SUPPORTING INFORMATION

Interpretation of the 1.9 ps DADS from Figure 9B.

Our aim is here to show analytically that, assuming a sequential model B* → P* → $P^+B_L^-$ → $P^+H_L^-$ → without back reactions, but with heterogeneous decay of P*, the DADS of the 1.9 ps component is proportional to the difference between the SADS of $P^+H_L^-$ and $P^+B_L^-$. Apart from the global analysis with independent decays $(1|2|\ldots|n_{\mathrm{comp}})$, (where n_{comp} is the number of components, in our case four) the simplest kinetic model is the unbranched, unidirectional model ($1 \rightarrow 2 \rightarrow \ldots \rightarrow n_{\mathrm{comp}} \rightarrow$). These models are also termed parallel and sequential. In the sequential model back-reactions are ignored on the assumption that the energy losses are large enough that the reverse reaction rates are negligible. Note that it is assumed that there are no losses in the chain $1 \rightarrow 2 \rightarrow \ldots \rightarrow n_{\mathrm{comp}} \rightarrow$. The sequential model can be solved to yield (e.g. [50]):

$$c_l(t) = \sum_{j=1}^{l} b_{jl} \exp(-k_j t) \qquad \text{Eq. S.1}$$

where $c_l(t)$ is the concentration of component *l* (from the sequential model), $\exp(-k_j t)$ is the concentration of component *j* from the parallel model (with decay rate k_j) and the amplitudes b_{jl} of the exponential decays are defined by $b_{11} = 1$ and for $j \le l$:

$$b_{jl} = \prod_{m=1}^{l-1} k_m \Big/ \prod_{\substack{n=1 \\ n \neq j}}^{l} (k_n - k_j) \qquad \text{Eq. S.2}$$

Because of the equivalence of the sequential and parallel model in describing the system we can write for all wavelengths λ and times *t*:

$$c_{\mathrm{S}}^T \varepsilon_{\mathrm{S}} = c_{\mathrm{P}}^T \varepsilon_{\mathrm{P}} \qquad \text{Eq. S.3}$$

where *c* and ε are n_{comp} (column) vectors, containing the concentrations and difference spectra of the components, and the subscripts S and P refer to the sequential and parallel model, respectively (the superscript T stands for transposed, thus c^T is a row vector).
Eq. S.1 expresses c_{S} in terms of c_{P}:

$$c_{\mathrm{S}}^T = c_{\mathrm{P}}^T B \qquad \text{Eq. S.4}$$

where the right triangular matrix *B* contains elements b_{jl} defined in Eq. S.2. Inserting Eq. S.4

into Eq. S.3 we find:

$$\varepsilon_P = B\varepsilon_S \qquad \text{Eq. S.5}$$

which expresses the DADS ε_P as a linear combination of SADS ε_S. In particular, we can use the elements of the one but last component described in the sequential model of Eq. S.2. We then find:

$$b_{l-1,l-1} = \prod_{m=1}^{l-2} k_m \Big/ \prod_{n=1}^{l-2} (k_n - k_{l-1}) = \left[\prod_{m=1}^{l-3} k_m \Big/ \prod_{n=1}^{l-3} (k_n - k_{l-1})\right] \frac{k_{l-2}}{k_{l-2} - k_{l-1}}$$

$$b_{l-1,l} = \left[\prod_{m=1}^{l-2} k_m \Big/ \prod_{n=1}^{l-2} (k_n - k_{l-1})\right] \frac{k_{l-1}}{k_l - k_{l-1}} = b_{l-1,l-1} \frac{k_{l-1}}{k_l - k_{l-1}} \qquad \text{Eq. S.6}$$

Now assuming a four compartmental sequential model ($l = 4$) we have for the third DADS

$$\varepsilon_{P,3} = b_{3,3}\varepsilon_{S,3} + b_{3,4}\varepsilon_{S,4} \sim \frac{k_2}{k_2 - k_3}\left(\varepsilon_{S,3} + \left(\frac{k_3}{k_4 - k_3}\right)\varepsilon_{S,4}\right) \qquad \text{Eq. S.7}$$

Since in the sequential model B* → P* → $P^+B_L^-$ → $P^+H_L^-$ → the rates $k_3 > k_2$ and $k_4 \ll k_3$ we have approximately

$$\varepsilon_{P,3} \sim -(\varepsilon_{S,3} - \varepsilon_{S,4}) = \varepsilon_{S,4} - \varepsilon_{S,3} \qquad \text{Eq. S.8}$$

Suppose (in a wavelength region where H_L^- does not absorb) that the final spectrum $\varepsilon_{S,4}$ is due to P^+ only, and that the third SADS $\varepsilon_{S,3}$ is due to P^+ and B_L^-, then the third DADS $\varepsilon_{P,3}$ will be proportional to minus the spectrum of B_L^-. Finally, we introduce heterogeneity of the charge separation rate k_2 only. As long as $k_3 > k_2$ we can consider this as a linear combination of systems for which Eq. S.8 holds. Thus the third DADS is still proportional to the difference of the fourth and third SADS. This, admittedly, lengthy argument thus allows us to interpret the DADS in Figure 9B as the negative of the shape of the spectrum of B_L^-.