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NITROGEN ION CLUSTERS IN TRITON'S ATMOSPHERE

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Abstract. The formation of nitrogen cluster ions [$N_2^+(N_2)_n$, $N^+(N_2)_n$] should occur easily in Triton's thin cold nitrogen atmosphere. These ions are formed stepwise as:

$$N_2^+ + N_2 \rightarrow N_2^+(N_2) \xrightarrow{+N_2} N_2^+(N_2)_2 \xrightarrow{+N_2} \cdots \xrightarrow{+N_2} N_2^+(N_2)_n$$

At low altitudes, thermodynamics (temperature and pressure) favor cluster sizes up to and including $N_2^+(N_2)_{40}$. Such ions are close to the threshold (critical size) to nucleate, forming a stable nitrogen ice aerosol seen as extended hazes in Voyager images of Triton's limb. The critical ion radius for nucleation is about 8.3 Å. As temperature increases and pressure decreases with altitude, cluster ion formation becomes less favorable and small cluster sizes predominate. At altitudes >200 km, clusters are thermodynamically unstable and only N_2^+ and N^+ are present. Because electron recombination with atomic ions (N^+) is very slow, a dense ionosphere should form where N^+ recombination via N^+ clustering with N_2 is unfavorable. Model calculations yield peak electron concentrations above 200 km, as detected by Voyager radio occultation measurements. The sharp ledge at the bottom of the ionosphere is caused by the onset of rapid electron-ion recombination associated with cluster ion formation.

Introduction

The first close-up images taken by Voyager 2 of Neptune's satellite Triton revealed a thin, hazy atmosphere. Clouds, patches of fog and local atmospheric phenomena such as venting plumes were observed, indicating that weather occurs on this satellite. The atmosphere is made up mostly of nitrogen, with small amounts of methane, as predicted by Cruikshank et al. (1983, 1984) six years earlier, and confirmed by the Voyager UVS experiment (Broadfoot et al. 1989). These hazes and clouds in the atmosphere result from local fluctuations in the thermodynamic state of the atmosphere, which induce nitrogen to nucleate on ions produced by cosmic ray- or magnetospheric particle-induced ionization, or on solid particles ejected by Triton's geysers. This paper describes the nitrogen ion chemistry that controls the ionospheric composition, and may be responsible for the hazes detected by the Voyager spacecraft.

The volatile gases -- in this case N_2 and CH_4 -- will tend toward their vapor pressure equilibria in accordance with the local temperature, which is determined by the radiative balance and dynamics of Triton's atmosphere. The temperature at the surface of Triton was determined to be roughly 37 K (Conrath et al, 1989), giving a nitrogen surface vapor pressure of about 10×10^{-6} bar, and CH_4 pressure of roughly 7×10^{-10} bar. As a result of this ratio of surface pressures, nitrogen dominates the composition, thermodynamics and meteorology of Triton's atmosphere.

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Ion Chemistry

As on Earth, the interaction of cosmic-rays or precipitating magnetospheric particles with nitrogen molecules results in the formation of ions and neutral atoms:

$$N_2 + e^* \rightarrow N_2^+ + e + e$$
$$N_2 + e^* \rightarrow N^+ + N + e + e \qquad (1)$$

The primary ions, N_2^+ and N^+, are transformed into larger ions by clustering with N_2 in a series of steps (Bohme et al., 1969; Headley et al., 1982):

$$N_2^+ + N_2 + M \underset{k_r}{\overset{k_f}{\rightleftharpoons}} N_2^+(N_2) + M$$
$$N_2^+(N_2) + N_2 + M \underset{k_r}{\overset{k_f}{\rightleftharpoons}} N_2^+(N_2)_2 + M \qquad (2)$$
$$N_2^+(N_2)_n + N_2 + M \underset{k_r}{\overset{k_f}{\rightleftharpoons}} N_2^+(N_2)_{n+1} + M$$

(species such as $N_2^+(N_2)_2$ can also be written N_6^+). Each forward clustering reaction step (k_f) has an associated reverse dissociation reaction step (k_r). Hence, the clusters will grow until they reach an equilibrium distribution of sizes, corresponding to the local temperature and pressure, in which cluster formation and thermal dissociation rates are in balance. The resulting distribution of cluster sizes is gaussian-like, with the peak corresponding to the thermodynamically "preferred" cluster size.

The thermodynamics of nitrogen cluster formation is described by Harioka and Nakajima (1988). The enthalpy of formation of N_4^+ from N_2^+ (reaction 1) is very high, 25.8 kcal/mole, and the reaction is strongly favored at low temperatures. The forward rate coefficient is given by Bohme (1969) as 1.9×10^{-29} cm^6/molec^2-sec at 280K; a temperature-dependent rate coefficient, 1.71×10^{-29} $(300/T)^{1.5}$ cm^6/molec^2-sec, was derived from the data of Bohme. Higher-order clusters have a lower enthalpy of formation (for example, 2.76 kcal/mole for the clustering of N_4^+ to N_6^+), but their entropy values remain almost constant from one size to the next. Nevertheless, higher clusters can still easily form at the cold temperatures of Triton's lower atmosphere. The equilibrium constant for each clustering step is given by,

$$K_{2,n}(T) = \frac{k_f}{k_r} = \frac{[N_2^+(N_2)_n]}{[N_2^+(N_2)_{n-1}][N_2]} = \exp\left(\Delta G^o_{2,n} / k_B T\right) \qquad (3)$$

where $K_{2,n}$ is the equilibrium constant for the nth clustering step, [ ] indicates a concentration in molecules/cm^3, ΔG^o is the Gibbs free energy change for the reaction, and k_B is the Boltzmann constant. It follows from Eq. (3) that the preferred cluster size increases with decreasing temperature and increasing nitrogen partial pressure, and thus varies rapidly with altitude.

Clustering reactions with N^+ as the core ion ($K_{1,n}$, n=1,...) yield a series of ions with an odd number of nitrogen atoms -- N_3^+, N_5^+, N_7^+, etc. This series of clusters has a slightly different rate constant for formation (Bohme, 1969), but in general behaves similarly to the N_2^+-based clusters. Recombination of the N^+ series of ions with electrons yields N atoms, which eventually recombine to form N_2. However, as this process is fairly slow, some build-up of N atoms in the Triton atmosphere is expected. In fact, ultraviolet emissions from N^+ as well as N atoms were detected at the top of the atmosphere by the Voyager UVS experiment (Broadfoot et al., 1989).

Forward rate coefficients in each cluster series were assumed to be similar for all clustering steps, being equal to the values of Bohme (1969) for the initial N_2 association reactions with N_2^+ and N^+. The reverse rate coefficients were calculated using the forward rate coefficient and equilibrium constant for each clustering step (see Eq. 3). The equilibrium constants were calculated using the thermodynamic data of Harioka and Nakajima (1989). Large clusters have enthalpies and entropies of reaction, ΔH and ΔS, respectively, that approach the latent heat of condensation and the entropy change, respectively, for condensation of N_2 (Harioka and Nakajima, 1988); the clusters are then acting as liquid surfaces for N_2 condensation. Accordingly, all clusters larger than N_{24}^+ were assigned bulk values for the enthalpy and entropy of formation.

The clustering of N *atoms* with N_2^+ was also included using a rate coefficient of 2.5×10^{-29} cm^6/molec^2-sec at 300 K (Good, 1975). (The reaction was assumed to have a similar temperature-dependence as for clustering reactions of N_2 with ions.) Charge exchange reaction rate coefficients (e.g., for $N + N_2^+ \rightarrow N^+ + N_2$) were taken from Delitsky et al. (1989).

The recombination coefficient for N_2^+ ions with electrons is $3.5\times10^{-7}(300/T)^{0.5}$ cm^3/molec-sec (Krasnopolsky, 1986). All cluster ion-electron recombination reactions were assumed to have a rate coefficient of $3.0\times10^{-6}(300/T)^{0.5}$ cm^3/molec-sec. Atomic ion-electron recombination, occurring at low pressures via photon emission, is at least 10^5 times slower than molecular ion-electron dissociative recombination; the N^+ recombination coefficient is $\sim10^{-12}$ cm^3/molec-sec. Hence, N^+ loss can be dominated by clustering to N_2 followed by electron/cluster-ion recombination ($\sim10^{-6}$ cm^3/molec-sec). Ions remain in the gas phase until they either recombine with electrons or nucleate into haze particles (see below).

The Voyager radio occultation experiment measured an unprecedented electron concentration of about 40,000/cm^3 at the peak in the ionosphere (Tyler et al.,1989), compared with the peak in Titan's ionosphere of about 3000/cm^3. Such a high electron density was unexpected in the thin atmosphere of Triton. The formation of cluster ions at low altitudes, and the accumulation of atomic ions (N^+) at high altitudes where clusters will not form, can explain these observations (see Results).

Ion Nucleation

A neutral gas can nucleate into an aerosol homogeneously when the partial pressure of the gas exceeds the vapor pressure of the condensed phase by a substantial margin (a factor of 2 or more). The gas may also nucleate heterogeneously onto the surfaces of solid particles (which might be injected into the atmosphere by geysers, for example), or onto large cluster ions. Ion nucleation theory is reviewed by Keesee (1989). Generally, the formation of aerosols on ions is aided by the electrostatic interaction between the core ion and the impinging gas molecules; this interaction reduces the free energy of the cluster (see below) and allows the formation of stable embryos. Heterogeneous nucleation of nitrogen above geysers would produce localized hazes. Ion-induced nucleation could occur wherever cluster ions are found, provided the atmosphere is sufficiently supersaturated (perhaps as a result of dynamical forcing). Hence, global haze layers seen in the Voyager Triton images may have their origin in ion nucleation.

The free energy expression for ion-induced nucleation upon a spherical cluster of radius r containing n nitrogen molecules (noting that $n=4/3\pi r^3\rho/m_o$, where ρ is the cluster density and m_o is the molecular mass of nitrogen) is given by,

$$\Delta G(r) = -nk_B T\ln S + 4\pi r^2\sigma + \left(\frac{q^2}{2}\right)\left(1-\frac{1}{\varepsilon}\right)\left(\frac{1}{r}-\frac{1}{r_i}\right) \quad (4)$$

where r_i is the radius of the ionic core of the cluster, with charge q, and ε is the dielectric constant. The first term relates the supersaturation (S), (i.e., the ratio of the vapor partial pressure to the thermodynamic equilibrium vapor pressure over the bulk condensed material) to the free energy, and the second term takes into account the surface tension of the nucleation embryo. Nitrogen has a much lower surface tension (10.5 dyne/cm) than does water (80 dyne/cm); hence, nucleation and particle formation is 'easier' in nitrogen clouds than in water clouds under the same relative conditions of supersaturation (i.e., the positive surface tension term in Eq. 4 is smaller for nitrogen). Since the radius of the cluster is always larger than the ionic core radius, the electrostatic contribution to the free energy is negative, and ion-induced nucleation is favored over homogeneous nucleation.

The ion-induced nucleation rate can be expressed as:

$$J = k_c[N_2]Z(r^*)Z(r_a)N_{ion}\exp\left[\frac{\Delta G(r_a)-\Delta G(r^*)}{k_B T}\right] \quad (5)$$

In this equation, k_c is the collision coefficient for N_2 with ion clusters, r^* is the critical size that a cluster must reach before it can nucleate and grow into a droplet, r_a is the preferred cluster size (i.e., the maximum in the distribution of sizes), $Z(r^*)$ is the Zeldovich factor (which is a correction for the small departure from an equilibrium distribution of cluster sizes due to nucleation of the largest ions), $Z(r_a)$ accounts for the equilibrium distribution of cluster sizes, N_{ion} is the ambient ion concentration, and the exponential term takes into account the difference in free energy between the preferred cluster size and the critical size for nucleation and phase change; if the difference in energies is large, then the ion clusters are not likely to nucleate into growing particles. They will simply add and subtract nitrogen molecules over time to change sizes, and so the cluster distribution will eventually reach a steady state.

Model Inputs and Calculations

Cluster size distributions were calculated with a standard Gear integration package (Gear, 1969). The Gear code is designed to solve a set of stiff chemical kinetic rate equations such as those encountered in ionization problems. The computations were run until equilibrium was achieved, typically within 1×10^5 seconds (~1 day). The model atmosphere used for these calculations has been taken from the Voyager UVS results (Broadfoot et al.,1989). The Triton surface temperature is 37 K, decreasing to a tropopause temperature of 32 K, and then increasing to an exospheric temperature of 95 K above 400 km. Atmospheric nitrogen partial pressures were calculated using the hydrostatic equation with the gravity constant for Triton. Temperature-dependent vapor pressures of nitrogen gas over solid nitrogen were obtained from the *AIP Handbook* (1972).

There are two principal sources of ionization in Triton's atmosphere: charged particles precipitating from Neptune's magnetosphere, and photoionization. The magnetospheric electrons dominate at low altitudes. Analysis of proton and

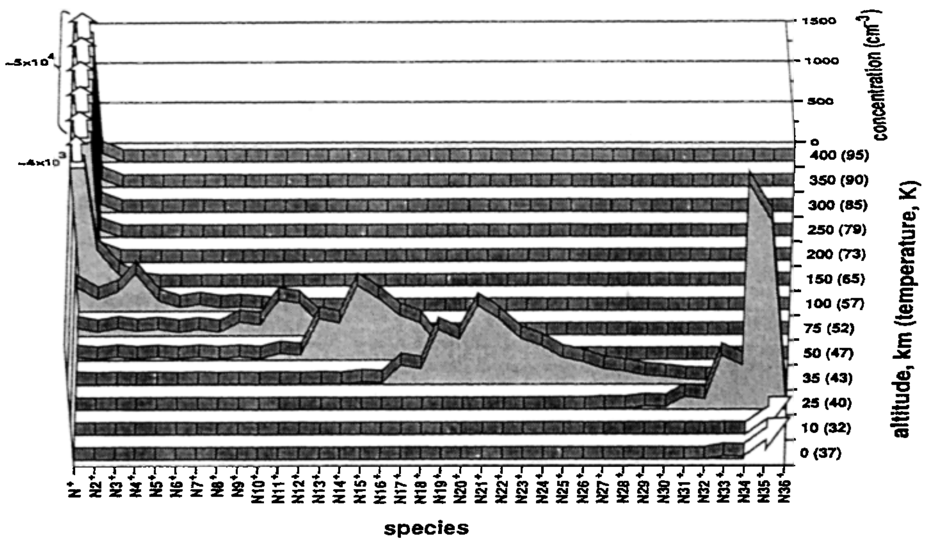

Fig. 1. Variation in nitrogen ion cluster sizes in Triton's atmosphere as a function of altitude. Near Triton's surface, large cluster sizes are favored at the very cold temperatures found there; at 10 km the peak size is roughly at N_{82}^+. The ion size distribution is well-resolved only above about 25 km. As altitude (and temperature) increases, intermediate ion sizes predominate, as is seen between 25 and 100 km. Cluster ion formation is not favored at higher altitudes, leading to large concentrations of N^+ (and an equivalent electron content).

electron spectra from the Voyager LECP experiment [Krimigis et al., 1989] gives an energy input of 7.5×10^{-8} erg/cm^3-sec for the magnetospheric electrons, and 4.1×10^{-9} erg/cm^3-sec for magnetospheric protons at Triton's surface. This yields an approximate ion-electron pair production rate of 1300/cm^3-sec for the electrons and 71/cm^3-sec for the protons (A. Eviatar, personal communication). The ion pair production rate is altitude dependent, and was scaled linearly with pressure.

Energy deposition rates for all other sources of ionization on Triton -- due to solar ultraviolet photolysis, interplanetary electron impact, and cosmic ray bombardment -- were obtained by scaling from the rates on Titan, correcting for differences in atmospheric temperatures, pressures and distances from the sun. The energy deposition rates for Titan are given by Sagan and Thompson (1984). To scale the energy deposition accurately, altiitudes of equivalent nitrogen overburden were calculated for the Titan and Triton atmospheres. The Titan atmosphere used in these calculations was obtained from Lellouch and Hunten (1987). The globally-averaged photoionization rates of Sagan and Thompson (1984) have been multiplied by a factor of four.

Reaction rate data were discussed in an earlier section.

Results

Figure 1 shows the calculated distribution of nitrogen ion cluster sizes as a function of altitude. The clusters are larger near the surface because the temperatures are colder; smaller sizes are more prevalent at higher altitudes because the temperatures are warmer. In the ionosphere, where temperatures are (relatively) high and pressures are low, precluding cluster ion formation, only N^+ and N_2^+ are present. However, N^+ is dominant because its electron recombination coefficient is some 10^{-5} smaller than that of N_2^+.

Calculated ion cluster sizes are plotted in Figure 1 to N_{36}^+ [$\equiv N_2^+(N_2)_{17}$]. At low altitudes, the preferred cluster sizes are larger than N_{36}^+. The peak in the ion size distribution under the conditions prevailing at these lower altitudes can be estimated from thermodynamic relationships given, for example, by Keesee (1989). At low levels of supersaturation, the preferred cluster size is much smaller than the critical cluster size. Hence, essentially no ions reach critical size and the nucleation (particle formation) rate is negligible. As the supersaturation increases, the preferred ion size increases, the number of critical-size clusters increases, and some nucleation can occur (limited by the rate that critical-size ions are formed from smaller clusters). As the preferred size approaches the critical size, essentially all of the ions may nucleate into growing particles; i.e., the thermodynamic barrier to nucleation has been removed.

To determine the radius of the critical-size clusters for ion nucleation, equation (21) from Keesee (1989) was solved. Near the surface of Triton, this cluster radius is around 8.3 Å, which corresponds to an ion cluster N_{82}^+ ($\equiv N_2^+[N_2]_{40}$).

In the range of Triton's surface temperature of 37 K, nitrogen has an extremely steep vapor pressure dependence with temperature. The vapor pressure at 37 K is 1×10^{-5} bar (10 μbar); at 34 K, the pressure is 1×10^{-6} bar, and at 31 K, 1×10^{-7} bar. Accordingly, the local surface temperature on Triton need only drop 2–3 degrees Kelvin for the atmosphere to suddenly achieve a supersaturation of 10. The critical cluster size and preferred cluster size are equal at a supersaturation of about 6.5 (i.e., at a temperature of about 35 K). If an air parcel at the surface of Triton cooled from 37 to 35 K, then the nucleation rate (Eq. 5) would increase from zero (4×10^{-14} particles/cm^3-sec at 36 K) to 5×10^8 particles/cm^3-sec (at 35 K).

The tropopause altitude of ~9 km, with its minimum temperature, is the point where haze particles are most likely to form by ion nucleation. This correlates with the Voyager observation that haze layers occur in the lowest ~10 km of Triton's atmosphere. The eruption of a geyser could generate a local disequilibrium by creating a high nitrogen supersaturation in the vicinity of the stabilizing plume. The nitrogen would then condense on ejected particles, or nucleate onto ions entrained into the plume.

Figure 2 gives the calculated electron concentration as a function of altitude, and compares the theoretical results with Voyager radio occultation measurements (Tyler et al., 1989). The predicted electron concentrations are $\leq 10^3$/cm^3 below 200 km and increase almost two orders of magnitude to 4×10^4/cm^3 near 350 km. The increase is due to the photoionization of N_2 and N, which creates N^+. The N^+ ions recombine very slowly

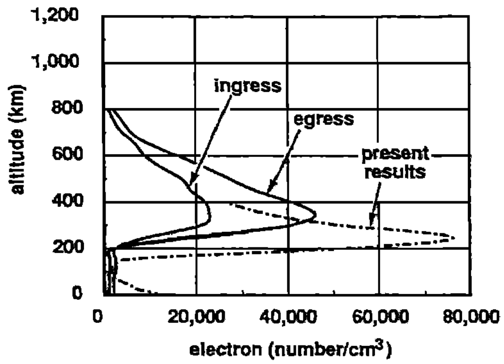

Fig. 2. Calculated versus observed electron density profiles for Triton's atmosphere. Solid curves labeled 'ingress' and 'egress' are from Voyager radio occultation measurements (Tyler et al., 1989). Ingress occultation was on the 'night' side of Triton, egress on the 'day' side. The dotted curve is the calculated electron concentration. The electron content is low at altitudes below 200 km due to the formation of ion clusters and their subsequent efficient electron recombination. Above 200 km, clusters can not form, and atomic ions, N^+, (and electrons) accumulate to form the observed ionosphere.

with electrons, and also very slowly form cluster ions at these altitudes (>200 km), because of the high temperatures and low nitrogen pressures. Accordingly, our model predicts the existence of a dense ionosphere above about 200 km. Small variations in temperature have a great effect on the availablity of cluster ions and, hence, predicted electron concentrations.

The addition of methane reactions into the ion chemistry scheme (using CH_4 concentrations deduced from the UVS experiment) had no effect on the calculated ion composition. Extrapolation of the UVS data yields a CH_4 concentration of about $10^2/cm^3$ at the electron ledge; a concentration of more than $10^6/cm^3$ would be needed to cause N^+ and electron depletion.

The ionosphere is not a simple Chapman layer because the ionization rate does not have a steep cutoff at low altitudes. The sharp ionization ledge at 200 km, observed by Voyager, is associated with the onset of cluster ion formation, which rapidly depletes electrons through electron-ion recombination.

Conclusions

1) Nitrogen cluster ion formation should readily occur in Triton's thin, cold atmosphere. Solar ultraviolet photoionization and magnetospheric particle bombardment create the core ions, N_2^+ and N^+, which accrete nitrogen molecules to form larger ion clusters; e.g., $N_2^+(N_2)_n$ and $N^+(N_2)_n$. These clustered ion species should be dominant below about 200 km in Triton's atmosphere.

2) The very low temperatures of Triton's atmosphere imply that these clustered ions can nucleate into solid nitrogen particles, creating the extended visible hazes recorded in the Voyager images of Triton's limb. Such haze formation is predicted to occur at altitudes below about 10 km where sufficient nitrogen supersaturation is likely to exist. At higher altitudes, cluster ions continue to form but remain gaseous, and no nitrogen hazes are forecast.

3) A model based on the chemical kinetics of nitrogen ions predicts a dense ionosphere at 200–400 km, as detected by Voyager radio occultation measurements. The ionized layer is produced by photoionization at these altitudes, which creates N^+ ions, as observed by the Voyager UVS instrument, that are not depleted effectively either by electron-ion recombination or ion clustering at the high temperatures and low pressures prevailing above 200 km.

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