

SUPPLEMENTARY MATERIALS

INFRARED SPECTROSCOPY OF AQUEOUS CARBOXYLIC ACIDS: COMPARISON BETWEEN DIFFERENT ACIDS AND THEIR SALTS

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1. THE WATER SPECTRUM SUBTRACTION

Since the water spectrum subtraction is a critical point in these spectral data treatment, we provide here some details on the procedure.

1.1 THE REFERENCE WATER SPECTRA AND METHOD

The water spectra used to subtract the water bands from experimental spectra are shown in Fig. S1A: (a) 2.23 M NaOH; (b) 1.54 M HCl; (c) pure water; (d) and 5.13 M NaCl. Table S1 lists the mean spectral ATR intensities (in a. u.) in the 2620–2580 and 1850–1800 cm⁻¹ regions that are the lowest of these species. Increasing the water spectrum subtraction from the acidic solutions spectra produced a low intensity absorption near 3200 cm⁻¹ (see Fig. 1) before a negative band appeared near 3660 cm⁻¹ (criterion (i), section 2.1). This led to an absolute maximum water subtraction. Similarly for the basic solutions, the amount of water subtraction using the alkaline solutions was made such that no negative band appeared near 3660 cm⁻¹ (criterion (i), section 2.1). After these water subtractions, some spectra still showed residual water bands. These are assigned to water close-bound to the solutes.

1.2 EXAMPLE OF THE 1.33 M GLYCINE TITRATION

Figure S2 shows 14 of the 26 ATR–IR spectra covering the 4800–700 cm⁻¹ range of 1.33 M glycine in the 0–14 pH range. We observe spectral changes with glycine ionic modifications in the 1800–1200 cm⁻¹ region. The results obtained after water spectral subtraction is shown in Fig. S3. The water MFs as a function of pH are given in Fig. S1B. On the subtracted spectra (Fig. S3), the OH stretch band is situated mainly between 3700 and 2500 cm⁻¹, but at the lowest pH the far

wing extends to almost 1700 cm⁻¹.

2. Spectral residues obtained from FA

Figure S4 presents the spectral residues resulting from FA made on the six IR titrations. An ordinate expanded scale illustrate the quality of the FA results obtained. All six figures show that the residues are almost at the zero level, which indicates that FA procedure is adequate.

3. Acetic Acid

3.1 CORRECTION FOR ACIDIC AND BASIC WATERS

The pH of the acetic acid stock solution was 2.10 (Table 3), indicating that H⁺ concentration is about 10⁻² mol/L. This is confirmed by the solution composition retrieved by FA. The stock solution is made of 100 ± 2% unionized acetic acid (Fig. 3A). However, as previously observed for malic acid,²⁷ acidic water was found in the solution at the level of 0.082 ± 0.012 mol/L equivalent HCl for each mol/L acetic acid (Table 4). Since this acidic water cannot be attributed to dissolved HCl (no titrant was added to the solution) nor can it be attributed to "free" protons (H⁺ or H₃O⁺, [H⁺] ~ 10⁻² mol/L), it must come from the solute, acetic acid (100%). Hence, a correction similar to that for malic acid²⁷ must be applied to the acetic acid spectrum (Fig. 1A_a). The corrected spectrum is displayed in Fig. 4a. In the same way, the spectrum of the aceto-acetate complex (Fig. 1A_c) was modified due to its acidic content (Fig. 6a). The sodium acetate species was found free of acidic and alkaline water, hence its spectrum (Fig. 1A_b) was unmodified (Fig. 5a).

4. Malic Acid

4.1 FACTOR ANALYSIS OF AQUEOUS MALIC ACID

Results obtained by FA on a series of 24 samples of aqueous malic acid have been reported²⁷

and are included here for comparison with the other acids. Three principal species were retrieved giving the spectra presented in Fig. 1B: (B_{aa}) acid; (B_{ab}) monosodium–; and (B_{bb}) disodium malate. Since the residues (Fig. S4B) are very low, it indicates that the FA procedure worked adequately. The titration curves (Fig. 2B) indicate that the FA results are coincident with the calculated ones using eq. (2).

4.2 CORRECTION FOR ACIDIC AND BASIC WATERS

After correcting the spectra for the over subtraction of acidic water, the real spectra of malic acid, mono–, and disodium malate are reproduced in Figs. 4–6, frames b.²⁷

5. Betaine

5.1 FACTOR ANALYSIS OF AQUEOUS BETAINES

FA applied to a series of 20 spectra obtained from the IR titration of 1.65 M betaine hydrochloride gave the results presented in Figs. 1C, 2C, 3C and S4C. Two principal species were retrieved: aqueous betaine hydrochloride and aqueous betaine zwitterion. The pK_a value retrieved by IR and pH was 1.65 (Table 3), which is close to the literature value of 1.83 (at 0 °C).³² The small difference between the two values is attributed to temperature, activity coefficient or both.

5.2 CORRECTION FOR ACIDIC AND BASIC WATERS

The pH of the stock solution was 0.60 (Table 3). The relative composition of this solution, as retrieved by FA, is 0.934 ± 0.005 and 0.073 ± 0.005 for betaine hydrochloride and betaine zwitterion, respectively (Fig. 3C). Such a composition indicates that 7.3% of the betaine hydrochloride dissociates in water. The total betaine concentration of the solution was 1.65 mol/L which gives a pH of 0.76 [$1.65 \times 0.073 = 0.120$ (± 0.009) mol/L of aqueous HCl]. The difference between this value and the pH meter one (0.60) comes from the activity coefficient differences.

According to FA, the stock solution contains acidic water at the level of 0.312 ± 0.008 mol/L equivalent HCl for each mol/L of betaine (Fig. 3C). The dissociation of 7.3% of betaine hydrochloride contributed 0.073 mol/L, leaving $0.312 - 0.073 = 0.239$ mol/L acidic water (equivalent HCl for each mol/L betaine). Therefore, this acidic water must be attributed to water in strong interaction with betaine hydrochloride. Furthermore, at +1 equivalent titrant, betaine hydrochloride is completely neutralized in the zwitterionic form, which is not associated with acidic or alkaline water (Fig. 3C). Thus, the only species responsible for the excess of acidic water observed in the stock solution is betaine hydrochloride. Then, $0.239 / 0.934 = 0.256$ mol/L equivalent HCl is associated to each mol/L betaine hydrochloride in water. The corrections (Appendix A) applied to the betaine hydrochloride spectrum (Fig. 1C_a) yielded spectrum Fig. 4c.

Zwitterionic betaine which is free from acidic and alkaline water (Fig. 1C) gives spectrum C_z in Fig. 1. This was reproduced in Fig. 6c.

Figure. 3C (■) shows the amount of NaCl-solvated water in the betaine titration. Since this amount follows the aqueous NaOH added until complete neutralization of betaine hydrochloride, we can conclude that it was produced by the neutralization of betaine hydrochloride by NaOH. This produced water, NaCl and betaine zwitterion. Furthermore, NaCl-solvated water was found unperturbed in the presence of both ionic species of betaine. This confirms the previously reported result that after a chemical equilibrium is obtained, saline, acidic and alkaline solvated waters are not perturbed in the mixtures by the presence of the other substances in the solutions.⁵ The recent study of Omta confirms this.²⁷

6. BOPA (*N,N*-((butyloxy) propyl) amino diacetic acid)

6. 1 FACTOR ANALYSIS OF AQUEOUS BOPA

FA applied to a series of 27 samples obtained from the IR titration of 0.95 M BOPA was

reported in ref. ¹⁵. Here we add the water quantitative IR analysis. The results are shown in Figs. 1F, 2F, 3F and S4F. Of the six titrations presented here, BOPA is the more complex one because 8 principal species are necessary in FA to obtain acceptable residues (Fig. S4F): BOPA hydrochloride, BOPA zwitterion, sodium BOPA, disodium BOPA, pure water, acidic and alkaline water and NaCl-solvated water. Since the pK_a 's of these are similar to the glycine's ones (Table 3) they make BOPA a member of the glycinate family.¹⁵

6. 2 CORRECTION FOR ACIDIC AND BASIC WATERS

Figure 3F indicates that mono- and di-sodium BOPA are not associated to acidic and alkaline waters. The unmodified spectra (Figs. 1F_{bb} and F_{bz}) are reported in Figs. 5f and 6f', respectively.

6.3 CORRECTION FOR BOPA HYDROCHLORIDE

At pH = 0.09, BOPA is completely in the hydrochloride ionic form since 2.56₂ HCl equivalents was added to the stock solution (Fig. 3F). FA indicates that the stock solution contains 95% sodium BOPA and 5% disodium BOPA. Therefore, from eq. 2, the complete transformation of BOPA into BOPA hydrochloride necessitates 2.05 HCl equivalent which gives (2.562 – 2.05 =) 0.512 mol/L equivalent HCl, a pH of 0.31 (= –log [0.512 × 0.95]). The difference between this value and the measured value of 0.09 is attributed to the activity coefficients of aqueous NaCl and BOPA.^{6,16}

Figure 3F indicates that when –2.562 titrant equivalent is added to the solution, 1.277 mol/L equivalent HCl for each mol/L BOPA is retrieved by FA. Consequently, an excess of (1.277 – 0.512 =) 0.765 mol/L equivalent HCl for each mol/L BOPA is retrieved by FA. This excess is due to water in strong interaction with BOPA hydrochloride which is taken care by applying a correction to the spectrum of Fig. 1F_{aa} (Appendix A) to give the spectrum of Fig. 4f.

6.4 CORRECTION FOR BOPA ZWITTERION

At pH = 2.27, three ionic species of BOPA are retrieved by FA (Fig. 2F): BOPA hydrochloride (14.1%), BOPA zwitterion (73.1%) and sodium BOPA (12.8%). In this solution, 0.824 HCl equivalent was added to the stock solution. Since sodium BOPA is not completely transformed into BOPA hydrochloride, only a low concentration of H⁺ is expected in the solution ($[H^+] < 10^{-2}$). The pH value of 2.27 confirms this. The amount of acidic water (0.208 mol/L equivalent HCl per mol/L BOPA) retrieved by FA in the IR spectrum of this solution is attributed to water in strong interaction with BOPA ionic species. Since no acidic water is associated to sodium BOPA, acidic water found in the solution at pH = 2.27 is attributed to both BOPA hydrochloride and zwitterion. We found that 0.765 mol/L equivalent HCl are associated to each mol/L BOPA hydrochloride giving $[(0.208 - 0.765 \times 0.141)/0.731 =]$ 0.137 mol/L equivalent HCl associated to BOPA zwitterion (in mol/L). A correction (Appendix A) is applied to BOPA zwitterion at pH = 2.27 which modifies spectrum of Fig. 1F_{az} to that of Fig. 6f.

In the previous reported results on BOPA,¹⁵ the acidic water correction was not made. This correction is now made to obtain the spectra **f** and **f'** of Figs 4, 5 and 6.

TABLE S1: Mean Intensity (in a. u. ^{*}) of the Water Principal Spectra (Fig. 1A) in Critical Regions.

Spectral region	Pure H ₂ O	2.23 M NaOH	1.54 M HCl	5.13 M NaCl
2620 – 2580 cm ⁻¹	0.03	0.28	0.17	0.01
1850 – 1800 cm ⁻¹	0.10	0.31	0.35	0.07

^{*} a. u.: absorbance unit, ATR absorbance using ZnSe crystal with 6.6 effective reflections.

FIGURE CAPTIONS

Figure S1. (A) Water ATR–IR principal spectra used in the water subtraction. (B) Water MFs of 1.33 M glycine at pH 0 to 14 (Figure S2). (a) 2.23 M NaOH for basic water (●); (b) 1.54 M HCl for acidic water (▲); (c) pure water (○); (d) 5.13 M NaCl for saline water (■, not present for glycine). Note that the spectra are shifted one from the others. Light vertical line at 1638 cm⁻¹ indicates the δ(H₂O) band.

Figure S2. Fourteen of the 26 ATR–IR spectra of 1.33 M glycine at pH 0 to 14 in the spectral range 4800 to 700 cm⁻¹. Intensity in ATR absorbance unit (a. u.). Note that the spectra are shifted.

Figure S3. Figure S2 spectra (1.33 M glycine) after water spectral subtractions (MFs shown in Fig. S1B). Light vertical line at 1638 cm⁻¹ indicates the δ(H₂O) band. Same presentation as in Fig. S2.

Figure S4. Residue spectra of FA applied to the IR titration of carboxylic acids: (A) acetic acid; (B) malic acid; (C) betaine; (D, E) 1.33, 2.66 M glycine; (F) BOPA (Note the 12× intensity scale).

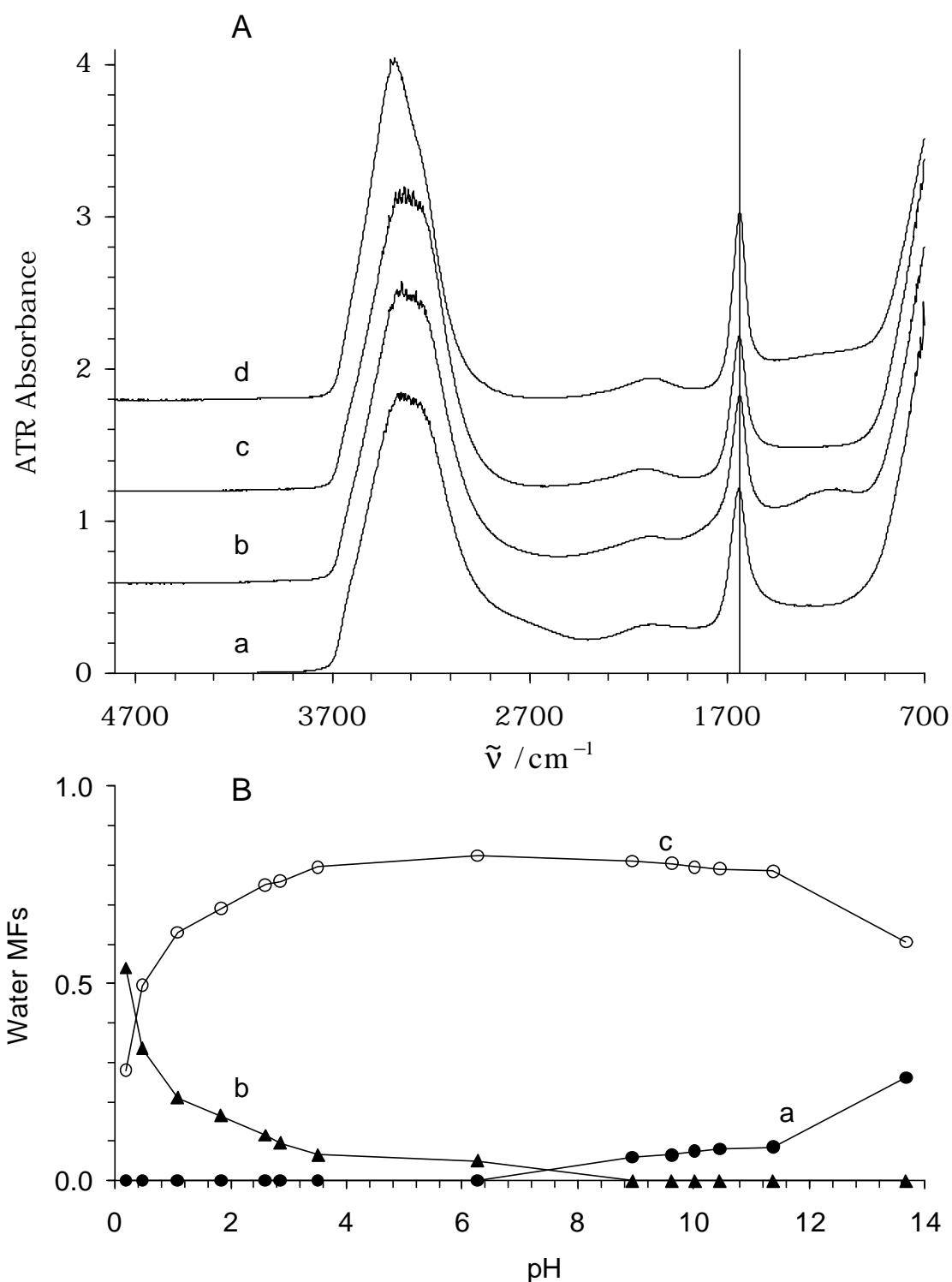


Figure S1. (A) Water ATR-IR principal spectra used in the water subtraction. (B) Water MFs of 1.33 M glycine at pH 0 to 14 (Figure 2). (a) 2.23 M NaOH for basic water (●); (b) 1.54 M HCl for acidic water (▲); (c) pure water (○); (d) 5.13 M NaCl for saline water (■). Spectra b–d are shifted 0.6 a. u. from the preceding ones. Light vertical line at 1638 cm^{-1} indicates the H_2O band. (saline water (■) is not present in the titration of glycine).

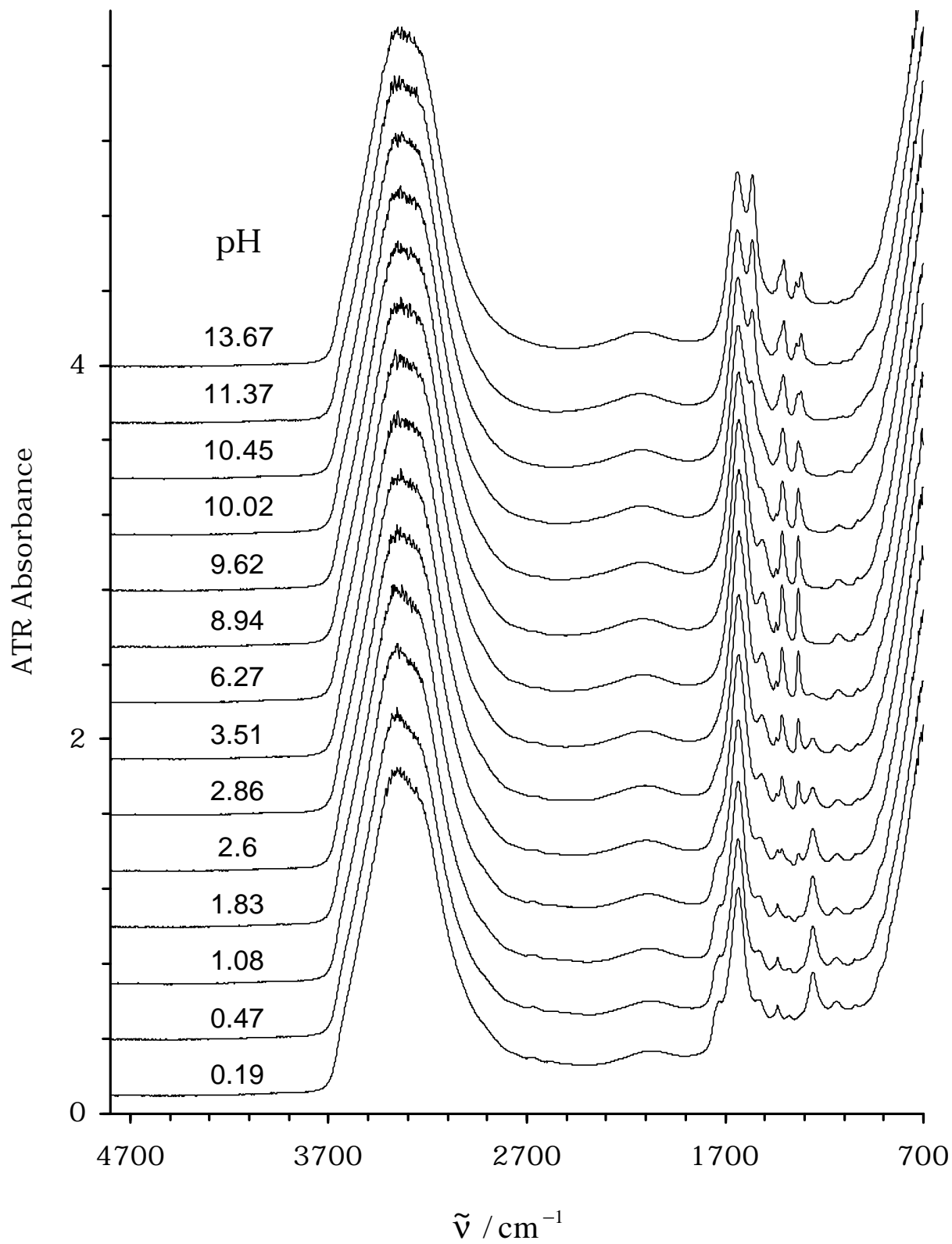


Figure S2. Fourteen of the 26 ATR-IR spectra of 1.33 M glycine at pH 0 to 14 in the spectral range 4800 to 700 cm^{-1} . Intensity in ATR absorbance unit (a. u.). The bottom spectrum is shifted 0.1 a. u., the other spectra are shifted 0.3 a. u. from the preceding ones.

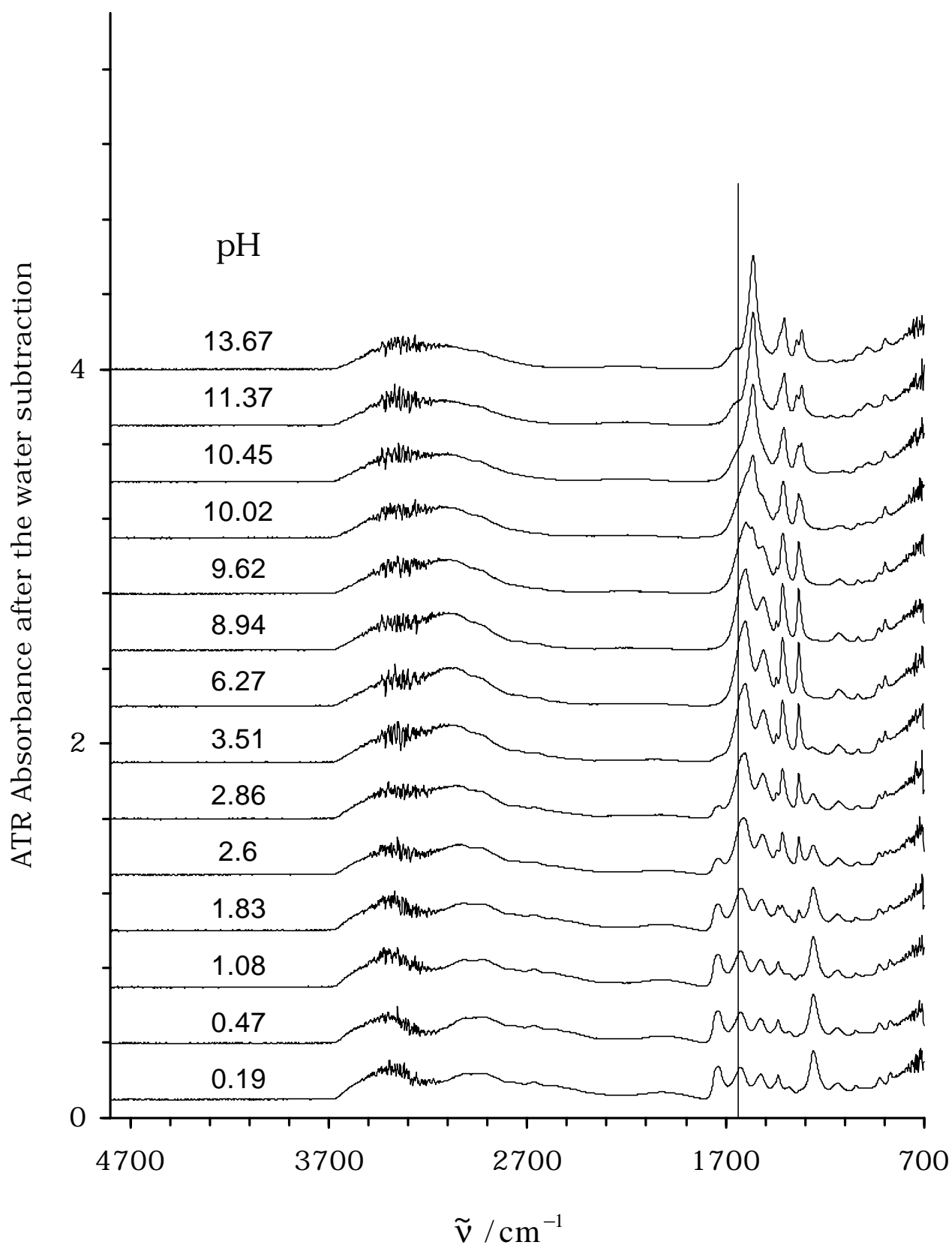


Figure S3. Figure 2 spectra (1.33 M glycine) after subtraction of the water spectra (MFs shown in Fig. 1B). The light vertical line at 1638 cm^{-1} indicates the $\delta(\text{H}_2\text{O})$ band. Same presentation as in Fig. S2.

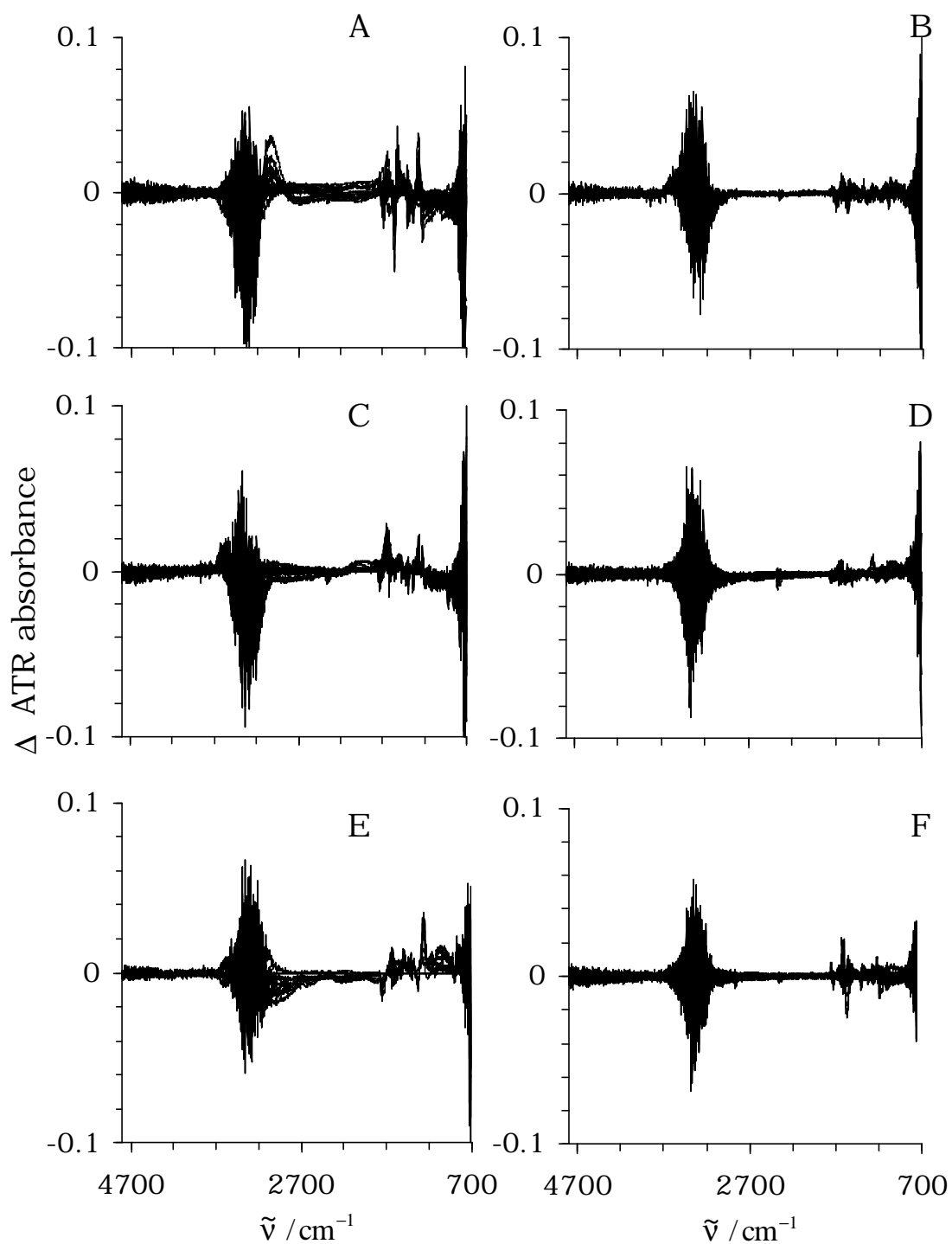


Figure S4. Residue spectra of FA applied to the IR titration of carboxylic acids: (A) acetic acid; (B) malic acid; (C) betaine; (D, E) 1.33, 2.66 M glycine; (F) BOPA (Note the 12× intensity scale).