Direct observation of quasi-liquid layers on ice surfaces by advanced optical microscopy: Effect of nitric acid gas

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Ice is one of the most abundant crystals on the earth, and hence the molecular-level understanding of ice crystal surfaces holds the key to unlocking the secrets of a number of fields. We and Olympus Engineering Co., Ltd. have developed laser confocal microscopy combined with differential interference contrast microscopy (LCM-DIM), by which we succeeded in the direct visualization of 0.37-nm-thick elementary steps on ice for the first time [1]. In addition, we could also visualize the quasi-liquid layers (QLLs) on ice crystal surfaces [2], which are covered with thin liquid layers even below the melting point (0°C). The direct observations of QLLs under nitrogen gas revealed the appearance temperatures and partial pressure of water vapor [3,4]. On the other hand, we also found that even trace acidic gas induced the stability of QLLs. In this study, we chose HNO₃ as a model atmospheric gas, and directly observed the QLLs on ice basal faces by advanced optical microscopy[5]. Because P_{HNO3} in the troposphere shows considerable variations (e.g., ranging from ~10⁻⁶ Pa in clean air to ~10⁻² Pa in polluted urban air [6,7]), the observations in this study were performed under some P_{HNO3} 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 ~1°. 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_{HNO3} 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.

Recently, we studied the effects of hydrogen chloride gas on the behavior of QLLs (HCI-QLLs) on ice basal faces [8,9]. We found that the HCI-QLLs were also aqueous hydrochloric acid solution, and that the temperature and HCI concentration of the HCI-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 [5]. We will present this study from other viewpoints in "A-AS07 Atmospheric Chemistry" and "M-IS23: Growth and dissolution of crystal" sessions.

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