THE NITROGEN CHEMISTRY OF TITAN'S UPPER ATMOSPHERE REVEALED

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ABSTRACT

Titan's atmosphere is unique because dissociation of N_2 and CH_4, the primary atmospheric constituents, provides the H, C, and N atoms necessary for the synthesis of complex organic molecules. The first steps in the synthesis of organic molecules occur in the upper atmosphere where energetic photons and electrons dissociate N_2 and CH_4. We determine the abundance of a suite of nitrogen-bearing molecules in Titan's upper atmosphere through analysis of measurements of the ionospheric composition made by the Ion Neutral Mass Spectrometer (INMS) on the *Cassini* spacecraft. We show that the density of ions in Titan's upper atmosphere depends closely on the composition of the neutral atmosphere and that, for many species, measurement of associated ions coupled with simple chemical models provides the most sensitive determination of their abundance. With this technique we determine the densities of C_2H_4, C_4H_2, HCN, HC_3N, CH_3CN, NH_3, C_2H_3CN, C_2H_5CN, and CH_2NH. The latter four species have not previously been detected in the gas phase on Titan, and none of these species have been accurately measured in the upper atmosphere. The presence of these species implies that nitrogen chemistry on Titan is more extensive than previously realized.

Subject headings: astrochemistry — planets and satellites: individual (Titan)

1. INTRODUCTION

The composition of the upper atmosphere is crucial to a complete understanding of Titan chemistry. Photocatalytic processes in the stratosphere dissociate CH_4 (Yung et al. 1984; Toublanc et al. 1995; Lara et al. 1996; Lebonnois et al. 2001), but energetic electrons and solar extreme-ultraviolet (EUV) radiation dissociate or dissociatively ionize N_2 primarily in the upper atmosphere above ~1000 km (Fox & Yelle 1997; Keller et al. 1998; Banaszkiewicz et al. 2000). Although they may have a complicated history, the N atoms contained in complex organic molecules on Titan are ultimately derived from this dissociation of N_2. It follows that the highest abundance of nitrogen-bearing molecules should be found in the upper atmosphere and that determination of the density of these species is necessary to an understanding of nitrogen chemistry at all levels of the atmosphere.

2. INMS OBSERVATIONS

2.1. *Description*

On 2005 April 16 the *Cassini* spacecraft penetrated deeply into the upper atmosphere of Titan, reaching an altitude of 1027 km. The closest approach point occurred at N74° latitude and 23:09 local time. During this encounter the Ion Neutral Mass Spectrometer (INMS) was configured to measure both neutral and ionized species. Ion measurements were conducted on the outbound leg of the trajectory in complete darkness. A robust ionosphere was detected, due exclusively to precipitating magnetospheric electrons (Cravens et al. 2006). Further description of the observations and some preliminary deductions have been presented elsewhere (Cravens et al. 2006). Here we analyze the composition of the ionosphere to identify the ion species and constrain the composition of the neutral atmosphere. Although data were collected up to mass-to-charge ratios $m/z = 100$, we confine our analysis to $m/z < 60$ because information on the chemistry of heavier species is too limited to permit useful analysis.

2.2. *Ion Identification*

Magnetospheric electrons ionize Titan's main atmospheric constituents, N_2 and CH_4, to form the primary ions N_x^+ ($x = 1, 2$) and CH_y^+ ($y = 1$–4), with a maximum rate near 1100 km (Fox & Yelle 1997; Keller et al. 1998). These initial ions quickly react with minor species in the neutral atmosphere. The atmospheric density near 1100 km is too low for 3-body association reactions to occur, and the dominant reactions are proton exchange between ions and neutrals. Essentially protons flow through the molecular species, ending on molecules with the largest proton affinity (PA). Thus, the stable ions are mostly protonated neutrals (closed-shell ions). Radical cations should have a low abundance because they are difficult to produce and are lost quickly through reactions with the main hydrocarbon species. Protonated closed-shell hydrocarbons have odd masses ($C_xH_y + H^+$, where y is an even integer), while ions containing a single N atom have even masses ($C_xH_yN + H^+$, where y is an odd integer). Previous models for Titan's ionosphere (Fox & Yelle 1997; Keller et al. 1998; Banaszkiewicz et al. 2000; Wilson & Atreya 2004) have been based on models for the neutral chemistry that included few nitrogen-bearing molecules of significant density, except for HCN (Yung et al. 1984; Toublanc et al. 1995; Lara et al. 1996). The predicted ionosphere consists mostly of hydrocarbons, such as CH_5^+ ($CH_4 + H^+$), $C_2H_5^+$ ($C_2H_4 + H^+$), $C_3H_3^+$, and $HCNH^+$ ($HCN + H^+$) (Keller et al. 1998). Consequently, the ion mass spectra predicted by pre-*Cassini* models have high-density odd masses, corresponding to hydrocarbon ions, alternating with absent or low-density even masses, corresponding to single nitrogen containing ions, with the single exception of $HCNH^+$ (Keller et al. 1998).

Figure 1 shows that the INMS spectrum is quite different. The most surprising feature of the spectrum is the richness of the ion population. Odd and even masses are equally represented, and the spectrum does not show the anticipated pattern of high-density odd masses and low-density even masses. The density of ions at $m/z = 18$, 30, 42, 54, and 56, for example, is quite striking compared with predictions based primarily on
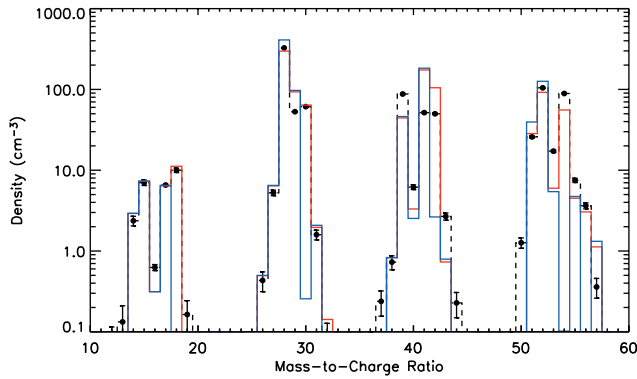
Fig. 1.—INMS mass spectra and models. The black dots represent the average spectrum measured by INMS on the 2005 April 16 flyby (T5) between the altitudes of 1027 and 1200 km, and the dashed line connects the points. Error bars reflecting the uncertainty due to counting statistics are included with the points but are smaller than the symbol size for larger densities. There is also a systematic error of ~20% uncertainty due to calibration uncertainties. The red solid line represents the modeled spectrum with densities of selected neutral species tuned to reproduce the observations. The blue solid line shows the same model calculation but with the mole fraction of NH_3, CH_2NH, CH_3CN, C_2H_3CN, and C_2H_5CN set to zero. These are the neutrals whose importance was not recognized in pre-*Cassini* models, and the resulting ion spectrum is similar to these previous results (Keller et al. 1998).

TABLE 1
PROTON AFFINITY (HUNTER & LIAS 1998), NEUTRAL MOLE FRACTIONS FROM THE WILSON & ATREYA (2004) PHOTOCHEMICAL MODEL, AND NEUTRAL MOLE FRACTIONS USED IN THIS MODEL

		MOLE FRACTION	
SPECIES	PROTON AFFINITY (kJ mol^{-1})	Wilson & Atreya (2004)	This Model
H_2	422.3	1.9×10^{-3}	4×10^{-3}
CH_4	543.5	$(4-10) \times 10^{-2}$	3×10^{-2}
C_2H_2	641.4	$(2-20) \times 10^{-4}$	3×10^{-4}
C_2H_4	680.5	$(0.6-3) \times 10^{-3}$	6×10^{-3}
C_2H_6	596.3	$(0.1-10) \times 10^{-4}$	1×10^{-4}
C_4H_2	737.2	$(0.1-1) \times 10^{-5}$	6×10^{-5}
HCN	712.9	$(3-10) \times 10^{-4}$	2×10^{-4}
HC_3N	751.2	$(0.08-0.4) \times 10^{-5}$	2×10^{-5}
CH_3CN	779.2	1×10^{-5}	1×10^{-5}
C_2H_3CN	784.7	0.1×10^{-5}	1×10^{-5}
C_2H_5CN	794.1	...	5×10^{-7}
NH_3	853.6	0.04×10^{-6}	7×10^{-6}
CH_2NH	852.9	...	$<1 \times 10^{-5}$

NOTES.—The mole fractions of CH_4, C_2H_2, C_2H_6, and H_2 are fixed at values determined by INMS neutral measurements on the 2005 April 16 flyby (T5). No major difference in composition was observed from the TA flyby on 2004 October 26 (Waite et al. 2005). The mole fractions of all other species are determined in this work for an altitude of 1100 km. C_2H_4, C_4H_2, HCN, HC_3N, and CH_3CN have previously been detected, while evidence for C_2H_3CN, C_2H_5CN, NH_3, and CH_2NH is first presented in this work.

hydrocarbon chemistry. The fact that the peaks missing from the modeled spectrum are all at even masses strongly suggests that the neutrals associated with these ions contain a single N atom. Titan's atmosphere contains far more nitrogen-bearing molecules than predicted.

In agreement with a preliminary analysis of Titan's ionospheric composition (Cravens et al. 2006), we identify $m/z = 18$ as NH_4^+, created by proton attachment to NH_3. NH_4^+ can be produced by reaction of almost any of the major ion species observed at Titan with NH_3 because of this neutral's high PA (Table 1). Although not previously detected on Titan, NH_3 has been produced in laboratory experiments simulating Titan's conditions (Bernard et al. 2003), and photochemical models predict its presence in the upper atmosphere (Wilson & Atreya 2004), although at a low density. Another possibility for $m/z = 18$ is H_2O^+, but this is highly unlikely. By considering a water input flux from micrometeorites, pre-*Cassini* models predicted the formation of H_2O^+, but with low density (Keller et al. 1998; Banaszkiewicz et al. 2000). Moreover, this ion was accompanied with H_3O^+ ($m/z = 19$) at a density 100 to 1000 higher. The ion at $m/z = 19$ is virtually absent in the measured spectra (Fig. 1), suggesting that it is unlikely that H_2O^+ accounts for any significant density at $m/z = 18$. There are no other ions with $m/z = 18$ formed from cosmically abundant elements; thus, it seems virtually certain that this ion is NH_4^+.

We identify $m/z = 30$ as $CH_2NH_2^+$, created by proton attachment to CH_2NH. Like NH_3, CH_2NH has a high PA (Table 1) and is expected to undergo proton transfer with protonated neutrals with lower PA. CH_2NH is formed in the reaction between $N(^2D)$ and CH_4 (Herron 1999) and has been recently suggested to be the major product in the $NH + CH_3$ reaction (Redondo et al. 2006). N, NH, and CH_3 are abundant in Titan's upper atmosphere, and CH_2NH should be a significant product of the neutral chemistry. The $m/z = 30$ ions could also be attributed to NO^+, formed by the reaction of precipitating O^+ with N_2 (Young et al. 2005). According to the Anicich & McEwan (1997) database, NO^+ does not react with any of the major constituents in Titan's atmosphere, so its main loss process must be electron recom-

bination (Rees 1989). Adopting an electron density of 10^3 cm^{-3}, we calculate that an NO^+ production rate of $\sim 3 \times 10^{-2}$ cm^3 s^{-1} is required to produce the observed $m/z = 30$ density. However, using a CH_4 mole fraction of 2.7% and reaction rates from the literature (Rees 1989), we calculate that O^+ is 60 times more likely to ionize CH_4 than react with N_2, giving a net O^+ production rate of ~ 4. This implies a CH_4 production rate a factor of 50 times larger than that required to explain the densities of the observed hydrocarbon ions, and therefore NO^+ cannot contribute to more than $\sim 2\%$ of $m/z = 30$. The only other possibility for $m/z = 30$ is $C_2H_6^+$, but this radical cation should be quickly destroyed by reactions with C_2H_4.

The identity of ions at $m/z = 28$, 42, and 56 is revealed by the fact that the masses are separated by 14 amu, corresponding to the addition of a $-CH_2$ unit. $HCNH^+$ at $m/z = 28$ was expected as the major ion by the pre-*Cassini* models (Fox & Yelle 1997; Keller et al. 1998; Banaszkiewicz et al. 2000; Wilson & Atreya 2004), and there is little doubt about its identification. $m/z = 42$ and 56 can then legitimately be attributed to CH_3CNH^+ and $C_2H_5CNH^+$, created respectively by proton attachment to CH_3CN and C_2H_5CN. CH_3CN has been previously detected in Titan's upper stratosphere (Marten et al. 2002), and C_2H_5CN has been tentatively identified in the condense phase (Khanna 2005). Finally, $m/z = 54$ is most probably due to $C_2H_3CNH^+$ created by proton attachment to C_2H_3CN. C_2H_3CN has not been detected in Titan's atmosphere but is predicted by neutral chemistry models (Lebonnois et al. 2002; Wilson & Atreya 2004) and has been observed in laboratory simulations (Coll et al. 1999). Other possibilities for $m/z = 42$, 54, and 56 such as hydrocarbon ions ($C_3H_6^+$, $C_4H_4^+$, $C_4H_6^+$) or O-bearing ions ($C_2H_2O^+$, C_3HO^+, $C_3H_3O^+$) are extremely unlikely. These radical cations are very reactive and should be quickly destroyed.

In summary, all of the unidentified ions can be explained through proton attachment to nitrogen-bearing neutral molecules. Other identifications are improbable because they require large densities of radical cations, which are unlikely in a highly reactive environment such as Titan's atmosphere. These conclusions are supported by kinetic models of the ionosphere,

TABLE 2
CALCULATED DENSITIES OF IONS (cm^{-3}) AT 1100 km FOR EACH MASS PEAK

m/z	Species	Density (cm^{-3})	Species	Density (cm^{-3})	Species	Density (cm^{-3})
12	C^+	1.13×10^{-2}	...	...	...	...
13	CH^+	2.98×10^{-2}	...	...	...	...
14	N^+	2.35×10^{0}	CH_2^+	5.72×10^{-1}	...	...
15	NH^+	7.24×10^{-3}	CH_3^+	7.30×10^{0}	...	...
16	CH_4^+	3.11×10^{-1}	NH_2^+	2.16×10^{-3}	...	...
17	CH_5^+	6.40×10^{0}	NH_3^+	9.34×10^{-3}	...	...
18	NH_4^+	1.04×10^{1}	...	...	...	...
25	C_2H^+	4.19×10^{-5}	...	...	...	...
26	$C_2H_2^+$	4.97×10^{-1}	CN^+	2.30×10^{-4}	...	...
27	$C_2H_3^+$	5.95×10^{0}	HCN^+	4.83×10^{-1}	...	...
28	$HCNH^+$	2.76×10^{2}	N_2^+	8.01×10^{0}	$C_2H_4^+$	4.94×10^{0}
29	$C_2H_5^+$	9.18×10^{1}	N_2H^+	2.38×10^{0}	H_3CN^+	4.93×10^{-2}
30	$CH_2NH_2^+$	6.16×10^{1}	...	...	...	...
31	$C_2H_7^+$	1.96×10^{0}	$CH_3NH_2^+$	1.08×10^{-1}	...	...
32	$CH_3NH_3^+$	1.34×10^{-1}	...	...	...	...
36	C_3^+	3.36×10^{-4}	...	...	...	...
37	C_3H^+	4.84×10^{-3}	...	...	...	...
38	C_2N^+	8.26×10^{-1}	$C_3H_2^+$	1.12×10^{-3}	...	...
39	$C_3H_3^+$	3.71×10^{1}	$CHCN^+$	8.04×10^{0}	...	...
40	CH_2CN^+	2.77×10^{0}	$C_3H_4^+$	6.03×10^{-1}	...	...
41	$C_3H_5^+$	1.73×10^{2}	CH_3CN^+	2.96×10^{0}	...	...
42	CH_3CNH^+	1.05×10^{2}	$C_3H_6^+$	4.75×10^{-2}	...	...
43	$C_3H_7^+$	7.25×10^{-1}	$C_2H_3NH_2^+$	2.57×10^{-2}	...	...
44	$C_3H_8^+$	5.43×10^{-4}	...	...	...	...
45	$C_3H_9^+$	1.65×10^{-2}	...	...	...	...
49	C_4H^+	2.29×10^{-6}	...	...	...	...
50	$C_4H_2^+$	1.76×10^{-2}	C_3N^+	2.15×10^{-5}	...	...
51	$C_4H_3^+$	2.76×10^{1}	HC_3N^+	3.11×10^{-2}	...	...
52	HC_3NH^+	9.02×10^{1}	$C_4H_4^+$	3.30×10^{-1}	$C_2N_2^+$	1.43×10^{-2}
53	$C_4H_5^+$	5.14×10^{0}	$HC_2N_2^+$	7.72×10^{-1}	$C_2H_3CN^+$	1.19×10^{-1}
54	$C_2H_3CNH^+$	5.94×10^{1}	$C_4H_6^+$	1.58×10^{-3}	...	...
55	$C_4H_7^+$	4.54×10^{0}	...	...	...	...
56	$C_2H_5CNH^+$	2.96×10^{0}	$C_4H_8^+$	6.24×10^{-5}	...	...
57	$C_4H_9^+$	1.21×10^{0}	...	...	...	...

described below, which further show that the required densities of the nitrogen-bearing species are quite reasonable.

3. CHEMICAL KINETIC MODEL

3.1. *Description*

We use a chemical kinetic model to infer the density of neutral species associated with the ions. The model assumes local chemical equilibrium and adopts atmospheric conditions appropriate for the 1100 km level. The densities of N_2, CH_4, H_2, C_2H_2, and C_2H_6 are fixed in the model at values determined by INMS neutral measurements. The densities of nine other neutrals, including the nitrogen-bearing species of interest here, are also held fixed but at values tuned to produce the observed ion densities. They are listed in Table 1. The relative abundance of the primary ions was calculated for a mixture of N_2 (97.3%) and CH_4 (2.7%) irradiated by 100 eV magnetospheric electrons, as measured by the CAPS instrument (Szego et al. 2005). Residual photoions remaining from daytime is not an issue since ion lifetimes are only ~3000 s, significantly shorter than the time the atmosphere has been in darkness. The magnitude of the ion production was scaled to reproduce the electron density measured by the *Cassini* Langmuir probe, which agrees precisely with the sum of the ion densities measured by INMS (Cravens et al. 2006; Wahlund et al. 2005). The electron temperature was taken as 500 K (Wahlund et al. 2005). The reaction list includes 23 neutral and 103 ion species containing hydrogen, carbon, and nitrogen atoms. Over 800 ion-neutral reaction rates and product branching ratios were retrieved from ion-molecule reaction databases (Anicich & McEwan 1997; Anicich et al. 2006), while electron-ion

recombination rates were compiled from the literature. The calculated densities of ions based on this neutral composition, ionization rate, and our list of reactions and rate constants are given in Table 2. The predicted mass spectrum can then be compared with INMS measurements.

3.2. *Neutral Densities*

The model spectrum shown in Figure 1 demonstrates that the measured densities at $m/z = 18$, 30, 42, 54, and 56 can be reproduced if the neutral atmosphere contains NH_3, CH_2NH, CH_3CN, C_2H_3CN, and C_2H_5CN with the mole fractions given in Table 1. NH_3 has a mole fraction of 7 ppm, whereas the CH_3CN and C_2H_3CN mole fractions are determined to be ~10 ppm. The C_2H_5CN abundance is lower with a mole fraction of 0.5 ppm. A preliminary analysis of Titan's ionospheric composition (Cravens et al. 2006) inferred an abundance for NH_3 of ~1 ppm, by assuming that NH_4^+ is produced by the reaction of all the ion species with NH_3 at a rate equal to that of $HCNH^+$. This provides a lower limit to the abundance, while our calculations may overestimate the NH_3 density because we do not include some heavy ions in our model. The actual mole fraction must lie between 1 and 7 ppm.

Because no information about the ion chemistry of CH_2NH is available in the literature, its reaction rates were assumed similar to that of other nitrogen-containing species. The CH_2NH mole fraction is estimated to be ~10 ppm if $CH_2NH_2^+$ accounts for the total density at $m/z = 30$, but because of the lack of reaction rate data and the possible contribution of NO^+ to $m/z = 30$, the inferred mole fraction of CH_2NH is quite uncertain.

Analysis of the ion spectra with the chemical model also allows us to better constrain the density of some previously detected molecules. The densities of HCN, HC_3N, and C_4H_2 are determined from the density of the $HCNH^+$, HC_3NH^+, and $C_4H_3^+$ ions at $m/z = 28$, 52, and 51. C_2H_4 is constrained primarily by CH_5^+ at $m/z = 17$, because this ion is lost through reactions with C_2H_4.

Mole fractions are probably determined to within a factor of 2–3 by our analysis. Examination of Figure 1 reveals that the models fits the ion densities to better than a factor of about 2. Numerical trials with the chemical model indicate that the ion densities vary linearly with neutral densities. There are other uncertainties related to potential inadequacies of the reaction database, but the overall good agreement suggests that these are small. More accurate determination of densities should follow from a more precise description of the electron flux and improvements to the reaction rate database.

4. DISCUSSION

A surprising conclusion from our analysis is that minor neutral species with mole fractions as small as ~1 ppm have a measurable effect on the ionosphere, making the approach described here the most sensitive method for the study of upper atmosphere composition. Although potentially of comparable sensitivity, INMS neutral measurements are not able to constrain the constituents studied here: C_2H_4 because its primary signature at mass 28 is masked by the much larger signal from N_2, and the other neutral species because of possible adsorption on the walls of the instrument (Waite et al. 2005). UV occultation measurements, which are able to detect species with mole fractions of order 10 ppm, have somewhat lower sensitivity and only for some species. The mole fraction of C_2H_4, HCN, and HC_3N determined in our analysis is in good agreement with the values inferred from the *Voyager 1* solar occultation experiment, although obtained at 100 km lower altitude for the latest two species (Vervack et al. 2004).

The mole fractions derived differ significantly from the predictions of photochemical models for the neutral atmosphere. Wilson & Atreya (2004) calculate a CH_3CN mole fraction in agreement with our value, but their predictions for HC_3N and C_2H_3CN are too low by a factor of ~10 and for NH_3 by a factor of ~250 (Table 1). Other photochemical models (Toublanc et al. 1995; Banaszkiewicz et al. 2000) underestimate the HC_3N mole fraction by a factor of a few, while they predict a CH_3CN mole fraction more than 3 orders of magnitude too small. The poor agreement implies that the models are missing production pathways for these molecules and that more work is required to properly describe the chemistry of these species. A CH_2NH production only ~6 times lower than the HCN production has been calculated (Lara et al. 1996). Unfortunately, its fate after pro-

duction is not followed in this model and its abundance cannot be retrieved. It may be presumed that CH_2NH is lost by photolysis and/or condensation. None of the photochemical models even consider C_2H_5CN since gas-phase production of C_2H_5CN has not been studied. Formation pathways similar to those forming CH_3CN such as insertion of $N(^2D)$ into C_3H_6 can be expected. These reactions will have to be included in future models.

Ground-based microwave spectroscopy provides constraints on the stratospheric abundance of several of the molecules identified here. A mole fraction of 4×10^{-8} at 450 km has been measured for CH_3CN, and upper limits of 2×10^{-9} were retrieved for C_2H_3CN and C_2H_5CN in the lower stratosphere (Hidayat et al. 1997; Marten et al. 2002). These values are 2–3 orders of magnitude smaller than that derived here for the upper atmosphere. This is to be expected as a consequence of production in the upper atmosphere and diffusion to lower altitudes, where species are lost through chemistry and condensation. For example, the HCN mole fraction decreases from $\sim 10^{-4}$ at 900 km (Vervack et al. 2004) to $\sim 10^{-7}$ in the lower stratosphere (Flasar et al. 2005). Large decreases from the upper atmosphere to the stratosphere are expected as well for the species identified here, but the details depend on chemical activity, photolysis rates, and eddy mixing rates and require further investigation. Ion chemistry initiated by Galactic cosmic rays may also contribute to the production of nitrogen-containing molecules in the lower stratosphere (Molina-Cuberos et al. 2002). Because of the large enhancement of mole fractions in the upper atmosphere over the stratosphere, diffusion of these molecules to the region studied here will not be important.

Once they reach lower altitudes, unsaturated species are expected to polymerize and form macromolecules (Lebonnois et al. 2002). NH_3 and HCN have recently been identified as the main pyrolysis products of Titan's aerosols (Israël et al. 2005), indicating the potential presence in the core molecular structure of nitrile groups (-CN), amino groups (-NH_2, -NH-, and -N<), and/or imino groups (-C=N-). This suggests that the molecules that we have identified in the upper atmosphere can be precursors of these aerosols and that knowledge of their abundance is crucial to an understanding of aerosol chemical formation pathways. Further down, the nitrogen-containing gas molecules that did not participate in polymerization processes are expected, because of their high polarity, to condense readily on the aerosols, coating them with a nitrogen-rich ice layer. Finally, the aerosols will accumulate on the surface, modifying the surface appearance and composition.

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