The primary photo-dissociation dynamics of lactate in aqueous solution: decarboxylation prevents dihydroxylation ESI

Jan Thøgersen,[a]* Veronica Vaida[b], Mikkel Bregnhøj,[a] Tobias Weidner[a] and Frank Jensen [a]

More details on the analysis of the ethanol/ethoxide content discussed on page 11:

As mentioned in the *protonation by secondary reactions* section, the transient absorption data in Fig. 5d show that the non-linear production of lactic acid following two-photon ionization of water is detectable and increasing after t = 50 ps. Fig. 4 shows that lactic acid absorbs at $\nu = 1042\ \mathrm{cm}^{-1}$, $\nu = 1093\ \mathrm{cm}^{-1}$ and $\nu = 1128\ \mathrm{cm}^{-1}$ and could potentially affect the estimated yields. However, the fact that similar ethanol yields are deduced from the time intervals t = 50-100 ps and t = 100-500 ps after the excitation indicate that contributions to the transient absorption from lactic acid are only minor in this region. This is likely because the lactate concentration used in the measurements presented in Fig. 5a-c and e-g is three times higher than that in Fig. 5d thereby significantly reducing the two-photon ionization of water and in turn the non-linear contribution from lactic acid.

Electron dynamics

The following gives a detailed analysis of the electron absorption dynamics discussed on pages 12-13. The analysis shows the electron contribution from one-photon excitation of lactate is separable from the two-photon ionization of water.

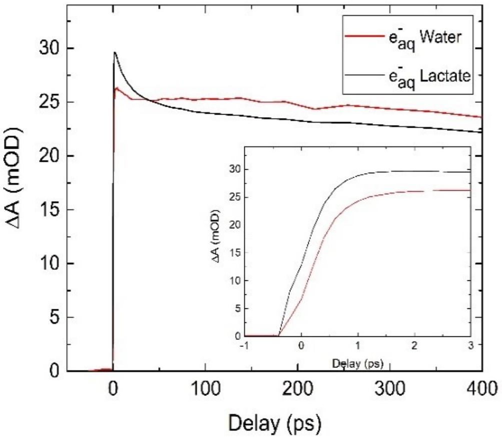


Fig. S1. Transient absorption at λ = 650 nm associated with hydrated electrons from aqueous lactate and pure water when excited by λ = 200 nm pump pulses under the same conditions. The pulse energy on the sample is E = 2.3 μJ. The Insert shows the first t = 3 ps after the excitation.

The transient absorption pertaining to hydrated electrons from the aqueous lactate solution following photoexcitation at λ = 200 nm is shown in Fig. S1. The transient absorption dynamics is recorded with the same pulse energy as the one used for recording the UV pump – IR probe transient data in Fig. 5 and Fig. 6. Fig. S1 also shows the transient absorption associated with hydrated electrons recorded in a pure water sample under the same experimental conditions. The induced transient absorption measurements in aqueous lactate and pure water are remarkably similar indicating that the induced absorption in aqueous lactate is dominated by the contribution of hydrated electrons from ionization of water. In both cases the transient absorption increases to a maximum in t = 1 ps and the absorption magnitudes of the two samples are nearly the same. However, the transient absorption recorded in aqueous lactate peaks at a slightly higher value than for pure water and drops by about 20 % during the subsequent t = 400 ps, whereas the transient absorption in pure water remains nearly constant. The different early absorption dynamics of aqueous lactate and pure water indicate the presence of electrons from lactate. This is confirmed by measurements of the electron yield as a function of the pump pulse energy shown below.

Since the excitation of lactate is a one-photon process, the electron yields grows linearly with the pump pulse energy, while the ionization of water is a two-photon process and the electron yield from water therefore increases non-linearly with the pump pulse energy. For a detailed discussion of the intensity dependence of the two-photon ionization of water the reader is referred to ref. ESI1. The pump pulse energy dependence of the transient absorption at λ = 650 nm in aqueous lactate and pure water is shown in Fig. S2. The energy dependence is recorded at t = 1 ps, t = 10 ps and t = 100 ps after the λ = 200 nm pump pulse. Each data set is fitted by a second order polynomium. Within the uncertainty of the fit, the pure water data at the three delays are well represented by the same polynomium ΔA = 7.0 (±0.9) mOD/μJ × E + 3.9 (±0.5) mOD/μJ^2 × E^2 with R^2= 0.997 or better, clearly showing the non-linear excitation of the water molecules. Note that the ratio between the linear and quadratic coefficients is r = 1.8. In contrast, the aqueous lactate data at t = 1 ps, t = 10 ps and t = 100 ps show significantly different energy dependencies. For the data after t = 1 ps the best polynomial fit is ΔA = 10.9 (±1) mOD/μJ × E + 1.3 (±0.5) mOD/μJ^2 × E^2 (R^2= 0.998), after t = 10 ps the best

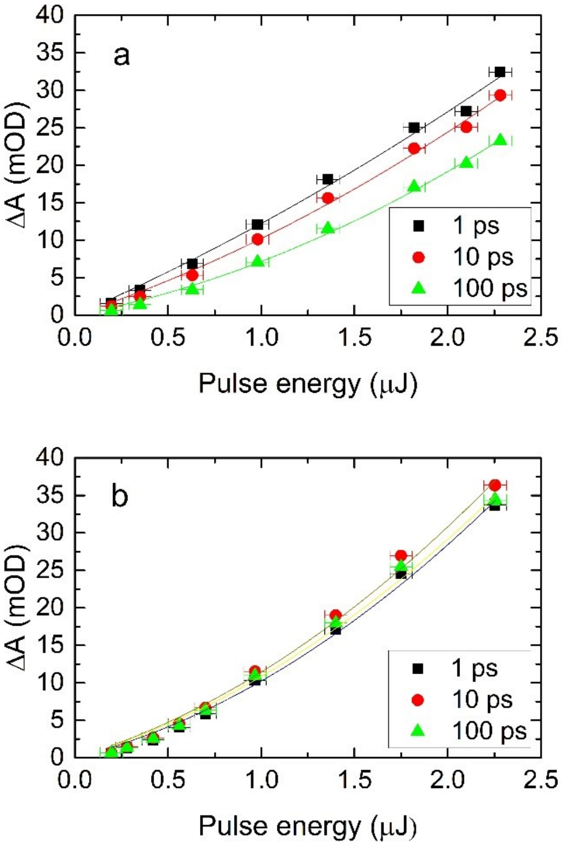


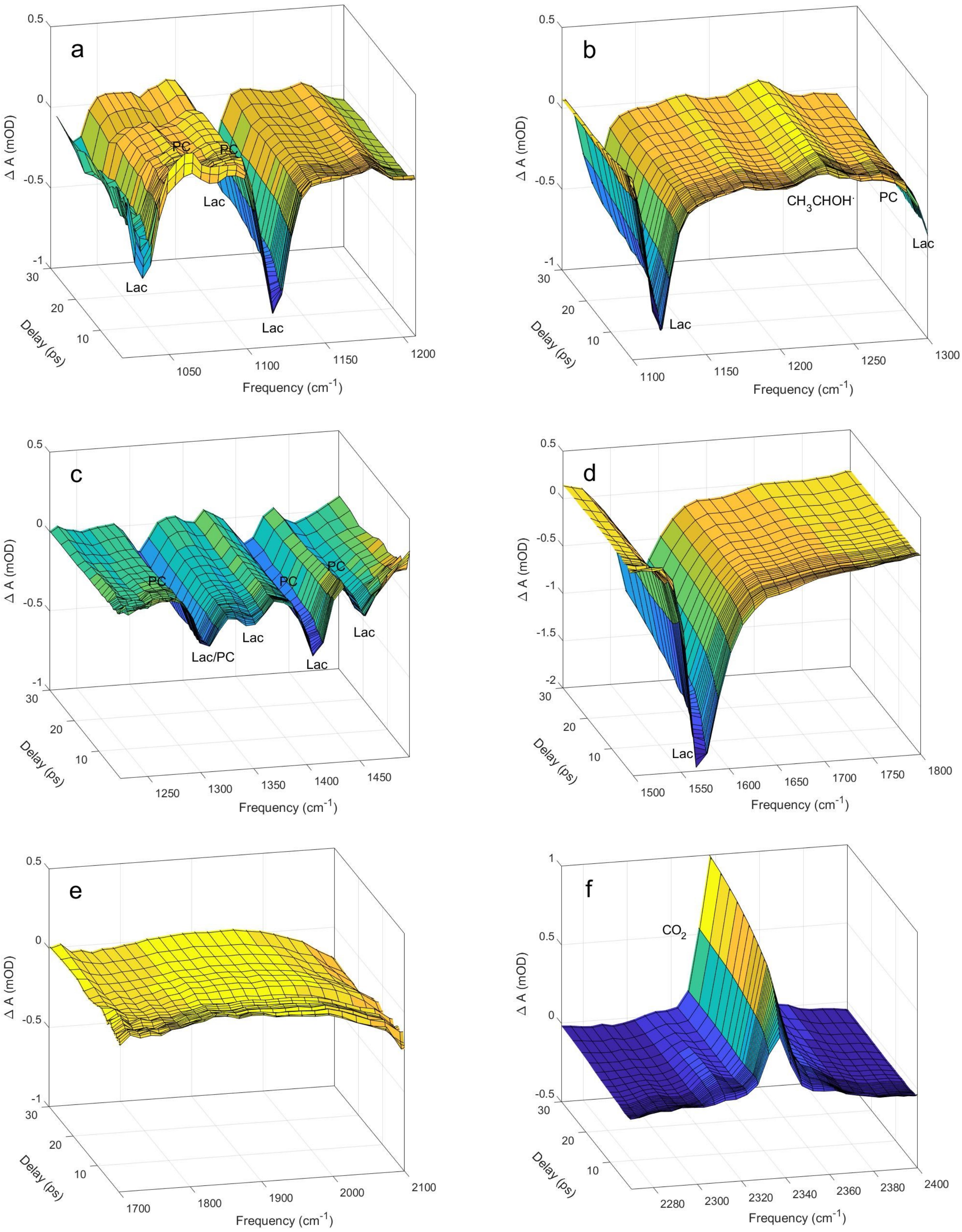
Fig. S2. Pump pulse energy dependence of the absorption at λ = 650 nm associated with a: aqueous lactate b: pure water.

polynomial fit is $\Delta A = 8.2\ (\pm 0.8)\ \mathrm{mOD}/\mu\mathrm{J} \times E + 2.0\ (\pm 0.4)\ \mathrm{mOD}/\mu\mathrm{J}^2 \times E^2$ ($R^2 = 0.998$), while the data after t = 100 ps is well fitted by $\Delta A = 4.8\ (\pm 0.5)\ \mathrm{mOD}/\mu\mathrm{J} \times E + 2.4\ (\pm 0.3)\ \mathrm{mOD}/\mu\mathrm{J}^2 \times E^2$ ($R^2=0.998$). Note that the ratio between the linear and quadratic coefficients here are r = 8.4 after 1 ps, r = 4.1 after 10 ps and r = 2.0 after 100 ps. The r = 2.0 ratio after 100 ps approaches the r = 1.8 ratio of pure water in line with the notion that the λ = 650 nm absorption in aqueous lactate at t = 100 ps is dominated by the contribution from water, while the initial absorption has a significant contribution from one photon excitation of lactate

ESI references.

1 A. Reuther, A. Laubereau, and D. N. Nikogosyan. *J. Phys. Chem.* 1996, **100**, 16794.

Figure S3. The first t = 30 ps of Fig. 5, page 7 on a linear time scale



Figur S3. The first t = 30 ps of Fig. 5 shown on a linear time scale.

The first 30 ps of the CO_2 dynamics on a linear time scale. Details of Fig. 5, page 7 and Fig. 6, page 9.

The data show little, if any, spectral narrowing with time and a modest initial blue-shift of about $\Delta\nu$ = 1 cm^{-1}. In addition, the absorption associated with the v = 1 -> v = 2 hot band at ν = 2315 cm^{-1} is a small fraction of that pertaining to the fundamental transition. Considering that the asymmetric stretch v = 0 -> v = 1 transition at 2343 cm^{-1} has approximately the same intensity as the v = 1 -> v = 2 transition (HITELOR database D. Scutaru et al. J. Quant. Spec. Radiat. Spectrosc. Trans. **52**, 765, (1994)), the majority of CO_2 molecules are in the vibrational ground state after 1 ps. Hence, the absorption dynamics after t = 1 ps essentially reflects the CO_2 formation kinetics.

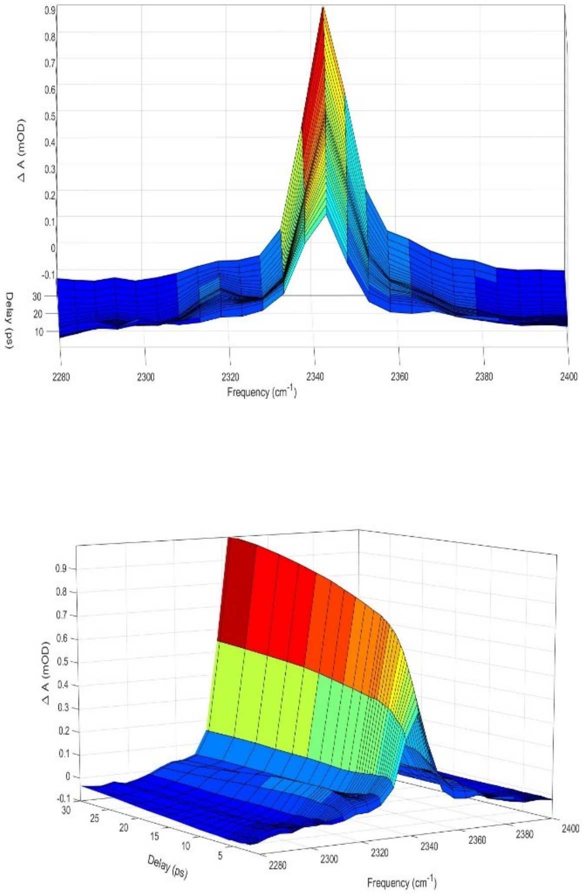


Fig. S4. Transient absorption associated with the asymmetric stretch of CO_2 shown on a linear time scale at two different angles.

Intensity dependence of excitation dynamics discussed on page 8.

Intensity dependence of the excitation of lactate exemplified by the transient absorption associated with the asymmetric stretch of lactate at $\nu = 1575$ cm^{-1}. The figures show that the excitation of lactate grows linearly with pump pulse energy for t< 100 ps, thus demonstrating that lactate is excited by one-photon absorption. The figures also show that the relative contribution from protonation of lactate induced by two-photon ionization of water decreases with decreasing pump pulse energy, since this depends non-linearly on the pump pulse energy.

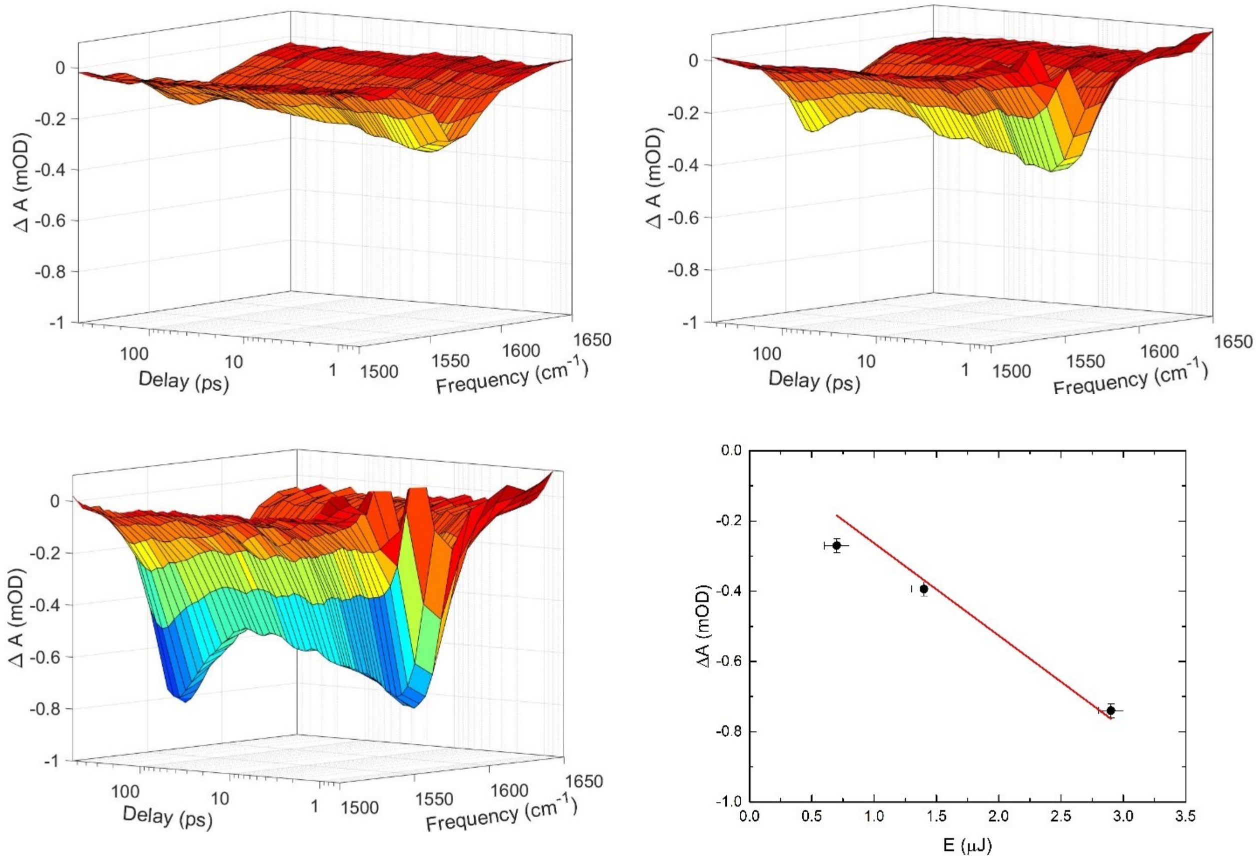


Fig. S5. The pump pulse energies in the three 3D plots are E = 0.7 ± 0.1 μJ (top left), E = 1.4 ± 0.1 μJ (top right) and E = 2.9 ± 0.1 μJ (bottom left). The induced absorption after t=1.4 ps as a function of pump pulse energy is shown in the plot (bottom right). The red line is a linear fit to the data points through origin.