Geophysical Research Abstracts,
Vol. 11, EGU2009-13419, 2009
EGU General Assembly 2009

Cubic ice and large humidity with respect to ice in cold cirrus clouds

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Recently several studies have reported about the possible formation of cubic ice in upper-tropospheric cirrus ice clouds and its role in the observed elevated relative humidity with respect to hexagonal ice, RH_i, within the clouds. Since cubic ice is metastable with respect to stable hexagonal ice, its vapour pressure is higher. A key issue in determining the ratio of vapour pressures of cubic ice P_c and hexagonal ice P_h is the enthalpy of transformation from cubic to hexagonal ice $\Delta H_{c\rightarrow h}$.

By dividing the two integrated forms of the Clausius-Clapeyron equation for cubic ice and hexagonal ice, one obtains the relationship (1):

$$\ln \frac{P_c}{P_h} - \ln \frac{P_c^*}{P_h^*} = \frac{\Delta H_{c\rightarrow h}}{R\left(\frac{1}{T} - \frac{1}{T^*}\right)} \tag{1}$$

from which the importance of $\Delta H_{c\rightarrow h}$ is evident. In many literature studies the approximation (2) is used:

$$\ln \frac{P_c}{P_h} = \frac{\Delta H_{c\rightarrow h}}{RT}. \tag{2}$$

Using this approximated form one can predict the ratio of vapour pressures by measuring $\Delta H_{c\rightarrow h}$. Unfortunately, the measurement of $\Delta H_{c\rightarrow h}$ is difficult. First, the enthalpy difference is very small, and the transition takes place over a broad temperature range, e.g., between 230 K and 260 K in some of our calorimetry experiments. Second, cubic ice (by contrast to hexagonal ice) can not be produced as a pure crystal. It always contains hexagonal stacking faults, which are evidenced by the (111)-hexagonal Bragg peak in the powder diffractogram. If the number of hexagonal stacking faults in cubic ice is high, then one could even consider this material as hexagonal ice with cubic stacking faults.

Using the largest literature value of the change of enthalpy of transformation from cubic to hexagonal ice, $\Delta H_{c\rightarrow h}$ $\approx$ 160 J/mol, Murphy and Koop (2005) calculated that P_c would be $\sim$10% higher than that of hexagonal ice $P_h$at 180 K – 190 K, which agrees with the measurements obtained later by Shilling et al. (2006). Based on this result Shilling et al. concluded that "the formation of cubic ice at T $<$ 202 K may significantly contribute to the persistent in-cloud water supersaturations" in the upper-tropospheric cold cirrus clouds. Using instead the value of $\Delta H_{c\rightarrow h}$ $\approx$ 50 J/mol (Handa et al., 1986; Mayer and Hallbrucker, 1987) the calculation gives that P_c is only $\sim$3% larger than that of P_h.

Recently it has been reported that emulsified water droplets freeze to cubic ice when being cooled at a rate of 10 K/min (Murray and Bertram, 2006,). We prepared emulsified droplets using the same emulsification technique and studied them with a differential scanning calorimeter (DSC) between 278 and 180 K using a scanning rate of 10 K/min. During the warming of the samples we observed a very broad, tiny exothermal peak approximately between 230 and 260 K. Kohl et al. (2000) observed exothermal peak at $\sim$230 K during the warming at 30 K/min of several samples of hyperquenched glassy water (HGW) prepared at temperature between 130 and 190 K. They attributed this peak to the cubic-to-hexagonal ice transition and estimated $\Delta H_{c\rightarrow h}$ to be between $\sim$33 and 75 J/mol. Johari (2005) used the value of $\Delta H_{c\rightarrow h}$ $\approx$ 37 J/mol. Assuming that in our case the broad peak between 230 and 260 K is also due to the cubic-to-hexagonal ice transition we obtained approximately between 10 and 25 J/mol for $\Delta H_{c\rightarrow h}$. This low enthalpy of transformation suggests that cubic ice in the atmosphere contains many hexagonal stacking faults. Using these values of $\Delta H_{c\rightarrow h}$ for cubic ice as produced at atmospheric cooling rates, the above mentioned formula gives that P_c is larger than that of P_h only by $\sim$1%. We, therefore, suggest that the difference

in the water vapor pressures between ice I_c and ice I_h is small and does not play a significant role in the elevation of RH_i in cold cirrus clouds.

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