A Novel Application of Dopants in Ion Mobility Spectrometry: Suppression of Fragment Ions of Citric Acid

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Figure S1. Schematic representation of different parts of the IMS used in this work and the paths of carrier, drift, and dopant gases.
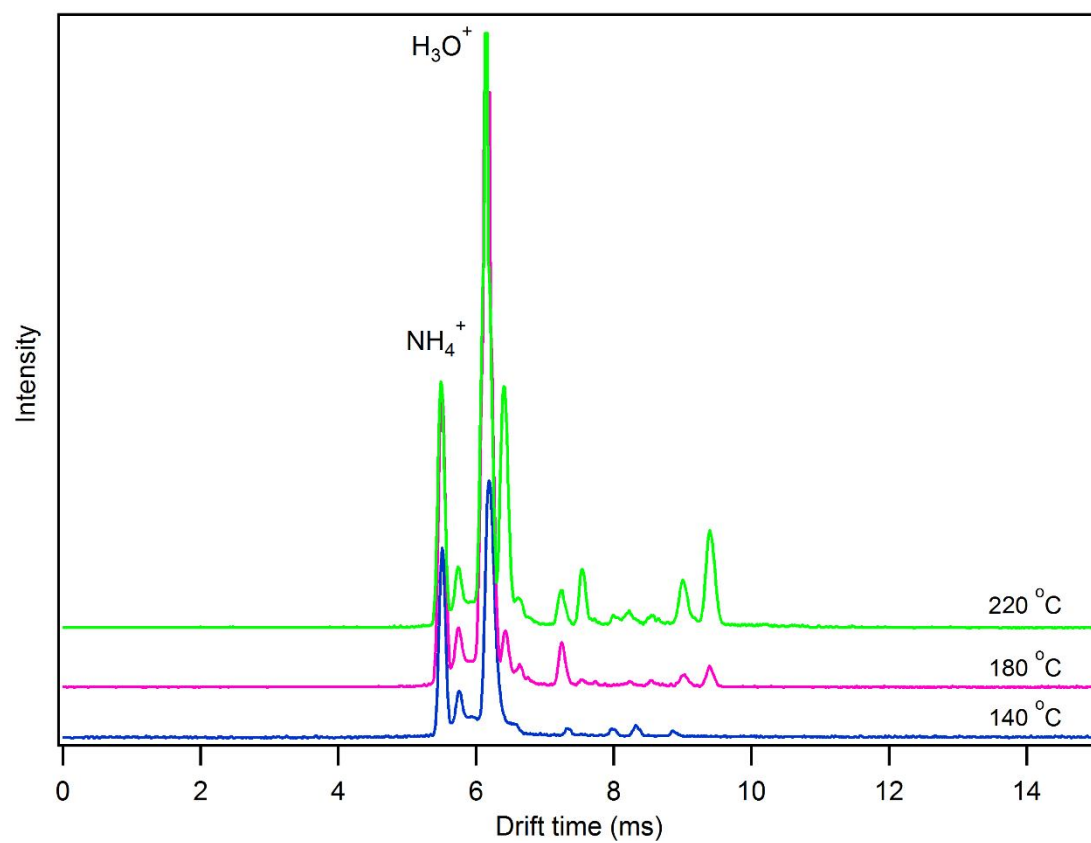
Figure S2. IMS spectra of citric acid (100 ppm) at different temperatures of the injection port with H_3O^+ as the main reactant ion RI. The drift tube temperature was 140 °C.
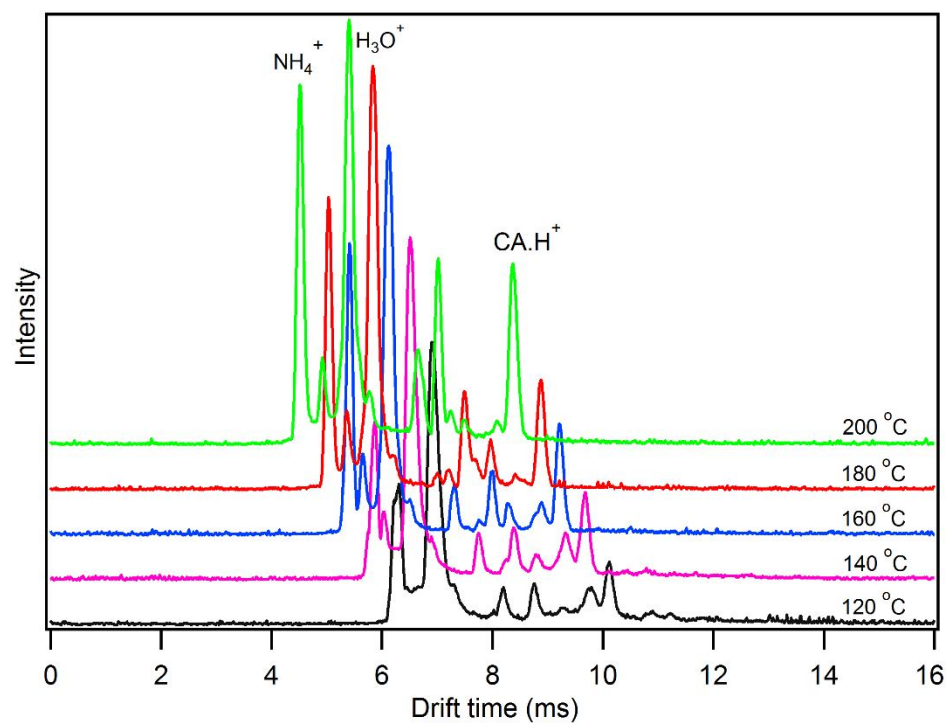
Figure S3. IMS spectra of citric acid at different temperatures of the drift tube in the absence of NH_3 dopant, i.e. the main reactant ion is H_3O^+. The injection port temperature was 220 ^oC.
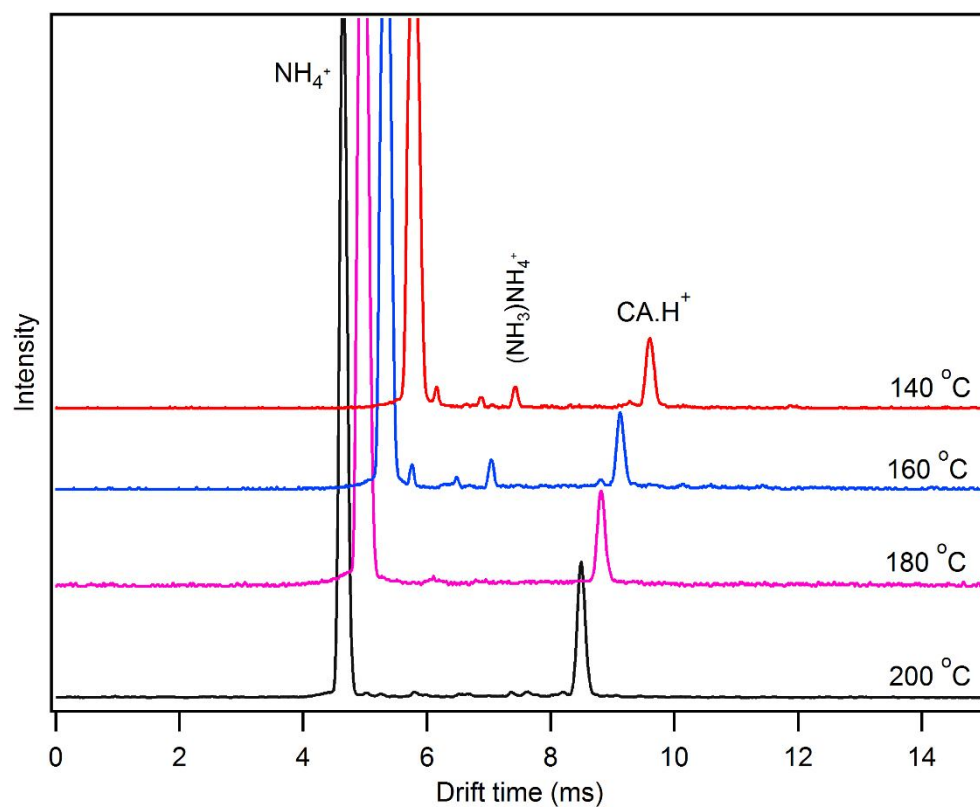
Figure S4. IMS spectra of citric acid (100 ppm) at different temperatures of the drift tube in the presence of NH_3 dopant. In this condition, the reactant ion is NH_4^+. The injection port temperature was 220 °C.
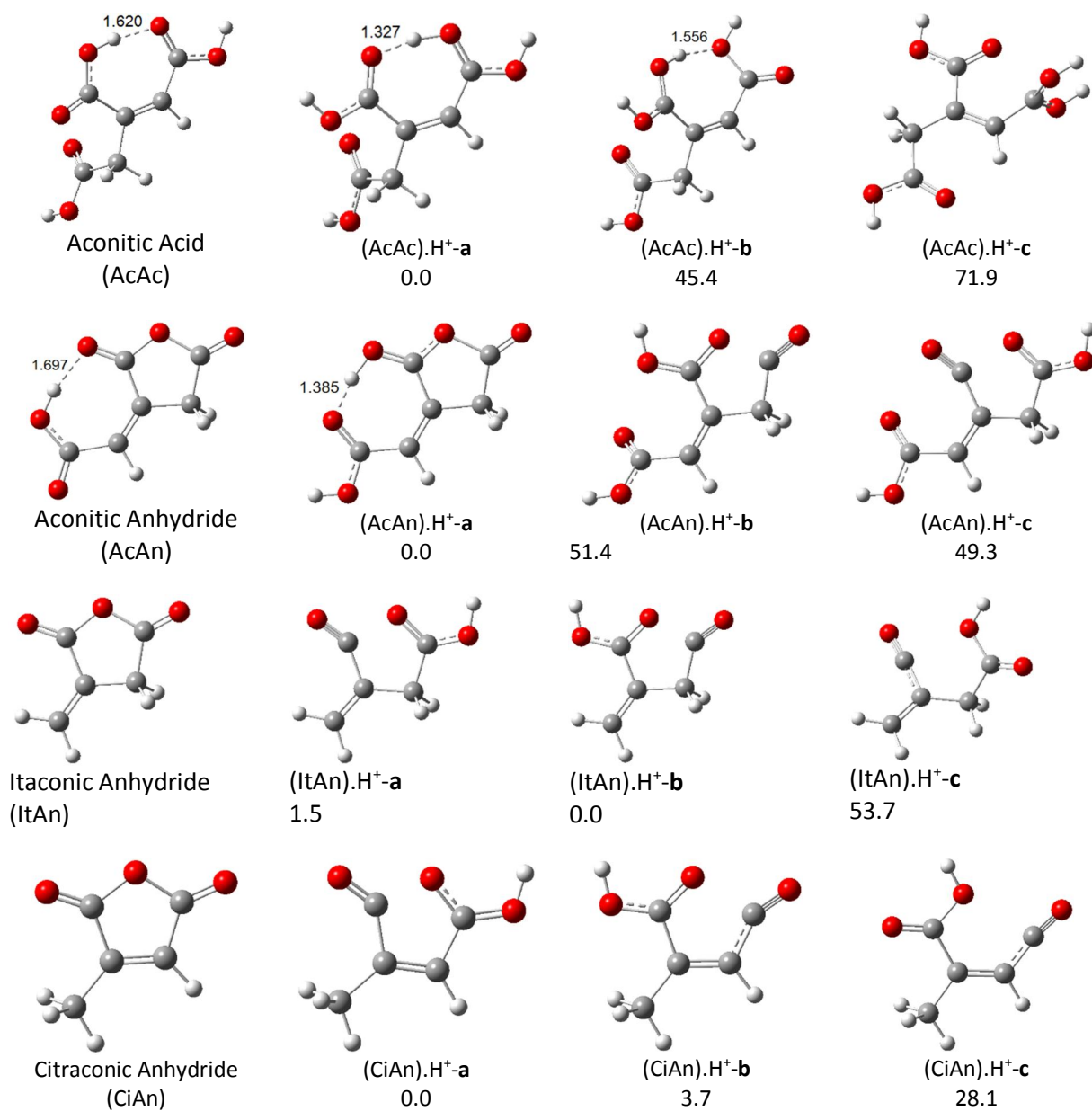
Figure S5. The optimized structures of the fragments of citric acid and their protonated forms. The relative energies and bond lengths are in kJ mol^{-1} and Å, respectively.
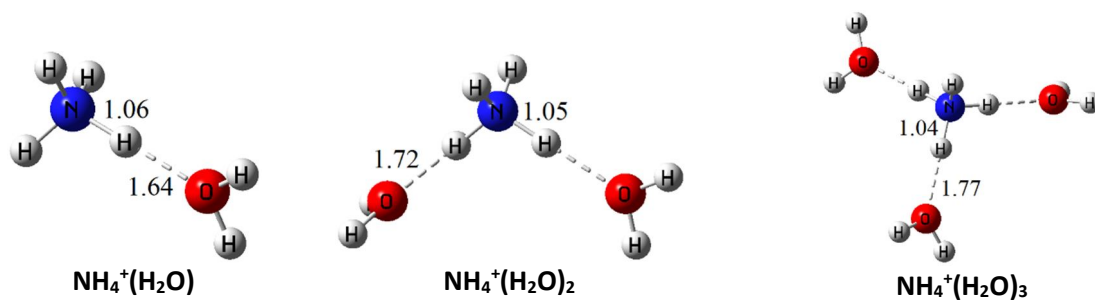
Figure S6. The optimized structures of $NH_4^+(H_2O)_n$ clusters. The bond lengths are in Å.

Table S1. The calculated values of ΔH, ΔG and equilibrium constant (K) for formation of $NH_4^+(H_2O)_n$ clusters in gas phase and at 298 K.

Hydration	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	K (1/atm)
$NH_4^+ + H_2O \rightarrow NH_4^+(H_2O)$	-89.5	-50.1	5.9×10^8
$NH_4^+(H_2O) + H_2O \rightarrow NH_4^+(H_2O)_2$	-66.9	-43.3	3.8×10^7
$NH_4^+(H_2O)_2 + H_2O \rightarrow NH_4^+(H_2O)_3$	-57.6	-23.3	1.2×10^4

Figure S7. The optimized structures of mono-, di-, and tri-hydrated form of CA.H$^+$ in gas phase. The relative energies and bond lengths are in kJ mol^{-1} and Å, respectively.
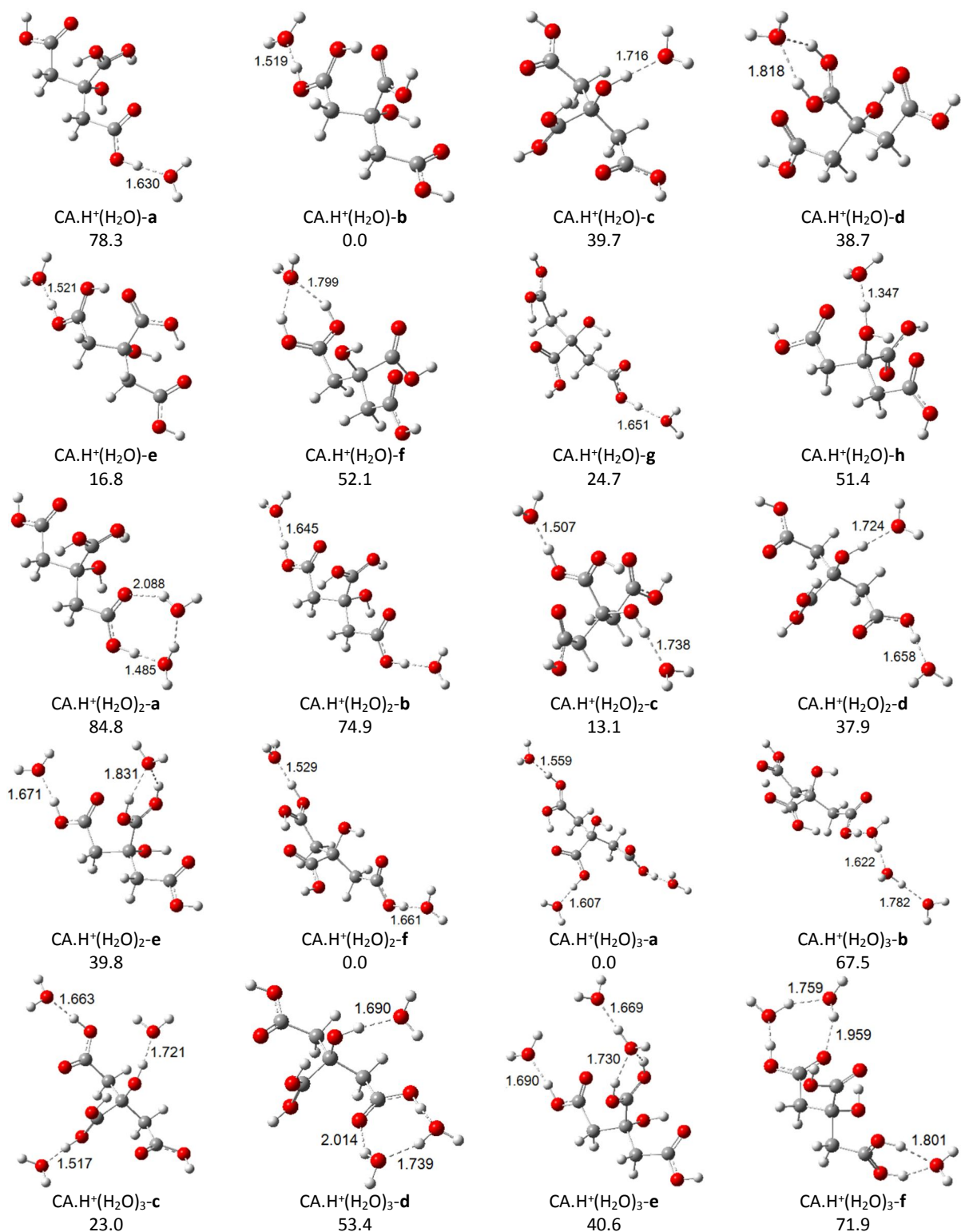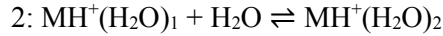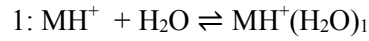
Table S2. The calculated values of ΔH, ΔG and equilibrium constant (K) for hydration of CA.H$^+$ in gas phase and at 298 K.
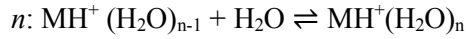
Hydration	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	K (1/atm)
CA.H$^+$ + H$_2$O → CA.H$^+$(H$_2$O)	-75.9	-42.9	3.3 x 10^7
CA.H$^+$(H$_2$O) + H$_2$O → CA.H$^+$(H$_2$O)$_2$	-64.8	-31.8	3.7 x 10^5
CA.H$^+$(H$_2$O)$_2$ + H$_2$O → CA.H$^+$(H$_2$O)$_3$	-61.3	-27.4	6.3 x 10^4

S-1 hydration model

Relative abundances, Y_i, of MH$^+$(H$_2$O)$_i$ can be calculated from equilibrium constants for following consecutive reactions

1: MH$^+$ + H$_2$O ⇌ MH$^+$(H$_2$O)$_1$

2: MH$^+$(H$_2$O)$_1$ + H$_2$O ⇌ MH$^+$(H$_2$O)$_2$

....

n: MH$^+$ (H$_2$O)$_{n-1}$ + H$_2$O ⇌ MH$^+$(H$_2$O)$_n$

The eqilibrium constant of each hydration reaction can be written as following

$$K_i = \frac{\left[MH^+\left(H_2O\right)_i\right]}{\left[MH^+\left(H_2O\right)_{i-1}\right]w} \tag{1}$$

Where w is water concentration. The eqilibrium constant, K_i, can be computed from ΔG° of each hydration reaction

$$K_i = exp(-\Delta G_i^o/RT) \tag{2}$$

where R is the gas constant and T is the absolute temperature.

Concentration of each ion can be obtained using equation (1)

MH$^+$(H$_2$O)$_1$ = [MH$^+$].w.K_1

MH$^+$(H$_2$O)$_2$ = [MH$^+$].w^2.K_1K_2

$$MH^+(H_2O)_j = [MH^+]w^j\prod_{i=1}^{j}K_i \tag{3}$$

The relative abundance for MH$^+$(H$_2$O)$_j$ is

$$Y_j = \frac{\left[MH^+(H_2O)_j \right]}{\sum_{i=0}^{n_{max}} \left[MH^+(H_2O)_i \right]} \tag{4}$$

Where n_{max} is the maximum number of water molecules in a $MH^+(H_2O)_n$. n_{max} was taken equal to 3 or 4.

Combination of equations (3) and (4) results in

$$Y_j = \frac{w^j \prod_{i=0}^{j} K_i}{\sum_{n=0}^{n_{max}} w^n \prod_{i=0}^{n} K_i} \tag{5}$$

where $K_o = 1$.

The van't Hoff equation was used to obtain the equilibrium constant, K_i, at the temperatures other than 25 °C (298 K):

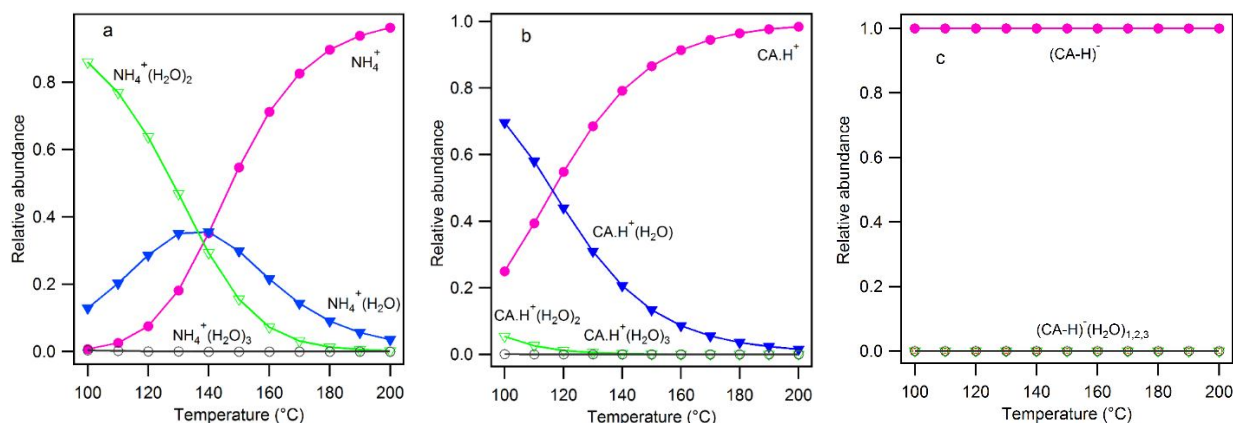$$\frac{d \ln K_i}{d(1/T)} = -\frac{\Delta H_i^{\circ}}{R} \tag{6}$$

Figure S8. The calculated relative abundances for (a) $NH_4^+(H_2O)_n$, (b) $CA.H^+(H_2O)_n$, and (c) $(CA-H)^-$ $(H_2O)_n$ in gas phase in the presence of 40 ppm water vapor.

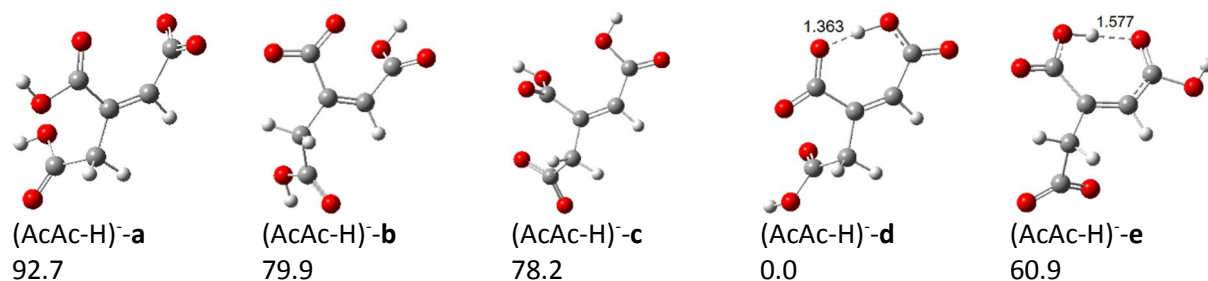| (AcAc-H)⁻-**a**	(AcAc-H)⁻-**b**	(AcAc-H)⁻-**c**	(AcAc-H)⁻-**d**	(AcAc-H)⁻-**e**
92.7	79.9	78.2	0.0	60.9

Figure S9. The optimized structures for different isomers of deprotonated form (conjugated bases) of aconitic acid in gas phase. The relative energies and bond lengths are in kJ mol^{-1} and Å, respectively.

Table S3. The calculated ΔH and ΔG values for protonation of the negative reactant ions (O_2^-, Cl^-, Br^-, I^-) and deprotonation of CA and its fragments in gas phase and at 298 K. The fragments with smaller deprotonation enthalpies are more acidic and deprotonated easier.

Protonation/deprotonation	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})
O_2^- + + H^+ → HO_2	-1461.9	-1437.0
Cl^- + H^+ → HCl	-1378.4	-1356.0
Br^- + H^+ → HBr	-1341.2	-1319.2
I^- + H^+ → HI	-1315.2	-1294.0
CA → (CA-H)$^-$ + H^+	1278.8	1256.4
AcAn → (AcAn-H)$^-$ + H^+	1355.3	1320.1
AcAc → (AcAc-H)$^-$ + H^+	1303.8	1275.2
CH_3COOH → CH_3COO^- + H^+	1446.1	1413.1
HCOOH → $HCOO^-$ + H^+	1426.4	1395.2

CA: Citric acid; AcAn: Aconitic anhydride; AcAc: Aconitic acid
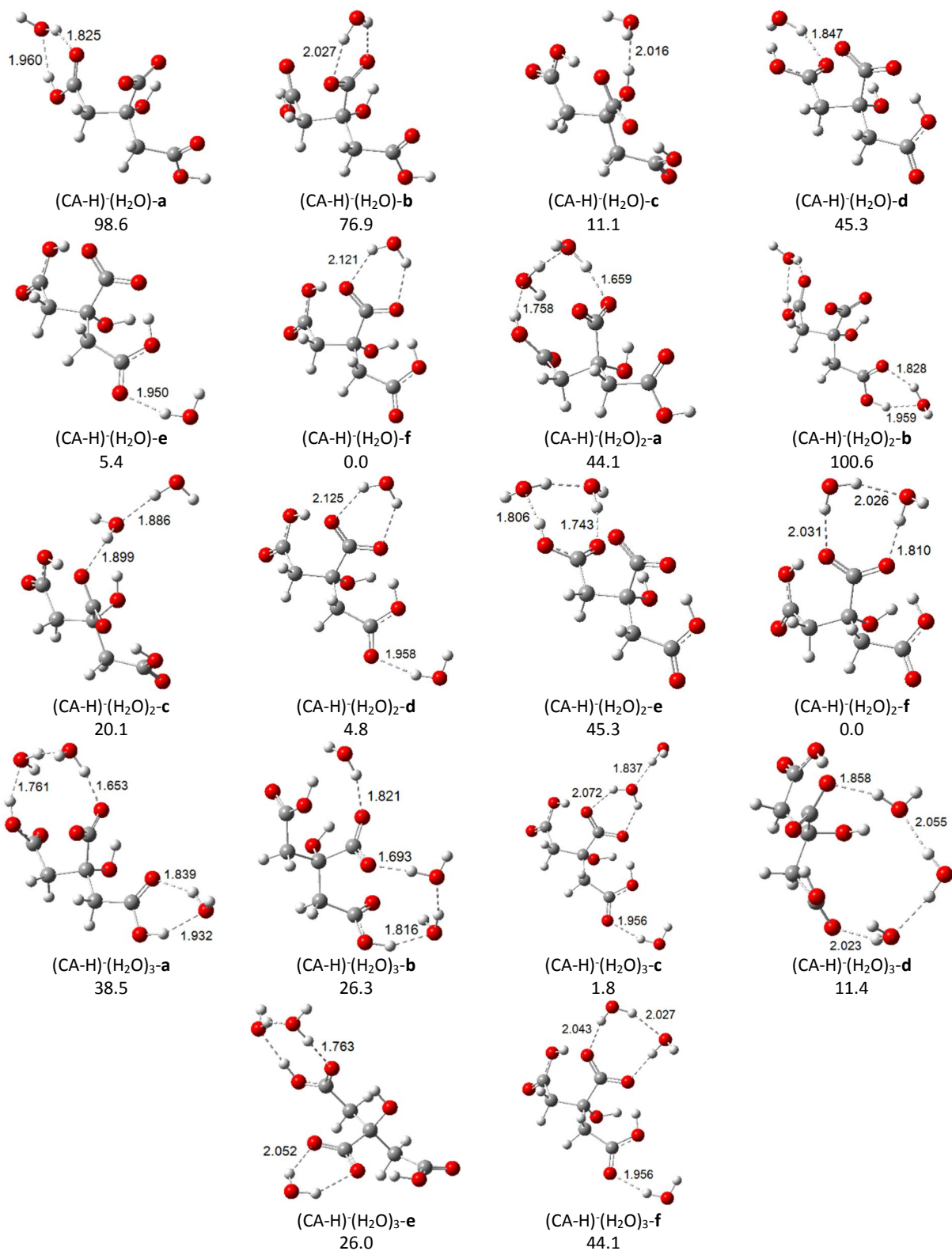
Figure S10. The optimized structures of mono-, di-, and tri-hydrated forms of (CA-H)$^-$ in gas phase. The relative energies and bond lengths are in kJ mol^{-1} and Å, respectively.

Table S4. The calculated values of ΔH, ΔG and equilibrium constant (K) for hydration of (CA-H)$^-$ in gas phase and at 298 K.

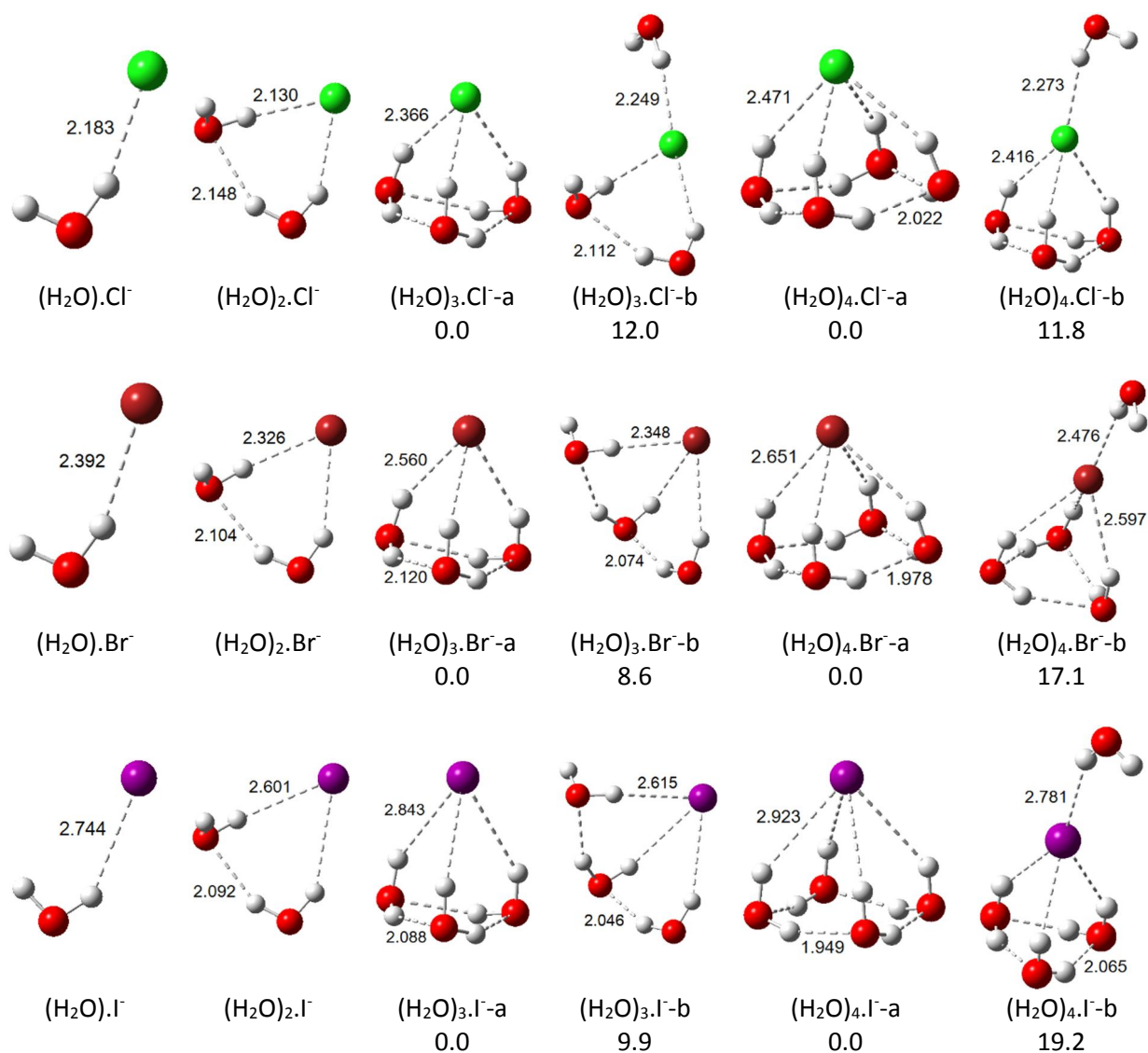| Hydration	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	K (1/atm)
(CA-H)$^-$ + H$_2$O → (CA-H)$^-$(H$_2$O)	-40.4	-6.6	1.4 x 10^1
(CA-H)$^-$H$_2$O) + H$_2$O → (CA-H)$^-$(H$_2$O)$_2$	-36.7	1.2	6.1 x 10^{-1}
(CA-H)$^-$(H$_2$O)$_2$ + H$_2$O → (CA-H)$^-$(H$_2$O)$_3$	-32.3	-0.4	1.2 x 10^0

Figure S11. The optimized structures of hydrated forms of Cl$^-$, Br$^-$, and I$^-$ with up to 4 water molecules in gas phase. The relative energies and hydrogen bond lengths are in kJ mol^{-1} and Å, respectively.

Table S5. The calculated values of ΔH, ΔG and equilibrium constant (K) for hydration of Cl⁻, Br⁻, and I⁻ in gas phase and at 298 K.

Hydration	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	K (1/atm)
$Cl^- + H_2O \rightarrow (H_2O)Cl^-$	-60.6 (61.5)[a]	-36.7 (-36.9)[a]	2.7×10^6
$(H_2O)Cl^- + H_2O \rightarrow (H_2O)_2Cl^-$	-53.1	-17.4	1.1×10^3
$(H_2O)_2Cl^- + H_2O \rightarrow (H_2O)_3Cl^-$	-52.4	-9.6	4.8×10^1
$(H_2O)_3Cl^- + H_2O \rightarrow (H_2O)_4Cl^-$	-49.2	-9.2	4.1×10^1
$Br^- + H_2O \rightarrow (H_2O)Br^-$	-51.8 (49.0)[a]	-28.7 (-30.6)	1.1×10^5
$(H_2O)Br^- + H_2O \rightarrow (H_2O)_2Br^-$	-48.1	-12.5	1.6×10^2
$(H_2O)_2Br^- + H_2O \rightarrow (H_2O)_3Br^-$	-50.1	-7.2	1.8×10^1
$(H_2O)_3Br^- + H_2O \rightarrow (H_2O)_4Br^-$	-47.2	-4.5	6.2×10^0
$I^- + H_2O \rightarrow (H_2O)I^-$	-43.1[a]	-23.8[a]	1.5×10^4
$(H_2O)I^- + H_2O \rightarrow (H_2O)_2I^-$	-39.7[a]	-17.8[a]	1.3×10^3
$(H_2O)_2I^- + H_2O \rightarrow (H_2O)_3I^-$	-38.5[a]	-3.1[a]	3.5×10^0
$(H_2O)_3I^- + H_2O \rightarrow (H_2O)_4I^-$	-38.5[a]	-2.2[a]	2.4×10^0

[a] From: Hiraoka, K.; Mizuse, S.; Yamabe, S., Solvation of Halide Ions with H_2O and CH_3CN in the Gas Phase, *J. Phys. Chem*., **1988**, *92*, 13, 3943.
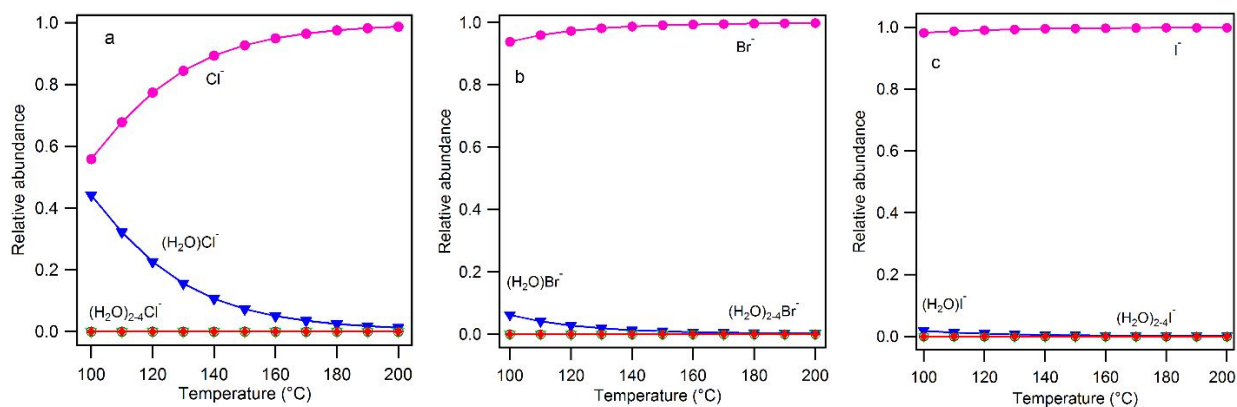

Figure S12. The calculated relative abundances for (a) $(H_2O)_nCl^-$, (b) $(H_2O)_nBr^-$, and (c) $(H_2O)_nI^-$ in gas phase in the presence of 40 ppm water vapor.
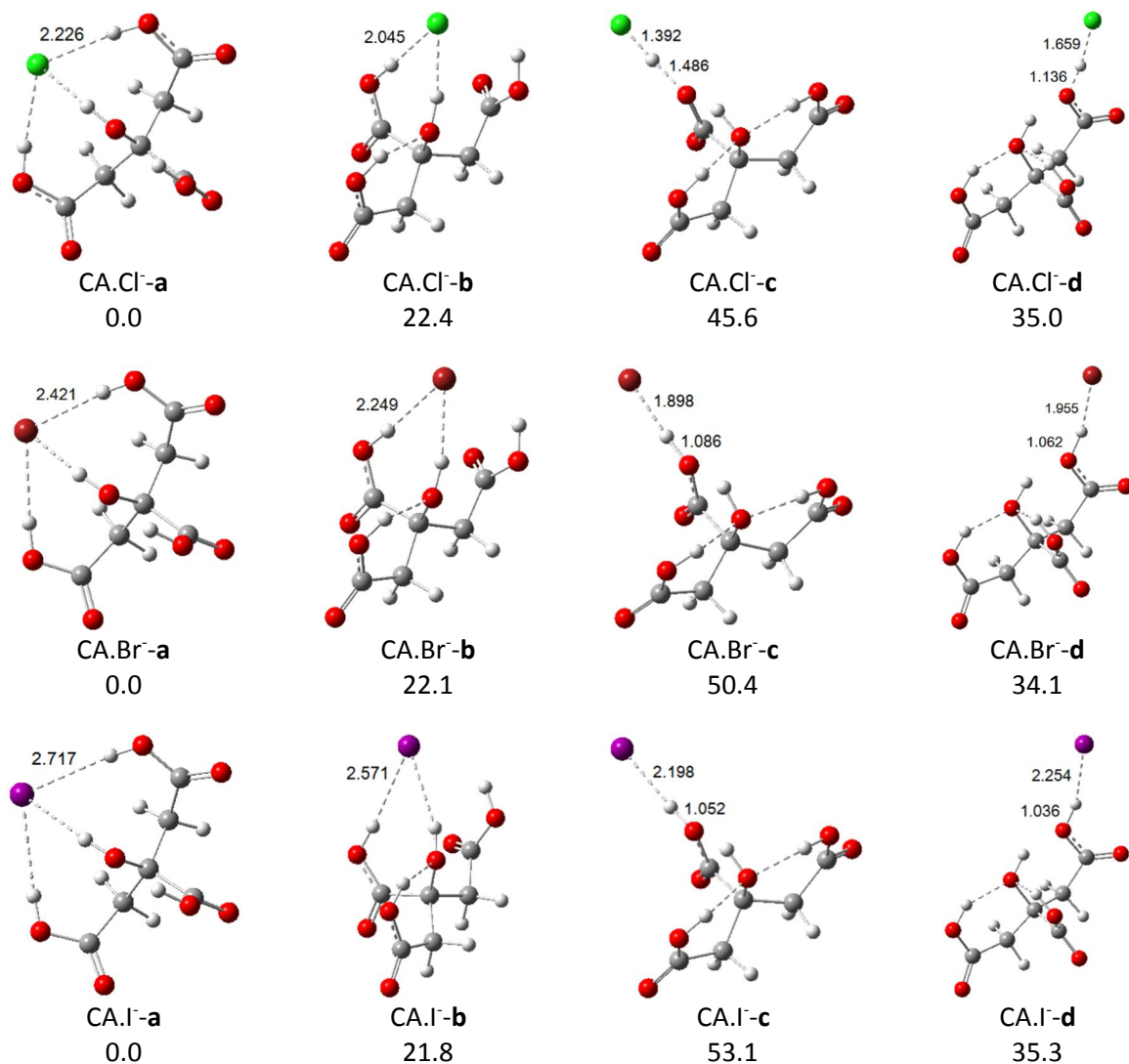
Figure S13. The optimized structures for different isomers of CA.Cl⁻, CA.Br⁻, and CA.I⁻ in gas phase. The relative energies and bond lengths are in kJ mol⁻¹ and Å, respectively.

Table S6. The calculated values of ΔH and ΔG for formation of the most stable isomers of CA.Cl⁻, CA.Br⁻, and CA.I⁻ in gas phase at 298 K.

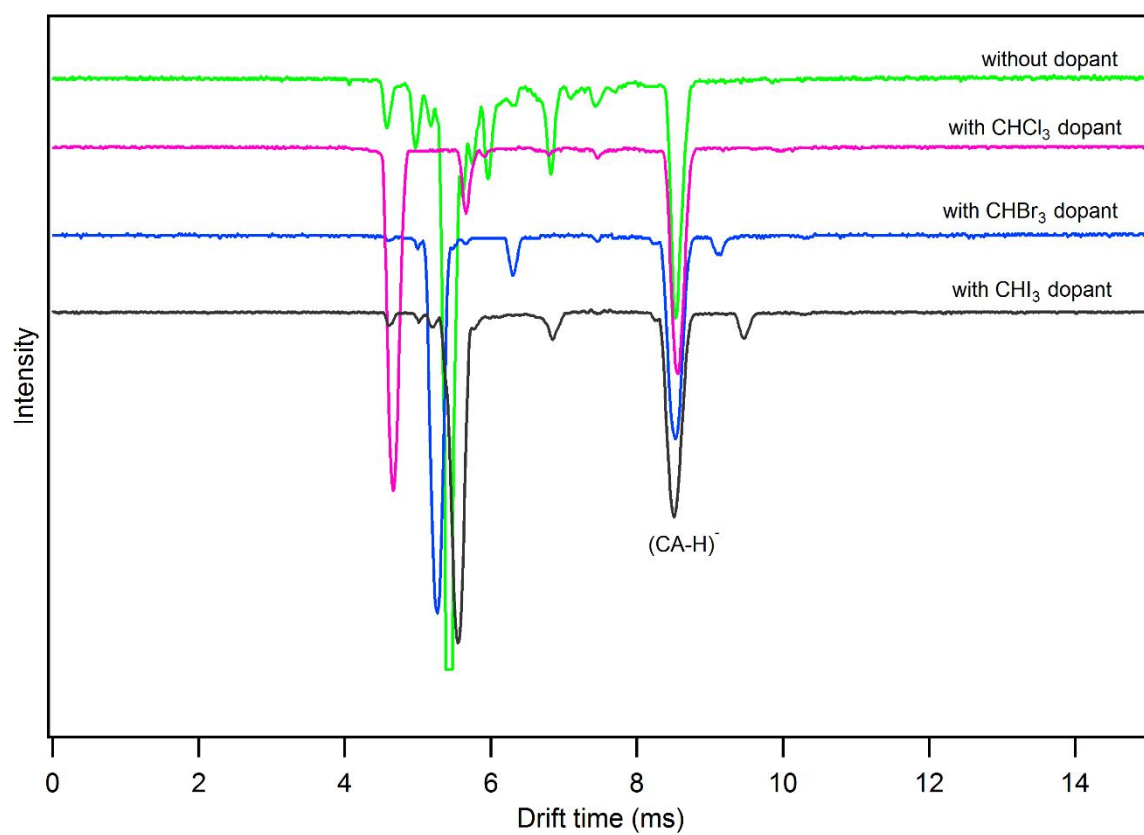| Halide attachment	ΔH (kJ mol⁻¹)	ΔG (kJ mol⁻¹)
CA + Cl⁻ → CA.Cl⁻	-150.4	-110.7
CA + Br⁻ → CA.Br⁻	-143.6	-104.0
CA + I⁻ → CA.I⁻	-148.6	-111.4

Figure S14. Comparison of IMS spectra of citric acid in negative mode with and without halomethane dopants (CHCl₃, CHBr₃, CHI₃) at drift tube temperature of 200 °C.
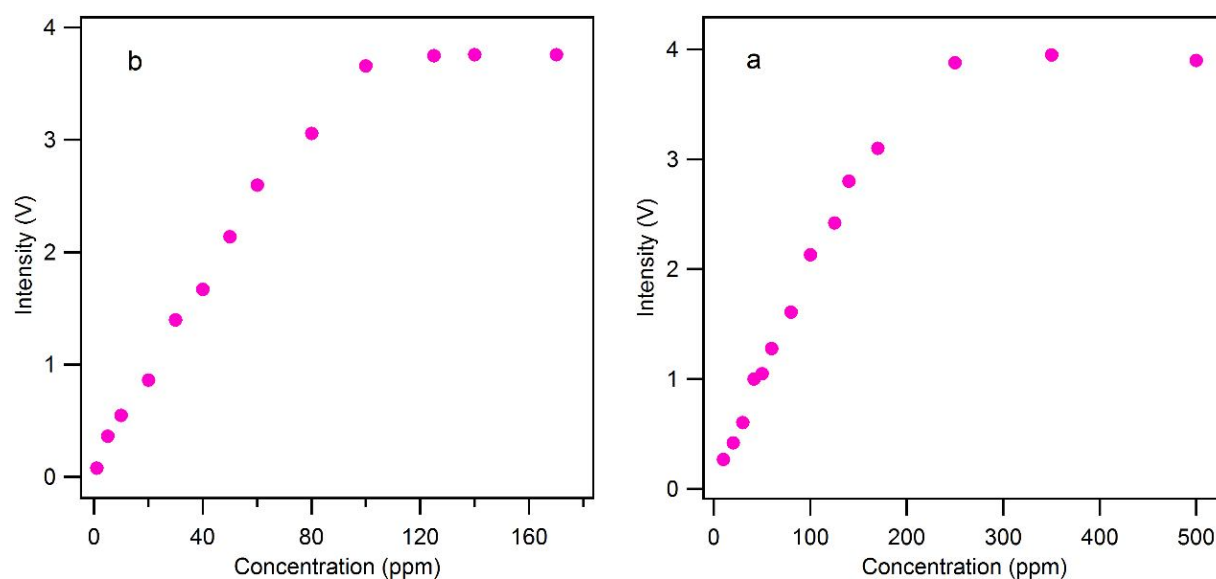
Figure S15. Calibration curves for citric acid obtained (a) in positive mode of IMS with NH3 dopant and (b) in negative mode of IMS with CHCl$_3$ dopant.

Figure S16. Manual preparation of fresh lemon juice for direct injection into IMS.