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(5.) $\lambda_{v_1} = 589.15788 \quad \lambda_{v2} = 589.75537\,nm$

$\lambda_v = \lambda_{air}\, n$

$\lambda_{air} = \frac{\lambda_v}{n} = \frac{589.15788}{1.0002926}\,nm = \boxed{588.98554\,nm}$

$\frac{589.75537}{1.0002926}\,nm = \boxed{589.58286\,nm}$

$\nu = \frac{c}{\lambda} = \frac{2.998 \times 10^8}{589.16 \times 10^{-9}} = \boxed{5.089 \times 10^{14}\ Hz}$

$= \frac{2.998 \times 10^8}{589.76 \times 10^{-9}} = \boxed{5.083 \times 10^{14}\ Hz}$

$\tilde{\nu} = \frac{1}{\lambda_{air}} = \frac{1}{588.98\,nm} \left| \frac{10^7\,nm}{1\,cm} \right. = \boxed{1.698 \times 10^4\ cm^{-1}}$

$\frac{1}{589.58} \left| \frac{10^7\,nm}{cm} \right. = \boxed{1.696 \times 10^4\ cm^{-1}}$

(9) At high absorbances the signal to noise ratio is very small - also, Beer's law may become non-linear At low absorbances there is not much difference between the absorbance due to sample & reference.

(10). $A = \varepsilon b c$

$\varepsilon = \frac{A}{bc} = \frac{0.822}{(1.00\,cm)(2.31 \times 10^{-5}\,M)} = \boxed{3.56 \times 10^4\ M^{-1}\,cm^{-1}}$

(13) a. for 325 nm $\sigma \cong 10^{-20}\ cm^2$

for 300 nm $\sigma \cong 3\times10^{-19}\ cm^2$

$$T = e^{-n\sigma b}$$

at 325 nm: $T = e^{-(8\times10^{18}\ molec/cm^3)(10^{-20}\ cm^2)(1\ cm)}$ $\boxed{= 0.92}$

$A = -\log T$ $\boxed{= 0.035}$

at 300 nm $T = e^{-(8\times10^{18})(3\times10^{-19})(1\ cm)}$ $=$ $\boxed{0.091}$

$A =$ $\boxed{1.04}$

b. $T = e^{-n\sigma b}$

$0.14 = e^{-(8\times10^{18})(\sigma)(1)}$

2.4576×10^{-19}

$\boxed{\sigma = 2.5\times10^{-19}\ cm^2}$

n decreased by 1% $\rightarrow$ n = 7.92×10^{18}

$T = e^{-(7.92\times10^{18})(\cancel{2.5}\ 2.4576\times10^{-19})(1)} = 0.143$

% increase in T is $\boxed{2\%}$

c. $290\ DU \left| \frac{2.69\times10^{16}}{DU} \right| = 7.801\times10^{18}\ molec/cm^3$

$350\ DU \left| \frac{2.69\times10^{16}}{DU} \right| = 9.415\times10^{18}\ molec/cm^3$

winter $T = e^{-(7.801\times10^{18})(2.5\times10^{-19})(1)} = 0.142$

summer $T = e^{-(9.415\times10^{18})(2.5\times10^{-19})(1)} = 0.0950$

$\frac{0.142 - 0.0950}{0.0950} = 49\%$ $\boxed{\text{greater transmittance is winter}}$

- fortunately the sun is at a lower angle in winter so the pathlength is much greater.

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(18) a. $A = \varepsilon bc$ $\quad \varepsilon = \dfrac{A}{bc} = \dfrac{(0.267 - 0.019)}{(1)(3.15\times10^{-6})} = \boxed{7.87\times10^{4}\ M^{-1}cm^{-1}}$

b. $A = \varepsilon bc$ $\quad c = \dfrac{A}{\varepsilon b} = \dfrac{(0.175 - 0.019)}{(7.87\times10^{4})(1)} = \boxed{1.98\times10^{-6} M}$

(22) Fluorescence is the emission of photon w/o a change in the spin state of the ~~ele~~ excited electron (singlet - singlet). The transition is fast $\sim 10^{-8}$ s. Phosphorescence involves a spin transition (triplet - singlet) The transition is slow; up to seconds.

~~(23)~~ (24) A fluorescence excitation spectrum involves scanning the source λ, and holding the emitted λ constant. A fluorescence emission spectrum involves holding the source λ constant and scanning the emitted λ.

· The excitation spectrum resembles an absorption spectrum.

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(1). Light source - provides radiation to be absorbed by sample

Scanning monochromator - chooses a particular λ from the source that will be absorbed by the sample

Motor - turns the beam chopper, which alternatively passes the radiation through the sample and reference

sample cuvet - holds the sample

reference cuvet - holds a reference solution and is identical to the sample cuvet

detector - generates an electrical signal proportional to the ~~absorbance by the sample~~ light transmitted through the sample

Amplifier - increases the detector signal so that it can easily be displayed.

(3) Deuterium lamp

(4) · Decreasing the distance between blazes
- Increasing the overall size (length) of the grating

(5) A filter can be used to remove higher order λ of light

(6) Advantage - better resolution
Disadvantage · lower signal to noise

(8) a. $n\lambda = d(\sin \overset{i}{\theta} + \sin \overset{r}{\phi})$

$$d = \frac{n\lambda}{\sin\theta - \sin\phi} = \frac{(1)(600\times10^{-9}\,m)}{\sin 40 + \sin 30} = 4.20\times10^{-6}\,m$$

$$\frac{\text{lines}}{cm} = \frac{1}{4.20\times10^{-6}\,m}\left|\frac{1m}{100cm}\right| = \boxed{2380\ \text{lines}/cm}$$

b. $1000\,cm^{-1} = 10\,000\,nm$ or $1\times10^{-3}\,cm$

$$d = \frac{(1)(\cancel{10\times10}\ 1\times10^{-3}\,cm)}{\sin 40 + \sin 30} = 7.00\times10^{-3}\,cm \Rightarrow \boxed{143\ \text{lines}/cm}$$

(9) 10^3 lines/cm $\Rightarrow d = 10\,\mu m$

$$D = \frac{n}{d\cos\overset{r}{\phi}} = \frac{1}{10\,\mu m \cos 10^\circ} = 0.102\frac{rad}{\mu m}\left(\frac{180^\circ}{\pi\,rad}\right) = \boxed{5.8^\circ/\mu m}$$

(10) a. $R = \frac{\lambda}{\Delta\lambda} = \frac{512.245}{0.03} = \boxed{1.7\times10^4}$

b. $10^4 = \frac{512.23\,nm}{x}$

$x = \boxed{5.122\times10^{-2}\,nm}$ or $2.0\times10^{8}\,cm^{-1}$

c. $R = nN$

$n = 4,\ N = 8.00\,cm\left|\frac{10\,mm}{1\,cm}\right|\frac{185}{mm}\right| = 14800$

$R = (4)(14800) = \boxed{5.9\times10^4}$

d. $D = \frac{\Delta\phi}{\Delta\lambda} = \frac{n}{d\cos\phi}$ $\qquad \frac{250}{mm} \Rightarrow d = 4\,\mu m$

$\Delta\lambda = 512.26 - 512.23 = 0.03\,nm$

$$\frac{\Delta\phi}{\Delta\lambda} = \frac{1}{4\,\mu m\cos 3^\circ} = \frac{0.250\,rad}{\mu m}\left(\frac{180^\circ}{\pi\,rad}\right) = \frac{14.3^\circ}{\mu m} \quad \Delta\phi = (0.03\,nm)\left(\frac{1\,\mu m}{10^3\,nm}\right)\left(\frac{14.3^\circ}{\mu m}\right) = \boxed{4.3\times10^{-4}\,deg}$$

For $n = 30$ the dispersion is $30\times$ greater $\boxed{= 1.3\times10^{-2}\,deg}$

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(12) $b = \frac{N}{2n} \cdot \frac{1}{\tilde{\nu}_2 - \tilde{\nu}_1} = \frac{30}{2 \cdot 1} \cdot \frac{1}{(1906-698)\,cm^{-1}} = \boxed{0.01242\ cm}$

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~~24~~ a. $\Delta = \pm 2\,cm$

b. the ability to tell the difference between closely spaced peaks

c. $R = 1/\Delta = \boxed{0.5\ cm^{-1}}$

d. $\delta = \frac{1}{2\Delta\tilde{\nu}} = \frac{1}{(2)(2000\,cm^{-1})} = \boxed{2.5\,\mu m}$