Example Questions involving Photochemistry

1. The energy gap between the triplet ground state and the excited singlet state for molecular oxygen is 90 kJ mol^{-1}. Calculate the wavelength of photons given off if an excited state singlet relaxes to the ground state with the emission of light. What region of the electromagnetic spectrum is this? Is the light emitted fluorescence or phosphorescence?

[*Ans: λ = 1330 nm; IR region; Phosphorescence*]

$^3O_2^*$ ——
$\updownarrow$ $\Delta E = 90$ kJ mol^{-1}
$^1O_2$ ——

$$\Delta E = E_{photon} \times N_A = \frac{hc}{\lambda} N_A$$

$$\therefore \lambda = \frac{hc\,N_A}{\Delta E} = \frac{(6.626\times10^{-34}\ \text{J s})(3.00\times10^{8}\ \text{m s}^{-1})(6.023\times10^{23}\ \text{mol}^{-1})}{90{,}000\ \text{J mol}^{-1}}$$

$$= 1.330\times10^{-6}\ \text{m}$$

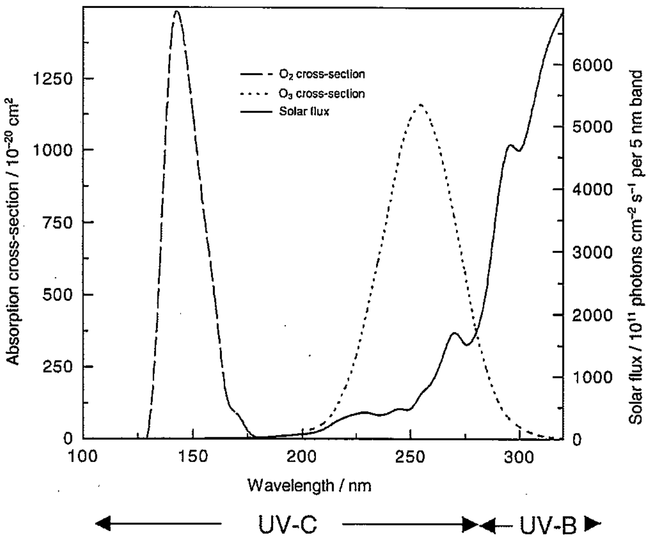
or

1330 nm

2. The bond dissociation energy of an **O=O** double bond is given in Appendix B3 (text) as 497 kJ mol^{-1}.

a) Calculate the maximum wavelength of photons capable of this dissociation.

b) Based on the information given in the figure below, (Fig 3.2; text), do you expect photodissociation to actually occur at this wavelength?



$$\lambda = \frac{hc\,N_A}{BDE}$$

$$= 2.409\times10^{-7}\ \text{m}$$

or

241 nm

[*Ans: λ < 241 nm; No, **O_2** does not absorb appreciably at λ > 200 nm*]

3. Consider the reactions below that correspond to the production of ground level ozone.

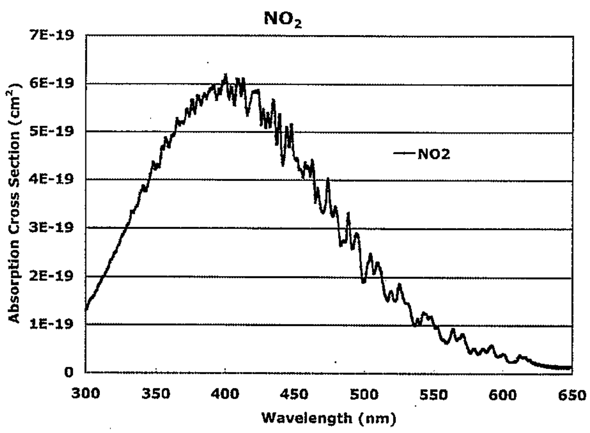
[1]	$NO_2 + h\nu \rightarrow NO + O$	f_1
[2]	$O + O_2 + M \rightarrow O_3 + M$	k_2
[3]	$NO + O_3 \rightarrow NO_2 + O_2$	k_3

a) Using the values of ΔH^o_f in Appendix B2 (text), calculate the maximum wavelength of light that is capable of photodissociating NO_2.

b) Given the absorption spectrum of NO_2 (below), do you expect this reaction to occur in the troposphere?

c) What colour do you expect for NO_2 to appear?

d) Appling the *steady state approximation* to the [NO], derive an expression for the steady state [O_3].



$$\Delta H^o_{rxn} = \Delta H^o_f(NO) + \Delta H^o_f(O) - \Delta H^o_f(NO_2)$$

$$= (90.3 + 249.2 - 33.2)\ kJ/mol$$

$$= 306.3\ kJ\ mol^{-1}$$

$$\lambda = \frac{hc N_A}{\Delta H^o_{rxn}} = 3.91 \times 10^{-7}\ m$$

or 391 nm

[*Ans: λ <391 nm; Yes, NO_2 has a strong absorption in the 300 – 500 nm and there plenty of UV-a photons in the troposphere to carry out this reaction; absorbs blue, ∴appears orange-brown; $[O_3]=f_1[NO_2]/k_3[NO]$*]

Applying the SSA to NO, we can say

rate production NO = rate destruction NO

$$\therefore f_1[NO_2] = k_3[NO][O_3]$$

rearranging to isolate $[O_3]$ yields,

$$[O_3] = \frac{f_1[NO_2]}{k_3[NO]}$$