Supporting information for

Polar solvent fluctuations drive proton transfer in hydrogen bonded complexes of carboxylic acid with pyridines: NMR, IR and ab initio MD study

B. Koeppe,[a] S.A. Pylaeva,[b] C. Allolio,[b] D. Sebastiani,[b] E.T.J. Nibbering,[c,*] G.S. Denisov,[d] H.-H. Limbach,[e] P.M. Tolstoy[f,*]

[a] – Department of Chemistry, Humboldt-Universität zu Berlin, Germany

[b] – Institute of Chemistry, Martin-Luther Universität Halle-Wittenberg, Germany

[c] – Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, Berlin, Germany

[d] – Department of Physics, St.Petersburg State University, Russia

[e] – Institute of Chemistry and Biochemistry, Freie Universität Berlin, Germany

[f] – Center for Magnetic Resonance, St.Petersburg State University, Russia

[*] – correspondence author, daniel.sebastiani@chemie.uni-halle.de, nibberin@mbi-berlin.de, peter.tolstoy@spbu.ru

Contents

Figure S1. Parts of ^{1}H NMR spectra of samples, containing chloroacetic acid and various N-bases in CD_2Cl_2 solution, measured at 180 K. Signals of the OH proton are shown, assigned to the **AHB01**-**AHB20** complexes (fee Fig. 1 in the main text for the structures).

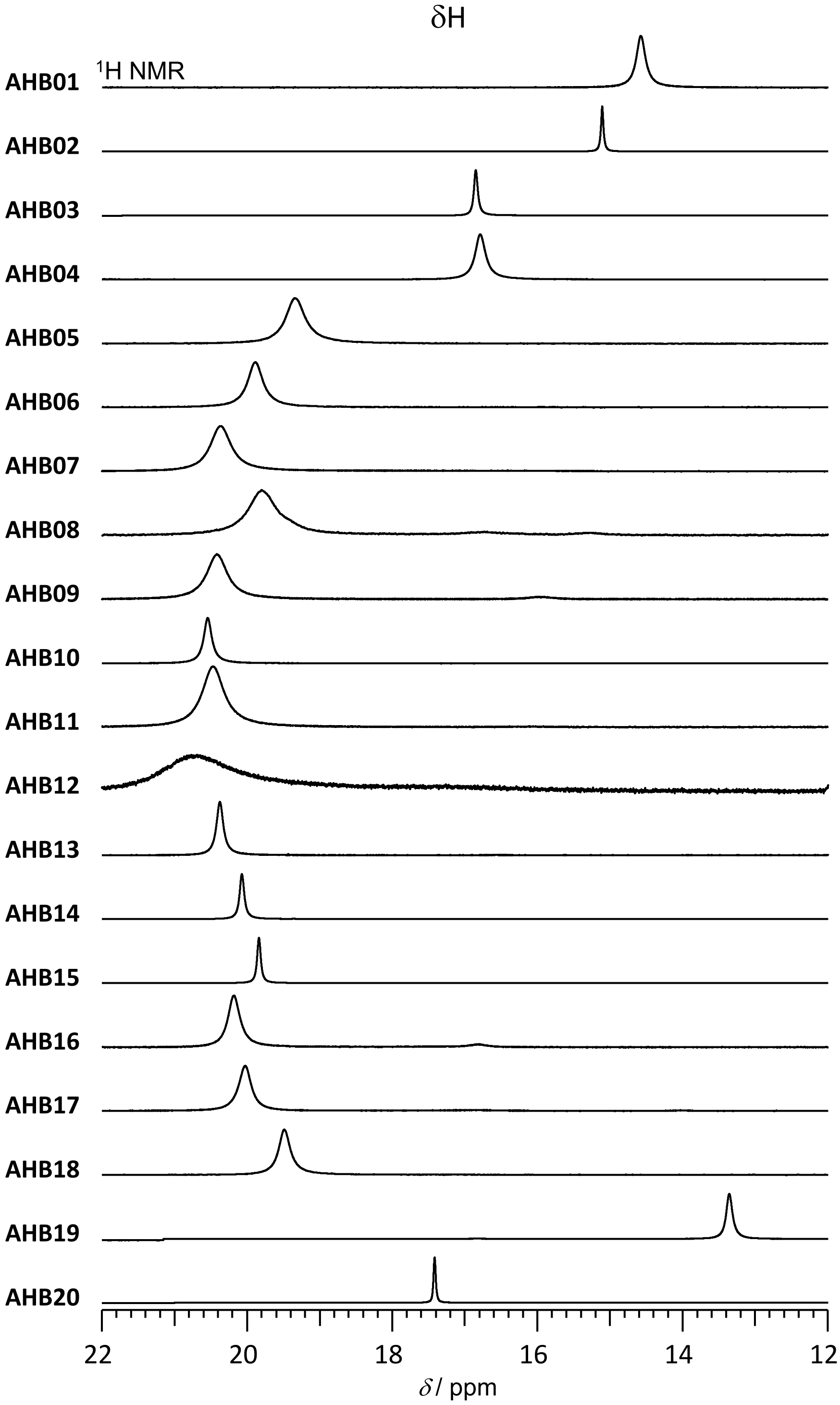


Figure S2. Parts of ^{13}C NMR spectra of samples, containing chloroacetic acid and various N-bases in CD_2Cl_2 solution, measured at 180 K. Signals C1 carbons are shown, assigned to the **AHB01**-**AHB20** complexes (fee Fig. 1 in the main text for the structures).

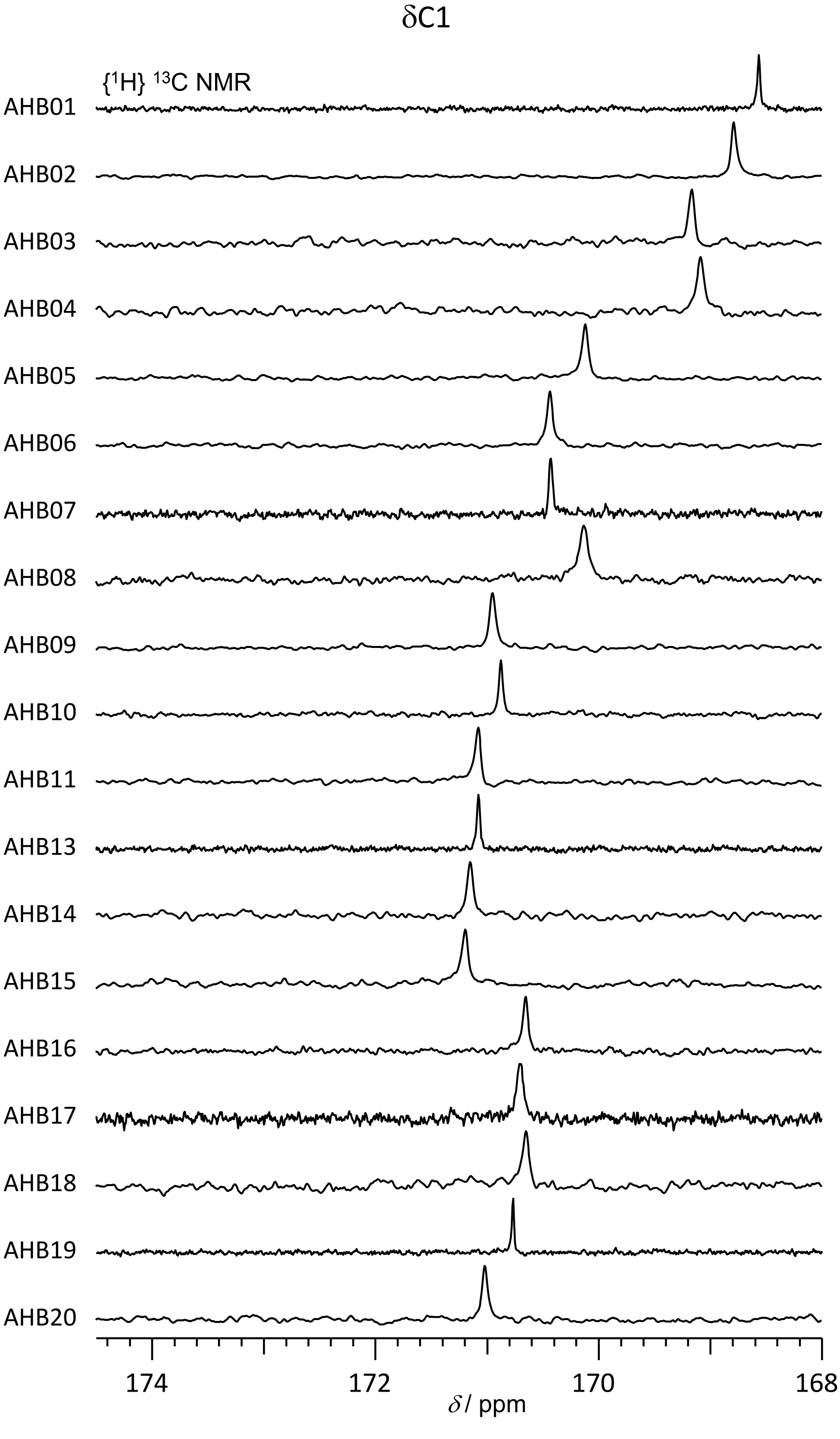
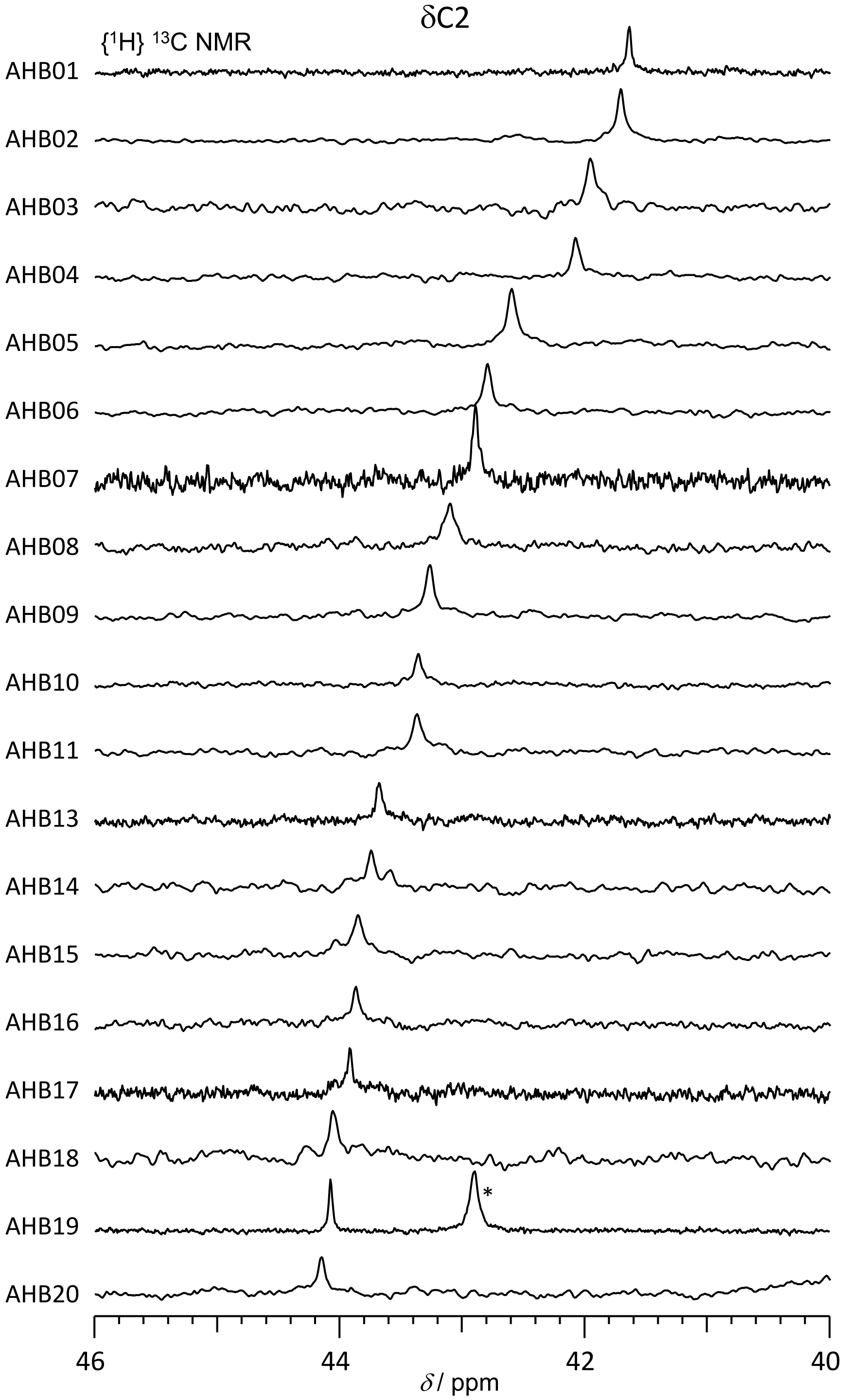


Figure S3. Parts of ^{13}C NMR spectra of samples, containing chloroacetic acid and various N-bases in CD_2Cl_2 solution, measured at 180 K. Signals C2 carbons are shown, assigned to the **AHB01**-**AHB20** complexes (fee Fig. 1 in the main text for the structures).



(*) CH_2 of TEA, identified by an additional HSQC experiment (not shown).

Figure S4. Parts of IR spectra in the region of C=O stretching vibration of samples, containing chloroacetic acid and various N-bases in CH_2Cl_2 solution, measured at around 180 K (see temperatures given for each spectrum) for complexes **AHB02-AHB03**, **AHB05-AHB07**, **AHB09-AHB10**, **AHB13-AHB20** (fee Fig. 1 in the main text for the structures). Spectra of the complexes containing ^{13}C-labelled chloroacetic acid are shown as green traces (long dashes), complexes containing non-labelled acid are shown as orange traces. Black solid traces correspond to the isotope difference spectra (the spectrum of ^{13}C-labelled species minus the spectrum of non-labelled species). Blue, red and dotted black traces correspond to the result of the fitting, as described in the Discussion section of the main text. Figure continued on the next page.

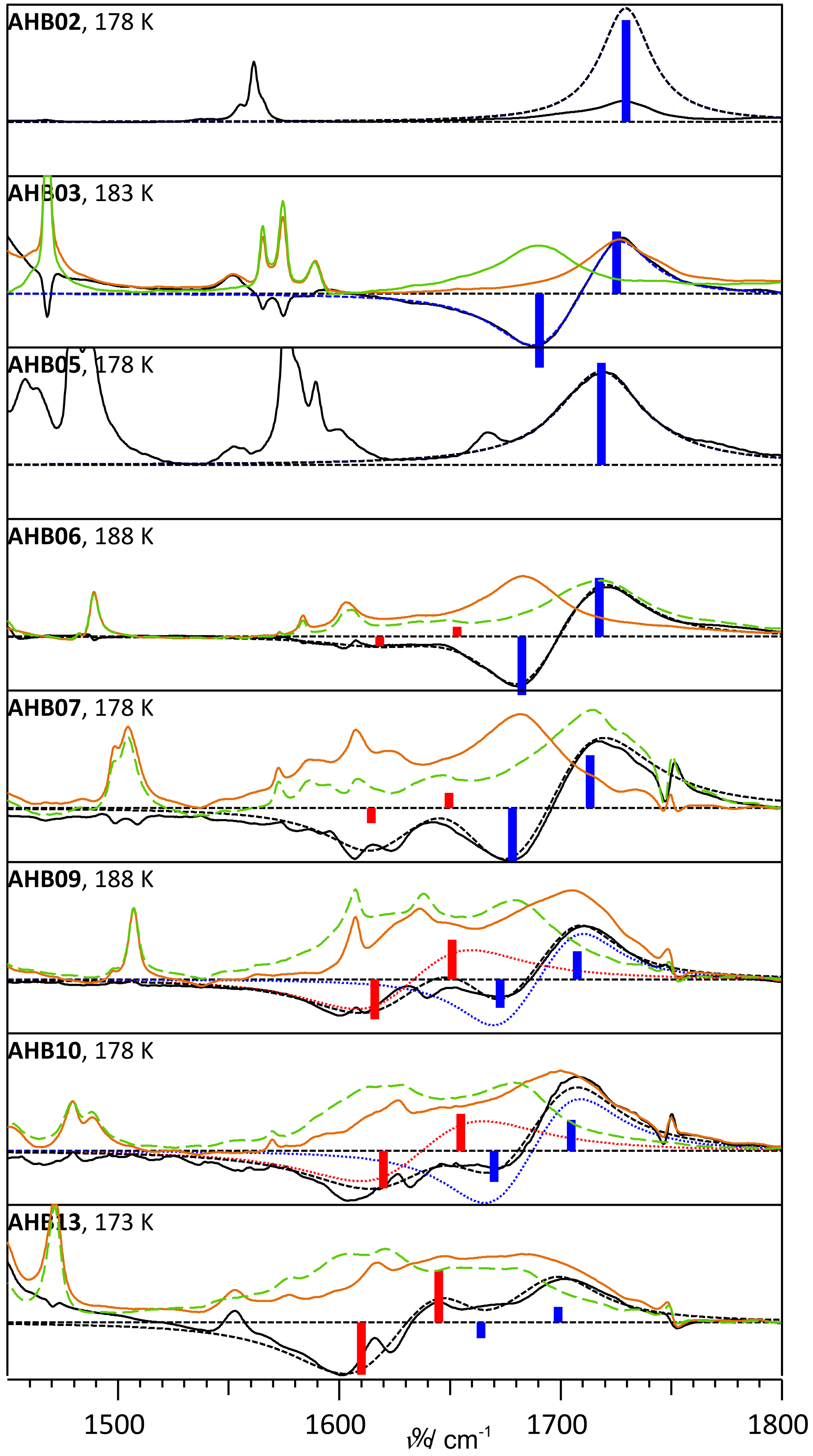

AHB02, 178 K
AHB03, 183 K
AHB05, 178 K
AHB06, 188 K
AHB07, 178 K
AHB09, 188 K
AHB10, 178 K
AHB13, 173 K
1500
1600
1700
1800
ν̃/ cm-1

Figure S4. Continued.

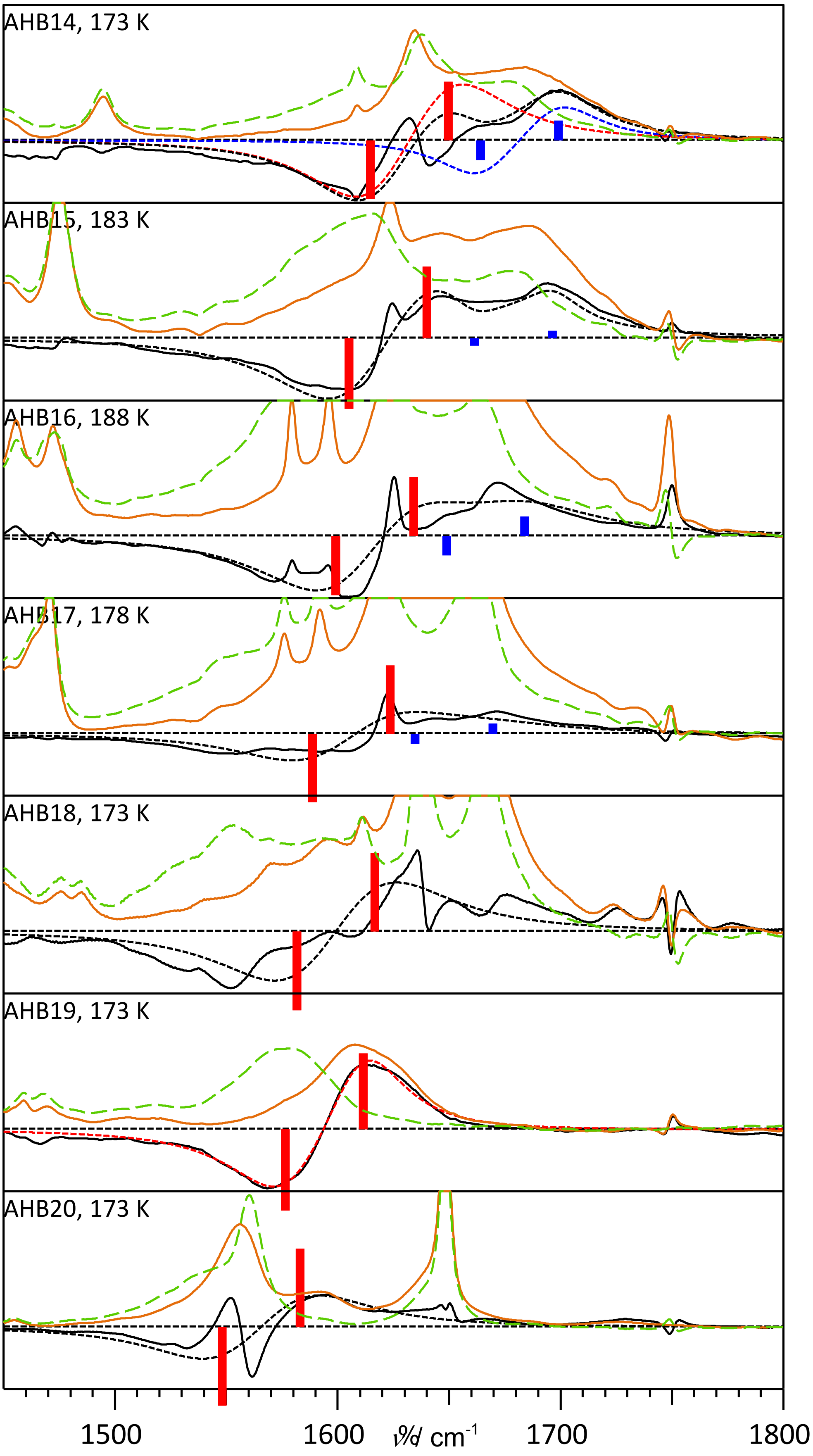
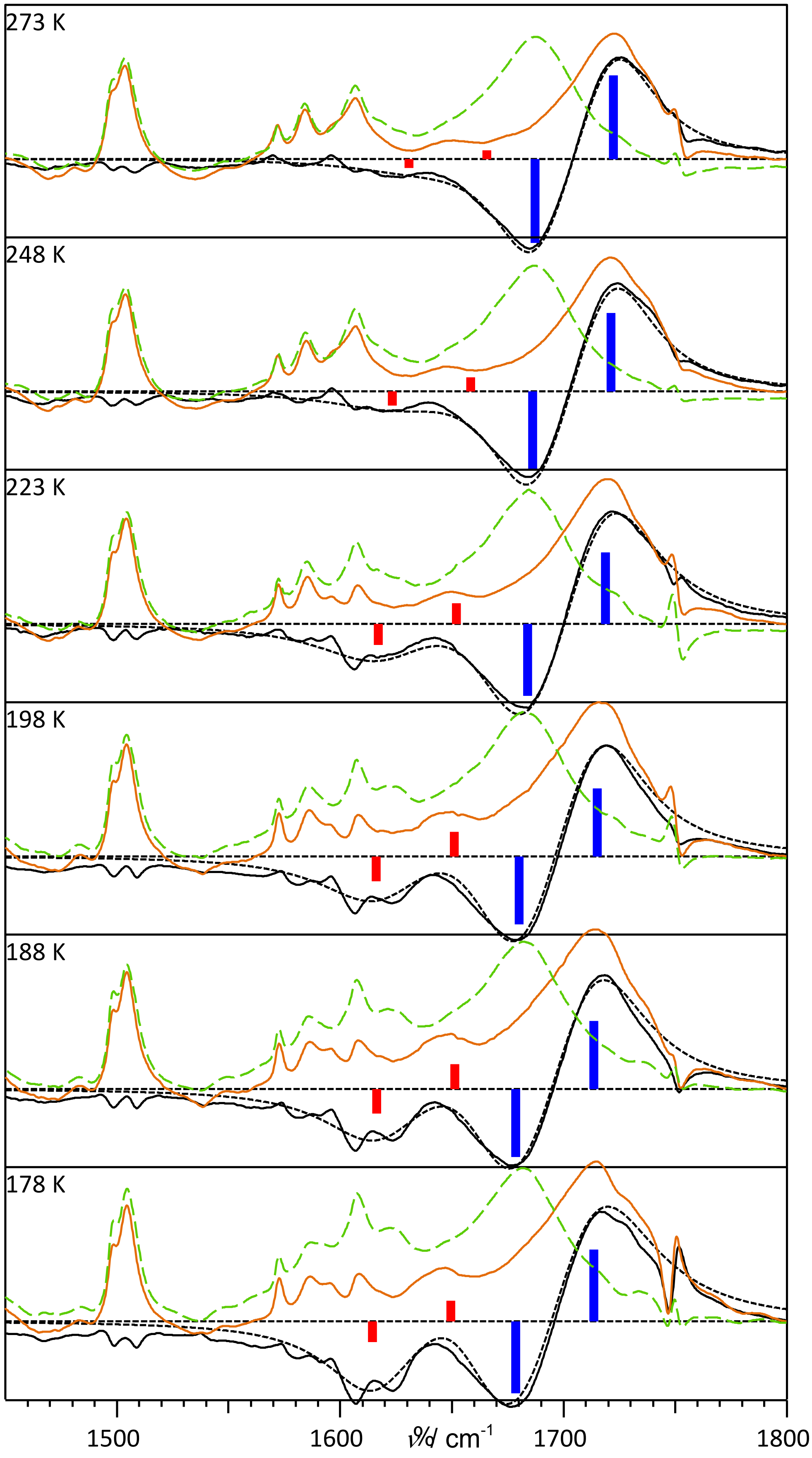
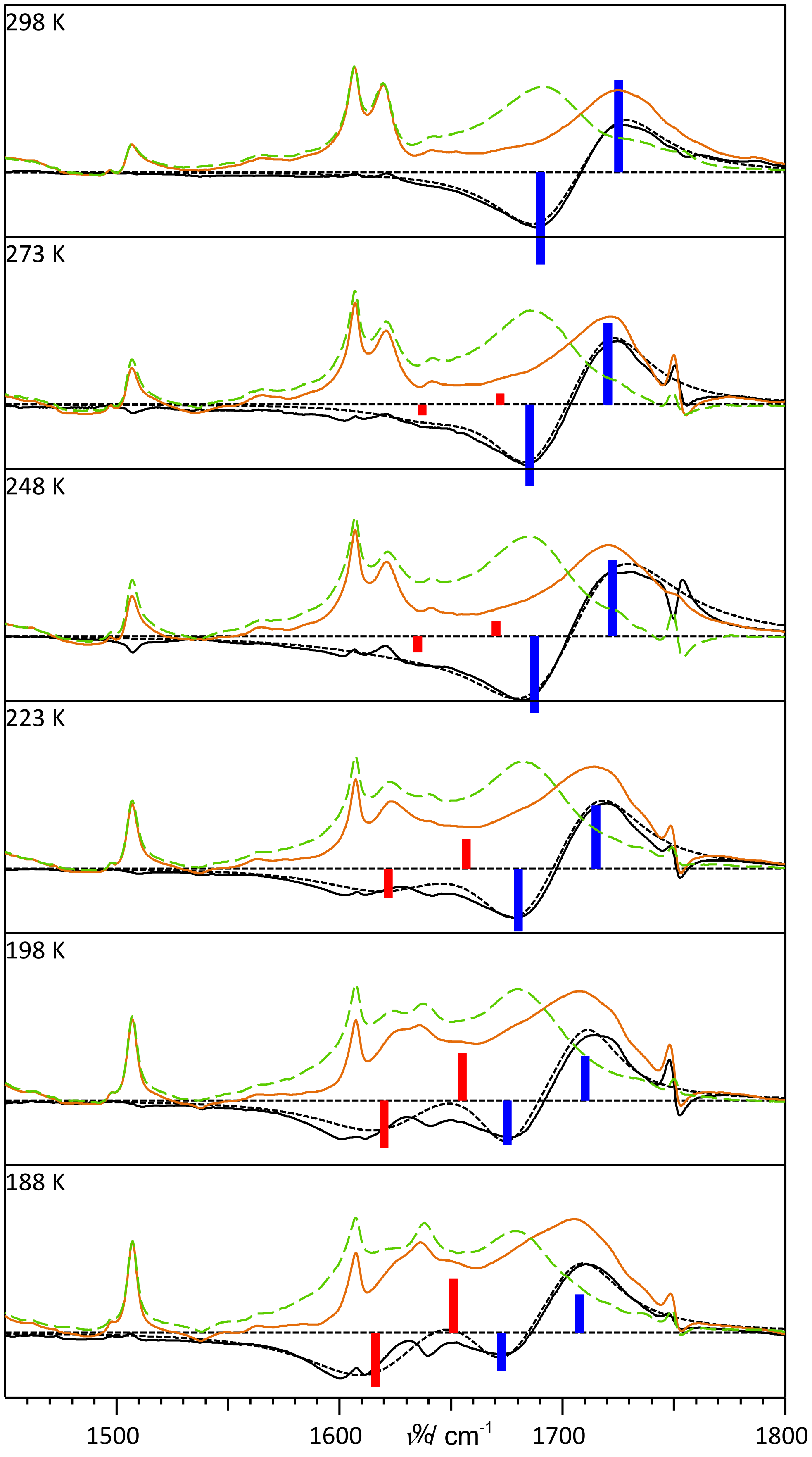


Figure S5. Parts of IR spectra in the region of C=O stretching vibration of samples, containing **AHB07** complex (fee Fig. 1 in the main text for the structure), measured at various temperatures. Spectra of the complexes containing ^{13}C-labelled chloroacetic acid are shown as green traces (long dashes), complexes containing non-labelled acid are shown as orange traces. Black solid traces correspond to the isotope difference spectra (the spectrum of ^{13}C-labelled species minus the spectrum of non-labelled species). Blue, red and dotted black traces correspond to the result of the fitting, as described in the Discussion section of the main text.


273 K
248 K
223 K
198 K
188 K
178 K
1500
1600
$\tilde{\nu}$ / cm^{-1}
1700
1800

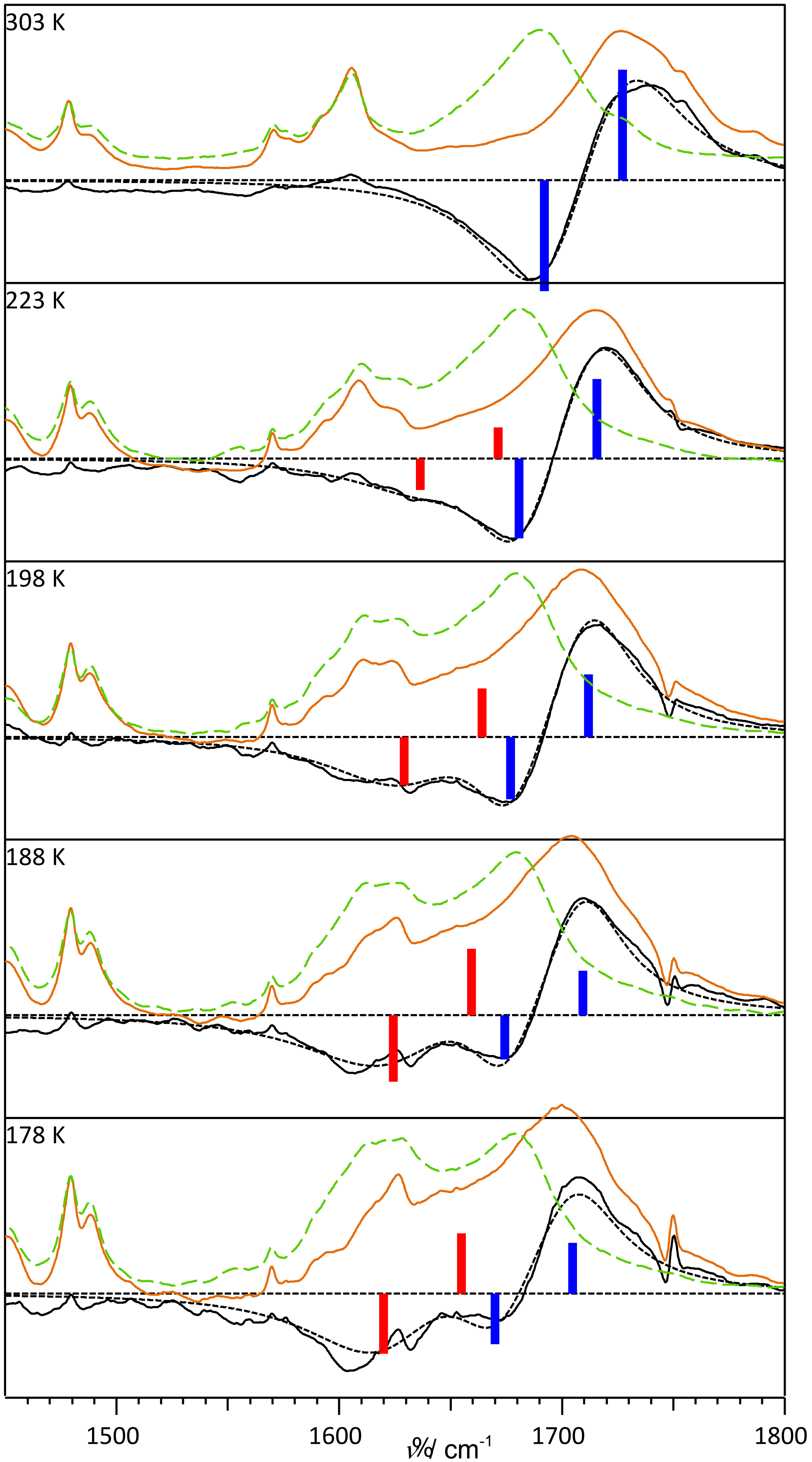
AHB07 var T

Figure S6. Parts of IR spectra in the region of C=O stretching vibration of samples, containing **AHB09** complex (fee Fig. 1 in the main text for the structure), measured at various temperatures. Spectra of the complexes containing ^{13}C-labelled chloroacetic acid are shown as green traces (long dashes), complexes containing non-labelled acid are shown as orange traces. Black solid traces correspond to the isotope difference spectra (the spectrum of ^{13}C-labelled species minus the spectrum of non-labelled species). Blue, red and dotted black traces correspond to the result of the fitting, as described in the Discussion section of the main text.



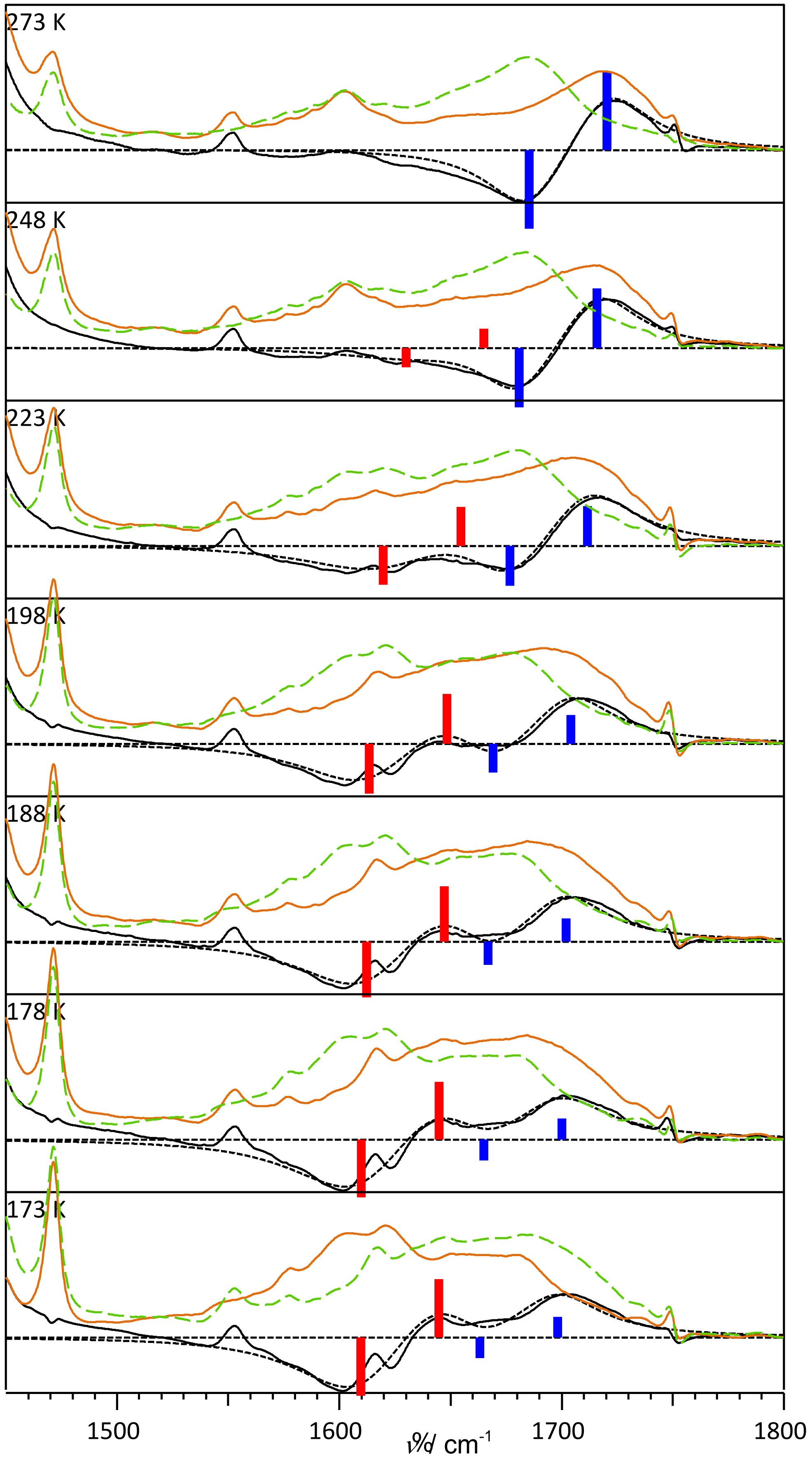
AHB9 var T

Figure S7. Parts of IR spectra in the region of C=O stretching vibration of samples, containing **AHB10** complex (fee Fig. 1 in the main text for the structure), measured at various temperatures. Spectra of the complexes containing ^{13}C-labelled chloroacetic acid are shown as green traces (long dashes), complexes containing non-labelled acid are shown as orange traces. Black solid traces correspond to the isotope difference spectra (the spectrum of ^{13}C-labelled species minus the spectrum of non-labelled species). Blue, red and dotted black traces correspond to the result of the fitting, as described in the Discussion section of the main text.



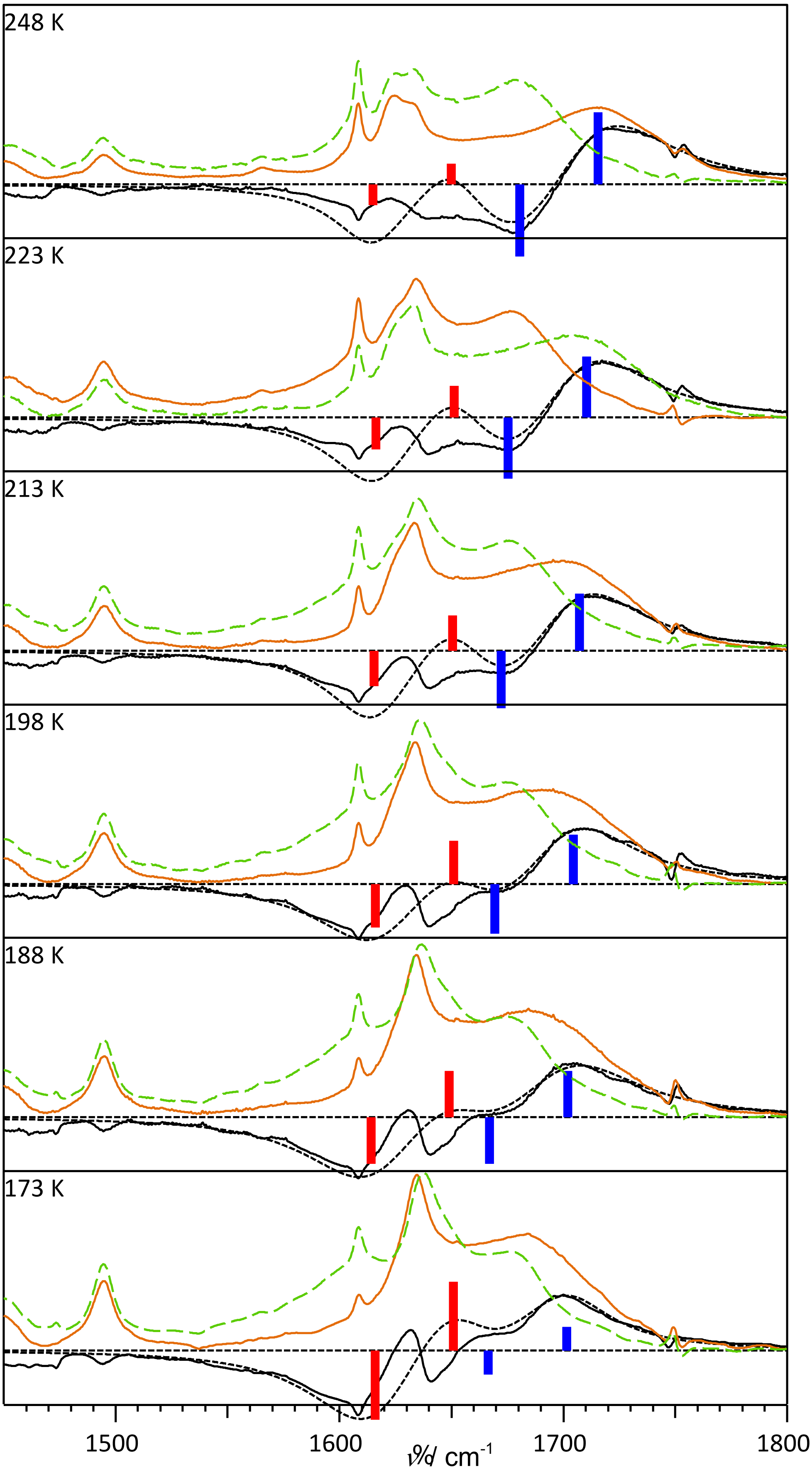
AHB10 var T

Figure S8. Parts of IR spectra in the region of C=O stretching vibration of samples, containing **AHB13** complex (fee Fig. 1 in the main text for the structure), measured at various temperatures. Spectra of the complexes containing ^{13}C-labelled chloroacetic acid are shown as green traces (long dashes), complexes containing non-labelled acid are shown as orange traces. Black solid traces correspond to the isotope difference spectra (the spectrum of ^{13}C-labelled species minus the spectrum of non-labelled species). Blue, red and dotted black traces correspond to the result of the fitting, as described in the Discussion section of the main text.



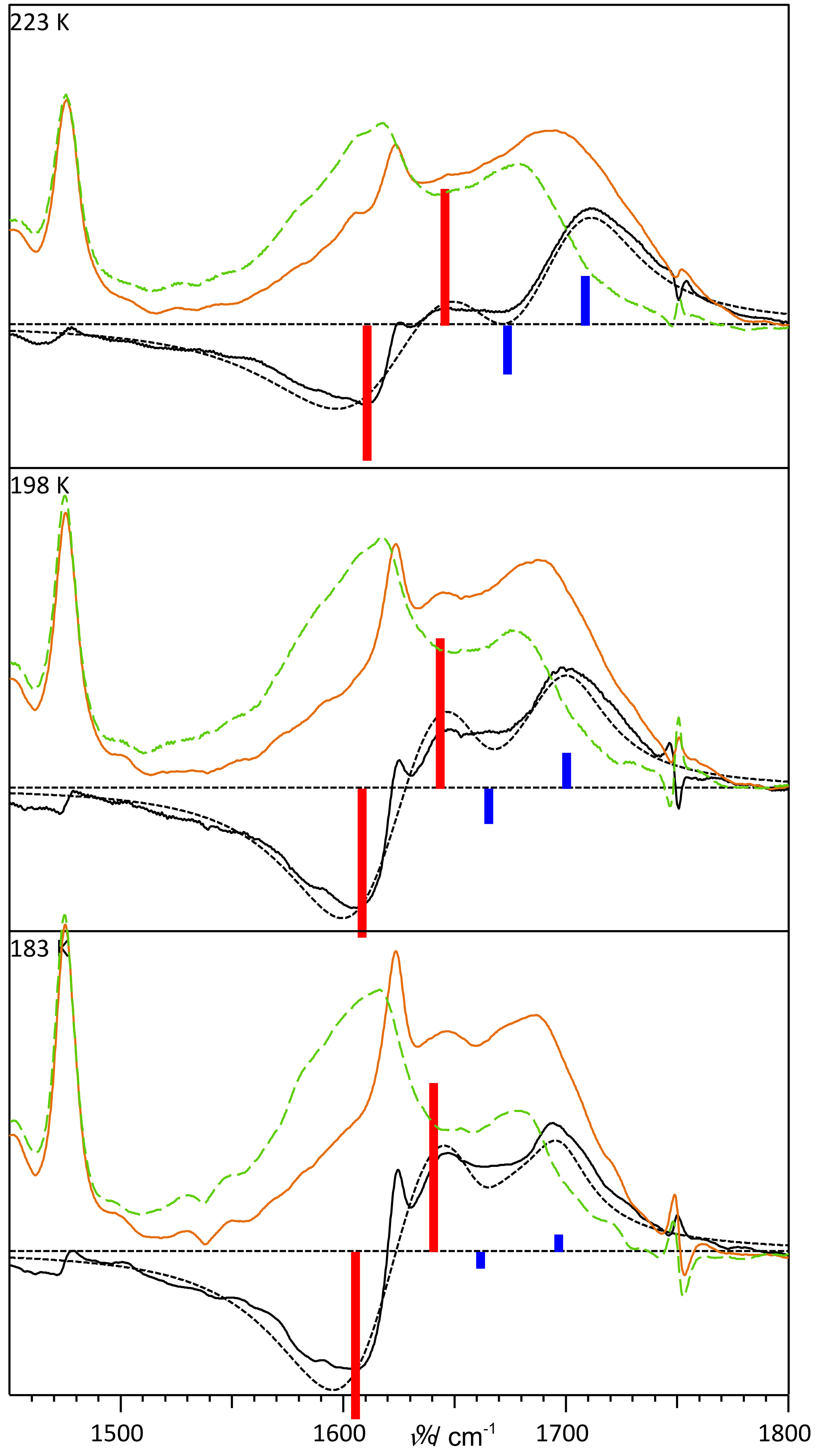
AHB13 var T

Figure S9. Parts of IR spectra in the region of C=O stretching vibration of samples, containing **AHB14** complex (fee Fig. 1 in the main text for the structure), measured at various temperatures. Spectra of the complexes containing ^{13}C-labelled chloroacetic acid are shown as green traces (long dashes), complexes containing non-labelled acid are shown as orange traces. Black solid traces correspond to the isotope difference spectra (the spectrum of ^{13}C-labelled species minus the spectrum of non-labelled species). Blue, red and dotted black traces correspond to the result of the fitting, as described in the Discussion section of the main text.



AHB14 var T

Figure S10. Parts of IR spectra in the region of C=O stretching vibration of samples, containing **AHB15** complex (fee Fig. 1 in the main text for the structure), measured at various temperatures. Spectra of the complexes containing ^{13}C-labelled chloroacetic acid are shown as green traces (long dashes), complexes containing non-labelled acid are shown as orange traces. Black solid traces correspond to the isotope difference spectra (the spectrum of ^{13}C-labelled species minus the spectrum of non-labelled species). Blue, red and dotted black traces correspond to the result of the fitting, as described in the Discussion section of the main text.



AHB15 var T

Table S1. IR spectral properties of chloroacetic acid base complexes **AHB** in dichloromethane solution: temperature, vibrational frequencies $\tilde{\nu}$ (in cm^{-1}) of the carbonyl stretching and asymmetric stretching vibrations of the ^{12}C isotopologs of neutral and anionic acid moieties, respectively; fractional integral intensity x_{red} of the band of the latter of the two modes.

complex	T / K	$\tilde{\nu}(^{12}\mathrm{C{=}O})$ ("blue")	$\tilde{\nu}_{\mathrm{as}}(^{12}\mathrm{CO_2^-})$ ("red")	x_{red}
AHB6	188	1719	1658	0
AHB7	273	1722	1666	0.09
AHB7	248	1721	1658	0.15
AHB7	223	1719	1652	0.23
AHB7	198	1715	1651	0.27
AHB7	188	1714	1651	0.27
AHB9	298	1725	1672	0.00
AHB9	273	1720	1672	0.12
AHB9	248	1722	1670	0.17
AHB9	223	1715	1657	0.32
AHB9	198	1710	1655	0.52
AHB10	303	1727		0.00
AHB10	223	1716	1672	0.28
AHB10	198	1712	1664	0.44
AHB10	188	1709	1659	0.60
AHB13	273	1720	1667	0.00
AHB13	248	1716	1665	0.24
AHB13	223	1712	1655	0.50
AHB13	198	1704	1648	0.63
AHB13	188	1702	1647	0.71
AHB13	178	1700	1645	0.74
AHB14	248	1716	1650	0.22
AHB14	223	1710	1650	0.27
AHB14	213	1707	1651	0.36
AHB14	198	1705	1651	0.41
AHB14	188	1702	1651	0.45
AHB15	223	1709	1651	0.10
AHB15	198	1700	1643	0.81

Table S2. Analysis of *ab initio* MD trajectory for chloroacetic acid complex with 2-methylpyridine (**AHB10**). The average residence times of O–H···N tautomer ($<t_{OH\cdots N}>$) and $O^-\cdots H–N^+$ tautomer ($<t_{O^-\cdots HN^+}>$) obtained for different values of τ. The latter is defined as time spent by the system without changing the sign of q_1 before and after the jump.

τ, fs	$<t_{OH\cdots N}>$, ps	$<t_{O^-\cdots HN^+}>$, ps
20	0.34	0.32
40	0.62	0.76
60	1.15	0.85
80	1.22	0.91
100	1.60	1.26
200	2.60	2.31

Figure S3. Time evolution of the bridging proton position ($q_1 = ½\,(r_{OH} - r_{HN})$) in the complex of chloroacetic acid with 2-methylpyridine (**AHB10**) according to *ab initio* MD simulations. Black trace: original computed data (same as in Figure 9). Red trace: 1 ps window average.

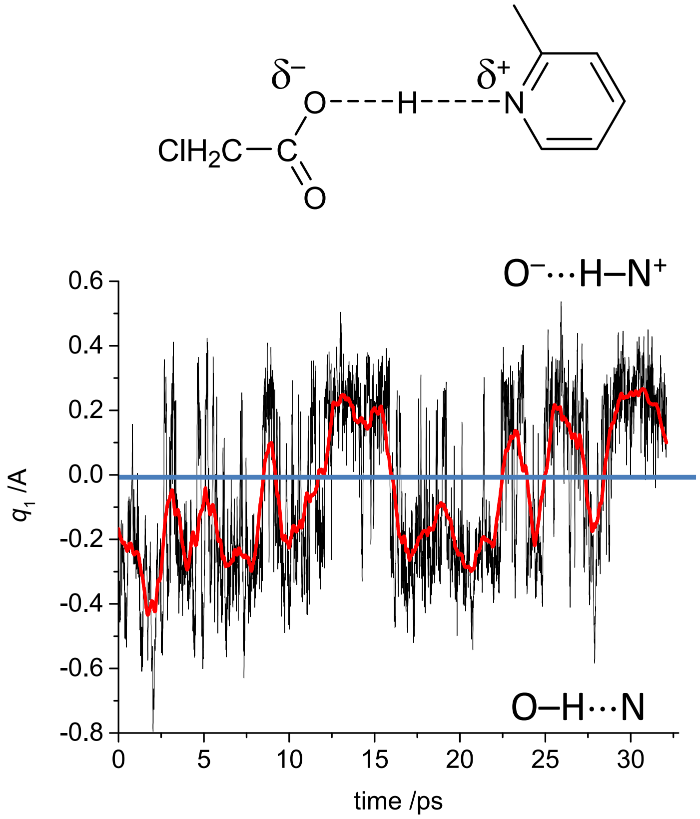
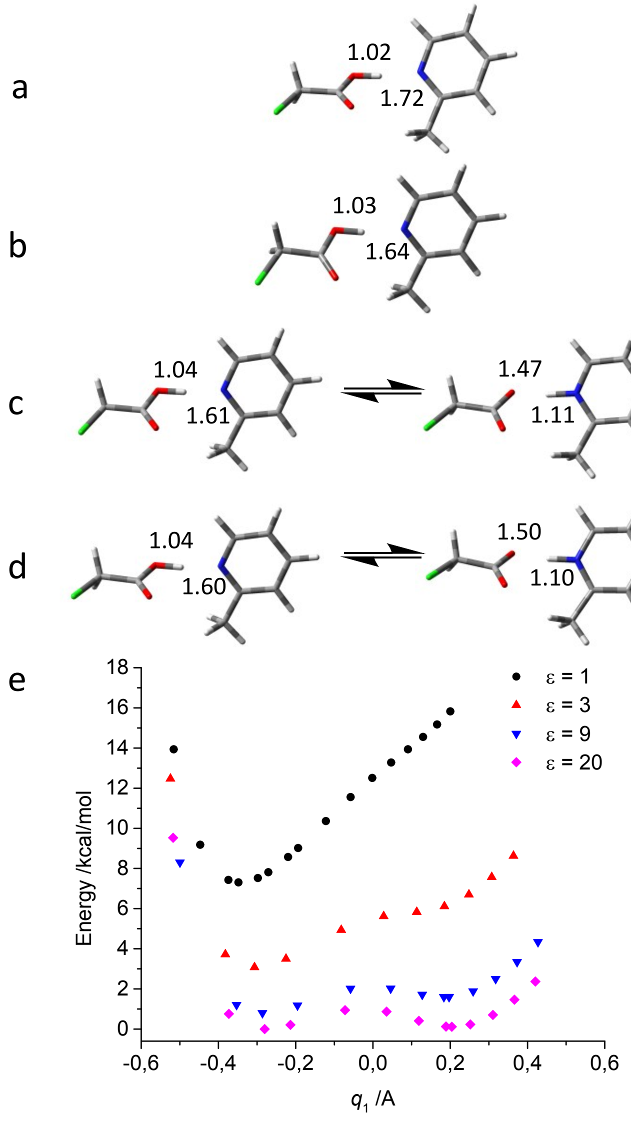


Figure S4. Results of B3LYP/6-311++G(d,p) calculations of optimized geometries and of adiabatic potential energy curves along the proton transfer coordinate for the chloroacetic acid complex with 2-methylpyridine (**AHB10**). Here, the term adiabatic refers to the fact that on each step of the calculations the distance from the bridging proton to oxygen atom was fixed while all other parameters were equilibrated. The complex was immersed into a cavity in infinite dielectric using polarizable continuum model.[1] The properties of the polarizable continuum were set to those of dichloromethane and the dielectric constant was changed. (a) Optimized geometry at ε = 1; (b) optimized geometry at ε = 3; (c) optimized geometries at ε = 9; (d) optimized geometries at ε = 1; (e) adiabatic potential energy curves along the proton transfer coordinate. The O…H distances are given above the OHN bond, the H…N distances are given below the OHN bond.



---

[1] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999.

Figure S5. Calculated NMR parameters of **AHB10** for 98 random snapshots of *ab initio* MD trajectory. Chemical shifts of chloroacetic acid C1 carbon (top) and C2 carbon (middle), as well as chemical shift of 2-methylpyidine nitrogen (bottom) are shown. Computational details are given in Experimental section. Horizontal red bars correspond to the values averaged over the range of q_1 values.