Supplementary Information for
A polarization scheme that resolves cross peaks with transient absorption and eliminates diagonal peaks in 2D spectroscopy

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Supplementary Information Text

Materials and Methods

Fig. S1. Configuration of waveplates and polarizers. \(\lambda/2\) waveplate setting probe polarization to 60°. \(\lambda/2\) waveplate setting pump polarization to 0°. Wire grid polarizer in pump path, accurately setting pump polarization to 0°. Wire grid polarizer in probe path, accurately setting pump polarization to 60°. Wire grid polarizer in probe path after the sample, projecting the probe and emitted fields onto -60°. Harrick cell holding the sample at the focus.

Fig S1 shows the configuration of the polarizers, waveplates, focusing optics, and sample stage. Two \(\lambda/2\) waveplates are used to control the pump and probe polarization prior to the first parabolic mirror. Polarizers are placed between the parabolic mirrors. The pump and probe polarizations are set prior to the sample cell. A polarizer is placed after the sample cell to project to emitted field onto a given axis. To correct for aberrations, it is best if the collimating parabolic mirror is oriented opposite of that used in our setup.

Theory
Fig. S2. Orientational correlation functions for cross peaks in an absorptive spectrum. a) Diagonal, b) off-diagonal and c) on-diagonal cross peaks as a function of $E_2$ and $E_3$ polarization for $E_1 = 0^\circ$. Black lines indicate polarizations for which diagonal peaks are removed. $\theta_{\alpha\beta}$ is set to $90^\circ$. d,e,f) Feynman diagrams for pathways plotted in a,b, and c, respectively. Orientational correlation factors were calculated using Eq. 2 in the main text. Black lines indicate polarizations where diagonal peaks are removed. At $<0^\circ,0^\circ,+60^\circ,-60^\circ>$ and $t_2=0$, the intensity ratio between off-diagonal
and on-diagonal should be 3:1, assuming a flat pump spectrum and infinitely narrow pulses. Additionally, the off-diagonal and on-diagonal cross peaks are opposite in sign.

Fig. S3. Effect of local oscillator attenuation on cross peaks. a) off-diagonal and b) on-diagonal cross-peak intensity. The gray curve is the cross-peak intensity before enhancement for polarizations that remove diagonal peaks. Blue curves simulate the enhanced signal due to local oscillator attenuation (E_{emit}/E_{LO}). Both panels share a common axis that is linear in $\theta_2$. The top axis displays the corresponding $\theta_3$ angle that removes diagonal peaks. $\theta_1$ is equal to zero. $\theta_{\alpha\beta}$ is set to 90º.

Fig. S3 shows the comparison between cross peak intensities before and after enhancement for polarizations that remove diagonal peaks. Fig. S3a is for off-diagonal cross peaks and Fig. S3b is for on-diagonal cross peaks. The gray curve is the cross-peak intensity before enhancement for polarizations that remove diagonal peaks. The cross peak intensity depends on the polarization scheme used. The blue curve is the intensity of the cross peaks due to LO enhancement, calculated using Eq. 5. Note that enhancement from LO attenuation enhances all peaks to a common value. For $\langle 0^\circ,0^\circ,\pm 60^\circ,\pm 60^\circ \rangle$ the cross peaks are enhanced 2-times. The enhancement factor can be calculated by dividing the blue curve by the gray curve. The oscillations
are due to numerical error (i.e. zero divided by zero) in $E_{\text{eml}}/E_{\text{LO}}$ as $E_{\text{LO}}$ approaches zero at 0 and 180 degrees.

Fig. S4. Dependence of absorptive cross peak dynamics on relative oscillator angle. a-d) Diagonal peak (yellow), off-diagonal cross peak (blue), and on-diagonal cross peak (red). a-d) Relative peak intensities for $< 0^\circ,0^\circ, +60^\circ, -60^\circ >$. e-h) Relative peak intensities for $< 0^\circ,0^\circ, \theta_2(t), -\theta_2(t) >$. Peak intensities are calculated for relative oscillator angles of 90, 60, 30, and 0 degrees.

Fig. S4 is the same plot as Fig. 4 in the main text, only at different relative oscillator angles. Diagonal peaks re-appear for $< 0^\circ,0^\circ, +60^\circ, -60^\circ >$ with a rate of 6D for all values of $\theta_{\text{up}}$ tested. The same is true for the decay rate of the cross peaks in the lower panels (Figs. 4e-h), which remains 6D. Note that the cross-peak intensities are largest for $\theta_{\text{up}}=90^\circ$ and approach zero as the relative oscillator angle approaches $\theta_{\text{up}}=0^\circ$. This is because $< 0^\circ,0^\circ, \theta_2(t_2), -\theta_2(t_2) >$ removes Feynman pathways where all four field interactions are with parallel oscillators.

The peak intensities in Fig. 4 and Fig. S4 are simulated as follows. As shown in Fig. 2, the diagonal, off-diagonal cross peaks, and on diagonal cross peaks have intensities given by,

$$S_{\text{diagonal}} = S_{iiii}$$  \hspace{1cm} (S1)

$$S_{\text{off-diagonal}} = S_{ijij} + 2S_{ijji}$$  \hspace{1cm} (S2)

$$S_{\text{on-diagonal}} = S_{ijji}$$  \hspace{1cm} (S3)

where, $S_{\text{diagonal}}$, $S_{\text{off-diagonal}}$, and $S_{\text{on-diagonal}}$ are the diagonal, off-diagonal cross peak, and on-diagonal cross peak intensities, respectively. $S_{ii}$, $S_{ij}$, $S_{ij}$, and $S_{ij}$ are the orientational correlation
functions of the \(iii,ijj,iiij\), and \(ijji\) pathways for a given polarization condition. The orientation correlation functions are given by.

\[
S_{iii} = a(X_iX_iX_iX_i) + b(X_iX_iY_iY_i) = a \frac{1}{45} [4e^{-6Dt_2} + 5] + b \frac{1}{45}[5 - 2e^{-6Dt_2}] \tag{S4}
\]

\[
S_{ijj} = a(X_iX_iX_jX_j) + b(X_iX_iY_jY_j) = a \frac{1}{45} [4P_2e^{-6Dt_2} + 5] + b \frac{1}{45}[5 - 2P_2e^{-6Dt_2}] \tag{S5}
\]

\[
S_{ijij} = a(X_iX_jX_iX_j) + b(X_iX_jY_iY_j) = a \frac{1}{27} [2P_2 + 1 + \frac{1}{5}e^{-6Dt_2}(P_2 + 5)] + b \frac{1}{27} [2P_2 + 1 - \frac{1}{5}e^{-6Dt_2}(P_2 + 5)] \tag{S6}
\]

\[
S_{ijji} = S_{ijij} \tag{S7}
\]

In Eqs. S4-S7, the time dependent orientational correlation functions including rotations were obtained from Ref. 4 in the main text. \(P_2=1/2(3cos^2(\theta_{\alpha \beta})-1)\). For \(<0,0,+60,-60>\), a and b were 1 and -3, respectively. For \(<0,0,+ \theta(t_2),-\theta(t_2)>\), a and b were \(\cos^2(\theta(t_2))\) and \(-\sin^2(\theta(t_2))\), respectively.

**Results**

1. **Projection of 2D spectrum onto the probe axis**

![Projection of 2D spectrum onto the probe axis](image)

**Fig. S5.** Projection of the 2D spectrum onto the probe axis matches the TA spectrum from the same measurement. Spectrum was collected in \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) (black) The TA spectrum obtained from the first coherence time delay of 0 ps. (blue) The normalized projection of the 2D spectrum onto the probe axis.

Figure S5 shows the overlay of the TA spectrum and the projection of the 2D spectrum onto the probe axis. Data was collected in \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) at \(t_2=0\) ps. The projection was
normalized to the maximum intensity of the TA spectrum to ensure the projection is plotted on the same scale. The 2D projection reproduces the TA spectrum well.

2. Verification of enhancement by local oscillator attenuation

In this section, we verify the effect local oscillator attenuation has on measured differential absorption. Enhancements are calculated by comparing \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) to a spectrum calculated separately from individual \(<0^\circ,0^\circ,0^\circ,0^\circ>\) (XXXX) and \(<90^\circ,90^\circ,0^\circ,0^\circ>\) (YYXX) measurements. Spectra were collected back-to-back. The XXXX-YYXX spectrum does not exhibit any enhancement because the local oscillator is not attenuated after interaction with the sample. Fig. S6 shows a horizontal slice of the 2D spectrum at \(\omega_1=2002\ \text{cm}^{-1}\) for the spectrum collected in XXXX-YYXX and \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\). This slice depicts the lower off-diagonal cross peaks.

![Graph showing ΔOD vs ω3 for XXXX-YYXX and <0°,0°,+60°,-60°> spectra.](image)

**Fig. S6.** Overlay of pump slices demonstrating enhancement from LO attenuation. a) Pump slice of the 2D spectrum for \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) and XXXX-YYXX. Pump slice was taken at \(\omega_1=2002\ \text{cm}^{-1}\).

There are two pieces of evidence verifying the effect of the local oscillator. First, the sign of the cross peaks for the XXXX-YYXX and \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) spectra are flipped. The local oscillator flips sign for \(\theta_2=60^\circ, \theta_3=-60^\circ\) compared to \(\theta_2=0^\circ, \theta_3=0^\circ\), resulting in the phase flip between \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) and XXXX-YYXX. This phase flip is apparent when comparing the blue and gray curves in Fig. S3. Second, the cross-peak intensity for \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) is roughly half the magnitude of the XXXX-YYXX. The local oscillator is attenuated 50% after the sample for \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) and should provide a 2x enhancement. Eq. 1 predicts that the signal strength should be a \(\frac{1}{4}\) the magnitude of XXXX-YYXX if LO enhancement is not considered. Therefore, the observation that \(<0^\circ,0^\circ,+60^\circ,-60^\circ>\) is \(\frac{1}{2}\) the magnitude of XXXX-YYXX is evidence of LO enhancement. Further support of LO enhancement is provided by the fact that the cross peak intensities appear unchanged for other polarizations that remove diagonal peaks, as predicted in Theory, in the main text. Spectra for some other these other polarizations are shown in Fig. S7.

Fig. S7a shows the XXXX-YYXX 2D spectrum calculated from separate measurements of XXXX and YYXX. Fig. S7b-h show the 2D spectrum at different polarization angles that remove diagonal peaks, indicated by the black lines in Fig. 3 in the main text. The diagonal peaks are
suppressed for all $<0^\circ,0^\circ,\theta_2,\theta_3>$ shown. Furthermore, the intensity and sign of these spectra are the same. The intensity of these spectra are approximately 2-times that of XXXX-3YYXX.

**Fig. S7.** 2D IR spectra collected at other angles that remove diagonal peaks at $t_2=0$. a) 2D spectrum calculated from separate measurements of XXXX and YYXX. b-h) 2D spectra collected at $<0^\circ,0^\circ,\theta_2,\theta_3>$, where angles $\theta_2$ and $\theta_3$ correspond to datapoints in panel a.