

PHOTODESORPTION AND PRODUCT FORMATION IN UV-IRRADIATED N₂ AND NH₃ ICES UNDER ULTRA-HIGH-VACUUM CONDITIONS

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Abstract. The accretion and desorption processes of gas molecules on cold grains play an important role in the evolution of dense clouds and circumstellar regions around YSOs. Given the low temperatures in dark cloud interiors (10–20 K), thermal desorption is negligible and most molecules are expected to stick to grains leading to depletion in the gas phase. Laboratory simulations of these processes under astrophysically relevant conditions are required for their understanding. The use of ultra-high-vacuum conditions minimalizes contamination by background water accretion. This introduces a radical improvement, allowing the study of photodesorption and the detection of products at very low abundances in a water-free ice matrix. We studied UV-photoprocessing of pure NH₃ and N₂ ices under ultra-high-vacuum conditions using the Interstellar Astrochemistry Chamber. The photodesorbed molecules, and the volatile products released upon photolysis and warm-up, were detected in situ by quadrupole mass spectroscopy.

1 Introduction

Laboratory simulations of dust processes in the interstellar medium can be seen as a bridge between theoretical studies and observational data. It helps us to understand what is really going on in space, but it also raises new questions.

Two qualitatively different types of ice mantle are expected to be present in dense clouds: one dominated by polar H-bonded molecules, and another one dominated by non-polar, or only slightly polar, highly unsaturated molecules. This is governed by the H/H₂ ratio, and in regions where this ratio is large species like NH₃ and H₂O are expected to dominate but when this ratio is much lower than unity molecules like N₂ and CO are abundant.

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Ammonia was one of the first polyatomic molecules detected in space (Cheung *et al.* 1968). In our solar system, it has been observed in the gas phase in Jupiter, Saturn, Uranus and Neptune. Molecular nitrogen is very difficult to detect in the infrared (IR) because it has no dipole moment. It was however observed in Triton and Pluto as a main component of their surfaces (Cruikshank *et al.* 1993).

The InterStellar Astrochemistry Chamber (ISAC) was designed for the study of solids (ice mantles, organics, and silicates) in simulated interstellar conditions: through characterization of their physico-chemical properties and monitoring of their evolution due to vacuum-UV irradiation and thermal processing. See Muñoz Caro *et al.* (2010) for a description of ISAC. The UV source is a microwave stimulated hydrogen flow discharge lamp (flux of $\sim 2.5 \times 10^{14}$ photons $\text{cm}^{-2} \text{s}^{-1}$, $E_{\text{photon}} = 7.3 - 10.5$ eV). The solid N_2 and NH_3 samples were deposited at 8 K. Their evolution during UV-irradiation and subsequent warm up was monitored using transmittance FTIR, and quadrupole mass spectroscopy (QMS). Here we only report the QMS data analysis.

2 Photodesorption and products formed by UV-irradiation

2.1 Irradiation of N_2

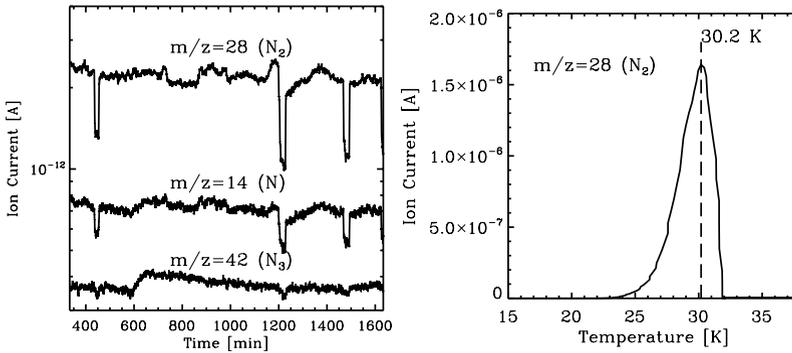


Fig. 1. *Left:* photo-desorption of N_2 corresponding to $m/z = 28$, 14 (N) and 42 (N_3) monitored by QMS. Turn on and turn off of the UV-lamp leads to a rising and fast decrease of the partial pressure. *Right:* TPD curve of irradiated N_2 ice.

The thickness of deposited N_2 ice, measured using the fringes method in the infrared spectrum, was $0.9 \mu\text{m}$. The ice was irradiated for 1362 minutes. The sample was warmed up with a heating rate of 1 K/min up to its sublimation temperature at ~ 30 K. The mass spectrum of N_2 during deposition was measured with the QMS. The main mass fragment was $m/z = 28$ (N_2), and $m/z = 14$ (N) represents only 5.1% of the total $m/z = 28$ due to fragmentation of N_2 in the filament of the QMS. The left panel of Figure 1 shows the different intervals where the UV-lamp was turned on, partial gas pressure increases, and later when turned

off, it decreases rapidly. It was observed that N_2 ($m/z = 28$) photo-desorbs when the UV-lamp is on.

The intensity of $m/z = 14$ (N) during irradiation is about 16% relative to that of $m/z = 28$ (N_2). This value is well above 5.1% for $m/z = 14$ measured during the deposition of N_2 . There is therefore also photo-desorption of atomic N. The azide radical N_3 ($m/z = 42$) also photo-desorbs.

The most energetic photons emitted by our H_2 -lamp, Ly- α (10.2 eV), are insufficient to dissociate N_2 . Dissociation is thus inefficient and occurs via $N_2 + N_2^* \rightarrow N_3 + N$. This reaction explains the observed photo-desorption of N_3 and N. The right panel of Figure 1 presents the temperature programmed desorption (TPD) curve of irradiated N_2 ice. The maximum of the thermal-desorption occurs at 30 K.

2.2 Irradiation of NH_3

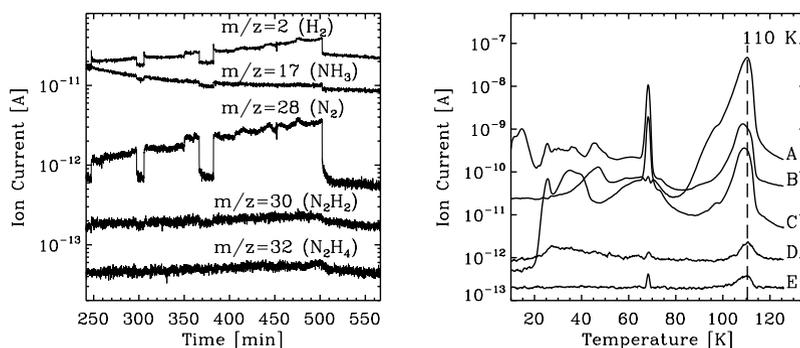


Fig. 2. *Left:* photo-desorption of NH_3 monitored by QMS. Turn on and turn off of the UV-lamp leads to a rising and fast decrease of the partial pressure. *Right:* TPD curves of irradiated NH_3 ice and its photo-products, where A is the TPD curve of $m/z = 17$ (NH_3), B is $m/z = 2$ (H_2), C is $m/z = 28$ (N_2), D is $m/z = 32$ (N_2H_4), and E is $m/z = 30$ (N_2H_2). The TPD curves were offset for clarity.

The same experimental protocol used for N_2 was employed for NH_3 . After deposition of NH_3 ice, it was UV-irradiated and then warmed up. The mass spectrum of NH_3 was measured by QMS during deposition. The main mass fragment was $m/z = 17$ followed by $m/z = 16$ (87.7% relative to $m/z = 17$), $m/z = 15$ (4.95%) and $m/z = 14$ (1.51%). The left panel of Figure 2 shows the effect of UV-irradiation of the sample as a function of irradiation time. Desorption of $m/z = 17$ (NH_3), $m/z = 2$ (H_2), $m/z = 28$ (N_2), $m/z = 30$ (N_2H_2), and $m/z = 32$ (N_2H_4) was observed. H_2 and N_2 are the main products while N_2H_2 and N_2H_4 are secondary products because it is easy to photo-dissociate the N-H bonds of NH_3 . The photo-desorption rate of H_2 and N_2 increases during irradiation. There is an excess in the $m/z = 17$ intensity which means that photodesorption is taking

place. The right panel of Figure 2 shows the sublimation temperature of NH_3 and the co-desorption of the different products near 110 K.

3 Conclusions

UV-irradiation of pure N_2 ice leads to formation of N and N_3 , and a fraction of these species photo-desorb. The main irradiation products of NH_3 ice are H_2 and N_2 , and the less abundant products are N_2H_2 and N_2H_4 . We could detect the photodesorption of these molecules. Future work will be aimed at the quantification of these results and comparison with infrared spectroscopic data of the ice.

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