Molecular Formula

1

Some definitions:

Nominal mass:

Elements: The *integer mass/mass number* of the most abundant naturally occurring stable isotope.

Molecules: The sum of the nominal masses of the elements in its molecular formula

Molecular mass is the mass of a given molecule, it is measured in units of daltons (Da) or amu (u).
1 Da = 1 u = 1.660 538 782(83)×10^{-27} kg

Molar mass is the mass of one mole of a substance. Molar mass is closely related to the molecular weight or the relative molar mass. Measured in grams (g/mol).

Numerically molecular mass and molar mass are very close.

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Monoisotopic mass

The monoisotopic mass is the sum of the masses of the atoms in a molecule where mass of the principal (most abundant) isotope for each element is used in the calculation. For typical organic compounds this also results in the lightest isotope being selected.

For some heavier atoms the principle isotope is not the lightest isotope.

Ions made up of the principal isotopes of atoms making up the molecule.

Monoisotopic mass is typically expressed in atomic mass units (u), also called Daltons (Da).

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Determination of the molecular formula of a compound is fundamental to chemists and material scientists. Three steps involved;

1. Qualitative analysis (for elements)
   Na fusion followed by chemical tests
   Combustion followed by GC (quantification)

2. Quantitative analysis (to find the elemental composition)
   Empirical formula (= molecular formula, sometimes)

3. Molecular mass
   Vapor density (gaseous compounds)

$$P = \frac{w}{(MW)V}RT$$

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Cryoscopic methods

$$\Delta T = Km \qquad m = molality$$

$$\pi = iMRT \qquad M = molarity$$

$$i = \text{number of moles of solute particles}$$

Vapor pressure osmometry
Use of Rault's Law

Neutralization reactions (titrations)
for acids and bases

Mass Spectrometry
Molecular ion

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Mass spectrometry (MS) is an analytical technique that that can measure of the mass of a molecule. The molecule is ionized (parent ion) usually by EI. Often it yields a radical uni-positive ion (OE ionic species) and detected. The mass of the un-fragmented molecular ion is the mass of the molecule.

The parent ion composition could change for CI (EE molecular ion).

MS is also used as any other spectroscopic method to elucidate the chemical structures of molecules.

The MS principle consists of ionizing chemical compounds to generate charged molecules or molecular fragments and measurement of their mass/charge ratio.

(MS measures the masses of all isotopic combinations)

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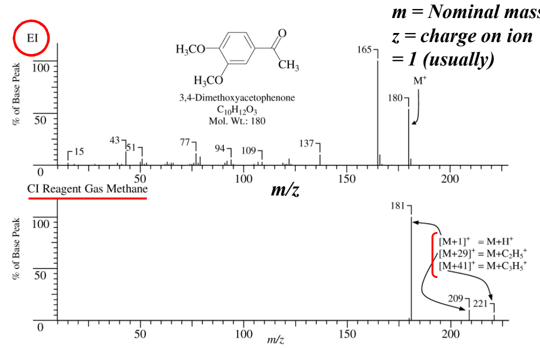
Molecular Mass to Molecular Formula



With the molecular mass, specially the mono-isotopic mass of the parent ion of the molecule in hand, a plausible molecular formula can be predicted.

These are available in tabulated form (e.g. Chapter 1 – Appendix A) and electronically.

http://library.med.utah.edu/masspec/elcomp.htm
http://www.colby.edu/chemistry/NMR/NMR.html

The electronic outputs must be accepted with caution. However they are extremely useful.

Fragment Finder.
Formula Finder

APPENDIX A FORMULA MASSES (FM) FOR VARIOUS COMBINATIONS OF CARBON, HYDROGEN, NITROGEN, AND OXYGEN[a]

	FM		FM		FM		FM
12		H_4N_2	32.0375	C_2H_6O	46.0419	CH_3N_2O	59.0246
C	12.0000	CH_4O	32.0262	**47**		CH_5N_3	59.0484
13		**33**		HNO_2	47.0007	$C_2H_3O_2$	59.0133
CH	13.0078	HO_2	32.9976	CH_3O_2	47.0133	C_2H_5NO	59.0371
14		H_3NO	33.0215	CH_5NO	47.0371	$C_2H_7N_2$	59.0610
N	14.0031	**34**		**48**		C_3H_7O	59.0497
CH_2	14.0157	H_2O_2	34.0054	[illegible]	[illegible]	C_3H_9N	59.0736
15		**38**		[illegible]	[illegible]	**60**	
HN	15.0109	C_3H_2	38.0157	[illegible]	[illegible]	CH_2NO_2	60.0085
CH_3	15.0235	**39**		CH_4O_2	48.0211	CH_4N_2O	60.0324
16		C_2HN	39.0109	**49**		CH_6N_3	60.0563
O	15.9949	C_3H_3	39.0235	H_3NO_2	49.0164	$C_2H_4O_2$	60.0211
H_2N	16.0187	**40**		**52**		C_2H_6NO	60.0450
CH_4	16.0313	C_2H_2N	40.0187	C_4H_4	52.0313	$C_2H_8N_2$	60.0688
17		C_3H_4	40.0313	**53**		C_3H_8O	60.0575
HO	17.0027	**41**		C_3H_3N	53.0266	C_5	60.0000
H_3N	17.0266	CHN_2	41.0140	C_4H_5	53.0391	**61**	
18		C_2H_3N	41.0266	**54**		CH_3NO_2	61.0164
H_2O	18.0106	C_3H_5	41.0391	$C_2H_2N_2$	54.0218	CH_5N_2O	61.0402
24		**42**		C_3H_2O	54.0106	CH_7N_3	61.0641
C_2	24.0000	N_3	42.0093	C_3H_4N	54.0344	$C_2H_5O_2$	61.0289
26		CNO	41.9980	C_4H_6	54.0470	C_2H_7NO	61.0528
CN	26.0031	CH_2N_2	42.0218	**55**		**62**	
C_2H_2	26.0157	C_2H_2O	42.0106	$C_2H_3N_2$	55.0297	CH_2O_3	62.0003
27		C_2H_4N	42.0344	C_3H_3O	55.0184	CH_4NO_2	62.0242
CHN	27.0109	C_3H_6	42.0470	C_3H_5N	55.0422	CH_6N_2O	62.0480
C_2H_3	27.0235	**43**		C_4H_7	55.0548	$C_2H_6O_2$	62.0368
28		HN_3	43.0170	**56**		**63**	
N_2	28.0062	CHNO	43.0058	C_2O_2	55.9898	HNO_3	62.9956

Nominal Mass → 60

Caution: With EI, in some cases, the highest mass peak in a mass spectrum is not the molecular ion. This is due to the instability of the high energy parent ion.

For example, alcohols sometimes give a parent peak that has a molar mass of M-18.

"Molar Mass Finder" provides a list of possible molecular ion molar masses from given fragment masses.

Molecular Property: Degree of Unsaturation, U

Also referred to as 'index of hydrogen deficiency, unsaturation index, double bond equivalents' is the number of pi bonds and rings in organic molecules and odd electron molecular ions. U is calculated from the *molecular formula*.

Structural feature	U
double bond	1
triple bond	2
ring	1

$$U = n + 1 - \frac{m - t}{2}$$

n = # of tetravalent atoms in formula
m = # monovalent atoms in formula
t = # trivalent atoms in formula

Example:

$C_8H_6ClNO_4$

$$U = n + 1 - \frac{m - t}{2}$$

$$U = 8 + 1 - \frac{7 - 1}{2} = 6$$

U<0 ; impossible combination for OE molecular ion/molecule, indicates O or N atom presence.

Fractional U vales are unlikely.

U is also a useful tool to ascertain whether a molecule is a odd or even electron molecular ion.

For EE molecular ions; calculate 'U' as above & subtract ½. 13

Nitrogen Rule (for molecules and OE molecular ions, $M^{+\bullet}$)

Nearly all molecules are ***even electron*** systems.

If the nominal mass is even, the compound contain an even number of N atoms; 0,2,4,6,…
If the nominal mass is odd, the compound contain an odd number of N atoms; 1,3,5,7,…

Nitrogen Rule (for EE molecular ions)

For EE precursor ions $(M+H)^+$, $(M+Na)^+$, $(M+Cl)^-$ etc; the N rule is;

if the nominal mass is odd, the compound contain an even number of N atoms; 0,2,4,6,…
If the nominal mass is even, the compound contain an odd number of N atoms; 1,3,5,7,… 14

Molecular Formula from The Rule of Thirteen

With ***nominal molecular mass***, (say from EI-MS; $M^{+\bullet}$) a *base formula* (algebraically valid and physically meaningful if compound contains C, H only) can be generated from the following relationship:

$$\frac{M}{13} = n + \frac{r}{13}$$

to give the base formula: C_nH_{n+r}

For this base formula, the U would be:

$$U = \frac{n - r + 2}{2}$$

Nominal mass = Mass of the fragment with lightest/abundant isotopes. 15

With the base formula in hand one can calculate the other possible molecular formulas that would correspond to the nominal molecular mass.

To obtain the other possible molecular formulae, add atoms and subtract an equivalent mass comprising of C and H atoms from the 'base formula'.

Element added	Subtract	ΔU	Element added	Subtract	ΔU
C	H_{12}	7	^{35}Cl	C_2H_{11}	3
H_{12}	C	-7	^{79}Br	C_6H_7; C_5H_{19}	-3; 4
O	CH_4	1	F	CH_7	2
N	CH_2	1/2	Si	C_2H_4	1
S	C_2H_8	2	P	C_2H_7	2
			I	C_9H_{19}; $C_{10}H_7$	0; 7

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Example:

If $M^{+\bullet}$ = 142 what are the possible molecular formulae.

a. only C and H are present

b. only C, H, and O are present

c. only C, H, and N, are present

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Calculate the base formula

n ↓ r ↓

Base formula: 142 / 13 = 10 + 12 / 13
$\mathbf{C_{10}H_{22}}$ with calculated U = 0

Some of other possible formula

add 1 C:
$C_{10}H_{22}$ + C - H_{12} = $\mathbf{C_{11}H_{10}}$
U =7 because ΔU=7

add 12 H:
$C_{10}H_{22}$ + H_{12} - C = C_9H_{34}
U = -7 because ΔU= -7
(impossible)

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add O:
$C_{10}H_{22}$ + O - CH_4 = $\mathbf{C_9H_{18}O}$
U = 1

add another O:
$C_9H_{18}O$ + O - CH_4 = $\mathbf{C_8H_{14}O_2}$
U = 2

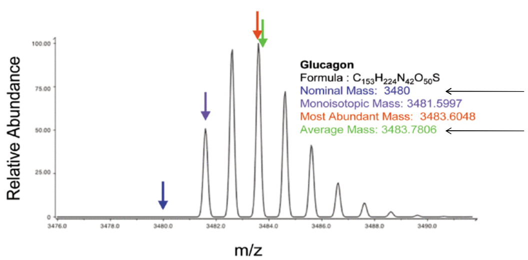
add another O:
$C_8H_{14}O_2$ + O - CH_4 = $\mathbf{C_7H_{10}O_3}$
U = 3

add another O:
$C_7H_{10}O_3$ + O - CH_4 = $\mathbf{C_6H_6O_4}$
U = 4
.
.

add N:
$C_{10}H_{22}$ + N - CH_2 = $C_9H_{20}N$
U = 0.5
(unlikely)

add another N:
$C_9H_{20}N$ - CH_2 = $\mathbf{C_8H_{18}N_2}$
U = 1

.
.
.



Isotope distribution of a very large molecule.

http://en.wikipedia.org/wiki/Image:Glucagon_mass.gif