Chemistry 416 "Spectroscopy"
Fall Semester 1993
Dr. Rainer Glaser

Third 1-Hour Examination
"Mass Spectroscopy"

Monday, November 1, 1993, 8:40 - 9:30

Name:

Question 1 (MS-MS)	30	
Question 2 (Carbonyls)	25	
Question 3 (Isotopes)	20	
Question 4 (Scenarios)	25	
Total	100	

Question 1. Tandem Mass Spectroscopy, MS-MS Analysis.

N-Methyl-*N*-isopropyl-*N*-butylamine, **1**, and *N*-methyl-*N*-ethyl-*N*-2-pentylamine, **2**, represent constitution isomers. Let's examine their fragmentation reactions after EI ionization (70 eV). (*Do only consider fragments with m/z > 40!*)

(a) For each isomers, draw the parent ion and precisely show the location of the charge. Show all electrons in every structure. Show the fragmentation reactions for **1** and **2**, indicate the m/z values for each cation, and also indicate what neutral molecules are being generated.

For **1**: (8 points)

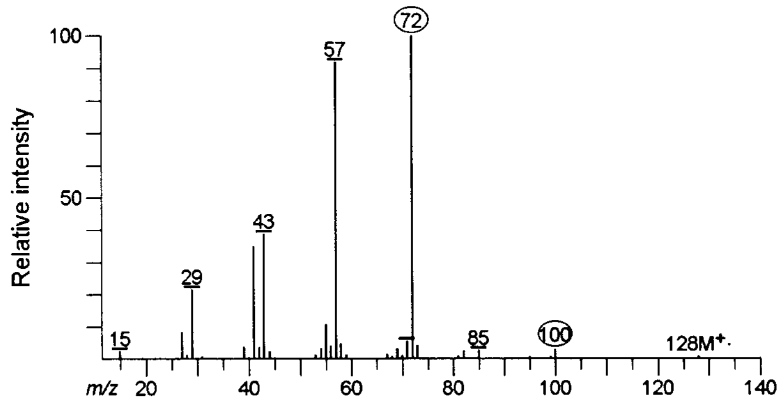
For **2**: (8 points)

(b) For **2** only, indicate every fragmentation reaction that is of the "α-cleavage" type. Answer this question in the box above. (4 points)

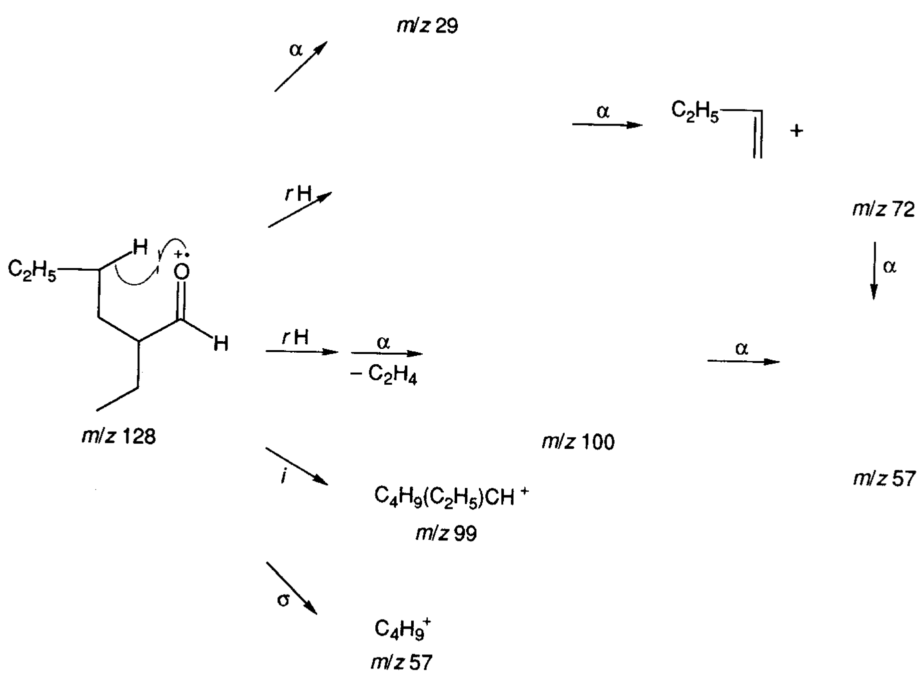
(c) How could MS-MS be used to distinguish between the isomers? Explain the principle of the ___________________ scan method of MS-MS and how it can be used here. (10 points)

Question 2. Aldehydes and Ketones.

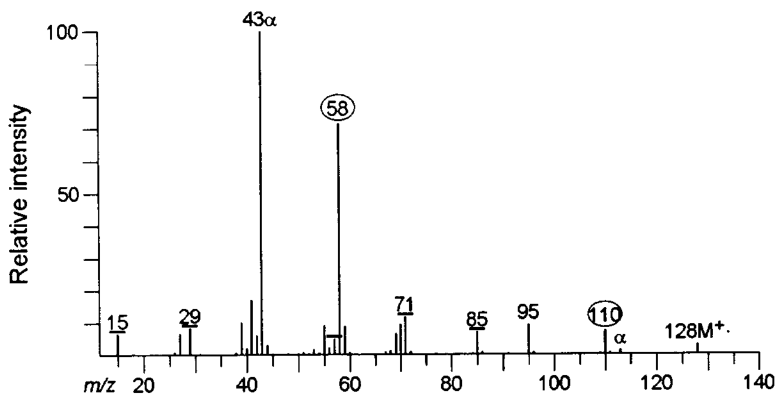
(a) The mass spectrum is shown of 2-ethylhexanal. The two strongest peaks occur at m/z = 72 and m/z = 57. Complete the fragmentation reaction diagram. (15 points)



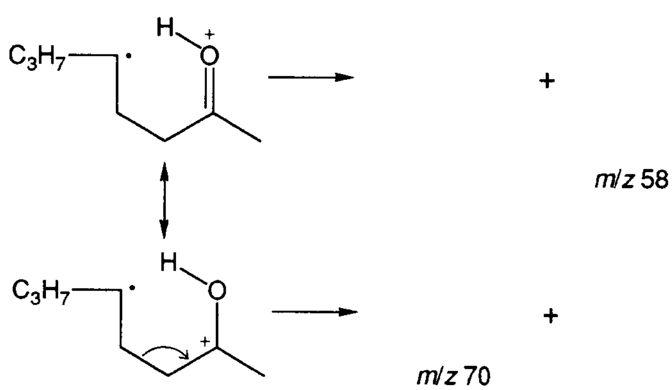
Mass spectrum of 2-ethylhexanal.



(b) Fragmentation of 6-methyl-2-heptanone leads to the intermediate radical cation shown. This cation can fragment in two ways. Complete these two ion reactions. State which of these two reactions occurs more often and explain why. (10 points)



Mass spectrum of 6-methyl-2-heptanone.



Explain:

Question 3. Isotopic Substitution Patterns.

Assume that the natural abundance of ^{14}C is zero. Assume that the two Br isotopes occur 50 percent each. Assume that the heavy isotope of Cl is 33 percent abundant.

(a) Deja vu! (9 points)

Predict the rel. intensities of the (M), (M+1), & (M+2) peaks for $C_{10}H_{22}$ based on the natural abundances of the heavy isotopes. (M) : (M+1) : (M+2) = 100 : ____ : ____. The (M+2) peak reflects the occurrence of ____________________________________ .
Predict the rel. intensities of the (M), (M+1), (M+2), (M+3), & (M+4) peaks for $C_{10}H_{21}Br$ based on the natural abundances of the heavy isotopes. (M) : (M+1) : (M+2) : (M+3) : (M+4) = 100 : ____ : ____ : ____ : ____
Predict the rel. intensities of the (M), (M+1), (M+2), (M+3), & (M+4) peaks for $C_{10}H_{20}Br_2$ based on the natural abundances of the heavy isotopes. (M) : (M+1) : (M+2) : (M+3) : (M+4) = 100 : ____ : ____ : ____ : ____ The (M+4) peak is due to ions that contain __________________________ of bromine.

(b) Chloral is reacted with bromobenzene and a product is formed with the composition $C_{14}H_9Br_2Cl_3$ (m/z = 440 for M^+). Schematically draw the isotopic peaks associated with the parent ion. Give the intensity ratios and briefly explain. (11 points)

Question 4. Scenarios. (5 points each)

(a) You have an extract from a plant that contains (among other compounds) several alkylnapthtols. How can you determine the number of different alkylnapthtols present using a tandem mass spectroscopy method?

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(b) You have a mixture that contains aromatic and aliphatic compounds. The LC-MS total ion chromatogram shows ten peaks. To find out which peaks in the total ion chromatogram correspond to *benzene* derivatives, it would be best to record a ____________________________ ______ chromatogram at m/z = _______ .

(c) You would like to perform a *quantitative* analysis of 1,3-dimethoxybenzene. What compound would you suggest as the *internal standard*?

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(d) You need to know the molecular weight of a new compound. The EI MS did not show any M^+ peak at all. What do you suggest to the MS operator?

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(e) You want to use CI for the MS analysis of an alcohol you made. The MS operator tells you that he could protonate your alcohol either with ammonium ions or with protonated trimethylamine. The PA(NH_3) = 205 kcal/mol and the PA(Me_3N) = 224 kcal/mol. Which one would be better to *keep fragmentation reactions low*.

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The END

of another exciting learning experience