Today

Mass Spectrometry

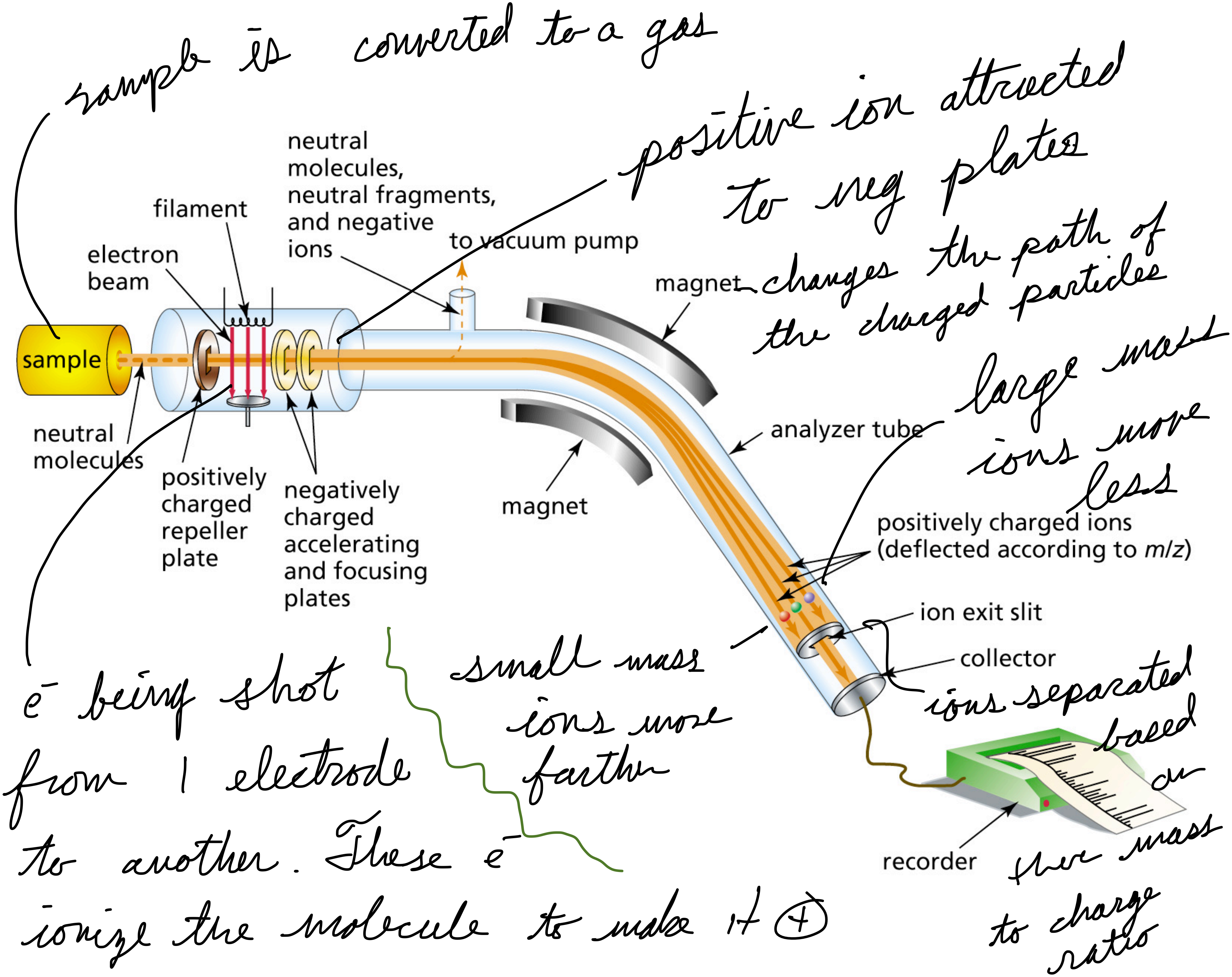
Next Class

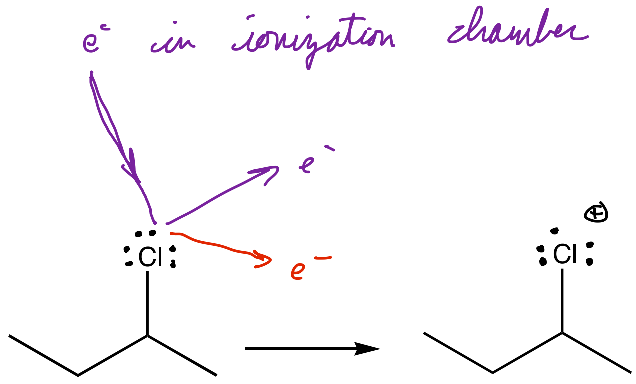
Mass Spectrometry
Practice interpreting Spectral Data

Test on Mass Spectrometry, Infrared Spectroscopy (Chap 13) and NMR Spectroscopy (Chap 14) on Feb 18 (1 week from today)

Spring 19 test 1
Spring 13 Quiz 4 and one question from Spring 13 Test 3
Spring 12 Test 4
Spring 11 Quiz 3, Test 3
Spring 09 Test 3
Spring 08 Quiz 3, Test 3
Spring 07 Test 4
Spring 06 Test 4
Spring 05 Test 4
Spring 04 Test 4
Spring 03 Test 4

Office Hours will remain online for a little while longer


sample
neutral molecules
electron beam
filament
positively charged repeller plate
negatively charged accelerating and focusing plates
neutral molecules, neutral fragments, and negative ions
to vacuum pump
magnet
magnet
analyzer tube
positively charged ions (deflected according to m/z)
ion exit slit
collector
recorder
sample is converted to a gas
positive ion attracted to neg plates
changes the path of the charged particles
large mass ions move less
small mass ions move farther
ions separated based on their mass to charge ratio
e⁻ being shot from 1 electrode to another. These e⁻ ionize the molecule to make it ⊕



an e⁻ gets knocked off the molecule + a cation results

a cation forms that is also a radical

very unstable

Spectral data obtained from

Spectral Database for Organic Compounds, SDBS

National Institute of Advanced Industrial Science and Technology (AIST), Japan

www.aist.go.jp/RIODB/SDBS/cgi-bin/cre_index.cgi

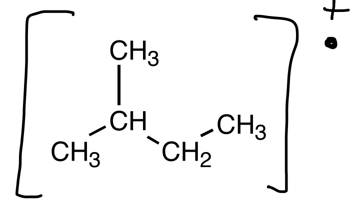
Fragmentation and Carbon Isotopes in MS

$5 \times 12 = 60$
$12 \times 1 = 12$
72

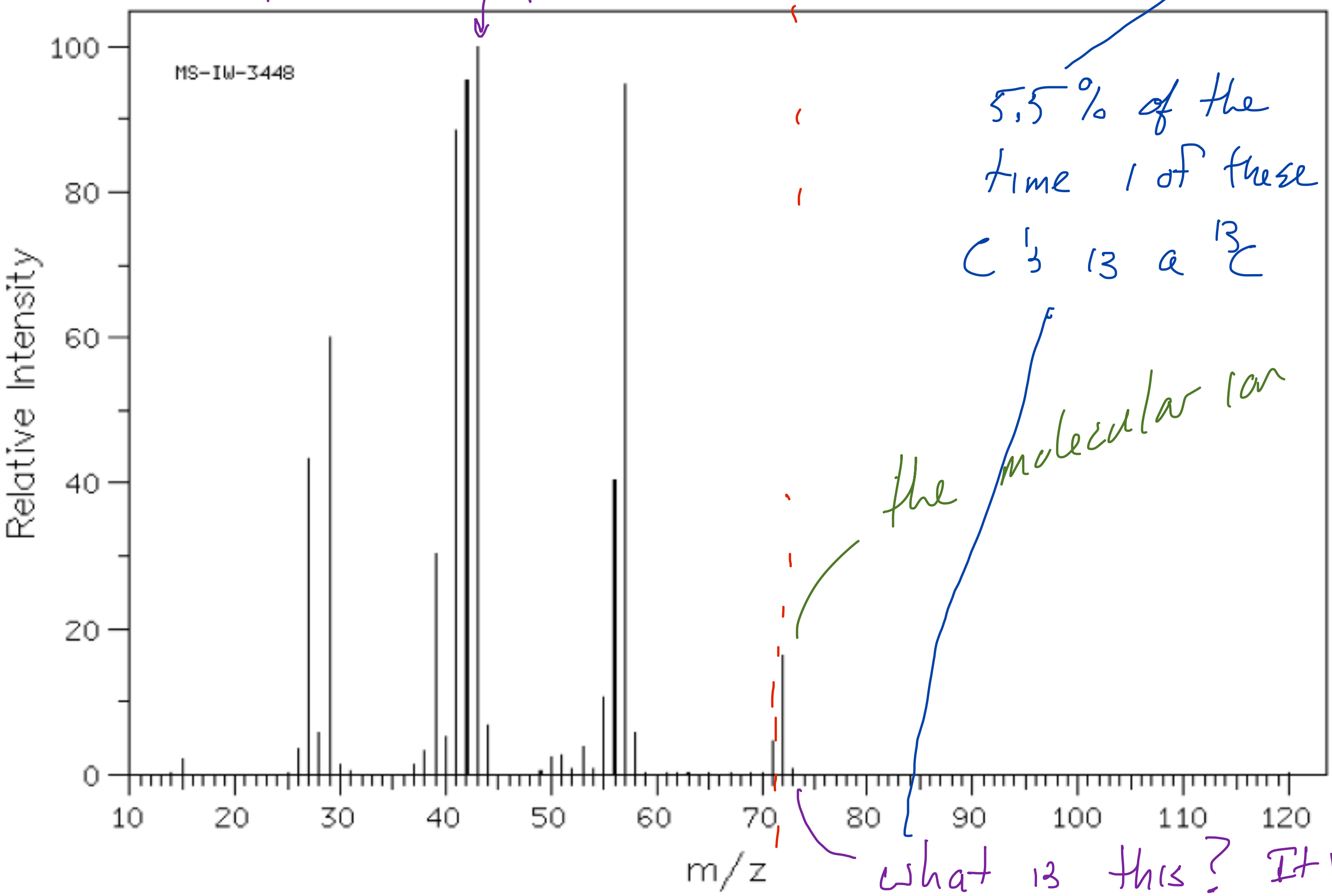
^{13}C NA is 1.1%

radical cations rip themselves apart and form fragments

base peak (tallest peak) assigned intensity of 100



5.5% of the time 1 of these C's is a ^{13}C



the molecular ion

what is this? It is an M+1 peak being caused by ^{13}C

m/z	Relative Intensity
72.0	16.4
73.0	0.9

mass to charge ratio = 72

$z = +1$

C, Cl, and Br isotopes in MS

1 ^{13}C in ion peak

be careful: N atoms and

^{12}C and ^{13}C

calculate # of C atoms

$$\# \text{ C atom} = \frac{\text{intensity of m + 1 peak}}{\text{intensity of m peak}} \quad \frac{1}{0.011}$$

no ^{13}C in ion peak

$$\frac{0.9}{16.4} \times 0.011 = 5$$

complicated fragmentation patterns can mess this up

^{35}Cl and ^{37}Cl

ave mass 35.453

3 : 1 m : m+2 means a Cl atom is present

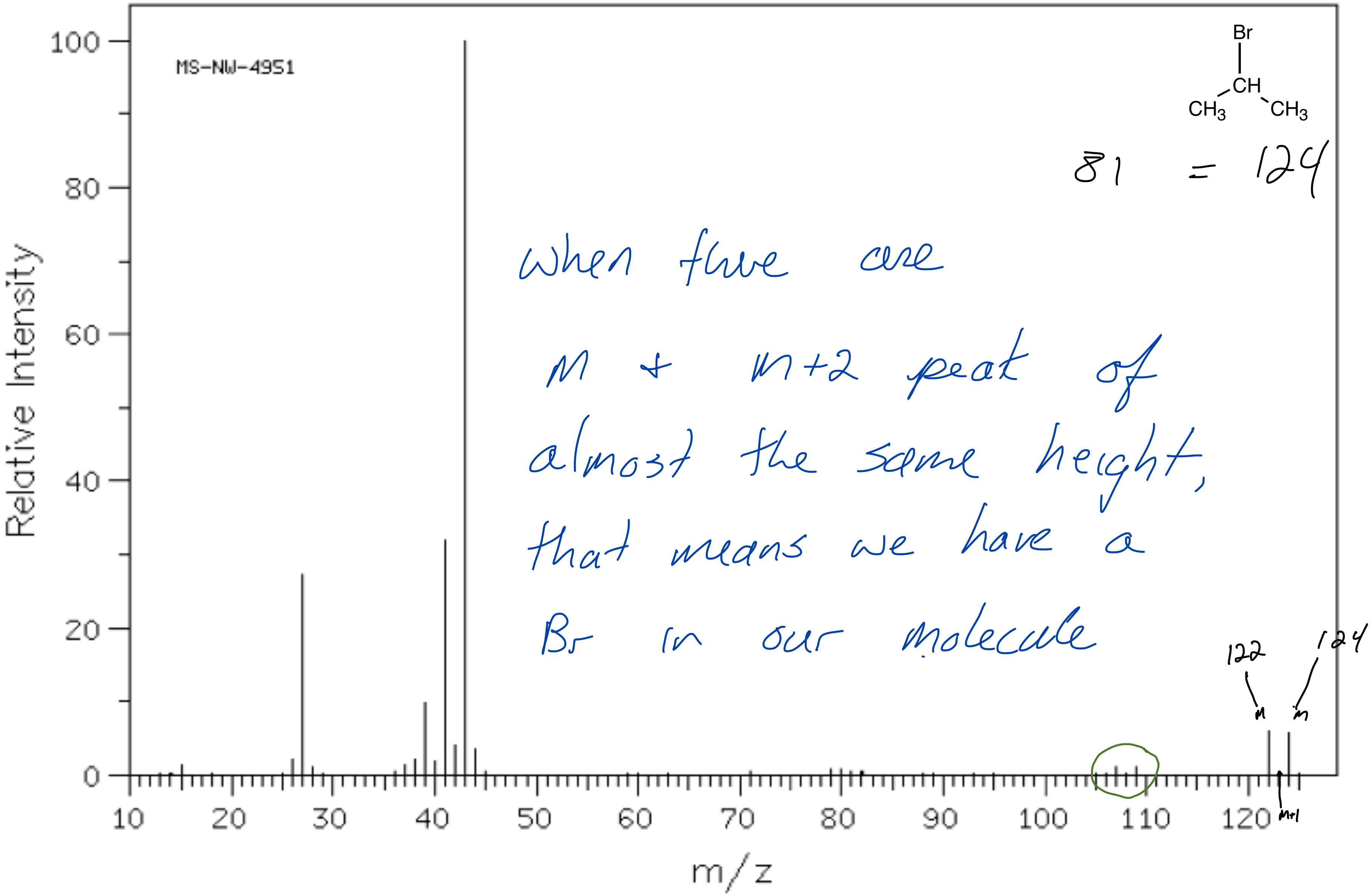
^{79}Br and ^{81}Br

ave mass 79.908 g/mol

1 : 1 m : m+2 means a Br atom is present

Bromine Isotopes in MS

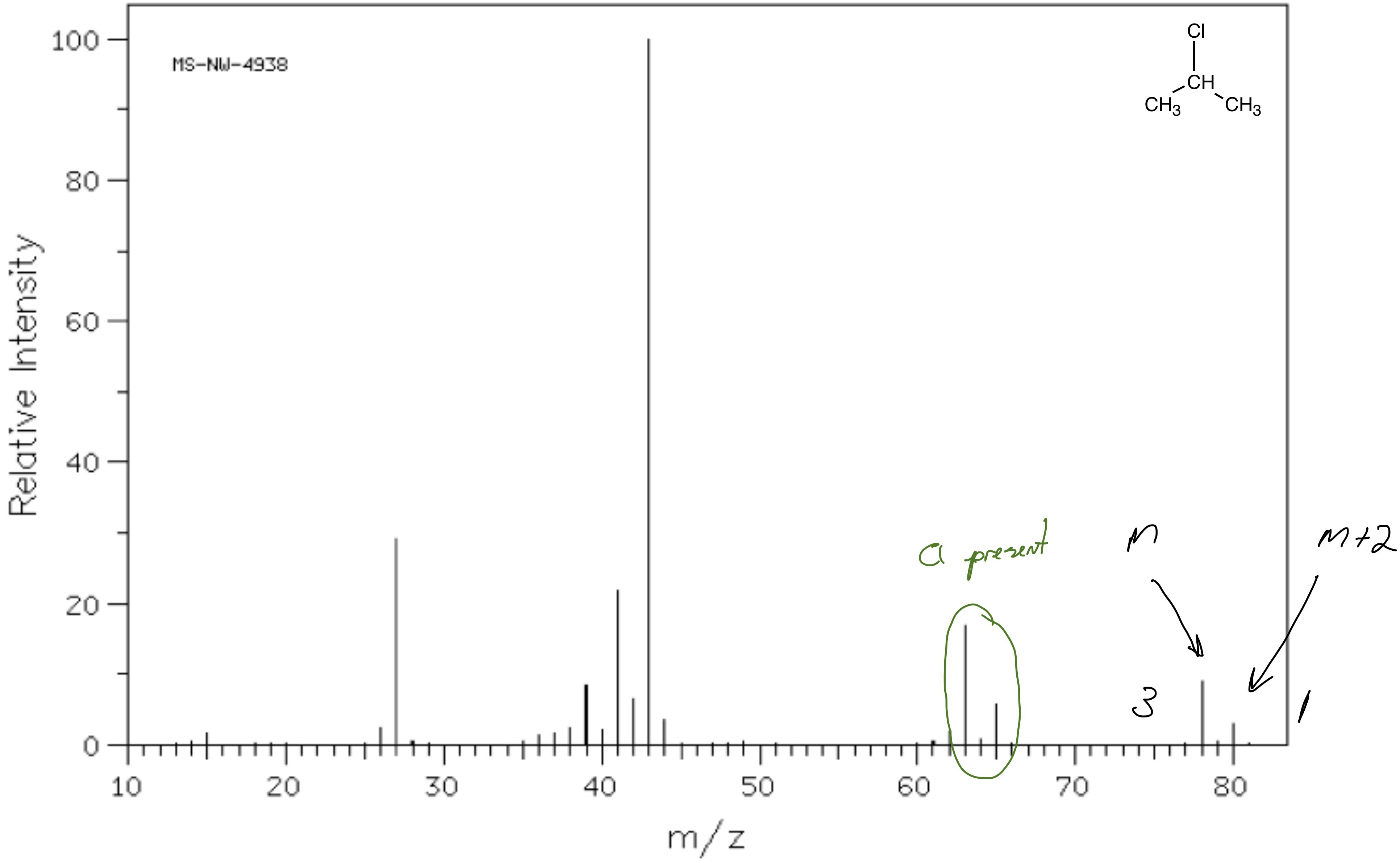
3 × 12 = 36
7 1 = 7
43 + 79 = 122
43 + 81 = 124



Chlorine Isotopes in MS

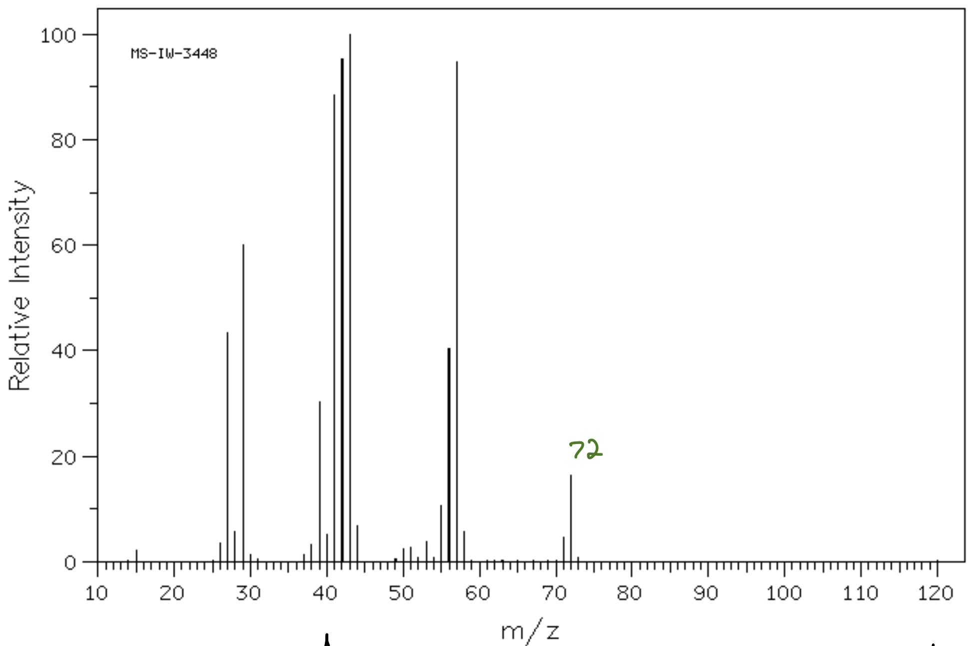
36 + 7 = 43 + 35 ⇒ 78

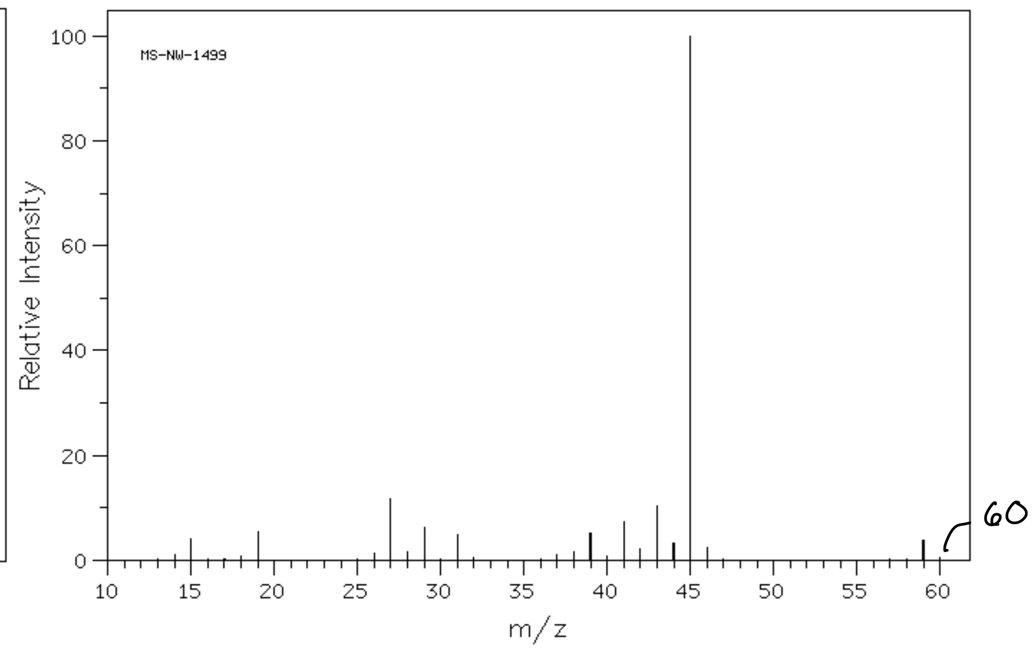
37 ⇒ 80



Formula from the "Rule of 13"

alcohol





CH how many CH units fit into 72

$m/z = 72$

$72 \div 13 = 5 \text{ r } 7$ ($72 - 65 = 7$)

$C_5H_{5+7} = C_5H_{12}$

$60 \div 13 = 4 \text{ r } 8$ ($60 - 52 = 8$)

$C_4H_{4+8} \Rightarrow C_4H_{12} \Rightarrow C_3H_8O$

O = 16 make "room" by removing 1C + 4H's

Using the Rule of 13

Determine the number of CH units that can fit into the molcular ion

The base formula is $C_{\frac{M}{13}} H_{\left(\frac{M}{13} + r\right)}$ where m/13 is a whole number and r is the remainder

$13 \overline{)\text{mass of peak}} = \frac{M}{13}$

If other elements are present, remove C's + H's to make room.

Start with the "Price is Right" rules; that is, remove C atoms to get as close as possible and then remove H atoms to finish. If not enough H's present remove C atoms to make room and add H's back in to account for the overage.

CH

C_7H_{14}

Practice

m/z =98 (only C and H)

$13 \overline{)98}$ = 7 r 7
91
—
7

m/z = 100 (one O atom)

$13 \overline{)100}$ = 7 r 9
91
—
9

$C_7H_{16} \Rightarrow C_6H_{12}O$

16 = 1 C + 4 H

1 Cl + 1 H = 36

m/z = 78 (contains Cl)

$13 \overline{)78}$ = 6
78
—
0

$C_6H_6 \Rightarrow C_3H_7Cl$

35
2×12 = 24
—
11

remove 2 C atoms and 11 H ?!

3×12 = 36 remove 3 C atoms is 1 amu too much so add back + 1 H

High Resolution Mass Spectrometry

Using exact isotopic masses to determine formulae

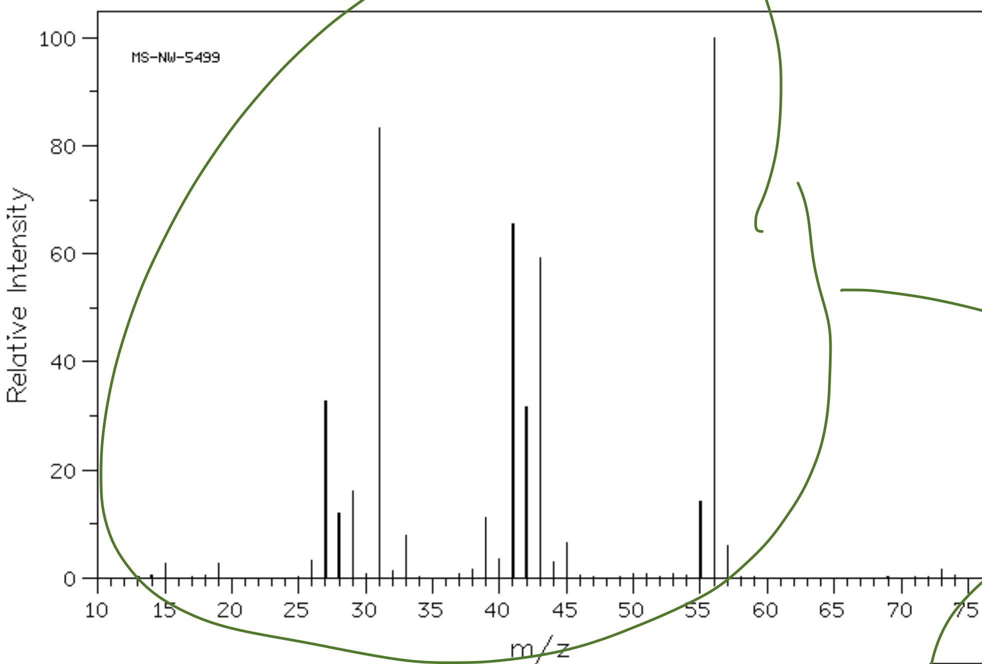
C_9H_{14}	$C_7H_{10}N_2$	$C_8H_{10}O$	$C_7H_6O_2$	$C_4H_{10}O_4$	$C_4H_{10}S_2$
122.1096 u	122.0845 u	122.0732 u	122.0368 u	122.0579 u	122.0225 u

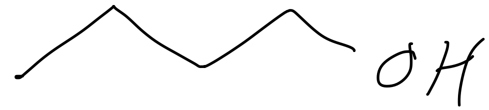
Based on an exact mass a computer can determine the formula by brute force

CH_3OCH_3	CH_3CH_2OH
Exact Mass: 46.0419	Exact Mass: 46.0419

high resolution mass spectrometry cannot tell isomers appart just by determing the formula

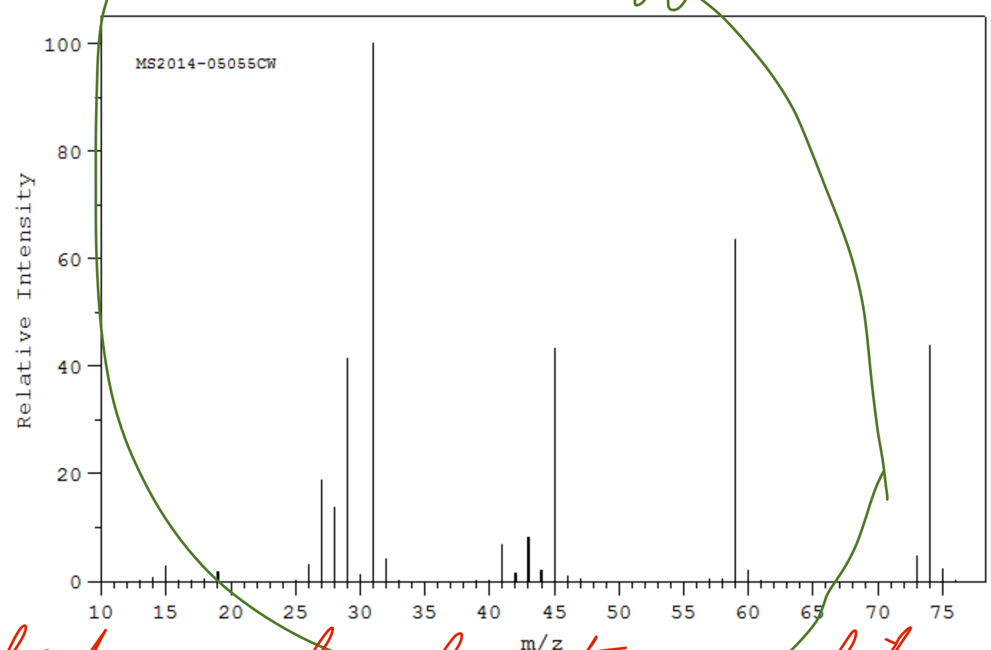
1-butanol





Fragmentation patterns are different

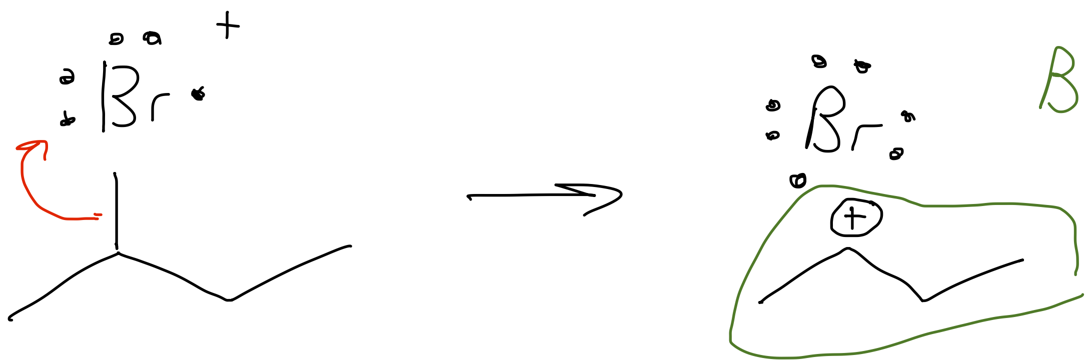
ethoxy ethane



collect data at a standard setting and computer can match molecule to a library

Heterolytic Cleavage Occurs Between α-Carbon and Heteroatom

e^-'s in bond are not distributed evenly

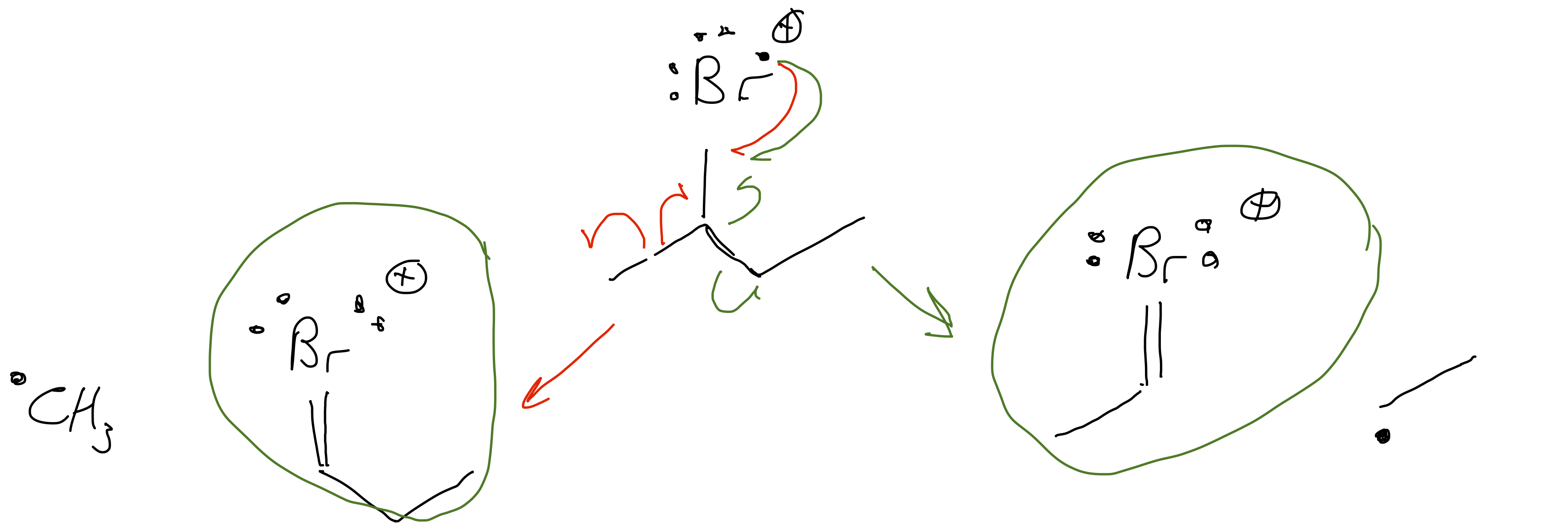


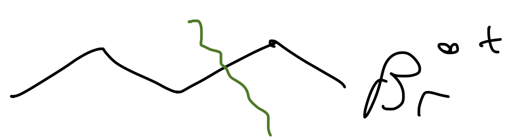
Br is better off because it isn't a cation anymore

The α-C to heteroatom (O, Cl, Br) bond breaks and both e^-'s go to the heteroatom.

Homolytic Cleavage Occurs Between α-Carbon and β-Carbon

e⁻ in bond are distributed evenly





Fragmentation Patterns