Exact Simulation of Pigment-Protein Complexes: Vibronic Renormalisation of Electronic Parameters in Ultrafast Spectroscopy

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The primary steps of photosynthesis generate, transport and trap delocalised electronic excitations (excitons) in pigment-protein complexes (PPCs). Generically, PPCs possess highly structured vibrational spectra with a large number of discrete intra- and quasi-continuous inter-pigment modes while exhibiting electronic (vibrionic) couplings that are comparable to electronic inter-pigment coupling. Consequently, establishing a quantitative connection between spectroscopic data and underlying microscopic models of PPC dynamics remains an outstanding challenge. We address this challenge with two numerically exact simulation methods that support an analytical theory of multimode vibronic effects. Vibronic coupling across the entire vibrational spectrum, including high-frequency modes, needs to be accounted for to ensure quantitatively correct description of optical spectra, where dynamic localization effects modulate the intensity of vibrational sidebands and multimode mixing shifts the absorption peaks. Furthermore, we show that high-frequency modes can support long-lived oscillations in multidimensional nonlinear spectra, which are not obtained in a coarse-grained description of the electronic-vibrational coupling.

Light-harvesting (LH) antennas and photo-chemical reaction centers (RC) provide the elementary building blocks of the photosynthetic apparatus of plants, algae and bacteria. Primarily these molecular aggregates consist of absorbing molecules (pigments) complexed with specific proteins to form a PPC. Despite its fundamental importance to biology, the dynamical characterization of these complexes to a degree that can reproduce all reported spectroscopic data in a single microscopic model remains an outstanding challenge.

Reduced models of excitonic dynamics subject to purely thermal fluctuations can achieve reasonable agreement with linear optical spectra. The quantitative explanation of all relevant aspects of multi-dimensional nonlinear spectroscopy though, requires a more detailed model of the system-environment interaction that takes into account the full complexity of the environmental structure. Indeed, spectroscopic studies of PPCs at low temperatures reveal the presence of vibrational environments that consist of a broad spectrum of low-frequency protein modes with room temperature energy scales, and several tens of discrete high-frequency modes that originate mainly from intra-pigment dynamics. Nonlinear optical experiments on monomer pigments in solution at both 77 K and room temperature as well as first-principles calculations further corroborate the underdamped nature of intra-pigment vibrational modes with picosecond lifetimes.

Recently, a range of vibronic models in which pigments are subject to the combined influence of a broad unstructured bosonic environment and a small number of vibrational modes with frequencies in the vicinity of excitonic transitions have been formulated. In this picture, vibrational lifetime borrowing can lead to long-lasting oscillatory dynamics of coherences between excitonic states and observations of long-lasting oscillatory features in multi-dimensional spectroscopy have been attributed to this effect. Notwithstanding, the identification of a universally accepted origin of these long-lived oscillations remains a subject of active discussion.

An important obstacle that prevents the conclusive resolution of this debate is the fact that the interpretation of spectroscopic data and their underpinning dynamical features can be influenced significantly by the specific choice of electronic and vibrational parameters that enter the PPC models. We will demonstrate that by accounting for the full environmental spectral density, involving more than 50 intra-pigment modes per site in addition to a broad background, the presence of high-frequency long-lived vibrational modes can lead to qualitatively significant modification of the calculated linear spectra of PPCs and consequently the estimated values of electronic parameters to recover a best fit with actual measurements. These corrections do not appear when considering only selected resonant modes and go well beyond predictions that can be obtained by using conventional lineshape theory.

To present our results, we provide an analytical theory of renormalisation effects due to multi-mode vibronic mixing in model excitonic systems of two prototypical PPCs, namely the water-soluble chlorophyll-binding protein (WSCP) of cauliflower and the special pair (SP) of bacterial reaction centers, depicted in Fig. 1. By considering realistic environmental spectral densities,
we corroborate our predictions using two independent numerically exact methods (the temperature-dependent time evolving density matrix using orthogonal polynomials algorithm, T-TEDOPA [22, 59–61], and the hierarchical equations of motion, HEOM [62]). We show that the hybridisation of electronic and vibrational degrees of freedom requires a significant renormalisation of electronic couplings. Importantly, this renormalisation of electronic parameters, in turn, is shown to have a significant impact on the dynamics of excitonic coherences, notably the lifetimes of their oscillatory dynamics.

**Electronic and vibronic couplings of PPCs** - Absorption spectra of PPCs are determined by the electronic energy-level structure of pigments, their mutual electronic interactions and the coupling of the resulting excitons to vibrational degrees of freedom of the pigment’s environment. In the following we will restrict our analysis to the $Q_y$ transition between electronic ground and first excited states of the pigments which suffices for the evaluation of the low-energy part of absorption spectra and is relevant for photosynthetic energy transfer [1]. For the dimeric WSCP and SP, the electronic Hamiltonian is then described by (see section I of the SI for details)

$$
H_e = \sum_{i=1}^{2} \varepsilon_i |\varepsilon_i\rangle \langle \varepsilon_i| + V(|\varepsilon_1\rangle \langle \varepsilon_2| + |\varepsilon_2\rangle \langle \varepsilon_1|).
$$

Here $|\varepsilon_i\rangle$ denotes the singly excited state of site $i$ with on-site energy $\varepsilon_i$ that is in the visible (WSCP) or in the near infrared spectrum (SP). The on-site energies depend on their local environment and therefore suffer from static disorder inducing ensemble dephasing that will be included in our numerical treatment. The electronic coupling $V$ leads to delocalised electronic eigenstates (excitons), $H_e|E_{\pm}\rangle = E_{\pm}|E_{\pm}\rangle$, and an excitonic splitting $\Delta = E_+ - E_- = \sqrt{4V^2 + (\varepsilon_1 - \varepsilon_2)^2}$. In WSCP, the mean site energies are identical, $\langle \varepsilon_1 \rangle = \langle \varepsilon_2 \rangle$, due to the symmetry of molecular structure, while in SP, the mean site energies are different as pigments are surrounded by nonidentical local protein environments. Another difference concerns the electronic coupling strength, which is stronger in SP due to electron exchange giving rise to short-range Dexter type contributions [63–64].

The exciton dynamics of PPCs is driven by vibrational modes that induce fluctuations in the transition energies $\varepsilon_i$ of pigments. The full electronic-vibrational interaction, induced by $N$ vibrational modes per site, is described by the Hamiltonian $H = H_e + H_v + H_{e-v}$ where

$$
H_v = \sum_{i=1}^{2} \sum_{k=1}^{N} \omega_k b_{i,k}^\dagger b_{i,k},
$$

$$
H_{e-v} = \sum_{i=1}^{2} \mbox{Re} \left( |\varepsilon_i\rangle \langle \varepsilon_i| \sum_{k=1}^{N} \omega_k \sqrt{\kappa_k} (b_{i,k} + b_{i,k}^\dagger) \right).
$$

Here the annihilation (creation) operators $b_{i,k}$ ($b_{i,k}^\dagger$) describe a local vibrational mode of frequency $\omega_k$ coupled to site $i$ with a strength quantified by the Huang-Rhys (HR) factor $\kappa_k$. For an environment initially in a thermal state, the ensuing dynamics is fully determined by the environmental spectral density $J(\omega) = \sum_k \omega_k^2 s_k \delta(\omega - \omega_k)$ whose structure needs to be determined experimentally or theoretically.

**Structure of the environmental spectral density** - Generally, in PPCs the spectral density $J(\omega)$ consists of a broad background and multiple sharp peaks distributed across a broad range of frequencies. These can be determined by fluorescence line-narrowing (FLN) and hole burning experiments which reveal that the environmental spectral densities of WSCP and SP consist of low-frequency broad features originating from protein motions, and 55 intra-pigment modes resulting in multiple narrow peaks in the high-frequency part of the spectrum. The contribution of the protein modes of WSCP may be described by log-normal distribution functions of the form $J_{\mathrm{WSCP}}(\omega) = \frac{\kappa}{\sqrt{2\pi}(\omega - \mu)^2} \exp(-\frac{(\ln(\omega - \mu))^2}{2\kappa^2})$.
\[ \sum_{m} \left( \frac{\omega_m}{\sigma_m} \right) \exp(-|\ln(\omega/\Omega_m)|^2/2\sigma_m^2), \]

which provides a satisfactory description of the low-energy part of experimentally measured FLN spectra of WSCP \[65, 66\]. Alternatively, the protein motions of WSCP have been modelled by the following functional form:

\[ \frac{S}{s_1 + s_2} \sum_{k=1}^{s_1} \omega_k^* e^{-(\omega/\omega_k)^2/2} \]

that has been extracted from FLN spectra of B777 photosynthetic complexes \[60\] and considered in the simulations of WSCP \[67\].

Every underdamped intra-pigment mode contributes a Lorentzian of width \( \gamma_k \approx 1 \) ps\(^{-1} \), resulting in

\[ J(\omega) = J_l(\omega) + J_h(\omega) \]

where

\[ J_h(\omega) = \sum_{k=1}^{55} \frac{4\omega_k s_k \gamma_k (\omega_k^2 + \gamma_k^2) \omega}{((\omega + \omega_k)^2 + \gamma_k^2)((\omega - \omega_k)^2 + \gamma_k^2)}, \]

and the reorganisation energy of the high-frequency modes is given by

\[ \lambda_h = \int_0^\infty d\omega J_h(\omega)/\omega = \sum_{k=1}^{55} \omega_k s_k. \]

The values of the environmental parameters of WSCP \[13, 65\] and SP \[15, 68\] are summarised in section IV of the SI. The presence of underdamped vibrational modes can lead to long-lived correlations between electronic and vibrational degrees of freedom that make the rigorous numerical treatment of the ensuing vibronic dynamics very costly. In non-perturbative HEOM simulations, where experimentally or theoretically estimated spectral densities are fitted by the sum of Drude-Lorentz peaks \[21, 69\], the simulation cost of a dimeric system exceeds several hundreds of terabytes when 55 intra-pigment modes are considered per site (see section III of the SI) and, therefore, is infeasible with current computer architectures. In this work, we employ T-TEDOPA method where an experimentally estimated vibrational spectral density is mapped to a one-dimensional chain of quantum harmonic oscillators whose complexity is unaffected by the number of long-lived intra-pigment modes in the spectral density. We also employ optimised HEOM method where simulation parameters are determined by fitting the bath correlation function of highly structured environments for a finite time window corresponding to the line width of experimentally measured absorption spectra. These two methods enable one to consider the full environmental structures of WSCP and SP with a moderate simulation cost of the order of a few gigabytes or less (see sections II and III of the SI).

In addition, numerically exact results obtained by these two independent methods coincide, demonstrating the high accuracy and reliability of our simulated data (see section V of the SI).

In order to reduce simulation costs, past studies of PPCs have severely coarse-grained actual structure of vibrational environments by smoothing out the low-frequency part induced by protein motions and neglecting the high-frequency intra-pigment modes except for the ones whose frequencies \( \omega_k \) are quasi-resonant with the excitonic splitting \( \Delta \). However, the accuracy of such a procedure depends on the ratio of the electronic-vibrational coupling, \( g_k = \omega_k \sqrt{s_k} \), and the detuning of the intra-pigment modes from the excitonic splitting, \( \Delta_k = \omega_k - \Delta \). For PPCs consisting of chlorophylls or bacteriochlorophylls, the HR factors of the intra-pigment modes are of the order of \( s_k \approx 0.01 \), independent of the vibrational frequencies \( \omega_k \). \[13, 15\] (see section IV of the SI). In case the excitonic splitting is significantly smaller than the vibrational frequencies of the intra-pigment modes, the detuning between them is well approximated by \( \Delta_k = \omega_k - \Delta \approx \omega_k \), thus exhibiting the same scaling in \( \omega_k \) as the electronic-vibrational coupling, \( g_k \). This case is realised in WSCP which implies that the coupling of higher-frequency modes increases with the detuning \( \Delta_k \) so that these modes cannot be considered more off-resonant from the excitonic splitting than the lower-frequency modes with smaller detunings. For \( s_k \ll 1 \), each mode acts perturbatively on the excitonic system yielding relative energy shifts of order \( (g_k/\Delta_k)^2 \). While the contribution of each individual mode may be small, the cumulative effect of the 55 modes on the excitonic transitions is of order \( \sum_{k=1}^{55} (g_k/\Delta_k)^2 \sim \sum_{k=1}^{55} s_k \sim 0.68 \) for WSCP, and hence cannot be considered as a weak perturbative contribution. In addition, when the excitonic splitting is of the order of typical vibrational frequency of the intra-pigment modes, the exciton states can be mixed strongly with a large number of off-resonant modes, as we will demonstrate for SP. As a consequence of these considerations, we are forced to re-evaluate the hypothesis that only quasi-resonant modes are involved in the vibronic mixing and responsible for long-lived quantum coherences observed in experiments \[30, 37, 45\].

**Multi-mode vibronic effects in site basis** — To explain the influence of multi-mode vibronic effects on absorption spectra, we consider the transition dipole moment operators of PPCs, describing the optical transition between electronic ground and excited states. Within the Franck-Condon approximation, the transition dipole moment operator of a dimeric system is written as

\[ \mu = \sum_{i=1}^{2} (\hat{e} \cdot \hat{\mu}_i) (|\varepsilon_i\rangle \langle g| + |g\rangle \langle \varepsilon_i|), \]

where \( \hat{e} \) is the unit vector in the direction of the electric field inducing absorption, \( \hat{\mu}_i \) the transition dipole moment of site \( i \), and \( |g\rangle \) the global electronic ground state.
state. The transition dipole moment operator describes the vertical optical transition from electronic ground to excited states, which launches the vibrational motions of PPCs, inducing 0-0 lines and vibrational sidebands in absorption spectra. The impact of the presence of vibrational modes on the strength of the 0-0 lines can be determined by decomposing the total Hamiltonian $H$ into $H = H_0 + H_I$ where $H_I = V(|\epsilon_i\rangle\langle\epsilon_i| + |\epsilon_2\rangle\langle\epsilon_2|)$ describes the electronic interaction between monomers, while $H_0$ determines the energy-level structure of each monomer. As detailed in section X of the SI, the Hamiltonian $H_0$ is diagonalised by the polaron transformation in site basis, $U = |g\rangle\langle g| + \sum_{i=1}^{255} |\epsilon_i\rangle\langle\epsilon_i|D_i$ with unitary displacement operators $D_i = \exp[\frac{1}{2}\sum_{k=1}^{55} \epsilon_k b_{i,k}^\dagger - b_{i,k}]$, leading to

$$H'_0 = \sum_{i=1}^{2} (\epsilon_i - \lambda_h) |\epsilon_i\rangle\langle\epsilon_i| + \sum_{i=1}^{2} \sum_{k=1}^{55} \omega_k b_{i,k}^\dagger b_{i,k},$$

where $\lambda_h = \sum_{k=1}^{55} \omega_k s_k$ denotes the reorganization energy of the intra-pigment modes. The eigenstates of $H'_0$ include the electronic ground (excited) states $|g,0\rangle$ and $|\epsilon_i,0\rangle$, where all the intra-pigment modes are in their vibrational ground states, and $|g,1_{i,k}\rangle$ and $|\epsilon_i,1_{i,k}\rangle$, where only one mode described by $b_{i,k}$ is singly excited. The transition dipole moment operator in the polaron basis, $\mu' = \sum_{i=1}^{255} (\hat{\epsilon} \cdot \hat{\mu}_i) |\epsilon_i\rangle\langle g|D_i + h.c.$, determines the transition dipole strengths between the eigenstates of $H'_0$. These transition strengths are given by the Franck-Condon factors of uncoupled monomers, such as $\langle g,0|\mu|\epsilon_i,0\rangle = (\hat{\epsilon} \cdot \hat{\mu}_i) \exp[-\frac{1}{2} \sum_{i=1}^{55} s_i^2]$ and $\langle g,0|\mu|\epsilon_i,1_{i,k}\rangle = (\hat{\epsilon} \cdot \hat{\mu}_i) \exp(-\frac{1}{2} \sum_{i=1}^{55} s_i^2)\sqrt{s_k}$, which describe the dipole strengths of the 0-0 transition and the 0-1 transitions (vibrational sideband) in monomer absorption spectrum, as schematically shown in Fig. 3A. This implies that the dipole strength of the 0-0 transition is reduced by the vibronic coupling to the intra-pigment modes by the factor $\exp(-\frac{1}{2} \sum_{i=1}^{55} s_i^2)$, as the total dipole strength of a monomer is redistributed to $n$-a transitions where $n$ vibrational excitations are present amongst the 55 intra-pigment modes. This is in line with the electronic interaction Hamiltonian in the polaron basis, $H'_I = V|\epsilon_1\rangle\langle\epsilon_2|\exp[\sum_{k=1}^{55} 2\epsilon_k (b_k^\dagger - b_k)] + h.c.$ with $b_k = (b_{1,k} - b_{2,k})/\sqrt{2}$, that includes the effective coupling between 0-0 transitions, $V_00 = \langle\epsilon_1,0|H'_I|\epsilon_2,0\rangle = V\exp(-\sum_{k=1}^{55} s_k) \approx 0.5V$ for WSCP, and the couplings $V_{01}$ between 0-0 and 0-1 transitions, such as $\langle\epsilon_1,0|H'_I|\epsilon_2,1_{i,k}\rangle$ and $\langle\epsilon_1,1_{i,k}|H'_I|\epsilon_2,0\rangle$, as schematically shown in Fig. 3B.

WSCP homodimer - The electronic parameters of PPCs have been estimated based on a comparison of experimentally measured spectroscopic data with approximate theoretical results where environmental structures are coarse-grained or vibronic couplings are treated perturbatively. Based on a coarse-grained spectral density $J^\text{UC}(\omega)$, shown in red in Fig. 3A, a best fit to the experimental absorption spectra of WSCP homodimers implies an electronic coupling strength estimate of $V \approx 70 \text{ cm}^{-1}$, as shown in red in Fig. 3B (see section VI of the SI for a more detailed discussion). Such an electronic coupling results in an excitonic splitting $\Delta \approx 2V \approx 140 \text{ cm}^{-1}$ which is consistent with the experimentally observed energy-gap between two absorption peaks at 656 nm and 662 nm, respectively. Since all the high frequency intra-pigment modes are neglected in the coarse-grained spectral density, the estimated value can be interpreted as the effective coupling $V_00$ between 0-0 transitions when the mixing of 0-0 and 0-1 transitions is sufficiently small. In this case, $V_00 \approx 70 \text{ cm}^{-1}$ corresponds to a bare electronic coupling $V = V_00\exp(\sum_{k=1}^{55} s_k) \approx 2V_00 \approx 140 \text{ cm}^{-1}$ under the full environmental spectral density $J^\text{UC}(\omega) + J^\text{h}(\omega)$, including the 55 intra-pigment modes shown in black in Fig. 3A. The renormalised electronic coupling $V \approx 140 \text{ cm}^{-1}$ yields a best fit to experimentally measured absorption spectra, as shown in black in Fig. 3B, when all the $M = 55$ intra-pigment modes are considered in simulations. The energy-gap between absorption peaks is gradually reduced from excitonic splitting $\Delta \approx 2V \approx 280 \text{ cm}^{-1}$ to $\Delta' \approx 2V_00 \approx 140 \text{ cm}^{-1}$, as the number $M$ of the lowest-frequency intra-pigment modes considered in simulations is increased from 20 via 40 to 55 (see Fig. 3A and C). The electronic coupling $V \approx 70 \text{ cm}^{-1}$ estimated based on the coarse-grained low-frequency spectral density cannot reproduce the experimental results when the full spectral density is considered in simulations, as shown in Fig. 3D. The energy-gap between absorption peaks shown in Fig. 3C and D can be quantitatively well described by the splitting of 0-0 transitions, $2V_00 = 2V\exp(-\sum_{k=1}^{M} s_k)$, implying that the mixing of the 0-0 and 0-1 transitions involved in vibronic eigenstates is small for WSCP. These results demonstrate that the electronic parameters should be renormalised before entering the PPC models for the interpretation of spectroscopic data when different vibrational parameters are considered, such as a vibronic model including the intra-pigment modes. In the case of WSCP the effect is simple, the much more complicated case of SP will be discussed below.

Reduced model analysis - To investigate how well the numerically exact absorption spectra of WSCP can be described by the effective coupling $V_00$ between 0-0 transitions and how the absorption lineshapes are modified by the mixing of 0-0 and 0-1 transitions, we consider a reduced vibronic model where the total Hamiltonian $H' = H'_0 + H'_I$ in the polaron basis is numerically diagonalised in the subspace that contains all states involving up to two vibrational excitations (see section X of the SI for details). This approach enables one to compute the transition energies and dipole strengths of vibronic eigenstates of $H'$ for the cases that the electronic interaction Hamiltonian $H'_I$ contains only the coupling $V_00$ between 0-0 transitions or includes all the vibronic couplings $V_{mn}$ between $m-n$ transitions with $m, n \in \{0, 1, 2\}$ where non-zero values of $m$ describe thermal populations of the intra-pigment modes at finite temperatures.
FIG. 3. (A) Experimentally estimated spectral density of WSCP, consisting of 55 intra-pigment modes $J_1^{\text{WSCP}}(\omega)$ and low-frequency protein modes $J_1^{\text{WSCP}}(\omega)$ [55], shown in black and blue, respectively. Experimentally estimated spectral density $J_1^{\text{B777}}(\omega)$ of B777 complexes is shown in red [67]. The position of the excitonic splitting $\Delta = 280 \text{ cm}^{-1}$ obtained for an electronic coupling $V = 140 \text{ cm}^{-1}$ is indicated by a black arrow. The 20th, 40th and 55th lowest vibrational frequencies of the intra-pigment modes are marked by black arrows with $\omega_{20}$, $\omega_{40}$ and $\omega_{55}$, respectively. (B) Experimental absorption spectrum of WSCP at 77 K, shown in green dots, and numerical results obtained by T-TEDOPA and HEOM, shown in black solid and red dashed lines, respectively, for $V = 69 \text{ cm}^{-1}$ and $J_{1}^{\text{WSCP}}(\omega)$ [67]. (C) For $V = 140 \text{ cm}^{-1}$ and $J_{1}^{\text{WSCP}}(\omega) + J_{0}(\omega)$, T-TEDOPA and HEOM results can reproduce the experimental absorption spectrum below 660 nm, as shown in black. Numerically exact absorption spectra for the $M \in \{20, 40, 55\}$ lowest frequency intra-pigment modes are displayed where $M = 55$ represents the full experimentally estimated spectral density. (D) For $V = 69 \text{ cm}^{-1}$ and $J_{1}^{\text{WSCP}}(\omega) + J_{0}(\omega)$, T-TEDOPA and HEOM results cannot reproduce the experimental absorption spectra. See section IV of the SI for details of the other molecular parameters used in these simulations. We note that the maximum amplitudes of simulated absorption spectra at 656 nm are normalised to unity for a comparison with experimental absorption lineshape.

When homogeneous broadening of the eigenstates is approximately described by a Lindblad equation, describing the noise induced by low-frequency protein modes $J_{1}^{\text{WSCP}}(\omega)$ and vibrational damping of the intra-pigment modes, the reduced model including all the $V_{mn}$ couplings can quantitatively well reproduce the numerically exact absorption lineshape of WSCP, as shown in red in Fig. 3A. Taking into account only $V_{00}$ leaves the low-energy part of absorption spectra (below 650 nm) unchanged, as shown in green in Fig. 3A. This implies that the low-energy part of absorption spectra of WSCP is mainly determined by the effective coupling $V_{00}$ between 0-0 transitions. The minor deviations in the high-energy part of absorption spectra is due to the mixing of 0-0 and 0-1 transitions, which redistributes transition dipole strengths from 0-0 lines to the vibrational sidebands. We note that the reduced model results are scaled by different factors to ensure that the maximum amplitudes of absorption spectra are unity at 656 nm, for a better comparison with numerically exact results. Whereas the high-energy part of absorption spectra is not sensitive to the low-frequency part of phonon spectral density, the low-energy part of approximate absorption spectra fits even better to the numerically exact results when a broad background $J_{1}^{\text{B777}}(\omega)$ is considered instead of $J_{1}^{\text{WSCP}}(\omega)$, as shown in Fig. 3B. The origin of the better performance of $J_{1}^{\text{B777}}(\omega)$ is the more realistic description of the lifetime broadening of the upper exciton state. As this spectral density covers the energy-gap (140 cm$^{-1}$) between exciton states and $J_{1}^{\text{WSCP}}(\omega)$ does not (see inset of Fig. 3A) the lifetime broadening of the upper exciton state is determined by exciton relaxation with one-quantum dissipation processes in case of $J_{1}^{\text{B777}}(\omega)$, whereas multiple quantum dissipation processes are needed in case of $J_{1}^{\text{WSCP}}(\omega)$. Since the Lindblad formalism, used to calculate the lifetime broadening in the reduced model, only includes one-quantum dissipation, the deviations with respect to the exact T-TEDOPA/HEOM, which includes the full dissipation, are larger for $J_{1}^{\text{WSCP}}(\omega)$. We note that the small value of $J_{1}^{\text{WSCP}}(\omega)$ at the transition frequency between exciton states is an artefact of the analysis of the $\Delta$FLN spectrum [65], which concentrated on the very low frequencies of this spectrum. The $\Delta$FLN spectrum at frequencies around the transition frequency between exciton states can be even better described by using $J_{1}^{\text{B777}}(\omega)$ (see Fig. 4B in Ref. [65]).

Since conventional lineshape theories [48–57] do not include the renormalisation of the excitonic coupling by the intra-pigment electron-vibrational coupling, the absorption spectrum calculated with the bare excitonic coupling $V = 140 \text{ cm}^{-1}$ cannot describe the numerically exact absorption spectrum, as shown in blue in Fig. 3B, where the energy-gap between absorption peaks in 0-0 line region is close to a bare excitonic splitting $\Delta \approx 2V \approx 280 \text{ cm}^{-1}$. Using, instead, the effective exciton coupling $V_{00}$ between 0-0 transitions results in a very reasonable agreement with the exact result in the low-energy region ($\lambda > 640 \text{ nm}$) of the absorption spectrum, if the Lamb shift arising from the imaginary part of the off-diagonal exciton-vibrational correlation function (see Refs. [55, 56, 66] and section X of the SI) is taken into account (green solid line in Fig. 3C). However, this theory results in a significantly too low intensity in the high-frequency part (600-620 nm) of the spectrum that contains the contributions from excitonically mixed vibronic transitions involving excited intra-pigment vibrations. This deviation highlights a critical shortcoming of the conventional lineshape theories, namely, all HR factors of an exciton transition are suppressed with respect to those of a localized electronic transition by
the inverse participation ratio of the exciton state \[48-51\]. For the present chlorophyll homodimer in WSCP the inverse participation ratio that corresponds to the inverse delocalization length is 1/2. Since the intensity of the vibrational sideband obtained with the conventional lineshape theory is roughly 1/2 that of the exact T-TEDOPA/HEOM calculations in Fig. 4C, we conclude that the underlying vibronic transitions are, in fact, localised. Obviously, the small effective excitonic coupling between these vibronic transitions cannot compete with the local exciton-vibrational coupling. Hence, the system can minimize the Gibbs free energy by localising these states. Such a localisation has been postulated in an earlier theory of optical spectra \[70-71\], where all intra-pigment vibronic transitions involving excited vibrational states are treated as “dynamically” localised and delocalisation is only taken into account for the 0-0 transitions (see also section X of the SI). Indeed, this theory results in a significantly improved agreement with the exact calculation (the green dashed and the black dashed curves in Fig. 4C). First direct evidence for such a localisation effect was reported recently in a model dimer study, where 58 discrete low- and high-frequency vibrational modes per monomer were included in a numerical diagonalisation of the Hamiltonian \[72\]. Whereas the latter study was still limited by the neglect of the lifetime broadening of optical transitions, the present non-perturbative T-TEDOPA/HEOM calculations are numerically exact in all aspects. On this basis, it is possible to systematically evaluate previous approximate lineshape theories. In the parameter range relevant for WSCP we find strong evidence for the localisation of intra-pigment vibronic transitions involving excited intra-pigment vibrational states. In order to distinguish this localisation from that resulting from static disorder we will term this effect dynamic localisation.

**Multi-mode vibronic mixing in exciton basis** - In contrast to WSCP, the bare excitonic splitting of SP is of the order of the typical vibrational frequencies of the intrapigment modes and the resulting redistribution of oscillator strengths and shifts of optical lines are much more difficult to predict. To qualitatively estimate these effects, we consider second-order perturbation theory starting from the full Hamiltonian \( H = H_e + H_v + H_{\sigma - \sigma} \) in the single-exciton manifold. In that case, the vibronic mixing is induced by the relative motion of the intrapigment modes with identical frequency \( \omega_k \), described by \( b_k = (b_{1,k} - b_{2,k})/\sqrt{2} \), as the center of mass motion, described by \( B_k = (b_{1,k} + b_{2,k})/\sqrt{2} \), merely induces the homogeneous broadening of absorption lineshapes without affecting exciton dynamics (see section I of the SI). Hence, we can discard the center-of-mass part of the total Hamiltonian to find \( H = H_0 + H_I \) where

\[
H_0 = H_e + H_v + \cos(\theta) \sum_{k=1}^{55} \omega_k \sqrt{s_k/2}(b_k + b_k^{\dagger}), \tag{7}
\]

with \( H_e = \sum_k \omega_k b_k^{\dagger} b_k \), and

\[
H_I = -\sin(\theta) \sum_{k=1}^{55} \omega_k \sqrt{s_k/2}(b_k^{\dagger} + b_k), \tag{8}
\]

Here \( \theta = \tan^{-1}[2(V/\varepsilon_1 - \varepsilon_2)] \), where \( \sigma_+ = |E_{+}⟩⟨E_{+}| + |E_{-}⟩⟨E_{+}| \) and \( \sigma_- = |E_{+}⟩⟨E_{-}| - |E_{-}⟩⟨E_{-}| \) are the Pauli matrices in the exciton basis. The Hamiltonian \( H_0 \) is diagonalised by the polaron transformation in the exciton basis, \( U = |E_{+}⟩⟨E_{+}|D_0 + |E_{-}⟩⟨E_{-}|D_0^{\dagger} \), with \( D_0 = \exp[\cos(\theta) \sum_k \sqrt{s_k/2}(b_k^{\dagger} - b_k)] \). For typical HR factors of PPCs, of the order of \( s_k \lesssim 0.01 \), the vibronic mixing is dominated by contributions from the single vibrational excitation subspace where it leads to eigenstates of \( \theta \) of the form

\[
|ψ_{\pm}⟩ = a_{\pm,0}|E_{\pm,0}\rangle + \sum_{k=1}^{55} a_{\mp,1k}|E_{\mp,1k}\rangle, \tag{9}
\]

with \( |0⟩ \) and \( |1_k⟩ \) representing vibrational states where all the intra-pigment modes are in their ground states or only one mode described by \( b_k \) is singly excited. In second-order perturbation theory, these vibronic eigenstates \( |ψ_{\pm}⟩ \) have energies

\[
E'_{±} = E_{±} + \alpha \frac{2V^2}{\Delta^2} \sum_{k=1}^{55} s_k \omega_k^2, \tag{10}
\]

and the purely excitonic splitting \( \Delta = E_{+} - E_{-} \) is shifted to a vibronic splitting

\[
\Delta' = E'_+ - E'_- = \Delta \left(1 + \frac{4V^2}{\Delta^2} \sum_{k=1}^{55} s_k \omega_k^2 \right), \tag{11}
\]

where \( \alpha = \exp(-2\cos^2(\theta) \sum_{k=1}^{55} s_k) \). These energetic corrections are in complete analogy to the well-known light shifts in atomic physics. The sign of these energy shifts is determined by the difference in excitonic splitting and vibrational frequency, \( \Delta - \omega_k \). For an excitonic splitting that is smaller than the vibrational frequencies, \( \Delta \lesssim \omega_k \), the energy-gap \( \Delta' \) between vibronic eigenstates \( |ψ_{+}⟩ \) and \( |ψ_{-}⟩ \) is reduced compared to the bare excitonic splitting \( \Delta \) (see Fig. 5A). This is in line with our numerically exact simulations of WSCP where the bare excitonic splitting \( \Delta \approx 2V \) is reduced to \( \Delta' \approx 2V_{00} \approx V \). When the excitonic splitting is larger than the vibrational frequencies, \( \Delta \gtrsim \omega_k \), the situation is reversed (see Fig. 5B), resulting in an increased vibronic splitting \( \Delta' \) compared to the bare excitonic splitting \( \Delta \). This implies that the mixing of 0-0 and 0-1 transitions can result in two absorption peaks with an energy-gap \( \Delta' \) being larger than the bare excitonic splitting \( \Delta \).

We note that the vibronic mixing of excitons with multiple intra-pigment modes is induced by off-diagonal vibronic couplings in the exciton basis, described by \( H_I \) in Eq. (8). In conventional lineshape theory \[35-67\], the diagonal vibronic couplings in the exciton basis, described
by \( H_0 \) in Eq. (7), are treated exactly, and perturbation theory is used for the off-diagonal vibronic couplings. In the simplest approach, a perturbative treatment of the off-diagonal couplings leads to dephasing constants, such as the relaxation rates between exciton states, contributing to homogeneous broadening \([45,51,53,54]\). In addition, the off-diagonal couplings can induce the energy-level shifts of exciton states \([55,56,60]\), described by the Lamb shift obtained from second-order perturbation theory with the Born-Markov approximations \([73,74]\). As detailed in section X of the SI, the Lamb shift also reduces (or enhances) the excitonic splitting when a bare excitonic splitting \( \Delta \) is smaller (or larger) than vibrational frequencies of protein and intra-pigment modes. However, the Born-Markov approximations, employed in the derivation of the Lamb shift, are not appropriate to describe the vibronic interaction between excitons and underdamped intra-pigment modes, and the Lamb shift significantly overestimates the energy-gap shift of WSCP (see section X of the SI). This implies that multi-mode vibronic effects induced by the intra-pigment modes can be better described by reduced vibronic models that include the intra-pigment modes as a part of system Hamiltonian, although approximate results have to be verified by numerically exact simulations given the complexity of the electronic-vibrational interaction in PPCs.

**Special pair.** The photosynthetic reaction center which drives exciton dissociation into free charges consists of the SP and four additional pigments \([75]\). The SP is a strongly coupled dimeric unit with an electronic coupling estimated to be \( V = 625 \text{ cm}^{-1} \), a difference in mean site energies of \( \langle \varepsilon_1 - \varepsilon_2 \rangle = 315 \text{ cm}^{-1} \) and consequently a bare excitonic splitting of \( \Delta \approx 1290 \text{ cm}^{-1} \). These electronic parameters have been estimated based on a best fit to absorption, linear dichroism and hole burning spectra of bacterial reaction centers using conventional lineshape theory \([57]\). In what follows, we neglect the order of magnitude weaker electronic coupling of the SP to the four additional pigments and do not aim to reproduce experimentally measured absorption spectra of the whole bacterial reaction centers and re-estimate electronic parameters. Rather we concentrate on the effect of multi-mode vibronic mixing on the SP and its consequences regarding the nature and lifetimes of excitonic coherence and long-lived oscillatory signals in 2D electronic spectra.

While in WSCP the excitonic splitting is far detuned from high-frequency modes, the situation is markedly different for the SP. Here the environmental spectral density contains high-frequency intra-pigment modes both above and below the bare excitonic gap, as shown in black in Fig. 6A. The smaller frequency differences between vibrational modes and excitonic splitting and the varying sign of their detuning makes the effect of multimode mixing harder to predict analytically. Indeed, the perturbation procedure for obtaining Eq. (11) will be inaccurate for a larger number of modes. The vibronic splitting can be estimated beyond the perturbation theory by numerically diagonalising the Hamiltonian \( H = H_0 + H_l \) in Eq. (78), leading to \( \Delta' \approx 1744 \text{ cm}^{-1} \) (see section VIII of the SI). This estimate is in line with numerically exact simulated results where the energy-gap between absorption peaks is approximately \( 1710 \text{ cm}^{-1} \) (see 780 nm and

---

**FIG. 4.** (A,B) For \( V = 140 \text{ cm}^{-1} \) and \( f_{WSCP}^{J1} + J_2(\omega), f_{WSCP}^{BB77}(\omega) + J_3(\omega) \), numerically exact absorption spectra of WSCP are shown in black, and approximate results obtained by reduced vibronic models, taking into account all \( V_{nn} \) couplings or only \( V_{00} \) are shown in red and green, respectively, where the Lamb shift induced by protein modes is included (see section X of the SI). (C) For \( f_{WSCP}^{BB77}(\omega) + J_3(\omega) \), numerical results obtained by conventional lineshape theory with \( V = 140 \text{ cm}^{-1} \) and \( V = 140 \text{ cm}^{-1} \exp\left(-\sum_{k=1}^{2} s_k\right) \approx 70 \text{ cm}^{-1} \) are shown in blue and green solid lines, respectively. The results obtained by the lineshape theory can be better matched to numerically exact results when \( m-n \) transitions associated with intra-pigment vibrational excitations are explicitly considered and 0-0 transitions are coupled by \( V_{00} \) as shown in a green dashed line (see section X of the SI and Refs. \([70,71]\) for more details). We note that the maximum amplitudes of simulated absorption spectra at 656 nm are normalised to unity for a comparison with numerically exact absorption lineshapes.

**FIG. 5.** (A,B) Effect of multi-mode vibronic mixing on vibronic energy-level structure when excitonic splitting \( \Delta \) is smaller (larger) than vibrational frequencies \( \omega_k \) of intra-pigment modes, leading to reduction (increment) of the energy-gap \( \Delta' \) between vibronic eigenstates.
FIG. 6. (A) Experimentally estimated spectral density of the SP \cite{15, 68} is shown in black for an intra-pigment mode vibrational damping rate $\gamma_k = (1 \text{ ps})^{-1}$. Coarse-grained version for $\gamma_k = (50 \text{ fs})^{-1}$ is shown in red and the excitonic and vibronic splittings, $\Delta \approx 1290 \text{ cm}^{-1}$ and $\Delta' \approx 1800 \text{ cm}^{-1}$, are highlighted. (B) Experimental absorption spectrum of the bacterial reaction center at 5 K, shown in green dots, and numerically exact absorption lineshape, obtained by TEDOPA and HEOM, of the SP, shown in black. Approximate absorption spectrum of the SP computed by second-order cumulant expansion is shown in red where the energy-gap between absorption peaks at 803 nm and 897 nm is approximately $\Delta \approx 900 \text{ cm}^{-1}$. (C) Excitonic coherence dynamics for the experimentally estimated and coarse-grained environmental structures, shown in black and red, respectively when only site 1 is initially excited. (D) Rephasing 2D spectra of the SP at waiting time $T = 0$. (E,F) 2D signals at a cross-peak R12, marked in (D), and corresponding Fourier transformation where ground and excited state signals are shown in red and blue, respectively. Note that excited state signals are dominated by vibronic coherence $|\psi_+\rangle\langle\psi_-|$, leading to 2D oscillations with frequency $\Delta' \approx 1800 \text{ cm}^{-1}$. The transient of the other cross-peak R21 is provided in section IX of the SI and all molecular parameters used in these simulations are given in section IV of the SI.

900 nm peaks in Fig. 6B, corresponding to $|\psi_+\rangle$ and $|\psi_-\rangle$, respectively and the oscillatory dynamics of excitonic coherence is dominated by 1755 cm$^{-1}$ frequency component (see Fig. 6C). We note that the difference between excitonic and vibronic splittings is significant, of the order of $\Delta' - \Delta \approx 465 \text{ cm}^{-1}$, and this shift cannot be described by conventional lineshape theory where multi-mode vibronic mixing is ignored and as a result the energy-gap between absorption peaks is reduced to the excitonic splitting (see the inset in Fig. 6B).

Long-lived multi-mode vibronic coherence. The considerable size of the multi-mode mixing effects on excitonic energy-gaps suggest a possibly significant influence on coherent excitonic dynamics. The coarse-grained spectral density shown in red in Fig. 6A, which corresponds to a vibrational lifetime of $\gamma_k = (50 \text{ fs})^{-1}$, yields short-lived oscillatory dynamics of excitonic coherence $\rho_\perp(t) = \langle E_- | \rho(t) | E_+ \rangle$ with $\rho_\perp(t)$ denoting reduced electronic density matrix (see red line in Fig. 6C). Even if a few intra-pigment modes near-resonant with excitonic splitting are selected to be weakly damped, $\gamma_k = (1 \text{ ps})^{-1}$, the vibronic mixing with the large number of remaining strongly-damped modes, $\gamma_k = (50 \text{ fs})^{-1}$, suppresses the lifetime of excitonic coherences, making the resulting dynamics essentially identical to that where all the modes are strongly damped (see section VIII of the SI for detailed analysis of multi-mode vibronic mixing of SP). In sharp contrast, when the picosecond lifetime of actual intra-pigment modes is considered, $\gamma_k = (1 \text{ ps})^{-1}$, the excitonic coherence dynamics is dominated by long-lived oscillations with frequency $\Delta' \approx 1755 \text{ cm}^{-1}$, associated with the vibronic coherence between $|\psi_+\rangle$ and $|\psi_-\rangle$ states (see black line in Fig. 6C).

In 2D electronic spectroscopy, the third order nonlinear optical response of molecular systems is measured by using a sequence of femtosecond pulses with controlled time delays \cite{76, 77}. As is the case of pump probe experiments \cite{78}, electronically excited state populations and coherences can be created by a pair of pump pulses, and the molecular dynamics in the electronic excited state manifold can be monitored by controlling the time delay $T$ between pump and probe. The additional time delay between two pump pulses enables one to monitor the molecular dynamics as a function of excitation and detection wavelengths for each waiting time $T$. The optical transitions induced by the pump pulses can also create vibrational coherences in the electronic ground state manifold, making it challenging to extract the information about coherent electronic dynamics from multidimensional spectroscopic data \cite{46}.

Our numerically exact simulations of the SP demonstrate that long-lived oscillatory signals in 2D electronic
spectra can originate from purely vibrational coherences or from vibronic coherences induced by multi-mode mixing. The latter have been ignored in previous numerical studies which considered only a few intra-pigment modes quasi-resonant with excitonic splitting and neglected all the modes that are far detuned from excitonic transitions as they were deemed to have a negligible effect \[79\]. However, the correct assessment of the nature of oscillatory 2D signals requires the computation of 2D spectra under the influence of the full spectral density. In order to make such computation feasible, in section IX of the SI, we provide an approximate master equation for vibronic dynamics, which takes into account multi-mode mixing effects and quantitatively reproduces numerically exact absorption lineshape of the SP. Fig. 6D shows the resulting rephasing 2D spectra at waiting time \( T = 0 \) in the presence of inhomogeneous broadening. The 2D lineshape, shown as a function of excitation and detection wavelengths, is dominated by a diagonal peak excited and detected at 900 nm which coincides with the position of the main absorption peak (see Fig. 6B). To investigate the excited state coherence between vibronic eigenstates \( |\psi_+\rangle \) and \( |\psi_-\rangle \), which induce the absorption peaks at 780 and 900 nm, respectively, we focus on a cross-peak R12 marked in Fig. 6D. Fig. 6E shows the transient of the cross-peak as a function of the waiting time \( T \) where the oscillatory 2D signals originating from electronic ground state manifold, shown in red, are comparable to those of excited state signals, shown in blue. The ground state signals consist of multiple frequency components below 1600 cm\(^{-1}\), corresponding to the vibrational frequencies \( \omega_k \) of underdamped intra-pigment modes, as shown in Fig. 6F. It is important to note that the excited state signals include a long-lived oscillatory component with frequency \( \sim 1800 \) cm\(^{-1}\), which is not present in the ground state signals and cannot originate from purely vibrational effects as they exceed the high-frequency cut-off of the environmental spectral density (see Fig. 6A). This component must therefore originate from long-lived vibronic coherence due to multi-mode mixing. While some oscillatory components in 2D spectra can originate from purely vibrational motions, our results demonstrate that long-lived 2D oscillations can also be the result of a strong vibronic mixing of excitons with a large number of underdamped intra-pigment modes.

Conclusions – Employing numerically exact methods and an analytical theory, we have investigated exciton-vibrational dynamics under the complete vibrational spectrum that has been estimated in earlier experiments. We considered two paradigmatic regimes. The first regime, represented by an excitonic dimer in WSCP, is characterized by an excitonic splitting that is smaller than vibrational frequencies of intra-pigment modes. In this case, one main effect of vibronic coupling to the intra-pigment modes is a reduction of the dipole strength of 0-0 transitions of monomers and of their effective coupling strength \( V_{00} \) that determines the splitting between absorption peaks in the low-energy spectrum. A second important effect concerns the non-uniform modulation of the vibrational sideband of optical transitions by the excitonic coupling. The high-energy vibronic transitions are much less affected indicating a dynamic localisation of the excited states that contain excited intra-pigment vibrations.

In the second regime, represented by the SP of the photosynthetic reaction center of purple bacteria, the excitonic splitting is located in the middle of the high frequency part of the intra-pigment vibrational spectrum. In this case, the splitting between main absorption peaks can be even larger that the bare excitonic splitting, due to multi-mode vibronic mixing effects. This regime is found to be particularly suitable for the discovery of new long-lived quantum coherences in photosynthesis. We found that the coherence time of excitonic dynamics is not simply governed by the lifetime of quasi-resonant intra-pigment modes. Rather it is determined by the lifetimes of individual intra-pigment modes involved in a multi-mode vibronic mixing. This implies that approximate theoretical models based on coarse-graining of the high frequency part of the vibrational environments \[21\] may underestimate the lifetime of excitonic coherences and could be inappropriate to analyse quantum coherences observed in nonlinear experiments on photosynthetic systems. Hence, we contend that previously ignored multi-mode vibronic effects must be included in the interpretation of nonlinear spectroscopic signals before the current debate regarding the presence and nature of long-lived quantum coherences in pigment-protein complexes can be settled conclusively.

The generality of the methods employed here suggest that our results have a broad scope and can be of relevance in a wide variety of scenarios involving strong hybridization of electronic and vibrational degrees of freedom, such as recent observations of nonadiabatic dynamics in cavity polaritonics \[80, 81\]. We expect that renormalization effects considered here may open an entirely new toolbox for vibrational reservoir engineering with possible applications in information technologies and polariton chemistry.

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I. VIBRONIC HAMILTONIAN AND POLARON TRANSFORMATION

In this section, we present the vibronic Hamiltonian that describes the interaction between excitons and vibrational modes in photosynthetic complexes in the exciton basis. This serves to define off-diagonal vibronic couplings that play an essential role in the multi-mode vibronic mixing discussed in the main text.

For simplicity, we consider an excitonically coupled dimer where the electronic excitation of each site is coupled to a local vibrational environment. The total Hamiltonian is modelled by \( H = H_e + H_v + H_{e-v} \). The electronic Hamiltonian \( H_e \) is characterized by on-site energies \( \varepsilon_i \) and inter-site electronic coupling \( V \)

\[
H_e = \sum_{i=1}^{2} \varepsilon_i |\varepsilon_i\rangle\langle\varepsilon_i| + V (|\varepsilon_1\rangle\langle\varepsilon_2| + |\varepsilon_2\rangle\langle\varepsilon_1|).
\]

(S1)

The vibrational environments are modelled by quantum harmonic oscillators

\[
H_v = \sum_{i=1}^{2} \sum_{k} \omega_k b_{i,k}^\dagger b_{i,k},
\]

(S2)

where \( b_{i,k} \) describes a vibrational mode with frequency \( \omega_k \), which is locally coupled to site \( i \). The coupling of the electronic degrees of freedom to their respective vibrational environment is described by

\[
H_{e-v} = \sum_{i=1}^{2} |\varepsilon_i\rangle\langle\varepsilon_i| \sum_{k} \omega_k \sqrt{s_k} (b_{i,k} + b_{i,k}^\dagger),
\]

(S3)

where the vibronic coupling strength is quantified by a Huang-Rhys factor \( s_k \). To identify the origin of the multi-mode vibronic mixing, we define \( B_k = \frac{1}{\sqrt{2}} (b_{1,k} + b_{2,k}) \) and \( b_k = \frac{1}{\sqrt{2}} (b_{1,k} - b_{2,k}) \), describing the center-of-mass and relative motions, respectively, of the local vibrational modes \( b_{1,k} \) and \( b_{2,k} \) with identical frequency \( \omega_k \). \( B_k \) and \( b_k \) satisfy the bosonic commutation relations and the total Hamiltonian can be expressed as \( H = H_e + H_c + H_r \)

\[
H_c = \sum_{k} \omega_k B_k^\dagger B_k + (|\varepsilon_1\rangle\langle\varepsilon_1| + |\varepsilon_2\rangle\langle\varepsilon_2|) \sum_{k} \omega_k \sqrt{s_k} (B_k + B_k^\dagger),
\]

(S4)

\[
H_r = \sum_{k} \omega_k b_k^\dagger b_k + (|\varepsilon_1\rangle\langle\varepsilon_1| - |\varepsilon_2\rangle\langle\varepsilon_2|) \sum_{k} \omega_k \sqrt{s_k} (b_k + b_k^\dagger).
\]

(S5)

Note that the center-of-mass modes \( B_k \) are coupled to both electronic excited states \( |\varepsilon_1\rangle \) and \( |\varepsilon_2\rangle \) with the same coupling strength and phase. This implies that the coupling to the center-of-mass motion, described by \( H_c \), does not affect electronic dynamics within the single excitation manifold. Instead, it induces dephasing of optical coherences between electronic ground and excited states, which broadens the absorption line shapes. The contribution of the center-of-mass motion to absorption line width can be taken into account analytically, as described in section III.

The vibronic coupling to the relative motion of vibrational modes, described by \( H_r \), affects electronic dynamics in the single excitation sector. Here we describe \( H_r \) in terms of exciton states \( |E_{\pm}\rangle \) that diagonalize the electronic Hamiltonian \( H_e = E_+ |E_+\rangle\langle E_+| + E_- |E_-\rangle\langle E_-| \) and are parameterized by

\[
|E_+\rangle = \cos(\theta/2) |\varepsilon_1\rangle + \sin(\theta/2) |\varepsilon_2\rangle,
\]

(S6)

\[
|E_-\rangle = -\sin(\theta/2) |\varepsilon_1\rangle + \cos(\theta/2) |\varepsilon_2\rangle,
\]

(S7)

where \( \tan(\theta) = 2V/|\varepsilon_1 - \varepsilon_2| \) and \( E_+ - E_- = \Delta = \sqrt{(\varepsilon_1 - \varepsilon_2)^2 + 4V^2} \). In the exciton basis, \( H_r \) is expressed as

\[
H_r = \sum_{k} \omega_k b_k^\dagger b_k + \sum_{i,j} A_{ij} |E_i\rangle\langle E_i| \sum_{k} \omega_k \sqrt{s_k} (b_k^\dagger + b_k),
\]

(S8)

where \( A_{ij} = \langle E_i|\varepsilon_1\rangle\langle E_j|E_1\rangle - \langle E_i|\varepsilon_2\rangle\langle E_j|E_2\rangle \), leading to \( A_{++} = -A_{--} = \cos(\theta) \) and \( A_{+-} = A_{-+} = -\sin(\theta) \). We call the terms proportional to \( |E_i\rangle\langle E_i| \) diagonal vibronic couplings, and the other terms proportional to \( |E_i\rangle\langle E_j| \) with \( i \neq j \) off-diagonal vibronic couplings.
We note that the diagonal vibronic couplings describe the shift of the equilibrium positions of the vibrational modes $b_k$ depending on electronic states. This can be seen more clearly in a displaced vibrational basis. We decompose the total Hamiltonian into two parts $H = H_0 + H_I$ where $H_0$ includes the diagonal vibronic couplings

$$H_0 = H_e + H_c + \sum_k \omega_k b_k^\dagger b_k + \cos(\theta) \langle |E_+\rangle \langle E_+| - |E_-\rangle \langle E_-| \rangle \sum_k \omega_k \sqrt{\frac{s_k}{2}} (b_k^\dagger + b_k),$$

(S9)

while $H_I$ consists of the off-diagonal vibronic couplings

$$H_I = -\sin(\theta) (|E_+\rangle \langle E_-| + |E_-\rangle \langle E_+|) \sum_k \omega_k \sqrt{\frac{s_k}{2}} (b_k^\dagger + b_k).$$

(S10)

By applying a unitary operator $U = |g\rangle \langle g| + |E_+\rangle \langle E_+| D_0 + |E_-\rangle \langle E_-| D_0^\dagger$ with $D_0 = \exp(\cos(\theta) \sum_k \sqrt{\frac{s_k}{2}} (b_k^\dagger - b_k))$ to the total Hamiltonian $H$ (the polaron transformation), it can be shown that $H_0$ is diagonalised as the diagonal vibronic couplings are reduced to the global energy-level shift of exciton states which is proportional to the reorganization energy $\sum_k \omega_k s_k$

$$UH_0 U^\dagger = H_e + H_c + \sum_k \omega_k b_k^\dagger b_k - \sum_i |E_i\rangle \langle E_i| \cos^2(\theta) \sum_k \omega_k \frac{s_k}{2},$$

(S11)

while $H_I$ describes the vibronic mixing between exciton states mediated by vibrational modes $b_k$

$$U H_I U^\dagger = -\sin(\theta) |E_+\rangle \langle E_-| D_0 \sum_k \omega_k \sqrt{\frac{s_k}{2}} (b_k^\dagger + b_k) D_0 + h.c.,$$

(S12)

where $h.c.$ stands for Hermitian conjugate. Neglecting these off-diagonal couplings is equivalent to the second order cumulant expansion technique [78], which has been employed to compute optical responses of multi-site systems approximately. To fully take into account the off-diagonal vibronic couplings in simulations, one needs to employ numerically exact methods, such as TEDOPA and HEOM discussed in section II and III respectively.

II. TEDOPA

The goal of this work is the numerical evaluation of absorption spectra in the presence of a structured environment as well as energetic and orientational disorder of the sample. To this end we will employ algorithms with controlled numerical error that can be reduced to any desired degree. The two methods that we choose are the time-evolving density matrix with orthogonal polynomials algorithm (TEDOPA) [22, 59, 61], to be described in this section, and a variation of the hierarchical equations of motion (HEOM) that we will describe in the following section [11].

The original formulation of TEDOPA for finite temperature environments requires the time consuming preparation of the thermal state of the environment and subsequent time evolution by means of matrix product operators (MPO) [24] as opposed to the zero temperature case for which the initial state of the environment is trivial and the system can be described by the more efficient matrix product state (MPS) formalism [22, 59]. Recently, however, it was demonstrated that there is an exact analytical mapping of the finite temperature case to the zero temperature case which allows for the direct computation of system observables [60, 61]. This approach, termed T-TEDOPA, leads to a major reduction in computational cost and, crucially, provides opportunities for further simplifications in the computations of absorption spectra that lead to additional significant reductions in computational cost by several orders of magnitude.

The calculation of the absorption spectrum requires the Fourier-Laplace transform of the correlation function $D(t)$ of the electronic transition dipole operator $\mu = \sum_i^{N} \hat{\mu}_i \cdot \hat{e} \langle \varepsilon_i \rangle \langle g | + h.c.$ averaged over orientational and energetic disorder where $\langle \varepsilon_i \rangle$ denotes the local excitation at site $i$, $| g \rangle$ the global electronic ground state, $\hat{\mu}_i$ the dipole moment of site $i$ and $\hat{e}$ the direction of polarisation of the electric field. This dipole-dipole correlation function is given by

$$\langle D(t) \rangle_{e,\varepsilon_i} = \langle \text{Tr} [\mu e^{-iHt} \rho_{th} e^{iHt}] \rangle_{e,\varepsilon_i},$$

(S13)

where $\rho_{th} = e^{-\beta H}/\text{Tr} [e^{-\beta H}]$. Even well beyond physiological temperatures $\rho_{th}$ is exceedingly well approximated by $\rho_{th} = |g\rangle \langle g| \otimes e^{-\beta H_e}/\text{Tr} [e^{-\beta H_e}]$ as the exciton energy is typically found to be in the eV range. With this assumption, the T-TEDOPA approach obtains identically the same dynamics of electronic observables under a mapping that takes the initial state to $|g\rangle \langle g| \otimes |\text{vac}\rangle \langle \text{vac}|$, where $|\text{vac}\rangle$ denotes the vacuum state of the environment for which all
vibrational modes are in their ground state and, simultaneously, takes the environmental spectral density from the original \( J(\omega) \) on the interval \([0, \infty]\) to

\[
J_\beta(\omega) = \frac{1}{2} \text{sign}(\omega) J(|\omega|) \left[ 1 + \coth \left( \frac{\beta |\omega|}{2} \right) \right],
\]

which is now defined on the entire real axis \([-\infty, \infty]\). Then the dipole-dipole correlation function is reduced to

\[
\langle D(t) \rangle_{\epsilon, \epsilon_i} = \langle \text{Tr}[e^{-iH_\beta t} \hat{\mu} |g\rangle \otimes |\text{vac}\rangle \langle \text{vac}| e^{iH_\beta t}] \rangle_{\epsilon, \epsilon_i}.
\]

Now making use of \( H|g\rangle \langle \text{vac}| = 0 \) and specialising to the case of a dimer \( (N=2) \) we find

\[
\langle D(t) \rangle_{\epsilon, \epsilon_i} = \langle \text{Tr}[e^{-iH_\beta t} \hat{\mu} |g\rangle \otimes |\text{vac}\rangle \langle \text{vac}| e^{iH_\beta t}] \rangle_{\epsilon, \epsilon_i},
\]

\[
= \left\langle \sum_{i,j=1}^{2} (\vec{\mu}_i \cdot \hat{\sigma}_j) \langle \text{vac}| e^{-iH_\beta t}|\epsilon_j\rangle |\text{vac}\rangle \langle \epsilon_i| e^{-iH_\beta t}|\epsilon_j\rangle \right\rangle_{\epsilon, \epsilon_i},
\]

\[
= \left\langle \sum_{i,j=1}^{2} \vec{\mu}_i \cdot \vec{\mu}_j \langle \text{vac}| e^{-iH_\beta t}|\epsilon_j\rangle |\text{vac}\rangle \langle \epsilon_i| e^{-iH_\beta t}|\epsilon_j\rangle \right\rangle_{\epsilon_i}.
\]

The computational effort of TEDOPA simulations typically grows stronger than linear with the simulated time \( t \), because it requires longer environmental chains and higher bond dimension of the employed matrix product states. Hence it proves advantageous to compute Eq. (S18) via

\[
|\psi_j(t/2)\rangle = e^{-iH_\beta t/2}|\epsilon_j\rangle |\text{vac}\rangle = \left( e^{iH_\beta t/2}|\epsilon_j\rangle |\text{vac}\rangle \right)^*,
\]

so that

\[
\langle D(t) \rangle_{\epsilon, \epsilon_i} = \langle \left| \left| \sum_{i=1}^{2} \vec{\mu}_j |\psi_j(t/2)\rangle \right|^2 \right|_{\epsilon_i} \rangle.
\]

For the parameters in our work, this rearrangement of the dipole-dipole correlation function leads to more than one order of magnitude reduction in the simulation time. The average over the energetic disorder can be simplified by two measures. First, instead of an independent average over site energies \( \epsilon_i \), described by

\[
\langle D(t) \rangle_{\epsilon, \epsilon_1} = \frac{1}{2 \sigma^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\xi_1 d\xi_2 \exp \left( -\frac{1}{2 \sigma^2} (\xi_1 - \langle \xi_1 \rangle)^2 - \frac{1}{2 \sigma^2} (\xi_2 - \langle \xi_2 \rangle)^2 \right) \left| \left| \sum_{i=1}^{2} \vec{\mu}_j |\psi_j(t/2)\rangle \right|^2 \right|_{\epsilon_1},
\]

we compute the ensemble average over \( \xi_1 = \epsilon_1 - \epsilon_2 \) and \( \xi_2 = \frac{1}{2}(\epsilon_1 + \epsilon_2) \)

\[
\langle D(t) \rangle_{\epsilon, \epsilon_1} = \frac{1}{2 \sigma^2} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\xi_1 d\xi_2 \exp \left( -\frac{1}{4 \sigma^2} (\xi_1 - \langle \xi_1 \rangle)^2 - \frac{1}{4 \sigma^2} (\xi_2 - \langle \xi_2 \rangle)^2 \right) \left| \left| \sum_{i=1}^{2} \vec{\mu}_j |\psi_j(t/2)\rangle \right|^2 \right|_{\epsilon_1, \langle \xi_2 \rangle},
\]

The ensemble average over \( \xi_2 = \frac{1}{2}(\epsilon_1 + \epsilon_2) \) does not require the repetition of simulations, as the global shift in site energies does not affect electronic dynamics, but simply induces a time-dependent phase factor, which can be taken into account analytically. In other words, after numerical simulation of \( \left| \sum_{i=1}^{2} \vec{\mu}_j |\psi_j(t/2)\rangle \right|^2 \) for \( \xi_1 = \epsilon_1 - \epsilon_2 \) and \( \xi_2 = \langle \xi_2 \rangle = \frac{1}{2}(\langle \epsilon_1 \rangle + \langle \epsilon_2 \rangle) \), the average over \( \xi_2 \) can be computed by

\[
\frac{1}{\sqrt{\pi} \sigma} \int_{-\infty}^{\infty} d\xi_2 e^{-\frac{1}{\sigma^2}(\xi_2 - \langle \xi_2 \rangle)^2} \left| \left| \sum_{i=1}^{2} \vec{\mu}_j |\psi_j(t/2)\rangle \right|^2 \right|_{\xi_1, \langle \xi_2 \rangle} = \exp \left( -\frac{1}{4 \sigma^2} \right) \left| \left| \sum_{i=1}^{2} \vec{\mu}_j |\psi_j(t/2)\rangle \right|^2 \right|_{\xi_1, \langle \xi_2 \rangle},
\]

where the Gaussian dephasing \( e^{-\frac{1}{4 \sigma^2} t^2} \) leads to a broadening of absorption line shapes. The numerical average over energy difference \( \xi_1 = \epsilon_1 - \epsilon_2 \) can be carried out most efficiently by means of a Gauss-Hermite interpolation of the integral over the frequency difference. Compared to a straightforward averaging with equidistant sampling points, this leads to a reduction of computational effort by almost one order of magnitude.

A further significant step in the optimisation of the T-TEDOPA simulation concerns an essential part of the time-evolving block-decimation (TEBD) algorithm. This step selects the best MPS-approximation with fixed bond dimension through a decimation technique that relies on the singular value decomposition (SVD). As the complexity of each time-evolution step is dominated by the SVD we follow Refs. [S2] and [S3] and apply a randomized version of
the SVD routine (rSVD) which trades a reduction in numerical accuracy for a significant increase in computational efficiency. At first sight, for the relatively moderate matrix sizes in our simulations, one may not expect significant computational gains due to the use of the rSVD. However, two specific aspects of the present problem lead to a different conclusion. As the absorption spectrum is obtained by the Fourier transform of the correlation function $D(t)$ and is further broadened due to the average over orientational and energetic disorder, small errors in the time evolution tend to be averaged out. Furthermore, the uncertainty in the experimentally determined environmental spectral density makes it unnecessary to aim for extremely high precision in the absorption spectra. A relative error of the order of about $10^{-3}$ suffices for our application. This allows us to accept a larger tolerated error in the rSVD which increases its speed significantly. As a result of the use of the rSVD we have been able to obtain more than one order of magnitude reduction in CPU time without noticeably affecting the quality of the results. As a result of these and some other minor measures, the computation of a single absorption spectrum fully averaged over energetic and orientational disorder for the full spectral density of WSCP takes about 3 minutes on 7 processors (2 GHz).

We note that the simulation cost of TEDOPA can be reduced further by transforming the two local baths to two effective baths describing the center-of-mass and the relative motion of the local modes with identical vibrational frequencies (see section [1]). As the influence of the center-of-mass modes on the reduced electronic system dynamics can be treated analytically, one can remove the center-of-mass modes from the dynamics and hence the TEDOPA simulations and consider a dimeric electronic system coupled to a single global bath describing the relative motion modes. The application of orthogonal polynomial algorithm [22, 59, 61] to this model leads to a single chain of coupled harmonic oscillators where the first oscillator is also coupled to the electronic states of a dimeric system. This enables one to reduce the simulation cost of TEDOPA compared to the case that two local baths are mapped to two chains coupled via the electronic states of the dimer. This also implies that one can consider a trimeric electronic system coupled to three local baths in TEDOPA simulations, as three local baths can be mapped to three global baths, including a bath describing the center-of-mass motions which can be neglected in simulations. In this case, the remaining two global baths, describing relative motion modes, can be mapped to two chains coupled via the electronic states of a trimer, which can be efficiently simulated within the framework of TEDOPA.

III. HEOM

Hierarchical equations of motion (HEOM) are a numerically exact method for computing reduced system dynamics where a quantum system is linearly coupled to a thermal environment consisting of quantum harmonic oscillators [62, 84]. In the following we will explain the specifics of our HEOM implementation including the measures that we have taken to optimise the calculation of absorption spectra.

It is assumed that at the initial time, system and environment are not correlated and the environment is in a thermal state at temperature $T$. In this work, we consider a local bath model where each site is coupled to an independent harmonic bath with an identical phonon spectral density $J(\omega)$, characterizing the system-environment coupling strength as a function of environmental mode frequencies $\omega$. The influence of such a harmonic bath on the reduced system dynamics is fully characterized by the bath correlation function

$$C(t) = \int_0^\infty d\omega J(\omega) \left( \coth \left( \frac{\beta \omega}{2} \right) \cos(\omega t) - i \sin(\omega t) \right).$$

(S23)

The parameters of HEOM simulations are determined by a multi-exponential fitting of the bath correlation function

$$C(t) \approx \sum_{j=1}^{N_C} (d_{j+} e^{-f_j t} + d_{j-} e^{-f_j^* t}) + \sum_{k=1}^{N_R} d_k e^{-\gamma_k t},$$

(S24)

where the fitting variables $d_{j+}$, $d_{j-}$, $f_j$, $d_k$ are complex-valued, while $\gamma_k$ is real-valued. The total number of exponentials is given by $2N_C + N_R$, which is one of the key factors determining the simulation cost. The HEOM simulations of reduced system dynamics within a finite time window, $0 \leq t \leq t_{\text{max}}$, requires the multi-exponential fitting of $C(t)$ within that time window, and the fitting quality outside of the time window of interest, namely $t > t_{\text{max}}$, does not affect the system dynamics for $0 \leq t \leq t_{\text{max}}$. The fitting quality can be checked by comparing simulated HEOM results with the analytical solutions of solvable models or the data obtained by alternative numerically exact methods. In this work, we consider an analytically solvable monomer model, namely a two-level system under dephasing noise [78], in order to monitor the fitting quality. For a given set of fitting parameters, the dynamics of the reduced system
density matrix $\hat{\rho}_0$ can be computed by using HEOM in the form

$$\frac{d\hat{\rho}_n}{dt} = -\frac{i}{\hbar}[H_s, \hat{\rho}_n] - \sum_{m=1}^{N_S} \left( \sum_{j=1}^{N_C} (n_{mj}+f_j + n_{mj}-f_j) + \sum_{k=1}^{N_R} n_{mk}\gamma_k \right) \hat{\rho}_n - i \sum_{m=1}^{N_S} \left( \hat{\sigma}_m^\dagger \hat{\sigma}_m, \sum_{j=1}^{N_C} (\hat{\rho}_{n_{mj}^+} + \hat{\rho}_{n_{mj}^-}) + \sum_{k=1}^{N_R} \hat{\rho}_{n_{mk}^+} \right)$$

$$- i \sum_{m=1}^{N_S} \sum_{j=1}^{N_C} n_{mj} \left( d_j^+ \hat{\sigma}_m^\dagger \hat{\rho}_{m_{mj}^+} - d_j^- \hat{\rho}_{m_{mj}^-} \hat{\sigma}_m^\dagger \right) - i \sum_{m=1}^{N_S} \sum_{j=1}^{N_C} n_{mj} \left( d_j^- \hat{\sigma}_m \hat{\rho}_{m_{mj}^-} - d_j^+ \hat{\rho}_{m_{mj}^+} \hat{\sigma}_m \right),$$

(S25)

where $N_S$ denotes the number of sites in the system ($N_S = 1$ for a monomer, $N_S = 2$ for a dimer, such as WSCP and the special pair in bacterial reaction centers), and $\hat{\sigma}_m$ ($\hat{\sigma}_m^\dagger$) is the annihilation (creation) operator of an electronic excitation at site $m$. The information about the reduced system dynamics and system-environment correlations is included in the auxiliary operators $\hat{\rho}_n$, which are labelled by the vectors $\mathbf{n} = (n_{mj}, \ldots, n_{mj}, \ldots, n_{mk}, \ldots)$ with non-negative integer elements. The sum of the integer elements of the vector $\mathbf{n}$ is denoted by $N_{\text{rank}}$. The reduced system density matrix is described by the lowest-rank operator $\hat{\rho}_0$, where all the integer elements of $\mathbf{n}$ are zero. All the other higher-rank auxiliary operators, describing system-environment correlations, have the same dimension as the reduced system density matrix and are taken to be null matrices at the initial time. The interaction between auxiliary operators is described by $\mathbf{n}_{mj}^+$, $\mathbf{n}_{mj}^-$, $\mathbf{n}_{mk}$, which are defined by $\mathbf{n}_{mj}^+ = (n_{mj}+ \pm 1, \ldots, n_{mj}^-, \ldots, n_{mk}, \ldots)$, $\mathbf{n}_{mj}^- = (n_{mj}^-, 
_{mj}^-, \ldots, n_{mk}, \ldots)$, $\mathbf{n}_{mk} = (n_{mj}, \ldots, n_{mj}^-, \ldots, n_{mk}^+, \ldots)$, and all of them are one-rank higher than $\mathbf{n}$. In HEOM simulations, the number of auxiliary operators, determined by the maximum $N_{\text{rank}}$, should be increased until the simulated system dynamics shows convergence in order to obtain numerically exact solutions.

In this work, the convergence of HEOM simulations is achieved for the maximum $N_{\text{rank}} = 10$.

In absorption simulations, we compute the dynamics of optical coherence in the form $\sum_{i=1}^{N_G} \psi_i(t)|\xi_i\rangle g_i\rangle$, where $|\xi_i\rangle$ denotes a singly excited state of site $i$, and $|g_i\rangle$ is the global electronic ground state. Note that $\hat{\sigma}_m^\dagger \hat{\sigma}_m |g_i\rangle = 0$ due to the absence of electronic excitations in the global ground state. This implies that in absorption simulations, the mathematical form of HEOM can be simplified to

$$\frac{d\hat{\rho}_n}{dt} = -\frac{i}{\hbar}[H_s, \hat{\rho}_n] - \sum_{m=1}^{N_S} \left( \sum_{j=1}^{N_C} (n_{mj}+f_j + n_{mj}-f_j) + \sum_{k=1}^{N_R} n_{mk}\gamma_k \right) \hat{\rho}_n - i \sum_{m=1}^{N_S} \hat{\sigma}_m^\dagger \hat{\sigma}_m \left( \sum_{j=1}^{N_C} (\hat{\rho}_{n_{mj}^+} + \hat{\rho}_{n_{mj}^-}) + \sum_{k=1}^{N_R} \hat{\rho}_{n_{mk}^+} \right)$$

$$- i \sum_{m=1}^{N_S} \sum_{j=1}^{N_C} n_{mj} \left( d_j^+ \hat{\sigma}_m^\dagger \hat{\rho}_{m_{mj}^+} - d_j^- \hat{\rho}_{m_{mj}^-} \hat{\sigma}_m^\dagger \right) - i \sum_{m=1}^{N_S} \sum_{j=1}^{N_C} n_{mj} \left( d_j^- \hat{\sigma}_m \hat{\rho}_{m_{mj}^-} - d_j^+ \hat{\rho}_{m_{mj}^+} \hat{\sigma}_m \right),$$

(S26)

where the auxiliary operators are described by $\hat{\rho}_n = \sum_{N_G=1}^N \psi_{n_i}(t)|\xi_i\rangle g_i\rangle$, similar to $N_S$-dimensional states with un-normalized amplitudes $\psi_{n_i}(t)$. We note that $H_s$ is the electronic Hamiltonian in this work, satisfying $H_s |g_i\rangle = 0$. It is notable that in Eq. (S25), $d_j^+$, namely the amplitude of $e^{-f_j t}$ considered in the multi-exponential fitting (see Eq. (S24)), induces the coupling between $\hat{\rho}_n$ and $\hat{\rho}_{n_{mj}^+}$ (see $d_j^+$ in Eq. (S25)) and that between $\hat{\rho}_n$ and $\hat{\rho}_{n_{mj}^-}$ (see $d_j^-$ in Eq. (S25)). This implies that even if we only consider $d_j^+ e^{-f_j t}$ in Eq. (S24) by setting $d_j^- = 0$, the auxiliary operators should be labelled by $\mathbf{n} = (n_{mj}, \ldots, n_{mj}, \ldots, n_{mk}, \ldots)$ with both $n_{mj}^+$ and $n_{mj}^-$ included, as is the case that both $d_j^+ e^{-f_j t}$ and $d_j^- e^{-f_j t}$ are considered in the fitting. Hence, setting $d_j^- = 0$ does not reduce the number of auxiliary operators of a given $N_{\text{rank}}$, determining simulation cost. This is contrary to the simplified HEOM formula for absorption simulations in Eq. (S26), where $d_j^+$ only induces the interaction between $\hat{\rho}_n$ and $\hat{\rho}_{n_{mj}^-}$, not the interaction between $\hat{\rho}_n$ and $\hat{\rho}_{n_{mj}^+}$. This implies that in absorption simulations, one does not need to fit the bath correlation function by using pair-wise exponentials, namely $d_j^+ e^{-f_j t} + d_j^- e^{-f_j t}$, but can consider a sum of fully independent exponentials

$$C(t) \approx \sum_{j=1}^{N_C} d_j e^{-f_j t},$$

(S27)

with complex-valued $d_j$ and $f_j$, for which the mathematical form of HEOM is simplified to

$$\frac{d\hat{\rho}_n}{dt} = -\frac{i}{\hbar}[H_s, \hat{\rho}_n] - \sum_{m=1}^{N_S} \sum_{j=1}^{N_C} n_{mj} f_j \hat{\rho}_n - i \sum_{m=1}^{N_S} \hat{\sigma}_m^\dagger \hat{\sigma}_m n_{mj} \hat{\rho}_n - i \sum_{m=1}^{N_S} \sum_{j=1}^{N_C} n_{mj} d_j \hat{\sigma}_m^\dagger \hat{\rho}_n \hat{\sigma}_m,$$

(S28)
where \( \mathbf{n} = (n_{m}, \cdots) \). This approach provides more flexibility in the multi-exponential fitting of the bath correlation function as it can reduce the number of exponentials required to achieve a desired fitting quality and therefore the overall simulation cost. We note that this approach cannot be employed when the population dynamics of electronic excited states is involved in the physical quantity of interest, such as nonlinear spectroscopic signals.

To further reduce the HEOM simulation cost, we map local vibrational modes to global modes making use of the fact that the influence of the center-of-mass modes on the reduced system dynamics can be computed analytically. This allows us to perform HEOM simulations without the explicit inclusion of the center-of-mass modes. As a result, the simulation cost is significantly reduced because \( N_{S} \) local baths can be mapped to \( (N_{S} - 1) \) global baths, as the center-of-mass modes are disregarded in the HEOM simulations. This reduces the dimension of the vectors \( \mathbf{n} \) labelling auxiliary operators \( \hat{\rho}_{n} \).

As an example, we consider a dimer model where each site is coupled to a single local mode with identical vibrational frequency \( \omega \) and Huang-Rhys factor \( s \)

\[
H = H_{e} + \sum_{i=1}^{2} \left( \omega b_{i}^{|} b_{i} + \omega \sqrt{s} |\varepsilon_{i}| \langle |\varepsilon_{i}| \otimes (b_{i}^{|} + b_{i}) \right).
\]

By introducing a center-of-mass mode \( B = \frac{1}{\sqrt{2}} (b_{1} + b_{2}) \) and a relative-motion mode \( b = \frac{1}{\sqrt{2}} (b_{1} - b_{2}) \), satisfying the bosonic commutation relations, the Hamiltonian can be expressed as

\[
H = H_{e} + \omega (B^{|}B + B^{b}b) + \omega \sqrt{s} A_{+} \otimes (B^{|} + B) + \omega \sqrt{s} A_{-} \otimes (b^{b} + b),
\]

where \( A_{\pm} = (|\varepsilon_{1}| \langle |\varepsilon_{1}| \pm |\varepsilon_{2}| \langle |\varepsilon_{2}|) / \sqrt{2} \). It is notable that \( A_{+} \propto |\varepsilon_{1}| \langle |\varepsilon_{1}| + |\varepsilon_{2}| \langle |\varepsilon_{2}| \) is proportional to the identity operator of the single excitation subspace. This means that the center-of-mass mode induces fully correlated fluctuations of the energy levels of different sites, without affecting the energy-level difference between them. Therefore the influence of the center-of-mass mode on the dynamics of optical coherence can be computed in an analytical way, as is the case of the Kubo’s line shape theory of a two-level monomer \([78]\). The influence of the relative-motion mode on the system dynamics, described by \( A_{-} \), still requires numerically exact simulations. The mapping from local to global modes can be generalized to a multi-mode case characterised by a phonon spectral density \([S5]\). For a dimer system coupled to identical local baths, the influence of the relative-motion modes on optical coherence can be computed by HEOM in the form

\[
\frac{d\hat{\rho}_{n}}{dt} = -\frac{i}{\hbar} \hat{H}_{s} \hat{\rho}_{n} - \sum_{j=1}^{N_{C}} n_{j} f_{j} \hat{\rho}_{n} - \frac{i}{\sqrt{2}} \sum_{j=1}^{N_{C}} \hat{\rho}_{n_{j}}^{+} - \frac{i}{\sqrt{2}} \sum_{j=1}^{N_{C}} n_{j} d_{j} |\varepsilon_{1}| \langle |\varepsilon_{1}| - |\varepsilon_{2}| \langle |\varepsilon_{2}| \hat{\rho}_{n_{j}}^{-},
\]

where \( \mathbf{n} = (n_{j}, \cdots) \). It is notable that the dimension of \( \mathbf{n} = (n_{j}, \cdots) \) of the relative-motion model is the half of the dimension of \( \mathbf{n} = (n_{1j}, \cdots, n_{2j}, \cdots) \) of the original local bath model. This significantly reduces the number of auxiliary operators for a given \( N_{\text{rank}} \) and therefore the simulation cost. This approach can be generalized to a multi-site system where \( \mathbf{n} = (n_{1j}, \cdots, n_{NS}, \cdots) \) is mapped to \( \mathbf{n} = (n_{1j}, \cdots, n_{NS-1, \cdots}) \) by removing a bath consisting of center-of-mass modes.

We note that the dynamics of the optical coherence \( \hat{\rho}_{0}(t) = \sum_{i=1}^{2} |\psi_{0,i}(t)\rangle \langle |\varepsilon_{i}| |g际 computed by Eq. (S31) only considers the dephasing induced by the relative-motion modes. The additional dephasing between the ground and excited state manifold caused by the center-of-mass modes can be taken into account analytically by multiplying an additional time-dependent factor that is independent of the excited states \( |\varepsilon_{i}| \), namely \( \sum_{i=1}^{2} |\psi_{0,i}(t)\rangle \langle |\varepsilon_{i}| |g \exp(-1/2 G(t) \rangle, \)

\[
G(t) = -i \lambda t + \int_{0}^{\infty} \frac{d\omega}{\omega} J(\omega) \left( (1 - \cos(\omega t)) \left( 1 + \frac{2}{\epsilon_{s}/k_{B}T - 1} \right) + i \sin(\omega t) \right), \tag{S32}
\]

with the reorganization energy \( \lambda = \int_{0}^{\infty} d\omega J(\omega) / \omega \). The factor \( 1/2 \) in \( \exp(-1/2 G(t)) \), which does not appear in the standard line shape theory \([S8]\), originates from the \( 1/\sqrt{2} \) factor in \( A_{+} \), describing the coupling to the center-of-mass modes. We note that this approach can be generalized to the simulations of nonlinear spectroscopic signals by taking into account the contribution of the center-of-mass modes analytically.

We would like to stress that the techniques devised to reduce the computational cost of absorption simulations by TEDOPA can also be applied to HEOM simulations. As explained in section [I] in TEDOPA the finite temperature environments can be mapped to zero temperature environments for which the initial state is a pure vacuum state, while the phonon spectral density becomes temperature-dependent. This enables one to compute the dipole-dipole correlation function up to time \( t \) by simulating the time evolution of a pure electronic-vibrational state up to time \( t / 2 \). This technique can be employed in HEOM simulations. In absorption simulations, the initial state of the system density matrix is given by \( \hat{\rho}_{0} = |g\rangle \langle g| \) and those of all the higher-rank auxiliary operators are taken to be null matrices,
\( \hat{\rho}_n = 0 \) for all \( n \neq 0 \). When a transition dipole moment operator \( \mu \) is multiplied to the left-hand side of the auxiliary operators, the lowest-rank operator becomes a linear combination of optical coherences, \( \hat{\rho}_0(0) = \sum_{i=1}^{N_S} \psi_{n,i}(0) \langle \varepsilon_i | g \rangle \). In this case, as shown in Eq. (S28), the time evolution of the auxiliary operators is governed by a propagator that is multiplied to the left-hand side of \( \hat{\rho}_n \). This makes it straightforward to define a high-dimensional vector \( \mathbf{\tilde{\rho}}(t) \), consisting of all the elements \( \psi_{n,i}(t) \) of the auxiliary operators \( \hat{\rho}_n(t) = \sum_{i=1}^{N_S} \psi_{n,i}(t) \langle \varepsilon_i | g \rangle \), and a propagator \( G \), governing the dynamics of \( \mathbf{\tilde{\rho}}(t) \), namely \( \frac{d}{dt} \mathbf{\tilde{\rho}}(t) = G \mathbf{\tilde{\rho}}(t) \). The dipole-dipole correlation function is then described by

\[
\langle D(t) \rangle_{\varepsilon,\varepsilon_i} = \langle \hat{\rho}_n(0) \cdot (e^{Gt} \hat{\rho}_n(0)) \rangle_{\varepsilon,\varepsilon_i} = \langle (e^{Gt/2} \hat{\rho}_n(0) \cdot (e^{Gt/2} \hat{\rho}_n(0))) \rangle_{\varepsilon,\varepsilon_i},
\]

(S33)
demonstrating that one can reduce the simulation time from \( t \) to \( t/2 \) in HEOM simulations, as is the case of T-TEDOPA. The reduced time window can decrease the number of auxiliary operators, required to obtain numerically exact absorption line shapes, as higher-rank auxiliary operators are initially null matrices and they are populated only through the interaction with lower-rank auxiliary operators. The other techniques for efficient disorder simulations, such as the Gauss-Hermite interpolation mentioned in section II, can also be employed in HEOM simulations.

The simulation cost of HEOM is determined by the number of the auxiliary operators, denoted by \( N_{\text{rank}} \), which should be increased until simulated system dynamics is converged. As detailed in section IV, we performed HEOM simulations up to \( N_{\text{rank}} = 10 \) to obtain fully converged absorption spectra where the bath correlation functions of WSCP and SP are fitted by the sum of 12 and 16 exponentials, respectively, to take into account experimentally estimated spectral densities consisting of low-frequency protein modes and 55 intra-pigment modes per site. For \( N_{\text{rank}} = 10 \) and \( N_{\exp} = 12 \) (or \( N_{\exp} = 16 \)) exponentials, the number of the auxiliary operators is evaluated as \( (N_{\exp} + N_{\text{rank}}) \). For absorption simulations of a dimeric system, one needs to consider the subspace spanned by optical coherences \( \langle \varepsilon_1 | g \rangle \) and \( \langle \varepsilon_2 | g \rangle \) for each auxiliary operator, leading to the total memory cost of the simulation of 20 MB and 170 MB, respectively, for WSCP and SP. We note that this is the memory cost required to keep the information about reduced system state and system-environment correlations, which does not include the additional cost required for computing system dynamics.

One the other hand, when the experimentally estimated spectral densities are fitted by Drude-Lorentz peaks [21, 69], one needs to consider at least two exponentials to describe each local intra-pigment mode [66], leading to 220 exponentials for 110 intra-pigment modes of a dimeric system. In this case, the memory cost of the simulation of 20 MB and 170 MB, respectively, for WSCP and SP. We note that this is the memory cost required to keep the information about reduced system state and system-environment correlations, which does not include the additional cost required for computing system dynamics.

IV. ELECTRONIC PARAMETERS AND PHONON SPECTRAL DENSITIES OF WSCP AND SP

Here we provide a summary of the electronic parameters and of the environmental spectral densities of WSCP and SP that entered our simulations.

In earlier work on WSCP homodimers reported in Ref. [67] it has been assumed that the mean site energies of two pigments are identical, \( \langle \varepsilon_1 \rangle = \langle \varepsilon_2 \rangle \), and the electronic coupling \( V = 69 \, \text{cm}^{-1} \) between pigments was estimated in Ref. [67] where the absorption spectra of WSCP were computed by cumulant expansion technique based on a coarse-grained spectral density

\[
J_{i}^{\text{B777}}(\omega) = \frac{S}{s_1 + s_2} \sum_{i=1}^{2} \frac{s_i}{72\omega_i^2} \omega^5 e^{-(\omega/\omega_i)^{1/2}},
\]

(S34)
where \( S = 0.8, s_1 = 0.8, s_2 = 0.5, \omega_1 = 0.069 \, \text{meV} \) and \( \omega_2 = 0.24 \, \text{meV} \). It is found that approximate simulated results based on second order cumulant expansion can reproduce the low-energy part of experimental absorption line shape when the angle between transition dipole moments of monomers is taken to be \( \phi = 39^\circ \).

The experimentally estimated environmental spectral density of WSCP consists of three log-normal distribution functions [65]

\[
J_{i}^{\text{WSCP}}(\omega) = \sum_{m=1}^{3} \frac{S_m}{\sigma_m \sqrt{2\pi}} \omega \exp \left(-\frac{[\ln(\omega/\Omega_m)]^2}{2\sigma_m^2}\right),
\]

(S35)
with \( S_1 = 0.39, S_2 = 0.23, S_3 = 0.23, \sigma_1 = 0.4, \sigma_2 = 0.25, \sigma_3 = 0.2, \Omega_1 = 26 \, \text{cm}^{-1}, \Omega_2 = 51 \, \text{cm}^{-1}, \Omega_3 = 85 \, \text{cm}^{-1}, \)
and 55 intra-pigment vibrational modes modelled by Lorentzian functions

\[ J_k(\omega) = \sum_{k=1}^{55} \frac{4\omega_k s_k \gamma_k (\omega_k^2 + \gamma_k^2) \omega}{((\omega + \omega_k)^2 + \gamma_k^2)((\omega - \omega_k)^2 + \gamma_k^2)^2}, \]

where vibrational frequencies and Huang-Rhys factors \[13\] are summarised in Table I, and vibrational damping rates are taken to be \(\gamma_k = (1 \text{ ps})^{-1}\).

For SP heterodimers, it has been estimated that the difference in mean site energies is \(\langle \varepsilon_1 - \varepsilon_2 \rangle = 315 \text{ cm}^{-1}\), electronic coupling is \(V = 625 \text{ cm}^{-1}\), and the angle between transition dipole moments of monomers \[57\] is 143°. Experimentally estimated spectral density consists of a log-normal distribution function \[68\]

\[ J_{SP}^l(\omega) = \frac{S_l}{\sigma_l \sqrt{2\pi}} \omega \exp \left( -\frac{[\ln(\omega/\Omega_l)]^2}{2\sigma_l^2} \right), \]

with \(S_l = 1.7\), \(\sigma_l = 0.47\), \(\Omega_l = 35 \text{ cm}^{-1}\), the special pair marker mode \[68\], modelled by vibrational frequency \(\omega_{SP} = 125 \text{ cm}^{-1}\), Huang-Rhys factor \(s_{SP} = 1.5\) and damping rate \(\gamma_{SP} = 15 \text{ cm}^{-1}\), and 55 intra-pigment vibrational modes of BChl pigments \[15\] with vibrational frequencies and Huang-Rhys factors \[13\] summarised in Table I. We assume that the damping rates of the intra-pigment modes are \(\gamma_k = (1 \text{ ps})^{-1}\). The special pair marker mode and 55 intra-pigment modes are modelled by Lorentzian spectral densities. In experiments where phonon spectral densities are estimated, the optical response may originate from the lowest-energy exciton rather than the lowest-energy pigment.

In the estimation of phonon spectral densities, we renormalise the Huang-Rhys factors of the local modes, \(s_k\), using the renormalised Huang-Rhys factor of the exciton state is given by \(s_{E_\text{exc}} = s(\sin^4(\theta/2) + \cos^4(\theta/2))\). Since experimental data are fitted by line shape functions based on the effective Huang-Rhys factor \(s_{E_\text{exc}}\) in the estimation of phonon spectral densities, we renormalise the Huang-Rhys factors of the local modes, \(s = s_{E_\text{exc}}/(\sin^4(\theta/2) + \cos^4(\theta/2)) \approx 1.9 s_{E_\text{exc}}\) based on the mean site energy difference \(\langle \varepsilon_1 - \varepsilon_2 \rangle = 315 \text{ cm}^{-1}\) and electronic coupling \(V = 625 \text{ cm}^{-1}\) of the SP. Since the Huang-Rhys factors \(S_i\) and \(s_{SP}\) of the log-normal distribution and special pair marker mode were estimated based

| \(k\) | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|------|----|----|----|----|----|----|----|----|----|----|
| \(\omega_k \text{ [cm}^{-1}]\) | 181 | 221 | 240 | 269 | 283 | 298 | 325 | 352 | 366 | 405 |
| \(s_k\) | 0.0173 | 0.0246 | 0.0182 | 0.0064 | 0.0036 | 0.0104 | 0.0112 | 0.0249 | 0.0112 | 0.0061 |
| \(k\) | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 |
| \(\omega_k \text{ [cm}^{-1}]\) | 430 | 470 | 488 | 515 | 537 | 572 | 598 | 620 | 641 | 700 |
| \(s_k\) | 0.0050 | 0.0075 | 0.0061 | 0.0045 | 0.0157 | 0.0132 | 0.0036 | 0.0047 | 0.0033 | 0.0019 |
| \(k\) | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 |
| \(\omega_k \text{ [cm}^{-1}]\) | 713 | 734 | 746 | 757 | 800 | 834 | 863 | 887 | 922 | 977 |
| \(s_k\) | 0.0025 | 0.0107 | 0.0112 | 0.0229 | 0.0022 | 0.0140 | 0.0033 | 0.0019 | 0.0291 | 0.0110 |
| \(k\) | 31 | 32 | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 |
| \(\omega_k \text{ [cm}^{-1}]\) | 998 | 1023 | 1045 | 1068 | 1108 | 1128 | 1150 | 1172 | 1186 | 1227 |
| \(s_k\) | 0.0036 | 0.0022 | 0.0056 | 0.0050 | 0.0087 | 0.0011 | 0.0244 | 0.0121 | 0.0226 | 0.0249 |
| \(k\) | 41 | 42 | 43 | 44 | 45 | 46 | 47 | 48 | 49 | 50 |
| \(\omega_k \text{ [cm}^{-1}]\) | 1243 | 1264 | 1288 | 1305 | 1326 | 1360 | 1393 | 1443 | 1484 | 1522 |
| \(s_k\) | 0.0090 | 0.0126 | 0.0224 | 0.0093 | 0.0509 | 0.0093 | 0.0328 | 0.0121 | 0.0107 | 0.0185 |
| \(k\) | 51 | 52 | 53 | 54 | 55 |
| \(\omega_k \text{ [cm}^{-1}]\) | 1550 | 1573 | 1628 | 1654 | 1681 |
| \(s_k\) | 0.0241 | 0.0182 | 0.0081 | 0.0135 | 0.0067 |
on experiments on excitonic systems [68], we multiply the renormalisation factor \( \sim 1.9 \) to \( S_l \) and \( s_{sp} \). Since the parameters in Table I were estimated based on experiments on BChl monomers [15], we do not renormalise the Huang-Rhys factors \( s_k \) of the intra-pigment modes.

V. NUMERICAL TEST & COMPARISON OF HEOM AND TEDOPA FOR STRUCTURED ENVIRONMENTS AT LOW TEMPERATURES

In this section we provide direct evidence that both HEOM and TEDOPA are capable of achieving numerically exact results for dimeric systems in contact with realistic, highly structured environmental spectral densities. To this end we apply both methods to WSCP and the special pair in bacterial reaction centers and show that the fully converged results coincide.

Fig. S1 presents the HEOM and TEDOPA results of numerically exact absorption line shapes of WSCP at 77 K. Fig. S1(a) shows the experimentally estimated spectral density of WSCP which consists of three log-normal functions at low vibrational frequencies [65] and 55 narrow Lorentzian functions corresponding to intra-pigment vibrational modes [13] (see section IV for all the parameters that enter this spectral density). For the HEOM simulation, the real and imaginary part of the corresponding bath correlation function at \( T = 77 \text{ K} \) is fitted by the sum of 13 exponentials, as shown in Fig. S1(b). The quality of the fit is confirmed by its ability to reproduce the analytical solution of monomer optical coherence dynamics, as shown in Fig. S1(c). Finally, Fig. S1(d) shows numerically exact absorption line shapes of WSCP that have been obtained by independent calculations using HEOM and TEDOPA. For two different electronic coupling strengths \( V = 69 \text{ cm}^{-1} \) and \( V = 140 \text{ cm}^{-1} \), we observe perfect overlap of the absorption spectra obtained by the two methods. This demonstrates the reliability of the two methods and our simulated data.

Fig. S2 presents HEOM and TEDOPA results of numerically exact absorption line shapes of the special pair in bacterial reaction centers at \( T = 5 \text{ K} \) under the highly structured environmental spectral density shown in Fig. S2(a). The corresponding bath correlation function at \( T = 5 \text{ K} \), shown in black in Fig. S2(b), is well fitted by the sum of 16 exponentials up to \( t = 200 \text{ fs} \), as shown in red. Fig. S2(c) shows that the fitting quality is good enough to reproduce the analytical solution of monomer optical coherence dynamics. Fig. S2(d) displays the absorption spectra of the special pair demonstrating that the results obtained by HEOM and TEDOPA are well matched. Our results demonstrate that low-temperature systems can be efficiently simulated by HEOM when the bath correlation function is numerically fitted. This contrasts the standard approach where the bath correlation function is expanded as a sum of exponentials in an analytical way for some model spectral densities. A well-known example is the Ohmic spectral density with the Lorentz-Drude cutoff function where the number of exponentials required to achieve a desired fitting

| \( k \) | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   | 9   | 10  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \( \omega_k \, [\text{cm}^{-1}] \) | 161 | 195 | 238 | 285 | 341 | 373 | 383 | 402 | 420 | 453 |
| \( s_k \) | 0.0150 | 0.0400 | 0.0100 | 0.0200 | 0.0230 | 0.0100 | 0.0070 | 0.0060 | 0.0030 | 0.0020 |

| \( k \) | 11  | 12  | 13  | 14  | 15  | 16  | 17  | 18  | 19  | 20  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \( \omega_k \, [\text{cm}^{-1}] \) | 483 | 531 | 565 | 592 | 676 | 711 | 724 | 742 | 760 | 772 |
| \( s_k \) | 0.0020 | 0.0040 | 0.0170 | 0.0070 | 0.0100 | 0.0060 | 0.0250 | 0.0100 | 0.0060 | 0.0120 |

| \( k \) | 21  | 22  | 23  | 24  | 25  | 26  | 27  | 28  | 29  | 30  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \( \omega_k \, [\text{cm}^{-1}] \) | 787 | 799 | 839 | 864 | 886 | 915 | 932 | 953 | 977 | 993 |
| \( s_k \) | 0.0026 | 0.0036 | 0.0120 | 0.0050 | 0.0030 | 0.0130 | 0.0068 | 0.0040 | 0.0007 | 0.0017 |

| \( k \) | 31  | 32  | 33  | 34  | 35  | 36  | 37  | 38  | 39  | 40  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \( \omega_k \, [\text{cm}^{-1}] \) | 1008 | 1031 | 1047 | 1062 | 1099 | 1115 | 1141 | 1154 | 1175 | 1185 |
| \( s_k \) | 0.0024 | 0.0007 | 0.0007 | 0.0040 | 0.0120 | 0.0090 | 0.0020 | 0.0100 | 0.0160 | 0.0090 |

| \( k \) | 41  | 42  | 43  | 44  | 45  | 46  | 47  | 48  | 49  | 50  |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| \( \omega_k \, [\text{cm}^{-1}] \) | 1223 | 1257 | 1287 | 1335 | 1351 | 1377 | 1388 | 1418 | 1442 | 1456 |
| \( s_k \) | 0.0130 | 0.0100 | 0.0020 | 0.0100 | 0.0120 | 0.0076 | 0.0100 | 0.0012 | 0.0026 | 0.0052 |

| \( k \) | 51  | 52  | 53  | 54  | 55  |
|------|-----|-----|-----|-----|-----|
| \( \omega_k \, [\text{cm}^{-1}] \) | 1484 | 1501 | 1541 | 1584 | 1598 |
| \( s_k \) | 0.0087 | 0.0104 | 0.0075 | 0.0044 | 0.0044 |
quality increases as temperature decreases, due to Matsubara terms, making HEOM simulations more challenging. Even in this case, the simulation cost can be significantly reduced by replacing multiple Matsubara (exponential) terms with a few damped oscillations based on numerical fitting.

It is notable that the input parameters for HEOM simulations are determined based on the fitting of the bath correlation functions. This implies that one needs to improve the fitting quality until simulated HEOM results show convergence, which requires the repetition of HEOM simulations and as a result increases the overall simulation cost. This is contrary to TEDOPA where the input parameters for simulations are computed by orthogonal polynomial algorithm [22, 59, 61], which makes it easier to control the accuracy of input parameters when compared to HEOM.

VI. COARSE-GRAINING ENVIRONMENTAL STRUCTURES

Recently in a treatment of the PC645 complex from marine algae the highly structured phonon spectral densities were severely coarse-grained to facilitate HEOM simulations of the multi-chromophoric PC645 complex [21]. Hence, we examine an approach in which the 55 narrow Lorentzian peaks of the high energy part of the environmental

![FIG. S1.](image)

(a) The experimentally estimated phonon spectral density $J(\omega)$ of WSCP consists of three log-normal functions at low frequencies $\omega \lesssim 150$ cm$^{-1}$ and 55 high-frequency underdamped modes modelled by Lorentzian functions with a vibrational damping rate of (1 ps)$^{-1}$. The inset shows the low energy part of the spectral density for better visibility. (b) The real and imaginary parts of the bath correlation function (BCF) $C(t)$ at $T = 77$ K, shown in black, are fitted up to 300 fs by the sum of 13 exponentials as shown in red dashed lines. The insets show the difference between target BCF and the fitting function, demonstrating that the fitting error is three orders of magnitude smaller than the amplitudes of the target BCF. (c) The dynamics of the real part of the optical coherence of a two-level monomer in the absence of static disorder. The simulated HEOM results, shown in red, are well matched to the analytical solution shown in black: the site energy of the monomer is taken to be zero for better visibility. The imaginary part of the coherence computed by HEOM is also well matched to the analytical solution (not shown here). (d) The absorption spectra of WSCP homodimers with $V = 140$ cm$^{-1}$ or $V = 69$ cm$^{-1}$. The simulated HEOM results shown in red are well matched to the TEDOPA results shown in black. The simulated optical coherence of the dimer system decays within 300 fs mainly due to the static disorder (not shown here), implying that the fitting of the BCF up to 300 fs is sufficient for HEOM simulations. Experimentally measured absorption spectrum of WSCP is shown in blue as a guide for the eye. For $V = 140$ cm$^{-1}$ ($V = 69$ cm$^{-1}$), the mean site energies $\langle \epsilon_1 \rangle = \langle \epsilon_2 \rangle$ are taken to be 631.5 nm (629.8 nm) and the standard deviation of the Gaussian static disorder is 80 cm$^{-1}$ (72 cm$^{-1}$). The angle between transition dipole moments of monomers [67] is taken to be 39°.
FIG. S2. (a) Experimentally estimated phonon spectral density $J(\omega)$ of the special pair in bacterial reaction centers. (b) The bath correlation function (BCF) at $T = 5\, \text{K}$, denoted by $C(t)$, is shown in black, which is fitted up to 200 fs by the sum of 16 exponentials as shown in red dashed lines. The difference between target BCF and fitting function is shown in blue, demonstrating that the fitting error is three orders of magnitude smaller than the amplitudes of the target BCF. (c) The dynamics of the real part of the optical coherence of a two-level monomer in the absence of static disorder. The simulated HEOM results shown in red are well matched to the analytical solution shown in black: the site energy of the monomer is taken to be zero for better visibility. (d) The absorption spectra of the special pair. The simulated HEOM results shown in red are well matched to the TEDOPA results shown in black. Experimentally measured absorption spectra of bacterial reaction centers are shown in blue as a guide for the eye. The mean site energies $\langle \epsilon_1 \rangle$ and $\langle \epsilon_2 \rangle$ of sites 1 and 2 are taken to be 814.2 nm and 835.7 nm, respectively, with the detuning of $\langle \epsilon_1 - \epsilon_2 \rangle = 315\, \text{cm}^{-1}$. The standard deviation of local static disorder is taken to be 105 cm$^{-1}$. The angle between transition dipole moments of monomers $^{[57]}$ is taken to be 143$^\circ$.

Spectral density of WSCP is approximated, as in Fig. S3(a), by a broad Lorentzian function

$$J_c(\omega) = \frac{4\gamma_c \omega_c (\omega^2 + \gamma_c^2) s_c \omega}{\pi[(\omega + \omega_c)^2 + \gamma_c^2][\omega - \omega_c]^2 + \gamma_c^2}.$$  

Here we have three variables ($\omega_c$, $s_c$, $\gamma_c$) and the sole constraint that we require the reorganization energy of the broad Lorentzian peak to be the same as the total reorganization energy induced by the original 55 modes, namely $\omega_c s_c = \sum_{k=1}^{55} \omega_k s_k$, so that the environmental coupling strength is conserved. The frequency of the broad Lorentzian peak is determined in such a way that the location of monomer’s phonon sideband is well matched to that of the original model without coarse-graining, resulting in $\omega_c = 1350\, \text{cm}^{-1}$ and $s_c \approx 0.49$. The width of the Lorentzian peak, described by $\gamma_c$, is also determined based on the monomer absorption line shape, as shown in Fig. S3(a) and (b), where $\gamma_c = (30\, \text{fs})^{-1}$ (see red lines) better reproduces the absorption line shape of the original model without coarse-graining (see black lines) than $\gamma_c = (15\, \text{fs})^{-1}$ and $(60\, \text{fs})^{-1}$ (see blue and green lines, respectively). The bath correlation function of the coarse-grained spectral density at $T = 77\, \text{K}$ is fitted by the sum of 12 exponentials, as shown in Fig. S3(c). The simulated HEOM results of dimer absorption spectra, shown in Fig. S3(d), demonstrate that the coarse-grained model can quantitatively reproduce the numerically exact absorption spectra of the original model in the low-energy 650 – 680 nm region, dominated by zero-phonon lines. However, the line shapes of phonon sidebands in the higher-energy region are not well matched, implying that the detailed vibrational structure is important, not only the overall coupling strength to the environment. We note that WSCP is a special case where zero-phonon lines are well separated from phonon sidebands due to a small excitonic gap. For larger excitonic splittings, zero-phonon lines can be spectrally overlapped with phonon sidebands, as is the case of the PC645 complex.

In Ref. $^{[67]}$ the electronic parameters of WSCP were estimated based on a coarse-grained spectral density, shown
FIG. S3. (a) Experimentally estimated phonon spectral density of WSCP is shown in black where the 55 high-frequency modes are replaced by a broad Lorentzian peak with a vibrational damping rate of $(15 \text{ fs})^{-1}$, $(30 \text{ fs})^{-1}$, $(60 \text{ fs})^{-1}$, displayed in blue, red, green, respectively. The three log-normal functions at low vibrational frequencies $\omega \lesssim 100 \text{ cm}^{-1}$ are not coarse-grained (see the inset). (b) Analytically computed absorption line shapes of a monomer coupled to the spectral densities shown in (a). The mean site energy of the monomer is taken to be $630 \text{ nm}$ and the standard deviation of the static disorder is $72 \text{ cm}^{-1}$. The vibrational damping rate of $(30 \text{ fs})^{-1}$ (shown in red) better reproduces the monomer absorption line shape of the original model without coarse-graining (black) than the other damping rates (blue, green). (c) In this work, we consider $(30 \text{ fs})^{-1}$ in HEOM simulations, for which the bath correlation function shown in black is fitted by the sum of 12 exponentials as shown in red. The fitting error is three orders of magnitude smaller than the amplitudes of the target BCF, as shown in the inset. (d) The dimer absorption spectra computed based on the coarse-grained spectral density are shown in red, which are quantitatively well matched to the results based on the original model, shown in black, around the zero-phonon lines below 650 nm (see the inset). The absorption line shapes of phonon sidebands around 600 – 640 nm are not well reproduced by the coarse-grained model, as it depends on the vibrational structure rather than the overall coupling strength to the high-frequency modes. For $V = 140 \text{ cm}^{-1}$ ($V = 69 \text{ cm}^{-1}$), the mean site energy is taken to be $632.2 \text{ nm}$ (630.4 nm) and the standard deviation of the static disorder is $80 \text{ cm}^{-1}$ ($72 \text{ cm}^{-1}$). The angle between transition dipole moments of monomers [67] is taken to be $39^\circ$.

VII. ESTIMATION OF ELECTRONIC PARAMETERS OF WSCP

Here we investigate the dependence of numerically exact absorption line shapes of WSCP on electronic parameters, including the angle $\phi$ between transition dipole moments of monomers, electronic coupling strength $V$ and the detuning
FIG. S4. (a) Coarse-grained spectral density from Ref. 67, shown in red (see Fig. 2(a) and (d) in the main text), and experimentally estimated spectral density of WSCP, shown in black. (b) The bath correlation function (BCF) $C(t)$ of the coarse-grained spectral density at $T = 77$ K, shown in black, is fitted up to 300 fs by the sum of 9 exponentials as shown in red dashed lines. The insets show the difference between target BCF and the fitting function, demonstrating that the fitting error is three orders of magnitude smaller than the amplitudes of the target BCF. (c) The dynamics of the real part of the optical coherence of a two-level monomer in the absence of static disorder. The simulated HEOM results, shown in red, are well matched to the analytical solution shown in black: the site energy of the monomer is shifted zero for better visibility. The imaginary part of the coherence computed by HEOM is also well matched to the analytical solution (not shown here). (d) The absorption spectra of WSCP homodimers with $V = 69$ cm$^{-1}$. The simulated HEOM results shown in red are well matched to the TEDOPA results shown in black where the angle between transition dipole moments of monomers [67] is taken to be 39°. Absorption above 640 nm is negligible due to the absence of the phonon sideband induced by high-frequency intra-pigment modes (see red line in (a)). The simulated results for 44°, shown in green, better reproduce experimental absorption spectra of WSCP, shown in blue dots, than those for 39° and 50°, shown in red and yellow, respectively. The mean site energies $\langle \varepsilon_1 \rangle = \langle \varepsilon_2 \rangle$ are taken to be 658 nm and the standard deviation of the Gaussian static disorder is 80 cm$^{-1}$.

$\langle \varepsilon_1 - \varepsilon_2 \rangle$ in mean site energies. Based on the comparison of theoretical and experimental absorption spectra, we investigate the optimal values of electronic parameters required to reproduce experimental absorption line shape around the zero-phonon lines. In simulations, we consider the experimentally estimated environmental spectral density of WSCP and Gaussian static disorder in site energies with the standard deviation of 80 cm$^{-1}$.

In Ref. 67, the electronic parameters of WSCP homodimers consisting of two Chl $b$ pigments were estimated based on the comparison of experimentally measured absorption spectra and approximate simulated results based on second order cumulant expansion. With the assumption that the mean site energies of two pigments are identical, $\langle \varepsilon_1 \rangle = \langle \varepsilon_2 \rangle$, due to the symmetric molecular structure of WSCP, the best agreement between theory and experiment was achieved for $\phi = 39^\circ$ and $V = 69$ cm$^{-1}$.

In Fig. S5(a), we compare experimental absorption spectra of WSCP, shown in blue dots, with numerically exact absorption line shapes where the angle $\phi$ between transition dipole moments is varied from 0° to 180°, while the other electronic parameters are fixed to $V = 69$ cm$^{-1}$ and $\langle \varepsilon_1 \rangle = \langle \varepsilon_2 \rangle = 630.2$ nm. The mean site energies are chosen in such a way that the simulated results for $\phi = 0^\circ$, shown in red, are well matched to the experimental absorption line shape around 655.5 nm originating from the absorption of higher-energy bright exciton state. As $\phi$ increases from 0° to 180°, the higher-energy exciton state $|E_+\rangle$ becomes darker, while the lower-energy exciton $|E_-\rangle$ becomes brighter, which results in a red-shift of the main absorption peak. It is notable that experimental results cannot be reproduced by varying $\phi$, as the exciton splitting $\Delta \approx 140$ cm$^{-1}$ is suppressed to $\Delta'$ by multi-mode vibronic mixing, which is smaller than the energy-level difference $\sim 140$ cm$^{-1}$ between zero-phonon lines observed in experiments.
FIG. S5. Experimental absorption spectra of WSCP homodimers at T = 77 K are shown in blue dots. Here we investigate how absorption spectra depend on electronic parameters of WSCP where experimentally estimated phonon spectral density of WSCP and static disorder in site energies with a FWHM of 80 cm$^{-1}$ are considered in simulations. (a) Numerically exact absorption line shapes of WSCP as a function of the angle $\phi$ between transition dipole moments of monomers where $V = 69$ cm$^{-1}$ and $\langle \varepsilon_1 \rangle = \langle \varepsilon_2 \rangle = 630.2$ nm. (b) Numerically exact simulated results as a function of electronic coupling strength $V$ where $\phi = 39^\circ$ and $\langle \varepsilon_1 - \varepsilon_2 \rangle = 0$. (c) Numerically exact simulated results as a function of the site energy difference $\langle \varepsilon_1 - \varepsilon_2 \rangle$ where $\phi = 39^\circ$ and $V = 69$ cm$^{-1}$. (d) Numerically exact simulated results for two parameter sets ($\phi = 39^\circ, V = 140$ cm$^{-1}$, $\langle \varepsilon_1 - \varepsilon_2 \rangle = 0$) and ($\phi = 30^\circ, V = 100$ cm$^{-1}$, $\langle \varepsilon_1 - \varepsilon_2 \rangle = 110$ cm$^{-1}$), shown in black and red, respectively, which give the best fit to the experimental spectrum.

In Fig. S5(b), the electronic coupling strength $V$ is increased from 69 cm$^{-1}$ to 140 cm$^{-1}$, while the other electronic parameters are fixed to $\phi = 39^\circ$ and $\langle \varepsilon_1 - \varepsilon_2 \rangle = 0$. For each case, the mean site energies $\langle \varepsilon_i \rangle$ are adjusted so that the main absorption peaks of theoretical and experimental data are well matched around 655.5 nm. As the electronic coupling $V$ becomes stronger, the energy-gap between zero-phonon lines increases in simulations, and it is found that the simulated results for $V = 140$ cm$^{-1}$ are well matched to experimental absorption spectra.

So far we have assumed that the mean site energies of two pigments are identical, $\langle \varepsilon_1 - \varepsilon_2 \rangle = 0$, as the molecular structure of WSCP homodimers is symmetric. In other PPCs, however, the local environments of pigments can be different from each other, leading to detuning in mean site energies, $\langle \varepsilon_1 - \varepsilon_2 \rangle \neq 0$. In Fig. S5(c), we change the mean site-energy difference from 0 cm$^{-1}$ to 150 cm$^{-1}$, while keeping $\phi = 39^\circ$ and $V = 69$ cm$^{-1}$. It is notable that the energy-gap between zero-phonon lines becomes larger as the detuning increases, but the simulated results cannot quantitatively reproduce experimental data. This implies that one needs to optimise the other electronic parameters $\phi$ and $V$ as well. As an example, in Fig. S5(d), we show numerically exact absorption spectra for two different parameter sets ($\phi = 39^\circ, V = 140$ cm$^{-1}$, $\langle \varepsilon_1 - \varepsilon_2 \rangle = 0$) and ($\phi = 30^\circ, V = 100$ cm$^{-1}$, $\langle \varepsilon_1 - \varepsilon_2 \rangle = 110$ cm$^{-1}$), shown in black solid and red dashed lines, respectively, which are well matched to experimental results, shown in blue dots.

VIII. REDUCED VIBRONIC MODEL FOR ABSORPTION SIMULATION

In the main text, we provide numerically exact absorption line shape of the special pair in bacterial reaction centers, consisting of two narrow peaks centered at 780 and 900 nm, respectively, and a relatively broad peak around 800 – 850 nm. Here we show that the 780 nm and 900 nm peaks originate from vibronic eigenstates $|\psi_+\rangle$ and $|\psi_-\rangle$, respectively.
FIG. S6. (a) Comparison of absorption line shapes of the special pair in bacterial reaction centers computed by HEOM (black) and reduced vibronic model (red). For each vibronic eigenstate of $\hat{H}$, the fidelity with a bare exciton state $|E^-\rangle$ ($|E^+\rangle$) is shown as green (blue) dots. For vibronic eigenstates A-D, the amplitude distributions in zero-phonon line $|E^\pm\rangle$ and phonon sideband $|E^\pm,1_k\rangle$ are displayed to visualize multi-mode vibronic mixing. (b) Reduced model results without higher-order interaction terms. The difference in approximate absorption line shapes obtained by reduced models with and without higher-order couplings is shown in the inset. (c) Reduced model results without off-diagonal vibronic couplings. (d) Reduced model results where double vibrational excitations are considered: in (a)-(c), a single vibrational excitation is considered.

resulting from the vibronic mixing of exciton states $|E^+\rangle$ and $|E^-\rangle$ with multiple intra-pigment modes, and the other vibronic eigenstates contribute to the phonon sideband in the 800 – 850 nm region.

To understand the origin of the three-peak structure, we consider a vibronic Hamiltonian which couples excitons to the relative motions of 55 intra-pigment modes (see section I) and the low-frequency part of phonon spectral density, originating from protein motions, is excluded

$$H \approx H_e + \sum_{k=1}^{55} \omega_k b_k^\dagger b_k + \sum_{i,j} A_{ij} |E_i\rangle \langle E_j| \sum_{k=1}^{55} \omega_k \sqrt{\frac{s_k}{2}} (b_k^\dagger + b_k).$$

(S39)

The influence of center-of-mass modes, which are not included in the above Hamiltonian, on absorption line shapes can be computed analytically, as the absorption line shape is determined by the Fourier transform of the dynamics of optical coherence, $\text{Tr} \{ \mu e^{-i\hat{H}t} \mu_\rho_1 e^{i\hat{H}t} \} \exp(-\frac{1}{2} G(t))$ where $G(t)$ describes the frequency shift and dephasing induced...
by the center-of-mass modes

\[ G(t) = -i \lambda + \int_0^\infty d\omega \frac{J(\omega)}{\omega^2} \left( 1 - \cos(\omega t) \right) \left( 1 + \frac{2}{e^{\omega/k_B T} - 1} \right) + i \sin(\omega t), \] 

(S40)

where \( J(\omega) \) denotes experimentally estimated phonon spectral density of the SP, and \( \lambda = \int_0^\infty d\omega J(\omega)/\omega \) is the reorganisation energy. To reduce the total number of vibrational excitations of the relative motion modes \( b_k \) required to obtain numerically converged absorption spectra, we consider the polaron transformation in section I where the vibronic Hamiltonian is transformed to

\[ \hat{H} = H_e + \sum_{k=1}^{55} \omega_k b_k^\dagger b_k - \sum_{k=1}^{55} \omega_k \langle E_i| \langle E_i| \left( \sum_{k=1}^{55} \frac{s_k}{2} A_k^2 \right) \] 

\[ + \langle E_+| E_- | A_+ \rangle \sum_{k=1}^{55} \omega_k \left( \sqrt{s_k} A_{++} \right) (b_k^\dagger + b_k) D_k \left( \sqrt{s_k} A_{--} \right) \prod_{k' \neq k} D_{k'} \left( \sqrt{s_k} (A_{++} - A_{--}) \right) + h.c. \] 

(S41)

Similarly the transition dipole moment operator is transformed to

\[ \hat{\mu} = (\hat{\epsilon} \cdot \hat{\mu}_{E+}) |E+/g\rangle \prod_{k=1}^{55} D_k \left( \sqrt{s_k} A_{++} \right) + (\hat{\epsilon} \cdot \hat{\mu}_{E-}) |E-/g\rangle \prod_{k=1}^{55} D_k \left( \sqrt{s_k} A_{--} \right) + h.c., \] 

(S42)

where \( \hat{\mu}_{E+} = \sum_{j=1}^{55} \hat{\mu}_j \langle E_i| \epsilon_j \rangle \) represent the transition dipole moment vectors of the exciton states \( |E+/g\rangle \) and \( |E-/g\rangle \) with \( \hat{\mu}_1 \) denoting the transition dipole moment vectors of monomers, and \( \hat{\epsilon} \) is a unit vector describing the electric field orientation of a laser pulse inducing the linear optical response of molecules. Here one needs to compute orientational average of absorption line shapes as the relative angle between \( \hat{\epsilon} \) and \( \hat{\mu}_{1,2} \) is random for isotropic samples. In simulations, one can take into account the orientational average exactly by considering \( \hat{\epsilon} \in \{ \hat{\epsilon}, \hat{\mu}_1, \hat{\mu}_2 \} \) for fixed \( \hat{\mu}_{1,2} \) and averaging the resultant optical coherence dynamics \( \text{Tr} \{ \mu e^{-i\hat{H}t} \mu_R \hat{H}_b e^{i\hat{H}t} \} \) with uniform weighting factors. This can be proved by considering the formal representation of the orientational average of absorption line shapes \( \int dR \text{Tr} \{(R_\epsilon) e^{-i\hat{H}t} (R_\mu) \hat{H}_b e^{i\hat{H}t}\} \), where \( R_\mu = \sum_{j=1}^{55} \hat{R}_j \langle \epsilon_j | \mu \rangle \langle g | h.c. \) denotes the transition dipole moment operator where monomer transition dipoles \( \hat{\mu}_j \) are randomly rotated by \( R \) in the lab frame. By applying the rotation matrix \( R \) to \( \hat{\epsilon} \) instead of \( \hat{\mu}_j \), namely \( \hat{\epsilon} \cdot (R_\mu \hat{\epsilon}) = (R_\epsilon \hat{\epsilon}) \cdot \hat{\mu}_j \), one can represent \( R^{\dagger} \hat{\epsilon} = \cos(\theta) \hat{\epsilon} + \sin(\theta) \hat{\mu}_j \) in the spherical coordinate. By substituting \( \hat{\epsilon} \) parameterized by \( (\theta, \phi) \) to \( \int dR \text{Tr} \{(R_\mu) e^{-i\hat{H}t} (R_\mu) \hat{H}_b e^{i\hat{H}t}\} \) and computing the orientational average in the spherical coordinate, one can show that the absorption line shape of isotropic samples can be computed exactly by considering three orientations, as stated above [16]. In 2D simulations, which will be discussed later, the orientational average of isotropic samples can be computed exactly by considering a few orientations, similar to the simulations of the absorption spectra [16]. The required orientations can be determined via the concept of spherical t-design which allows the average of any polynomial of the order \( t \) over a sphere to be obtained by an average over a discrete set of specific orientations [56, 57].

In Fig. S6(a), we consider a single vibrational excitation subspace where all the relative-motion modes are in their vibrational ground states or only one of the 55 modes is singly excited. In simulations, we average the dynamics of optical coherences \( \text{Tr} \{ \mu e^{-i\hat{H}t} \hat{R}_b e^{i\hat{H}t} \} \) for 1000 random realizations of site energies, and then multiply \( \exp(-\frac{1}{2} G(t)) \) induced by center-of-mass modes, as the latter does not depend on static disorder. The eigenvalues and eigenstates of the Hamiltonian \( \hat{H} \) determine, respectively, the transition energy and dipole strength of vibronic eigenstates. The eigenvalue spectrum depends on the random realizations of site energies, inducing ensemble dephasing of optical coherences. Fig. S6(a) shows that the prediction of the absorption line shape based on the reduced model, shown in red, quantitatively reproduces the numerically exact absorption line shape of the SP, shown in black.

To understand the origin of the three-peak structure in absorption spectrum, we investigate four vibronic eigenstates in the absence of static disorder, including state A appearing at 900 nm, state B at 817 nm, and states C and D at 780 nm, highlighted in Fig. S6(a). The state A is well approximated by \( |E_-, 0\rangle \) where \( |E_0\rangle \) is the lower-energy exciton state and \( |0\rangle \) denotes the global vibrational ground state. It is notable that the vibronic mixing between \( |E_-, 0\rangle \) and \( |E_+, 1_k\rangle \), which can be induced by off-diagonal vibronic couplings, is negligible due to the large energy-gap between \( |E_-, 0\rangle \) and \( |E_+, 1_k\rangle \), where \( |1_k\rangle \) denotes a composite vibrational state with a single vibrational excitation in the \( k \)-th mode. For all the eigenstates of \( \hat{H} \), the fidelity with \( |E_-, 0\rangle \) is shown in green dots, demonstrating that the mixing with \( |E_-, 0\rangle \) is negligible for all the eigenstates except for A. The state B is one of the vibronic eigenstates contributing to the broad phonon sideband in the 800 – 850 nm region. The state B is mainly described by \( |E_-, 1_{1008 \text{ cm}^{-1}}\rangle \) with a single vibrational excitation in the 1008 cm\(^{-1}\) mode, which is weakly mixed with quasi-resonant \( |E_+, 0\rangle \) and multiple \( |E_-, 1_k\rangle \) states mediated by off-diagonal vibronic couplings. The states C and D, on the other hand, have relatively
large fidelity with $|E_+,0\rangle$, as shown in blue dots. Both the states C and D show a strong mixing between $|E_+,0\rangle$ and $|E_+,1_{453\text{ cm}^{-1}}\rangle$, and relatively weak mixing with multiple $|E_-,1_k\rangle$ states. It is notable that the mixing between $|E_+,0\rangle$ and $|E_+,1_{453\text{ cm}^{-1}}\rangle$ cannot be directly created by the off-diagonal vibronic couplings proportional to $|E_+\rangle\langle E_-|$ or $|E_-\rangle\langle E_+|$, hinting that it is due to the higher-order interactions mediated by $|E_-,1_k\rangle$ states.

To clarify the origin of the strong mixing between $|E_+,0\rangle$ and $|E_+,1_{453\text{ cm}^{-1}}\rangle$ in the states C and D, in Fig. S6(b) we turn off the higher-order interaction terms in Eq. (S11) by neglecting the couplings proportional to $|E_+,1_k\rangle\langle E_-,1_l|$ with $k \neq l$, which induces the transition between exciton states and, at the same time, the exchange of a single vibrational excitation between different modes $k$ and $l$. Note that the absorption line shapes computed with and without the higher-order interaction terms, shown in Fig. S7(a) and (b), respectively, are almost identical (see the inset in Fig. S6(b)), implying that the higher-order terms are weak couplings. It is also notable that when the higher-order terms are removed from the Hamiltonian $H$, the states A and B are almost unchanged, but the mixing between $|E_+,0\rangle$ and $|E_+,1_{453\text{ cm}^{-1}}\rangle$ is completely suppressed in the states C and D. These results can be rationalised as follows. In the absence of the higher-order interaction terms, the energy-level of higher-energy exciton state $|E_+,0\rangle$ is increased by 447 cm$^{-1}$ due to the vibronic mixing with excited $|E_-,1_k\rangle$ states, leading to the state C in Fig. S6(b), while the vibronic mixing of a vibrationally hot state $|E_+,1_{453\text{ cm}^{-1}}\rangle$ with $|E_-,0\rangle$ is negligible due to the relatively large energy-gap between them, leading to the state D in Fig. S6(b) whose energy-level is almost identical to that of $|E_+,1_{453\text{ cm}^{-1}}\rangle$. This leads to small energy-gap of around 6 cm$^{-1}$ between states C and D, which can be strongly mixed even by weak higher-order couplings, as shown in Fig. S6(a). However, the energy-level shifts of the states C and D by the higher-order interaction terms are negligible due to the weak coupling strength, which makes the resulting absorption line shapes insensitive to the presence of the higher-order couplings.

Since the vibronic mixing induced by a weak coupling is likely to be sensitive to energy-level fluctuations induced by environments, such as protein motions, we performed numerically exact simulations of excitonic coherence dynamics of the SP and controlled the vibrational damping rate of the 453 cm$^{-1}$ modes in order to check if there is a strong vibronic mixing between excitons and 453 cm$^{-1}$ modes. It is found that the lifetime of the 453 cm$^{-1}$ modes does not affect excitonic coherence dynamics (not shown here), implying that the vibronic mixing with the 453 cm$^{-1}$ modes is negligible under actual environments. Therefore we will ignore the higher-order interaction terms, $|E_+,1_k\rangle\langle E_-,1_l|$ with $k \neq l$, in the following approximate simulations of absorption and 2D spectra to avoid weak coupling effects.

Fig. S6(c) shows absorption spectra in the absence of off-diagonal vibronic couplings. It is notable that the absorption line shape computed by the reduced vibronic model is similar to the results obtained by second order cumulant expansion (see Fig. 3(b) in the main text), where the energy-gap between zero-phonon lines is close to the bare excitonic splitting $\Delta \approx 1300$ cm$^{-1}$.

Fig. S6(d) shows absorption line shapes computed by the reduced vibronic model within double vibrational excitation subspace, which includes doubly excited vibrational states where only the $k$-th mode is doubly excited, $|2_k\rangle$, or two different modes $k$ and $l$ are singly excited at the same time, $|1_k,1_l\rangle$. We note that the inclusion of doubly excited vibrational states in simulations does not qualitatively change absorption line shapes, but improves the quantitative agreement between approximate and numerically exact absorption line shapes, shown in red and black, respectively.

IX. REDUCED VIBRONIC MODEL FOR 2D SIMULATION

Here we investigate the nonlinear optical response of the SP based on the reduced vibronic model in section VIII, which can quantitatively reproduce numerically exact absorption spectra of the SP. Contrary to the dynamics of optical coherence of the SP, which determines absorption line shape and decays within 200 fs, 2D optical responses are governed by electronic-vibrational dynamics on a picosecond time scale and therefore the noise induced by relative motion modes plays an essential role. Here we will consider the noise caused by vibronic coupling to the low-frequency part of the phonon spectral density of the SP, including protein motions, and the vibrational damping of 55 intra-pigment modes. The noise will be approximately described by a Lindblad equation where decoherence rates are computed based on a microscopic Hamiltonian. The influence of center-of-mass modes on 2D spectra will be considered analytically [78], as is the case of absorption simulations. We will compute rephasing 2D spectra of the SP based on the reduced vibronic model in order to demonstrate that oscillatory 2D signals are a mixture of $\Delta^* \approx 1800$ cm$^{-1}$ frequency component induced by vibronic coherence $|\psi_+\rangle\langle \psi_-|$, and multiple components with frequencies $\omega_k \lesssim 1600$ cm$^{-1}$ originating from vibrational coherences of the 55 intra-pigment modes.

As schematically shown in Fig. S7(a), we will consider two noise-inducing processes. Firstly, the vibronic coupling between electronic states and low-frequency part $J_l(\omega)$ of the phonon spectral density of the SP induces electronic dephasing. In the displaced vibrational basis defined by $U = |g\rangle\langle g| + |E_+\rangle\langle E_+| \prod_{k=1}^{55} D_k \left( \sqrt{\frac{g}{2}} A_{++} \right) + \ldots$, the 2D optical response can be written as $\text{Tr}(U \rho U^\dagger H)$.
The electronic dephasing is described by the interaction Hamiltonian in the form

$$\hat{H}_{ed} = U H_{ed} U^\dagger = U \left( \sum_{i=1}^{2} (-1)^{i-1} |\varepsilon_i\rangle \langle \varepsilon_i| \right) U^\dagger \sum_l f_l (b_l + b_l^\dagger),$$

(S43)

where $b_l$ represent the relative motions associated with low-frequency phonons including log-normal and marker mode. Secondly, the vibrational damping of the relative motions of high-frequency intra-pigment modes is described by the coupling of each mode to an independent secondary bath, modelled by

$$\hat{H}_{vd} = U H_{vd} U^\dagger = \sum_{k=1}^{55} (b_k + b_k^\dagger) \sum_l g_{k,l} (c_{k,l}^\dagger + c_{k,l}),$$

(S44)

where $c_{k,l}^\dagger$ denote the bath modes inducing the vibrational damping of the $k$-th intra-pigment mode $b_k$. The phonon spectral density $J_{vd,k}(\omega)$ of the $k$-th secondary bath, characterized by $g_{k,l}$, determines the damping rate of the $k$-th intra-pigment mode. We consider a Lorentzian spectral density centered at the vibrational frequency $\omega_k$ of the intra-pigment mode, so that the coupling strength between intra-pigment mode $b_k$ and environmental modes $c_{k,l}$ is maximized when environmental mode frequencies are resonant with $\omega_k$. The width of the Lorentzian spectral density is taken to be $(50 \text{ fs})^{-1}$, so that the corresponding bath correlation function quickly decays compared to the picosecond timescale of mode damping. It is found that simulated results are not sensitive to the width of the Lorentzian spectral density when it is broader than $(50 \text{ fs})^{-1}$. The amplitude of the Lorentzian spectral density is determined in such a way that the damping rate of the $k$-th mode is taken to be $(1 \text{ ps})^{-1}$ when the mode is decoupled from electronic states, resulting in a single mode under damping induced by a secondary bath.

To construct a Lindblad equation, the interaction Hamiltonians $\hat{H}_{ed}$ and $\hat{H}_{vd}$ are expressed as

$$\hat{H}_{ed} = A_{ed} \sum_l f_l (b_l^\dagger + b_l),$$

(S45)

$$\hat{H}_{vd} = \sum_{k=1}^{55} A_{vd,k} \sum_l g_{k,l} (c_{k,l}^\dagger + c_{k,l}),$$

(S46)

where $A_{ed} = U \left( \sum_{i=1}^{2} (-1)^{i-1} |\varepsilon_i\rangle \langle \varepsilon_i| \right) U^\dagger$ and $A_{vd,k} = b_k^\dagger + b_k$. We represent the system operators $A_{ed}$ and $A_{vd,k}$ in the eigenbasis of the vibronic system Hamiltonian, $\hat{H} |\psi_j\rangle = \varepsilon_j |\psi_j\rangle$, and define $A_\alpha(\omega) = \sum_\epsilon \Pi(\epsilon) A_\alpha(\epsilon')$ for each system operator where $\Pi(\epsilon)$ describes the projection onto the subspace belonging to the eigenvalue $\epsilon$. The noise is described by dissipators in a Lindblad form [74]

$$\frac{dho(t)}{dt} = -i [\hat{H}, \rho(t)] + \sum_\alpha \sum_\omega \gamma_\alpha(\omega) \left( A_\alpha(\omega) \rho(t) A_\alpha^\dagger(\omega) - \frac{1}{2} \{ A_\alpha^\dagger(\omega) A_\alpha(\omega), \rho(t) \} \right),$$

(S47)

where decoherence rates are given by $\gamma_\alpha(\omega) = 2\pi J_\alpha(\omega) n(\omega) (n(\omega) + 1)$ with $n(\omega) = (\exp(\hbar \omega/k_B T) - 1)^{-1}$, which is characterized by the corresponding spectral density, namely $J_\alpha(\omega) = J_{ed}(\omega)$ or $J_\alpha(\omega) = J_{vd,k}(\omega)$ for $k \in \{1, 2, 3, \ldots, 55\}$, and temperature $T$.

Fig. 5 shows absorption line shapes of SP computed by HEOM and reduced vibronic models without and with noise, shown in black, red and blue, respectively. Note that the reduced model results with noise are similar to those without noise. This implies that absorption line widths are dominated by inhomogeneous broadening and dephasing induced by center-of-mass modes, and the decoherence rates of the Lindblad equation are negligible within the lifetime of optical coherences, which is approximately $\sim 200 \text{ fs}$.

In 2D electronic spectroscopy, a molecular sample is perturbed by three excitation pulses with controlled time delays, which generates third-order optical responses propagating along several phase-matched directions [76, 77]. Here we will focus on rephasing 2D signals, which can be measured at a particular phase-matched direction [76, 77]. The time delay between first and second pulses enables one to resolve excitation frequencies. The time interval between second and third pulses, called waiting times, allows for monitoring molecular dynamics within electronic ground and excited state manifolds. In simulations, we will consider ground state bleaching (GSB) and stimulated emission (SE) pathways, describing electronic ground and excited state dynamics, respectively [78]. This includes purely vibrational ground state coherences and the excited state coherences between vibronic eigenstates, which lead to oscillatory 2D signals [40, 88, 89].

Fig. 5 shows rephasing 2D spectra at waiting time $T = 0$ in the presence of inhomogeneous broadening. The 2D line shape, shown as a function of excitation and detection frequencies, is dominated by a diagonal peak excited
FIG. S7. (a) Schematic representation of a vibronic model in the presence of noise. The vibronic system is characterized by the interaction between electronic states of a dimer and 55 oscillators associated with the relative motions of intra-pigment modes. The coupling between electronic states and low-frequency phonons induces electronic dephasing. Each oscillator is coupled to an independent secondary bath, causing vibrational damping. (b) Absorption spectra of SP computed by HEOM and reduced vibronic models without and with noise are shown in black, red and blue, respectively, where double vibrational excitation subspace is considered. (c) Rephasing 2D spectra at waiting time $T = 0$. (d) 2D signals at a cross-peak R12, marked in (c), and corresponding Fourier transformation where total, ground and excited state signals are shown in black, red and blue, respectively. Note that excited state signals as well as total 2D signals, namely the sum of ground and excited state signals, are dominated by vibronic coherence $|\psi^-\rangle\langle \psi^-|$, leading to 2D oscillations at $\Delta' \approx 1800$ cm$^{-1}$. (e) 2D signals at a cross-peak R21, marked in (c). Note that excited state signals are dominated by 2D oscillations at $\Delta' \approx 1800$ cm$^{-1}$, while ground state coherences are dominated by multiple components with frequencies $\omega_k \lesssim 1600$ cm$^{-1}$, which are lower than $\Delta' \approx 1800$ cm$^{-1}$. The offset values of transients and FTs are shifted for better visibility.

and detected at both $\sim 900$ nm. The 2D peak location coincides with the transition energy of the main absorption peak A1 marked in Fig. S7(b). To investigate the excited state coherence between vibronic eigenstates $|\psi^-\rangle$ and $|\psi^+\rangle$, inducing absorption peaks A1 and A2, respectively, we will focus on cross peaks R12 and R21 highlighted in Fig. S7(c). R12 (R21) is excited at the transition energy of A1 (A2) and then detected at that of A2 (A1).

Fig. S7(d) shows the transient of R12 and its Fourier transformation visualizing frequencies involved in the transient. It is notable that excited state signals, shown in blue, are dominated by oscillations at $\Delta' \approx 1800$ cm$^{-1}$ induced by the vibronic coherence between $|\psi^-\rangle$ and $|\psi^+\rangle$, which are brighter than the other vibronic eigenstates due to excitonic characters. This is contrary to the ground state signals shown in red, which are dominated by low-frequency oscillations at $\sim 125$ cm$^{-1}$ close to the vibrational frequency of the marker mode. This makes the total 2D signals, namely the sum of ground and excited state signals, dominated by the excited state coherence $|\psi^+\rangle\langle \psi^-|$ and the vibrational coherences induced by the marker mode, leading to $\Delta' \approx 1800$ cm$^{-1}$ and $\omega_{\text{sp}} = 125$ cm$^{-1}$ oscillations, respectively.

Fig. S7(e) shows the transient of the other cross-peak R21 and its Fourier transformation. Contrary to the case of R12, the oscillation amplitudes of ground state signals, shown in red, are comparable to those of excited state signals at R21. We note that the ground state oscillations include multiple components with frequencies lower than $\sim 1600$ cm$^{-1}$, as the vibrational frequencies $\omega_k$ of underdamped intra-pigment modes considered in simulations are lower than $\sim 1600$ cm$^{-1}$ and the Huang-Rhys factors of these modes are of the order of 0.01, which are too small to induce ground state coherences at double vibrational frequencies $\omega_k + \omega_k'$. Note that the excited state signals at R21 include oscillatory components at $\Delta' \approx 1800$ cm$^{-1}$, which are not present in the ground state signals.

Our 2D results demonstrate that long-lived 2D oscillations can be dominated by vibronic coherences even if the frequency of 2D oscillations is not near-resonant with the vibrational frequencies of underdamped modes, namely $\omega_k \lesssim 1600$ cm$^{-1} \ll \Delta' \approx 1800$ cm$^{-1}$. This implies that even if experimentally observed frequency of 2D oscillations is not matched to vibrational frequencies $\omega_k$ of intra-pigment modes observed in monomer experiments, there is
possibility that the 2D oscillations originate from vibronic coherences induced by multi-mode mixing, rather than from purely electronic coherences [90]. In this work, we do not aim to compare our simulated results with experimental 2D spectra, as it requires absorption and 2D simulations of bacterial reaction centres, including the SP, and re-estimation of electronic parameters, as demonstrated for WSCP.

X. DESCRIPTION OF MULTI-MODE VIBRONIC EFFECTS IN SITE BASIS

In the main text, the influence of high-frequency intra-pigment modes on absorption line shape of WSCP is explained based on vibronic Hamiltonian represented in exciton basis (see section I of the SI). Here we provide alternative explanation based on vibronic Hamiltonian in site basis. We show that a local vibronic coupling to high-frequency intra-pigment modes induces dipole strength redistributions amongst 0-0 and 0-n transitions with \( n \geq 1 \) (phonon sideband) of each monomer, leading to Franck-Condon factors. This makes the effective coupling strength \( V_{00} = V \exp\left(-\frac{i}{2} \sum_k (s_{1,k} + s_{2,k})\right) \) between 0-0 transitions of sites 1 and 2 smaller than bare electronic coupling strength \( V \), where \( s_{i,k} \) denote the Huang-Rhys factors of intra-pigment modes of site \( i \). We demonstrate that for WSCP where the energy-gap \( \Delta' \approx 2V_{00} \) between 0-0 transitions is sufficiently smaller than vibrational frequencies of intra-pigment modes, a multi-mode vibronic mixing amongst 0-0 and 0-n transitions with \( n \geq 1 \), occurring mediated by electronic coupling \( V \), does not significantly modify the energy-gap between absorption peaks in zero-phonon line region, but redistributes the transition dipole strengths of zero-phonon lines and phonon sideband. This makes the energy-gap \( \Delta' \approx 2V_{00} \) between absorption peaks in zero-phonon line region smaller than bare excitonic splitting \( \Delta \approx 2V \), which is consistent with the explanation provided in the main text. Contrary to the case of WSCP, when a strong multi-mode vibronic mixing of 0-0 and 0-n transitions occurs, the energy-gap \( \Delta' \) between absorption peaks in zero-phonon line region can be significantly different from the energy-gap estimated based on the effective coupling \( V_{00} \) between 0-0 transitions, and \( \Delta' \) can become even larger than bare excitonic splitting \( \Delta \), as demonstrated for SP. In addition, using reduced models where vibronic coupling to low-frequency protein motions is approximately described by second order perturbation theory, we show that the low-frequency protein modes whose frequencies are smaller than \( \Delta' \approx 2V_{00} \) increase the energy-gap \( \Delta'' \) between absorption peaks, mediated by Lamb shift, making \( \Delta'' \) larger than \( \Delta' \approx 2V_{00} \). This is in line with the explanation provided in the main text where low-frequency vibrational modes increase the energy-gap between exciton states. These results demonstrate that the effective coupling strength between 0-0 transitions of different pigments is reduced by the local vibronic coupling to intra-pigment modes, and the energy-gap between absorption peaks can be significantly changed by the multi-mode vibronic mixing of 0-0 and 0-1 transitions induced by high-frequency intra-pigment modes and low-frequency protein motions.

A. Line shape theory with an effective coupling between 0-0 transitions

We consider polaron transformation in site basis where the total Hamiltonian \( H = H_e + H_v + H_{e-v} \) in section I is transformed by a unitary operator \( U = |g\rangle\langle g| + \sum_{i=1}^{2} \sum_{k=1}^{55} |\varepsilon_i\rangle\langle \varepsilon_i| D_i \) with \( D_i = \exp(\sum_{k=1}^{55} \sqrt{s_k(b^\dagger_{i,k} - b_{i,k})}) \) where \( b_{i,k} \) denote intra-pigment vibrational modes locally coupled to site \( i \). We decompose the transformed Hamiltonian into two parts \( UHU^\dagger = H_0 + H_I \) where \( H_0 \) is a diagonalised Hamiltonian in site basis

\[
H_0 = \sum_{i=1}^{2} (\varepsilon_i - \lambda_i) |\varepsilon_i\rangle\langle \varepsilon_i| + \sum_{i=1}^{2} \sum_{k=1}^{55} \omega_k b^\dagger_{i,k} b_{i,k},
\]

with \( \lambda_i = \sum_{k=1}^{55} \omega_k s_k \). The eigenstates of \( H_0 \) are characterised by the number of vibrational excitations of the intra-pigment modes. In simulations, we consider double vibrational excitation subspace spanned by \( |\varepsilon_i, 0\rangle \) where all the intra-pigment modes are in their ground states, \( |\varepsilon_i, 1_j, k\rangle \) where only the \( b_{j,k} \) mode is singly excited, \( |\varepsilon_i, 2_j, k\rangle \) where only the \( b_{j,k} \) mode is doubly excited, and \( |\varepsilon_i, 1_j, k, 1_{j', k'}\rangle \) where different \( b_{j,k} \) and \( b_{j',k'} \) modes are singly excited at the same time while all the other modes are in their ground states. The transition dipole strengths of the eigenstates of \( H_0 \) are determined by the polaron transformed transition dipole moment operator

\[
U_\mu U^\dagger = \sum_{i=1}^{2} (\hat{\varepsilon} \cdot \vec{\mu}_i) |\varepsilon_i\rangle\langle g| \exp\left(\sum_{k=1}^{55} \sqrt{s_k(b^\dagger_{i,k} - b_{i,k})}\right) + h.c.,
\]

where \( \hat{\varepsilon} \) denotes the orientation of polarisation of electric field inducing absorption, \( \vec{\mu}_i \) the transition dipole moment vector of monomer \( i \), and \( |g\rangle \) electronic ground state. The unitary displacement operator \( \exp(\sum_{k=1}^{55} \sqrt{s_k(b^\dagger_{i,k} - b_{i,k})}) \) describes dipole strength redistributions amongst the eigenstates of \( H_0 \), leading to the Franck-Condon factors of
uncoupled monomers. On the other hand, $H_I$ describes the interaction between the eigenstates of $H_0$ mediated by electronic coupling $V$

$$H_I = V|\varepsilon_1\rangle\langle\varepsilon_2| \exp\left(\sum_{k=1}^{55} \sqrt{s_k}((b_{1,k}^\dagger - b_{1,k}) - (b_{2,k}^\dagger - b_{1,k}))\right) + \text{h.c.},$$  \hspace{1cm} (S50)

which includes an effective coupling $V_{00} = V \exp(-\sum_{k=1}^{55} s_k)$ between $|\varepsilon_1, 0\rangle$ and $|\varepsilon_2, 0\rangle$ states. For WSCP, the total Huang-Rhys factor of 55 intra-pigment modes is $\sum_{k=1}^{55} s_k \approx 0.68$ (see Table [I]), leading to $V_{00} \approx 0.508V$. $H_I$ also contains the couplings between vibrationally excited eigenstates of $H_0$, such as the coupling between $|\varepsilon_1, 1_i\rangle$ and $|\varepsilon_2, 1_i\rangle$ where vibrational states are identical, and that between $|\varepsilon_1, 0\rangle$ and $|\varepsilon_2, 1_i\rangle$ where the numbers of vibrational excitations are different.

To investigate how absorption line shape of WSCP is affected by $H_I$, we start with a minimal model where the initial state is approximated by $|g, 0\rangle$, where all the intra-pigment modes are in their vibrational ground states, and all the couplings in $H_I$ are neglected except for $V_{00}(|\varepsilon_1, 0\rangle\langle\varepsilon_2, 0| + \text{h.c.})$. In this case, the 0-0 transitions from global ground state $|g, 0\rangle$ to electronically excited states $|\varepsilon_i, 0\rangle$ are mixed by the effective coupling $V_{00}$, while the other optical transitions from $|g, 0\rangle$ to vibrationally excited eigenstates of $H_0$ are simply characterised by the Franck-Condon factors of monomers. The broadening of optical transitions is induced by static disorder in site energies and the coupling to low-frequency protein motions described by

$$UH_{ed}U^\dagger = \sum_{i=1}^{2} |\varepsilon_i\rangle\langle\varepsilon_i| \sum_l f_l(b_{i,l} + b_{i,l}^\dagger)$$

$$= \sum_{i=1}^{2} \left(|\varepsilon_i, 0\rangle\langle\varepsilon_i, 0| + \sum_{j=1}^{55} \sum_{k=1}^{55} |\varepsilon_i, 1_j\rangle\langle\varepsilon_i, 1_j| + \sum_{j=1}^{55} \sum_{k=1}^{55} |\varepsilon_i, 2_j\rangle\langle\varepsilon_i, 2_j| + \cdots \right) \sum_l f_l(b_{i,l} + b_{i,l}^\dagger),$$  \hspace{1cm} (S51)

(S52)

where $b_{i,l}$ describe protein modes locally coupled to site $i$, characterised by three log-normal distribution functions of WSCP (see section [V]). For vibrationally excited eigenstates of $H_0$, such as $|\varepsilon_i, 1_j\rangle$, which are assumed to be decoupled from the other eigenstates of $H_0$, the homogeneous broadening of associated 0-n transitions induced by low-frequency protein motions can be computed non-perturbatively by using the line shape function obtained from second order cumulant expansion

$$\sum_\xi |\tilde{\mu}_\xi|^2 \int_{-\infty}^{\infty} dt \exp(i(\omega - \tilde{\omega}_\xi + \lambda_\xi)t + G(t) - G(0) - \gamma_{pd}|t|),$$  \hspace{1cm} (S53)

where $\tilde{\omega}_\xi$ denote the eigenvalues of vibrationally excited eigenstates of $H_0$, $|\tilde{\mu}_\xi|^2$ associated transition dipole strengths determined by the Franck-Condon factors of monomers, and $\gamma_{pd}$ an empirical pure dephasing rate. $G(t)$ is characterised by the phonon spectral density $J_l(\omega) = \sum_l f_l^2 \delta(\omega - \omega_l)$ of low-frequency protein modes with frequencies $\omega_l$

$$G(t) = \int_0^\infty d\omega \omega^{-2} \left(J_l(\omega)(n(\omega) + 1)e^{-i\omega t} + J_l(\omega)n(\omega)e^{i\omega t}\right),$$  \hspace{1cm} (S54)

where $n(\omega) = (\exp(\omega/k_B T) - 1)^{-1}$ and $\lambda_l = \int_0^\infty d\omega J_l(\omega)/\omega$ is the reorganisation energy of protein modes.

On the other hand, the effective coupling $V_{00}$ between $|\varepsilon_1, 0\rangle$ and $|\varepsilon_2, 0\rangle$ states leads to delocalised eigenstates over two pigments, denoted by $|E_{0, +}\rangle$ and $|E_{0, -}\rangle$, and their coupling to low-frequency protein motions is described by

$$\sum_{i=1}^{2} |\varepsilon_i, 0\rangle\langle\varepsilon_i, 0| \sum_l f_l(b_{i,l} + b_{i,l}^\dagger) = \sum_{j,k=\pm} |E_{0,j}\rangle\langle E_{0,k}| \sum_{i=1}^{2} |\varepsilon_i, 0\rangle\langle\varepsilon_i, 0| \sum_l f_l(b_{i,l} + b_{i,l}^\dagger).$$  \hspace{1cm} (S55)

When the off-diagonal couplings proportional to $|E_{0,j}\rangle\langle E_{0,k}|$ with $j \neq k$ are treated perturbatively by using Markov and secular approximations, the second order cumulant expansion enables one to approximately describe the homogeneous broadening of 0-0 transitions from $|g, 0\rangle$ to $|E_{0, +}\rangle$ by a line shape function in the form $[66, 70]$

$$\sum_{j=\pm} |\tilde{\mu}_{0,j}|^2 \int_{-\infty}^{\infty} dt \exp \left(i(\omega - \tilde{\omega}_{0,j} - \tilde{\omega}_{LS,j})t + G_j(t) - G_j(0) - \frac{1}{2}\gamma_{j \rightarrow k} + \gamma_{pd}|t| \right).$$  \hspace{1cm} (S56)

Here $\tilde{\omega}_{0,j}$ is the eigenvalue of $|E_{0,j}\rangle$ state, $|\tilde{\mu}_{0,j}|^2$ associated transition dipole strength, $G_j(t) = \sum_{i=1}^{2} |\langle\varepsilon_i, 0|E_{0,j}\rangle|^4 G(t)$, and $\gamma_{pd}$ the empirical pure dephasing rate. We note that within the Redfield formalism, the log-normal distribution
functions of WSCP, describing the coupling to protein motions, do not lead to pure dephasing noise, but induce the relaxation from $|E_{0,j}\rangle$ to $|E_{0,k}\rangle$ with an incoherent population transfer rate given by

$$\gamma_{j \to k} = 2\pi \sum_{i=1}^{2} |\langle E_{0,j}|\epsilon_{i}, 0\rangle\langle \epsilon_{i}, 0|E_{0,k}\rangle|^{2} (J_{i}(\Delta \omega_{jk})(n(\Delta \omega_{jk}) + 1) + J_{i}(-\Delta \omega_{jk})n(-\Delta \omega_{jk})),$$  \hfill (S57)

where $\Delta \omega_{jk} = \omega_{0,j} - \omega_{0,k}$ is the energy-gap between $|E_{0,j}\rangle$ and $|E_{0,k}\rangle$ states, satisfying $|\Delta \omega_{jk}| = \Delta' = \sqrt{(\epsilon_{1} - \epsilon_{2})^{2} + 4V_{00}^{2}}$, and $J_{i}(\omega) = 0$ for $\omega < 0$. Importantly, the Lamb shift $\tilde{\omega}_{LS,j}$ in Eq. (S56) describes the energy-level shift of $|E_{0,j}\rangle$ state due to the interaction with protein motions

$$\tilde{\omega}_{LS,j} = -\frac{2}{\omega} \sum_{i=1}^{2} |\langle E_{0,j}|\epsilon_{i}, 0\rangle\langle \epsilon_{i}, 0|E_{0,k}\rangle|^{2} \int_{-\infty}^{\infty} d\omega \frac{J_{i}(\omega)(n(\omega) + 1) + J_{i}(-\omega)n(-\omega)}{\Delta \omega_{jk} - \omega},$$  \hfill (S58)

where $P$ denotes the Cauchy principal value. This implies that the energy-gap between $|E_{0,+}\rangle$ and $|E_{0,-}\rangle$ states is shifted by low-frequency protein motions from $\Delta' = \sqrt{(\epsilon_{1} - \epsilon_{2})^{2} + 4V_{00}^{2}}$ to

$$\Delta'' = (\tilde{\omega}_{0,+} + \tilde{\omega}_{LS,+}) - (\tilde{\omega}_{0,-} + \tilde{\omega}_{LS,-})$$  \hfill (S59)

$$= \Delta' + \sum_{i=1}^{2} |\langle E_{0,+}|\epsilon_{i}, 0\rangle\langle \epsilon_{i}, 0|E_{0,-}\rangle|^{2} \int_{-\infty}^{\infty} d\omega \frac{J_{i}(\omega)(n(\omega) + 1) + J_{i}(-\omega)n(-\omega)}{\Delta' - \omega}$$

$$- \sum_{i=1}^{2} |\langle E_{0,+}|\epsilon_{i}, 0\rangle\langle \epsilon_{i}, 0|E_{0,-}\rangle|^{2} \int_{-\infty}^{\infty} d\omega \frac{J_{i}(\omega)(n(\omega) + 1) + J_{i}(-\omega)n(-\omega)}{\Delta'' - \omega},$$  \hfill (S60)

where $\sum_{i=1}^{2} |\langle E_{0,+}|\epsilon_{i}, 0\rangle\langle \epsilon_{i}, 0|E_{0,-}\rangle|^{2} \leq 0.5$ with the equality satisfied when site energies are identical, $\epsilon_{1} = \epsilon_{2}$, where $|E_{0,+}\rangle$ and $|E_{0,-}\rangle$ states are fully delocalised over two pigments. This is similar to the energy-level shift induced by high-frequency intra-pigment modes, which requires delocalisation of exciton states (see the main text).

In Fig. (SSa), approximate absorption line shapes computed by cumulant expansion within single vibrational excitation subspace are displayed in solid lines for several values of the empirical pure dephasing rate $\gamma_{pd}$. Numerically exact absorption line shape of WSCP is shown in a black dashed line for a comparison with approximate results. It is notable that absorption above 580 nm is negligible in approximate absorption line shapes, contrary to numerically exact results, implying that doubly excited vibrational states contribute to the high-energy part of the absorption spectra of WSCP. In Fig. (SSb), approximate absorption line shapes computed within double vibrational excitation subspace are displayed, which are better matched to numerically exact results above 580 nm. It is notable that in the absence of the empirical pure dephasing rate, $\gamma_{pd} = 0$, approximate absorption line shapes shown in red are not well matched to numerically exact results shown in black. The agreement between approximate and exact results can be improved by considering a non-zero empirical pure dephasing rate. Approximate simulated results in zero-phonon line region below 650 nm are well matched to numerically exact results when $\gamma_{pd} \approx (150 \text{fs})^{-1}$, as shown in green, although the transition dipole strength of phonon sideband around 600 nm is underestimated.

In Fig. (SSc), we consider the influence of the Lamb shift induced by protein motions on absorption line shapes. For the optimal pure dephasing rate $\gamma_{pd} = (150 \text{fs})^{-1}$, approximate absorption line shapes in the presence and absence of the Lamb shift are shown in green solid and yellow dashed lines, respectively. It is notable that when site energies are optimised in such a way that the main absorption peak is located at 655.5 nm, the Lamb shift enhances absorption below 665 nm, implying that the energy-gap between 0-0 transitions is increased by the coupling to protein motions. To clarify the energy-level shift of 0-0 transitions induced by protein motions, we show the transition dipole strengths of the eigenstates of $H_{0} + V_{00}(|\epsilon_{1}, 0\rangle\langle \epsilon_{2}, 0| + h.c.)$ as a function of transition energy in the presence and absence of the Lamb shift (see green circles and yellow triangles, respectively). When the Lamb shift is not included in simulations, the energy-gap between 0-0 transitions is given by $\Delta' = 2V_{00} \approx 142 \text{ cm}^{-1}$ for $V = 140 \text{ cm}^{-1}$ (see yellow triangles). When the Lamb shift is considered, the energy-gap between 0-0 transitions is increased to $\Delta'' \approx 200 \text{ cm}^{-1}$ (see green circles).

To identify the origin of the energy-level shift $\Delta'' - \Delta'$ induced by low-frequency protein motions, we show $g(\Delta') = \frac{1}{2} P \int_{-\infty}^{\infty} d\omega J_{i}(\omega)(n(\omega) + 1) + J_{i}(-\omega)n(-\omega))/(\Delta' - \omega)$ as a function of $\Delta'$ in Fig. (SSd). As shown in Eq. (S58), when site energies are identical, $\epsilon_{1} = \epsilon_{2}$, the energy-levels of $|E_{0,+}\rangle$ and $|E_{0,-}\rangle$ are given by $\tilde{\omega}_{0,+} - \lambda_{i}/2 + g(\Delta')$ and $\tilde{\omega}_{0,-} - \lambda_{i}/2 + g(-\Delta')$, respectively. This leads to $\Delta'' = (\tilde{\omega}_{0,+} - \tilde{\omega}_{0,-}) + g(\Delta') - g(-\Delta') = \Delta' + g(\Delta') - g(-\Delta')$. In Fig. (SSc), the energy-level shift $\Delta'' - \Delta' = g(\Delta') - g(-\Delta')$ induced by protein modes is shown as a function of $\Delta'$ in black, and the phonon spectral density $J_{i}(\omega)$ describing the coupling to protein motions is shown in red. It is notable that $\Delta'' - \Delta' > 0$ when the energy-gap $\Delta'$ between 0-0 transitions is larger than the vibrational frequencies of protein
FIG. S8. (a) Numerically exact absorption spectra of WSCP at $T = 77$ K shown in a black dashed line, and approximate absorption line shapes computed by second order cumulant expansion within single vibrational excitation subspace. An empirical pure dephasing rate is taken to be $\gamma_{pd} \in \{0, (200 \text{ fs})^{-1}, (150 \text{ fs})^{-1}, (100 \text{ fs})^{-1}\}$, corresponding to red, orange, green, blue solid lines, respectively. (b) Approximate absorption line shapes computed by cumulant expansion within double vibrational excitation subspace. (c) For $\gamma_{pd} = (150 \text{ fs})^{-1}$, approximate absorption line shapes in the presence and absence of the Lamb shift induced by low-frequency protein motions are shown in green solid and yellow dashed lines, respectively. The transition dipole strengths of the eigenstates of $H_0 + V_{00}(|\varepsilon_1, 0\rangle \langle \varepsilon_2, 0| + h.c.)$ in the presence and absence of the Lamb shift are shown in green circles and yellow triangles, respectively, as a function of transition energy. (d) The Lamb shift induced by the coupling to protein motions of WSCP. (e) The phonon spectral density of low-frequency protein modes, modelled by three log-normal distribution functions, shown in red, and associated energy-level shift $\Delta'' - \Delta'$ shown in black.

modes, which is the case of WSCP where $\Delta' = 2V_{00} \approx 142 \text{ cm}^{-1}$. When $\Delta'$ is smaller than the vibrational frequencies of protein modes, the energy-gap between 0-0 transitions can be decreased by the Lamb shift, leading to $\Delta'' - \Delta' < 0$. These features are similar to the energy-level shift induced by high-frequency intra-pigment modes where vibronic splitting $\Delta'$ becomes smaller (larger) than bare excitonic splitting $\Delta$ when $\Delta$ is smaller (larger) than the vibrational frequencies of intra-pigment modes (see the main text).

So far we have assumed that all the intra-pigment modes are initially in their vibrational ground states. We now consider a thermal state of the intra-pigment modes at temperature $T = 77$ K. In Fig. S9(a), approximate absorption line shape computed by the second order cumulant expansion is shown in red where the empirical pure dephasing rate is taken to be $\gamma_{pd} = 0$. The contributions of 0-$n$, 1-$n$ and 2-$n$ transitions to the total absorption line shape are shown in blue solid, blue dashed and blue dotted lines, respectively, where the optical transitions from electronic ground state with $m$ vibrational excitations to electronic excited states with $n$ vibrational excitations are called $m$-$n$ transitions with $m, n \in \{0, 1, 2\}$. It is notable that the contribution of 1-$n$ transitions is not negligible, implying that initial thermal populations of the intra-pigment modes are important even at $T = 77$ K. As shown in Fig. S9(b), the cumulant expansion results are better matched to numerically exact results when the empirical pure dephasing rate is taken to be $\gamma_{pd} \approx 150 \text{ cm}^{-1}$.

We now consider the standard second order cumulant expansion method where absorption line shape is modelled by the optical responses of excitons

$$
\sum_{j=\pm} \langle \mu_{XT,j} \rangle^2 \int_{-\infty}^{\infty} dt \exp \left( i(\omega - E_j - E_{LS,j})t + G_j(t) - G_j(0) - \left( \frac{1}{2} \gamma_{j \rightarrow k} + \gamma_{pd} \right) t \right), \quad (S61)
$$
FIG. S9. (a) Approximate absorption line shape of WSCP at \( T = 77 \) K is shown in red where \( \gamma_{pd} = 0 \) and the initial state of the intra-pigment modes is modelled by a thermal state, instead of a global vibrational ground state \(|0\rangle\) considered in Fig. S8. The contributions of \( 0-n, 1-n \) and \( 2-n \) transitions to the total approximate absorption line shape are shown in blue solid, blue dashed and blue dotted lines, respectively. (b) Approximate absorption spectra in the presence of empirical pure dephasing, which are better matched to numerically exact results shown in a black dashed line. (c) Approximate absorption spectra computed by the standard second order cumulant expansion method where the optical responses of exciton states are determined by the coupling to the total vibrational environments including both protein and intra-pigment modes. Absorption line shapes in the presence and absence of the Lamb shift are shown in red and blue, respectively. (d) The total phonon spectral density of WSCP is shown in red, and the renormalisation of excitonic splitting, \( \Delta'' - \Delta \), by the Lamb shift is shown in black as a function of bare excitonic splitting \( \Delta \).

The Lamb shift \( E_{LS,j} \) describes the energy-level shift of exciton states due to the interaction with the full vibrational environments

\[
E_{LS,j} = -\sum_{i=1}^{2} |\langle \varepsilon_i | E_j \rangle|^2 \lambda_i + \sum_{i=1}^{2} |\langle E_+ | \varepsilon_i \rangle |^2 \lambda_0 \int_{-\infty}^{\infty} d\omega \frac{J(\omega)(n(\omega) + 1) + J(-\omega)n(-\omega)}{\Delta - \omega}. \tag{S63}
\]

As shown in Fig. S9(c), the energy-gap between excitons is reduced from a bare excitonic splitting \( \Delta \approx 2V = 280 \text{ cm}^{-1} \) to \( \Delta'' \approx 102 \text{ cm}^{-1} \) by the Lamb shift where approximate absorption line shapes in the presence and absence of the Lamb shift are shown in red and blue, respectively. This implies that the Lamb shift induced by high-frequency intra-pigment modes suppresses the energy-gap between excitons (see Fig. S9(d)), although the Markov approximation considered in the derivation of the Lamb shift is not appropriate to describe the long-lived correlations between excitons and underdamped intra-pigment modes. It is notable that the suppression of the excitonic splitting is overestimated by the standard cumulant expansion method, implying that the minimal model described in a vibronic basis with an effective coupling \( V_{00} \) between 0-0 transitions is more appropriate to describe the energy-level shift by intra-pigment modes.
FIG. S10. (a) Numerically exact absorption spectra of WSCP at \( T = 77 \text{ K} \) shown in a black dashed line, and approximate absorption line shape computed by numerical diagonalisation of vibronic Hamiltonian \( H_0 + V_{00}(|\varepsilon_1, 0\rangle\langle\varepsilon_2, 0| + h.c.) \). The total approximate absorption line shape is a sum of 0-\( n \), 1-\( n \) and 2-\( n \) transitions shown in blue solid, blue dashed and blue dotted lines, respectively. (b) Approximate absorption line shape obtained by numerical diagonalisation of \( H_0 + H_j^{(nn)} \) where \( H_j^{(nn)} \) contains the couplings between local electronic excitations with identical vibrational states. The transition dipole strengths of 0-\( n \) transitions are displayed in yellow triangles as a function of transition energy. (c) Approximate absorption spectra based on the full Hamiltonian \( H_0 + H_I \) including the couplings amongst 0-0 and 0-1 transitions. (d) Approximate absorption spectra based on \( H_0 + H_I + H_{LS} \) including Lamb shift. Approximate results in the absence and presence of an empirical pure dephasing rate, \( \gamma_{pd} = 0 \) and \( \gamma_{pd} = (2 \text{ ps})^{-1} \), are shown in red and green solid lines, respectively. The transition dipole strengths of 0-\( n \) transitions in the presence of the Lamb shift are shown in grey dots.

B. Multi-mode vibronic mixing of 0-0 and 0-1 transitions

So far we have investigated the influence of the effective coupling \( V_{00} \) between 0-0 transitions on absorption line shapes of WSCP by neglecting all the other couplings in \( H_I \). We now consider the other couplings in simulations by numerically diagonalising the total Hamiltonian \( UHU^\dagger = H_0 + H_I \) within double vibrational excitation subspace and computing the energy-levels and transition dipole strengths of vibronic eigenstates. The broadening of absorption peaks is induced by static disorder in site energies and homogeneous broadening induced by the coupling to low-frequency protein motions and vibrational damping of intra-pigment modes. The center-of-mass motions of protein modes are treated non-perturbatively, while the relative motions of protein modes are considered approximately by using a Lindblad equation (see sections VIII and IX). In addition, the vibrational damping of each intra-pigment mode is considered within the Lindblad formalism where each intra-pigment mode is coupled to an independent secondary bath in a thermal state, similar to the reduced model for SP (see section IX). We assume that the intra-pigment modes are initially in a thermal state at temperature \( T = 77 \text{ K} \).

In Fig. S10(a), we consider only the \( V_{00} \) coupling between 0-0 transitions and neglect all the other couplings in \( H_I \), as is the case of the cumulant expansion simulations. Numerically exact absorption spectrum of WSCP is shown in a black dashed line, while approximate absorption line shape is shown in a red solid line. The contributions of 0-n, 1-n and 2-n transitions to the total approximate absorption spectra are shown in blue solid, blue dashed and blue dotted lines, respectively. The 1-1 transitions lead to a single peak at 659 nm due to the absence of the interaction between \( |\varepsilon_1, 1_j, k\rangle \) and \( |\varepsilon_2, 1_j', k'\rangle \). Note that the total approximate absorption line shape shown in red is not well matched to numerically exact results shown in black.
In Fig. S10(b), we consider the interaction between local electronic excitations when associated vibrational states are identical, such as the coupling between $|\varepsilon_1, n_{j,k}\rangle$ and $|\varepsilon_2, n_{j,k}\rangle$ with $n_{j,k} \in \{0, 1, 2\}$, and that between $|\varepsilon_1, 1_{j,k}, 1_{j',k'}\rangle$ and $|\varepsilon_2, 1_{j,k}, 1_{j',k'}\rangle$ where different modes $b_{j,k}$ and $b_{j',k'}$ are singly excited at the same time. This modifies the absorption line shape of 1-n transitions, leading to two absorption peaks in zero-phonon line region below 650 nm, similar to 0-n transitions. To clarify the energy-gap between 0-0 transitions, the transition dipole strengths of all 0-n transitions are shown in yellow triangles as a function of transition energy, where the splitting between 0-0 transitions is $\Delta' = 2V_{00} \approx 142 \text{ cm}^{-1}$. Note that approximate absorption spectra are still not well matched to numerically exact results.

In Fig. S10(c), we now consider the full $H_I$, containing the couplings between local electronic excitations with different number of vibrational excitations. This leads to a multi-mode vibronic mixing between 0-0 and 0-1 transitions, which redistributes the transition dipole strengths of the bright 0-0 transition at 655.5 nm and relatively dark 0-1 transitions around 650 nm (compare yellow triangles in Fig. S10(b) and (c)). This makes the main absorption peak at 655.5 nm darker, and the phonon sideband around 650 nm brighter. As a result, approximate absorption line shape shown in red is quantitatively well matched to numerically exact absorption spectrum shown in black, although the approximated results underestimate absorption in the low-energy region below 662 nm. This implies that the energy-gap $\Delta' \approx 134 \text{ cm}^{-1}$ between absorption peaks in zero-phonon line region is underestimated when compared to numerically exact results.

So far we have not included the Lamb shift in reduced model simulations. Within the Lindblad formalism, the energy-level shift induced by the interaction with environmental degrees of freedom is described by

$$H_{LS} = \sum_{\omega} \sum_{\alpha} S_\alpha(\omega)A_\alpha^{\dagger}(\omega)A_\alpha(\omega)$$

$$= -\sum_j |\psi_j\rangle\langle\psi_j|\sum_{\alpha} \lambda_\alpha |\psi_j\rangle A_\alpha |\psi_j\rangle|^2 + \sum_{\epsilon_i \neq \epsilon_j} |\psi_k\rangle\langle\psi_k|\sum_{\alpha} S_\alpha(\epsilon_k - \epsilon_j)|\langle\psi_j|A_\alpha|\psi_k\rangle|^2,$$

where $|\psi_j\rangle$ represent the vibronic eigenstates of the total Hamiltonian $UHU^{\dagger} = H_0 + H_I$, satisfying $UHU^{\dagger}|\psi_j\rangle = |\epsilon_j\rangle$, $A_\alpha$ noise operators describing the coupling to low-frequency protein motions or vibrational damping of intra-pigment modes, $S_\alpha(\Delta') = P \int_{-\infty}^{\infty} d\omega J_\alpha(\omega)(n(\omega) + 1) + J_\alpha(-\omega)n(-\omega))/(\Delta' - \omega)$ and $\lambda_\alpha = \int_{-\infty}^{\infty} d\omega J_\alpha(\omega)/\omega$ with $J_\alpha(\omega)$ denoting the environmental spectral density describing the noise process associated with $A_\alpha$ (see section IX). When all the couplings in $H_I$ are neglected except for $V_{00}$, the Lamb shift $H_{LS}$ is reduced to the energy-level shift in second order cumulant expansion (see Eq. S58). Fig. S10(d) shows that when the Lamb shift is included in simulations, the energy-gap $\Delta' \approx 134 \text{ cm}^{-1}$ renormalised by intra-pigment modes is increased to $\Delta'' \approx 188 \text{ cm}^{-1}$. The difference between approximate and numerically exact absorption line shapes can be further reduced by introducing a small empirical pure dephasing rate $\gamma_{pd} = (2 \text{ ps})^{-1}$, as shown in a green solid line. Within the Lindblad formalism, the phonon spectral density of protein motions of WSCP does not induce a pure dephasing rate, as log-normal distribution functions are super-Ohmic, which may underestimate the pure dephasing effect in numerically exact simulations.

These results demonstrate that the interaction between 0-0 transitions is significantly suppressed by a local vibronic coupling to high-frequency intra-pigment modes, and a multi-mode vibronic mixing of 0-0 and 0-1 transitions can modify absorption line shapes even if the mixing is not strong enough to change the energy-gap between absorption peaks. This is similar to the properties of bare exciton states where the energy-gap between excitons is close to the difference in site energies, $|\varepsilon_2 - \varepsilon_1|$, when the electronic coupling $V$ between monomers is sufficiently weak, but such a weak coupling can induce notable redistribution of oscillator strengths, leading to large difference in transition dipole strengths of exciton states [21]. We note that in photosynthetic systems, pigments may be coupled to non-identical vibrational environments, characterised by different spectral densities. Even in this case, one can generalise our approach and show that the effective coupling between 0-0 transitions of sites $i$ and $j$ is given by $V_{ij}/\exp(-\frac{1}{2} \sum_{k}(s_{i,k} + s_{j,k}))$ where $V_{ij}$ denotes the bare electronic coupling between sites $i$ and $j$ of a multi-chromophoric system, and $s_{i,k}$ the Huang-Rhys factors of the intra-pigment modes locally coupled to site $i$. The Lamb shift induced by low-frequency protein motions can increase or decrease the energy-gap between absorption peaks, similar to the multi-mode vibronic mixing induced by intra-pigment modes, hinting that characterisation of the environmental structures of photosynthetic pigment-protein complexes is essential to understand the optical responses of these systems.

C. Vibrational environments of WSCP modelled by B777 spectral density

In this work, we considered three log-normal distribution functions to model low-frequency protein motions of WSCP. Here we consider an alternative model where the three log-normals are replaced by Eq. S44, which is the
FIG. S11. (a) Vibrational environments of WSCP modelled by the sum of B777 spectral density shown in red (see Eq. (S34)) and 55 high-frequency underdamped modes modelled by Lorentzian functions with a vibrational damping rate of (1 ps)$^{-1}$, leading to the total spectral density $J(\omega)$ shown in black. The B777 spectral density is broader than three log-normal distribution functions shown in blue, considered in all the other WSCP simulations in this work. (b) The real and imaginary parts of the bath correlation function (BCF) $C(t)$ at $T = 77$ K, shown in black, are fitted up to 300 fs by the sum of 16 exponentials as shown in red dashed lines. The insets show the difference between target BCF and the fitting function, demonstrating that the fitting error is three orders of magnitude smaller than the amplitudes of the target BCF. (c) The dynamics of the real part of the optical coherence of a two-level monomer in the absence of static disorder. The simulated HEOM results, shown in red, are well matched to the analytical solution shown in black: the site energy of the monomer is taken to be zero for better visibility. The imaginary part of the coherence computed by HEOM is also well matched to the analytical solution (not shown here). (d) The absorption spectra of WSCP homodimers where $V = 140$ cm$^{-1}$, the angle between transition dipole moments of monomers is taken to be 39°, and the standard deviation of the Gaussian static disorder is 80 cm$^{-1}$. The simulated HEOM results in the presence and absence of 55 intra-pigment modes are shown in black and red, respectively, where site energies are optimised in such a way that the main absorption peak at 655.5 nm coincide. It is notable that when intra-pigment modes are not considered, the energy-gap between 0-0 transitions is determined by an excitonic splitting $\Delta \approx 2V$ as shown in red, which is suppressed by the coupling to the high-frequency intra-pigment modes as shown in black. Cumulant expansion results based on the effective coupling $V_{00}$ between 0-0 transitions are shown in a green dashed line where the empirical pure dephasing rate is not considered, $\gamma_{pd} = 0$. Approximate results obtained by diagonalization of vibronic Hamiltonian are shown in a dashed orange line. We note that the maximum amplitudes of simulated absorption spectra are normalised to unity and mean site energies are adjusted, so that the main absorption peaks are overlapped at 655.5 nm, implying that the absorption spectra computed based on different spectral densities are normalised independently by different factors.
to be $V = 140\text{ cm}^{-1}$. The excitonic splitting $\Delta \approx 2V$ is suppressed by the coupling to high-frequency intra-pigment modes, as shown in red. These results demonstrate that vibronic renormalisation of the energy-gap between absorption peaks induced by high-frequency intra-pigment modes is a general phenomenon independent of the shape of the low-frequency part of the total spectral density. Approximate absorption line shape computed by second order cumulant expansion with an effective coupling $V_{\text{exp}}$ between $|E_0^+\rangle$ and $|E_0^-\rangle$ states with $\gamma_{21} \approx 92\text{ cm}^{-1}$ and $\gamma_{12} \approx 6\text{ cm}^{-1}$. Approximate results obtained by numerical diagonalisation of vibronic Hamiltonian without the empirical pure dephasing rate ($\gamma_{pd} = 0$), shown in orange, are also well matched to numerically exact results shown in black.

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