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.

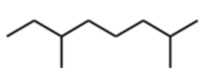
And ^{16}O mass is lower than 16 amu.

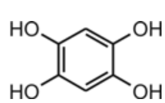
Isotopes vary from unit masses by “mass defect”.

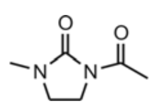
^{1}H has positive mass defect; **^{16}O** has negative mass defect.

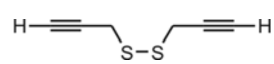
Exact Masses and Molecular Formulae

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

<u>How to determine a molecular formula from an exact mass:</u>

- Look up in a table, *or*

142

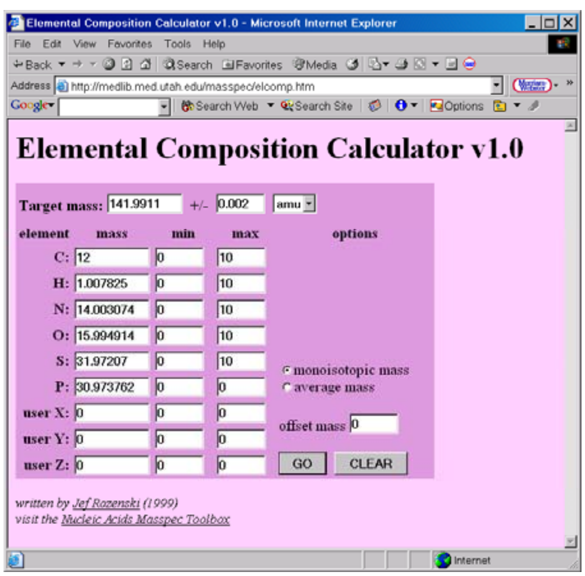
$C_4H_4N_3O_3$	142.0253	$C_7H_{12}NO_2$	142.0868
$C_4H_6N_4O_2$	142.0491	$C_7H_{14}N_2O$	142.1107
$C_5H_4NO_4$	142.0140	$C_7H_{16}N_3$	142.1346
$C_5H_6N_2O_3$	142.0379	$C_8H_{14}O_2$	142.0994
$C_5H_8N_3O_2$	142.0617	$C_8H_{16}NO$	142.1233
$C_5H_{10}N_4O$	142.0856	$C_8H_{18}N_2$	142.1471
$C_6H_6O_4$	142.0266	$C_9H_6N_2$	142.0532
$C_6H_8NO_3$	142.0504	$C_9H_{18}O$	142.1358
$C_6H_{10}N_2O_2$	142.0743	$C_9H_{20}N$	142.1597
$C_6H_{12}N_3O$	142.0981	$C_{10}H_8N$	142.0657
$C_6H_{14}N_4$	142.1220	$C_{10}H_{22}$	142.1722
$C_7H_{10}O_3$	142.0630	$C_{11}H_{10}$	142.0783

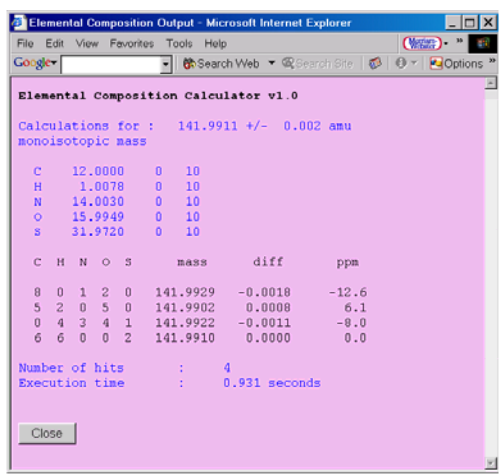
From R. M. Silverstein, F. X. Webster, *Spectrometric Identification of Organic Compounds* (Wiley, 1998), 6th ed.

Exact Masses and Molecular Formulae

<u>How to determine a molecular formula from an exact mass:</u>

- Look up in a table, *or*
- 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.

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Oxygen	15.9994	^{16}O	15.9949	100.0
		^{17}O	16.9991	0.04
		^{18}O	17.9992	0.20
Chlorine	35.453	^{35}Cl	34.9689	100.0
		^{37}Cl	36.9659	31.98
Bromine	79.909	^{79}Br	78.9183	100.0
		^{81}Br	80.9163	97.3
Iodine	126.904	^{127}I	126.9045	100.0

For some, isotope abundance is low.

For others, isotope abundance is high.

These differences are exhibited in peak intensities in mass spec.

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Iodine	126.904	^{127}I	126.9045	100.0

For some, isotope mass difference is 1.

For others, mass difference is >1.

These differences are exhibited as multiple peaks in mass spec.

Isotopic Abundance and Peaks

Atoms are nicknamed "A + *n*" in mass spec, based on most prevalent higher isotope mass.

Element	*Atomic Weight*	*Nuclide*	*Mass*	*Relative Abundance*
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		D(^{2}H)	2.01410	0.015
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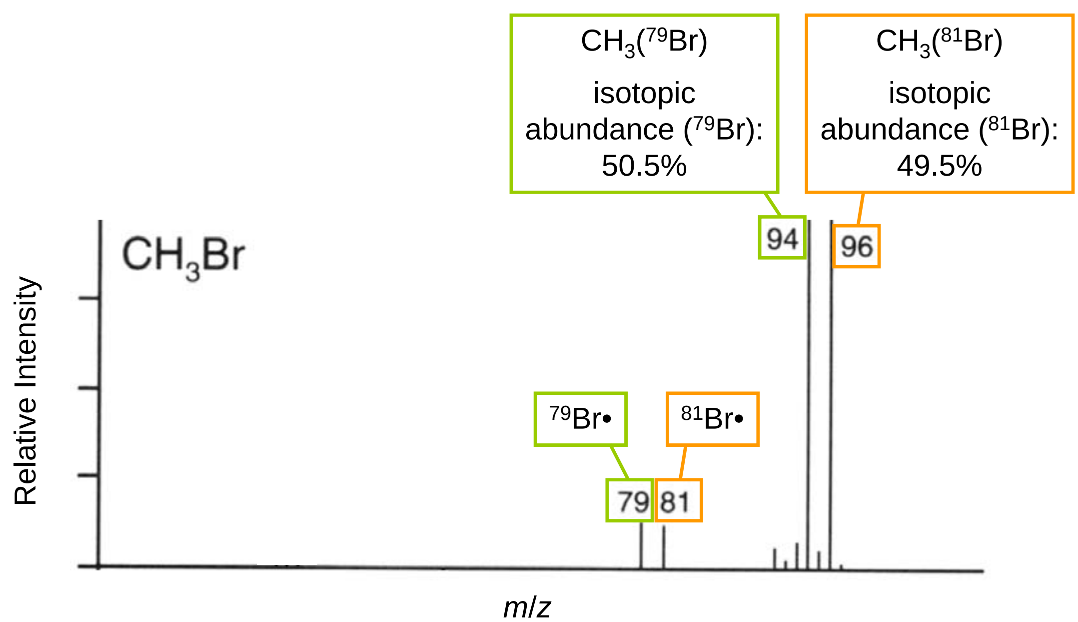
		^{81}Br	80.9163	97.3
Iodine	126.904	^{127}I	126.9045	100.0

H: "A + 1". Contributes to peak at M + 1 in MS.

Br: "A + 2". Contributes to peak at M + 2 in MS.

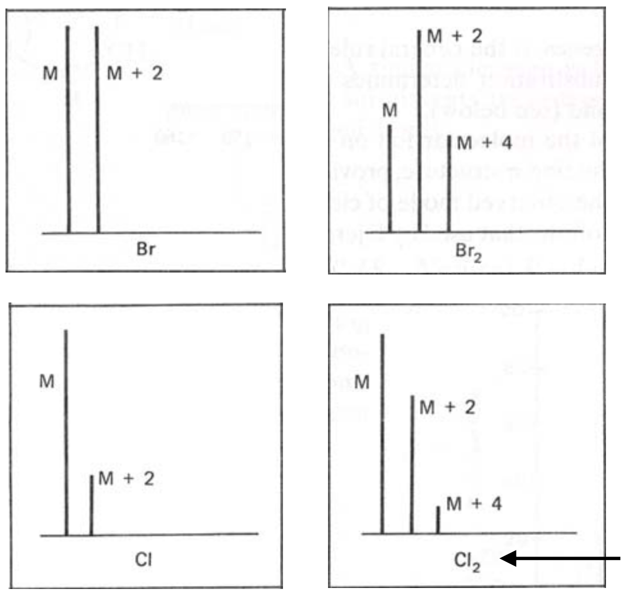
Isotopic Abundance and Peaks

A + *n* isotopes generate characteristic patterns in mass spectra.



Isotopic Abundance and Peaks

Halogen isotopes generate characteristic patterns in mass spectra.

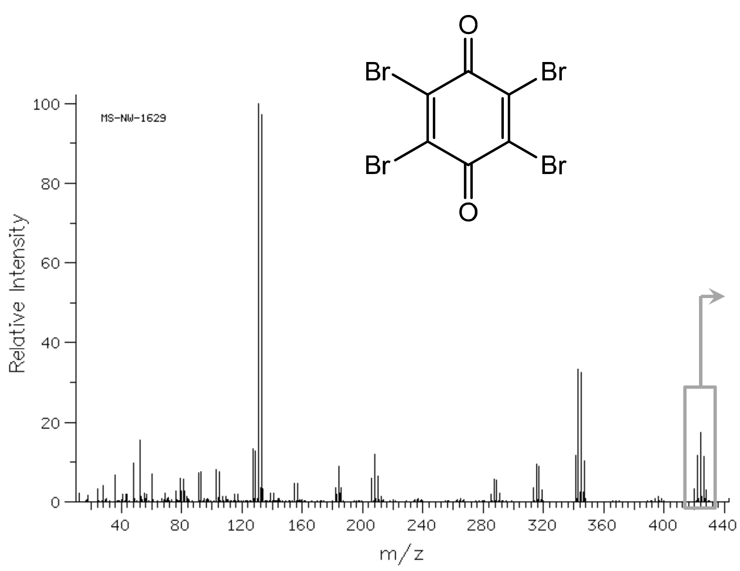


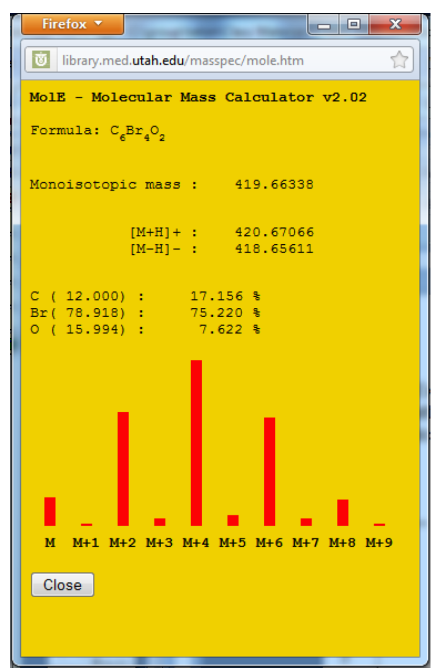
Pictures of these patterns available in textbook, Pretsch.

(Refers to two chlorines in any molecule, not just Cl_2.)

Isotopic Abundance and Peaks

Expected isotope patterns can also be calculated with online calculators.





Isotopic Abundance and Peaks

Though isotopic contributions of ^{13}C, ^{2}H to MS are small, they add up.

If, for a carbon-containing compound, peak A has intensity 100, then higher-mass peaks have intensity:

	(A + 1)	(A + 2)		(A + 1)	(A + 2)	(A + 3)
C_1	1.1	0.00	C_{16}	18	1.5	0.1
C_2	2.2	0.01	C_{17}	19	1.7	0.1
C_3	3.3	0.04	C_{18}	20	1.9	0.1
C_4	4.4	0.07	C_{19}	21	2.1	0.1
C_5	5.5	0.12	C_{20}	22	2.3	0.2
C_6	6.6	0.18	C_{22}	24	2.8	0.2
C_7	7.7	0.25	C_{24}	26	3.3	0.3
C_8	8.8	0.34	C_{26}	29	3.9	0.3
C_9	9.9	0.44	C_{28}	31	4.5	0.4
C_{10}	11.0	0.54	C_{30}	33	5.2	0.5
C_{11}	12.1	0.67	C_{35}	39	7.2	0.9
C_{12}	13.2	0.80	C_{40}	44	9.4	1.3
C_{13}	14.3	0.94	C_{50}	55	15	2.6
C_{14}	15.4	1.1	C_{60}	66	21	4.6
C_{15}	16.5	1.3	C_{100}	110	60	22

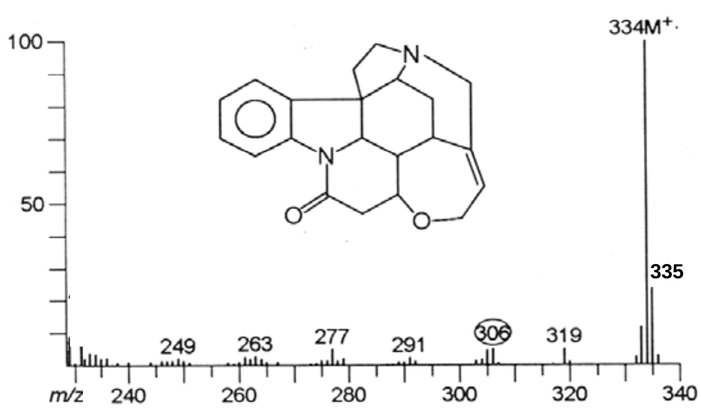
For each additional element present, add *per atom*:
(A + 1): N, 0.37; O, 0.04; Si, 5.1; S, 0.79.
(A + 2): O, 0.20; Si, 3.4; S, 4.4; Cl, 32.0; Br, 97.3.
Typical values for (A + 4): C_{25}, 0.02; C_{40}, 0.13; C_{100}, 5.7.

For a large enough number of carbons, M is no longer most intense peak.

McLafferty, F. W.; Turecek, F. *Interpretation of Mass Spectra.*

Isotopic Series in Large Molecules

For the EI-MS of strychnine ($C_{21}H_{22}N_2O_2$),
what should the intensity of (M + 1),
m/z = 335, be?



$P_{^{13}C} = 21(1.1\%)$

$P_{^{2}H} = 22(0.015\%)$

$P_{^{15}N} = 2(0.37\%)$

$P_{^{17}O} = 2(0.04\%)$

= **24%**