14.E: Spectroscopy (Exercises)

14.1: Vocabulary

Q14.2

Find the wave number and frequency of light with a wavelength of 700 nm (to three significant figures).

S14.2

1. Wave number is equal to the reciprocal of wavelength. Its units are inverse centimeters.

$$ \tilde \nu = \dfrac{1}{\lambda} $$

$$ \tilde \nu = \dfrac{1}{700\ nm} \times \dfrac{10^9\ nm}{100\ cm} $$

$$ \tilde \nu = 1.43\ \times 10^4\ cm^{-1} $$

2. Use the relationship between frequency, speed, and wavelength to solve for frequency.

$$ \nu = \dfrac{c}{\lambda} $$

$$ \nu = \dfrac{2.998\ \times 10^8\ m/s}{700\ nm \times \dfrac{m}{10^9\ nm}} $$

$$ \nu = 4.28 \times 10^{14}\ s^{-1} $$

Q14.2a

Convert $3 \times 10^4\ cm^{-1}$ to wavelength. Identify what kind of spectroscopy?

Q14.2a

What is the frequency and wavenumber of a 740 nm photon?

Q14.2b

The wavelength of the red line in the Hydrogen spectrum is 656 nm ($656 \times 10^{-9}\ m$). What is the wavenumber and frequency of it?

S14.2b

The wave number $=1/\lambda = 1/656 \times 10^{-9}$ m $= 1.5 \times 10^6$ m^{-1}

Q14.2c

Convert 533 nm to wavenumber and frequency.

Q14.4a

Convert the following absorbance to percent transmittance: (a) 0.56, (b) 1.5, (c) 6.8.

Q14.4b

Calculate percent transmittance from the following values of absorbance:

a. 4.0
b. 0.23
c. 1.6

S14.4b

Solve, using the relationship between transmittance and absorbance.

$$ -\log_{10}T = A $$

$$ T = 10^{-A} $$

For percent transmittance, multiply T by 100%

(a)

$$ T = 10^{-4.0} \times 100\% $$

$$ T = 0.010\% $$

(b)

$$ T = 10^{-0.23} \times 100\% \]

$$ T = 59\%\]

(c)

$$ T = 10^{-1.6} \times 100\% \]

$$ T = 2.5\% \]

Answers: 0.010%, 59%, 2.5%

Q14.4c
Convert the following from percent transmittance to absorbance.

  a. 0.10%
  b. 23%
  c. 84%

Q14.4c

What is the percent transmitter of the following absorbance

  a. 0.4
  b. 1.2

S14.4c

We have A = 2- log %T

a. 0.4 = 2-log%T -->%T= $10^{(2-0.4)}$

%T= 39.8

b. 1.2 = 2-log%T ---> %T = 6.3%

Q14.6a
When molecules are exposed to radiation with frequency, v, such that $\Delta E = h\upsilon$, do they travel through a transition from a higher to lower state, or lower to higher state?

Q14.6b

Find the uncertainty of simultaneously measuring the frequency and wavelength of an emission, if the wavelength is 430 nm and the excited state lifetime is 0.50 nanoseconds.

S14.6b

1. Use Heisenberg's uncertainty principle and the relationship between energy and frequency to find the uncertainty of frequency.

$$ \Delta E \Delta t \geq \dfrac{h}{4 \pi} \]

$$ \Delta E = h \Delta \nu \]

$$ h \Delta \nu \Delta t \geq \dfrac{h}{4 \pi} \]

$$ \Delta \nu \geq \dfrac{1}{4 \pi \Delta t} \]

The maximum value for Δt is the lifetime of the excited state.

$$ \Delta \nu \geq \dfrac{1}{4 \pi 0.50 ns \times \dfrac{s}{10^9\ ns}} \]

$$ \Delta \nu \geq 1.6 \times 10^8\ s^{-1} \]

2. Use the uncertainty of frequency and the relationship between frequency and wavelength to find the uncertainty of the wavelength.

$$ \lambda = \dfrac{c}{\nu} \]

$$ | \Delta \lambda | = \dfrac{c}{\nu^2} | \Delta \nu | \]

$$| \Delta \lambda | = \dfrac{\lambda ^2 | \Delta \nu | }{c}$$

$$| \Delta \lambda | = \dfrac{(430\ nm)^2 \times 1.6 \times 10^8\ s^{-1}}{2.998 \times 10^8\ m/s} \times \dfrac{m}{10^9\ nm}$$

$$| \Delta \lambda | = 2.3 \times 10^{-7}\ nm$$

Q14.6c

Calculate the wavelength emission of an electronically excited molecule with uncertainties in frequency (Δv) is $5.6 \times 10^6\ s^{-1}$ and the wavelength ($\Delta \lambda$) 4×10^{-6} nm? $c = 3 \times 10^8 ms^{-1} = 3 \times 10^{17} nms^{-1}$

S14.6c

We have:

$$| \Delta \lambda | = \frac{\lambda | \Delta v|}{v} \tag{14.E.1}$$

Since

$$\nu = \frac{c/}{\lambda} \tag{14.E.2}$$

then

$$| \Delta \lambda | = \frac{\lambda^2 | \Delta v|}{c} \tag{14.E.3}$$

$=> 4 \times 10^{-6} nm = (\lambda^2 \times 5.6 \times 10^6\ \cancel{s^{-1}})/ 3 \times 10^{17} nm\cancel{s^{-1}}$

$=> \lambda = 463$ nm

Q14.8a
In the gas phase, using electronic spectroscopy, what is observed on the electronic spectra of diatomic molecules at high resolution in terms of structure and bands?

Q14.8b

Explain why the decreasing of temperature will increase the resolution of visible and UV spectra?

S14.8b

Decreasing temperature will lower the kinetic energy of molecules. Thus the effect of Doppler and collisional broadening decrease, making the resolution enhances.

Q14.8c
Measuring the spectrum of the UV light at low temperature is a good way to enhance the resolution of the UV light. Explain. Give one more example.

Q14.10

In a 5.0 mM solution, a solute absorbs 90% of a visible light as the beam passes through a 80 mm cell. Calculate the molar absorptivity of this solute.

S14.10

We can calculate the transmittance:

$$T = 1.00 - 0.9 = 0.10 \tag{14.E.4}$$

Also, the absorbance is

$$A = -\log T = -\log(0.10) = 1.0 \tag{14.E.5}$$

Next step, use Beer-Lambert law to determine the molar absorptivity,

$$\epsilon = \frac{A}{bc} \tag{14.E.6}$$

$$\epsilon = \frac{1}{(8.0\,cm)(5.0\,mM)} = 2.5 \times 10^{-2}\,L\,mol^{-1}\,cm^{-1} \tag{14.E.7}$$

Q14.10

Calculate the absorbance (A) with the molar absorptivity= $6.17\,Lmol^{-1}cm^{-1}$, c= 0.52 M when a certain wavelength passes through 2.3-cm cell.

S14.10

$$A = \epsilon bc = (6.17)(2.3)(0.52) = 7.38 \tag{14.E.8}$$

Q14.12

Calculate E_{vib} for a harmonic oscillator if $v = 2$ and $\nu = 3.24 \times 10^{13}\ Hz$

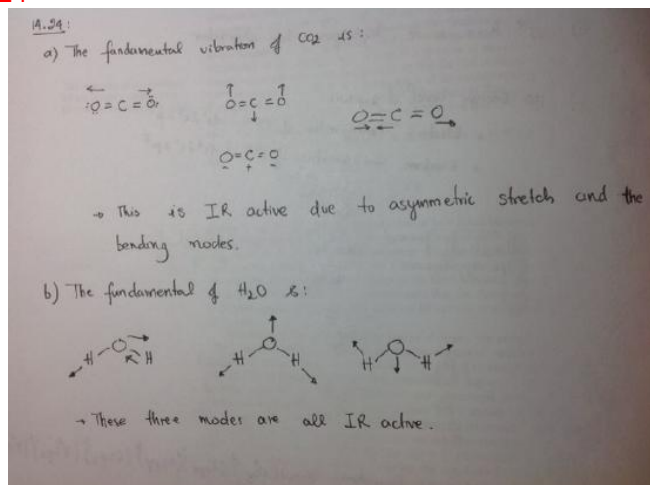### S14.12

$$E_{vib} = (v + \frac{1}{2})h\nu = (2 + \frac{1}{2})6.626 \times 10^{-34} \times 3.24 \times 10^{13} = 5.37 * 10^{-20}\,Hz \tag{14.E.9}$$

Q14.24
Given the following molecules: CO_2, H_2O. Show the fundamental vibration modes for each of the molecule and explain which one are IR active or both.

S14.24

Q14.26
Given the following molecules: He_2, F_2, H_2, O_2 and Li_2. Rank these molecules from lowest to highest fundamental frequency of vibration? Show works.

S14.26
This can be determined by looking at the mass of the molecules. The one with the lowest mass will have the highest fundamental frequency of vibration and vice versa. $\mu_{He_2} = \frac{(4.003amu)(4.003amu)}{(4.003amu) + (4.003amu)} = 2.0015$ and the similar calculation can be applied for other molecules, and the rank is as the following: Lowest --- $F_2 < O_2 < Li_2 < He_2 < H_2$ ---- highest

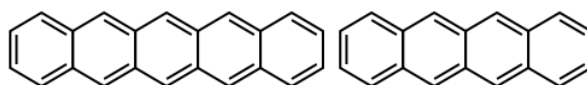## 14.5: Nuclear Magnetic Resonance

Q14.12
A chemist used the NMR machine to scan his sample and he obtained a signal-to-noise (S/N) ratio of 2.0. How long would it takes the chemist to generate a spectrum with a S/N ratio of 40? Assumed he spent 5 minutes per scan.

S14.12

We are looking at the $\left(\frac{S}{N}\right)_n$. This mean the ratio of signal to noise would change according to the number of n scans Thus,

$\left(\frac{S}{N}\right)_n = \frac{nS}{\sqrt{n}N} = \sqrt{n}\left(\frac{S}{N}\right)_1 \sqrt{n} = \left(\frac{S}{N}\right)_n \div \left(\frac{S}{N}\right)_1 = 40 \div 2 = 20$ $n = 400$ Since 400 scans at the interval of 5 mins, it would take 400 × 5min = 2000min (1h/60min) = 33.3 h to generate this spectrum
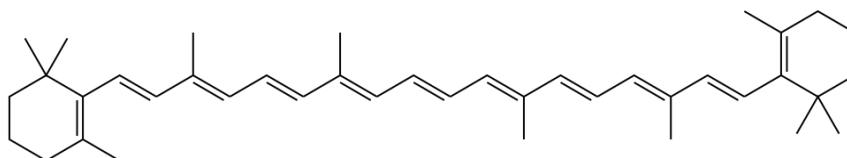
Q14.28

Explain why pentacene crystals are blue in color, but tetracene crystals are orange.

pentacene tetracene

Q14.29

Use the particle in a one-dimensional-box model to calculate the longest wavelength peak in the absorption spectrum of ß-carotene (structure shown below).

Q14.32a
What does chemical shift measure? What can influence chemical shift?

S14.32a

Chemical shift measures the difference in resonance frequencies between a nucleus of interest and a reference nucleus. It is influenced by electron shielding; the more electrons are pulled away from a proton of interest (the smaller the electron density around the nucleus of interest), the greater the chemical shift.
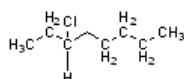
Q14.32b
Assume you are doing an NMR spectroscopy. You operate the spectrometer at 100 Hz, but you find a signal of a compound at an unknown frequency downfield from TMS peak. However, you know its chemical shift is 6.5 ppm. Calculate the unknown frequency for your lab report.

Q14.34b
Assuming the precession frequency is 100 MHz and $\gamma = 10.0\times10^5\,T^{-1}s^{-1}$, calculate the Larmor frequency for ^{17}O .

Q14.32c

Identify the most shielded and deshielded hydrogen for this compound:

S14.32c

The hydrogen groups on the far right end are the most shielded and the hydrogen group on the carbon with the chlorine group is the most deshielded.

Q14.32d

The NMR signal of coumpound is 280 Hz downfield from TMS is 70 MHZ. find its chemical shifl in ppm.

S14.32d

$$\delta = \frac{\nu - \nu_{ref}}{\nu_{spec}} \times 10^6 \qquad\qquad (14.E.10)$$

$$\delta = \frac{280\ Hz}{70 \times 10^6} \times 10^6 = 4.0\ ppm \qquad\qquad (14.E.11)$$

Q14.34

a. Calculate the magnetic field, B_0 that corresponds to a precession frequency of 600 MHz for ^1H.
b. What is the field strength (in tesla) needed to generate a ^1H frequency of 500 MHz?
c. How do spin-spin relaxation and spin-lattice relaxation differ from each other?
d. The ^1H NMR spectrum of toluene shows that it has two peaks because of methyl and aromatic protons recorded at 60 MHz and 1.41 T. Given this information, what would be the magnetic field at 400 MHz?
e. What is the difference between ^{13}C and ^1H NMR?

S14.34

a. B_0= 14.1 T.
b. Using the equation used in problem 1 and solving it for B_0 we get a field strength of 11.74 T.
c. Look under relaxation.
d. Since we know that the NMR frequency is directly proportional to the magnetic strength, we calculate the magnetic field at 400 MHz: B_0 = (400 MHz/60MHz) x 1.41 T = 9.40 T
e. Look under applications.

Q14.34

calculate the field strength in tesla to generate ^1H frequency of 300 MHz?

S14.34

$$B_0 = 2\pi\nu/\gamma = 2\pi(300 \times 10^6\ s^{-1})/\ 26.75 \times 10^7\ T^{-1}s^{-1}$$

$$B_0 = 7.04\ T$$

Q14.36

Given 4.7 T, calculate the diference in frequency for 2 protons whose § value differ 1.25 and 400 MHz
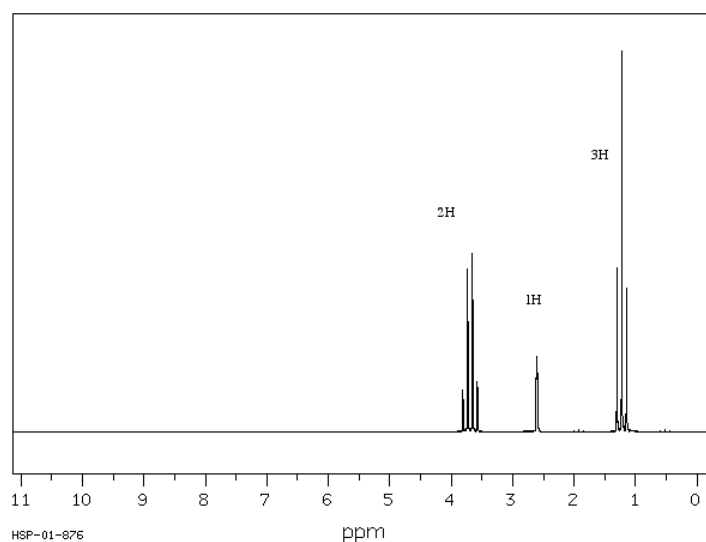
S14.36

$$B_0 = (\Delta\delta \times v_{spec})\ /\ 10^6 = (1.25\ (200 \times 10^6\ Hz))\ /\ 10^6$$

$$B_0 = 2.5 \times 10^2\ Hz$$

Q14.38

Draw the NMR spectrum of isobutyl alcohol with chemical shift -CH 0.90 ppm, -A-H 1.68ppm, -CH2 3.26 ppm, O-H 4.49 ppm

S14.38

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14.6: Electron Spin Resonance

Q14.42

You performed an electron spin resonance (ESR) experiment with di-*tert*-butyl nitroxide radical and get 3 lines of equal intensity. Then, you combine di-*tert*-butyl nitroxide radical with ascorbic acid and was about to run another ESR experiment but Jill stopped you. Why did Jill stop you?

14.7: Fluorescence and Phosphorescence

Q14.43

Someone has handed you data of the luminescence of a material as a function of time. How can you decide whether the luminescence process was fluorescence or phosphorescence?

14.8: Lasers

14.9: Optical Rotatory Dispersion and Circular Dichroism

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