

Supplementary Information for

Observation of Distinct Carboxylic Acid Conformers in Aqueous Solution

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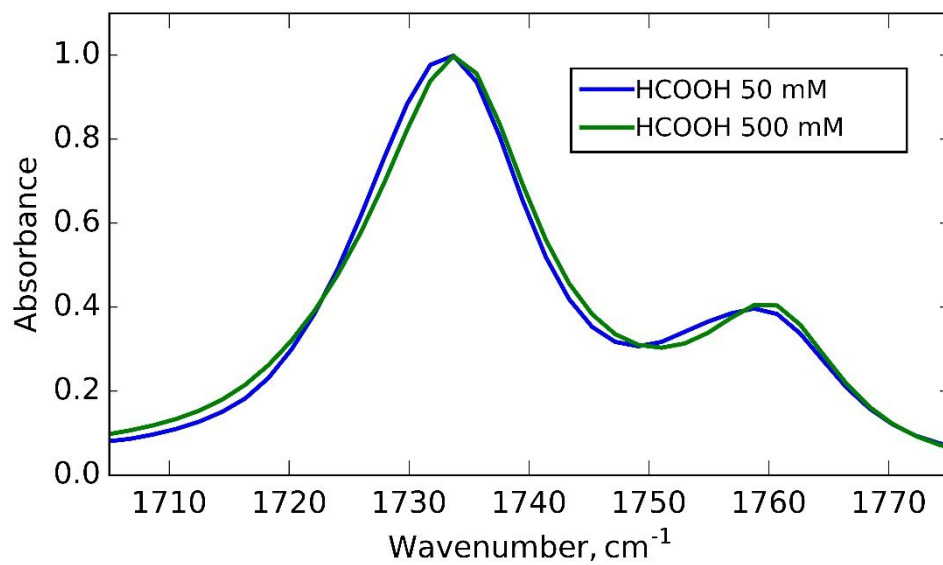
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Experimental approach

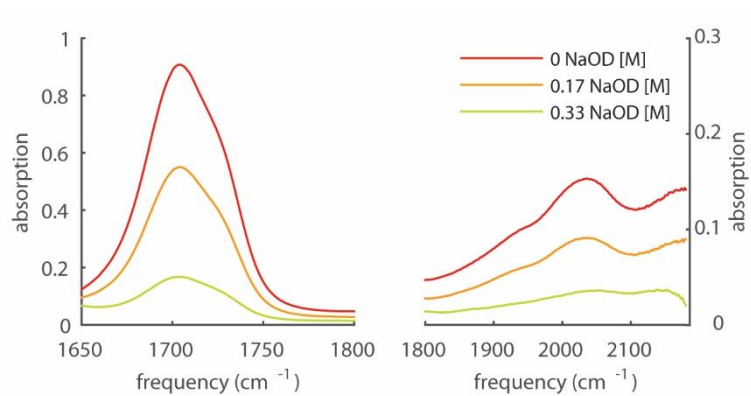
One and two-color 2D-IR measurements were performed in pump-probe geometry on the same sample. We first measured in the region of the carbonyl vibrations by tuning both the pump and the probe to 1720 cm^{-1} . Secondly, we move the probe to the O-D region, adjusting the polarization, and compensating the chirp by adding calcium fluoride windows in the probe optical path. In both types of measurements, 2D-IR spectra are obtained by averaging over at least 10 scans, and for every scan at every time delay we scan the interferometer at least 30 times. This results in a total measurement time of approximately 10 hours.

Signals in parallel and perpendicular polarizations are acquired simultaneously. The resulting anisotropy is described by the following equation:

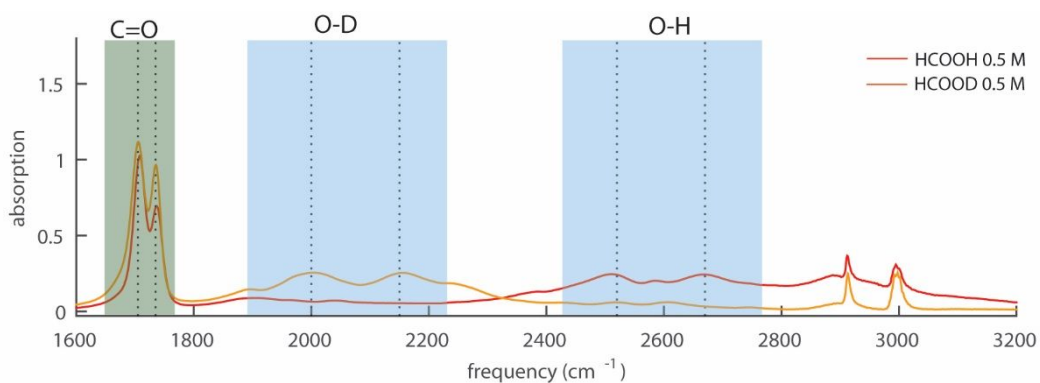
$$R = \frac{\Delta\alpha_{par} - \Delta\alpha_{per}}{\Delta\alpha_{par} + 2\Delta\alpha_{per}}$$



Supplementary Figure 1: Scaled linear infrared spectra of 50 and 500 mM solution of formic acid in acetonitrile-d₃.



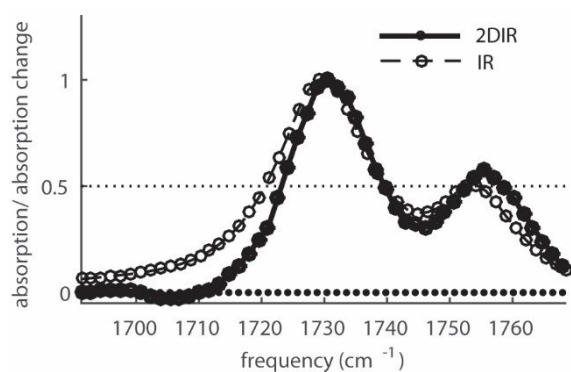
Supplementary Figure 2: Linear infrared spectra of 0.5 M formic acid in heavy water with different amounts of added NaOD (D₂O background is subtracted). We observe a strong decrease in absorption at 2050 cm⁻¹, which supports the assignment of this band to the O-D stretch vibration of formic acid.



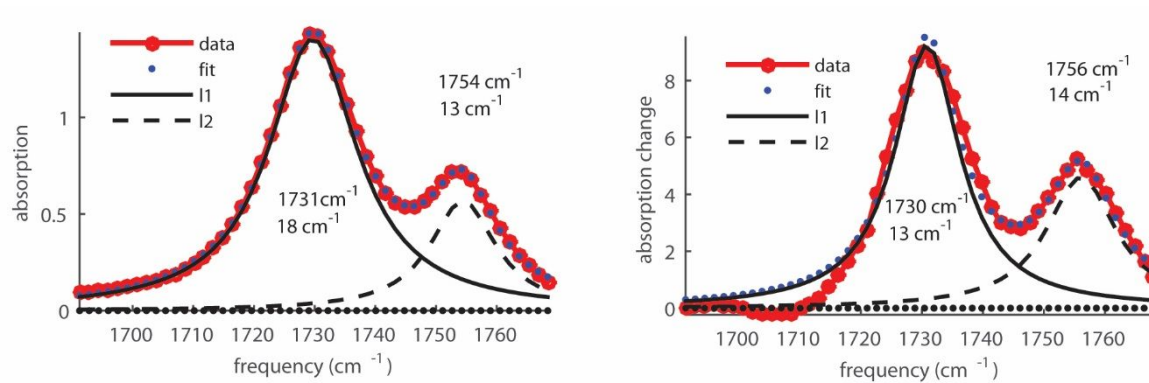
Supplementary Figure 3: Linear infrared spectra of 0.5 M solutions of deuterated and non-deuterated formic acid in DMSO (solvent background is subtracted). In both solutions the double-peak structure of the carbonyl band is clearly observed. The broad structured bands at 1900-2300 cm^{-1} and 2400-2800 cm^{-1} are assigned to O-D and O-H stretch vibrations of deuterated and non-deuterated formic acid, respectively.

Relative concentration of the two conformers

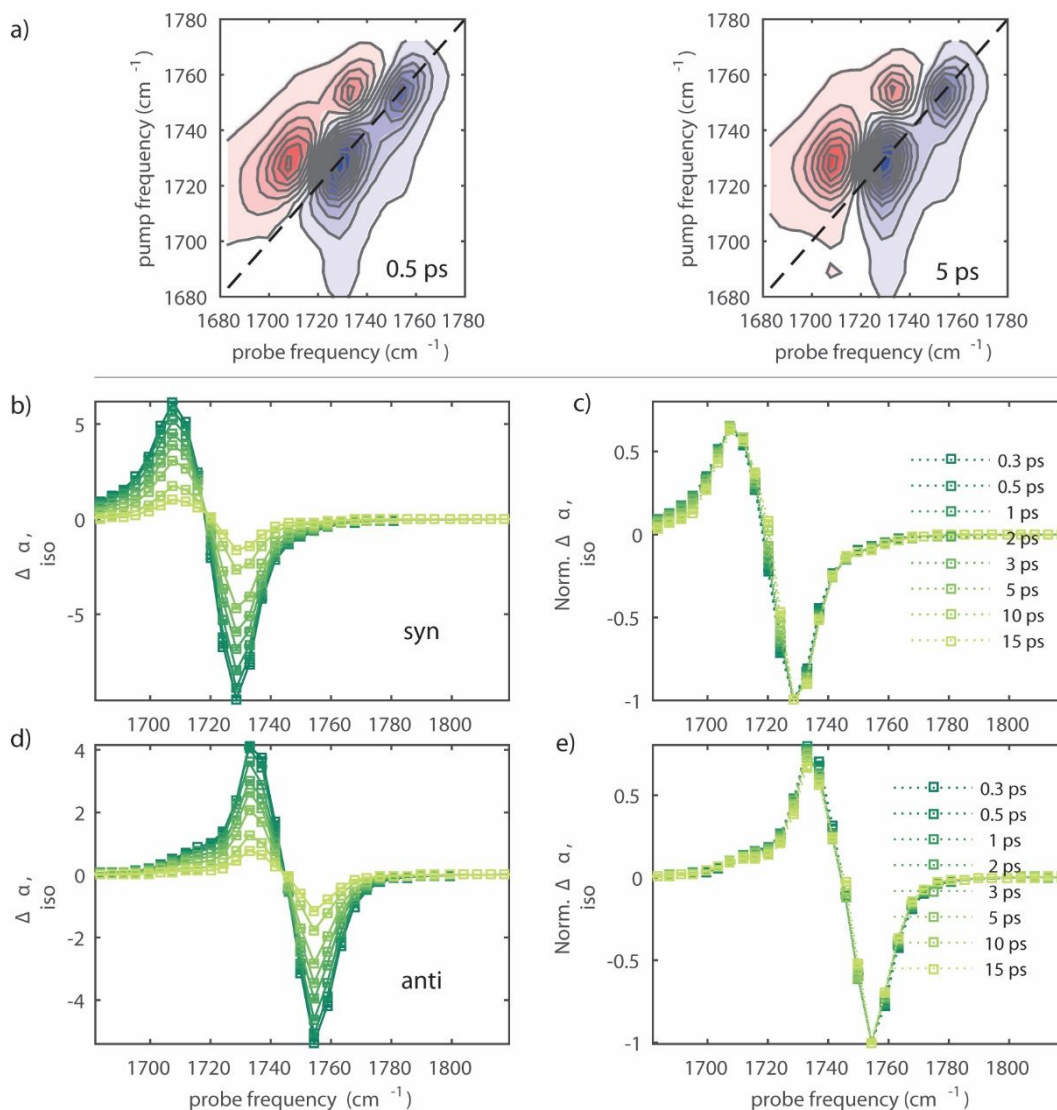
The relative concentration of the conformers cannot be determined from the linear infrared spectrum as the cross-sections of the carbonyl vibrations of the two conformers are not known. However, we can make use of the fact that the linear infrared absorption spectrum scales as μ^2 (where μ is the vibrational transition dipole moment), while the 2D-IR spectrum scales as μ^4 , thus providing an additional relation between the measured signals, cross-sections and concentrations. The linear IR spectrum and the diagonal 2D-IR spectrum (pump frequency = probe frequency) are shown together in Supplementary Figure 4. The diagonal 2D-IR spectrum (and in fact all presented 2D-IR spectra) is normalized with respect to the pump spectrum. We observe a very similar ratio of the two bands in the linear IR spectrum and the diagonal 2D-IR spectrum, which indicates that the two bands have similar cross-sections. To obtain the precise ratio between the cross-sections of the peaks we fit the linear spectrum and the 2D-IR slice with two Lorentzian-shaped bands (Supplementary Figure 5). We find that the ratio of the two cross-sections is close to 1, meaning that the two carbonyl vibrations have a similar transition dipole moment. We then calculate the areas under the bands of the two carbonyl vibrations by fitting the linear spectrum.



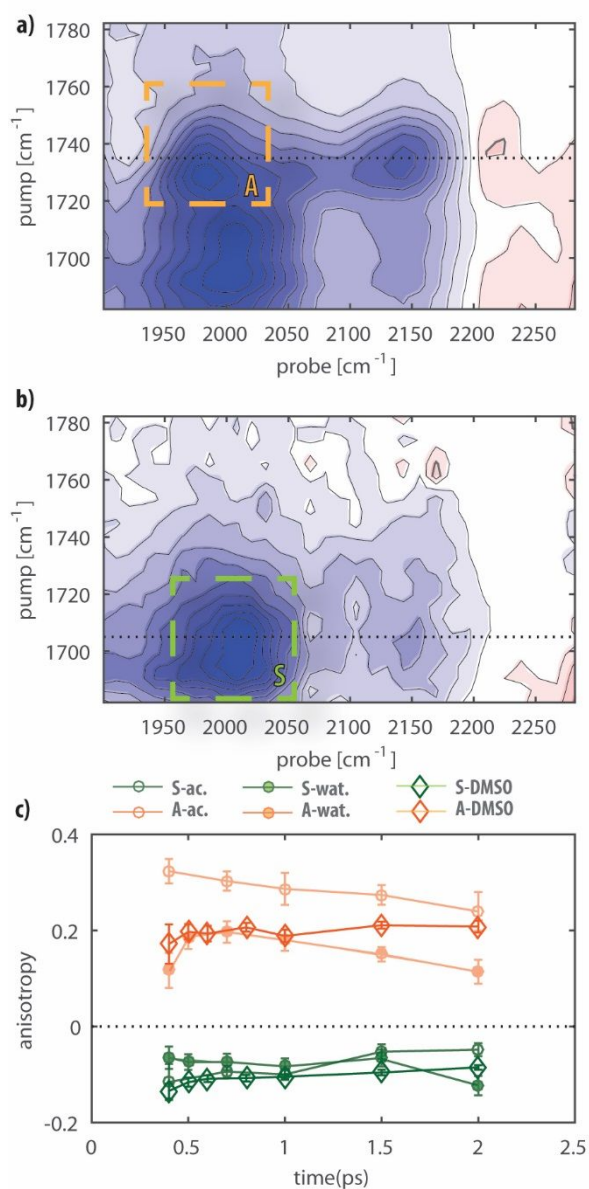
Supplementary Figure 4: Linear infrared spectrum and a diagonal slice of the 2D-IR spectrum of formic acid in acetonitrile- d_3 . The similar shape of the spectra indicates that the carbonyl stretch vibration has a similar absorption cross section for the *syn*- and *anti*-conformers.



Supplementary Figure 5: Decomposition of the linear infrared spectrum (left) and 2D-IR diagonal slice (right) of formic acid in acetonitrile- d_3 into two lorentzian-shaped bands, corresponding to two formic acid conformers.



Supplementary Figure 6: a) Isotropic degenerate 2D-IR spectra of formic acid in d-acetonitrile at 0.5 and 5 ps. b) Isotropic transient spectra as a function of probe frequency taken at a pump frequency of 1727 cm^{-1} , which is the central frequency of the carbonyl vibraton of the syn-conformer. c) Transient spectra reported in b) normalized at the maximum intensity of the cross-peak. d) Isotropic transient spectra as a function of probe frequency taken at a pump frequency at 1754 cm^{-1} , which is the central frequency of the carbonyl vibration of the anti-conformer. e) Transient spectra reported in d) normalized at the maximum intensity of the cross-peak. The transient spectra do not show any sign of ingrowing cross-peaks. Hence, the conformers do not show chemical exchange on a picosecond time scale.



Supplementary Figure 7: 2D-IR spectra of 0.5 M of formic acid in DMSO obtained by excitation of the carbonyl stretch vibration and probing of the O-D stretch modes with a) parallel and b) perpendicular probe polarization; c) comparison of the anisotropies of O-D/C=O cross-peaks of formic acid in acetonitrile-d₃, heavy water, and DMSO solution.