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Vibronic Enhancement of Exciton Sizes and Energy Transport in Photosynthetic Complexes ANDREW MORAN, JORDAN WOMICK, BRANTLEY WEST, STEPHEN MILLER, University of North Carolina — This talk investigates the impact of vibronic couplings on the electronic structures and relaxation mechanisms of two cyanobacterial light harvesting proteins, allophycocyanin (APC) and c-phycocyanin (CPC). Both APC and CPC possess three pairs of pigments (i.e., dimers), which undergo electronic relaxation on the sub-picosecond time scale. Electronic relaxation is approximately 10 times faster in APC than in CPC despite the nearly identical structures of their pigment dimers. Femtosecond laser spectroscopies conducted in conjunction with a Frenkel exciton model find that photo-induced electronic relaxation in these two proteins is understood on the same footing only when the vibronic couplings in high-frequency modes are properly taken into account. In addition to incorporating high-frequency intramolecular modes in the spectral density, we simulate electronic relaxation dynamics using a model in which the excitons delocalize in a vibronic basis. General implications of the present findings for energy transport in artificial systems (e.g., crystalline organic semiconductors) are discussed.

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