Supplemental Figure Captions for S. T. Shipman (et al.), "Vibrational dynamics of carboxylic acids in gas and dilute solution".

Fig. S1. A van Hoft plot of the equilibrium between monomeric and dimeric formic acid (squares) and trifluoroacetic acid (circles). The data for this plot were taken in a heated gas cell under constant volume conditions, and so the intercept of the best-fit line yields the entropy change on dimerization, which is -185 ± 21 J / (mol K) for TFA and -163 ± 29 J / (mol K) for FA. The slope gives $-\Delta U$ for the same process; ΔU is -69 ± 8 kJ / mol for TFA and -44 ± 21 kJ / mol for FA. By way of comparison, the entropy change on dimerization from *ab initio* calculations is -166 J / (mol K) for TFA and -155 J / (mol K) for FA at the B3LYP/6-311++G(2d,p) computational level.

Fig. S2. Plots of the residuals for the unconstrained best fits of the gas phase FA and TFA transient absorption data. All other residuals are available as figure insets of the main text. Best fit parameters are given in Table 1 of the text.

Fig. S3. Contour plots showing error surfaces of constrained fits to the FA and TFA gas phase acyclic and free O–H bands. The data were fit across a grid of fast and slow time constants, spanning 5 – 100 ps for the fast constant and 50 – 1000 ps for the slow constant, with grid spacing of 5 ps along each axis. Note that the TFA acyclic data were fit to a triexponential to account for interference from the cyclic dimer band bleach. This time constant was allowed to freely vary, but restrictions were placed on the signs of the amplitudes to force the fast time constant to be a rise and the slow and dimer-bleach-related constants to be decays. This was the only data set were amplitude sign restrictions were imposed.

Fig. S4. Frequency-resolved spectra of gas phase formic acid (top panel) and trifluoroacetic acid (bottom panel) acquired at fixed pump-probe delay times after pumping the dimer band at 3107 / 2953 cm^{-1} (FA / TFA). These spectra show the decay of the band attributed to the acyclic dimer and, in TFA, show the rise of the free O–H signal. The vertical lines in each panel indicate the probe pulse frequencies used to monitor the acyclic dimer band, chosen to minimize contamination by the cyclic dimer bleach at lower frequencies.

Fig. S5. Fits of the trifluoroacetic acid data presented in Figure 8 of the manuscript to the sum of a sloping baseline (representing the high frequency tail of the acyclic dimer hydrogen-bonded O–H absorption) and a Gaussian. The two vertical lines in each panel are positioned at 3572 and 3578 cm^{-1} to more clearly illustrate the slight shift to higher frequency of this feature with increasing pump-probe delay time. The data points are given by circles and the fits by solid lines.

Fig. S6. A plot of the log of the number of vibrational states from a direct state count using scaled harmonic frequencies (scale factor = 0.9613) for dimers of formic acid and trifluoroacetic acid as a function of internal energy.

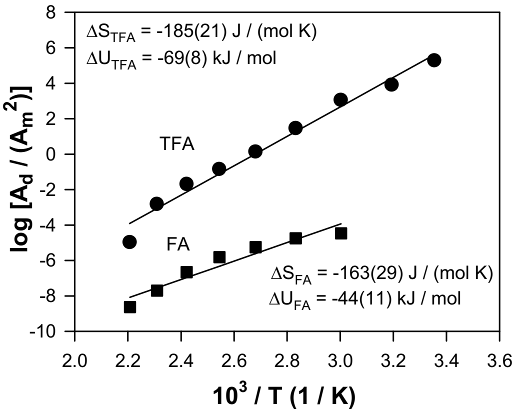
ΔS_TFA = -185(21) J / (mol K)
ΔU_TFA = -69(8) kJ / mol
TFA
FA
ΔS_FA = -163(29) J / (mol K)
ΔU_FA = -44(11) kJ / mol
log [A_d / (A_m^2)]
10^3 / T (1 / K)
8
6
4
2
0
-2
-4
-6
-8
-10
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6

Figure S1

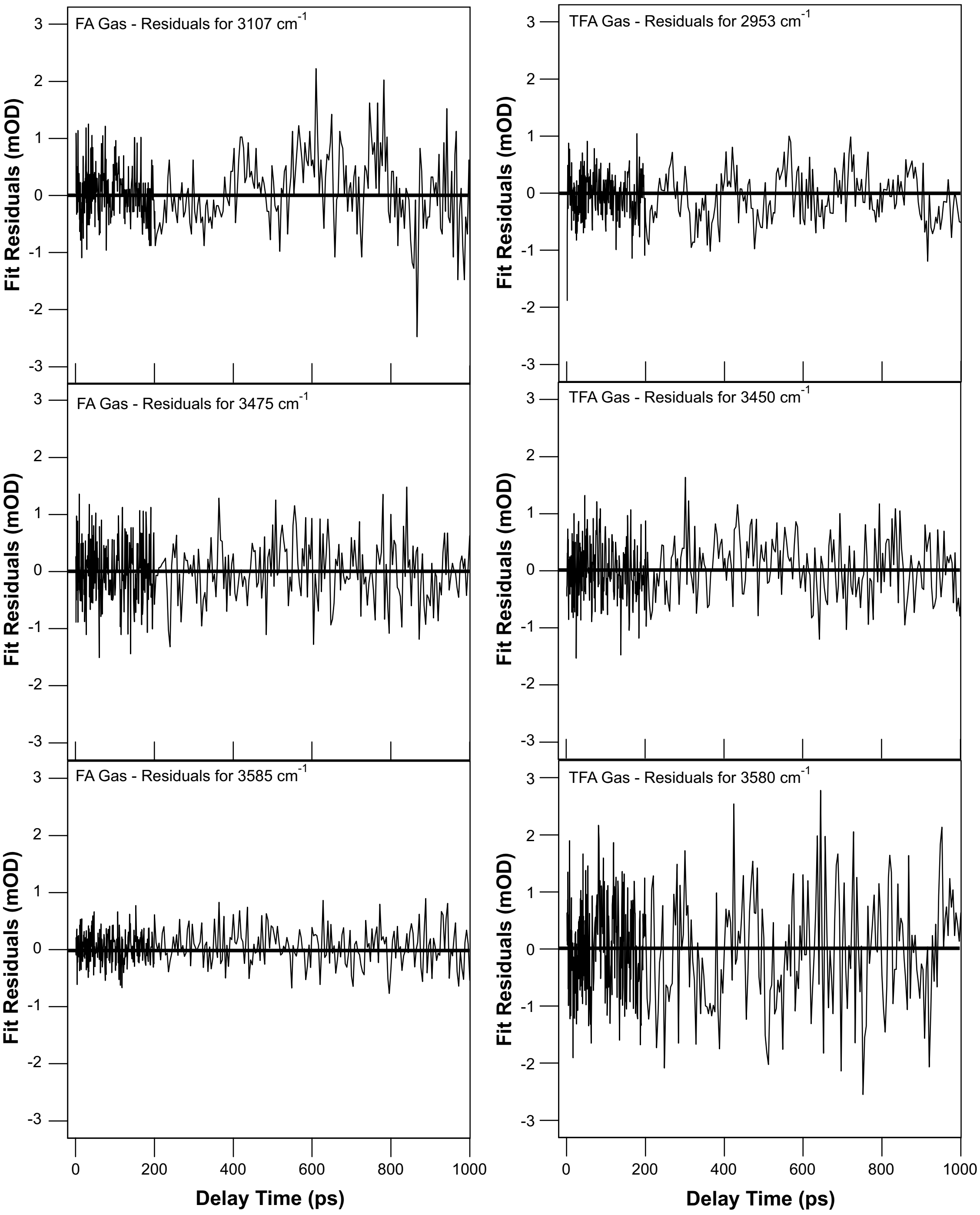
FA Gas - Residuals for 3107 cm-1
TFA Gas - Residuals for 2953 cm-1
FA Gas - Residuals for 3475 cm-1
TFA Gas - Residuals for 3450 cm-1
FA Gas - Residuals for 3585 cm-1
TFA Gas - Residuals for 3580 cm-1
Fit Residuals (mOD)
3
2
1
0
-1
-2
-3
0
200
400
600
800
1000
Delay Time (ps)

Figure S2

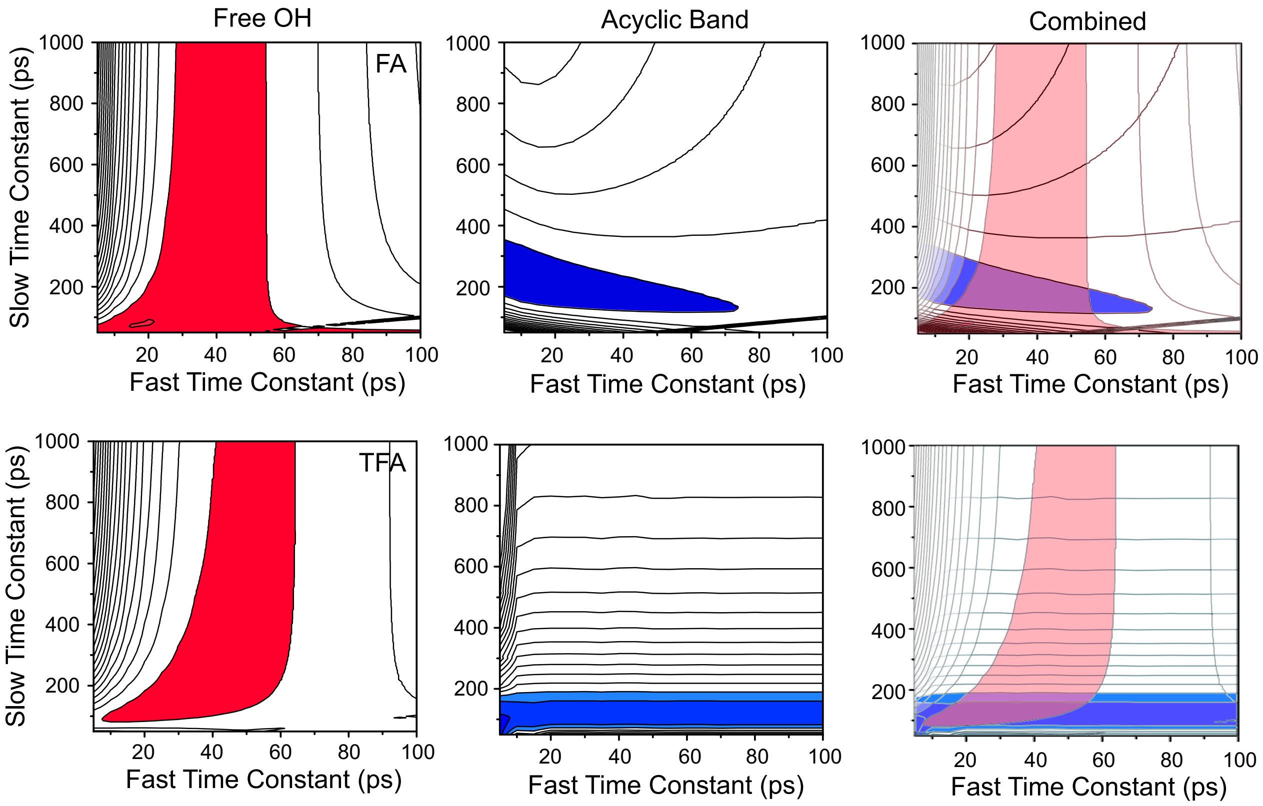
Free OH
Acyclic Band
Combined
FA
TFA
Slow Time Constant (ps)
Fast Time Constant (ps)
1000
800
600
400
200
20
40
60
80
100

Figure S3

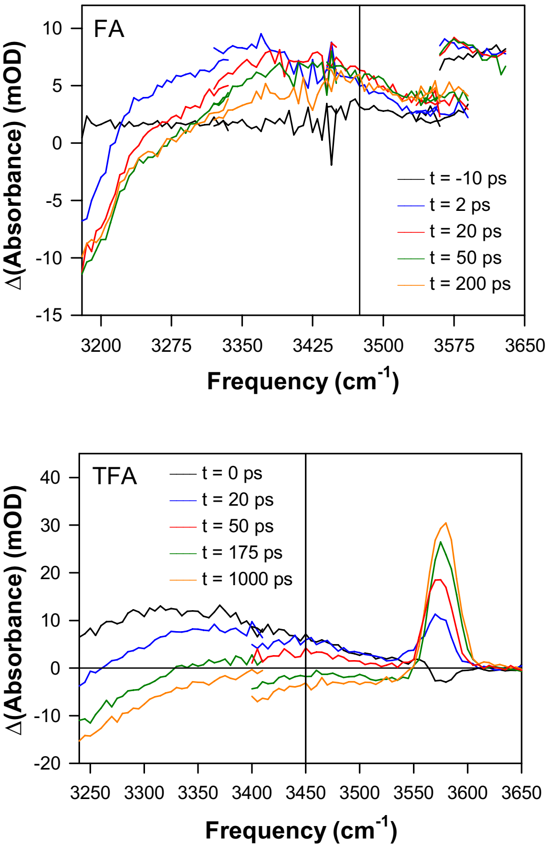
FA
Δ(Absorbance) (mOD)
10
5
0
-5
-10
-15
t = -10 ps
t = 2 ps
t = 20 ps
t = 50 ps
t = 200 ps
3200
3275
3350
3425
3500
3575
3650
Frequency (cm^{-1})
TFA
t = 0 ps
t = 20 ps
t = 50 ps
t = 175 ps
t = 1000 ps
Δ(Absorbance) (mOD)
40
30
20
10
0
-10
-20
3250
3300
3350
3400
3450
3500
3550
3600
3650
Frequency (cm^{-1})

Figure S4

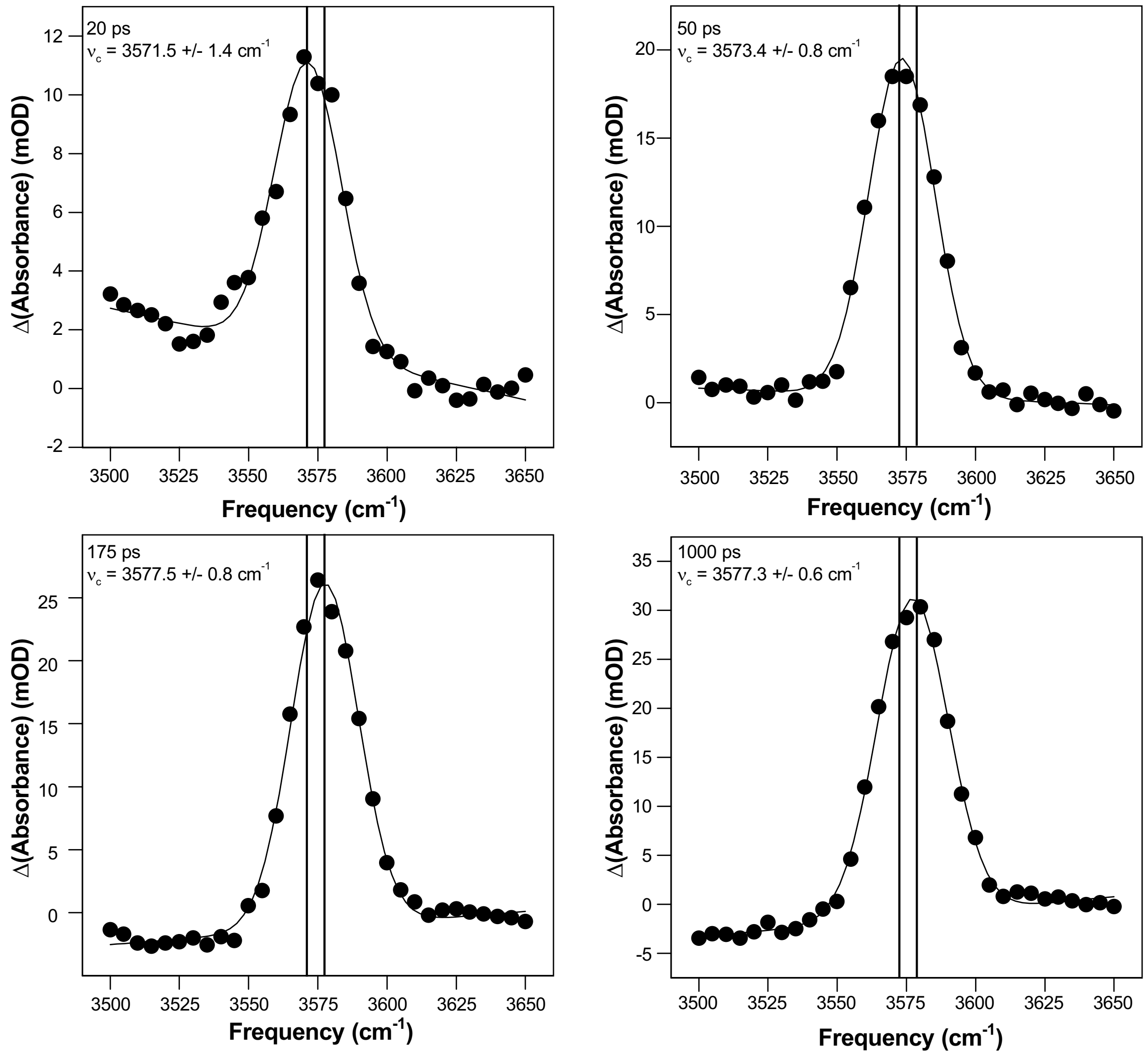
20 ps
ν_c = 3571.5 +/- 1.4 cm⁻¹
50 ps
ν_c = 3573.4 +/- 0.8 cm⁻¹
175 ps
ν_c = 3577.5 +/- 0.8 cm⁻¹
1000 ps
ν_c = 3577.3 +/- 0.6 cm⁻¹
Δ(Absorbance) (mOD)
Frequency (cm⁻¹)
3500
3525
3550
3575
3600
3625
3650
-2
0
2
4
6
8
10
12
5
15
20
25
30
35
-5

Figure S5

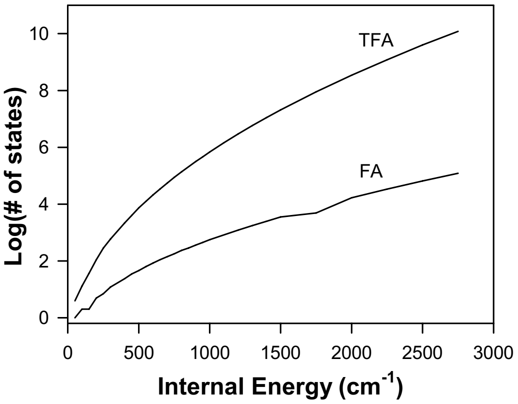
TFA
FA
Log(# of states)
0
2
4
6
8
10
0
500
1000
1500
2000
2500
3000
Internal Energy (cm^{-1})

Figure S6