

Course: CY51003: Spectroscopic Methods of Structure Determination

Mid-Autumn Semester Examination 2014-2015

Department of Chemistry

Total Time: 2 hours

Total Marks: 30

Answer the following questions.

6x5 = 30

NOTE: Supporting data are provided at the end.

1. a) A hydrocarbon show intense molecular ion peak $[MH^+]$ at 105.0701 in MS. It undergoes easy and very selective hydrogenation (at room temperature under 2 atm hydrogen pressure using Pd on charcoal catalyst) to provide hydrogenated product which show molecular ion peak at 106 in EI-MS. Predict the structure of the hydrocarbon. [3]

b) Why acid anhydrides display two stretching bands in the carbonyl region? What are their absorption values in cm^{-1} ? [1.5]

c) To increase your chance to get very prominent molecular ion peak in mass spectrum, which reagent gas would you like to use in case of chemical ionization technique and why? (Chose three reagent gases and then discuss very briefly) [1.5]

2. a) Calculate the intensity of $[M+4]$ peak with respect to $[M]$ for 1-bromo-2-chloropropane and 1-bromo-3-chloropropane. [3]

b) Explain the isotope distribution pattern of $[Ru(p\text{-cymene})OAc]^+$ as shown below. [3]
p-cymene is 4-isopropyltoluene ligand and OAc is acetate.

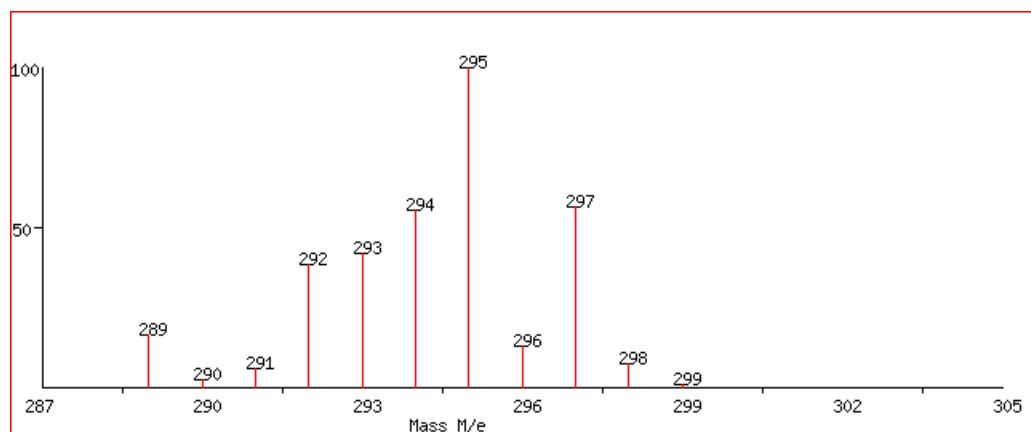
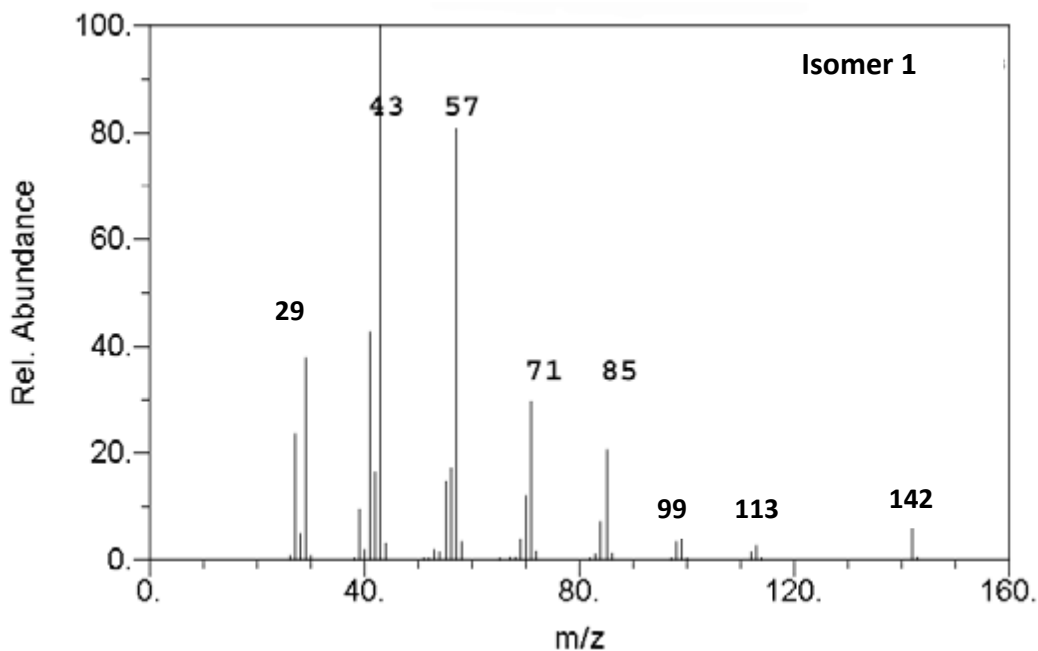


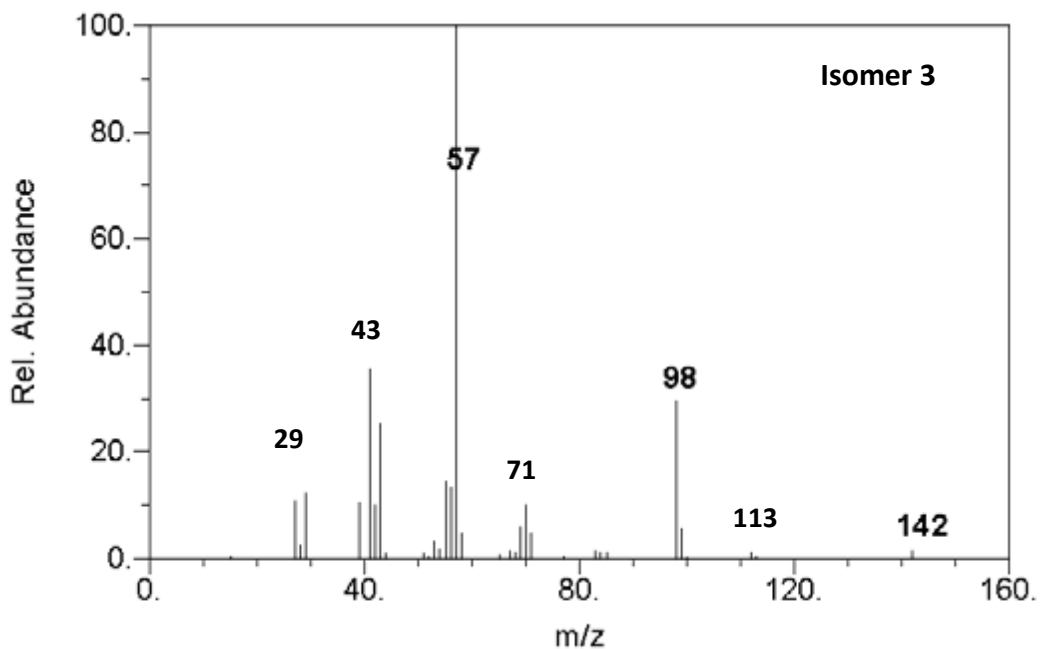
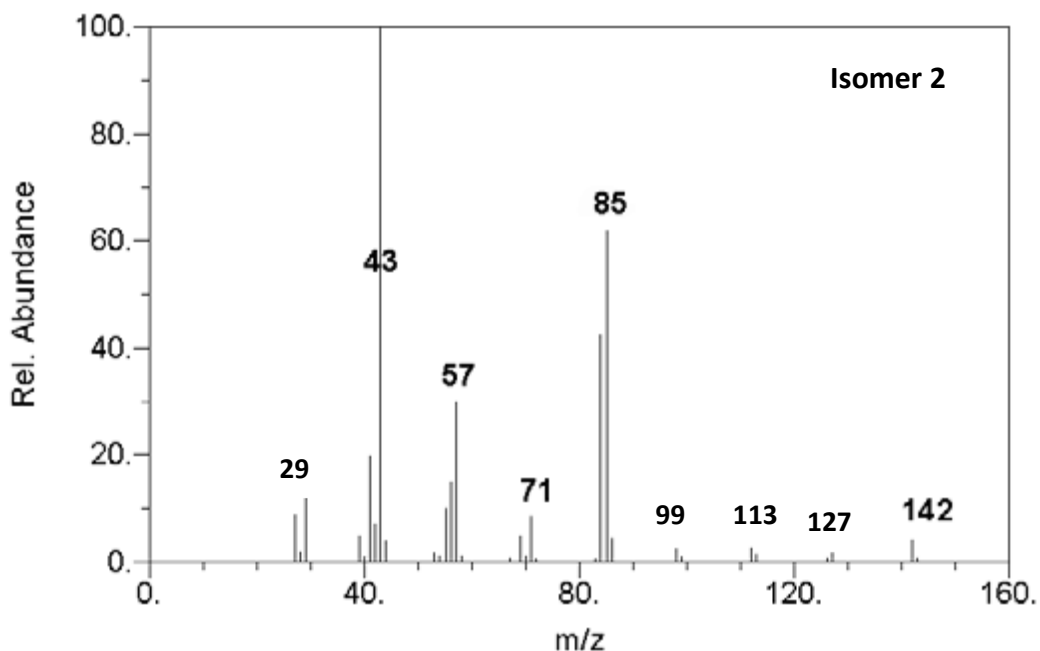
Figure 1. Isotope distribution pattern of $[\text{Ru}(p\text{-cymene})\text{OAc}]^+$.

Peaks (m/z): 289 (16.2%), 290 (2.1%), 291 (5.7%), 292 (38.1%), 293 (42%), 294 (55.3%), 295 (100%), 296 (13%), 297 (56.1%), 298 (7.3%), 299 (0.6%). (In bracket intensity values are given).

3. The fragmentation pattern of the three saturated isomeric hydrocarbon are given below (EI-MS spectra). What are those hydrocarbons? Here m/z 142 belongs to the molecular ion peak.

$$[2 + 2 + 2 = 6]$$





4. a) A molecule made of carbon and hydrogen, showed sharp absorption peak at 3300, 2951, 2848, 2150 cm^{-1} . In Mass Spectrum, for molecular peak, first isotope peak (M+1) is 11.2% intense than the corresponding molecular ion peak M. Proposed suitable structure or structures for this molecule with proper justification. [3]

b) What are the basic differences between ESI and EI technique in MS? [2]

c) What is mass analyzer and what is its role? [1]

5. a) Between UV, IR and NMR, discuss about their relative sensitivity by using mathematical calculation. [3]

b) What is the physical meaning of θ -, 90° - and 180° pulses? [2]

c) What is net or overall magnetization? [1]

Isotope, Abundance and Mass of elements required for your exam:

Element	Isotope 1, mass, abundance	Isotope 2, mass, abundance	Isotope 3, mass, abundance
Hydrogen	^1H , 1.00783, 99.985%	^2H or D, 2.0141, 0.015%	--
Carbon	^{12}C , 12.00, 98.90%	^{13}C , 13.00336, 1.1%	---
Nitrogen	^{14}N , 14.0031, 99.62%	^{15}N , 15.0001, 0.38%	--
Oxygen	^{16}O , 15.9949, 99.76%	^{17}O , 16.9991, 0.04%	^{18}O , 17.9992, 0.20%
Fluorine	^{19}F , 18.9984, 100%	--	--
Silicon	^{28}Si , 27.9769, 92.22%	^{29}Si , 28.9765, 4.69%	^{30}Si , 29.9738, 3.09%
Phosphorous	^{31}P , 30.9738, 100%	--	--
Sulfur	^{32}S , 31.9721, 95.02%	^{33}S , 32.9715, 0.75%	^{34}S , 33.9679, 4.21%
Chlorine	^{35}Cl , 34.9689, 75.77%	^{37}Cl , 36.9659, 24.23%	--
Bromine	^{79}Br , 78.9183, 50.69%	^{81}Br , 80.9163, 49.31%	--
Iodine	^{127}I , 126.9045, 100%	--	--
Ruthenium (total seven isotopes)	^{96}Ru , 95.91, 5.54% ^{98}Ru , 97.91, 1.87% ^{99}Ru , 98.91, 12.76%	^{100}Ru , 99.90, 12.60% ^{101}Ru , 100.91, 17.06%	^{102}Ru , 101.90, 31.55% ^{104}Ru , 103.91, 18.62%