Infrared Spectroscopy and Mass Spectrometry

Introduction
It is fundamental for an organic chemist to be able to identify, or characterize, the new compound that he/she has just made.

Sometimes this can be achieved by a chemical means, such as determining the elemental composition and molecular weight.

If the compound has been made previously, it is possible to compare physical properties (boiling points / melting points, etc) with literature values.

Chemical tests can be used to determine whether certain functionalities are present or absent.

But, these are not sufficient for either complex molecules or new molecules that have never been made before.

Tests can be either destructive or non-destructive. (Combustion which gives elemental analysis is destructive, whereas NMR is non-destructive - you can recover your sample).

Ideally, chemists want techniques that use small amounts of compounds, are non-destructive, quick and give unambiguous results.

Spectroscopic techniques generally meet almost all of these requirements.

The four most common are:

Infrared spectroscopy (IR spectroscopy observes the vibration of bonds, and gives information about which functionalities are present).

Mass Spectrometry (MS provides information concerning the mass of the molecule, and sometimes about its structure).

Nuclear Magnetic Resonance Spectroscopy (NMR spectroscopy provides information about the numbers and environments of all the hydrogens (and Carbons and Fluorines) in a molecule. Probably the most important technique).
**Ultra Violet Spectroscopy** (UV Spectroscopy deals with electronic transitions, and gives information mainly about multiple bonds and conjugation).

The **Electromagnetic Spectrum**
Visible, IR and UV light, microwaves and radio waves are all examples of electromagnetic radiation.

They all travel at the same speed (the speed of light, $3 \times 10^8$ m/s), but differ in their wavelength and frequency.

The frequency, $\nu$, is the number of complete wavecycles to pass a fixed point in one second. (Usually in Hz, which means cps).

The wavelength, $\lambda$, is the distance between any two peaks of the wave.

Diagram 12-2

Wavelength and frequency are inversely proportional.

$$\lambda = \frac{c}{\nu}$$

where $c$ is the speed of light.

Electromagnetic waves travel as **photons**, which are packets of energy of zero mass.

The energy of a photon is the product of its frequency and Planck's constant.

$E = h \nu$

$H = $ Planck's constant $1.58 \times 10^{-37}$ kcal-sec
Under certain conditions, when a photon of correct energy strikes a molecule, it can be absorbed and this leads to reaction. This is why we write photochemical reactions involving $h\nu$.

The electromagnetic spectrum covers all possible frequencies, ranging from radio waves that are low energy and cause nuclear spin transitions, up to X-rays that are of high energy and cause ionization of molecules.

**The InfraRed Region**
Infrared radiation is of slightly shorter frequency than visible light.

Typical IR wavelengths range from $8 \times 10^{-5}$ cm to $1 \times 10^{-2}$ cm, and this corresponds to energies of around 1-10 kcal.

This energy is sufficient to make atoms vibrate, but not enough to cause electronic transitions.

These vibrational transitions correspond to specific energies, which give rise to specific absorptions. Therefore, IR provides information about how atoms are bonded together.

The position of an IR band is specified by its wavelength, measured in microns ($\mu$m = $10^{-6}$ m). Although more commonly, the term wavenumber is used, $\nu$ (nu bar) the reciprocal of the wavelength in cm.

E.g. eqn 12-3
Molecular Vibrations
A covalent bond between two atoms can be envisaged as a spring holding them together.
If the bond is compressed, there is a restoring force which pushes the atoms apart, back to the equilibrium bond length.

Similarly, if the bond is stretched, there is a restoring force that forces the atoms back closer together, again restoring the equilibrium bond length.

The frequency of the stretching vibration depends on two factors:
(1) The mass of the atoms
(2) The stiffness of the bond

Heavier atoms vibrate more slowly than lighter ones, so a C-D bond will vibrate at a lower frequency than a C-H bond.

Stronger bonds are stiffer than weaker bonds, and therefore require more force to stretch or compress them.

Thus, stronger bonds generally vibrate faster than weaker bonds.

So O-H bonds which are stronger than C-H bonds vibrate at higher frequencies.

Table 12-1 (SLIDE)

The IR spectra of even simple molecules contain many different absorptions (not just one for each bond). These absorptions result from not only the stretching of the molecule as a whole, but also from bending vibrations.

In general for a non-linear molecule containing n atoms, there are 3n-6 fundamental vibrational modes.
### TABLE 12-1 Bond Stretching Frequencies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy [kcal (kJ)]</th>
<th>Stretching Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C—H</td>
<td>100 (420)</td>
<td>3000</td>
</tr>
<tr>
<td>C—D</td>
<td>100 (420)</td>
<td>2100</td>
</tr>
<tr>
<td>C—C</td>
<td>83 (350)</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td>Frequency dependence on atomic masses</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C—C</td>
<td>83 (350)</td>
<td>1200</td>
</tr>
<tr>
<td>C≡C</td>
<td>146 (611)</td>
<td>1660</td>
</tr>
<tr>
<td></td>
<td>Frequency dependence on bond energies</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C—N</td>
<td>73 (305)</td>
<td>1200</td>
</tr>
<tr>
<td>C≡N</td>
<td>147 (615)</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2200</td>
</tr>
<tr>
<td>C—O</td>
<td>86 (360)</td>
<td>1100</td>
</tr>
<tr>
<td>C≡O</td>
<td>178 (745)</td>
<td>1700</td>
</tr>
<tr>
<td></td>
<td>Note: In a group of bonds with similar bond energies, the frequency decreases with increasing atomic weight. In a group of bonds between similar atoms, the frequency increases with bond energy. Bond energies and frequencies are approximate.</td>
<td></td>
</tr>
</tbody>
</table>

#### Diagrams

1. **Symmetric Stretching**
2. **Antisymmetric Stretching**
3. **Bending (Scissoring)**
Consider the water molecule  
(non-linear, 3 atoms → 3 fundamental vibrational modes).

Figure 12-2

These are only the fundamental vibrational modes, these can combine and multiply to give rise to numerous other modes of vibration.

These more complicated modes give rise to the numerous absorptions in an IR spectra, and since different molecules will have different IR spectra, we can use IR to help identify molecules.

The most complex (and informative) region is called the fingerprint region (600-1400cm⁻¹), and this contains the wagging, twisting, scissoring and rocking vibrations.

The region that contains the simple stretching vibrations is typically from 3500 to 1600cm⁻¹, and this is the area we will focus our studies on.

IR Active and IR Inactive Vibrations
Not all molecular vibrations absorb IR radiation.

To understand which ones do (and which do not) absorb we need to consider how an electromagnetic field interacts with the chemical bond.

Important points are:
(1) A chemical bond which is polarized has a dipole moment (i.e. charge separation).
(2) An electric field will interact with the polar bond, causing it either to stretch or compress.
(3) An electromagnetic wave has a rapidly reversing electric field, so this radiation rapidly compresses and stretches the polar bond.
(4) If the frequency of the stretching and compression is at the frequency of the molecule's natural rate of vibration, then energy may be absorbed.

Vibrations of bonds with dipole moments normally result in the absorption of IR radiation, and are said to be IR active.
However, if a bond is symmetrical, and has zero dipole moment, the electric field does not interact with this bond.

If the symmetrical bond is stretched, the dipole moment still remains zero, the vibration produces no change in the dipole moment, there is no absorption of energy.

This vibration is said to be IR inactive.

To recap:
In general, if a bond has a dipole moment, its stretching frequency causes an absorption in the IR spectrum.

If a bond is symmetrically substituted and has zero dipole moment, its stretching vibration will (essentially) be absent from the spectrum.

Measurement of an IR spectrum
An IR spectrometer measures the frequency of IR radiation which is absorbed by a compound.

A simple IR spectrometer consists of two beams of light which pass through a reference and a sample cell.
These beams alternately pass through a monochromatic and a detector and the information is converted to a print out on a chart recorder.
The output signal is equal to the sample signal minus the reference signal (i.e. it corrects for the "background" - air or solvent absorption).
The monochromator allows only one frequency of light to enter at any given time. It scans the range of IR frequencies from 4000 - 600\,cm\(^{-1}\).

The vertical axis is **percentage** transmittance and the horizontal axis contains the wavenumber. Typically the higher wavenumber are to the left of an IR spectrum.

**IR Spectroscopy of Hydrocarbons**

**Carbon-Carbon Bond Stretching**
Since stronger bonds are generally stiffer, they absorb at higher frequencies than weaker bonds.

- Single C-C bonds absorb around 1200\,cm\(^{-1}\)
- Double C=C bonds absorb around 1660\,cm\(^{-1}\)
- Triple CC bonds absorb around 2200\,cm\(^{-1}\).

The absorptions of C=C bonds can provide more information about the double bond.

Conjugation (and more so, aromaticity) cause there to be **less** double bond character in the C=C bond, which results in absorption at a **lower** wavenumber.
Isolated C=C  1640-1680 cm\(^{-1}\)
Conjugated C=C  1620-1640 cm\(^{-1}\)
Aromatic C=C  \(~1600\) cm\(^{-1}\)

**Carbon-carbon Triple Bonds**
CC triple bonds only absorb if they are terminal, since internal alkynes have very small (almost zero) bond dipole moments.

**Carbon Hydrogen Bond Stretching**
The C-H bond stretch is subtly affected by the hybridization of the C-H bond.

The more s character a bond has, the stronger it is, and so the higher wavenumber it should absorb at.

- \(\text{sp}^3\) is one quarter s, absorbs at 2800-3000 cm\(^{-1}\)
- \(\text{sp}^2\) is one third s, absorbs at 3000-3100 cm\(^{-1}\)
- sp is one half s, absorbs at \(~3300\) cm\(^{-1}\).

**Interpretation of IR Spectra**

Figures 12-6, 12-7 (SLIDES)

**Characteristic Absorptions of Alcohols and Amines**
The O-H and N-H bonds are strong and therefore stiff, so they occur at high frequencies, usually above 3000 cm\(^{-1}\).

**Typical Stretching Frequencies**
- Amine N-H  3300 cm\(^{-1}\), broad and with spikes
- Acid O-H  3300 cm\(^{-1}\), broad
- Alcohol O-H  3000 cm\(^{-1}\), broad.

These are almost always broad since these molecules exhibit extensive hydrogen bonding, giving rise to many differing bonds, and so many different stretching frequencies.

Figures 12-8, 12-9 (SLIDES)
(a) 1-octyne

3313

2119

\[ \text{H} - \text{C} \equiv \text{C} \text{-(CH}_2\text{)_3CH}_3 \]

(b) 4-octyne

\[ \text{CH}_3\text{(CH}_2\text{)}_2\text{C} \equiv \text{C}-\text{(CH}_2\text{)_3CH}_3 \]

I-butanol

\[ \text{CH}_3\text{(CH}_2\text{)}_2\text{OH} \]

O-H stretch

C-H stretch
Carbonyl Compounds
The C=O double bond has a large dipole moment, and produces intense IR absorptions (~1700 cm\(^{-1}\)).

Simple Ketones. Aldehydes and Carboxylic Acids
The C=O bond is slightly stiffer than the C=C bond, and so absorbs at slightly higher frequency (~1710 cm\(^{-1}\)).

An aldehyde also shows a characteristic set of two C-H stretches at 2700 and 2800 cm\(^{-1}\). (Obviously ketones and acids do not have these peaks).

Diagram 12-9a,

Carboxylic acids also have very strong O-H absorptions, seen as very broad peaks around 3000 cm\(^{-1}\).

Figure 12-10 (SLIDE)

Resonance Lowering of Frequencies
Just as conjugation (resonance) lowers the stretching frequency of C=C, the same is true for C=O double bonds.

Delocalisation of the \(\pi\) electrons reduces the electron density of the C=O double bond, which weakens it, and lowers the stretching frequency from 1710 to about 1680 cm\(^{-1}\).

E.g. amides and \(\alpha,\beta\) unsaturated carbonyls.
Some carbonyl groups absorb above 1710 cm$^{-1}$, and this is characteristic of either esters, or strained cyclic ketones.

**Diagram 12-9c**

**Characteristic absorptions of C-N bonds**
Carbon-nitrogen stretching frequencies are similar to carbon-carbon frequencies, except the absorptions are usually stronger.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-N Single bond</td>
<td>1200</td>
</tr>
<tr>
<td>C=N Double bond</td>
<td>1600</td>
</tr>
<tr>
<td>CN Triple bond</td>
<td>&gt;2200</td>
</tr>
</tbody>
</table>

**Summary**
It may seem like there is just too much data to learn, but just learn the general areas, and remember how strain and conjugation affects the frequencies.

**Diagram 12-11 and table 12-2. (SLIDES)**

IR spectroscopy is valuable since
(a) it shows what functional groups are present
(b) it indicates the absence of other functional groups
(c) by comparison with an authentic sample, it can confirm the identity of a compound.
Mass Spectrometry (MS)
MS provides information concerning the molecular weight of a molecule (and often other structural information).

Very small sample sizes are required (2mg, "if you can see it, you can MS it", but a destructive technique), and high resolution mass spectrometry (HRMS) can determine molecular weight to 3-4 decimal places.

E.g. OFP-CO$_2$H = C$_{17}$H$_8$F$_8$O$_2$ should be 396.03965

![Structure of OFP-CO$_2$H](image)

Found from HRMS: 396.0391

Spectrometry is different from spectroscopy since spectroscopy involves the absorption or emission of light waves. Spectrometry does not.

A sample is struck by high energy electrons, the molecules fragment, and are then analyzed.

From the fragments it is possible to compile a picture of the molecule. ("Rifle and a vase")

The Mass Spectrometer

Figure 12-14 (SLIDE)

A mass spectrometer ionizes molecules in a high vacuum, and sorts the ions according to their masses, and records the abundance of the ions of each mass.

A mass spectrum has the mass of the ions on the x axis, and the relative number of the ions on the y axis. (Most abundant ion being 100% - base peak).
There are actually several different methods (techniques) for the ionization of molecules - we will only discuss electron impact ionization (EI).

An electron strikes a neutral molecule, and knocks out an electron - thus generating a radical cation.

E.g. methane
Eqn 12-13a

It is the positively charged species that are bent through the flight tube into the detector. (Not radicals, radicals are neutral).

The radical cation which corresponds the mass of the original molecule is called the molecular ion (or parent ion), M⁺.

In addition to ionization, the impact can also fragment the molecule (break it apart), but certain fragments are "invisible" since they are not charged and therefore not detected.

E.g. ethane
Separation of Ions of Different Masses
The ions are separated by magnetic deflection.

The positive ions are accelerated into the flight tube by a negatively charged accelerated plate. The flight tube is curved, with a powerful magnet, and this curves the flight of appropriately weighted species (a heavier ion bends less than a lighter ion).

The radius of curvature of an ion depends on the mass-to-charge ratio \((m/z)\). Where \(m=\)mass, and \(z=\)charge.

Since (almost always) the ion has a charge of +1, we assume the ions are separated only according to their mass.

At the end of the flight tube is a slit and an ion detector. The slit allows only ions of one particular mass to pass through into the detector.

By varying the magnetic field of the magnet, the spectrometer can scan all possible masses.

A Mass Spectrum

![Mass Spectrum Image]

Notice the 2 axes, and also that the base peak is normally not the parent ion.

HRMS
Normal mass spectrometry gives masses rounded to the nearest figure. Often this is sufficient to identify compounds or distinguish between two compounds.

However, sometimes this is not always the case, and HRMS can give formula masses correct up to several decimal places.
Exact Masses

\begin{align*}
^{12}\text{C} & \quad 12.000000 \\
^{1}\text{H} & \quad 1.007825 \\
^{16}\text{O} & \quad 15.994914 \\
^{14}\text{N} & \quad 14.003050
\end{align*}

Consider a product of mass 44.

It could be \(\text{C}_3\text{H}_8\), \(\text{C}_2\text{H}_4\text{O}\), \(\text{CO}_2\) or \(\text{CN}_2\text{H}_4\).

By performing HRMS, we can differentiate between these 4 formulae:

\begin{align*}
\text{C}_3\text{H}_8 & = 44.06260 \\
\text{C}_2\text{H}_4\text{O} & = 44.02620 \\
\text{CO}_2 & = 43.98983 \\
\text{CN}_2\text{H}_4 & = 44.03740
\end{align*}

If the HRMS was measured as 44.029, we would conclude the compound is \(\text{C}_2\text{H}_4\text{O}\).

**Heavier Isotope Peaks**

Molecular ion (parent ion) peaks can often also provide information about molecular formula.

Most elements do not exist as one single isotope, but have several isotopes of differing masses.

These heavier isotopes gives rise to small peaks at slightly higher mass values in mass spectra.

A peak one mass unit higher than the \(M^+\) ion is called an \(M+1\) peak; two units heavier is called an \(M+2\) peak.

Certain elements have characteristic isotope patterns (larger than normal \(M+1\) or \(M+2\) peaks) and these can be easily recognized.

\begin{itemize}
  \item \text{Br} has an \(M+2\) as large as \(M^+\)
  \item \text{Cl} has \(M+2\) as large as \(M^+\)
  \item \text{S} has a slightly increased \(M+2\) (4\% of \(M^+\))
\end{itemize}