

# CHEMPHYSICHEM

## Supporting Information

### **The Role of Resonant Vibrations in Electronic Energy Transfer**

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## SUPPORTING INFORMATION

### Bath transformation

In this section the transformation process of including several vibrational modes from the bath explicitly into the system Hamiltonian is presented. The logic proceeds as follows: first we start with the bath decomposition we want to achieve, that is a few explicit modes and many other modes, with bilinear interaction between the two. Then we transform the bath Hamiltonian into the normal modes, which present non-interacting modes. In this basis we present the form of the bath Hamiltonian in the system ground and excited state as is usual in the spectroscopical treatment. Then we invert the transformation, insert the two kinds of modes, and derive the new form of the system-bath interaction. The result presents the two terms of system bath interaction discussed in the main text, one coupling the bath modes to the electronic degrees of freedom, the other to the prominent vibrational coordinate.

We start with the vibrational part of the total Hamiltonian separated into the system part (a few prominent modes) and the environment part (typically many more modes):

$$\begin{aligned} H_B^S &= \sum_k \frac{\hbar\Omega_k}{2} (P_k^2 + Q_k^2) \\ H_B^E &= \sum_n \frac{\hbar\omega_n}{2} (p_n^2 + q_n^2). \end{aligned} \quad (1)$$

Here  $\Omega_k$  and  $\omega_n$  is the mode frequency,  $P_k$ ,  $p_n$  and  $Q_k$ ,  $q_n$  are the canonical coordinates. The interaction between the modes is assumed to be bilinear:

$$H_B^{int} = \sum_{kn} \kappa_{kn} Q_k q_n. \quad (2)$$

The bath Hamiltonian  $H_B = H_B^S + H_B^E + H_B^{int}$  can be always transformed into the vibrational normal modes[1]:

$$\begin{aligned} H_B^{(g)} &= \sum_{\xi} \frac{\hbar\omega_{\xi}}{2} (p_{\xi}^2 + q_{\xi}^2) \\ H_B^{(e)} &= \sum_{\xi} \frac{\hbar\omega_{\xi}}{2} (p_{\xi}^2 + (q_{\xi} - d_{\xi})^2). \end{aligned} \quad (3)$$

The excited state is displaced by  $d_{\xi}$  with respect to the ground state. The excited state bath can be expressed by the ground state bath as

$$H_B^{(e)} = H_B^{(g)} - \sum_{\xi} \hbar\omega_{\xi} d_{\xi} q_{\xi} + \lambda_e; \quad \lambda_e = \sum_{\xi} \frac{\hbar\omega_{\xi}}{2} d_{\xi}^2. \quad (4)$$

Here  $\lambda_e$  is usually called the reorganization energy and the linear coupling to the bath modes  $q_{\xi}$  is apparent now. This form of the bath is typically used for describing the spectroscopically relevant energy-gap  $\Delta V = H^{(e)} - H^{(g)}$  fluctuations. Using the backward transformation,

$$q_{\xi} = \sum_n a_n^{(\xi)} q_n + \sum_k b_k^{(\xi)} Q_k, \quad (5)$$

we get for the excited state bath

$$H_B^{(e)} = H_B^{(g)} + \lambda - \sum_n D_n q_n - \sum_k D_k Q_k. \quad (6)$$

Here  $D_n = \sum_{\xi} \hbar\omega_{\xi} d_{\xi} a_n^{(\xi)}$  and  $D_k = \sum_{\xi} \hbar\omega_{\xi} d_{\xi} b_k^{(\xi)}$  are the new potential shifts in the excited state. Now we define new quantities such as the excited state vibrations equilibria

$$Q_k^0 = \frac{D_k}{\hbar\Omega_k}, \quad (7)$$

the total reorganization energy

$$\lambda = \lambda_e - \sum_k \frac{D_k^2}{2\hbar\Omega_k}, \quad (8)$$

and the new bath operators for the 'electronic' environment bath

$$\Phi^{(2)} = - \sum_n D_n q_n + \sum_{kn} \kappa_{kn} \frac{D_k}{\hbar\Omega_k} q_n \quad (9)$$

and the 'vibrational' environment bath

$$\Phi_k^{(1)} = \frac{1}{\sqrt{2}} \sum_n \kappa_{kn} q_n. \quad (10)$$

Using these quantities, the total Hamiltonian of one two-level system can be written as

$$\begin{aligned} H = H_B + [e_g + H_{vib}(\{Q_k\})] |g\rangle \langle g| \\ + [e_e + \lambda + H_{vib}(\{Q_k - Q_k^0\}) + \Phi^{(2)}] |e\rangle \langle e|, \end{aligned} \quad (11)$$

where

$$H_{vib}(\{Q_k\}) = \sum_k \frac{\hbar\Omega_k}{2} (P_k^2 + Q_k^2) + Q_k \sqrt{2}\Phi_k^{(1)}. \quad (12)$$

This is the Hamiltonian of Eqs. (1) and (2) in the main text. A similar form of interaction Hamiltonian with the two baths was used by Novoderezhkin et al.[2].

### Vibronic basis expressions

The system-bath interaction terms are transformed:

$$\begin{aligned} \Phi_{ij}^{(2)} &= \sum_{n=1}^N \sum_{\nu_1 \dots \nu_N} c_{n,\nu_1 \dots \nu_N}^i c_{n,\nu_1 \dots \nu_N}^j \Phi_n^{(2)}, \\ \Phi_{ij}^{(1)} &= \sum_{n=1}^N \sum_{\nu_1 \dots \nu_N} \sum_{\mu_1 \dots \mu_N} c_{n,\nu_1 \dots \nu_N}^i c_{n,\mu_1 \dots \mu_N}^j \sum_k \mathcal{K}_{k,\nu_1 \dots \nu_N \mu_1 \dots \mu_N} \Phi_k^{(1)}. \end{aligned} \quad (13)$$

In the vibronic basis, the dipole transitions to the one-exciton block will be given by the transformation coefficients and the vibration wavefunction overlap:

$$\langle \varepsilon_i | \mu | g^{\nu_1 \dots \nu_N} \rangle = \mu_{i,g\nu_1 \dots \nu_N} = \sum_n \mu_n \sum_{\mu_1 \dots \mu_N} c_{n,\mu_1 \dots \mu_N}^i \langle \chi_n^{(e)\mu_n} | \chi_n^{(g)\nu_n} \rangle \prod_{l \neq n} \delta_{\mu_l \nu_l}. \quad (14)$$

### Dynamics of the vibronic wavepacket - projection

To get further illustration of the relaxation of the vibronic wavepacket in the lower state, we can calculate a projection of the wavepacket on the abscissa connecting the minima of the potential energy surfaces of excited state 1 and 2. The resulting dynamics can be found in Fig. S1.

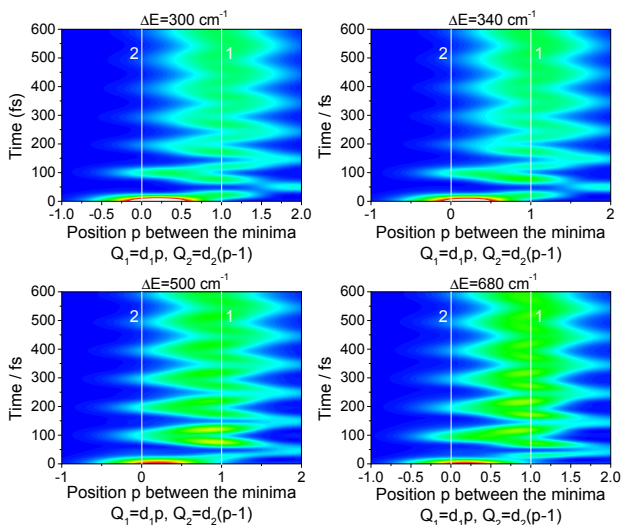


Figure S1. Vibronic wavepacket dynamics projected on the abscissa between the state 1 and 2, see Fig. 1 for definition of the coordinates.

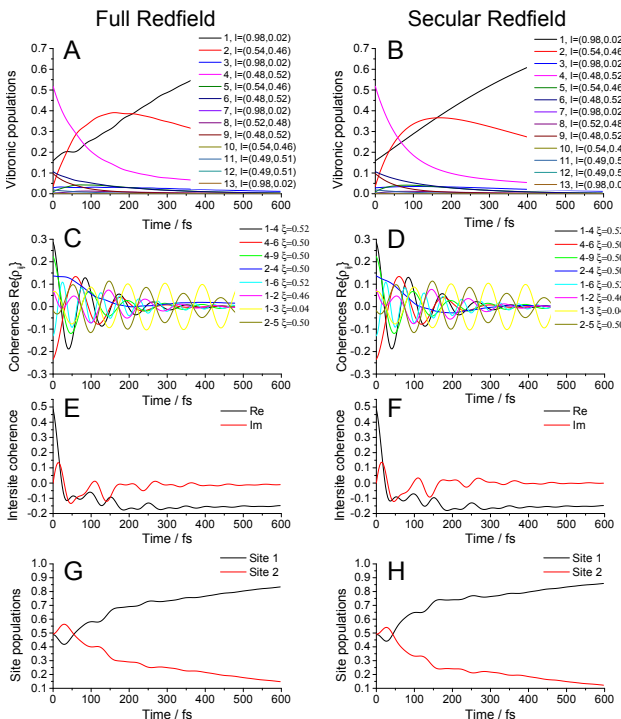


Figure S2. Comparison of the 'Secular' and Full Redfield dynamics of the system,  $\Delta E = 340 \text{ cm}^{-1}$

### Role of secular approximation

Here in Fig. S2 we give the detailed comparison of the system dynamics for the full and secular Redfield description. In the secular case, where there is no interplay between the vibronic populations and coherences, the population dynamics is given by rate equations only. The 'wiggles' on the vibronic populations are therefore characteristic for the coherences affecting their dynamics. The most pronounced difference is thus the significantly faster transfer between sites in the secular case.

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- [1] Garg, A., Onuchic, J.N., and Ambegaokar, V. (1985) Effect of friction on electron transfer in biomolecules. *J. Chem. Phys.*, **83** (1985), 4491.
- [2] Novoderezhkin, V.I., Yakovlev, A.G., Van Grondelle, R., and Shuvalov, V.a. (2004) Coherent nuclear and electronic dynamics in primary charge separation in photosynthetic reaction centers: A Redfield theory approach. *J. Phys. Chem. B*, **108**, 7445–7457.