

Ammonia-water ices: spectroscopic signatures in the near infrared

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Abstract

A study of the near infrared reflection and transmission spectra of ammonia-water ice mixtures grown by vapor deposition at various temperatures and with different $\text{NH}_3/\text{H}_2\text{O}$ ratios has been conducted. Variations in positions and widths of the $2.2 \mu\text{m}$ and $2.0 \mu\text{m}$ bands of NH_3 and of the $2.0 \mu\text{m}$ and $1.65 \mu\text{m}$ bands of H_2O in the mixtures will be discussed. These findings are expected to be relevant for the comparison with astrophysical data to estimate the concentration of ammonia in outer solar system ices, and their temperature.

1. Introduction

The existence of ammonia on icy satellites in the outer solar system had been predicted a long time ago, although its identification in the solid phase is recent, e.g. in Charon [1], Enceladus [2] and in a few other icy objects. The identification was made via a near-IR absorption feature at $2.2 \mu\text{m}$ attributed to solid NH_3 . NH_3 has an equally intense band at $2.0 \mu\text{m}$, nearly coincident with the $2.0 \mu\text{m}$ overtone band of H_2O , the dominant ice material in many of these objects. On the other hand the $1.65 \mu\text{m}$ band of H_2O ice is used to determine the fraction of amorphous versus crystalline ice in different objects [3]. This band is almost undetectable in amorphous water ice but it has a significant intensity in crystalline ice. In the lab, these features have been recently studied by Zheng et al. [4], among others.

Solid ammonia presents three different phases. Condensation at $T < 50 \text{ K}$ produces a highly distorted amorphous solid, whereas at intermediate temperatures a metastable phase is created. Both phases transform to the crystalline structure above 80 K (see [5] and references therein). With water, three stoichiometric solids are known: the dihydrate $\text{NH}_3\cdot 2\text{H}_2\text{O}$; the monohydrate $\text{NH}_3\cdot \text{H}_2\text{O}$ and the hemihydrate $2\text{NH}_3\cdot \text{H}_2\text{O}$. Moreover, non-

stoichiometric solids with different $\text{H}_2\text{O}/\text{NH}_3$ ratios can be formed, but they do not present unique hydrogen bondings as those found in the hydrates [6].

We study in this work the near-IR spectra of stoichiometric and non-stoichiometric $\text{H}_2\text{O}/\text{NH}_3$ mixtures generated at different temperatures from 14 K to 90 K , and we analyze also their temperature evolution.

2. Experimental part

Grazing angle reflection-absorption infrared (RAIR) and transmission spectroscopy are employed with the experimental setup available in our laboratory. A detailed description is given in [7]. We present here a short summary of the experimental arrangement and deposition techniques.

We use a UHV cylindrical chamber, evacuated by a turbomolecular pump and provided with a closed-cycle He cryostat in contact to a deposition substrate, a gold plate for RAIR experiments and an infrared transparent silicon wafer for transmission. The substrate temperature can be controlled between 14 K and 300 K with 1 K accuracy. The chamber base pressure is in the 10^{-8} mbar range. Spectra are recorded with a Bruker Vertex 70 FTIR spectrometer, equipped with a liquid nitrogen cooled Mercury Cadmium Telluride detector, by addition of between 100 and 500 scans, at 2 cm^{-1} apodized resolution. In the reflection configuration the IR beam is directed onto the Au surface at 75° from the surface normal and the specularly reflected light is collected by a parabolic mirror onto the detector. In transmission the IR beam is perpendicular to the substrate surface.

Samples of mixed $\text{NH}_3/\text{H}_2\text{O}$ ices were prepared by simultaneous introduction into the chamber of water and ammonia vapors, at the appropriate ratio, through two independent inlets, and deposition on the substrate at the desired temperature. The purity of the species is measured with a quadrupole mass

spectrometer. The ice film thickness can be approximately measured calibrating the QMS for the masses 17 and 18, following the procedure described previously [7, 8]. The ice mixtures were prepared for water to ammonia ratios with partial pressures in the 10^{-6} - 10^{-5} mbar range. The approximate ice growing rate was 8 nm/s and the film thickness ranged between 5 and 10 μm .

3. Results and discussion

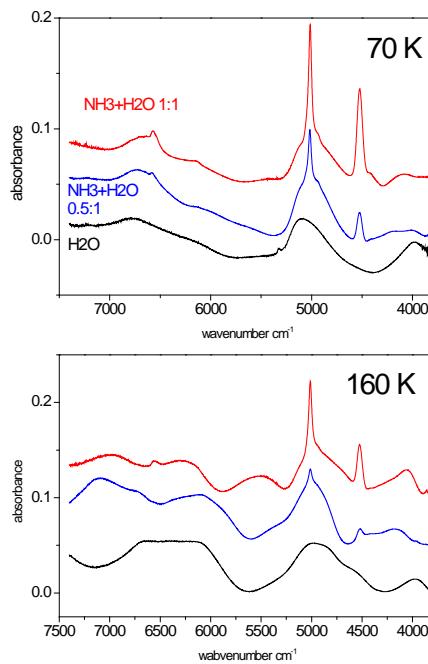


Figure 1. Grazing angle (75°) RAIRS spectra of various $\text{NH}_3:\text{H}_2\text{O}$ ice mixtures, $\sim 7 \mu\text{m}$ thick. Above: spectra recorded at the generation temperature, 70 K. Below: after annealing at 160 K. The spectra of the mixtures have been offset vertically for clarity.

In Figure 1 we present NIR spectra of the $\text{NH}_3:\text{H}_2\text{O}$ monohydrate (red trace), of a non-stoichiometric $\text{NH}_3:\text{H}_2\text{O} \sim 0.5$ mixture (blue trace) and of pure water ice (black trace), at a generation temperature of 70 K and after annealing the samples to 160 K.

It can be seen from the intensity of the two main NH_3 features, at 2.2 and $2.0 \mu\text{m}$, that most ammonia is retained in the monohydrate after warming, whereas in the non-stoichiometric mixture, the fraction of NH_3 has almost vanished. This fact, which was

already appreciated by Moore et al [6], reveals the larger strength of the ammonia-water bondings in the monohydrate. Water, on its side, undergoes a crystallization process during the warming, evidenced by the appearance of the $1.65 \mu\text{m}$ peak in the bottom panel.

Other results of this investigation will be presented at the meeting, where emphasis will be placed upon the astrophysical relevance of this work.

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References

- [1] Brown, M.E. and Calvin, W.M., *Science*, 287, 107, 2000.
- [2] Emery, J.P. et al, *A&A*, 435, 353, 2005.
- [3] Newman, S.F., et al., *Icarus*, 193, 397, 2008.
- [4] Zheng, W., Jewit, D., and Kaiser, R.I., *Ap. J. Sup. Series*, 181, 53-61, 2009.
- [5] Holt, J.S., Sadoskas, D., and Pursell, C.J., *J. Chem. Phys.*, 120, 7153, 2004.
- [6] Moore, M.H. et al., *Icarus*, 190, 260, 2007.
- [7] Maté, B. et al., *J. Phys. Chem. B*, 107, 11098, 2003.
- [8] Gálvez, O., Maté, B., Herrero, V.J. and Escribano, R., *Astrophys. J.*, 703, 2101, 2009.