Analysis and Control of Excitation Energy Dynamics in Photosynthetic Antenna Systems

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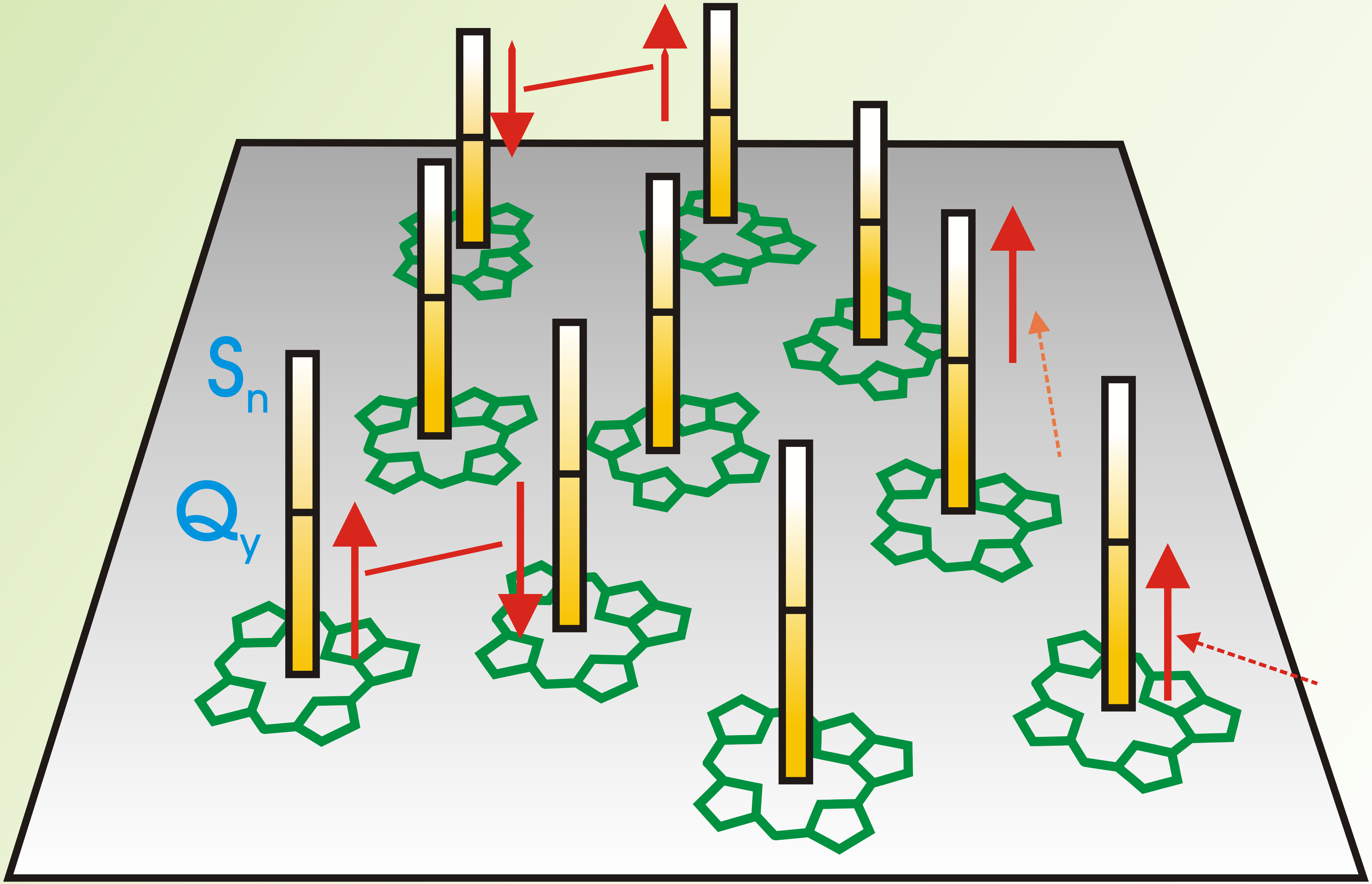
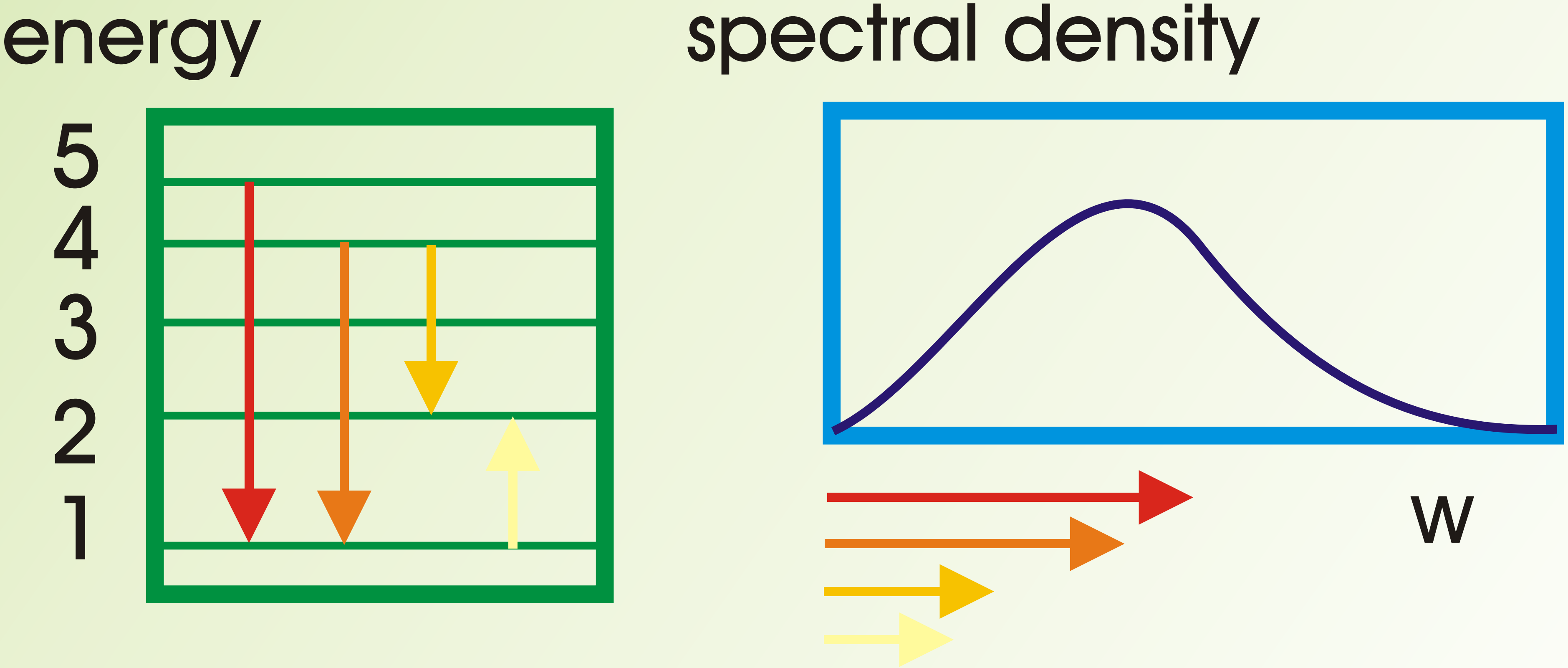
The Model

Electronic Level Scheme



Exciton Relaxation and the Spectral Density



Multiexciton Density Matrix Theory

The Multiexciton Density Matrix

$$\rho(\alpha_M, \beta_N; t) = \langle \alpha_M | \mathrm{tr}_{\mathrm{intra-Chl}} \{ \mathrm{tr}_{\mathrm{protein}} \{ \hat{W}(t) \} \} | \beta_N \rangle$$

Single Exciton State

$$|\alpha_1\rangle = \sum_m C_{\alpha_1}(m) | m Q_y \rangle$$

Two Exciton State

$$|\alpha_2\rangle = \sum_{m,n} C_{\alpha_2}(m,n) | m Q_y, n Q_y \rangle + \sum_m C_{\alpha_2}(m) | m S_n \rangle$$

Single Exciton Relaxation Rates for Localized and Delocalized Protein Vibrations

$$k_{\alpha\to\beta}^{(\text{deloc vib})} = 2\pi\omega_{\alpha\beta}^2 \left(1 + n(\omega_{\alpha\beta})\right) \left[j_{\alpha\beta}(\omega_{\alpha\beta}) - j_{\alpha\beta}(-\omega_{\alpha\beta})\right]$$

spectral density of delocalized vibrations

$$j_{\alpha\beta}(\omega) = \sum_{\xi} \mid g_{\alpha\beta}(\xi) \mid^2 \delta(\omega - \omega_\xi)$$

$$k_{\alpha\to\beta}^{(\text{local vib})} = 2\pi\omega_{\alpha\beta}^2 \left(1 + n(\omega_{\alpha\beta})\right) \sum_m \mid C_\alpha(m) C_\beta(m) \mid^2 \left[j_m(\omega_{\alpha\beta}) - j_m(-\omega_{\alpha\beta})\right]$$

spectral density of localized vibrations

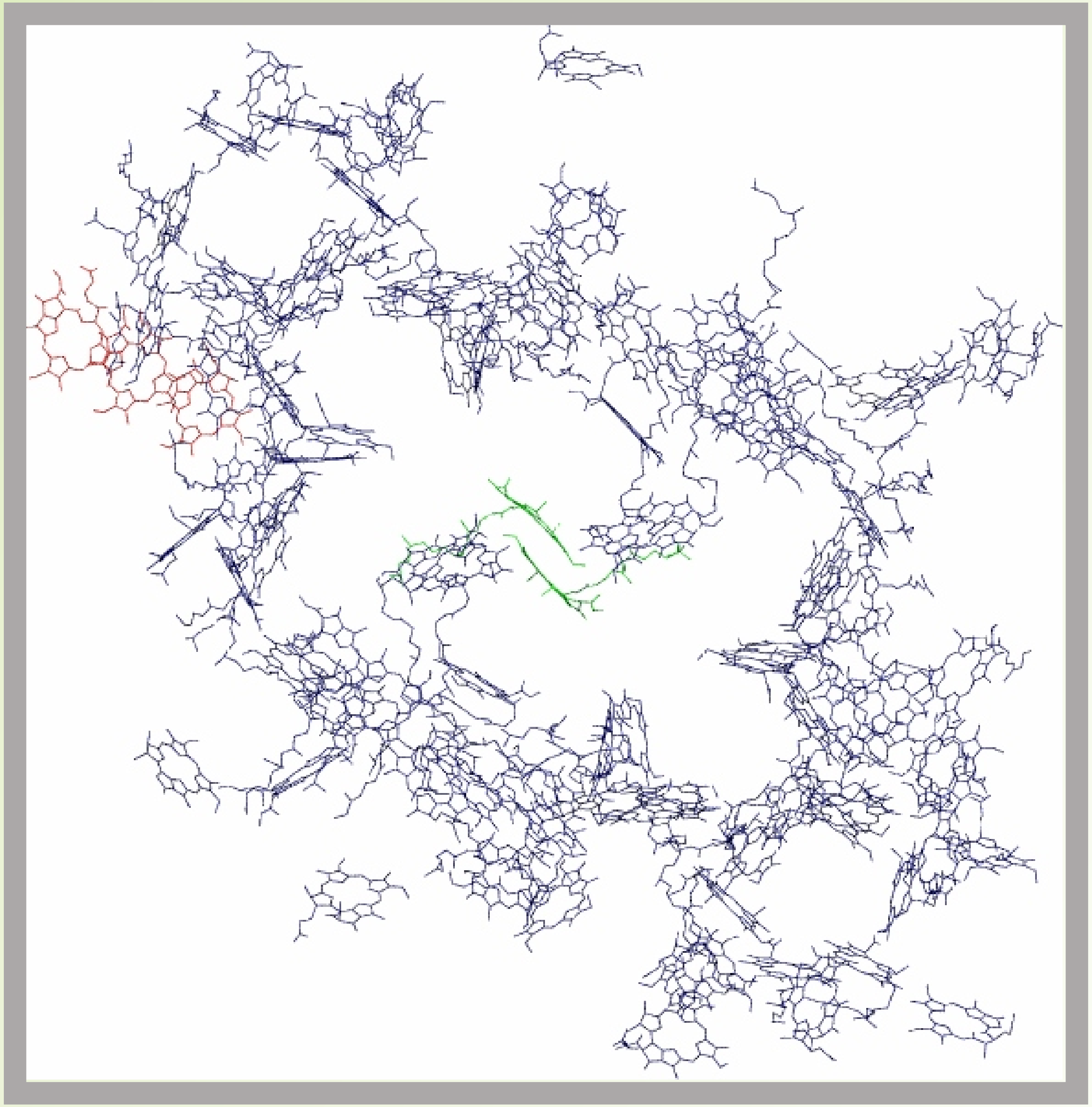
$$j_m(\omega) = \sum_{\xi(m)} g_m^2(\xi(m)) \delta(\omega - \omega_{\xi(m)})$$

Exciton Exciton Annihilation Rate

$$k^{(\mathrm{EEA})}_{\alpha_2 \to \beta_1} = \left| \sum_m C^*_{\alpha_2}(mS_n) C_{\beta_1}(mQ_y) \right|^2 k^{(\mathrm{IC})}_{S_n \to Q_y}$$

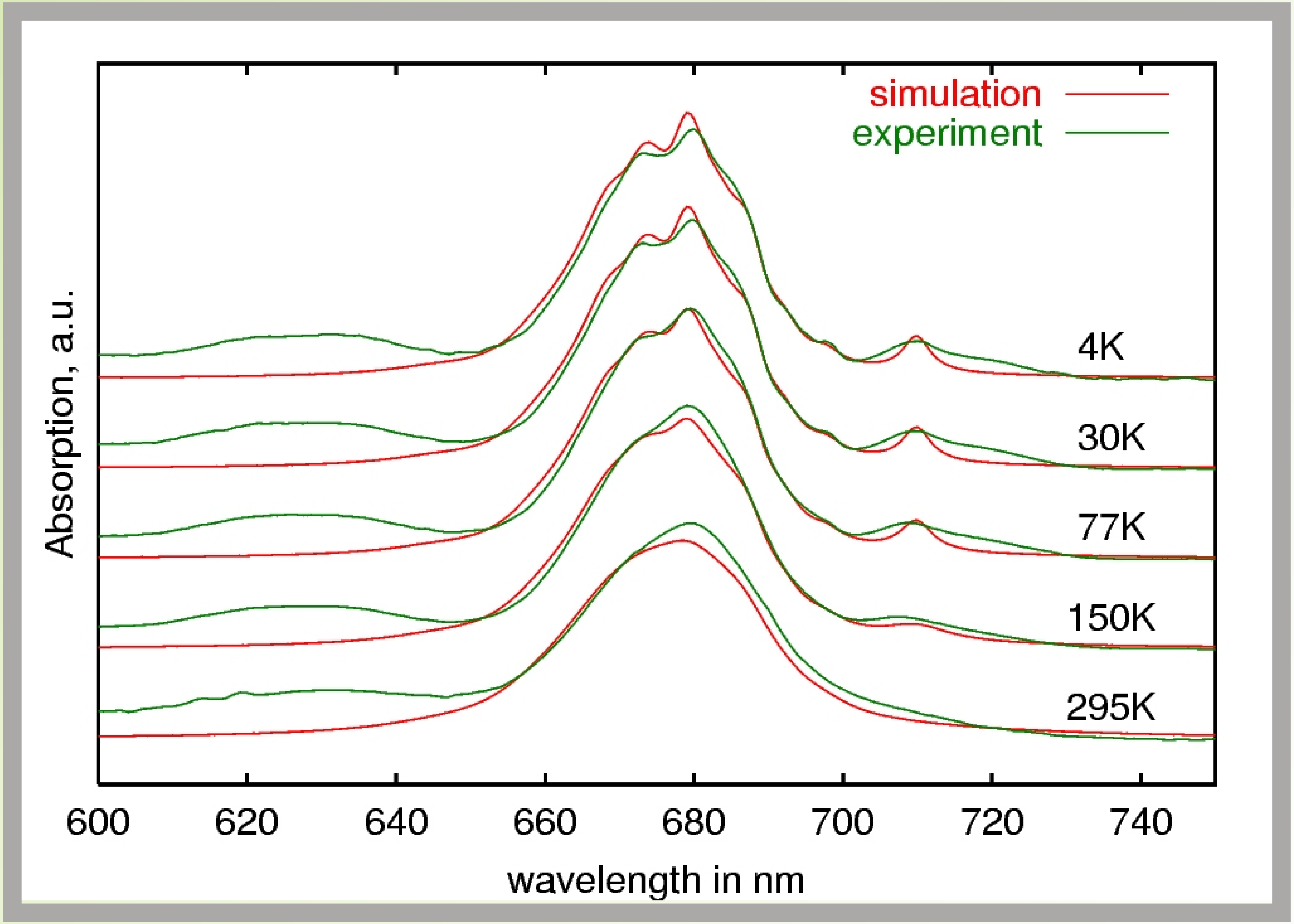
Exciton Model for the Ps1 Antenna

Photosystem 1 of *Synechococcus elongatus*

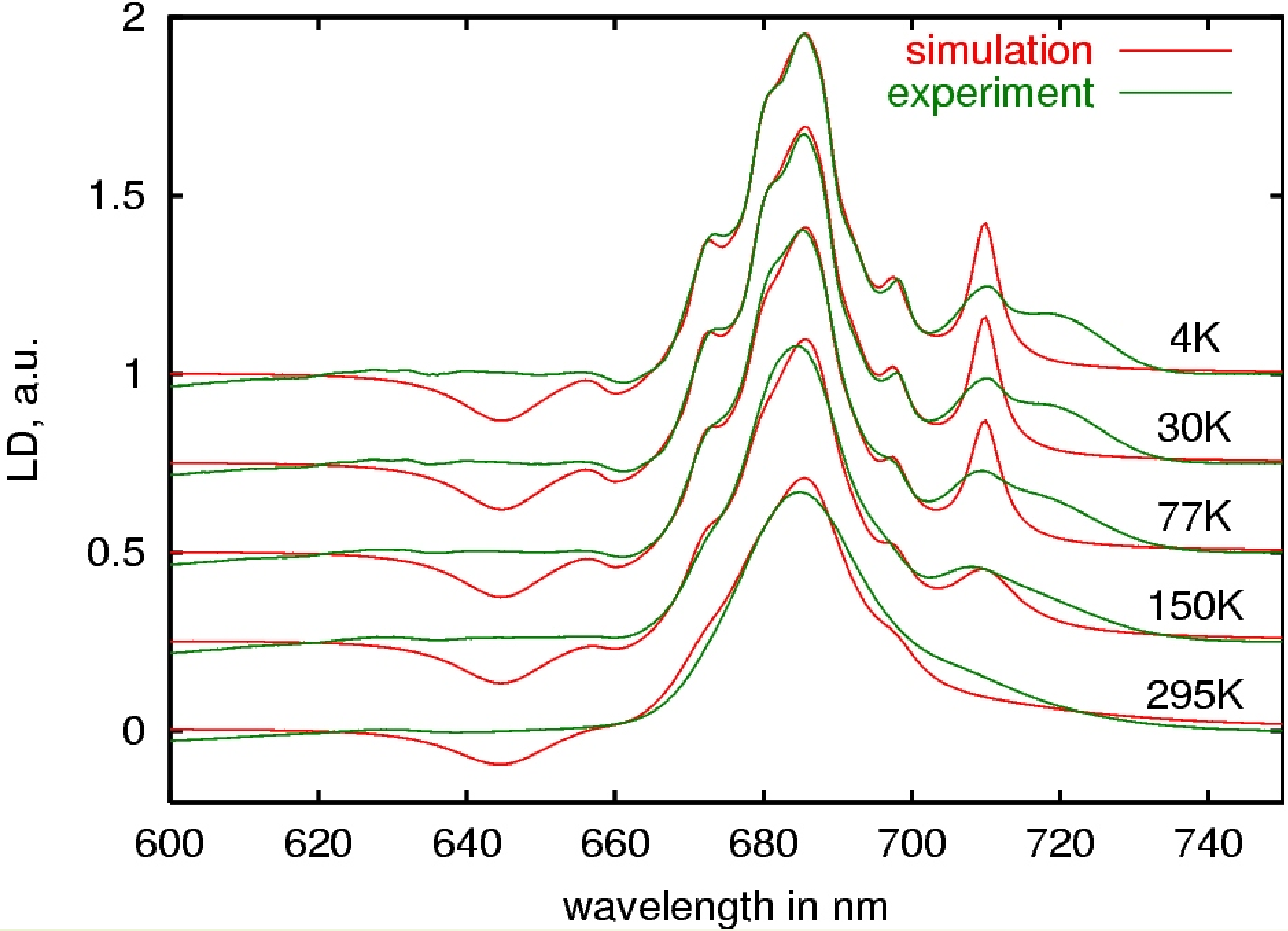


Fit of Frequency Domain Spectra

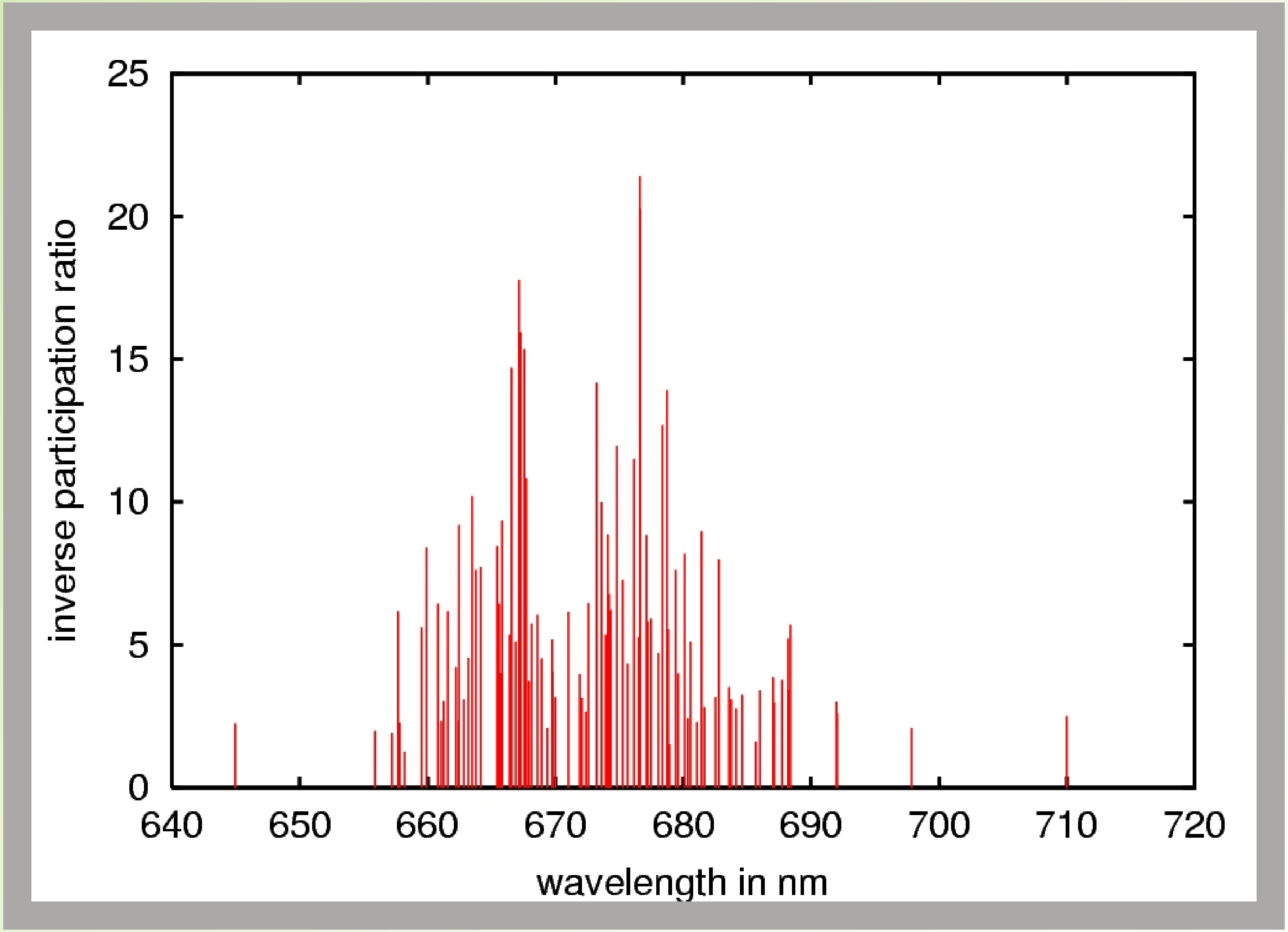
Linear Absorption of PS1



Linear Dichroism of PS1

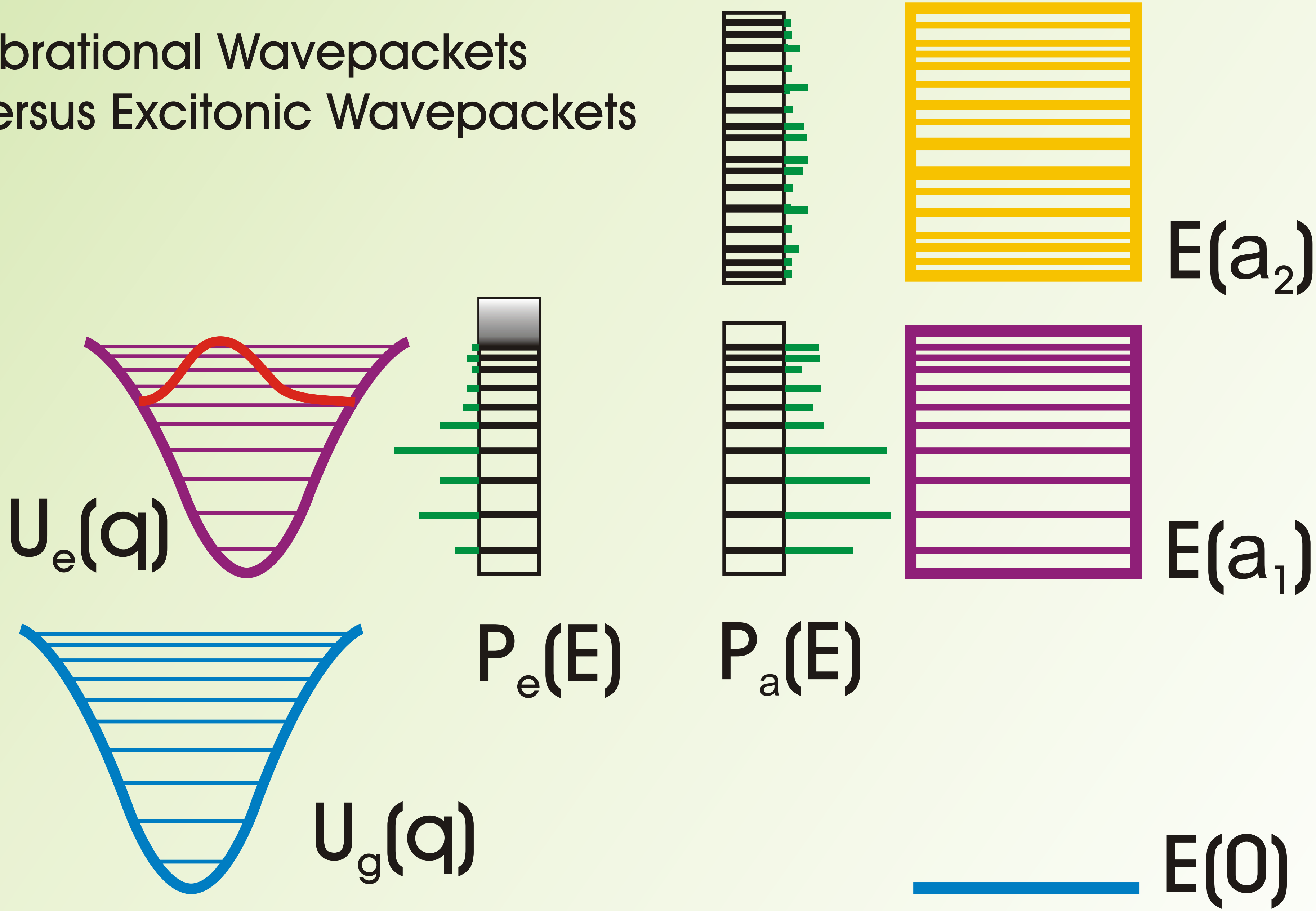


Inverse Participation Ratio of Q_y Excitons in the PS1

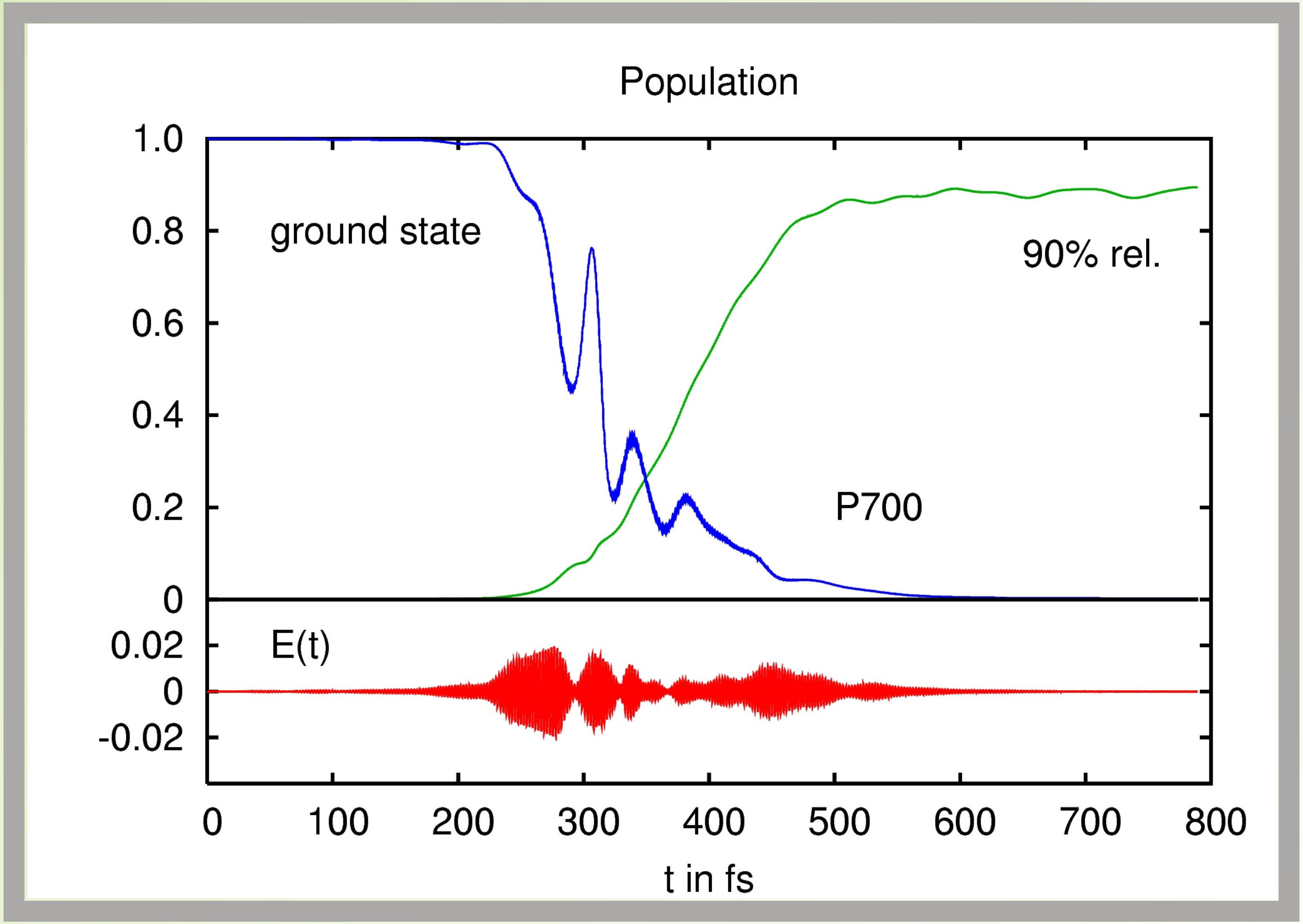


Fs-Laser Pulse Control of Exciton Dynamics

Vibrational Wavepackets
versus Excitonic Wavepackets



population at t = 800 fs:
98% 1-exciton manifold + 2 % ground-state



population at t = 800 fs:
60% 1-exciton manifold + 40% ground-state