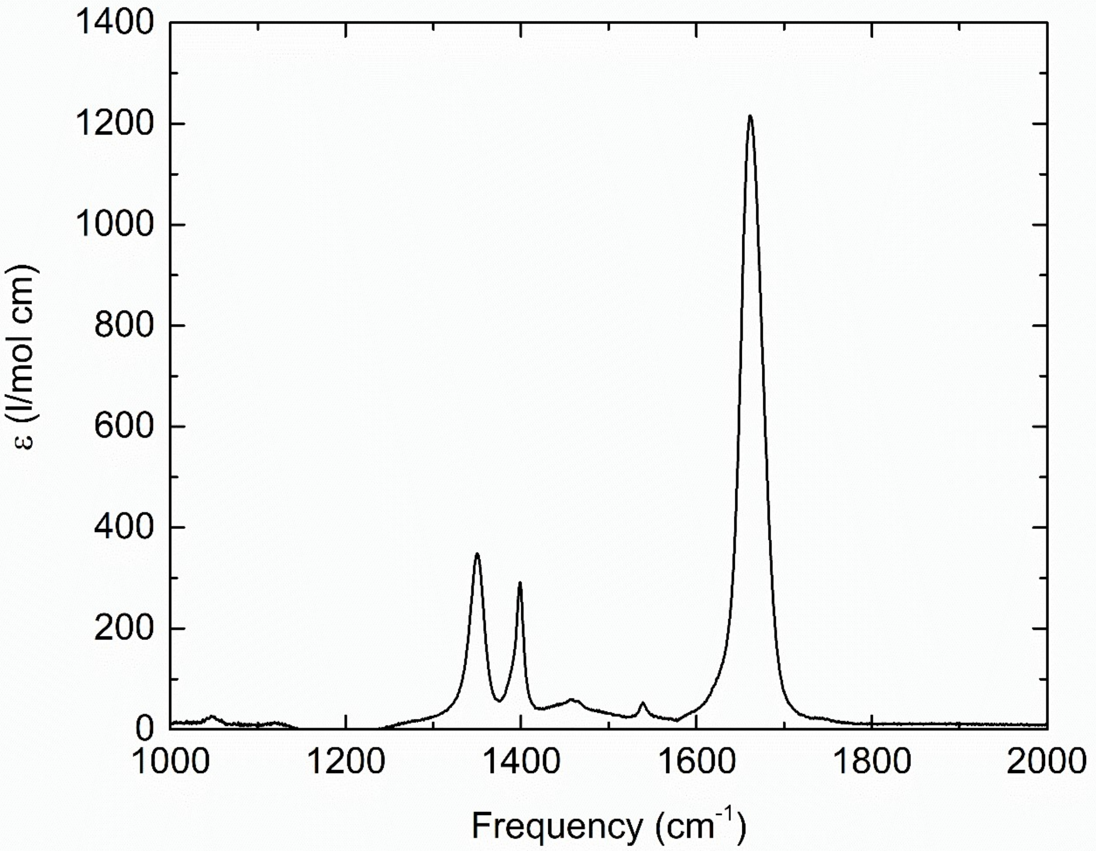
Supplementary information to “**The primary photo-dissociation dynamics of aqueous formamide and dimethylformamide**”

by Jan Thøgersen, Tobias Weidner and Frank Jensen.

Fig. SI 1.



The infrared absorption spectra of formamide in D_2O.

Fig. SI 2

Infrared spectrum of Dimethylamine in D_2O

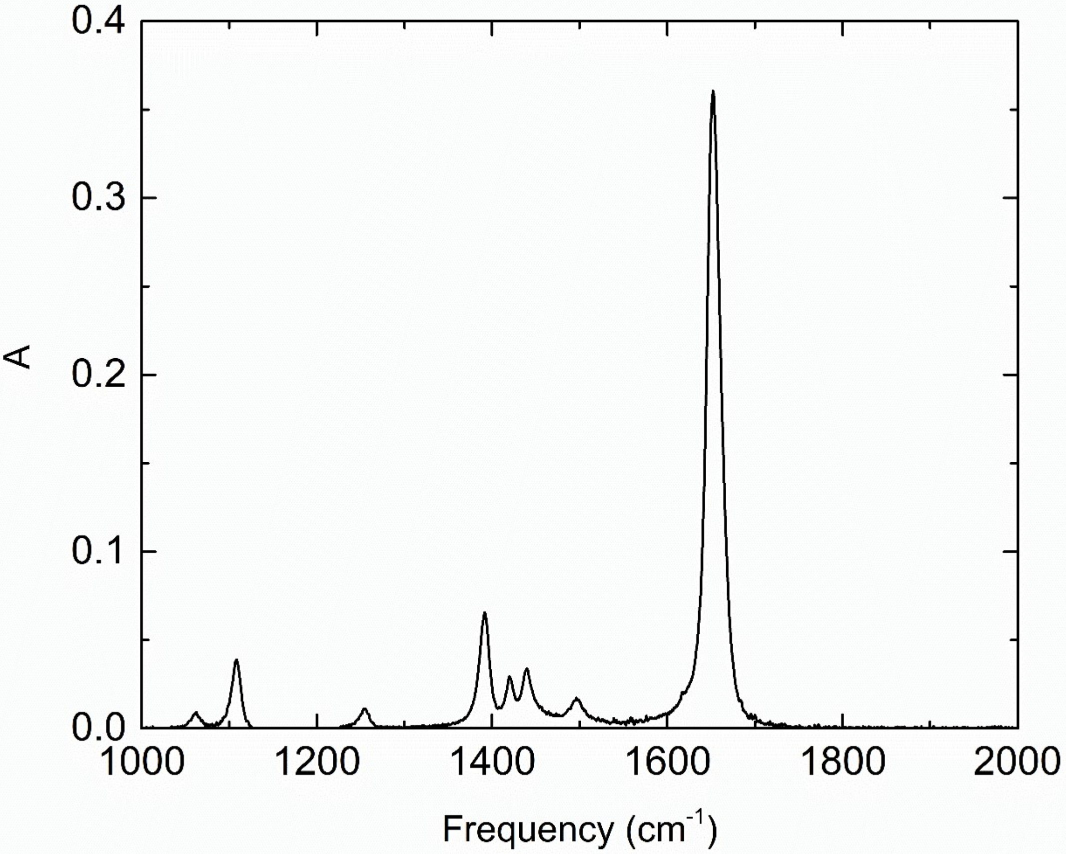


Table SI 1. Calculated transition frequencies and intensities for the CO stretch transition in isolated CO

^{12}C-^{16}O:

Mode(n)	E(harm)	E(anharm)	I(harm)	I(anharm)
1(1)	2244.824	2216.274	86.07996330	85.83573205

^{13}C-^{16}O:

Mode(n)	E(harm)	E(anharm)	I(harm)	I(anharm)
1(1)	2194.784	2167.484	82.28503140	82.05687976

Table SI 2

Selected calculated transition frequencies and intensities for the isolated dimethylamine radical:

Mode(n)	E(harm)	E(anharm)	I(harm)	I(anharm)
1(1)	3146.657	3146.657	12.01247568	12.01247568
2(1)	2984.294	2984.294	16.96124969	16.96124969
3(1)	1485.262	1565.616	2.80475471	2.73854023
4(1)	1404.591	1397.450	31.05893307	31.82715729
5(1)	1219.992	1278.499	0.05882885	15.44094307
6(1)	954.405	954.405	7.66082399	7.66082399
7(1)	448.961	448.961	2.37158077	2.37158077
8(1)	3047.492	3047.492	0.00000000	0.00000000
9(1)	1462.383	1426.203	0.00000000	0.00000000
10(1)	1016.135	1109.930	0.00000000	0.00000000
11(1)	31.059	31.059	0.00000000	0.00000000
12(1)	3050.853	3050.853	45.19678315	45.19678315
13(1)	1482.951	1487.795	27.02608970	23.73462033
14(1)	943.324	943.324	0.78364205	0.78364205
15(1)	144.186	144.186	1.94749158	1.94749158
16(1)	3145.287	3145.287	44.02101166	44.02101166
17(1)	2977.007	2977.007	16.51944231	16.51944231
18(1)	1461.345	1581.886	0.88337644	1.65333538
19(1)	1385.945	1389.605	0.32414295	2.67026041
20(1)	1247.279	1230.314	4.27652269	1.54002207
21(1)	1041.306	1091.436	0.07802245	0.09818501

Table SI 3. Calculated transition frequencies for the dimethylamine radical with one explicit water molecule

	E(harm)	E(anharm)
10(1)	1484.981	1457.672
11(1)	1478.650	1584.209
12(1)	1460.184	1431.289
13(1)	1457.224	1373.949
14(1)	1404.541	1499.396
15(1)	1387.377	1524.970
16(1)	1265.387	1072.102
17(1)	1227.477	1271.020
18(1)	1042.756	1007.745
19(1)	1017.640	1111.454

Table SI 4

Selected calculated transition frequencies and intensities for isolated dimethylamine:

Mode(n)	E(harm)	E(anharm)	I(harm)	I(anharm)
11(1)	1518.766	1482.986	22.87140575	11.93726936
12(1)	1506.404	1429.725	14.33260770	8.96130503
13(1)	1490.722	1441.930	14.70274912	17.73048621
14(1)	1481.219	1425.195	2.76261297	13.89618226
15(1)	1472.319	1421.335	4.69318170	2.15310950
16(1)	1468.483	1463.386	9.01277890	3.33167411
17(1)	1443.087	1385.182	0.00805202	0.04988853
18(1)	1274.965	1255.547	0.25839152	1.01605078
19(1)	1214.168	1155.132	12.45016276	7.94156646
20(1)	1205.669	1168.154	31.02478160	24.14318249
21(1)	1108.866	1074.930	0.21895369	0.14096097
22(1)	1050.705	998.602	11.58348187	11.48538847

Table SI 5

Selected calculated transition frequencies and intensities for dimethylamine with one explicit water molecule:

Mode(n)	E(harm)	E(anharm)	I(harm)	I(anharm)
11(1)	1518.766	1482.986	22.87140575	11.93726936
12(1)	1506.404	1429.725	14.33260770	8.96130503

13(1)	1490.722	1441.930	14.70274912	17.73048621
14(1)	1481.219	1425.195	2.76261297	13.89618226
15(1)	1472.319	1421.335	4.69318170	2.15310950
16(1)	1468.483	1463.386	9.01277890	3.33167411
17(1)	1443.087	1385.182	0.00805202	0.04988853
18(1)	1274.965	1255.547	0.25839152	1.01605078
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20(1)	1205.669	1168.154	31.02478160	24.14318249
21(1)	1108.866	1074.930	0.21895369	0.14096097
22(1)	1050.705	998.602	11.58348187	11.48538847

Fig. SI 3

The first 20 ps of the transient absorption associated with the C-O stretch of formamide

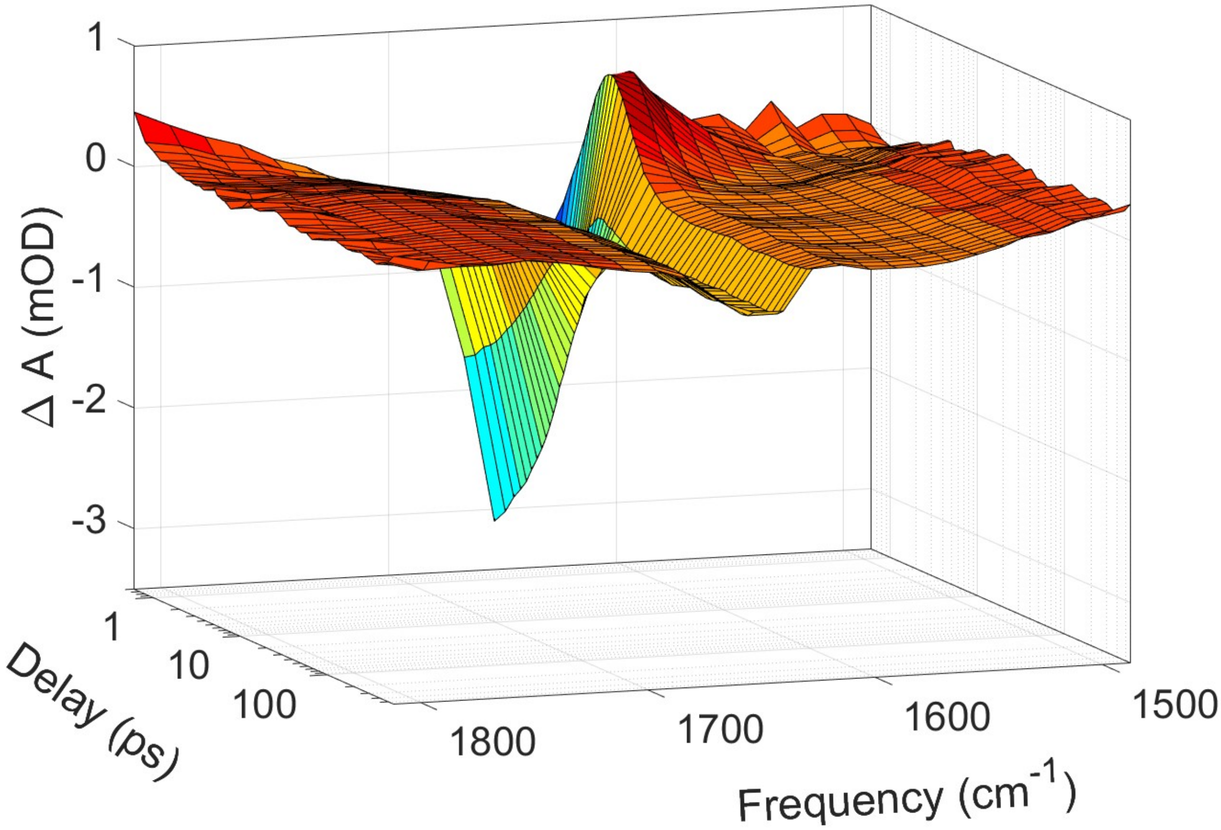


Fig. SI 4

The first 20 ps of the transient absorption of formamide from ν = 1220 cm^{-1} to ν = 1480 cm^{-1}.

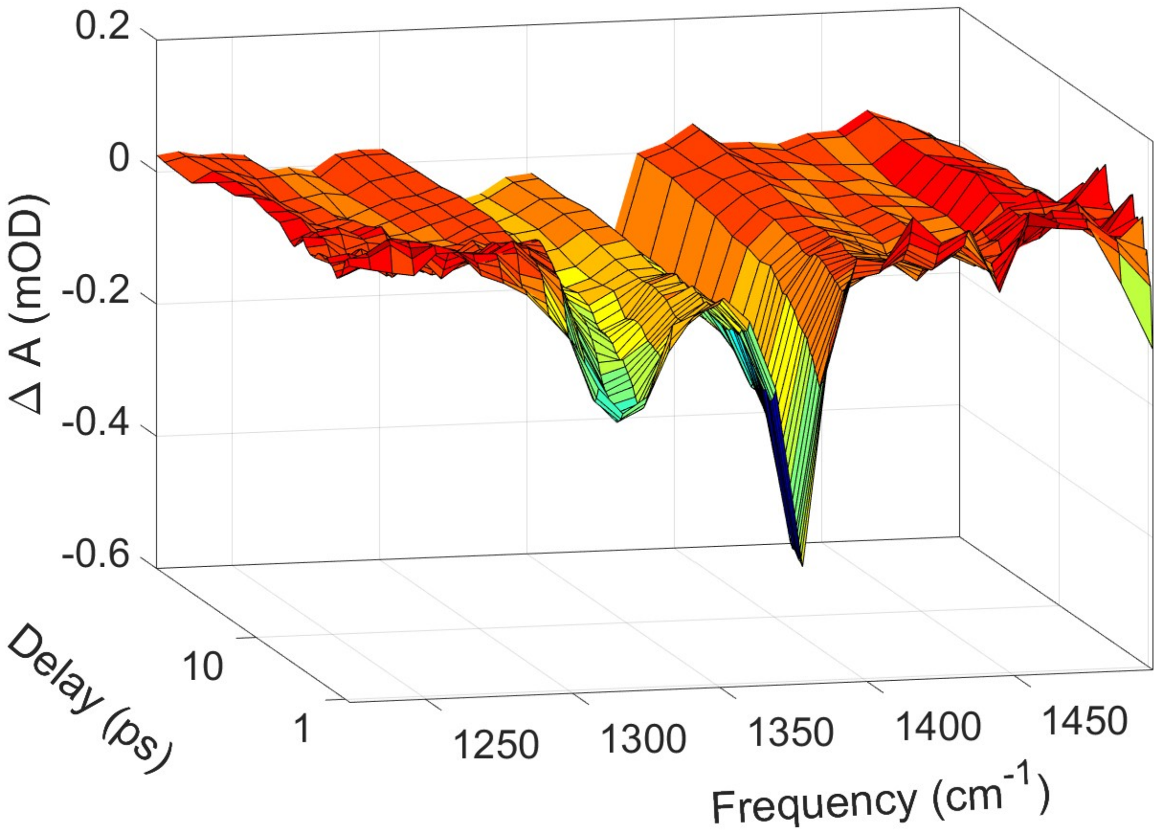


Fig. SI 5

The first 20 ps of the transient absorption of formamid from ν = 1300 cm^{-1} to ν = 1520 cm^{-1}.

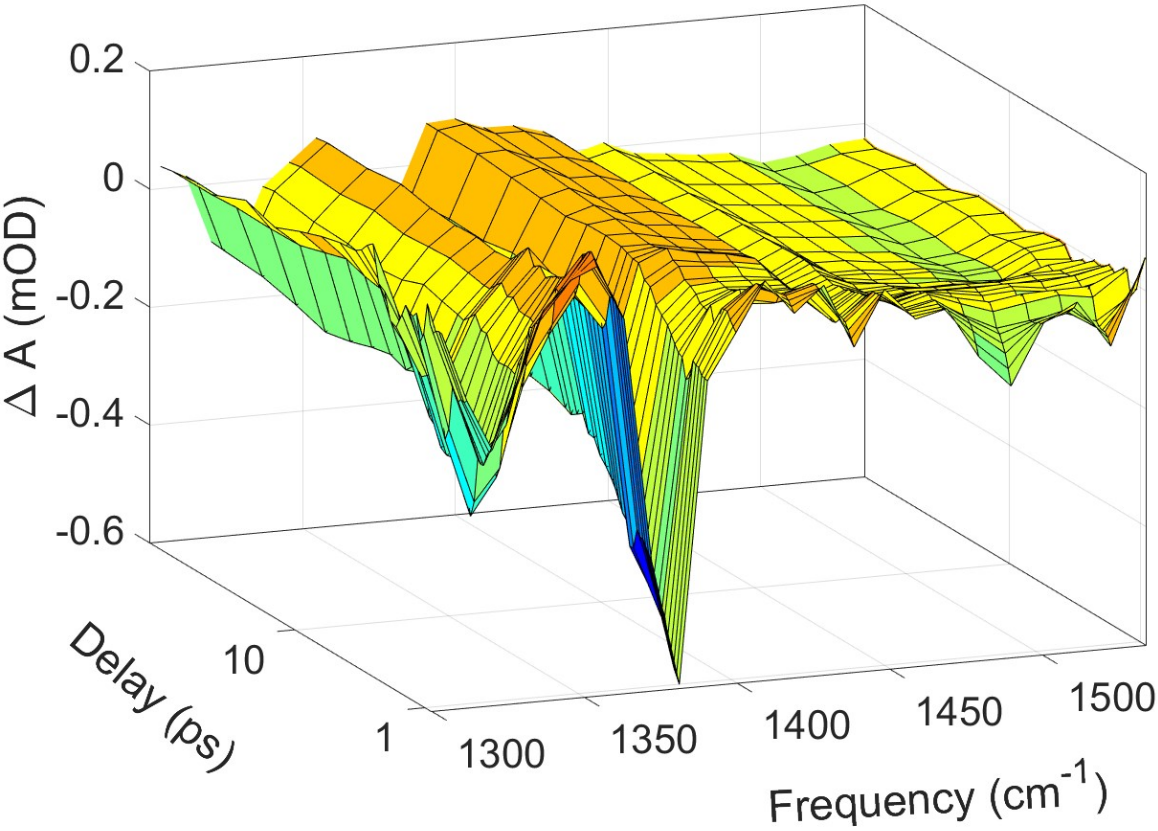
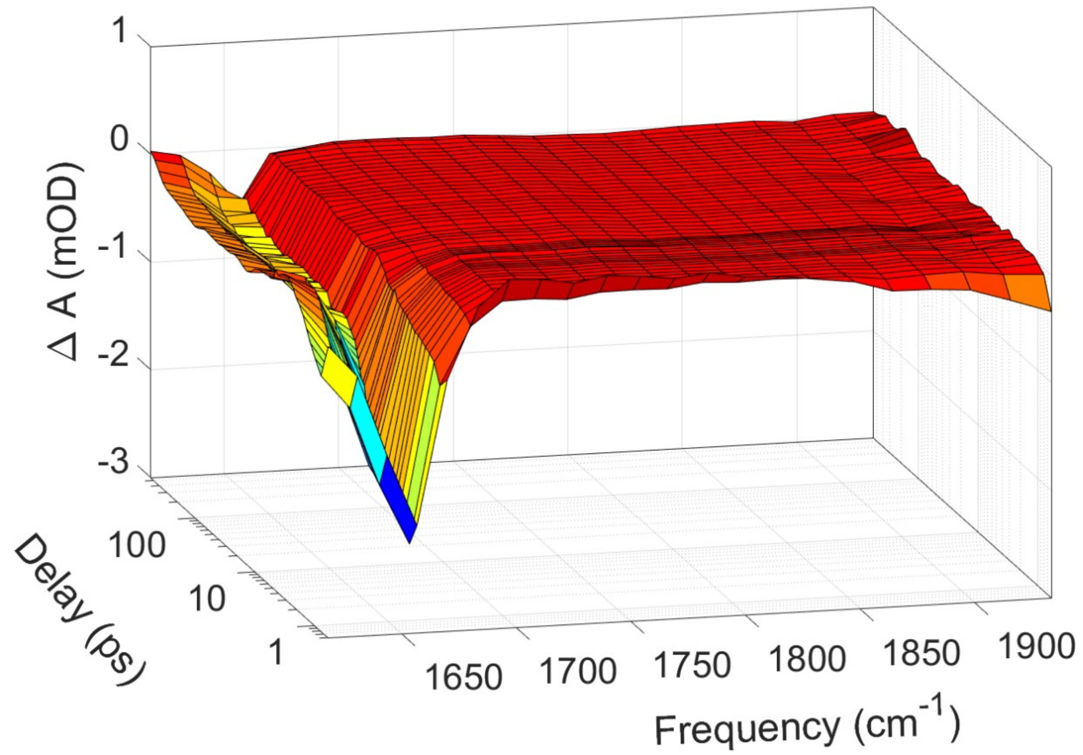


Fig. SI 6



The transient absorption of formamide in D_2O recorded from ν = 1600 cm^{-1} to ν = 1950 cm^{-1}.

SI ES 1

Estimate of ammonia yield:

Using the measured transient absorption of NH_3(aq) at ν = 1111 cm^{-1} and formamide at ν = 1387 cm^{-1} together with the corresponding measured extinction coefficients, we estimate the fraction of excited formamide molecules that have dissociated to NH_3 after t = 20 ps to $\Phi(NH_{3,}$ t = 20 ps) = - (ΔA(ν= 1111 cm^{-1}, t = 20 ps)) × ε_{FA}(ν = 1387cm^{-1}) /(ΔA(ν = 1387 cm^{-1}, t = 1 ps) × ε_{NH3}(ν = 1111 cm^{-1})) = -(0.042 mOD×190 l/mol cm /(-0.65 mOD × 54 l/mol cm) = 0.23 ± 0.10. Using formamide's transient absorption dip at ν = 1055 cm^{-1} instead of that at ν = 1387 cm^{-1} still yields $\Phi(NH_{3,}$ t = 20 ps) = 0.23 ± 0.10.

SI ES 2

Estimate of expected CO absorption:

We can make a rough estimate of the expected induced absorption from CO assuming that every NH_3 molecule is accompanied by a CO molecule. If we apply the induced absorption of NH_3, $\Delta A(NH_3)$ = 0.06 mOD, and the calculated transition strengths of $\delta(NH_3)$ (I = 161 km/mol) and νCO (I = 86 km/mol) together with their assumed spectral widths of $\Delta\nu$ = 64 cm^{-1} and $\Delta\nu$ = 42 cm^{-1}, respectively, we find a value of ΔA (CO) ≈ 0.05 mOD. The $\Delta\nu$ = 42 cm^{-1} spectral width of the CO absorption band is taken from the Dimethylformamide data.

Fig. SI 7.

The difference between the induced transient absorption of ^{13}C and ^{12}C formamide measured from ν = 2160 cm^{-1} to ν = 2310 cm^{-1}.

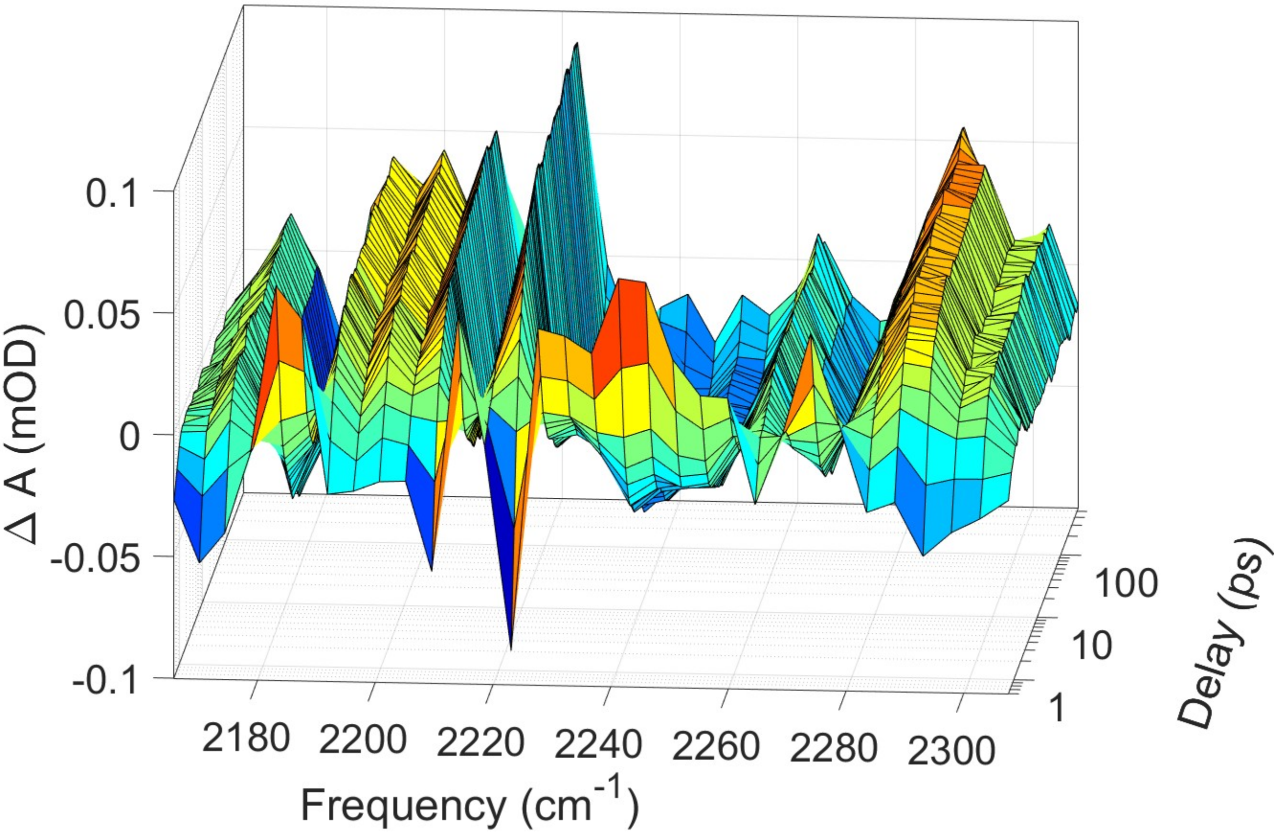
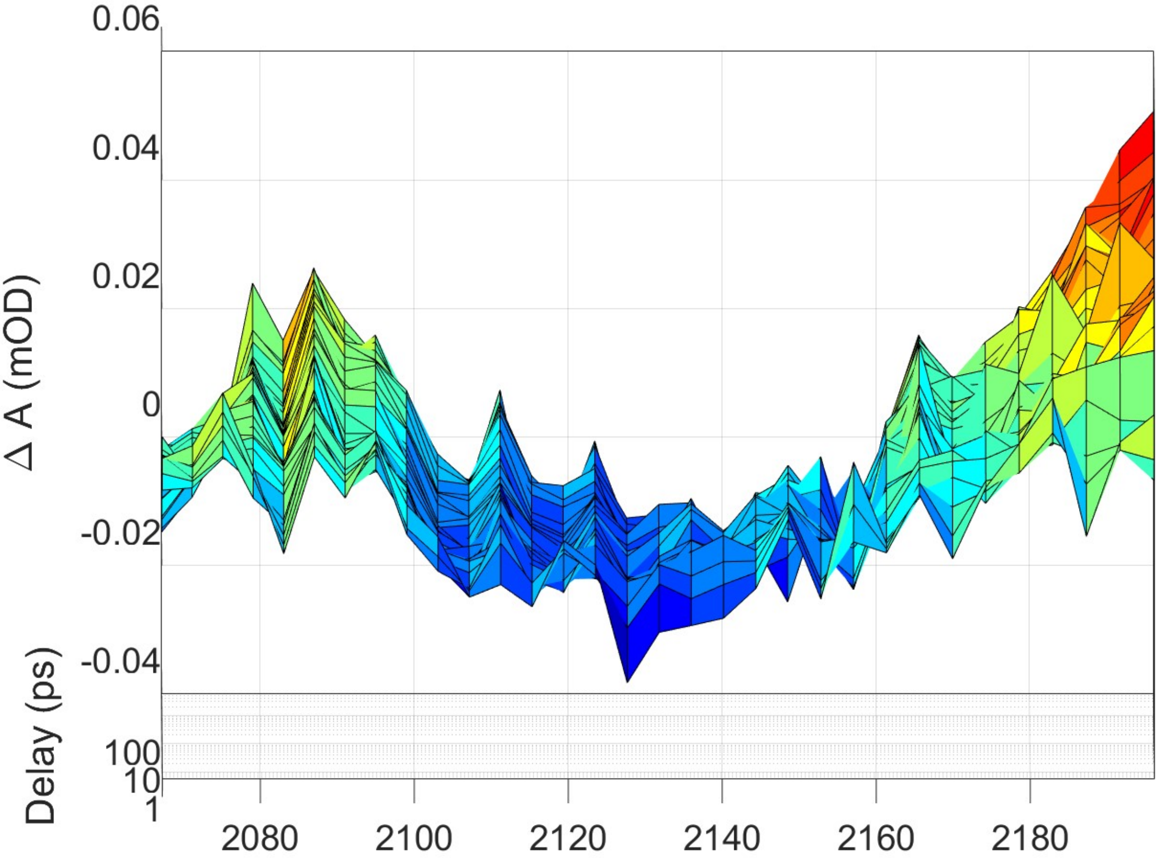


Fig. SI 8.

The difference between the induced transient absorption of ^{13}C and ^{12}C formamide measured from ν = 2070 cm^{-1} to ν = 2200 cm^{-1}.



SI ES 3

Detectivity of NH_2(aq)

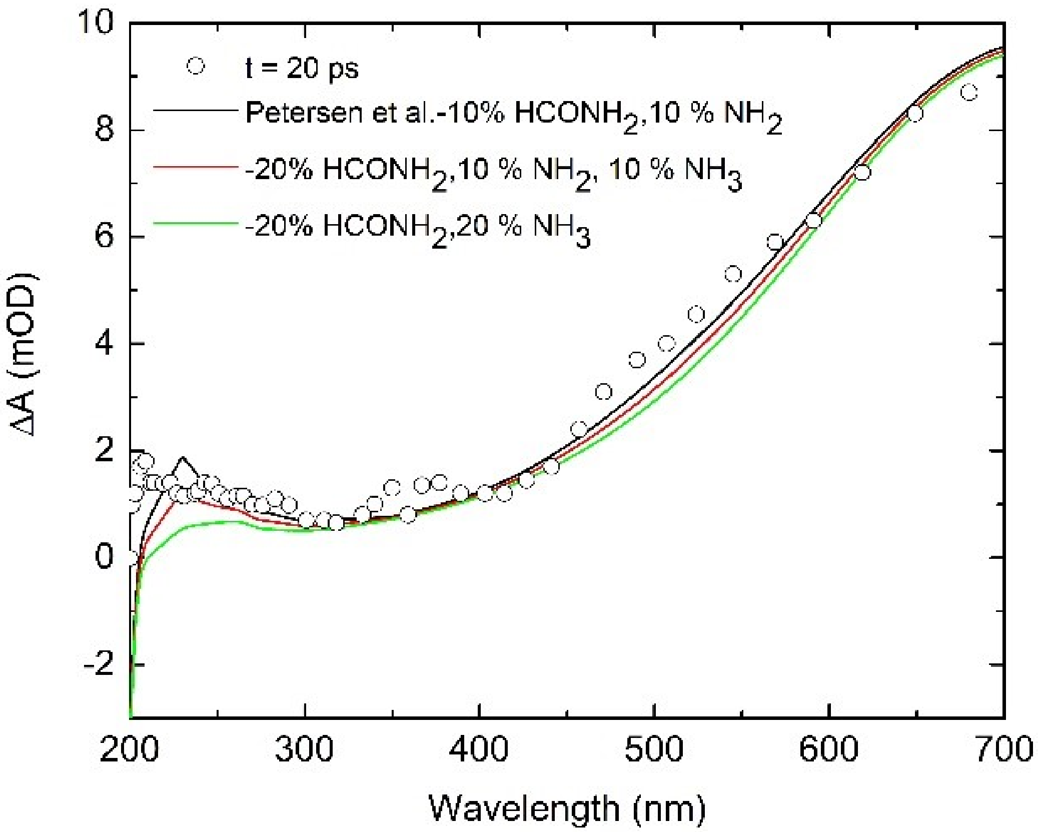
The calculated intensity of the NH_2 bending transition is I = 23 km/mol and thus only 1/7 of the NH_3(aq) intensity of I = 161 km/mol. Assuming the same spectral width and yield for NH_2(aq) and NH_3(aq), the formation of NH_2 will results in an induced absorption ΔA = 0.009 mOD. This is below the detection limit of our infrared transient absorption spectrometer.

Furthermore, at transition frequencies higher than ν = 1534 cm^{-1} (not shown) the transient absorption spectrum is dominated by the contribution from the heat induced absorption change of the H_2O bending mode. If therefore the calculated transition value is low by more than ν = 10 cm^{-1}, NH_2 cannot be identified by our transient absorption spectrometer, even if the yield is higher or the assumed spectral width and intensity are off by a factor of two.

SI ES 4

Comparison with previous experiments

The primary photolysis of aqueous formamide at 200 nm has previously been studied by Petersen et al.[SI1] Using femtosecond UV/Vis transient absorption spectroscopy, the authors showed that the majority of excited formamide molecules (~80%) decay to the vibrationally excited electronic ground state, followed by efficient vibrational relaxation towards the ground state in just a few picoseconds. The recombination yield is in good agreement with the value derived from the present data and the vibrational relaxation time reported by Petersen et al. also agrees with the present relaxation data. Based on meticulous spectral analysis Petersen et al. assigned the photoproducts to NH_2 + HCO. HCO was not observed directly, but good agreement between the recorded



UV-Vis transient absorption data reproduced from Petersen et al. [SI1] compared to the total absorption assuming $HCONH_2$ dissociate to HCO+ NH_2 (black), both HCO + NH_2 and CO + NH_3 (red) and only CO + NH_3 (green). In addition, the absorption from e_{aq}^-, OH^- and H^+ formed by two-photon ionization and dissociation are added to the spectra using the relative yields reported by Thomsen et al. [SI2] transient absorption spectrum and the distinctive spectrum of NH_2(aq) gave strong evidence for the formation of NH_2. NH_2 is not identified by the present IR measurements for reasons discussed already. Our measurements show the formation of NH_3. This product was not reported by Petersen et al.. The figure shows the UV-Vis transient absorption spectrum after t = 20 ps reported by Petersen et al..[SI1] The experimental data are compared to the total absorption assuming different dissociation yields of NH_2 and NH_3. The black curve is calculated assuming $HCONH_2$ dissociate to HCO + NH_2 like in the analysis by Petersen et al.. The red curve assumes $HCONH_2$ dissociates to equal yields of both HCO + NH_2 and CO + NH_3, while the green curve assumes only CO + NH_3 are produced. Like Petersen et al we furthermore add the absorption from e_{aq}^-, OH^- and H^+ to account for the contribution from two-photon ionization and dissociation of the water solvent. This contribution is added assuming the same relative yields of the products as those reported by Thomsen et al.[SI2.] following two photon excitation of water at λ = 266 nm. The figure shows acceptable agreement between the transient data and the calculated curves calculated for dissociation into equal yields of the HCO + NH_2 and CO + NH_3 and for dissociation into HCO + NH_2 alone. The curve calculated for the case of dissociation into solely CO + NH_3 fails to catch the UV part of the transient data and this scenario is thus incompatible with the measurements. Hence, the UV-Vis transient spectrum can accommodate the contribution from NH_3(aq) and the identification of NH_3(aq) in the present measurements is not in conflict with the data presented by Petersen et al.

SI references

1 C. Petersen, N. H. Dahl, S. Knak Jensen, J. Aa. Poulsen, J. Thøgersen and S. R. Keiding. *J. Phys. Chem. A.* 2008**, 112***,* 3339.

2 C. Thomsen, D. Madsen, S. R. Keiding. J. Thøgersen. *J. Chem. Phys.* 1999, **110**, 3453.