Infrared Spectroscopy

More detailed information about functional groups

Infrared Spectroscopy

An infrared spectrum is obtained by passing infrared radiation through the sample

$$E = h\upsilon = \frac{hc}{\lambda}$$

Wavenumber (υ) is another way to describe the frequency of electromagnetic radiation absorbed.

High frequencies, large wavenumbers, and short wavelengths are associated with high energy.

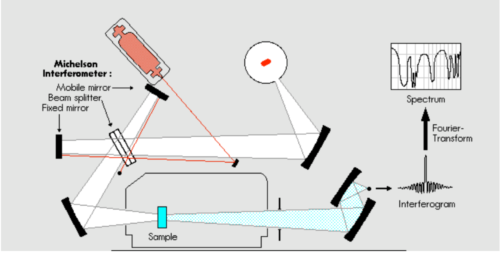
Infrared Spectroscopy Review

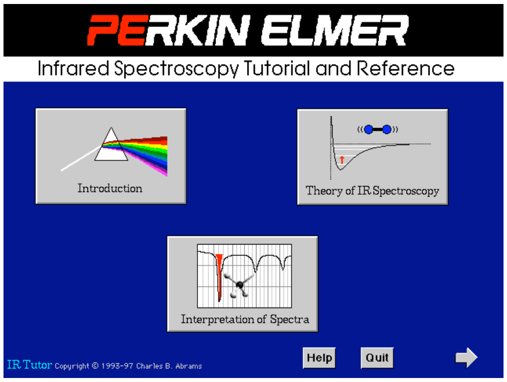
- Region of infrared that is most useful lies between 2.5-16 μm (4000-625 cm^{-1})
- Depends on transitions between vibrational energy states

  Stretching

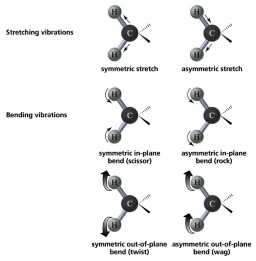
  Bending

Infrared Absorbance





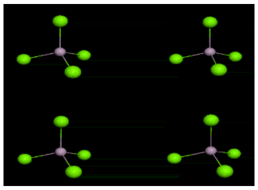
Atoms/covalent bonds are in constant motion. (*Vibrate*)



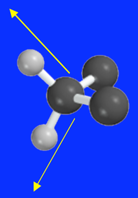
Each stretching and bending vibration occurs with a distinct quantized energy

Infrared Absorbance & Molecular Vibrations for CCl_4

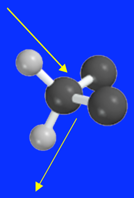
Stretching & Bending



Stretching Vibrations



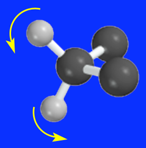
Symmetric



Antisymmetric

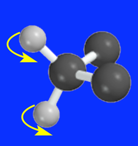
Bending Vibrations

In plane

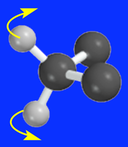


In plane

Bending Vibrations

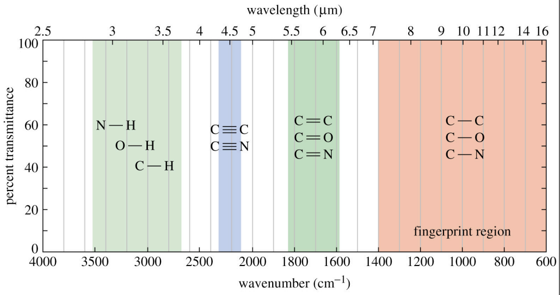


Out of plane



Out of plane

Stretching takes more energy than bending.



Bond order affects the position of absorption bands

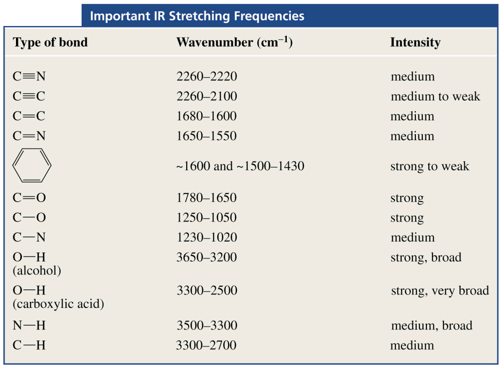
The approximate wavenumber of an IR absorption peakcan be calculated from Hooke's law

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

$\tilde{\nu}$ = the wavenumber of the stretching vibration

f = force constant

m_1 and m_2 = masses of the respective atoms



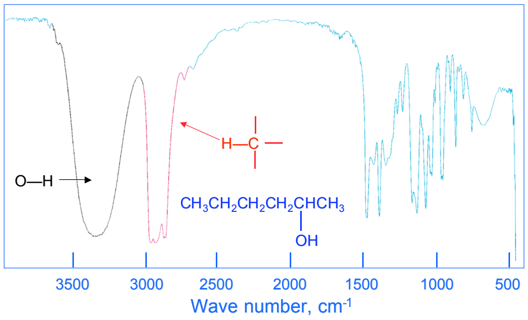
Important IR Stretching Frequencies

Type of bond	Wavenumber (cm^{-1})	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
⌬	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

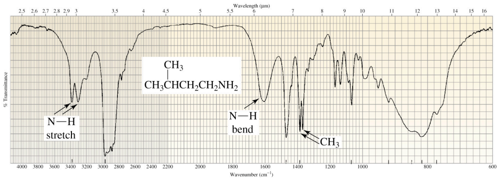
Empirical Table
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
O—H (alcohols)	3200-3600
O—H (carboxylic acids)	3000-3100
N—H	3350-3500

IR Spectrum of 2-Hexanol



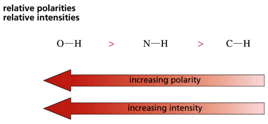
IR Spectrum of a Primary Amine (1º)



- A bond must have a dipole or an induced dipole in order to have a visible absorbance in the IR spectrum.

- When a bond stretches, the increased distance between the atoms increases the dipole moment

- Therefore, the greater the dipole, the more intense the absorption. (i.e., The greater the molar extinction coefficient (ε) in Beer's law, A= εbc)



relative polarities
relative intensities

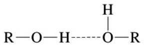
O—H > N—H > C—H

increasing polarity

increasing intensity

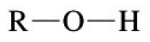
- The energy (IR frequency) and intensity of the absorption band also depends on the concentration of the solution from Beer's law, A= εbc.

- Therefore, it takes less energy to stretch an O–H or N-H bond if it is hydrogen bonded.



$$R—O—H\cdots\overset{\displaystyle H}{\overset{|}{O}}—R$$

concentrated solution
a hydrogen-bonded O—H bond
3550–3200 cm^{-1}



R—O—H

dilute solution
a non-hydrogen-bonded O—H bond
3650–3590 cm^{-1}

Question

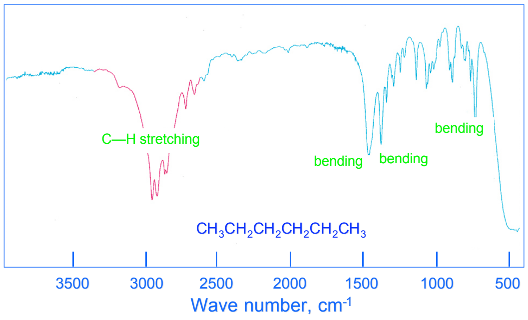
What is the difference in the O-H stretching peak between a 1° alcohol's liquid phase spectrum and its spectrum in the gas phase?

A) none
B) The gas phase peak is more intense.
C) The gas phase peak is >4000 cm^{-1}.
D) The gas phase peak is much less intense.

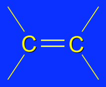
Empirical Table
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp C—H	3310-3320
sp^2 C—H	3000-3100
sp^3 C—H	2850-2950
sp^2 C—O	1200
sp^3 C—O	1025-1200

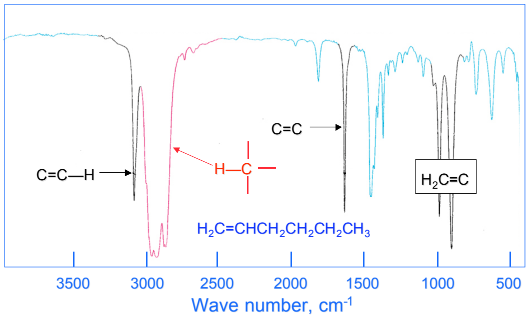
IR Spectrum of Hexane



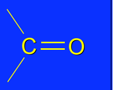
Empirical Table
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (multiple bonds)	
	1620-1680
—C≡C—	2100-2200
—C≡N	2240-2280

IRSpectrum of 1-Hexene

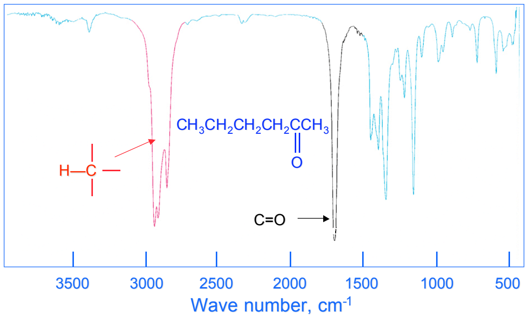


Empirical Table
Infrared Absorption Frequencies

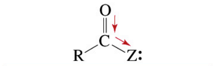


Structural unit	Frequency, cm^{-1}
Stretching vibrations (carbonyl groups)	
Aldehydes and ketones	1710-1750
Esters	1730-1750
Amides	1680-1700
Carboxylic acids	1700-1725
Acid anhydrides	1800-1850 and 1740-1790

IR Spectrum of 2-Hexanone



- An atom other than carbon next to the carbonyl group causes the position of the carbonyl absorption band to shift



inductive electron withdrawal

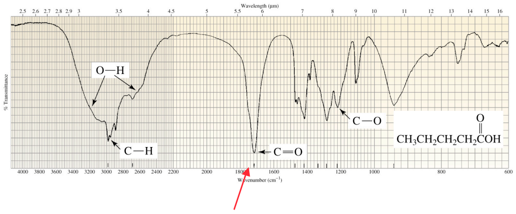
- The nitrogen of an amide is less electronegative.

1680-1700 cm^{-1} (longer C=O bond)

- The oxygen of an ester is more electronegative.

1730-1750 cm^{-1} (shorter C=O bond)

What would explain the difference in the C=O stretching absorbances between an anhydride 1800-1850 cm^{-1} and 1740-1790 cm^{-1} *and a carboxylic acid* 1700-1725 cm^{-1}*?*

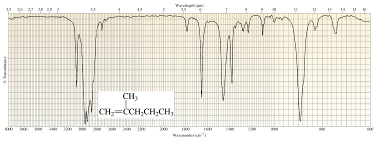


~ 1720 cm^{-1}

(1725-1700 cm^{-1})

Empirical Table
Infrared Absorption Frequencies

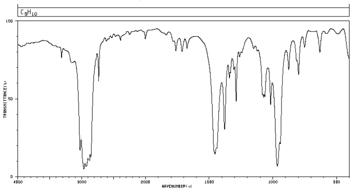
Structural unit	Frequency, cm^{-1}
Bending vibrations of alkenes	
$RCH{=}CH_2$	910-990
$R_2C{=}CH_2$	890
cis-$RCH{=}CHR'$	665-730
trans-$RCH{=}CHR'$	960-980
$R_2C{=}CHR'$	790-840



wavenumber (cm^{-1})	assignment
3075	*sp*^{2} CH
2950	*sp*^{3} CH
1650 and 890	a terminal alkene with two substituents

Question

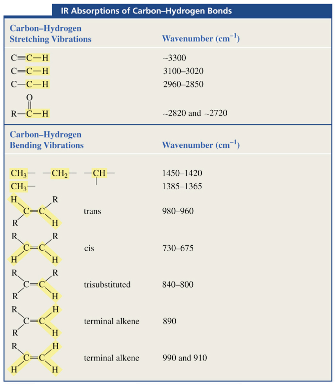
Is the following IR of cis or trans 2-pentene?



3317 72	2734 68	1674 79	1289 46	966 6	
3025 16	2616 84	1454 13	1261 74	876 66	
2965 4	2527 86	1441 17	1152 79	814 72	
2937 6	2390 84	1379 29	1082 60	799 62	
2922 6	2001 84	1342 60	1074 49	752 79	
2877 10	1761 77	1334 84	1063 49	631 77	
2867 12	1713 77	1306 66	1018 44		H

A) cis B) trans

SUMMARY:
C–H bond absorption and hybridization of the carbon atom

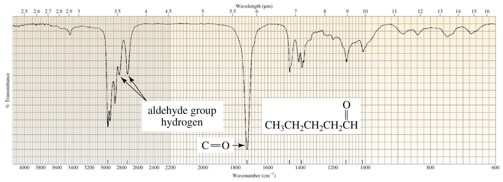


IR Absorptions of Carbon–Hydrogen Bonds

Carbon–Hydrogen Stretching Vibrations		Wavenumber (cm^{-1})
$C{\equiv}C{-}H$		~3300
$C{=}C{-}H$		3100–3020
$C{-}C{-}H$		2960–2850
$R{-}\overset{O}{\overset{\Vert}{C}}{-}H$		~2820 and ~2720

Carbon–Hydrogen Bending Vibrations		Wavenumber (cm^{-1})
$CH_3{-}$ $-CH_2-$ $-CH-$		1450–1420
$CH_3{-}$		1385–1365
	trans	980–960
	cis	730–675
	trisubstituted	840–800
	terminal alkene	890
	terminal alkene	990 and 910

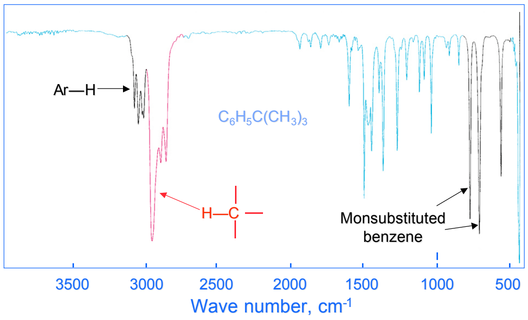
Distinctive Stretch of C–H Bond in an Aldehyde (the “waggle” vibration)



Empirical Table
AROMATIC IR Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Bending vibrations of derivatives of benzene	
Monosubstituted	730-770 and 690-710
Ortho-disubstituted	735-770
Meta-disubstituted	750-810 and 680-730
Para-disubstituted	790-840

IR Spectrum of tert-butylbenzene



Analyzing Structure: Functions & Infrared Spectra

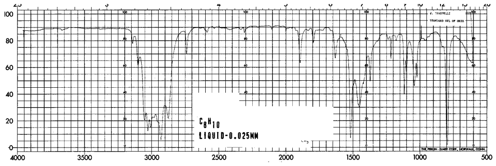
The molecular formula is a critical piece of information, which limits the functional possibilities.

The presence & absence of absorption bands are must be considered in identifying a possible structure in IR spectroscopy.

NOTE: Bonds, which lack dipole moments, are not detected.

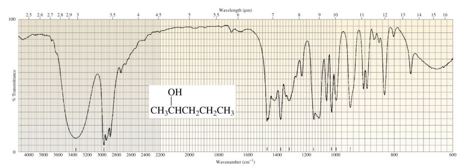
Question

The following IR is most likely?



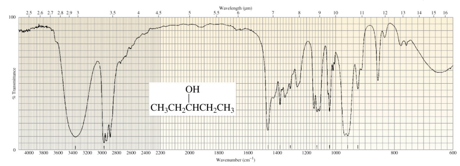
A) o-xylene
B) m-xylene
C) p-xylene
D) ethyl benzene

a.



Subtle differences can make some distinctions very difficult.

b.

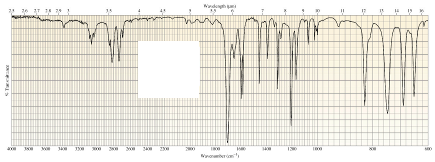


Therefore IR is used with other methods; NMR being most important.

Analyzing Infrared Spectra : Structure & Function Questions

Question

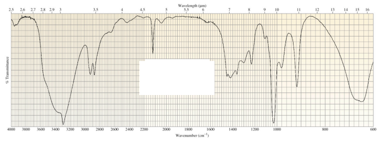
The following IR is most likely?



A) methylbenzamide
B) benzoic acid
C) methylphenylketone
D) ethyl benzene
E) benzaldehyde

Question

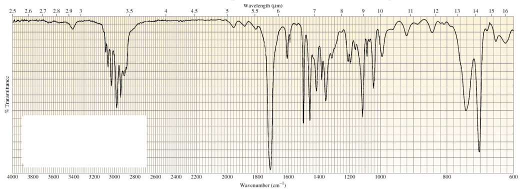
The following IR is most likely?



A) propylamine
B) propenoic acid
C) 2-propanol
D) 2-propenaldehyde
E) 2-propyne-1-ol

Question

The following IR is most likely?



A) methylbenzamide
B) benzoic acid
C) benzaldehyde
D) ethylbenzylketone
E) methylbenzoate