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## Laboratory Experiments on Heterogeneous Nucleation and Growth Rates of pure H<sub>2</sub>O ice and hydrates of HCl and HNO<sub>3</sub> in the range 165-195 K .

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A multidagnostic Stirred Flow Reactor has been used to investigate heterogeneous nucleation of pure H<sub>2</sub>O ice from water vapor depositing on a silicon substrate mounted in a cryostat at controlled temperatures. The gas phase has been monitored using residual gas mass spectrometry, the cryogenic deposit was investigated using FTIR spectroscopy in transmission in the range 650 to 4000 cm<sup>-1</sup> across typically 0.5 to 2 micrometer thick ice films. Subsequent to ice deposition controlled amounts of HCl and HNO<sub>3</sub> were deposited on top of the previously deposited thin ice film all the while monitoring both FTIR absorption as well as the partial pressures of H<sub>2</sub>O and HCl or HNO<sub>3</sub> using m/e 18, 36 and 46 amu, respectively. Ice deposition on the Si substrate of the cryostat required a supersaturation ratio  $r$  (with respect to pure ice) varying from 2.22 to 16.45 with decreasing temperature at a typical growth rate of 2 monolayers (ML) s<sup>-1</sup>. The data lie on a straight line when plotted as  $\ln(1/r)$  vs.  $1/T$  with an activation energy of  $20.2 \pm 2.6$  kJ mol<sup>-1</sup> (Arrhenius plot). The underlying idea of the rate model for ice nucleation is that  $1/r$  is proportional to the encounter probability (or rate) of individual H<sub>2</sub>O molecules adsorbed on the thin (hydroxylated) SiO<sub>2</sub> (quartz) surface of the Si window. Low temperature leads to a high surface coverage of adsorbed H<sub>2</sub>O and to a large encounter probability to form a viable ice embryo at the SiO<sub>2</sub> interface. However, the surface self-diffusion of adsorbed H<sub>2</sub>O is an activated process whose rate slows down with decreasing temperature. The measured activation energy of 20.2 kJ mol<sup>-1</sup> corresponds to the bond energy of a single Hydrogen bond between a H<sub>2</sub>O molecule adsorbed onto a surface OH-group of SiO<sub>2</sub>. In contrast, when depositing HCl from the gas phase onto the thin H<sub>2</sub>O ice film we observe barrierless, that is spontaneous nucleation of HCl hexahydrate (HCl•6H<sub>2</sub>O or HH) at  $T < 173$  K monitored by FTIR absorption in situ. With increasing HCl deposition the growth rate of HH, typically 2 ML s<sup>-1</sup>, slows down owing to the decrease of the surface diffusion rate of adsorbed HCl across the existing HH film and comes to a halt after approximately 500 ML of deposited HCl. When depositing HNO<sub>3</sub> on pure thin ice films we essentially observe barrierless spontaneous formation of alpha-NAT (HNO<sub>3</sub>•3H<sub>2</sub>O) or NAD (HNO<sub>3</sub>•2H<sub>2</sub>O) at typical growth rates of 0.6 ML s<sup>-1</sup> akin to the HCl/ice system. In some cases a very small supersaturation is required to initiate crystal growth. The key message from this work is that spontaneous, that is barrierless, nucleation enables the formation of HCl and HNO<sub>3</sub> hydrates (type II Polar Stratospheric Clouds or PSC's) in the presence of stratospheric ice (type I PSC's).

### Significance statement

This work's key message is that spontaneous nucleation enables the formation of HCl and HNO<sub>3</sub> hydrates in the presence of stratospheric ice. The efficiency of this process is at variance with the reported difficulty to nucleate HCl and HNO<sub>3</sub> hydrates in the laboratory starting with the gas-phase components.

**Author:** Dr ROSSI, Michel J. (Paul Scherrer Institute (PSI))

**Co-author:** Dr IANNARELLI, Riccardo (EPFL)

**Presenters:** Dr ROSSI, Michel J. (Paul Scherrer Institute (PSI)); Dr IANNARELLI, Riccardo (EPFL)

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