



Characteristic Group Vibrations of Organic Molecules



Information obtained from IR spectra

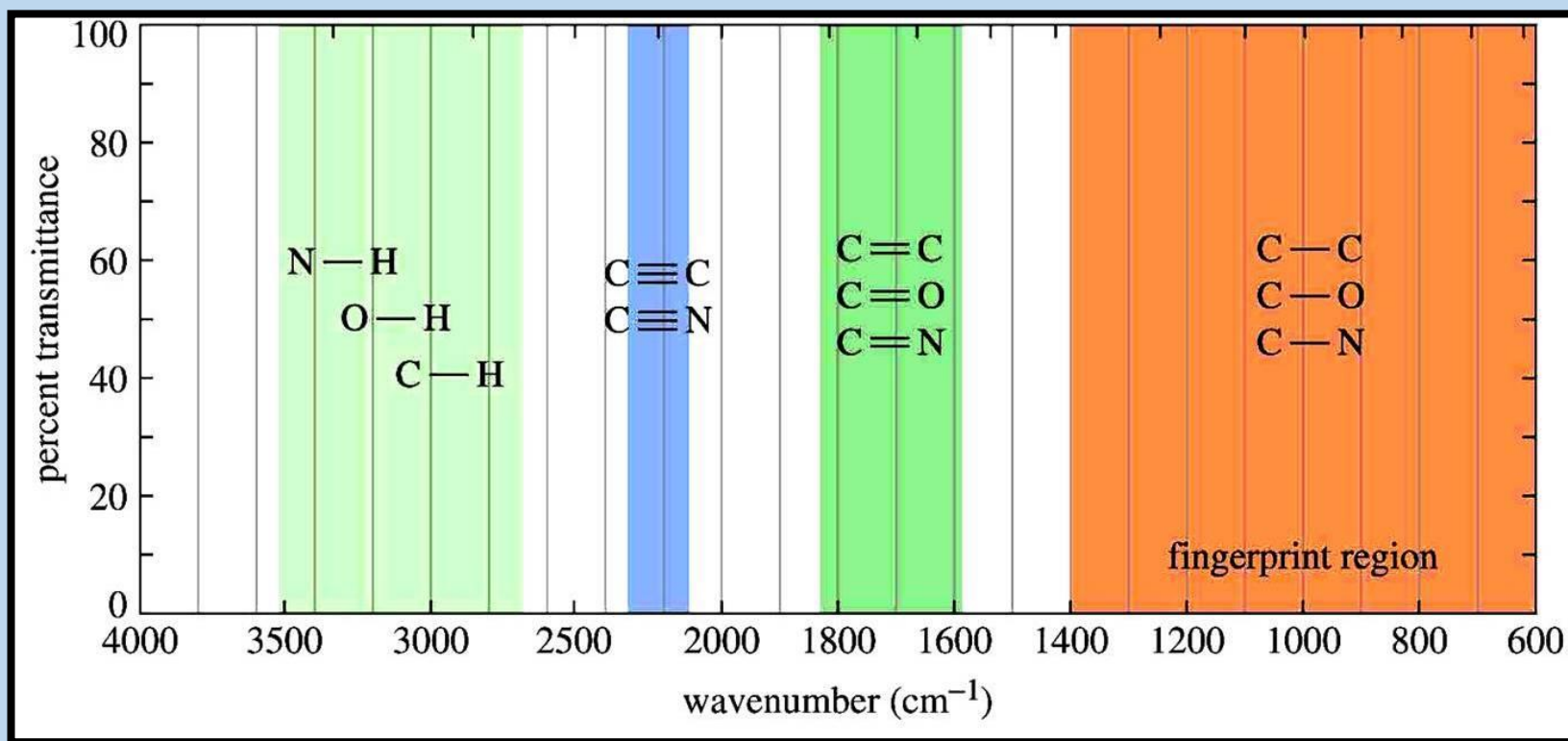


- ❖ IR is most useful in providing information about the presence or absence of specific **functional groups**.
- ❖ IR can provide a **molecular fingerprint** that can be used when comparing samples. If two pure samples display the same IR spectrum it can be argued that they are the same compound.
- ❖ IR **does not** provide detailed information or proof of molecular formula or structure. It provides information on molecular fragments, specifically functional groups.
- ❖ Therefore it is *very limited* in scope, and must be used in conjunction with other techniques to provide a more complete picture of the molecular structure.



IR absorption range

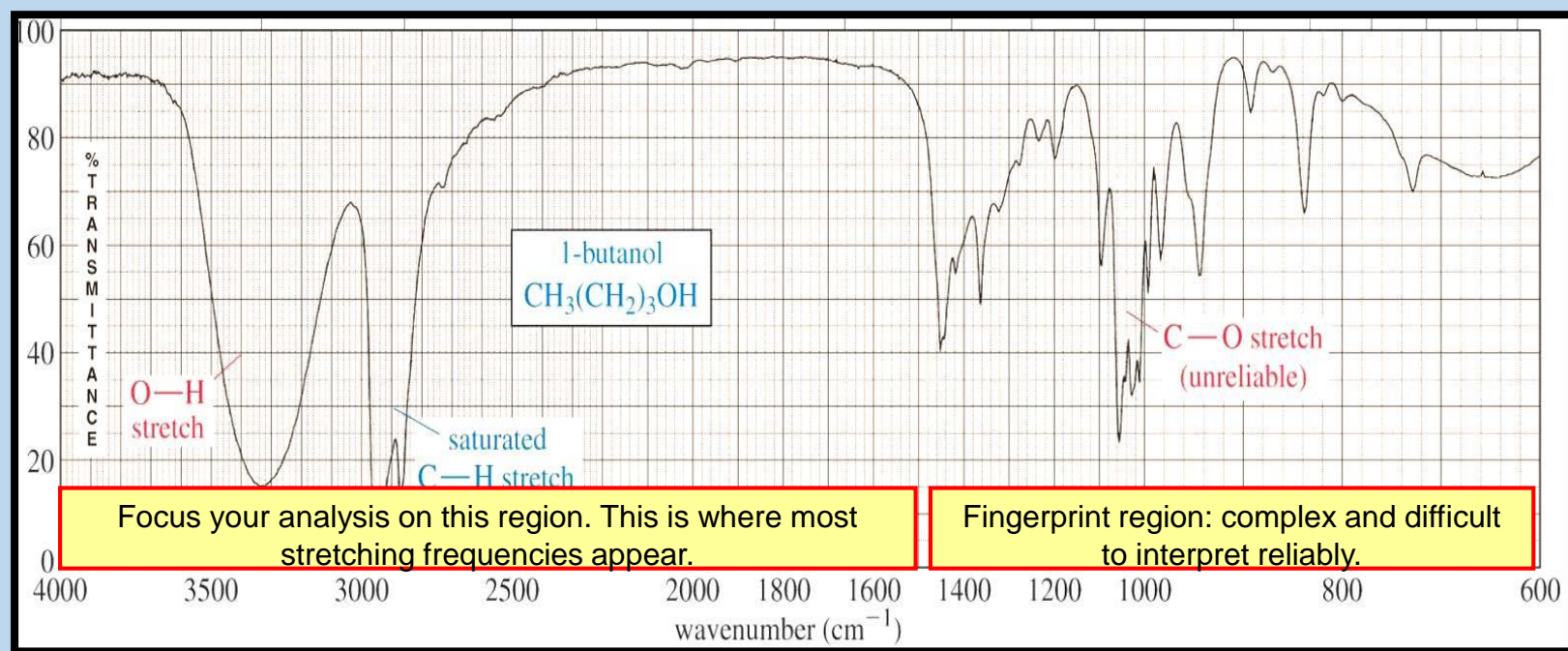
- The typical IR absorption range for covalent bonds is **600 - 4000 cm^{-1}** . The graph shows the regions of the spectrum where the following types of bonds normally absorb. For example a sharp band around **2200-2400 cm^{-1}** would indicate the possible presence of a **$\text{C}\equiv\text{N}$** or a **$\text{C}\equiv\text{C}$** bond.





The fingerprint region

- Although the entire IR spectrum can be used as a fingerprint for the purposes of comparing molecules, the **600 - 1400 cm^{-1}** range is called the **fingerprint region**. This is normally a complex area showing many bands, frequently overlapping each other. This complexity limits its use to that of a fingerprint, and should be ignored by beginners when analyzing the spectrum.





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- The region above 1400 cm^{-1} often *provides easily recognizable bands of various functional groups* and thus much valuable structural evidence from relatively few of these bands is obtained and total interpretation of the complete spectrum is seldom required.



Hydrocarbons C-H and C-C stretching and bending vibrations

Alkanes:

In simple hydrocarbons, only two types of atoms C and H and only two types of bonds (**C-C**) and (**C-H**) are present..

A hydrocarbon containing a methyl group (**CH₃**) usually shows two distinct bands, one at **2960 cm⁻¹ due to asymmetric stretching** and the other at **2870 cm⁻¹ due to symmetric stretching**.

The C -H bonds in methylene group (**CH₂**) undergo number of stretching and bending vibrations. The two stretching vibrations – asymmetrical and symmetrical occur at **2925 cm⁻¹** and appear in the spectrum.

The **C-H bending** vibrations of the methyl groups in the hydrocarbons normally occur at **1450 and 1375 cm⁻¹**. The band at 1375 cm⁻¹ is due to methyl on the carbon atom and is quite sensitive to the electronegativity of the substituent present at the methyl group. within a range of ± 10 cm⁻¹.

The (**C-C**) bond vibrations appear as weak bands in **1200-800 cm⁻¹** region and are seldom used for structural study. Whereas the (**C-C**) **bending** absorptions occur at **< 500 cm⁻¹** and are usually below the range of IR – instrument.



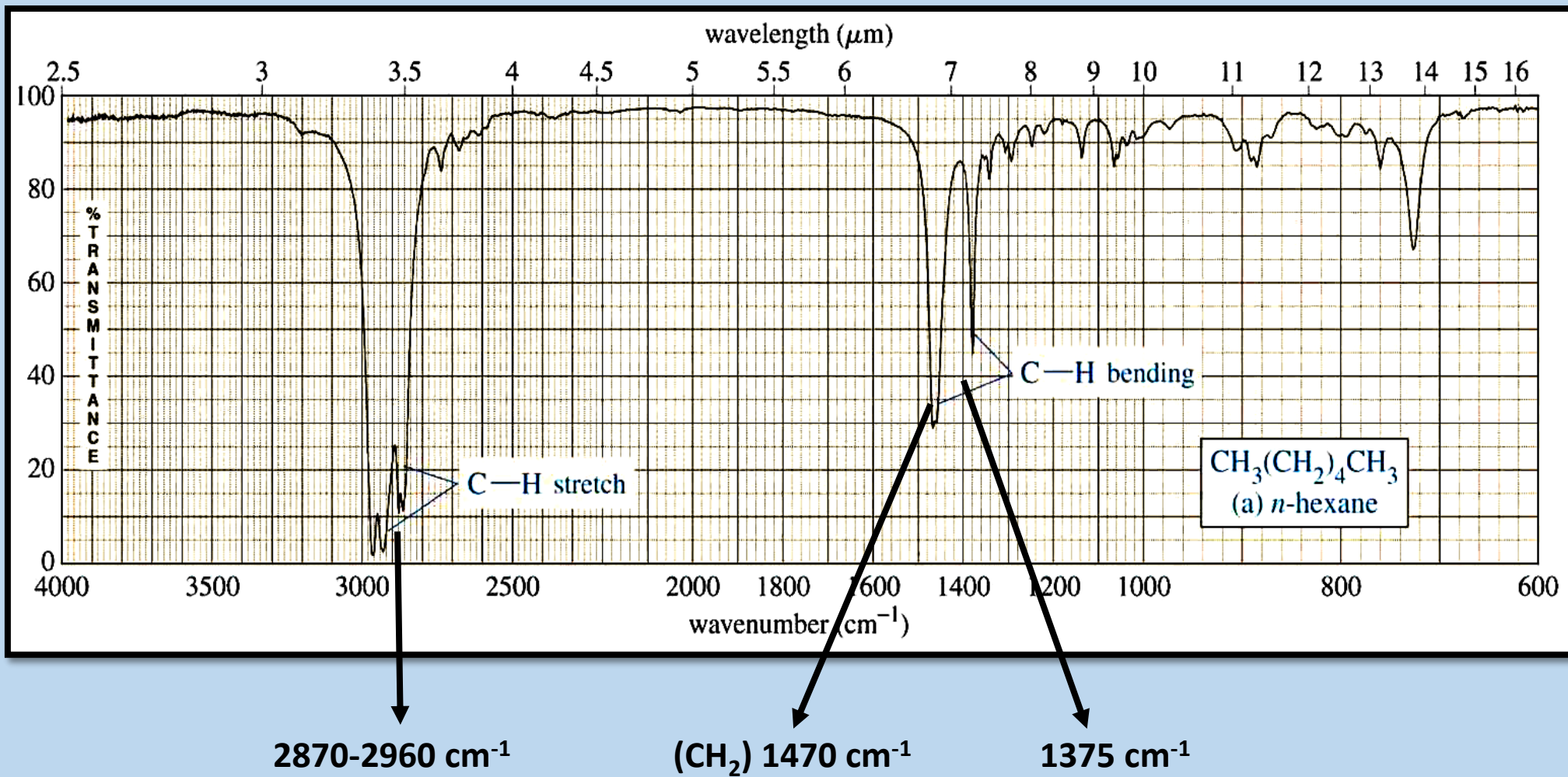
The band shifts from as high as **1475 cm⁻¹ in CH₃-F** to as low as **1150 cm⁻¹ in CH₃-Br**. This band is extremely useful in detecting the presence of methyl group in a compound because it is sharp and of medium intensity and is rarely overlapped by absorptions due to methylene or methane deformations.

The intensity of this band usually *increases* with the number of methyl groups in the compound. However, **the presence of two or more methyl groups on one aliphatic carbon atom (isopropyl or t-butyl groups) results in splitting of this band due to in-phase or out of phase interactions of the two symmetrical methyl deformations.**

The methylene group, C-H bending vibrations such as scissoring, twisting, wagging and rocking normally appear at fairly different frequencies. **If two or more CH₂ groups are present**, the usually strong scissoring and rocking absorption bands appear at **1465 and 720 cm⁻¹**, respectively. Whereas **weak bands due to twisting and wagging vibrations appear at 1250 ± 100 cm⁻¹**. So, the scissoring absorption band of methylene around 1465 cm⁻¹ often overlaps with asymmetric bending vibration of methyl at 1450 cm⁻¹.



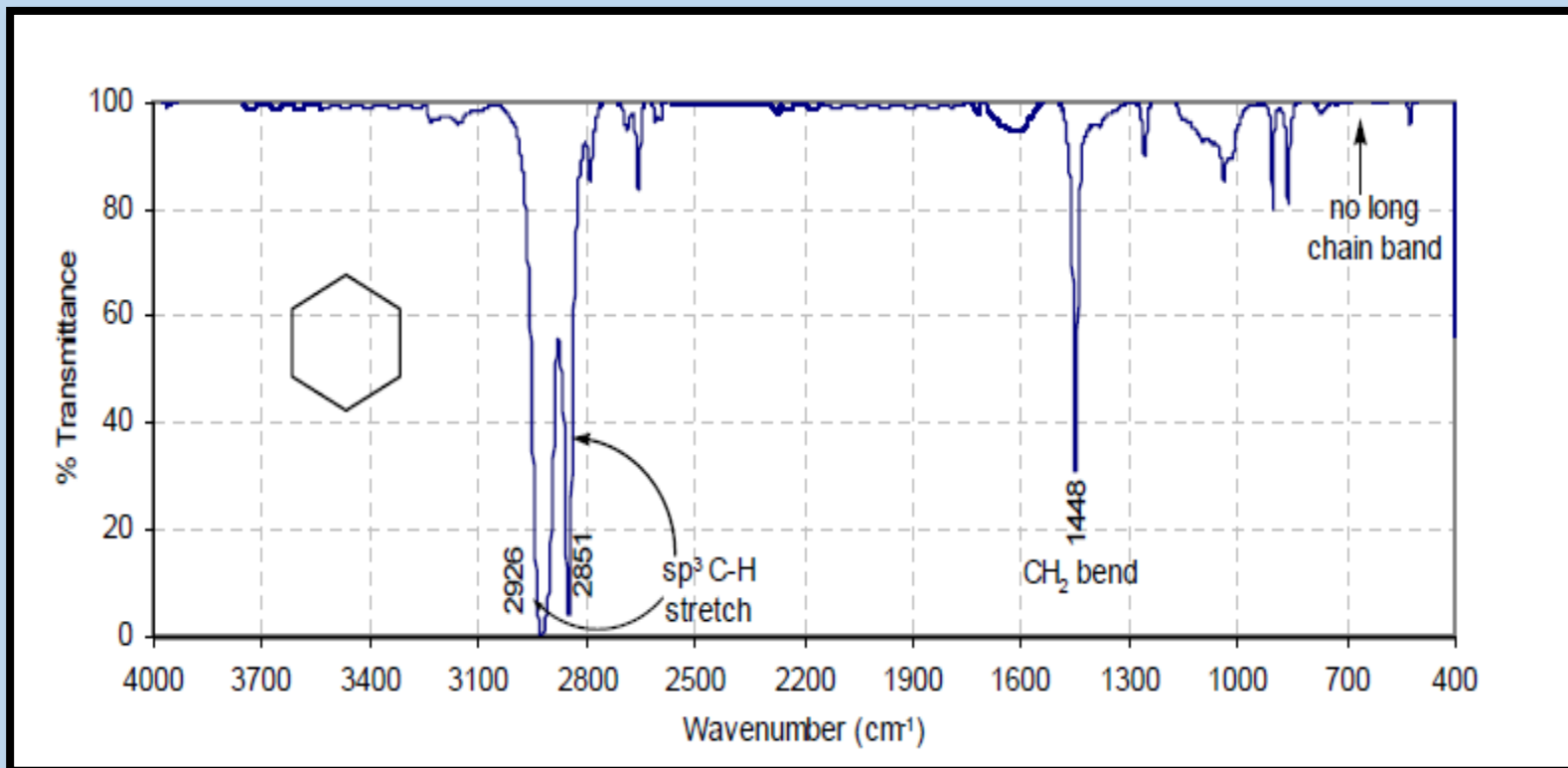
n-Hexane





Cyclic aliphatic hydrocarbons

The C-H stretching frequencies are the same ($2800 - 3000 \text{ cm}^{-1}$) as in the case of acyclic compounds, if the ring is unstrained. However, **methylene (CH_2)** scissoring bands shift slightly to smaller wavenumber (1470 cm^{-1} in hexane and 1448 cm^{-1} in cyclohexane). In satirically strained cyclic compounds, the **C-H stretching** normally occurs at slightly higher wavenumber e.g. $3080 - 3040 \text{ cm}^{-1}$ in cyclopropane.





Alkenes:

- The (C=C) bond has a higher force constant than a (C-C) bond and in a non-conjugated olefin.

(C=C) stretching > (C-C) stretching
(1680-1620 cm⁻¹) (1200-800 cm⁻¹)

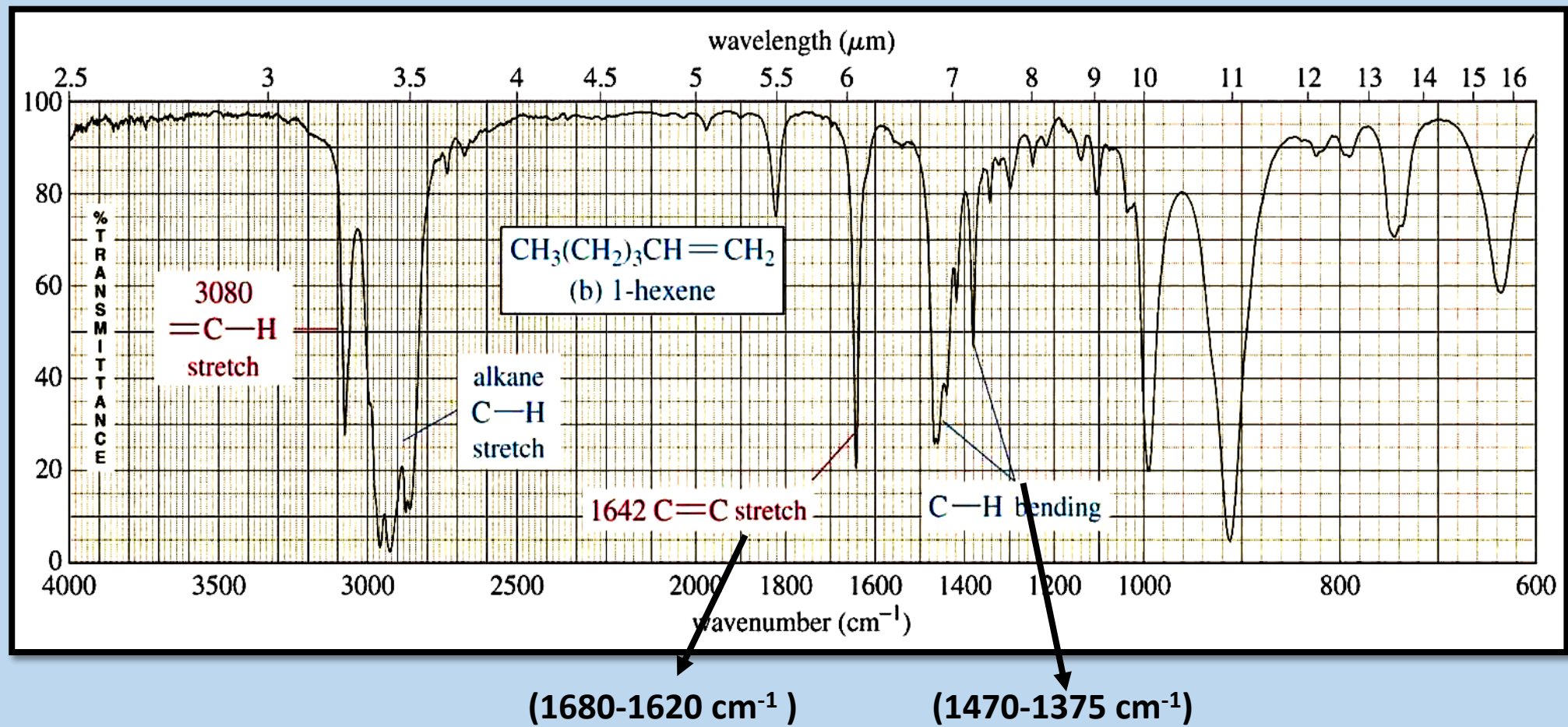
- In completely **symmetrical alkenes**, such as ethylene, tetrachloroethylene etc., (C=C) stretching band is absent, due to lack of change in dipole moment in completely symmetrical molecule.
- **Non-symmetrically** substituted double bonds exhibit strong absorption bands. The absorption bands are **more intense for cis isomers than for trans isomers**; for mono or tri substituted olefins than for di and tetra substituted ones.

(C=C) terminal olefins > (C=C) internal olefins

- Similarly (C=C) groups conjugated with certain unsaturated group show **stronger** band than for non-conjugated ones.

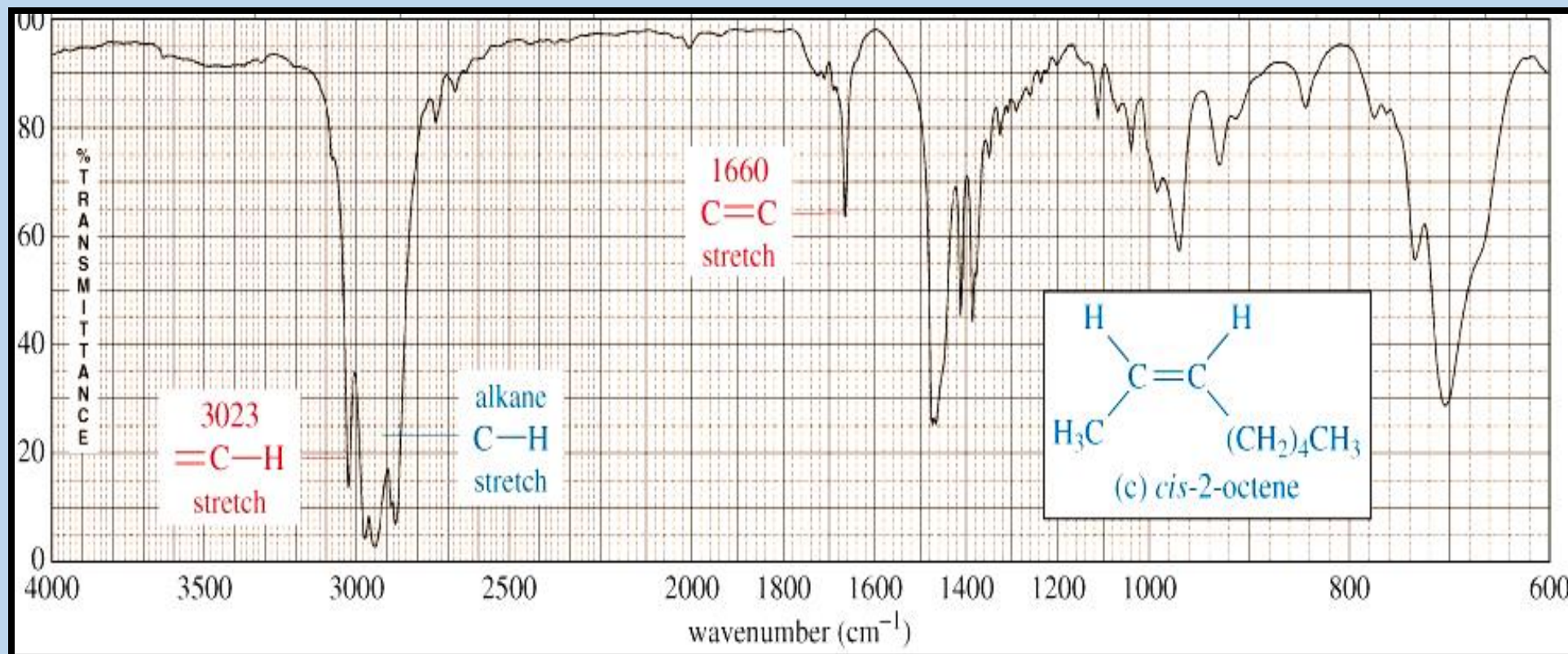


IR spectrum of alkene



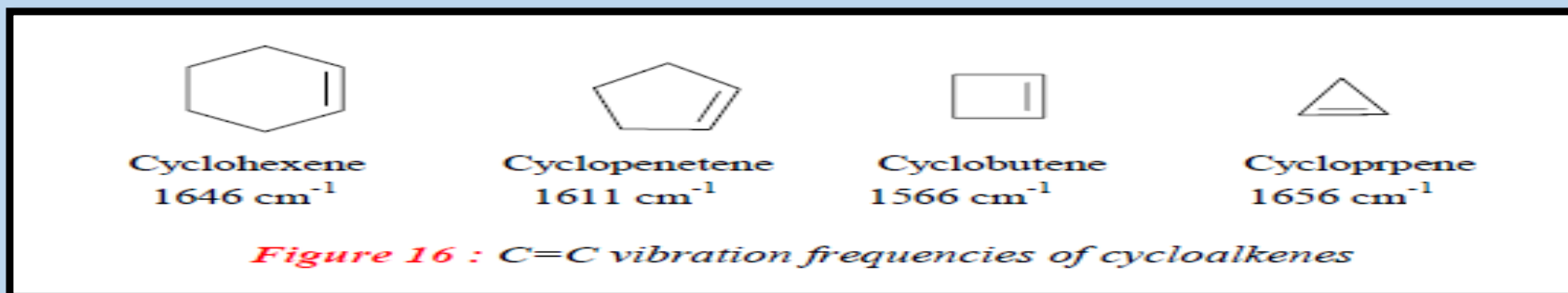


This spectrum shows that the band appearing around 3080 cm^{-1} can be obscured by the broader bands appearing around 3000 cm^{-1} .



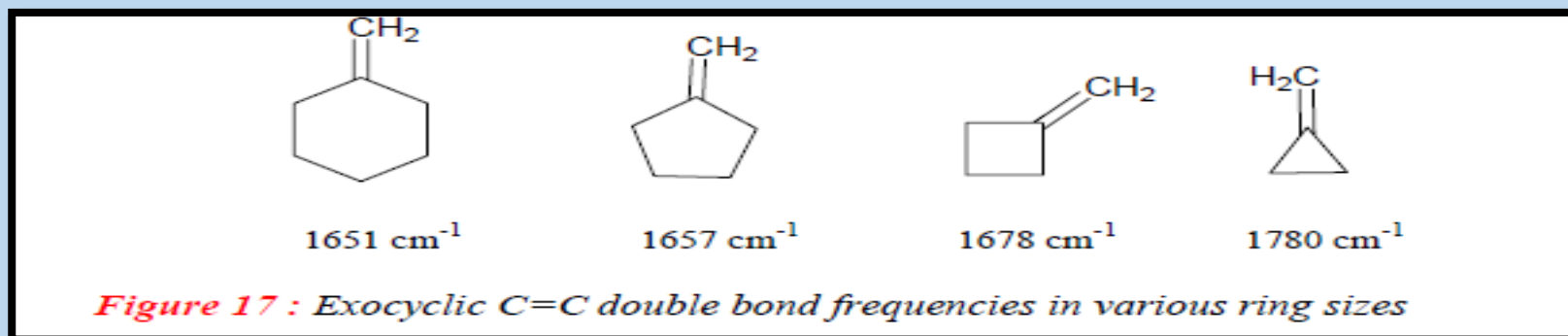


- ❖ In case of olefins, conjugated with an aromatic ring, the **(C=C) stretching** appears at **1625 cm⁻¹** (s) and an additional band **at ~1600 cm⁻¹** is observed due to aromatic double bond.
- ❖ In compounds containing both olefinic and alkyl C-H bonds, the bands above **3000 cm⁻¹** are generally attributed to **aromatic or aliphatic (C-H) stretching**, whereas between **3000-2840 cm⁻¹** are generally assigned to the **alkyl C-H stretching**.
- ❖ The absorption frequency of a **(C=C)** bond in a **cyclic ring** is very sensitive to ring size. The absorption frequency decreases as the internal angle decreases and is lowest in cyclobutene (90° angle). The frequency increases again for cyclopropane





- ❖ The exocyclic (C=C) bonds exhibit an increase in frequency with decrease in ring size. The exocyclic double bond on six-membered ring absorbs at 1651 cm^{-1} and it is shifted to 1780 cm^{-1} in case of exocyclic (C=C) bond on **cyclopropane**.





Alkynes:

- The most prominent band in alkynes corresponds to the **(C≡C) bond**. It shows as a sharp, weak band at about **2100 cm⁻¹**. The reason it's weak is because the triple bond is not very polar.
- In **highly symmetrical alkynes**, it may not show at all due to the low polarity of the triple bond associated with those alkynes.
- **Terminal alkynes**, (**≡C-H**) involving the *sp* carbon (the carbon that forms part of the triple bond). Therefore they may also show a **sharp, weak band at about 3300 cm⁻¹ corresponding to the C-H stretch**.
- **Internal alkynes**, do not have C-H bonds to the *sp* carbon and therefore lack the aforementioned band.



A comparison between an unsymmetrical terminal alkyne (1-octyne) and a symmetrical internal alkyne (4-octyne).

