

Is there a link between the dissociation degree of nitric acid adsorbed to ice under tropospheric conditions and its photolytic activity at the air-ice interface?

YANISHA MANOHARAN, LUCA LONGETTI, LUCA ARTIGLIA, MARKUS AMMANN AND THORSTEN BARTELS-RAUSCH

Paul Scherrer Institut

Presenting Author: yanisha.manoharan@psi.ch

A major source of tropospheric nitrogen oxides (NO_x) and nitrous acid (HONO) in polar regions is the nitric acid (HNO₃) photochemistry at the air-ice interface. It plays a pivotal role in modifying not only the nitrogen oxide budget but also the oxidative capacity of the atmosphere. The interest of our study comes from the lack of understanding of the speciation and hydration of HNO₃ adsorbed to ice under tropospheric conditions and its enhanced photolytic activity at the air-ice interface. Previous spectroscopic work of our group revealed that acidic trace gases adsorbed on ice exist in molecular and ionic forms. The current hypothesis is that the flexibility in the hydrogen-bonding network structure at the air-ice interface drives the dissociation. We investigated the dissociation state of HNO₃ at the air-ice interface by means of depth profiling with near-ambient pressure core level X-ray photoelectron spectroscopy (XPS), and characterized changes in the hydrogen bonding environment due to the adsorption of HNO₃ by means of near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. We also acquired a preliminary data set of flow tube experiments, focusing on the photochemical products, yields, and kinetics of HNO₃ adsorbed on ice films. For achieving low, atmospherically relevant concentrations of HNO₃ we worked with a home-built synthesis and dosing set-up for dosing dinitrogen pentoxide (N₂O₅), that undergoes fast heterogeneous hydrolysis on ice to HNO₃. The results aim to deepen our understanding of the interaction of HNO₃ with the ice and allow discussing the impact of HNO₃-air-ice-photochemistry on the nitrogen oxide budget in polar regions.