NAME _____

ID # _____

# INTERPRETATION OF ORGANIC SPECTRA (4361/8361)

## 9:05 – 9:55 am, December 10, 2012

## Exam 4

This exam is open book and open note. You are permitted to use any written materials you have brought as aids on this exam. You may also use a simple calculator. Other than this, please do not use any other electronic devices (cell phones, computers, recording devices, etc.) during the exam.

You may use pen or pencil. However, re-grades will be considered only for exams completed in pen.

Please write your answers in the boxes/spaces provided. If your answer is not in the appropriate space (say, for example, it's on the back of the page), draw us an arrow and/or note telling us where to look.

Feel free to remove the corner staple if this helps you analyze the spectra; you will have the opportunity to re-staple your exam at the end. You will be given 50 minutes total to finish the test. This exam contains <u>two</u> main problems, which are split into parts. Many of these parts can be answered independently. *Do not get stuck* on one part and then assume that you will be unable to answer the rest of the question—move on. In addition, partial credit will be given for incorrect but still plausible answers, so *guess* on problems you cannot answer perfectly.

At the end of the 50 minute exam period you will be asked to return your exam to the proctor. Please do not take any part of the exam packet with you when you are done; everything will be returned to you after the exams are graded. This packet should contain 7 pages, including this one. Please check to make sure that your packet contains 7 pages before beginning your exam.

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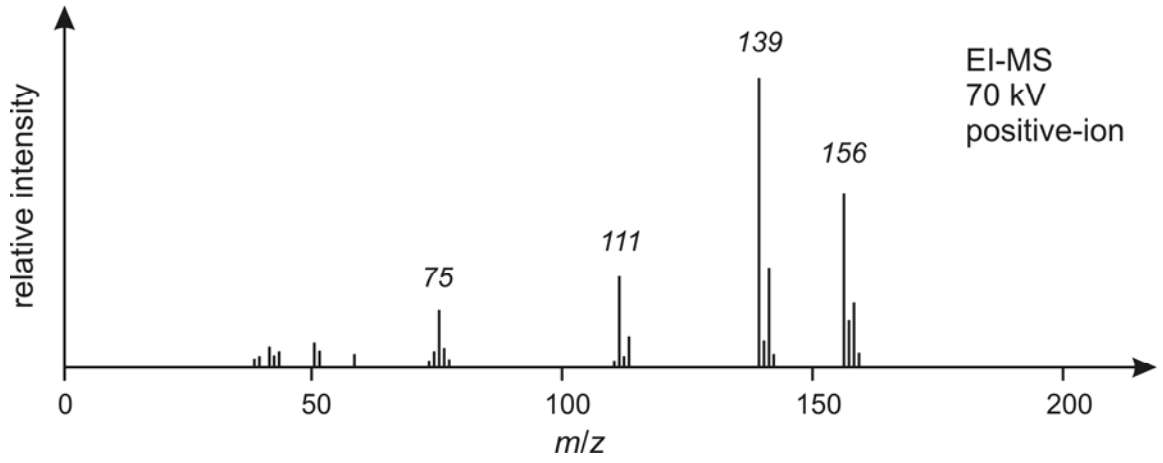
NAME _____

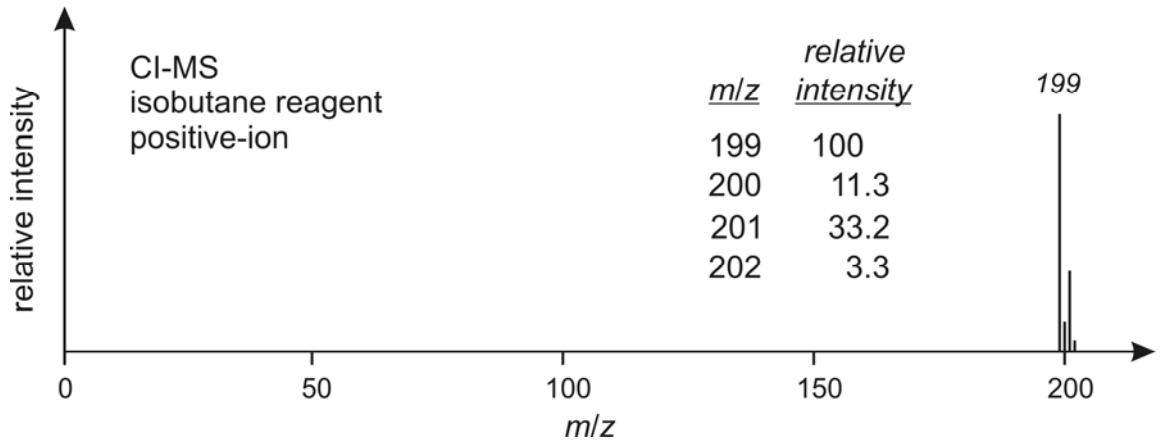
Scoring:

1. _____ / 10
2. _____ / 8
3. _____ / 24
4. _____ / 10
5. _____ / 8
6. _____ / 20
7. _____ / 20

**Total Score: _____ / 100**

The electron-ionization mass spectrum (EI-MS) and chemical-ionization mass spectrum (CI-MS) of an unknown molecule are shown below. (CI-MS was carried out because the parent ion was not observed in the EI-MS.) Problems 1-3 refer to these spectra.

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1. High-resolution mass spectrometry, yielded *m*/*z* = 199.0522 for the highest intensity peak in the CI-MS. When you plug this into an online mass calculator, it gives a molecular formula of $\mathbf{C_{10}H_{12}ClO_2}$ for this *m*/*z* = 199 ion.

   What are the most likely molecular formulae of the *m*/*z* = 200 and *m*/*z* = 201 ions? In each formula, give not only the atomic symbol for each element, but also the isotope number for any element that is not >90% abundant in nature. Also make sure to indicate the charge state of the ion.

   Example of answer format:

   *m*/*z* = 18: $CH_4(^2H)^+$

   *m*/*z* = 200:

   *m*/*z* = 201:

2. The odd-electron parent ion was not observed in the EI-MS, presumably because it fragmented before it could be detected. In the box on the right, propose a molecular structure for this odd-electron parent. Make sure you illustrate any unpaired electrons and charges in your structure.

3. In the boxes on the next page, draw mechanisms (using “electron pushing”) that explain the fragmentation of the odd-electron parent ion into fragment ions with *m*/*z* = 156, 111, and 75. In each box, use either the parent ion or one of the fragment ions you’ve already drawn as your starting material. (So, there is no need to draw the same fragmentation over and over again.)

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***m/z = 156***

***m/z = 111***

***m/z = 75***

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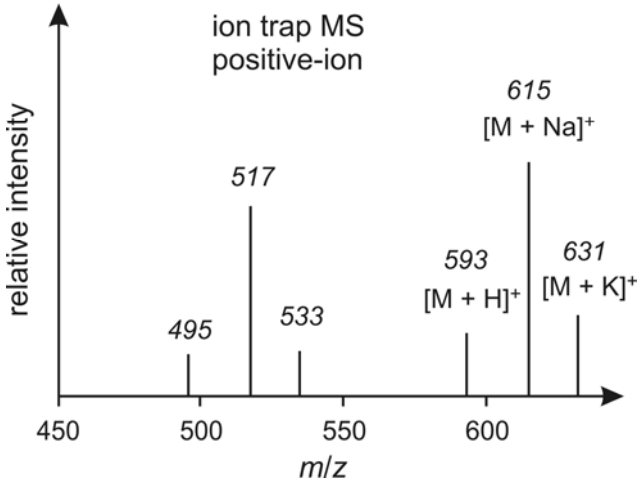
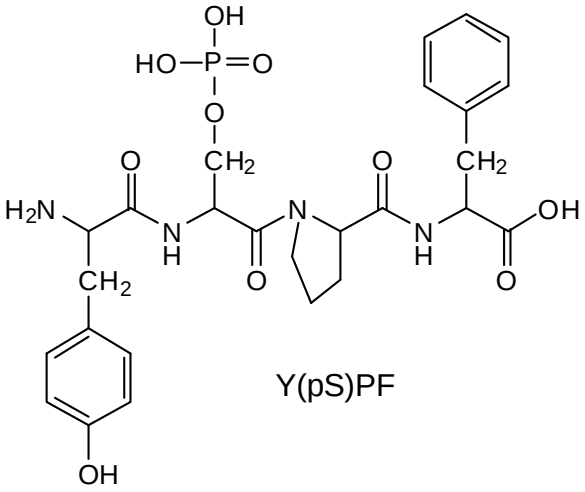
A small signaling peptide was extracted from a biological sample and subjected to positive-ion MS analysis in an ion-trap mass spectrometer; the mass spectrum of this pure peptide is shown below. The mass spectrum of the peptide showed two sets of three peaks; each set was assumed to correspond to $[M + H]^+$, $[M + Na]^+$, and $[M + K]^+$ ions. In Problems 4-7, you will try to use this and other MS data to determine whether the molecule is the phosphorylated peptide **Y(pS)PF**.




Y(pS)PF

4. The lower-mass set of peaks looks like it could arise from loss of $H_3PO_4$ from the parent (which is characteristic of phosphorylated peptides in MS). Draw a mechanism that shows how this fragmentation would yield an *m*/*z* = 517 fragment ion from the *m*/*z* = 615 parent. You do not need to draw the entire peptide; just draw the part involved in your mechanism.

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5. What is the molecular structure of the *m*/*z* = 517 ion?

6. The ions at *m*/*z* = 517 were selected and, in the ion-trap instrument, subjected to a tandem, MS/MS experiment via collision-induced dissociation (CID).

   a. What do ions encounter in the CID step?

   b. What happens to ions after they undergo CID?

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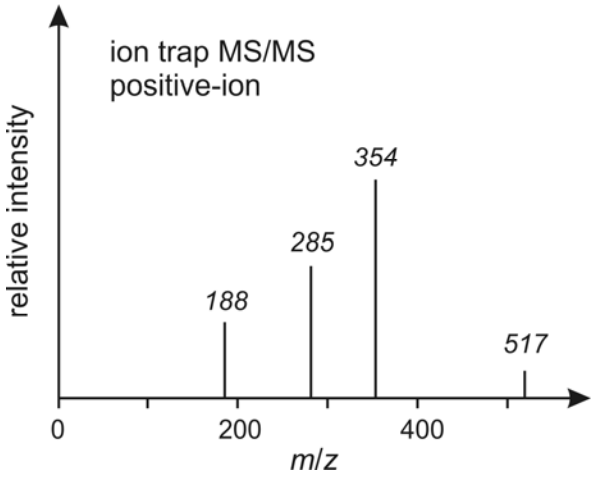
7. The resulting MS/MS spectrum of the selected *m*/*z* = 517 ions is shown at right.




What are the structures of the ions with *m*/*z* = 354 and 285? Make sure you illustrate any formal charge, and don't abbreviate any atoms other than carbon and hydrogen.

***m/z = 354***

***m/z = 285***

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