Photochemistry I – Problems

Series D

1. A solution of an organic compound belonging to the family of coumarin dyes is characterized by a decadic extinction coefficient ε = 6.7×10^4 mol^{-1}·L·cm^{-1} at λ_{max} = 470 nm, corresponding to the maximum of its absorption spectrum. The radiative lifetime of the compound's singlet excited state is τ_r^0 = 885 ps.

   Postulating that the dye's absorption band is Lorentzian and that its width at half height is Γ = 60 nm, determine the fluorescence quantum yield Φ_f of the compound.

   Refractive index of the solvent: n = 1.33.

2. The relative fluorescence intensities I_f of 10^{-5} M solutions of an acridinium dye in acetonitrile have been measured in the presence of increasing concentrations of naphthalene. Using the numerical values listed here below, calculate the excited state lifetime τ_f of the dye.

[Naphtalene] / (mol·L^{-1})	0	10^{-3}	10^{-2}	2×10^{-2}	5×10^{-2}	10^{-1}	2×10^{-1}
I_f (arbitrary units)	435	407	343	311	238	145	109

3. Quantum yields for energy transfer Φ_{ET} were measured for a series of compounds in which an energy donor and an energy acceptor are covalently linked by a rigid molecular linker of variable and known length r.

r / nm	1.2	1.5	1.8	2.8	3.1	3.4	3.7	4.0	4.3	4.6
Φ_{ET}	0.99	0.94	0.97	0.82	0.74	0.65	0.40	0.28	0.24	0.16

   a) Express literally Φ_{ET} as a function of the rate constants k_r^0, k_{nr}, and k_{ET}.

   b) Test whether this data is adequately described by the Förster theory.

   c) Why the Dexter mechanism for energy transfer is not considered here ?