

Lifetime Extension of Cirrus Cloud Ice Particles upon Contamination with HCl and HNO₃ under conditions of the Upper Troposphere and Lower Stratosphere

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Ice particles in the Upper Troposphere/Lower Stratosphere (UT/LS) are the seat of heterogeneous chemical processes that are important in polar ozone chemistry. Estimated evaporative lifetimes of typical pure ice particles of a few micrometers radius in Cirrus clouds are on the order of a minute or so at 80% relative humidity, too short to allow significant heterogeneous processing. We took this as a motivation to systematically measure absolute rates of evaporation and condensation of H₂O in 1 to 2 micrometer thick ice films taken as proxies for small atmospheric ice particles under controlled conditions of HCl and HNO₃ trace gas contamination. We have used a multidagnostic reaction vessel equipped with residual gas mass spectrometry (MS), FTIR absorption spectroscopy in transmission and a quartz crystal microbalance (QCM) in order to simultaneously observe both the gas and condensed phases under relevant atmospheric conditions. The rates (Rev(H₂O)) or fluxes of evaporation (Jev(H₂O)) of H₂O from thin ice films contaminated by a measured amount of HCl in the range of 10% of a formal monolayer to 20 formal monolayers decreased by factors of between 2 and 50 depending on parameters such as temperature of deposition (Tdep), rate (RHCl) and dose (NHCl) of contaminant doping. Experiments with HCl fell into two categories as far as the decrease of Jev with the average mole fraction of contaminant (χ_{HCl}) in the remaining ice slab was concerned: one group where Jev(H₂O) decreased gradually after pure ice evaporated, and another group where Jev(H₂O) abruptly changes with χ_{HCl} after evaporation of excess ice. FTIR spectroscopy revealed an unknown, yet crystalline form of HCl hydrate upon HCl doping that does not correspond to a known crystalline hydrate. Of importance is the observation, that the equilibrium vapor pressure of these contaminated ices correspond to that of pure ice even after evaporation of excess ice at the characteristic rate of pure ice evaporation until very late in their evaporation history. Therefore, measurements of vapor pressure cannot identify lightly contaminated ices that may be responsible for evaporative lifetime extension. The presentation will include a critical comparison with HNO₃-contaminated ices that present some interesting differences to HCl contaminated ices.