Exc.1 (a) $\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8 \text{ m s}^{-1}}{670 \times 10^{-9} \text{ m}} = 4.47 \times 10^{14} \text{ s}^{-1} = \boxed{447 \text{ THz}}$

(b) $\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{670 \times 10^{-9} \text{ m}} = 1.49 \times 10^6 \text{ m}^{-1} = \boxed{1.49 \times 10^4 \text{ cm}^{-1}}$

Exc.2 (a) $\tilde{\nu} = \frac{\nu}{c} = \frac{92.0 \times 10^6 \text{ s}^{-1}}{2.998 \times 10^8 \text{ m s}^{-1}} = \boxed{0.307 \text{ m}^{-1}}$

(b) $\lambda = \frac{1}{\tilde{\nu}} = \frac{1}{0.307 \text{ m}^{-1}} = \boxed{3.26 \text{ m}}$

Exc.3 $\varepsilon = \frac{A}{[\text{J}]L}$ [12.5] $= -\frac{\log T}{[\text{J}]L}$ [12.4a and b]

$\varepsilon_{410 \text{ nm}} = -\frac{\log(0.715)}{(0.433 \times 10^{-3} \text{ mol dm}^{-3}) \times (2.5 \text{ mm})} = \boxed{13\bar{5} \text{ dm}^3 \text{ mol}^{-1} \text{ mm}^{-1}}$

Expressing all lengths in cm yields: $\boxed{1.3\bar{5} \times 10^6 \text{ cm}^2 \text{ mol}^{-1}}$

Exc.4 $[\text{J}] = \frac{n}{V} = \frac{0.0302 \text{ g}/(602 \text{ g mol}^{-1})}{0.500 \text{ dm}^3} = 1.00 \times 10^{-4} \text{ mol dm}^{-3}$

(a) $\varepsilon = \frac{A}{[\text{J}]L}$ [12.5]

$\varepsilon = \frac{1.011}{(1.00 \times 10^{-4} \text{ mol dm}^{-3}) \times (1.00 \text{ cm})} = \boxed{1.01 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$

(b) Since the solution is twice as concentrated, the absorbance must be twice as large. Thus,

$A = 2.022$ and $T = 10^{-A}$ [12.5] $= 10^{-2.022} = 0.00951$ or $\boxed{0.951\%}$

Exc.5 (a) Since $I = \frac{1}{2} I_0$, we calculate that $T = I/I_0 = \frac{1}{2}$ and $A = -\log T = 0.301$

For water, $[\text{H}_2\text{O}] \approx \frac{1.00 \text{ kg/dm}^3}{18.02 \text{ g mol}^{-1}} = 55.5 \text{ mol dm}^{-3}$

$$\text{Depth, } L = \frac{A}{\varepsilon[\text{H}_2\text{O}]}$$

$$= \frac{0.301}{(6.2 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (55.5 \text{ mol dm}^{-3})}$$

$$= \boxed{87 \text{ cm}}$$

(b) Since $I = \frac{1}{10} I_0$, we calculate that $T = I/I_0 = \frac{1}{10}$ and $A = -\log T = 1.00$

$$\text{Depth, } L = \frac{A}{\varepsilon[\text{H}_2\text{O}]}$$

$$= \frac{1.00}{(6.2 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}) \times (55.5 \text{ mol dm}^{-3})}$$

$$= \boxed{2.9 \text{ m}}$$

Exc.6 Let [tryptophan] = [A] and [tyrosine] = [B] in the following analysis. The data using a cell of thickness 1.00 cm is:

At 240 nm, $\varepsilon_{A,240} = 2.00 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, $\varepsilon_{B,240} = 1.12 \times 10^4\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, $A_{240} = 0.660$

At 280 nm, $\varepsilon_{A,280} = 5.40 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, $\varepsilon_{B,280} = 1.50 \times 10^3\ \mathrm{dm^3\ mol^{-1}\ cm^{-1}}$, $A_{280} = 0.221$

Substitution of these values into eqn 12.7 yields the concentrations of A and B.

$$[\text{tryptophan}] = [A] = \frac{\varepsilon_{B,280}A_{240} - \varepsilon_{B,240}A_{280}}{(\varepsilon_{A,240}\varepsilon_{B,280} - \varepsilon_{A,280}\varepsilon_{B,240})L}$$

$$= \frac{\{(1.50\times10^3)\times(0.660) - (1.12\times10^4)\times(0.221)\}\ \mathrm{mol\ dm^{-3}\ cm}}{\{(2.00\times10^3)\times(1.50\times10^3) - (5.40\times10^3)\times(1.12\times10^4)\}\times(1.00\ \mathrm{cm})}$$

$$= \boxed{25.8\ \mu\mathrm{mol\ dm^{-3}}}$$

$$[\text{tyrosine}] = [B] = \frac{\varepsilon_{A,240}A_{280} - \varepsilon_{A,280}A_{240}}{(\varepsilon_{A,240}\varepsilon_{B,280} - \varepsilon_{A,280}\varepsilon_{B,240})L}$$

$$= \frac{\{(2.00\times10^3)\times(0.221) - (5.40\times10^3)\times(0.660)\}\ \mathrm{mol\ dm^{-3}\ cm}}{\{(2.00\times10^3)\times(1.50\times10^3) - (5.40\times10^3)\times(1.12\times10^4)\}\times(1.00\ \mathrm{cm})}$$

$$= \boxed{54.3\ \mu\mathrm{mol\ dm^{-3}}}$$

Exc.7 Using the definitions and thought processes illustrated in text *Justification* 12.1, we write

$$\frac{\mathrm{d}I}{I} = -\kappa[\mathrm{J}]\,\mathrm{d}x$$

To obtain the intensity that emerges from a sample of thickness L when the intensity incident on one face of the sample is I_0, we sum all the successive changes. Because a sum over infinitesimally small increments is an integral, we write

$$\int_{I_0}^{I}\frac{\mathrm{d}I}{I} = -\kappa\int_0^L[\mathrm{J}]\,\mathrm{d}x$$

We make the substitution $[\mathrm{J}] = [\mathrm{J}]_0 e^{-x/\lambda}$ and analytically perform the integrals.

$$\int_{I_0}^{I}\frac{\mathrm{d}I}{I} = -\kappa[\mathrm{J}]_0\int_0^L e^{-x/\lambda}\mathrm{d}x$$

$$\ln\frac{I}{I_0} = \frac{-\kappa[\mathrm{J}]_0}{-1/\lambda}e^{-x/\lambda}\Big|_{x=0}^{x=L}$$

$$= \kappa\lambda[\mathrm{J}]_0\{e^{-L/\lambda} - 1\}$$

But $e^{-L/\lambda} \approx 0$ when $L \gg \lambda$, so the expression simplifies to

$$-\ln\frac{I}{I_0} = \kappa\lambda[\mathrm{J}]_0$$

Because the relation between natural and common logarithms is $\ln x = \ln 10 \times \log x$, we can write $\varepsilon = \kappa/\ln 10$ and substitute $A = -\log\frac{I}{I_0}$ to obtain

$$\boxed{A = \varepsilon\lambda[\mathrm{J}]_0}$$

Exc.8 $\nu = \frac{1}{2\pi}\left(\frac{k_f}{\mu}\right)^{1/2}$ [12.13b; isotopic masses are found in the *CRC Handbook of Chemistry and Physics*]

(a) $\mu = \frac{m_{^{12}C}m_{^{16}O}}{m_{^{12}C}+m_{^{16}O}} = \frac{(12.0000\ m_u)\times(15.9949\ m_u)}{(12.0000+15.9949)\ m_u}\times(1.66054\times10^{-27}\ \text{kg}\ m_u^{-1}) = 1.139\times10^{-26}\ \text{kg}$

$$\nu = \frac{1}{2\pi}\left(\frac{908\ \text{N m}^{-1}}{1.139\times10^{-26}\ \text{kg}}\right)^{1/2} = 4.49\times10^{13}\ \text{s}^{-1} = \boxed{4.49\times10^{13}\ \text{Hz}}$$

(b) $\mu = \frac{m_{^{13}C}m_{^{16}O}}{m_{^{13}C}+m_{^{16}O}} = \frac{(13.0034\ m_u)\times(15.9949\ m_u)}{(13.0034+15.9949)\ m_u}\times(1.66054\times10^{-27}\ \text{kg}\ m_u^{-1}) = 1.191\times10^{-26}\ \text{kg}$

$$\nu = \frac{1}{2\pi}\left(\frac{908\ \text{N m}^{-1}}{1.191\times10^{-26}\ \text{kg}}\right)^{1/2} = 4.39\times10^{13}\ \text{s}^{-1} = \boxed{4.39\times10^{13}\ \text{Hz}}$$

Exc.9 Select those molecules in which a vibration gives rise to a change in dipole moment. It is helpful to write down the structural formulas of the compounds. The molecules that show infrared absorption are:

$\boxed{\text{(b) HCl, (c) CO}_2\text{, (d) H}_2\text{O, (e) CH}_3\text{CH}_3\text{, (f) CH}_4\text{, and (g) CH}_3\text{Cl}}$

Exc.10 For non-linear molecules the number of normal modes is given by $3N-6$ where N is the number of atoms in the molecules; for linear molecules the number of normal modes is $3N-5$. Thus, we need to establish the linearity of the molecules listed. Molecules (c) and (d) are clearly non-linear. From the Lewis structures of molecules (a) and (b) and VSEPR we decide that they are non-linear and linear, respectively.

(a) NO_2, non-linear, $3N-6=9-6=\boxed{3}$

(b) N_2O, linear, $3N-5=9-5=\boxed{4}$

(c) C_6H_{12}, non-linear, $3N-6=3\times18-6=\boxed{48}$

(d) C_6H_{14}, non-linear, $3N-6=3\times20-6=\boxed{54}$

Exc.11 The laser is delivering photons of energy

$$E = h\nu = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ \text{J s})\times(2.998\times10^{8}\ \text{m s}^{-1})}{488\times10^{-9}\ \text{m}} = 4.07\times10^{-19}\ \text{J}$$

Since the laser is putting out 1.0 mJ of these photons every second, the rate of photon emission is:

$$\nu = \frac{1.0\times10^{-3}\ \text{J s}^{-1}}{4.07\times10^{-19}\ \text{J}} = 2.5\times10^{15}\ \text{s}^{-1}$$

The time it takes the laser to deliver 10^6 photons (and therefore the time the dye remains fluorescent) is

$$t = \frac{10^6}{2.5\times10^{15}\ \text{s}^{-1}} = 4\times10^{-10}\ \text{s} = \boxed{0.4\ \text{ns}}$$