10.

HW Review:

**Diffraction and crystallography**

11.2 Describe the "phase problem" in X-ray crystallography, and at least one way the problem can be addressed (or at least circumvented to solve X-ray structures).

See Page 420 for phase problem, See Page 421 for the way the problem can be addressed.

11.20 Draw a set of points as a rectangular array based on unit cells of side a and b, and mark the planes with Miller indices (1,0,0), (0,1,0), (1,1,0), (1,2,0), (2,3,0), (4,1,0).

Here's an example...

$$(1, 2, 0) = (k, h, l) \implies (\frac{a}{h}, \frac{b}{k}, 0) = (\frac{a}{1}, \frac{b}{2}, 0)$$

$$\implies 2 \times (\frac{a}{1}, \frac{b}{2}, 0) = (2a, b, 0)$$
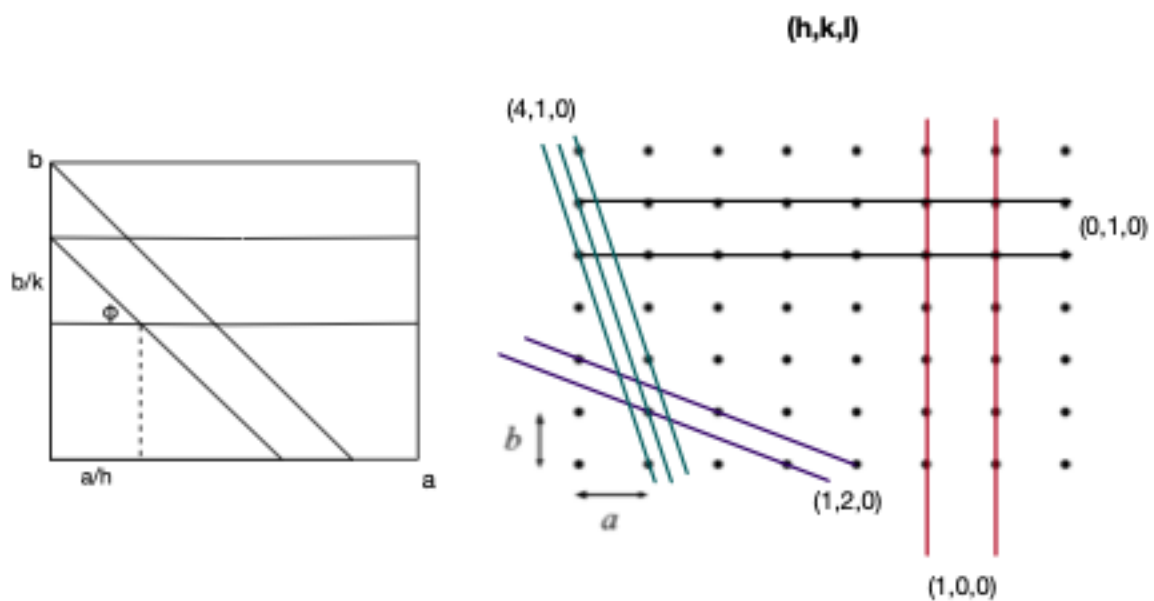
Chapter 12

12.12 A swimmer enters a gloomier world (in one sense) on diving to greater depths. Given that the mean molar absorption coefficient of seawater in the visible region is $6.2 \times 10^{-5} \ dm^3 \ mol^{-1} \ cm^{-1}$, calculate the depth at which a diver will experience (a) half the surface intensity of light and (b) one-tenth that intensity.

Derivation of Beer's Law:

Here is an image of the situation we wish to model:
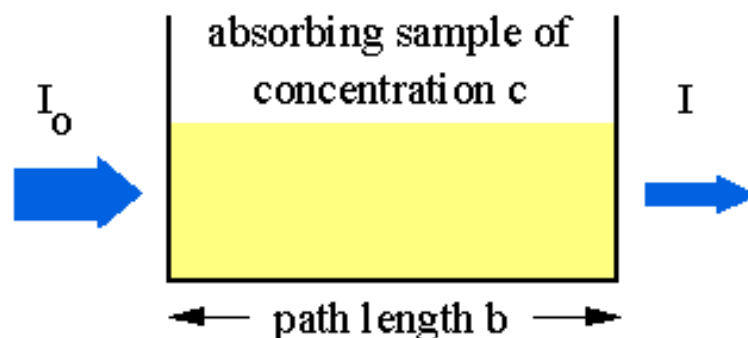
The density of particles, ρ and the absorption coefficient, α multiplied by the intensity, I shown in the 1st order differential equation:

$$-\frac{\partial I}{\partial x} = I\alpha\rho$$

Combine like-terms to each side of the equation:

$$\int_{I_0}^{I} \frac{\partial I}{I} = -\int_{0}^{x} \alpha\rho\partial x$$

We know that $\int \frac{1}{x}dx = ln(x)$, so

$$ln(\frac{I}{I_0}) = -\alpha\rho x,$$

To get the general solution of the D.E we can take the exponential of both sides

$$\frac{I}{I_0} = e^{-\alpha\rho x}$$

General Solution to the D.E:

$$I(x) = I_0 e^{-\alpha\rho x}$$

Otherwise, to continue deriving Beer's Law we can use the property of logarithms:

$$-ln(\frac{I}{I_0}) = ln(\frac{I_0}{I}) = \alpha\rho x,$$

and since we know the following

$$log_{10}(x) = \frac{ln(x)}{ln(10)},$$

then we can say

$$log_{10}(\frac{I_0}{I}) = \frac{\alpha\rho x}{ln(10)}$$

Finally, we can say that $\rho \propto c$. We can also simplify further by saying $\epsilon = \frac{\alpha}{\ln(10)}$, which has units of $M^{-1}cm^{-1}$ and $x = b$, where b is in cm.

$$A = \ln(\frac{I_0}{I}) = \epsilon bc$$

Now, solving for the path length b gives the following expression with $c_{H_2O} = \rho/MW$ and $I = 0.5I_0$.

$$b = \frac{\ln(\frac{I_0}{0.5I_0})}{\epsilon(\rho/MW)} = \frac{0.301}{(6.2x10^{-5}dm^3.\,mol^{-1}.\,cm^{-1})(55.5mol.}$$

Note, since the information regarding salt water concentration is not provided in the question we approximated the concentration by with values for H_2O.

12.25 How many normal modes of vibration are there for (a) NO_2, (b) N_2O, (c) cyclohexane, and (d) hexane?

There are $3N - 6$ and $3N - 5$ vibrational modes (in which N is the number of atoms in molecule) for non-linear and linear molecules; respectively.

(a) NO_2, Non-linear; $3N - 6 = 3(3) - 6 = 3$

(b) N_2O, linear; $3N - 5 = 3(3) - 5 = 4$

(c) cyclohexane, non-linear; $3N - 6 = 3(18) - 6 = 48$

(d) hexane, non-linear; $3N - 6 = 3(20) - 6 = 54$

SIDE NOTES:

Rates of various processes

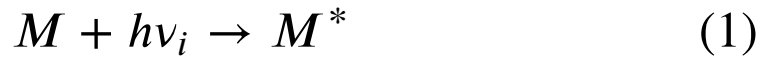| Process	Timescales (s)	Radiative	Transition
IC	$10^{-14} - 10^{-11}$	N	$S_n \rightarrow S_1$
Vib Relax	$10^{-14} - 10^{-11}$	N	$S_n{}^* \rightarrow S_n$
Abs	10^{-15}	Y	$S_0 \rightarrow S_n$
Fluor	$10^{-9} - 10^{-7}$	Y	$S_1 \rightarrow S_0$
ISC	$10^{-8} - 10^{-3}$	N	$S_1 \rightarrow T_1$
Phos	$10^{-4} - 10^0$	Y	$T_1 \rightarrow S_0$

- timescale of FRET are typically in ns

12.37 When benzophenone is illuminated with ultraviolet radiation, it is excited into a singlet state. This singlet changes rapidly into a triplet, which phosphoresces. Triethylamine acts as a quencher for the triplet. In an experiment in methanol as solvent, the phosphorescence intensity Iphos varied with amine concentration as shown below. A time-resolved laser spectroscopy experiment had also shown that the half-life of the fluorescence in the absence of quencher is 29 ms. What is the value of k_Q?

Species			
$[Q]/(mol\ dm^{-3})$	0.0010	0.0050	0.0100
$I_{phos}/(A.\,U.\,)$	0.41	0.25	0.16

First, we need to write out the mechanism that is given in the question:

When benzophenone is illuminated with ultraviolet radiation, it is excited into a singlet state.

$$M + h\nu_i \rightarrow M^* \tag{1}$$

This singlet changes rapidly into a triplet, which phosphoresces.

$$M^* \rightarrow M + h\nu_{phos} \tag{2}$$

Triethylamine acts as a quencher for the triplet.

$$M^* + Q \rightarrow M + Q \tag{3}$$

To model this process, we apply the steady state approximation on $[M^*]$ to obtain I_{phos}... (Do this to get your own "stern-volmer" equation that models what the questions provides).

Steady State is an assumption that the rate of (production/destruction) is equal to zero i.e., at equilibrium.

$$\frac{d[M^*]}{dt} = I_{abs} - k_Q[Q][M^*] - k_{phos}[M^*] = 0$$

$$\implies (-k_Q[Q] - k_{phos})[M^*] = -I_{abs} \implies [M^*] = \frac{}{k_Q}$$

and we know that $I_{phos} = k_{phos}[M^*]$, so

$$I_{phos} = k_{phos} \frac{I_{abs}}{k_Q[Q] + k_{phos}}$$

We can take the inverse of I_{phos} to get the equation in the form of a line:

$$\frac{1}{I_{phos}} = \frac{1}{I_{abs}} + \frac{k_Q[Q]}{k_{phos}I_{abs}}$$

Now, we plot the data that was given and extract the slope...

```python
%matplotlib inline
import plot as p
import numpy as np
Q = np.array([0.0010,0.0050, 0.0100])
Iphos = np.array([0.41, 0.25, 0.16])
x,y = Q,1/Iphos
p.simple_plot(x,y,xlabel=r'$[Q]$',ylabel=r'${I_{phos}}^{-1}$',Type='scatter',color=False,fig_size=(8,4),
              fit=True, order=1, annotate_text=r"$slope=k_{Q}/(k_{phos}I_{abs})$",annotate_x=-0.005, annotate_y=5.5)
```

```
LINEST data:
y=424.530188*x+(1.965514)
LinregressResult(slope=424.5301879248300
5, intercept=1.9655137944822072, rvalue=
0.9992022644095554, pvalue=0.02543041691
2291167, stderr=16.967310989778486)
<scipy.stats._distn_infrastructure.rv_fr
ozen object at 0x1a21538ef0>
Ttest_indResult(statistic=-3.81908198801
46667, pvalue=0.0187930819162 7094)
```
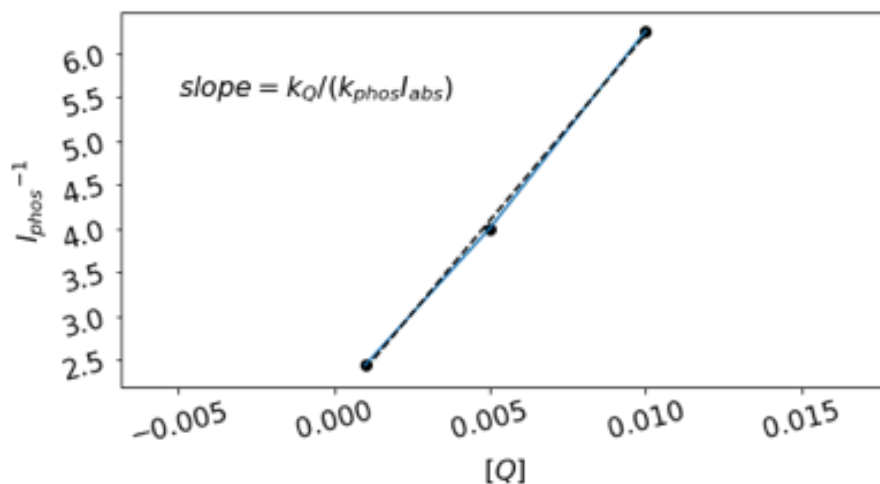
Therefore, the linear fit gives:
$$I_{phos}^{-1} = (424.5302 dm^3 mol)[Q] + (1.966),$$

where $\dfrac{k_Q}{k_{phos} I_{abs}} = 424.5302 dm^3 mol.$

Therefore,
$$k_Q = \frac{(24.5302 dm^3 mol)(2.39 \times 10^4 s^{-1})}{1.97} = 5.2 \times 10^6 dm^3 mo$$

What kind of information can be obtained using FRET spectroscopy? What is the distance dependence of the FRET effect?

Förster resonance energy transfer (FRET) spectroscopy is useful for studying processes involving inter and intra-molecular energy transfer and can be used to measure distances (ranging from 1 to 9 nm) in biological systems. Furthermore, conformational changes can be studied, and also good for studying bulk distances. Single molecule FRET —create histograms of binned FRET distances, ultimately revealing states.See Pages 500,501 for more information.

12.39 The Förster theory of resonance energy transfer and the basis for the FRET technique can be tested by performing fluorescence measurements on a series of compounds in which an energy donor and an energy acceptor are covalently linked by a rigid molecular linker

of variable and known length. L. Stryer and R.P. Haugland, Proc. Natl. Acad. Sci. USA 58, 719 (1967), collected the following data on a family of compounds with the general composition dansyl-(l-prolyl)n-naphthyl, in which the distance R between the naphthyl donor and the dansyl acceptor was varied by increasing the number of prolyl units in the linker:

R/nm	1.2	1.5	1.8	2.8	3.1	3.4	3.7	4.0	4.3	4.6
η_T	0.99	0.94	0.97	0.82	0.74	0.65	0.40	0.28	0.24	0.16

Are the data described adequately by the Förster theory (eqns 12.26 and 12.27)? If so, what is the value of R_0 for the naphthyl–dansyl pair?

Förster theory:

States that the efficiency of resonance energy transfer is related to the distance R between donor-acceptor pairs by

$$\eta_T = \frac{R_0{}^6}{R_0{}^6 + R^6},$$

where R_0 is the distance at which 50% of the energy is transfered from donor to acceptor, and R is the distance between donor and acceptor.

First, we need to rearrange the Förster theory equation into a linearized form.

$$\frac{1}{\eta_T} = \frac{R_0{}^6 + R^6}{R_0{}^6} = 1 + (\frac{R}{R_0})^6$$

Now, we are able to plot the data:

```
%matplotlib inline
import plot as p
import numpy as np
R = np.array([1.2, 1.5, 1.8, 2.8, 3.1, 3.4, 3.7, 4.0
, 4.3, 4.6])
nT = np.array([0.99, 0.94, 0.97, 0.82, 0.74, 0.65, 0
.40, 0.28, 0.24, 0.16])
x,y = R**6,1/nT
p.simple_plot(x,y,xlabel=r'$(R/(nm))^{6}$',ylabel=r'
${\eta_{T}}^{-1}$',Type='scatter',
              color=False,fig_size=(8,4),fit=True, o
rder=1)
```
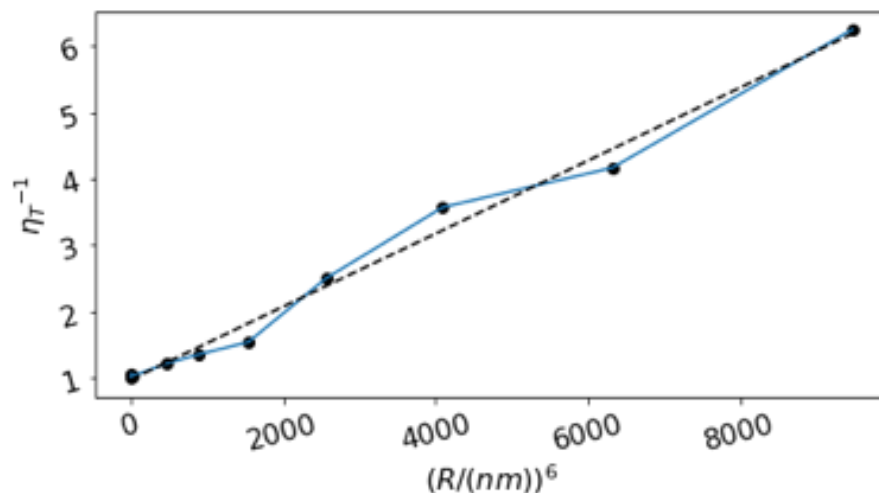
```
LINEST data:
y=0.000550*x+(0.971320)
LinregressResult(slope=0.00055031827065
7045, intercept=0.9713203050354837, rval
ue=0.9942902411662985, pvalue=4.61817449
9727511e-09, stderr=2.0881362169084858e-
05)
<scipy.stats._distn_infrastructure.rv_fr
ozen object at 0x1a216ce0f0>
Ttest_indResult(statistic=2.513617012289
7212, pvalue=0.021684950976179403)
```

Using the slope of the line
$y = 0.000550 * x + (0.971320)$, where the slope is
$0.000550 = (\frac{1}{R_0})^6$.

$$R_0 = (\frac{1}{0.000550nm^{-6}})^{1/6} = 3.5nm$$