2.14: Solvent Effect of Fluorescence

The concept of solvation can be understood from interactions between a fluorophore (the solute), and the surrounding solvent molecules. The dominating solute-solvent interactions arise from electrostatic dipole-dipole interactions, which lead to lowering the potential energies of all energy levels involved in absorption and fluorescence processes.

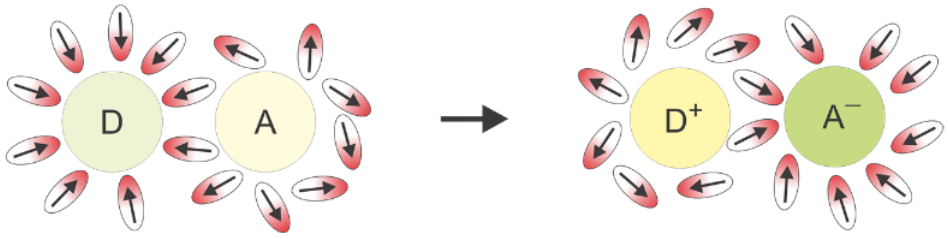

Figure 1: Changes in solute-solvent interactions lead to solvatochromic shifts in absorption and fluorescence spectra of the same fluorophore. (CC BY-SA-NC; Andrei Tokmakoff)

This effect can be explained by **Onsager's model of solvation**. According to this model, the dipole moment of the fluorophore in the ground state, μ_g, interacts with the dipole moments of the surrounding solvent molecules, rearranging them in a way that minimizes the potential energy of the whole system. If we would "freeze" the molecules for a while and remove the fluorophore, the special arrangement of the solvent dipole moments would result in a non-balanced electric field R_g, called the "reaction field" or "vacuum field"

Solvation Energies

In Onsager's model, the solute-solvent interaction is identified as an interaction of the fluorophore dipole moment, μ_g, with the reaction field R_g, namely:

$$U_g^{\text{rel}} = -\vec{\mu}_g \cdot \vec{R}_g$$

The energy level of the ground state is therefore lowered by this value. The symbol 'rel' indicates that the solvent is in a state of thermodynamic equilibrium (relaxed).

Electronic excitation of the fluorophore causes a rapid (~10^{-15} s) change of its dipole moment to μ_e. This time is much too short for the solvent molecules to rearrange their orientations. Thus, immediately after excitation the interaction energy will be:

$$U_e^{FC} = -\vec{\mu}_e \cdot \vec{R}_g$$

indicating that the reaction field will be still the same as it was before excitation. The symbol 'FC' indicates a non-equilibrated, Franck-Condon state. The solvent molecules need usually picoseconds (10^{-12}-10^{-10} s) to perform solvent relaxation achieving finally the solute-solvent interaction energy (Figure 2):

$$U_e^{\text{rel}} = -\vec{\mu}_e \cdot \vec{R}_e$$

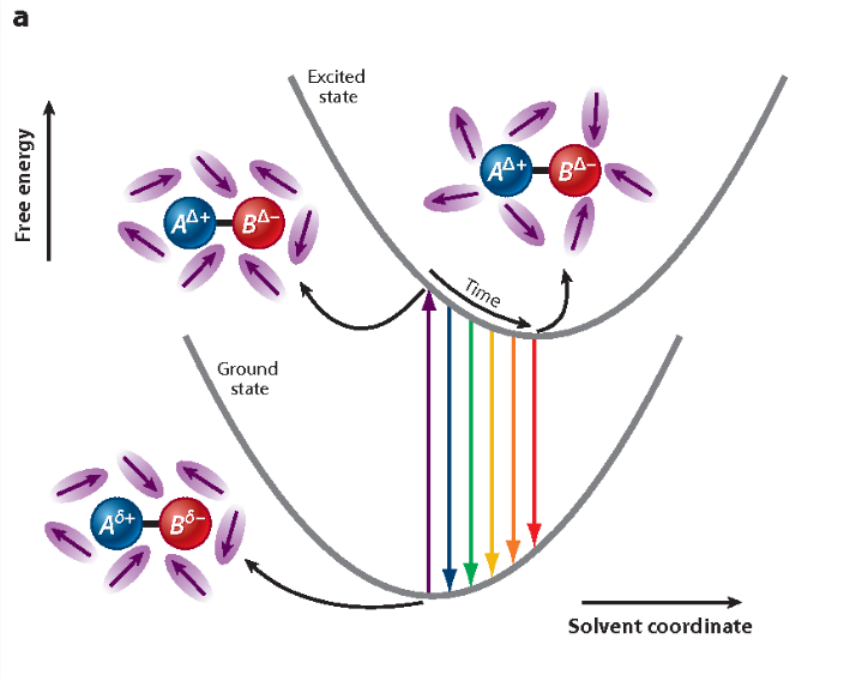

Figure 2: Schematic description of the time-dependent fluorescence (TDF) process. (a) The absorption and TDF are depicted for a dye molecule, represented as A-B with a charge-transfer transition (> δ). The purple arrows indicate solvent molecule permanent dipole moments that reorganize after excitation as measured by a collective solvent coordinate. https://www.semanticscholar.org/pape...c0d32/figure/0

The process of fluorescence brings the fluorophore dipole moment back to its ground-state value μ_g, so just after fluorescence:

$$U_e^{FC} = -\vec{\mu}_e \cdot \vec{R}_e$$

which finally evolves during ground-state solvent relaxation to U_g^{rel} . Direct consequences of the different solute-solvent interaction energies at different stages of absorption and fluorescence events are the spectral shifts in absorption (ΔU_{abs} and fluorescence (ΔU_{flu}) spectra (Figure 3):

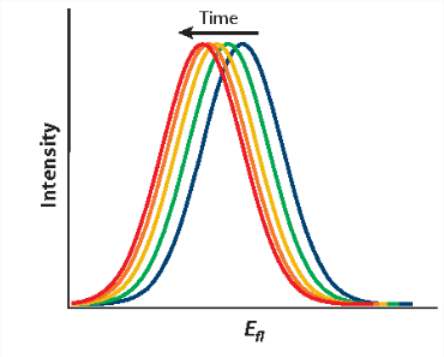

Figure 3: The typical time dependency of the fluorescence spectrum

which finally evolves during ground-state solvent relaxation to U_g^{rel} . Direct consequences of the different solute-solvent interaction energies at different stages of absorption and fluorescence events are the spectral shifts in absorption (ΔU_{abs}) and fluorescence (ΔU_{flu}) spectra:

$$\Delta U_{abs} = U_e^{FC} - U_g^{rel}$$
$$\Delta U_{flu} = U_g^{FC} - U_e^{rel}$$

Reorganization Energy

If we assume the stabilization energies in the excited and ground state are identical, we can assign them to the **reorganization energy** (λ) of the system:

$$U_g^{rel} = U_e^{rel} = \lambda$$

Reorganization energies are critical parameters in Marcus theory for charge transfer.
