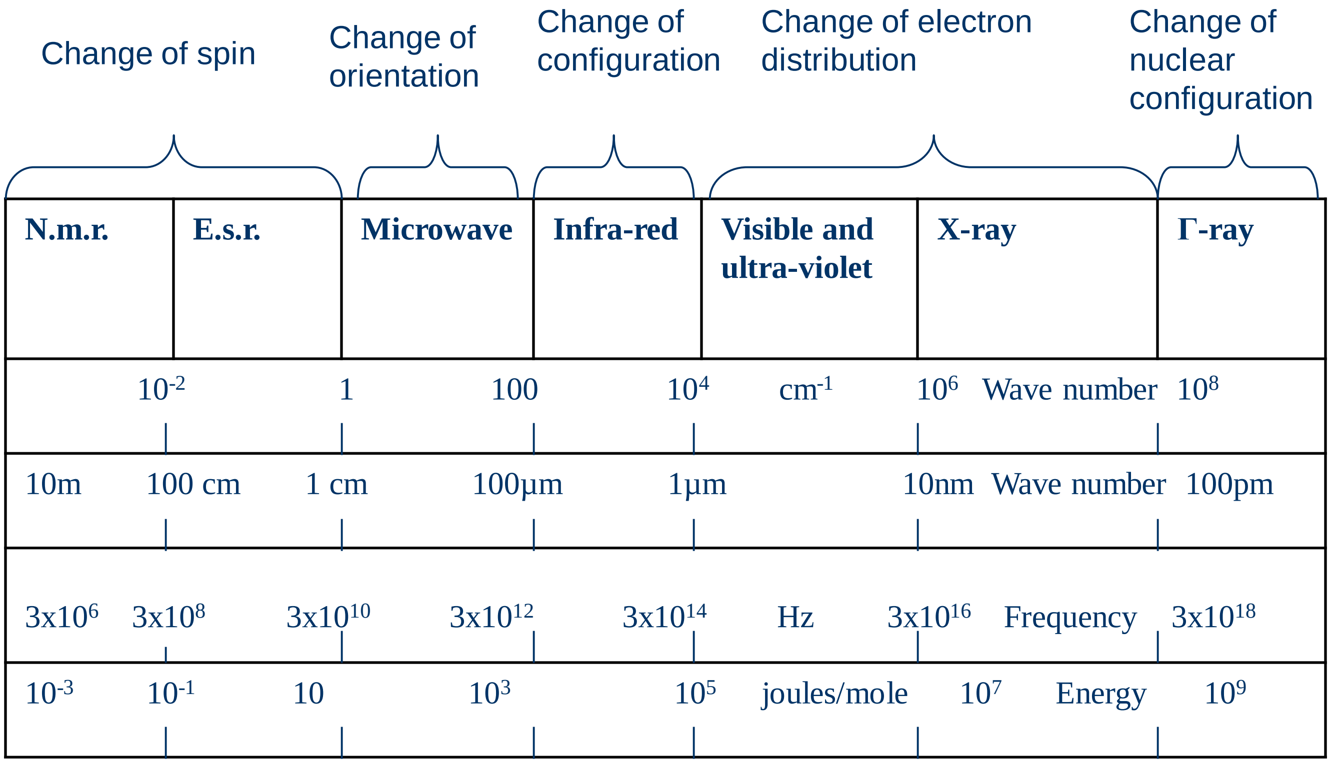
Vibrational Spectroscopy

Dr.V.A.Kalantre

The regions of the electromagnetic spectrum



Change of spin

Change of orientation

Change of configuration

Change of electron distribution

Change of nuclear configuration

N.m.r. | **E.s.r.** | **Microwave** | **Infra-red** | **Visible and ultra-violet** | **X-ray** | **Γ-ray**

10^{-2} 1 100 10^{4} cm^{-1} 10^{6} Wave number 10^{8}

10m 100 cm 1 cm 100µm 1µm 10nm Wave number 100pm

$3x10^{6}$ $3x10^{8}$ $3x10^{10}$ $3x10^{12}$ $3x10^{14}$ Hz $3x10^{16}$ Frequency $3x10^{18}$

10^{-3} 10^{-1} 10 10^{3} 10^{5} joules/mole 10^{7} Energy 10^{9}

Raman spectroscopy, yields information similar to that obtained in microwave and I.R. regions although the experimental method is such that observations are made in visible regions.

1] Rotational Spectroscopy

2] Infra-red Spectroscopy

3] Raman Spectroscopy

4] UV and Visible region

5] NMR Spectroscopy

6] ESR Spectroscopy

7] Mossbauer Spectra or Nuclear Gamma Resonance Fluorescence (NRF) spectroscopy

Infra-Red Spectroscopy

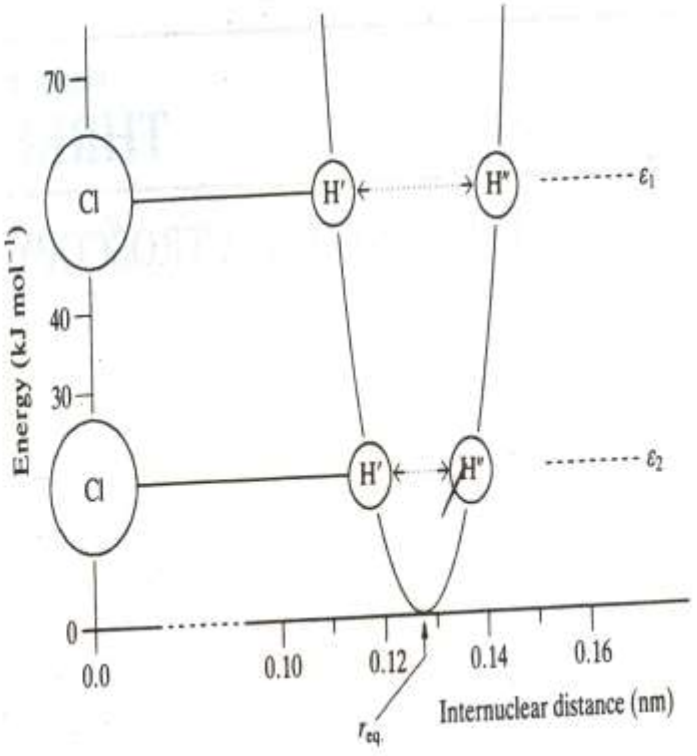


Figure 3.1 The energy of HCl as the bond is compressed or extended.

The compression and extension of a bond (like spring) obeys Hooks law i.e. $f = -K (r - r_{eq})$
Where f is restoring force, K is force constant and r is inter nuclear distance. The energy curve is parabolic and has the form
$E = \frac{1}{2} K (r - r_{eq})^2$
This mode of vibrating diatomic molecule is called simple harmonic oscillates.

v

The oscillation frequency is

$$\omega_{osc} = 1/2\pi \ \sqrt{k/\mu} \qquad \text{Hz}$$

Where μ is reduced mass of system

$$\omega_{osc} = 1/2\pi c \ \sqrt{k/\mu} \qquad \text{cm-1}$$

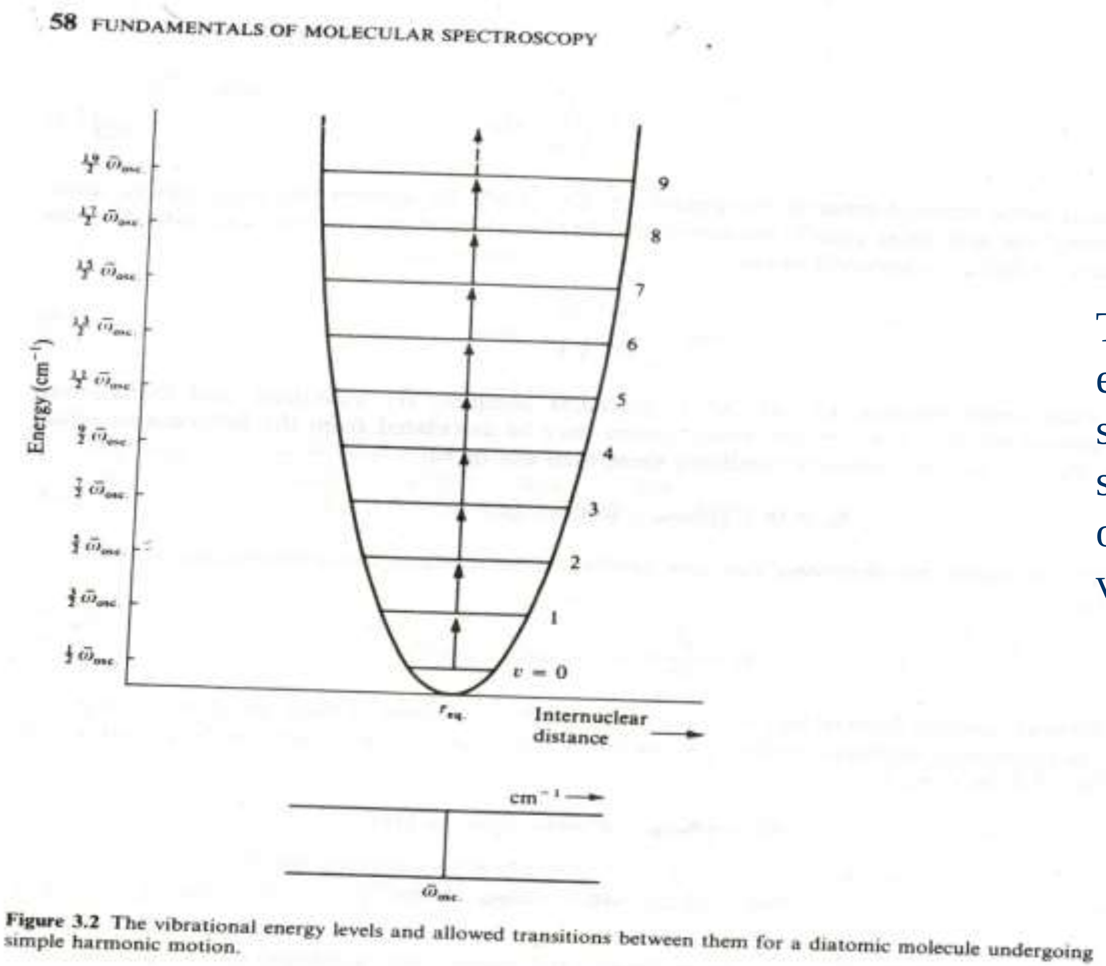
Vibrational energies are quantized.The allowed vibrational energies for a particular system is calculated from Schrodinger equation. For simple harmonic oscillator

$$Ev = \left(v + \frac{1}{2}\right) h\omega_{osc} \qquad \text{joules} \qquad v = (0,1,2, \dots \dots \dots .)$$

where v is vibrational quantum number.

$$\varepsilon\, v \quad = Ev/hc \quad = \quad \left(v + \frac{1}{2}\right) h\omega_{osc} \qquad \text{cm-1}$$

are the energies allowed to a simple harmonic vibrator.



58 FUNDAMENTALS OF MOLECULAR SPECTROSCOPY

Figure 3.2 The vibrational energy levels and allowed transitions between them for a diatomic molecule undergoing simple harmonic motion.

The Schrodinger equation leads to the simple selection rule for simple harmonic oscillator undergoing vibrational changes

$$\Delta v = \pm 1$$

Anharmonic oscillator

An empirical expression for anharmonic oscillator was derived by P.M.Morse is

$$E = Deq[1 - \exp a(req - r)]2$$

where a is constant for a particular molecule and Deq is called dissociation energy

$$\varepsilon v = \left(v + \frac{1}{2}\right) \omega e - \left(v + \frac{1}{2}\right) 2\ \omega e\ xe \quad \text{cm-1} \qquad v = (0,1,2, \dots \dots \dots .)$$

The simple selection rule for the anharmonic oscillator undergoing vibrational changes

$$\Delta v = \pm 1, \pm 2, \pm 3, \dots \dots$$

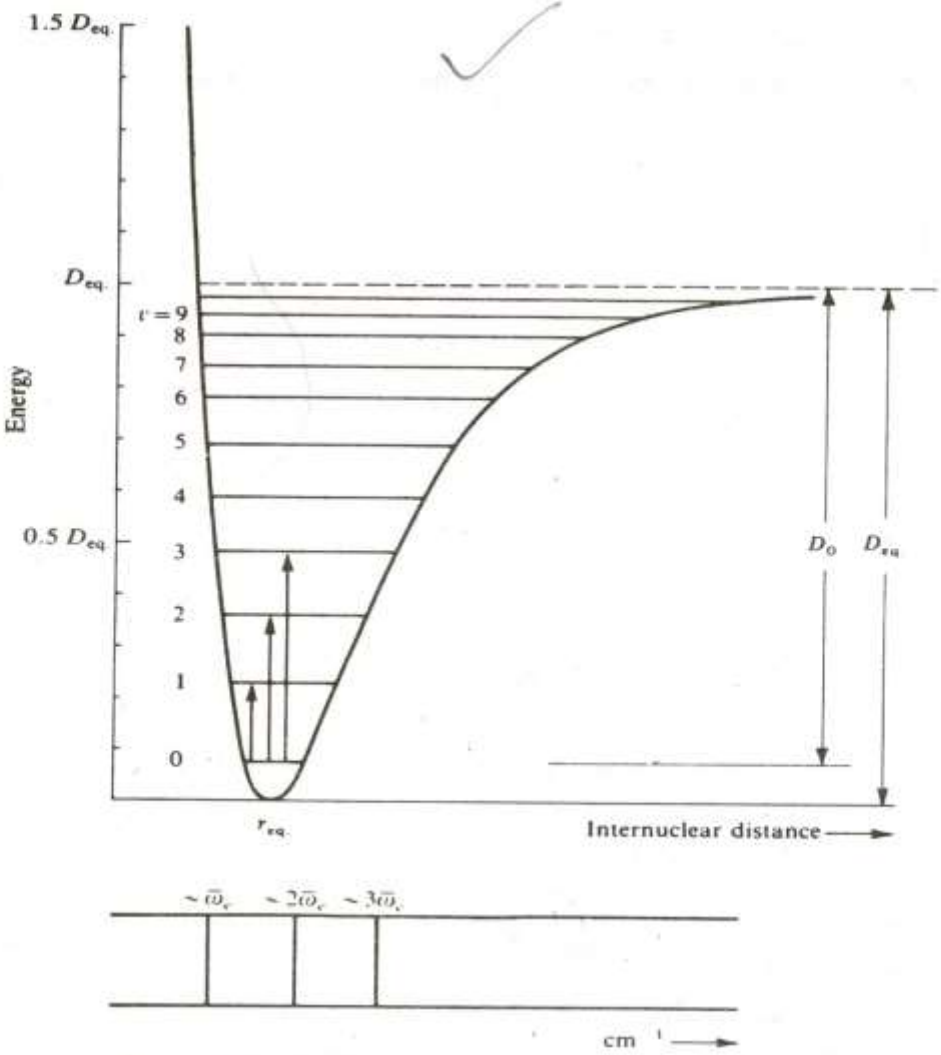


Figure 3.4 The vibrational energy levels and some transitions between them for a diatomic molecule undergoing inharmonic oscillations.

v = 0 to *v* =1, Δ*v*=+1 with considerable intensity

Δε = ε*v* =1 - ε*v* =0

$\omega e \ (1 - 2xe)$ cm-1

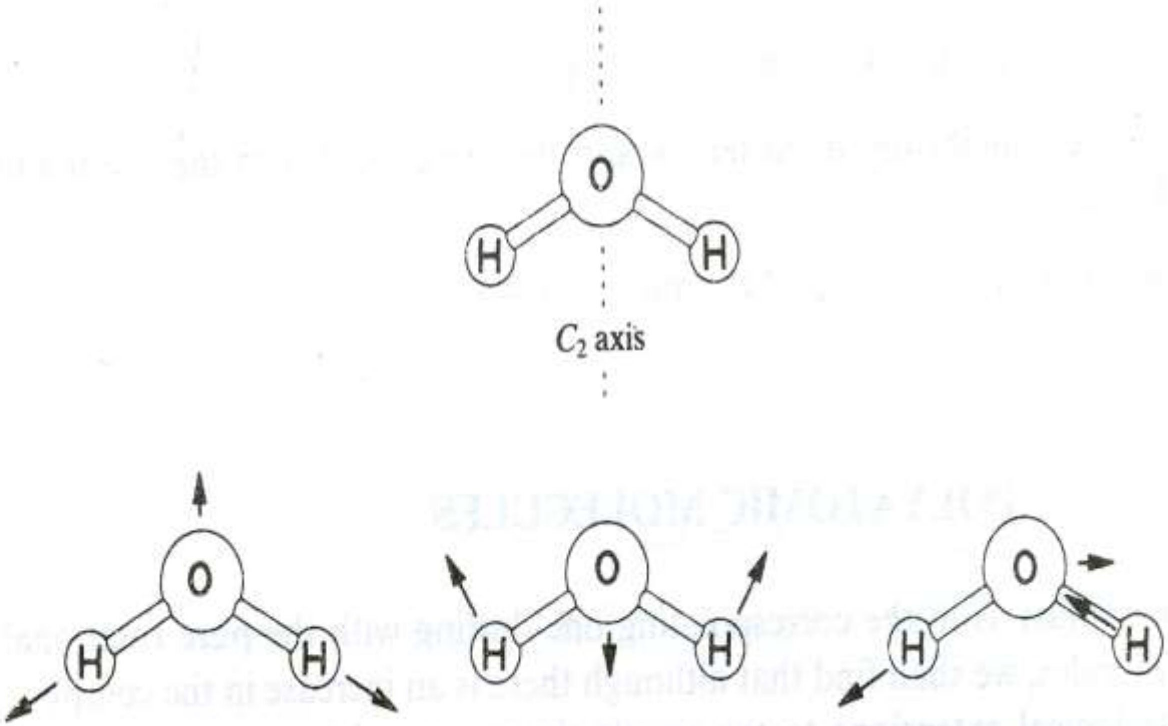
v = 1 to *v* =2 Δ*v*=+2 with small intensity

$2\omega e \ (1 - 3xe)$ cm-1

v = 2 to *v* =2 Δ*v*=+3 with normally negligble intensity

$3\omega e \ (1 - 4xe)$ cm-1

Since $xe \approx 0.01$ the line near is called the fundamental absorption , while those near 2ωe and 3ωe are called the first overtones and second overtones respectively



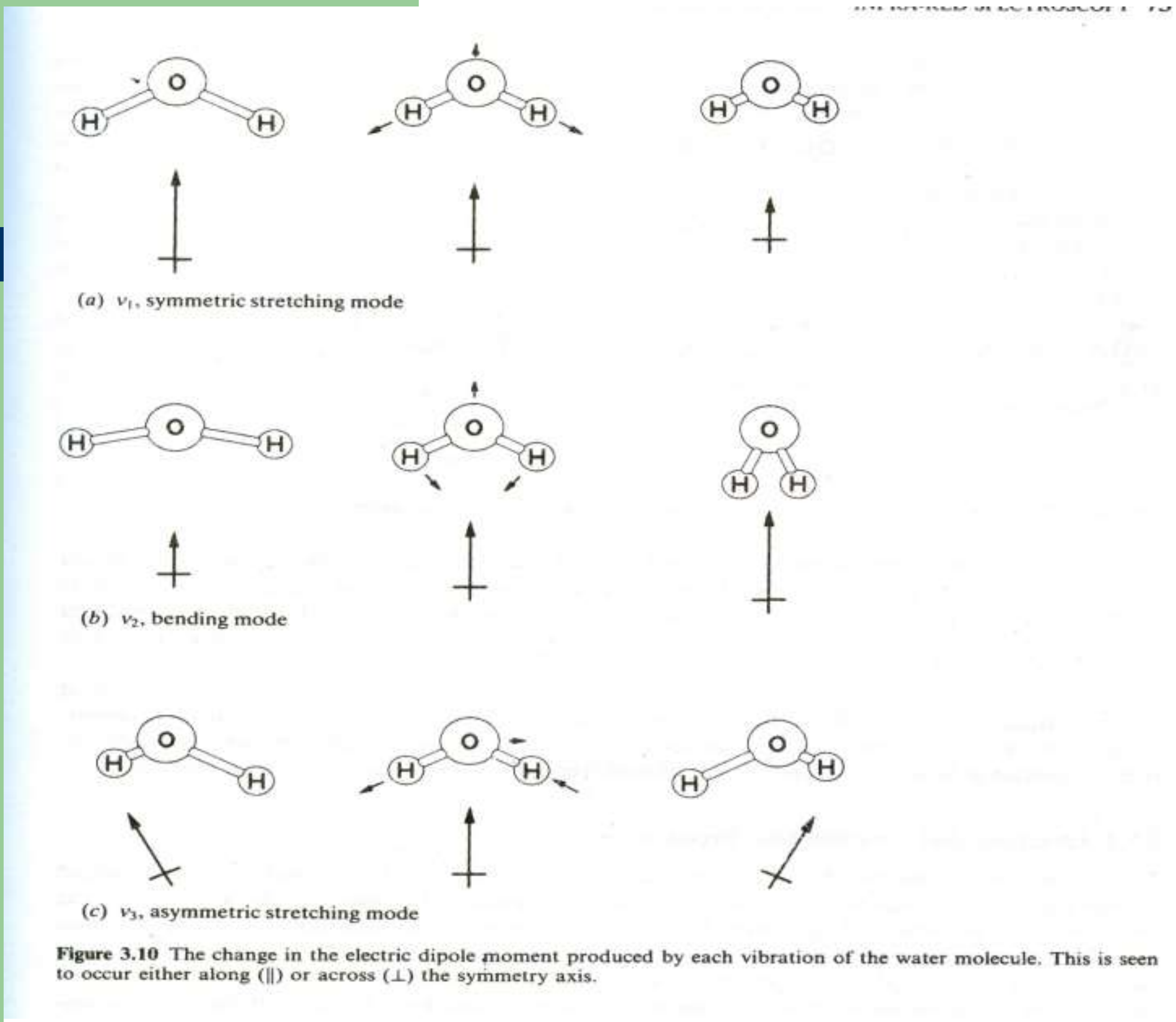
(*a*) Symmetric stretch
3651.7 cm^{-1}
ν_1, parallel (∥)

(*b*) Symmetric bend
1595.0 cm^{-1}
ν_2, parallel (∥)

(*c*) Antisymmetric stretch
3755.8 cm^{-1}
ν_3, perpendicular (⊥)

Figure 3.9 The symmetry of the water molecule and its three fundamental vibrations.

or intensity of overtone vibrations—these are governed

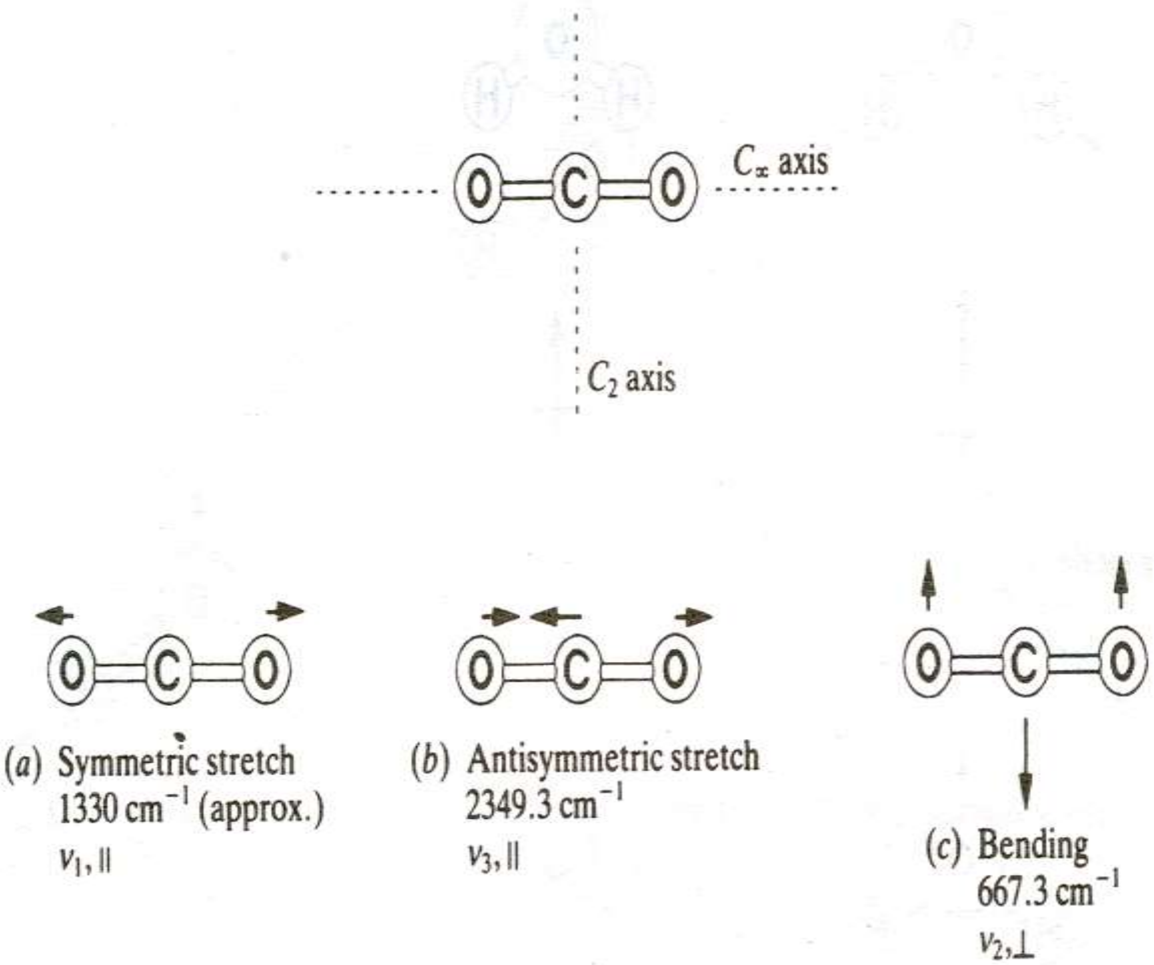


(*a*) ν_1, symmetric stretching mode

(*b*) ν_2, bending mode

(*c*) ν_3, asymmetric stretching mode

Figure 3.10 The change in the electric dipole moment produced by each vibration of the water molecule. This is seen to occur either along (‖) or across (⊥) the symmetry axis.



(*a*) Symmetric stretch
$1330\ \mathrm{cm}^{-1}$ (approx.)
$\nu_1, \parallel$

(*b*) Antisymmetric stretch
$2349.3\ \mathrm{cm}^{-1}$
$\nu_3, \parallel$

(*c*) Bending
$667.3\ \mathrm{cm}^{-1}$
$\nu_2, \perp$

Figure 3.11 The symmetry and fundamental vibrations of the carbon dioxide molecule.

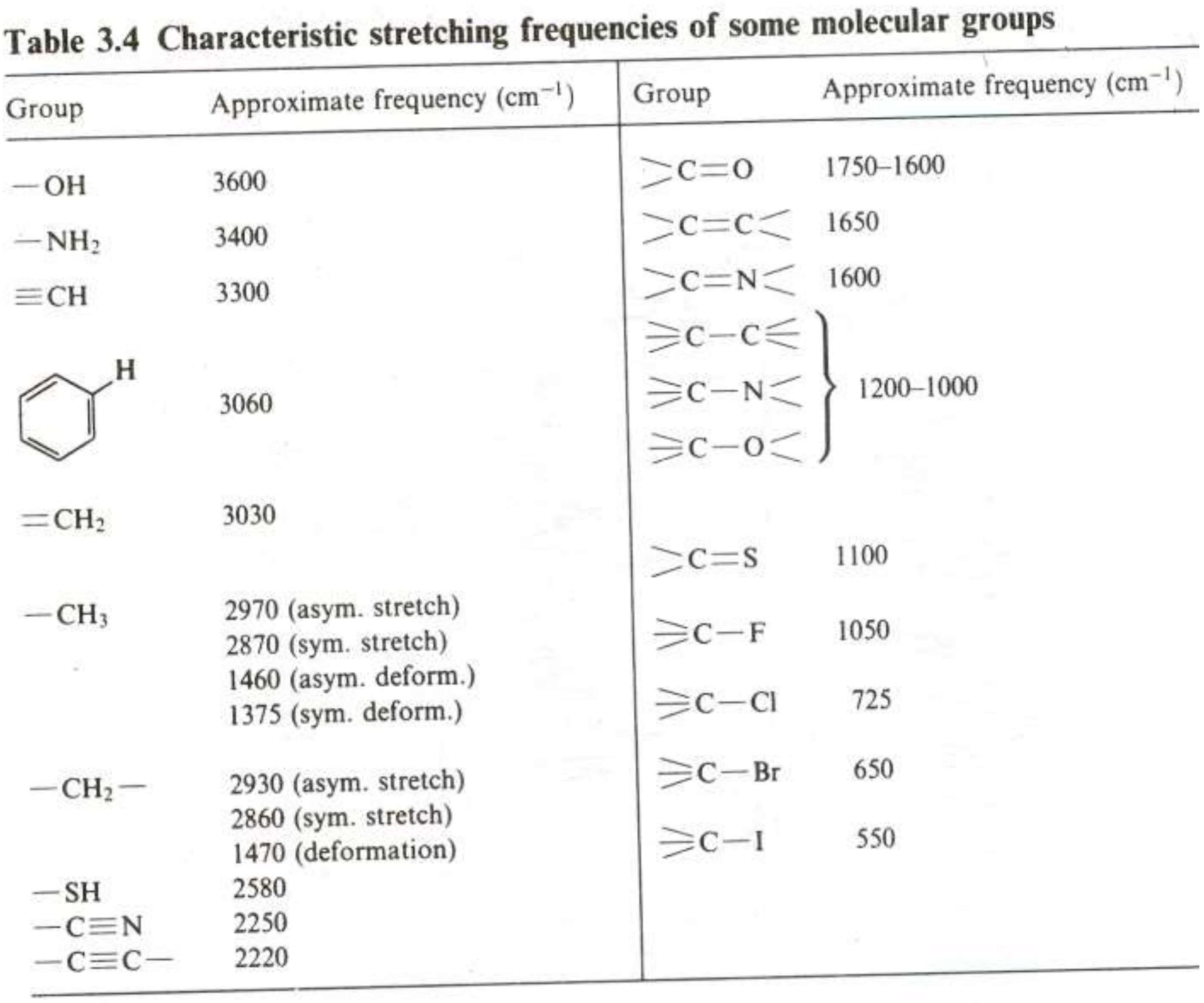
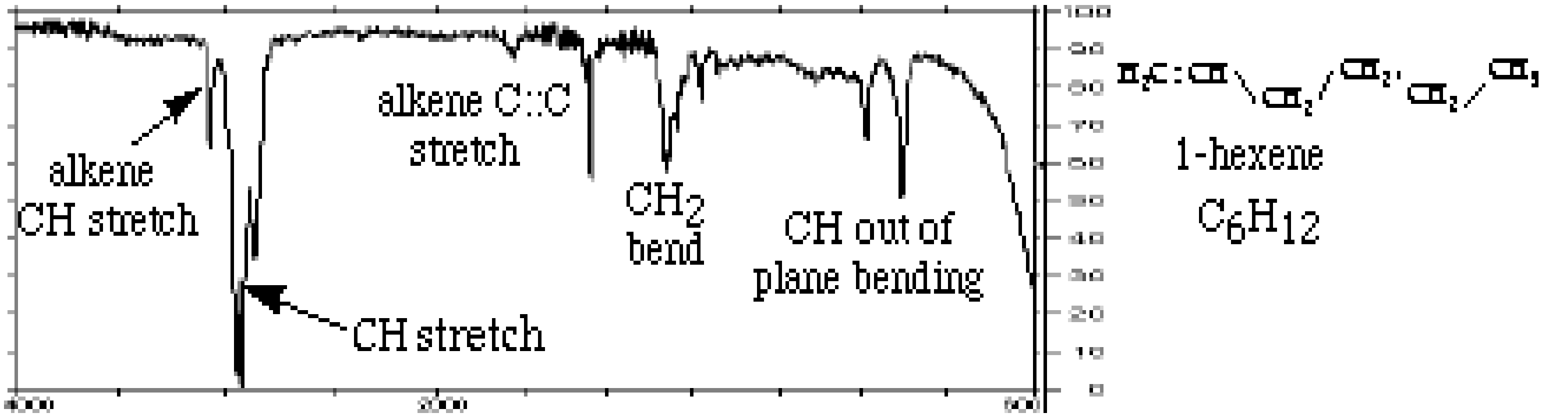


Table 3.4 Characteristic stretching frequencies of some molecular groups

Group	Approximate frequency (cm^{-1})	Group	Approximate frequency (cm^{-1})
$-OH$	3600	$>C=O$	1750–1600
$-NH_2$	3400	$>C=C<$	1650
$\equiv CH$	3300	$>C=N<$	1600
H	3060	$\geqslant C-C \leqslant$ $\geqslant C-N<$ $\geqslant C-O<$	1200–1000
$=CH_2$	3030	$>C=S$	1100
$-CH_3$	2970 (asym. stretch) 2870 (sym. stretch) 1460 (asym. deform.) 1375 (sym. deform.)	$\geqslant C-F$ $\geqslant C-Cl$	1050 725
$-CH_2-$	2930 (asym. stretch) 2860 (sym. stretch) 1470 (deformation)	$\geqslant C-Br$ $\geqslant C-I$	650 550
$-SH$	2580		
$-C\equiv N$	2250		
$-C\equiv C-$	2220		

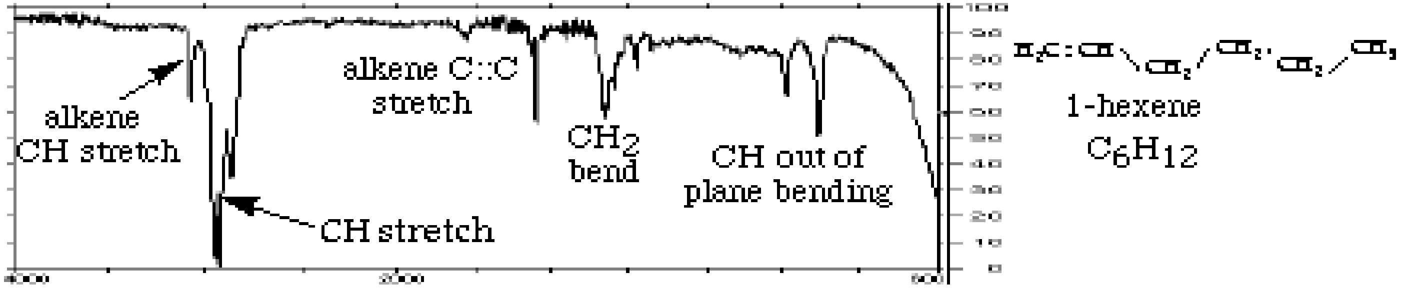
IR spectrum for the alkene

The spectrum for 1-hexene, C_6H_{12}, has few strong absorption bands. The spectrum has the various C-H stretch bands that all hydrocarbons show near 3000 cm^{-1}. There is a weak alkene C-H stretch above 3000 cm^{-1}. This comes from the C&H bonds on carbons 1 and 2, the two carbons that are held together by the double bond. The strong CH stretch bands below 3000 cm^{-1} come from C-H bonds in the CH_2 and CH_3 groups. There is an out-of-plane CH bend for the alkene in the range 1000-650 cm^{-1}. There is also an alkene C-C double bond stretch at about 1650 cm^{-1} .



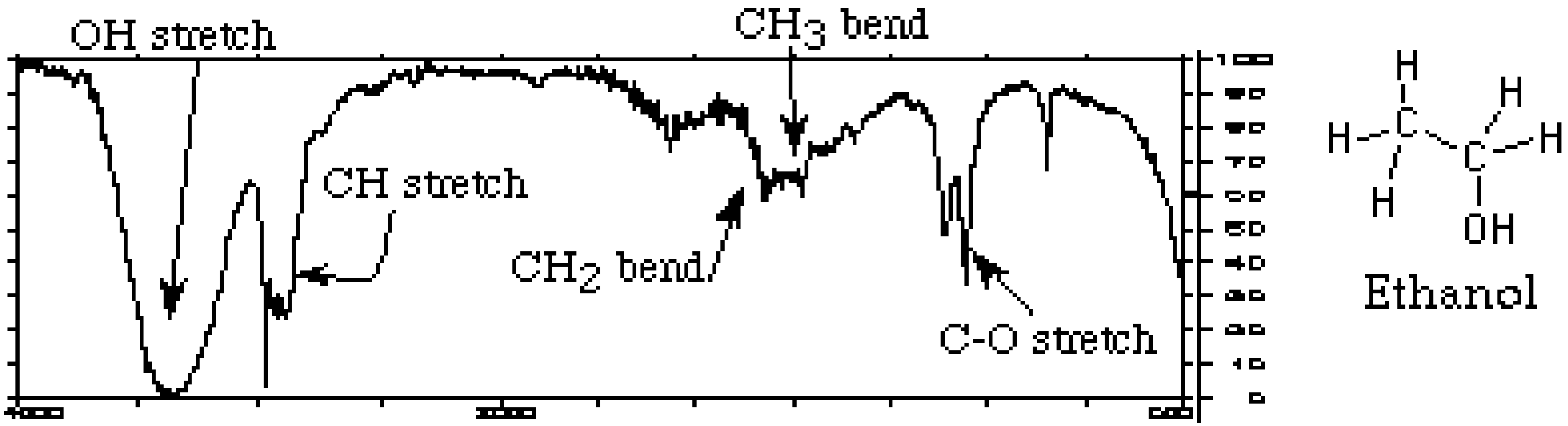
IR spectrum for benzene

The IR spectrum for benzene, C_6H_6, has only four prominent bands because it is a very symmetric molecule. Every carbon has a single bond to a hydrogen. Each carbon is bonded to two other carbons and the carbon-carbon bonds are alike for all six carbons. The molecule is planar. The aromatic CH stretch appears at 3100-3000 cm^{-1} There are aromatic C-C stretch bands at about 1500 cm^{-1}. Two bands are caused by bending motions involving C-H bonds at approx. 1000 cm^{-1} and at about 675 cm^{-1}.



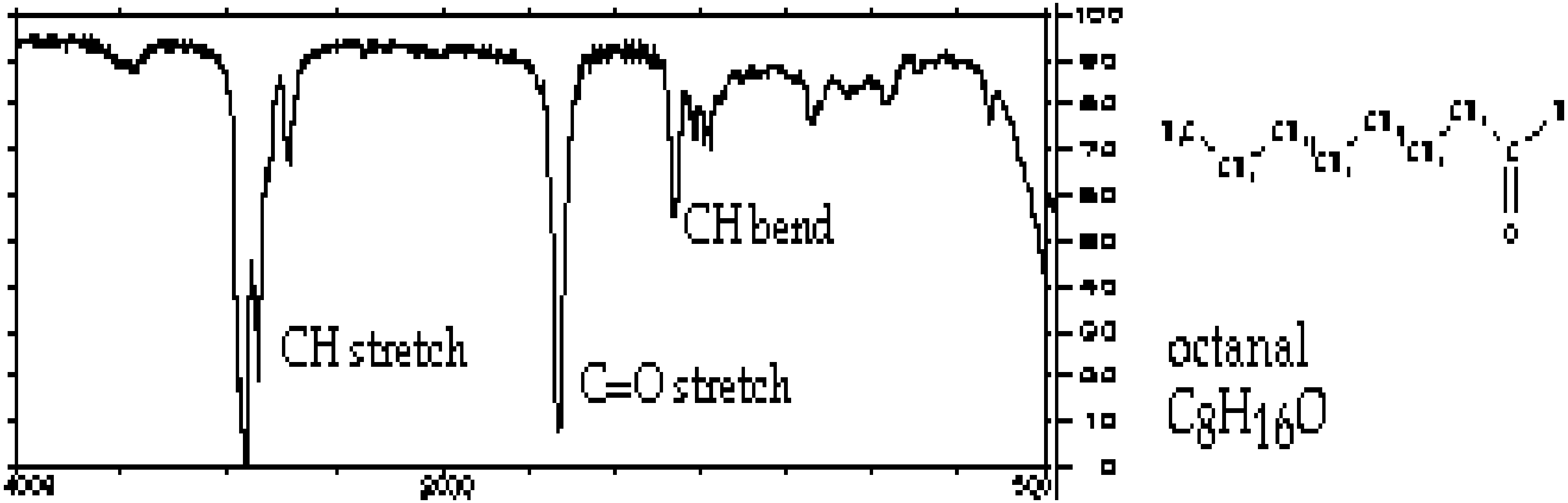
IR spectrum for the alcohol

The IR spectrum for ethanol (CH_3CH_2OH), is more complicated. It has a C-H stretch, an O-H stretch, a C-O stretch and various bending vibrations. The important point to learn here is that no matter what alcohol molecule you deal with, the O-H stretch will appear as a broad band at approximately 3300-3500 cm^{-1}. Likewise the C-H stretch still appears at about 3000 cm^{-1}.



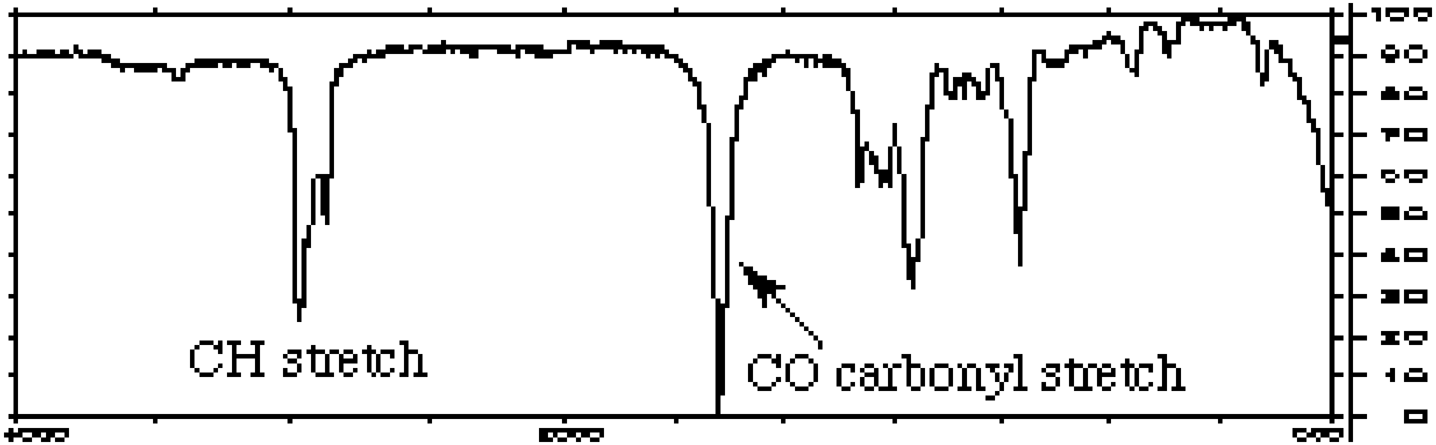
The spectrum for an aldehyde

The spectrum for octanal ($CH_3(CH_2)_6CHO$), is shown here. The most important features of the spectrum are carbonyl C=O stretch near 1700 cm^{-1} and the C-H stretch at about 3000 cm^{-1}. If you see an IR spectrum with an intense strong band near 1700 cm-1 and the compound contains oxygen, the molecule most likely contains a carbonyl group,



The IR spectrum for ketone

The spectrum for the ketone, 2-pentanone, appears below. It also has a characteristic strong carbonyl CO stretch at 1700 cm^{-1}. The CH stretch still appears at about 3000 cm^{-1}, and the CH2 bend shows up at approximately 1400 cm^{-1}. You can also see that this spectrum is different from the spectrum for octanal. At this point in your study of IR spectroscopy, you can't tell which compound is an aldehyde and which is a ketone. You can tell that both octanal and a 2-pentanone contain C-H bonds and a carbonyl group.



When you analyze the spectra, it is easier if you follow a series of steps in examining each spectrum.

1. Look first for the carbonyl C=O band. Look for a strong band at 1820-1660 cm-1. This band is usually the most intense absorption band in a spectrum. It will have a medium width. If you see the carbonyl band, look for other bands associated with functional groups that contain the carbonyl .If no C=O band is present, check for alcohols
2. If a C=O is present you want to determine if it is part of an acid, an ester, or an aldehyde or ketone.

ACID	A n O-H is also present. It has a broad absorption near 3300-2500 cm^{-1}. This actually will overlap the C-H stretch.
ESTER	Look for C-O absorption of medium intensity near 1300-1000 cm^{-1}. There will be no O-H band.
ALDEHYDE	Look for aldehyde type C-H absorption bands. These are two weak absorptions to the right of the C-H stretch near 2850 cm^{-1} and 2750 cm^{-1} and are caused by the C-H bond that is part of the aldehyde functional group.
KETONE	The weak aldehyde C-H absorption bands will be absent. Look for the carbonyl C=O band around 1725-1705 cm^{-1}.

3. If no carbonyl band appears in the spectrum, look for an alcohol O-H band.

4. If no carbonyl bands and no O-H bands are in the spectrum, check for double bonds, C=C, from an aromatic or an alkene.

ALKENE

Look for weak absorption near 1650 cm^{-1} for a double bond. There will be a CH stretch band near 3000 cm^{-1}.

AROMATIC

Look for the benzene, C=C, double bonds which appear as medium to strong absorptions in the region 1650-1450 cm^{-1}. The CH stretch band is much weaker than in alkenes.

5. If none of the previous groups can be identified, you may have an alkane.

ALKANE

The main absorption will be the C-H stretch near 3000 cm^{-1}. The spectrum will be simple with another band near 1450 cm^{-1}.

Thank You

Raman Spectroscopy

Classical Theory of the Raman Effect : Molecular Polarizability.

When a molecule is put into a static electric field it suffers some distortion, the positively charged nuclei being attracted towards the negative pole of the field, the electrons to the positive pole. This separation of charge centers causes an induced electric dipole moment to be set up in the molecule and the molecule is said to be Polarized. The size of the induced dipole μ, depends both on the magnitude of the applied field, E, and on the ease with which the molecule can be distorted. We many write

$$\mu = \alpha E$$

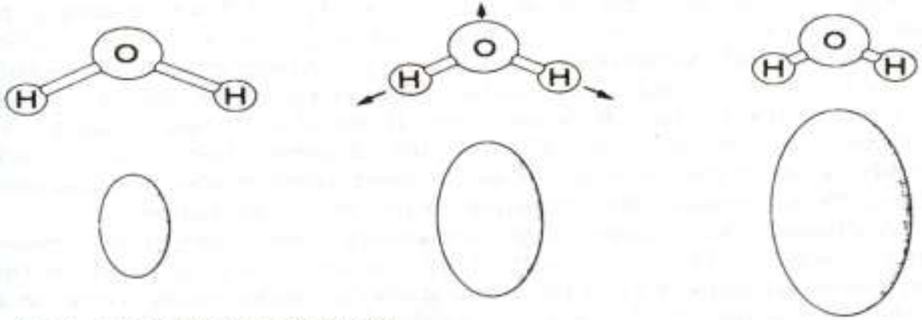
where α is the polarizability of the molecule.

When a sample of such molecule is subjected to a beam of radiation of frequency ν the electric field experienced by each molecule varies according to the equation

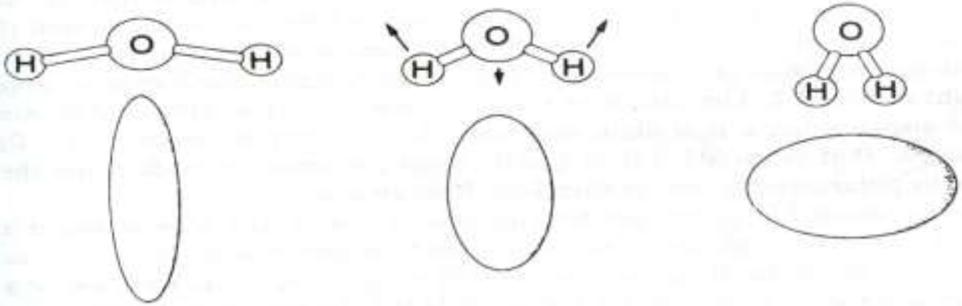
$$E = E_0 \sin 2\pi\nu t$$

and thus the induced dipole also undergoes oscillations of frequency ν :

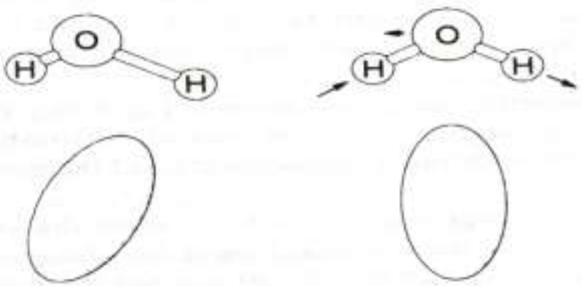
$$\mu = \alpha E = \alpha E_0 \sin 2\pi\nu t$$



(*a*) ν_1, symmetric stretching mode

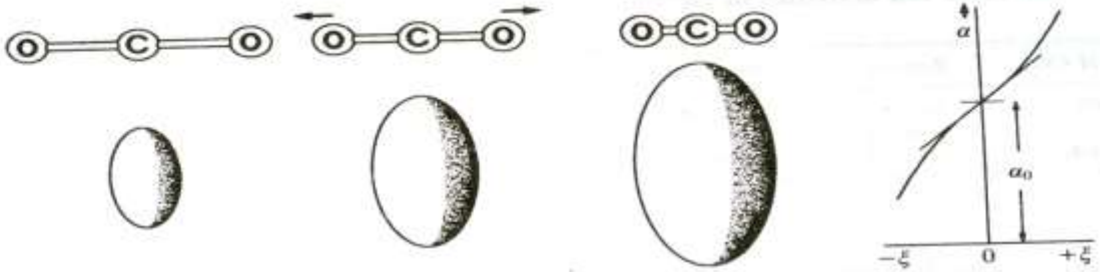


(*b*) ν_2, bending mode

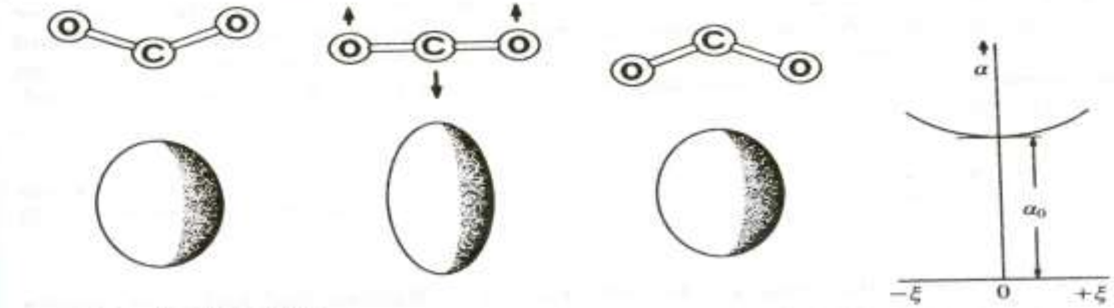


(*c*) ν_3, asymmetric stretching mode

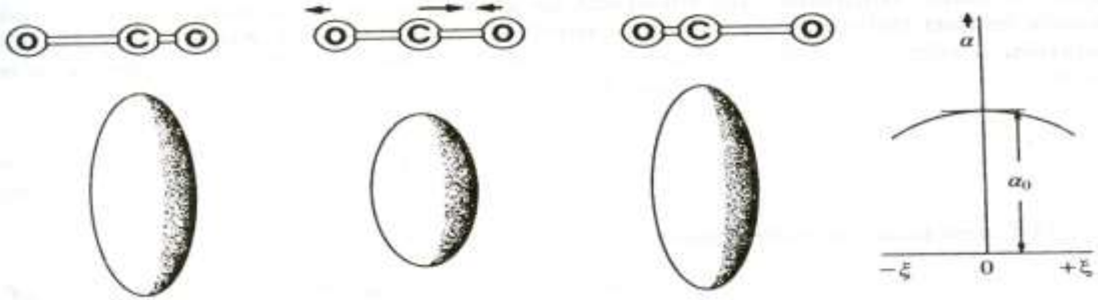
Figure 4.6 The change in size, shape, or direction of the polarizability ellipsoid of the water molecule during each of its three vibrational modes. The centre column shows the equilibrium position of the molecule, while to right and left are the (exaggerated) extremes of each vibration.



(*a*) ν_1, symmetric stretching mode



(*b*) ν_2, bending mode



(*c*) ν_3, asymmetric stretching mode

Figure 4.7 The changes in the polarizability ellipsoid of carbon dioxide during its vibrations, and a graph showing the variation of the polarizability, α, with the displacement coordinate, ξ, during each vibration.

Thank You