Supplementary Material

Does electronic coherence enhance anticorrelated pigment vibrations under realistic conditions?

Hong-Guang Duan[1,2,3], Michael Thorwart[1,3], and R. J. Dwayne Miller[2,3,4]

[1] *I. Institut für Theoretische Physik, Universität Hamburg, Jungiusstraße 9, 20355 Hamburg, Germany*
[2] *Max Planck Institute for the Structure and Dynamics of Matter,*
Luruper Chaussee 149, 22761 Hamburg, Germany
[3] *The Hamburg Center for Ultrafast Imaging, Luruper Chaussee 149, 22761 Hamburg, Germany*
[4] *The Departments of Chemistry and Physics, University of Toronto,*
80 St. George Street, Toronto Canada M5S 3H6

(Dated: August 29, 2019)

In this Supplementary Material, we provide additional details on the time evolution of 2D electronic spectra of the vibronically coupled dimer. We introduce the global fitting approach and decay associated spectrum. Moreover, we show the decay associated spectra of the vibronically coupled dimer both for the resonant and off-resonant case and compare to the purely excitonic dimer model without vibrational coupling. With the same parameters, we calculate the 2D electronic spectra of dimer model at low temperature (80 K). The associated vibrations are presented as well. In addition, we also calculate the 2D electronic spectra of a monomer coupled to a vibrational mode and show its vibrational dynamics.

I. TIME EVOLUTION OF THE 2D ELECTRONIC SPECTRUM WITH A RESONANT VIBRATIONAL MODE

In this section, we show the time dependent 2D electronic spectra of the vibronically coupled dimer model when the electronic transition is in resonance with the vibrational model, i.e., for $\Omega = 200$ cm^{-1}. Temperature is set to 300 K. In Fig. S1, the sequence of 2D spectra for the waiting times $T = 0, 50, 100$ and 200 fs is shown. Two diagonal and two off-diagonal peaks are labeled as A, B and C, D at $T = 0$ fs. Inhomogeneous broadening is clearly identified at $T = 0$ fs by the stretching along the diagonal direction and it disappears after $T \geq 50$ fs.

II. DECAY-ASSOCIATED SPECTRUM OBTAINED FROM GLOBAL FITTING APPROACH

Here, we provide more details of the global fitting approach. Multidimensional global fits of both experimentally measured and theoretical calculated arrays of 2D spectra have been performed by using the previously developed algorithm [1]. A detailed description can be found in the Supplementary Information of Ref. [2]. In this method, a sequence of 2D spectra taken at different waiting times T is collected to form a three-dimensional array $S(\omega_\tau, \omega_t, T)$. This 3D array is then decomposed into a sum of two-dimensional decay-associated spectra (DAS) $A_i(\omega_t, \omega_\tau)$ with individual exponential decays with correspondingly associated lifetimes τ_i according to

$$S(\omega_\tau, \omega_t, T) = \sum_i A_i(\omega_\tau, \omega_t) \exp(-T/\tau_i).$$
(S1)

In Fig. S2, we show the decay-associated spectra of the dimer model in three different configurations. In (a), the DAS of the vibronic dimer under resonant condition is depicted, i.e., with $\Omega = 200$ cm^{-1}, which equals the electronic energy gap between the two monomers in the exciton basis. It consists of two components, one with a life time of $\tau_1 = 61$ fs and one with $\tau_2 = \infty$. For comparison, the pure electronic dimer model without the vibrational mode is analyzed in (b). Also here, the result shows that the population transfer can be separated into two exponentials with a life time of $\tau_1 = 64$ fs and $\tau_2 = \infty$. In (c), the DAS of the off-resonant case is shown. The results show again two decay-associated components with timescale of $\tau_2 = 69$ fs and $\tau_2 = \infty$. Based on the global fitting analysis, we demonstrate that the transfer of electronic population is not modified by the vibronic coupling of the pigment to vibrations of a local mode.
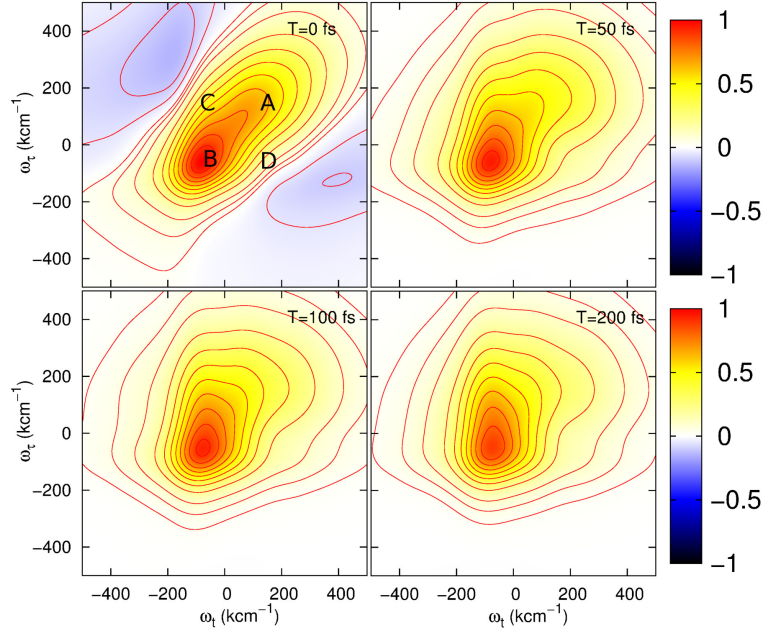
FIG. S1. Real part of the 2D electronic spectra of the vibronically coupled dimer model for the waiting times $T = 0, 50, 100$ and 200 fs under resonant condition, i.e., $\Omega = 200$ cm^{-1}. The diagonal and off-diagonal peaks are labeled as A, B and C, D, respectively, in 2D spectrum at $T = 0$ fs. Each spectrum is normalized with respect to is own spectral maximum.
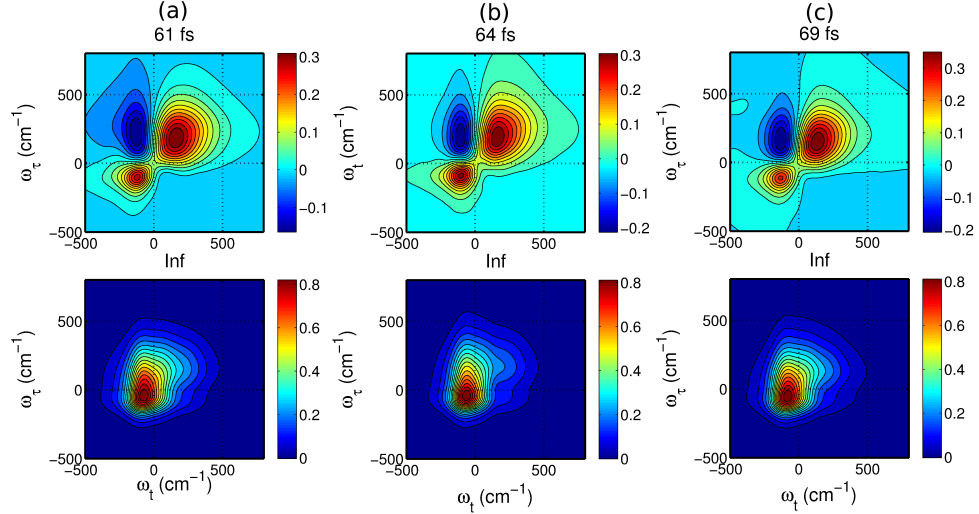

FIG. S2. The decay-associated spectra of three dimer models: (a) two coupled electronic states which are vibronically coupled to their own molecular vibrational mode under resonant condition, i.e., $\Omega = 200$ cm^{-1}. (b) The purely electronically coupled dimer without a molecular vibrational mode. (c) Two electronic states are coupled to their own molecular vibrational mode under off-resonant condition, i.e., $\Omega = 500$ cm^{-1}. The resulting life times are $\tau_1 = 61, 64$ and 69 fs, and $\tau_2 = \infty$ for the three cases, respectively.

III. STICK SPECTRUM FOR RESONANT VIBRATIONAL COUPLING

We show the stick spectum of the dimer in which the each of the two monomers is resonantly coupled to the respective vibrational mode in Fig. S3. It indicates the clearly separated electronic (black color) and the vibrational (magenta color) parts of which the wavefunctions of the eigenstates are composed. The sticks at 200 cm^{-1} and 400 cm^{-1} are purely vibrational. Hence, the narrow peaks at 200 cm^{-1} and 400 cm^{-1} shown in Figs. 1 (F) and (G) of

the main paper only stem from vibrational coherence of each monomer. No vibronic coupling is noticeable.
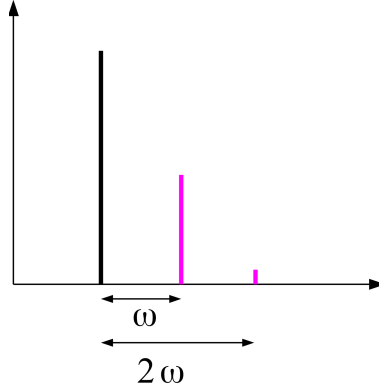

FIG. S3. Stick spectrum of the dimer corresponding to Figs. 1 (F) and (G) in the main paper, with the two monomer resonantly coupled to the respective vibrational mode.

IV. LOW-TEMPERATURE CALCULATIONS

With the same model and parameters, we show in this section the calculated results for the case of low temperature (80 K) under resonant conditions. First, we show the 2D electronic spectrum of the vibronically coupled dimer model at $T = 0$ fs in Fig. S4 (a) for $\Omega = 200$ cm^{-1}. The kinetics of the population transfer is analyzed by the global fitting approach and two DAS. One DAS with a life time of 121 fs is shown in Fig. S4(b). In addition, the time traces of selected peaks of the 2D spectrum are shown in Fig. S4(c). Four traces show rather long-lived oscillations. To resolve the spectral information, the Fourier transforms of the residuals are calculated to obtain the frequencies of electronic and vibrational coherent oscillations. In Fig. S4(d), the signal with frequency at 200 cm^{-1} is well resolved in all peaks. Moreover, for the peak D, the Fourier transform shown in Fig. S4(d) reveals one additional peak at 400 cm^{-1} (marked by black circle in Fig. S4 (d)). This proves that the long-lived oscillations solely originate from vibrational coherence. The mechanism is the same as in the case of room temperature.

For comparison, we have furthermore calculated the 2D electronic spectra of the purely electronic dimer without any vibrational mode. The results are shown in Fig. S5. In Fig. S5(a), the real part of the 2D electronic spectrum is shown at $T = 0$ fs. It does not show any significant difference compared to the one of the vibronically coupled model in Fig. S4(a). Moreover, the kinetics has been analyzed again and the first decay associated spectrum is shown in Fig. S5(b) with a life time of $\tau_1 = 161$ fs, which is slightly longer than the one observed in Fig. S4(b). It is caused by the overlap of the electronic and vibrational coherence in the kinetics in the regime of short times.

V. VIBRATIONAL DYNAMICS OF THE MONOMER

In this section, we study the coherent dynamics of a vibronically coupled monomer, in which, only the vibrational coherence is present in the model. In Fig. S6(a), the 2D electronic spectrum of the monomer with $\omega = 200$ cm^{-1} is shown for $T = 0$ fs. To study the time dependence of its vibrational dynamics, we select one spectral component in the 2D spectrum, marked by "D", which is related to the coupling between $0 - -0$ and $0 - -1$ transitions from the electronic ground to the excited state. The associated kinetics of peak D is presented in Fig. S6(b), together with a fit to an exponential. In addition, the frequency spectrum of peak D is obtained by the Fourier transform of the residual and is shown in Fig. S6(c). The vibrational frequency of 200 cm^{-1} is clearly revealed, together with another peak at 400 cm^{-1} with a small magnitude, which is marked by one purple circle in Fig. S6(c).

[1] V. I. Prokhorenko, *European Photochemistry Association Newletter*, issue June 2012, 21.
[2] F. Milota, V. I. Prokhorenko, T. Mancal, H. von Berlepsch, O. Bixner, H. F. Kauffmann, and J. Hauer, J. Phys. Chem. Lett. **117**, 6007 (2013).
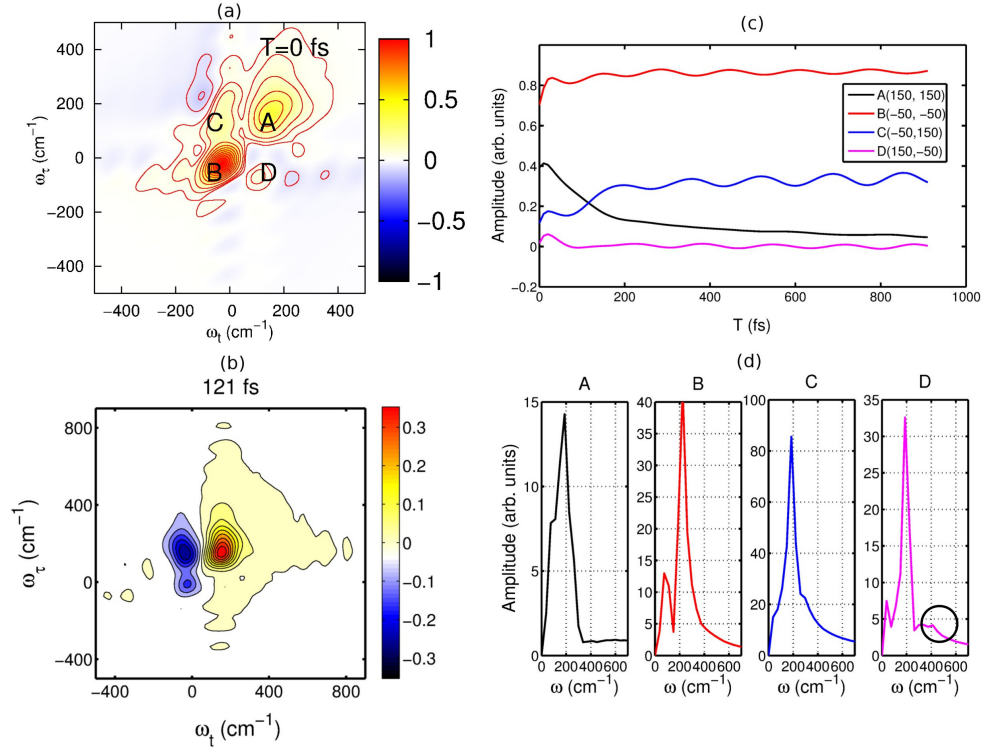
FIG. S4. (a) Calculated 2D spectrum of the vibronically coupled dimer model under resonant condition and at low temperature (80 K) at $T = 0$ fs. Selected peaks are labeled as A, B, C and D. (b) Decay-associated spectrum for the life time $\tau_1 = 121$ fs obtained from the global fitting approach (the second component with $\tau_2 = \infty$ is not shown here). (c) Time evolution of selected peaks in the 2D spectrum. (d) Associated spectral components of the vibrations of the selected peaks obtained by performing the Fourier transform of the residuals after subtracting the kinetics.
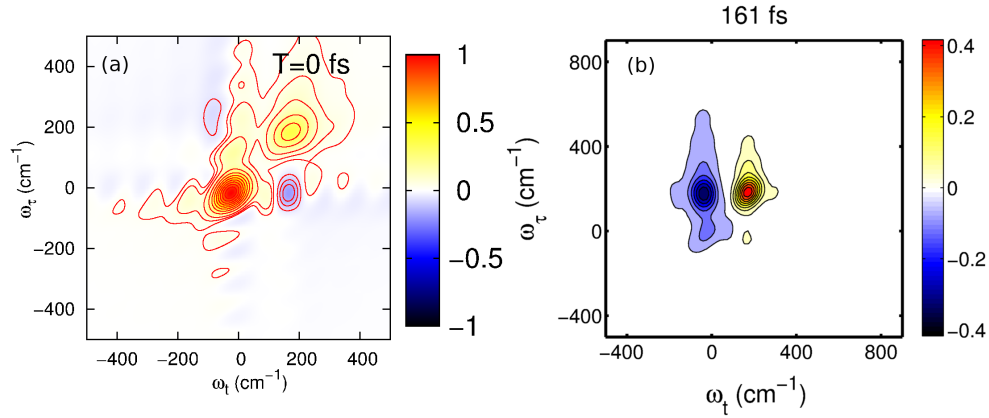

FIG. S5. (a) Calculated 2D spectrum of the purely electronically coupled dimer without vibrational modes at low temperature (80 K) at $T = 0$ fs. (b) Decay-associated spectrum for the life time $\tau_1 = 161$ fs obtained from the global fitting approach (the second component with $\tau_2 = \infty$ is not shown here).
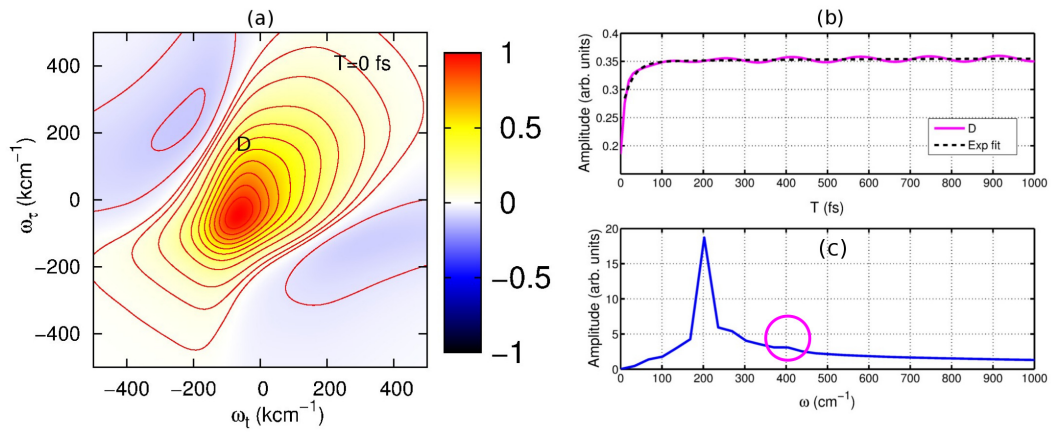
FIG. S6.   Vibrational dynamics of a monomer coupled to a single vibrational mode. In (a), the 2D electronic spectrum at $T = 0$ fs is shown. We label one spectral position by "D", which is chosen in correspondence to the coupling between $0 - -0$ and $0 - -1$ transitions. In (b), the associated trace of the signal D is presented, together with a fit to an exponential. In (c), the corresponding Fourier spectrum of the residual is shown.