

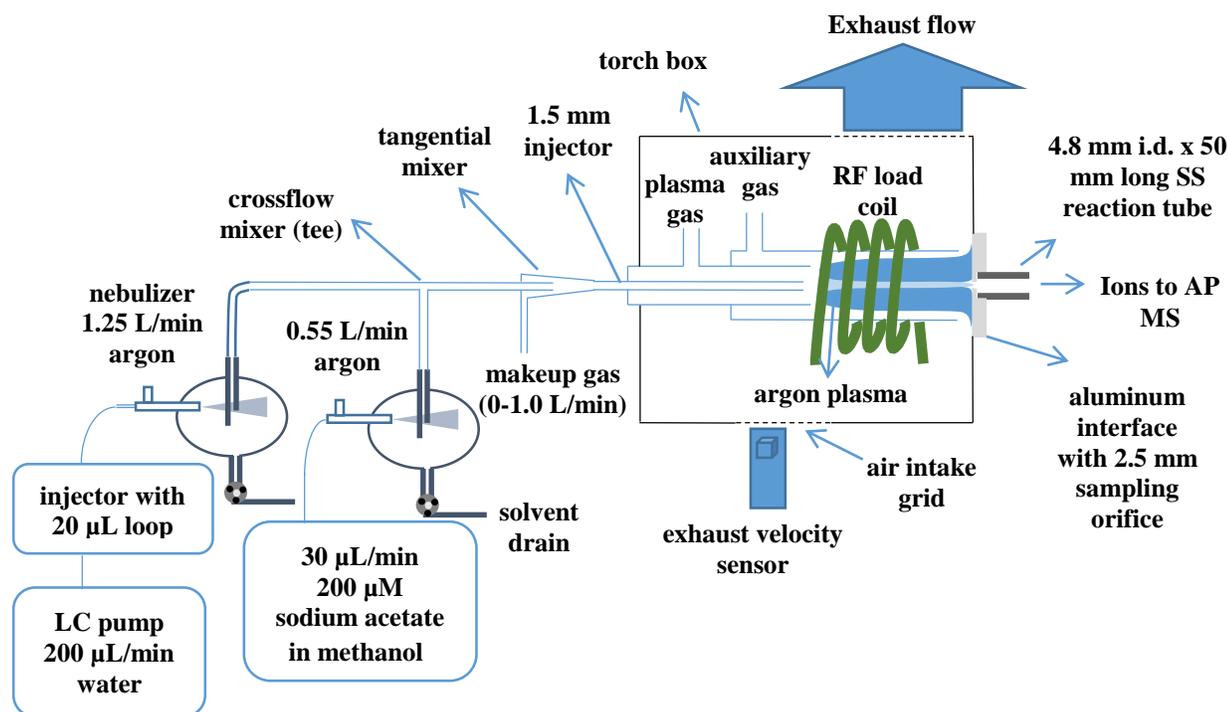
## Supplementary Information

# Mechanistic Insights into Chloride Ion Detection from the Atmospheric-Pressure Afterglow of an Argon Inductively Coupled Plasma

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**Figure S1.** Schematic diagram of ICP-PARCI ion source. Note that diagram is not to scale.

## Argon gas velocity and temperature measurements

To measure the argon gas velocity at the center of the reaction tube, we utilized a particle tracking approach. Water droplets with a diameter of  $\sim 30\ \mu\text{m}$  were created on demand and were entrained in the gas flow emerging from the reaction tube. The on-demand droplet generator consisted of a 0.5 mL polypropylene water reservoir connected through a 50-cm fused silica capillary (i.d.:  $100\ \mu\text{m}$ , o.d.:  $360\ \mu\text{m}$ , Polymicro Technologies, Phoenix, AZ, USA) to a borosilicate pulled glass tip (i.d.:  $10\ \mu\text{m}$ ,  $\pm 20\%$ , WPI, Sarasota, FL, USA). The glass tip was encased by a ceramic piezoelectric tube (PI Ceramic, Lederhose, Germany) and was positioned face up and orthogonal to the reaction tube approximately 6 mm below the center of the tube. The piezoelectric actuator was driven by a trapezoidal pulse (amplitude: 55.6 V, rise time:  $35\ \mu\text{s}$ , duration:  $80\ \mu\text{s}$ , fall time:  $60\ \mu\text{s}$ ) created by an arbitrary waveform generator (Dataman, Model: 530, Orange City, FL, USA) coupled to an amplifier (Trek, Model 2205, Lockport, New York, USA). Droplets were imaged using a triggered camera (Model DMK 42BUC03, The Imaging Source, LLC, Charlotte, NC) attached to the objective of a stereoscopic microscope.

Two green LEDs synchronized with the droplet generation were used for illumination and droplet tracking. Timing events were controlled using a microprocessor (UNO, Arduino AG, Turin, Italy) at 20 Hz cycle time, starting with camera trigger followed by a  $350\ \mu\text{s}$  delay (camera ready time) before triggering the waveform generator for droplet production. A delayed pulser (PM 5715, Philips, Eindhoven, Netherlands) simultaneously triggered with the droplet generator provided the illumination and image capture pulses to LEDs ( $8.2\ \mu\text{s}$  duration, 4 V pulse). The droplet trajectory was tracked by varying the delay time of the LED pulser.

The droplets were ejected orthogonal to the gas flow and droplet entrainment was achieved 2 mm downstream of the tube evident from horizontal movement of the droplets with the gas flow. Once entrained, the droplets were captured at two LED firing times. The time difference between the two firings (1-6 ms) was measured using a digital oscilloscope (DS1102E, Rigol, Beaverton, OR). Five replicate images were captured for each LED firing time to provide an average location of the droplets for each setting. The droplet travel distance between the two LED firings was measured using Image J software

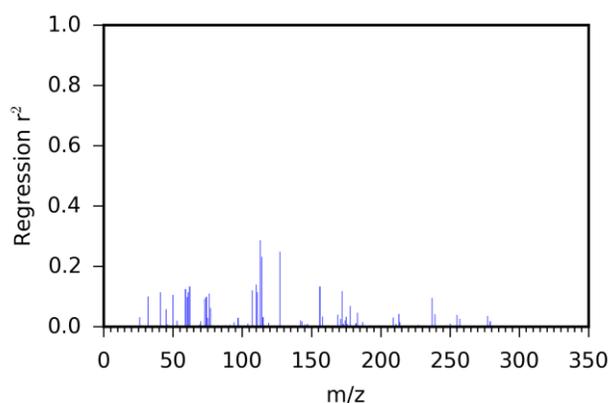
package in pixels and then converted to mm (3-6 mm) based on calibration using a calibrated microscope slide (model SK2, OptixCam, Roanoke, VA). The measurements provided relative standard deviations of 2-9% for the calculated velocity.

The gas temperature at the end of the reaction tube was measured using a thermocouple positioned at the center of the tube.

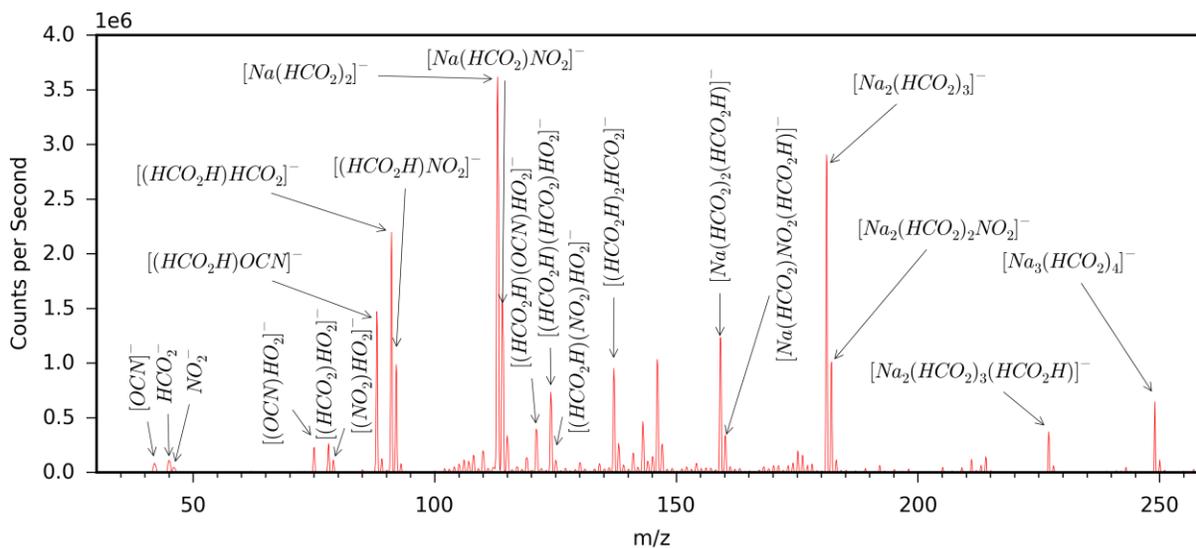
### Sample preparation and data analysis

All solvents used were LC-MS grade (Chromasolv, Sigma-Aldrich, St. Louis, MO). Chloramphenicol and sodium chloride were purchased from Sigma-Aldrich, St. Louis, MO. Analyte solutions were prepared by dissolving in methanol to concentrations of ~40-80 mM followed by dilution in water to final concentration of 25  $\mu$ M chlorine in water.

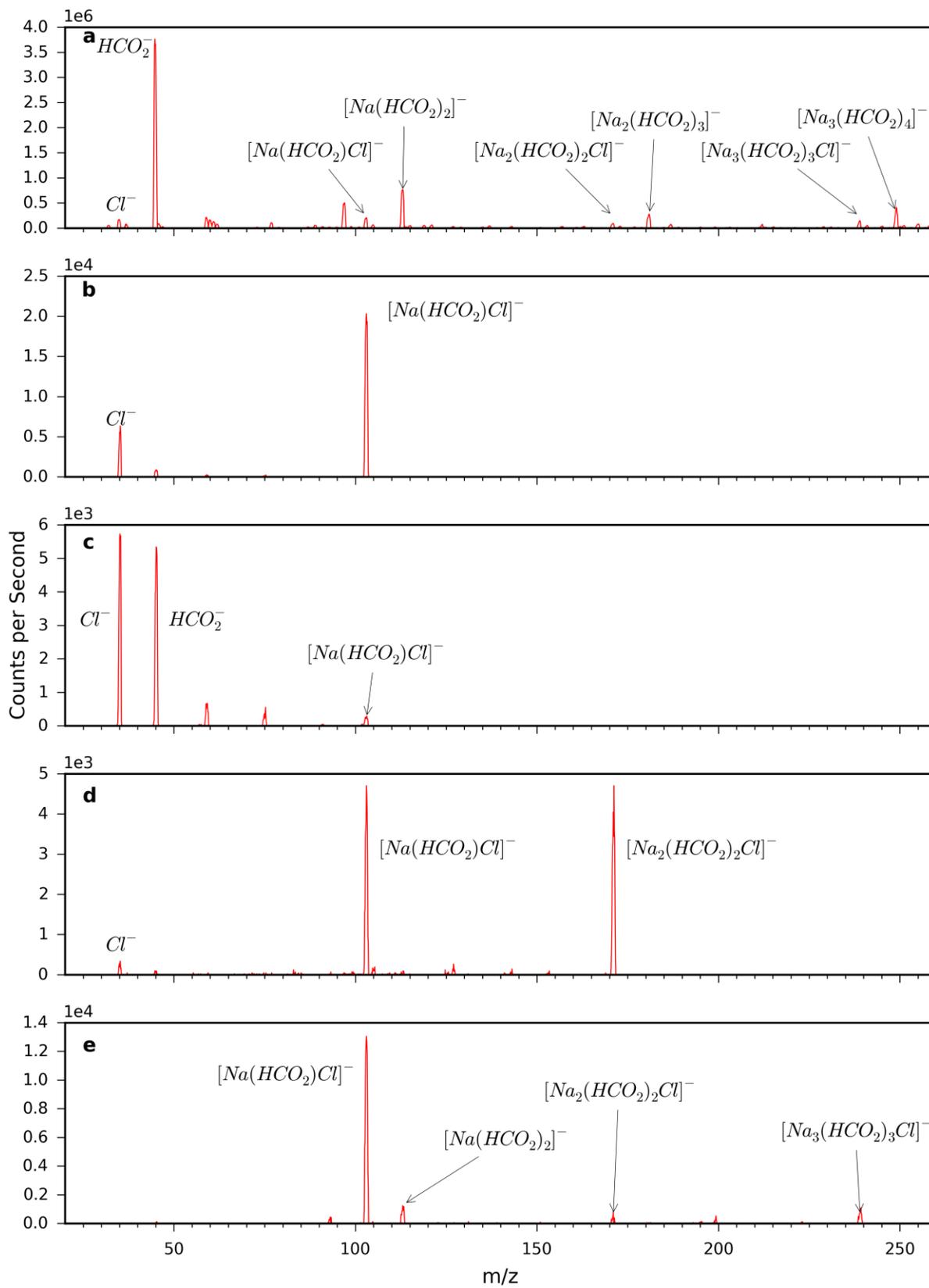
Ionization reagent solution was prepared using ACS grade sodium acetate (Fisher, Waltham, MA) by dissolving to a concentration of ~ 96 mM in methanol, followed by dilution to 200  $\mu$ M in methanol. All selected ion chromatograms from flow injections were exported as text files, and then manually integrated using the trapezoid rule by selecting the beginning and end points of a baseline for each peak. The background spectra were centroided and extracted as .csv files for linear regression analyses of ion intensities.



**Figure S2.** Correlation of background ion intensities with  $\text{Cl}^-$  sensitivity indicated by  $r^2$  values for linear regressions. All ions with > 100000 cps intensity were considered in regressions.



**Figure S3.** Background spectrum collected using soft ion sampling conditions (declustering potential of 10 V) at carrier gas flow rate of 2.4 SLPM and exhaust flow setting of 3.8 m/s. Compared to Figure 3, new clusters are detected, indicating formation of HCO<sub>2</sub>H in these conditions. Further, [Na<sub>n</sub>(HCO<sub>2</sub>)<sub>n+1</sub>]<sup>-</sup> and [Na<sub>n</sub>(HCO<sub>2</sub>)<sub>n</sub>NO<sub>2</sub>]<sup>-</sup> clusters with n > 1 are enhanced relative to clusters with n=1 compared to the data in Figure 3, showing a higher extent of clustering with HCO<sub>2</sub>Na.



**Figure S4.** a) MS spectrum of clusters generated by nano-ESI from an aqueous solution of sodium chloride and sodium formate, b) MS/MS spectrum of  $[\text{NaHCO}_2\text{Cl}]^-$  at collision energy of 12 eV showing  $\text{Cl}^-$  as a major fragment ion, c) MS/MS spectrum of  $[\text{NaHCO}_2\text{Cl}]^-$  at collision energy of 20 eV, indicating competitive generation of formate and chloride at higher collision energies, d) MS/MS spectrum of  $[\text{Na}_2(\text{HCO}_2)_2\text{Cl}]^-$  at collision energy of 20 eV, showing loss of  $\text{NaHCO}_2$  as the major fragmentation pathway from the second order cluster, e) MS/MS spectrum of  $[\text{Na}_3(\text{HCO}_2)_3\text{Cl}]^-$  at collision energy of 20 eV, showing successive loss of  $\text{NaHCO}_2$  as the major fragmentation pathway from the third order cluster. Experiments were performed using a Sciex API3000 instrument with a homebuilt nanospray source composed of a pulled glass capillary with a tip size of 3  $\mu\text{m}$ . An aqueous solution of 1 mM  $\text{NaHCO}_2$  and 100  $\mu\text{M}$   $\text{NaCl}$  was loaded into the capillary. A platinum wire was inserted into the capillary to apply -1100 V to the solution while a voltage of -200 V was applied to the curtain plate of the instrument using an external power supply. Nitrogen was used as CAD gas at an instrument setting of 4.