



Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

Schriftliche Prüfung 529-0041-00S Moderne MS Winter 2016

Vorname : _____ Name : _____

- Zeit: 60 Min. Teilen Sie sich Ihre Zeit gut ein.
Time: 60 min, organize your time carefully.
- Sie können auf Englisch oder Deutsch antworten
Answers are accepted in German or English.
- Es sind alle Hilfsmittel mit Ausnahme von Computern und Telekommunikation erlaubt.
It is allowed to use all resources except for computers and communication devices.
- Unleserliche Texte, unklare Formulierungen oder unsaubere Skizzen können nicht bewertet werden. Bitte bemühen Sie sich um eine saubere Darstellung.
Unreadable text, unclear formulations or graphs are not graded. Please try to use clear illustrations and descriptions
- Schreiben Sie jedes abzugebende Blatt einzeln mit Ihrem Namen und Vornamen an.
Label every page with name and surname.
- Dieses Deckblatt ist ausgefüllt abzugeben. Die Aufgabenstellung ist ebenfalls einzureichen.
Please fill in the first page. Hand in all pages including cover page and questions.
- Wir bitten Sie um Fairness und wünschen Ihnen viel Erfolg!
We ask you for fairness and wish you good luck!

Recently, a new cell design for achieving ultrahigh resolution FT-ICR mass measurements has been proposed (E. N. Nikolaev et al., J. Am. Soc. Mass Spectrom. 22 (2011), 1125). One key element of it is that instead of only a pair of excitation plus a pair of detection electrodes, the new design has multiple excite and detect electrodes arranged in a segmented fashion, as shown in **Figure 1**. In some cases, a mass resolution in excess of 40'000'000 has been reached with this new cell design, allowing so-called peak fine structure (**Figure 2**) to be measured.

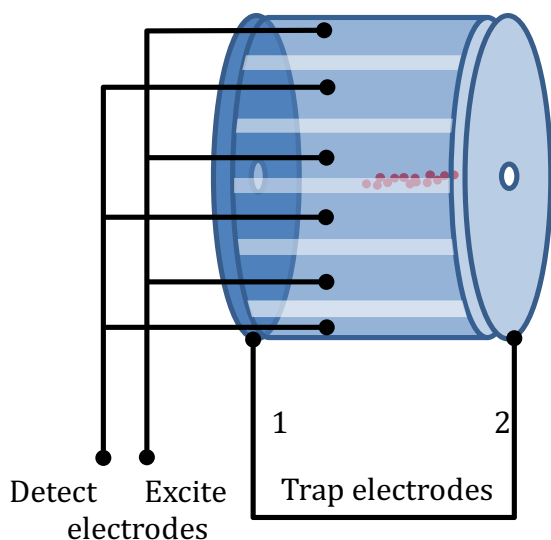
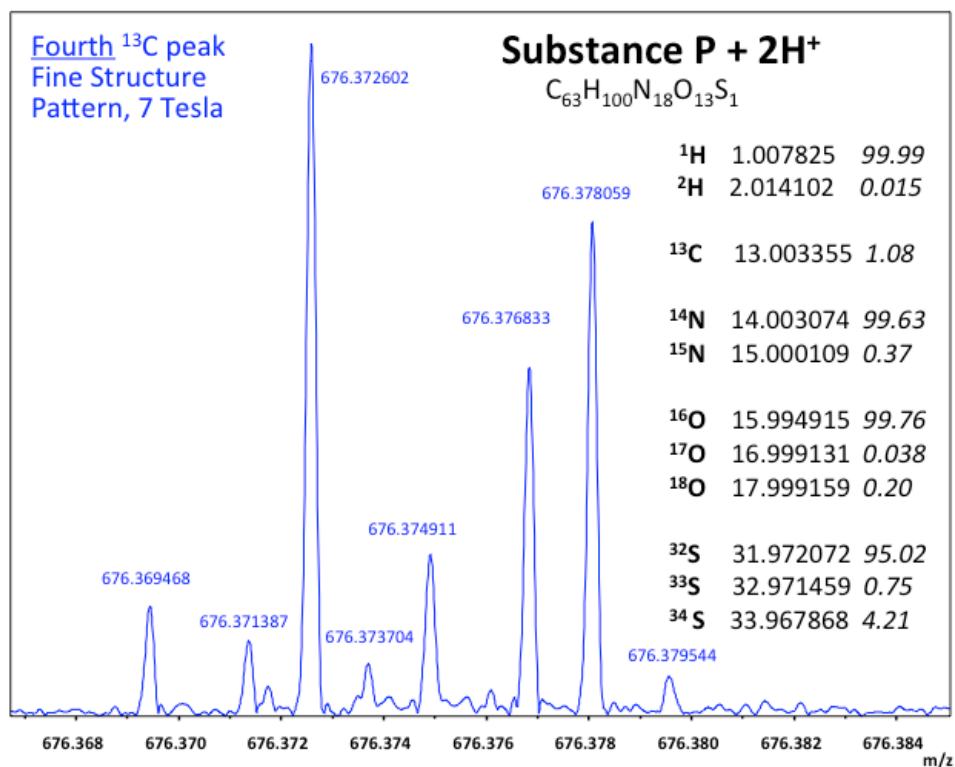


Figure 1 (left) Schematic of the new “dynamically harmonized” trap for ultrahigh resolution FTICR mass spectrometry.

Figure 2 (below) Fine structure of 4th ¹³C peak in the isotope distribution pattern of doubly protonated substance P. The inset (table) gives the exact atomic weights and relative abundance of all relevant isotopes.



Answer the following questions:

- a) Name some of the factors/problems that limit the obtainable mass resolution in FT-ICR. Which problem does the new cell design directly address?
- b) Which ionization method was probably used to produce the data for substance P shown in Figure 2?
- c) Why is ^{12}C missing in the table (inset) in Figure 2?
- d) Calculate the mass resolution of the data shown in Figure 2 using the FWHM of the peaks.
- e) The elemental composition of substance P is $\text{C}_{63}\text{H}_{98}\text{H}_{18}\text{O}_{13}\text{S}$; in Figure 2 one of the isotopic peaks in the isotope pattern of doubly protonated substance P ($\text{C}_{63}\text{H}_{100}\text{H}_{18}\text{O}_{13}\text{S}$) is shown. Explain why this peak fine structure shows up at $m/z \approx 676.375$, and roughly estimate the relative abundance of the highest sub-peak (676.372602 compared to the monoisotopic peak of substance P
- f) Determine the isotopic composition of three peaks of your choice in Figure 2. The labels above the signals are measured exact masses, not theoretical ones.