

# Infrared (IR) spectroscopy

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# Introduction

- IR refers to the part of electromagnetic spectrum between the visible and microwave (mw) regions.
- The useful range of IR for an organic chemist is between 4000-625  $\text{cm}^{-1}$ .
- Many functional groups have vibration frequencies, characteristic of that functional group, within well-defined regions of this range.

# Theory

- IR radiation in the range from about  $10,000\text{-}100\text{ cm}^{-1}$  is absorbed and converted into energy of molecular vibration.
- This absorption is quantized but vibrational spectra appear as bands rather than lines.
- These bands in IR spectra presented as wavenumber ( $\bar{\nu}$ ).

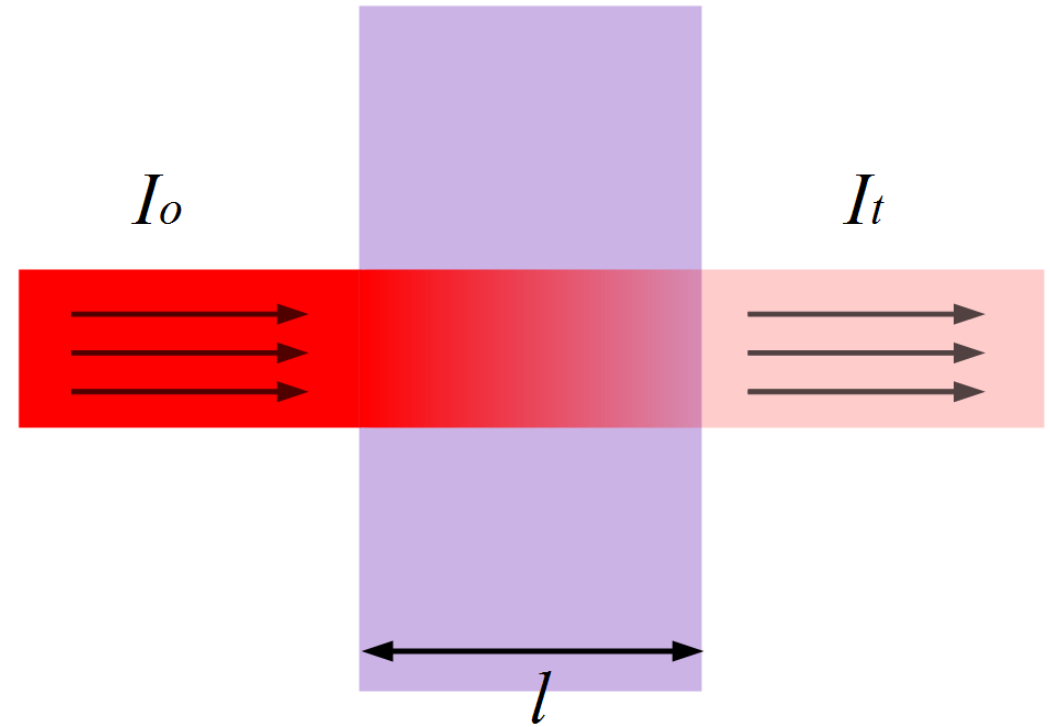
# Theory

- Band intensities can be expressed either as transmittance ( $T$ ) or absorbance ( $A$ ).

- *Transmittance* ( $T$ ) =  $\frac{I_t}{I_o}$

- % *Transmittance* ( $T$ ) =  $\left(\frac{I_t}{I_o}\right) \times 100$

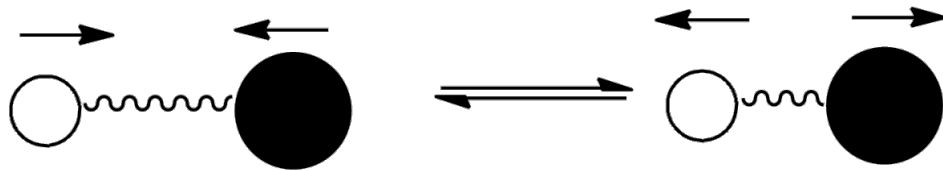
- *Absorbance* ( $A$ ) =  $\log \frac{1}{T}$



# Theory

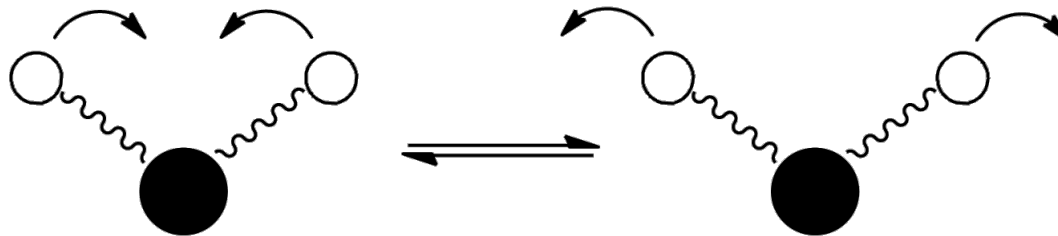
- There are two types of molecular vibrations:

- Stretching



stretching vibrations

- Bending



bending vibrations

# Theory

- The covalent bonds in a molecule can be described in similar way with a 2 balls (atoms) that connected with a spring (the bond).
- The natural frequency of vibration of a bond is given by the equation:

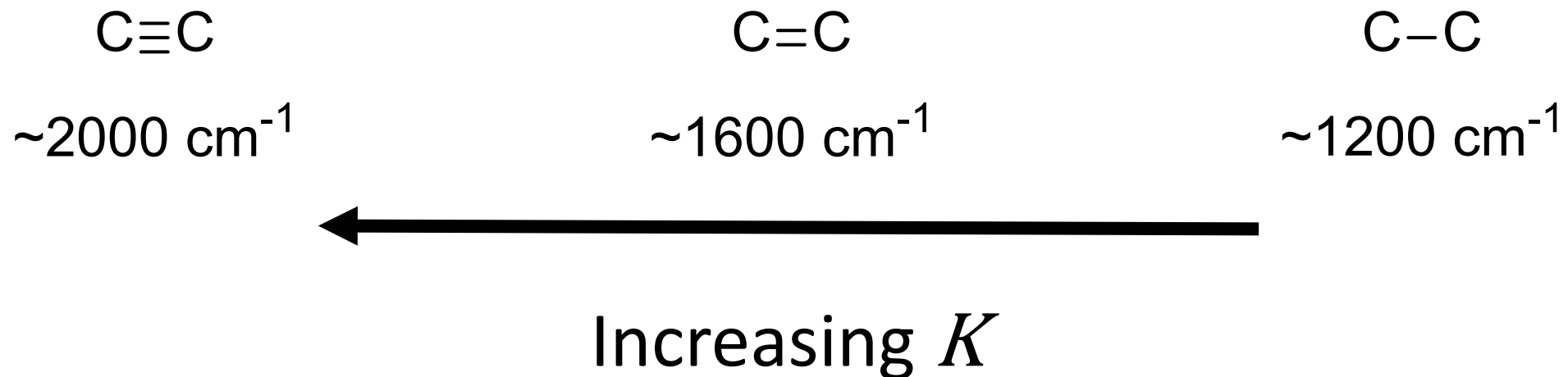
$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

- Where the reduced mass ( $\mu$ ) is given by:

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

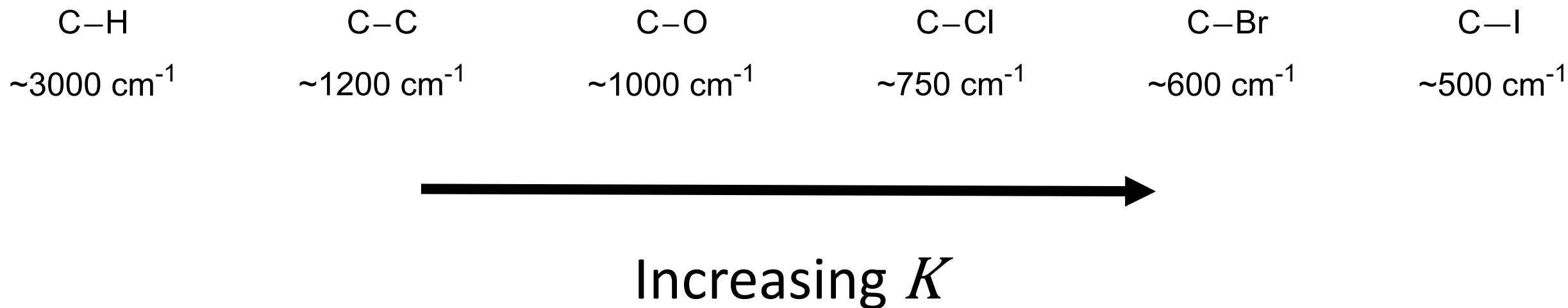
# Theory

- From the previous equations, two things should be noticed:
  1. Stronger bonds have a larger force constant  $K$  and vibrate at higher frequencies than weaker bonds



# Theory

2. Heavier atoms vibrate at lower frequencies than bonds between lighter atom, i.e. larger  $\mu$  values



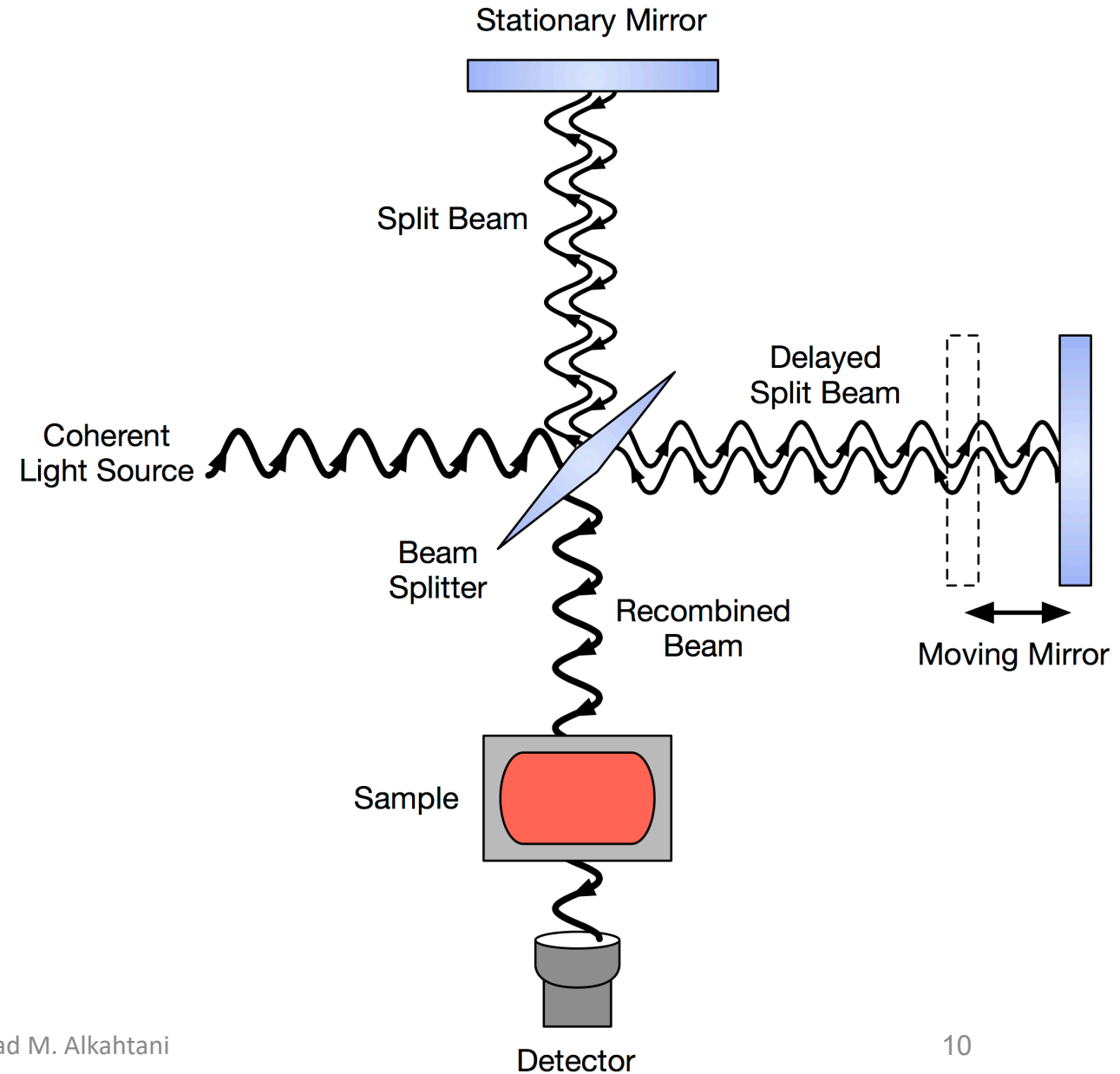


# Theory

Bond	Bond Energy [kcal (kJ)]	Stretching Frequency (cm <sup>-1</sup> )
<i>Frequency dependence on atomic masses</i>		
C—H	100 (420)	3000
C—D	100 (420)	2100
C—C	83 (350)	1200
	↓ heavier atoms	↓ $\bar{\nu}$ decreases
<i>Frequency dependence on bond energies</i>		
C—C	83 (350)	1200
C=C	146 (611)	1660
C≡C	200 (840)	2200
	↓ stronger bond	↓ $\bar{\nu}$ increases
C—N	73 (305)	1200
C=N	147 (615)	1650
C≡N	213 (891)	2200
C—O	86 (360)	1100
C=O	178 (745)	1700

# Instrumentation

- IR spectrometers composed of:
  - IR source
  - Monochromator (interferometer)
  - Detector
  - Recorder



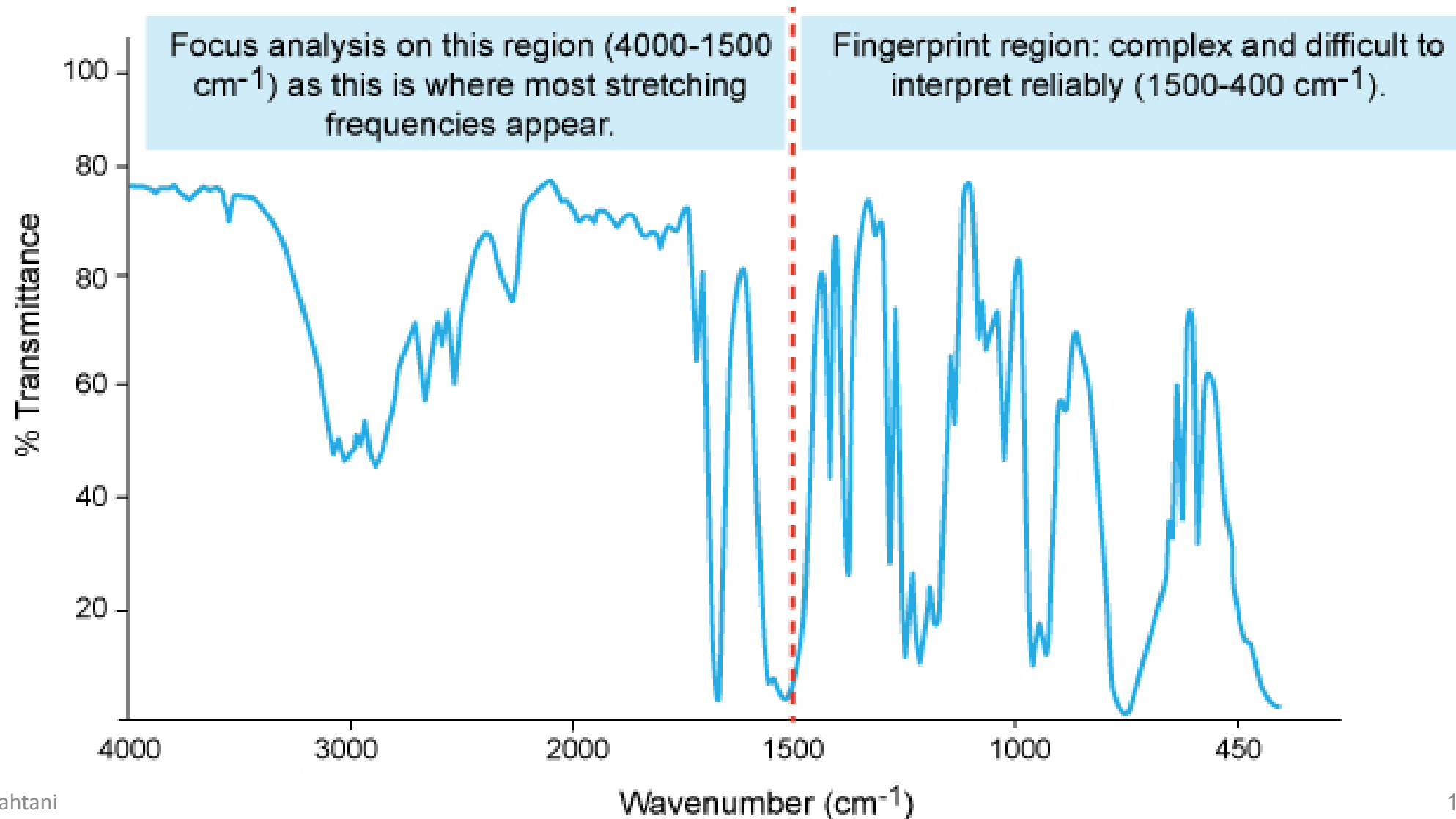
# Sample preparation

- Compounds may be examined:
  - In vapour phase
  - As a liquid
  - In solution
  - In the solid state

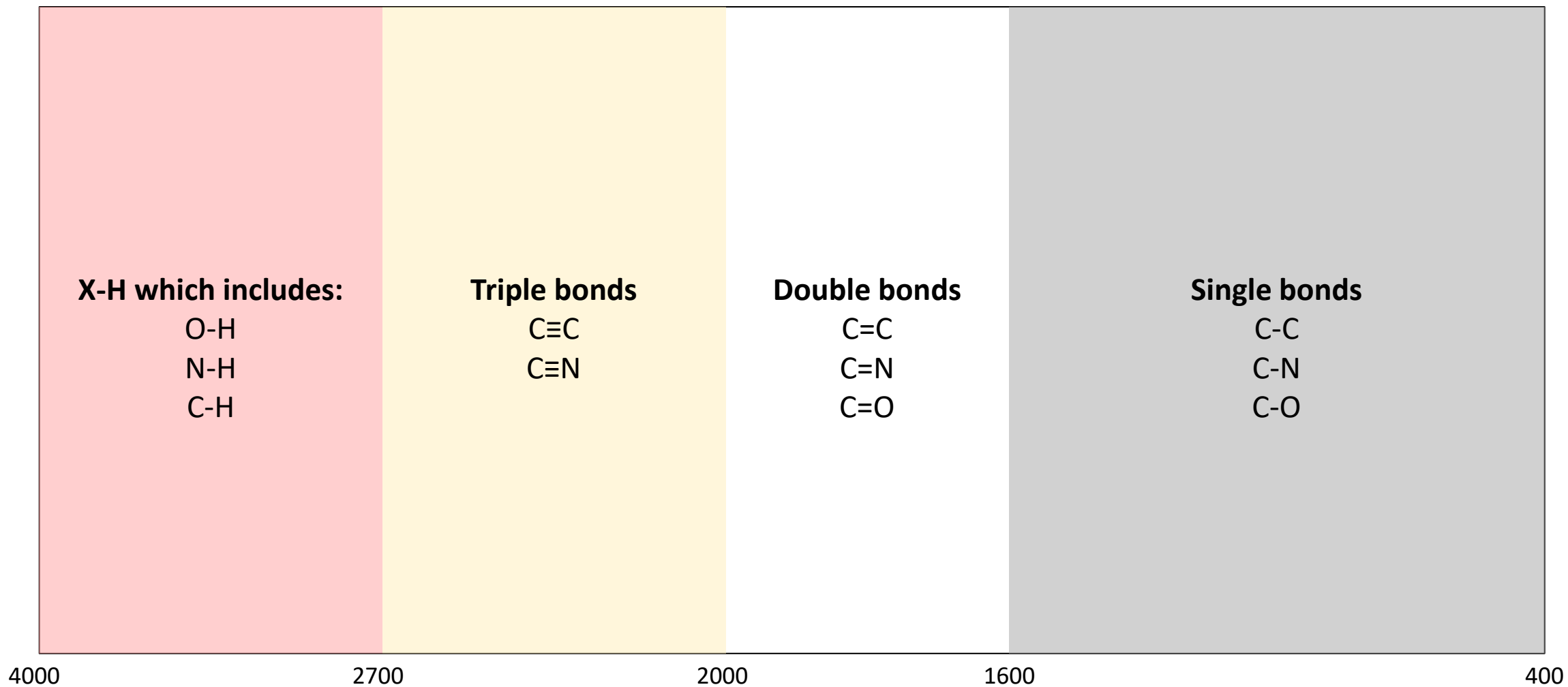
# Interpretation of IR spectra

- IR spectrum can be divided into two regions:
  1. Functional group region ( $4000\text{-}1500\text{ cm}^{-1}$ )
  2. Fingerprint region ( $1500\text{-}400\text{ cm}^{-1}$ )

# Interpretation of IR spectra



# Interpretation of IR spectra

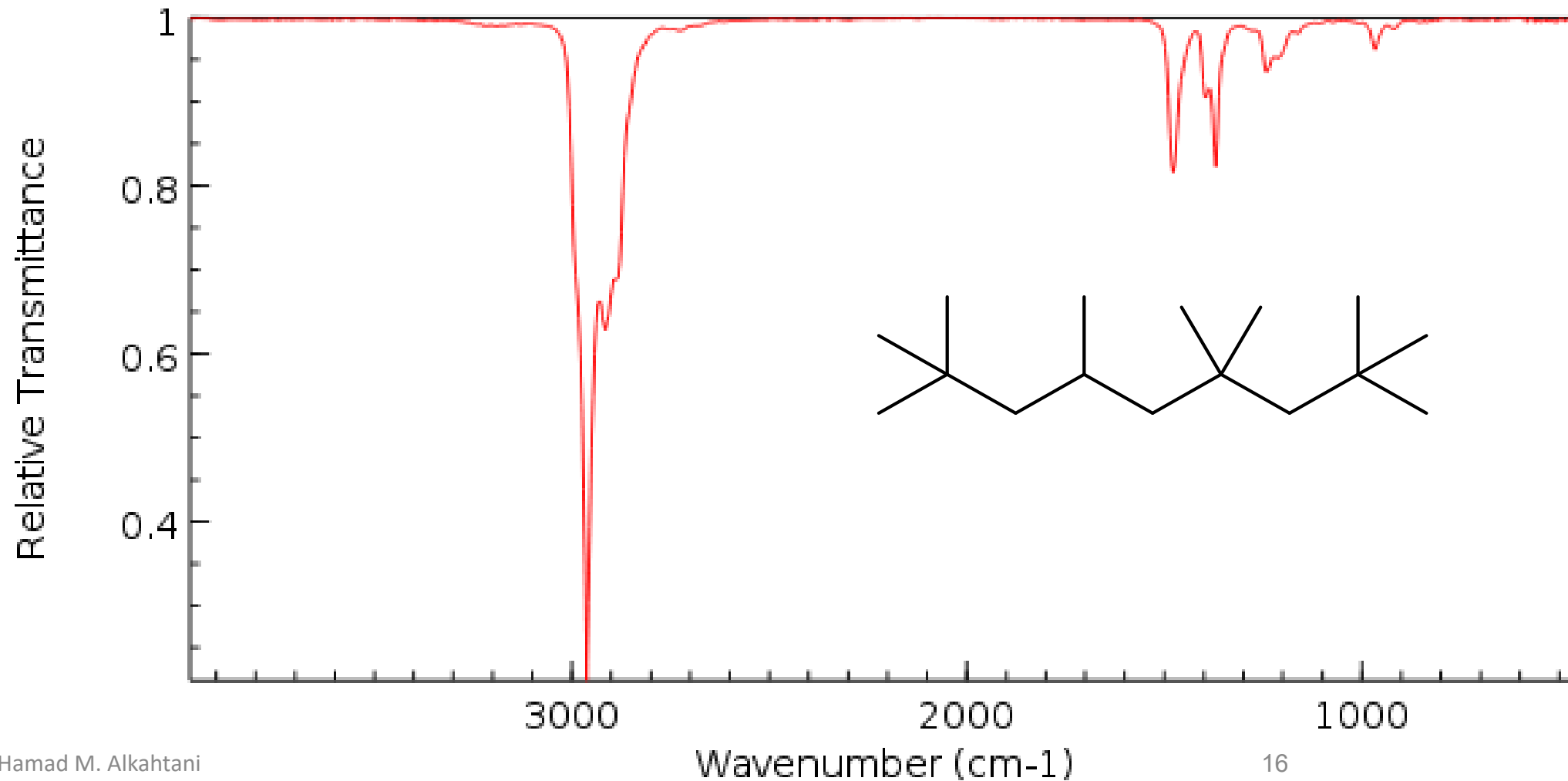


# Interpretation of IR spectra: 1. Alkanes

- C-H stretching in the alkanes occurs in the general region of 3000-2800  $\text{cm}^{-1}$ .
- C-C stretching vibrations are weak and appear in the broad region of 1200-800  $\text{cm}^{-1}$  (fingerprint region).

# Interpretation of IR spectra: 1. Alkanes

Nonane, 2,2,4,4,6,8,8-heptamethyl-  
INFRARED SPECTRUM

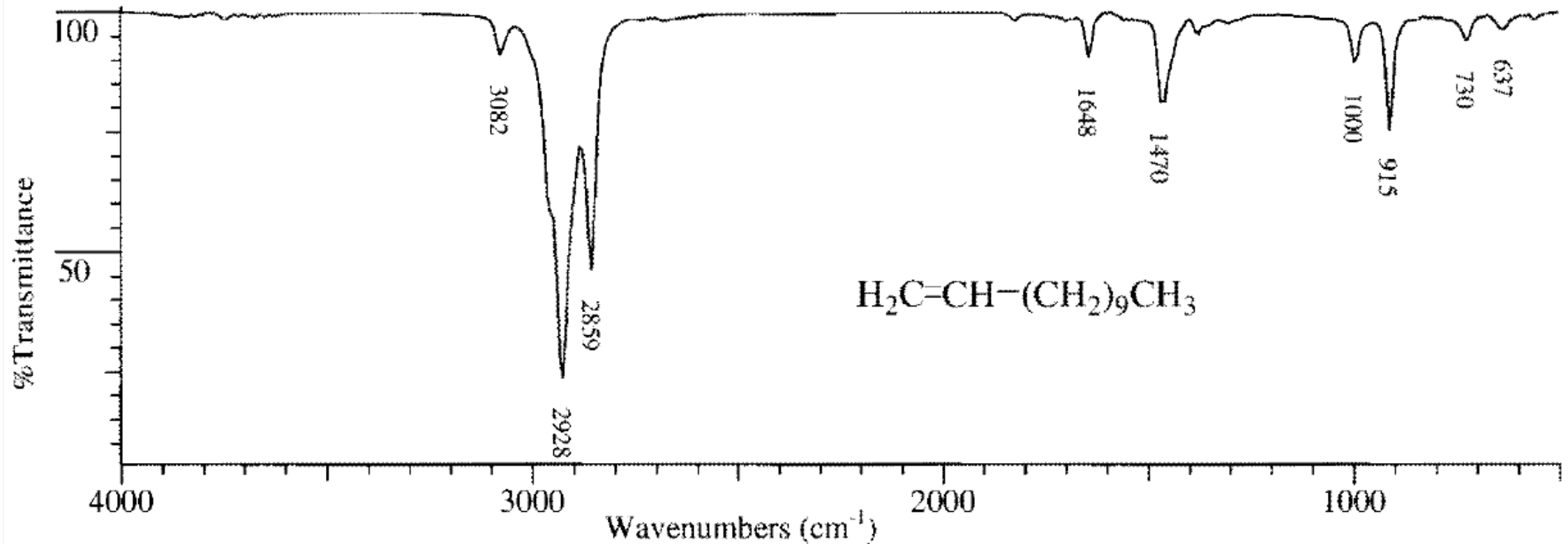




# Interpretation of IR spectra: 2. Alkenes

- Any C-H stretching bands above  $3000\text{ cm}^{-1}$  result from aromatic, heteroaromatic, alkyne, or alkene C-H stretching.
- C=C absorb in the range  $1680\text{-}1620\text{ cm}^{-1}$ .

# Interpretation of IR spectra: 2. Alkenes

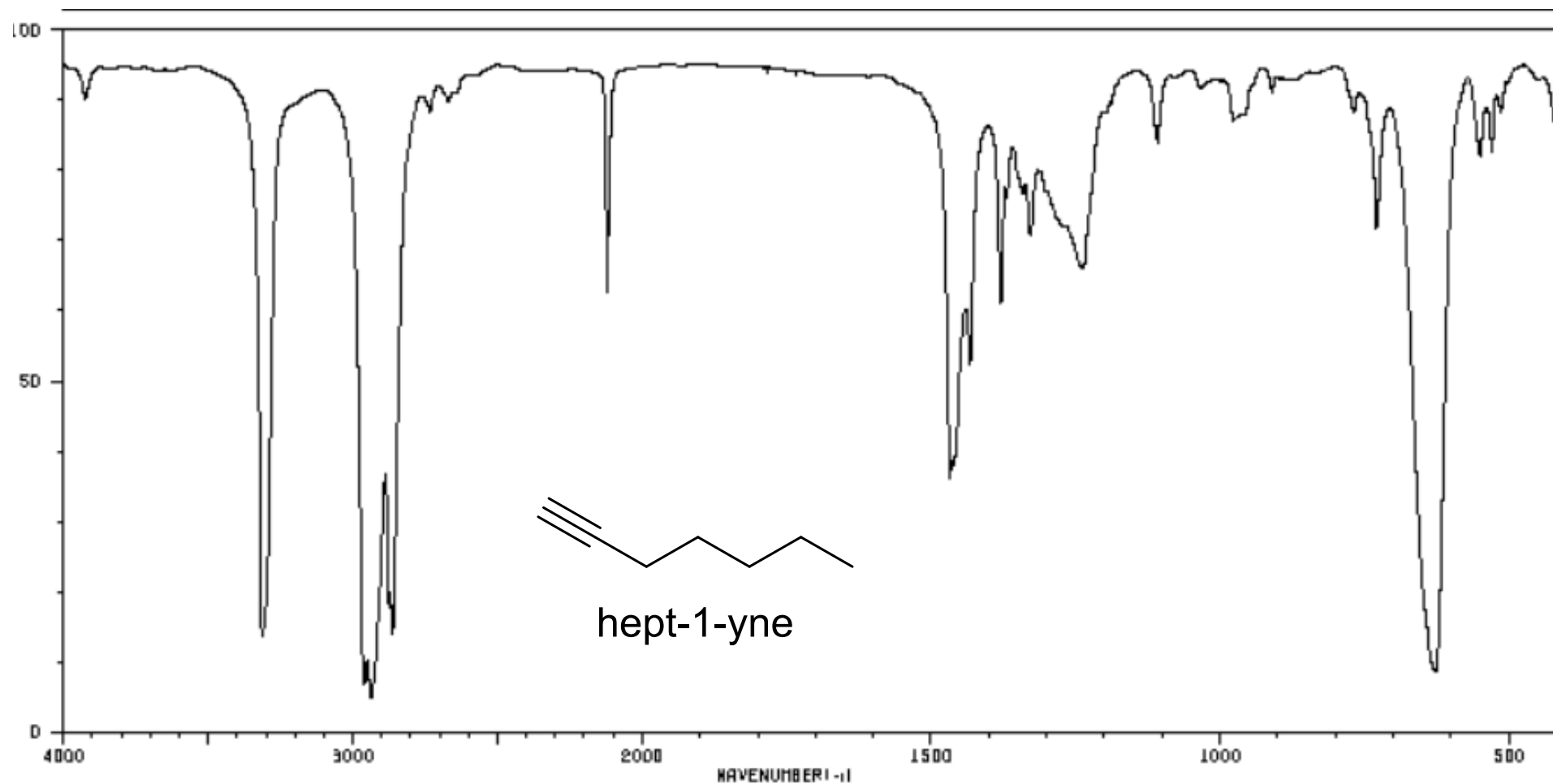


- C=C-H stretch: 3082  $\text{cm}^{-1}$
- C=C stretch: 1648  $\text{cm}^{-1}$

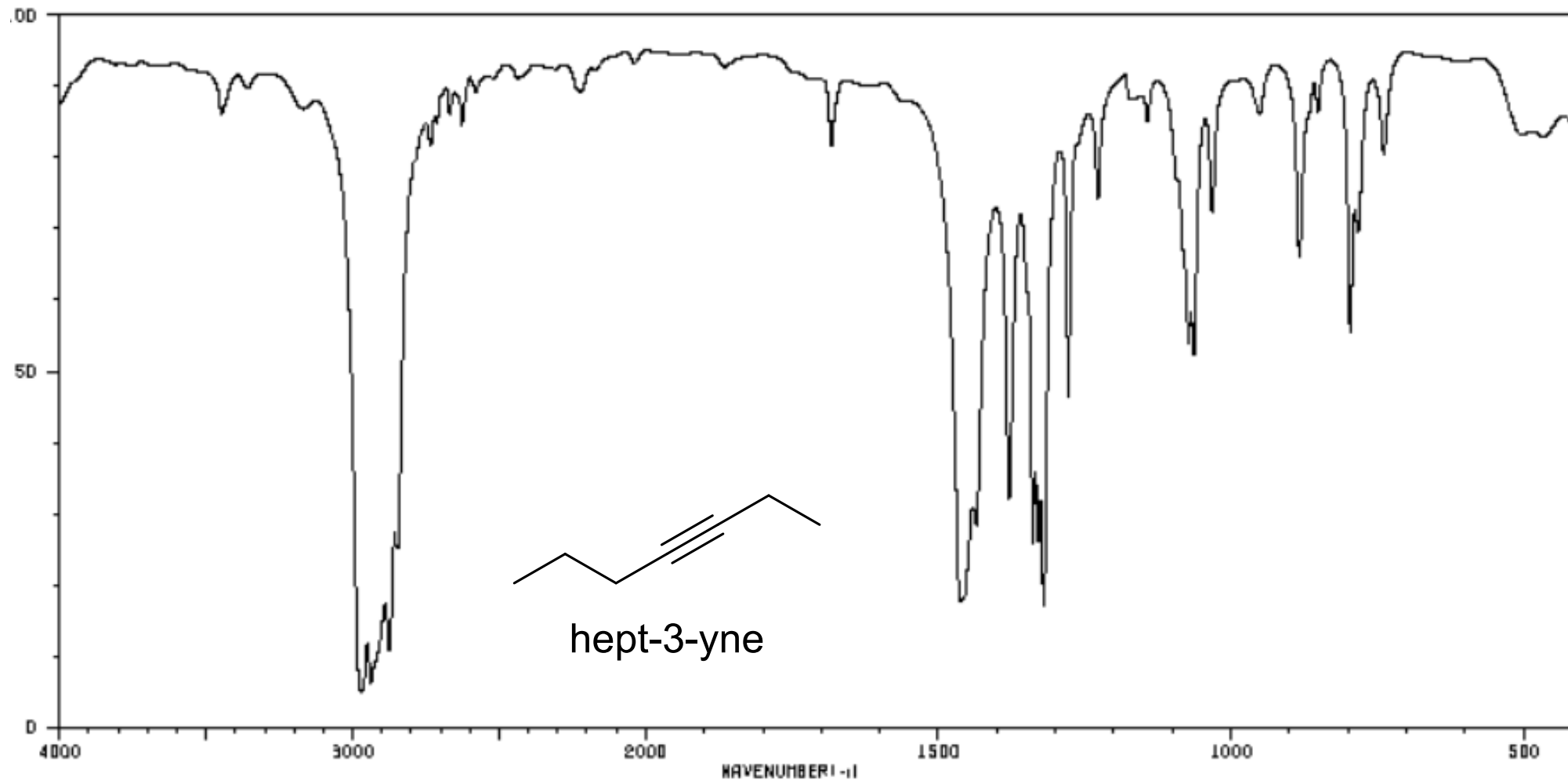
# Interpretation of IR spectra: 3. Alkynes

- $\text{C}\equiv\text{C}$  stretching vibrations occur in the region of  $2260\text{-}2100\text{ cm}^{-1}$ .
- Terminal  $\text{C}\equiv\text{C}$  shows stronger band than internal one.
- $\text{C}\equiv\text{C-H}$  stretching vibrations occur in the general region of  $3333\text{-}3267\text{ cm}^{-1}$  (This is a strong band and is narrower than the hydrogen bonded OH and NH bands occurring in the same region).

# Interpretation of IR spectra: 3. Alkynes



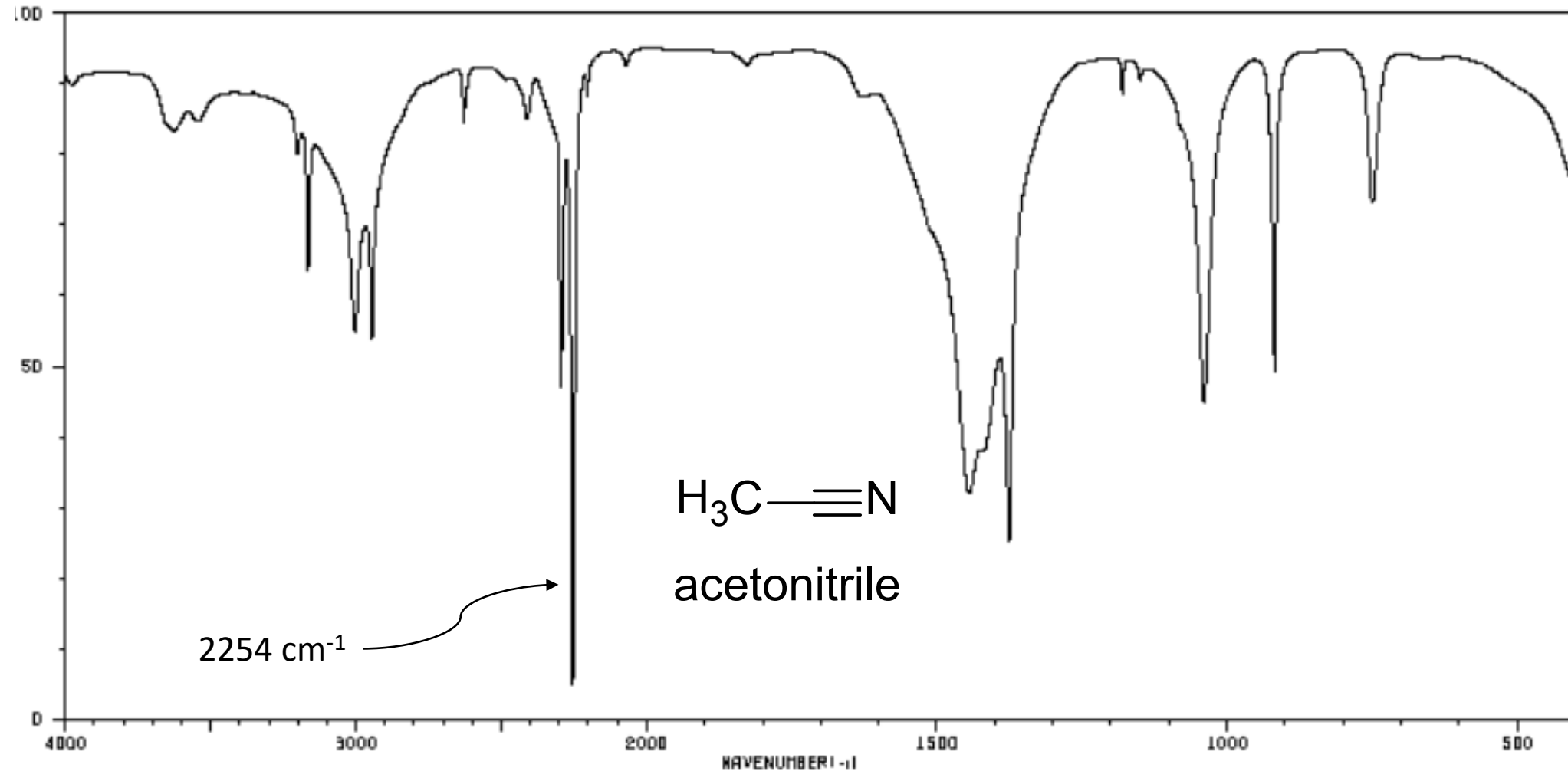
# Interpretation of IR spectra: 3. Alkynes



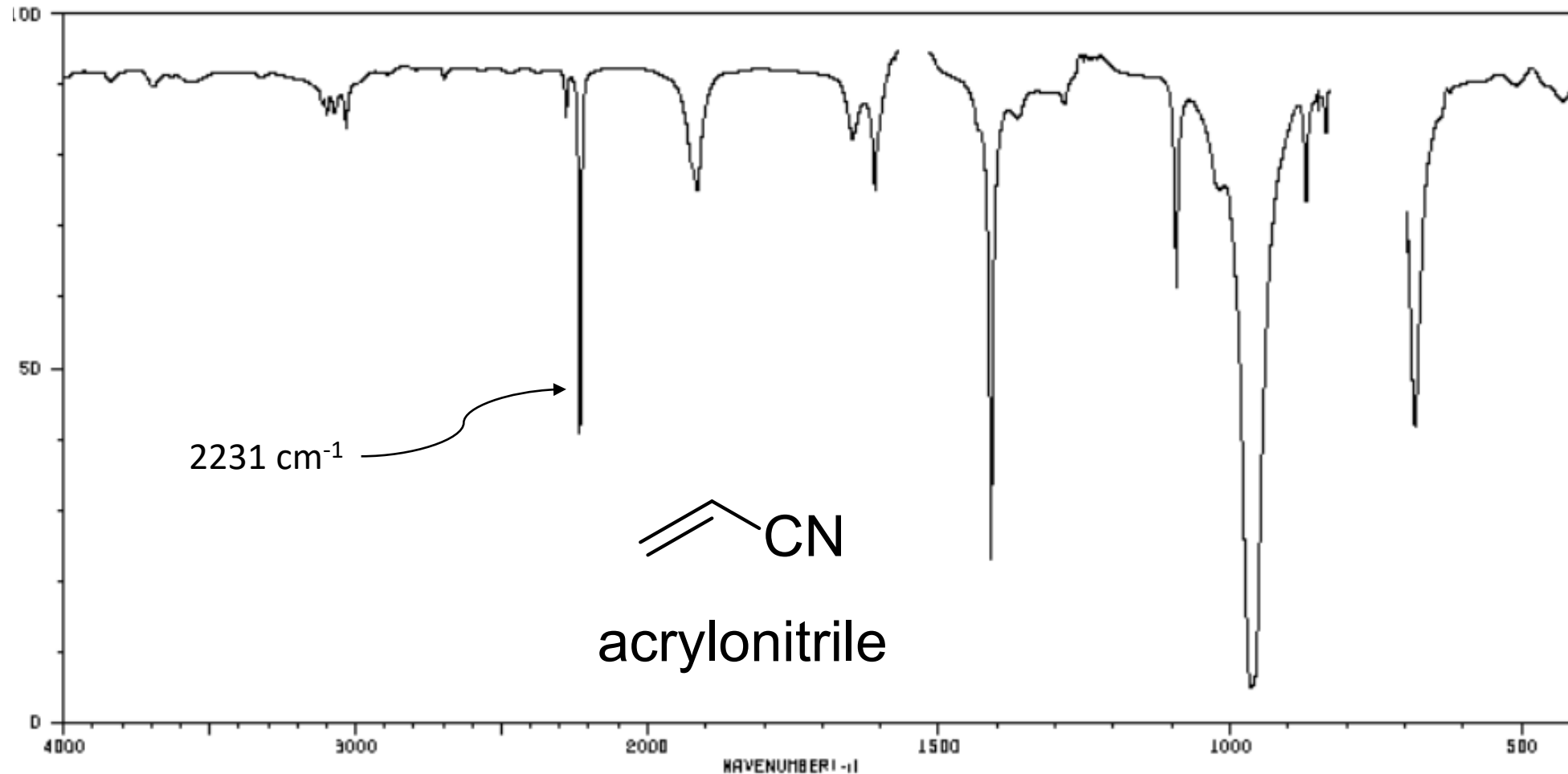
# Interpretation of IR spectra: 4. Nitriles

- Nitriles absorb in the range 2260–2200  $\text{cm}^{-1}$  (weak to medium).
- Conjugation usually reduces frequency and increases intensity.
- EWG groups attached to the  $\alpha$  carbon to the  $\text{C}\equiv\text{N}$  reduce band intensity.

# Interpretation of IR spectra: 4. Nitriles

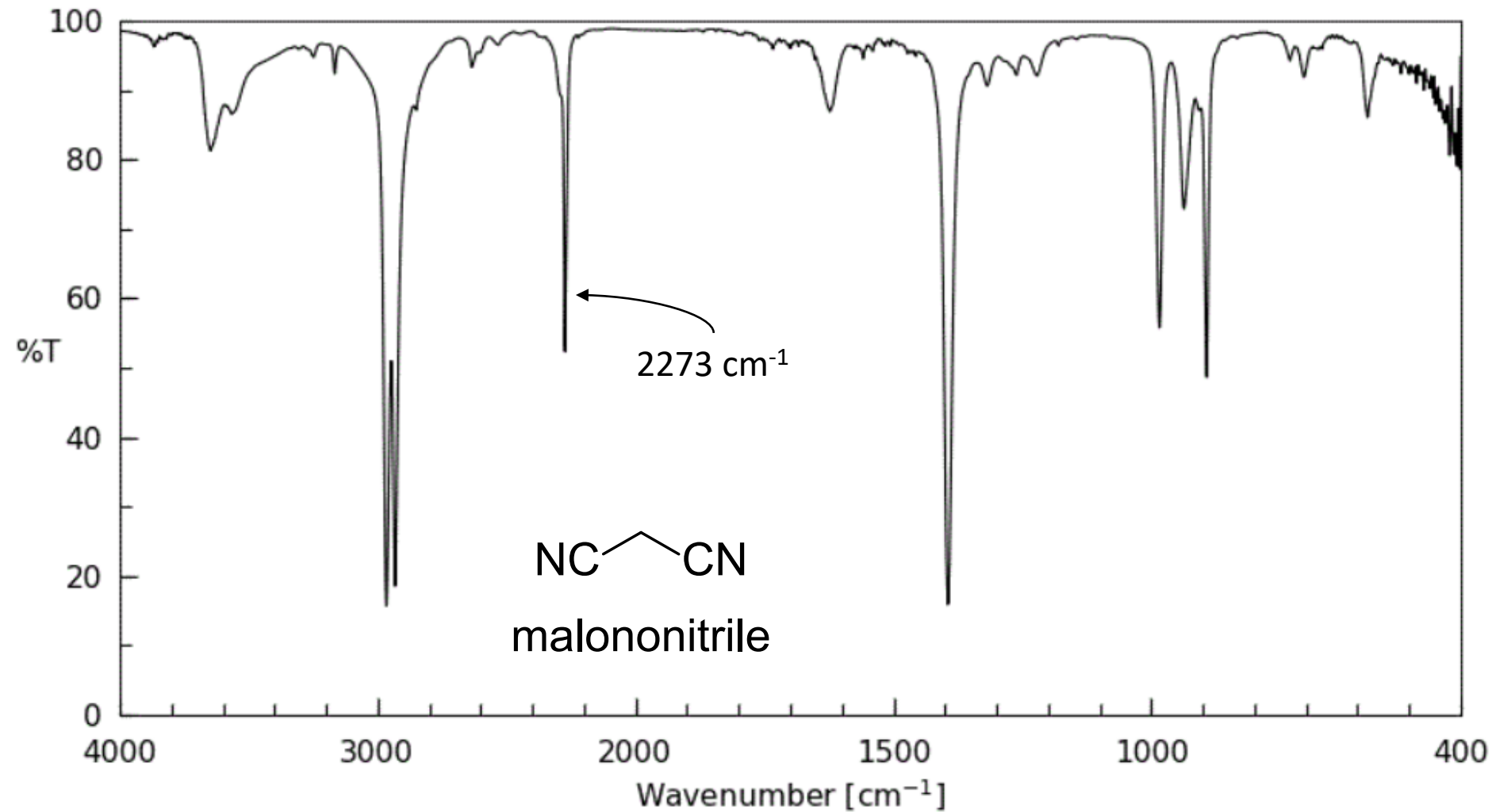


# Interpretation of IR spectra: 4. Nitriles





# Interpretation of IR spectra: 4. Nitriles



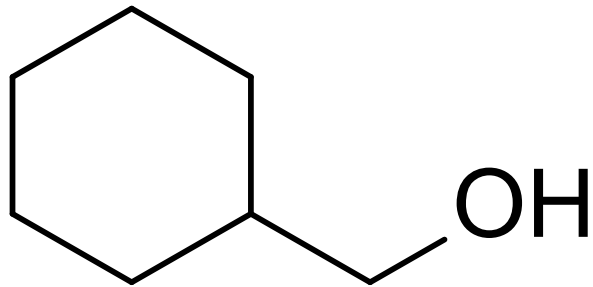
# Interpretation of IR spectra: 5. O-H

- These vibrations are sensitive to H-bonding.
- The stronger the H-bond the longer O-H bond, the lower the vibration frequency and the broader and the more intense the absorption band.
- The non-H-bonded hydroxyl group of alcohols and phenols absorbs strongly in the 3700-3584  $\text{cm}^{-1}$  region.

# Interpretation of IR spectra: 5. O-H

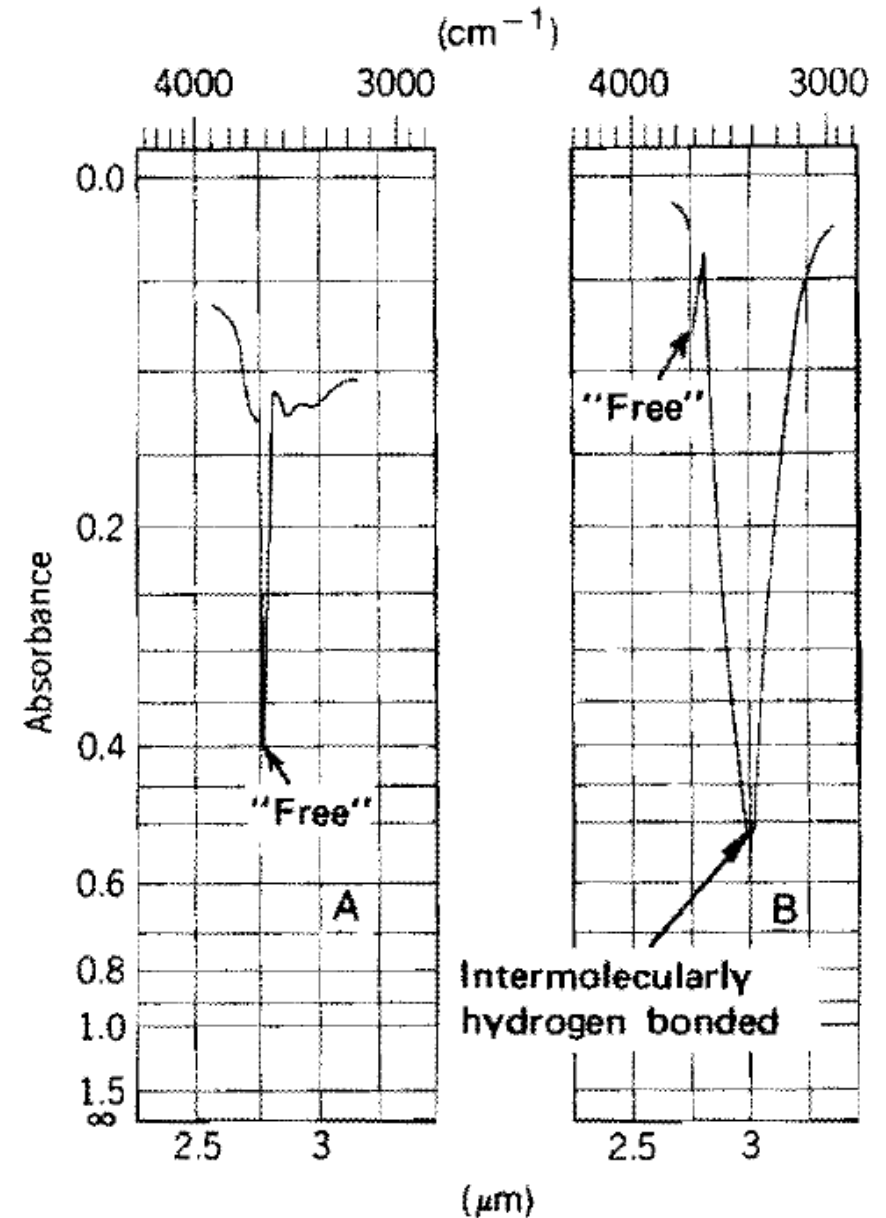
- Intermolecular H-bonding increases as the concentration of the solution increases, and additional bands start to appear at lower frequencies, 3550-3200  $\text{cm}^{-1}$ .

# Interpretation of IR spectra: 5. O-H



Cyclohexylcarbinol

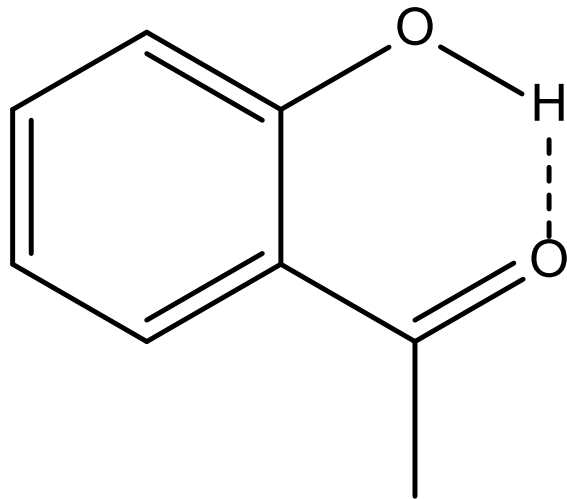
IR spectrum of the O-H stretching region of cyclohexylcarbinol in  $\text{CCl}_4$ : **A** at 0.03 M and **B** at 1.00 M



# Interpretation of IR spectra: 5. O-H

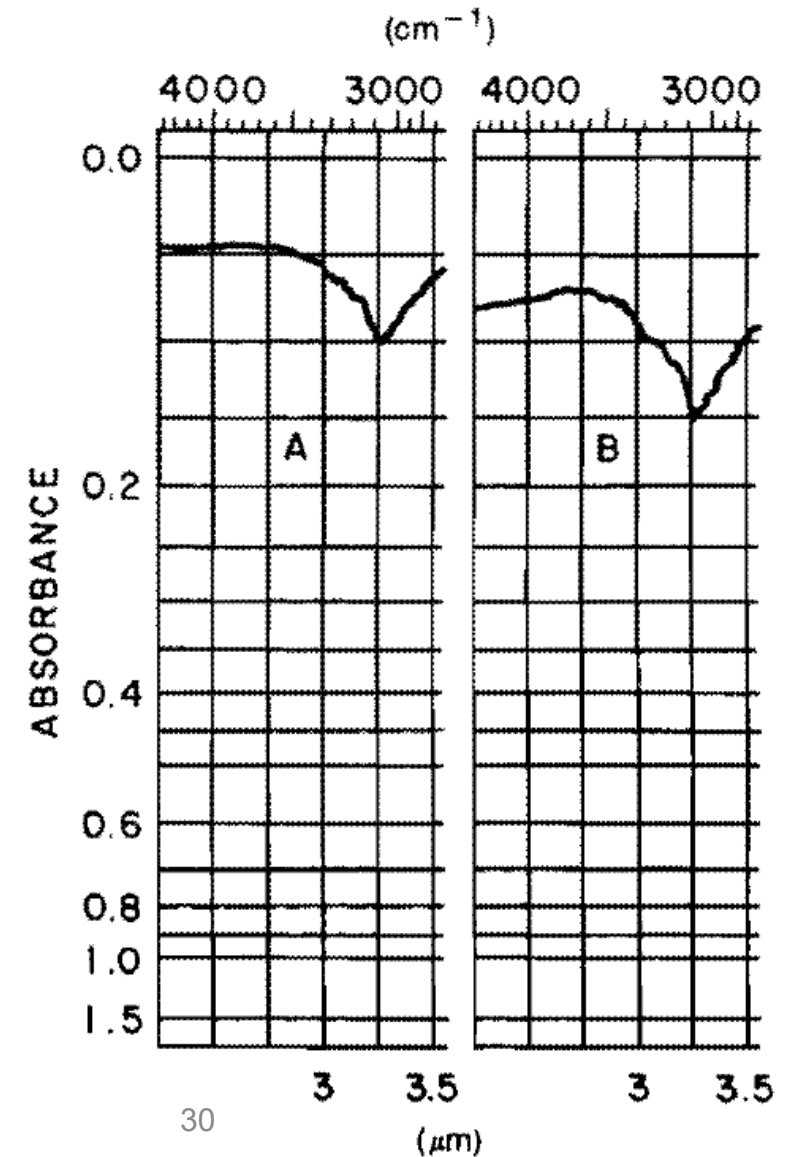
- Strong intramolecular H-bonding occurs in *o*-hydroxyacetophenone.  
The resulting absorption at  $3077\text{ cm}^{-1}$  is broad, shallow, and independent of concentration.

# Interpretation of IR spectra: 5. O-H

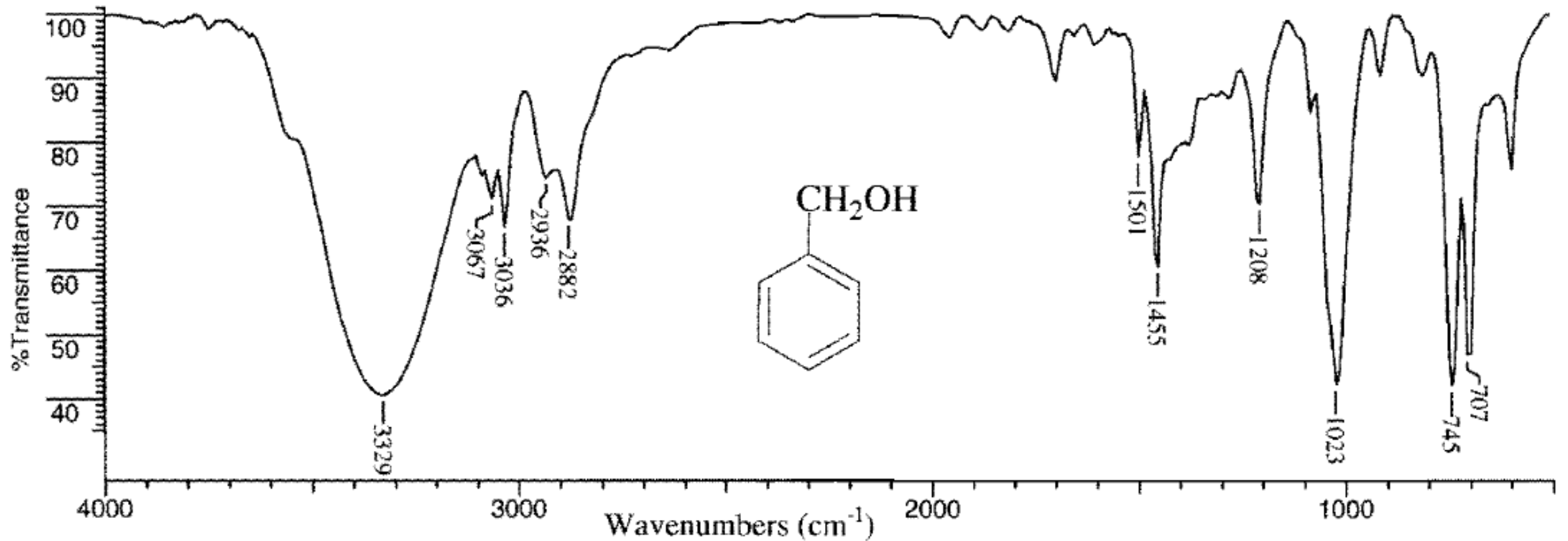


*o*-Hydroxyacetophenone

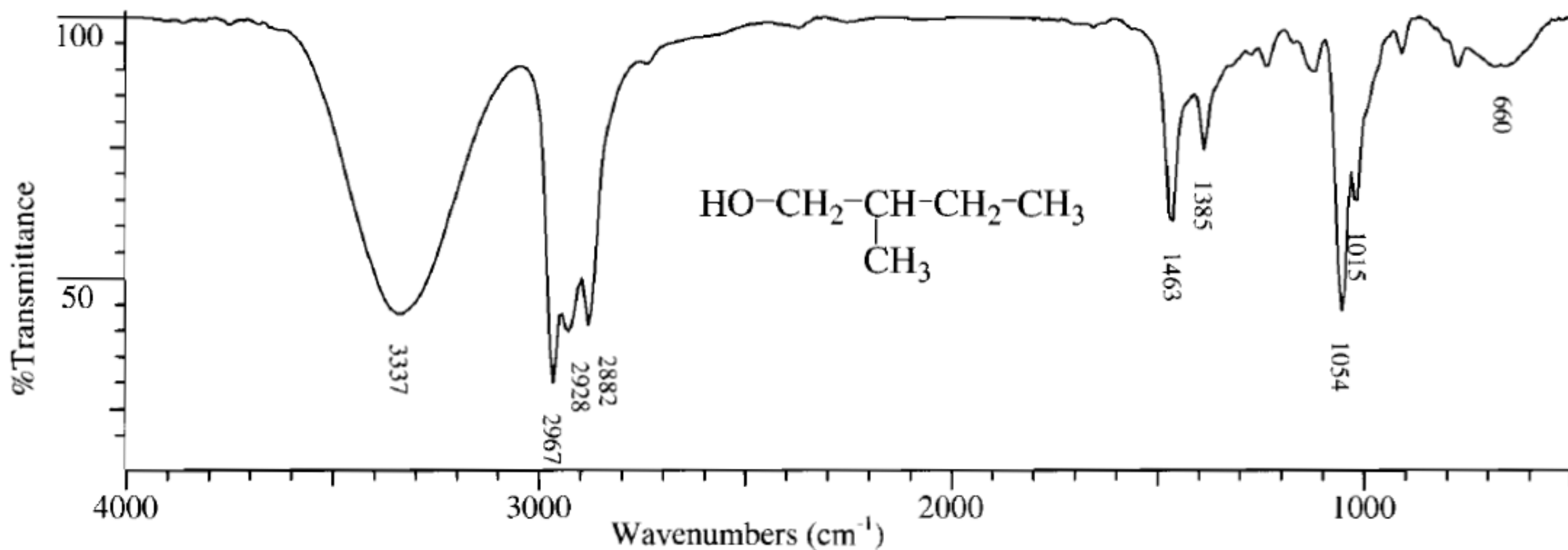
A portion of the IR spectra of *o*-hydroxyacetophenone: **A** at 0.03 M and **B** at 1.0 M



# Interpretation of IR spectra: 5. O-H

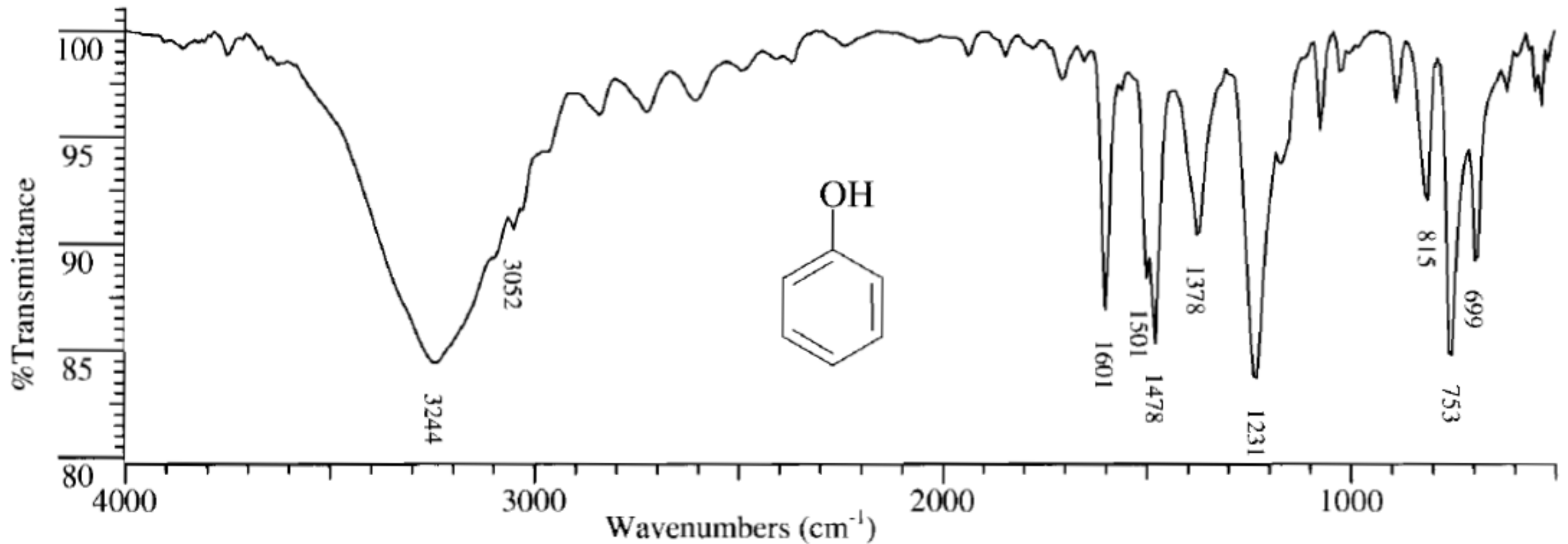


# Interpretation of IR spectra: 5. O-H



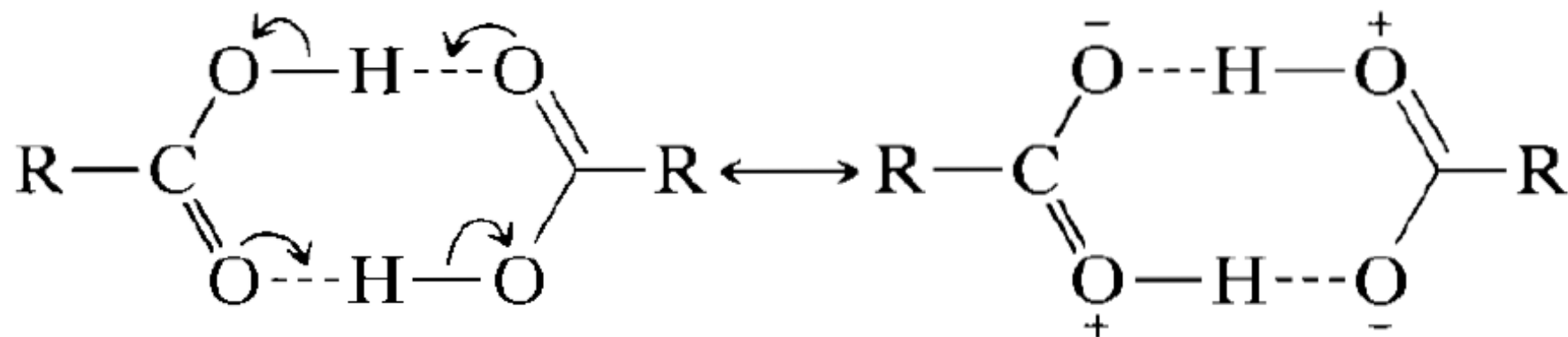


# Interpretation of IR spectra: 5. O-H



# Interpretation of IR spectra: 5. O-H

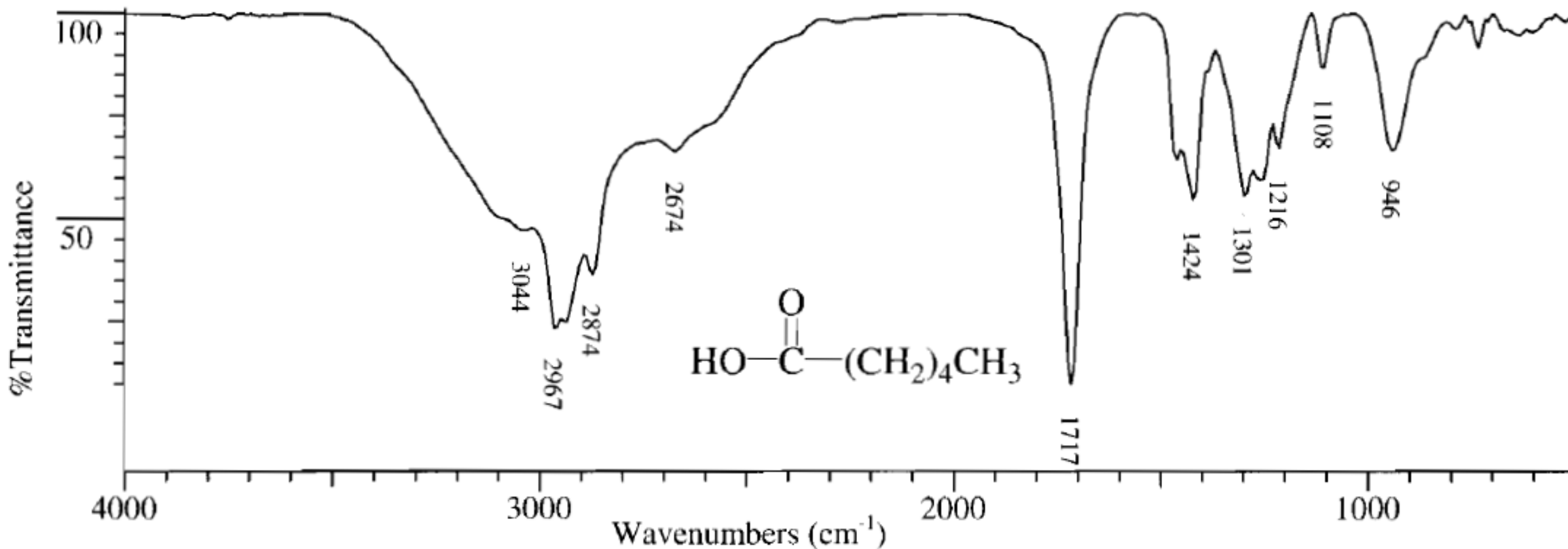
- In the liquid or solid state, and in  $\text{CCl}_4$  solution at conc.  $> 0.01 \text{ M}$ , carboxylic acids exist as dimers due to strong H-bonding.



# Interpretation of IR spectra: 5. O-H

- Carboxylic acids dimers display broad and intense O-H stretching absorption in the region of 3200-2500  $\text{cm}^{-1}$ .
- Free O-H stretching vibration (near 3520  $\text{cm}^{-1}$ ) is observed only in very dilute solution in nonpolar solvent or in the vapour phase.

# Interpretation of IR spectra: 5. O-H



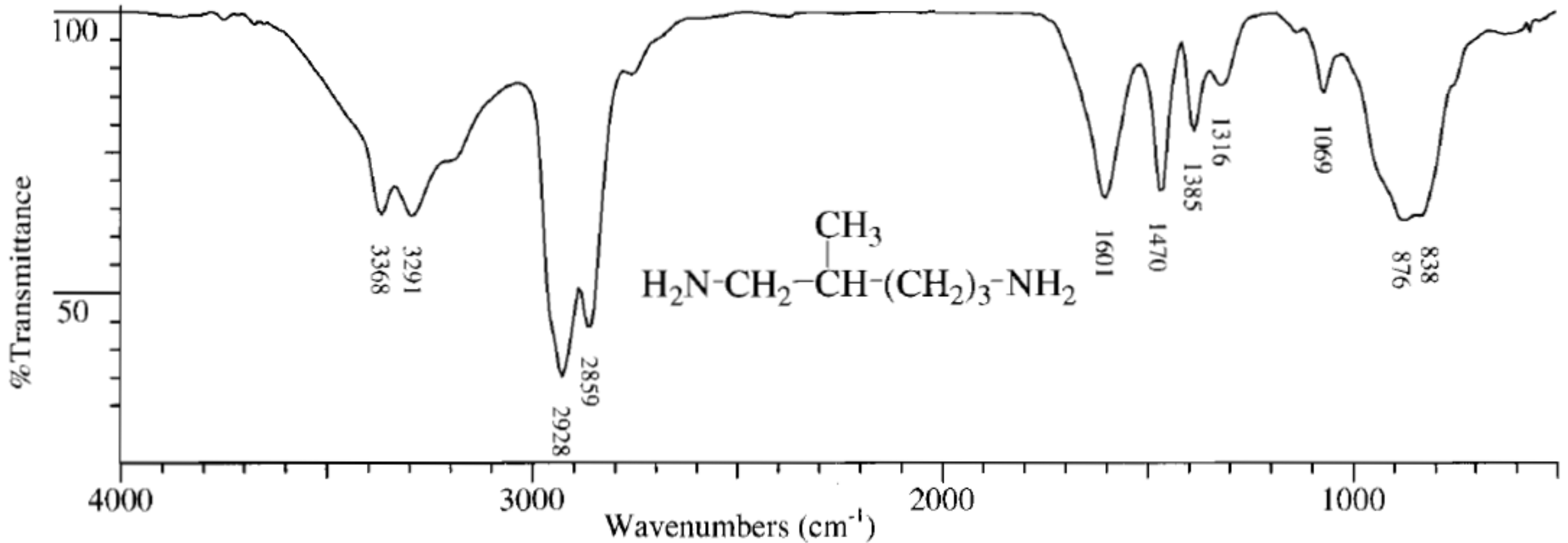
# Interpretation of IR spectra: 6. N-H

- The stretching frequencies of the N-H bonds of amines are typically in the range 3500-3300  $\text{cm}^{-1}$ .
- They are less intense than O-H stretching.
- Because an N-H has a weaker tendency to form a H-bond, its absorption is often sharper.

# Interpretation of IR spectra: 6. N-H

- Primary amines display two peaks: one near  $3500\text{ cm}^{-1}$  and the other near  $3400\text{ cm}^{-1}$ .
- This is because asymmetric and symmetric stretching modes, respectively.
- Secondary amines show a single weak band in  $3350\text{-}3310\text{ cm}^{-1}$  region.

# Interpretation of IR spectra: 6. N-H

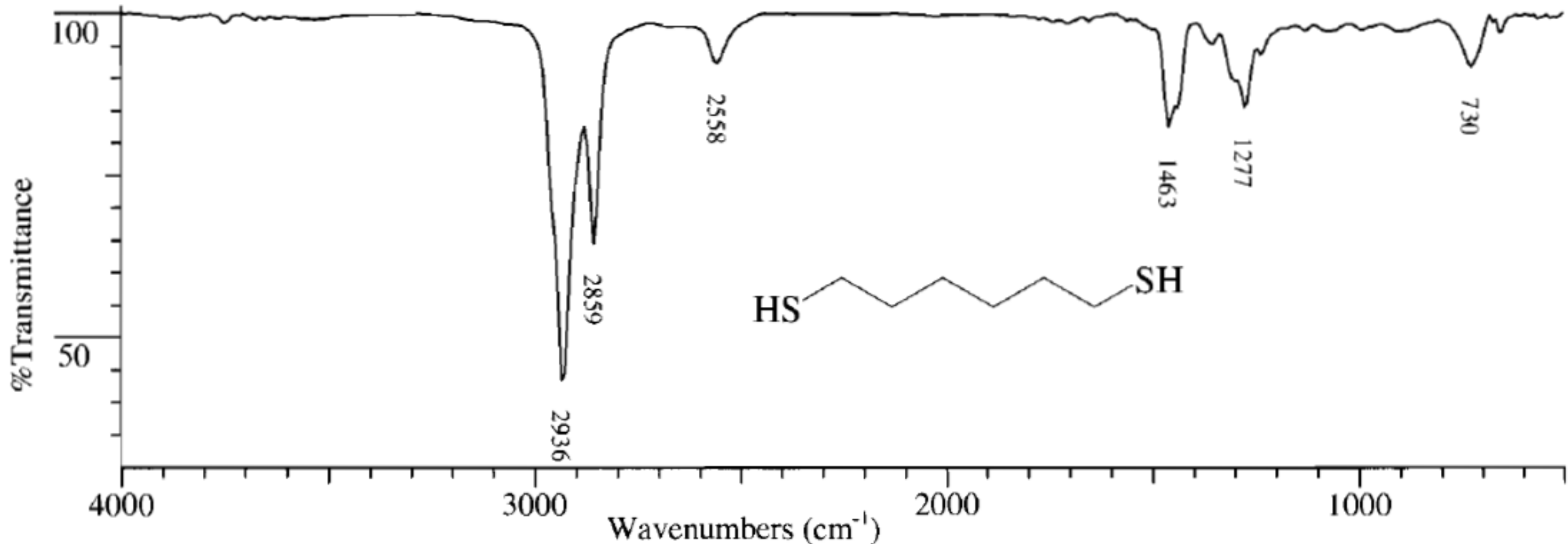


# Interpretation of IR spectra: 7. S-H

- Thiols and thiophenols show S-H stretching absorption in the range 2600-2550  $\text{cm}^{-1}$ .
- S-H stretching is weak and may go undetected (especially in dilute solutions).



# Interpretation of IR spectra: 7. S-H



# Interpretation of IR spectra: 8. C=O

- Carbonyl bands are always strong with the following order of strength:

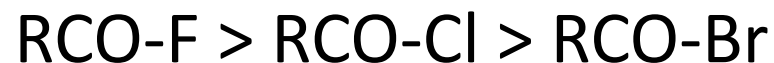


- The precise position of C=O absorption is governed by the following factors:
  - a. Electronegativity
  - b. H-bonding
  - c. Conjugation
  - d. Ring strain

# Interpretation of IR spectra: 8. C=O

## a. Electronegativity

- The more electronegative the group X in the system R-CO-X, the higher is the frequency.
- Therefore:



# Interpretation of IR spectra: 8. C=O

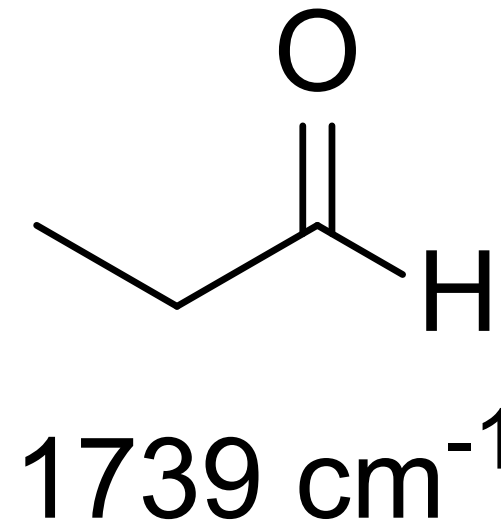
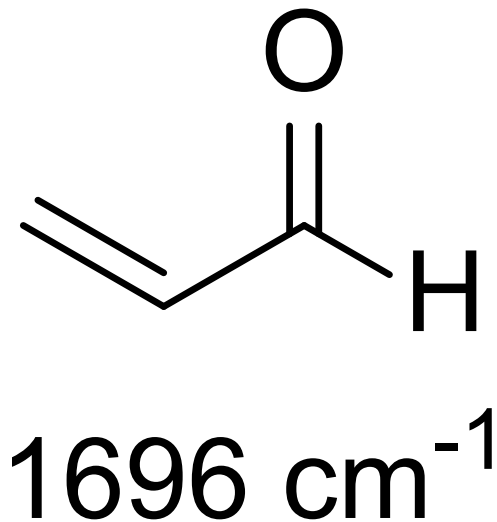
## b. H-bonding

- H-bonding to C=O results in absorption at lower frequencies.
- H-bonding reduces absorption by  $\sim 40\text{-}60\text{ cm}^{-1}$ .
- C=O of acids and amides show this effect clearly.

# Interpretation of IR spectra: 8. C=O

## c. Conjugation

- $\alpha,\beta$ -unsaturation causes a lowering frequency of 15-40  $\text{cm}^{-1}$ .
- This effect is similar to that of amides.



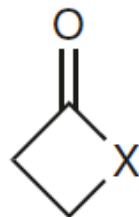
# Interpretation of IR spectra: 8. C=O

## d. Ring strain

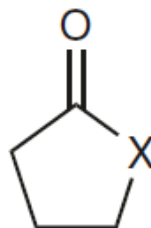
- Ring strain in cyclic compounds causes a relatively large shift to higher frequency.
- Therefore, this provides a reliable test of ring size.



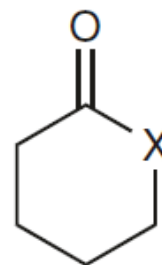
1813



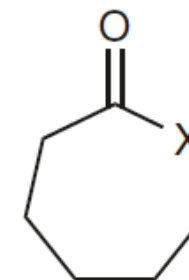
X=CH<sub>2</sub> 1775  
X=O 1841  
X=NH 1750



X=CH<sub>2</sub> 1750  
X=O 1774  
X=NH 1717



X=CH<sub>2</sub> 1715  
X=O 1750  
X=NH 1673



X=CH<sub>2</sub> 1710  
X=O 1727  
X=NH 1669