Introduction to Mass Spectrometry
(Dr. Pahlavan's old handout with 4 good introductory examples)

Chapter 12&13
Structural Determination
(MS, IR, and NMR)

Chemistry laboratory tasks:

I) product purification(direct method)
  a) Crystallization or distillation
  b) Chromatography

II) Structural elucidation(spectroscopy method)
  a) Mass spectroscopy(MS)-determine the size and formula.
  b) Infrared(IR)-determine the type of functional groups.
  c) Nuclear magnetic resonance(NMR)-determine the Carbon and Hydrogen framework.
  d) Ultraviolet(uv)-determine type of conjugated pi electron.(not discussed in this chapters)

a) Mass spectroscopy(MS)

MS is a technique that allows us to measure the mass(molecular weight) of a molecule and formula of unknown samples.
In MS , molecules are first ionized by collision with high energy e^- beam, then the ions fragment into smaller pieces, which are magnetically sorted according to their mass-to-charge ratio (m/e^- or m/z). The ionized sample molecule is called molecular ion, $M^{+\bullet}$, and measurement of its mass gives the molecular weight of the sample.
A high-energy e^- strikes an organic molecule, it dissociates a valance e^- from the molecule, producing a cation- radical.
This is called Cation because has lost a negatively charged particle(e^-) and radical because the molecule now has an odd number of electrons.

$$\underset{\text{organic molecule}}{RH} \xrightarrow{e^-} \underset{\text{cation-radical}}{RH^{+\bullet}} + e^-$$

Electron bombardment transfers such a large amount of energy to the sample molecules that the cation radicals fragment after ionization ,deflected through a curved pipe according to their m/e^- ratio. Neutral fragments (radicals) are not deflected by magnetic field and are lost on the walls of the pipe, but not positively charged fragments which are sorted by MS. onto a detector, which records them as peaks at the proper m/e^- ratios. Since the number of charges z=1 or $1e^-$, the peaks of the Mass spectrum of a compound is usually presented as a bar graph with unit masses(m/e^- or m/z values) on the x-axis and intensity(the # of ions of a given m/e^- striking) on the y-axis.
In general, the last largest peak on the spectrum corresponds to molecular weight of the molecule, and is called the parent peak or molecular ion($M^{+\bullet}$) and the largest peak of the spectrum is called the base peak.
How a molecule or ion breaks into fragments depends upon the carbon skeleton and functional groups present. Therefore the structure and mass of the fragments give clues about the structure of the parent molecule. Also, it is frequently possible to determine the molecular weight of a compound from its mass spectrum.

Example-methanol, CH_3OH

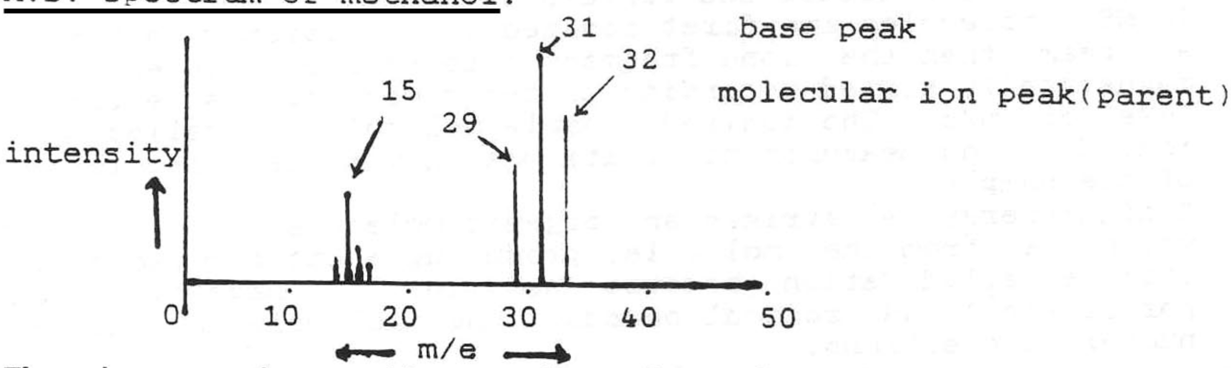
When CH_3OH bombard with high-energy electrons, one of the valance electrons is lost.
the result is an ion-radical, a species with one unpaired e^- and a charge of +1. An ion-radical is `symbolized by (+), the ion-radical that results from abstraction of one e^- of a molecule is called the molecular ion and symbolized $M^{+\bullet}$. The mass of the molecular ion is the molecular weight of the compound. The molecular ion of methanol has a mass of 32 and a charge of +1. Its mass-to-charge ratio (m/e) is 32.

$CH_3\text{-O-H} \longrightarrow 1e^- + [CH_3\text{-O-H}]^{+}$ usually written as $[CH_3OH]^{+\bullet}$. (molecular ion, m/e=32)

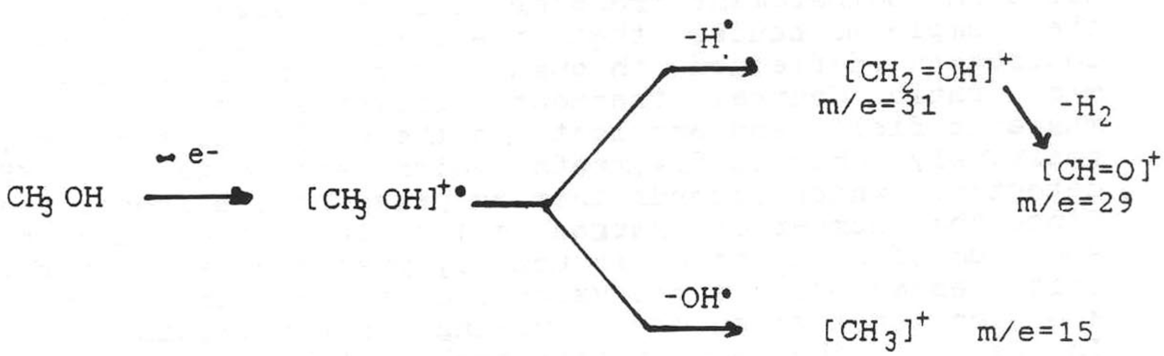
fragments;

$[CH_3OH]^{+\bullet} \longrightarrow H^\bullet + CH_2{=}OH^+$ (fragment ion, m/e=31)

M.S. spectrum of methanol:

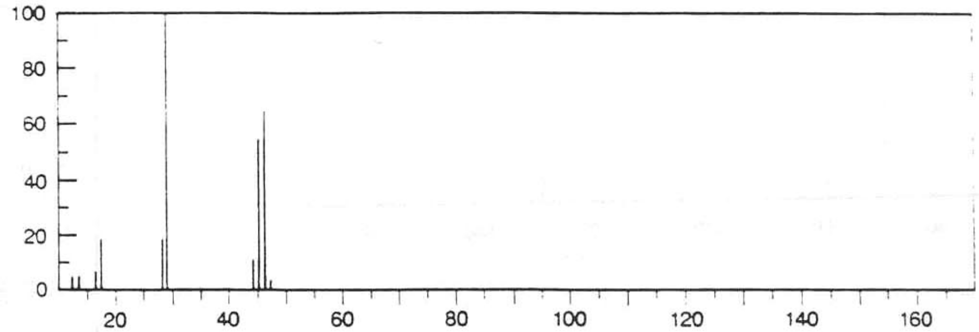


The base peak sometimes arises from the molecular ion, but often it arises from smaller fragment.

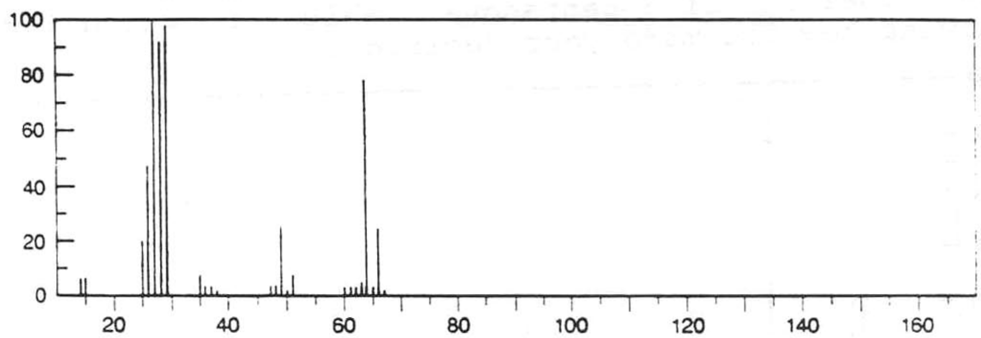


Mass spectroscopy problems

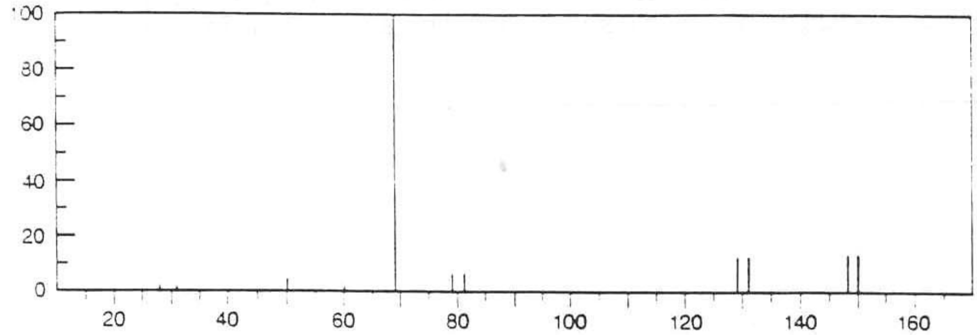
1. The mass spectrum of a carboxylic acid is shown in figure below, assign a structure to the acid and write equations showing the formation of any ions(frgment ions) having an abundance greater than 40% .



2. The mass spectrum of a haloalkane is given ,assign a structure to the compound.



3. The compound for which a mass spectrum appears in following figure contains only one carbon atom and two types of halogen. After consulting given table ,assign a structure to the compound, and account for the peaks that appear in the spectrum.



	Most Common Isotopes			
Element	**Mass**	**%**	**Mass**	**%**
H	1	100	2	0.016
C	12	100	13	1.08
N	14	100	15	0.36
O	16	100	18	0.20
F	19	100	—	—
Cl	35	100	37	32.5
Br	79	100	81	98.0
I	127	100	—	—

The "percentage" of the more abundant isotope is scaled to 100 in this table.

The true abundances can be obtained by rescaling the total percentages to 100.

Example:
True % Cl-35 = 100/1.325 = 75.5%
True % Cl-37 = 32.5/1.325 = 24.5%

4. Given the following mass spectra . One is that of 2-pentanone; the other is of 3-pentanone. Which is which ?Write equations showing how you made your decision.