Chapter 15

Textbook questions

Question 15-5

Why do some absorbing compound fluoresce but others do not?

Compounds that fluoresce have structures that slow the rate of nonradiative relaxation to the point where there is time for fluorescence to occur.

Compounds that do not fluoresce have structures that permit rapid relaxation by nonradiative processes.

Question 15-6

Discuss the major reasons why molecular phosphorescence spectrometry has not been as widely use as molecular fluorescence spectrometry?

The triplet state has a long lifetime which makes it susceptible to collisional deactivation.
Thus, most phosphorescence measurements are made at low temperature in a rigid matrix or in solutions containing micelles.
Also, electronic methods must be used to discriminate phosphorescence from fluorescence.
Not as many molecules give good phosphorescence signals as fluorescence signals.
As a result, the experimental requirements to measure phosphorescence are more difficult than those to measure fluorescence and the applications are not as large.

訊號弱、反應時間慢、易將能量傳給 solvent ，所以不好測

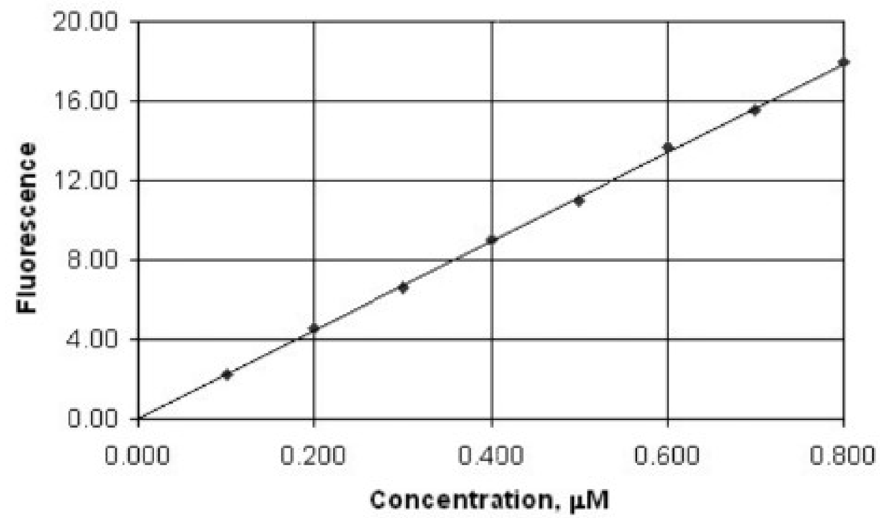
15-7

The reduced form of NADH is an important and highly fluorescent coenzyme. It has an absorption maximum of 340 nm and an emission maximum at 465 nm. Standard solutions of NADH gave the following fluorescence intensities

	Intensity / a.u.
0.100	2.24
0.200	4.52
0.300	6.63
0.400	9.01
0.500	10.94
0.600	13.71
0.700	15.49
0.800	**17.91**

A) Construct a spreadsheet and use it to draw a calibration curve for NADH
B) Find the least squares slope and intercept for the plot
C) Calculate the standard deviation of the slope and the standard deviation about regression for the curve
D) An unknown exhibit a relative fluorescence intensity of 12.16. Use the spreadsheet to calculate the concentration of NADH
E) Calculate the relative standard deviation for the result in (D)
F) Calculate the relative standard deviation for the result in (D) if the result of 7.95 was the mean of three measurements

	A	B	C
1	**Determination of NADH**		
2	Part (a)		
3	Concentration in μM	Fluorescence	
4	0.100	2.24	
5	0.200	4.52	
6	0.300	6.63	
7	0.400	9.01	
8	0.500	10.94	
9	0.600	13.71	
10	0.700	15.49	
11	0.800	17.91	
12	unknown	12.16	
13	Part (b)		
14	**Regression equation**		
15	Slope	22.3464	
16	Intercept	3.571E-04	
17	Concentration of unknown	0.544	
18	Parts (c), (d), (e), and (f)		
19	**Error Analysis**		
20	s_r (standard error in y)	0.175	
21	N	8	
22	S_{xx}	0.42	
23	s_m	0.27	
24	y bar (average fluoresence)	10.056	
25	M for part (e)	1	
26	M for part (f)	3	
27	Standard deviation in c for part (e)	0.008	
28	RSD in c for part (e)	0.015	
29	Standard deviation in c for part (f)	0.005	
30	RSD in c for part (f)	0.010	
31	**Spreadsheet Documentation**		
32	Cell B15==SLOPE(B4:B11,A4:A11)		Cell B24 =AVERAGE(B4:B11)
33	Cell B16=INTERCEPT(B4:B11,A4:A11)		Cell B25= Replicates part (e) (entry)
34	Cell B17=(B12-B16)/B15		Cell B26=Replicates part (f)
35	Cell B20=STEYX(B4:B11,A4:A11)		Cell B27 =B20/B15*SQRT(1/B25+1/B21+((B12-B24)^2)/((B15^2)*B22))
36	Cell B21=COUNT(B4:B11)		Cell B28=B27/B17
37	Cell B22=B21*VARP(A4:A11)		Cell B29=B20/B15*SQRT(1/B26+1/B21+((B12-B24)^2)/((B15^2)*B22))
38	Cell B23=SQRT(B20^2/B22)		Cell B30=B29/B17



(b) $F = 22.35c + 3.57 \times 10^{-4}$ (c) 0.27, 0.175

(d) 0.544 µM (e) 1.5% (f) 1%

Chapter 16

Textbook questions

16-2

Gaseous HCl exhibits an IR absorption at 2890 cm-1 due to the hydrogen-chlorine stretching vibration.

a) Calculate the force constant for the bond

b) Calculate the wavenumber of the absorption band for DCl assuming the force constant is the same as that calculated in part (a).

(a)

Using the following equation to get $\bar{\nu} = \dfrac{1}{2\pi c}\sqrt{\dfrac{k}{\mu}}$ $\quad \mu = \dfrac{m_1 m_2}{m_1 + m_2}$

$$m_1 = \frac{1.00\times10^{-3}\ \text{kg /mol H}}{6.02\times10^{23}\ \text{atom H/molH}} = 1.66\times10^{-27}\ \text{kg}$$

$$m_2 = \frac{35.5\times10^{-3}\ \text{kg /mol Cl}}{6.02\times10^{23}\ \text{atom Cl/mol Cl}} = 5.90\times10^{-26}\ \text{kg}$$

$$\mu = \frac{1.66\times10^{-27}\ \text{kg}\times5.90\times10^{-26}\ \text{kg}}{1.66\times10^{-27}\ \text{kg}+5.90\times10^{-26}\ \text{kg}} = 1.62\times10^{-27}\ \text{kg}$$

Rearranging Equation 16-15 and substituting yields

$$k = (2\bar{\nu}\pi c)^2\mu = (2\pi\times2890\ \text{cm}^{-1}\times\ 3.00\times10^{10}\ \text{cm s}^{-1})^2\times1.62\times10^{-27}\ \text{kg}$$

$$= 4.81\times10^2\ \text{kg s}^{-2} = 4.81\times10^2\ \text{N/m}$$

16-2

Gaseous HCl exhibits an IR absorption at 2890 cm-1 due to the hydrogen-chlorine stretching vibration.

a) Calculate the force constant for the bond

b) Calculate the wavenumber of the absorption band for DCl assuming the force constant is the same as that calculated in part (a).

(b)

(b) The force constant in HCl and DCl should be the same and

$$m_1 = \frac{2.00\times10^{-3}}{6.02\times10^{23}} = 3.32\times10^{-27}\ \text{kg}$$

$$\mu = \frac{3.32\times10^{-27}\ \text{kg}\times5.90\times10^{-26}\ \text{kg}}{3.32\times10^{-27}\ \text{kg} + 5.90\times10^{-26}\ \text{kg}} = 3.14\times10^{-27}\ \text{kg}$$

$$\bar{\nu} = \frac{1}{2\pi\times3.00\times10^{10}\ \text{cm/s}}\sqrt{\frac{4.81\times10^{2}\ \text{kg s}^{-2}}{3.14\times10^{-27}\ \text{kg}}} = 2075\ \text{cm}^{-1}$$