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Supplement of

Heterogeneous kinetics of H₂O, HNO₃ and HCl on HNO₃ hydrates (α-NAT, β-NAT, NAD) in the range 175–200 K

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Supplement A

Langmuir adsorption isotherms for H₂O, HNO₃ and HCl on stainless-steel reactor walls at 315 K

Figures

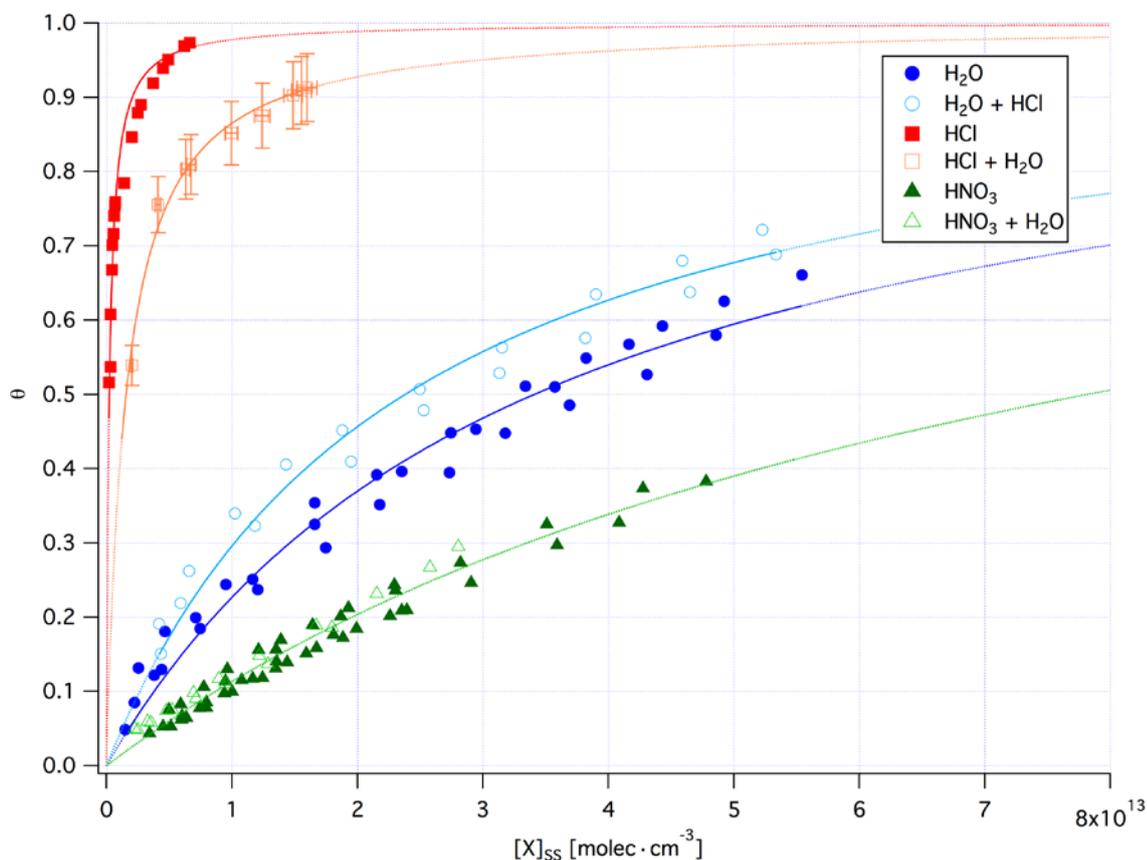


Figure S1: Wall coverage as a function of gas X concentration interacting with the reactor walls according to Langmuir adsorption. The dark and light blue symbols represent the interaction of pure H₂O and of H₂O in the presence of an additional HCl flow admitted into the reactor, respectively. Similarly, the red and orange symbols represent the interaction of pure HCl and of HCl in the presence of an additional H₂O flows admitted into the reactor. The dark and light green symbols represent the interaction of pure HNO₃ and of HNO₃ in the presence of an additional H₂O flow. The additional flows as well as parameters for the best fit curves are reported in Table 2 in the main text.

Supplement B

Thermodynamic Considerations for α -NAT

A van t'Hoff plot of the corresponding vapor pressures $P_{\text{eq}}(\text{H}_2\text{O})$ is displayed in Figure S2 and the best linear fit for two-orifice and PV measurements are reported in Eqs. (S1) and (S2):

$$\log P_{\text{eq}}(\text{H}_2\text{O}) [\text{Torr}] = (15.2 \pm 4.0) - \frac{(70.3 \pm 14.1) \times 10^3}{2.303 RT} \quad (\text{S1})$$

$$\log P_{\text{eq}}(\text{H}_2\text{O}) [\text{Torr}] = (11.8 \pm 1.5) - \frac{(56.5 \pm 5.1) \times 10^3}{2.303 RT} \quad (\text{S2})$$

The two temperature dependent regimes are not clearly evident in the vapor pressures, as the temperature dependences of $\alpha(\text{H}_2\text{O})$ and $R_{\text{ev}}(\text{H}_2\text{O})$ tend to compensate each other at low temperatures. For this reason, we may also calculate the best fit line for PV experiments excluding points at temperatures lower than 180 K. We display the results of the fit for this reduced dataset as the black dashed line in Figure S1

We calculate the enthalpies of evaporation for two-orifice (TO) and PV experiments as $\Delta H_{\text{ev,TO}}^0(\text{H}_2\text{O}) = (70.3 \pm 14.1) \text{ kJ mol}^{-1}$ and $\Delta H_{\text{ev,PV}}^0(\text{H}_2\text{O}) = (56.5 \pm 5.1) \text{ kJ mol}^{-1}$, respectively. For comparison, the enthalpy of evaporation corresponding to the dashed black line is $\Delta H_{\text{ev,TO}}^0(\text{H}_2\text{O}) = (82.0 \pm 30.0) \text{ kJ mol}^{-1}$. The values calculated are the same within experimental uncertainty, and if we take the average value for the two measurements techniques of $\Delta H_{\text{ev}}^0(\text{H}_2\text{O}) = (63.4 \pm 9.6) \text{ kJ mol}^{-1}$ we estimate an activation energy of the accommodation process of H_2O on α -NAT of $E_{\text{acc}}(\text{H}_2\text{O}) = E_{\text{ev}}(\text{H}_2\text{O}) - \Delta H_{\text{ev}}^0(\text{H}_2\text{O}) = (75.3 - 63.4) = (11.9 \pm 9.8) \text{ kJ mol}^{-1}$, a positive activation energy similar to the case of HCl hexahydrate, for which $E_{\text{acc}}(\text{HCl}) = (21.2 \pm 17.0) \text{ kJ mol}^{-1}$ (Iannarelli and Rossi, 2014). In analogy with the case of $\text{HCl} \cdot 6\text{H}_2\text{O}$, the positive activation energy may have to do with the high value of activation energy $E_{\text{ev}}(\text{H}_2\text{O})$ out of the crystalline environment of α -NAT.

Bibliography

Iannarelli, R. and Rossi, M. J.: H_2O and HCl trace gas kinetics on crystalline HCl hydrates and amorphous HCl/ H_2O in the range 170 to 205 K: The HCl/ H_2O phase diagram revisited, *Atmos. Chem. Phys.*, 14(10), 5183-5204, 2014.

Supplement C: Additional Figures

Van't Hoff Plot for $P_{\text{ev}}(\text{H}_2\text{O})$ for α -NAT

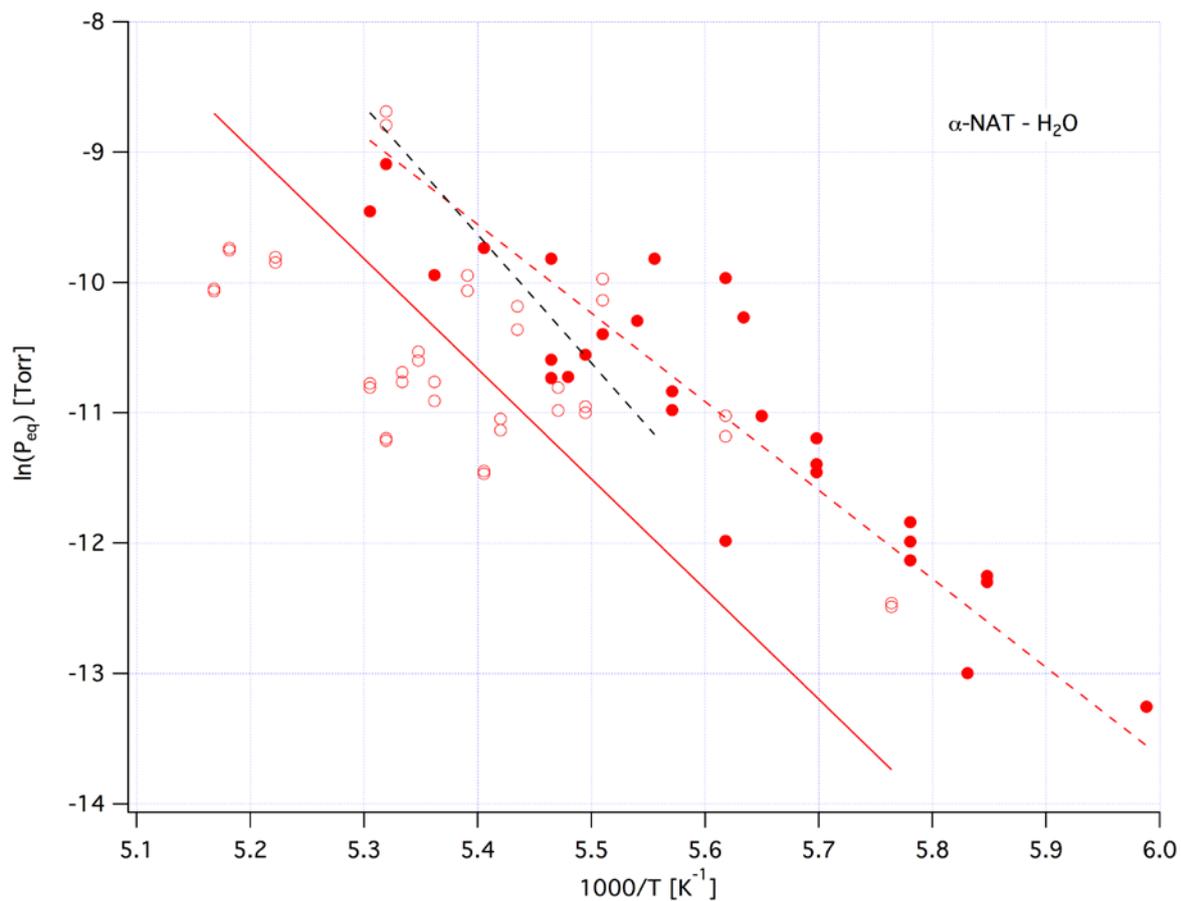


Figure S2: Summary van t'Hoff plot of $P_{eq}(\text{H}_2\text{O})$ for α -NAT. Full and empty red circles represent results of PV (Pulsed Valve) and TO (Two Orifice) experiments, respectively. The equations for the linear fits may be found in Equations (13) and (14). The black dashed line represent the best fit of PV results above 180 K.

Pulsed Valve Experiments and Saturation

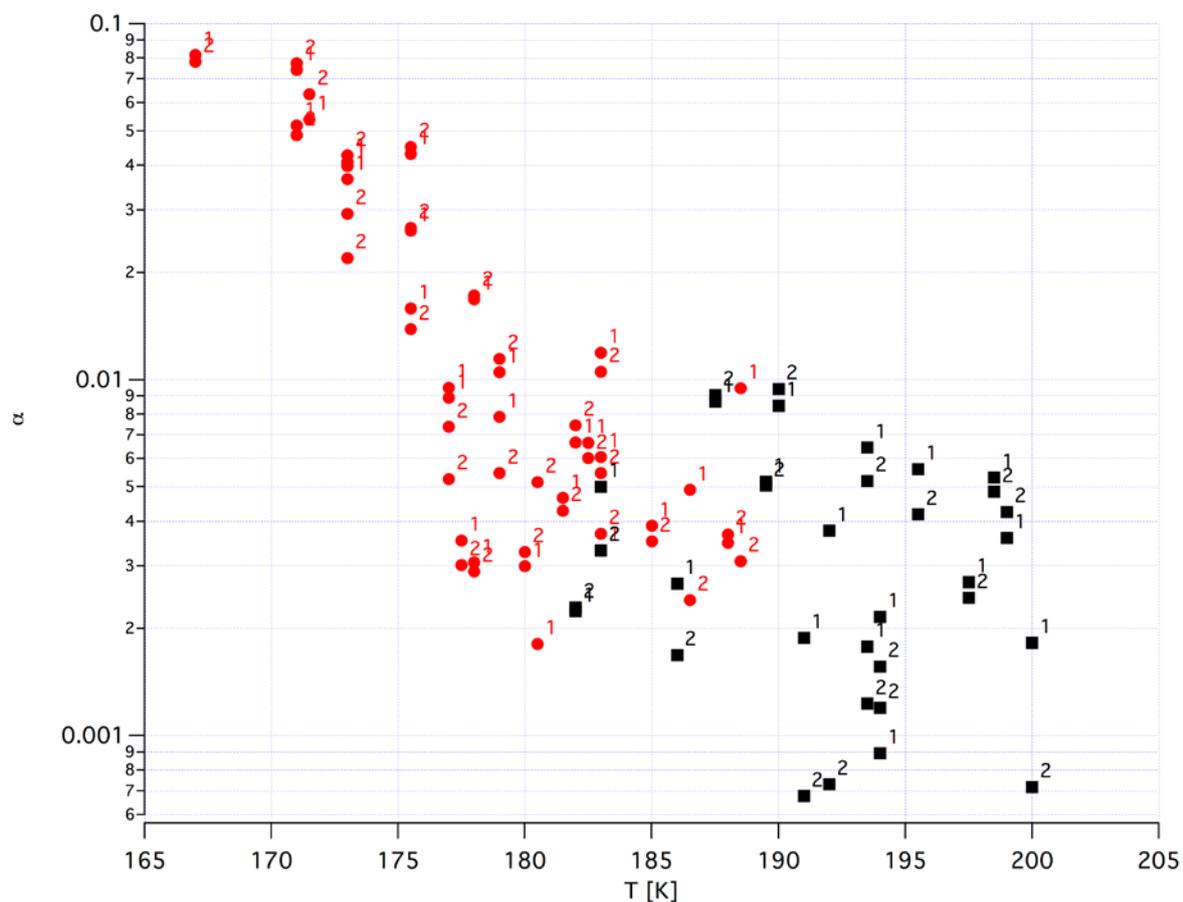


Figure S3: H_2O pulse series on α -NAT and β -NAT substrates. Red circles and black squares represent series of H_2O pulses on α - and β -NAT, respectively. The numbers label the first and second pulse of a series.

Summary van't Hoff Plot for HNO₃ and adsorbed HCl on α - and β -NAT

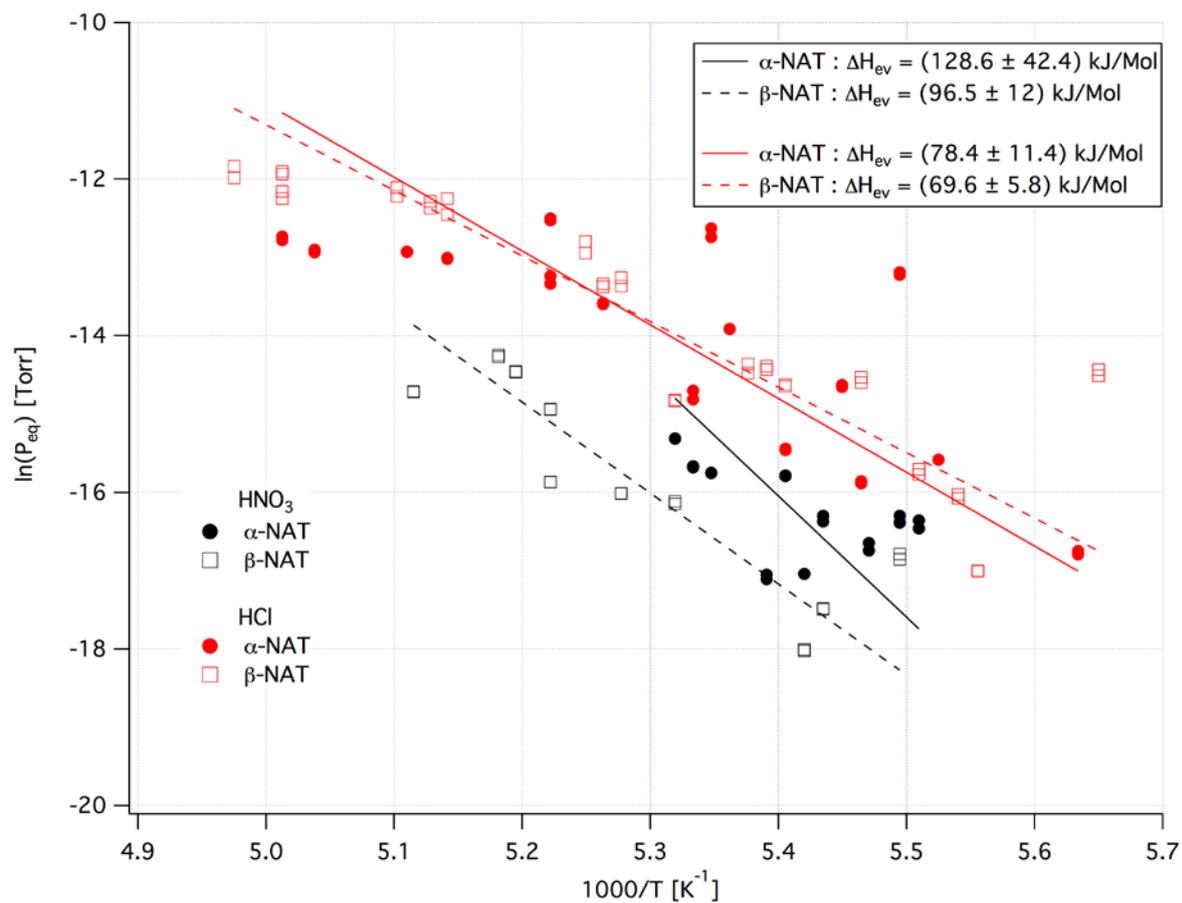


Figure S4: Summary of van t'Hoff plots of $P_{eq}(\text{HNO}_3)$ and $P_{eq}(\text{HCl})$ for α - and β -NAT, respectively. HNO₃ and HCl experiments correspond to TO and PV experiments, respectively. The equations for the linear fits may be found in the text.

Binary Phase Diagram HNO₃/H₂O

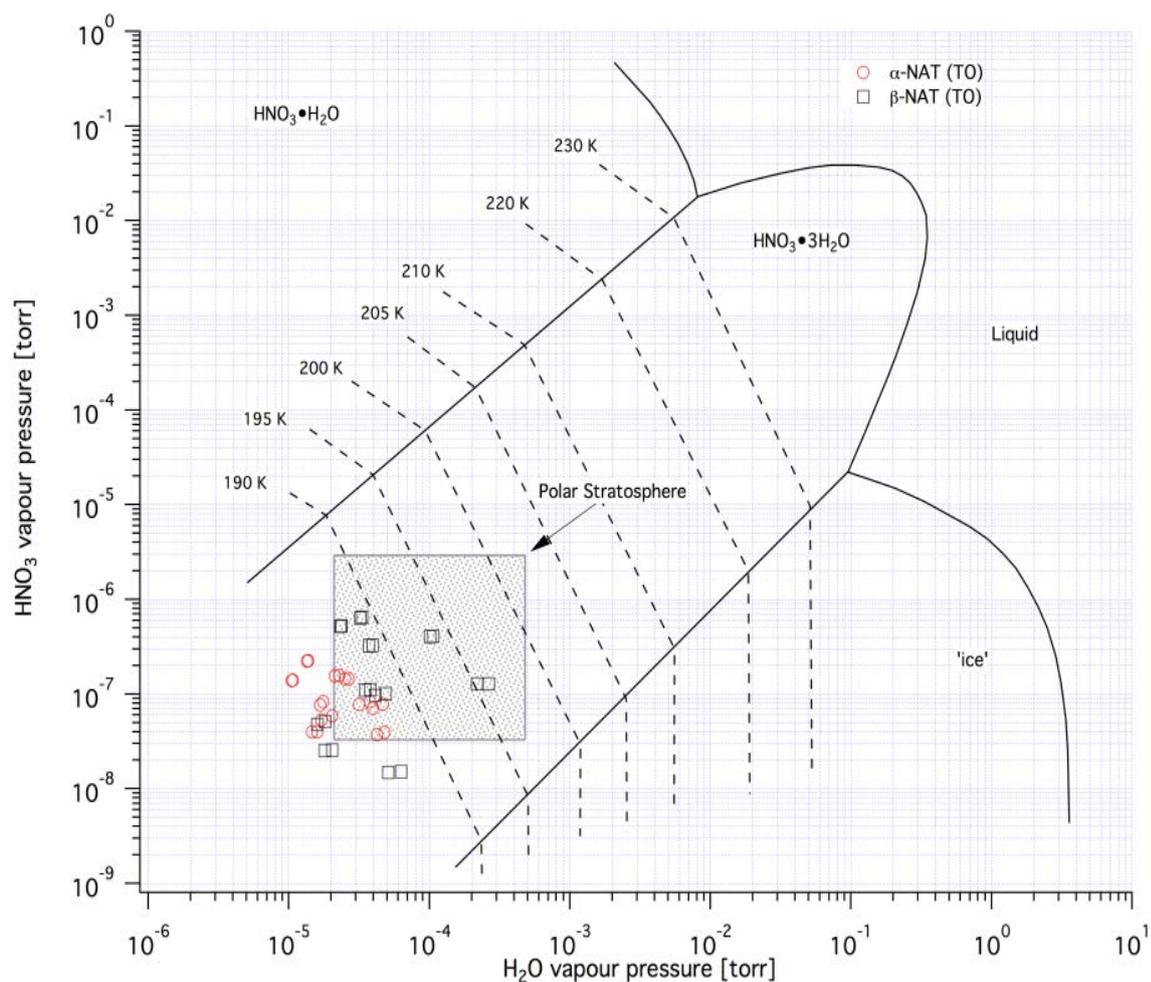


Figure S5: Binary Phase Diagram of the HNO₃/H₂O system reconstructed from Hanson and Mauersberger (1988). Empty red circles and black squares represent calculated values of equilibrium vapor pressures $P_{\text{eq}}(\text{H}_2\text{O})$ and $P_{\text{eq}}(\text{HNO}_3)$ for α - and β -NAT, respectively. In both cases $P_{\text{eq}}(X)$ values have been taken from TO (Two Orifice) experiments according to Equations (7) and (8). The solid lines represent the coexistence conditions for two phases and the dashed lines are isotherms. The shaded gray represents polar stratospheric conditions.

Raw Data of HCl pulses monitored at m/e 36 interacting with α - and β -NAT

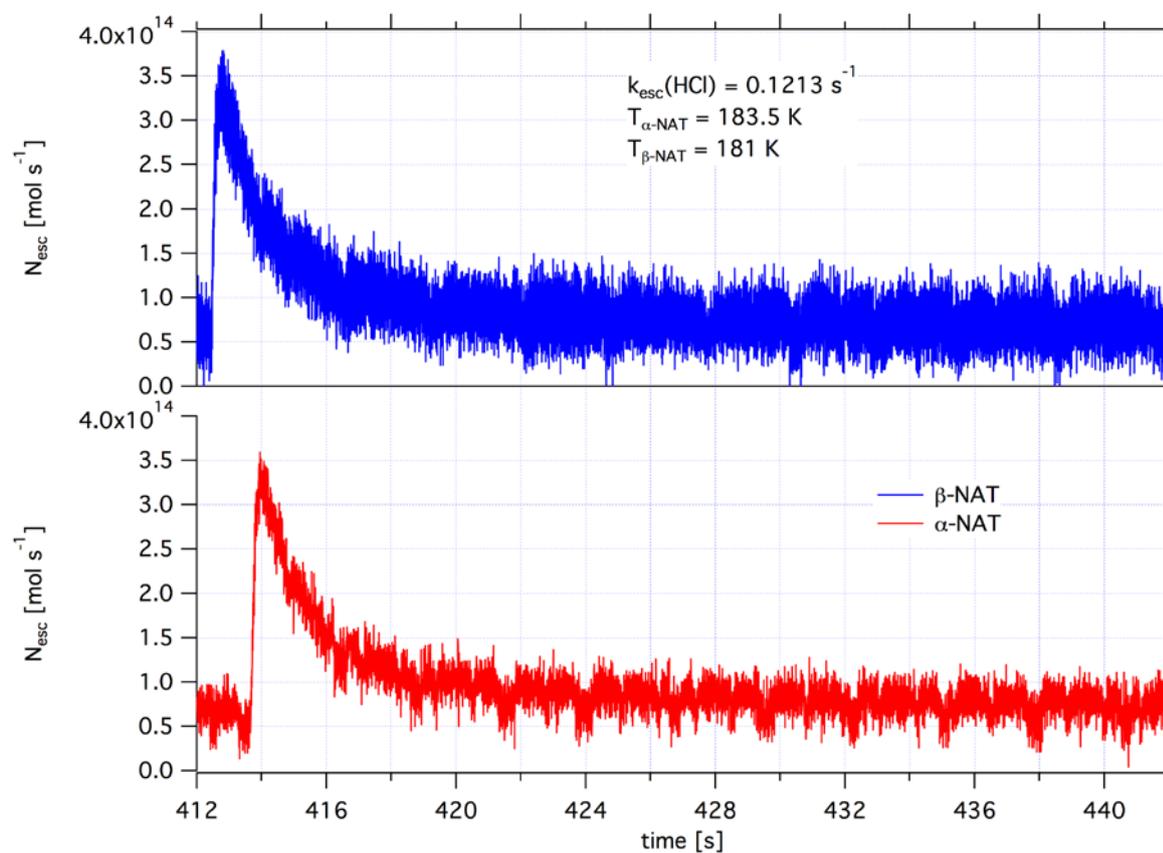


Figure S6: Detailed view of raw data of MS signals of HCl pulses monitored at m/e 36 released onto α - and β -NAT, lower (red trace) and upper (blue trace) panel at 183.5 and 181 K, respectively. The lower and upper trace approximately correspond to 4×10^{16} and 6×10^{16} molecule per pulse, respectively, at a SFR gas phase residence time of 8.24 s corresponding to the small orifice (long residence time). See also Table 1 in the main text.