6.6: Exact Mass

Exact Mass. In most mass spectrometry experiments the nominal mass is used and the mass to charge ratio of an ion is rounded to the nearest whole number. High resolution instruments, including double focusing and FT-ICR mass spectrometers, are capable of determining the "exact mass" of an ion. This is useful for interpretation because each element has a slightly different mass defect. This "mass defect" is the difference between the mass of the isotope and the nominal mass (which is equivalent to the number of protons and neutrons).

Recall that the atomic mass scale is defined by carbon-12 with a mass of exactly $12.0000\,\text{u}$. The exact mass of a specific isotope is determined relative to ^{12}C by high resolution mass spectrometry (see Table $6.6.1$). High resolution mass spectrometry can distinguish compounds with the same nominal mass but different exact mass caused by different elemental composition.

For example, C_2H_6, CH_2O, and NO all have a nominal mass of 30 u. Because they have the same nominal mass, a mass spectrometer with unit mass resolution can not distinguish these three ions. However, the exact masses for $C_2H_6(30.04695039)$, $CH_2O(30.01056487)$ and NO^2 (29.99798882) are different and a high resolution mass spectrometer can distinguish these three compounds.

Table $6.6.1$ lists the exact mass for the most abundant isotopes of several common elements. The Isotope Distribution Calculator on the SIS website will also calculate the exact mass for any chemical formula. This is available online at: https://www.sisweb.com/mstools/isotope.htm

Table $6.6.1$: Adopted from DiFlippo, F.; et. al. Phys Rev Lett. 1994, 73, 1482 .

Element	Isotoope	Mass
H	^{1}H	1.007 825 031 6 (5)
	^{2}H	2.014 101 777 9 (5)
He	^{4}He	4.002 603 36
	^{3}He	3.016 0
C	^{12}C	12.000 000 000 0 (0)
	^{13}C	13.003 354 838 1 (10)
N	^{14}N	14.003 074 004 0 (12)
	^{15}N	15.000 108 897 7 (11)
O	^{16}O	15.994 914 619 5 (21)
	^{17}O	17.999 2
P	^{31}P	30.973 763 3
S	^{32}S	31.972 072 8
	^{34}S	33.967 9

Values in parentheses indicate error in last digit.

This section is only an introduction to the interpretation of mass spectra. A full analysis of fragmentation patterns is beyond the scope of this text but with practice interpretation becomes much easier. Several excellent references include McLafferty's book (35) and the ACOL book on mass spectrometry (36). These contain additional information on mass spectral interpretation and many more practice problems.