# Solar Control of the Upper Atmosphere of Triton

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**If the upper atmosphere and ionosphere of Triton are controlled by precipitation of electrons from Neptune's magnetosphere as previously proposed, Triton could have the only ionosphere in the solar system not controlled by solar radiation. However, a new model of Triton's atmosphere, in which only solar radiation is present, predicts a large column of carbon atoms. With an assumed, but reasonable, rate of charge transfer between $N_2^+$ and C, a peak $C^+$ abundance results that is close to the peak electron densities measured by Voyager in Triton's ionosphere. These results suggest that Triton's upper atmospheric chemistry may thus be solar-controlled. Measurement of key reaction rate constants, currently unknown or highly uncertain at Triton's low temperatures, would help to clarify the chemical and physical processes occurring in Triton's atmosphere.**

Ultraviolet spectrometer observations of Triton (1), Neptune's largest satellite, by the Voyager spacecraft detected a thin $N_2$ atmosphere with a trace abundance of $CH_4$. Radio propagation experiments with Voyager's communication link discovered (2) an extensive ionosphere on Triton. This ionosphere was a surprising find because similar experiments with Titan, Saturn's largest satellite, showed no evidence for an ionosphere (3). Photochemical modeling (4, 5) of Triton's atmosphere by several groups suggested that $N^+$, produced by dissociative ionization of $N_2$, is the principal ion present. The proposed ionization source is precipitation of magnetospheric electrons, which occurs when Triton passes through Neptune's magnetic equatorial plane. For these models it was necessary to invoke electron precipitation because photodissociation of $CH_4$ in the first few scale heights of the atmosphere (6) yields an upward flux of $H_2$ that rapidly consumes $N^+$ in the ionosphere. The solar extreme ultraviolet (EUV) flux is insufficient by about an order of magnitude to produce enough $N^+$ to explain the electron densities observed in Triton's ionosphere. If this scenario were true, Triton would be the first planetary body discovered in the solar system whose upper atmospheric chemistry is clearly controlled by a nonsolar source.

To maintain an $N^+$ ionosphere, the energy flux of precipitating electrons required (4, 5) to reproduce the observed peak electron density of $4 \times 10^4$ cm$^{-3}$ is $\sim 10^{-2}$ erg cm$^{-2}$ s$^{-1}$. On the other hand, the temperature gradient observed in Triton's upper atmosphere implies (7) that the downward energy flux from the ionosphere is only $1.1 \times 10^{-3}$ erg cm$^{-2}$ s$^{-1}$. For typical terrestrial heating efficiencies (8) of about 50%, the required influx of magnetospheric electrons produces heating greater by a factor of 5 than is consistent with the thermospheric energy balance on Triton. Although heating efficiencies for the Triton atmosphere may be different from those of the terrestrial atmosphere (9), we explore in this report an alternative photochemical scheme for Triton's ionosphere in which $C^+$ is the principal ion and solar EUV radiation is the dominant ionization source.

A major weakness of the earlier models of Triton's atmosphere was the lack of coupling between C and N chemistry. We therefore developed a comprehensive one-dimensional photochemical model of Triton's atmosphere and ionosphere with 39 neutral and ion species and 193 reactions (10); nitrile and C atom chemistry were included (Table 1). The model extends from the ground to the exobase (~1000 km) and includes vertical transport due to molecular and eddy diffusion. The solar flux that was adopted was for solar maximum conditions (11). Condensation of supersaturated species is accounted for by an approximate method described in (12). A condensation time of $10^6$ s was assumed for all supersaturated species at all altitudes of the model. This value is based on the opacity of hazes observed on Triton's limb (6).

The model predicts that the bulk of solar ionizing radiation (wavelength $\lambda < 1000$ Å) is absorbed above 250 km by the major gas $N_2$. Photolysis of $N_2$ and dissociative recombination of $N_2^+$ with electrons produce N atoms. At longer wavelengths (Lyα to 1450 Å) the photons are absorbed by $CH_4$ near the surface. The downward flux of N atoms from the ionosphere and an upward flux of $CH_4$ photodissociation products combine to produce nitriles primarily by the reactions

$$N + CH_2 \rightarrow HCN + H$$

$$N + CH_3 \rightarrow H_2CN + H$$

The first of these two reactions accounted for 95% of the HCN production in the model. A small amount of nitriles is also produced in ion-molecule reactions. In the upper atmosphere of Triton, HCN readily dissociates to produce CN radicals. In the lower atmosphere, HCN is greatly supersaturated and is eventually lost by condensation to ice. The column-integrated loss rate of HCN in the model was $1 \times 10^7$ cm$^{-2}$ s$^{-1}$, which suggests that HCN may contribute to the coloration of Triton's surface (13). Odd nitrogen is also lost by escape to space. The thermal escape flux of N atoms at the upper boundary of the model was $2 \times 10^7$ cm$^{-2}$ s$^{-1}$; thus, N (probably as $N^+$) is an important constituent of Neptune's magnetosphere (14–16).

Carbon atoms are produced from two species, CN and $CH_4$, primarily in the lowest 100 km of the atmosphere (17, 18). The CN radicals react with N atoms via

$$CN + N \rightarrow C + N_2$$

We assumed that the measured (19) rate constant of $1 \times 10^{-10}$ cm$^3$ s$^{-1}$ at 300 K for this reaction applies on Triton. Photolysis of $CH_4$ produces C atoms with a quantum

**Table 1.** Selected list of reactions for C and nitrile species in the atmosphere of Triton. The units for rate coefficients are per second and centimeters cubed per second for dissociative and two-body reactions, respectively. The photodissociation coefficients refer to globally averaged values at the top of the atmosphere.

| | Reaction | Rate constant | Reference |
|---|---|---|---|
| R1 | $CH_4 + h\nu \rightarrow C(^1D) + 2H_2$ | $4.1 \times 10^{-11}$ | (20) |
| R2 | $C(^1D) + N_2 \rightarrow C + N_2$ | $2 \times 10^{-12}$ | (21) |
| R3 | $CN + N \rightarrow C + N_2$ | $1 \times 10^{-10}$ | (19) |
| R4 | $C + N \rightarrow CN + h\nu$ | $1 \times 10^{-18}$ | Assumed |
| R5 | $C + N_2^+ \rightarrow C^+ + N_2$ | $1 \times 10^{-9}$ | Assumed |
| R6 | $C + h\nu \rightarrow C^+ + e$ | $1.6 \times 10^{-9}$ | (32) |
| R7 | $C^+ + CH_4 \rightarrow C_2H_3^+$ | $1.0 \times 10^{-9}$ | (23) |
| | $C^+ + CH_4 \rightarrow C_2H_2^+ + H_2$ | $3.3 \times 10^{-10}$ | (23) |
| R8 | $C^+ + C_2H_2 \rightarrow C_3H^+ + H$ | $2.2 \times 10^{-9}$ | (23) |
| R9 | $C^+ + HCN \rightarrow C_2N^+ + H$ | $3.4 \times 10^{-9}$ | (23) |
| R10 | $C^+ + e \rightarrow C + h\nu$ | $5 \times 10^{-12}$ | Assumed |

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yield of 0.4% at Lyα (*20*). The C atoms are initially in the $^1D$ electronic state but are rapidly quenched to the ground $^3P$ state by collisions with $N_2$ (*21*). In the upper atmosphere, C atoms are lost primarily by ionization and by escape to space (*22*). Additional losses by radiative association and three-body recombination with N, C, and H atoms occur in the lower atmosphere. Incorporating the above chemistry in the photochemical model results in the vertical distributions of key neutral species shown in Fig. 1. The C atom column abundance in the model was $5 \times 10^{14}$ cm$^{-2}$, which is insufficient to produce an EUV airglow detectable by Voyager.

A significant column of C atoms has important implications for Triton's ionosphere and upper atmosphere. $C^+$ is formed from C by direct photoionization and by charge transfer with $N_2{}^+$ ions in the reaction

$$C + N_2{}^+ \rightarrow C^+ + N_2$$

We have assumed that the rate constant for this reaction is $1 \times 10^{-9}$ cm$^3$ s$^{-1}$, which should be near the upper limit for charge transfer. This reaction is exothermic by 4.3 eV; all other possible products yield endothermic reactions. Because large exothermicity does not necessarily imply that the rate constant for charge transfer between atomic-diatomic species is also large, a measurement of the rate of this reaction is needed. In a photochemical model in which solar radiation is the only source of ionization and in which the solar flux is diurnally averaged, a peak $C^+$ density of $3 \times 10^4$ cm$^{-3}$ was produced at an altitude of 250 km.

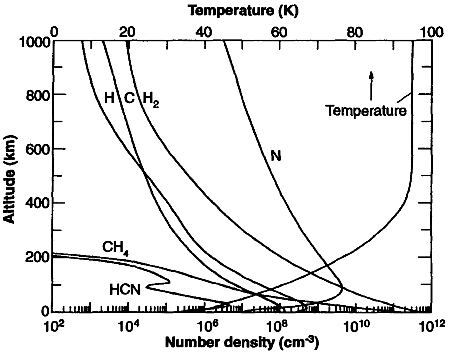

**Fig. 1.** Number densities of the key neutral species in the model. The model temperature profile is shown on the upper scale (*5*). The density profile for the principal atmospheric species $N_2$ is not shown here but is given in (*5*). In the model, $N_2$ has a surface density of $3.3 \times 10^{15}$ cm$^{-3}$. Other significant species not shown include $CH_2$, $C_2H_2$, $C_2H_4$, and $C_2H_6$ (*6*).

As the length of a day on Triton is only $5 \times 10^5$ s, and the molecular diffusion time constant at 200 km is $H^2/D \approx 1 \times 10^7$ s (for scale height $H \approx 65$ km and molecular diffusion coefficient $D \approx 6 \times 10^6$ cm$^2$ s$^{-1}$), we do not expect the present ionosphere to exhibit a large diurnal variation. Because reaction of $C^+$ with $H_2$ is extremely slow (*23*) ($<1 \times 10^{-15}$ cm$^3$ s$^{-1}$), $C^+$ ions are lost primarily by reacting with $CH_4$ (R7 in Table 1) in the bottom side of the ionosphere, and the resulting products consist of molecular ions that are rapidly lost by dissociative recombination (Fig. 2). On the top side, above the peak, $C^+$ is consumed slowly by radiative recombination (R10).

To address uncertainties in the production of $C^+$ in the model, we performed sensitivity studies of key reaction rates and possible additional loss mechanisms for C atoms. The calculated peak $C^+$ density was roughly linearly dependent on the assumed value for the rate constant of reaction R5 and the integrated solar flux below 1000 Å. Decreasing the rate of reaction R3 by a factor of 2 had a negligible effect on the peak $C^+$ density; decreasing the rate by a factor of 100 yielded a peak $C^+$ density of $3 \times 10^{-3}$ cm$^{-3}$. At Triton's low temperatures ($\approx$50 K) a reduction in the rate by a factor of 100 corresponds to an activation energy of about 300 K. Thus, even a moderate activation barrier for reaction R3 will have a significant impact on the model. Scavenging of atomic species (N, H, and C) by aerosol particles (*24*) and three-body recombination of C atoms with $N_2$ (*25–27*) may also affect the C atom profile but will not alter the model prediction that $C^+$ is the dominant ion.

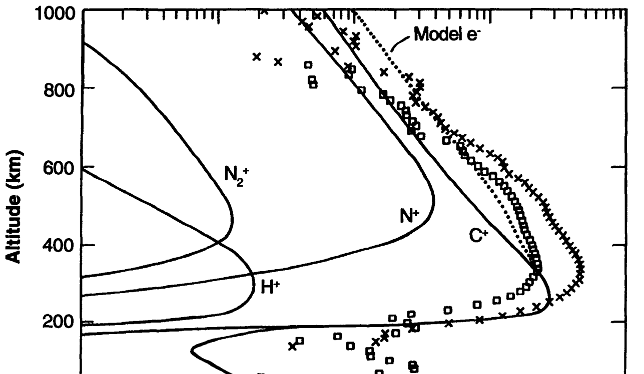

**Fig. 2.** Ion and electron densities computed in the model. The measured electron density profile for Triton's summer and winter hemispheres are from the Voyager radio occultation experiment (*2*). The squares and crosses are data from ingress (winter) and egress (summer) observations, respectively. The uncertainty in the data is $\pm 2.3 \times 10^3$ cm$^{-3}$.

An increase in the $CH_4$ abundance in the ionosphere could cause the dominant ion to switch from $C^+$ to $N^+$ or a molecular ion. The lower peak electron density ($2 \times 10^4$ cm$^{-3}$) observed by Voyager in the winter hemisphere may be a result of the higher $CH_4$ abundance in the winter hemisphere (*1*). The reduced rate of photodissociation of $CH_4$ on Triton's nightside (*6*) or a meridional flow from the summer to winter hemisphere may produce the larger winter $CH_4$ abundance. Uncovering of buried $CH_4$ ice or gas release associated with vigorous geyser activity could also lead to an increase in $CH_4$ levels. Thus, Triton's ionosphere may be dependent on events at the surface. Furthermore, if large seasonal variations in Triton's atmosphere occur as a result of Triton's unusual orbital parameters (*28*), the $CH_4$ mixing ratio could vary by as much as an order of magnitude on decadal time scales. Because of the sensitivity of the $C^+$ ionosphere to $CH_4$ abundance, we do not expect that Titan, the largest moon of Saturn, for which $CH_4$ makes up 8% of the upper atmosphere (*29*), would have comparably high concentrations of $C^+$ in the ionosphere. Indeed, the presence of an ionosphere on Titan could not be detected (*3*). We expect that Pluto also lacks a large ionosphere because the $CH_4$ fractional abundance is comparable to or greater than that of Titan (*30*).

We have shown that the peak ionization observed in the Triton atmosphere can be sustained by solar EUV even at a distance of 30 astronomical units from the sun. However, these results do not preclude the occurrence of some precipitation. The globally averaged solar EUV flux incident on Triton is $\approx 1 \times 10^{-3}$ erg cm$^{-2}$ s$^{-1}$, which is too small by about a factor of 2 to account for the observed thermospheric temperature, for a heating efficiency of 50%. This comparison suggests that electron impact, at a much lower level than previously suggested, may be important in Triton's atmosphere or that another source of heating is present in Triton's upper atmosphere.

The low temperatures in Triton's atmosphere present a considerable challenge to photochemical modeling. In order to elucidate the physics and chemistry of the upper atmosphere and ionosphere, measurements of the assumed rate coefficients for reactions in Table 1 are needed. Low temperatures and strong coupling of neutral and ion processes make photochemical modeling of Triton's atmosphere similar, in spirit at least, to modeling of chemical processes in comets and interstellar molecular clouds (*31*).

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25. Early measurements of three-body reactions of C atoms with $N_2$ to produce CNN and with $H_2$ to produce $CH_2$ have been made (*26*) at 300 K. We are not aware of data regarding the electronic structure of CNN, so we assumed that C simply attaches to $N_2$ without disturbing the $N_2$ triple bond. In trial model runs we then assumed that loss of CNN occurs by photolysis (rate $\sim 5 \times 10^{-4}$ $s^{-1}$) to yield C and $N_2$, and by reaction with N and H atoms (rates $\sim 1 \times 10^{-10}$ $cm^3$ $s^{-1}$) to yield CN, CH, and $N_2$. The resulting column abundance of C atoms in the model was reduced by an order of magnitude, and the peak $C^+$ density decreased to about $7 \times 10^3$ $cm^{-3}$. However, it must be emphasized that the lack of laboratory data on gas-phase CNN makes this result highly uncertain; most likely, CNN does not form at Triton's low temperatures. The recombination reaction of C atoms with $H_2$ is thought to have a large activation energy (*27*) and is assumed to be negligible in Triton's atmosphere.
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# A New Type of Meteoritic Diamond in the Enstatite Chondrite Abee

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**Diamonds with $\delta^{13}C$ values of −2 per mil and less than 50 parts per million (by mass) nitrogen have been isolated from the Abee enstatite chondrite by the same procedure used for concentrating Cδ, the putative interstellar diamond found ubiquitously in primitive meteorites and characterized by $\delta^{13}C$ values of −32 to −38 per mil, nitrogen concentrations of 2,000 to 12,500 parts per million, and $\delta^{15}N$ values of −340 per mil. Because the Abee diamonds have typical solar system isotopic compositions for carbon, nitrogen, and xenon, they are presumably nebular in origin rather than presolar. Their discovery in an unshocked meteorite eliminates the possibility of origins normally invoked to account for diamonds in ureilites and iron meteorites and suggests a low-pressure synthesis. The diamond crystals are ~100 nanometers in size, are of an unusual lath shape, and represent ~100 parts per million of Abee by mass.**

The presence of diamond in extraterrestrial samples [ureilites (*1*) and an iron meteorite (*2*)] was first reported over a century ago. It now seems that a number of processes must have been involved in the formation of such meteoritic diamonds. A mechanism similar to that for the formation of diamonds on Earth at high pressures is unlikely in meteorites because their parent bodies are believed to be no more than a few hundred kilometers in diameter and so would not reach the required high pressures. In Canyon Diablo, the iron meteorite from Meteor Crater, Arizona, cubic diamond is intergrown with hexagonal lonsdaleite, which is usually associated with shock processing. The diamonds were thus believed to be produced in the terrestrial impact event (*3*). Recognition of the diamond polymorphs in an Antarctic iron meteorite that showed no evidence of terrestrial shock, however, implied that at least some diamonds were formed before the iron meteorite reached Earth (*4*). Most, but not all, ureilites [for example, ALHA 78019 (*5*) is an exception] contain diamond in amounts up to 1% by weight (*1*) in matrix veins intergrown with graphite and lonsdaleite (*6*). The favored explanation for the origin of these diamonds is formation by shock during collisions in space (*6*, *7*). An alternative mechanism to shock, akin to chemical vapor deposition (CVD), has also been suggested (*8*).

Whatever the exact mechanism of formation of the ureilite and iron meteorite diamonds, their existence can almost certainly be explained by processes acting in the solar system at some time. The situation is clearly different for the carrier of isotopically anomalous N (*9*) and Xe [Xe (HL) (*10*)], sobriquet Cδ, which was identified as diamond with a particle size of typically 3 nm (*11*). Cδ diamond is present in virtually all types of primitive carbonaceous and ordinary chondrites (*12*, *13*) and the enstatite chondrites Indarch (*13*, *14*) and Qingzhen (*13*); Cδ diamonds from different meteorite classes show a variation of a factor of 6 in N content and a 5 per mil range in C isotopic composition (*15*). The N and Xe isotopic compositions suggest that Cδ diamonds were produced as circumstellar

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