Chapter 3: Rotational and vibrational spectroscopy

3.1 For the peak at λ = 255nm in the UV-vis spectrum of benzene, the value of the absorbance (A) is 1.65. Use $A = \varepsilon cd$, with d as 10^{-2} m and the value of c worked out in mol m^{-3} [this is $(0.6/78) \times 10^3$]. This gives the answer for ε, in units of m^2 mol^{-1} as follows:

$$\varepsilon = A/cd$$

$$= 1.65/ (7.69 \times 10^{-3} \times 10^{3}) \times 10^{-2} = 0.21 \times 10^{2} = 21 \text{ (see Table 3.1)}$$

3.2 a) For pentane-2-4-dione in ethanol (Figure 3.7), λ_{max} is *ca*. 270 nm, with A 0.92. Given the value of d as 10^{-2}m and c, the concentration of *diketone*, 10^{-2} g dm^{-3} [i.e. $10^{-2}/100$ (the molecular weight of the ketone), i.e. 10^{-4} mol dm^{-3} or 10^{-1} mol m^{-3}] the *apparent* molar decadic absorptivity ε is A/cd, i.e. $0.92/10^{-2} \times 10^{-1} = 920$ m^2 mol^{-1}.

b) Since A is proportional to c, the concentration of chromophore (the enol form in this case), the values of A in the different solvents give the percentage *enol* in each case. Given 73% as the percentage enol in ethanol (with A 0.92) the values of A in hexane and water (*ca*. 1.10 and 0.16 respectively) give percentage of enol in these solvents as 87% and 13% respectively. (i.e. a higher proportion in the non-hydrogen-bonding solvent hexane.)

3.3 When aniline (phenylamine) is protonated, to give the anilinium cation $C_6H_5NH_3^+$, the proton bonds to the lone-pair of electrons on nitrogen which are thus no longer available to be conjugated with the π-electrons in the benzene ring. Thus the ($\pi \rightarrow \pi^*$) absorptions in the anilinium cation at 200 nm (ε 750 m^2 mol^{-1}) and 250 nm (ε 16 m^2 mol^{-1}) now closely resemble those observed for benzene itself (see Table 3.1) with considerably lower values of λ and ε than for aniline (in which the lone pair and the electrons in the ring are conjugated.)

3.4 Firstly, by inspection of Figure 3.8, you should be able to see that at pH *ca*. 5, the overall absorption spectrum contains approximately equal concentrations of both acid and base forms (the former contributing largely to the peak at *ca.* 550, the latter to the maximum at *ca*. 400 nm). Let's now work out the amounts of each form at a given pH by first choosing a value of λ at which only *one* form exhibits absorption (say 560 nm for the acid form) and assume that at pH 3, it is effectively all in in this form). Then, at pH 5, say, the ratio of the concentration of (the remaining) acid and the base form (by difference) can be calculated and fed into the equation relating K, H^+, [HA] and $[A^-]$.

$$K = \frac{[H^+][A^-]}{[HA]}$$

From measurement of the A values for pH 3 and 5 at 560 nm, you should be able to confirm that, at pH5, $[A^-] = [HA]$, so that $K = [H^+] = 10^{-5}$, i.e. pK = 5.0.