Vibrational Spectroscopy 2

Polyatomic Molecules

Recommended Reading:

Banwell and McCash Chapter 3

Atkins Chapter 16

Vibrational Modes

Diatomic molecules have 1 bond ⇒1 vibrational mode = bond stretch.

In polyatomic molecules bond lengths and angles can change

⇒ many different modes.

How many vibrational modes does a molecule have?

Consider a molecule with N atoms.

1. Need 3 co-ordinates (x,y,z) to specify position of each atom

⇒ 3N co-ordinates to specify shape of molecule

⇒ 3N degrees of freedom

2. Need 3 co-ordinates to specify translational motion (centre of mass)

⇒ 3N -3 degrees of freedom left

3. Need 3 co-ordinates (angles) to specify orientation of molecule

⇒ 3N -6 vibrational modes (non-linear)

4. If molecule is linear only need 2 angles to specify orientation

⇒ 3N -5 vibrational modes (linear)

Bending and Stretching Modes

If molecule has N atoms, then it will have N-1 bonds and each bond can undergo a stretching vibration.

⇒ N-1 stretching modes

this then leaves

⇒ (3N -6)-(N-1) = 2N-5 bending modes modes (non-linear molecule)

⇒ (3N -5)-(N-1) = 2N-4 bending modes modes (linear molecule)

A Normal Mode is a vibration that can be excited without exciting any of the other modes ⇒ no energy transfer between normal modes.

Any vibration of the molecule can be expressed as a linear sum of the Normal Modes of the molecule

Each normal mode can be considered as an independent oscillator with its own values of k, μ, and $\tilde{\nu}_0$

Each vibrational mode has its own set of energy levels

Each vibrational degree of motion corresponds to a separate type of coordinated overall motion of all of the atoms in the molecule, which is called a normal mode of vibration. For a general polyatomic molecule the total vibrational energy is conventionally written as

$$\boxed{\varepsilon_{vib}(n_1,n_2,n_3,\ldots)=\sum_i \tilde{\nu}_i\left(n_i+\frac{1}{2}\right)+\sum_i\sum_{j>i}\chi_{i,j}\left(n_i+\frac{1}{2}\right)\left(n_j+\frac{1}{2}\right)+\ldots}$$

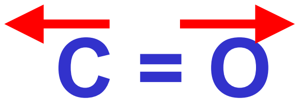
where n_i is the vibrational quantum number for mode i, ν_i and $\chi_{i,j}$ are the harmonic and leading anharmonic vibrational constants.

So in order to calculate the actual vibrational spacing associated with any particular mode it is necessary to know both the constants ν_i and $\chi_{i,i}$ associated with that mode but also all of the mixed anharmonicity constants $\chi_{i,j}$ for $j \neq i$.

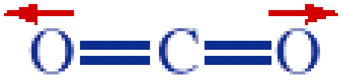
We now look at some specific simple examples:

Types of Vibration

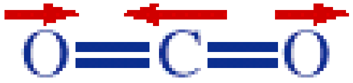
In diatomic molecules the only vibrational mode is a simple stretching mode.



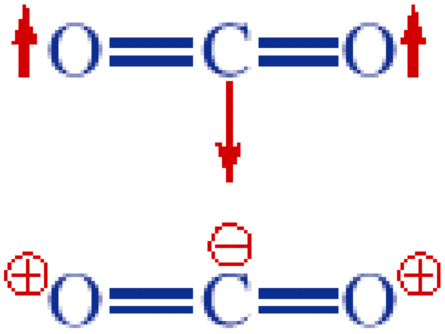
More unusual vibrational motions exist for the polyatomic case



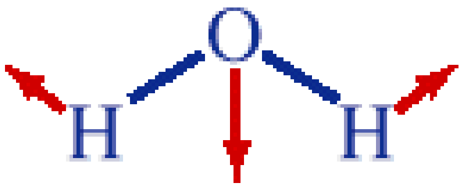
Symmetric stretch (breathing) mode



Antisymmetric stretch



Degenerate bending modes



symmetric deformation

Web site for animations:

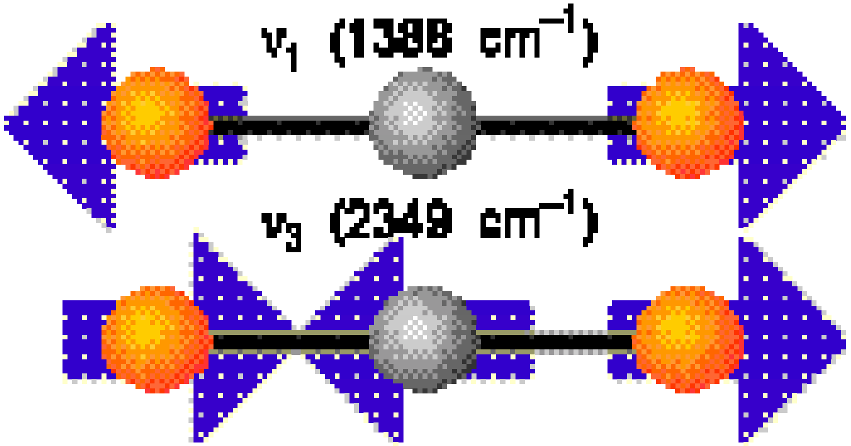
http://www.ems.psu.edu/~bannon/moledyn.html

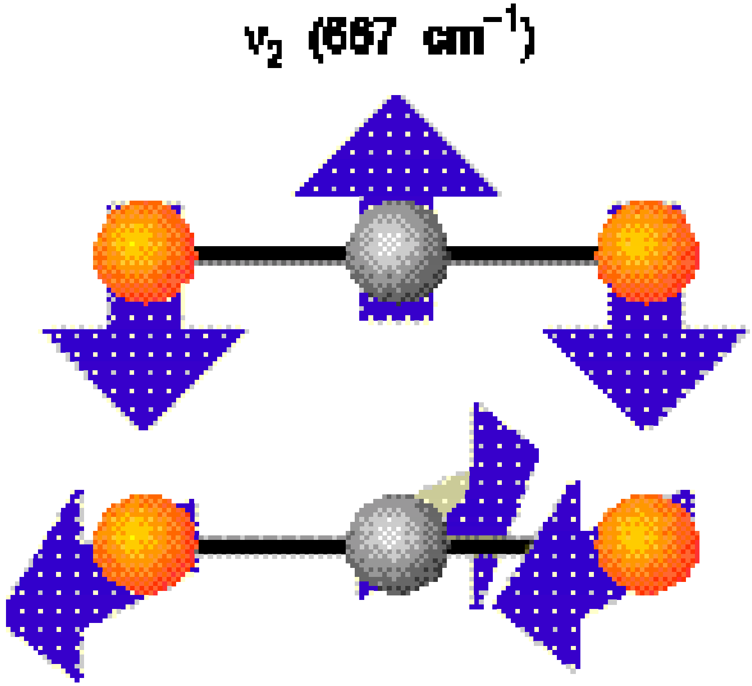
Example: Vibrational Modes of CO_2

Three atoms, linear molecule: N = 3 ⇒ 3N-5 = 4 vibrational modes

N-1 Stretching Modes: ⇒ 2

2N-4 Bending modes: ⇒ 2





Note that wavenumbers are in IR region of EM spectrum.

Bending modes are degenerate so they occur at the same energy (wavenumber).

How many lines would we see in the vibrational spectrum of CO_2?

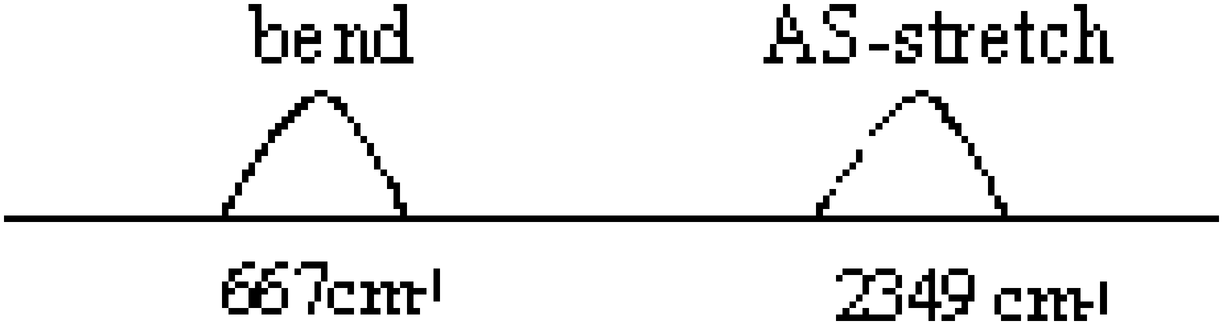
Hint: Don’t forget selection rules!

IR Spectrum of CO_2

Only see TWO vibrational bands.

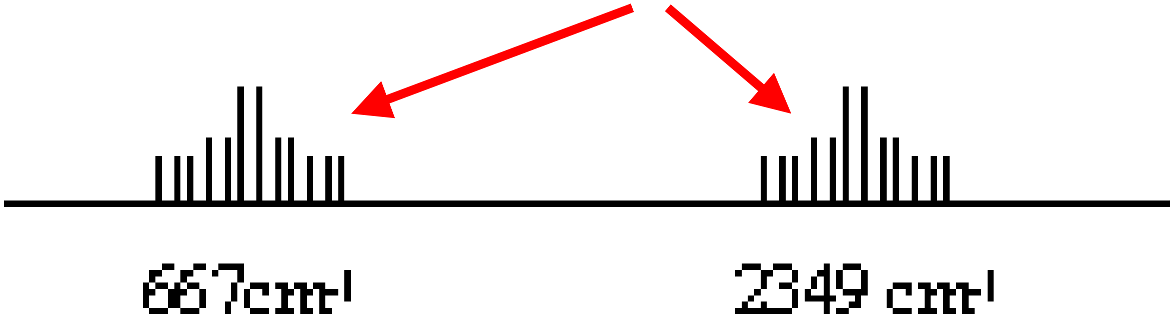
The symmetric stretch mode does not have a changing dipole moment. Not IR active.

In Solution: Low resolution, see two absorption bands



In Gas Phase: High resolution

Rotational fine structure



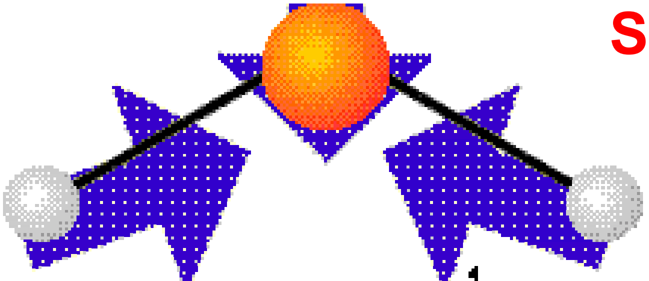
See notes later on vibrational-rotational spectra

Example: Vibrational Modes of Water H_2O

Three atoms, nonlinear molecule: $N = 3 \Rightarrow 3N-6 = 3$ vibrational modes

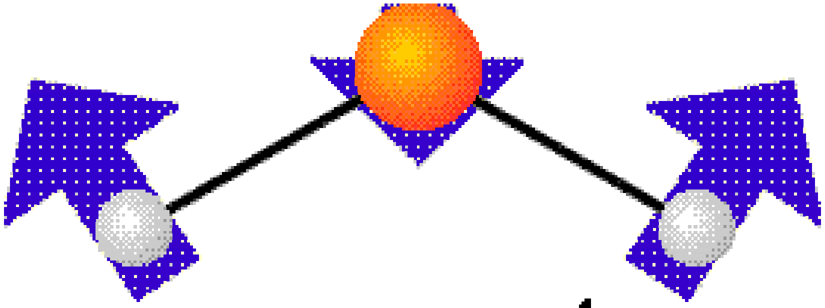
N-1 Stretching Modes: $\Rightarrow 2$

2N-5 Bending modes: $\Rightarrow 1$



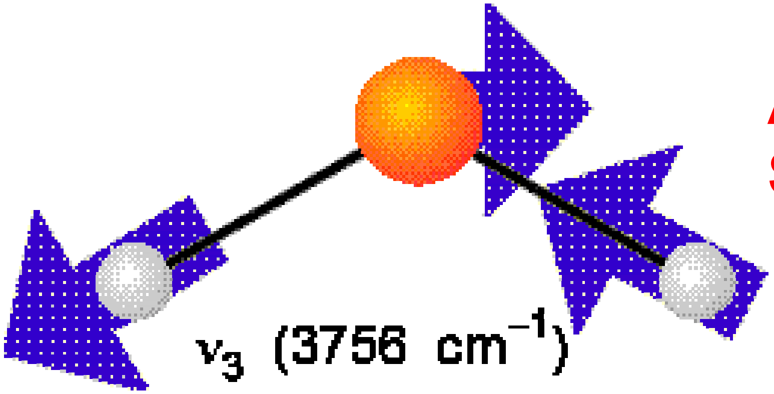
ν_1 (3652 cm^{-1})

Symmetric Stretch



ν_2 (1595 cm^{-1})

Bend

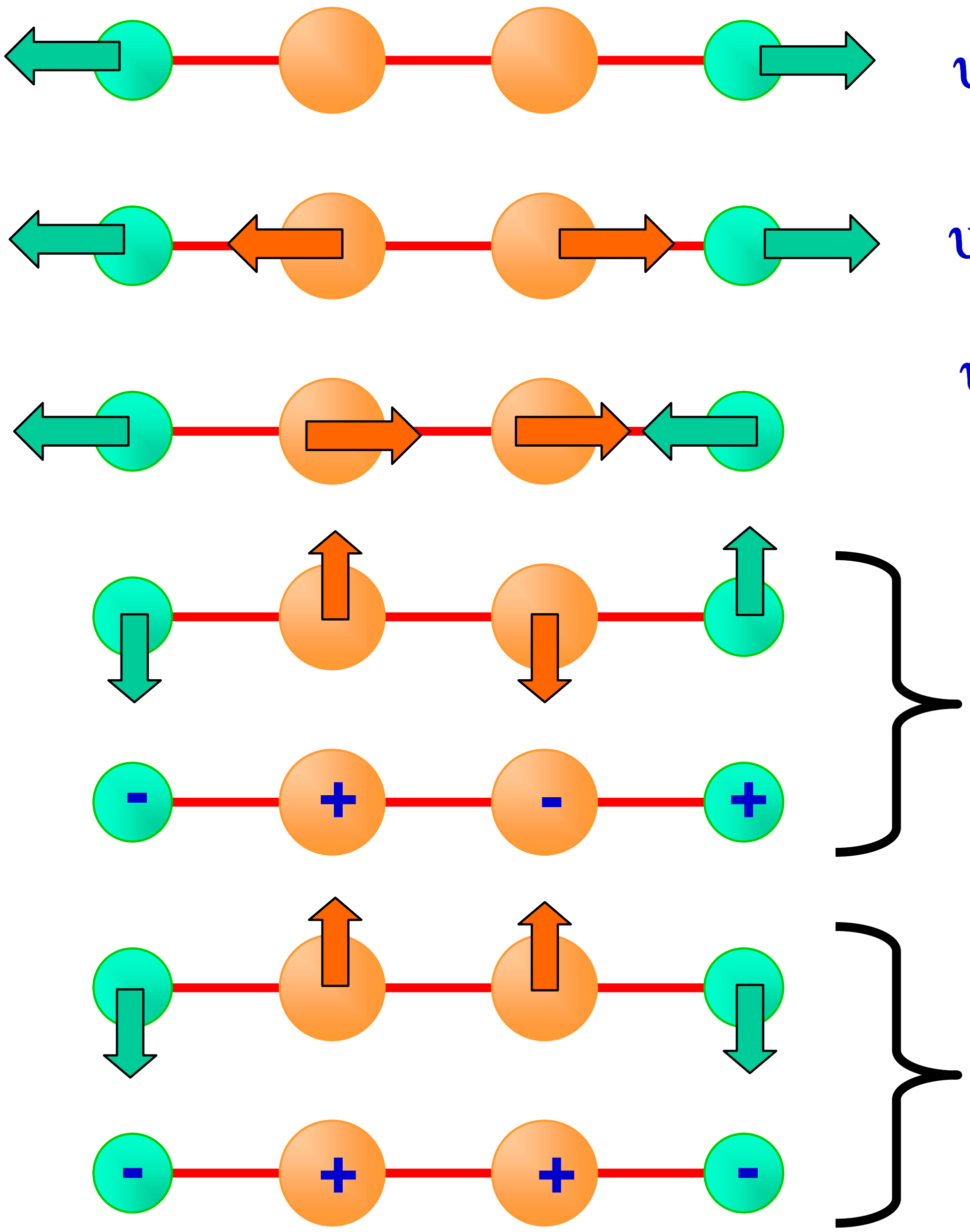


ν_3 (3756 cm^{-1})

Anti-symmetric Stretch

Vibrational Modes of Acetylene C_2H_2

Linear molecule: N = 4 ⇒ 3N-5 = 7 modes: 3 stretching and 4 bending



υ_1 , C-H symmetric stretch, 3347 cm^{-1}

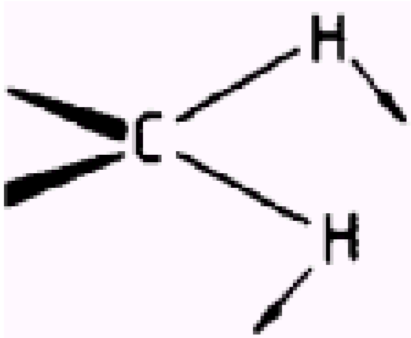
υ_2 , C=C stretch, 1974 cm^{-1}.

υ_3 , C-H antisymmetric stretch
3287 cm^{-1}

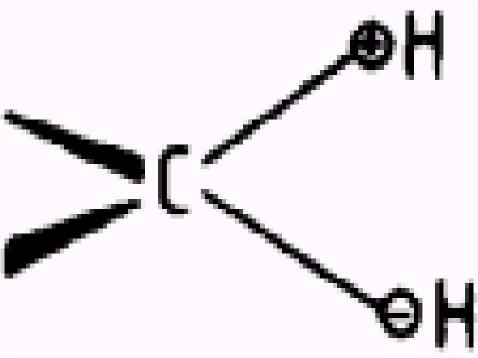
υ_4 , trans bend, 612 cm^{-1}
doubly degenerate

υ_5 , cis bend, 729 cm^{-1}
doubly degenerate

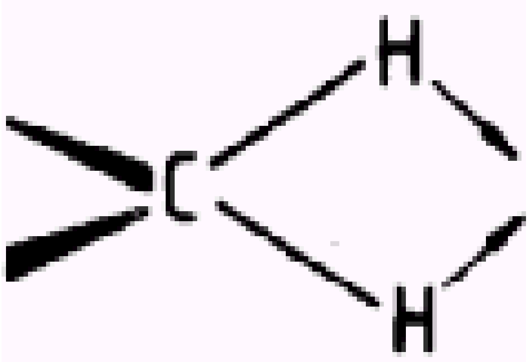
Many Types of Vibration



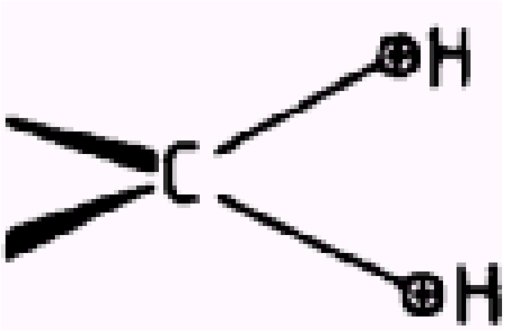
-CH$_2$ Rocking



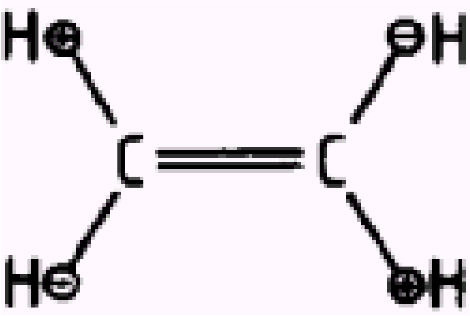
-CH$_2$ Twisting



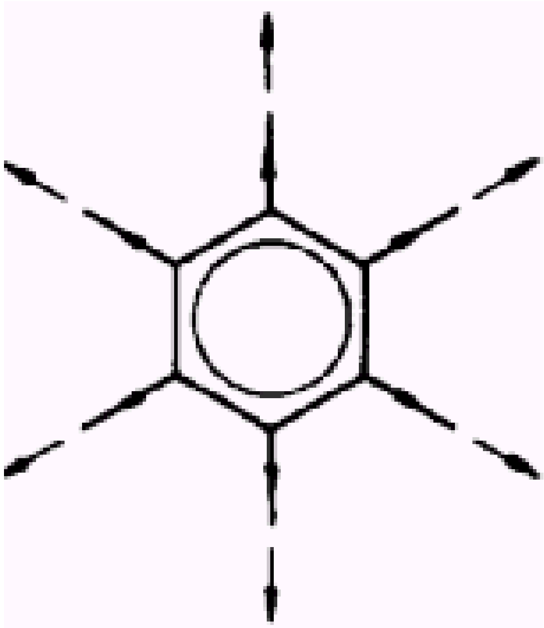
-CH$_2$ Scissoring



-CH$_2$ Wagging



Torsional
Vibrationa



Breathing Mode

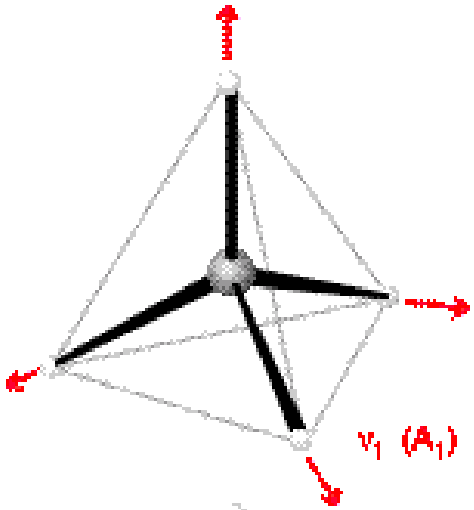
Inversion
(umbrella)
vibrationa

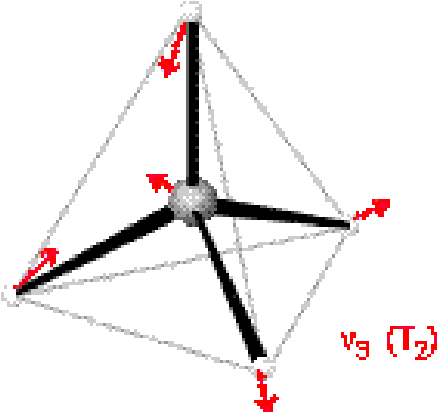
Example: Vibrational Modes of CH_4

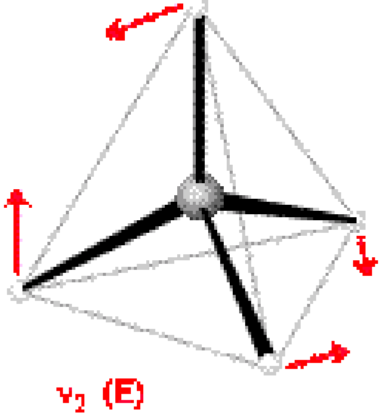
Five atoms, non-linear molecule: $N = 5 \Rightarrow 3N-6 = 9$ vibrational modes

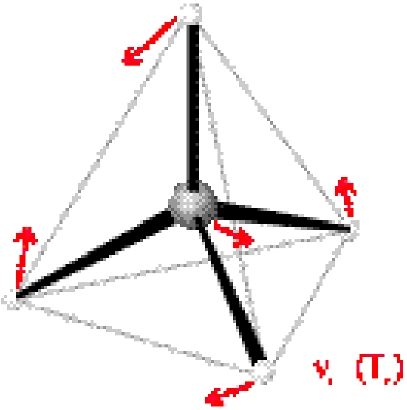
N-1 Stretching Modes: $\Rightarrow$ 4

2N-5 Bending modes: $\Rightarrow$ 5









Some modes are degenerate so only 4 different modes observed.

Not all modes are infra red active - ν3 and ν4 are observed in infra red spectrum.

How do we know this?

GROUP THEORY - a full course by itself

Larger Molecules

Recall that $\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$ **So each mode will have its own value of k and μ**

3N-6 vibrational modes, so for a large molecule (N > 4) the IR spectrum can be very complex

Vibrational modes can be localised in parts of the molecule.

In some modes ALL of the atoms undergo displacements.

In other modes only small groups of atoms are vibrating

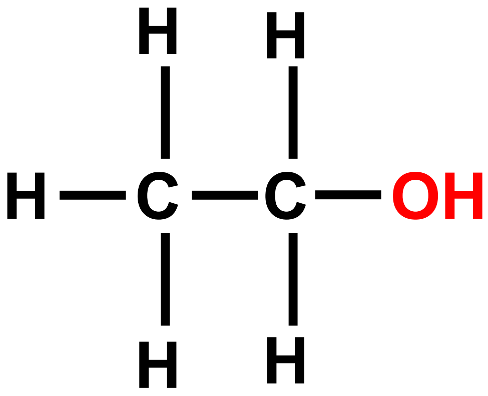
⇒ Two classes

1) SKELETAL Vibrations: Arise from strong coupling between stretching or bending motions of atoms in straight chains, branched chains or in a ring. Many atoms involved, all undergoing approximately the same displacement.

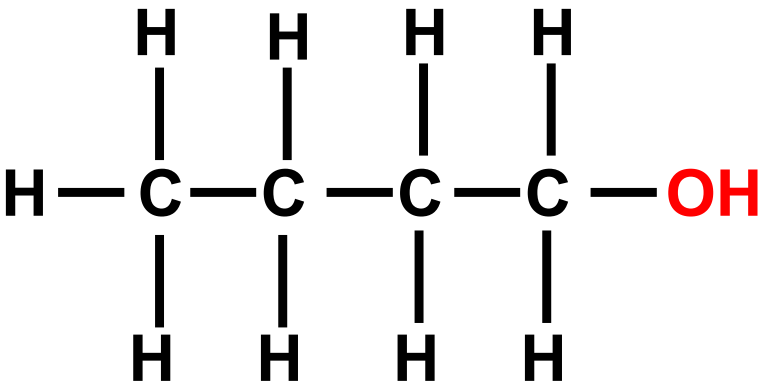
2) CHARACTERISTIC GROUP Vibrations: Almost independent of the structure of the molecule as a whole and just depend on the structure of the group undergoing vibration

Group Vibrations

Consider the following molecules (alcohols) C_2H_5OH, C_4H_9OH...

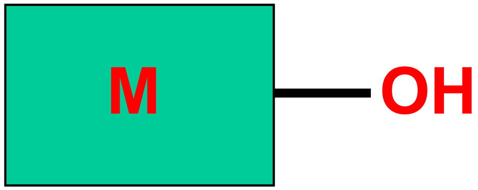


$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$



$$\mathrm{H-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-OH}$$

As far as the OH group is concerned we can represent both these molecules as



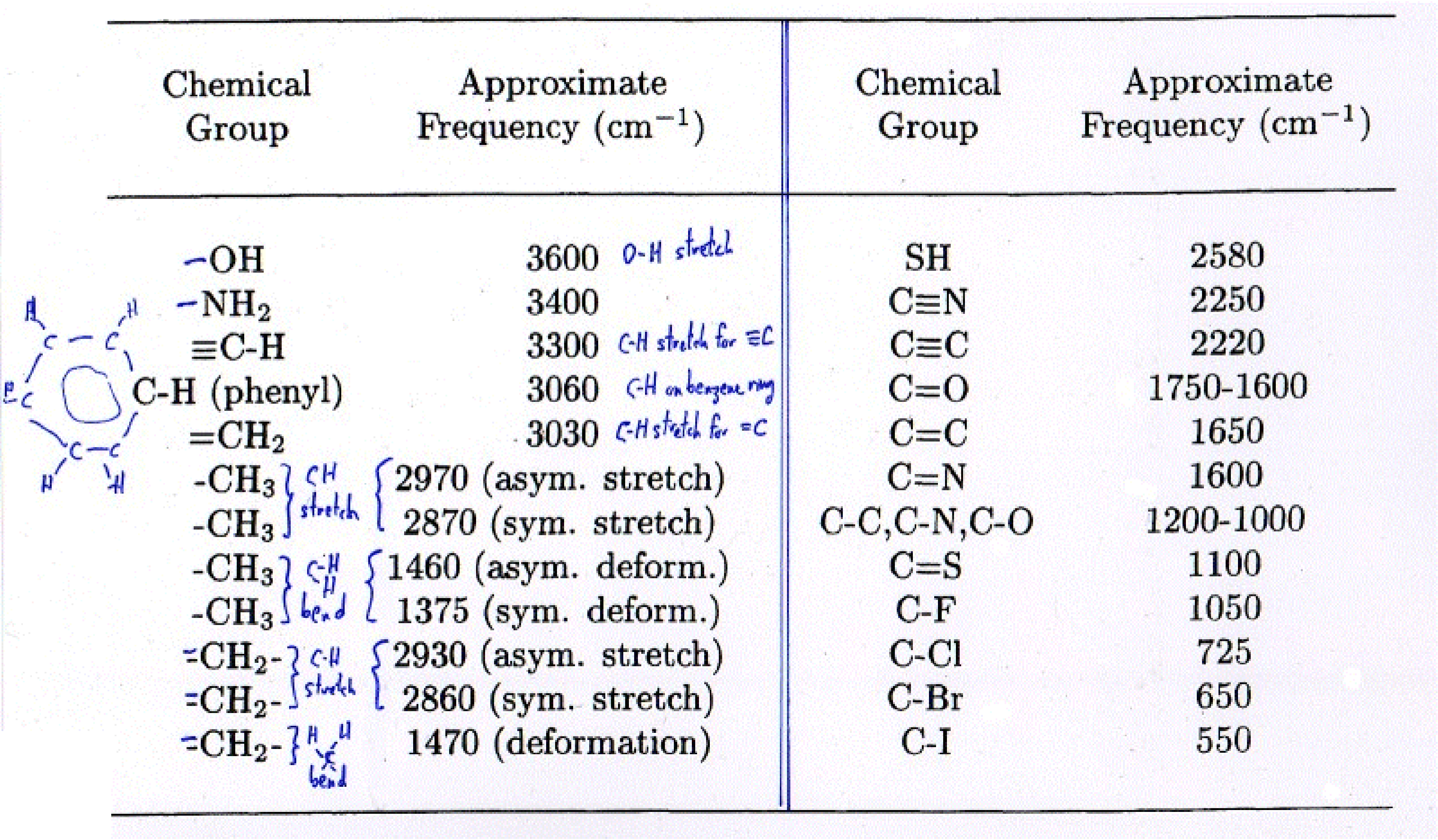
Where M is the 'large' mass of the molecule. The vibrational frequency of the OH group will then be given by

$$\boxed{\omega_o = \sqrt{\frac{k}{\mu}}} \quad \text{with} \quad \boxed{\mu = \frac{M.m_{OH}}{M+m_{OH}} \approx m_{OH}}$$

so to a first approximation, the vibrational frequency is independent of the overall size of the molecule and only depends on the mass of the vibrating group (OH in this case)

Characteristic Group Vibrations

IR absorption frequencies are characteristic of certain functional groups on the molecule.



Chemical Group	Approximate Frequency (cm^{-1})	Chemical Group	Approximate Frequency (cm^{-1})
$-\mathrm{OH}$	3600 O-H stretch	SH	2580
$-\mathrm{NH}_2$	3400	$\mathrm{C{\equiv}N}$	2250
$\equiv\mathrm{C{-}H}$	3300 C-H stretch for ≡C	$\mathrm{C{\equiv}C}$	2220
C-H (phenyl)	3060 C-H on benzene ring	C=O	1750-1600
$=\mathrm{CH}_2$	3030 C-H stretch for =C	C=C	1650
$-\mathrm{CH}_3$ } C-H stretch	2970 (asym. stretch)	C=N	1600
$-\mathrm{CH}_3$	2870 (sym. stretch)	C-C,C-N,C-O	1200-1000
$-\mathrm{CH}_3$ } C-H H bend	1460 (asym. deform.)	C=S	1100
$-\mathrm{CH}_3$	1375 (sym. deform.)	C-F	1050
$-\mathrm{CH}_2-$ } C-H stretch	2930 (asym. stretch)	C-Cl	725
$-\mathrm{CH}_2-$	2860 (sym. stretch)	C-Br	650
$-\mathrm{CH}_2-$ } H C H bend	1470 (deformation)	C-I	550

See Banwell and McCash Table 3.4

Trends in Group Frequencies

Recall that $$\tilde{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

Increasing the mass of the atom undergoing vibration within the group will tend to decrease the frequency (wavenumber). e.g

-C-H > -C-F > -C-Cl > -C-Br ...

C=O > C=S ...

Increasing the strength of the bond, and hence the value of k, increases the frequency. e.g

$-C\equiv X$ > -C = X > -C-X …

wavenumbers are in the ratio

2220 : 1650 : 1200

1.85 : 1.38 : 1

$\sqrt{3} : \sqrt{2} : 1$

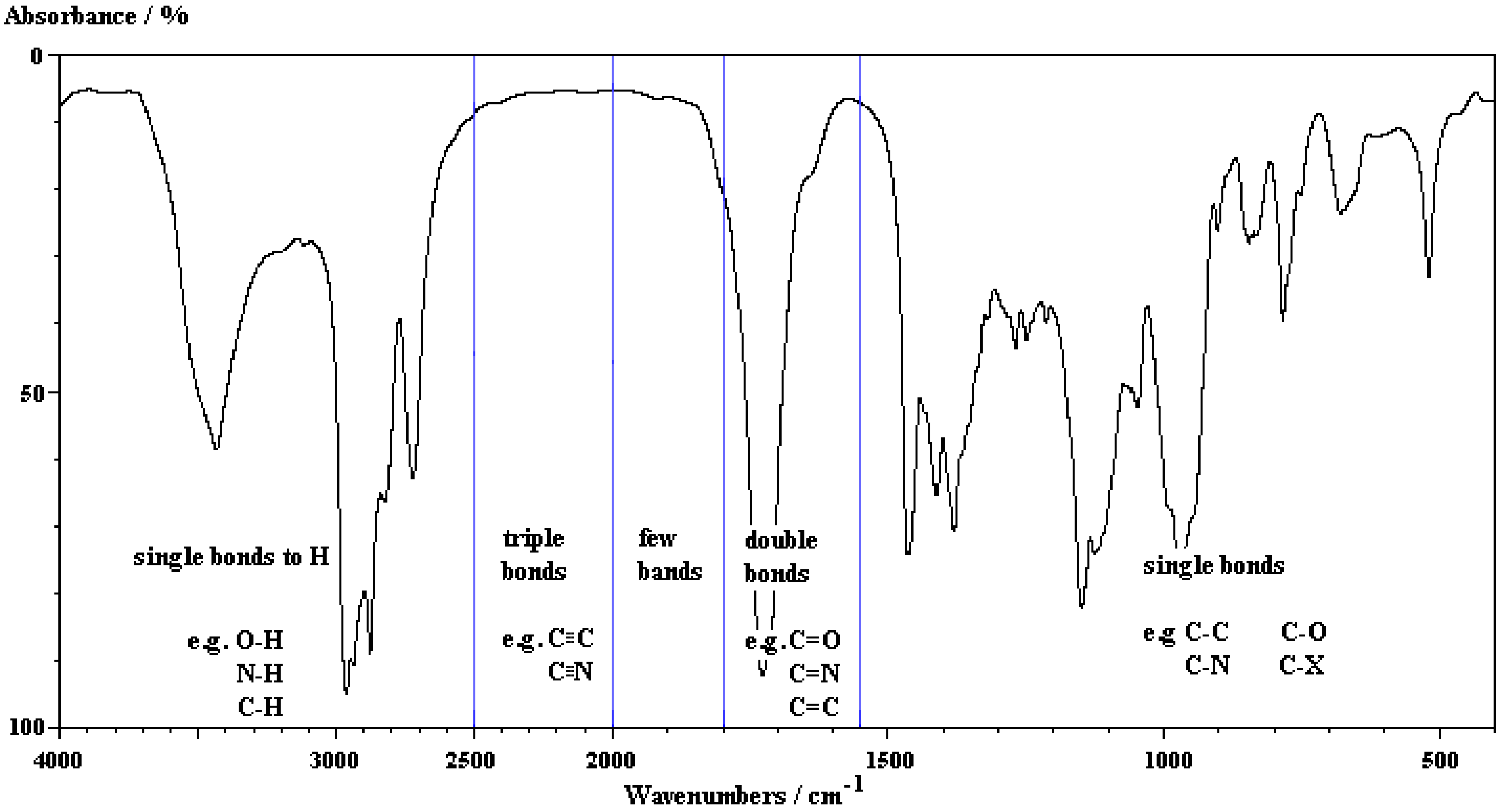
as expected since $\tilde{\nu} \propto \sqrt{k}$

Intensities of the bands in the IR spectrum depends on the magnitude of the change in the dipole moment. In general the more polar the bond the larger the dipole moment and the stronger the band, e.g.

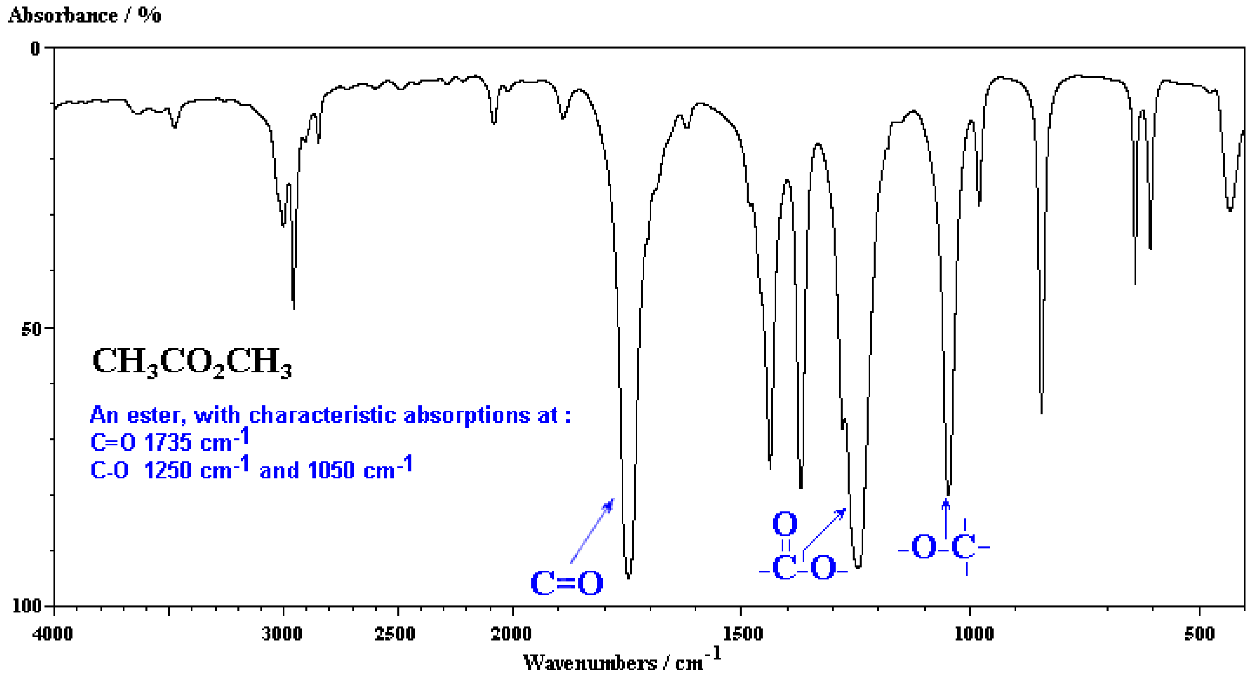
-C = O > -C = N > -C = C ...

-O - H > -N - H > -C - H ...

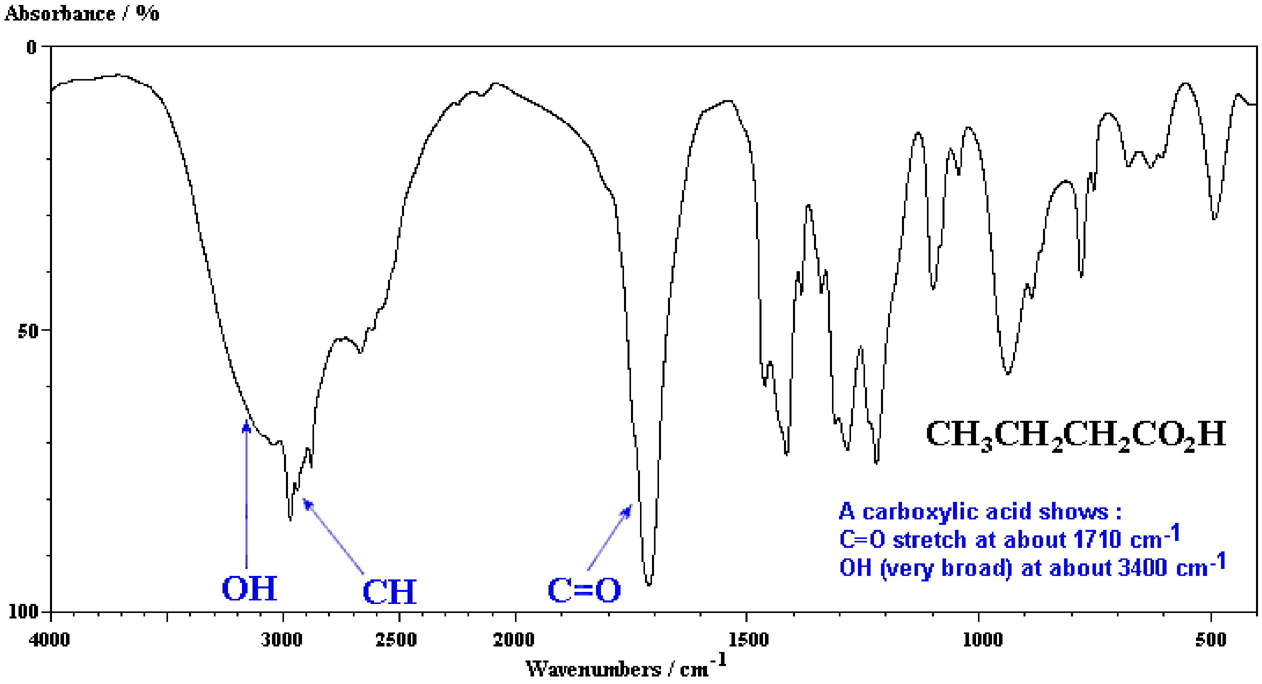
Examples


Absorbance / %
0
50
100
4000
3000
2500
2000
1500
1000
500
Wavenumbers / cm^{-1}
single bonds to H
e.g. O-H
N-H
C-H
triple bonds
e.g. C≡C
C≡N
few bands
double bonds
e.g. C=O
C=N
C=C
single bonds
e.g C-C
C-N
C-O
C-X

Examples

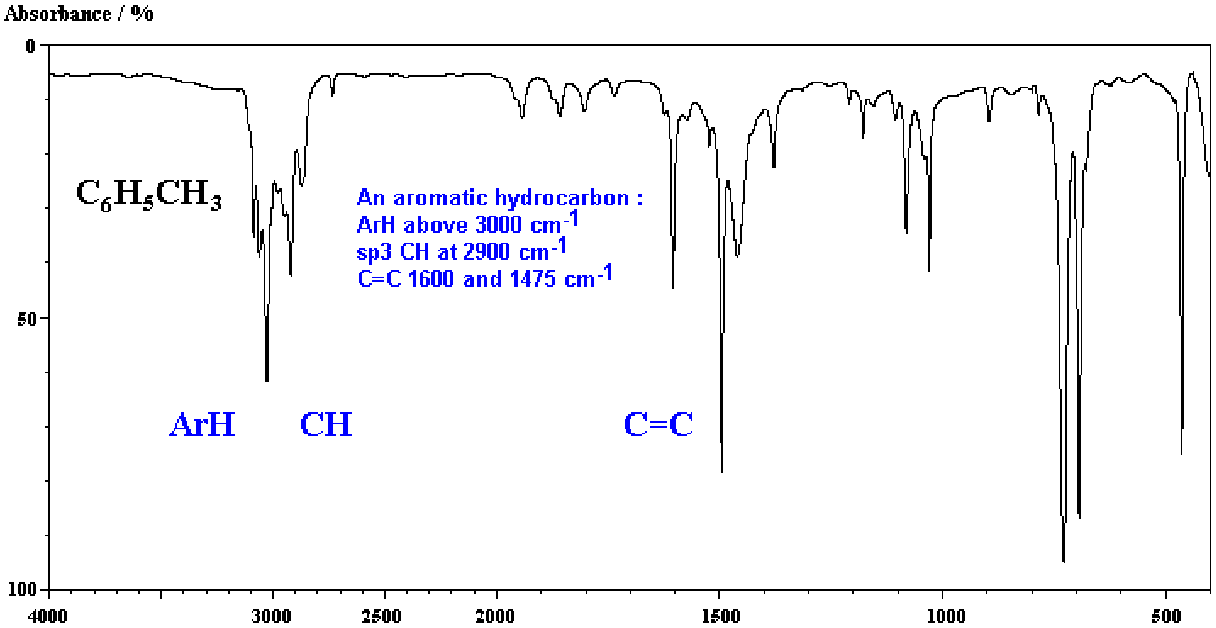

$CH_3CO_2CH_3$

An ester, with characteristic absorptions at :
C=O 1735 cm^{-1}
C-O 1250 cm^{-1} and 1050 cm^{-1}

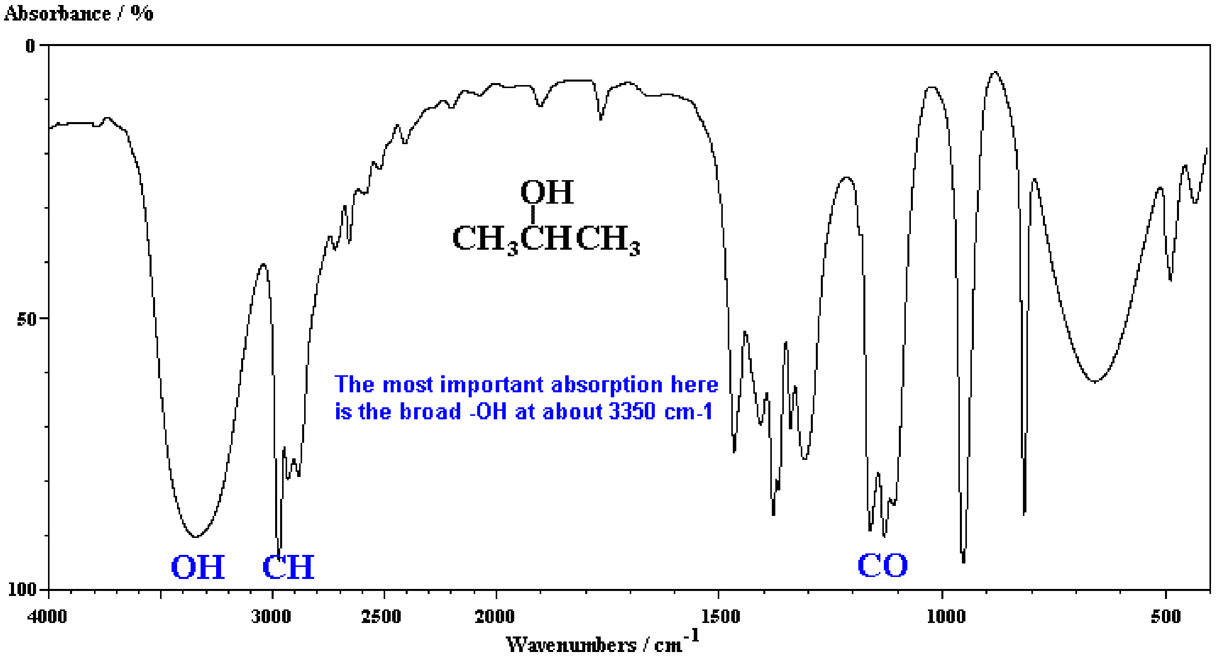

$CH_3CH_2CH_2CO_2H$

A carboxylic acid shows :
C=O stretch at about 1710 cm^{-1}
OH (very broad) at about 3400 cm^{-1}

Examples



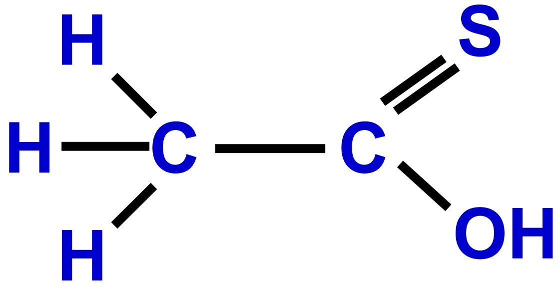
An aromatic hydrocarbon :
ArH above 3000 cm^{-1}
sp3 CH at 2900 cm^{-1}
C=C 1600 and 1475 cm^{-1}



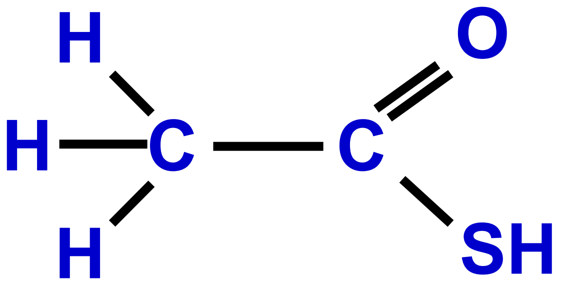
The most important absorption here is the broad -OH at about 3350 cm-1

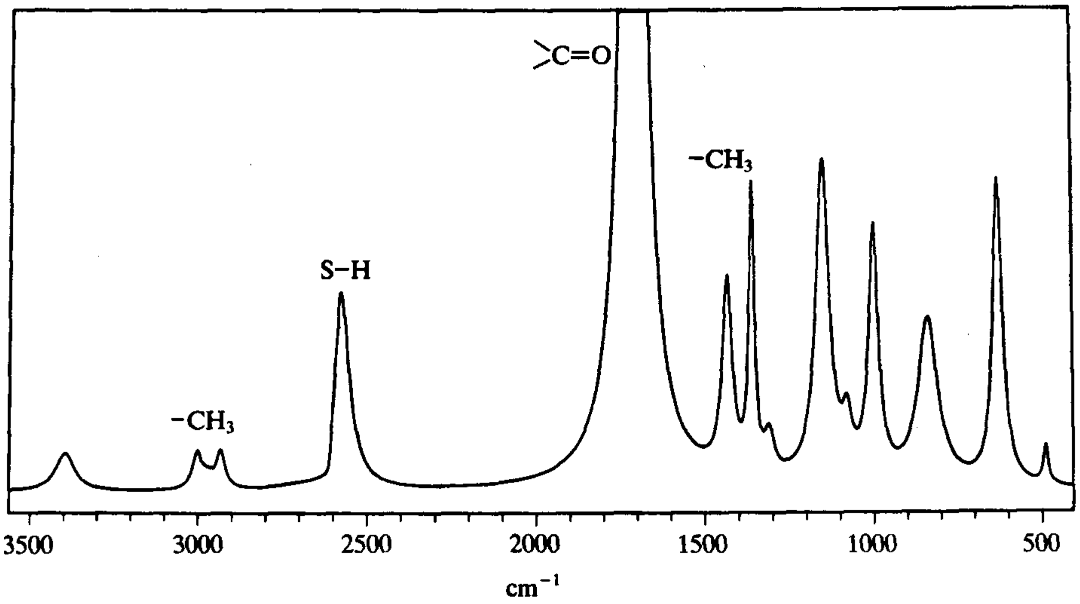
Example: Thioacetic Acid C_2H_4OS

Which structure?



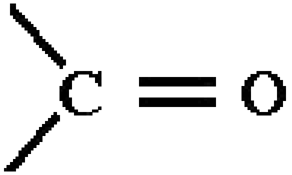
or





IR spectrum shows sharp absorption bands at

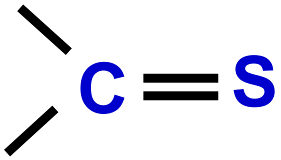
$1730\ cm^{-1}$ ⇒



and

$2600\ cm^{-1}$ ⇒ -SH group

No absorption near $1100\ cm^{-1}$ ⇒ no

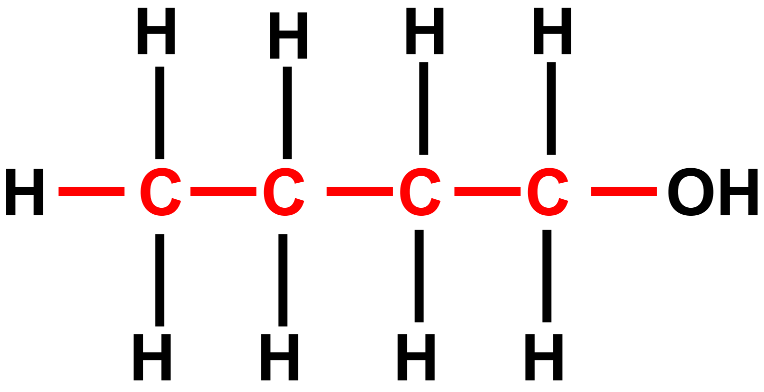


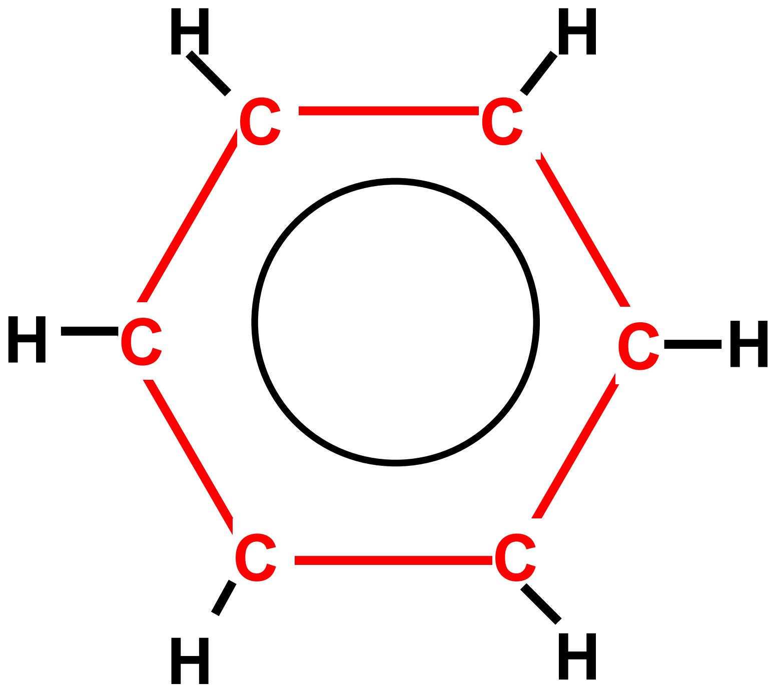
group

See Banwell and McCash figure 3.19(c)

Skeletal Vibrations

Arise from branched or linear chain structures. These are vibrations of the whole chain or along a side arm to a chain or ring structure. Because many atoms are involved in the vibration, the mass is high and therefore the vibrational frequency (and wavenumber) is low





Usually in the range 1400 - 700 cm^{-1} for organic molecules