4.3: Solvation Dynamics and Reorganization Energy

Some of the practical challenges of describing solvation through thermodynamic cycles include dealing with strong solute–solvent interactions, flexible solutes, and explicit solvents. Additionally, it does not reflect the fact that solvation is a highly dynamic process involving motion of the solvent. Perhaps the most common example is in charge transfer processes (i.e., electrons and protons) in which water's dipoles can act to drive and stabilize the position of the charge. For instance, consider the transfer of an electron from a donor to an acceptor in solution:

$$\mathrm{D} + \mathrm{A} \longrightarrow \mathrm{D}^{+} + \mathrm{A}^{-}$$

We most commonly consider electron transfer as dependent on a solvent coordinate in which solvent reorganizes its configuration so that dipoles or charges help to stabilize the extra negative charge at the acceptor site. This type of *collective* coordinate is illustrated in the figure below. These concepts are reflected in the Marcus' theory of electron transfer. The free energy change to relax the solvent configuration after switching the charges in the initial configuration is known as the **reorganization energy** λ.