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Modeling of synchrotron-based laboratory simulations of Titan's ionospheric photochemistry

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ABSTRACT

The APSIS reactor has been designed to simulate in the laboratory with a VUV synchrotron irradiation the photochemistry occurring in planetary upper atmospheres. A $N_2—CH_4$ Titan-like gas mixture has been studied, whose photochemistry in Titan's ionospheric irradiation conditions leads to a coupled chemical network involving both radicals and ions. In the present work, an ion–neutral coupled model is developed to interpret the experimental data, taking into account the uncertainties on the kinetic parameters by Monte Carlo sampling. The model predicts species concentrations in agreement with mass spectrometry measurements of the methane consumption and product blocks intensities. Ion chemistry and in particular dissociative recombination are found to be very important through sensitivity analysis. The model is also applied to complementary environmental conditions, corresponding to Titan's ionospheric average conditions and to another existing synchrotron setup. An innovative study of the correlations between species concentrations identifies two main competitive families, leading respectively to saturated and unsaturated species. We find that the unsaturated growth family, driven by C_2H_2, is dominant in Titan's upper atmosphere, as observed by the Cassini INMS. But the saturated species are substantially more intense in the measurements of the two synchrotron experimental setups, and likely originate from catalysis by metallic walls of the reactors.

1. Introduction

Titan's ionosphere extends above 800 km of altitude, with local pressures no higher than 10^{-5}–10^{-6} mbar. In such diluted conditions, the efficient organic chemistry detected by mass spectrometers onboard the Cassini orbiter was unexpected, and revived our understanding of the organic chemistry occurring in Titan's atmosphere [1–18]. Large condensable molecules responsible for the nucleation leading to solid atmospheric aerosols are now known to be produced in the ionosphere [9,19–22]. The reason for the chemical growth in spite of the low molecular density has been found in the chemical coupling between radicals and reactive charged species present in the ionosphere, *i.e.* positive ions, negative ions and electrons [22].

The complexity of the chemistry is however far from being charted, as illustrated by the absence of data on the dissociative recombination products for species larger than four carbon and/or nitrogen atoms [23–25], or even for modest size ions of importance in Titan's ionosphere, such as $CH_2NH_2^+$ [17]. The initial steps of molecular growth following EUV photolysis of $N_2/CH_4/C_2H_2$ mixtures were studied, at the second time-scale, in an ion trap by Thissen et al. [26]. No substantial growth was observed in these conditions, unless C_2H_2 was present in the initial mixture. On the other hand, at the much longer time-scale of Titan's ionosphere, a correlation analysis of the positive ions densities recorded by Cassini's Ion and Neutral Mass Spectrometer (INMS) enabled Westlake et al. [18] to infer small growth units having one or two carbon atoms.

To complete and more easily approach in the laboratory this partially ionized chemistry starting with N_2/CH_4, a new generation of photochemical reactors has been developed [27,28]. In this case, VUV synchrotron sources are used to simulate the VUV part of the solar spectrum, the major source of ionization in Titan's ionosphere. A first series of results was obtained with the "Atmospheric Photochemistry Simulated by Synchrotron" (APSIS) experiment using a mass spectrometer for neutrals detection, and compared with Cassini's data [28]. The trends on the neutral species are in

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agreement with Titan's observations: an efficient organic growth and the formation of nitrogen-bearing products.

However no analytical device enabled the direct detection of the ions in the reactive medium. Knowing their central role in the organic growth in Titan's atmosphere, our aim is to design a fully coupled model to theoretically probe the ion content in the APSIS reactor and interpret the results observed on the neutral species. Building an exhaustive chemical model involving all the known and partially known processes, as well as their uncertainties to perform uncertainty propagation and sensitivity analysis, prevents from a complex description of the dynamics within the APSIS reactor.

As a first approach, the study is performed with a 1-cell model, run in reference conditions corresponding to the experiments reported in Peng et al. [28]. These results are used to validate the model and perform uncertainty and sensitivity analysis to highlight prominent processes explaining the observed chemical growth. Complementary model runs have been performed for different conditions of the physical parameters (irradiation spectrum, pressure, temperature) and compared to the reference one to infer the impact of these parameters in laboratory simulations and different environments. Finally, the model has been run in conditions similar to the experiments of Imanaka & Smith [27] for comparison with APSIS, and in Titan-like conditions.

The model is established in Section 2, describing the main characteristics of the APSIS reactor, the chemical scheme, the chemistry-transport 1-cell model, and the generation of electron-impact mass spectra. The probabilistic description of the uncertain chemical parameters, and notably new wavelength-dependent photolysis branching ratios, and the method to handle it are also developed in this section. Application of the model to the APSIS reactor is presented in Section 3.1. The stationary state mole fractions of the products are analyzed and compared to experimental data. Exploration of the Monte Carlo samples generated for uncertainty analysis is performed with several objectives: (i) identification of the main uncertainty sources, in terms of reaction type and specific reactions (key reactions); (ii) detection of species communities in the chemical network to identify dominant growth pathways. This section is completed with the analysis of simulations in different physical conditions (irradiation spectrum, pressure and temperature). The following sections are devoted to the analysis of simulations of Imanaka & Smith's reactor (Section 3.2), and to a proxy of Titan's ionospheric conditions (Section 3.3). The conclusion outlines the main results of this research in relation with the detailed chemical modeling of N_2/CH_4 plasmas and the representativity of laboratory simulations of Titan's ionospheric chemistry.

2. The N_2/CH_4 photochemical plasma model

2.1. The APSIS reactor

The APSIS reactor is described in detail in Peng et al. [28]. It is a stainless-steel parallelepiped with internal dimensions (length × width ce:hsp sp="0.25"/>× height) of 500 mm × 114 mm × 92 mm. The experimental conditions chosen for the modeling are reported in Table 1. A reactive gas mixture $N_2/CH_4 = 90/10$ (purity > 99.999%, Air Liquide) is flowed into the reactor at a gas flow of 7 standard cubic centimeter per minute (sccm), controlled by a MKS mass flow controller. A primary pumping unit ensures a stationary flow of reactive gas whose partial pressure reaches 4.5 mbar and a residence time of the gas mixture of about 180 s.

The APSIS chamber is coupled *windowless* to the DISCO beamline at SOLEIL synchrotron facility [29], using a differential pumping system [30]. A non-reactive carrier gas (He) is continuously injected between the beamline and the APSIS chamber in order to prevent the reactive mixture to be diffusing out of the reactor into the differential pumping system and leading to a total pressure of 7.0 ± 0.1 mbar in the reactor. The experiments are conducted at room temperature.

In situ measurement of the gas phase composition is achieved using a Pfeiffer QME 200 quadrupole mass spectrometer (MS). The MS detector has a resolution of 1 u and covers the 1–100 u range. Electron energy is 70 eV. Gas is sampled by a capillary tube mobile along the reactor length and probing at about 1 cm from the irradiated column. This tube is long enough to reduce the conductance between the reactor chamber and the MS, with the consequence that only stable molecules can be detected with this setup.

The photon flux of the DISCO beamline (a few 10^{11} ph s^{-1} for 0.1 nm bandwidth) leads to a N_2 dissociation ratio of less than 10^{-4}. The signal at m/z 28 of N_2 is therefore constant enough throughout the experiments to be considered as a fixed reference, and it is used to normalize the mass spectra (Section 2.4).

2.2. The reaction scheme

The present chemical scheme incorporates the complete neutral chemistry, *i.e.* photodissociation, bimolecular thermal reactions and trimolecular thermal recombinations, from Hébrard et al. [31,32], with new developments for the photodissociation branching ratios of $CH_4, N_2, H_2, C_2H_2, C_2H_4, C_2H_6$ and HCN, following Gans et al. [33], as described in Section 2.2.1. In addition, the model implements the ion chemistry database established by Carrasco et al. [34] and Plessis et al. [23], including photo-ionizations, ion–molecule reactions and dissociative recombinations involving C, H and N. Oxygen chemistry is excluded, since O_2 is just a trace gas in the reactor and, according to GC–MS analysis, does not play a significant role in APSIS photochemistry [28]. The single electron source in the APSIS reactor being photoelectrons, with insufficient energy to ionize the medium, electron impact reactions are not included.

The present chemical scheme considers only positive, singly charged ions. The DISCO spectrum intensity is vanishing below 50 nm, which prevents the double ionization of N_2 [35] and CH_4 [36], and therefore a sizeable production of dications. Negative ions have been identified as interesting vectors for the formation of heavy particles in Titan's ionosphere [14] and chemical plasmas [37], but their formation by attachment of thermal electrons involves essentially minor radical species and proceeds at very small rates [14].

In total, the model includes 244 species (125 neutrals and 119 ions) reacting with each other through 1708 reactions (33 photolysis, 415 bimolecular reactions, 82 termolecular reactions, 574 dissociative recombinations, 604 ion–molecule reactions). All the parameters describing the rate constants of these processes are uncertain (some of them unknown). They are represented by random variables with prescribed distributions, following Hébrard et al. [31,32], Carrasco et al. [34] and Plessis et al. [23].

The present model is original for two reasons: (1) it implements a new consistent treatment of the separation between photolysis cross-section and branching ratios, which are typically measured in different experiments (see next section); and (2) it is the single ion–neutral coupled model implementing the state-of-the-art dissociative recombination scheme developed by Plessis et al. [23], which for the first time includes all available data for this process, notably the partial measurements of branching ratios.

2.2.1. Representation of photolysis cross-sections and branching ratios

In previous works, photolysis rate constants were treated as lognormally distributed uncertain parameters [38,32,31,39]. In Peng et al. [40] and Gans et al. [33], the separation of photolysis cross-sections and branching ratios was proposed for several