Lecture XXVI: Spring 2009 Chem 3331 04/23/2009

So far, we talked about the structures and reactivities of organic compounds. But how do we know that the structures we put on paper are actual structures?

Today: ① Mass spectrometry – principles and applications
② Electromagnetic spectrum
③ IR spectroscopy
④ Interpretation of IR spectra

Determining the structure of an organic compound can be done through either chemical tests or through physical – spectroscopic methods. The latter are better since they are more sensitive and less destructive.

What are we looking for?

- Size – mass : MASS SPECTROMETRY
- Functional groups: IR SPECTROSCOPY
- Carbon-hydrogen skeleton: NMR SPECTROSCOPY
  ↳ most powerful!

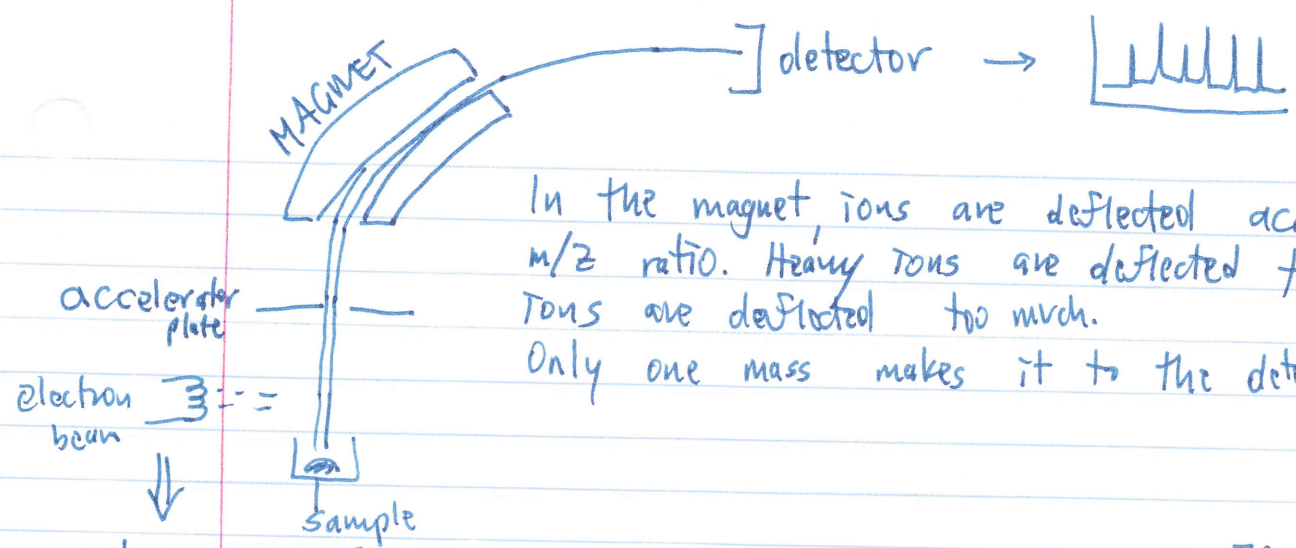
① Mass Spectrometry

Elemental analysis, aka combustion analysis, will give us molecular formula:

$$C_x H_y \xrightarrow{O_2} x CO_2 + \frac{y}{2} H_2O$$

But we cannot tell if this is C_xH_y or $C_{2x}H_{2y}$ or $C_{3x}H_{3y}$. To figure out which one is it, we need to know the mass of the molecule. Mass spectrometry can tell us that.

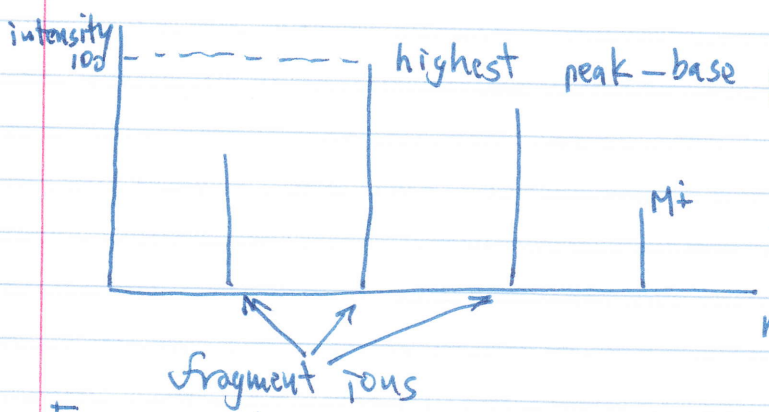
Mass Spectrometer is an instrument that is used:



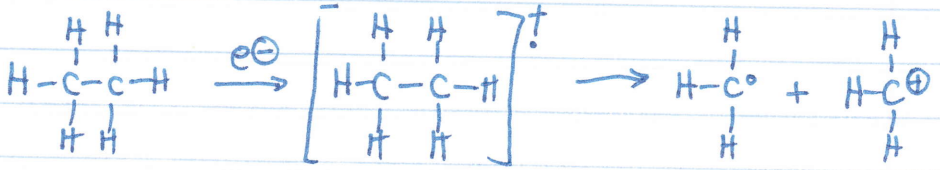
In the magnet, ions are deflected according to their m/z ratio. Heavy ions are deflected too little, light ions are deflected too much.
Only one mass makes it to the detector

creates ions from the sample: $M + e^- \rightarrow 2e^- + [M]^{\dot{+}}$
ELECTRON IMPACT IONIZATION

$M^{\dot{+}}$ – molecular ion, tells us molecular weight

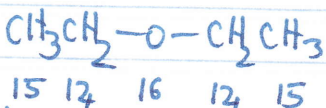


For example:

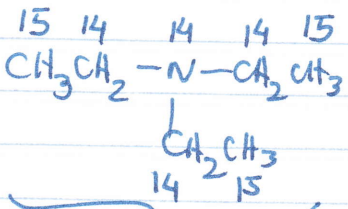


What other information can we get from a mass spectrum?

a) Whether we have nitrogens or not:



even number

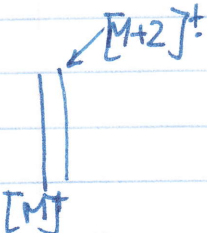


odd number

b) Whether we have Br or Cl in our molecules:

Br is a mixture of ^{79}Br and ^{81}Br, 1:1
Cl " " " " ^{35}Cl and ^{37}Cl, 3:1

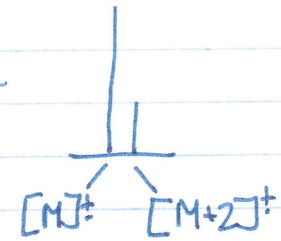
In spectra of compounds with Br, we will see:



very characteristic 1:1

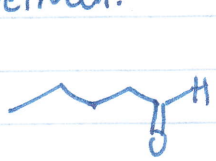
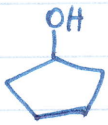
In spectra of compounds with Cl, we will see:

If we see such a pattern, that is a sign that we have a Cl in our molecule.



Mass spectrometry is a destructive technique, but that is OK, since it uses a fraction of a milligram of compounds.

But mass spectrometry only tells us the mass. It would not tell us the difference between:

86 g/mol  and  86 g/mol

We need to be able to figure out functional groups too.

(2) Electromagnetic spectrum

- Visible light, UV light, radio waves, X-rays, microwaves — all are forms of electromagnetic radiation

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

E: energy; ν: frequency; λ: wavelength

$nm = 10^{-9}\ m$

long-wave radio ← ~km-s

γ-rays	X-rays	UV light	visible	IR light	microwaves	FM-AM radi
10^{-16}–10^{-18} m	10^{-11}–10^{-8} m	10^{-9}–10^{-7} m	400–700 nm	10^{-6}–10^{-3} nm	10^{-3}–1 m	1 – 10^{2} m

A) Light of different energy interacts differently with chemical compounds
B) Light is easily measured and quantified.

⇓

Light is used as an ANALYTICAL tool in chemistry:

ENERGY (↑)

γ-rays: destroy molecules, break chemical bonds

X-rays: excite some 1s (very low-lying) electrons to high energy levels – we typically ignore this

UV-rays: excite external, highest-level electrons: ELECTRONIC TRANSITIONS

Visible light: roughly the same as UV, depending on the molecule

IR light: causes stretching and bending of chemical bonds: VIBRATIONAL TRANSITIONS

Microwaves: cause rotations around the bonds ROTATIONAL TRANSITIONS

Radiowaves: cause very small (but important) changes in nuclear spin

In this course, we will study IR and Radio (aka NMR) spectroscopy. In 3332, UV/Visible

③ Infrared Spectroscopy (IR)

useful IR region: $\lambda = 2.5 \cdot 10^{-6}\,m \leftrightarrow 2.5 \cdot 10^{-5}\,m$ (2500 – 25000 nm)
visible: $\lambda = 300 - 700$ nm

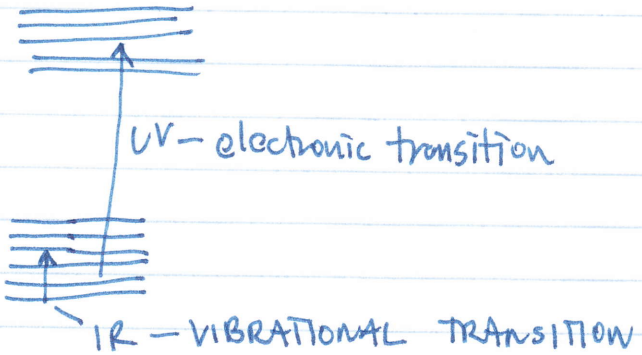
Wavenumbers ($\bar{\nu}$) are more commonly used in IR spectroscopy:

$\bar{\nu} = 1/\lambda$ [m^{-1}, more commonly cm^{-1}]

IR: 400 – 4000 cm^{-1}; wavenumbers are directly proportional to energy

Some materials, like water, snow, glass, absorb IR light strongly and are "IR-black". That is why glass cannot be used in IR spectrometers – instead, finely polished blocks of NaCl or KBr is used.

So, what does IR light do to a molecule?



$\Delta E = h\nu = h\frac{c}{\lambda} = hc\bar{\nu}$

this is proportional to the energy between the vibrational levels

⇓

Molecule's signature!

Stronger bonds need more energy to stretch:

$\bar{\nu}(C{=}O) > \bar{\nu}(C{-}O)$

1700 cm^{-1} > 1100 cm^{-1}

$\bar{\nu} = a\sqrt{\frac{k}{\mu}}$ Hooke's law

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ ↑ REDUCED MASS

Lighter atoms need more energy to stretch:

$\bar{\nu}(C{-}H) > \bar{\nu}(C{-}C)$

3000 cm^{-1} > 1200 cm^{-1}

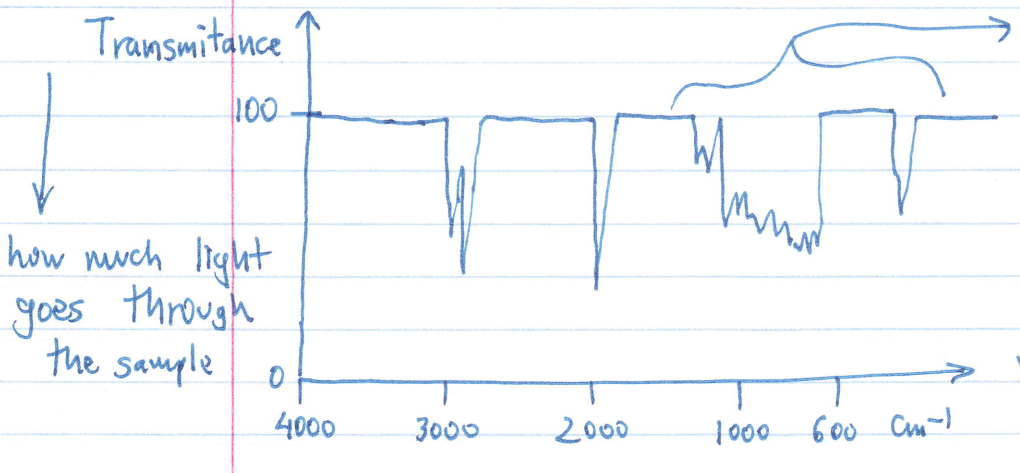
$\bar{\nu}(C{-}H) > \bar{\nu}(C{-}D)$

3000 cm^{-1} 2100 cm^{-1}

Let's see how does a typical IR spectrum look like:

$CH_3{-}C{\equiv}C{-}CH_3$ IMPORTANT – Completely symmetric vibrations are invisible in IR!!!

④ Interpretation of IR Spectra



1500–400 cm^{-1}
FINGERPRINT REGION
no two molecules have it the same; but it is very complex and difficult to interpret ⇒ ignore it!

Each functional group has a specific position:

$>C=O$	1630–1820 cm^{-1} strong	$-N(-H)-H$	3100–3550 cm^{-1} medium-strong	$-C(=O)-H$	2720 cm^{-1} strong
$-O-H$	3200–3650 cm^{-1} strong, broad	$-C(sp^3)-H$	2850–3000 cm^{-1} medium		
$-C(sp^2)-H$	3000–3100 cm^{-1} medium	$-C(sp)-H$	3300 cm^{-1} medium-strong		
$-C=C-$	1600–1800 cm^{-1} medium-weak	$-C\equiv C-$	2100–2250 weak, might be absent if the compound is too symmetric		

WE WILL PROVIDE YOU WITH A TABLE OF THESE VALUES FOR THE EXAM.

For now, let's practice some interpretation:

IR: 1700 cm^{-1} (strong), 2890 cm^{-1}
MASS: 58 g/mol

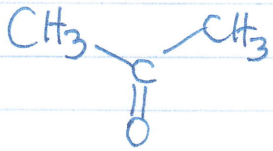
??? 1700 cm^{-1} ⇒ $>C=O$ Mass ⇒ 58

$-C=O$ (12+16)

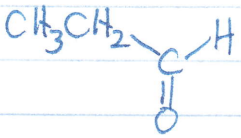
30 g/mol

2890 cm^{-1} ⇒ $C-H$ (sp^3)

$2 \times 15 = 2 \times CH_3$


acetone

But could it be:


Nah. We should see 2720 cm^{-1} for aldehyde hydrogen

SHOW EXAMPLES OF IR SPECTRA AND THEIR INTERPRETATION, MORE COMPLEX SPECTRA TOO! — NEXT WEEK:

NMR

HOMEWORK-CHAPTER 12: 16, 18, 19, 20, 23, 24.