Supporting Information to "Vibronic and Vibrational Coherences in Two-Dimensional Electronic Spectra of Supramolecular J-Aggregates"

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1. Description of Decay Associated Spectrum Analysis

For the evaluation of the two-dimensional electronic spectra (2D-ES), collected at different population times t_2, a multi-dimensional global fit was used. Global fit analysis for time-resolved data like e.g. pump-probe or fluorescence (two-dimensional in these cases) has been shown to be a useful tool for recovering spectroscopic and kinetic information about the investigated systems (for more information and algorithms see e.g. Ref. 1). In a conventional global treatment of data the light-induced dynamics of the excited system is described as a sum of several spectral forms with distinguishable spectral shapes $A(\lambda)_i$ and individual decay times τ_i. A two-dimensional array of experimental data $F(\lambda,t)$, like a spectrally-resolved pump-probe, can be approximated as:

$$F_{\lambda,t} = \sum_i A_{\lambda,i} e^{-t/\tau_i}$$

$$(1)$$

Here we assume infinitesimally-short excitation pulses. $A_{\lambda,i}$ is the spectrum associated with the decay constant τ_i (Decay Associated Spectrum, DAS). In a global fit approach, the fitting of experimental data to a model as described by Eq. 1, only a few decay times are varied at a time, which makes the fit procedure robust. For the case of 2D-ES the experimental data have three dimensions since each "snapshot" at time t_2 has already two dimensions (2D-spectrum).

Recently, a generalization of global analysis for multi-dimensional data ($N_{dim} > 2$) was performed theoretically [2]. For 3D-data, organized as a sequence of 2D-spectra measured at different population times t_2, the overall data set can be described, in similarity to Eq. 1, as:

$$S_{\omega_1,\omega_3,t_2} = \sum_i A_{\omega_1,\omega_3,i} e^{-t_2/\tau_i},$$

$$(2)$$

where $S_{\omega_1,\omega_3,t_2}$ is the measured 2D-spectrum at time t_2, and $A_{\omega_1,\omega_3,i}$ is the ith *two-dimensional* decay-associated spectrum (2D-DAS). These can be obtained by using fitted decay times as (see for detail Ref 2):

$$A_{\omega_1,\omega_3,i} = \sum_{t_2} S_{\omega_1,\omega_3,t_2} D_{t_2,i}^{-1} \qquad . \qquad (3)$$

Here, D^{-1} is the inverse matrix of the model response function $D_{t_2,i} = e^{-t_2/\tau_i}$ which assumes an infinitesimally-short excitation pulse. Convolution of this function with an instrument response function (IRF) results in even more reliable results. In this study we did not account for the IRF because (i) its form was not measured and (ii) its influence is important only for very short population times ($t_2 <= 20$ fs) where the 2D-spectra can strongly be affected by the non-linear response of the solvent. Therefore, the fit of the experimental data to the model (Eq. 2) was performed for $t_2 > 30$ fs.

We found that the real part of the 2D-spectra can be fitted satisfactorily using only three decay components with 146 fs, 454 fs, and a long-lived (>5 ps; not resolved due to limited t_2 scan range) with confidence intervals of +/- 3 fs and +/- 30 fs, respectively. The fit´s quality is demonstrated in Figure 3 (B, C) of the main text where we show several experimental traces together with the fitted results. Figures SI-1(A-C) show the recovered 2D-DAS for these decay components. Figure SI-1 (D) shows the 2D-DAS-projections onto the ω_3 axis. When performing conventional DAS-analysis of the measured pump-probe traces (see figure 2 in the main text for selected pump-probe spectra), we retrieve almost identical traces to the projections shown in figure SI-1 (D). This agreement between DAS and 2D-DAS-analysis proves the robustness of the latter.
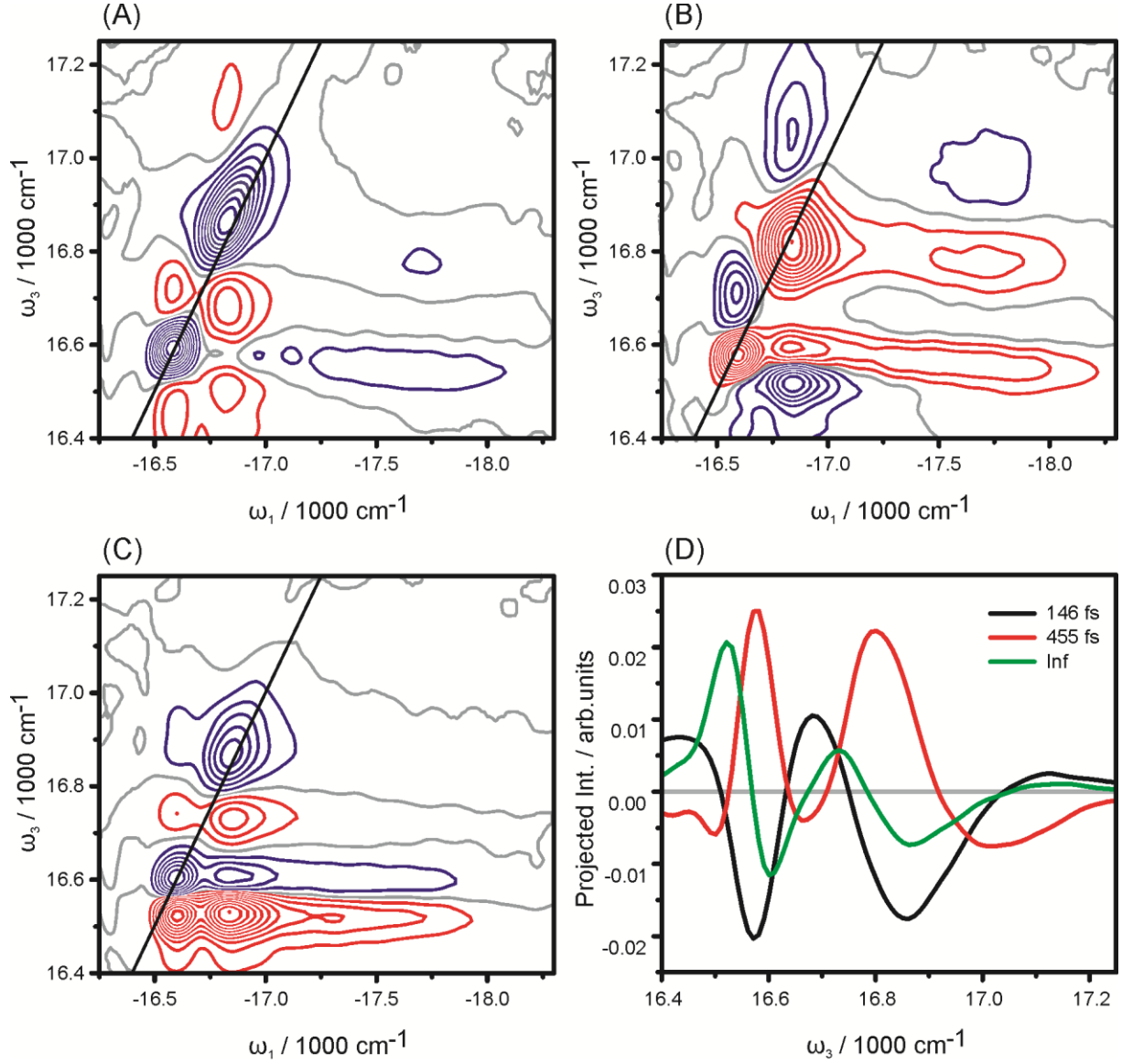
Fig. SI-1. 2D-DAS for the 146 fs (A), 454 fs (B) and >5 ps (C) life time component. Positive (negative) signals are shown in red (blue) in 10% intervals. The gray line marks the nodal line at zero intensity. The diagonal $\omega_1 = \omega_3$ is shown as the thin black line. Panel (D) shows the projection of the 2D-DAS onto the ω_3 axis.

The residuals of the fit

$$\Delta S_{\omega_1,\omega_3,t_2} = S_{\omega_1,\omega_3,t_2} - \sum_i A_{\omega_1,\omega_3,i} e^{-t_2/\tau_i} \qquad (4)$$

were further analyzed using Fourier transform along t_2 resulting in a *three-dimensional* spectrum of residuals. Figure 5 in the main text shows two slices from this 3D-spectrum.

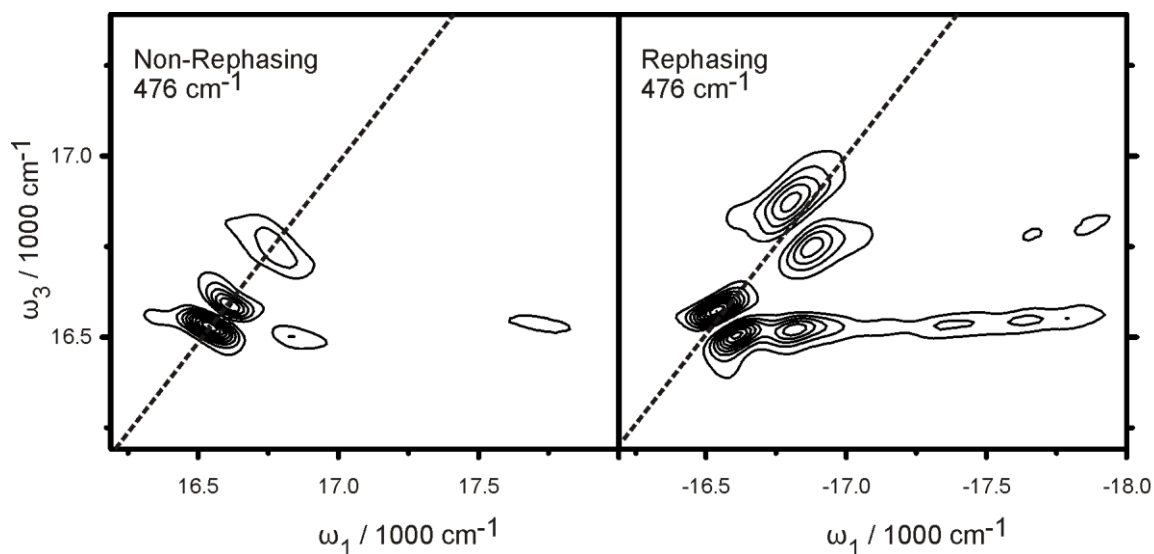## 2. Rephasing and Non-Rephasing FFT-Power Spectrum at 476 cm^{-1}

Fig. SI-2. Non-Rephasing and rephasing components of the strongest oscillatory component at 476 cm^{-1} of the FFT-power spectrum. Fourier-transformation along t_2 was performed for each point in the 2D-spectra.

After subtraction of the slowly varying signal contribution determined by the 2D-DAS-routine described above, the remaining signal consists of fast oscillatory components. After Fourier-transformation along t_2, the strongest modulation was found at 476 cm^{-1}, as described in the discussion of figure 3 in the main text. Splitting up the signal in rephasing and non-rephasing contributions can help in determining the nature of the observed oscillations, as discussed in reference 47 of the main text. If the observed 476 cm^{-1} modulation was of purely electronic nature, the non-rephasing diagonal peaks should oscillate but not their rephasing counterparts. Figure SI-2 shows that this is not the case. This observation rules out a purely electronic nature of the 476 cm^{-1} oscillation.

References

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