Modeling of an Abnormal Glow Discharge to Characterize the Atmospheric Ion Chemistry of Saturn's Moon Titan

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Abstract: The Cassini spacecraft measured the molecular masses of positively- and negatively-charged species between 950-1500 km in the upper atmosphere of Saturn's largest moon, Titan. These measurements highlighted the important role of charged molecular species which are an important source for radical and neutral-ion chemistry, eventually leading to the formation of the organic haze layer surrounding Titan. Photochemical models have substantially advanced our understanding of the gas phase chemistry and gas-solid coupling occurring in Titan's ionosphere. However, these models have faced obstacles due to limited reaction rate data. Many laboratory experiments, on the other hand, have examined chemical pathways involved in Titan's atmospheric chemical growth. Here, we utilized a 1D chemical network model using a fluid mechanical framework derived from the Titan Haze Simulation (THS) experiment developed on the COsmic Simulation Chamber (COSmIC) at NASA Ames Research Center to investigate Titan's low-temperature (150 K) gas phase chemistry in ionized conditions. This model simulates the chemical reactivity occurring in the COSmIC abnormal glow plasma discharge. Our study focuses on N_2-CH_4-based gas mixtures relevant to Titan's upper atmosphere. We have incorporated updated reaction rates into our numerical model and expanded on the plasma parameter space from previous studies to assess the sensitivity of changing plasma conditions on the resulting ion chemistry. C/N elemental composition of the gas-phase products and comparisons with recently published solid-phase C/N ratios will be presented. The sensitivity of our calculations with source voltage variations and its impact on the chemistry will also be discussed. Finally, the implications of these results will be juxtaposed with other laboratory and numerical simulations of planetary and astrophysical environments where plasma chemistry plays a key role in the astrochemical inventory.

Keywords: Astrochemistry, Plasma chemistry, Modeling, Chemical network

1. Introduction and Background

Titan is the largest moon orbiting around Saturn. It is also the only moon in the solar system to have its own atmosphere, an atmosphere mainly composed of molecular nitrogen (N_2) and methane (CH_4). This reducing atmosphere consists of five main atmospheric layers (troposphere, stratosphere, mesosphere, thermosphere and exosphere) hosting planetary-like dynamical, thermal, chemical and seasonal variations on a global scale. The haze surrounding Titan is ultimately controlled by the regulatory gas phase molecular precursors produced in the upper atmosphere resulting from high-altitude N_2 and CH_4 photo-dissociation. These precursors consist of hydrocarbon radicals (*e.g.* CH_2, CH_3) and more complex hydrocarbons, nitriles and even polycyclic aromatic hydrocarbons [1]. Other energetic sources triggering high-altitude photochemistry include solar X-rays, galactic cosmic rays, Saturn's magnetospheric energetic electrons and solar wind [*e.g.* 2]

The Cassini spacecraft studied Titan for 13 years and directly measured the molecular mass of ions for the first time in Titan's upper atmosphere [1]. These observations uncovered the complexity of Titan's upper atmospheric chemistry, consisting of radicals, ions and the preliminary stages of solid haze particle formation. Photochemical models have helped explain the gas phase chemistry involved in the production of these aerosols [*e.g.* 3]. Alongside those models, laboratory experiments have helped fill gaps in the reaction networks through specific channels involving neutral and charged hydrocarbons. Furthermore, photochemical and microphysical models [4] have demonstrated the dusty nature of Titan's ionosphere (> 900 km in the atmosphere) thus characterizing the interaction between the aerosols and charged particles. This has helped consolidating the important contributions plasma-based (laboratory and numerical) studies can bring to refine characterizing the molecular growth in Titan-like conditions [5,6].

Ion-molecule reactions are thought to produce most of the positive ions present in Titan's ionosphere, and are thus controlled by the two initial neutral main constituents, N_2 and CH_4. The direct ionization of N_2 and CH_4 and formation of the N^+ and N_2^+ primary ions make CH_3^+ readily available, an ion predicted to participate in the production of the first light hydrocarbons such as $C_2H_5^+$, one of the major ions produced:

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$$

A large number of positive ions making up the bulk composition of Titan's ionosphere (> 900 km) have been proposed based on Cassini observations complemented with numerical simulations and laboratory measurements, and include species up to C6 hydrocarbons and nitriles [7 *and references therein*] near the ionospheric peak region. The processes, however, coupling ion and neutral chemistry and aerosol production are still mostly unknown at the moment. Using plasma-based laboratory techniques with carrier gas mixtures, it is possible to influence the chemistry and thus constrain formation of $C_xH_yN_z$ species in analogous Titan conditions. Plasma simulations have been able to constrain chemical pathways using instruments with a higher resolution than Cassini's.

2. The COSmIC Facility at the NASA Ames Research Center

Our numerical model is based on the Titan Haze Simulation (THS) experiment developed on the COsmic Simulation Chamber (COSmIC) abnormal glow plasma discharge at NASA Ames Research Center to investigate Titan's low-temperature (150 K) gas phase chemistry in ionized conditions [8 *and references therein*]. In this setup, a pulsed discharge nozzle (PDN) is used as an external ionization source, and the plasma-generated ions travel through a free-jet planar expansion before being collected by a Time-of-Flight mass spectrometer. This setup thus generates a unique pulse-dependent, low-temperature (~ 150 K) truncated chemistry which enables us to study the first steps of the long chemical chain of reactions and even the solid organic particles. These particles, analogues of Titan's atmospheric solid aerosols, are called *tholins*. Experimental mass spectra obtained with the THS in N_2-CH_4-based gas mixing ratio conditions relevant to Titan's ionosphere can then directly be compared to computed mass spectra obtained from our model.

3. Numerical Description

A fluid mechanics-based framework was developed to model the THS abnormal glow discharge and its truncated chemistry in the active region (Figure 1) of the plasma discharge [9].

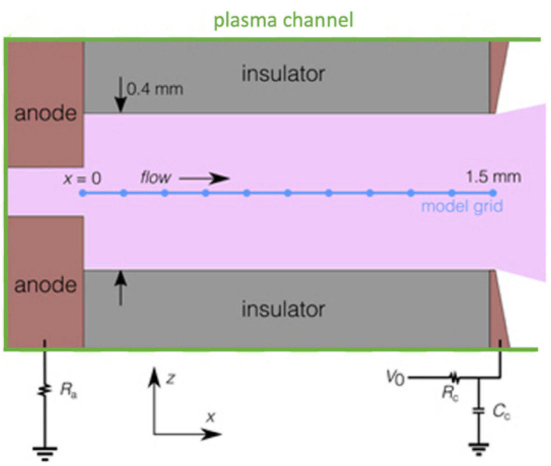

Fig. 1. Geometry of the pulsed discharge nozzle used in the model, with the 1D grid along which the spatial derivatives are calculated (in blue) between the anode and cathode [adapted from 9].

It assumes a one-dimensional flow regime and tracks the evolution of reaction products in space and time (Figure 2). Building on earlier reaction pathways involving neutrals and positive ions, the ongoing study addresses new precursors and recently-published reaction rates [3].

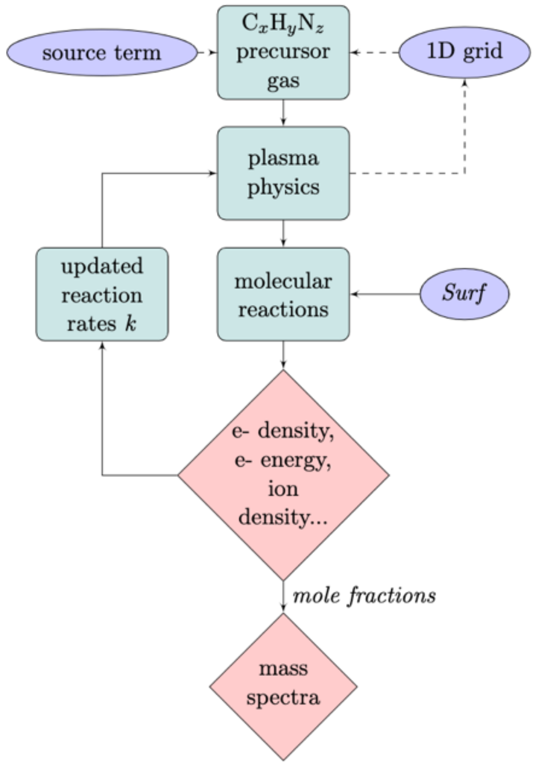

Fig. 2. Simplified schematic representation of the THS model. Main inputs consist of a predefined molecular reaction list with the associated reaction coefficients. Input molecular reactions also include surface reactions which comprise neutralization reactions and secondary electrons formed near the cathode.

Ions, radicals, neutrals are calculated using the following formalism:

$$\rho\frac{\partial\omega_k}{\partial t} + \rho(u\cdot\nabla)\omega_k = \nabla\cdot\left[\rho\omega_k \mathrm{D_k}\frac{\nabla\omega_k}{\omega_k} - \mathrm{z_k}\mu_\mathrm{k}\mathrm{E}\right] + \mathrm{R_k}$$

where ω_k represents the species mass fraction of the kth molecular species and R_k corresponds to the source term for heavy species. The mixture-average diffusion coefficient D_k, as in [9], is considered negligible ($D_k = 0$) since the supersonic expansion dominates the continuous flow. Finally, R_k is obtained by computing a network of chemical rate equations.

4. Implications

We conducted computations in N_2-CH_4-based mixtures to (i) derive mass spectra presenting the first light and intermediate ions indicative of the truncated nature of the plasma, (ii) compare these mass spectra to experimental and previous theoretical spectra, (iii) determine the sensitivity of the chemical outputs to the plasma parameter space, and (iv) characterize the gas phase elemental composition and thus the precursors leading to the formation of *tholins*. These recent developments and results will be discussed and placed in the context of laboratory/numerical simulations of Titan and, by extension, astrophysical environments where plasma chemistry plays a key role in the chemical inventory of the solar system.

5. Acknowledgements

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