

IR and Mass Spectrometry

Reading: Wade chapter 12, sections 12-1- 12-15

Study Problems: 12-15, 12-16, 12-23, 12-25

Key Concepts and Skills:

- Given an IR spectrum, identify the reliable characteristic peaks
- Explain why some peaks are strong and some are weak or absent..
- Identify functional groups by IR spectra.
- determine molecular weights and molecular structures from mass spectra

Lecture Topics:

I. IR spectroscopy

Absorption spectroscopy involves the measurement of the amount of light absorbed by a compound as a function of its wavelength.

Infrared spectroscopy observes the vibrations of bonds and provides evidence for the presence of certain functional groups within a structure.

Specifically, the infrared region of the electromagnetic spectrum has radiation energetic enough to cause the **stretching** and **bending** of bonds in molecules. *Note: infrared light does not cause electronic transitions to take place. Excitation of electrons in pi bonds is observed in UV-visible spectroscopy; excitation of electrons in sigma bonds require far UV and X-ray photons, which are much more energetic than infrared photons*

Remember:

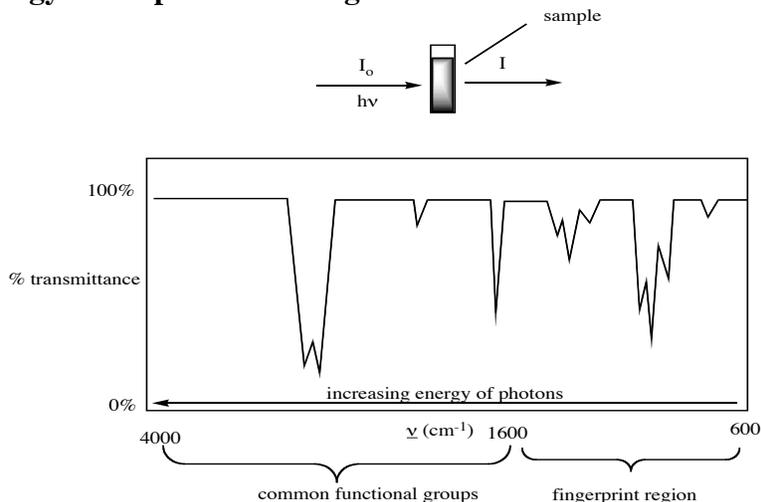
$$E=hf$$

Where frequency $\nu = c/\lambda$

In an IR spectrum, we are measuring % transmission of light versus wavenumbers, $\underline{\nu}$, which is the reciprocal of wavelength (note ~~wavenumbers~~ wavenumbers are proportional to frequency):

$$\underline{\nu} (\text{cm}^{-1}) = 1/\lambda$$

The wavenumber range of an IR spectrum is 4000 cm^{-1} to 600 cm^{-1} or $2,500 \text{ nm}$ to $16,000 \text{ nm}$. Note that **the higher the wavenumber, the shorter the wavelength and the greater the energy of the photon causing the bond vibration**



•The frequency of the stretching vibration depends on the masses of the atoms making up the bond and also the stiffness (strength) of the bond

•Heavier atoms vibrate more slowly than lighter ones, and thus the frequency of stretching vibration decreases with increasing atomic weight:

bond	stretching frequency
C-H	3000 cm^{-1}
C-D	2100 cm^{-1}
C-C	1200 cm^{-1}

Thus, less energetic photons are required to stretch a C-C bond than a C-H bond

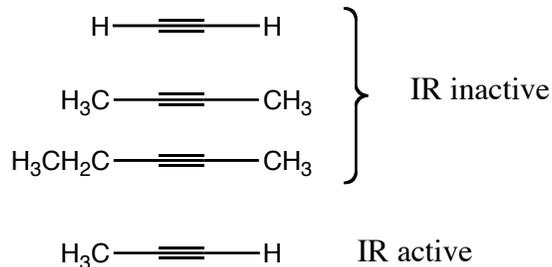
•Stronger bonds are stiffer and thus require more force (requiring more energetic photons) to stretch and compress those bonds; the frequency of light required to stretch a bond increases with bond energy:

bond	stretching frequency
C-C	1200 cm^{-1}
C=C	1660 cm^{-1}
C≡C	2200 cm^{-1}
C-N	1200 cm^{-1}
C=N	1650 cm^{-1}
C≡N	2200 cm^{-1}
C-O	1100 cm^{-1}
C=O	1700 cm^{-1}

The simple stretching vibrations (in the 1600 cm^{-1} to 3500 cm^{-1} region) are the most characteristic and predictable, and absorptions in this region are used to identify functional groups in molecules. The region of an IR spectrum below 1600 cm^{-1} is called the fingerprint region and contains a unique set of absorptions (yet less predictable) for a given molecule; this region can be used for identifying unknown substances by comparison with spectra of known compounds.

IR active bonds/functional groups

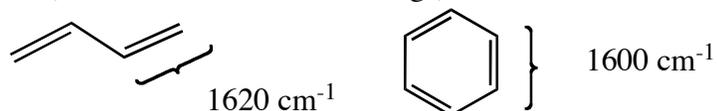
For bonds to be IR active (that is, to absorb a photon of infrared light), they **must** possess a dipole moment, and furthermore, bond vibrations must change the dipole moment of the molecule. The electromagnetic field of an IR photon must be able to interact with a bond in order for absorption of energy to occur. Because one of the components of an electromagnetic wave is a rapidly reversing electric field, there can only be an interaction with a bond when the bond has a dipole moment. Bonds which have little or no dipole moment give rise to extremely weak (or absent) absorptions in infrared spectra. This is seen most frequently with internal alkynes:



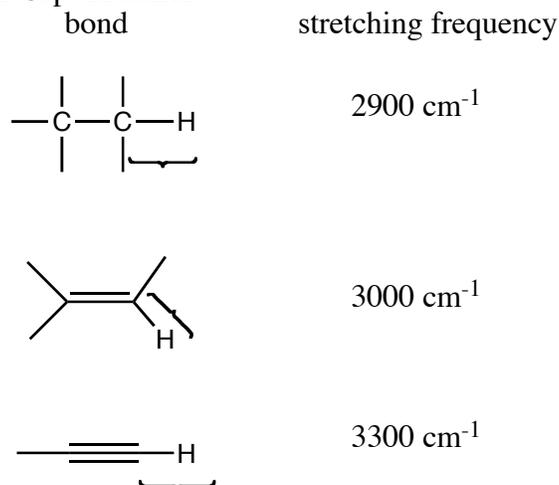
Hydrocarbons

For hydrocarbons, we can most readily observe C=C (1660 cm⁻¹) and C≡C (2200 cm⁻¹); the C-C stretch is usually buried in the fingerprint region (1200 cm⁻¹) and so is not diagnostic.

Conjugation generally lowers the absorption frequency, since electron delocalization in conjugated systems (dienes, trienes, aromatic rings) leads to weaker bonds:



For the C-H stretching frequency, we find a rough correlation with the strength of the chemical bond: C^{sp}-H bonds are stronger (more tightly held electrons) than the C^{sp²}-H bonds which are stronger than C^{sp³}-H bonds.



Again, from IR spectra we get an idea of bond strengths: compare C-H bonds (100 kcal/mol) at 2900 cm⁻¹ to C-C bonds (80 kcal/mol) at 1200 cm⁻¹.

Alcohols and Amines

The OH bond stretch in the IR spectrum is one of the most recognizable absorptions. It occurs at around 3300 cm⁻¹ and is broad due to hydrogen bonding. Note that the C-O stretch is buried in the fingerprint region (1000-1200 cm⁻¹)

Bond	stretching frequency
C-N	1200 cm ⁻¹
C=N	1600 cm ⁻¹
C≡N	2200 cm ⁻¹ strong
C≡C	2200 cm ⁻¹ weak or absent:

Summary

1600 – 1800 cm ⁻¹	C=C, C=O, C=N
2100 – 2300 cm ⁻¹	C≡C, C≡N
2800 – 3500 cm ⁻¹	C-H, O-H, N-H

Utility:

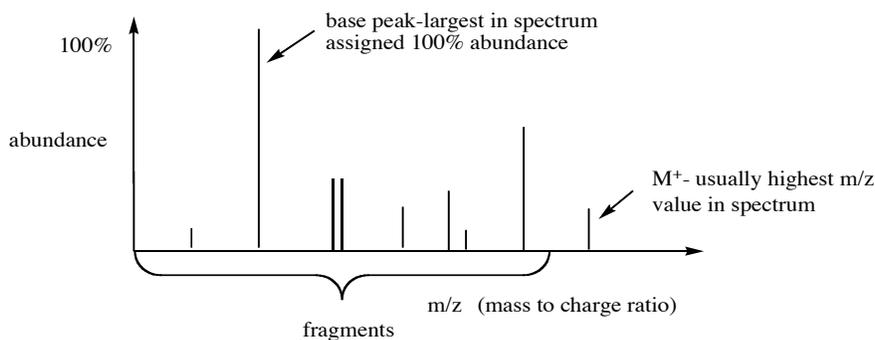
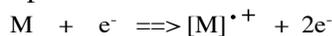
- IR spectroscopy indicates the functional groups in an organic compound
- Can confirm the identity of a compound by comparison with a known sample, taking note of the fingerprint region
- Says nothing about the connectivity of the carbon skeleton of the molecule or stereochemistry.

2. Mass spectrometry

- Provides the molecular weight and valuable information about the molecular formula using a very small amount of sample.
- Not absorption spectroscopy!

In mass spectrometry, molecules are ionized in a vacuum, the ions are sorted according to their masses, and the abundance of each mass is recorded

In electron- impact (EI-MS), electrons are used to bombard molecules, resulting in ejection of two electrons to form the molecular ion (M⁺). The molecular ion may undergo fragmentation to produce multiple lower-mass ions.



GC-MS

A GC-MS is an instrument which first passes the sample through a gas chromatography (GC) column, allowing for separation of the compounds in a mixture prior to injection into the mass spectrometer.

Determination of molecular formula.

High resolution mass spectrometry detects particle mass to 1 in 20,000 and provides an exact mass for the molecular ion. One can then compare the exact mass with masses calculated from various molecular formulas. For example, if high-resolution analysis gives an exact mass of 44.029, the following information allows us to conclude that our molecular formula is C_2H_4O :

	mass
^{12}C	12.0000
1H	1.007825
^{16}O	15.994914
^{14}N	14.003050

	C_3H_8	C_2H_4O	CO_2	CN_2H_4
Calculated mass:	44.06260	44.02620	43.98983	44.03740

Heavy isotope peaks

Further information can be gleaned from analysis of heavy isotope peaks ($M+1$, $M+2$), whose abundance depends on the natural abundance of the isotope. The presence of Br, Cl, I, S, and N can all be distinguished based on peaks close to M^+ :

Compounds containing	have
Br	$M+2$ as large as M^+
Cl	$M+2$ 1/3 as large as M^+
I	a peak at 127 for I^+
N	an odd number for M^+
S	$M+2$ 4% of M^+

Summary

- Mass spectrometry allows us to determine the molecular weight of a substance; high-resolution mass spectrometry allows us accurately to determine the molecular formula of a substance
- Analysis of heavy isotope peaks in the mass spectrum ($M+1$, $M+2$) signals the presence of I, Cl, Br, and S. An odd molecular weight signals the presence of an odd number of nitrogens in a molecule (trivalent)

Additional Problems for practice:

1. match the following IR spectra with the compounds listed below:

1,3-cyclohexadiene

Diphenylacetylene

1-octene

2-pentene

2. match the following IR spectra with the compounds listed below

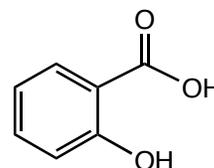
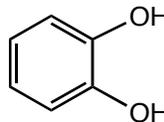
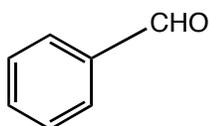
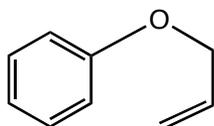
butyl acetate

butyramide

isobutyl amine

lauric acid

3. Match the following IR spectra with the compounds listed below



- The mass spectrum of 2-butenal shows a peak at m/z 69 that is 28.9% as intense as the base peak. Propose at least one fragmentation route to account for this peak, and explain why this fragment would be reasonably stable
- The exact mass of a compound determined by high-resolution mass spectra is 212.0833. Given the following table, what is the molecular formula? Given the spectrum below, what is the structure of the compound?