Exercise Sheet 7 – Computational mass spectrometry
Introduction to mass spectrometry

1. Mass spectrometry (5.0 points)

a) Name the core components of a mass spectrometer and describe their function briefly (max 4 sentences). (3 points)

Ion source: ionizes and vapourizes the analytes into the vacuum of the mass spectrometer (e.g. electrospray or MALD)

Mass analyzer: induces differences in flight path of the ion dependent on their m/z ratio by e.g. deflecting them in a magnetic field or trapping them (orbitrap).

Detector: detects the current induced by the deflected ions or counts them.
Can be e.g. a Faraday cup, a microchannel plate or (for orbitraps) metal strips for ion current detection.

a) Explain concisely (in 2 sentences) what a mass spectrum is and what information it depicts. Use the following terms: *m/z*, intensity, peak(s). (2 point)

A mass spectrum is a plot of m/z vs intensity that plots the intensity of the signal detected by the mass spectrometer for each m/z value (often as a count of detected particles).

Peaks in the spectrum correspond to fragments of a certain mass at a given ionization level; depending on the resolution, peaks may be resolved into multiple subpeaks for each isotopic composition of the fragment.

2. Peptides, fragmentation, peaks and masses (10.0 points)

a) Write a small program/script/function (language of your choice) which calculates and returns all possible tryptic peptides for any protein sequence. The function may look similar to "String[] getTrypticPeptides(String proteinSequence)". Provide your source code and its output (as PDF at the end) and the number of peptides generated (fill in here) for the protein P00533-1. Download the protein sequence from UniProt.org. (4.0 points) You will re-use the source code in the next exercise.

Number of tryptic peptides: _82 peptides above 500 Da, 122 without a mass filter_

b) Write a small program/script/function (language of your choice) which calculates and returns the monoisotopic masses of all possible singly charged y- and b-fragment peaks with at least 7 significant figures for any given input peptide. The function may look similar to "double[] getFragmentMasses (String sequence)". Provide your source code and its output (as PDF at the end) and the output for the peptide "MAINHTGEK" (fill in table). (4.0 points) You will re-use the source code in the next exercise.

b+	m/z	AAS	m/z	y+
1	150.05879	M	1000.4885	9
2	221.0959	A	869.4480	8
3	334.1800	I	798.4108	7
4	448.2229	N	685.3268	6
5	585.2818	H	571.2839	5
6	686.3295	T	434.2250	4
7	743.3509	G	333.1773	3
8	872.3935	E	276.1558	2
9	1000.4885	K	147.1132	1

b) The first isotope (peak) of ethanol ($C_2H_5O_1H_1$) contains 1 additional neutron. Let's assume that the neutron is either incorporated in form of a heavy H (^2H) or heavy C (^{13}C). Assume you pick two molecules from the first isotope, one containing a single heavy H ($C_2H_5O_1{}^2H_1$) and the other containing

a single heavy C ($^{13}C_1C_1H_5O_1H_1$). The difference between the two molecules is which atom contains the additional neutron. With the information at hand, what do you expect the mass of $^{13}C_1C_1H_5O_1H_1$ to be in relation of $C_2H_5O_1{}^2H_1$? Smaller, equal or bigger? Explain your reasoning (1 sentence). (2.0 points)

☒ $^{13}C_1C_1H_5O_1H_1$ is lighter (smaller m/z) than $C_2H_5O_1{}^2H_1$

☐ $^{13}C_1C_1H_5O_1H_1$ is equal (same m/z) than $C_2H_5O_1{}^2H_1$

☐ $^{13}C_1C_1H_5O_1H_1$ is heavier (bigger m/z) than $C_2H_5O_1{}^2H_1$

Explanation:

The mass difference between 13C and 12C is 13.0033 - 12.0000 = 1.0033; the mass difference between deuterium and protonium is 2.0141 - 1.0078 = 1.0063.

~~We would expect the mass difference to be equal in ethanol, as the molecular environ~~ment does not significantly affect the nuclear binding energy.

Therefore, deuterated ethanol is heavier than ethanol substituted with 13C.