Chapter 11. End-of-Chapter Solutions

1.
Different regions of the electromagnetic spectrum interact with matter in different ways. Infrared photons will excite vibrations, and this region is useful for identifying molecular functional groups. The broad absorption and fluorescence bands of molecules in the UV/Vis region are useful for quantitative measurements. The sharp lines in a proton NMR spectrum are useful because they shift and split depending on the local environment and proximity to other protons.

2.
A mass spectrum shows peaks for the molecular ion and fragment ions. If two molecules contribute to the mass spectrum, all these ions will appear in one spectrum. The molecular ion of the higher-mass molecule can be identified, but the molecular ion of the lower-mass molecule will be difficult to distinguish from fragment ions. The fragmentation pattern for a given molecule can be reproducible and a molecule can be identified by comparing an experimental mass spectrum to reference spectra in a search library. Additional fragment ions due to a second molecule will make this search less reliable.

3.
A mass spectrum will show peaks for the molecular ion and fragment ions. (The molecular ion can be missing if the molecular ion is particularly unstable. It might be viewable on changing ion source conditions or, in the case of GC-MS, obtaining the spectrum by LC-MS.)

The parent ion mass should correspond to the molecular mass. For large molecules, the isotope pattern due to ^{13}C, ^{2}H, etc can be compared to calculations to confirm an empirical formula. Numerous isotope pattern calculators can be found via an internet search.

The fragment ions will be pieces of the molecule that are stable as ions. For example, a fragment ion peak at $m/z = 77$ is generally due to a $C_6H_5^+$ ion. Seeing this peak suggests that the molecule has a phenyl group in the structure. Another common motif is a series of peaks separated by 14. These are alkyl fragments such as propyl$^+$ ($m/z = 43$), butyl$^+$ ($m/z = 57$), and pentyl$^+$ ($m/z = 71$). Observing these peaks in a spectrum indicate an alkyl chain is present.

4.
The main components of a mass spectrometer and their principles are summarized in the following table. All instruments have a vacuum system to operate at reduced pressure, ion lenses to accelerate and focus an ion beam, and electronics to measure detector current or count rate. Depending on the details of the sample and instrument, there is also some type of interface to introduce analyte into the ion source.

Component	Operating Principles
Ion source	Neutral atoms or molecules are converted to an ion by either using energy to remove an electron or by an electron or proton transfer to the neutral species. A plasma is the most common energy source to create atomic ions. There are numerous types of ion sources for molecules, depending on the thermal stability, size, and polarity of the analytes.
Mass analyzer	The mass analyzer separates ions of different m/z in space or time. On doing so, the ions of different m/z can be counted individually by the detector.
Detector	Most mass spectrometer detectors convert the number of ions striking it per unit time to a count rate or an electric current. Detection in an orbitrap is an exception where an electrode picks up an image current for further processing.

5.

m/z is mass-to-charge ratio. The physical processes that accelerate or deflect ions depend on both mass and charge. Mass analyzers therefore separate ions based on this ratio.

The molecular ion is the ion observed in the spectrum that has no fragmentation. In ionization methods that create an ion by a proton transfer, the peak will be labeled as $[M+H]^+$.

The fragmentation pattern is the relative intensity of all peaks in a mass spectrum. It is very reproducible for 70 eV electron ionization in GC-MS. The fragmentation pattern is more variable for LC-MS ionization methods.

The isotope pattern is the relative intensity of the higher mass peaks immediately adjacent to a peak. The higher mass peaks occur due to the natural relative abundance of higher mass isotopes, e.g., ^{13}C, ^{2}H, ^{18}O, etc. A notable example is the ^{35}Cl to ^{37}Cl isotopes, which occur in a 3 to 1 ratio. Observing two peaks in a 3:1 ratio separated by two mass units is an indication that a molecule contains Cl.

6.

The time-of-flight ($R > 10,000$) and the orbitrap ($R > 100,000$) mass spectrometers are the two most common lab-based instruments that can achieve accurate mass determinations. The other common mass analyzers are limited to nominal mass determinations ($R \approx 1000$).

7.

As in mass spectra and other spectroscopies, an impurity will contribute additional lines to the spectrum of the target analyte. An impurity at the 1% level or less will probably not be noticeable in an infrared spectrum. An impurity present at 10% or greater might show new peaks or change the relative intensity of peaks with which it has overlapping lines. The effect of an

impurity will depend on the degree of overlap and relative intensity of lines for the two molecules. As an example, the spectrum of a 50:50 mix of ethanol and toluene was barely different from pure ethanol. The presence of relatively weak absorption bands due to aromatic vibrations was the only indication that another compound was present.

8.
An overtone absorption is the upward transition from the $v'' = 0$ vibrational ground state to an excited vibration greater than $v'' = 1$. The $v'' = 0$ to $v'' = 1$ transition shown in Figure 11.3 is called the fundamental absorption. Overtone absorption bands are generally weak. However, it is important to recognize them in spectra, so they are not erroneously assigned as a functional group that is not present in the molecule.

9.
I list the most obvious vibrations from the functional group region for these molecules in the following table.

	Types of protons	Approximate peak position (cm^{-1})
(a) isooctane	C–H stretch	2850 – 2950
(b) benzene	Aromatic C–H stretch C–C ring mode	3050–3100 1500
(c) phenol	O–H stretch	3300 (broad)
(d) polyvinyl alcohol	C–H stretch O–H stretch	2850–2950 3400 (broad)
(e) isopentyl acetate	C–H stretch C=O stretch	2850–2950 1750 (strong)
(f) benzaldehyde	Aromatic C–H stretch Alkyl C–H stretch C=O stretch	3050–3100 2700–2900 1700 (strong)

10.
An NMR experiment excites all nuclei with a broad-band pulse of RF energy. One coil provides this excitation pulse. After excitation, the second coil, called the receiver coil, picks up an induced current as the nuclei relax back to an equilibrium population distribution.

11.
Since the position of a peak in an NMR spectrum is a delta value relative to a reference, a given nuclei will occur at the same delta for any magnetic field. The advantage of using a higher

magnetic field is that it improves both resolution and sensitivity. The resolution increases because spreading the peaks over a larger spectral region narrows the peaks when converted to delta values. The larger energy level splitting at higher magnetic field increases sensitivity because the population difference between the lower and higher levels will be greater.

12.

Use Table 11.7 or similar information from literature sources to predict peak positions for the different types of protons in these molecules. Confirm your predictions by viewing NMR spectra in one of the databases listed on page 403.

	Types of protons	Approximate peak position (δ)
(a) isooctane	methyl	1.0
	methylene	1.3
(b) benzene	aromatic	7.3
(c) phenol	hydroxyl	Near 5 (variable depending on solvent)
	aromatic	7.0–7.5 (multiple proton environments)
(d) polyvinyl alcohol	methylene	1.6
	methylene with OH	4.0
(e) isopentyl acetate	methyl	1.0
	methylene	1.5
	methyl next to C=O	2.0
	methylene next to O	4.1
(f) benzaldehyde	aromatic	7.5–8 (multiple proton environments)
	aldehyde	10