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Why does large ice supersaturation persist in cold cirrus clouds?

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The upper tropospheric cold cirrus clouds (T< 210K) are thought to limit the accumulation of water vapor in the upper troposphere (UT), because the growth and sedimentation of cirrus ice crystals redistribute moisture to lower levels. However, observations often reveal persistent ice supersaturation, S_i >100% (corresponding to relative humidity with respect to hexagonal ice RH_i > 200%) outside (in clear-sky) and inside cold cirrus clouds[1] formed near the tropopause region in-situ i.e., not influenced by a deep convective water vapour source[1]. Such cirrus can be formed by homogeneous freezing of the pre-existing H_2SO_4/H_2O aerosol droplets[2]. Below T ≈ 203 K, the condensation of HNO_3 can combine with H_2SO_4/H_2O to form $H_2SO_4/HNO_3/H_2O$ droplets. The UT droplets can also contain $(NH_4)_2SO_4$, $(NH_4)HSO_4$, NH_4NO_3, and $(NH_4)_3H(SO_4)_2$ which are formed by the neutralization of H_2SO_4 and HNO_3 by NH_3.

The existence of the clear-sky $S_i >> 0$ % is not surprising, considering that cold cirrus clouds are formed by homogeneous freezing aqueous droplets. Laboratory measurements of micrometer-scaled droplets of H_2SO_4/H_2O[2], $(NH_4)HSO_4/H_2O$[3], and $(NH_4)_2SO_4/H_2O$[4] have predicted that before cirrus clouds start developing the clear-sky S_i can reach ∼70%. What is really surprising is how $S_i >> 0$ % can persist within cirrus clouds which consist of numerous ice crystals formed by homogeneous freezing of aqueous droplets. According to current knowledge, the ice crystals rapidly consume water vapor and lower in-cloud moisture to $S_i \approx 0$ %[5]. Now there is no physical explanation for the nature of the observed clear-sky and in-cloud $S_i >> 0$ %.

Recently using differential scanning calorimeter (DSC), we showed that the cold cirrus formed by homogeneous freezing H_2SO_4/H_2O droplets may consist of mixed-phase particles: an ice core + a H_2SO_4/H_2O coating[6]. Our new DSC measurements indicate that the cirrus formed by homogeneous freezing of aqueous droplets containing H_2SO_4, HNO_3, and ammonium salts $(NH_4)HSO_4$, $(NH_4)_2SO_4$, NH_4NO_3, and $(NH_4)_3H(SO_4)_2$ may also consist of the mixed-phase particles.

In the absence of any deep convective water vapor sources, the temperature of the onset of the freezing of UT aqueous droplets will determine the highest clear-sky S_i. Assuming that the UT droplets have a composition similar to that of the laboratory droplets, we calculated the S_i which would exist immediately prior to the formation of cold cirrus. The calculations were performed using the measured freezing temperatures of ice, T_i, and the thermodynamic model of the system [7] $H^+ - NH_4^+ - SO_4^{2-} - NO_3^- - H_2O$.

The calculations show that $S_i > 100$ % can be formed prior to the formation of cold ice cirrus by homogeneous freezing of aqueous droplets containing H_2SO_4, HNO_3, $(NH_4)_2SO_4$, $(NH_4)HSO_4$, NH_4NO_3, and $(NH_4)_3H(SO_4)_2$.

In the UT, the growth rate of coated ice crystals will differ from that of uncoated ones since the coating can serve as a 'shield' reducing the flux of H_2O molecules to the ice surface. The uncoated ice crystals experience rapid growth due to fast deposition of H_2O *directly* on the ice surface. In the case of coated ice, H_2O molecules first condense on the coating, dilute it, diffuse to the ice core, and only then become incorporated into the ice lattice.

The calculations of the thickness of the coating around ice crystals and the impact of the coating on the rate of ice growth, and consequently on the rate of the consumption of moisture inside cold cirrus, were made for H_2SO_4/H_2O droplets. The H_2SO_4/H_2O system has been well studied and its thermodynamic data are well documented. We find that the coating can slow down the rate of ice growth by $\sim 10^3$ in comparison with uncoated ice and this can be a

reason for the persistent in-cloud $S_i >> 0$ %.

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