

CHUKA



UNIVERSITY

UNIVERSITY EXAMINATIONS

**EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN
CHEMISTRY**

CHEM 437: ORGANIC SPECTROSCOPY

STREAMS:

TIME:2 HOURS

DAY/DATE: THURSDAY 13/04/2023

11.30 A.M. –1.30 P.M.

INSTRUCTIONS

Answer question one and any other two questions

Useful data are provided

General data and fundamental constants

Quantity	Symbol	Value	Power of ten	Units
Speed of light	c	2.997 925 58*	10^8	m s^{-1}
Elementary charge	e	1.602 176	10^{-19}	C
Faraday's constant	$F = N_A e$	9.648 53	10^4	C mol^{-1}
Boltzmann's constant	k	1.380 65	10^{-23}	J K^{-1}
Gas constant	$R = N_A k$	8.314 47		$\text{J K}^{-1} \text{mol}^{-1}$
		8.314 47	10^{-2}	$\text{dm}^3 \text{bar K}^{-1} \text{mol}^{-1}$
		8.205 74	10^{-2}	$\text{dm}^3 \text{atm K}^{-1} \text{mol}^{-1}$
		6.236 37	10	$\text{dm}^3 \text{Torr K}^{-1} \text{mol}^{-1}$
Planck's constant	h	6.626 08	10^{-34}	J s
	$\hbar = h/2\pi$	1.054 57	10^{-34}	J s
Avogadro's constant	N_A	6.022 14	10^{23}	mol^{-1}
Atomic mass constant	m_u	1.660 54	10^{-27}	kg
Mass				
electron	m_e	9.109 38	10^{-31}	kg
proton	m_p	1.672 62	10^{-27}	kg
neutron	m_n	1.674 93	10^{-27}	kg
Vacuum permittivity	$\epsilon_0 = 1/c^2 \mu_0$	8.854 19	10^{-12}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
	$4\pi\epsilon_0$	1.112 65	10^{-10}	$\text{J}^{-1} \text{C}^2 \text{m}^{-1}$
Vacuum permeability	μ_0	4π	10^{-7}	$\text{J s}^2 \text{C}^{-2} \text{m}^{-1} (= \text{T}^2 \text{J}^{-1} \text{m}^3)$
Magneton				
Bohr	$\mu_B = e\hbar/2m_e$	9.274 01	10^{-24}	J T^{-1}
nuclear	$\mu_N = e\hbar/2m_p$	5.050 78	10^{-27}	J T^{-1}
g value	g_e	2.002 32		
Bohr radius	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	5.291 77	10^{-11}	m
Fine-structure constant	$\alpha = \mu_0 e^2 c/2h$	7.297 35	10^{-3}	
	α^{-1}	1.370 36	10^2	
Second radiation constant	$c_2 = hc/k$	1.438 78	10^{-2}	m K
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k^4/15h^3 c^2$	5.670 51	10^{-8}	$\text{W m}^{-2} \text{K}^{-4}$
Rydberg constant	$R = m_e e^4/8h^3 c \epsilon_0^2$	1.097 37	10^5	cm^{-1}
Standard acceleration of free fall	g	9.806 65*		m s^{-2}
Gravitational constant	G	6.673	10^{-11}	$\text{N m}^2 \text{kg}^{-2}$

*Exact value

QUESTION ONE (30 MARKS)

a (i) Why are quantitative analytical methods based on NIR radiation often more precise and accurate than methods based on mid-IR radiation? (1.5 marks)

(ii) Distinguish between decoupling and Nuclear Overhauser Effect (NOE) experiments. (2 marks)

b(i) In the room-temperature ^1H spectrum of methanol, no spin-spin coupling is observed, but when a methanol sample is cooled to -40°C , the exchange rate of the hydroxyl proton slows sufficiently so that splitting is observed. Sketch spectra for methanol at the two temperatures. (3 marks)

(ii)

The proton NMR spectrum in Figure 19. 40 is for a compound having an empirical formula $C_4H_7BrO_2$. Identify the compound.

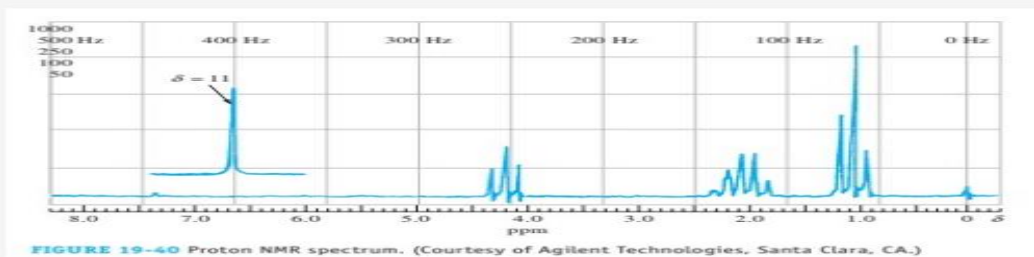


FIGURE 19-40 Proton NMR spectrum. (Courtesy of Agilent Technologies, Santa Clara, CA.)

(2.5 marks)

(iii) From the proton spectrum given in Figure 19-45, determine the structure of this compound, a commonly used pain killer; its empirical formula is $C_{10}H_{13}NO_2$.

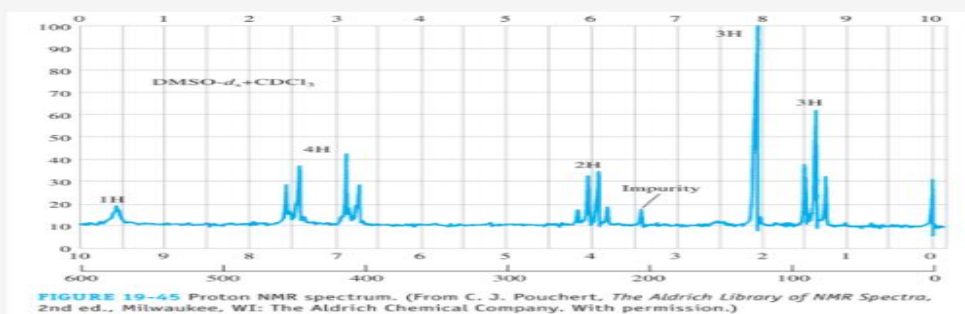
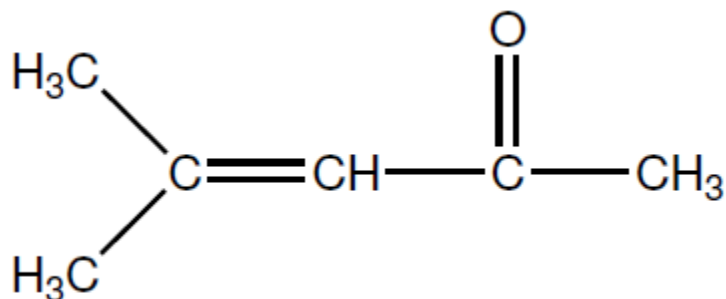


FIGURE 19-45 Proton NMR spectrum. (From C. J. Pouchert, *The Aldrich Library of NMR Spectra*, 2nd ed., Milwaukee, WI: The Aldrich Chemical Company. With permission.)

(4 marks)

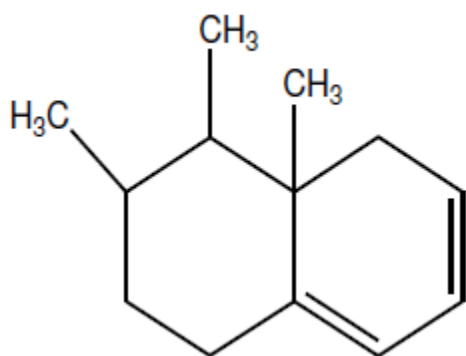
c) Calculate λ_{\max} of the following structures using Woodward Fischer rules

(i)



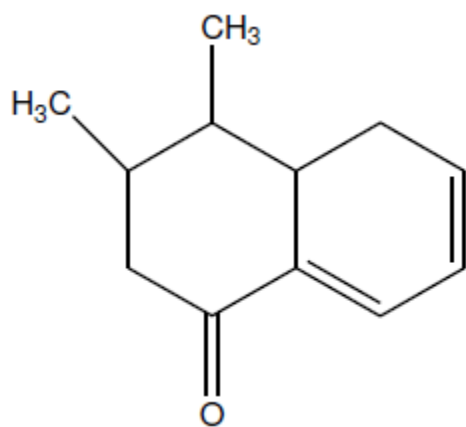
(1.5 marks)

(ii)



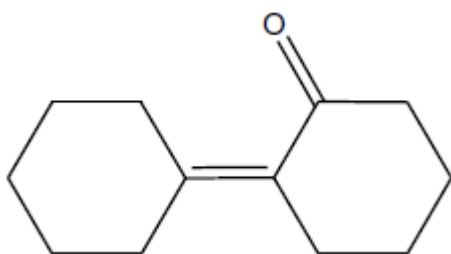
(2 marks)

(iii)



(2.5 marks)

(iv)



(2.5 marks)

d)

Calculate the resolution required to resolve peaks for:

a. CH_2N ($M = 28.0187$) and N_2^+ ($M = 28.0061$).

b. C_2H_4^+ ($M = 28.0313$) and CO^+ ($M = 27.9949$).

c. $\text{C}_3\text{H}_7\text{N}_3^+$ ($M = 85.0641$) and $\text{C}_5\text{H}_9\text{O}^+$ ($M = 85.0653$).

d.

androst-4-en-3,17-dione (M^+) at $m/z = 286.1930$ and an impurity at 286.1240 .

(a) 1 mark

(b) 1 mark

(c) 1 mark

(d) 0.5 marks

e) Calculate the ratio of the $(M+2)^+$ to M^+ and the $(M+4)^+$ to M^+ peak heights for

(i) $\text{C}_{10}\text{H}_6\text{Br}_2$ (0.5 marks)

(ii) $\text{C}_3\text{H}_7\text{ClBr}$ (0.5 marks)

(iii) $\text{C}_6\text{H}_4\text{Cl}_2$ (0.5 marks)

e) In a magnetic sector (single-focusing) mass spectrometer, it might be reasonable under some circumstances to monitor one m/z value, to then monitor a second m/z , and to repeat this pattern in a cyclic manner. Rapidly switching between two accelerating voltages while keeping all other conditions constant is called peak matching.

(i) Derive a general expression that relates the ratio of the accelerating voltages to the ratio of the corresponding m/z values. (2 marks)

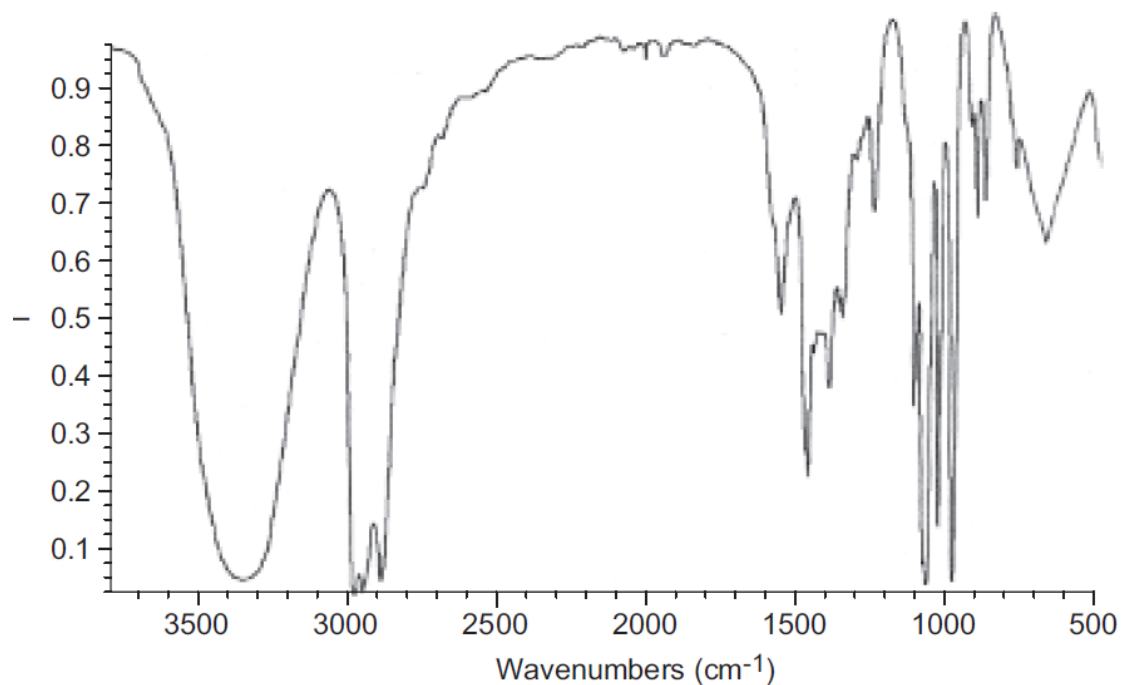
(ii) Use this equation to calculate m/z of an unknown peak if m/z of the ion used as a standard, CF_3^+ is 69.00 and the ratio of $V_{\text{unknown}}/V_{\text{standard}}$ is 0.965035. (1 mark)

(iii) Based on your answer in part (ii), and the assumption that the unknown is an organic compound that has a mass of 143, draw some conclusions about your answer in part (ii), and about the compound. (0.5 marks)

QUESTION TWO (20 MARKS)

a (i)

Stretching frequencies of O–H bonds in carboxylic acids and alcohols, (depending upon the extent of hydrogen bonding), appear as broad and strong absorptions between $3571\text{--}3195\text{ cm}^{-1}$ ($2.80\text{--}3.13\text{ }\mu\text{m}$). The C=O stretching frequencies of acids, esters, ketones, etc., appear as strong and conspicuous absorptions between $1870\text{--}1540\text{ cm}^{-1}$ ($5.3\text{--}6.50\text{ }\mu\text{m}$). Using this information, label [Figs. 1.8, 1.9,](#) and [1.10](#) as corresponding to an organic acid, ketone, or alcohol.

**Figure 1.8**

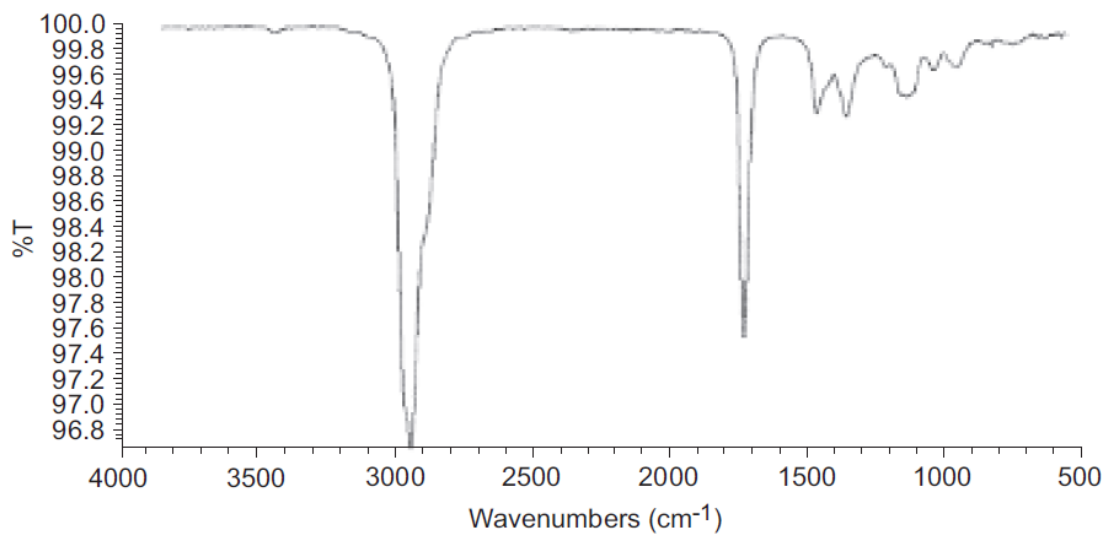


Figure 1.9

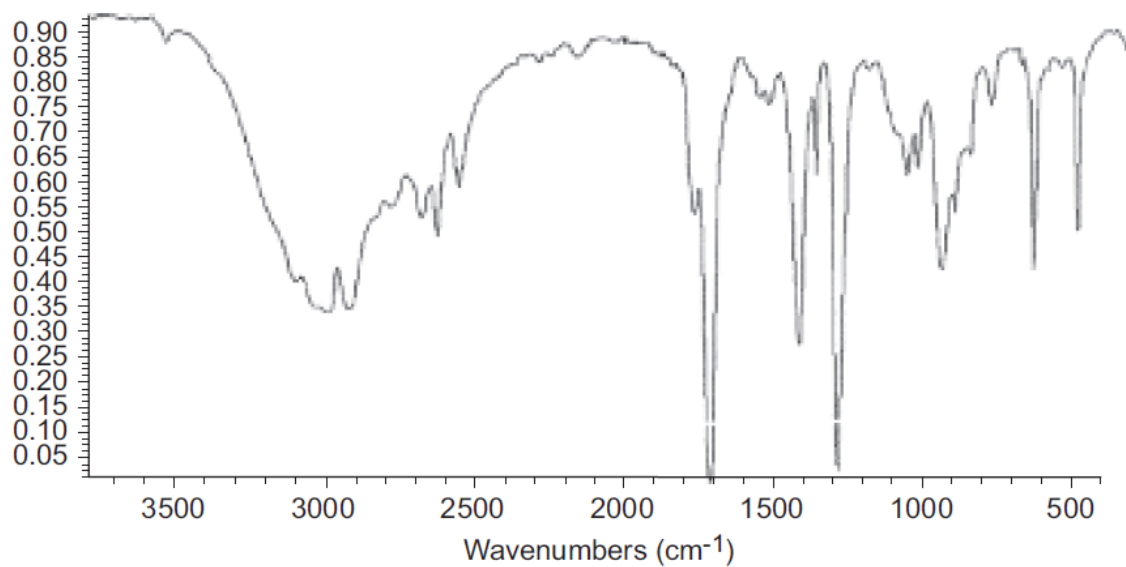


Figure 1.10

(4 marks)

b) The spectrum in Figure 17-21 is for an acrid-smelling liquid that boils at 50°C and has a molecular weight of about 56. What is the compound? What impurity is clearly present?

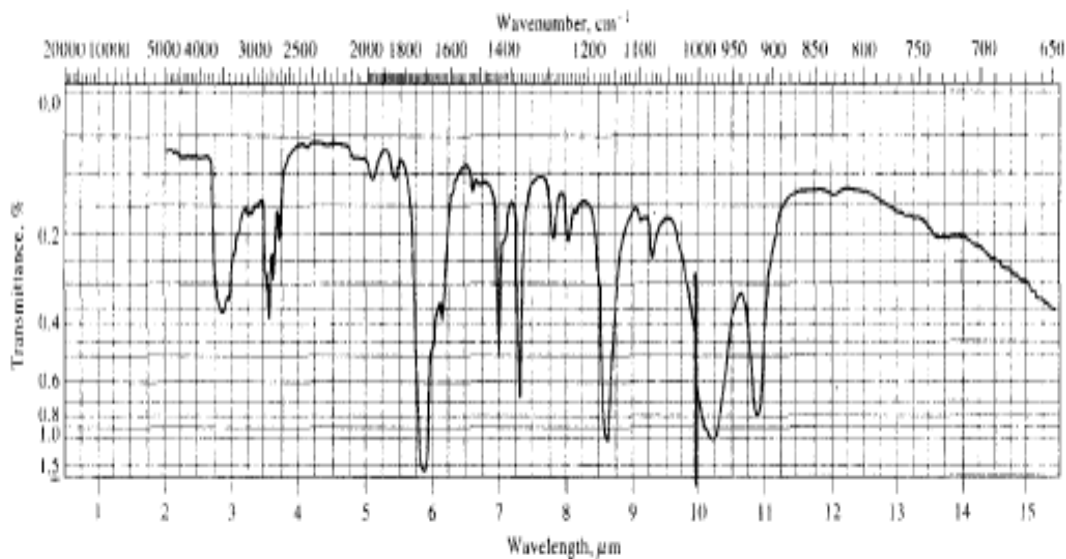


Figure 17-21

(2.5 marks)

c) Cyclohexanone exhibits its strongest IR absorption band at 5.86 μm , and at this wavelength there is a linear relationship between absorbance and concentration.

(i) Identify the part of the molecule responsible for the absorbance at this wavelength. (1 mark)

(ii) Suggest a solvent that would be suitable for a quantitative analysis of cyclohexanone at this wavelength. (1 mark)

(iii) A solution of cyclohexanone (4.0 mg/mL) in the solvent selected in part

(ii) exhibits a blank-corrected absorbance of 0.800 in a cell with a path length of 0.025 mm.

What is the detection limit for this compound under these conditions if the noise associated with the spectrum of the solvent is 0.001 absorbance units? (1 mark)

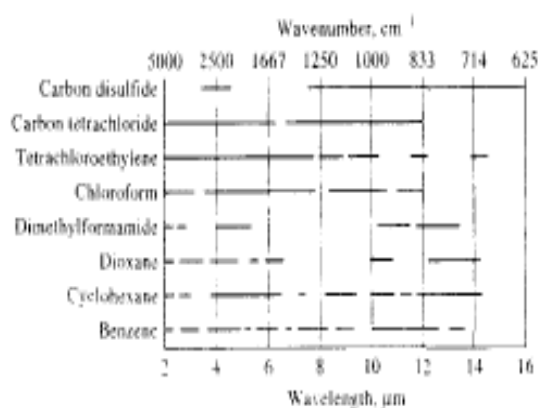


FIGURE 17-1 Solvents for IR spectroscopy.
Horizontal lines indicate useful regions.

TABLE 17-3 Abbreviated Table of Group Frequencies for Organic Functional Groups

Bond	Type of Compound	Frequency Range, cm^{-1}	Intensity
C—H	Alkanes	2850–2970	Strong
		1340–1470	Strong
C—H	Alkenes (>C=C<H)	3010–3095	Medium
C—H	Alkynes ($\text{—C}\equiv\text{C—H}$)	675–995	Strong
C—H		3300	Strong
C—H	Aromatic rings	3010–3100	Medium
		690–900	Strong
O—H	Monomeric alcohols, phenols	3590–3650	Variable
	Hydrogen-bonded alcohols, phenols	3200–3600	Variable, sometimes broad
	Monomeric carboxylic acids	3500–3650	Medium
	Hydrogen-bonded carboxylic acids	2500–2700	Broad
N—H	Amines, amides	3300–3500	Medium
C=C	Alkenes	1610–1680	Variable
	Aromatic rings	1500–1600	Variable
C≡C	Alkynes	2100–2260	Variable
C—N	Amines, amides	1180–1360	Strong
C=N	Nitriles	2210–2280	Strong
C—O	Alcohols, ethers, carboxylic acids, esters	1050–1300	Strong
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760	Strong
NO ₂	Nitro compounds	1500–1570	Strong
		1300–1370	Strong

d) The following Raman data were obtained for CHCl_3 with the polarizer of the spectrometer set (1) parallel to the plane of polarization of the laser and (2) at 90° to the plane of the source.

	Relative Intensities		
	$\Delta\nu, \text{cm}^{-1}$	(1) I_{\parallel}	(2) I_{\perp}
(a)	760	0.60	0.46
(b)	660	8.4	0.1
(c)	357	7.9	0.6
(d)	258	4.2	3.2

Calculate the depolarization ratio and indicate which Raman lines are polarized. (4 marks)

e) Predict the appearance of the high-resolution proton NMR spectrum of

(i) cyclohexane. (1.5 marks)

(ii) diethyl ether. (1.5 marks)

(iii) 1, 2-dimethoxyethane, $\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_3$. (1.5 marks)

f) Briefly compare the ^1H and ^{31}P NMR spectra of methyl phosphorous acid $\text{P}(\text{OCH}_3)_3$ at 7.05 T.

There is a weak spin-spin coupling between phosphorus and hydrogen nuclei in the compound.

(2 marks)

QUESTION THREE (20 MARKS)

The following questions all deal with the similarities and differences between IR spectrometry and Raman spectrometry.

- a) What are the requirements for a vibrational mode in a molecule to show IR absorption? What are the requirements for a vibrational mode to be Raman active? Why do these requirements differ? Under what circumstances will vibrational modes by both Raman and IR be active? Under what circumstances will vibrational modes be Raman active but not IR active and vice versa? (4 marks)
- b) Consider the molecule chloroacetonitrile (ClCH_2CN). How many vibrational modes should this molecule have? Why might one observe fewer Raman bands than expected? (3 marks)
- c) Chloroacetonitrile shows a strong Raman band at 2200cm^{-1} due to the C-N stretching mode. The corresponding IR absorption is very weak or absent. By comparing spectra in the 2200cm^{-1} region, what can you conclude about the C-N stretching mode in chloroacetonitrile? (2 marks)
- d) Compare and contrast IR and Raman spectrometry with respect to optics, cell materials, sample handling, solvent compatibility, and applicability to various sample types. (5 marks)
- e) Compare and contrast the sources and transducers used in Raman spectrometers to those used in FTIR instruments. Consider both FT-Raman and dispersive Raman spectrometers in your comparison. (2 marks)

- f) Compare and contrast IR and Raman spectrometry with respect to qualitative usefulness, detection limits, quantitative analysis, and instrumental complexity. (4 marks)

QUESTION FOUR (20 MARKS)

Figure 20-29 shows the mass spectrum of the same compound from an EI source and a CI source.

- a. Which mass spectrum would be best for determining the molecular mass of the compound? Why? (3 marks)
- b. Which mass spectrum would be best for determining the chemical structure? Why? (3 marks)

c. The EI source was a pulsed source used with a TOF mass analyzer. If the flight tube were 1.0 m long and the accelerating voltage were 3000 V, what would the flight time be for the ion at $m/z = 58$?

d. For two ions of m/z values m_1/z and m_2/z , derive an equation for the difference in flight times Δt_F as a function of the two masses, the charges, and the accelerating voltage.

e. For the same TOF analyzer as in part (c), calculate the difference in flight times between ions of m_1/z and m_2/z .

c) 3 marks

d) 3 marks

e) 3 marks

- f. To get more structural information, the compound of Figure 20-29 was subjected to tandem mass spectrometry. Which ionization source, EI or CI, would be most suitable for this purpose? Why? (2 marks)
- g. Using the ionization source chosen in part (f), describe the types of mass spectra that could be obtained from an MS/MS experiment by:

1. holding the first mass analyzer constant and scanning the second analyzer.
2. scanning both analyzers with a small m/z offset between them.
3. scanning the first analyzer while holding the second analyzer constant.
4. scanning the second mass analyzer for every mass selected by the first analyzer.

In your answer, use features of the mass spectrum of Figure 20-29 to illustrate your description.

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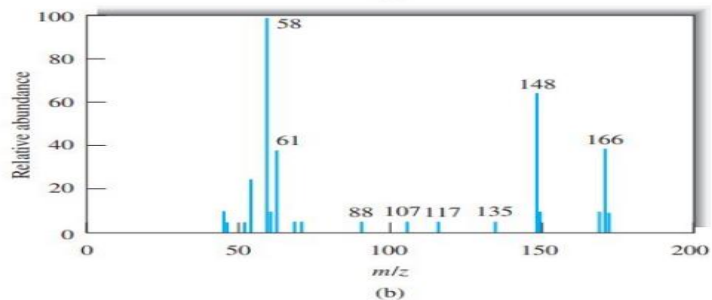
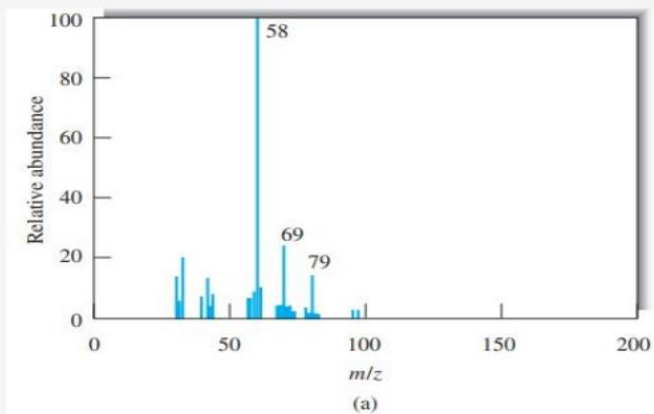
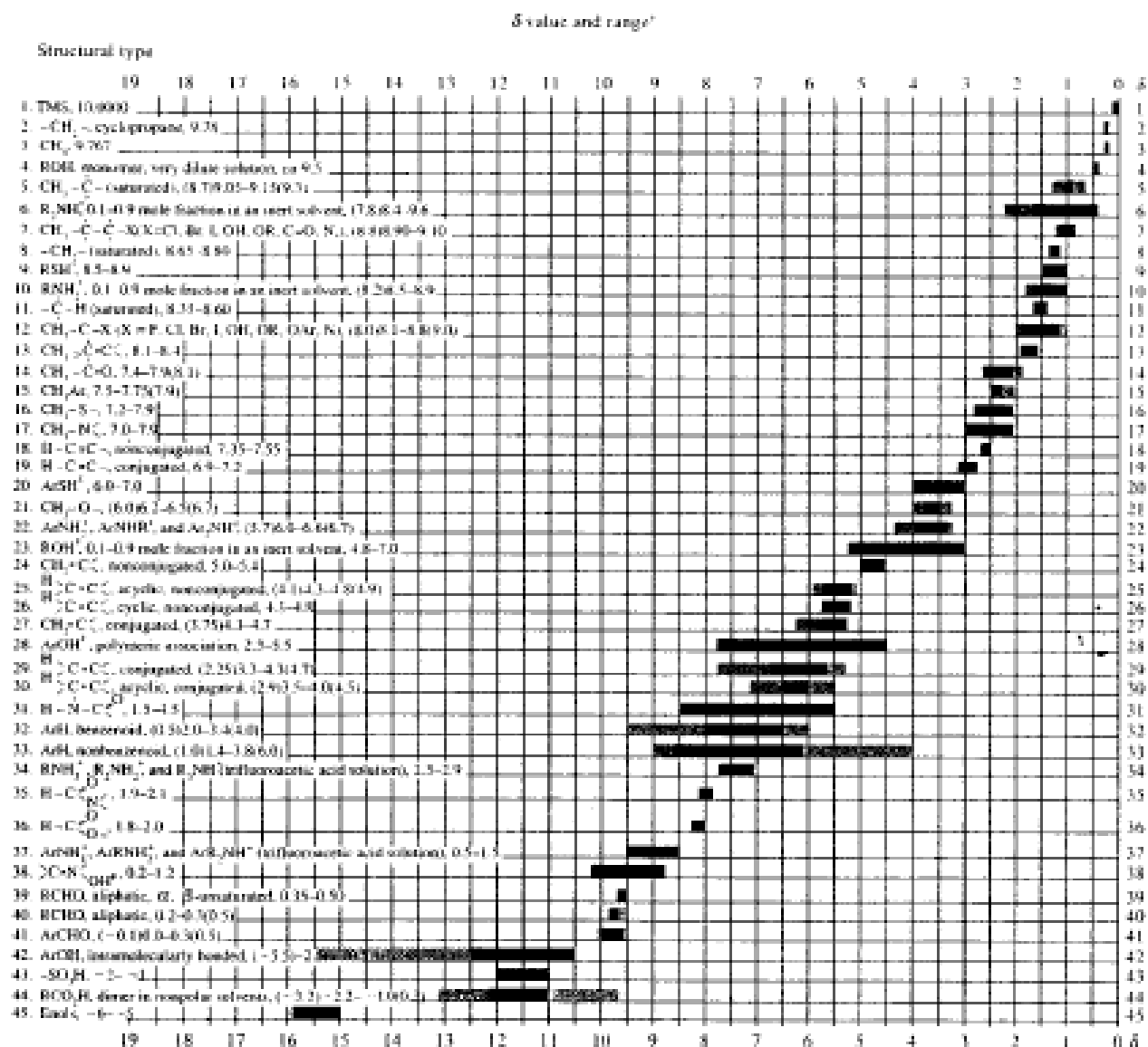


FIGURE 20-29 EI spectrum (a) and CI spectrum (b) of the same biologically important compound. (From H. M. Fales, H. A. Lloyd, and G. A. W. Milne, *J. Amer. Chem. Soc.*, **1970**, *92*, 1590–1597, DOI: 10.1021/ja00709a028. American Chemical Society.)

(3 marks)



*Normally, absorptions for the functional groups indicated will be found within the range shown. Occasionally, a functional group will absorb outside this range. Approximate limits for this are indicated by absorption values in parentheses and by blue shading in the figure.

*The absorption positions of these groups are concentration-dependent and are shifted to higher δ values in more dilute solutions.

FIGURE 19-17 Absorption positions of protons in various structural environments. (Table taken from J. R. Dyer, *Applications of Absorption Spectroscopy by Organic Compounds*, p. 85, Englewood Cliffs, NJ: Prentice-Hall, 1965. With permission.)

TABLE 19-2 Approximate Chemical Shifts for Certain Methyl, Methylene, and Methine Protons

Structure	δ , ppm		
	M = CH ₃	M = CH ₂	M = CH
Aliphatic α substituents			
M—Cl	3.0	3.5	4.0
M—Br	2.7	3.4	4.1
M—NO ₂	4.3	4.4	4.6
M—OH (or OR)	3.2	3.4	3.6
M—O—C ₆ H ₅	3.8	4.0	4.6
M—OC(=O)R	3.6	4.1	5.0
M—C=C	1.6	1.9	—
M—C≡C	1.7	2.2	2.8
M—C(=O)H	2.2	2.4	—
M—C(=O)R	2.1	2.4	2.6
M—C(=O)C ₆ H ₅	2.4	2.7	3.4
M—C(=O)OR	2.2	2.2	2.5
M—C ₆ H ₅	2.2	2.6	2.8
Aliphatic β substituents			
M—C—Cl	1.5	1.8	2.0
M—C—Br	1.8	1.8	1.9
M—C—NO ₂	1.6	2.1	2.5
M—C—OH (or OR)	1.2	1.5	1.8
M—C—OC(=O)R	1.3	1.6	1.8
M—C—C(=O)H	1.1	1.7	—
M—C—C(=O)R	1.1	1.6	2.0
M—C—C(=O)OR	1.1	1.7	1.9
M—C—C ₆ H ₅	1.1	1.6	1.8

Woodward - Fischer Rules

Parent value and increments for different groups and substituents:

- **Parent Value**
 - a) Butadiene or cyclic conjugated butadiene 217 nm
 - b) Acyclic triene 245 nm
 - c) Homoannular conjugated diene 253 nm
 - d) Heteroannular conjugated diene 215nm
- **Increments for substitution**
 - a) Alkyl substituents 5 nm
 - b) Ring residue 5 nm
 - c) Exocyclic double bond 5 nm
 - d) Double bond extending conjugation 30nm
 - e) Bicyclic or strain correction 15 nm
- **Auxochrome**
 - Cl,-Br +5nm
 - OR +6nm
 - SR +30 nm
 - NR₂ +60 nm
 - OCOCH₃ 0 nm
- ❖ If the cyclic diene or open chain conjugated diene is substituted by -Cl or -Br then 17nm is added in basic value.
- ❖ The difference between calculated value and observed value of (λ_{\max}) should be lower than 5 nm.

Woodward - Fischer Rules for calculating (λ_{\max}) in α , β carbonyl compounds

Woodward Fischer suggested some empirical rule for the calculation of λ_{\max} in α , β unsaturated compound, which was modified by Scott, which are as follows

- In α , β unsaturated ketone is taken as 215nm.
- In a cyclic ketone, if α , β unsaturated carbonyl group is a part of six member cyclic ring then basic value is taken as a 215 nm, but if α , β unsaturated carbonyl group is a part of five member ring then base value is taken as 202 nm. The (λ_{\max}) for such compounds are generally 10^4

Structural increments for calculation of (λ_{\max}) for given α , β unsaturated carbonyl compound

- 1) Exo-cyclic double bond +5 nm
- 2) For each double bond extending conjugation +30 nm
- 3) For a homo-anular conjugated diene +39 nm
- 4) For each double bond endocyclic. +5nm
- 5) **Increment of various auxochrome:**

Chromophore	α	β	γ	δ
Ring residue	+10	+12	+18	+18
-R	+10	+12	+18	+18
-OR	+35	+30	+17	+31
-OH	+35	+30	-	+50
-OCH ₃	+6	+6	+6	+6
-Cl	+15	+12	-	-
-Br	+25	+35	-	-
-SR	-	+85	-	-
-NR ₂	-	+95	-	-