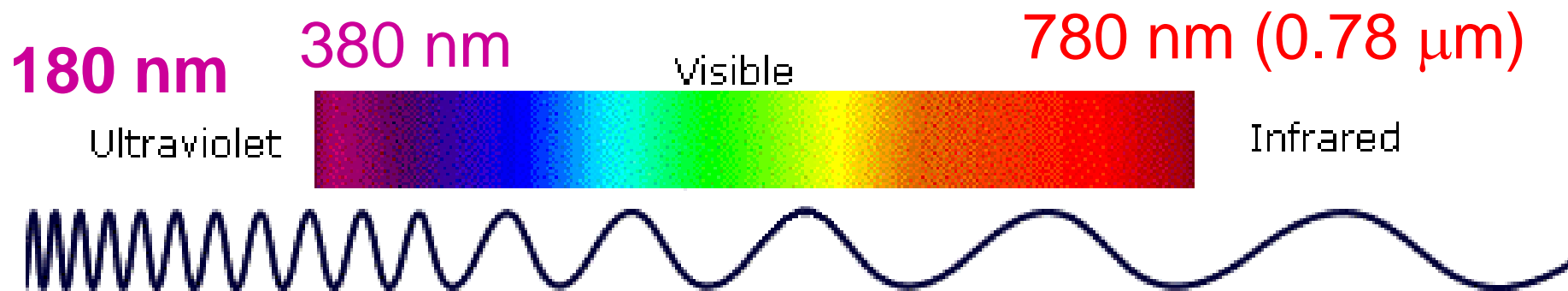


INFRARED (IR) SPECTROSCOPY



$$1\text{m} = 10^2\text{cm} = 10^6\mu\text{m} = 10^9\text{nm}$$

$$1\mu\text{m} = 10^3\text{nm}$$

$$\tilde{\nu} = \frac{1}{\lambda}$$

$\tilde{\nu}$ = wavenumber (cm⁻¹)

$$1\text{cm} = 10^4\mu\text{m}$$

$$1\mu\text{m} = 10^{-4}\text{cm}$$

$$\tilde{\nu} = 1/10^{-4}\mu\text{m} = 10^4/\mu\text{m}$$

Region	Energy (kJ/mol)	Wavenumber (cm ⁻¹)	Wavelength (μm)
Near IR	150-50	12,800-4000	0.78-2.5
Mid IR	50-2.5	4000-200	2.5-50
Far IR	2.5-0.1	200-10	50-1000

The portion of the infrared region most useful for analyses of organic compounds is **4000-666 cm⁻¹**

Photon energies associated with this part of the infrared are **not large enough to excite electrons**, but may **induce vibrational excitation** of covalently bonded atoms and groups.

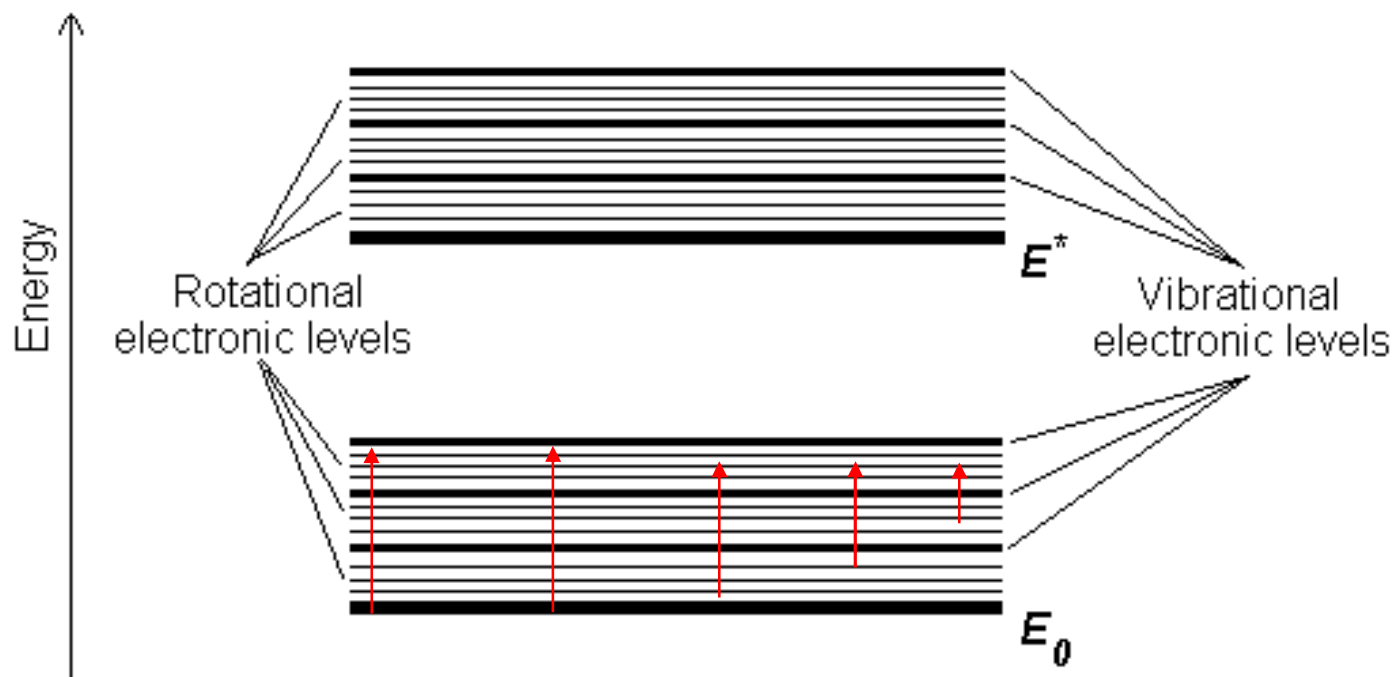
The covalent bonds in molecules (**A-B**) are **not** rigid sticks or rods, but are more like **stiff springs** that can be **stretched** and **bent**.



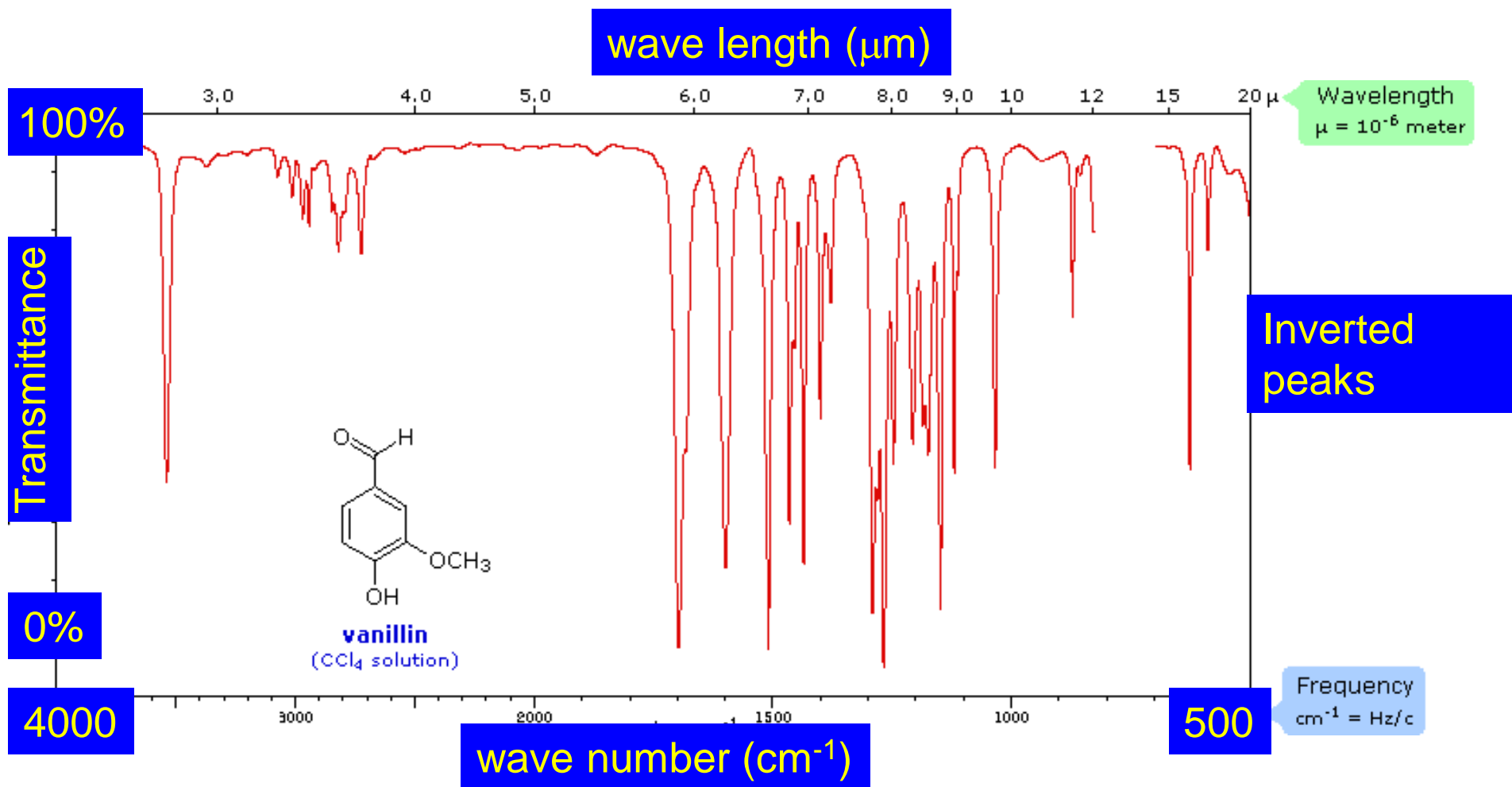
In addition to **rotation** of groups about single bonds, molecules experience a wide variety of **vibrational motions**, characteristic of their **component atoms**.

Consequently, **organic compounds** will **absorb** infrared radiation that corresponds in energy to these vibrations.

Absorption in this region implies the occurrence of **vibrational transitions** in the molecule while it remains in its **ground state**.



- IR spectroscopy permit chemists to obtain absorption spectra of compounds that are a **unique reflection** of their **molecular structure**.



The **complexity** of this spectrum is typical of most infrared spectra, and illustrates their use in **identifying substances**.

No two compounds have identical IR spectrum, except enantiomers.

The **inverted display of absorption**, compared with **UV-Visible**, is characteristic of **IR spectra**.

Thus a sample that did not absorb at all would record a horizontal line at **100%**

The frequency scale at the bottom of the chart is given in units of **reciprocal centimetres (cm⁻¹)** rather than **Hz**, because the numbers are more **manageable**.

$$\tilde{\nu} = \nu/c$$

Interaction of Molecules with IR Radiation

Vibrational frequencies of molecules correspond to the **frequencies of absorbed radiation**.

i.e. Infrared light is absorbed when the **oscillating dipole moment** (due to molecular vibration) interacts with the **oscillating electrical vector** of the infrared beam.

Band intensities are expressed as **transmittance (T)**
($T = I/I^\circ$)

I = intensity of light **transmitted**

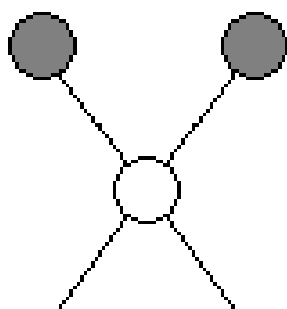
I° = Intensity of **initial light** from the source

Band intensities are described as **w** (for **weak**), **m** (for **medium**) and **s** (for **strong**)

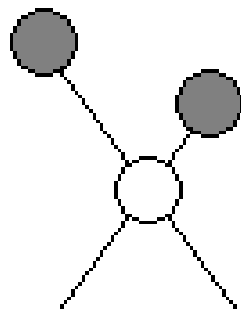
Types of Molecular Vibration

- **Two types** of molecular vibration:
- 1) **Stretching**:- a rhythmic movement along the bond axis such that the **interatomic distance** is **increased** or **decreased**.

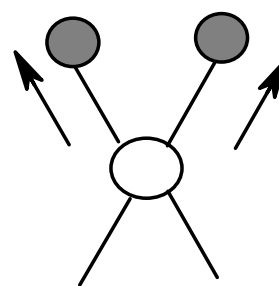
Stretching vibrations



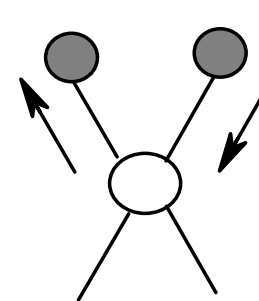
Symmetric



Asymmetric



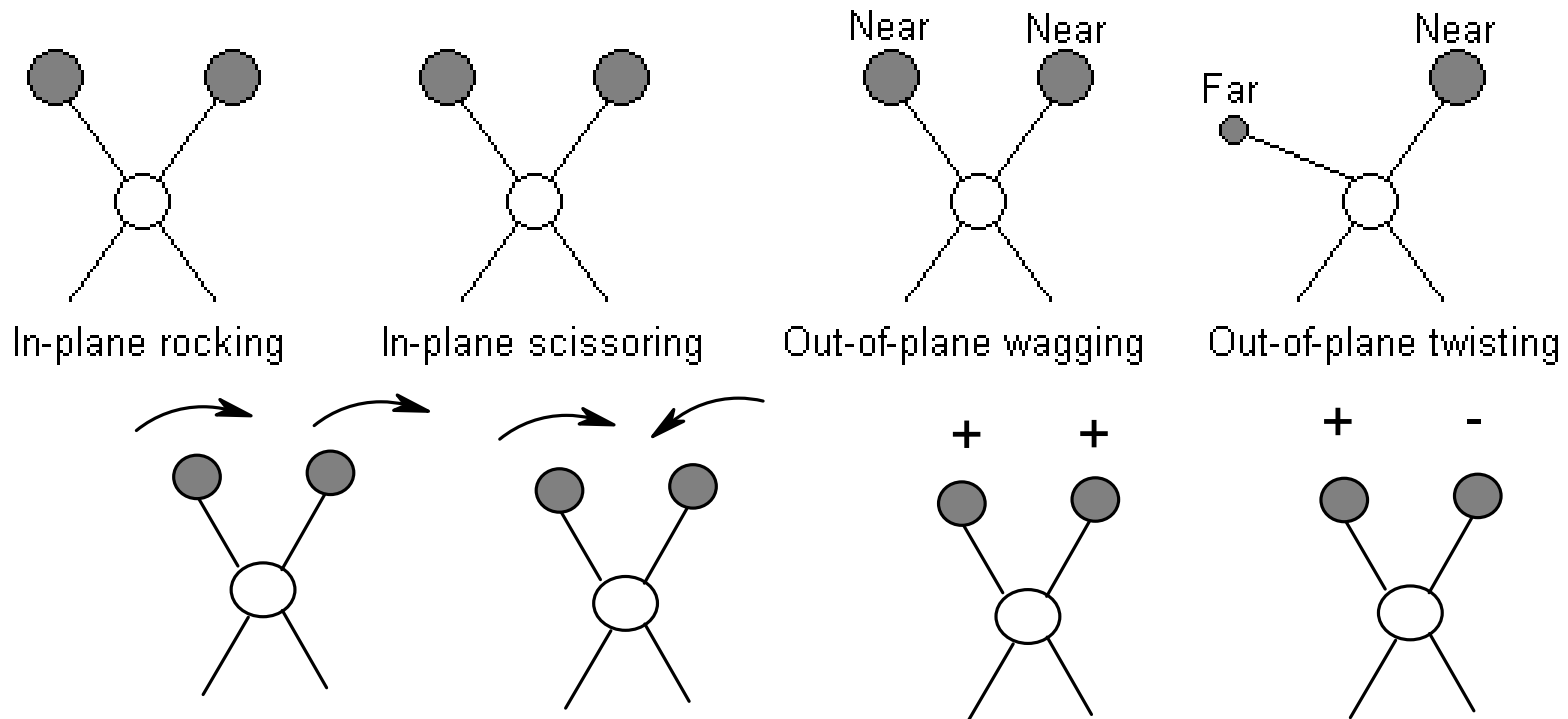
Symmetric



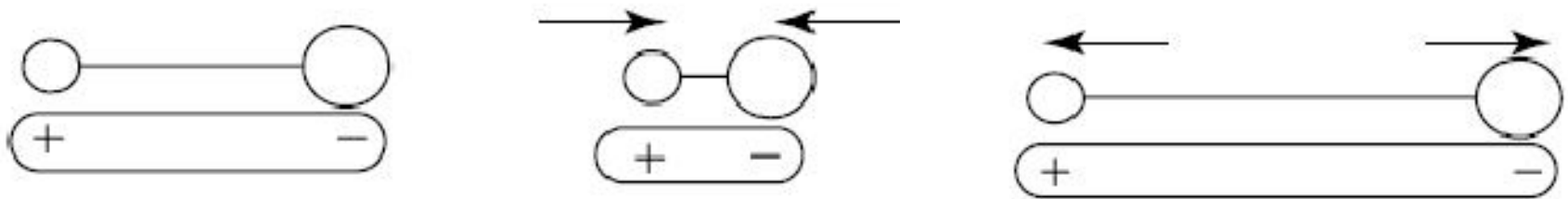
Asymmetric

- 2) **Bending**:- a **change in bond angle** between bonds with a common atom or
- the **movement of a group of atoms** with respect to the remainder of the molecule,
- with out movement of the atoms in the group with respect to one another.

Bending vibrations

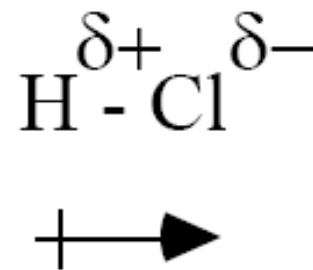


- Only those vibrations that result in **change of dipole moment** of the molecule are observed in IR.



Homonuclear diatomic molecules such as H_2 or O_2 **do not absorb IR radiation** (they are **IR-inactive**), since there is **no over-all electric (Dipole) moment** in the molecule.

$\text{O} - \text{O}$
No dipole
moment



HCl, H₂O, NO

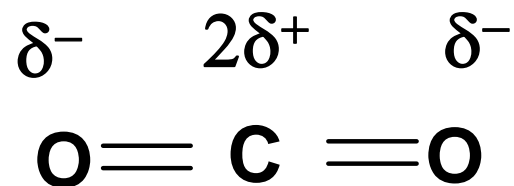
IR active

Atoms, O₂, H₂, Cl₂

IR inactive

- It is **not necessary** for polyatomic molecules to **possess permanent dipole moment** in order exhibit IR absorption,
- provided that **some polar bonds** are present in the molecule.

Example





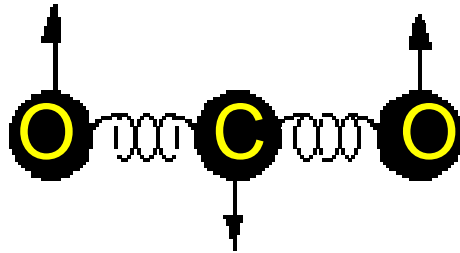
A

Symmetrical stretching



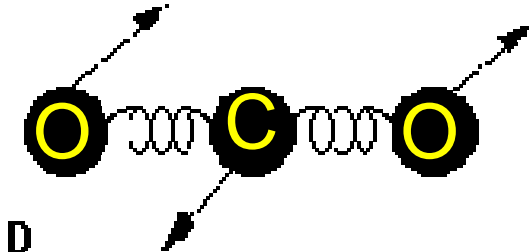
B

Anti-symmetrical stretching



C

In plane bending



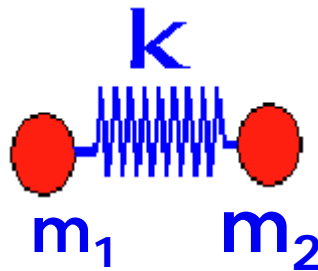
D

Out of plane bending

- A is **not IR active**
- B, C and D are **IR active**
- its **positive and negative electrical centres** are no longer coincident,
- a **dipole moment** is **temporarily induced**.

Simple Harmonic Oscillator

1st Approximation, a covalent bond behaves as a weightless spring and obeys **Hooke's Law** :- the **restoring force** acting upon it when it is stretched is **proportional** to the **degree of stretching**.



A molecule can be regarded as a collection of **balls** and **springs**, where the **balls** are the **atoms** and the **springs** are the **chemical bonds**.

Hooke's law

μ is the reduced mass

$$\tilde{\nu} = \frac{1}{2\pi c} \left(\frac{\kappa}{\mu} \right)^{1/2} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

$\tilde{\nu}$ = **wave number** of the stretching vibration

κ = the **force constant (bond strength)**

m_1, m_2 = **masses** of atoms joined by the bond

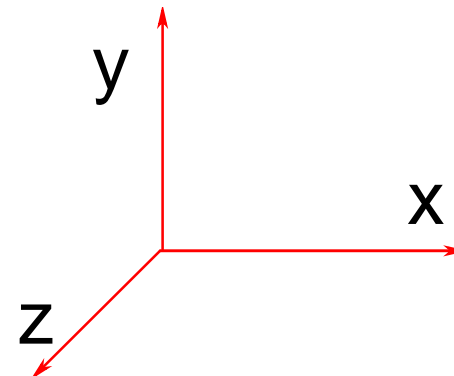
c = speed of light

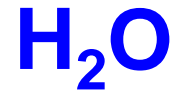
The exact **wave number** at which a given vibration occurs is determined by:

- 1) the **strengths of the bonds** involved and
- 2) the **masses** of the component **atoms**.

Fundamental Vibrations

- Molecules of n atoms will have $3n$ degrees of freedom.
- Since its atoms may have its movement resolved along x , y and z axes.
- Movement of the whole molecule as a rigid unit
- will take up six of these degrees of freedom,
- three translational and three rotational
- (two rotational in the case of linear molecules).
- So, for vibrational motions where atoms move relative to each other, we have $3n-6$ ($3n-5$ for linear molecules) fundamental vibrations
- (vibrations responsible for number of theoretically expected absorption bands in IR).





- Three atoms (non-linear).
- $3 \times 3 = 9$ degrees of freedom.
- $3n-6$ (fundamental vibrations).
- $9 - 6 = 3$ (fundamental vibrations).



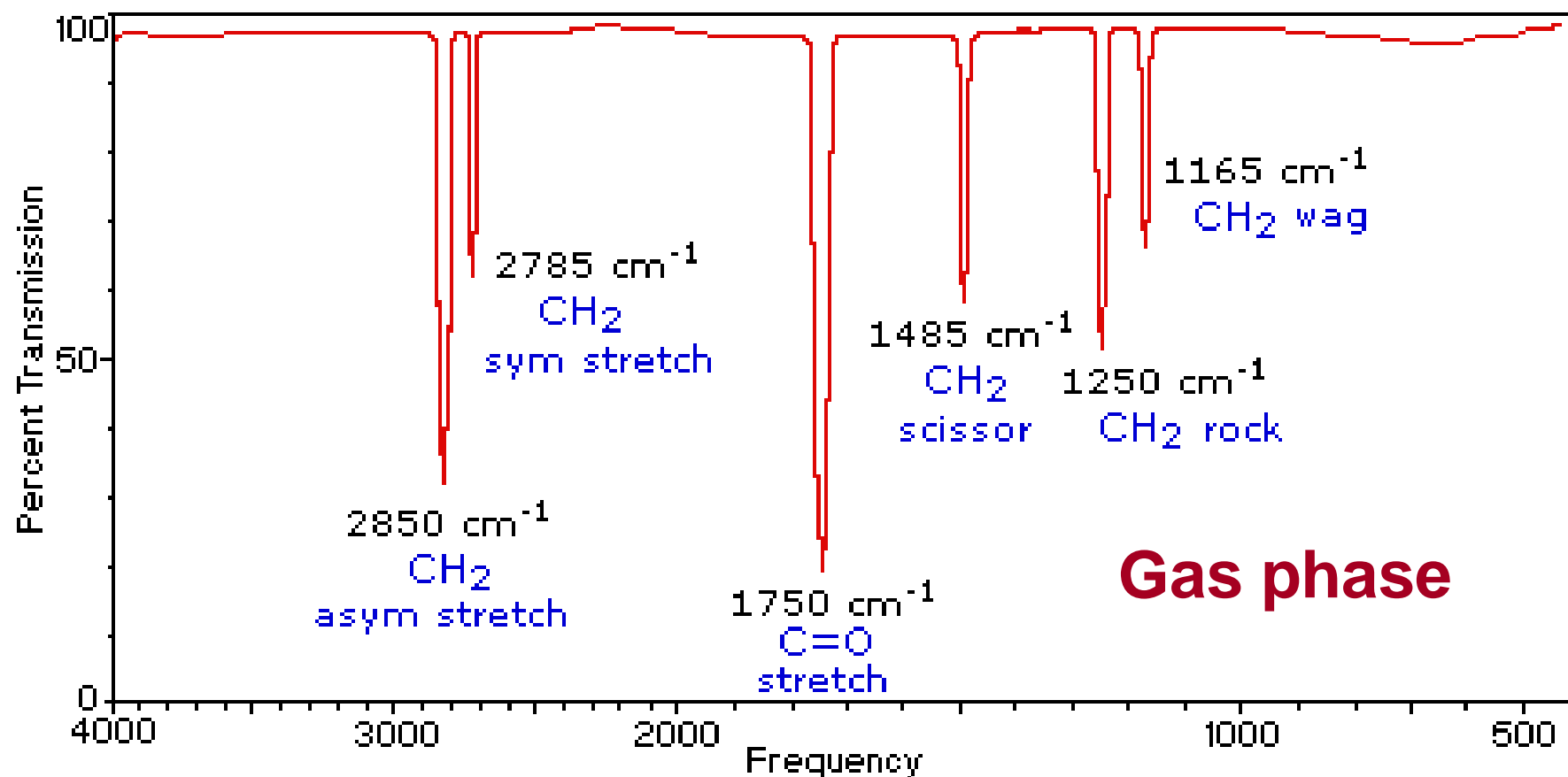
- Three atoms (linear).
- $3 \times 3 = 9$ degrees of freedom.
- $3n-5$ (fundamental vibrations).
- $9 - 5 = 4$ (fundamental vibrations).

Formaldehyde, $\text{H}_2\text{C}=\text{O}$

Four atoms (non-linear).

$3 \times 4 = 12$ degrees of freedom.

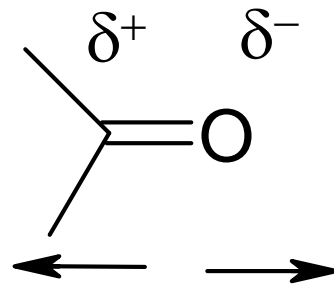
$12 - 6 = 6$ (fundamental vibrations).



- In practice, IR spectra **do not** normally **display separate absorption signals** for **each of the $3n-6$** fundamental vibrational modes of a molecule.
- I) Absorption signals may be **increased** by:
 - **additive** and **subtractive** interactions of the fundamental vibrations (**overtones**),
- II) Absorption signals, may be **decreased** by:
 - a) **Molecular Symmetry** (identical group in the same molecule will have the same value),
 - **b) Spectrometer limitations**
 - **c) Selection rules** (only those vibrations which results in a **change of dipole moment** will show absorption bands).

Band Intensity:

- Described as **w** (for **weak**), **m** (for **medium**) and
- **s** (for **strong**).
- One **selection rule** that **influences the intensity**
- is that a **change** in **dipole moment** should occur for a vibration to absorb infrared radiation.
- Absorption of **C=O bond** stretching are usually very strong.



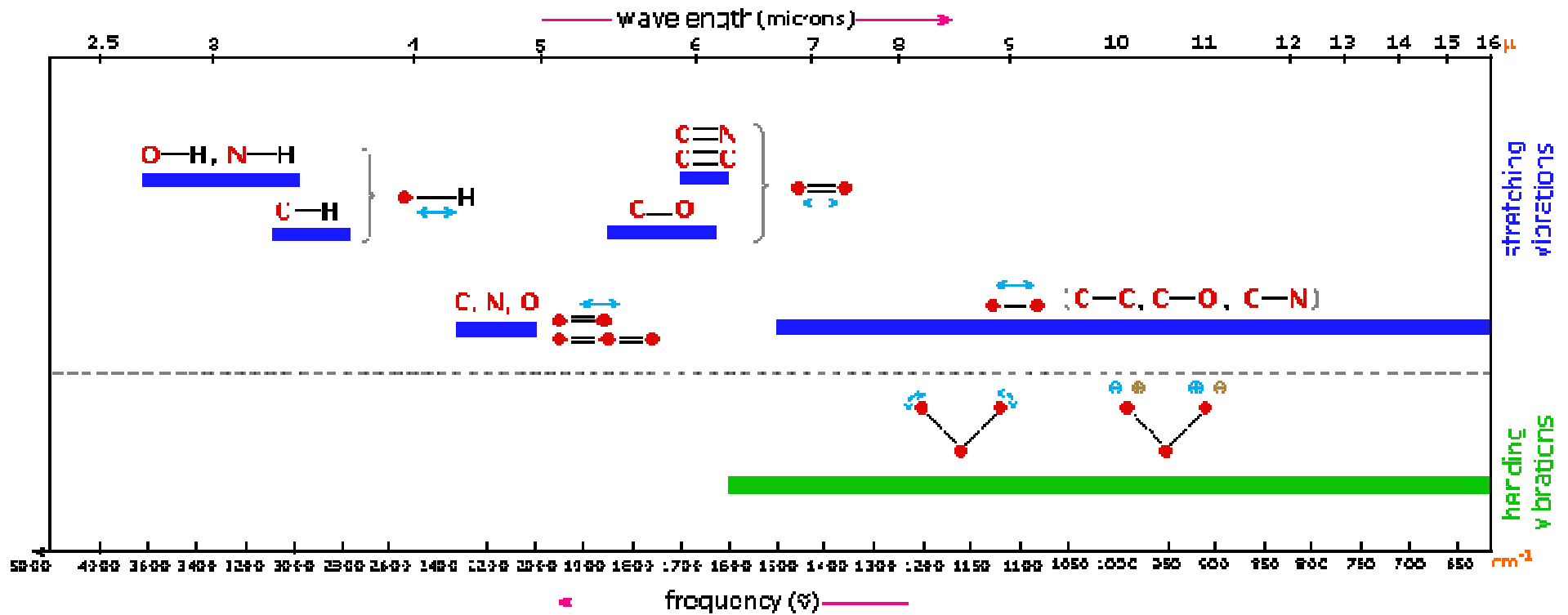
because a **large change** in the **dipole moment** takes place in that mode.

Some General Trends

- i) **Stretching frequencies** are **higher** than the corresponding **bending frequencies**.
 - (It is easier to bend a bond than to stretch or compress it)
- ii) **Asymmetrical stretching** frequencies are **higher** than **symmetrical stretching** frequencies.

$$\tilde{\nu} = \frac{1}{2\pi c} \left(\frac{\kappa}{\mu} \right)^{1/2} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

- iii) Bonds to **hydrogen** have **higher stretching frequencies** than those to **heavier atoms**.
- iv) **Triple bonds** have **higher stretching frequencies** than **double bonds**, which in turn have higher frequencies than **single bonds (except for bonds to hydrogen)**.



Blue colours refer to **stretching vibrations**,

Green coloured band encompasses **bending vibrations**.

- The **1450 to 666 cm⁻¹** region is complex.
- It is **difficult to assign all** the absorption bands.
- Because of the unique patterns,
- this region is often called the **fingerprint** region.
- It is characteristic of the **molecule as a whole**;
- useful as **confirmatory evidence** than **identification**.
- Absorption bands in the **4000 to 1450 cm⁻¹** region are usually due to **stretching vibrations** of **diatomic units**,
- and this is sometimes called:
- the **group frequency** region.
- Useful for **identification of functional groups**.

Interpretation of IR Spectra

- IR spectroscopy is **one of several aids** to the elucidation of structures.
- **Physical**, **chemical** and other **spectroscopic data** are necessary.

Points to consider during interpretation.

- 1) Begin at the **high-frequency end** of the chart. (most reliable correlations occur here)
- 2) Use the **fingerprint region** mainly for confirmation.
- 3) **Do not** expect to assign every band in the spectrum.
- (only **10-20% of bands** can usually be assigned).

- 4) place more reliance upon **negative evidence**,
- (that is **absence of absorption** in a particular region).
- Because the presence of a band may have **several possible origins**.
- 5) Continually **cross-check** the evidence against other spectroscopic methods.
- 6) Treat published descriptions of **band intensities** with **caution**.
- 7) Study any **variation between spectra** obtained by different **sampling techniques**.

Characteristic Group Frequencies

	Stretching Vibrations		
<u>Functional Class</u>	Range (cm ⁻¹)	Intensity	Assignment
Alkanes	2850-3000	str	CH ₃ , CH ₂ & CH 2 or 3 bands
<u>Alkenes</u>	3020-3100 1630-1680 1900-2000	med var str	=C-H & =CH ₂ (usually sharp) C=C (symmetry reduces intensity) C=C asymmetric stretch

- **Tables** of characteristic group frequencies **are available**. (prepared following **examination of many compounds**).
- **Precise frequencies** of absorption for a group is dependent on its **environment** within the molecule and on its **physical state of measurement**.

Alkanes

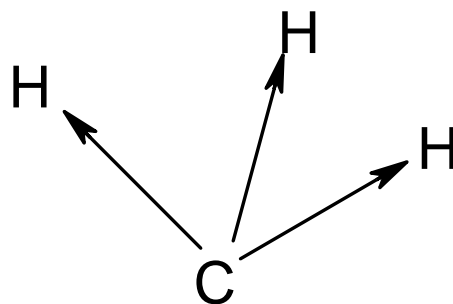
Two types of bonds (**C-H** and **C-C**)

Spectra can be interpreted in terms of **four vibrations**:

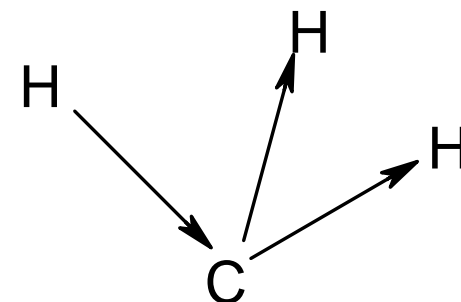
- **1) C-H stretching**
 - **2) C-H bending**
 - **3) C-C stretching**
 - (are weak, and appear in the broad region
 - **1200-800 cm⁻¹)**
- C-C stretching is of **little value** for identification.
- **4) C-C bending**
 - (**below 500 cm⁻¹**, do not appear in normal spectra).
 - Thus the **most characteristic** vibrations are those of **C-H stretching** and **C-H bending**.

C-H Stretching Vibration (ν)

Methyl group

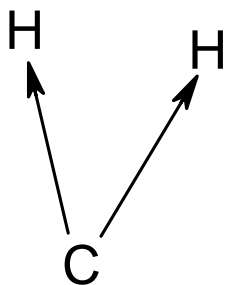


Symmetrical stretching (ν_s)
2885-2860 cm^{-1}

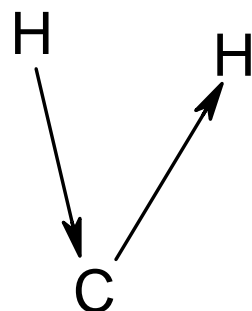


Asymmetrical stretching (ν_{as})
< 2975-2950 cm^{-1}

Methylene group

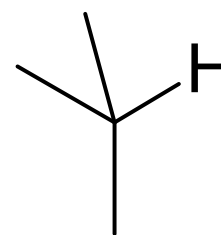


Symmetrical stretching (ν_s)
2870-2845 cm^{-1}



Asymmetrical stretching (ν_{as})
< 2940-2915 cm^{-1}

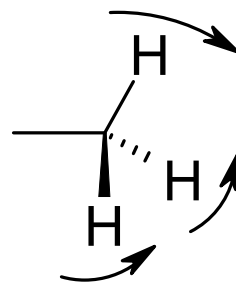
methine



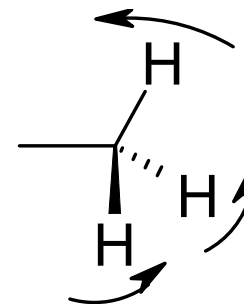
2890 cm^{-1}

C-H bending vibration (δ)

Methyl group

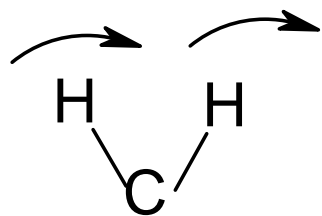


Symmetrical bending (δ_s)
ca. 1375cm^{-1}

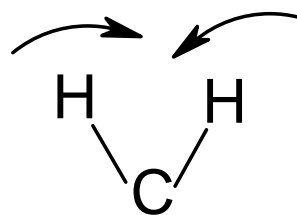


Asymmetrical bending (δ_{as})
ca. 1450cm^{-1}

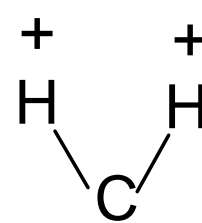
Methylene group



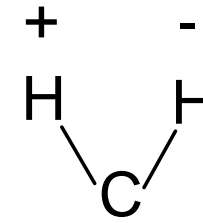
rocking
 $720\text{-}725\text{cm}^{-1}$



scissoring
 $1470\text{-}1465\text{cm}^{-1}$



wagging



twisting

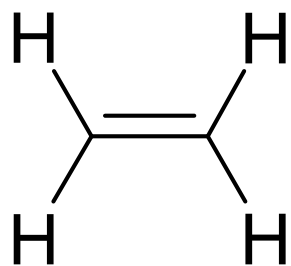
$1390\text{-}1350\text{cm}^{-1}$

Alkenes

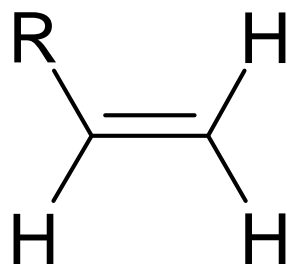
- New modes of vibrations are:
 - 1) **C=C stretching**,
 - 2) **C-H stretching** (C in olefinic linkage) and
 - 3) In-plane and out-of-plane **bending** of the olefinic C-H bond

C=C stretching

- 1667-1600 cm^{-1}
- (**moderate to weak**)

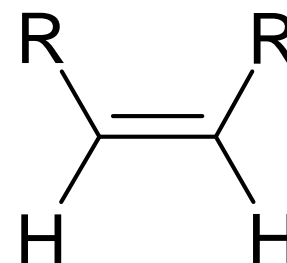


IR inactive
(1600 cm⁻¹)



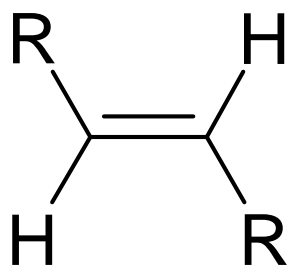
1640cm⁻¹

(moderate intensity)



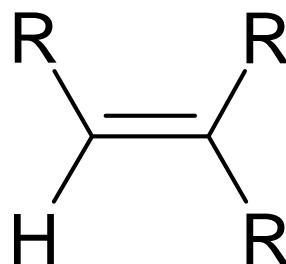
1650cm⁻¹

(moderate intensity)



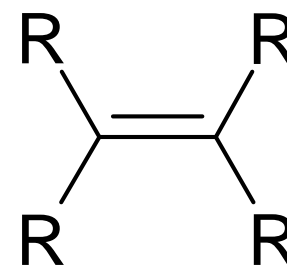
1670cm⁻¹

weak or absent



1670cm⁻¹

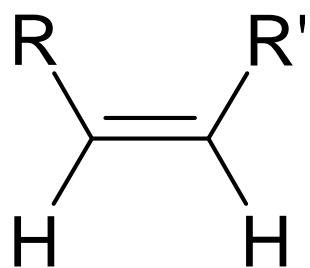
(moderate intensity)



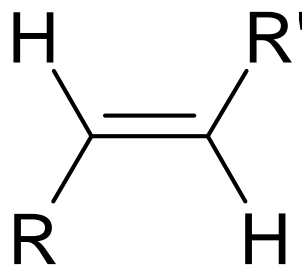
1670cm⁻¹

weak or absent

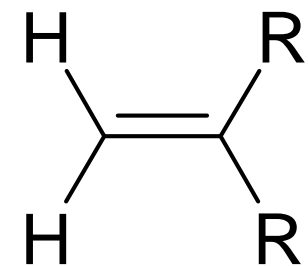
More alkyl substitution, shift towards **high frequency**,
due to more **coupling interaction** between **C=C**
and **C-C** vibrational frequencies.



1650cm⁻¹
(medium)



1670cm⁻¹
(weak)

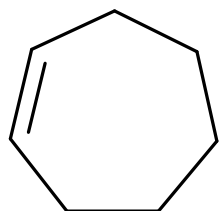


1670cm⁻¹
(medium)

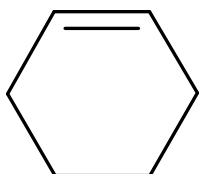
cis-double bonds which lack the symmetry of the *trans* structure **absorb more strongly**.

Internal double bonds absorb **more weakly** than **terminal double bonds**, because of *pseudo-symmetry*

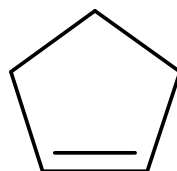
Cycloalkenes



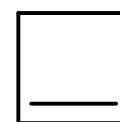
1650cm⁻¹



1646cm⁻¹



1611cm⁻¹



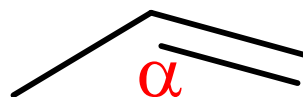
1566cm⁻¹

Decreasing bond angle

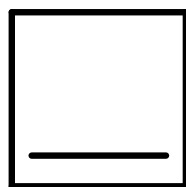
Decreasing order of C=C stretching frequency

The C=C stretching vibration is **coupled** with **C-C stretching vibration** of the adjacent bonds.

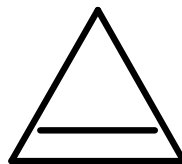
Coupling is dependent on bond angle α



As the angle (α) becomes smaller the coupling interaction becomes less until it is minimum at 90° (the attached C-C bond is orthogonal to C=C bond)



1566cm^{-1}

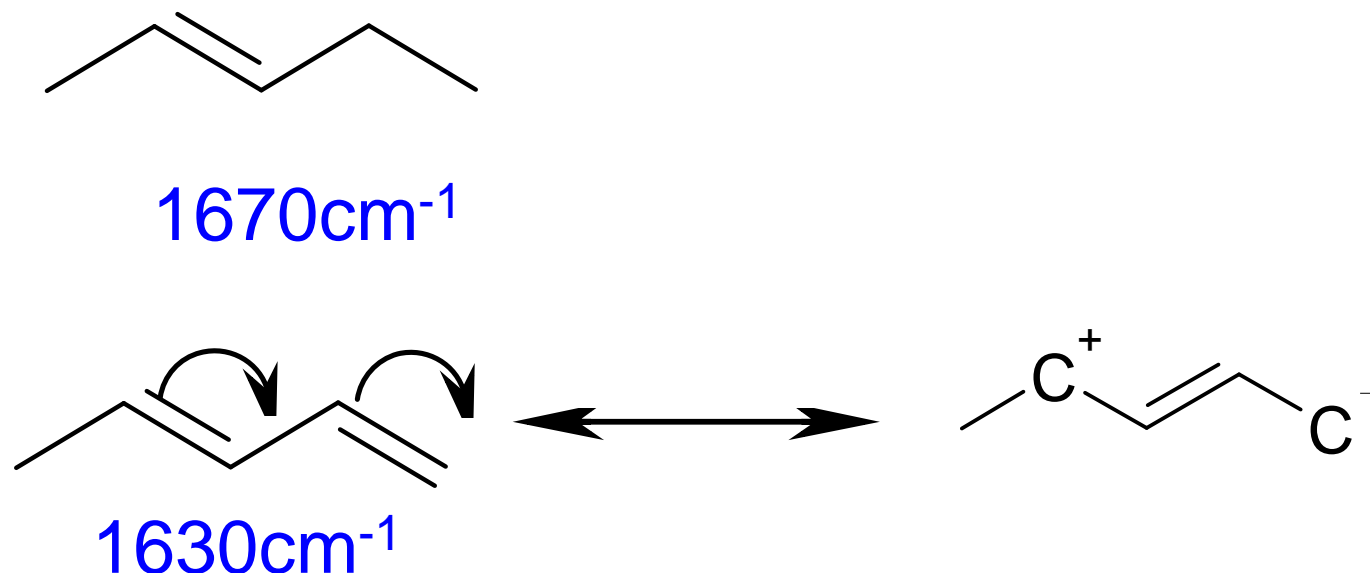


1641cm^{-1}

In cyclopropene, interaction becomes again appreciable (1641cm^{-1})

The C=C vibration is strongly coupled to the attached C-C single bond vibration

Effect of Conjugation



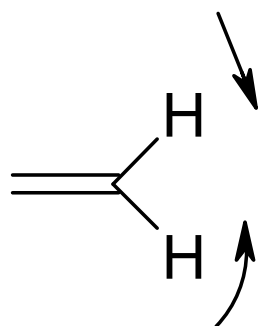
Conjugation of a double bond provides a **single bond character** through resonance, which **lowers** force constant **K**, thus a **lower frequency** of vibration.

Olefinic C-H stretching vibration

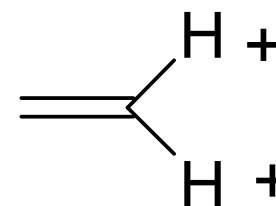
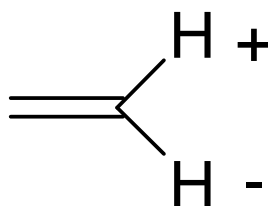
-C=C-H at $3100-3000\text{ cm}^{-1}$

In general, only C-H stretching bonds **above 3000 cm^{-1}** result from **aromatic, acetylenic** or **olefinic** C-H stretching.

Olefinic C-H bending vibration



Scissoring vibration
(**same plane**)
 $\text{ca. } 1416\text{cm}^{-1}$



Out of plane bending
(**Twisting and wagging**)
 $1000-650\text{cm}^{-1}$
Strongest in alkenes

Alkynes

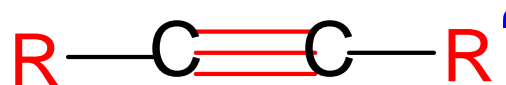
Contains $\text{C}\equiv\text{C}$ group

Three characteristic bands are present

1) $\text{C}\equiv\text{C}$ stretching (2260-2100 cm^{-1})

In symmetrical substituted alkynes $\text{R}-\text{C}\equiv\text{C}-\text{R}$ stretching vibration is **not observed**.

Even in non-symmetrical substituted alkynes stretching vibration is **very weak**, due to ***pseudo-symmetry***.



Only in **mono-substituted** alkynes this is observed.

2) C-H stretching



(3300-3250 cm^{-1})

Observed in **mono-substituted** acetylenes
(Strong band).

Narrower than **hydrogen-bonded O-H** and **N-H bands** which occurring in the same region.

3) C-H bending



(700-600 cm^{-1})

Observed in **mono-substituted** acetylenes

Aromatic Compounds

Show characteristic bands in **five regions**

1) The **C-H stretching** appear **above 3000 cm^{-1}** (aliphatic C-H stretching (below 3000 cm^{-1})).

2) In **$2000-1700\text{ cm}^{-1}$** region, a series of weak **combination** bands (**overtones**) appear.

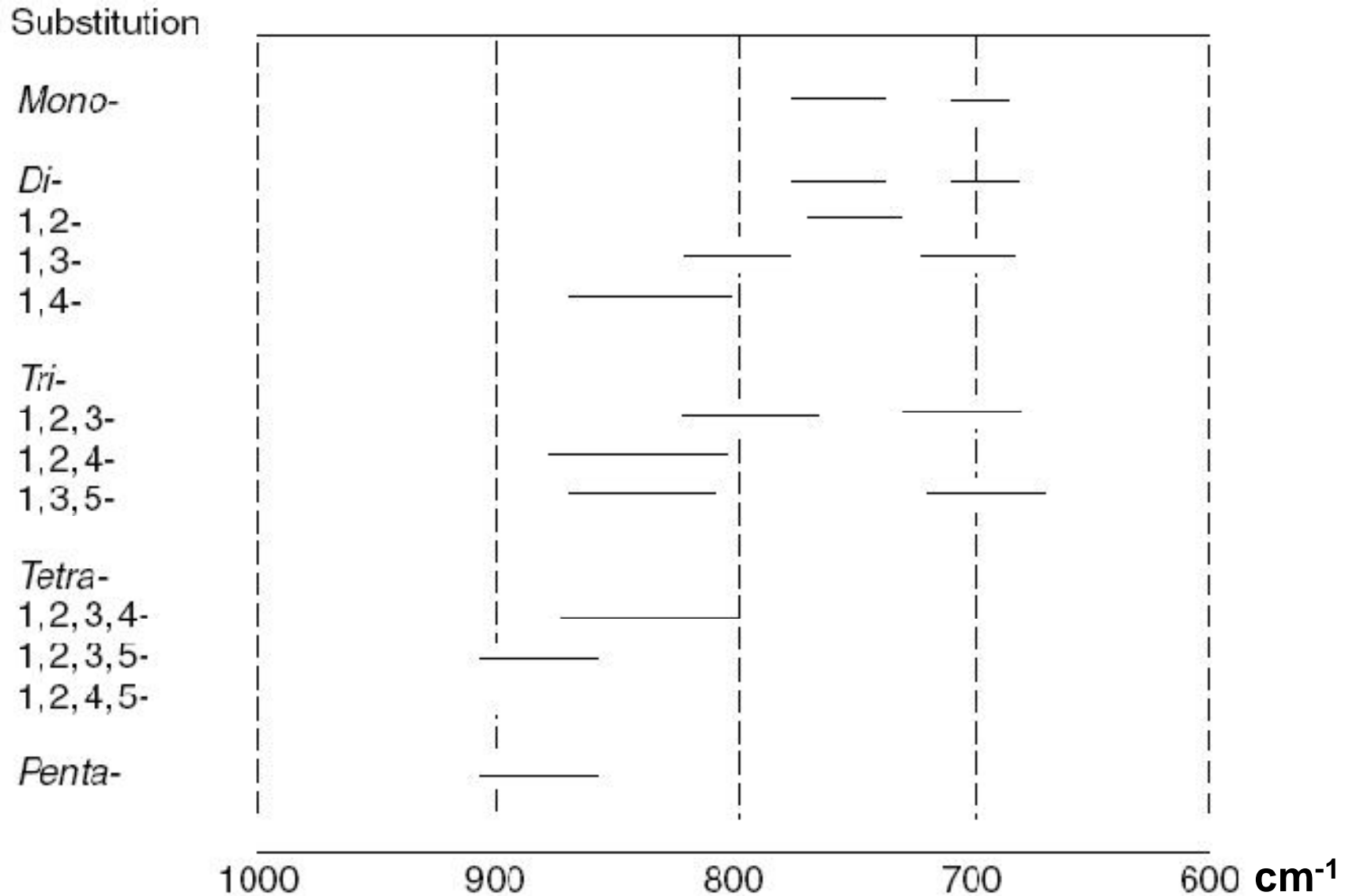
3) **Skeletal vibration**, representing C=C stretching absorb in the **$1650-1430\text{ cm}^{-1}$** .

4) The **C-H bending bands** appear in the regions **$1275-1000\text{ cm}^{-1}$** (**in-plane bending**) and

5) **$900-690\text{ cm}^{-1}$** (**out-of-plane C-H bending**).

These bands are strong and characteristic of the **number of hydrogen atoms** in the ring.

Bands of the out-of-plane bending in substituted benzene



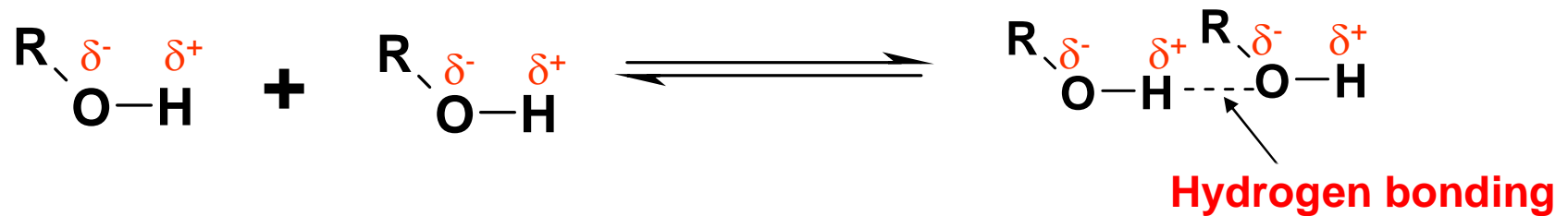
Alcohols and Phenols

- Characteristic bands due to O-H and C-O stretching.

O-H stretching

- Affected by **hydrogen bonding**
- 'Free' hydroxyl groups absorb between
- 3650-3585 cm^{-1} (**strong and sharp**).
- 'Free' OH bands are only observed in the **vapour phase** or **very dilute solution** of **non-polar** solvents (eg. CCl_4).
- **Intermolecular H-bonding increases** as the **concentration** of the solution increases or when the sample is analysed **neat**.
- This **lowers frequency** of absorption
- to 3550-3200 cm^{-1} .

Reason:

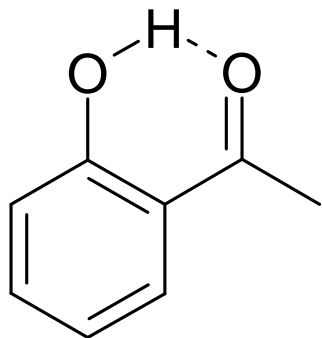


- The **stronger** the hydrogen-bonding
- the **longer** the O-H bond (**more polarized**)
- the **lower** the **force constant**
- the **lower** the **vibrational frequency**
- the **broader** the band (**H-bonding is not uniform throughout the sample**) and
- the **more intense** (due to **increased polarization** of the O-H bond) the absorption band.

Can IR spectroscopy distinguish these isomers?

Intramolecular H-bonding

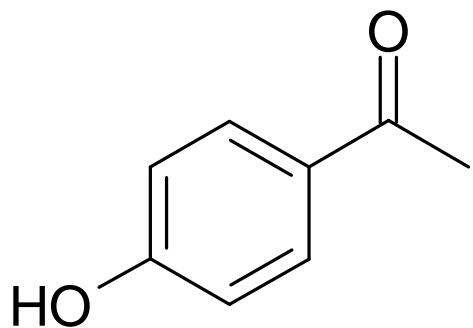
occurs in *O*-Hydroxyacetophenone



at **3077 cm⁻¹** (lower frequency)
(independent of concentration)

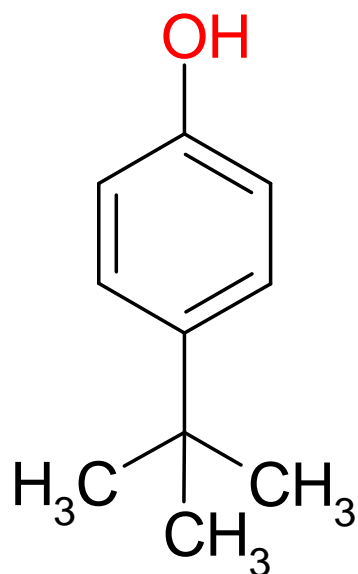
O-Hydroxyacetophenone

'free' hydroxyl peak at **3600 cm⁻¹**
(**Sharp**) in dilute solution of CCl₄.



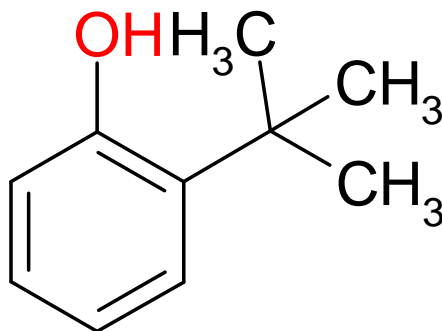
p-Hydroxyacetophenone

intermolecular H-bonded peak
at **3100 cm⁻¹** (**broad**) when run
neat sample (high concentration)



3105cm⁻¹

H-bonded OH

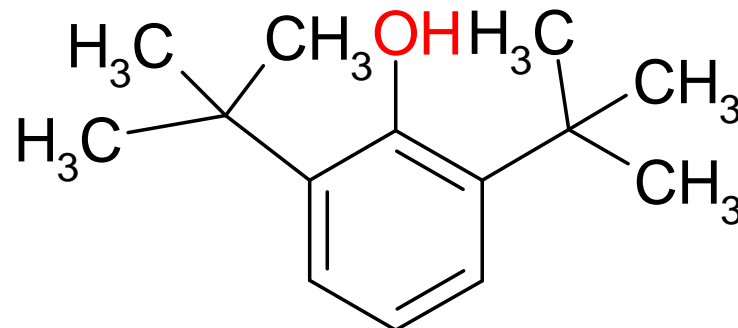


3105cm⁻¹

3643cm⁻¹

partly

H-bonded OH



3643cm⁻¹

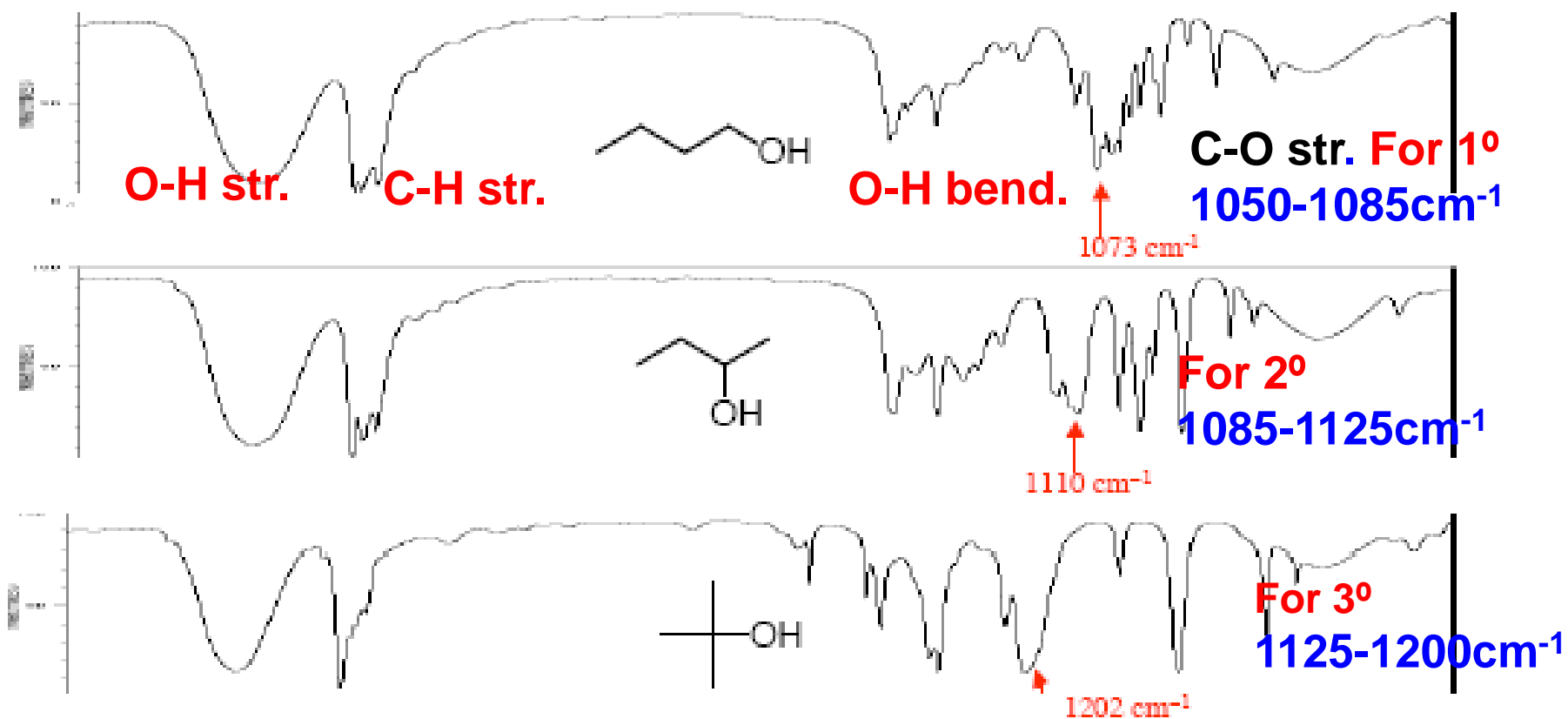
No H-bonding

Why the difference in absorption position?

2,6-di-*t*-butylphenol in which **steric hindrance prevents hydrogen-bonding**,

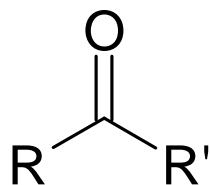
No **H-bonded** hydroxyl band is observed, not even in spectra of **neat samples**.

- **C-O stretching** appear at **1300-1000 cm^{-1}** .
- **O-H bending** also occurs but such bands **couple with other vibrations** and produce complex bands in the fingerprint region (**1420-1330 cm^{-1}**).



Carbonyl Compounds

- show **strong C=O** stretching absorption band in the region **1870-1540 cm⁻¹**.
- **High intensity** and relatively **free from interfering bands**.
- One of the **easiest** bands **to recognise**.
- **Neat sample** of saturated aliphatic ketone,
- **1715 cm⁻¹** as '**normal**'.



aliphatic ketone
(1715 cm⁻¹)

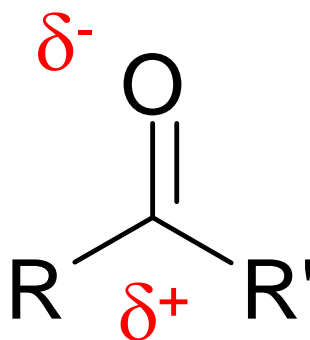
Change in the environment of the carbonyl can either **lower** or **raise** the absorption frequency.

Factors affecting position of C=O absorption

- 1) The **physical state** of measurement (solid, neat, dilute solution, conc. solution);
- 2) **Electronic effect** of substituents;
- 3) **Conjugation**;
- 4) **Hydrogen bonding**;
- 5) **Ring strain**.

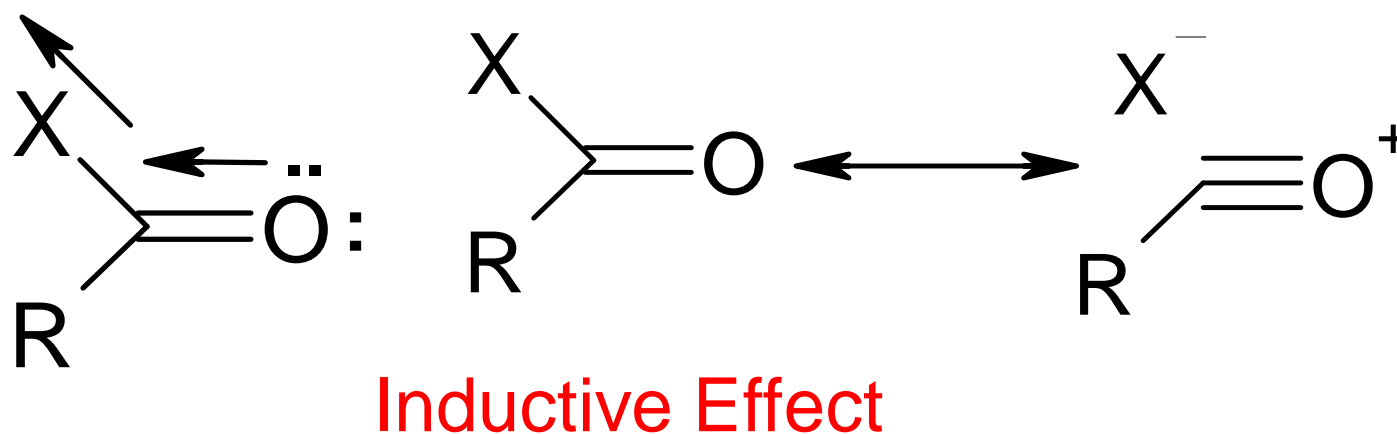
1) Physical State

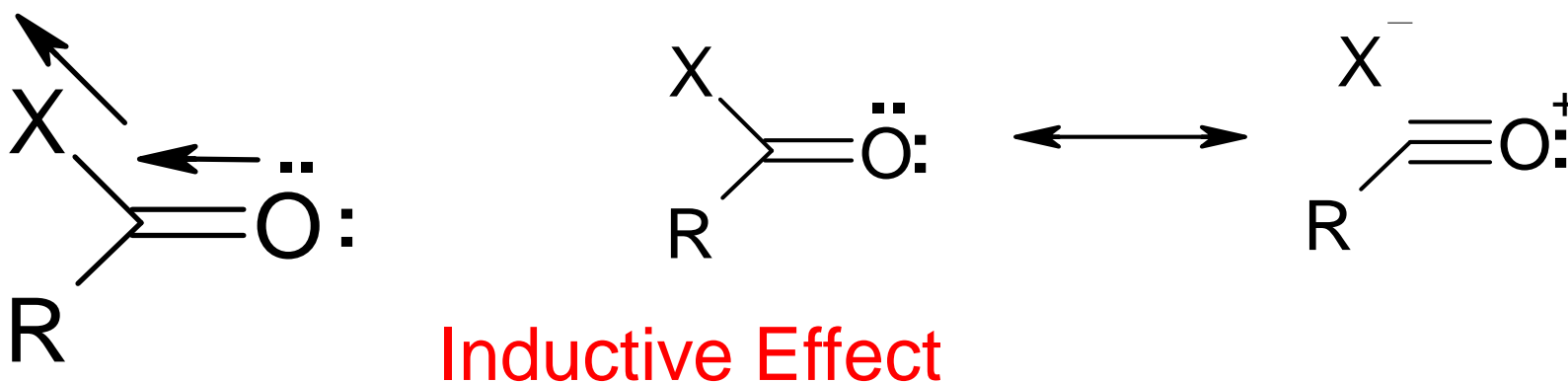
- Non-polar solvents increase absorption frequency.
- Polar solvents decrease absorption frequency.
- Due to **solvent-carbonyl** interaction.
- Overall range of solvent effect **does not exceed** 25 cm^{-1} .



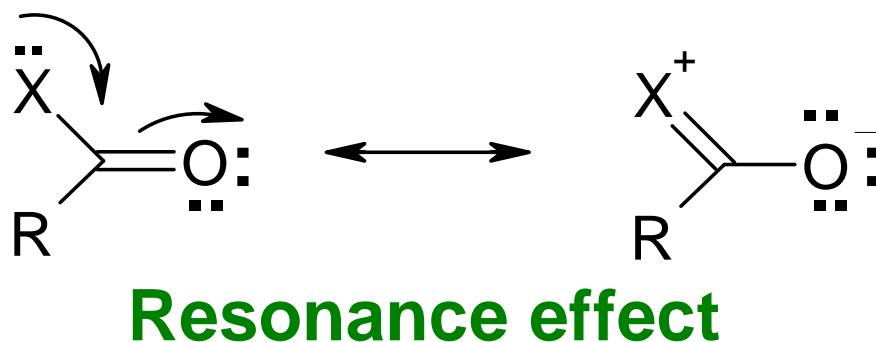
2) Electronic Effect of Substituents

- Replacement of an **alkyl group** of a saturated aliphatic ketone by **heteroatom (X)** shifts the carbonyl absorption.
- The direction of the shift depends on whether **inductive effect** or **resonance effect** predominates.



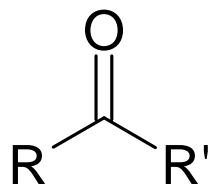


- Inductive effect** reduces the length of the C=O bond
- increases its force constant
 - the frequency of absorption will **increase**.

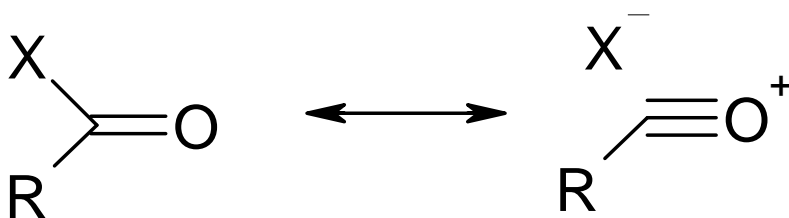


- Resonance effect** increases the length of the C=O bond
- reduces its force constant.
 - the frequency of absorption will **decrease**.

Substituent effects predominantly inductive



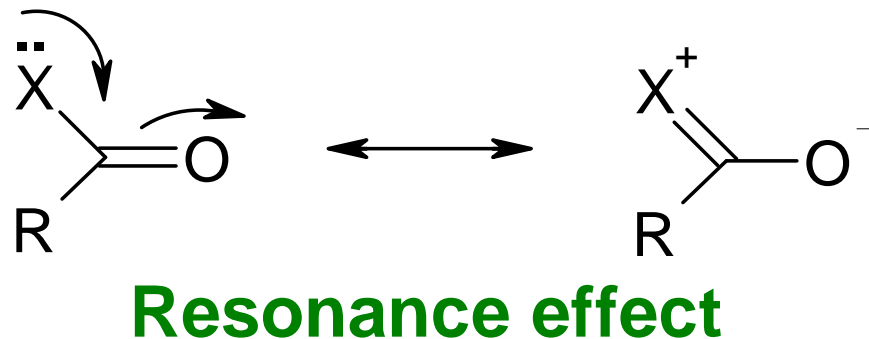
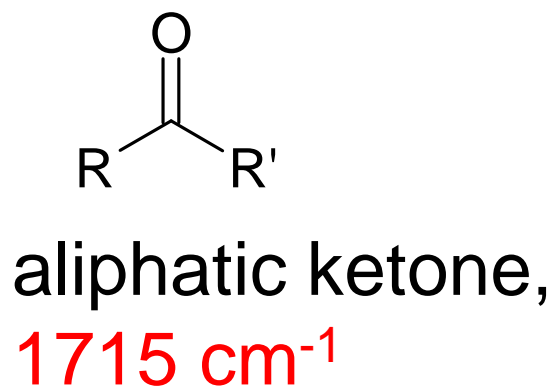
aliphatic ketone,
1715 cm⁻¹



Inductive Effect

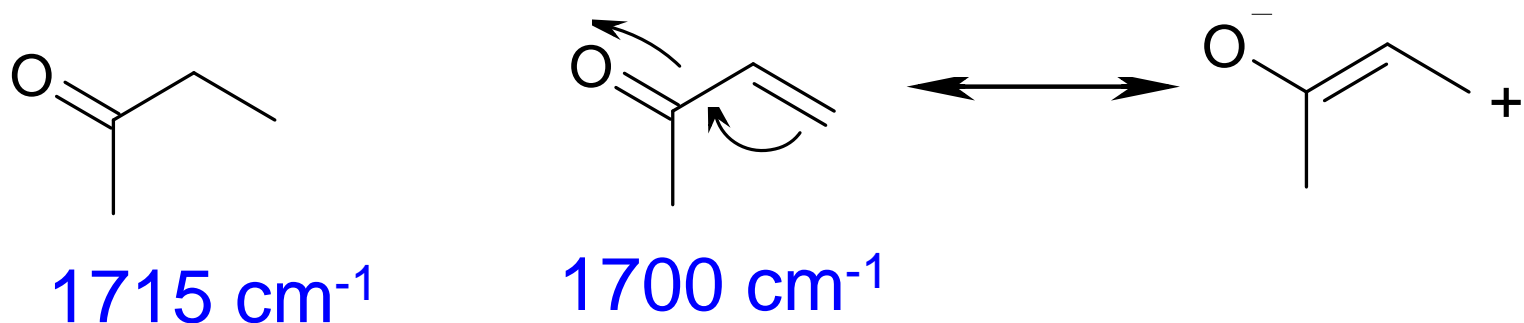
X	C=O absorption (cm ⁻¹)
F	1869
Cl	1815-1785
Br	1812
OH	1760
OR	1750-1735

Substituent effects predominantly resonance



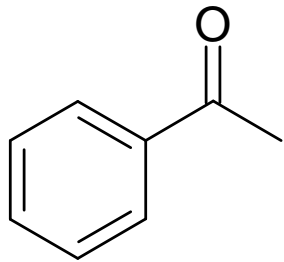
X	C=O absorption (cm ⁻¹)
NH ₂	1695-1650
SR	1710-1690

3) Conjugation

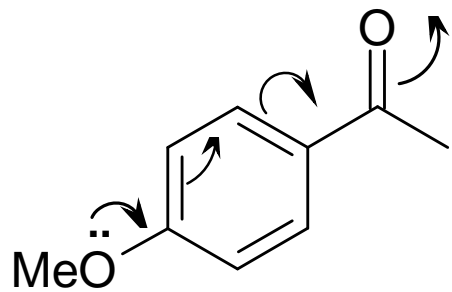


Conjugation **lowers** the stretching frequency of carbonyl by **15-40 cm^{-1}** .

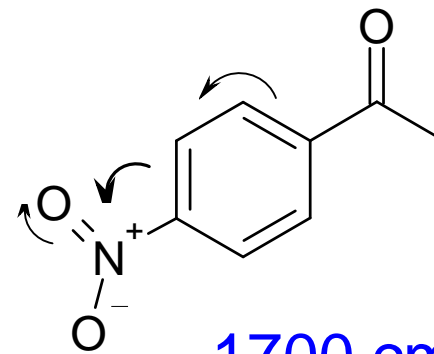
This is because the carbonyl **bond order** (double bond character) is **reduced** and hence the **force constant falls** (reduces).



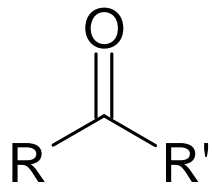
1685 cm^{-1}



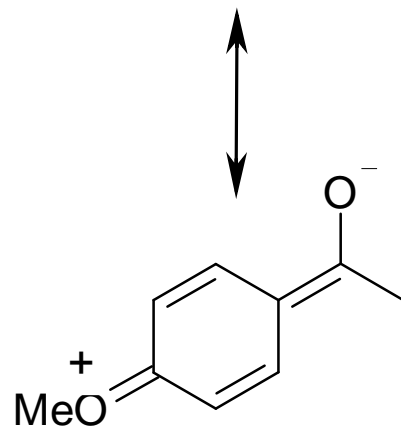
1650 cm^{-1}



1700 cm^{-1}

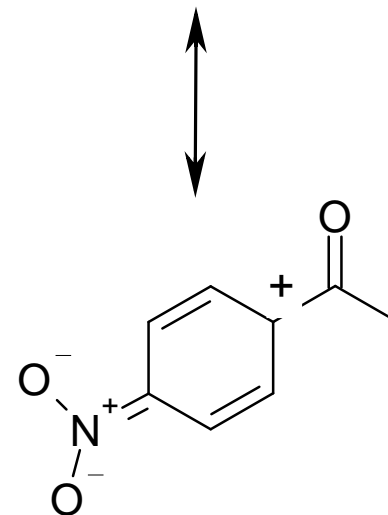


1715 cm^{-1}



Increased conjugation
with carbonyl group

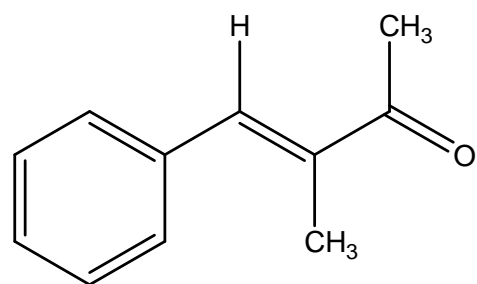
Lowers frequency



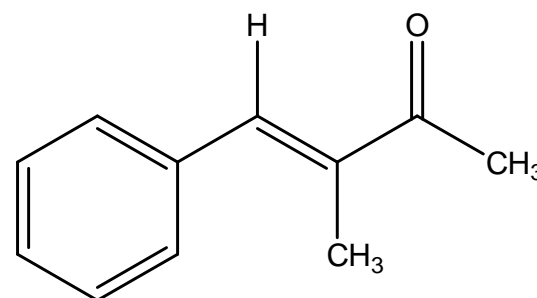
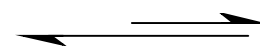
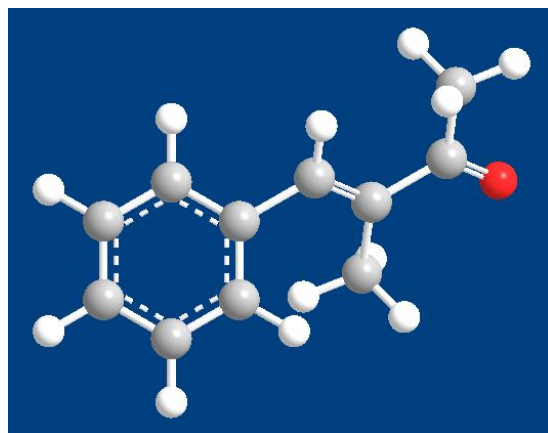
Decreased conjugation
with carbonyl group
Increases frequency

(E)-3-Methyl-4-phenylbut-3-en-2-one

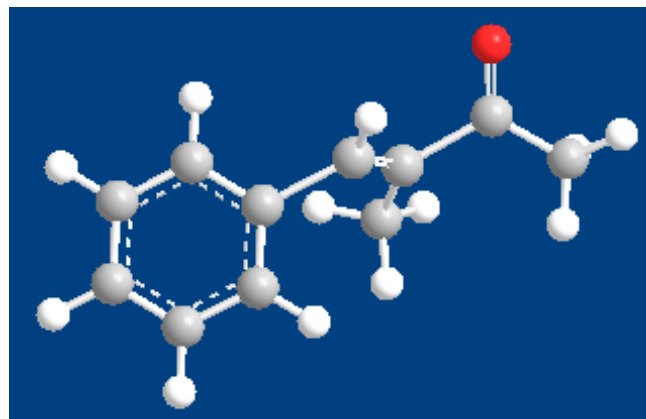
Shows two C=O bands at **1674** and **1699 cm⁻¹** . Why?



s-trans **1674 cm⁻¹**

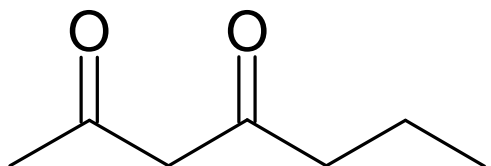


s-cis **1699 cm⁻¹**



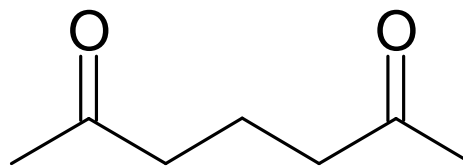
Sterric effects in s-cis reduces co-planarity of the conjugated system and **reduces** the **effect of conjugation**

How can you distinguish the two isomers using IR?



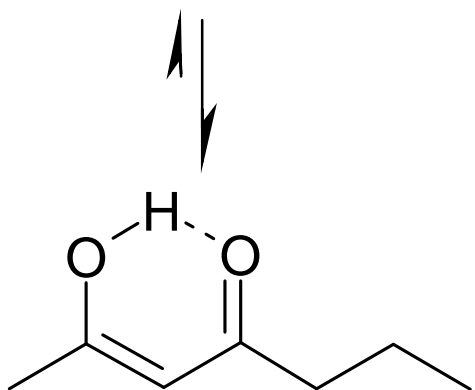
Heptane-2,4-dione

36% 1725 cm^{-1}



Heptane-2,6-dione

1715 cm^{-1}

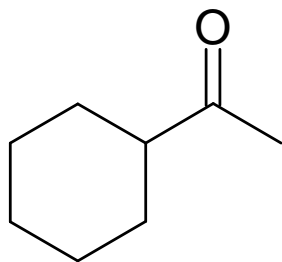


64%

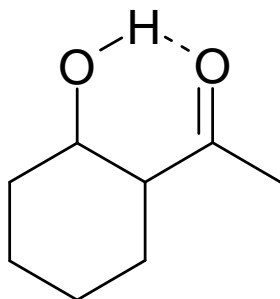
1613 cm^{-1}

3077 cm^{-1} for O-H stretching (H-bonded)

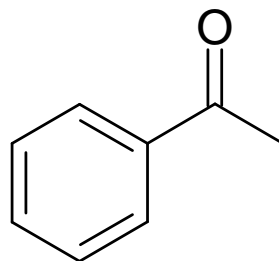
4) Hydrogen Bonding



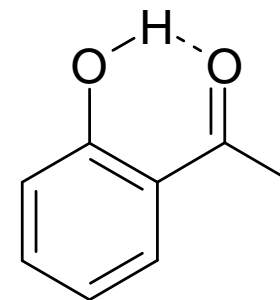
1715 cm^{-1}



1688 cm^{-1}



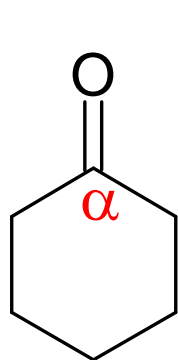
1685 cm^{-1}



1658 cm^{-1}

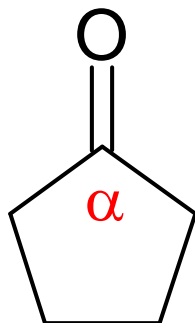
H-bonding reduces C=O stretching frequency.
This is because the carbonyl **bond order is reduced**
and the **force constant falls**..

5) Ring Strain



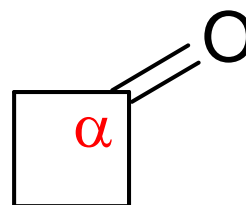
Cyclohexanone

1715 cm⁻¹



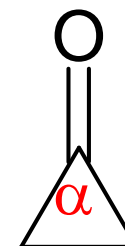
Cyclopentanone

1751 cm⁻¹



Cyclobutanone

1775 cm⁻¹



Cyclopropanone

1815 cm⁻¹

The bond angle (α) influences the absorption frequency of C=O.

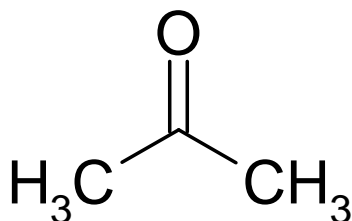
In **non-cyclic ketones** and in **cyclohexanone** $\alpha = 120^\circ$

In strained rings in which $\alpha < 120^\circ$

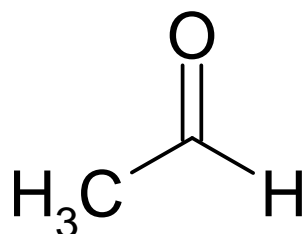
The **energy** of C=O stretching **increases**,

Hence **stretching frequency** is **increased**.

Aldehydes



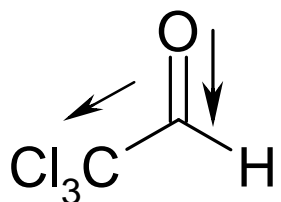
1715 cm^{-1}



1730 cm^{-1}

C=O stretching vibrations of **aldehydes** absorb at slightly **higher frequencies** than that of ketones.

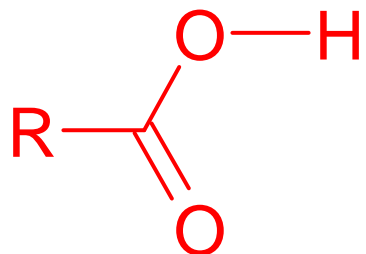
Hyperconjugation (which reduces vibrational frequency) is **higher in ketones** than in aldehydes



1768 cm^{-1}

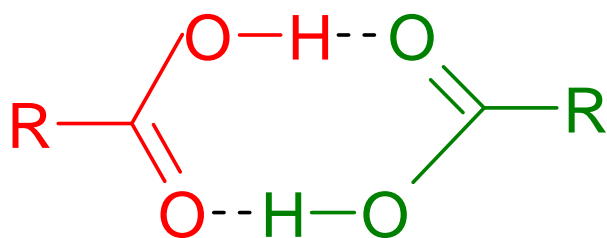
Electronegative substituents on **α -carbon** **increases the frequency** of carbonyl absorption

Carboxylic acids



Monomers of saturated aliphatic
Carboxylic acids absorb at 1760 cm^{-1}

In liquid or solid state and in solutions ($>0.01\text{M}$),
carboxylic acids **exist as dimers**
due to **strong H-bonding**

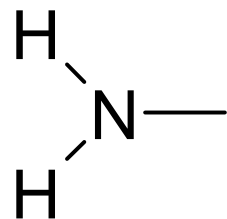


O-H stretching at 3000 cm^{-1}
(**very broad, intense**)

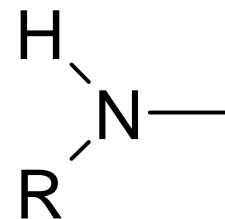
Dimerized saturated aliphatic
Carboxylic acids absorb at $1720\text{-}1706\text{ cm}^{-1}$

Amines

N-H stretching



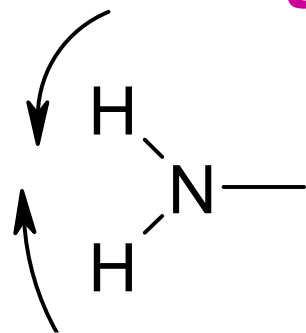
ν_s 3400 cm⁻¹
 ν_{as} 3500 cm⁻¹



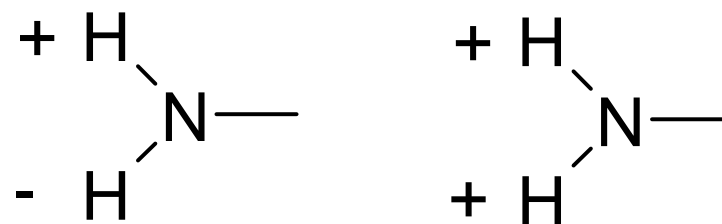
ν 3550 - 3310 cm⁻¹

Shifted to lower frequency by hydrogen bonding
N-H bands are **weaker** and **sharper** than O-H bands.

N-H bending



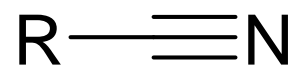
scissoring 1650 -1580 cm⁻¹
(medium to strong)



wagging 909-666 cm⁻¹
(medium to strong)

The position is affected by H-bonding

Nitriles



Aliphatic nitriles absorb near **2260-2240 cm^{-1}** .

Conjugation (aromatic nitriles) at **2240-2222 cm^{-1}** .

Index of Hydrogen Deficiency

(Double Bond Equivalence)

gives the sum of the number of π -bonds and rings

$$\text{Index of hydrogen deficiency} = \frac{\left(\begin{array}{c} \text{Number of H's} \\ \text{in reference} \\ \text{(C}_n\text{H}_{2n+2}) \end{array} \right) - \left(\begin{array}{c} \text{Number of H's} \\ \text{in compound} \end{array} \right)}{2}$$

Note: a saturated acyclic alkane (i.e. molecular formula: $\text{C}_n\text{H}_{2n+2}$) is used as the reference.

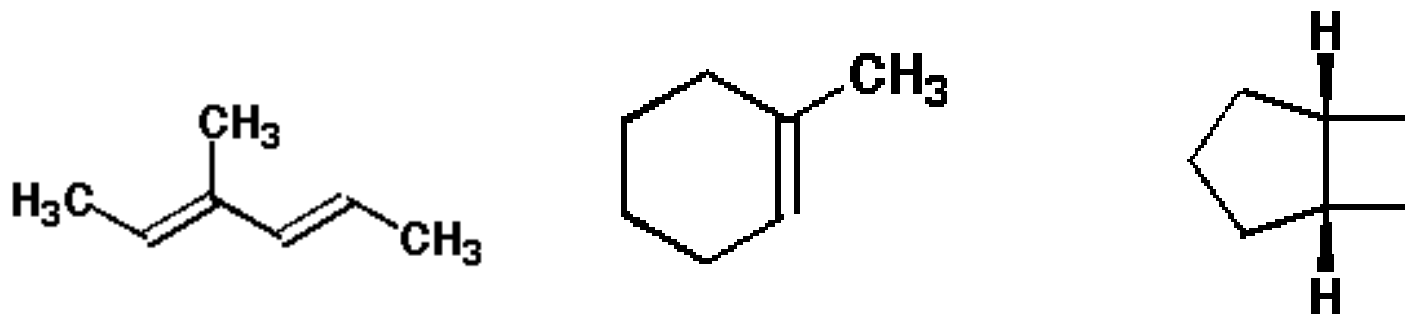
e.g. A compound X has a molecular formula C_7H_{12}

the reference compound has 16 Hydrogens

$$\therefore \text{Index of hydrogen deficiency} = \frac{16 - 12}{2} = 2$$

∴ the compound contains either 2 π -bonds,
1 π -bond and 1 ring, or 2 rings

possible formulas include:



Which are easily distinguished by $^1\text{H NMR}$ spectroscopy

Another way of expressing this
is that for a molecular formula: C_nH_m

$$\text{Index of hydrogen deficiency} = \frac{2n + 2 - m}{2}$$

Effect of Heteroatoms

Group VII elements ($X = \text{F, Cl, Br, I}$) are equivalent to one proton in the reference. i.e. the number of H's in the reference formula must be corrected by subtracting 1 for each X present.

Group VI elements ($Y = \text{O, S}$): no correction to the reference formula is necessary.

Group V elements ($Z = \text{N, P}$): the number of H's in the reference formula must be corrected adding 1 for each Z present.

∴ For a molecular formula: $C_n H_m X_x Y_y Z_z$

$$\text{Index of hydrogen deficiency} = \frac{2n + 2 + z - x - m}{2}$$

Example

$$C_{10}H_6N_2Br_4Cl_2 \quad \text{Index of hydrogen deficiency} = \frac{(20 + 2) + 2 - 6 - 6}{2} = 6$$

the exact structure has not yet been fully identified, but it probably has a structure such as:

