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Evidence for Slow Structural Relaxation and Related Non-Equilibrium Dynamic Effects in pre-illuminated Photosynthetic Reaction Centers ANTHONY J. MANZO, Chem. Dept., UC Riverside, A.O. GOUSHCHA, Semicoa, Costa Mesa, CA and Chem. Dept., UC Riverside, G.W. SCOTT, Chem. Dept., UC Riverside, N.M. BEREZETSKA, V.N. KHARKYANEN, Inst. of Physics, Natl. Academy of Sciences of Ukraine, Kyiv, Ukraine — The charge recombination time of photosynthetic reaction centers (RCs) increases significantly upon lengthy illumination, allowing for non-equilibrium dynamic effects (non-equilibrium structural transitions) in the protein-cofactor system. Experimental verification of such effects was made by applying photoexcitation of varying duration from .1 to hundreds of seconds, resulting in repeated cycles of the charge separation and recombination within isolated RCs. The charge recombination kinetics was monitored by transient absorption spectroscopy. The kinetic curves were analyzed using the maximum entropy method for optimization of fitting results and the relaxation spectra were calculated. These spectra for RCs with both quinone acceptors active had two or more pronounced peaks in a frequency domain for short illumination times. The peaks centered at around $\sim 1 \text{ s}^{-1}$ and $\sim 10 \text{ s}^{-1}$ were well distinguished. With increasing actinic pulse duration, the low frequency part of the distribution broadened and shifted gradually towards still lower frequencies, reaching values smaller than 0.02 s^{-1} for illumination times longer than 100 s. The results strongly support the idea of illumination-controlled coupling of electron transfer to macromolecule conformation in photosynthetic RCs.

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