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Neutral production of hydrogen isocyanide (HNC) and hydrogen cyanide (HCN) in Titan's upper atmosphere

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Abstract

Following the first detection of hydrogen isocyanide (HNC) in Titan's atmosphere, we have devised a new neutral chemical scheme for hydrogen cyanide (HCN) and hydrogen isocyanide (HNC) in the upper atmosphere of Titan. To improve the chemistry of HNC and HCN, a careful review of the literature has been performed to retrieve critical reaction rates and to evaluate their uncertainty factors. We have also estimated the reaction rates of 48 new reactions using simple capture theory. Our photochemical model gives abundances of HNC and HCN in reasonable agreement with observations. An uncertainty propagation study shows large uncertainties for HNC. A global sensitivity analysis pinpoints some key reactions to study as a priority to improve the predictivity of the model. In particular, our knowledge of the isomerization of HNC via the reaction H + HNC → HCN + H and the chemistry of H_2CN needs to be improved [9].

1. Introduction

It was first hypothesized that hydrogen isocyanide (HNC) could be formed by the dissociative recombination of $HCNH^+$ in Titan's upper atmosphere where it might be detectable and might also play a part in the formation of more complex nitriles found on Titan [10] . Recently, observations of Titan performed with the HIFI heterodyne submillimeter instrument aboard the Herschel Space Observatory [5]), allowed the first detection of HNC in Titan's atmosphere [11]. These measurements suggest that the bulk of this emission must originate at altitudes above 300 km. However, the observations cannot strictly establish a HNC vertical profile [12]. It was argued that HNC was likely to be formed almost entirely by an ion-molecule mechanism and that neutral formation pathways were not viable [10]. As a consequence, it was suggested that the concentration profile for HNC as a function of altitude would follow the typical profile for a polyatomic ion rather than a neutral molecule and that it might be located mainly in the ionosphere with a peak of abundance around 1200 km [10].

2. Photochemical scheme

Since the neutral composition of the atmosphere is a prerequisite for ionospheric models, it is of prime importance to study carefully the neutral processes leading to the production and loss of both HCN and HNC. In this present study, we have therefore focused on the reactions which are essential for the study of HCN and HNC, either because they are important for the neutral production of these two species and/or loss or because they contribute significantly to the uncertainties on their abundances. To improve the chemistry of HNC and HCN, a careful review of the literature has been performed to retrieve critical reaction rates and to evaluate their uncertainty factors, which might be quite sizeable the low temperatures found in Titan's atmosphere [6, 8]. Our updated chemical scheme contains 137 compounds and 788 reactions (including 91 photodissociation processes). The reaction rates of 48 of these reactions have been estimated using simple capture theory. The complete list of the reactions is available upon request or can be downloaded from the KInetic Database for Astrochemsity (KIDA, http://kida.obs.u-bordeaux1.fr).

3. Uncertainty propagation and sensitivity analysis

The methodology used to study the propagation of uncertainties in the model is described in details elsewhere [7, 8]. For this present study, we have focused exclusively on its chemical sources through the uncertainties of the photodissociation and reaction rates. These uncertainties originate in their experimental or theoretical determination, and are generally quantified by a standard deviation or a relative uncertainty. Because of the profoundly non-linear nature of the photochemical model and the potentially large uncertainties displayed by many parameters, a linear uncertainty propagation is not expected to produce valid results [4]. Propagation of distributions by Monte Carlo sampling is better adapted to such problems [1].

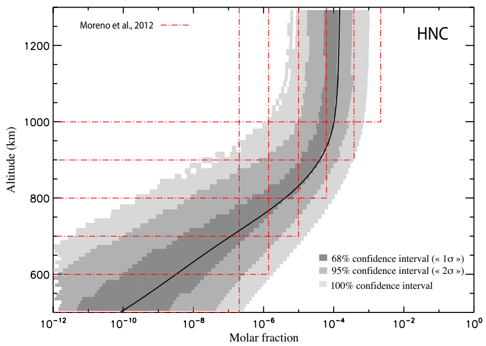

Figure 1: Abundance profiles of HNC in the upper atmosphere of Titan. Nominal model (solid line) and the different acceptable profiles derived from recent Herschel observations [12] (red dotted lines). Grey shaded areas correspond to the abundance profiles og HNC obtained after 1000 Monte-Carlo runs.

The technique used to pinpoint the key reactions of our chemical scheme is based on the computation of the Rank Correlation Coefficients (RCCs) between rate constants and abundances at different altitudes [2, 8]. The power of this technique, based on the uncertainty propagation study and the knowledge of RCCs, to improve photochemical models has been demonstrated for Titan [8] and for Neptune [3]. Among the few key reactions we give here, H_2CN + H, HNC + H and $N(^2D)$ + HNC/HCN are clearly the most important ones for HNC and HCN in the upper atmosphere of Titan.

4. Summary and conclusions

We have investigated as exhaustively as possible the neutral chemistry of HNC and HCN in order to construct a chemical scheme as complete as possible. We have shown that a purely neutral source is efficient enough to produce HNC and HCN in the upper atmosphere of Titan in agreement with current observations. We have shown that the precision on the HCN abundance predicted by photochemical models is currently strongly limited by the poor knowledge of some reaction rates, especially the isomerization reaction H + HNC $\rightarrow$ HCN + H. Further studies of the reactivity of H_2CN with H and the reactivity of $N(^2D)$ with HNC and HCN are also very important. Our study does not mean that ion-molecule mechanisms are not relevant to produce HNC but it shows that neutral reactions are competitive processes in the upper atmosphere.

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