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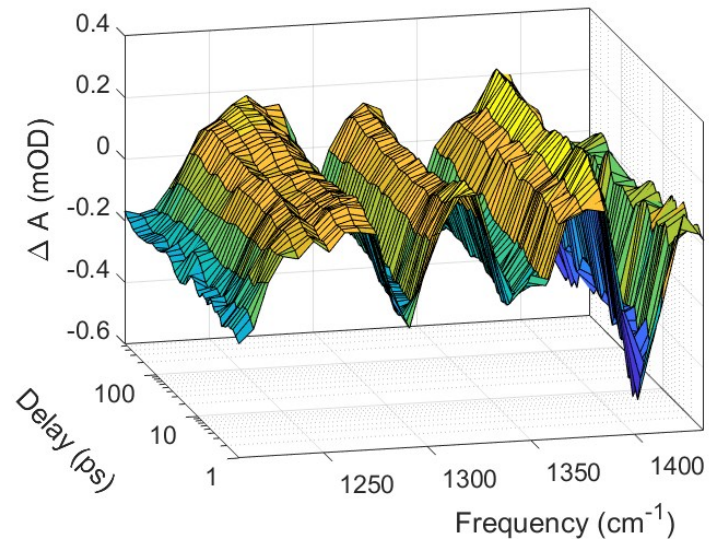
Signal linearity.

All absorption transients except the ones associated with the protonation results from one-photon excitation of aqueous alanine.

Two-photon artifacts are always a concern when photolysing weakly absorbing species at 200 nm. Given that the one-photon extinction coefficients of the investigated amino acids are only of the order of 100 l/mol cm, two-photon absorption in the amino acids or the water solvent may potentially contribute to the photodynamics. In order to assess the contribution from two-photon excitation, we initiate our transient absorption spectroscopy measurements with a thorough investigation of the intensity dependence of the amplitude as well as the dynamics of the induced infrared absorption signal.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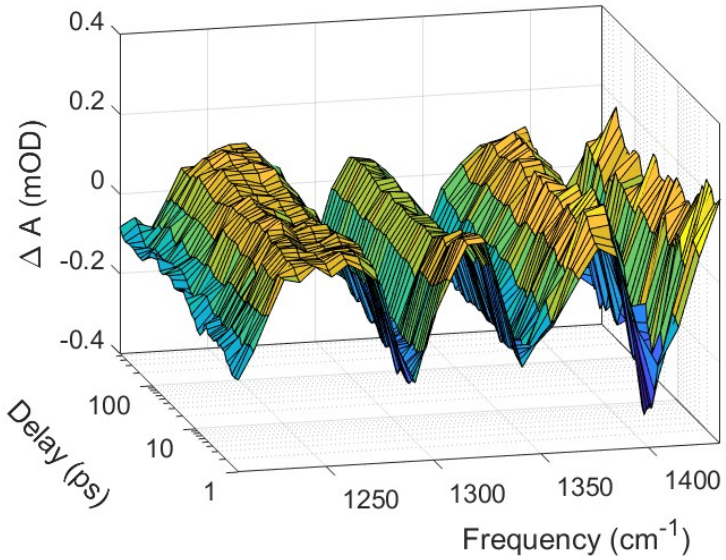
0.2
0
-0.2
-0.4
-0.6
Δ A (mOD)
100
10
1
Delay (ps)
1250
1300
1350
1400
Frequency (cm-1)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0.2
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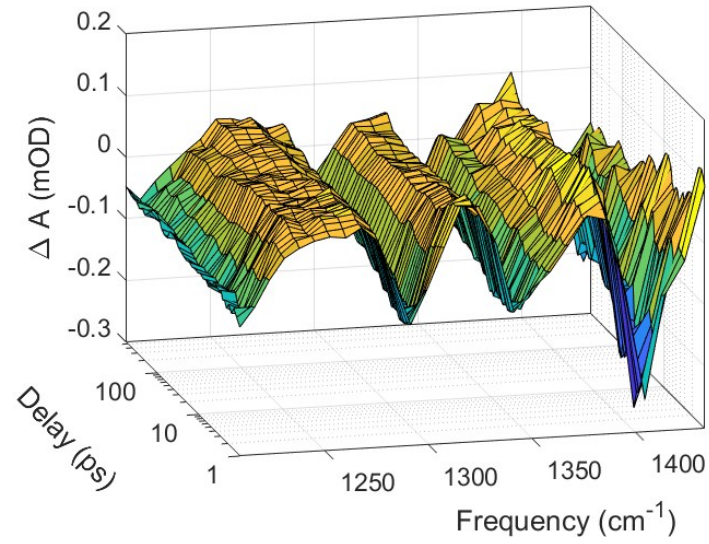
Frequency (cm-1)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0.1
0
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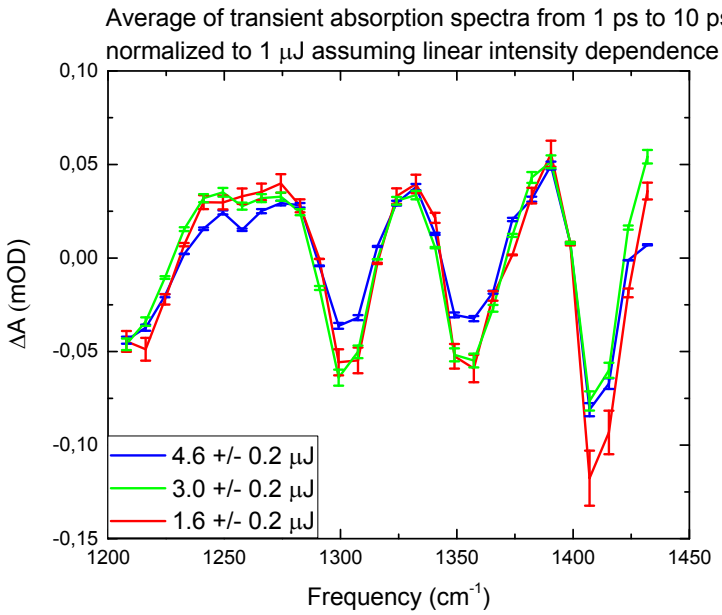
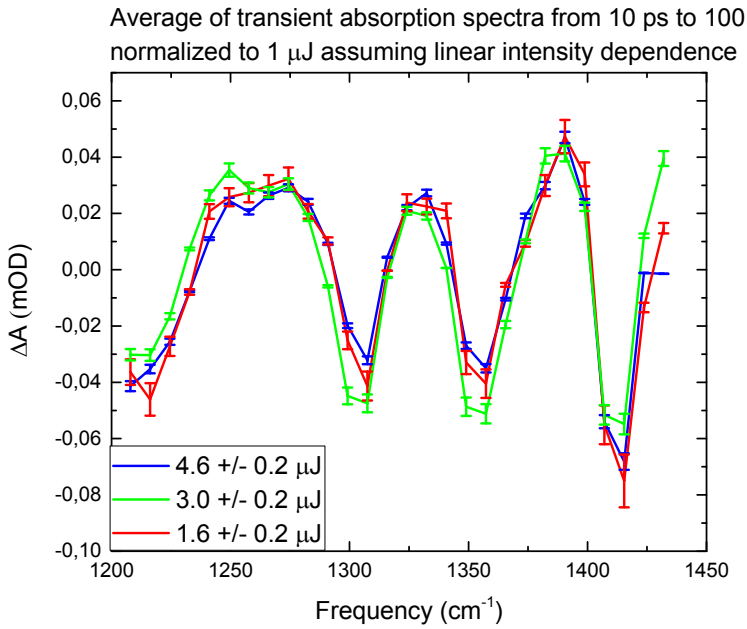
Δ A (mOD)
100
10
1
Delay (ps)
1250
1300
1350
1400
Frequency (cm-1)

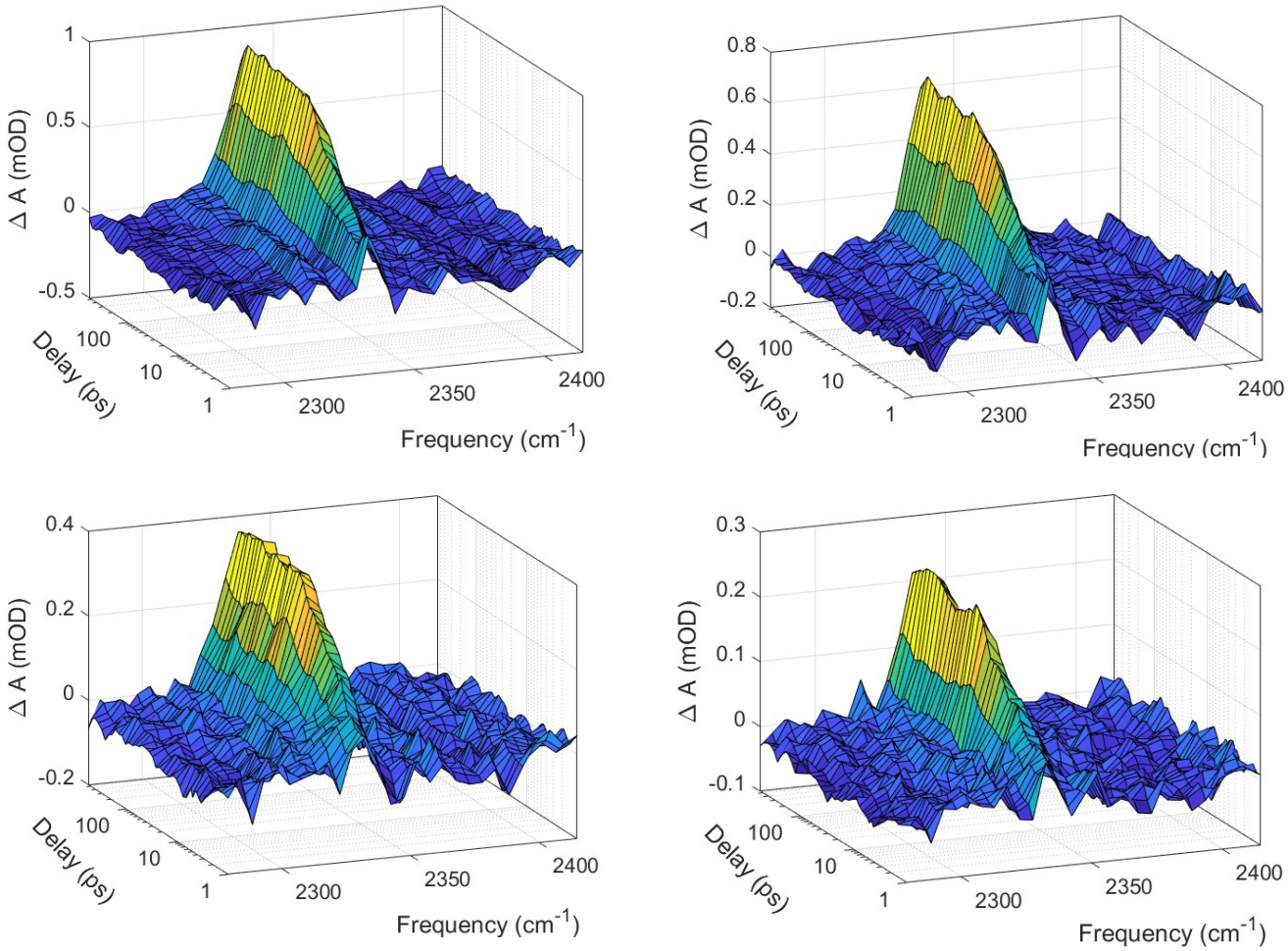
First, we discuss the pump pulse energy dependence of the excitation of ground state alanine: The figures above show the transient absorption dynamics from 1200 to 1430 cm^{-1} measured at three different pump pulse energies: 4.6 μJ (top), 3.0 μJ (middle) and 1.6 μJ (bottom). The first 100 ps of the transient absorption dynamics is similar in the three measurements thus demonstrating that the absorption dynamics is independent of the pump pulse energy. Accordingly, the transient absorption is induced exclusively by one-photon excitation or exclusively by two-photon (or higher) excitation. Only after some 100 ps does the protonation of alanine due to two-photon ionization of water become discernable at the symmetric COOH stretch transition at 1260 cm^{-1}, but only for the highest pump pulse energy (i.e. the induced absorption dynamics depends on the pump pulse energy). The slow protonation is also reflected in a late decrease in the infrared absorption induced at the highest pump pulse energies. This is not visible from the viewing angle used in the 3D figures above.



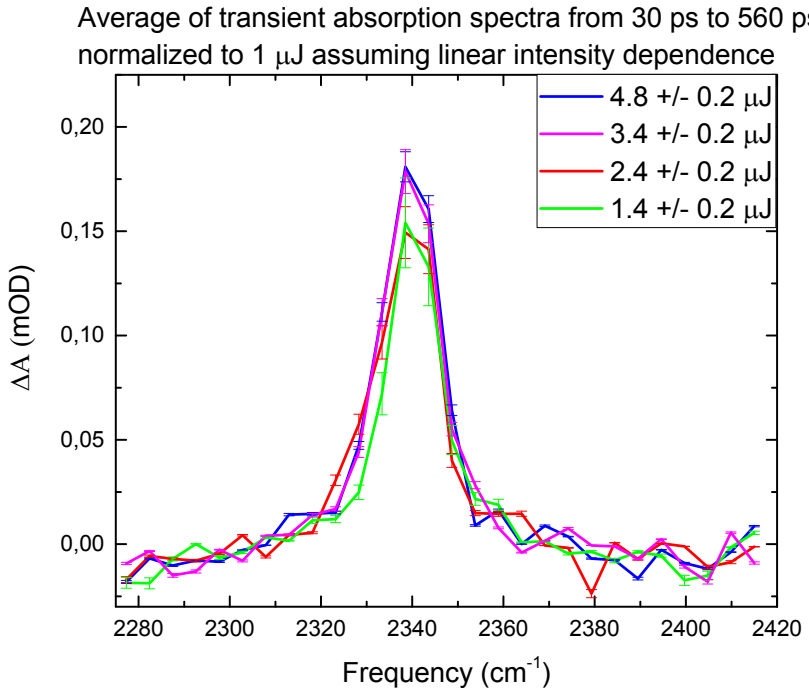


Now, the induced absorption signal from 1 to 100 ps scales linearly with the pump energy: The two figures above show the pump pulse energy dependence of the average transient absorption spectra from 1200 to 1430 cm^{-1} from 1 to 10 ps and from 10 to 100 ps. The spectra are measured at pump pulse energies of 1.6, 3.0 and 4.6 μJ. The spectra in the figures are normalized to a pump pulse energy of 1 μJ assuming a linear pump pulse energy dependence. The error bars represent the uncertainty in the pulse energy measurement. The three spectra coincide nicely. This shows that the induced transient absorption is due to one-photon excitation

The one-photon photo-dissociation of alanine results in decarboxylation:



The transient infrared absorption dynamics pertaining to the asymmetric stretch transition of CO_2 at 2338 cm^{-1} are shown above. The transients are recorded at four different pump energies: 4.8 μJ (top left), 3.4 μJ (top right), 2.4 μJ (bottom left) and 1.4 μJ (bottom right). They all display the same absorption dynamics, thus demonstrating that the decarboxylation dynamics is independent of the pump pulse energy. Moreover, the amplitude of the absorption signal increases linearly with the pump pulse energy as shown below.



The figure above shows the average of the transient absorption spectra recorded from 30 to 560 ps at four different pump pulse energies 4.8 μJ, 3.4 μJ, 2.4 μJ and 1.4 μJ. The four spectra are normalized to a pump pulse energy of 1 μJ assuming linear energy dependence. Again, the error bars indicate the uncertainty of the pump pulse energy measurement. The four traces coincide within the experimental uncertainty thus showing that the decarboxylation of alanine is induced by one-photon excitation at 200 nm.