Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information for: Nonadibatic sunlight harvesting

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1 Redfield master equation

The Redfield master equation reads

$$\frac{\mathrm{d}\rho_{ab}(t)}{\mathrm{d}t} = -\mathrm{i}\omega_{ab}\rho_{ab}(t) - \sum_{c,d}\left(R^{\mathrm{PB}}_{ab,cd} + R^{\mathrm{BB}}_{ab,cd}\right)\rho_{cd}(t). \tag{1}$$

Here, the first term of the right-hand side accounts for the unitary dynamics, and the Redfield relaxation tensors $R^{\mathrm{PB}}_{ab,cd}$ and $R^{\mathrm{BB}}_{ab,cd}$ describe the dephasing and relaxation energy processes due to the vibrational environment (phonon bath) and the incoherent radiation environment (blackbody bath), respectively. These are given by

$$R^{\mathrm{PB,BB}}_{ab,cd} = \delta_{ac}\sum_{e}\Gamma^{\mathrm{PB,BB}}_{be,ed}(\omega_{de}) + \delta_{b,d}\sum_{e}\Gamma^{\mathrm{PB,BB}}_{ae,ec}(\omega_{ce}) - \Gamma^{\mathrm{PB,BB}}_{ca,bd}(\omega_{db}) - \Gamma^{\mathrm{PB,BB}}_{db,ac}(\omega_{ca}). \tag{2}$$

The damping matrix elements that determine the time span for correlations are defined by

$$\Gamma^{\mathrm{PB,BB}}_{ab,cd}(\omega) = \sum_{u,v}\int_0^\infty \mathrm{d}\tau \mathrm{e}^{\mathrm{i}\omega\tau} C^{\mathrm{PB,BB}}_{u,v}(\tau)\hat{K}^{\mathrm{PB,BB}}_{u,ab}\hat{K}^{\mathrm{PB,BB}}_{v,cd}. \tag{3}$$

Here, $\hat{K}^{\mathrm{PB,BB}}_{u,ab}$ denote the observables of the system of interest that are coupled to the phonon and blackbody baths. Thus, the system-phonon bath and system-blackbody bath can be written as $\sum_u \hat{\Phi}^{\mathrm{PB,BB}}_{u,ab} \otimes \hat{K}^{\mathrm{PB,BB}}_{u,ab}$, where $\hat{\Phi}^{\mathrm{PB,BB}}_{u,ab}$ represent the observables of the phonon and blackbody baths that are coupled to the system of interest (vibronic dimer). The bath correlation function is defined by $C^{\mathrm{PB,BB}}_{u,v}(\tau) = \frac{1}{\hbar^2}\left\langle \hat{\Phi}^{\mathrm{PB,BB}}_{u,ab}(t)\hat{\Phi}^{\mathrm{PB,BB}}_{v,ab}(0)\right\rangle_{\mathrm{PB,BB}}$, where $\left\langle \hat{\mathcal{O}}\right\rangle_{\mathrm{PB,BB}} = \mathrm{tr}\left[\hat{\rho}^{\mathrm{PB,BB}}_{\mathrm{equi}}\hat{\mathcal{O}}\right]$ and $\left\langle \hat{\Phi}^{\mathrm{PB,BB}}_{u,ab}\right\rangle_{\mathrm{PB,BB}} = 0$. The real part of $\Gamma_{ab,cd}$ describes an irreversible redistribution of the amplitudes contained in the various parts of reduced density matrix. The imaginary part introduces terms that can be interpreted as a modification of the transition frequencies and of the respective mean-field matrix elements. The correlation function for each environment phonon/photon mode is given by

$$C^{\mathrm{PB,BB}}_{i}(t) = \int_0^\infty \mathrm{d}\omega\omega^2 J^{\mathrm{PB,BB}}_{i}(\omega)\left[\coth\left(\frac{\hbar\omega\beta}{2}\right)\cos(\omega t) - \mathrm{i}\sin(\omega t)\right]. \tag{4}$$

The blackbody radiation bath is characterized by the super-Ohmic spectral density [1]

$$\omega^2 J^{\mathrm{BB}}_{j}(\omega) = \frac{2\hbar\omega^3}{3(4\epsilon_0\pi^2c^3)}. \tag{5}$$

The spectral density of the phonon-baths reads

$$\omega^2 J^{\mathrm{PB}}_{j}(\omega) = \frac{2\Omega^{(\mathrm{e,v})}_{j}\Lambda^{(\mathrm{e,v})}_{j}\omega}{\hbar(\omega^2 + \Omega^{(\mathrm{e,v})2}_{j})}, \tag{6}$$

where $\Omega^{(\mathrm{e,v})}$ represents the cutoff frequency and $\Lambda^{(\mathrm{e,v})}$ the reorganization energy of the phonon baths coupled to the electronic (e) and intramolecular vibrational (v) degrees of freedom.

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2 Comparison between the Redfield master equation and the hierarchical equations of motion method

Figure 1 shows the vibronic dynamics of the PEB dimer solved with the Redfield master equation (RME) and the hierarchical equations of motion (HEOM) method [2, 3] for several values of the reorganization energy $\Lambda^{(\mathrm{e})}$ of the phonon bath coupled to the electronic degrees of freedom (e), and characterized by the spectral density $\omega^2 J_j^{\mathrm{PB}}(\omega) = 2\Omega_j^{(\mathrm{e})}\Lambda_j^{(\mathrm{e})}\omega/\hbar(\omega^2 + \Omega_j^{(\mathrm{e})2})$. The subspace of vibronic single exciton states can be described by the effective Hamiltonian [4]

$$\hat{H} = \frac{\Delta\epsilon}{2}\sigma_z + V\sigma_x - \frac{g}{\sqrt{2}}(\hat{b}_{\mathrm{ac}}^{\dagger} + \hat{b}_{\mathrm{ac}})\sigma_z + \omega_{\mathrm{ac}}\hat{b}_{\mathrm{ac}}^{\dagger}\hat{b}_{\mathrm{ac}}, \tag{7}$$

being $\Delta\epsilon$ the site energy difference, V the electronic coupling and g the vibronic coupling. Here, $\sigma_z = \sigma_2^+\sigma_2^- - \sigma_1^+\sigma_1^-$ and $\sigma_x = \sigma_1^+\sigma_2^- + \sigma_2^+\sigma_1^-$, where $\sigma_{i=1,2}^+$ ($\sigma_{i=1,2}^-$) creates (annihilates) an electronic excitation at the site $i = 1, 2$. The creation (annihilation) operator $\hat{b}_{\mathrm{ac}}^{\dagger}$ ($\hat{b}_{\mathrm{ac}}$) of the anticorrelated vibrational mode of frequency $\omega_{\mathrm{ac}} = \omega_1 = \omega_2$ reads $\hat{b}_{\mathrm{ac}}^{\dagger} = (\hat{b}_1^{\dagger} - \hat{b}_2^{\dagger})/\sqrt{2}$ $\left(\hat{b}_{\mathrm{ac}} = (\hat{b}_1 - \hat{b}_2)/\sqrt{2}\right)$, where $\hat{b}_{i=1,2}^{\dagger}$ ($\hat{b}_{i=1,2}$) creates (annihilates) an intramolecular vibrational excitation at the site $i = 1, 2$.

Figure 1 shows the population dynamics of the reduced lowest energy single exciton state $|\, e \,\rangle$ and coherence dynamics between the reduced single exciton states $|\, e \,\rangle$ and $|\, e' \,\rangle$, assuming as initial electronic state, the state prepared by the incoherent blackbody radiation bath only after 2.0 [ps], and a equilibrium thermal state ($T = 300$ K) for the anticorrelated vibrational mode. The values adopted for the simulations are $\Delta\epsilon = 1042\ \mathrm{cm}^{-1}$, $V = 92\ \mathrm{cm}^{-1}$, $g = 267.1\ \mathrm{cm}^{-1}$, $\omega_{\mathrm{ac}} = 1058\ \mathrm{cm}^{-1}$ and $T_{\mathrm{PB}}^{(\mathrm{e})} = 300\,\mathrm{K}$.

References

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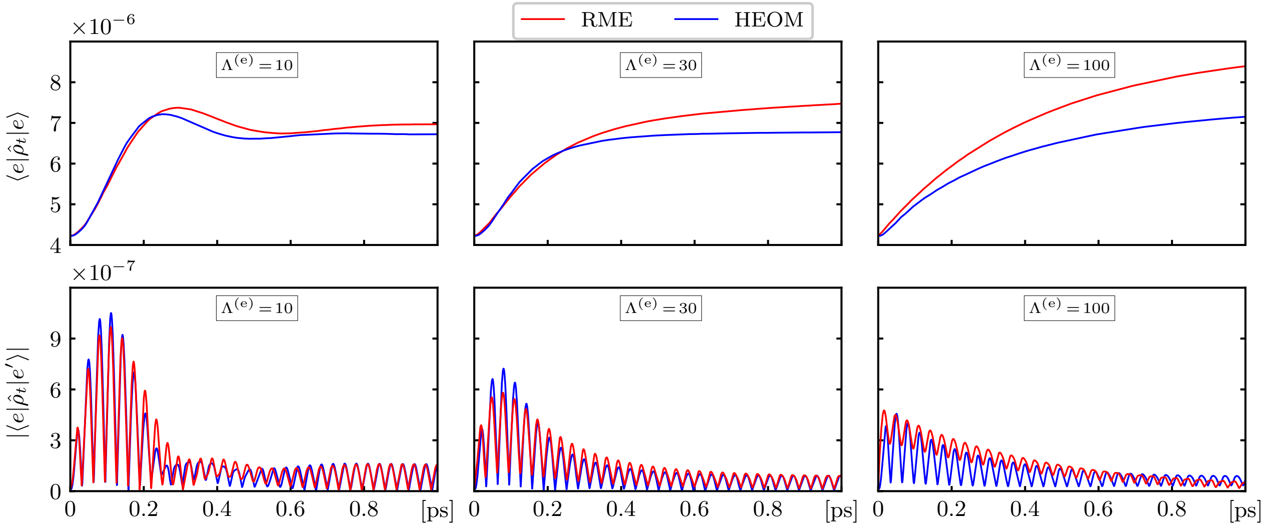

Figure 1: Comparison between the Redfield master equation (RME) and the hierarchical equations of motion (HEOM) method for several values of reorganization energy $\Lambda^{(e)}$ [cm^{-1}] of the PEB dimer. Top panels: Population dynamics of the reduced lowest energy single exciton state $|\,e\,\rangle$. Bottom panels: Coherence dynamics (absolute value) between the reduced single exciton states $|\,e\,\rangle$ and $|\,e'\,\rangle$.

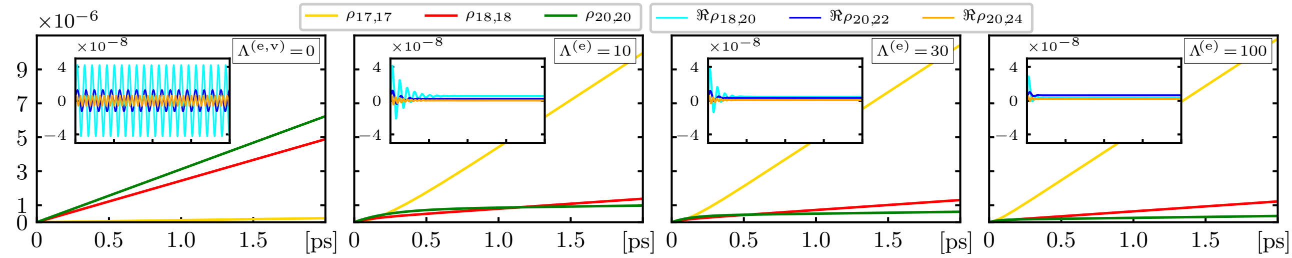

Figure 2: Vibronic single exciton states populations $\rho_{aa} = \langle\psi_a\,|\hat{\rho}|\,\psi_a\rangle$ and coherences (inset figures) $\Re\rho_{ab} = \Re\,\langle\psi_a\,|\hat{\rho}|\,\psi_b\rangle$ (color coding is shown on top) in the DBV dimer for the reorganization energies $\Lambda^{(e)} = 0, 10, 30, 100$ cm^{-1} and $\Lambda^{(v)} = 10$ cm^{-1}. Baths parameters are $T^{(e,v)}_{\rm PB} = 300\,$K, $T_{\rm BB} = 5600\,$K.

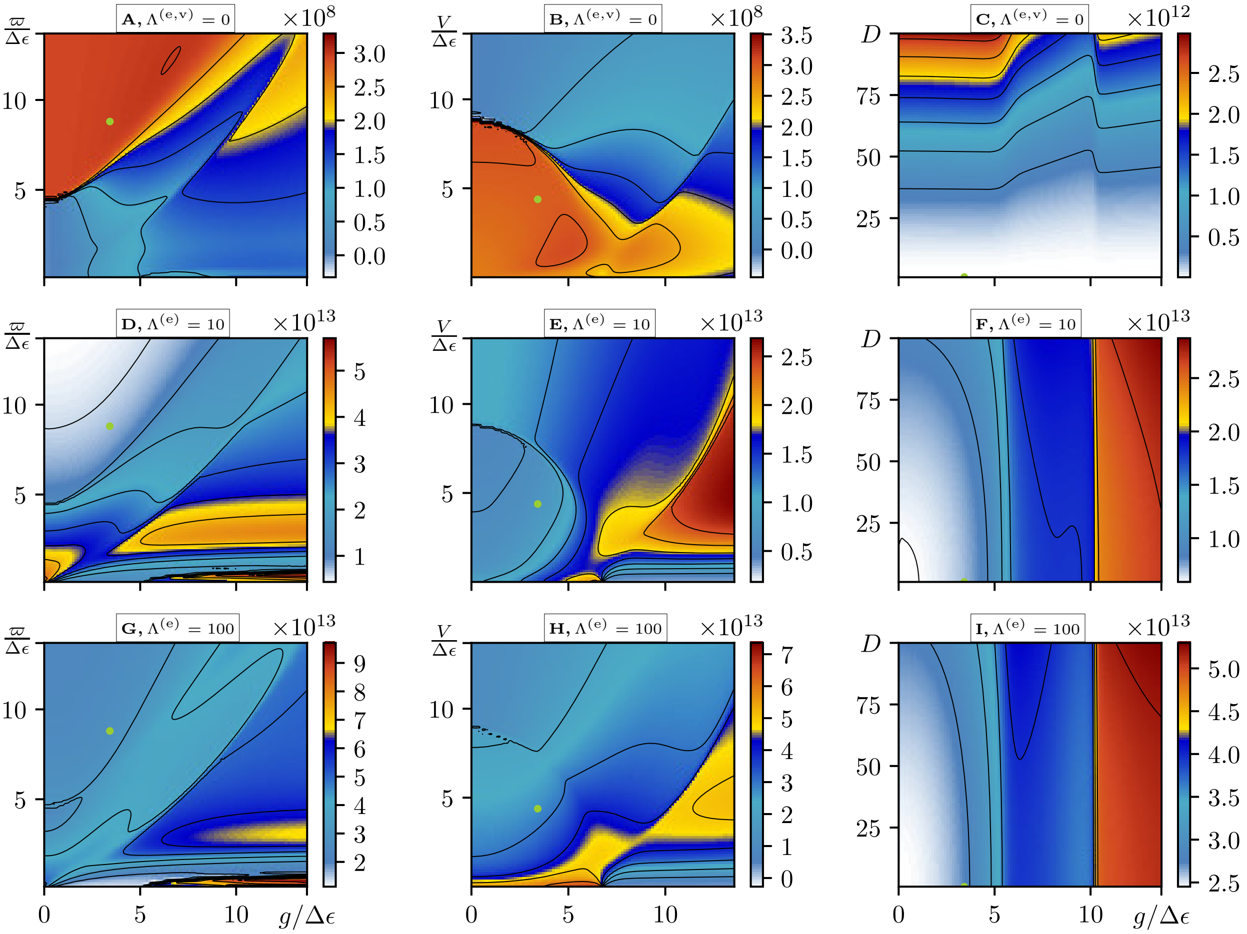

Figure 3: Decoherence rate $\gamma_{18,20}$ [s^{-1}] (color map) for the DBV dimer with the reorganization energies $\Lambda^{(e,v)} = 0\,\mathrm{cm}^{-1}$ (top panels), $\Lambda^{(e)} = 10\,\mathrm{cm}^{-1}$, $\Lambda^{(v)} = 10\,\mathrm{cm}^{-1}$ (middle panels) and $\Lambda^{(e)} = 100\,\mathrm{cm}^{-1}$, $\Lambda^{(v)} = 10\,\mathrm{cm}^{-1}$ (bottom panels), as a function of the ratios $g/\Delta\epsilon$, $\varpi/\Delta\epsilon$, $V/\Delta\epsilon$ and the transition dipole moment amplitude D, where $\Delta\epsilon$ represents the site energy difference. Green points represent the values adopted for the simulations of the density matrix dynamics in the vibronic single exciton, exciton and sites bases, discussed throughout the paper. Baths parameters are $T_{\mathrm{PB}}^{(e,v)} = 300$ K, $T_{\mathrm{BB}} = 5600$ K.