

## Embedding of HCl droplets on ice crystal surfaces under atmospheric-concentration HCl gas

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Surfaces of ice act as sites of various chemical reactions of atmospheric acidic gases, which cause serious environmental issues, such as the catalytic ozone depletion by hydrogen chloride (HCl) gas. As a means of direct observation of QLLs on ice surfaces, we and Olympus Engineering Co. Ltd., have developed laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM), which can directly visualize 0.37-nm-thick elementary steps [1] and QLLs on ice crystal surfaces [2].

Recently, we studied effects of HCl gas ( $10^2$  Pa) on the behavior of QLLs on ice basal faces by LCM-DIM [3-4]. Then we found that the QLLs were not pure water but an HCl aqueous solution, whose HCl concentration was very close to that of a liquidus line of a binary phase diagram of water and HCl. Therefore, the HCl droplets did not disappear and were embedded in ice crystals stably without freezing [4]. However, in our previous studies, we used the HCl gas of  $10^2$  Pa HCl partial pressure, which is extremely higher than ordinary atmospheric partial pressure of HCl. Here, we show direct observations of ice basal faces by advanced optical microscopy under atmospheric-concentration HCl gases of from  $10^{-4}$  to  $10^{-2}$  Pa. Then, we investigated the appearance/disappearance of liquid water on ice surfaces and their effects on the growth of ice crystals [5].

Under atmospheric-concentration HCl gas, we found that liquid droplets and thin layers appeared/disappeared on the ice basal faces at about  $-1$  °C with increasing/decreasing temperatures. These behaviors were similar to those in the absence of the HCl gases. In contrast, at temperatures below  $-10$  °C, surprisingly we found that with decreasing temperature, the HCl gases induced the appearance of droplets of an HCl aqueous solution on the basal faces. In addition, the HCl droplets pinned the lateral advancement of spiral steps, resulting in the formation of bunched steps. The HCl droplets were finally embedded in the ice crystals by further growth of the bunched steps. In contrast, with increasing temperatures, the HCl droplets and the bunched steps disappeared at  $-10$  °C.

These results indicate that a bulk of an ice crystal plays an important role in the uptake of HCl. So far, it has been believed that the contribution of a bulk of an ice crystal to the HCl uptake is less important than that of an ice surface, because of the small solubility of HCl and the slow diffusion of chloride ions in an ice crystal. Hence, the results found in this study suggest that the uptake of HCl in an ice crystal can be promoted via the bunching and embedding mechanism at temperatures below  $-10$  °C. Our findings will give significant insights into various environmental issues caused by acidic gases in polar regions. However, it is crucially important to study whether the similar phenomena occur at  $-70$  °C, at which temperature HCl on ice crystals plays an important role in the ozone depletion by the heterogeneous photochemical reactions in polar stratospheric clouds.

[1] Sazaki et al. (2010) PNAS 107, 19702.

[2] Sazaki et al. (2012) PNAS 109, 1052.

[3] Nagashima et al. (2016) Cryst. Growth Des. 16, 2225.

[4] Nagashima et al. (2018) Cryst. Growth Des. 18, 4117.

[5] Nagashima et al., Cryst. Growth Des. submitted.

We will present this study from other viewpoints in " M-IS17 Growth and dissolution of crystal".

Keywords: ice crystal, air-snow interaction, atmospheric-concentration HCl gas, bunched step, HCl uptake, advanced optical microscopy