Spectroscopy

1. In the following diagram of a light wave what distance is defined as the wavelength?

A) 1 to 2  
B) 1 to 3  
C) 1 to 4  
D) none of the above

2. Which of the following compounds has three different sets of structurally equivalent hydrogen atoms?

![Compounds]

3. Four major spectroscopic tools are listed below. Which makes use of the longest wavelength radiation?

A) infrared  
B) ultraviolet  
C) visible  
D) proton nmr

4. You have three dyes. One is green, one is blue and one is yellow. Which absorbs the shortest wavelength of visible light, and which absorbs the longest?

A) longest = yellow; shortest = blue  
B) longest = blue; shortest = green  
C) longest = yellow; shortest = green  
D) longest = green; shortest = yellow

5. Of the following general statements concerning vibrational frequencies and intensities, which is incorrect?

A) stretching vibrations have a higher frequency than equivalent bending vibrations.  
B) stretching vibrations of double bonds have a higher frequency than those of equivalent single bonds.  
C) the stretching vibration of a Y-Y bond is more intense than that of a Y-Z bond. (Y and Z are different atoms)  
D) stretching vibrations of a Y-H bond have a higher frequency than those of a Y-Z bond. (Y and Z are heavier atoms than H)
6 Which of the following compounds will display spin-spin splitting in the 1H-NMR?
A) (CH₃)₂COCH₃
B) Br(CH₂)₃Br
C) para-xylene, CH₃C₆H₄CH₃
D) none of these

7 The 1H-NMR of 1,1-dibromoethane consists of two well-separated signals, one large and the other small.
Which of the following descriptions is correct?
A) the large signal is a quartet and the small signal is a doublet.
B) the large signal is a triplet and the small signal is a singlet.
C) the large signal is a singlet and the small signal is a triplet.
D) the large signal is a doublet and the small signal is a quartet.

8 Which spectroscopic tool would be best for distinguishing a sample of 1,2,2-trichloropropane from 1,1,2-trichloropropane?
A) 1H-NMR
B) infrared spectroscopy
C) none of them
D) mass spectrometry

9 Which spectroscopic tool would be best for distinguishing a sample of chlorocyclopentane from bromocyclopentane?
A) 1H-NMR
B) infrared spectroscopy
C) none of them
D) mass spectrometry

10 Combustion analysis of an organic compound shows it to be 64.3% carbon. It displays a molecular ion at m/z=112 amu in the mass spectrum. Which of the following is a plausible molecular formula for this compound?
A) C₈H₁₆
B) C₇H₁₂O
C) C₆H₈O₂
D) C₅H₄O₃

11 An unknown compound has the following spectroscopic properties:
Mass Spectrometry: m/z 102 (very small), 87 & 43 are the largest ions
1H-NMR: δ 1.4 & 3.9 ppm (both singlets, intensity ratio 3:2)
13C-NMR: δ 108, 64 & 25 ppm,
Infrared Spectroscopy: several strong absorptions in the 1000 to 1300 cm⁻¹ region
Which of the following is the most likely formula of this compound?
12 Which type of C–H has the highest stretching frequency in the infrared spectrum?
A) RCHO
B) RCH₃
C) R₂C=CH₂
D) RC≡CH

13 Which C=O function has the lowest stretching frequency in the infrared spectrum?
A) acyl chloride
B) aldehyde
C) amide
D) ester

14 Which hydrocarbon gives the lowest field ¹H-NMR signal?
A) cyclohexane
B) benzene
C) 1,4-cyclohexadiene
D) 1-butyne

Questions 15 through 22 refer to the 90 MHz ¹H-NMR spectrum shown here (specific signals are labeled a through f).

15 Of all six signal groups in this spectrum, what is the multiplicity of the lowest field signal?
A) singlet
B) doublet
C) triplet
D) quartet
16 Which of the six signal groups in this spectrum is located at the highest frequency?
A) a
B) c
C) e
D) f

17 How far from the TMS reference signal is the singlet at c (δ 3.8 ppm)?
A) 23.7 Hz
B) 23.7 MHz
C) 342 Hz
D) 342 MHz

18 The two sharp signals that constitute the resonance marked a have chemical shifts of 7.82 and 7.95. What is the coupling constant, J, for this doublet?
A) 0.13 MHz
B) 11.7 Hz
C) 11.7 MHz
D) 13 Hz

19 Which of the six signal groups in this spectrum is most shielded?
A) a
B) c
C) e
D) f

20 Ignoring the TMS reference signal what, is the mutiplicity of the highest field signal?
A) singlet
B) doublet
C) triplet
D) quartet

21 The ratio of the number of hydrogens generating doublet a to the hydrogens generating quartet d is measured how?
A) x/y (distance in mm)
B) 7.88/2.85 (chemical shifts in ppm)
C) x/z (distance in mm)
D) none of the above

22 If this spectrum is from a C_{10}H_{12}O_{2} compound, having a strong absorption at 1680 cm^{-1} in the infrared, what is its likely structure?
23 Which statement about the NMR reference compound TMS is not correct?
A) TMS stands for tetramethylsilane.
B) all the hydrogens in TMS have the same chemical shift.
C) TMS is relatively unreactive with most functional groups.
D) TMS has a high boiling point, so it is not easily lost when handling the NMR sample.

24 A C₂H₂BrCl compound gives a ¹H-NMR spectrum consisting of two equal sized doublets, J=16 Hz
What is this compound?
A) (Z)-1-bromo-2-chloroethene
B) (E)-1-bromo-2-chloroethene
C) 1-bromo-1-chloroethene
D) none of the above

25 The ¹H-NMR spectrum of diethyl ether shows?
A) two peaks, one a triplet, the other a quartet
B) two peaks, one a triplet, the other a doublet
C) four peaks, all doublets
D) four peaks, all triplets

26 The ¹H-NMR spectrum of a C₆H₈ hydrocarbon displays a single sharp signal. The ¹³C-NMR spectrum has two resonance signals. Which of the following compounds would fit this evidence?

27 Consider four C₃H₅Cl₃ isomers.
Which has two ¹H-NMR singlets and three ¹³C-NMR signals?
A) CH₃CH₂CCl₃
B) CH₂CICH₂CH₂Cl
C) CH₃CHCICCHCl₂
D) CH₃CCl₂CH₂Cl
28 Consider four C₃H₆Cl₂ isomers. Select those compounds having two ¹³C-NMR signals. Which of these displays no molecular ion in the mass spectrum, but has ions at 99 & 101 m/z as well as 77 & 79 m/z (ratio of lower to higher mass is 3:1 in each case)?
A) CH₃CCl₂CH₃
B) CH₃CH₂CHCl₂
C) CH₂ClCH₂CH₂Cl
D) CH₃CHClCH₂Cl

29 Four C₁₀H₁₄ isomers are named below. Which of these would display the following ¹H-NMR signals?
δ 1.22 (t) 6H, δ 2.60 (q) 4H, δ 7.12 (s) 4H (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet)
A) tert-butylbenzene.
B) isobutylbenzene.
C) para-diethylbenzene.
D) 1,2,3,4-tetramethylbenzene.

30 Four C₁₀H₁₄ isomers are named below. Which of these would display the following ¹H-NMR signals?
δ 2.18 (s) 12H, δ 6.88 (s) 2H (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet)
A) tert-butylbenzene.
B) 1,2,4,5-tetramethylbenzene.
C) 1,2,3,5-tetramethylbenzene.
D) 1,2,3,4-tetramethylbenzene.

31 An unknown compound has a molecular ion at m/z=79 amu in its mass spectrum. Analysis shows its composition to be 17.7% nitrogen. What is the molecular formula of this compound?
A) C₅H₅N
B) C₄H₃N₂
C) C₃H₇N₃
D) C₄H₁₇N

32 The infrared spectrum of a hydrocarbon has a strong absorption at 3297 cm⁻¹. What structural feature does this indicate?
A) sp³ C–H
B) sp² C–H
C) sp C–H
D) C≡C

33 Four C₁₀H₁₄ isomers are named below. Which of these would display the following ¹H-NMR signals?
δ 0.88 (d) 6H, δ 1.86 (m) 1H, δ 2.45 (d) 2H, δ 7.2-7.3 (s) 5H (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet)
A) para-isopropyltoluene.
B) isobutylbenzene.
C) sec-butylbenzene.
D) meta-diethylbenzene.
A compound has a molecular ion at m/z = 142 amu, and displays only one 1H-NMR signal (a sharp singlet).
Which of the following satisfies these facts?
A) methyl iodide
B) 1,1,2,2-tetra fluorocyclopentane
C) para-disulphydrylbenzene [C₆H₄(SH)₂]
D) 2,4-hexadiyne-1,6-diol

Which of the following statements is the best definition of the base peak in a mass spectrum?
A) the molecular ion peak
B) the lowest m/z peak
C) the highest mass rearrangement ion
D) the ion peak of greatest intensity

Assuming all the compounds listed below yield an observable molecular ion, which would have an odd number m/z value for this ion?
A) C₉H₁₅F
B) C₇H₁₀N₂O
C) C₈H₁₀NI
D) all the above have odd mass molecular ions

The mass spectrum of 3-pentanone has a very large ion peak at m/z = 57.
Which of the following ions is thought to be responsible for this peak?

\[
\begin{align*}
\text{A} & : \text{CH}_3\text{CH}_2\text{CHCH}_3^+ \\
\text{B} & : (\text{CH}_3)_3\text{C}^+ \\
\text{C} & : \text{C}_2\text{H}_5\text{C}\equiv\text{O}^+ \\
\text{D} & : \text{CH}_3\text{CH}\equiv\text{C}≡\text{OH}^+
\end{align*}
\]

Four methyl compounds are listed below. Which has the lowest field methyl resonance in the 1H NMR spectrum?
A) (CH₃)₄Si
B) (CH₃)₃N
C) (CH₃)₂S
D) (CH₃)₂O

The following hydrocarbons all have 1H NMR spectra consisting of a single sharp peak. Which exhibits the greatest shielding?
A) 2-butyne
B) benzene
C) 1,2,3-butatriene
D) 1,3-butadiyne

Infrared spectroscopy examines energy excitations in which of the following ranges?
A) 0.01 to 0.1 kcal/mol
B) 1 to 10 kcal/mol
C) 10 to 50 kcal/mol
D) 50 to 100 kcal/mol
41 A C₅H₁₂O₂ compound has strong infrared absorption at 3300 to 3400 cm⁻¹.
The ¹H NMR spectrum has three singlets at δ 0.9, δ 3.45 and δ 3.2 ppm; relative areas 3:2:1.
Addition of D₂O to the sample eliminates the lower field signal.
The ¹³C NMR spectrum shows three signals all at higher field than δ 100 ppm.
Which of the following compounds best fits this data?
A) 1,5-pentanediol
B) 1,3-dimethoxypropane
C) 2,2-dimethyl-1,3-propanediol
D) 2,4-pentanediol

42 A C₉H₁₄O₃ compound has two strong infrared absorptions between 1100 and 1250 cm⁻¹ and at 1600 cm⁻¹.
The ¹H NMR spectrum has sharp singlet peaks at δ 3.6 and 6.6 ppm (intensity ratio 3:1).
The ¹³C NMR spectrum shows three lines at δ 165, 115 and 55 ppm.
Which of the following compounds best fits this data?
A) 1,3,5-trimethoxybenzene
B) 1,2,3-trimethoxybenzene
C) 2,4,6-trimethyl-1,3,5-benzenetriol
D) 1-phenyl-1,2,3-propanetriol

43 An infrared spectrum has a strong absorption at 5.85 μ. Which of the following frequencies corresponds to this wavelength?
A) 3300 cm⁻¹
B) 1710 cm⁻¹
C) 1200 cm⁻¹
D) 890 cm⁻¹

44 Which of the following statements is not correct?
A) frequencies in cm⁻¹ are much smaller numbers than frequencies in Hz
B) wavelengths in μ are smaller numbers than wavelengths in Å
C) frequency varies inversely with wavelength
D) wavelengths given in nm are larger numbers than wavelengths in Å

45 Which of the following trienes will have the simplest ¹Hnmr spectrum?

MASS SPECTROMETRY

Question 1:
Which of the following compounds will give a molecular ion having m/z = an odd number?
A) CH₃CH₂OH
B) CH₂BrCl
C) CH₃CO₂H
D) CH₃CH₂NH₂
E) (CH₃)₂NCH₂C≡N

Question 2:
What class of compounds is most likely to give a fragment ion at m/z = M-18?

A) Alkenes
B) cycloalkanes
C) alcohols
D) alkyl iodides
E) benzene derivatives

Question 3:
Which of the following compounds is most likely to have its base peak at m/z = 43?

A) CH₃(CH₂)₄CH₃
B) (CH₃)₂CCH₂CH₃
C) cyclohexane
D) CH₃)₂CHCH(CH₃)₂

Question 4: Two mass spectra of gaseous compounds are shown here:
1. Enter the name or formula of a compound that would give mass spectrum 1.

2. Enter the name or formula of a compound that would give mass spectrum 2.

**Question 5:** Two mass spectra of pure liquid compounds are shown here:
1. Enter the name or formula of a compound that would give mass spectrum 1.

2. Enter the name or formula of a compound that would give mass spectrum 2.

**Question 6:** Two mass spectra of pure liquid compounds are shown here:
1. Enter the name or formula of a compound that would give mass spectrum 1.

2. Enter the name or formula of a compound that would give mass spectrum 2.

Question 7: Two mass spectra of pure liquid compounds are shown here:
1. Enter the name or formula of a compound that would give mass spectrum 1.

2. Enter the name or formula of a compound that would give mass spectrum 2.