Chemistry 5652

Spectroscopic Identification of Organic Compounds

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Text: **Introduction to Spectroscopy, Pavia, Lampman, Kriz**

Go to the web at: www.umsl.edu/~chickosj/

Open Chem 5652

What is the first thing we need to know to determining molecular structure?

Elemental Composition

Determination of Empirical Formula

a. How is empirical formula determined

Combustion Analysis

Example: Suppose 15.2 mg sample of an unknown compound was burned in an excess of oxygen to produce 43.0 mg CO_2 and 15.6 mg H_2O. What is a possible empirical formula?

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mass of H in H_2O 2/18 = 0.1111; mass of C in CO_2 12/44= 0.2727

0.1111*15.6 = 1.73 mg H;
0.2727*43.0 = 11.7 mg C
13.43 mg
15.2-13.43 = 1.77 mg O, S, N ?

Simplest ratio H: 1.73 mg/1mg/mmol = 1.73 mmol
C: 11.7 mg/12mg/mmol = 0.975 mmol
O: 1.77 mg/16 mg/mmol = 0.111 mmol

Which mmol value is best known?

C: 0.975/0.975 =	1.0	5.0	6.0	7.0	8.0	9.0
H: 1.74/0.975 =	1.78	8.92	10.7	12.5	14.2	16.0
O: 0.111/0.975 =	0.114	0.56	0.67	0.78	0.89	1.0

Empirical formula: $C_9H_{16}O$ or $C_{18}H_{32}S$

Possible molecular formulas: $C_{9n}H_{16n}O_n$ or $C_{18n}H_{32n}S$

where n = 1, 2, 3, ...

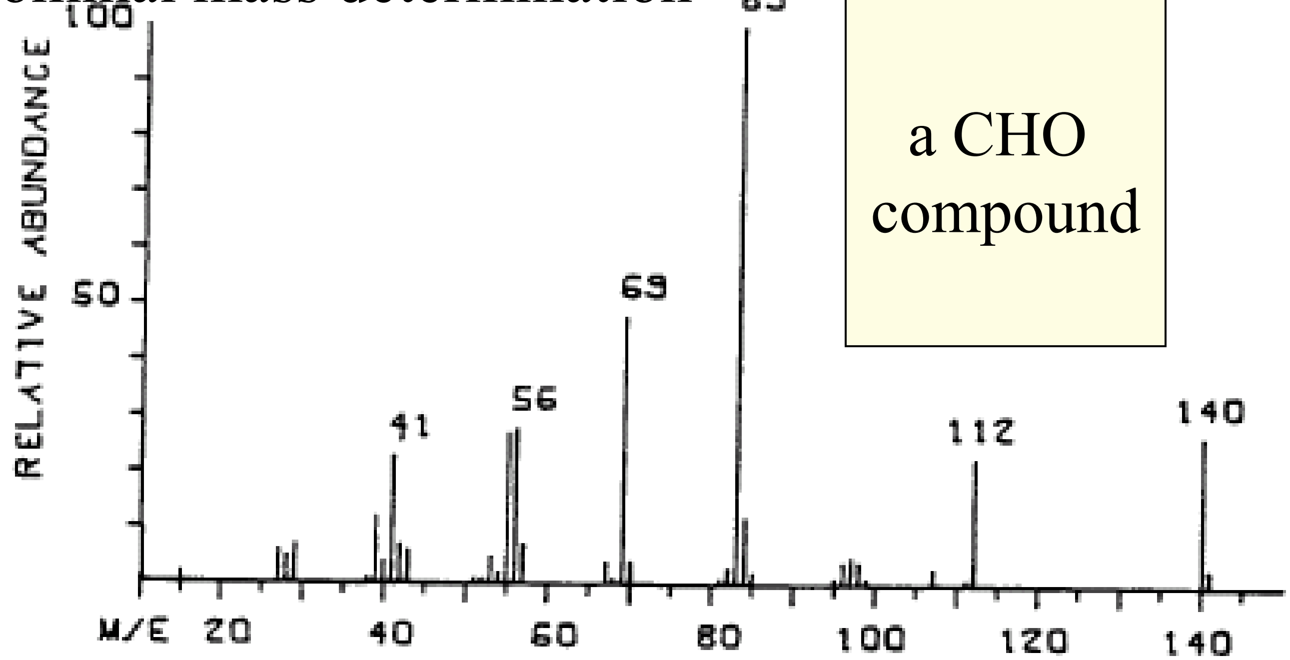
Determination of Molecular Formula

a. Nominal mass determination (combustion analysis coupled with: pH titration, freezing point depression, mass spectrometry)

b. Exact mass measurement

   Measurement of molecular formula and molecular weight is frequently accomplished by measuring the exact mass by mass spectrometry.

Nominal mass determination



a CHO compound

The nominal mass of a substance is 140. What is its molecular formula?

The rule of 13:

1. Divide the nominal mass by 13: 140/13 = 10.769; A hydrocarbon with this molecular weight would have 10 C atoms
2. Multiply the remainder by 13: 0.769*13 = 9.997 or 10; A hydrocarbon with this molecular weight would have (10+10) or 20 H
3. For every O subtract 16 (1C + 4 H or 16 H) = $C_9H_{16}O$; $C_8H_{12}O_2$;
4. $C_7H_8O_3$; $C_6H_4O_4$

Summary

Rule of 13

number of C = MW/13 (the digits before the decimal point)

number of H = (the number of C atoms plus 13*digits after the decimal)

Once determining the number of carbons and hydrogens, subtract

for each oxygen: 16 (1C+4H; 16 H)

for each sulfur   : 32 (2C+8H; 32 H)

for each nitrogen: 14 (C+2H, 14 H)

...

Exact Mass Measurements

Masses of Isotopes

Element	Atomic Weight	Isotope	Exact Mass
Hydrogen	1.0080	^{1}H	1.0080
		^{2}D	2.0141
Carbon	12.0111	^{12}C	12.000(std)
		^{13}C	13.0034
Oxygen	15.9994	^{16}O	15.9949
		^{17}O	16.9991
Nitrogen	14.0067	^{14}N	14.0031
		^{15}N	15.0001
Sulfur	32.064	^{32}S	31.9721
		^{33}S	32.9715
		^{34}S	33.9679
Phosphorus	30.974	^{31}P	30.9738
Fluorine	18.9984	^{19}F	18.9984
Chlorine	35.453	^{35}Cl	34.9689
		^{37}Cl	36.9659
Bromine	79.909	^{79}Br	78.9183
		^{81}Br	80.9163
Iodine	126.9045	^{127}I	126.9045

Periodic Table of the Elements

1 1IA 11A																	18 VIIIA 8A
1 H Hydrogen 1.0079	2 IIA 2A											13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	2 He Helium 4.00260
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.847	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.732	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [208.9824]	85 At Astatine 209.9871	86 Rn Radon 222.0176
87 Fr Francium 223.0197	88 Ra Radium 226.0254	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Uuq Ununquadium [289]	115 Uup Ununpentium unknown	116 Uuh Ununhexium [298]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

Lanthanide Series	57 La Lanthanum 138.9055	58 Ce Cerium 140.115	59 Pr Praseodymium 140.90765	60 Nd Neodymium 144.24	61 Pm Promethium 144.9127	62 Sm Samarium 150.36	63 Eu Europium 151.9655	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93032	68 Er Erbium 167.26	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.0278	90 Th Thorium 232.0381	91 Pa Protactinium 231.03588	92 U Uranium 238.0289	93 Np Neptunium 237.0482	94 Pu Plutonium 244.0642	95 Am Americium 243.0614	96 Cm Curium 247.0703	97 Bk Berkelium 247.0703	98 Cf Californium 251.0796	99 Es Einsteinium [254]	100 Fm Fermium 257.0951	101 Md Mendelevium 258.1	102 No Nobelium 259.1009	103 Lr Lawrencium [262]

Alkali Metal | Alkaline Earth | Transition Metal | Basic Metal | Semimetals | Nonmetals | Halogens | Noble Gas | Lanthanides | Actinides

Why is the atomic weight of C not exactly 12.000?

Carbon consists of two isotopes, ^{12}C (99 %) and ^{13}C (1%)

Remember atomic weight is defined as an weighted average of all isotopes

Exact Mass Measurements

What is exact mass? m

mass of a proton: $1.672623 * 10^{-24}$ g

mass of a neutron: $1.674927 * 10^{-24}$ g

mass of a deuteron: $3.3427 * 10^{-24}$ g

Avogadro's Number (AN): $6.0254 * 10^{23}$

Molar mass of $^{2}D = AN * m_D = 6.0254*10^{23} * 3.3427 *10^{-24}$ g

$= 2.0141$ g mol^{-1}

Carbon = 6 ^{2}D = $6*2.0141$ = 12.0846;

Carbon = 6(P +N) = 6(1.672623+1.674927)*0.60254 =12.1022

Exact mass of carbon = 12.0 Why the discrepancies?

$E = \Delta m\, C^2$

Where E is the energy given off from a mass discrepancy of m and C is the speed of light.

$E = 0.0846\ g \cdot (3 * 10^{10}\ cm\ sec^{-1})^2$

$E = g \cdot cm \cdot (sec^{-1})^2 \cdot cm$

$E = force \cdot distance$

stability. In Figure 2 this quantity B.E./A is plotted as a function of A. The maxima at certain values (e.g., 4, 12, etc.) reflect unusual stability for these values of A. Calculations of this type may be used to demonstrate that above bismuth, emission of alpha particles is exoergic. This accounts for alpha activity in the heavy elements.

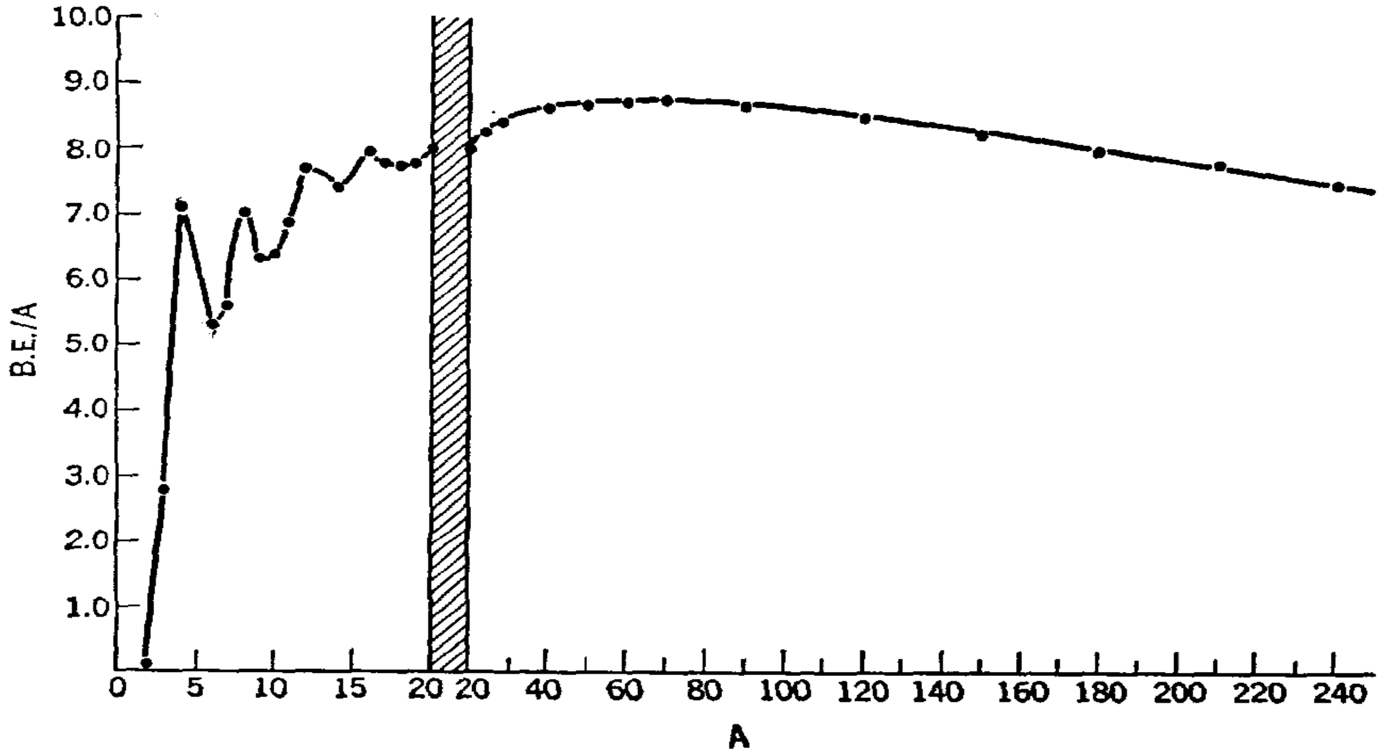


Figure 2. Plot of the binding energy per nucleon (Mev/nucleon) as a function of the mass number.

Using Exact Mass Measurements

Suppose you determined the exact mass of an ion by mass spectrometry to be 56.0376. Nominal mass 56

How can you figure out all the possible formulas that add to 56?

First use the Rule of 13

Divide the nominal mass by thirteen; the number in front of the decimal is the number of carbons; multiply the number following the decimal by 13 and add it to the number of carbons; this equals the number of hydrogens.

a. To add an oxygen: remove a carbon and 4 hydrogens
b. To add a nitrogen: remove a carbon and 2 hydrogens
c. To add a sulfur: remove two carbons, 6 hydrogens; or 2 oxygens
d. …

Mass of 56

56/13 = 4.3076;   The number of carbons is 4

13*0. 3076 = 4; therefore the number of hydrogens is 4 + 4

Therefore the hydrocarbon formula is C_4H_8

Other possible molecular formulas are:

C_4H_8 - CH_4 = C_3H_4O

C_4H_8 - CH_2 = C_3H_6N X

C_4H_8 - $2CH_4$ = C_2O_2 ; C_4H_8 - $2CH_4$ = C_2S ;

C_4H_8 - $2CH_2$ = $C_2H_4N_2$

C_4H_8 - CH_4, CH_2 = C_2H_2NO X

C_4H_8 - $3CH_2$ = CH_2N_3 X

C_4H_8 - C = C_3H_{20} X

All compounds with an odd number of nitrogen atoms must have an odd molecular weight

C_4H_8 - CH_4, $2CH_2$ = CN_2O C_4H_8 - $4CH_2$ = N_4

The exact mass of an ion by mass spectrometry was determined to be 56.0376 amu

Nominal mass 56		exact mass
N_4	4*14.0031	56.0124
CN_2O	12.00+2*14.0031+ 15.9949	56.0011
CH_2N_3	…	56.0249
C_2O_2		55.9898
C_2H_2NO		56.0136
$C_2H_4N_2$		56.0375
C_3H_4O		56.0262
C_3H_6N		56.0501
C_4H_8		56.0626

Determining Molecular Formulas and Degree of Unsaturation

What is the degree of unsaturation of this compound?

$C_{19}H_{17}ClN_2O$ prazepam

Draw a structure of a compound with the same number of carbons and heteroatoms that contains no rings or double bonds; each carbon should have 4 bonds, each O should have 2 bonds each nitrogen should have three bonds …

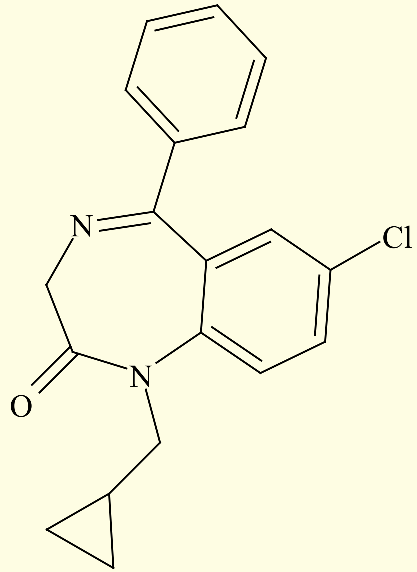
$NH_2CH_2CHOHCHClCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$

|

$H_2NCH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2$

Molecular formula is $C_{19}H_{41}ClN_2O$

$C_{19}H_{41}ClN_2O$ - $C_{19}H_{17}ClN_2O$ = 24/2 = 12 degrees of unsaturation


N
Cl
O
N

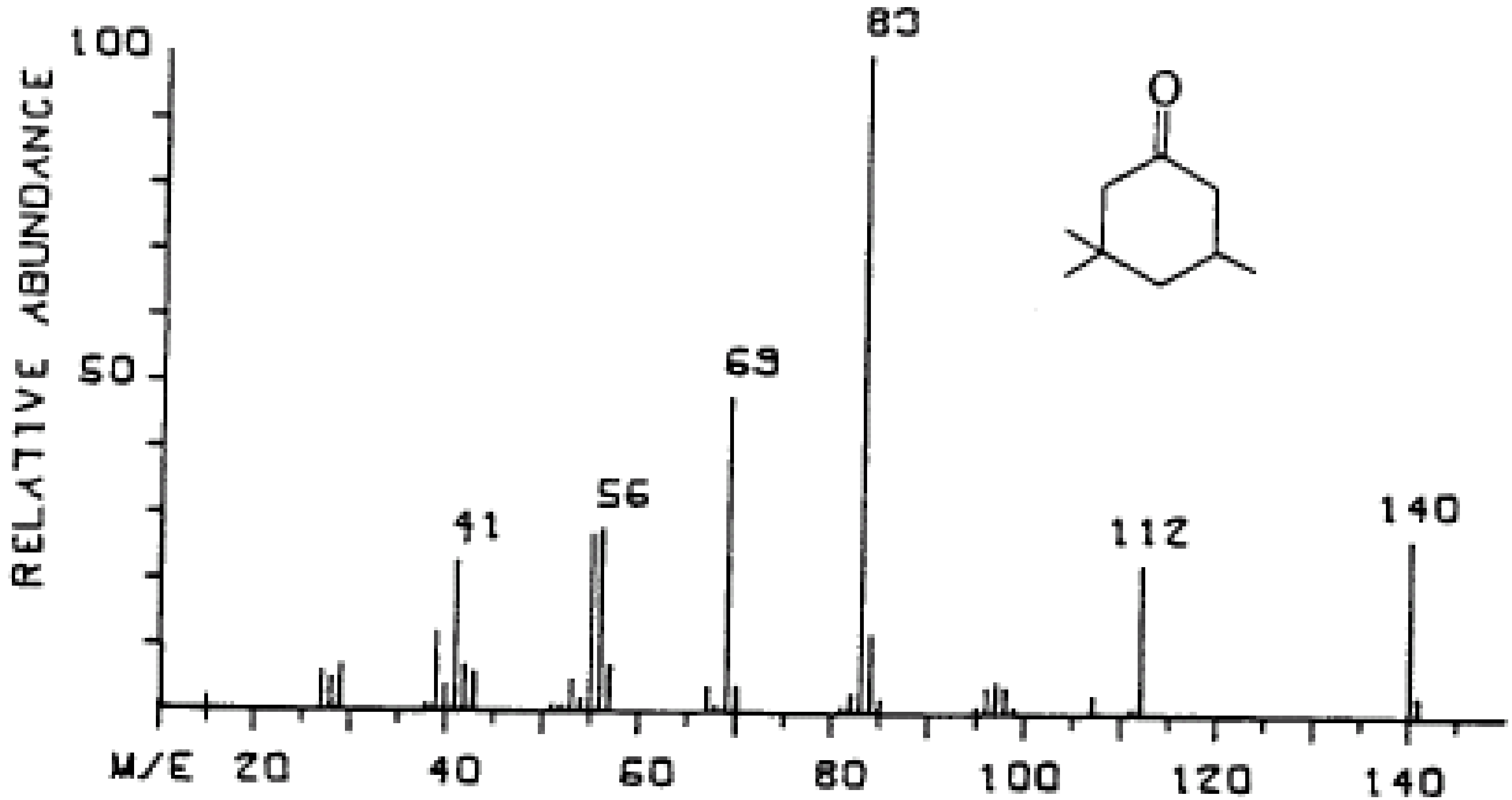


FIGURE 6-14 Mass spectrum of 3,3,5-trimethylcyclohexanone.

What is the origin of the small peak at m/e of 141

Table 2.1 Relative Isotope Abundances of Common Elements

Elements	Isotope	Relative Abundance	Isotope	Relative Abundance	Isotope	Relative Abundance
Carbon	^{12}C	100	^{13}C	1.11		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.20
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.10	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.40
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98.0
Iodine	^{127}I	100				

What is the origin of the peak at 141; called the P+1 peak

For a molecular formula of $C_9H_{16}O$, what's the probability of having 1 ^{13}C?

Probability is $(X+Y)^n$ where X and Y is the probability of having isotope ^{12}C and ^{13}C, respectively and n is the number of C atoms

$(^{12}C + {}^{13}C)^9$

1	n =0
1 1	n = 1
1 2 1	n = 2
1 3 3 1	n = 3
1 4 6 4 1	n = 4
1 5 10 10 5 1	n = 5
1 6 15 20 15 6 1	n = 6
1 7 21 35 35	n = 7
1 8 28 56 56	n = 8
1 9 36 84	n = 9

$(^{12}C)^9 + 9(^{12}C)^8(^{13}C) + 36(^{12}C)^7(^{13}C)^2$

All ^{12}C 1 ^{13}C 2 ^{13}C

$(0.989)^9 = 0.905$; $9(0.989)^8(0.011) = 0.091$; $36(0.989)^7(0.011)^2 = 0.004$

$(0.905/0.905)*100 = 100\%$ $(0.091/0.905)*100 = 10\%$ $(0.004/0.905)*100 = 0.45\%$

The parent ion is reported as 100 %

Then $(0.989)^9 = 100(0.905/0.905) = 100\ \%$

$9(0.989)^8(0.011) = 100(0.091/0.905) = 10.0\ \%$

$36(0.989)^7(0.011)^2 = 0.004/.905 = 0.45\ \%$

Including 1 oxygen: $^{17}O = 0.04$

$^{18}O = 0.2$

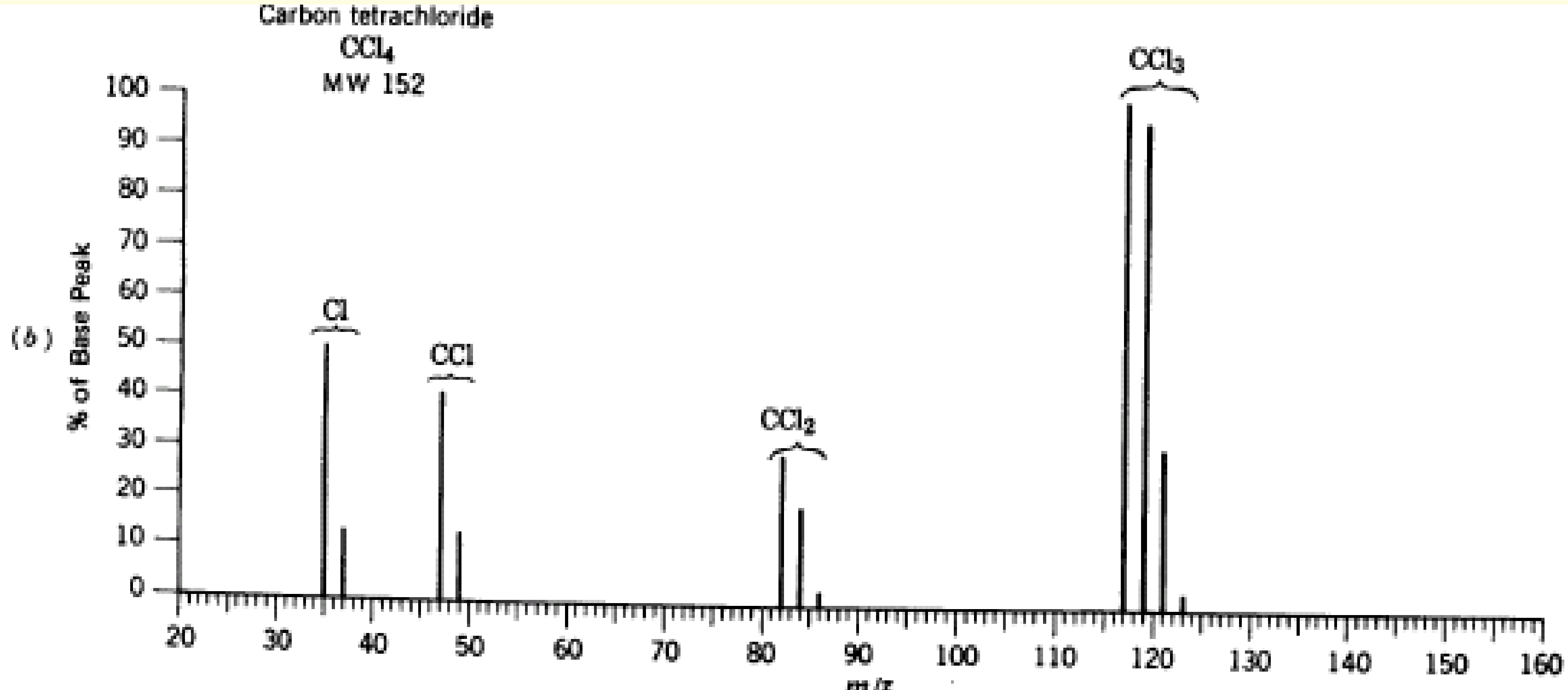
P = 100 %

P+1 = 10.04 %

P+2 = 0.65 %

The contribution of ^{2}H is pretty small

Electron impact mass spectrum of CCl_4



152-117 = 35

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Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.20
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.10	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.40
Chlorine	^{35}Cl	100			^{37}Cl	32.5
Bromine	^{79}Br	100			^{81}Br	98.0
Iodine	^{127}I	100				

100%/(100+32.5) = 0.7547 ^{35}Cl

1.0-7547 = .2452 ^{37}Cl

$(^{35}Cl + {}^{37}Cl)^3$

				1					
			1		1				n = 1
		1		2		1			n = 2
	1		3		3		1		n = 3
1		4		6		4		1	n = 4

$(0.7547)^3$	$3(0.7547)^2(0.2453)$	$3(0.7547)(0.2453)^2$	$(0.2453)^3$
0.43	0.419	0.136	0.0148
100%	97.5%	31.7%	3.4%

For CCl_4

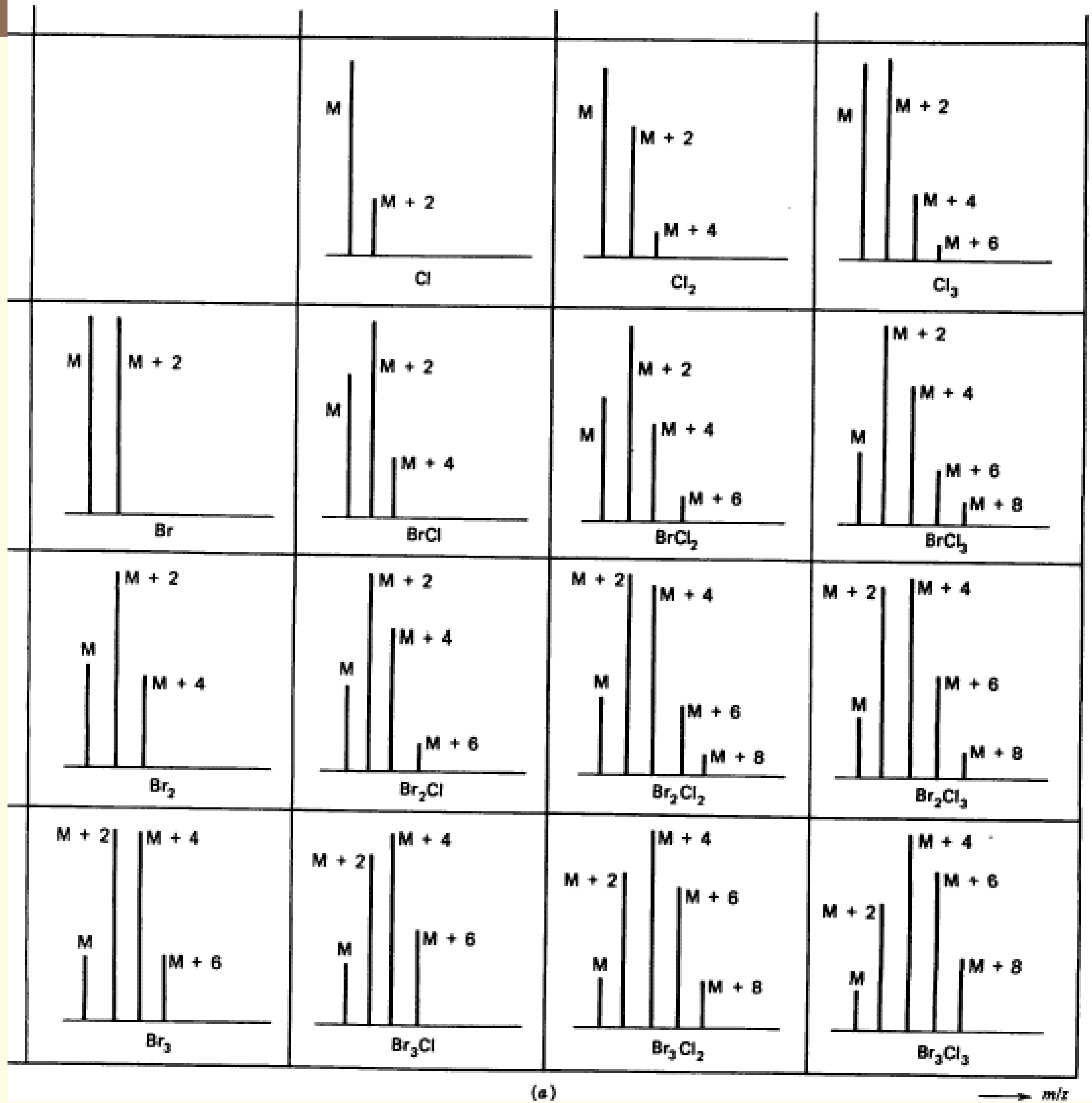
$(0.7547)^4$	$4(0.7547)^3(0.2453)$	$6(0.7547)^2(0.2453)^2$	$4(0.7547)(0.2453)^3$
0.324	0.4226	0.206	0.045
100%	130%	63.4%	13.7%

$(0.2453)^4$

0.0036

1.1%

What about other elements?



Organic Spectroscopy

Our knowledge of the universe has come about primarily as a result of our studies of how light interacts with matter

Unlike our macroscopic world in which things seem continuous, events occur at the atomic scale in discrete steps

Models

A More Extensive View of The Electromagnetic Spectrum