

# Depletion of ammonia gas onto Jovian ices

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## Abstract

The microwave spectrum of Jupiter is consistent with supersolar ammonia deeper than 6 bar, and subsolar ammonia at pressures less than 2 bar (de Pater et al. 2001). Because the Galileo Probe Mass Spectrometer measured a deep  $\text{NH}_3/\text{H}_2$  mixing ratio of  $6.4 \times 10^4$  (Wong et al. 2004)—or five times the protosolar ratio (Grevesse et al. 2007)—the microwave data show that there must be a global-scale depletion mechanism for ammonia gas, operating between the 2 and 6 bar levels. Candidate depletion mechanisms include dynamics, condensation of species with higher nitrogen fractions than  $\text{NH}_3$  (including clathrates; see Romani et al. 2000), and adsorption of ammonia onto  $\text{NH}_3$  or water ices.

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## Experimental approach

The uptake coefficient of ammonia on water ice and water ice mixtures is measured with a Knudsen cell. Our Knudsen cell is a low-pressure flow reactor with an inlet for trace gases (here: ammonia) and a sealable compartment for an ice substrate. It is operated under molecular flow conditions (pressures  $\sim 20$  mtorr). Under these conditions the collision frequency of the ammonia with the ice substrate can be calculated and is the same as the collision frequency with an escape orifice. The composition of the escaped gases is analyzed with a residual gas analyzer (RGA) mass spectrometer. Uptake of ammonia on ice appears as a depletion of gas phase ammonia in the signal detected by the RGA.

**Cooling method.** The measurements are performed in the temperature range of 165–200 K. The ice compartment of the Knudsen Cell is cooled with a mixture of ethanol/liquid  $\text{N}_2$ .

**Ice preparation.** The ice is prepared in the ice compartment of the Knudsen Cell. 15 ml of deionized water (pH = 7) are frozen rapidly by cooling the

We have begun laboratory experiments designed to measure the uptake of ammonia by  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}-\text{NH}_3$  ice mixtures. We also plan model calculations to apply the experimental results to Jupiter's atmosphere and quantify the effect of ammonia uptake by ices. The laboratory study uses a Knudsen cell apparatus in a temperature regime appropriate to the troposphere of Jupiter around the 2–4 bar pressure level, where the microwave data indicate depletion of ammonia gas. We discuss the key parameters and processes that influence the ammonia uptake and their relevance to Jupiter's atmosphere.

compartment to 200 K. The ice freezes in sections, starting with the layers in contact with the cold compartment walls. As a result small cracks can be seen in the ice. After the experiment the surface of the ice is basic with a pH  $\approx 9$ . The ice surface is  $A_{\text{ice}} = 28 \text{ cm}^2$ .

**Temperature measurement.** The temperature is measured with two thermocouples (TC) in the cooling mixture and the ice compartment. The temperatures differ by  $\sim 20$  K, suggesting that the ice has an intermediate temperature. The water vapor pressure in the Knudsen Cell changes with the ice temperature and can be used to calculate the ice temperature  $T_{\text{ice}}$  via:

$$\frac{P_{\text{H}_2\text{O},T(\text{ice})}}{\sqrt{T_{\text{ice}}}} = \frac{P_{\text{H}_2\text{O},\text{measured}}}{\sqrt{T_{\text{KnudsenCell}}}}$$

where  $p_{\text{H}_2\text{O},T(\text{ice})}$  is the saturated vapor pressure of water at the temperature of the ice,  $p_{\text{H}_2\text{O}}$  measured is the vapor pressure measured by the RGA and pressure sensors, and  $T_{\text{KnudsenCell}}$  is the temperature of the rest of the cell (293 K; room temperature).

## Uptake: definitions

The uptake coefficient for solids,  $\gamma$ , is defined as the number of molecules sticking to the surface divided by the number of collisions with the surface.

The equivalent process for liquids is described by the mass accommodation coefficient,  $\alpha$ , which is the number of molecules incorporated in the liquid divided by the number of collisions with the surface of the liquid. Solvation and diffusion into the bulk liquid allows uptake into liquids to be much more efficient than uptake on solids, so  $\alpha \gg \gamma$ .

Figure 1 compares uptake of ammonia into liquid water and onto solid pure water ice. A previous study by Jin and Chu (2007) found that the uptake coefficient for ammonia on water ice is  $3.8 \pm 1.4 \times 10^{-4}$  at 190 K. Their work was intended to study climatologically significant processes affecting the Earth's atmosphere.

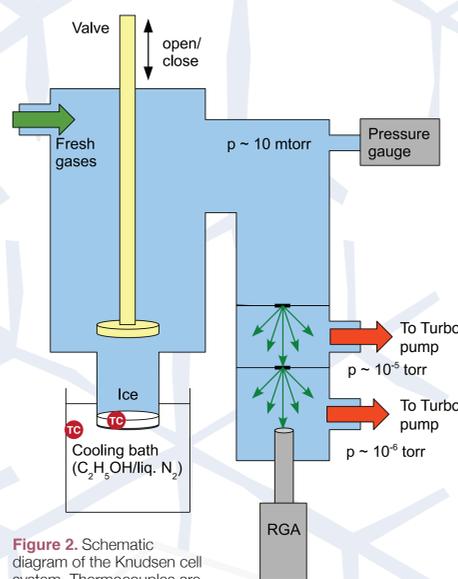


Figure 2. Schematic diagram of the Knudsen cell system. Thermocouples are marked "TC."

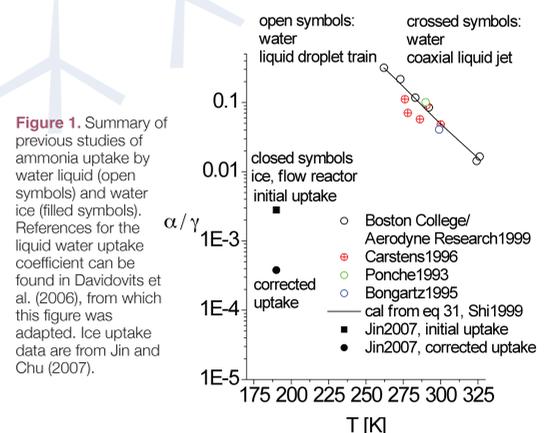


Figure 1. Summary of previous studies of ammonia uptake by water liquid (open symbols) and water ice (filled symbols). References for the liquid water uptake coefficient can be found in Davidovits et al. (2006), from which this figure was adapted. Ice uptake data are from Jin and Chu (2007).

## Calculating the uptake coefficient $\gamma$

The  $\text{NH}_3$  pressure in the Knudsen cell is the balance of the ammonia flow in and out of the reactor and the ammonia adsorbed on the walls and the ice. The net rate of each of the various loss processes is described by the Hertz-Knudsen equation (Kennard 1938),

$$\dot{N}_{b,\text{NH}_3} = A_b f_b \frac{\bar{v}_{\text{NH}_3} P_{b,\text{NH}_3}}{4}$$

where  $A$  is the surface area,  $p$  is the partial pressure,  $v$  is the average velocity,  $f$  is a constant for a single loss process or for a combination of processes, and the  $b$  subscript identifies the loss process, e.g., adsorption onto  $\text{NH}_3$  ice (in which case  $f_b = \gamma$ ).

The uptake coefficient can be derived from comparison of the ammonia pressures in two relative measurements at the same ammonia flow:

$$\gamma_{\text{ice,NH}_3} = \frac{A_{\text{orifice}} k_{\text{orifice}}}{A_{\text{ice}}} \left[ \frac{P_{\text{NH}_3,\text{no ice}}}{P_{\text{NH}_3,\text{ice}}} - 1 \right]$$

$$\gamma_{\text{ice,NH}_3} = \frac{1}{A_{\text{ice}}} \frac{A_{\text{orifice}} k_{\text{orifice}} - [A_{\text{orifice}} k_{\text{orifice}}]_{\text{ice}}}{\left[ \frac{P_{\text{orifice,NH}_3,\text{ice}}}{P_{\text{orifice,NH}_3,\text{ice}}} - 1 \right]}$$

$k$  is the Clausing correction for orifice geometry (Kennard 1938), and "ice" or "no ice" subscripts on partial pressures indicate whether the ice sample is exposed or not during the measurements. Wall adsorption is ignored in all cases; the Knudsen cell walls are made of Pyrex and are passivated by a Teflon coating.

## Measurements

The RGA signal (Figure 3) is proportional to the Knudsen cell pressure and is converted to pressure units.

Two corrections must be made to the raw RGA data. Background contributions from residual gases in the RGA compartment of the Knudsen cell must be subtracted, and mass interference must be removed when multiple gases produce signal at the same mass to charge ratio ( $m/z$ ) measured by the RGA. For example, at  $m/z = 17$ , there is signal from both water (the  $\text{OH}^+$  ion) and ammonia (the  $\text{NH}_3^+$  ion):  $[17] = [17]_{\text{H}_2\text{O}} + [17]_{\text{NH}_3}$ . Measured fragmentation ratios (which unfortunately depend on parent molecule partial pressure in the current RGA) are used to correct for mass interference.

**The current data yield an uptake coefficient  $\gamma < 1 \times 10^{-3}$  in the temperature range between 165 K and 195 K.**

The uncertainties are large in these initial experiments and warrant a qualitative rather than quantitative discussion. During all experiments the temperature changed  $\sim 0.3$  K/min due to the warming of the cooling mix. The warming rate is slow compared to the reaction rates, and the data are believed to be valid. The experiment duration was about 90 minutes per run. The two thermocouple temperatures differ by  $\pm 10$  K.

The mass interference from water to the ammonia signal complicates the data reduction at high temperatures and large water vapor pressures. In addition, water sublimation changes the gas composition. These complications mainly affect the uptake coefficients calculated from signal ratios for exposed vs. not exposed ice. Because the interactions remain approximately the same when the orifice size changes, measurements comparing the RGA signal for different escape orifices yield more reliable uptake coefficient values. We use argon (which does not interact with ice or surfaces in the cell) as a reference gas to distinguish between gas composition changes and ammonia partial pressure changes due to adsorption on the ice sample.

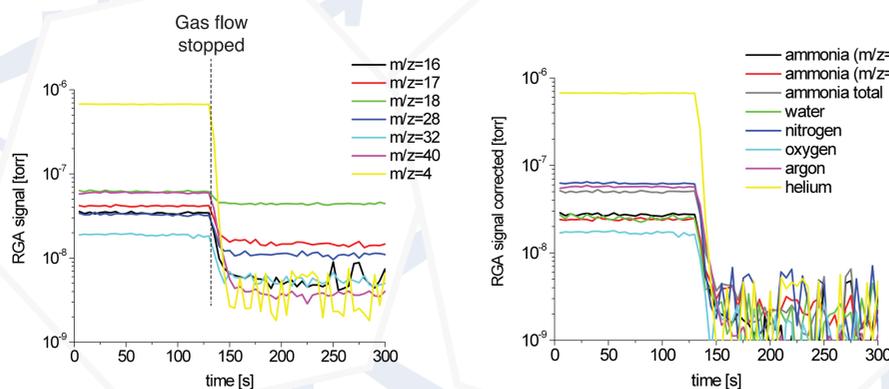


Figure 3. RGA signal levels before (left) and after (right) calibration for background signal and for mass interference.

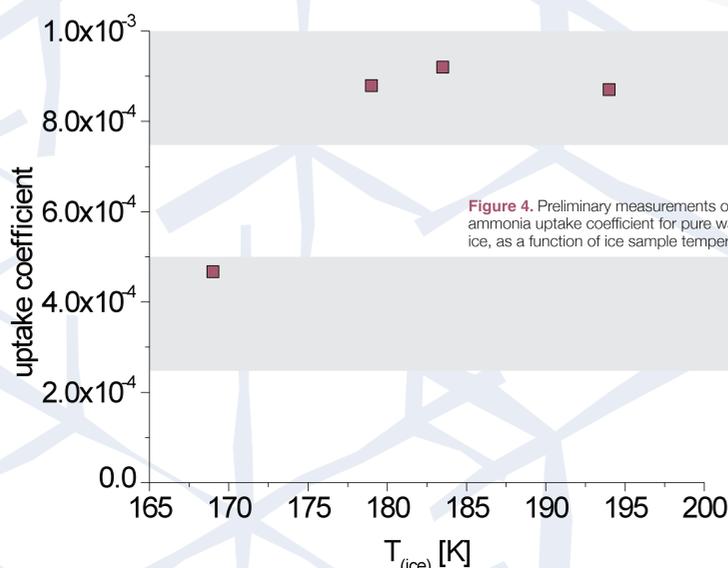


Figure 4. Preliminary measurements of ammonia uptake coefficient for pure water ice, as a function of ice sample temperature.

## Future work

We are at an early stage in the laboratory experiments. Significant improvements will result from upgrades to the cooling apparatus and the data reduction procedures. Once these steps are taken, we will measure the temperature dependence of ammonia uptake and investigate the effect of pH and dissolved ammonia salts on the uptake coefficient. Perhaps most relevant to Jupiter studies is the measurement of the surface coverage: the maximum amount of  $\text{NH}_3$  that can be adsorbed before the ice surface is saturated. Figure 5 shows a simple atmospheric model prediction for the depletion of ammonia, as a function of surface coverage. A depletion of about 90% is needed to be consistent with globally averaged ammonia concentrations derived from microwave measurements (de Pater et al. 2001).

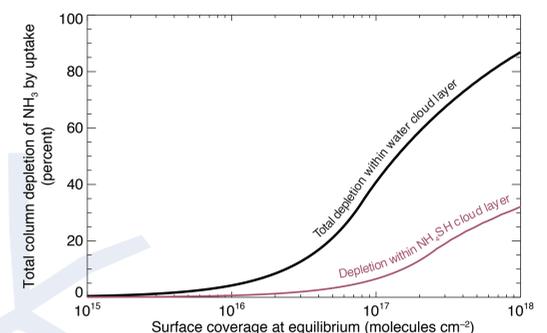


Figure 5. Percentage of ammonia gas column density depleted by uptake onto ice particles, as a function of surface coverage. A constant uptake coefficient of  $7 \times 10^{-4}$  was used, consistent with our laboratory results. "Water cloud layer" is defined by  $T \leq 273$  K and  $p \leq 2.12$  bar;  $\text{NH}_3$  cloud layer is bounded by  $2.12 \text{ bar} < p < 0.675$  bar. Cloud particle surface area assumes  $1\text{-}\mu\text{m}$  spheres and cloud mass densities from the equilibrium cloud condensation model of Atreya and Romani (1986); aerosols in the model atmosphere then adsorbed  $\text{NH}_3$  gas until saturation. Jin and Chu (2007) find a surface coverage of  $2 \times 10^{15}$  to  $2 \times 10^{16}$  molecules  $\text{cm}^{-2}$  at 190 K, with the caveat that their experiment did not run long enough to achieve steady-state equilibrium.

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