Direct Evidence For Ammonium Ion Formation in Ice Through Ultraviolet-induced Acid–base Reaction of NH_3 With H_3O^+

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➢ Introduction…

- Astronomical observations obtained in Orion with the infrared spectrometer on the *Spizer Space Telescope* confirmed that the 6.85 μm band can be observed

- Several studies have been carried out to elucidate the origin of the band, and various classes of compounds have been proposed as candidates, such as saturated hydrocarbons, CH_3OH, HCHO, NH_4^+, and inorganic compounds such as carbonate and calcium oxide

- NH_4^+ has recently come under careful consideration as a contributor to the observed 6.85 μm band

- Warming up the photolyzed products formed through UV photolysis of astrophysical ice analogs consisting of different mixing ratios for H_2O, CO_2, NH_3, O_2; the NH_4^+ ν_4 band shows a pronounced redshift from ~6.76 μm to ~7.04 μm with an increase in intensity of a factor of 2, which results in a better match to the interstellar 6.85 μm band

- UV photolysis of ice generates H_3O^+ as protonic defects in the lattice; H_3O^+ may have the important role of providing a proton to NH_3, which could result in the formation of NH_4^+ in interstellar ice in the absence of acids such as HNCO and HCOOH

- **In this paper…**

- Direct evidence for ammonium ion (NH_4^+) formation through ultraviolet (UV) photolysis of NH_3–H_2O mixture ice that does not contain acid

- NH_4^+ forms by the reaction of NH_3 with protonic defects (H_3O^+) in the UV-photolyzed ice

- H_3O^+ may play an important role in the acid–base chemistry of interstellar ice in UV-irradiating environments

- IR absorption results suggest that NH_4^+ is a potential contributor to the interstellar 6.85 μm band but is not a dominant component

➢ Experimental…

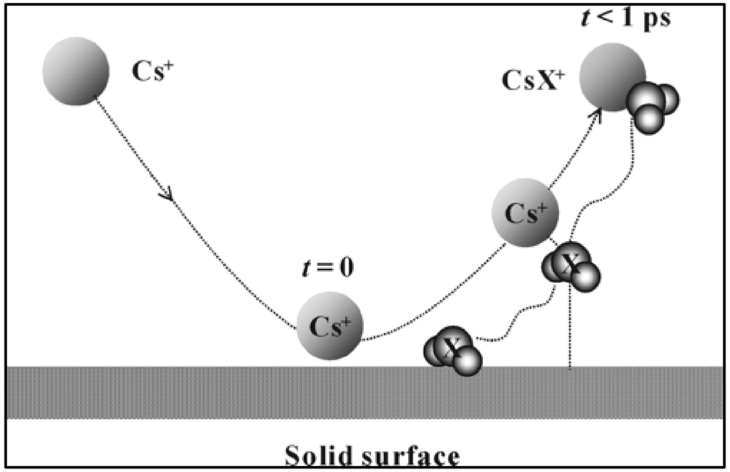
a. *RIS and LES Measurements*

- ❖ Reactive ion scattering (RIS) and low-energy sputtering (LES) experiments were carried out using an ultrahigh vacuum chamber (base pressure 1 10^{-10} torr) equipped with instruments for RIS, LES, and temperature programmed desorption

- ❖ Ice samples for RIS and LES experiments were grown on a Ru(0001) substrate surface by the backfilling method at an H_2O partial pressure of 1 10^{-8} torr

- ❖ The ice samples were prepared to have typical thicknesses of 5 monolayers, as measured by TPD

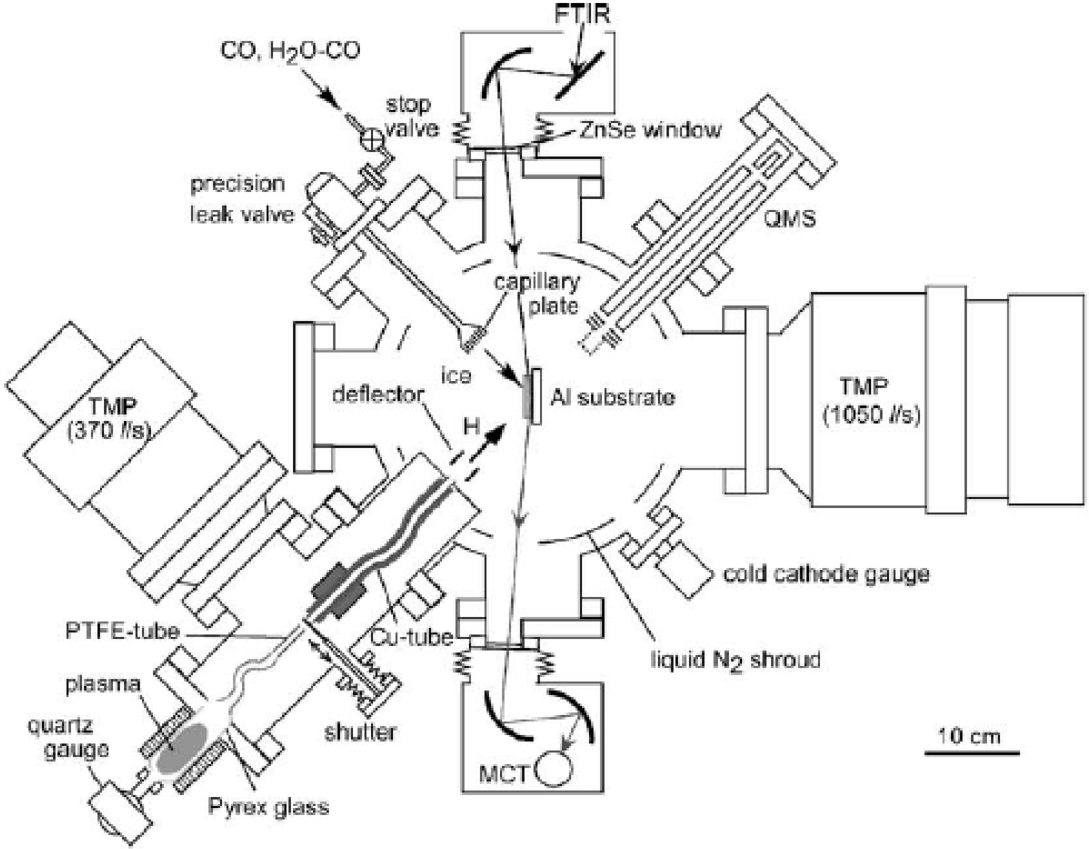
- ❖ A radio frequency (RF)-powered Kr lamp was adopted as the UV light source



H Kang, *Acc. Chem. Res*. **2005**, *38*, 893

b. FTIR Measurement

- Sample solids were created on an Al substrate(was maintained at 10 or 70 K during each experi-ment) by vapor depo-sition of NH_3–H_2O mixed gases (1:1) through a capillary plate located approximately 5 cm from the substrate
- Thickness of the mixed ice was approximately 20 MLs
- The UV photon source was a deuterium (D_2) lamp with an MgF_2 window



Schematic representation of ASURA experimental apparatus: top view

N. Watanabe *et al*. *Planet. Space Sci*. **2006**, *54*, 1107

Result and discussion…

a. RIS and LES Measurements

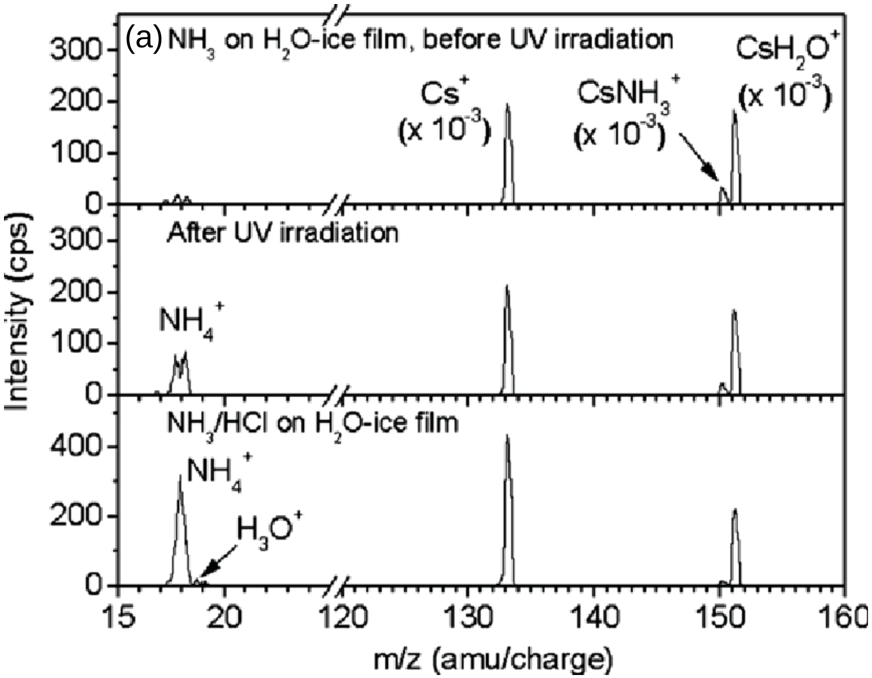


Figure 1. (a) RIS and LES spectra taken from a sample with NH_3 adsorbates (0.14 ML) on an H_2 O–ice film. (b) Spectrum after (0.14 ML) on an H_2 O–ice film. (c) Spectrum from an H_2 O–ice film with HCl (0.1 ML) and NH_3 (0.1 ML) adsorbates without UV exposure. The sample temperature was maintained at 67 K during the adsorption of NH_3, UV irradiation, and surface analysis. The Cs^+ beam energy was 30 eV.

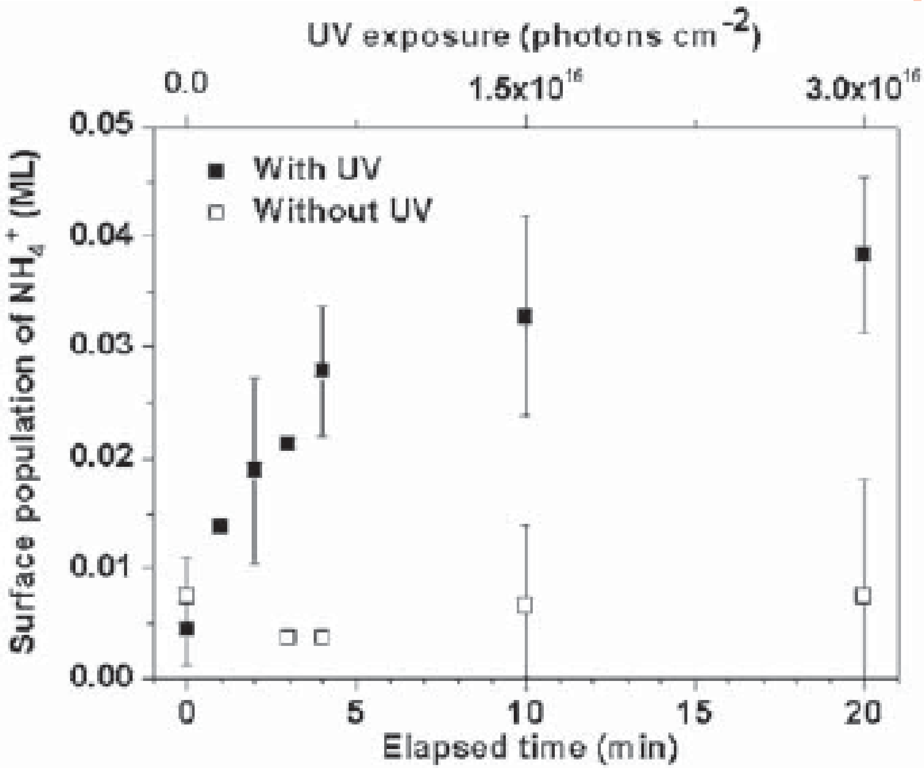


Figure 2. NH_4 $^+$ formation progress as a function of UV exposure. The sample was prepared to have the same structure as that used for Figures 1(a) and (b), with NH_3 adsorbed on an H_2 O film. Without UV exposure, the NH_4 $^+$ intensity was weak and did not increase over the same amount of elapsed time ($_3$). The error bars indicate the fluctuations in NH_4 $^+$ population measured from repeated experiments. Cs^+ energy was 30 eV.

b. FTIR measurement

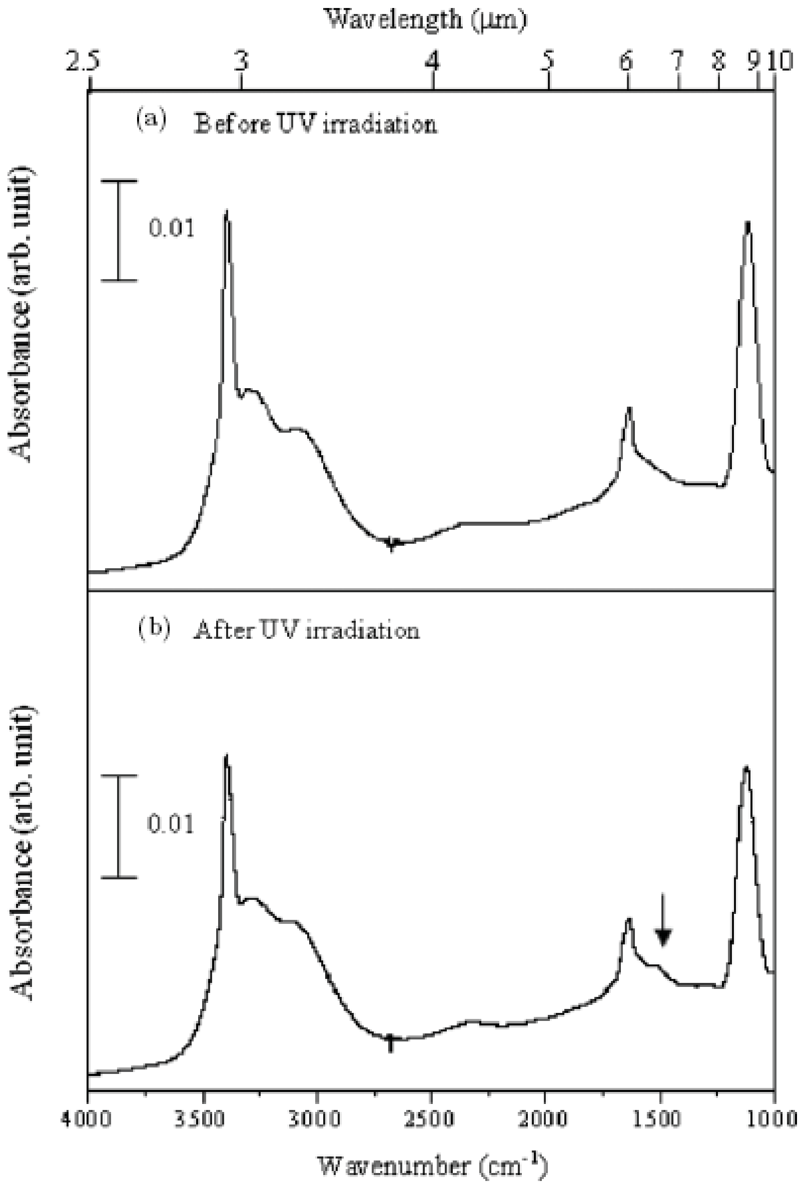


Figure 3. IR spectra of (a) an NH_3 –H_2 O (1:1 mixture) ice film vapor-deposited at 10 K and (b) the ice film irradiated with UV light for 120 minutes at 10 K. The arrow indicates the v_4 band of $NH_4{}^+$ produced by UV photolysis.

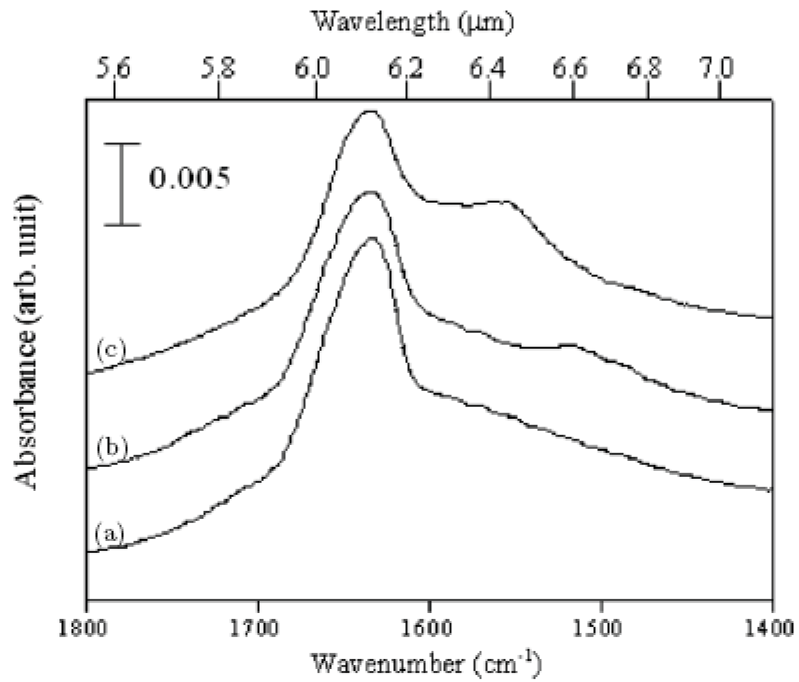


Figure 4. IR spectra of an NH_3 –H_2 O (1:1) mixed ice (a) before and (b) after UV irradiation for 120 minutes at 10 K. (c) Spectrum after warming the sample in (b) at 130 K.

c. Mechanism and Efficiency of NH_4^+ Formation

- NH_4^+ formation in NH_3–H_2O ice samples is considered to occur via acid–base reaction between H_3O^+ and NH_3 as UV photolysis of H_2O–ice generates H_3O^+ as protonic defects in the lattice

- Proton transfers occur via a proton-tunneling mechanism along the hydrogen bonding network of the ice lattice; therefore, they can occur even at low temperatures

- Photogenerated NH_4^+ disappears upon warming of the ice sample to ∼100 K

- NH_4^+ is transformed back to NH_3 by donating a proton to OH^- ions or OH radical species in the ice

- The high temperature condition also enhances the solvation efficiency of NH_3 by water molecules, which leads to the formation of ammonia hydrates; this is indicated by the appearance of the absorption feature at 1550 cm^{-1} in Figure 4.

Summary

- Ammonium ions (NH_4^+) have been previously proposed as a candidate for the interstellar 6.85 μm band
- This study shows that NH_4^+ can be formed by UV processing of a simple binary mixture of NH_3 and H_2O
- Another implication of the observations in this study is that H_3O^+ may act as an acid in "invisible" interstellar ice in UV-irradiating environments
- Although NH_4^+ is a possible contributor to the interstellar 6.85 μm band, it may not be the major component
- No complete match to the 6.85 μm band by any single component has yet been established in laboratory experiments
- Complex mixing of candidate species such as NH_4^+, CH_3OH, hydrocarbons, and inorganic compounds may be able to explain the peak position and intensity of the interstellar 6.85 μm band
- Investigations are required to better match the IR spectrum between laboratory and interstellar 6.85 μm bands.

THANK YOU