

Intramolecular Vibrational Modes in Excitation Energy Transfer and Spectroscopy of Molecular Aggregates

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Aggregates of light-absorbing molecules (pigments) embedded in proteins form the functional basis of natural photosynthesis. Transfer of excitation energy collected by such pigment-protein complexes occurs both in the spatial and energy domains along an energy funnel leading towards the so-called reaction center, which converts excitation energy into separated charges. It has been long accepted that protein degrees of freedom form a heat bath into which excess energy is irreversibly damped when excitation crosses energy gaps between states. This basic picture of photosynthetic energy transfer has prevailed in the debates over its quantum nature during the past decade [1, 2], and its essential features remain in place even as a more elaborate scheme involving the active role of intramolecular vibrational modes of pigments is emerging [3-5]. In this contribution, we will discuss recent developments in a research effort to characterize the involvement of intramolecular vibrational modes in excitation energy transfer in photosynthesis by spectroscopic means. Early work concentrated on linking the vibrational motion with long-lived oscillations in the coherent electronic two-dimensional spectra [6-9] without necessarily making conclusions on their influence on energy transfer. Building upon these results, we will discuss how additional vibrational resonances between energy gaps may help smoothen the energy landscape to allow energy transfer across very large energy gaps [4,10] and avoid trapping states[5]. Theoretical analysis of recent experiments performed on bacterial reaction centers by the Ogilvie group [11] reveals signatures of the same states that previous work [4] implied in an efficient energy transfer. Based on the past decade of development, we will try to speculate about the general role of intramolecular vibrational modes in the design of photosynthetic pigment-protein complexes.

Literature

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