0.1 Extraction of pure dephasing from thin film measurement

- For simplicity, we reduce our analysis to certain components of the dataset: ...
- Observables we focus on: transient duration and peak shift
- A striking feature in our ultrafast measurements is the short duration of the coherence trace. At $T > 50$ fs, the transient has a FWHM of ~ 80 fs. For comparison, our instrumental response is estimated to be $70 - 90$ fs, depending on the exact value of our pulse duration ($35 - 45$ FWHM, intensity level). This suggests pure dephasing is only a small fraction of the pulse duration, but analysis is complicated by the presence of inhomogeneity.
- The existence of a finite peak shift in spite of a nearly pulse-width limited transient demonstrates that inhomogeneous broadening is significant. Ensemble dephasing could be significantly affecting the duration of the coherent transient.
- To separate the ensemble and pure dephasing contributions, we simulated the 2D delay transient through numerical integration of the Liouville equation. Integration was performed on a homogeneous, three-level system with whose coherent dynamics described by $\Gamma_2 = \Gamma_1/2 + \Gamma_2^*$. A three-level system was used because a two-level system cannot explain the fast, but incomplete, population relaxation observed. Ensemble dephasing was incorporated by convolving the homogeneous response with a Gaussian distribution function of width Δ_{inhom}. Through fitting we found $T_1 = 70$ fs, a result that was independent of the coherent dynamics.
- To understand the interplay between ensemble dephasing and pure dephasing on our observables, we simulated the coherent transient for a variety of Δ_{inhom} and T_2 values. The results for $\Delta_t = 40$ fs are mapped out in Figure X. The lines of constant T_2 span from $\Delta_{\text{inhom}} = 0$ (left ends of the curves) to the limit $\Delta_{\text{inhom}} \to \infty$ (right ends of the curves). The lines of constant T_2 demonstrate that ensemble dephasing acts to both reduce the transient duration and introduce a peak shift. The influence of inhomogeneity on the observables vanishes as $T_2 \to 0$.
- We performed simulations analogous to those in Figure X for a range of viable pulse durations $\Delta_t \in [35, 45]$ fs. The case of $\Delta_t = 40$ fs (Figure X) is a threshold; longer pulse durations produce a domain of solutions that do not intersect our experimental point, but shorter pulse durations do. Shorter pulse durations produce the transient duration and peak shift with a larger pure dephasing rate and a smaller inhomogeneity. The range of solutions compatible with our measurements is shown in Table X. We

Table 1: Fitted parameters for the coherent transient. The FWHM of the homogeneous line shape is $2\hbar T_2^{-1}$

Δ_t (fs)	T_2 (fs)	$\hbar T_2^{-1}$ (meV)	Δ_{inhom} (meV)
45	–	–	–
40	10	66	∞
35	18	36	43

cannot establish an upper limit for the extent of inhomogeneous broadening.

- Though we are only interested in extracting the pure dephasing component of our spectra, it is worth noting that the model system does an excellent job of reproducing the entire 2D transient observed, even during pulse overlap where the description of the interaction is more complex due to the congestion of signals (Figure Y). Our system description does not account for signal contributions in regions II/IV, which might be due to strong double quantum coherence resonances. Regardless, these contributions do not affect our analysis.