Vibrational spectra:

The diatomic molecules can vibrate in just one mode , to and fro along the axis joining their atomic centers , polyatomic molecules comprising (n) atoms have (3n-6) vibrational modes . If the molecule is also linear it has one more mode ,i.e., (3n-5)modes altogether (fig. 7)

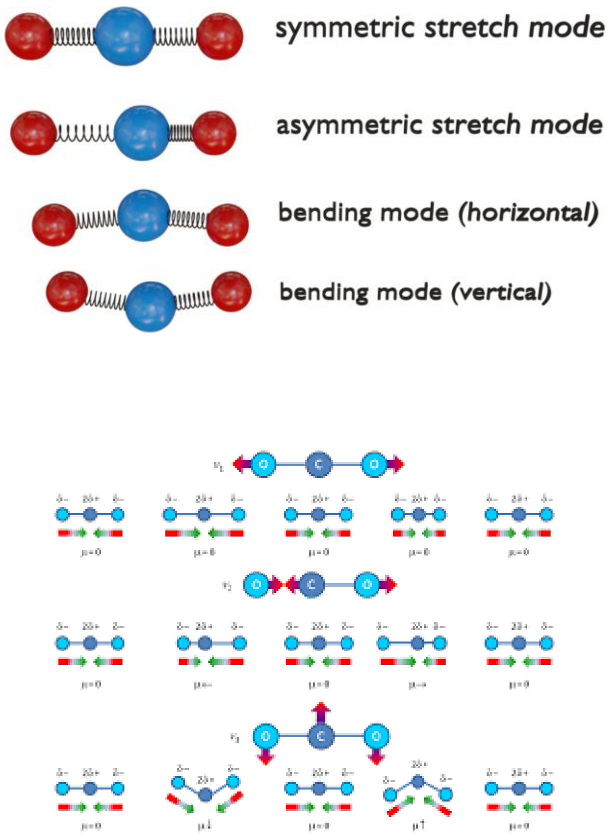

Fig. 7 The vibrational modes of a diatomic and tiatomic molecules

At low energies, the vibrations of a diatomic molecule can be described in terms of a harmonic oscillator. According to Planck's quantum hypothesis, the energy, E, of a harmonic oscillator of natural frequency ν_0 can only take the values E=$nh\nu_o$ where n= 0,1,2,3, …… This implies that in its ground state , n=0 , the energy of the oscillator should equal zero and that the oscillator should be completely at rest .However, this would contravene the Heisenberg Uncertainty principle ; complete rest implies no uncertainty whatsoever as to the system's position and linear momentum .

The correct expression for the energy , E_{vib} of the oscillator is obtained from quantum mechanics . The potential energy, U , of a simple harmonic oscillator is given by :

$$U = k\,\frac{x^2}{2} \quad \text{…………..(8)}$$

where k is the oscillator (spring) constant . Substituting this expression for the potential energy in the one-dimensional time independent Schrodinger equation gives :

$$\frac{d^2\varphi}{dx^2} + \frac{8\pi^2 m'}{\text{ɳ}2}\left[\mathrm{E_{vib}} - \frac{\mathrm{kx}^2}{2}\right]\varphi = 0 \qquad \text{………. (9)}$$

The energy eigenvalues given by the solution to this equation are

$$E_{vib} = (\mathrm{n} + \tfrac{1}{2})\mathrm{h}\nu_o \qquad \text{……… (10)}$$

Where the oscillator' s natural frequency , ν_o ,is given by

$$v_o = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} \qquad \ldots\ldots\ldots\ldots\ldots(11)$$

The integer n is called the vibrational quantum number and can take the values n = 0,1,2,3, ……. Thus , in its ground state, n= 0 , the oscillator has a 'zero point' energy of $hv_o/2$ and so is never completely at rest .

At low energies , where the diatomic molecule can be regarded as a harmonic oscillator , the vibrational energy levels are equally spaced . However , at higher energies , i.e. , higher vibrational quantum numbers , the oscillator becomes an harmonic as is shown in fig.   and the energy levels close up . As the energy increases , so does the amplitude of the vibrations . At the energy corresponding to the quantum number , n_c , the bond linking the atoms breaks.

In practice, the vibrational spectra of diatomic molecules are very simple , usually comprising just a single strong line called the fundamental line . There are two reasons for this :

1. The selection rule for radiative vibrational transitions is $\Delta n = \pm 1$. It follows , from equation (10) that only photons of frequency v_o will be absorbed or emitted in transitions between low energy vibrational states .

2. A typical value for the difference between two adjacent vibrational energy levels is $\Delta E_{vib} = 0.5$ eV

Fig. 8

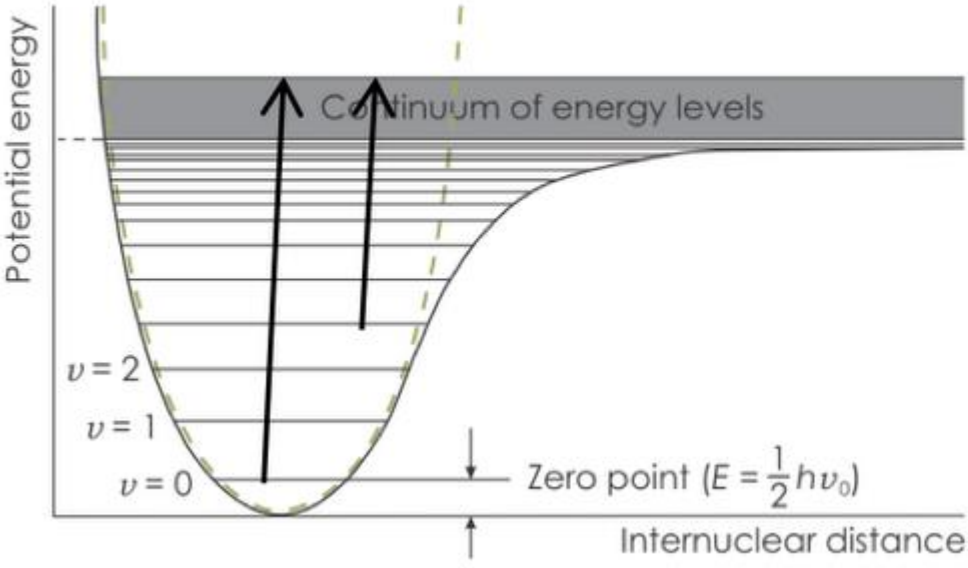

Fig. 8 The potential energy of a diatomic molecule

At low resolution, the fundamental line appears as a broad band. This is because the transitions between the vibrational states are accompanied by transitions between rotational states (fig.). In these transitions , photons with energies in the range $E_{\text{photon}} = \Delta E_{vib}+\Delta E_{rot}$ where ΔE_{rot} is the energy involved in these rotational transitions , are absorbed or emitted by the molecule. This range of photon energies shows up as a broadening of the fundamental line.

Electronic Spectra

Transitions between molecular electronic levels(ΔE_{elec}=1-10eV) are usually accompanied by transitions between the molecule′ s vibrational and rotational levels . Accordingly , the frequencies of the photons emitted and absorbed in such transitions are given by :

$$v = \frac{\Delta E elec + \Delta E vib + \Delta E\, rot}{h}$$

These frequencies are in the visible and the near ultra-violet . Transitions between electronic states appear as a spectral band . At higher resolutions these bands are seen to comprise closely packed lines corresponding to the various upper and lower vibrational and rotational levels .

Raman Spectra

In 1928 , Raman discovered that the light scattered by molecules contains frequencies other than those of the incident radiation ; the phenomenon is called Raman scattering . The source of the additional frequencies is in the internal structure of the scattering particles . Molecules both vibrate and rotate , and these motions can add to the vibrations induced by the electric field in the incident radiation . The phenomenon is best understood in terms of photons .

As a first possibility , a photon of energy hv striking a molecule will be scattered without any change in its energy (frequency). The molecule rises to a higher energy state form which it returns at once to its ground state by emitting an identical photon .

This is the mechanism of the normal Rayleigh scattering . A second possibility is that the excited molecule emits a photon of lower energy (frequency) than that which struck it , using the surplus to enhance the energy of its vibrations and rotations . In this case , the energy of the emitted photon is $h(\nu - \nu_{vib})$ and the increase in the molecule' s vibrational and/or rotational energy is $h\nu_{vib}$ (see fig.)

In rare instances , the incident photon will strike a molecule whose vibrational and/or rotational energy has already been enhanced . In this case , the molecule can emit a photon of energy $h(\nu - \nu_{vib})$. Thus , the scattered radiation can contain frequencies that are both slightly higher , $\nu - \nu_{vib}$, and slightly lower , $\nu - \nu_{vib}$, than that of the incident radiation .

Raman scattering is employed in the elucidation of molecular structures .

For example , the molecule N_2O has two possible configurations : NON and NNO. The first configuration is symmetrical ; the second is asymmetrical. This difference in their structures expresses itself as a difference in their vibrational modes . The Raman scattering of N_2O corresponds to vibrations of the asymmetrical configuration and thus the molecule 's structure was determined .