Structural analysis (CH-314)

Week 1

Problems and Solutions

Problem 1. Calculate the nominal and monoisotopic masses as well as the atomic weights of the following elements: a) iodine (I), b) oxygen (O), and c) lithium (Li).

Solution:

Iodine has only one stable isotope: ^{127}I (126.90447 Da, 100%). Therefore, its nominal mass is 127 Da and both monoisotopic and relative masses equal 126.90447 Da.

Oxygen has three stable isotopes: ^{16}O (15.99491 Da, 99.76%), ^{17}O (16.99913 Da, 0.04%), ^{18}O (17.99916 Da, 0.2%). The most abundant isotope is ^{16}O. Therefore, the nominal mass of oxygen is 16 Da and its monoisotopic mass is 15.99491 Da. The relative mass (atomic weight) equals $0.9976 \cdot 15.99491\ \mathrm{Da} + 0.0004 \cdot 16.99913\ \mathrm{Da} + 0.002 \cdot 17.99916\ \mathrm{Da} = 15.99932\ \mathrm{Da}$.

Lithium has two stable isotopes: ^{6}Li (6.01512 Da, 7.5%), ^{7}Li (7.016 Da, 92.5%). The most abundant isotope is ^{7}Li. Therefore, the nominal mass of lithium is 7 Da and its monoisotopic mass is 7.016 Da. The relative mass (atomic weight) equals $0.075 \cdot 6.01512\ \mathrm{Da} + 0.925 \cdot 7.016\ \mathrm{Da} = 6.94093\ \mathrm{Da}$.

Problem 2. Calculate the nominal and monoisotopic masses as well as the molecular weights of the following molecules: a) sodium iodide (NaI) and b) amino acid glycine ($C_2H_5NO_2$).

Solution:

Sodium has only one stable isotope: ^{23}Na (22.98976 Da, 100%). Therefore, its nominal mass is 23 Da and both monoisotopic and relative masses equal 22.98976 Da. The masses of iodine were calculated in Problem 1. Thus, the masses of NaI are calculated as follows: $23\ \mathrm{Da} + 127\ \mathrm{Da} = 150\ \mathrm{Da}$ (nominal), $22.98976\ \mathrm{Da} + 126.90447\ \mathrm{Da} = 149.89423\ \mathrm{Da}$ (both monoisotopic and average).

Hydrogen, carbon, and nitrogen have two stable isotopes each: ^{1}H (1.007825 Da, 99.985%) and ^{2}H (2.014101 Da, 0.015%), ^{12}C (12 Da, 98.89%) and ^{13}C (13.00335 Da, 1.11%), ^{14}N (14.00307 Da, 99.64%) and ^{15}N (15.00011 Da, 0.36%). The nominal masses are, thus, 1 Da, 12 Da, and 14 Da, respectively. The monoisotopic masses are 1.007825 Da, 12 Da, and 14.00307 Da, respectively. And the atomic weights are $0.99985 \cdot 1.007825\ \mathrm{Da} + 0.00015 \cdot 2.014101\ \mathrm{Da} = 1.007976\ \mathrm{Da}$, $0.9889 \cdot 12.0\ \mathrm{Da} + 0.0111 \cdot 13.00335\ \mathrm{Da} = 12.01114\ \mathrm{Da}$, $0.9964 \cdot 14.00307\ \mathrm{Da} + 0.0036 \cdot 15.00011\ \mathrm{Da} = 14.00666\ \mathrm{Da}$, respectively. The masses of oxygen were calculated in Problem 1. Thus, the masses of glycine are calculated as follows: $2 \cdot 12\ \mathrm{Da} + 5 \cdot 1\ \mathrm{Da} + 14\ \mathrm{Da} + 2 \cdot 16 = 75\ \mathrm{Da}$ (nominal), $2 \cdot 12.0\ \mathrm{Da} + 5 \cdot 1.007825\ \mathrm{Da} + 14.00307\ \mathrm{Da} + 2 \cdot 15.99491 = 75.032015\ \mathrm{Da}$ (monoisotopic), $2 \cdot 12.01114\ \mathrm{Da} + 5 \cdot 1.007976\ \mathrm{Da} + 14.00666\ \mathrm{Da} + 2 \cdot 15.99932 = 75.06746\ \mathrm{Da}$ (average).

Problem 3. Consider various types of molecular ions that can be produced from aminobenzoic acid ($H_2N\text{-}C_6H_4\text{-}COOH$). Calculate their monoisotopic masses.

Solution:

Using the masses of all the elements (see Problem 1 and Problem 2) that aminobenzoic acid consists of, one can calculate the monoisotopic mass of neutral aminobenzoic acid: $7 \cdot 12.0\ \mathrm{Da} + 7 \cdot 1.007825\ \mathrm{Da} + 14.00307\ \mathrm{Da} + 2 \cdot 15.99491 = 137.047665\ \mathrm{Da}$. To calculate the masses of the open-shell ions, one adds or subtracts the mass of an electron (0.00054858 Da): 137.04821 Da (radical anion) and 137.04712 Da (radical cation). To calculate the masses of the closed-shell ions, one adds or subtracts the mass of a proton (1.007276 Da): 138.05494 Da (protonated) and 136.04039 Da (deprotonated).

Problem 4. Calculate the exact masses and the abundances of all hydrogen sulfide (H_2S) isotopologues (consider only the naturally occurring isotopes).

Solution:

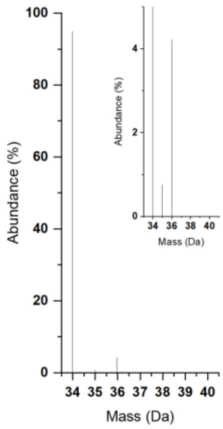
Hydrogen has two natural isotopes: ^1H (1.007825 Da, 99.985%) and ^2H (2.014101 Da, 0.015%), and sulfur has four natural isotopes: ^{32}S (31.97207 Da, 95.0%), ^{33}S (32.97146 Da, 0.76%), ^{34}S (33.96786 Da, 4.22%), ^{36}S (35.96709 Da, 0.014%). First, consider separately isotopologues corresponding to hydrogen and to sulfur:

	Exact mass	Abundance
$^1H_2$	$2 \cdot 1.007825\ \mathrm{Da} = 2.01565\ \mathrm{Da}$	$0.99985^2 \approx 0.9997$
$^1H^2H$	$1.007825\ \mathrm{Da} + 2.014101\ \mathrm{Da} = 3.021926\ \mathrm{Da}$	$2 \cdot 0.99985 \cdot 0.00015 \approx 3 \cdot 10^{-4}$
$^2H_2$	$2 \cdot 2.014101\ \mathrm{Da} = 4.028202\ \mathrm{Da}$	$0.00015^2 = 2.25 \cdot 10^{-8}$

	Exact mass	Abundance
^{32}S	31.97207 Da	0.95
^{33}S	32.97146 Da	0.0076
^{34}S	33.96786 Da	0.0422
^{36}S	35.96709 Da	0.00014

Then, all the isotopologues of H_2S can be generated by combining a row from the left table with a row from the right table. Their exact masses and abundances are sums of the masses and products of the abundances of the constituents, respectively. Thus, one gets:

Isotopologue	Exact mass	Abundance
$^1H_2{}^{32}S$	$2.01565\ \mathrm{Da} + 31.97207\ \mathrm{Da} = 33.98772\ \mathrm{Da}$	$0.9997 \cdot 0.95 = 0.94972$
$^1H_2{}^{33}S$	$2.01565\ \mathrm{Da} + 32.97146\ \mathrm{Da} = 34.98711\ \mathrm{Da}$	$0.9997 \cdot 0.0076 = 0.0076$
$^1H_2{}^{34}S$	$2.01565\ \mathrm{Da} + 33.96786\ \mathrm{Da} = 35.98361\ \mathrm{Da}$	$0.9997 \cdot 0.0422 = 0.04219$
$^1H_2{}^{36}S$	$2.01565\ \mathrm{Da} + 35.96709\ \mathrm{Da} = 37.98274\ \mathrm{Da}$	$0.9997 \cdot 0.00014 = 0.00014$
$^1H^2H^{32}S$	$3.021926\ \mathrm{Da} + 31.97207\ \mathrm{Da} = 34.994\ \mathrm{Da}$	$3 \cdot 10^{-4} \cdot 0.95 = 0.00029$
$^1H^2H^{33}S$	$3.021926\ \mathrm{Da} + 32.97146\ \mathrm{Da} = 35.99339\ \mathrm{Da}$	$3 \cdot 10^{-4} \cdot 0.0076 = 2.3 \cdot 10^{-6}$
$^1H^2H^{34}S$	$3.021926\ \mathrm{Da} + 33.96786\ \mathrm{Da} = 36.98979\ \mathrm{Da}$	$3 \cdot 10^{-4} \cdot 0.0422 = 0.00001$
$^1H^2H^{36}S$	$3.021926\ \mathrm{Da} + 35.96709\ \mathrm{Da} = 38.98902\ \mathrm{Da}$	$3 \cdot 10^{-4} \cdot 0.00014 = 4.2 \cdot 10^{-8}$
$^2H_2{}^{32}S$	$4.028202\ \mathrm{Da} + 31.97207\ \mathrm{Da} = 36.00027\ \mathrm{Da}$	$2.25 \cdot 10^{-8} \cdot 0.95 = 2.1 \cdot 10^{-8}$
$^2H_2{}^{32}S$	$4.028202\ \mathrm{Da} + 32.97146\ \mathrm{Da} = 36.99966\ \mathrm{Da}$	$2.25 \cdot 10^{-8} \cdot 0.0076 = 1.7 \cdot 10^{-10}$
$^2H_2{}^{32}S$	$4.028202\ \mathrm{Da} + 33.96786\ \mathrm{Da} = 37.99606\ \mathrm{Da}$	$2.25 \cdot 10^{-8} \cdot 0.0422 = 9.5 \cdot 10^{-10}$
$^2H_2{}^{32}S$	$4.028202\ \mathrm{Da} + 35.96709\ \mathrm{Da} = 39.99529\ \mathrm{Da}$	$2.25 \cdot 10^{-8} \cdot 0.00014 = 3.1 \cdot 10^{-12}$

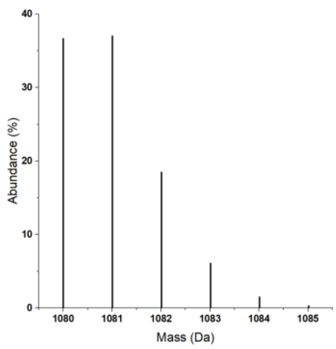


Note the second most intense peak is A+2, not A+1.

Problem 5. Calculate the abundances of the five lightest isotopologues (including the monoisotopic species) of the C_{90} fullerene.

Solution:

Carbon has two natural isotopes: ^{12}C (98.89%) and ^{13}C (1.11%). As the total number of carbon atoms in the molecule is 90, the abundances of the isotopologues are calculated as follows:



$$p(^{12}C_{90}) = 0.9889^{90} = 0.3662\ (36.6\%),$$

$p(^{12}C_{89}{}^{13}C) = 90 \cdot 0.9889^{89} \cdot 0.0111 = 0.3699\ (37.0\%)$,

$p(^{12}C_{88}{}^{13}C_2) = \frac{90 \cdot 89}{2} \cdot 0.9889^{88} \cdot 0.0111^2 = 0.1848\ (18.5\%)$,

$p(^{12}C_{87}{}^{13}C_3) = \frac{90 \cdot 89 \cdot 88}{2 \cdot 3} \cdot 0.9889^{87} \cdot 0.0111^3 = 0.0608\ (6.1\%)$,

$p(^{12}C_{86}{}^{13}C_4) = \frac{90 \cdot 89 \cdot 88 \cdot 87}{2 \cdot 3 \cdot 4} \cdot 0.9889^{86} \cdot 0.0111^4 = 0.0149\ (1.5\%)$.

Note that A+1 peak is already larger than A peak and that other peaks are quite noticeable.

Problem 6. For peptides, isotopic distribution is mainly due to ^{13}C. Estimate the minimum number of atoms that a peptide should contain for its A+1 peak to be the most abundant. And for its A+2 peak?

Solution:

Consider a molecule containing n carbon atoms (denote the abundance of ^{12}C by α). Then, the abundance of its A peak equals α^n. And the abundance of its A+1 peak equals $n \cdot \alpha^{n-1} \cdot (1-\alpha)$. For A+1 peak to be the most abundant the following inequality should hold: $n \cdot \alpha^{n-1} \cdot (1-\alpha) > \alpha^n$, which means that n should be greater than $\frac{\alpha}{1-\alpha}$. For carbon, $\alpha = 0.9889 \Rightarrow n > \frac{0.9889}{0.0111} = 89.1 \Rightarrow n_{min} = 90$ (which is consistent with the abundances calculated in Problem 5).

The abundance of A+2 peak equals $\frac{n \cdot (n-1)}{2} \cdot \alpha^{n-2} \cdot (1-\alpha)^2$. For A+2 peak to be the most abundant the following inequality should hold: $\frac{n \cdot (n-1)}{2} \cdot \alpha^{n-2} \cdot (1-\alpha)^2 > n \cdot \alpha^{n-1} \cdot (1-\alpha)$, which means that n should be greater than $\frac{2\alpha}{1-\alpha} + 1$. For carbon, one gets $n_{min} = 180$.

From the statistical analysis of the natural abundances of amino acids, it follows that an average amino acid contains about 5 carbon atoms, which means that A+1 peak becomes the most abundant for a 18 amino acid peptide and A+2 – for a 36 amino acid peptide.

Problem 7. There are two sulfur-containing standard amino acids, methionine and cysteine. Considering isotopic distribution only due to the isotopes of sulfur, estimate the minimum number of such residues that a peptide should contain for its A+2 peak to be the most abundant.

Solution:

Sulfur has four natural isotopes: ^{32}S (31.97207 Da, 95.0%), ^{33}S (32.97146 Da, 0.76%), ^{34}S (33.96786 Da, 4.22%), ^{36}S (35.96709 Da, 0.014%). If a molecule contains n sulfur atoms, the abundance of its A peak equals α_{32}^n, where α_{32} is the abundance of ^{32}S. For A+2 peak, there are two possible isotopologues: $^{32}S_{n-2}{}^{33}S_2$ and $^{32}S_{n-1}{}^{34}S_1$. Their abundances are $\frac{n \cdot (n-1)}{2} \cdot \alpha_{32}^{n-2} \cdot \alpha_{33}^2$ and $n \cdot \alpha_{32}^{n-1} \cdot \alpha_{34}$, respectively. For A+2 peak to be the most abundant, the following should hold:

$$\frac{n \cdot (n-1)}{2} \cdot \alpha_{32}^{n-2} \cdot \alpha_{33}^2 + n \cdot \alpha_{32}^{n-1} \cdot \alpha_{34} > \alpha_{32}^n$$

Taking into account the abundances of the isotopes of sulfur, one gets:

$$3.2 \cdot 10^{-5} \cdot n^2 + 0.0444 \cdot n > 1$$

For a peptide (n is relatively small), one may ignore the quadratic term in this equation and finally get $n > 22.5$, which means $n_{min} = 23$.

From the statistical analysis of the natural abundances of amino acids, it follows that an average amino acid contains about 0.04 sulfur atoms, which means that A+2 peak becomes the most abundant for a peptide containing more than 550 amino acids (this is already a protein, not a peptide).