

Nitric acid gas captured in quasi-liquid layers on ice surfaces

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Ice crystal surfaces act as “reaction fields” for heterogeneous chemical reactions that involve atmospheric acidic gases, thereby causing serious environmental issues such as the catalytic ozone depletion by hydrogen chloride gas and the generation of nitrogen oxide gases (NO_x) from the photolysis of nitric acid/nitrates. These chemical reactions cannot be explained solely by homogeneous processes. In addition, the surfaces of ice crystals near the melting point are covered with thin liquid water layers, called quasi-liquid layers (QLLs), which may play crucial roles in various chemical reactions. In this study, we chose HNO₃ as a model atmospheric gas, and directly observed the QLLs on ice basal faces by advanced optical microscopy [1]. Because P_{HNO_3} in the troposphere shows considerable variations (e.g., ranging from $\sim 10^{-6}$ Pa in clean air to $\sim 10^{-2}$ Pa in polluted urban air [2,3]), the observations in this study were performed under some P_{HNO_3} conditions (0, 10^{-4} and 10^{-2} Pa).

Irrespective of the presence/absence of the HNO₃ gas, the pure-QLLs and HNO₃-QLLs appeared with increasing temperature and disappeared with decreasing temperature. The shape of pure-/HNO₃-QLLs showed spherical dome and the contact angle of them on the ice basal face was $\sim 1^\circ$. The appearance temperatures of the pure-/HNO₃-QLLs were not so different (-1.9 and -0.5 to -1.8 °C, respectively). Although the disappearance temperature of pure-QLLs (-2.2 °C) was almost same as the appearance temperature, the disappearance temperature of the HNO₃-QLLs (-6.4 °C) was significantly lower than the appearance temperature of them under high- P_{HNO_3} condition (10^{-2} Pa). The large thermal hysteresis between the appearance and disappearance temperatures suggests that the disappearance mechanisms of the pure-/HNO₃-QLLs were different. We found that the HNO₃-QLLs are not composed of pure water, but rather of aqueous HNO₃ solutions, and also that the HNO₃-QLL and the ice crystal were in equilibrium. The evidence and the disappearance mechanism are showed as follows.

The size of the HNO₃-QLLs decreased immediately after we started reducing the temperature. We could not observe such changes in the sizes of pure-QLL with temperature in the absence of the HNO₃ gas. When we assumed that the mass of HNO₃ in the HNO₃-QLL was constant during the relatively short observation time period, the volume reduction of the HNO₃-QLLs with decreasing temperature meant increasing of HNO₃ concentration of the HNO₃-QLL. We calculated the volume reductions as a function of temperature by using the HNO₃-H₂O phase diagram. The calculated volume reductions were in good agreement with the volume reductions determined experimentally.

One of the plausible causes for the disappearance of HNO₃-QLLs could be the evaporation of HNO₃ from the HNO₃-QLLs. We calculated the equilibrium HNO₃ partial vapor pressure, $P_e(\text{HNO}_3)$, of the HNO₃-QLLs. As temperature decreases, $P_e(\text{HNO}_3)$ increases. It is very reasonable to expect that when $P_e(\text{HNO}_3)$ exceeds P_{HNO_3} in the observation chamber with decreasing temperature, HNO₃ evaporates from the HNO₃-QLLs, resulting in the disappearance of the HNO₃-QLLs.

Recently, we studied the effects of hydrogen chloride gas on the behavior of QLLs (HCl-QLLs) on ice basal faces [4,5]. We found that the HCl-QLLs were also aqueous hydrochloric acid solution, and that the temperature and HCl concentration of the HCl-QLLs were also very close to those of a liquidus line: these

results were similar to those found in this study. Therefore, ice crystal surfaces would capture large amount of acidic gas components in the acidic-QLLs.

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The details of this study are shown in our paper [1]. We will present this study from other viewpoints in “A-CC39 Glaciology” and “M-IS23: Growth and dissolution of crystal” sessions.

Keywords: Ice, quasi-liquid layer, nitric acid gas, optical microscopy