

HOW SOLVENT CONTROLS ELECTRONIC ENERGY TRANSFER AND LIGHT HARVESTING

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Understanding solvent effects, which cause line broadening and screen electronic interactions, is fundamentally important because of its central role in the control of electronic energy transfer (EET) dynamics. Recent work has furthermore shown that simple models for solvation may not be sufficient to explain effects that go beyond Förster theory, such as coherent contribution to energy transfer.^{1,2} Here results obtained from novel quantum-mechanical methodologies will be reported as a starting point for an atomistic description of the interplay between solvation and electronic energy transfer. First, we will present results obtained with a quantum-mechanical method that accounts for the actual shape of the molecules inside the dielectric environment through the Polarizable Continuum Model (PCM), thus overcoming the point-dipole assumption of Förster theory. This model predicts an exponential distance-dependent attenuation of the solvent screening in chromophore pairs taken from light harvesting antenna proteins,^{3,4} thus indicating a substantial underestimation of EET rates by Förster theory at separations less than about 20 Å. As a further step towards a realistic model of solvation in EET, we will present a QM/MM method that adopts an atomistic description of the solvent, thus going beyond the continuum dielectric approximation. This approach allows the study of EET in highly heterogeneous dielectric environments such as proteins. Moreover, a fundamental advantage of the QM/MM model is the ability to explore the solvent-induced fluctuations on the electronic coupling and the site energies, thus providing detailed insights on the role of solvation in electronic energy transfer.

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