Hello students and welcome for the module , Amplitude of diatomic molecular vibrations in the topic molecular spectroscopy I of Section B of the course CHC105 Physical chemistry. In this particular topic we will be learning the vibrational energy levels for a simple harmonic oscillator, zero point energy, vibrational transitions, selection rule followed by the summary of the module.

After learning this topic, you will be able to quantify the vibrational energy for a simple harmonic oscillator , you will be able to understand what is zero point energy and will be able to visualize vibrational transitions and also apply selection rule for different vibrational transitions.

Consider here a simple diatomic molecule having atoms one and two connected by a bond between them. These atoms have masses $m_1$ and $m_2$ and the molecule is vibrating back and forth relative to their center of mass in opposite directions like a one dimensional simple harmonic oscillator.

So here the diatomic molecule is considered as a simple harmonic oscillator. Now when this molecule is oscillating, it is oscillating with a frequency and the frequency of this vibration is given by the formula in equation (1) that is

$$\nu = \frac{1}{2\pi}\left(\frac{k}{\mu}\right)^{1/2}$$

Where γ is the frequency in second$^{-1}$, K is the force constant of the bond between atom one and two, given in newtons per meter and μ is the reduced mass of the atoms one and two in kilograms.

This particular diatomic molecule behaves like a simple harmonic oscillator having potential energy which is given by Hooke's law equation as shown in equation (2),

$V(x)= ½ Kx^2$ -----(2)

where x is the displacement that occurs when the molecule undergoes vibration. Now for this particular system of a simple diatomic molecule we apply Schrodinger equation and the solution of Schrodinger equation for this molecule gives quantized vibrational energy levels which are given in equation (3)

$$E_V = \left(V + \frac{1}{2}\right)hv$$

where V is the vibrational quantum number which can have values from 0,1, 2, 3 and so on. From this we can make out that the simple harmonic oscillator has quantized vibrational energy. That means the energy levels for a simple harmonic oscillator are quantized and they are given according to equation (3).

Now the equation (3) is giving us energy in joules, so converting this energy in frequency in terms of wave number , we get

$$E_V = \left(V + \frac{1}{2}\right) hv = \left(V + \frac{1}{2}\right) hc\omega_e \qquad \text{----------------(4)}$$

Where ωe is the vibrational frequency in wave number and ωe is given by ν by C. So what we have done in equation (4) is we have replaced ν by ωe multiplied by C.So in equation (4) where we have hν, it is substituted with ωe C and so we get the equation Ev equal to (V+1/2)hcωe.

Next, using this equation (4) we can deduce the value of vibrational energy for different vibrational levels for a simple harmonic oscillator. So at vibrational level zero we get energy as half ωe. Now at zero level we should ideally not expect any vibration from a molecule because the molecule is at zero vibrational level. But as we can see in the table for the zeroth vibrational level the energy is not equal to 0 but it is equal to half ωe in terms of wavenumber and so, this particular energy is referred to as zero point energy.

Next coming to the vibrational level 1, substituting equation (4) in that we get the vibrational energy as 3/2 ωe. Similarly for the second vibrational level, the energy obtained is 5/2 ωe, for the third energy level, the energy obtained is 7 /2 ωe and if we try to get the difference in the energies of each of these levels we observe that the difference is constant. The difference in energy of each of the level is ωe .Hence we can conclude that the spacings between the adjacent vibrational levels are equidistant and they depend upon force constant and reduced mass of the molecule.

Coming to the vibrational transitions, whenever a molecule is in lower vibrational energy level and it is exposed to infrared radiation, the molecule absorbs radiation and goes to the excited state.

The selection rules are the rules which are applicable for this molecule undergoing transition from
one level to the other level. So for vibrational spectroscopy the selection rule is ΔV equal to±1. So at a time a molecule can go one level up or one level down.

So let us consider that this particular molecule is undergoing transition from level V " to level V'. So the difference in the vibrational level energies of the two levels will be, energy for V' level minus energy for V" level, so substituting here in equation (5)

$$\Delta E_V = \left(V' + \frac{1}{2}\right) hc\omega_e - \left(V'' + \frac{1}{2}\right) hc\omega_e = (V' - V'')hc\omega_e$$

Now converting this into frequency,

$$v = \frac{\Delta E_V}{h} = (V' - V'')c\omega_e$$

Therefore, frequency ν is equal to V' minus V'' Cωe. Converting this into wave number,

$$v^- = \frac{(V' - V'')}{c} c\omega_e = (V' - V'')\omega_e$$

Therefore from this it is clear that there's only one absorption line obtained in the spectrum for the transition which is equal to vibrational frequency of the diatomic molecule. So summarizing what we have studied in this module, a diatomic vibrating molecule undergoes simple harmonic motion. The vibrational energy levels are quantized and they are given by the formula ,

$$E_V = \left(V + \frac{1}{2}\right)hv$$

The energy of the lowest vibrational level of the molecule is not zero but has a finite value and it is referred as zero point energy. Considering the vibrational transitions, we apply selection rule which is Δ V
=±1 and according to this we know that there is only one absorption line obtained in the spectrum which is with wavenumber equal to the equilibrium vibrational frequency of the molecule.
These are the books that have been referred for making the notes. Thank you.