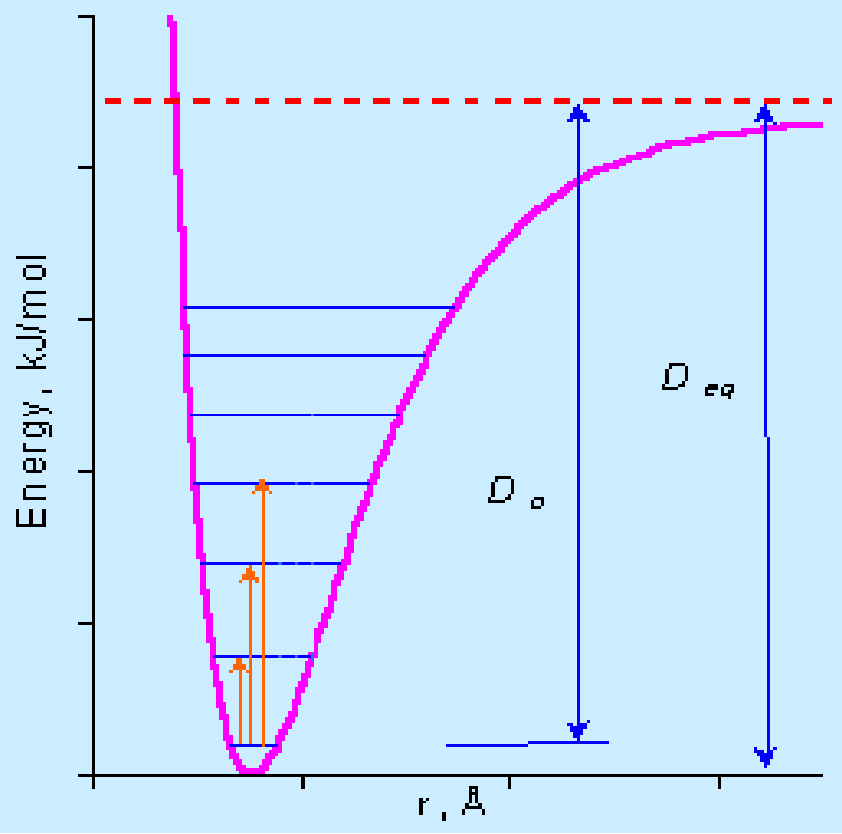
First OvertoneTransition

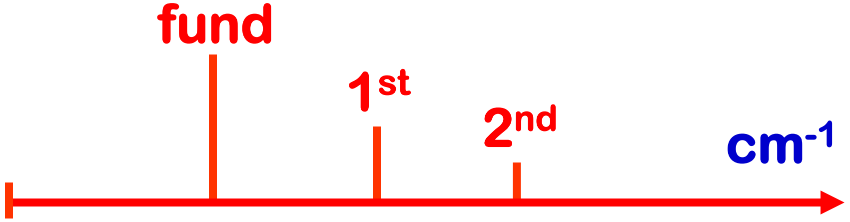
$$\boxed{\tilde{\nu}_{n=0\rightarrow n=2} = G(2) - G(0) = 2\tilde{\nu}_0\left(1-3\chi_e\right)}$$

Second OvertoneTransition

$$\boxed{\tilde{\nu}_{n=0\rightarrow n=3} = G(3) - G(0) = 3\tilde{\nu}_0\left(1-4\chi_e\right)}$$

Can calculate energies of higher overtone transitions, intensity decreases rapidly for higher overtones.





Maximum vibrational quantum number

In general the transition energies are given by

$$\Delta\varepsilon_n = \varepsilon_{n+1} - \varepsilon_n = \tilde{\nu}_0 - 2\tilde{\nu}_0\chi_e(n+1)$$

This shows that as the vibrational quantum number n increases the energy levels get systematically closer together and go to zero at the dissociation limit. Another way of seeing this is to recognise that the energy function is a parabolic function of n whose limit lies at D_{eq}.

$$\varepsilon_n = \left(n + \frac{1}{2}\right)\tilde{\nu}_o - \left(n + \frac{1}{2}\right)^2 \chi_e \tilde{\nu}_o$$

Taking the derivative with respect to n and setting it equal to zero gives

$$\frac{d\varepsilon_n}{dn} = \tilde{\nu}_o - 2\left(n + \frac{1}{2}\right)\chi_e\tilde{\nu}_o = 0$$

solving gives the vibrational index associated with the dissociation limit

$$n_D = \frac{\tilde{\nu}_o}{2\chi_e\tilde{\nu}_o} - \frac{1}{2}$$

round down to the nearest integer to find n_{max} the maximum vibrational quantum number.

Example: Overtone bands in HCl

The infrared spectrum of HCl has vibrational lines at 2886cm^{-1} (strong, fundamental), 5668 cm^{-1} (weak, 1st overtone) and 8347 cm^{-1} (very weak, second overtone). Find χ_e and $\tilde{\nu}_0$

From data given we have

$$\text{Fundamental} = G(1) - G(0) = \tilde{\nu}_0 (1 - 2\chi_e) = 2886\ \text{cm}^{-1}$$

$$1^{st}\ \text{Overtone} = G(2) - G(0) = 2\tilde{\nu}_0 (1 - 3\chi_e) = 5668\ \text{cm}^{-1}$$

$$2^{nd}\ \text{Overtone} = G(3) - G(0) = 3\tilde{\nu}_0 (1 - 4\chi_e) = 8347\text{cm}^{-1}$$

Three equations, two unknowns, can solve equations to find

$$\tilde{\nu}_0 = 2990\ \text{cm}^{-1}$$

$$\chi_e = 0.0174$$

$\tilde{\nu}_0$ = vibrational frequency of simple harmonic oscillator

Note that χ_e is dimensionless

Hot Bands

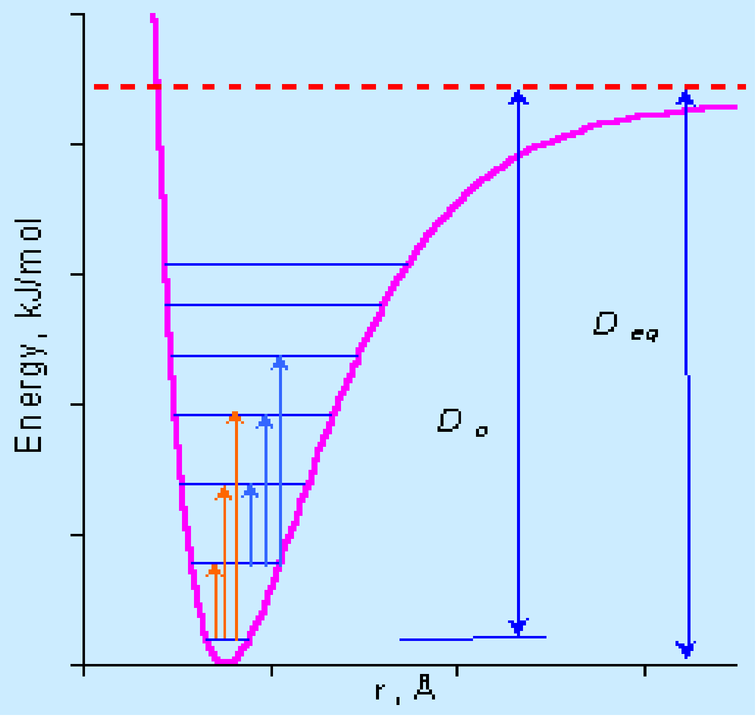
At low temperature only the n = 0 state has a significant population, so only transitions from n = 0 occur. However as temperature increases then some of the molecules will be in the n = 1 state and absorption transitions out of the n = 1 state will be observed. These are called Hot Bands and their intensities depend on the temperature of the gas.

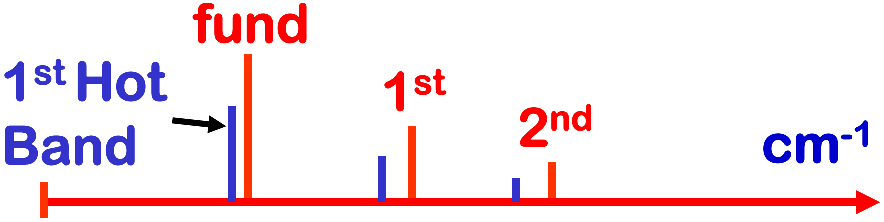
First Hot BandTransition

$$\boxed{\tilde{\nu}_{n=1\rightarrow n=2} = G(2) - G(1) = \tilde{\nu}_0\left(1-4\chi_e\right)}$$

Second Hot BandTransition

$$\boxed{\tilde{\nu}_{n=1\rightarrow n=3} = G(3) - G(1) = 2\tilde{\nu}_0\left(1-5\chi_e\right)}$$





The Birge-Sponer Plot

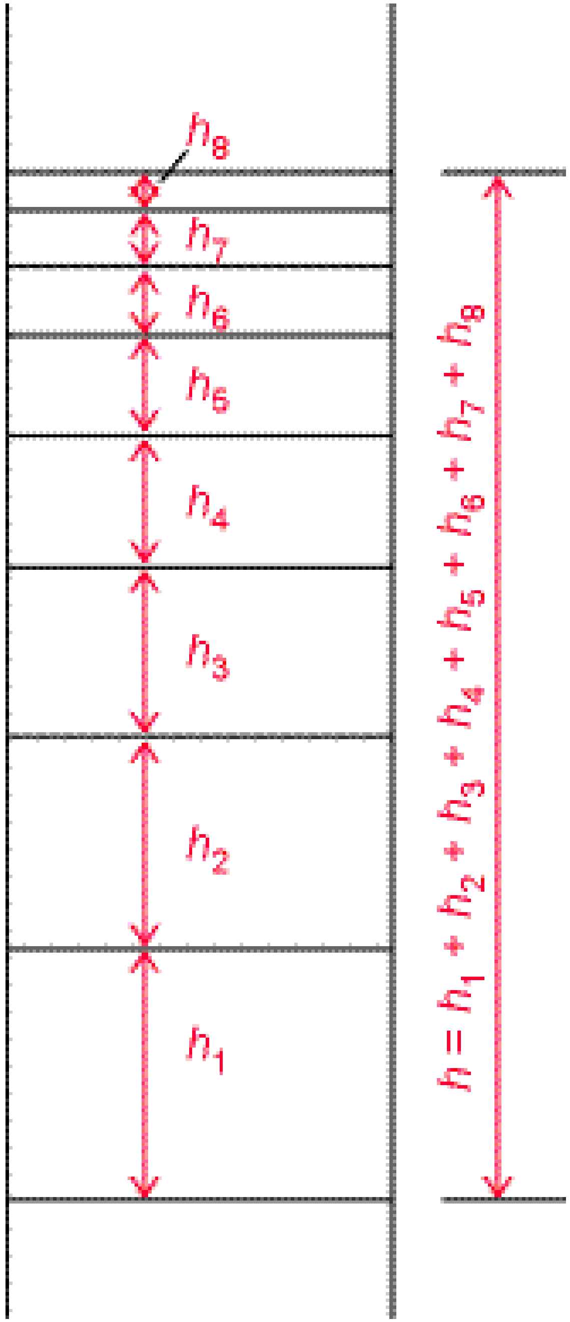
When several vibrational transitions are detectable in a spectrum then a graphical technique called a Birge-Sponer plot may be used to determine the dissociation energy of the molecule.

The basis of the Birge-Sponer plot is that the sum of successive intervals ΔG from the zero-point energy to the dissociation limit is the Dissociation energy.

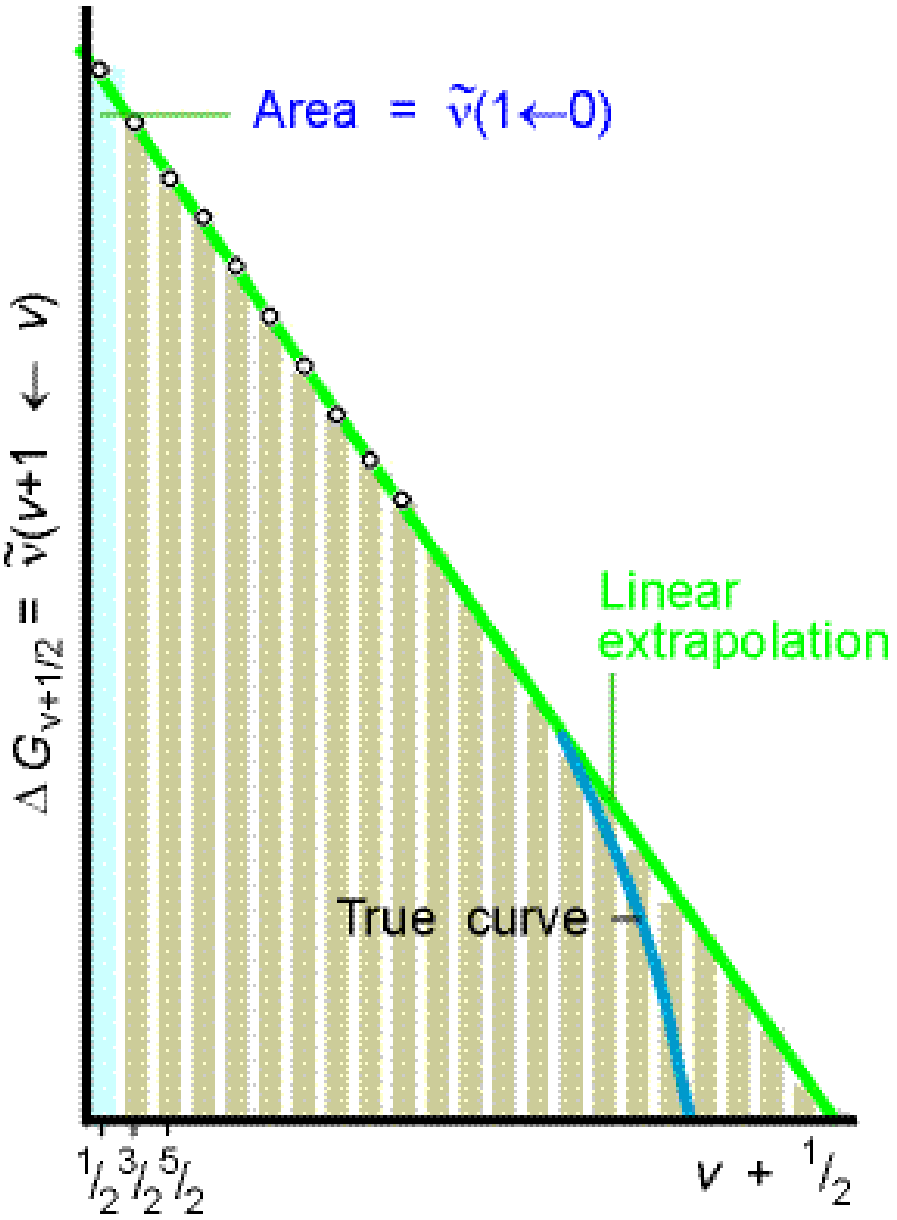
$$\boxed{D_0 = \Delta G_{1/2} + \Delta G_{3/2} + \ldots. = \sum_{n} \Delta G_{n+1/2}}$$

The area under the plot of $\Delta G_{n+1/2}$ against n+1/2 is equal to this sum and therefore to D_0 (see plot on next page).

The plot decreases linearly when only the χ_e term is taken into account and then Do can be found by extrapolation. In real systems the plots are nonlinear and therefore overestimate D_0.



The Birge-Sponer Plot



Example using the Birge-Sponer plot

The observed vibrational transitions in H_2^+ are observed at the following values:

0 → 1	2191 cm^{-1}
1 → 2	2046 cm^{-1}
2 → 3	1941 cm^{-1}
3 → 4	1821 cm^{-1}
4 → 5	1705 cm^{-1}
5 → 6	1591 cm^{-1}
6 → 7	1479 cm^{-1}
7 → 8	1368 cm^{-1}
8 → 9	1257 cm^{-1}
9 → 10	1145 cm^{-1}
10 → 11	1033 cm^{-1}
11 → 12	918 cm^{-1}
12 → 13	800 cm^{-1}
13 → 14	677 cm^{-1}
14 → 15	548 cm^{-1}
15 → 16	411 cm^{-1}

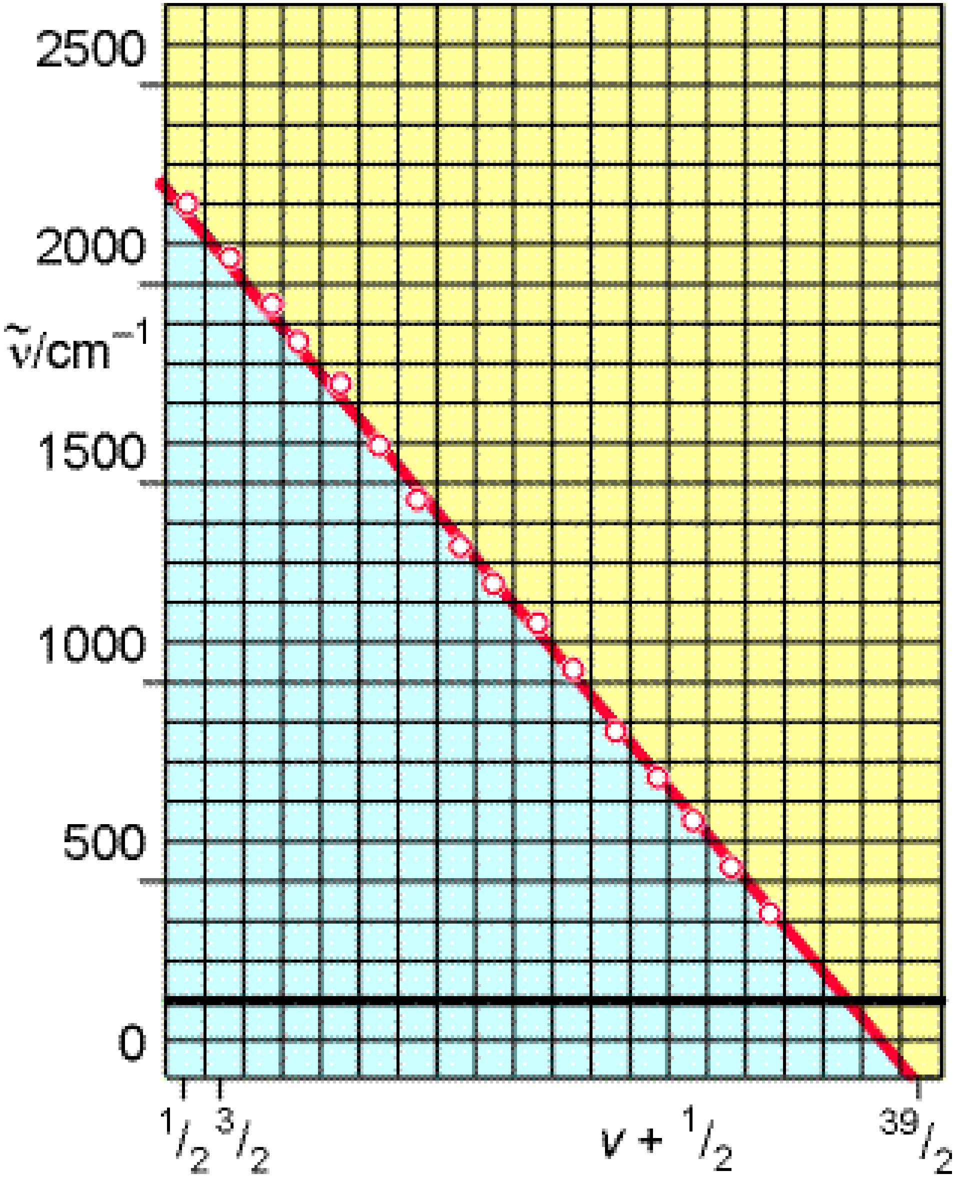
Determine the dissociation energy of the H_2^+ molecule.

Birge-Sponer Method:

Plot the line separations against n + 1/2, extrapolate linearly to the horizontal axis then measure the area under the curve (use formula for triangle or count the squares).

(See Birge-Sponer plot for this problem on next page).

Dissociation energy of H_2^+



Birge-Sponer Method:

The total area under the curve is 214 squares.

Each square corresponds to 100 cm^{-1},

so the dissociation energy is 21,400 cm^{-1}.