Supplementary Information

Hydrogen chloride (HCl) at ground sites during CalNex 2010 and insight into its thermodynamic properties

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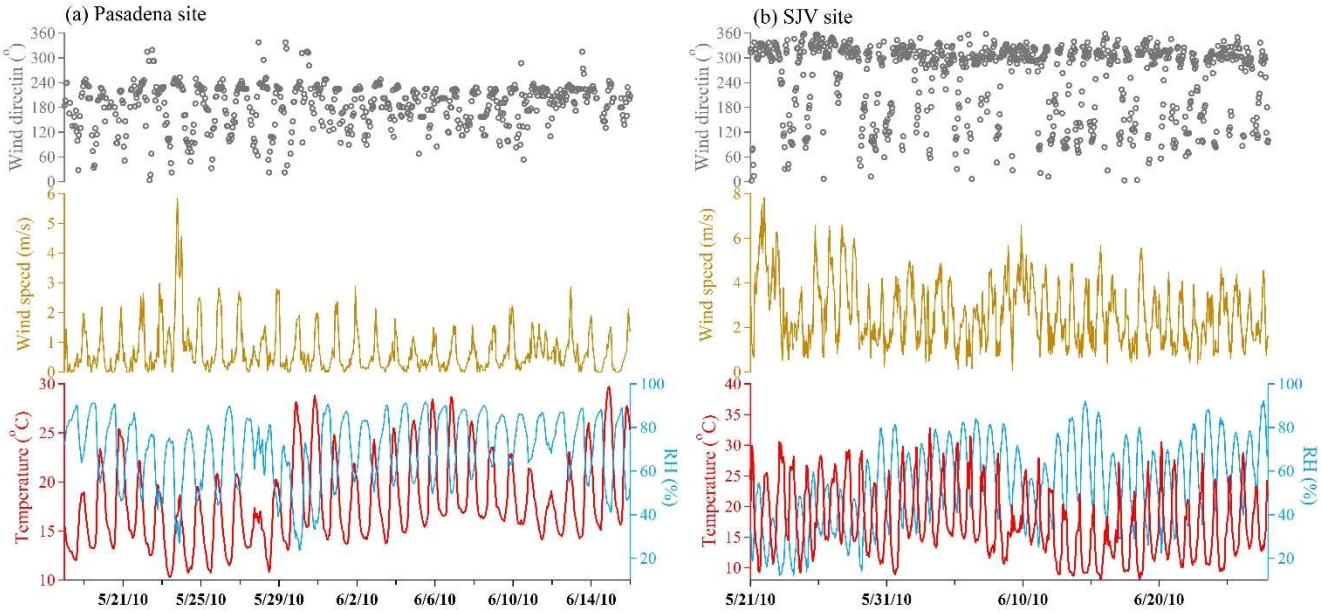

Figure S1. Meteorological parameters of 1-hour resolution including temperature, relative humidity, wind speed and wind direction at a) Pasadena and b) San Joaquin Valley (SJV) sites.

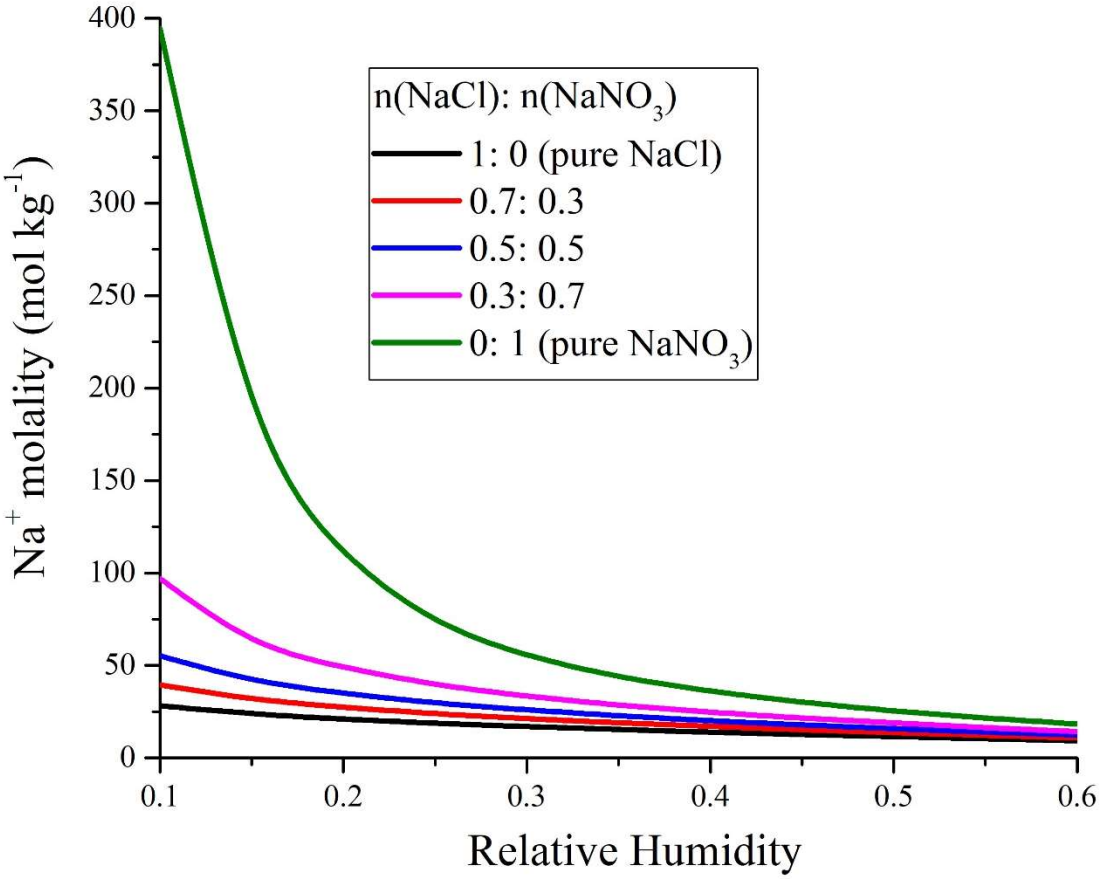

Figure S2. E-AIM III calculation results of Na^+ molality in metastable state particles as a function of RH under different molar ratios of NaCl:$NaNO_3$. Chloride-displacement reaction can significantly increase the Na^+ molality (also ionic strength) in aerosol liquid water in low RH conditions.

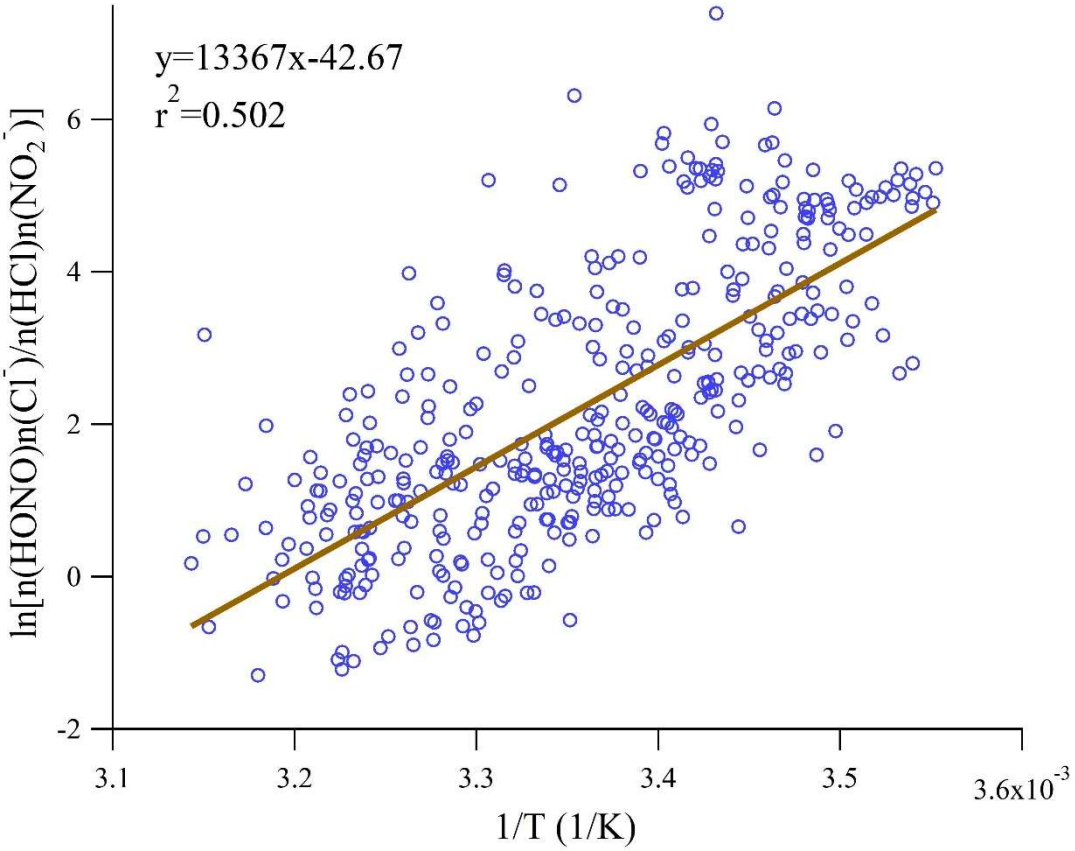

Figure S3. The linear regression of ln[n(HONO)n(Cl^-)/n(HCl)n(NO_2^-)] against 1/T in SJV site to study the coupled phase partitioning between HCl/Cl^- and HONO/NO_2^-.

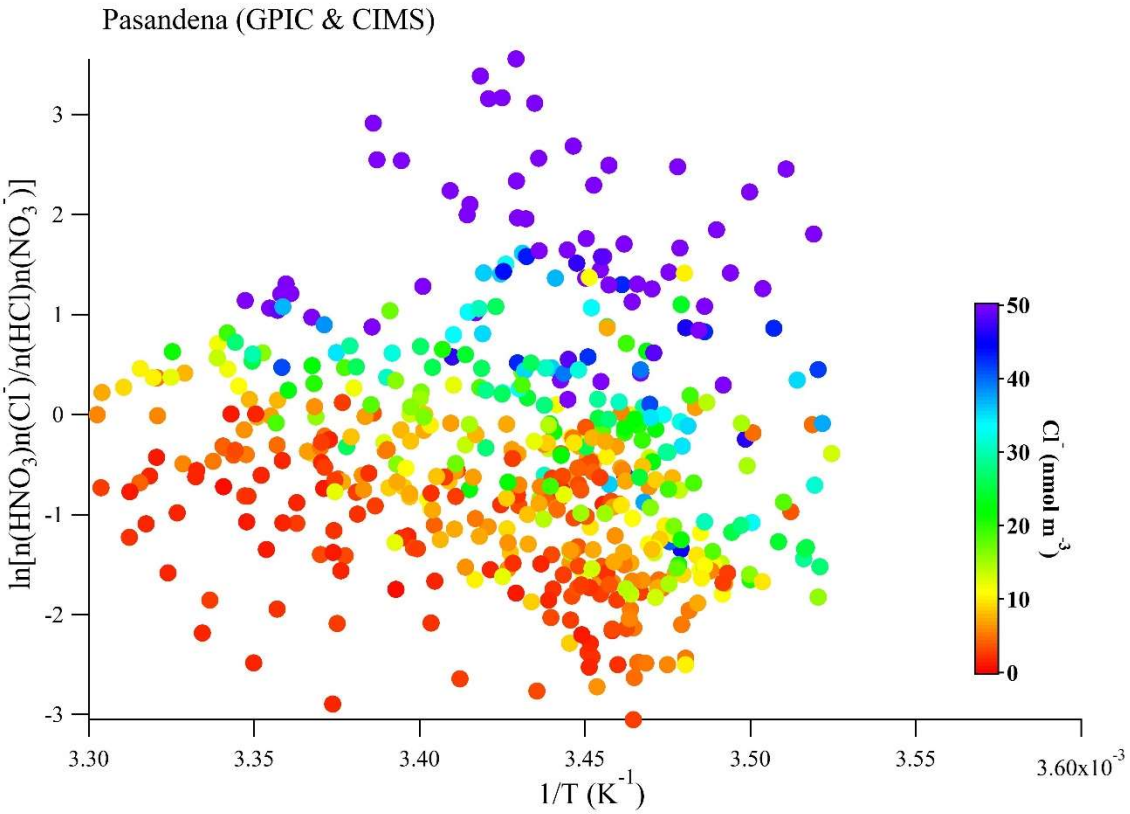

Figure S4. The plot of $\ln[n(HNO_3)n(Cl^-)/n(HCl)n(NO_3^-)]$ against 1/T at Pasadena site.

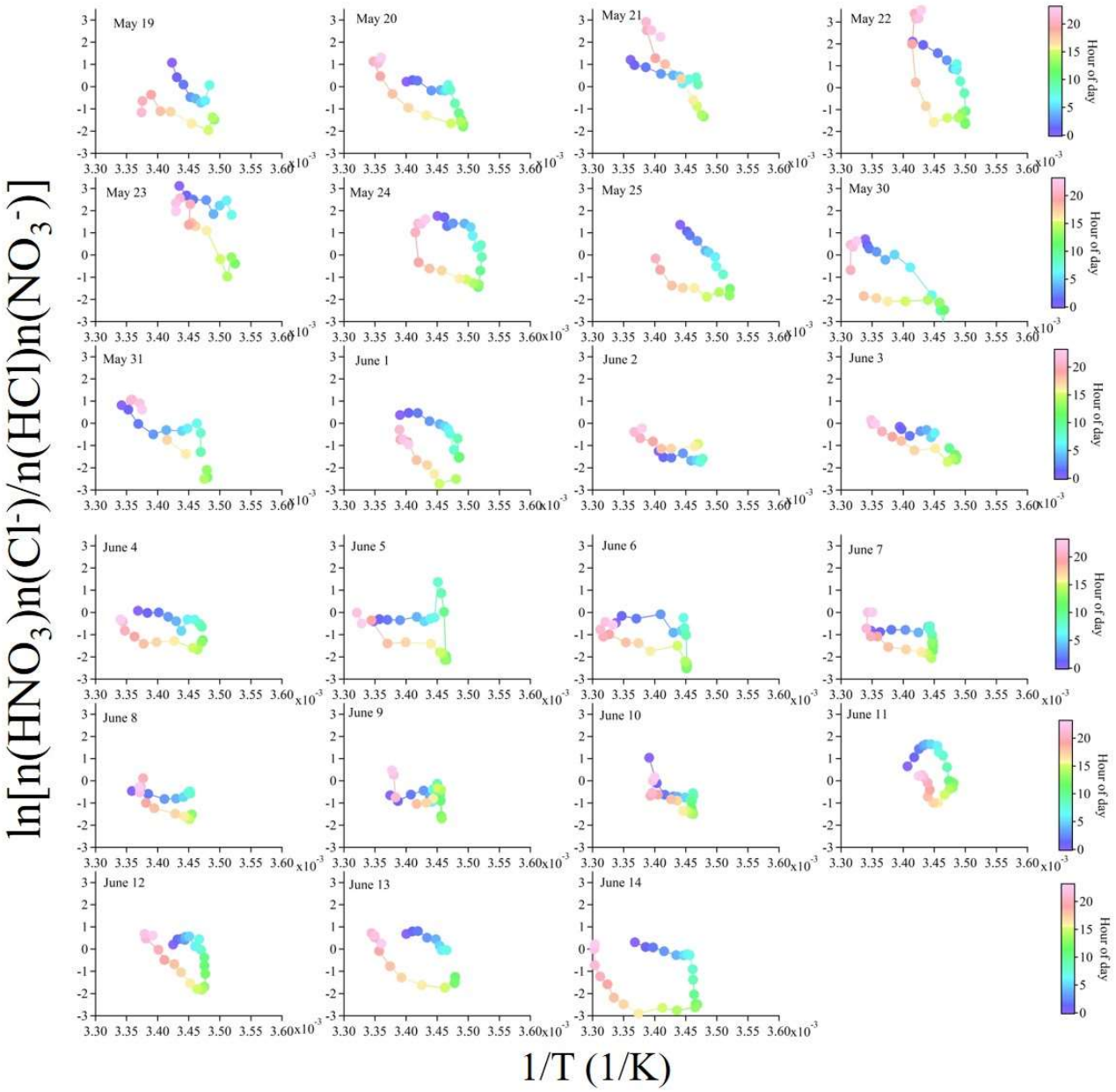

Figure S5. Day-by-day relationship between $\ln[n(HNO_3)n(Cl^-)/n(HCl)n(NO_3^-)]$ and 1/T in Pasadena. Data points were colored by the hour of the day.

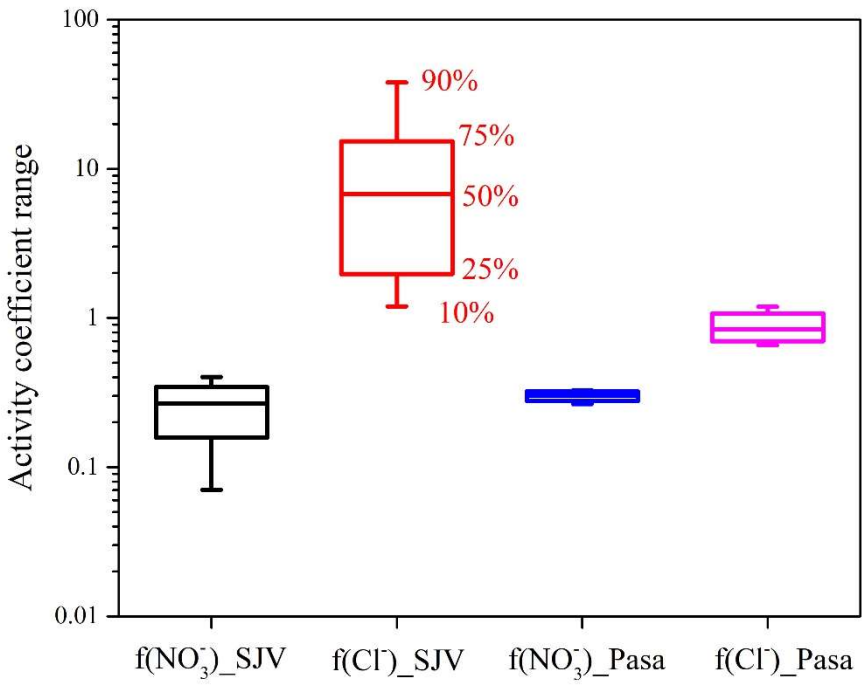

Figure S6. The activity coefficient range of particulate NO_3^- and Cl^- in SJV site and Pasadena site. The calculation was performed by E-AIM III for SJV site (due to low RH, temperature was set constant at 298.15 K) and E-AIM IV for Pasadena site.

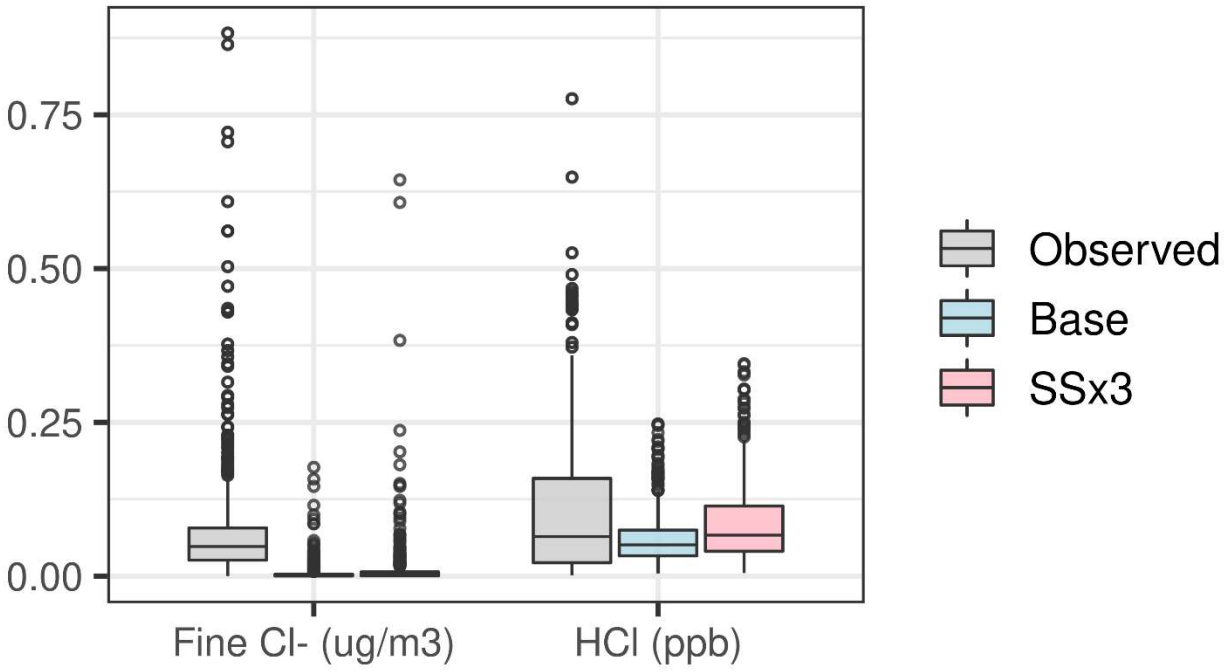

Figure S7. Modeled distributions of HCl and fine particulate Cl^- and at the SJV site. Circles represent values greater than 1.5 times the interquartile range from either end of the box.

Table S1. Summary of Effective Henry's Law Constant at 298K $K^{\theta}(298K)$ (atm^{-1}) and temperature dependence $\Delta_r H$ (kJ mol^{-1})

$HNO_3(g) \leftrightarrow H^+(aq) + NO_3^-(aq)$		$HCl(g) \leftrightarrow H^+(aq) + Cl^-(aq)$		$HNO_2(g) \leftrightarrow H^+(aq) + NO_2^-(aq)$		Reference
$K^{\theta}(298K)$	$\Delta_r H$	$K^{\theta}(298K)$	$\Delta_r H$	$K^{\theta}(298K)$	$\Delta_r H$	
853.1	-70.468	662.1	-72.561			[*Carslaw et al.*, 1995; *Clegg and Brimblecombe*, 1990]
814.9	-72.307	639.7	-74.860			[*Fountoukis and Nenes*, 2007]
786.7	-72.331	$607 \sim 8.3 \times 10^5$				[*Sander*, 2015; *Young et al.*, 2013]
		811.4	-43.299			[*Haskins et al.*, 2018]
1180.7	-73.014	658.8	-74.103	8.11×10^{-6}	-29.272	[*Seinfeld and Pandis*, 2006]
		973~2369	-51.7~ -86.3			[*McGrath et al.*, 2013]
				8.6×10^{-7}	-33.9	[*Rubio et al.*, 2009]
				8.04×10^{-6}		[*Becker et al.*, 1998]
				8.42×10^{-6}	-25.94	[*Park and Lee*, 1988]

Section 1: Semi-volatile NH_4Cl formation prediction:

An accurate description of HCl gas-particle equilibrium can be instructive in understanding the cycling of chlorine in the atmosphere and to the prediction of the magnitude and distribution of Cl^- available for activation, thereby impacting levels of photolabile reactive chlorine. The ammonia measurements that were made at both sites were used along with the HCl measurements to assess the extent to which formation of ammonium chloride (NH_4Cl) governs transport of HCl into the condensed phase as Cl^-. Gas phase NH_3 and HCl are in equilibrium with fine mode particulate NH_4Cl (solid or aqueous) to an extent dependent on temperature and relative humidity [*Meng and Seinfeld*, 1996]. The product $[NH_3][HCl]$ is depicted as a function of 1/T and RH, along with the equilibrium data reported by *Pio and Harrison* [1987], for the simplest case of pure NH_4Cl (Figure S8). In this plot, points that are below and to the left of the corresponding line for a given RH do not form a solid or droplet phase at equilibrium. At the Pasadena site, there was no $NH_4Cl(s)$ predicted for RHs below deliquescence and $NH_4Cl(aq)$ was predicted only when RH was above about 90% at the lowest temperatures from the campaign, i.e., at night and early morning at this surface site. As a consequence, NH_4Cl in aerosol represents a storage mechanism for soluble chloride only under cool damp conditions. At the SJV site, however, the dry conditions prevented any formation of NH_4Cl either as solid or aqueous aerosol. As a result, the measured condensed phase NH_4^+ and Cl^- depends on other processes.

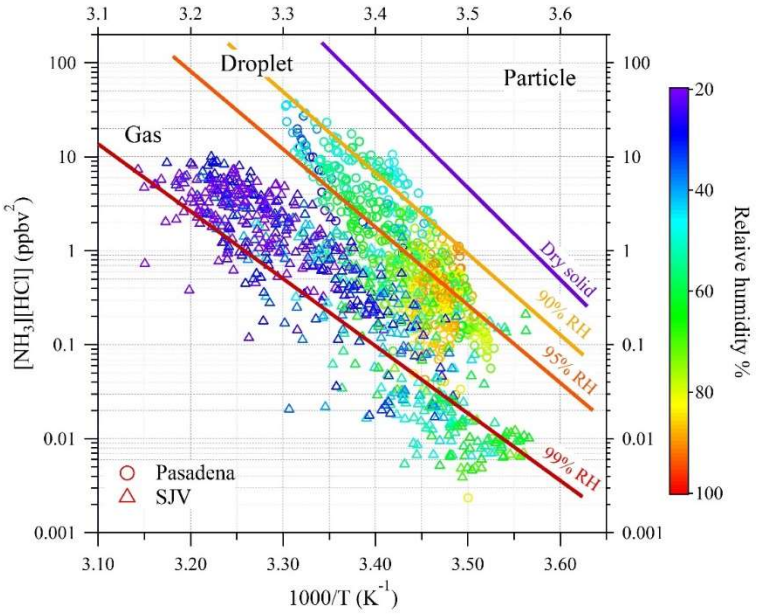

Figure S8. The product $[NH_3][HCl]$ in $ppbv^2$ versus 1/T for the Pasadena data (circle) and SJV site (triangle) color coded by relative humidity. The colored lines correspond to the division between gas and condensed phases (either solid or droplet) for the RHs = 99%, 95%, 90% and dry conditions as given by *Pio and Harrison* [1987], respectively. Points above and to the right of the lines of their corresponding color indicate the presence of a condensed phase (either solid or droplet).

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