Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Perturbed free induction decay signal from ambient CO_2(g).

The perturbed free induction (PFID) signal is common in UV pump - IR probe transient absorption spectroscopy of liquids. The PFID signal usually pertains to vibrations in solvent and solute.[S1] When probing in the spectral range around 2350 cm^{-1} an additional PFID signal arises from the asymmetric stretch vibration of ambient gas-phase CO_2.

The short probe pulse excites the CO_2(g) molecules as it propagates through air, thereby inducing a coherent polarization of the CO_2(g) molecules. This polarization dephases during the free induction decay with a dephasing time T_2, which for CO_2(g) is many picoseconds. The infrared detector records the coherent sum of the infrared light of the probe pulse and the infrared light emitted by the decaying polarization pertaining to the CO_2(g) molecules. If the system consisting of the probe pulse and the CO_2(g) molecules is left alone during the free induction decay, the detector measures no induced absorption change. However, if the pump pulse interrupts the light emission during the free induction decay of the CO_2(g) molecules or changes the transmission through the liquid sample within ~T_2 after the probe pulse, the detector records an induced absorption change at times $t < 0$ – the perturbed free induction decay signal. In reality, the PFID signal persists for as long as there is a temporal overlap between the pump and the probe pulse, and PFID may thus be observed slightly after $t = 0$.

Fig. S1 below shows the raw data recorded in aqueous acetate. The figure shows an enormous $t = 0$ coherence signal preceded by a strong (and in this graph under-sampled) PFID signal. These signals are much stronger than the transient absorption pertaining to the photolysis of acetate, and small remnants of the signals persist 2 ps after $t = 0$ because of the finite width of Gaussian pump and probe pulses.

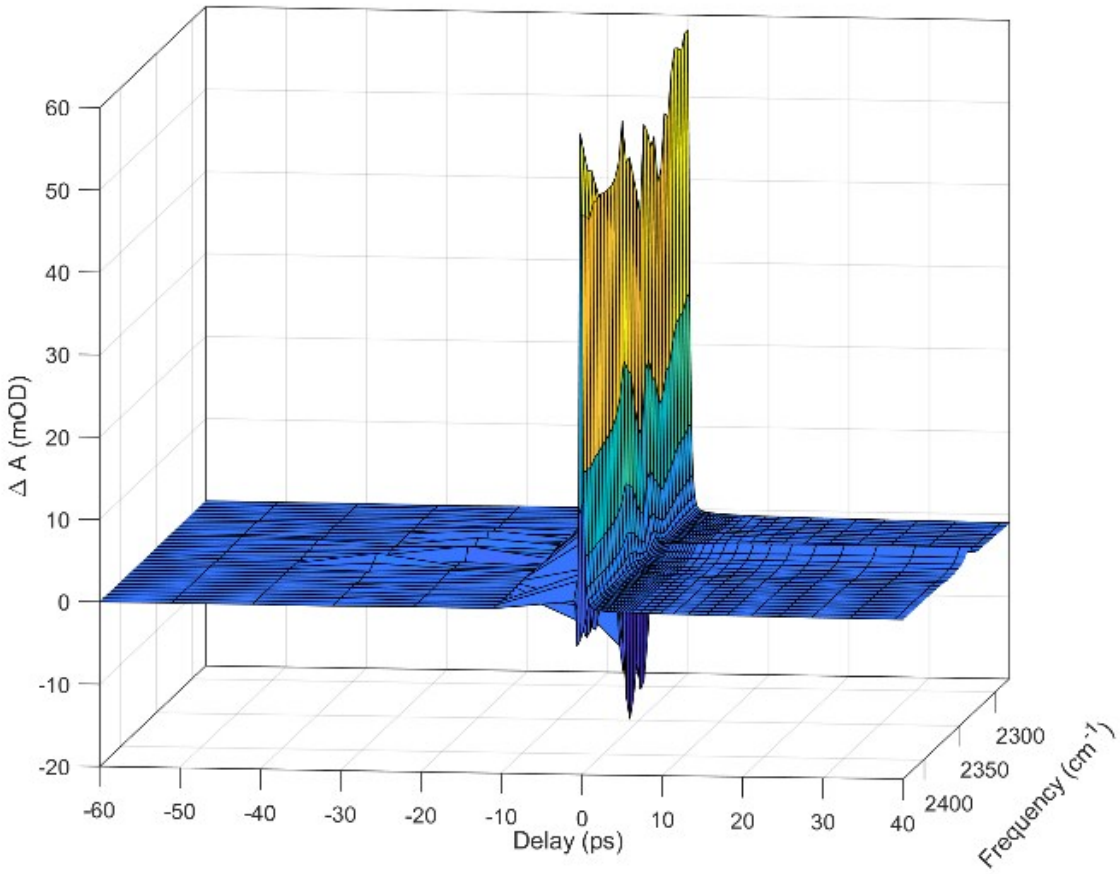
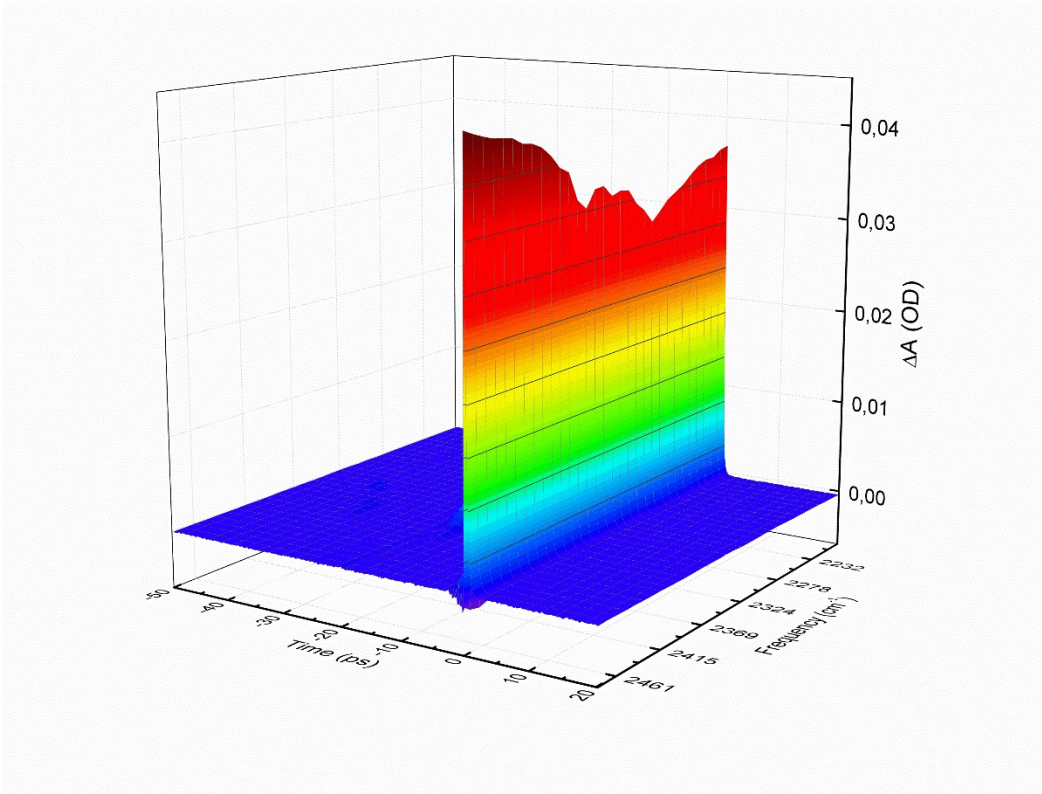


Fig. S1. Raw data recorded in aqueous acetate showing (under-sampled) PFID signal at $t < 0$ and the coherence signal at $t = 0$ together with the induced absorption associated with aqueous CO_2(aq) at $t > 0$.

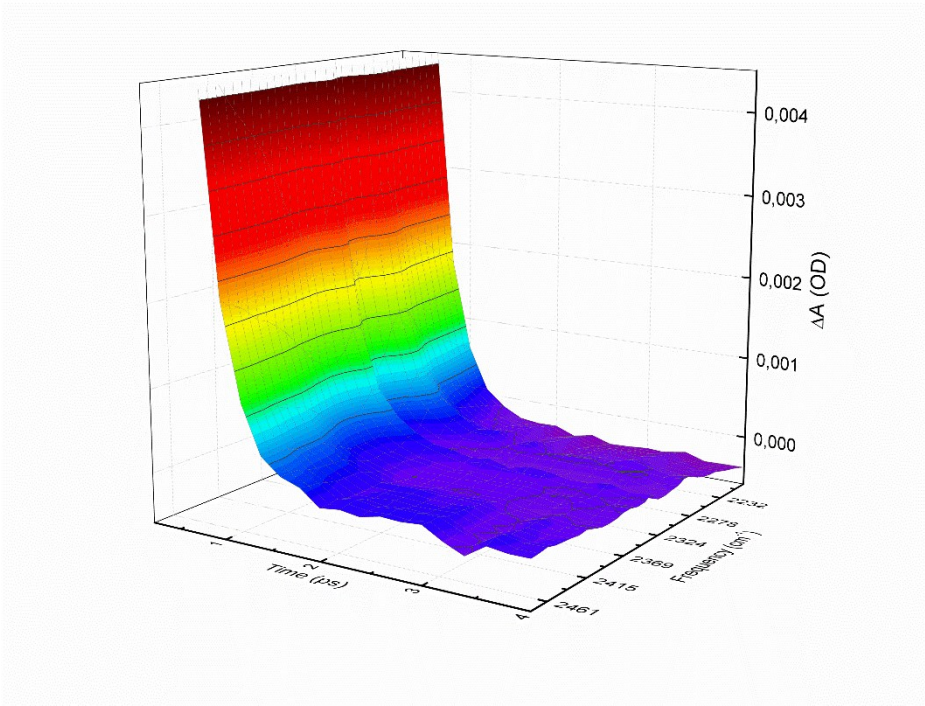
The origin of the t = 0 coherence signal and the PFID signal is clearly demonstrated in data recorded in neat water, shown in Fig. S2-S6 below. Note that these data lack the induced absorption pertaining to the asymmetric stretch of



CO_2(aq) observed in the photolysis of acetate.

Fig. S2. The t = 0 coherence signal and the PFID signal recorded in neat water.

Fig. S3. Close-up of the t = 0 coherence signal and the PFID signal recorded in neat water. Since the PFID signal related CO_2(g) and the coherence signal are strong and the Gaussian pump and probe pulses have a FWHM cross-correlation of about 0.3 ps the t = 0 coherence signal and the PFID signal are detectable for 2 ps after t = 0. That is, until the temporal overlap between pump and probe pulses becomes insignificant. The graph is truncated at ΔA = 0.0045 OD.



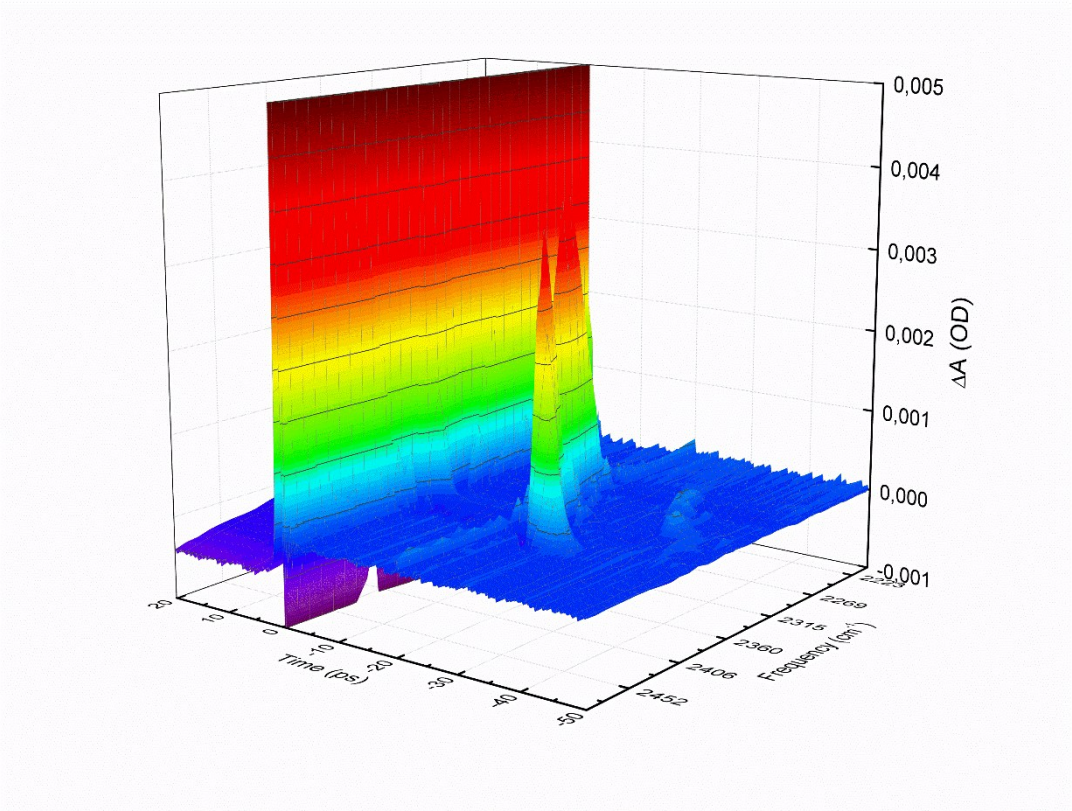


Fig. S4. The t = 0 coherence signal and the PFID signal recorded in neat water. Note the significant PFID signal from CO_2(g) appears already at t = - 40 ps. The graph is truncated at ΔA = 0.005 OD.

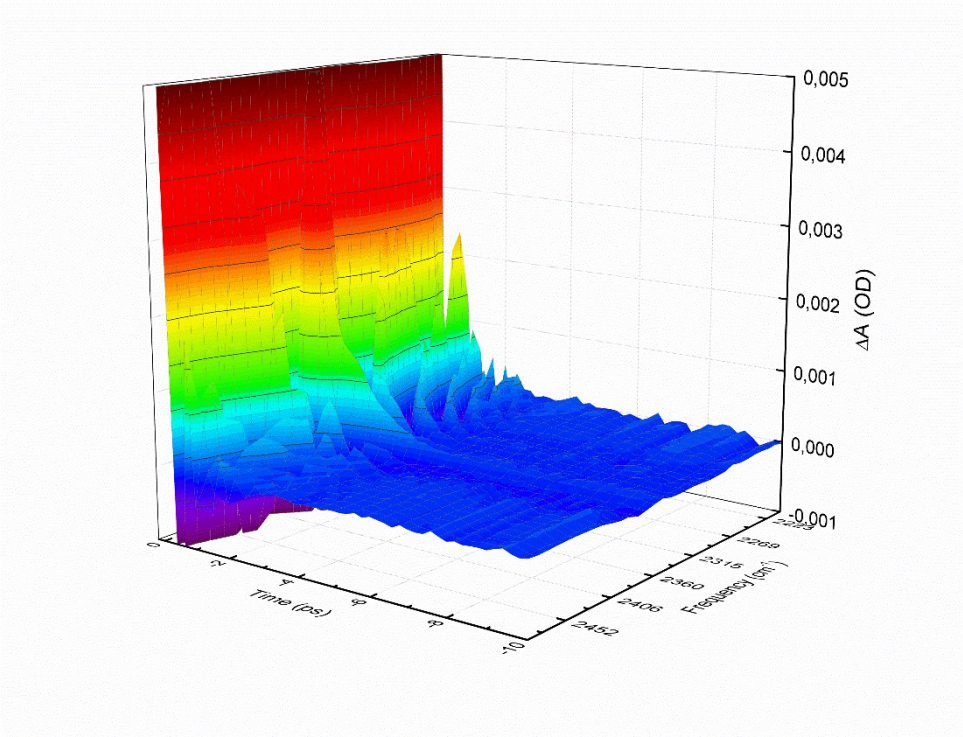


Fig. S5. The last –10 ps of the t = 0 coherence signal and the PFID signal recorded in neat water. The graph is truncated at ΔA = 0.005 OD.

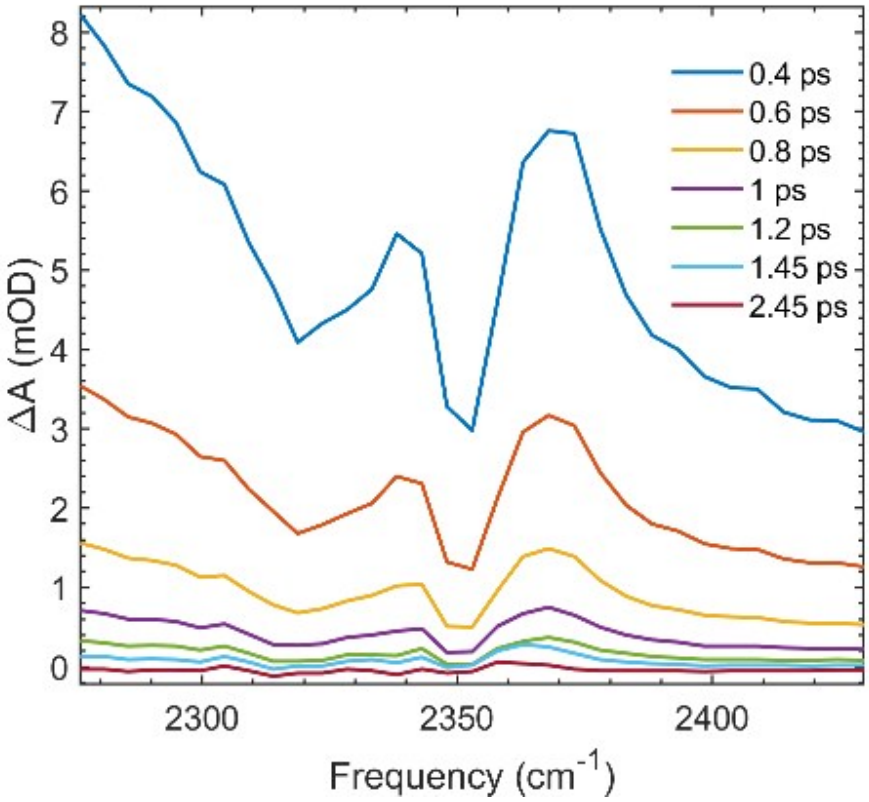


Fig. S6. The coherence signal and PFID signal recorded in neat water shown at selected times at t > 0. The data representation is similar to that of Fig. 2 and Fig. 3 in the manuscript.

References:

S1. P. Hamm. *Chem. Phys.* , 1995, **200**, 415.