Chapter 4. End-of-Chapter Solutions

1.
(a) Rearranging $c = \lambda\nu$

650 nm:
$\nu = \frac{2.998\times10^{8}\ \text{m/s}}{650\times10^{-9}\ \text{m}} = 4.61\times10^{\mathbf{14}}\ \text{Hz or 461 GHz}$

405 nm:
$\nu = \frac{2.998\times10^{8}\ \text{m/s}}{405\times10^{-9}\ \text{m}} = 7.40\times10^{\mathbf{14}}\ \text{Hz or 740 GHz}$

(b) Using $E = h\nu$, where h is Planck's constant, 6.626×10^{-34} J s.

650 nm:
$E = (6.626\times10^{-34}\ \text{J s})(4.61\times10^{\mathbf{14}}\ \text{s}^{-1}) = 3.06\times10^{-19}\ \text{J}$

$E = \frac{1}{650\times10^{-9}\ \text{m}} \quad \frac{1\ \text{m}}{100\ \text{cm}} = 15{,}400\ \text{cm}^{-1}$

405 nm:
$E = (6.626\times10^{-34}\ \text{J s})(7.40\times10^{\mathbf{14}}\ \text{s}^{-1}) = 4.90\times10^{-19}\ \text{J}$

$E = \frac{1}{405\times10^{-9}\ \text{m}} \quad \frac{1\ \text{m}}{100\ \text{cm}} = 24{,}700\ \text{cm}^{-1}$

Both wavelengths are in the visible spectral region and are of the same order of magnitude in energy. You will want to develop a sense of scale of the different spectral regions. The wavenumbers or inverse centimeter unit, cm^{-1}, is a common unit in spectroscopy because of the convenient scale in the infrared through visible regions.

2.
(lowest energy) radio, microwave, infrared, visible, ultraviolet, X-ray, γ-ray (highest energy)

3.
The H atom has one proton and one electron. The highest charge that it can have is +1. Maybe the writer meant "highly excited."

4.
$\lambda = \frac{1}{3100\ \text{cm}^{-1}} \quad \frac{1\ \text{m}}{100\ \text{cm}} = 3.2\times10^{-6}\ \text{m} = 3.2\ \mu\text{m}$

The energy of a 280 nm photon is

$$E = \frac{1}{280\times10^{-9}\ \text{m}} \quad \frac{1\ \text{m}}{100\ \text{cm}} = 35{,}700\ \text{cm}^{-1}$$

Dividing this energy by the IR photon energy gives:

$$\frac{35{,}700\ \text{cm}^{-1}}{3100\ \text{cm}^{-1}} = 11.5\ \text{IR photons}$$

This example shows that the scale of energies between the infrared and the visible differs by roughly ten-fold.

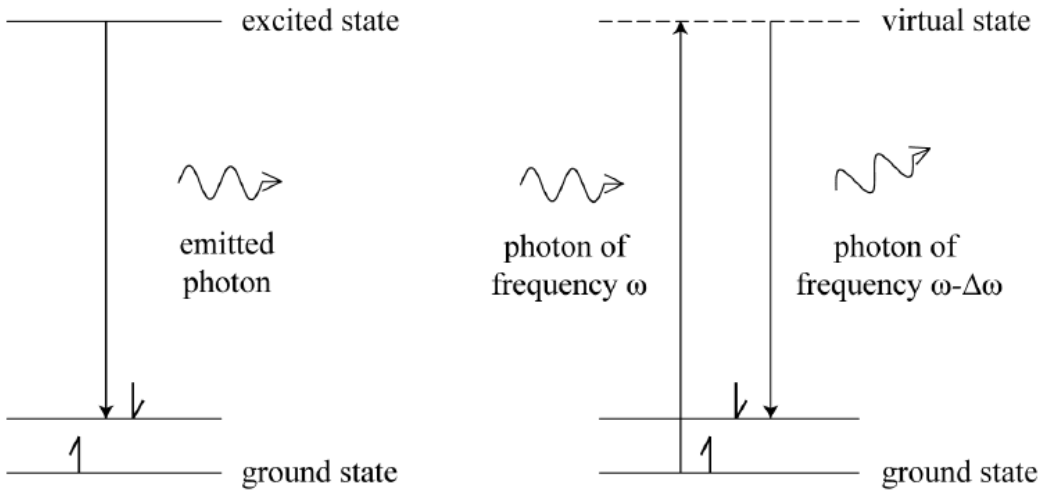
5.

(a) a filled antibonding orbital – No, once an orbital is full it is full and no further electrons may be added.

(b) an empty antibonding orbital – Yes, an empty orbital can accept an electron.

6.

Schematic of emission (left) and Raman scattering (right). The electron symbols show the occupied levels after the transition occurs. In the emission example, one electron was placed in the excited state by some means, such as absorbing collisional, thermal, or light energy. In the scattering example, the photon is shown at an angle to indicate a change in direction after interacting with the electronic system. (Raman scattering is a weak process, and most scattered photons return to their original energy level, the ground state in this example.)



7.

Bond length is inversely related to bond energy. The shortest bond in the series, C−F, will be the strongest and require the highest IR energy to be excited.

8.
The equation for the best fit line to the calibration data is

$$y = (-0.8432\ \text{mL/mg})x + 0.6148$$

where x is glucose concentration in mg/mL and y is the unitless absorbance measurement.

For a measurement of 0.521 the expression becomes

$$0.521 = (-0.8432\ \text{mL/mg})[\text{glucose}] + 0.6148$$

and the result is [glucose] = 0.111 mg/mL.

9.
n-hexane. C_6H_{14} has no non-bonding or π electrons and therefore can only have the short wavelength $\sigma \rightarrow \sigma^*$ transitions.

10.
(a) $A = abc$, so in a 5-cm cuvette A will be 5(0.333) = 1.67 AU.

(b) $A = -\log(T)$ so $T = 10^{-1.67} = 0.0216$, which is equivalent to 2.16 %-transmittance.

(c) In a 2-cm cuvette A will be 2(0.333) = 0.666 AU and $T = 10^{-0.666} = 0.216$ or o 21.6 %-transmittance.

Note that the linear relationship for A versus b or c is true only for A, not for transmittance.

11.
Absorbance is proportional to path length, so first determine the absorbance at 1.0 cm.

P = 398 photons and P_o = 1000 so:

$$A = -\log \frac{348}{1000} = 0.458$$

The absorbance at 2.0 cm will be twice the 1.0-cm absorbance or 0.916. Now reversing our calculation:

$$0.916 = -\log \frac{\text{photons}}{1000}$$

leads to 121 photons at 2.0 cm, and therefore a transmittance of 0.121 or percent-transmittance of 12.1 %.

12.
The stain on the cuvette will appear as an absorbance in addition to the analyte absorbance, so the measurements will be erroneously higher than the true value.

13.
$A = 0.1 = -\log(T)$, $T = 0.79$
and
$A = 1.0 = -\log(T)$, $T = 0.10$
These transmittance values provide a range where lamp noise in subtracting two large values (for the high T region) and stray light (for the low T region) are unlikely to affect the measurement.

14.
Array spectrometers acquire the whole spectrum simultaneously and are therefore very rapid. Their disadvantage is that the spectral resolution is fixed for the pixel width of the detector. Scanning instruments are more flexible and can provide higher resolution and greater sensitivity by varying the slit width and changing the type of detector, respectively.

15. Using the data point for a distance of 1.0 cm:

$$A = -\log \frac{348}{1000} = 0.458$$

Using the Beer-Lambert law:
$0.458 = \varepsilon(1.00\text{ cm})(4.0\times10^{-5}\text{ M})$
$\varepsilon = 11{,}500\text{ M}^{-1}\text{ cm}^{-1}$

The result should be the same for any data point, but doing a number of calculations and taking the mean will average random scatter.

16.
(a) Inserting the unknown measurement into the equation for the calibration curve.
$0.271 = -0.8432[\text{glucose}] + 0.6148$
[riboflavin] = 0.408 mg/mL

(b) The background of 0.009 must be subtracted from the measurement, then calculating as before:
$(0.271 - 0.009) = -0.8432[\text{glucose}] + 0.6148$
[riboflavin] = 0.418 mg/mL

17.
A very weak absorbance will attenuate the light power passing through the test portion a very small amount. The light measurements of P and P_o will be nearly identical. The noise fluctuations of the lamp source will limit the ratio of P and P_o that can be distinguished.

18.
Note that the trendline equation does not show the units of the slope and intercept. Since the fluorescence signal is given in arbitrary units, the slope is 50.466 ppm^{-1}. Inserting the unknown measurement into the equation for the calibration curve:
$14.5 = (50.466\ ppm^{-1})[riboflavin] + 0.7505$
[riboflavin] = 0.272 ppm

19.
(a) Using the Beer-Lambert law:
$0.549 = \varepsilon(1.00\ cm)(4.00\times10^{-5}\ M)$
$\varepsilon = 13{,}720\ M^{-1}\ cm^{-1}$
(I carry an extra significant digit in intermediate calculations that I will drop in the final result.)

(b) Again using the Beer-Lambert law and the molar absorptivity from the calibration above.
$0.455 = (13720\ M^{-1}\ cm^{-1})(1.00\ cm)[Fe(phen)_3^{2+}]$

$$[Fe(phen)_3^{2+}] = \frac{0.455}{(13720\ M^{-1}\ cm^{-1})(1.00\ cm)}$$

$[Fe(phen)_3^{2+}] = 3.32\times10^{-5}\ M$

(c) The water sample was diluted by 10 to add the other reagents for the absorbance measurement, so
$[Fe^{2+}] = (3.32\times10^{-5}\ M)(10) = 3.32\times10^{-4}\ M$

(d) This absorbance value is above the linear range for most spectrophotometers. The test portion should be diluted until the absorbance is less than or near 1.0.

(e) This absorbance measurement will be lower than a test portion that was all Fe^{2+}. The calculated concentration will be less than the true iron concentration in the water sample.