Exact Masses and Molecular Formulae

Element	Atomic Weight	Nuclide	Mass	Relative Abundance
Hydrogen	1.00797	^{1}H	1.00783	100.0
		$D(^{2}H)$	2.01410	0.015
Carbon	12.01115	^{12}C	12.00000[b]	100.0
		^{13}C	13.00336	1.11
Nitrogen	14.0067	^{14}N	14.0031	100.0
		^{15}N	15.0001	0.37
Oxygen	15.9994	^{16}O	15.9949	100.0
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
Fluorine	18.9984	^{19}F	18.9984	100.0
Silicon	28.086	^{28}Si	27.9769	100.0
		^{29}Si	28.9765	5.06
		^{30}Si	29.9738	3.36
Phosphorus	30.974	^{31}P	30.9738	100.0
Sulfur	32.064	^{32}S	31.9721	100.0
		^{33}S	32.9715	0.79
		^{34}S	33.9679	4.43

^{12}C mass set to 12 amu, exactly.

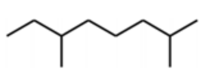
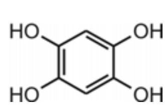
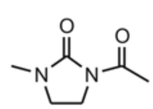
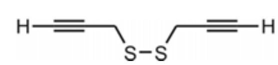
As a result, ^{1}H mass is actually higher than 1 amu.

And ^{16}O mass is lower than 16 amu.

Isotopes vary from unit masses by "mass defect".
^{1}H has positive mass defect; **^{16}O** has negative mass defect.

Exact Masses and Molecular Formulae

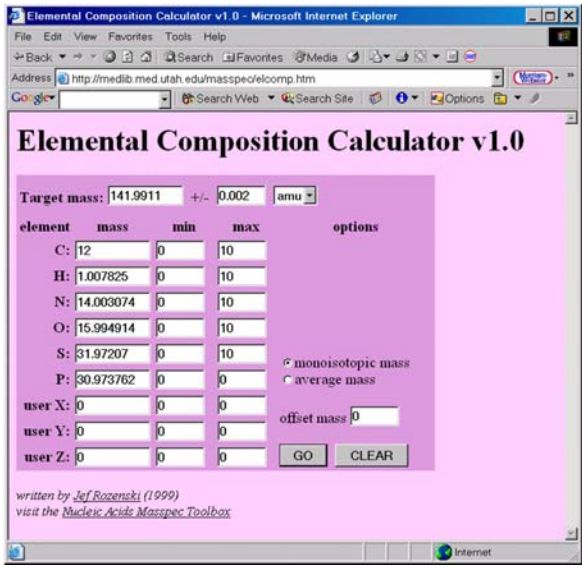
So, molecules with different molecular formulae have different exact masses.

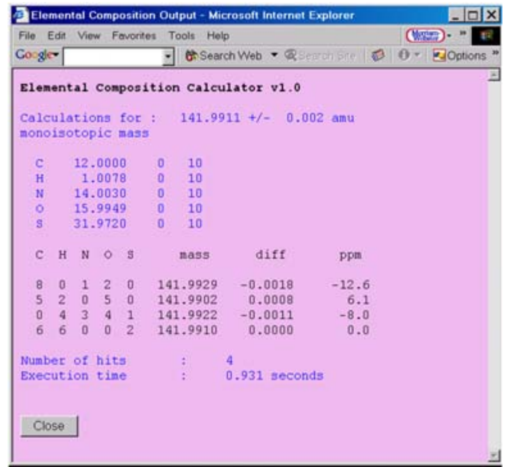
				
molecular formula	$C_{10}H_{22}$	$C_6H_6O_4$	$C_6H_{10}N_2O_2$	$C_6H_6S_2$
m/z (unit)	142	142	142	142
m/z (exact mass)	142.1723	142.0264	142.0743	141.9911

Exact Masses and Molecular Formulae

How to determine a molecular formula from an exact mass:

• Use a web-based calculator.





$C_6H_6S_2$ is closest match.

Isotopic Abundance and Peaks

- For nearly all elements, there are multiple isotopes with some natural abundance.
- Every atom in a molecule has a chance of being one of these isotopes. So, there will be some fraction of molecules that will be heavier than expected parent mass.

Element	*Nuclide*	*Mass*	*Relative Abundance*
Hydrogen	^{1}H	1.00783	100.0
	$D(^{2}H)$	2.01410	0.015
Carbon	^{12}C	12.00000^{b}	100.0
	^{13}C	13.00336	1.11
Nitrogen	^{14}N	14.0031	100.0
	^{15}N	15.0001	0.37
Oxygen	^{16}O	15.9949	100.0
	^{17}O	16.9991	0.04
	^{18}O	17.9992	0.20
Chlorine	^{35}Cl	34.9689	100.0
	^{37}Cl	36.9659	31.98
Bromine	^{79}Br	78.9183	100.0
	^{81}Br	80.9163	97.3
Iodine	^{127}I	126.9045	100.0

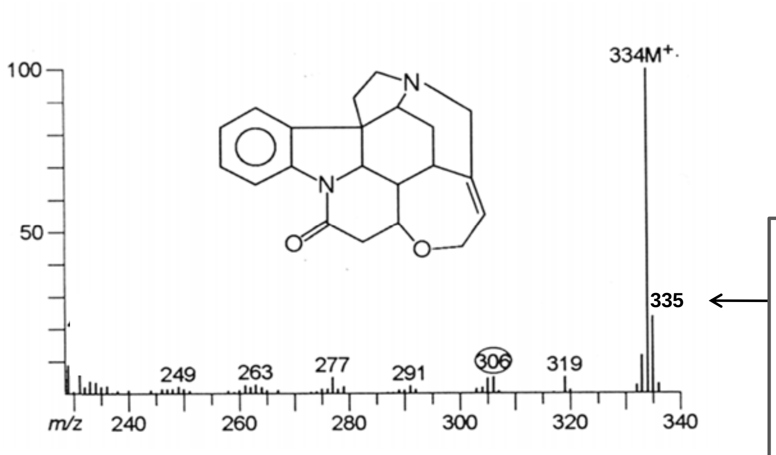
So, if a molecule has 50 carbon atoms, then there is ~50% chance it will be 1 amu heavier than expected.

If a molecule has 1 bromine atom, there is ~50% chance it will be 2 amu heavier than expected.

These differences are exhibited in peak intensities in mass spec.

Isotopic Series in Large Molecules

EI-MS of strychnine ($C_{21}H_{22}N_2O_2$, MW = 334):



Represents strychnine with one ^{13}C;

About 22% of molecules have one, so peak is 22% height of parent.