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## Prediction of a $N_2^{++}$ layer in the upper atmosphere of Titan

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[1] Calculations of dication  $N_2^{++}$  density in the atmosphere of Titan is performed for the first time. The metastable lifetime of this species is 3 seconds in its ground state. The density of the  $N_2^{++}$  layer centred around 1100–1200 km altitude can reach  $10^4 \text{ m}^{-3}$ . The ions are produced by both the double photoionisation and the photoelectron impact of  $N_2$ . They are lost by dissociative recombination with the thermal electrons and chemical reactions with  $N_2$  and  $CH_4$ . The most recent chemical reaction rate constants, given by laboratory experiments, were used in this study. Finally, we explore the possible detection of this ion layer by a spectrophotometer and show that the UVIS instrument onboard CASSINI could be capable to observe it.  
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### 1. Introduction

[2] Studying planetary ionospheres is amongst the major scientific goals of all planetary missions. The Cassini-Huygens mission payload includes several instruments which will give us new insights into the ionosphere of Titan. Within the scope of this work three instruments are of particular interest: The Ion and Neutral Mass Spectrometer (INMS) will analyze ion and neutral particles. The Radio and Plasma Wave Science (RPWS) instrument will provide information on the electric and magnetic wave fields and determine the electron density and temperature. The Ultraviolet Imaging Spectrograph (UVIS) will measure ultraviolet energy from the atmosphere to study its composition.

[3] The modelling the ionosphere requires a set of complex equations based on magnetohydrodynamics. Of the different plasma parameters those of interest in this study are the plasma densities. These are function of production and loss mechanisms as well as dynamics. Production can be of chemical or physical origin. In the latter case we consider two sources: photoabsorption (called primary photo-production) and electron impact (called secondary production). The primary production is easy to solve, because for the satellites and the telluric planets, the

atmospheres are optically thin, allowing the Beer-Lambert law to be solved. The secondary production requires a kinetic transport equation described in detail by *Lilensten and Blelly* [2002]. Such an approach has been developed for Titan by *Galand et al.* [1999]. In work by *Witasse et al.* [2002], this approach was adapted to Mars and allowed the authors to predict the existence of a  $CO_2^{++}$  layer. Recent information on the modelling of the Titan ionosphere may be found in work by *Wilson and Atreya* [2004], *Cravens et al.* [2004], and *Fox and Yelle* [1997].

[4] This paper aims at presenting the calculation of the stable doubly-charged  $N_2^{++}$  ion density. Up to now the existence of stable molecular dications in Titan's ionosphere had never been considered, as it was generally assumed that they were negligible or unstable. However, laboratory measurements show that dication production by Vacuum Ultraviolet photons or electron impact can represent up to 10 or 15% of the total ionisation processes. Moreover, molecular dications have been shown to possess very stable electronic states. In the case of  $N_2$ , which is a major neutral component of Titan's atmosphere, the ground state lifetime of  $N_2^{++}$  was measured to be 3 seconds for the principal component of the decay function [*Mathur et al.*, 1995]. As a consequence, these cations, when produced, can be involved in collisions with electrons and neutral molecules and can play a part in the overall chemistry of the ionosphere. Very little is known about the chemical processes involving these dications, so that laboratory work has been performed to measure electron recombination and chemical reaction rates. The expected detectability of  $N_2^{++}$  ions in Titan's atmosphere offers a unique opportunity to compare modelling work and observations. No other significant stable molecular doubly-charged ions are expected to be produced in Titan's ionosphere. Double ionisation of  $CH_4$  probably yields only unstable doubly-charged ions which quickly dissociate into singly-charged fragmented ion pairs [*Rabrenovic et al.*, 1983].

[5] In the first part, we describe the photochemical model. Then,  $N_2^{++}$  density profiles are presented and compared to Titan's other ions. The sensitivity to different parameters is then analyzed. The potential detection of this dication layer is considered in the last section.

### 2. Modelling $N_2^{++}$ Density

[6] The ground state of  $N_2^{++}$ , noted  $X^1\Sigma_g^+$ , is 43.00 eV above the ground neutral state. So far, 9 excited electronic states have been identified, such as  $a^3\Pi_u$  and  $b^3\Sigma_g^-$  situated at 0.57 and 1.48 eV respectively above  $N_2^{++}$ 's ground state [*Taylor and Partridge*, 1987]. The lifetimes of all other electronic excited states are less than 50 microseconds [*Ahmad*, 2002]. As a result they are unstable under ionospheric conditions. Only the ground state has a lifetime long

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enough to allow collisions with electrons or the neutral gas ( $\tau = 3$  seconds) as stated by *Mathur et al.* [1995]. Therefore, here we only model the density of the ground state with the longest lifetime.

## 2.1. Photochemistry

[7] In our model, we assume that N<sub>2</sub><sup>++</sup> ions are produced by photoionisation and photoelectron impact ionisation of molecular nitrogen. They are predominantly lost by chemical reaction with N<sub>2</sub>, CH<sub>4</sub> and by dissociative recombination with thermal electrons. Collisions with other neutral components are not considered here as their density is much lower than N<sub>2</sub> and CH<sub>4</sub>'s. Their collision rates are not expected to exceed that of N<sub>2</sub> and CH<sub>4</sub>, which is already close to the maximum collision rate value (Langevin rate). Moreover, penetrating electrons from the solar wind are not considered here: the computation is performed for a diurnal atmosphere and only deals with the total production due to EUV inputs. Assuming photochemical equilibrium at these altitudes, the doubly charged ion concentration expression is given by

$$N_{N_2^{++}} = \frac{P_{N_2}^{photo} + P_{N_2}^{impact}}{N_e k_{DR} + N_{N_2} k_{N_2} + N_{CH_4} k_{CH_4} + \frac{1}{\tau}} \quad (1)$$

with the notations:

- $P_{N_2}^{photo}$ : ion production by photoionisation.
- $P_{N_2}^{impact}$ : ion production by electron impact.
- $N_e$ : thermal electron density.
- $N_{N_2}$ : nitrogen density.
- $N_{CH_4}$ : methane density.
- $k_{DR}$ : dissociative recombination rate.
- $k_{N_2}$ : chemical reaction rate constant with N<sub>2</sub>.
- $k_{CH_4}$ : chemical reaction rate constant with CH<sub>4</sub>.
- $\tau$ : lifetime of the ion state = 3 s [*Mathur et al.*, 1995].

[8] The chemical reaction rate constants  $k_{N_2}$ ,  $k_{CH_4}$  and  $k_{DR}$  are defined below.

## 2.2. Laboratory Measurements

[9] Laboratory experiments have been performed in order to measure the reaction rate of N<sub>2</sub><sup>++</sup> ions. Chemical reactions of dications represent the opening of a new and exciting class of mechanism [*Mrázek et al.*, 2000, and references therein]. The experimental procedure is described by *Nicolas et al.* [2002]. Very briefly, molecular dications are produced by electron impact and introduced in an octopole ion guide where the reaction takes place with the neutral target gas (N<sub>2</sub> or CH<sub>4</sub>). The reaction rate constants (in cm<sup>3</sup> s<sup>-1</sup>) for the reaction of N<sub>2</sub><sup>++</sup> with N<sub>2</sub> and with CH<sub>4</sub> have been measured to be:

$$k_{N_2} = 2.7 \times 10^{-9} \pm 25\% \quad (2)$$

$$k_{CH_4} = 1.8 \times 10^{-9} \pm 25\% \quad (3)$$

[10] The dissociative recombination of N<sub>2</sub><sup>++</sup> with electrons has also recently been studied by *Seiersen et al.* [2003], using the heavy-ion storage ring ASTRID. Low-energy electrons are scattered on N<sub>2</sub><sup>++</sup> which yields an absolute cross-section, from which a recombination rate constant is

deduced. The experiment is described in detail by *Seiersen et al.* [2003]. The total recombination rate is (in cm<sup>3</sup> s<sup>-1</sup>),

$$k_{DR} = 5.8 \times 10^{-7} \sqrt{\frac{300}{T_e}} \pm 25\% \quad (4)$$

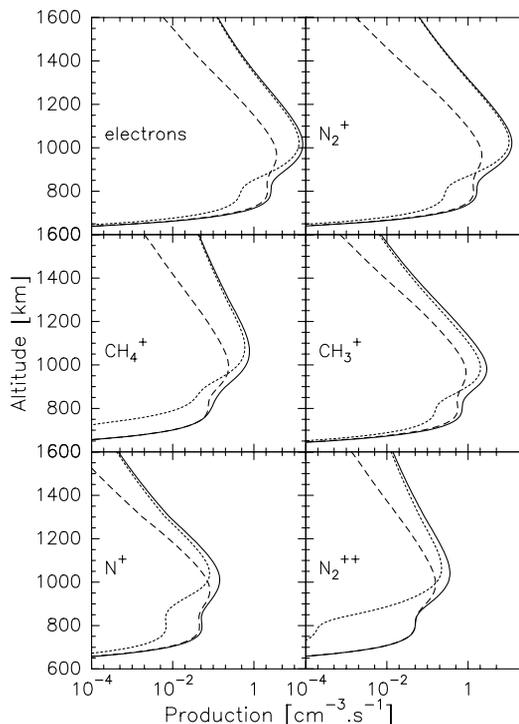
with  $T_e$  being the electron temperature.

## 2.3. Ion Production

[11] The computation of ion production is fully described by *Galand et al.* [1999]. It consists of primary production through photoabsorption and secondary production through electron impacts. The neutral atmosphere is described by *Muller-Wodarg et al.* [2000]. The exospheric temperature is 175 K. The altitude range covered by our computation is 600 km to 1600 km. The photon absorption cross sections come from *Torr and Torr* [1985] and *Fennelly and Torr* [1992] for N<sub>2</sub> and from *Samson et al.* [1989] for CH<sub>4</sub>. For the double ionisation of nitrogen, and as photoionisation cross-sections have not yet been measured nor calculated, we put forward a ratio of:

$$\frac{\sigma_e(N_2^{++})}{\sigma_e(N_2)} = \frac{\sigma_{hv}(N_2^{++})}{\sigma_{hv}(N_2)} \quad (5)$$

to yield  $\sigma_{hv}(N_2^{++})$  where  $\sigma_{hv}$  represents the photoabsorption cross section and  $\sigma_e$  is the electron impact cross section. The set of electron impact cross sections for N<sub>2</sub> is detailed by *Lummerzheim and Lilensten* [1994]. It comes from *Davies et al.* [1989] for CH<sub>4</sub> (with 6 excitation states) and *Märk* [1975] for the double ionisation of the nitrogen molecule. The computation is performed for a diurnal atmosphere and only concerns the total production due to EUV inputs. Most of the current EUV models rely only on a few data sets obtained by the Dynamics Explorer missions [*Hinteregger et al.*, 1973]. A first representation of Solar EUV fluxes for aeronomical applications was given by *Hinteregger* [1981] and *Hinteregger and Katsura* [1981]. A first reference flux SC#21REF was assembled from measurements performed in July 1976 (f10.7 = 70), and given in 1659 wavelengths. An extrapolation model (SERF 1) allows the flux during other periods of solar activity to be estimated. *Torr and Torr* [1979, 1985] proposed two reference fluxes for aeronomy called F79050N (f10.7 = 243) and SC#REFW (f10.7 = 68). We estimate the flux at other activity levels by interpolating. Since then, several authors have developed their codes in order to take better advantage of the AE data base. Amongst them, two must be emphasized. *Tobiska* [1993] and *Tobiska and Eparvier* [1998] developed a model which takes data from other sources into account (SME, OSO; AEROS; rockets and ground-based facilities) as well as the solar emission zone of each line, through a specific parameter. They propose a formula to retrieve a solar flux from the gift of the decimetric index and its average. The second improved model is EUVAC [*Richards et al.*, 1994]. Its main difference with previous models is the reference flux chosen, and the interpolation formula. The coronal flux is also constrained to be at most 80% of the total. We tested all the solar flux models. They give very little differences on the productions and actually none on the N<sub>2</sub><sup>++</sup> density results. In this paper, we use the Torr and Torr model where the solar EUV flux is interpolated in terms of the decimetric index from measurements taken from the Atmosphere



**Figure 1.** Total ion productions (full lines), primary photo-productions (dotted lines) and secondary electron impact productions (dashed lines).

Explorer satellites during solar minimum and solar maximum conditions [Hinteregger, 1981; Hinteregger et al., 1981]. The values used are those parameterized and modified by Torr and Torr [1985] into 37 energy values from 248 eV down to 12.02 eV. Following Tobiska [1993], two values have been added at 2.327 nm and 3.750 nm to take into account the ionisation due to high-energy photons. The  $f_{10.7}$  value is 150. It stands for a mean solar activity and allows for comparisons with the previous work by Galand et al. [1999]. However, it is probably an upper value of what may be expected during Cassini–Huygens’ lifetime.

[12] The model results are shown in Figure 1 for a solar zenith angle of  $45^\circ$ . This angle has been chosen to represent a planetary average [Lebennois and Toubanc, 1999]. The behaviour is somewhat classical, with the secondary production dominating over the primary production mechanism below typically 850 to 950 km. The  $CH_4^+$  and  $CH_3^+$  cases are special in that the primary electron production is very small compared to the secondary production. However, the overall total is small, of the order of 0.05 ion per cubic centimetre.

### 3. Density Results

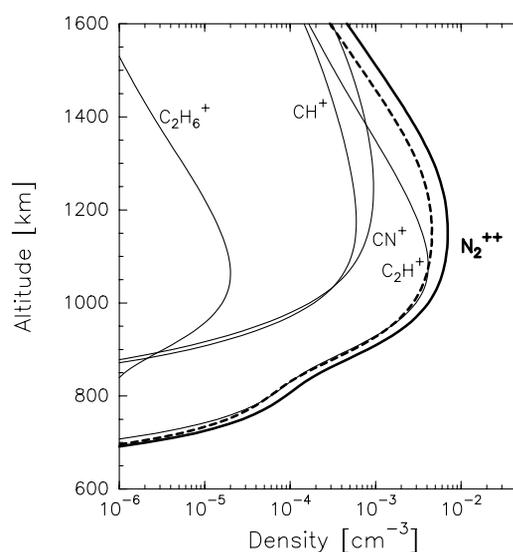
[13] The modelled  $N_2^{++}$  densities are presented in Figure 2. As a first guess, we have set the electron temperature to the neutral temperature. Then,  $N_2^{++}$  density reaches values of  $\pm 1 \times 10^4 \text{ m}^{-3}$  at about 1100 km. This represents only  $\pm 1 \times 10^{-4}$  of the total ion density [Galand et al., 1999]. However, when compared to minor ion densities, this dication is not the least abundant. Ions such as  $CH^+$ ,  $C_2H^+$ ,  $C_2H_6^+$ , or  $CN^+$  have smaller densities. Let us note that  $N_2^{++}$  reactions with neutrals often lead to the formation of pairs of singly-charged ions with large translational energy [Mrázek et al.,

2000]. This can have several implications: the modification of the chemical reaction rates of  $N^+$  and  $N_2^+$  ions produced by these reactions due to collision energy, and the possible escape of some ions towards the exosphere. We evaluated in a first run the effect of different physical parameters and set the reaction rate constant of the reaction  $N_2^{++} + CH_4$  to zero. In a second run, we set the electron temperature to twice the neutral temperature since this parameter is unknown. These two approaches result in a very small increase (less than 10%) of the  $N_2^{++}$  density above 1300 km. When we set the lifetime of the ion state to be infinite, i.e., no spontaneous dissociation ( $\tau^{-1} = 0$ ), the effect is more important leading to an increase of about 60% at around 1300 km. However, the effect on the peak density is in any case very small. Below the altitude of this maximum, there are no effects at all, as the reaction with molecular nitrogen is the most important process. Finally, we computed the  $N_2^{++}$  density for reduced solar activity (decimetric index of 100), close to what is expected during the Cassini–Huygens operating phase. This is also shown in Figure 2. It results in the peak density decreasing by a factor of around one third, from  $8.8 \times 10^{-3} \text{ cm}^{-3}$  down to  $5.6 \times 10^{-3} \text{ cm}^{-3}$ .

### 4. Detectability of Doubly-Charged Ions

[14] The Cassini–Huygens mission will provide new insights into Titan’s ionosphere in 2004–2008. The question remains: is it possible to detect  $N_2^{++}$ ? The ion mass spectrometer technique cannot be used here. As a matter of fact, this method allows the ion selection by their mass-to-charge ( $m/q$ ) ratio. For  $N_2^{++}$  this number is equal to that of  $N^+$ : this overlapping makes it impossible to discriminate between the two ions while the contribution of  $N_2^{++}$  compared to  $N^+$  remains tiny.

[15] Fluorescence is generally a scarce phenomenon for dications but was at least observed for  $N_2^{++}$  [Cossart et al., 1985; Olsson et al., 1988; Ahmad, 2002; Ehresmann et al., 2000, 2003]. The excited state of specific interest to us is



**Figure 2.** Ion densities. The two bold lines are the  $N_2^{++}$  densities (full line:  $f_{10.7} = 150$ ; dashed line:  $f_{10.7} = 100$ ). Thin lines represent some minor ions [from Galand et al., 1999].

D<sup>1</sup>Σ<sub>u</sub><sup>+</sup>, 7.8 eV above the ground state [Ahmad, 2002; Olsson et al., 1988]. Two bands corresponding to the D<sup>1</sup>Σ<sub>u</sub><sup>+</sup>-X<sup>1</sup>Σ<sub>g</sub><sup>+</sup> (0, 0) and (1, 1) transitions have already been observed experimentally in the 158.7–159.4 nm range [Cossart et al., 1985; Olsson et al., 1988]. Using the results of Ehresmann et al. [2003], a rough approximation leads us to suppose that nearly 10% of the total of N<sub>2</sub><sup>++</sup> ions created by double photoionisation at the cross-section peak near 65 eV are produced in the D<sup>1</sup>Σ<sub>u</sub><sup>+</sup> state. From a simple altitude integration we would expect a mere 0.2 Rayleigh produced in the fluorescence state in quiet conditions, and 0.27 Rayleigh in mean solar conditions. Onboard Cassini, the UVIS instrument makes observations in the UV–EUV windows. At around 160 nm, the detection limit for a one-hour observation time is about 0.08 Rayleigh [Esposito et al., 2005]. Therefore, we expect that our prediction could be confirmed by observations.

## 5. Conclusions

[16] For the first time, the presence of N<sub>2</sub><sup>++</sup> doubly charged ions is modelled in the atmosphere of Titan. Their density has been calculated by using a kinetic code for the production rates and a simple chemical scheme for the chemical losses. The chemical reaction rate constants have been measured in recent laboratory experiments. These ions are produced in the dayside through the ionisation of nitrogen. They are essentially lost by dissociative recombination with thermal electrons and by chemical reactions with N<sub>2</sub> and CH<sub>4</sub>. Consequently, a layer is created with a peak density of ±1 × 10<sup>4</sup> m<sup>-3</sup> around 1100 km. With 10% of these ions created in the excited fluorescence state D<sup>1</sup>Σ<sub>u</sub><sup>+</sup>, this layer could well be detected in the near future by the UVIS instrument onboard Cassini.

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