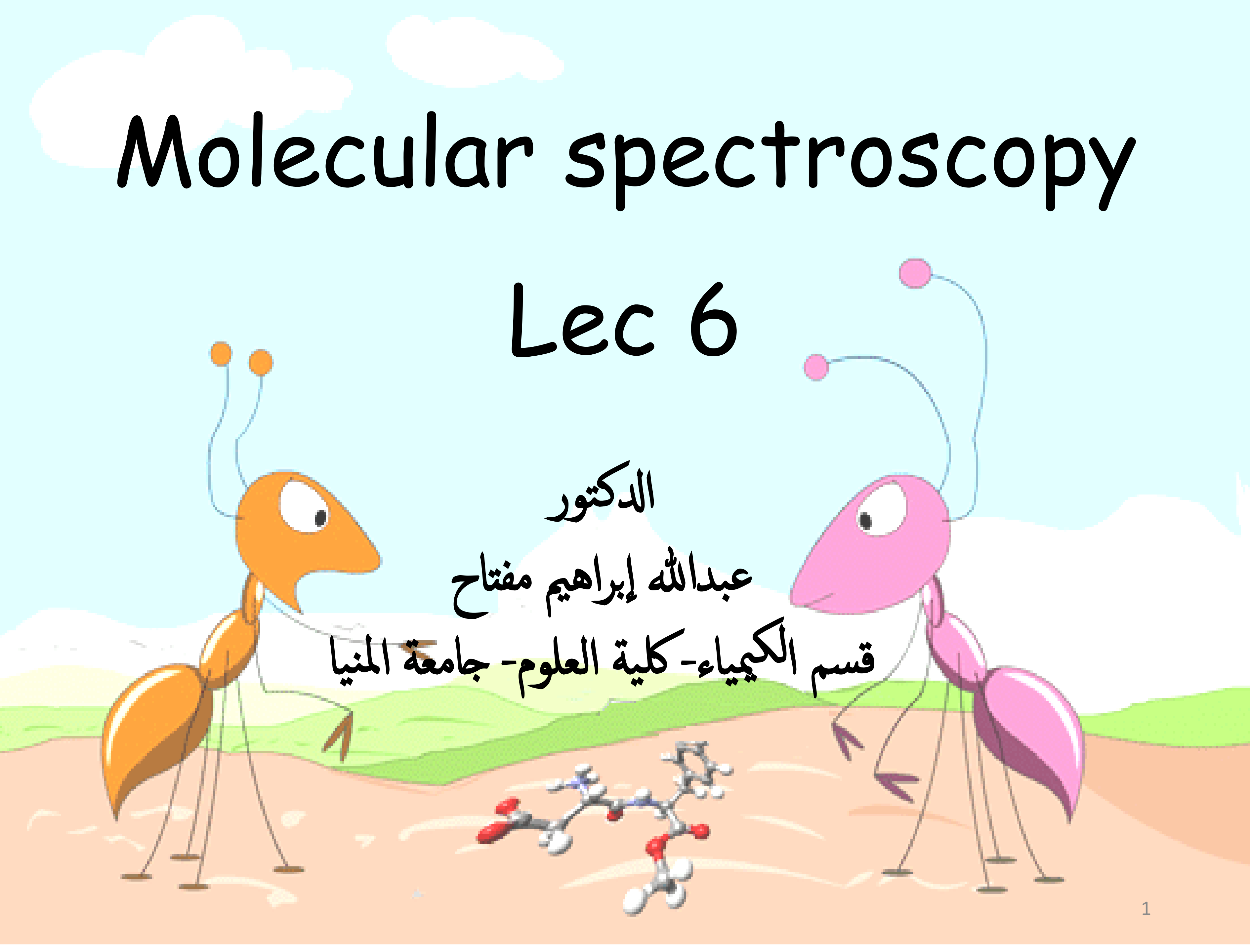

Molecular spectroscopy

Lec 6

الدكتور

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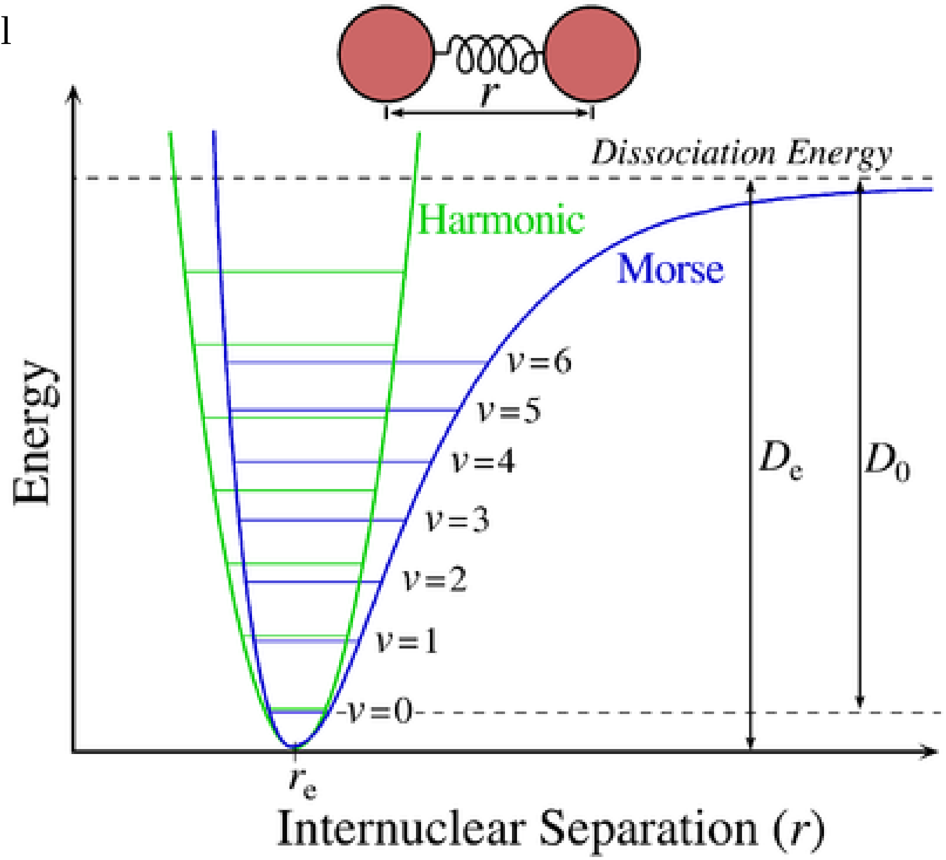
Anharmonic Oscillator Model

- The energy levels in a harmonic oscillator are equally spaced by an energy $\bar{\upsilon}$. The effect of anharmonicity is that the levels get increasingly closer together as the vibrational quantum number v increases, until eventually there is no difference in energy between successive quantum states. The energy at which this occurs (known as the dissociation energy) coincides with the point at which the potential energy function reaches zero and the molecule is no longer bound (this is the reason why the energy levels are no longer quantized).
- Real bonds, although elastic, do not exactly obey Hook’s law especially at higher vibrational levels.
- If the bond between atoms is stretched there comes a point at which it will break – the molecule will dissociate into atoms.
- As we stretch a bond the bond itself gets weaker (the restoring force is reduced)
- The dissociation energy may be measured either from the bottom of the potential, in which case it is called D_e, or from the zero point energy, in which case it is called D_0.



Anharmonic Oscillator Model

An empirical expression for this curve was derived by P. M. Morse and is called the Morse function

$$E_{Morse} = D_{eq}(1-e^{-a(r-r_e)})^2$$

The curve is called the Morse Curve

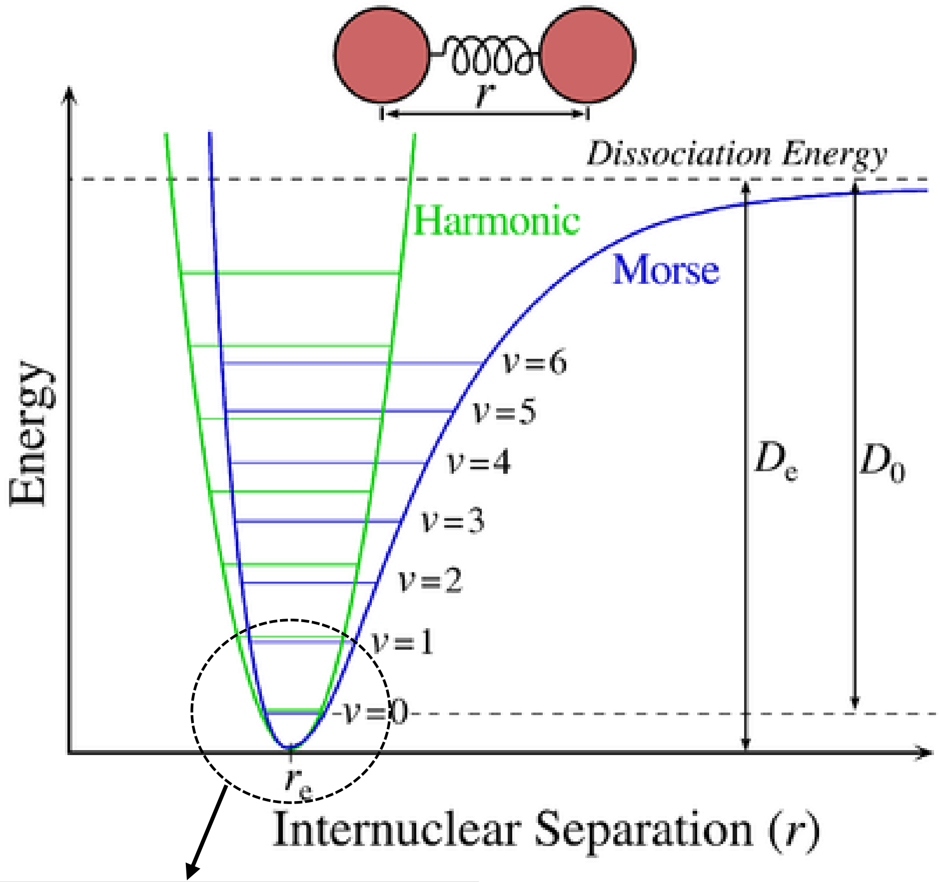
D_e is the dissociation energy

a is a constant for a particular molecule

By solving Schrodinger equation for an anharmonic oscillator we get the allowed vibrational energy levels:

$$E_v = \left(v+\frac{1}{2}\right)\bar{\upsilon}_e - \left(v+\frac{1}{2}\right)^2 x_e\bar{\upsilon}_e \qquad cm^{-1}$$

x_e = anharmonicity constant. It has small positive magnitude



behaves like Simple Harmonic Oscillator at small y (low *v*)

$$E_{v=0} = \frac{1}{2}\bar{v}_e \quad - \frac{1}{4}x_e\bar{v}_e \qquad cm^{-1}$$

$$E_{v=1} = \frac{3}{2}\bar{v}_e \quad - \frac{9}{4}x_e\bar{v}_e \qquad cm^{-1}$$

$$E_{v=2} = \frac{5}{2}\bar{v}_e \quad - \frac{25}{4}x_e\bar{v}_e \qquad cm^{-1}$$

The vibrational levels crowd more closely together with increasing v.

- ❑ To determine the dissociation energy, we set $\frac{dE}{dv}$ equal to zero to determine the maximum value of the vibrational quantum number *v*.

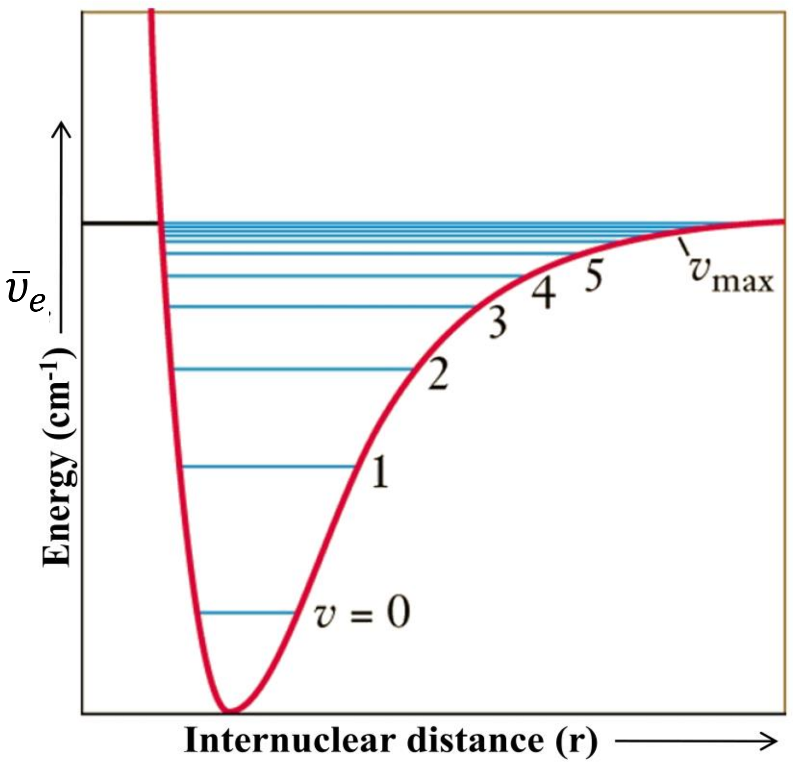
$$\frac{dE}{dv} = 0 = v_e - 2\left(v_{max} + \frac{1}{2}\right)x_e v_e$$

$$\Rightarrow \left(v_{max} + \frac{1}{2}\right) = \frac{v_e}{2x_e v_e}$$

Substituting back into the energy expression above gives

$$D_e = E(v_{max}) = \frac{v_e^2}{4x_e v_e}$$

D_e and D_0 are related by



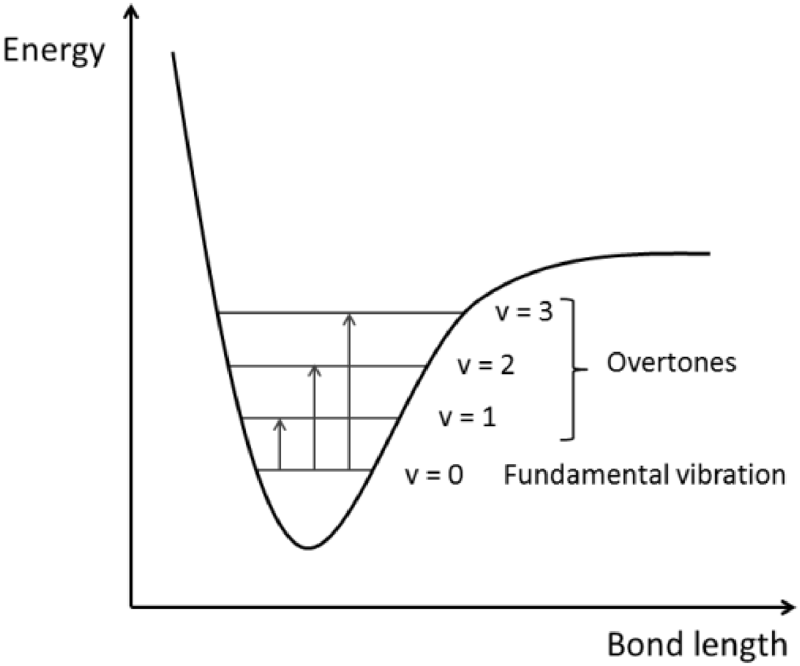
The experimental dissociation energy,
$D_0 = D_e$ -ZPE

Selection rule for the anharmonic oscillator

$\Delta v = \pm 1, \pm 2, \pm 3, \ldots$
$\Delta v = +1, +2, +3 \ldots$ (absorption)
$\Delta v = -1, -2, -3 \ldots$ (emission)

- ❑ Boltzmann distribution says the population of the v =1 state is around 1% of the ground state population.

- ❑ Consider only the transitions from v = 0 state Only the lines of $\Delta v = \pm 1, \pm 2, \pm 3$ have observable intensity; transition probability rapidly diminishes for higher jumps

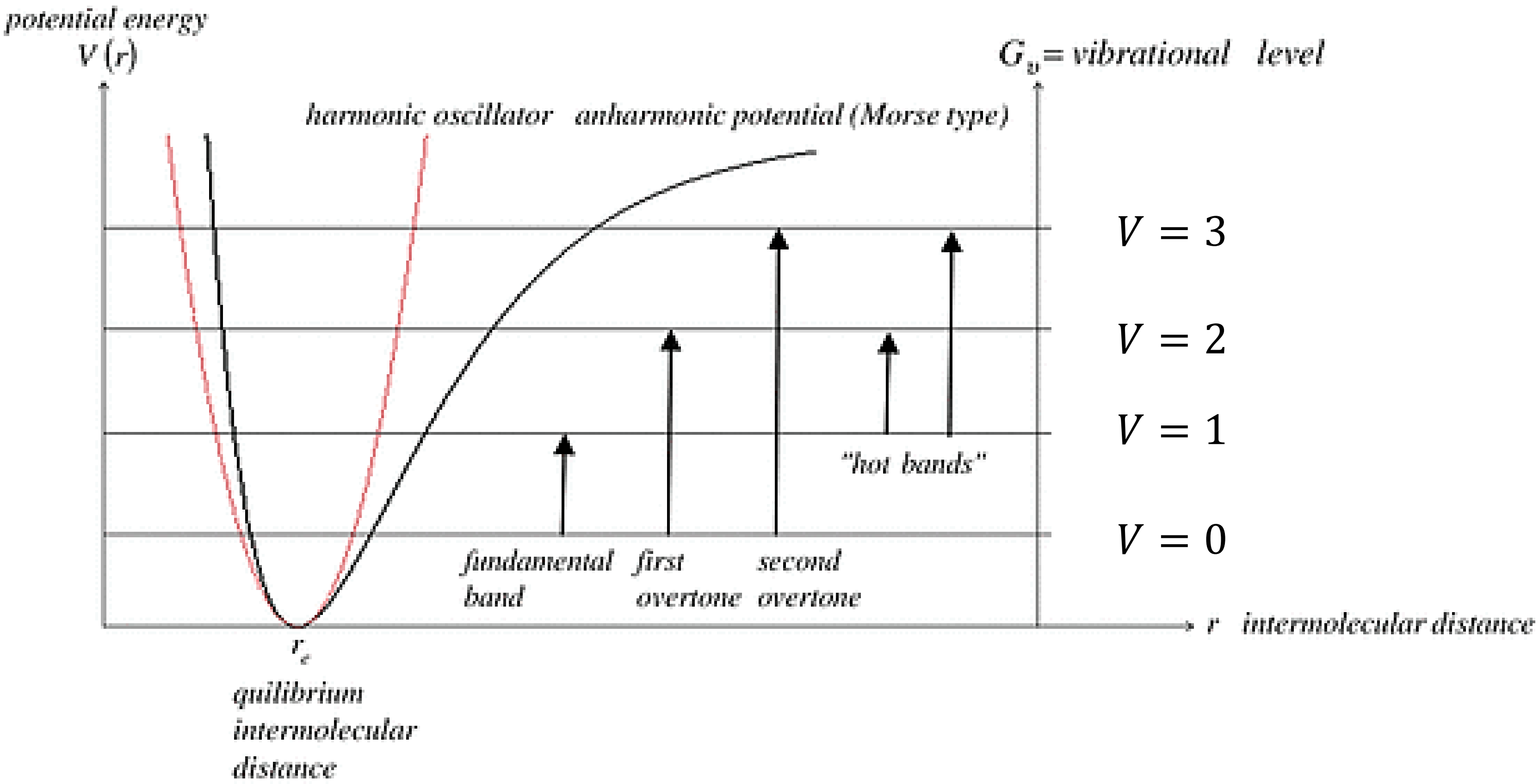


- ➢ $E_{0\to1} = \bar{\upsilon}_e(1-2x_e)$ cm^{-1} $v = 0 \to v = 1$ $(\Delta v = +1)$: fundamental absorption
- ➢ $E_{0\to2} = 2\bar{\upsilon}_e(1-3x_e)$ cm^{-1} $v = 0 \to v = 2$ $(\Delta v = +2)$: first overtone band
- ➢ $E_{0\to3} = 3\bar{\upsilon}_e(1-4x_e)$ cm^{-1} $v = 0 \to v = 3$ $(\Delta v = +3)$: second overtone band

} weaker

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.



Example: Overtone bands in CO

Explain the difference between overtone bands and hot bands in infrared spectroscopy. The fundamental and first overtone transitions of $^{12}C^{16}O$ are at 2143.2 cm^{-1} and 4259.9 cm^{-1}, respectively. Evaluate: (a) the equilibrium vibration wavenumber, $\bar{\upsilon}_e$ (b) the anharmonicity constant, x_e, (c) the anharmonic zero point energy and (d) the force constant of the molecule.

Answer

- ✓ **Overtone bands** arise from transitions with $\Delta v = \pm 2, \pm 3, \ldots$ and they are forbidden for a simple harmonic oscillator, but are allowed as a result of the anharmonicity of real potential energy curves. Overtone bands are significantly weaker than the fundamental $\Delta v = \pm 1$ transition and occur at approximate multiples of the fundamental wavenumber $\bar{\upsilon}$.
- ✓ **Hot band absorptions** are all $\Delta v = +1$ arising from vibrational levels other than the ground vibrational level, *e.g.* the first hot hand is $\Delta v_{2,1}$ and the second hot band is $\Delta v_{3,2}$. They are generally much weaker than the fundamental as the large vibrational energy spacing compared with thermal energies results in negligible population of excited vibrational levels at room temperature as given by the Boltzmann distribution.

Ref. Chemistry: Quantum Mechanics and Spectroscopy II (J. E. Parker)

Hot bands will only be significant at elevated temperatures, or for molecules with very low vibrational wavenumbers such as I_2 with $\bar{\upsilon}e = 214.5 \text{ cm}^{-1}$ where a significant excited state population exists even at 298 K. Hot bands are all close to, but less than, the fundamental transition $\Delta v_{1,0}$.

$$E_v = \left(v + \frac{1}{2}\right)\bar{\upsilon}_e - \left(v + \frac{1}{2}\right)^2 x_e\bar{\upsilon}_e \qquad cm^{-1}$$

$$E_{v=0} = \frac{1}{2}\bar{\upsilon}_e - \frac{1}{4}x_e\bar{\upsilon}_e \qquad cm^{-1}$$

$$E_{v=1} = \frac{3}{2}\bar{\upsilon}_e - \frac{9}{4}x_e\bar{\upsilon}_e \qquad cm^{-1}$$

$$E_{v=2} = \frac{5}{2}\bar{\upsilon}_e - \frac{25}{4}x_e\bar{\upsilon}_e \qquad cm^{-1}$$

Three equations, two unknowns, can solve equations to find $\boldsymbol{x_e}$ and $\boldsymbol{\bar{\upsilon}_e}$

$$\boxed{\Delta E_{1,0} = E_{v=1} - E_{v=0} = \bar{\upsilon}_e - 2x_e\bar{\upsilon}_e = 2143.2 \qquad cm^{-1}}$$

$$\boxed{\Delta E_{2,0} = E_{v=2} - E_{v=0} = 2\bar{\upsilon}_e - 6x_e\bar{\upsilon}_e = 4259.9 \qquad cm^{-1}}$$

Ref. Chemistry: Quantum Mechanics and Spectroscopy II (J. E. Parker)

$$3\Delta E_{1,0} - \Delta E_{2,0} \qquad gives \qquad \boldsymbol{\bar{\upsilon}_e = 2169.7\ cm^{-1}}$$

$$2\Delta E_{1,0} - \Delta E_{2,0} \qquad gives \qquad 2x_e\bar{\upsilon}_e = 26.5\ \ cm^{-1}$$

The anharmonicity constant $\boldsymbol{x_e = 6.1068 \times 10^{-3}}$

(c) The zero point energy is the energy of the lowest vibrational level, *v* = 0.

$$E_{v=0} = \frac{1}{2}\bar{\upsilon}_e - \frac{1}{4}x_e\bar{\upsilon}_e = \frac{1}{2} \times 2169.7 - \frac{1}{4}13.25 = \boldsymbol{1081.5\ \ cm^{-1}}$$

(d) The force constant of the molecule *k* is related to the vibrational wavenumber and reduced mass *μ*.

$$\mu = \frac{m_O m_C}{m_O + m_C} = \frac{15.9949 \times 12}{15.9949 + 12} \times 1.66605 \times 10^{-27} = 1.1385 \times 10^{-26}\,Kg$$

$$\bar{\upsilon}_e = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \Rightarrow k = 4\pi^2 c^2 \bar{\upsilon}_e^2\,\mu$$

$$\boldsymbol{k} = 4\pi^2(2.9979 \times 10^{10})^2(2169.7)^2\ \ (1.1385 \times 10^{-26}) \quad \boldsymbol{= 1901.6\,Nm^{-1}}$$

Ref. Chemistry: Quantum Mechanics and Spectroscopy II (J. E. Parker)

The molecule $^{14}N^{16}O$ has an equilibrium vibration wavenumber $\bar{\upsilon}_e$ = 1904.2 cm^{-1} and an anharmonicity term $x_e\bar{\upsilon}_e$ = 14.08 cm^{-1}. Calculate the dissociation energy D_e assuming that the vibrational energy E(v) is given by the Morse potential and then calculate D_0. Use

1 cm^{-1} = 11.958 kJ mol^{-1}.

$$E_v = \left(v + \frac{1}{2}\right)\bar{\upsilon}_e - \left(v + \frac{1}{2}\right)^2 x_e\bar{\upsilon}_e = \left(\boldsymbol{v} + \frac{\mathbf{1}}{\mathbf{2}}\right)\bar{\boldsymbol{\upsilon}}_{\boldsymbol{e}} - \left(\boldsymbol{v}^{\mathbf{2}} + \boldsymbol{v} + \frac{\mathbf{1}}{\mathbf{4}}\right)\boldsymbol{x}_{\boldsymbol{e}}\bar{\boldsymbol{\upsilon}}_{\boldsymbol{e}}$$

$$E_{v+1} = \left(v + \frac{3}{2}\right)\bar{\upsilon}_e - \left(v + \frac{3}{2}\right)^2 x_e\bar{\upsilon}_e = \left(\boldsymbol{v} + \frac{\mathbf{3}}{\mathbf{2}}\right)\bar{\boldsymbol{\upsilon}}_{\boldsymbol{e}} - \left(\boldsymbol{v}^{\mathbf{2}} + \mathbf{3}\boldsymbol{v} + \frac{\mathbf{9}}{\mathbf{4}}\right)\boldsymbol{x}_{\boldsymbol{e}}\bar{\boldsymbol{\upsilon}}_{\boldsymbol{e}}$$

$$\Delta E_{v+1,v} = \bar{\upsilon}_e - (2v + 2)x_e\bar{\upsilon}_e$$

$$(2v_{max} + 2)x_e\bar{\upsilon}_e = \bar{\upsilon}_e$$

$$2v_{max}x_e\bar{\upsilon}_e = \bar{\upsilon}_e - 2\,x_e\bar{\upsilon}_e$$

$$v_{max} = \frac{1}{2\,x_e} - 1 = \frac{1}{2 \times \left(\frac{140.8}{1904.2}\right)} - 1 = 66.6 \sim 66$$

Ref. Chemistry: Quantum Mechanics and Spectroscopy II (J. E. Parker)

$$D_e = E_{v_{max}} = \left(66 + \frac{1}{2}\right)1904.2 \;\; - \left(66 + \frac{1}{2}\right)^2 14.08 = 64364\ cm^{-1}$$

$$E_{v=0} = \left(\frac{1}{2}\right)1904.2 \;\; - \left(\frac{1}{4}\right)14.08 = 948.6\ cm^{-1}$$

$$D_0 = D_e\text{-}\ E_{v=0} = 63415 \quad cm^{-1}$$

Ref. Chemistry: Quantum Mechanics and Spectroscopy II (J. E. Parker)