Photochemistry

Photochemistry involves the interaction of a substance with electromagnetic radiation (EM) mainly in the UV-Vis region.

The energy of one photon is E=hv where h=6.626x10^{-34} Js. We can modify this to take into account wavelength instead of frequency e.g. v=c/λ so E=hc/ λ where c=3x10^{8} m s^{-1}.

Interaction of light with matter- light has intensity with I_o being initial intensity. As the initial light travels through a sample, the sample may be able to absorb some of the light. If some or all of the light particles (photons) can be absorbed by the sample, then the transmitted light intensity (I_t) will be less than the I_o. If there is no absorption, then I_t will be about equal to I_o however scattering and reflection are likely to happen. The intensity of the absorbed light is $I_{abs}=I_o-I_t$.

The Beer-Lambert Law says that the intensity of light decreases exponentially with the concentration of the absorbing species and the pathlength. E.g. A=εcl where A is dimensionless, ε is the molar absorptivity constant with units dm^3 mol^{-1} cm^{-1}, l is length in cm, and c is concentration in mol dm^{-3}.Absorbance is described as $A = log \frac{I_0}{I_t}$.

E is a measure of the electronic transition of the absorbing species. High ε values indicate allowed transitions such as pi→pi* whereas low ε values indicate forbidden transitions such as non-bonding e^-→pi*. The energy of the photons absorbed corresponds to the energy of the electronic transition. The incident light must contain photons with this energy in order for absorption to happen.

The main difference between ground state and excited state is that an atom at ground state is where electrons are found at their lowest energy levels, whereas at excited state the electrons in that atom contain higher energy than in ground state.

A triplet state means that an electron is promoted with a spin state parallel to the electron in the orbital that it was previously in, a triplet state is usually lower in energy than a singlet state as repulsion between electrons is lower.

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Photophysical processes are parallel processes that compete for the energy of S_1 and T_1, they are internal conversion, intersystem crossing, fluorescence, and phosphorescence.

Internal conversion is going from S_n→S_1 and/or S_1→S_0

Intersystem crossing is going from S_1→ T_1 and then T_1→ S_0

Fluorescence is going from S_1→S_0+hv

Phosphorescence is going from T_1→ S_0+hv

A substance that accelerates the decay of an electronically excited state to a lower state is a quencher (Q) and is said to quench the excited state.

Lecture 2-

Quantum yield can be given in terms of the rate at which events occur relative to the rate at which photons are absorbed or number of events that occur relative to number of photons absorbed.

$$\Phi = \frac{rate\ of\ process}{rate\ of\ photon\ absorption} = \frac{v}{I_{abs}} = \frac{number\ of\ events, i}{number\ of\ photons\ absorbed} = \frac{N_i}{N_{abs}}$$