(11) **Today**

Chap 12: Mass Spectrometry and Infrared Spectroscopy

Next Class (12)

Test 1 on Substitution and Elimination

(13) **Second Class from Today**

Chap 12: Mass Spectrometry and Infrared Spectroscopy

Third Class from Today (14)

Chap 12: Mass Spectrometry and Infrared Spectroscopy

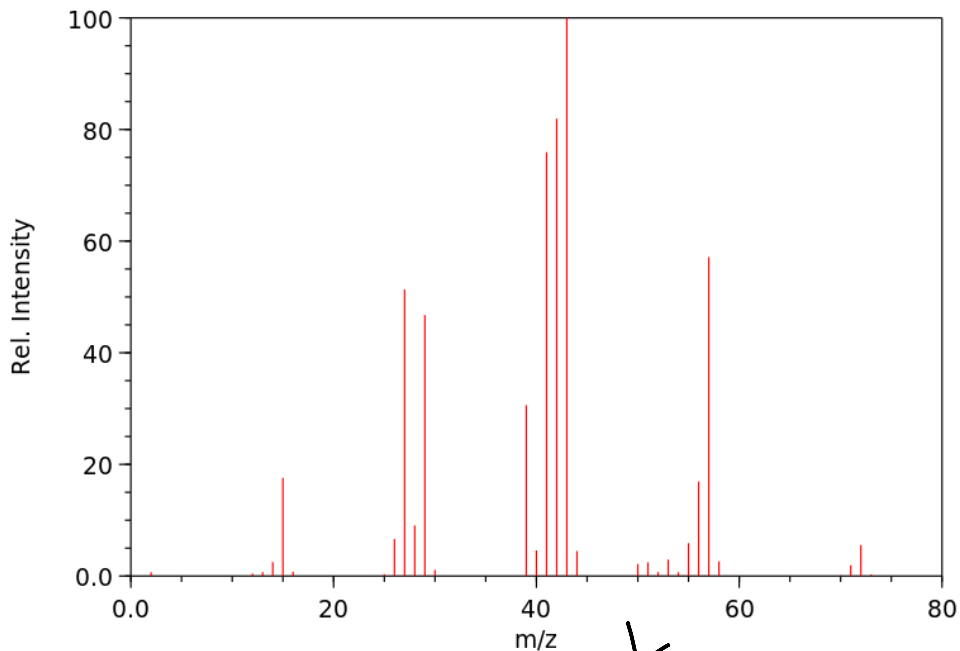
Test on substitution and elimination on Friday

Review session over Zoom Thursday 7:30 pm to 9:00 pm at the regular class URL.
I will send a new email with the link.

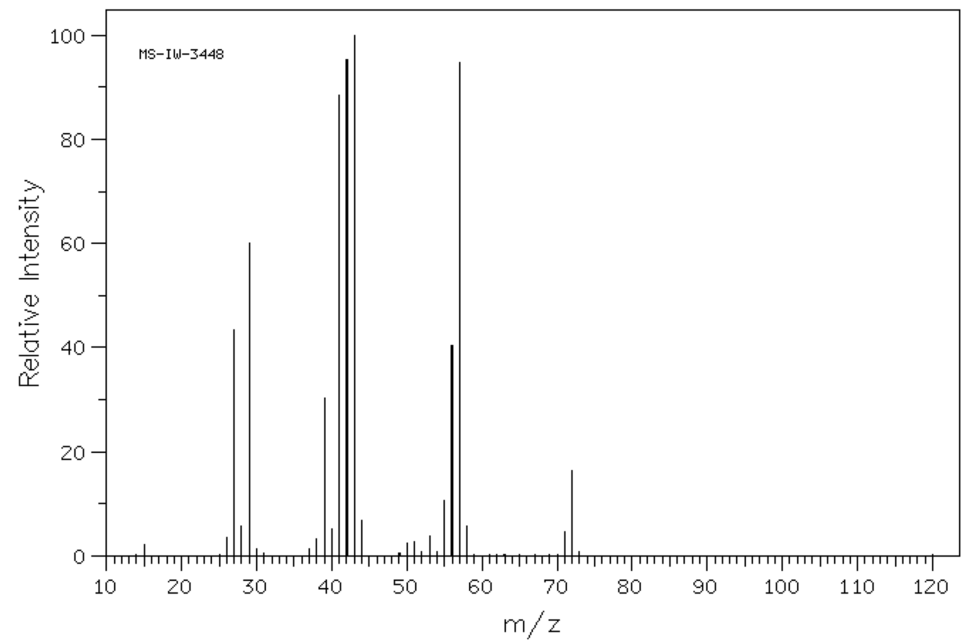
Why Mass Spectrometry?

Identify known compounds: Fingerprinting

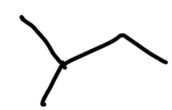
C_5H_{12}

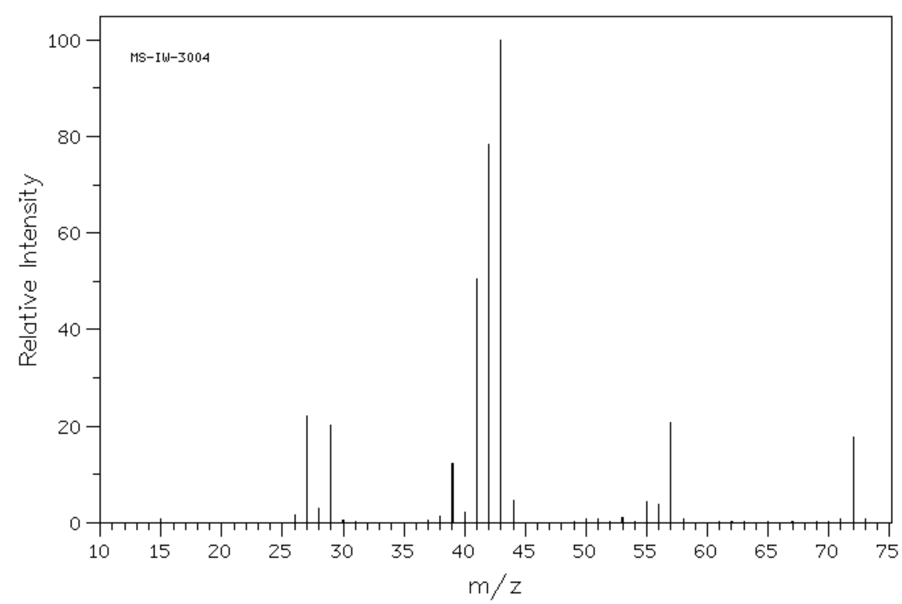


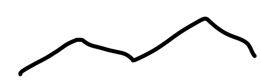
NIST Chemistry WebBook (https://webbook.nist.gov/



SDBSWeb : https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, March 2006)

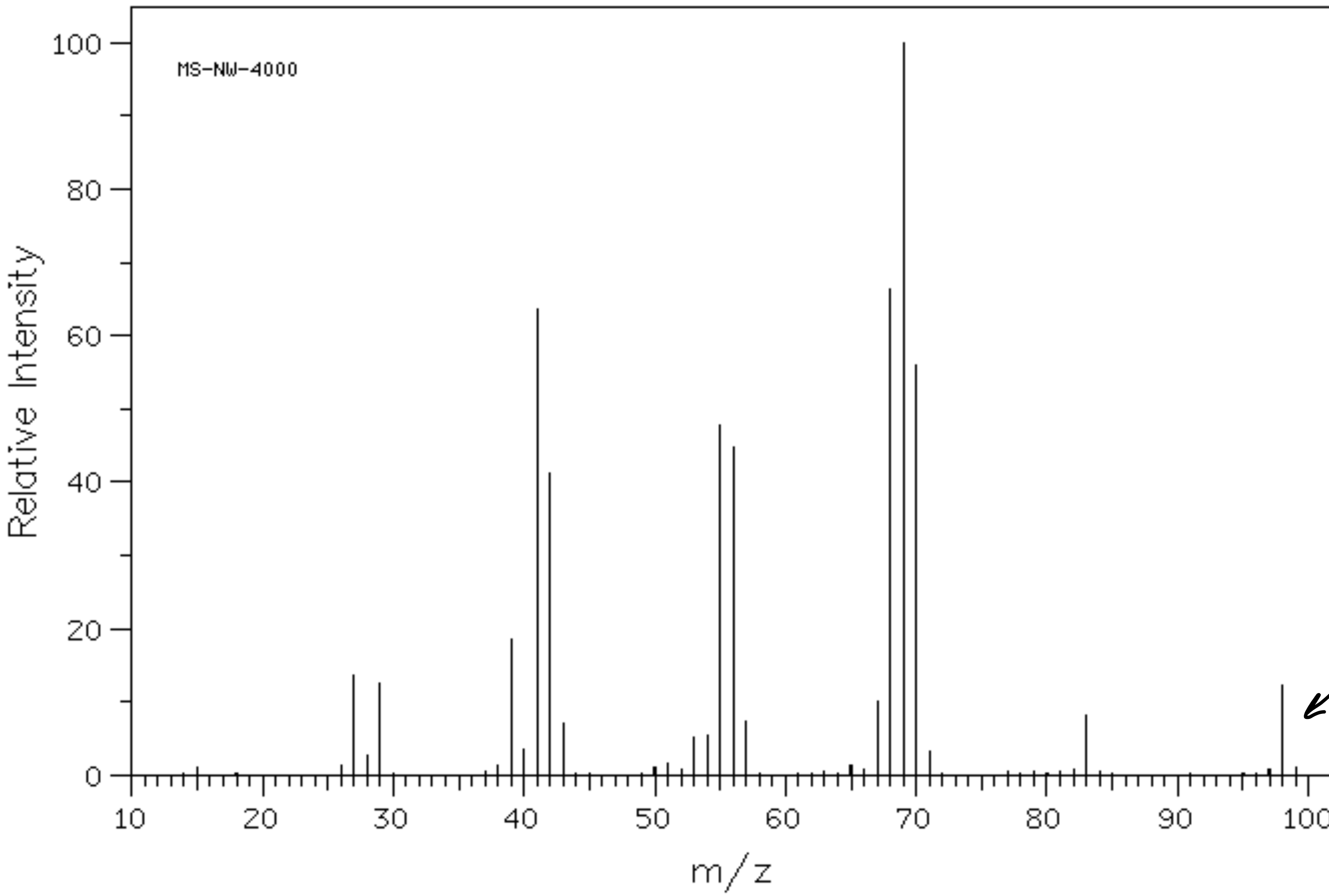






Why Mass Spectrometry?

Determine molar mass and structure of unknown compounds.



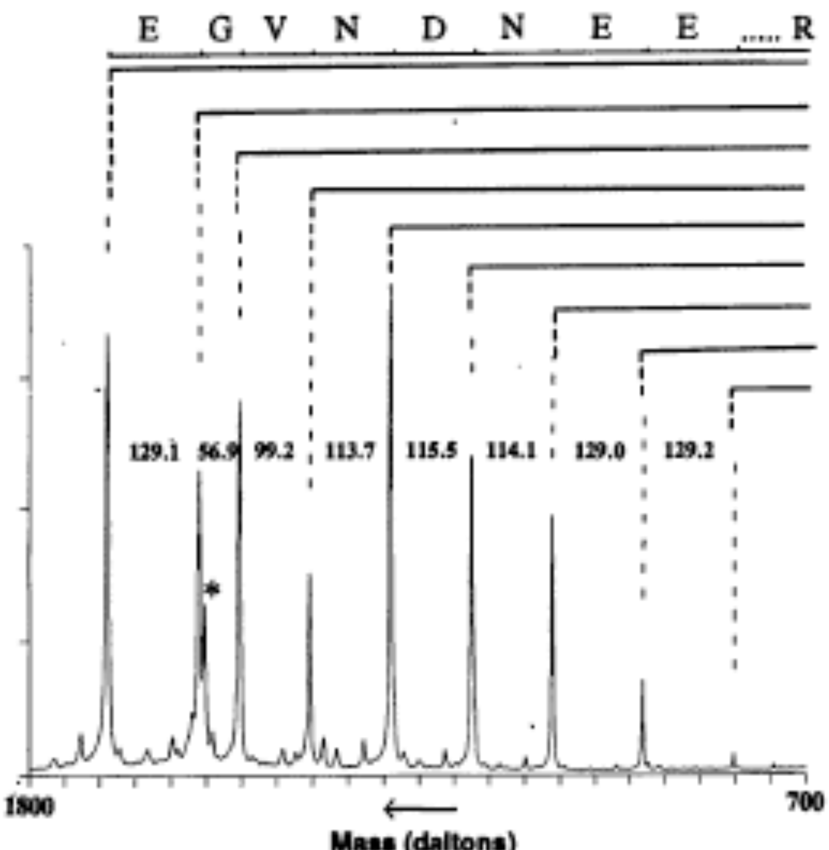
SDBSWeb : https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology, Jan 2019)

peak furthest to the right often tells us the mass of the molecule

Why Mass Spectrometry?

Determine 1° structures of polypeptides (protein ladder sequencing).

1. 5% phenylisocyanate 95% phenylisothiocyanate (PC)
2. Trifluoroacetic acid
3. repeat



PC-Glu-Gly-Val-Asn-Asp-Asn-Glu-Glu-Gly-Phe-Phe-Ser-Ala-Arg

PC-Gly-Val-Asn-Asp-Asn-Glu-Glu-Gly-Phe-Phe-Ser-Ala-Arg

PC-Val-Asn-Asp-Asn-Glu-Glu-Gly-Phe-Phe-Ser-Ala-Arg

PC-Asn-Asp-Asn-Glu-Glu-Gly-Phe-Phe-Ser-Ala-Arg

PC-Asp-Asn-Glu-Glu-Gly-Phe-Phe-Ser-Ala-Arg

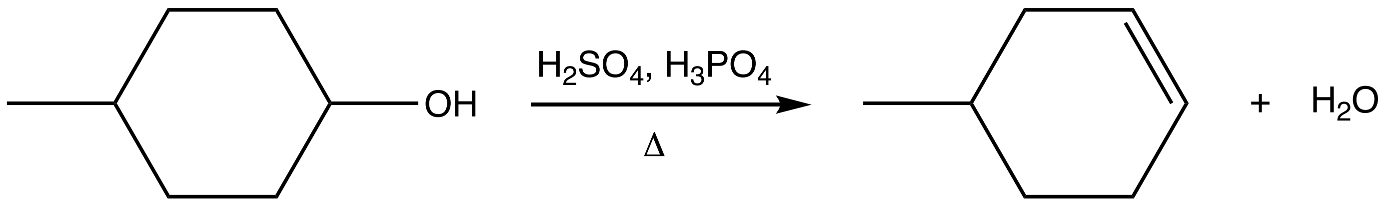
PC-Asn-Glu-Glu-Gly-Phe-Phe-Ser-Ala-Arg

Brian T. Chait; Rong Wang; Ronald C. Beavis; Stephen B. H. Kent

Science, New Series, Vol. 262, No. 5130, Genome Issue. (Oct. 1, 1993), pp. 89-92.

Why Mass Spectrometry?

Confirm synthesis of target compound.



IR Data: OH vs no OH, no C=C vs C=C

MS Data: molar mass and high-resolution mass spectrometry to confirm formula

NMR Data

Why Mass Spectrometry?

HRAM GC-MS/MS

For comprehensive characterization of samples in a single analysis with high-confidence compound discovery, identification and quantitation, a GC system can be combined with a high resolution accurate mass (HRAM) mass spectrometer.

https://www.thermofisher.com/us/en/home/industrial/mass-spectrometry/gas-chromatography-mass-spectrometry-gc-ms/gc-ms-systems/high-resolution-accurate-mass-gc-ms.html

Overview

Describe the basics of how mass spectrometry works.

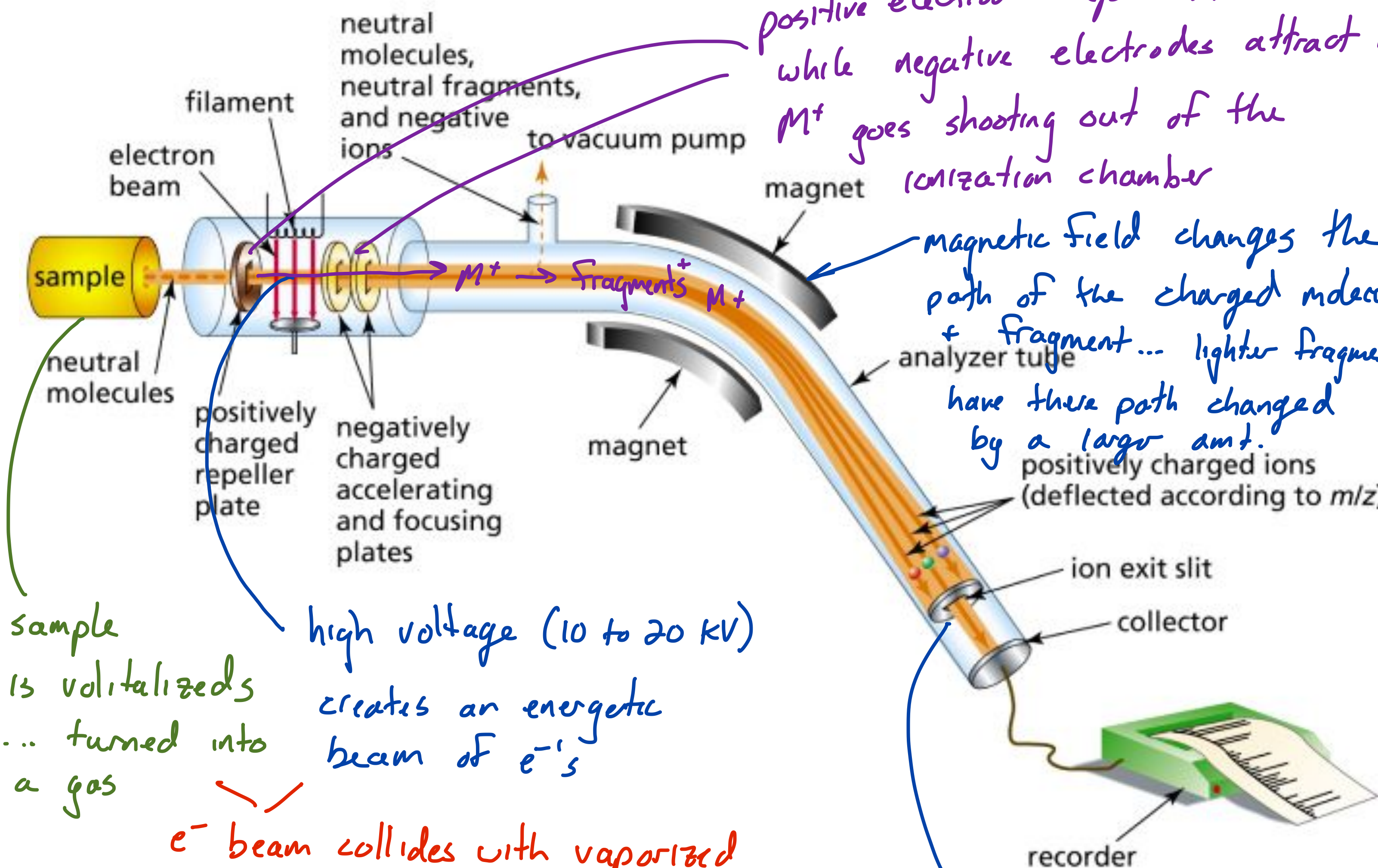
Examine the affects that isotopes and their natural abundance has on the mass spectrum

Consider methods for determining the formulas of compounds

Predict common fragmentation patterns for different functional groups

Unless indicated otherwise, all mass spectra that follow have been downloaded from the SDBSWeb : https://sdbs.db.aist.go.jp (National Institute of Advanced Industrial Science and Technology)

Schematic Representation of a Mass Spectrometer



positive electrode repels m+ while negative electrodes attract it.. M+ goes shooting out of the ionization chamber

magnetic field changes the path of the charged molecule + fragment... lighter fragments have there path changed by a larger amt.

M+ → fragments+ M+

sample is volitalized... turned into a gas

high voltage (10 to 20 kV) creates an energetic beam of e-'s

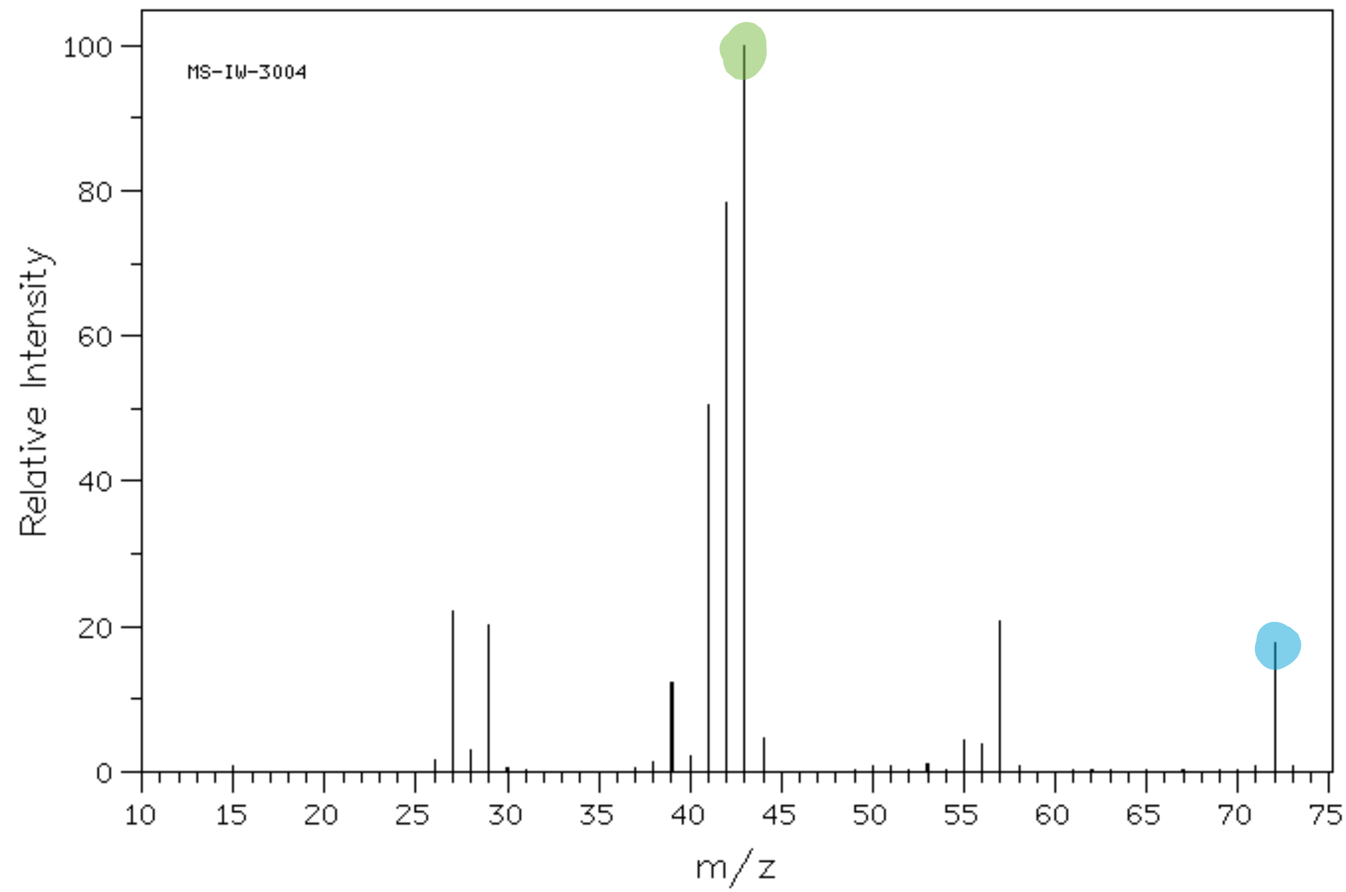
e- beam collides with vaporized molezules and an e- gets knocked off the molecules

$M \xrightarrow{e^-} M^+ + e^- \; e^-$

molecules + fragments are separated based on their mass +1

Organic Chemistry, 8th ed., Bruice, Pearson 2016

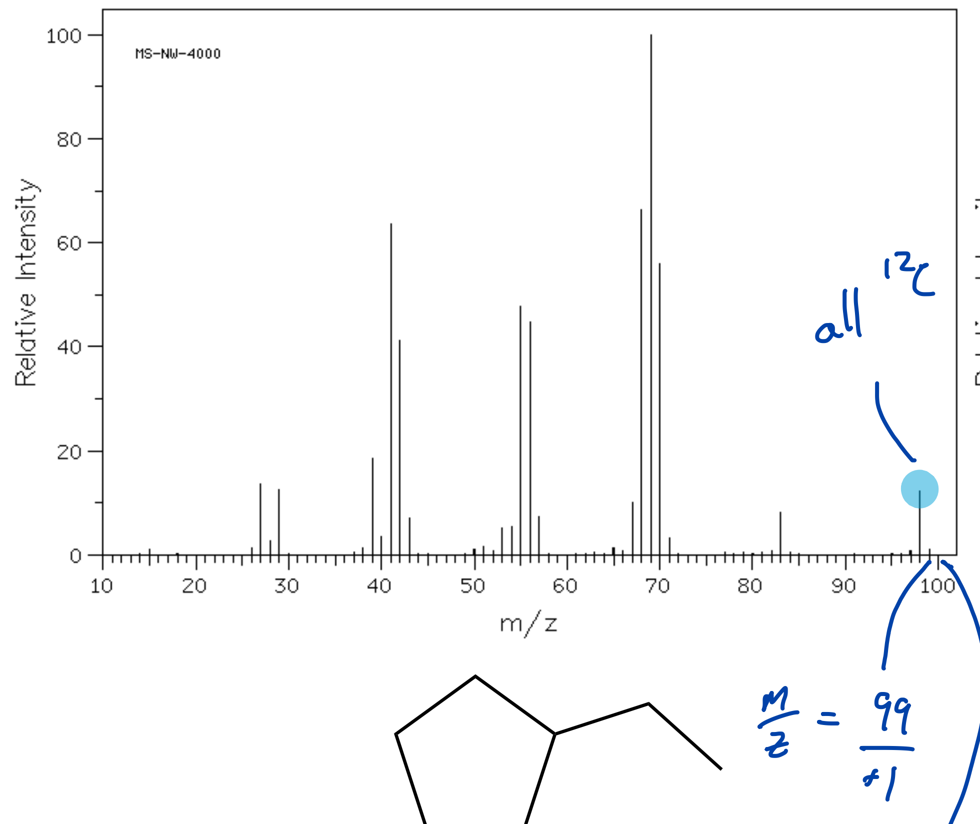
Mass Spectrum of Pentane



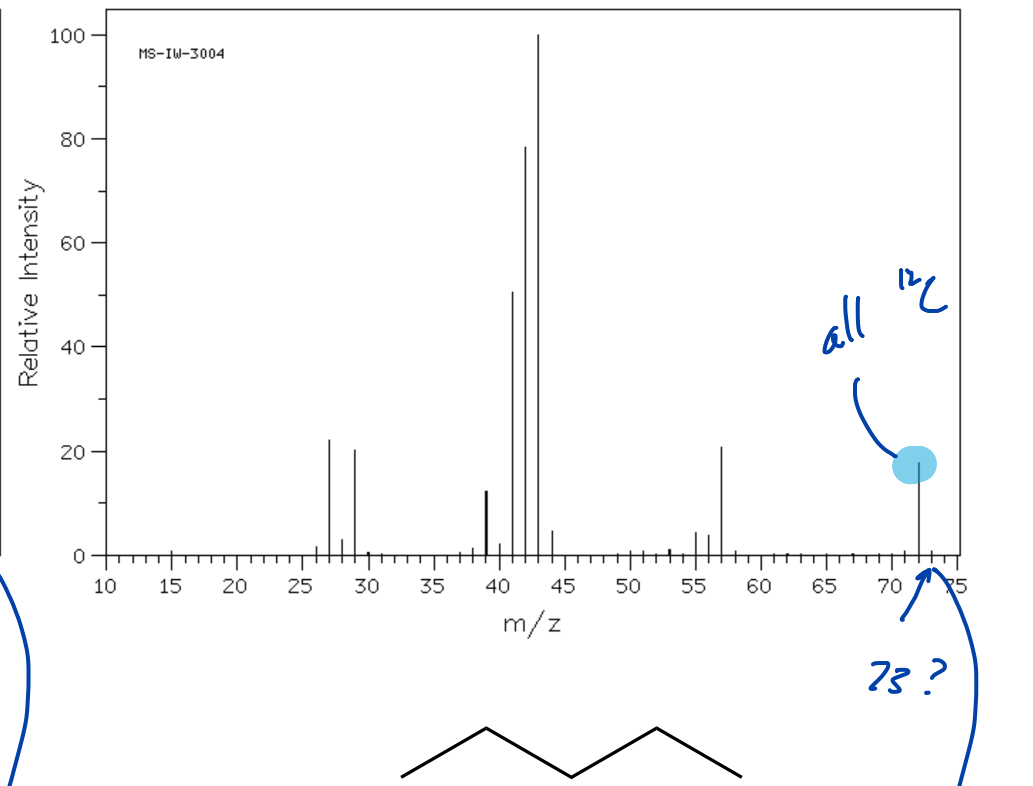
The Scale is set based on the height of the largest peak...

The Base Peak is the largest peak... typically the most easily produced fragment

The Molecular Ion is often the peak that is farthest to the right
Frequently the molecular ion does not survive long enough to be detected



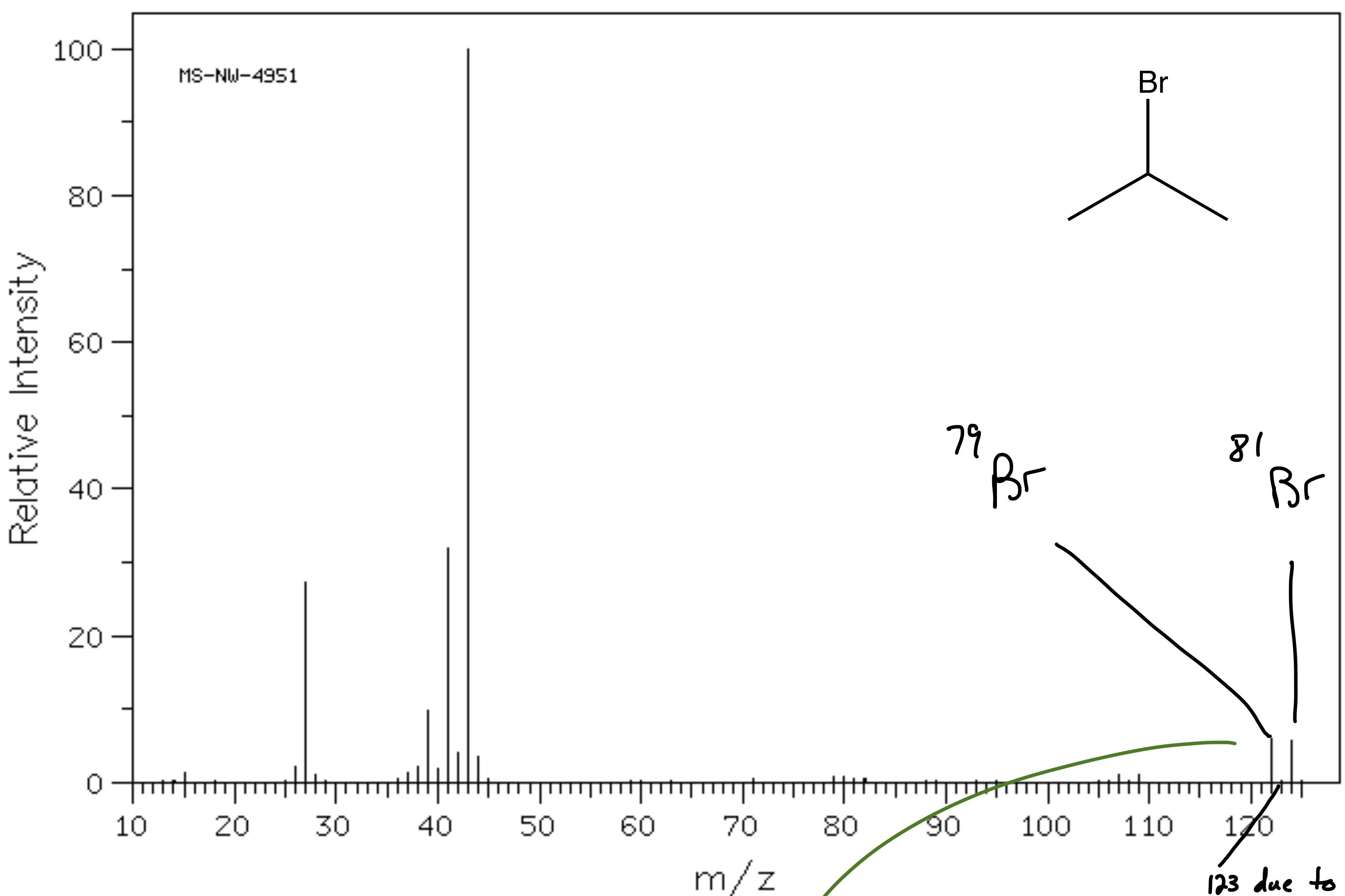
Molecular Weight: 98.1890



Molecular Weight: 72.1510

1 C atom is ^{13}C

1 C atom is ^{13}C

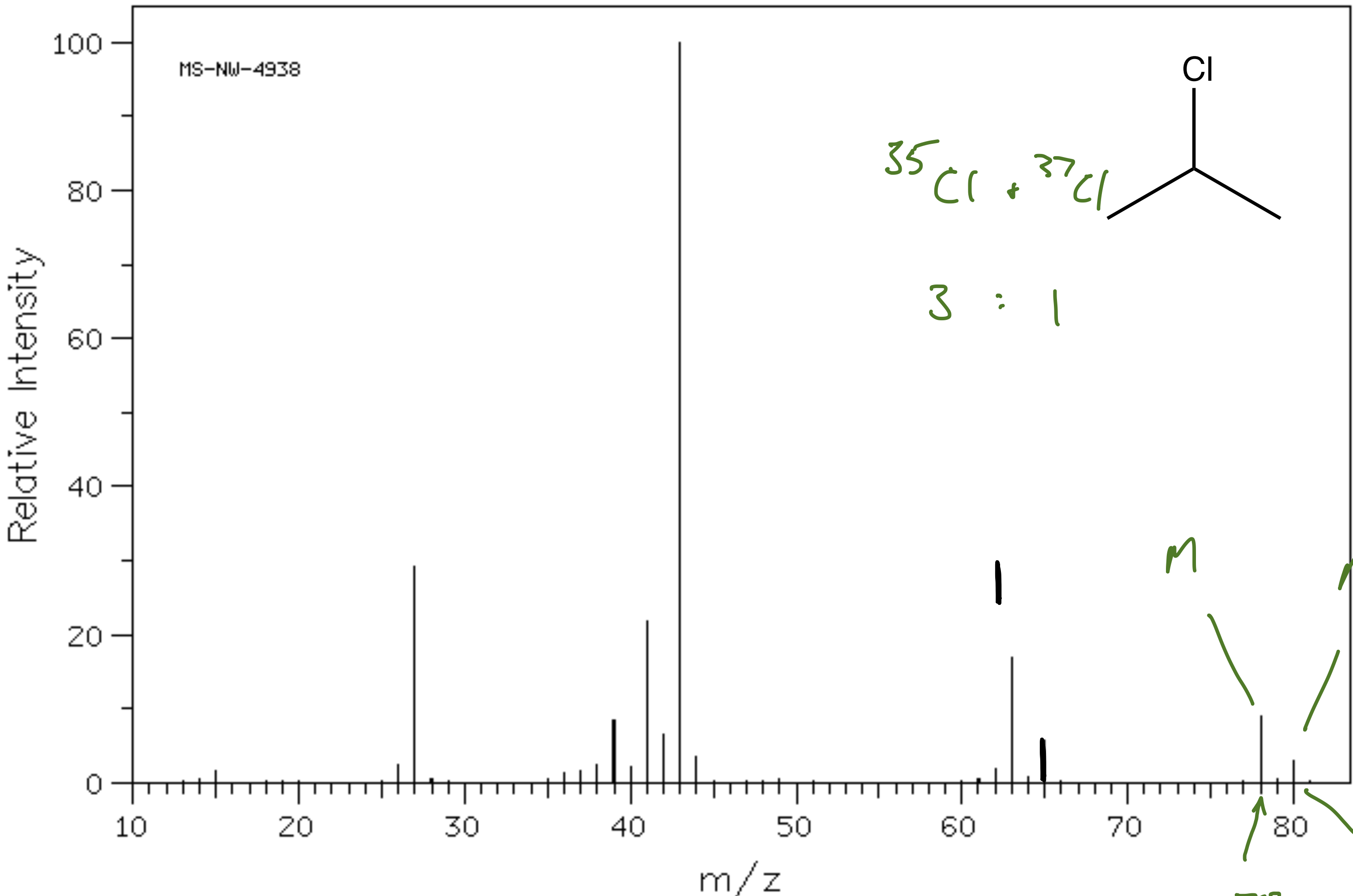


3×12 36
7×1 7
79.9
80 80
123

^{79}Br ^{81}Br
51 : 49

this almost 50:50 ratio is unique to Br m + m+2 at same height is probably Br in your molecule

Isotopic Fingerprint for Chlorine Atoms



$^{35}Cl + ^{37}Cl$

3 : 1

M

M+2

35.45

$3 \times 12 = 36$

$7 = 7$

43

$78 - 43 = 35$

$80 - 43 = 37$

M + M+2 in 3:1 ratio

ratio is unique to Cl, so Cl atom present

Comparing m and m+1 peaks

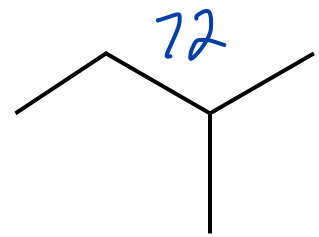
The "Rule of 13"

High Resolution Mass Spectrometry

CH_4 1% of CH_4's are $^{13}CH_4$

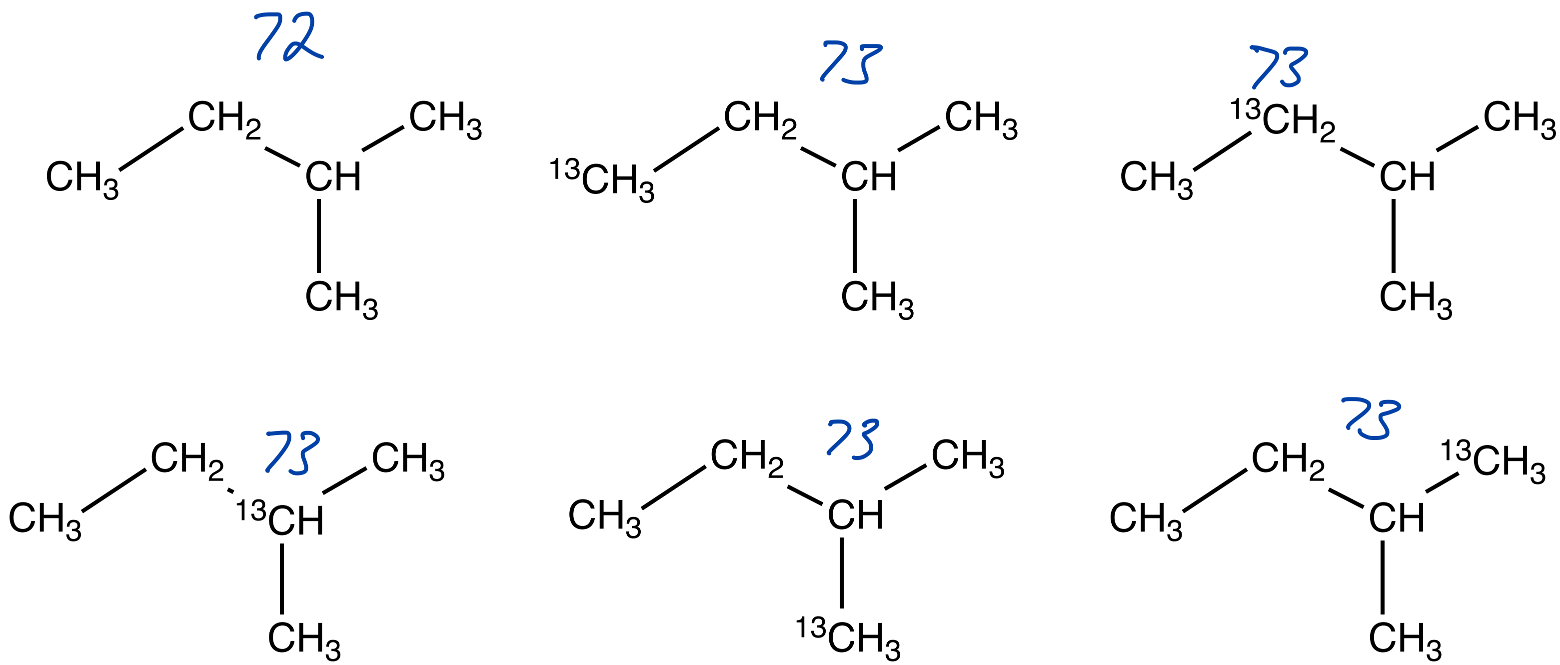
$^{13}CH_3-^{13}CH_3$ 0.0001

0.01 %



CH_3-CH_3 1% + 1%   here   here

$^{13}CH_3-CH_3$ 2%



5 different ways to get a ^{13}C atom into a molecule with 5 C atoms...

Determining Formulas Using m+1 Peaks

$$\# \text{ C atoms} = \frac{\text{intensity of m+1 peak}}{\text{intensity of (m) + (m+1) peaks}} \cdot \frac{1}{0.0106}$$

1.5

(22.4 + 1.5)

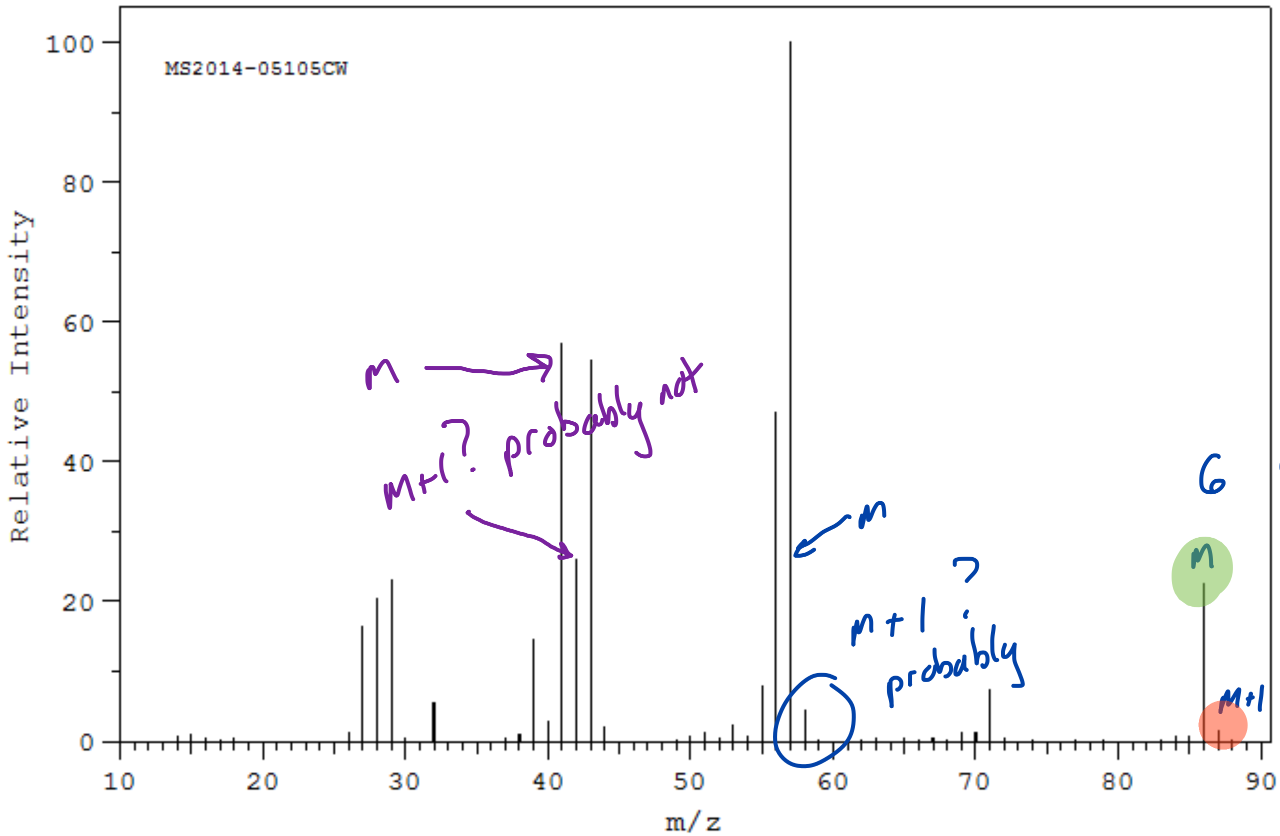
= 5.92

= 6

problems using this technique

overlapping peaks confusing size of m+1 peak

other atoms, like N, with isotopes that have a +1



m/z	%
26.0	1.3
27.0	16.5
28.0	20.3
29.0	23.1
32.0	5.6
38.0	1.0
39.0	14.5
40.0	2.9
41.0	56.8
42.0	25.9
43.0	54.4
44.0	2.0
51.0	1.3
53.0	2.3
55.0	7.9
56.0	47.0
57.0	100.0
58.0	4.4
69.0	1.2
70.0	1.1
71.0	7.3
86.0	22.4
87.0	1.5