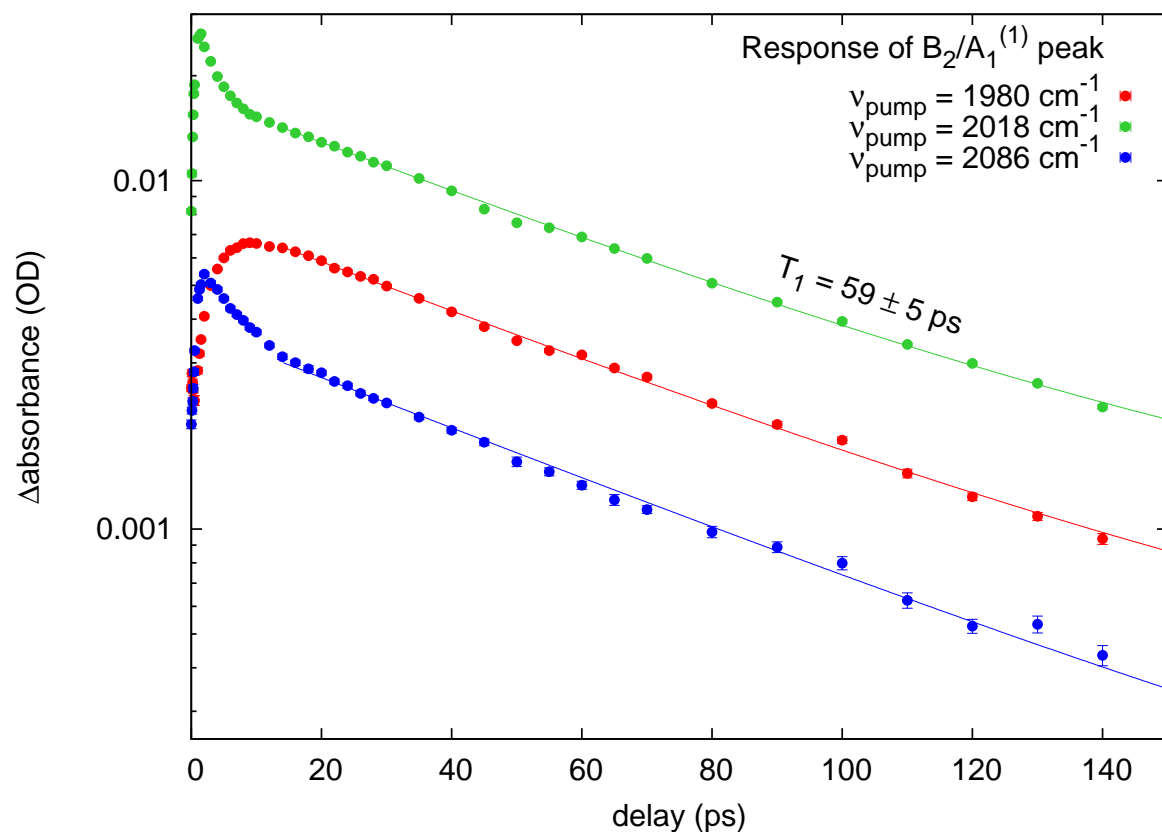


–Electronic Supporting Information–  
Ultrafast Dynamics in Iron Tetracarbonyl Olefin Complexes  
investigated with Two-Dimensional Vibrational Spectroscopy

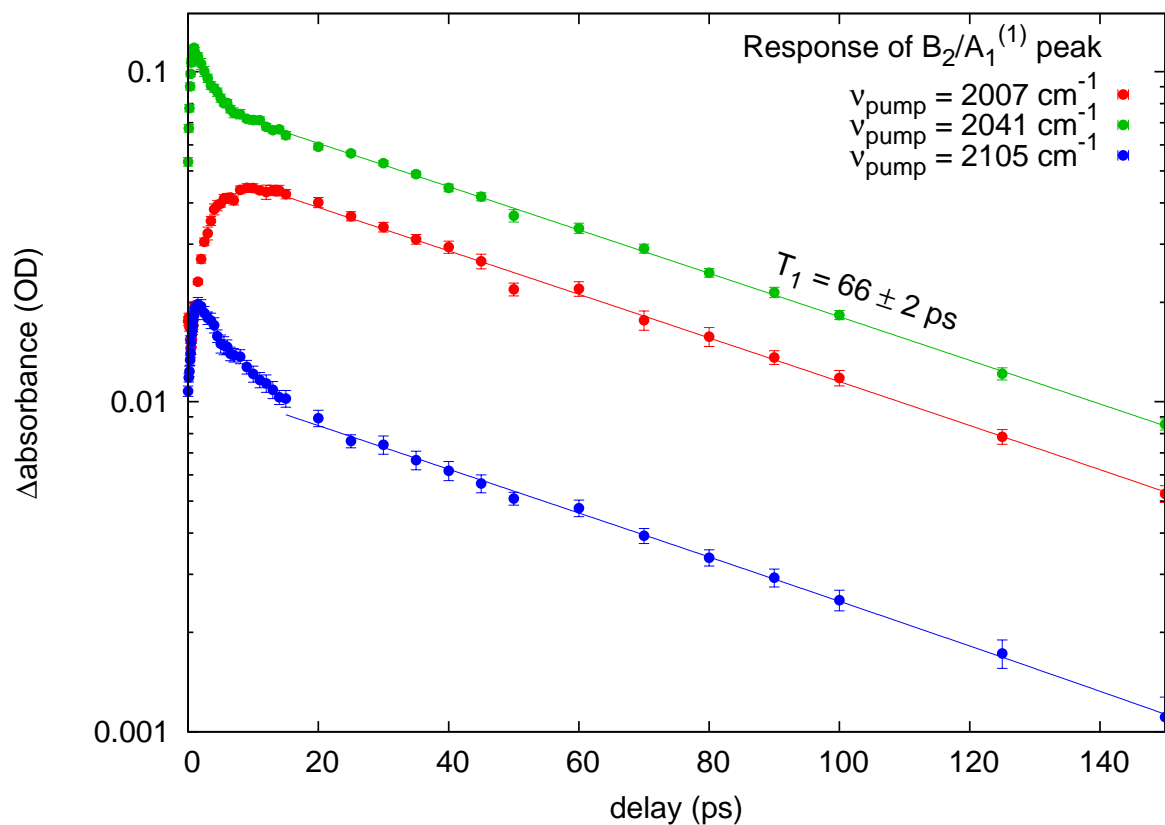
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# 1 Determination of the $T_1$ relaxation time of the vibrational modes

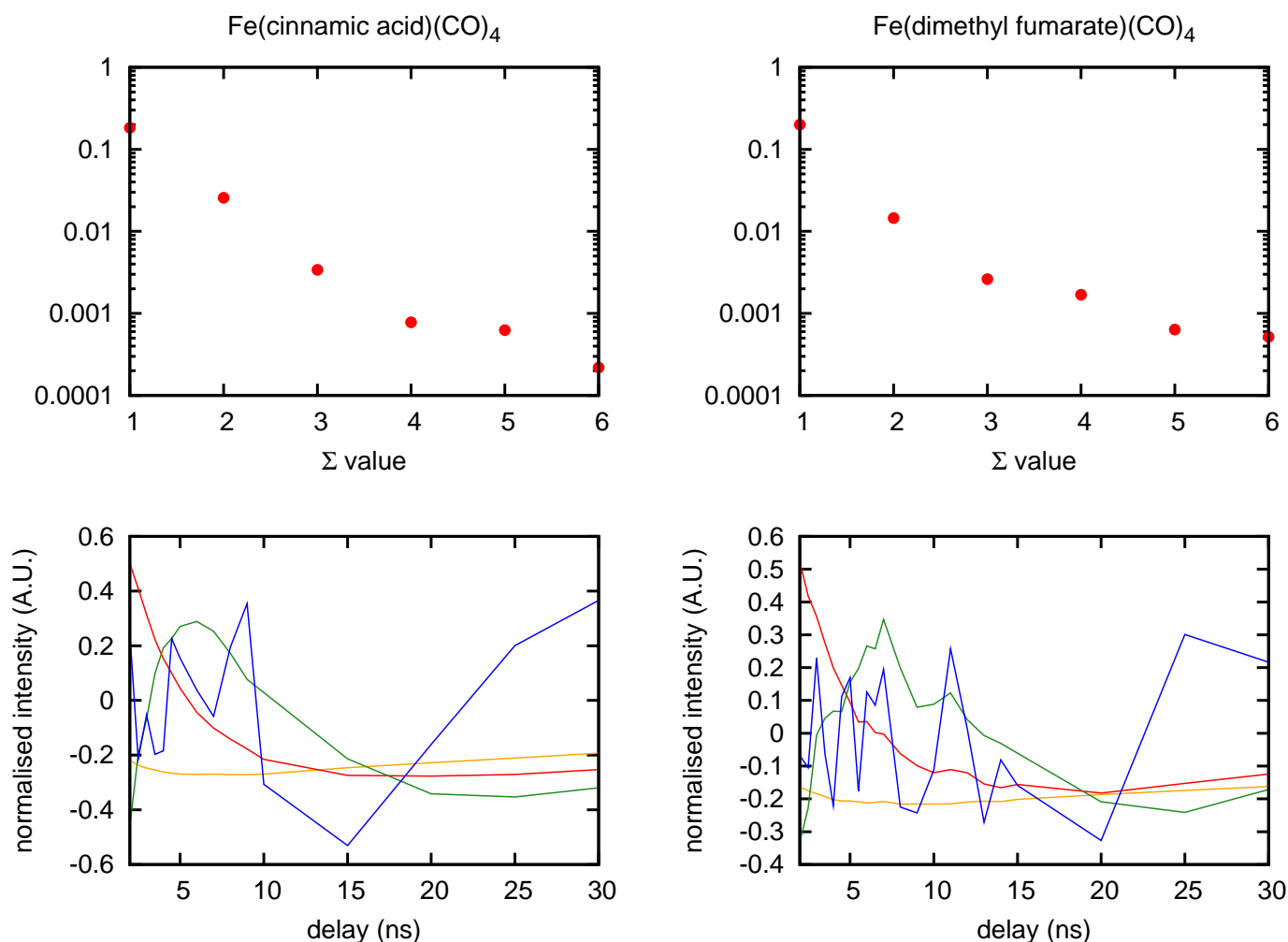


**Figure S1** Delay-dependent intensity of the  $B_2/A_1^{(1)}$  modes of  $\text{Fe}(\text{CO})_4(\text{cinnamic acid})$  when pumped at 1980, 2034, and  $2086 \text{ cm}^{-1}$ . The intensity is plotted on a log scale. The curves represent a least-squares fit of a single exponential decay from 14–150 ps. The  $T_1$  lifetime of the overall vibrational relaxation of the carbonyl stretch modes of  $\text{Fe}(\text{CO})_4(\text{cinnamic acid})$  is  $59 \pm 5 \text{ ps}$ .



**Figure S2** Delay-dependent intensity of the  $B_2/A_1^{(1)}$  modes of  $\text{Fe}(\text{CO})_4(\text{dimethyl fumarate})$  when pumped at 2007, 2041, and 2105  $\text{cm}^{-1}$ . The intensity is plotted on a log scale. The curves represent a least-squares fit of a single exponential decay from 14–150 ps. The  $T_1$  lifetime of the overall vibrational relaxation of the carbonyl stretch modes of  $\text{Fe}(\text{CO})_4(\text{dimethyl fumarate})$  is  $66 \pm 2$  ps.

## 2 Singular Value Decomposition of the cross peaks



**Figure S3** Top: Weights of the principal components obtained from a Singular Value Decomposition (SVD) of the delay-dependence of the cross peaks of Fe(CO)<sub>4</sub>(cinnamic acid) (left) and Fe(CO)<sub>4</sub>(dimethyl fumarate) (right) 2D-IR spectra. The magnitude of the weights are plotted on a log scale. Bottom: First four target vectors of the SVD of Fe(CO)<sub>4</sub>(cinnamic acid) (left) and Fe(CO)<sub>4</sub>(dimethyl fumarate) (right). In both complexes, the first three components are the most significant. The delay dependent behavior of the fourth component suggests it is an uncorrelated noise contribution to the data. The target vectors of both complexes are very similar in relative magnitude and delay dependence which indicates their dynamics follow the same mechanism. The Fe(CO)<sub>4</sub>(dimethyl fumarate) measurement is noisier compared to that of Fe(CO)<sub>4</sub>(cinnamic acid). This is evident from the higher magnitude of the fourth singular value.