EPSC Abstracts
Vol. 6, EPSC-DPS2011-196-2, 2011
EPSC-DPS Joint Meeting 2011

Effects of uncertain photolysis parameters on predictions of Titan's photochemistry models

Z. Peng (1), F. Cailliez (1), N. Carrasco (2), E. Hébrard (3), M.Dobrijevic (3) and **P. Pernot** (1)
(1) Laboratoire de Chimie Physique, UMR 8000, CNRS, Univ Paris-Sud, F-91405 Orsay; (2) Laboratoire Atmosphères, Milieux, Observations Spatiales, Université de Versailles Saint-Quentin, UMR 8190, F-78280 Guyancourt; (3) Laboratoire d'Astrophysique de Bordeaux, CNRS, UMR 5408, Université de Bordeaux, Observatoire Aquitain des Sciences de l'Univers, 2 rue de l'Observatoire, BP 89, F-33271 Floirac. (pascal.pernot@u-psud.fr)

Abstract

The precision of the rates of the photolytic processes initiating the complex chemistry of Titan's upper atmosphere conditions strongly the predictivity of photochemical models. However, there was no thorough investigation of the impact of the different parameters describing these processes. For the first time, we deal here directly with uncertainty in the photolysis cross-sections and branching ratios to estimate the photolysis rate constants and reassess their impact on model predictions.

1. Introduction

Photolysis of N_2 and CH_4 in the upper atmosphere of Titan by EUV/VUV photons initiates a complex chemistry. Photolysis rates have been shown to be responsible for an important part of the uncertainty on the predicted densities of numerous compounds [1, 2].

The calculation of the partial photodissociation rate of a compound i to products j is based on the absorption cross-section $\sigma_i^a(\lambda)$, the branching ratio $b_{ij}(\lambda)$ and the incident solar flux at every level in the atmosphere, $I_\lambda(z)$. The photodissociation rate constant $J_{ij}(z)$ is modeled in the parallel plane approximation and at zenith solar angle by

$$J_{ij}(z) = \int_0^\infty \mathrm{d}\lambda \, I_\lambda(z)\sigma_i^a(\lambda)b_{ij}(\lambda), \quad (1)$$

$$I_\lambda(z) = I_\lambda^\infty \exp\left[-\tau(\lambda, z)\right], \quad (2)$$

$$\tau(\lambda, z) = \sum_i \sigma_i^a(\lambda) \int_z^{z_u} \mathrm{d}z' \, c_i(z'), \quad (3)$$

where $c_i(z)$ is the density profile of species i, $\tau(\lambda, z)$ is the optical depth, and I_λ^∞ is the photon flux at the top of the atmosphere (altitude z_u). As $\sum_j b_{ij}(\lambda) = 1$, the photolysis rate $J_i(z) = \sum_j J_{ij}(z)$ does not depend on the branching ratios.

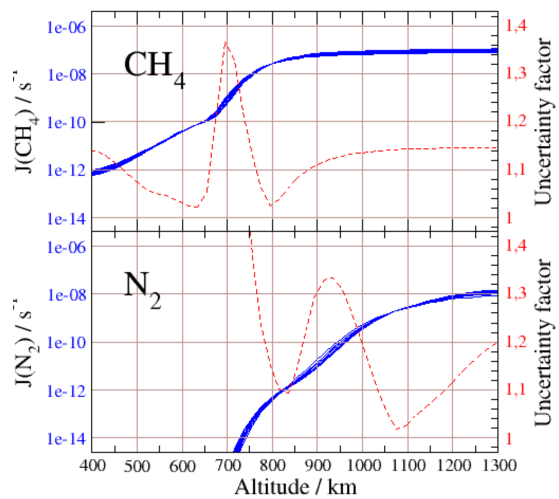

Figure 1: Samples of altitude-dependent photolysis rate coefficients for N_2 and CH_4 (lines; left scale) and their uncertainty factors (dashed lines; right scale).

Because of the feedback between the densities of the absorbing species and the photodissociation processes in the actinic flux calculation, uncertainties are difficult to evaluate without an exhaustive investigation. This work had been postponed in previous studies on the effects of chemical uncertainties in Titan's photochemistry, which assigned a constant uncertainty factor to each photolysis pathway, corresponding to its uncertainty at the top of the atmosphere [1]. This approximate treatment has two main drawbacks: it ignores possible altitudinal variations of the uncertainty and does not account for the sum-to-one constraint on the branching ratios. The present study goes beyond this approximation to assess the direct impact of cross-section and branching ratios uncertainty on the predicted densities.

2 Photolysis *sweet-spots*

Here, we compute explicitly the photolysis rates, $J_i(z)$, and their altitude-dependent uncertainty factors, $F_{J_i}(z)$, in a 1D radiative transfer model. Using a Monte Carlo procedure, we generated a sample of rate coefficients $J_{\mathrm{N}_2}(z)$ and $J_{\mathrm{CH}_4}(z)$, from which we derived the $F_{J_{\mathrm{N}_2}}(z)$ and $F_{J_{\mathrm{CH}_4}}(z)$ uncertainty factors. A subset of rates profiles is shown in Fig. 1, along with the uncertainty factors. For N_2, we observe neatly localized curve crossings, at about 1100 km and 800 km. For CH_4, a similar curve crossing occurs slightly below 800 km, and a less localized one occurs between 600 and 650 km. These features are reflected as dips in the uncertainty factors (Fig. 1). Clearly, the approximation of altitude-independent uncertainty of photolysis rate constants has to be revised, at least for the major absorbers.

As the occurence of specific altitudes with very small uncertainty factors on the photodissociation rate coefficients seems to be a general property of notable interest for the uncertainty budget of photochemical models, we named them "sweet-spots".

A simple model for species with barometric distribution and monochromatic irradiation enables to derive an explicit expression of uncertainty factors

$$F_J(z) = F_\sigma^{\ |1-\tau(z;\overline{\sigma})|}, \qquad (4)$$

where $\overline{\sigma}$ is the reference value of the absorption cross-section and F_σ is its uncertainty factor. This reveals the particular role of the unity optical depth. Generalization to polychromatic irradiation leads to

$$F_J(z) = F_\sigma^{\ \left|1-\int_0^\infty \left[J_\lambda(z;\bar{\sigma})/\bar{J}(z)\right]\tau(z;\overline{\sigma}(\lambda))\mathrm{d}\lambda\right|}, \qquad (5)$$

where $J_\lambda(z;\bar{\sigma}(\lambda))$ is the photolysis rate constant at wavelength λ, and $\bar{J}(z)$ its λ-integered value.

Major species (N_2 and CH_4) with a barometric distribution present thus photolysis sweet-spots. As their photolysis rates are major key parameters in sensitivity analysis of photochemical models [1, 2], the sweet-spots provide reference altitudes for sensitivity analysis where these rates should not contribute to prediction uncertainty, enabling to focus on other parameters. Moreover, a sweet-spot being also the altitude of maximal photolysis rate, it is reasonable to expect a significant improvement in the prediction accuracy of models for Titan's photochemistry.

3 Photolysis branching ratios

It has been shown previously that the sum-to-one constraint is an essential feature in the representation of uncertain branching ratios for ion-neutral [3, 4] reactions and dissociative recombinations [5]. This applies also to photolysis, where branching ratios/quantum yields and photolysis cross-sections are typically measured in different experiments. The same scheme, based on knowledge-based Dirichlet distributions, was therefore implemented for the main photolysis processes, with the additional complexity of wavelength-dependence of branching ratios. The model for CH_4 is presented in a companion poster [6]. This new representation has a noticeable impact on the predicted densities for most species, but this has to be balanced by the effect of other uncertainty sources.

4 Conclusion

We will present results of a photochemical model including the sources of uncertainty described above, in addition to the more usual reaction rates [1, 2]. Taking advantage of the sweet-spots, we will identify the key parameters in the photochemical modeling of Titan's upper atmosphere and compare with earlier treatments.

References

[1] E. Hébrard, P. Pernot, M. Dobrijevic, N. Carrasco, A. Bergeat, K. M. Hickson, A. Canosa, S. D. Le Picard, and I. R. Sims. *J. Phys. Chem. A*, 113:11227–11237, 2009.

[2] Z. Peng, M. Dobrijevic, E. Hébrard, N. Carrasco, and P. Pernot. *Faraday Discuss.*, 147:137–153, 2010.

[3] N. Carrasco and P. Pernot. *J. Phys. Chem. A*, 111:3507h–3512, 2007.

[4] N. Carrasco, C. Alcaraz, O. Dutuit, S. Plessis, R. Thissen, V. Vuitton, R. Yelle, and P. Pernot. *Planet. Space Sci.*, 55:1644–1657, 2008.

[5] S. Plessis, N. Carrasco, and P. Pernot. *J. Chem. Phys.*, 133: 134110, 2010.

[6] Z. Peng, B. Gans, N. Carrasco, S. Lebonnois, D. Gauyacq, and P. Pernot. Poster EPSC-DPS2011-119 (2011).