Supplementary Information to the paper: The primary photolysis dynamics of oxalate in aqueous solution: decarboxylation by Jan Thøgersen, Tobias Weidner and Frank Jensen

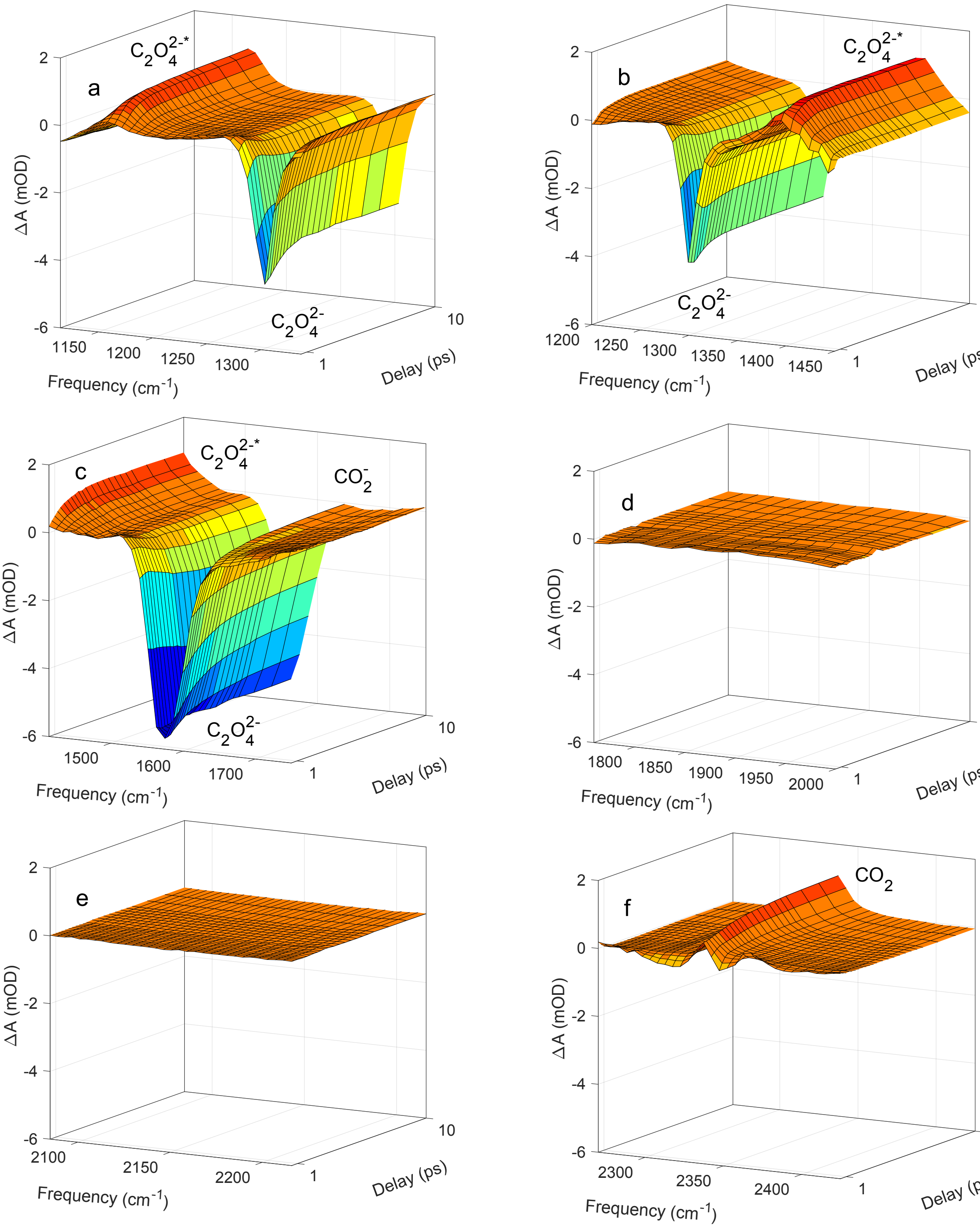

Fig. SI1. The first 10 ps of the transient absorption spectra of aqueous oxalate as a function of time after the 200 nm excitation pulse. a: The positive absorption associated with excited state oxalate transition at1180 cm^{-1} and the negative absorption related to $\nu_s CO_2^-$ of ground state oxalate at 1313 cm^{-1}. b: The negative absorption related to $\nu_s CO_2^-$ of ground state oxalate at 1313 cm^{-1} and the positive absorption associated with excited state oxalate transition at 1400 cm^{-1}. c: The negative absorption pertaining to the $\nu_{as} CO_2^-$ transition of ground state oxalate and the positive absorption at 1650 cm^{-1} is assigned to $\nu_{as} CO_2^{\bullet-}$ of $CO_2^{\bullet-}$. d+e: No transitions are observed in the frequency region 1750-2220 cm^{-1}. f) The $CO_2(aq)$ asymmetric stretch transition in H_2O at 2338 cm^{-1}. The spectra a+b and d-f are recorded in H_2O, while c is recorded in D_2O.

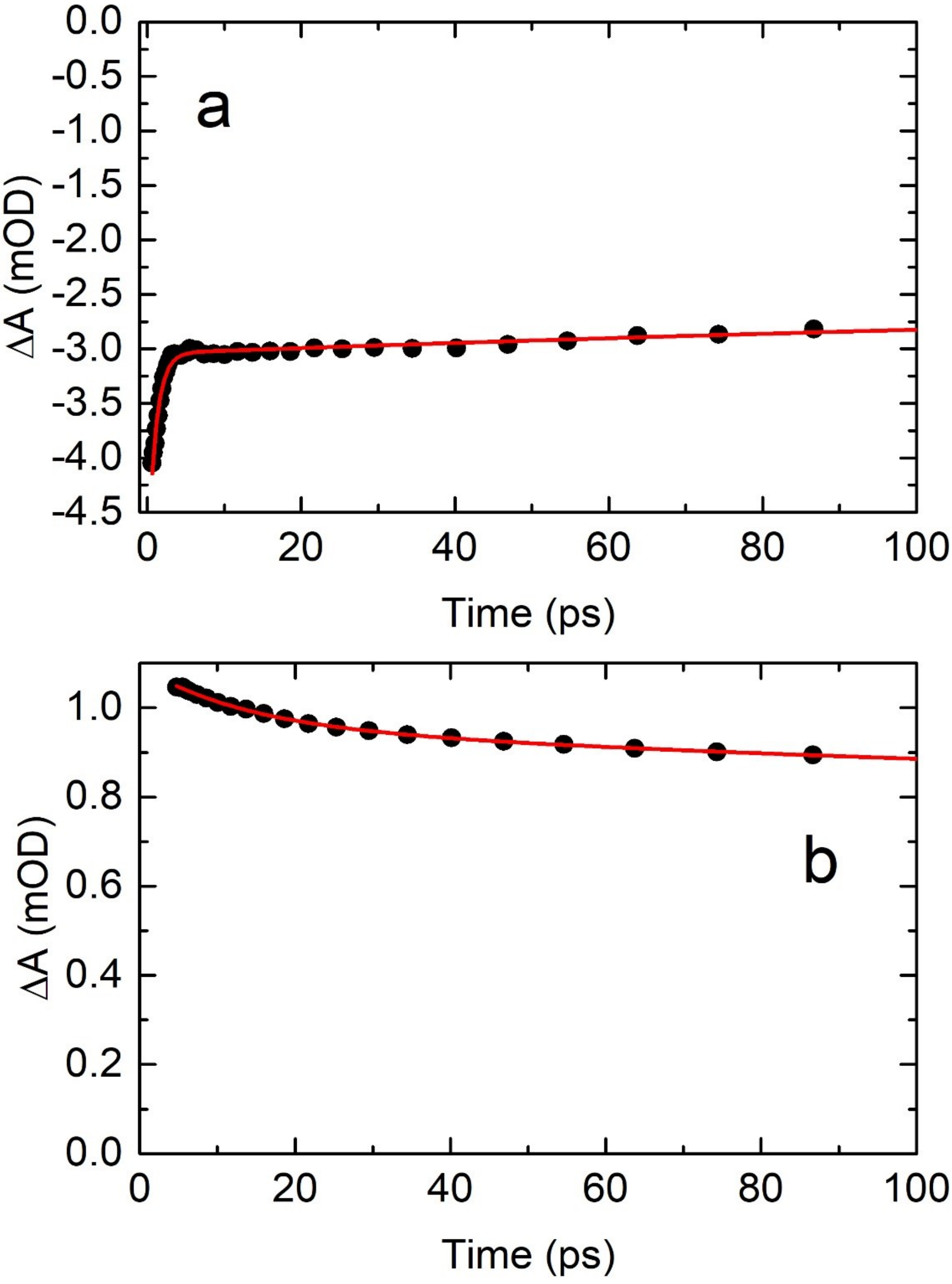

Fig. SI2. The first 100 ps of the transients shown in Fig. 6. a: Transient absorption dynamics of ground state oxalate represented by the symmetric stretch transition at 1313 cm^{-1} (dots). The absorption is well described by a double exponential function $\Delta A(t)$=-1.95mOD×exp(-t/1.1±0.5ps) -0.74mOD×exp(-t/0.28±0.05ns)-2.3 mOD (red line). b: transient absorption dynamics of the triplet excited state represented by the transition at 1400 cm^{-1} (dots). The decay of the transient absorption follows a tripple exponential curve: $\Delta A(t)$=0.094mOD×exp(-t/13.7±0.5ps)+0.15mOD×exp(-t/0.23±0.05ns) +0.80mOD×exp(-t/5.3±1.7 ns) (red line).

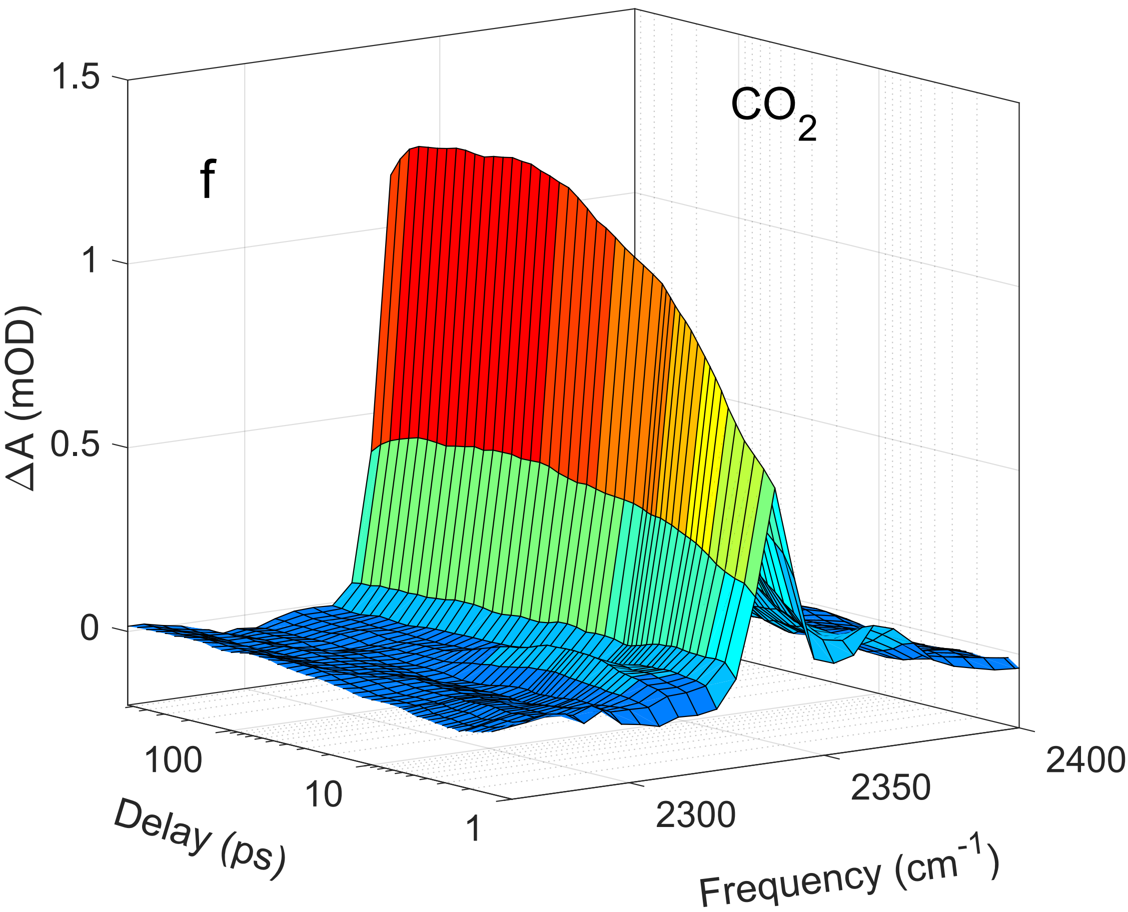

Fig. SI3. The CO_2 absorption dynamics from Fig. 5f shown from a different angle. The v=2 → v=1 hot band is seen in the foreground.