

## Experimental Studies of Heterogeneous Gas-to-Particle Reactions Using Novel Particle-on-Substrate Stagnation Flow Reactor Approach

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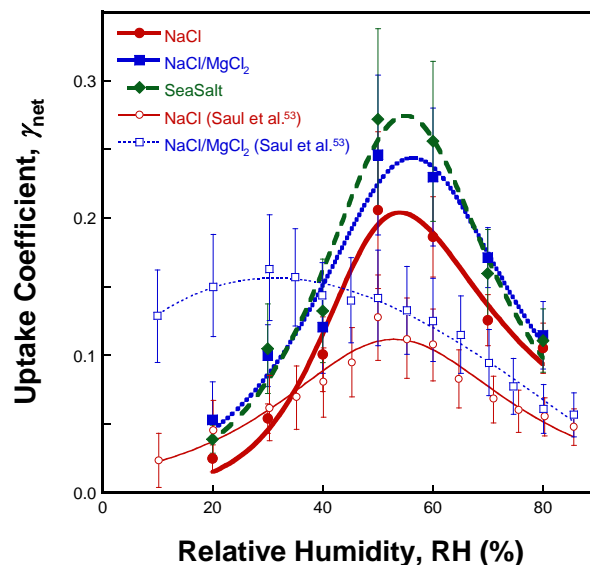
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A novel experimental method for measuring net gas-to-particle reaction probabilities has been developed and applied to a number of reactions relevant to atmospheric aerosol chemistry. Systematic studies focused on definitive and quantitative characterization of nitric acid uptake of NaCl, sea salt and CaCO<sub>3</sub> particles under a wide range of relative humidity have been reported using this method.

A novel Particle-on-Substrate Stagnation Flow Reactor (PS-SFR) experimental approach has been developed by staff and users of EMSL to study the kinetics of heterogeneous, gas-to-sea salt particle reactions. In this new approach, substrate-deposited particles are exposed to reactive gases, followed by chemical analysis of the particles, using advanced instrumentation in EMSL. The reactor design and flow parameters were guided by computational fluid dynamics performed by team members from the University of Southern California to ensure that the diffusion flux was uniform for all particles undergoing reaction. The experimental protocol and data interpretation were successfully implemented in laboratory studies focused on heterogeneous gas-to-particle reactions relevant the atmospheric chemistry of sea salt and mineral dust. A complementary combination of the reported results with previously published single particle mass spectrometry data was essential to understanding uptake kinetics over a wide range of particle sizes and experimental conditions. The developed experimental approach offers options for multi-instrumental analyses of particle samples and therefore can be applicable to a wide variety of reactions of interest not only for the atmospheric chemistry community but also for the surface science and catalysis communities.

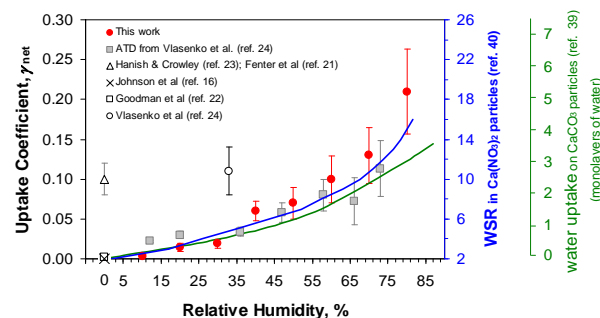
Heterogeneous reactions between nitric acid and aerosol particles, such as sea salt and carbonates present in mineral dust, serve as major sinks for gaseous metric acid and nitrogen oxides, which impact the overall chemical balance of the



**Figure 1.** Values of uptake coefficient as a function of relative humidity for HNO<sub>3</sub> reaction with an NaCl, mixture of NaCl/MgCl<sub>2</sub> and sea salt particles (Liu et al, 2007).

## Research Highlights

troposphere. Results from our studies using the PS-SFR approach show that NaCl and CaCO<sub>3</sub> have a similar reactive HNO<sub>3</sub> uptake at RH < 40% but exhibits a very different humidity dependence. The uptake of HNO<sub>3</sub> onto NaCl was found to increase with the decreasing RH and peak around a relative humidity of 55%, and then below the efflorescence relative humidity (~45% RH) the uptake coefficient decreases rapidly (Figure 1). While uptake of HNO<sub>3</sub> onto CaCO<sub>3</sub> was found to increase monotonically with an increase in relative humidity due to hygroscopic growth of the reaction product Ca(NO<sub>3</sub>)<sub>2</sub> (Figure 2). As a result, if CaCO<sub>3</sub> and NaCl aerosol particles are present in the same HNO<sub>3</sub> polluted air mass, both heterogeneous reaction channels could occur. They may take place equivalently or competitively, depending on specific conditions. Sea salt and mineral dust particles are the largest components, by mass, of global aerosol burden and contribute substantially to atmospheric chemistry, air quality, and climate change issues.



**Figure 2.** Experimentally determined uptake coefficient as a function of the relative humidity for HNO<sub>3</sub> reaction with CaCO<sub>3</sub> particles (Liu et al. 2008).

The developed approach is expected to be applicable to a variety of reactions of interest not only for the atmospheric research community but also for the surface science and catalysis communities. Details of this research have been recently published in the *Journal of Physical Chemistry A*.

### Citations

Liu Y, JP Cain, H Wang, and A Laskin. 2007. "Kinetic Study of Heterogeneous Reaction of Deliquesced NaCl Particles with Gaseous HNO<sub>3</sub> Using Particle-on-Substrate Stagnation Flow Reactor Approach." *Journal of Physical Chemistry A* 111(40):10026-10043.

Liu Y, ER Gibson, JP Cain, H Wang, VH Grassian, and A Laskin. 2008. "Kinetics of Heterogeneous Reaction of CaCO<sub>3</sub> Particles with Gaseous HNO<sub>3</sub> over a Wide Range of Humidity." *Journal of Physical Chemistry A* 112(7):1561-1571.