Assignment VI, p.1

- Dansyl chloride, which absorbs maximally at 330nm and emits maximally at 510nm, can be used to label amino acids. Tabulated below is the variation of fluorescence intensity of its aqueous solution after excitation with a short laser pulse.

t, ns	**5.0**	**10.0**	**15.0**	**20.0**
I_f/I_0	0.45	0.21	0.11	0.05

(a) calculate the observed fluorescence life time. I_0 is the initial fluorescence intensity.
(b) The fluorescence yield of dansil chloride in water is 0.7. Calculate the fluorescence rate constant.

Assignment VI, p.2

- The following radical chain mechanism proposed for the initial stages of gas-phase oxidation of silane by nitrous oxide

(1) $N_2O \rightarrow N_2 + O$

(2) $O + SiH_4 \rightarrow SiH_3 + OH$

(3) $OH + SiH_4 \rightarrow SiH_3 + H_2O$

(4) $SiH_3 + N_2O \rightarrow SiH_3O + N_2$

(5) $SiH_3O + SiH_4 \rightarrow SiH_3OH + SiH_3$

(6) $SiH_3 + SiH_3O \rightarrow (H_3Si)_2\,O$

(a) Label each step with its role in the chain

(b) Use steady state approximation to show that (provided k_1 and k_6 are small): $\frac{d[SiH_4]}{dt} = -k[N_2O][SiH_4]^{1/2}$