EPSC Abstracts
Vol. 6, EPSC-DPS2011-119, 2011
EPSC-DPS Joint Meeting 2011

Impact of a new wavelength-dependent representation of methane photolysis branching ratios on the modeling of Titan's atmospheric photochemistry

Z. Peng (1), B. Gans (2), N. Carrasco (3), S. Lebonnois (4), D. Gauyacq (2) and P. Pernot (1)
(1) Laboratoire de Chimie Physique, UMR 8000, CNRS, Univ Paris-Sud, F-91405 Orsay; (2) Institut des Sciences Moléculaires d'Orsay, UMR 8214, CNRS, Univ Paris-Sud, F-91405 Orsay; (3) Laboratoire Atmosphères, Milieux, Observations Spatiales, Université de Versailles Saint-Quentin, UMR 8190, F-78280 Guyancourt; (4) Laboratoire de Météorologie Dynamique, Université Paris 6, F-75006 Paris. (pascal.pernot@u-psud.fr)

Abstract

New measurements of methane photolysis branching ratios at 121.6 nm and 118.2 nm are used to design a wavelength-dependent model between 100 and 140 nm. Results for this model are compared with the standard model where $b_{CH_3} \equiv 1$ outside of Ly-α.

1. Introduction

The precision of the rates of the photolysis processes initiating the complex chemistry of Titan's upper atmosphere conditions strongly the predictivity of photochemical models. Recent studies point out the photolysis rate constants and branching ratios of CH_4 as a key parameters [1].

Recently, new measurements of methane photolysis branching ratios have been performed at 121.6 nm and 118.2 nm by Gans *et al.* [2]. This study has been focused on the major channels leading to CH_3 and CH_2 radicals with careful uncertainty determination. The main results of this study are reported in Table 1. A key finding is that these branching ratio are strongly energy-dependent and thus *special care has to be taken to describe this process in photochemical models*.

The aim of this study is to quantify the impact of the new measurements of CH_4 photolysis branching ratios on the predictions of a photochemical model of Titan's atmosphere, and on their precision. To do this, we apply Monte Carlo uncertainty propagation using the original representation of uncertain branching ratios developped by Carrasco and Pernot [3] and extended by Plessis *et al.* [4] to complex sets of branching ratios. This work is further generalized here to deal with wavelength-dependent branching ratios. The methodology is exposed in the next section and applied to a 1D photochemical model of Titan's atmosphere. Results are compared with those of the standard representation, where $b_{CH_3} \equiv 1$ outside of Ly-α.

	Channel	$\Phi_{121.6}$	$\Phi_{118.2}$
(1)	$CH_3(X^2A_2'') + H$	0.42 ± 0.05	0.26 ± 0.04
(2)	$CH_2(a^1A_1) + H_2$	0.48 ± 0.05	0.17 ± 0.05
(3)	$CH_2(a^1A_1) + 2H$	≈ 0	(2)+(3)
(4)	$CH_2(b^1B_1) + H_2$	≈ 0*	≈ 0*
(5)	$CH_2(X^3B_1) + 2H$	0.03 ± 0.08	0.48 ± 0.06
(6)	$CH(X^2\Pi) + H + H_2$	0.071**	0.097**
(7)	$C(^1D) + 2H_2$	$0(+0.006)$	$0(+0.006)$

Table 1: Branching ratios for methane photolysis at 121.6 nm and 118.2 nm with 1 σ standard uncertainties from Gans *et al.* [2], * from Lee *et al.* [5] and ** interpolated from Rebbert *et al.* [6].

2 Modeling branching ratios

From the available information on CH_4 photolysis, *i.e.* separate measurements for $\Phi_\lambda(6)$ and the other non-zero branching ratios ($\Phi_\lambda(1)$, $\Phi_\lambda(2)$ and $\Phi_\lambda(5)$), we built a *probabilistic tree* accounting for the four observed products

$$CH_4 + h\nu(\lambda) \longrightarrow \begin{cases} \xrightarrow{B_1(\lambda)} \begin{cases} \xrightarrow{B_{11}(\lambda)} CH_3 + H \\ \xrightarrow{B_{12}(\lambda)} CH_2(a) + H_2/2H \\ \xrightarrow{B_{13}(\lambda)} CH_2(X) + H_2 \end{cases} \\ \xrightarrow{B_2(\lambda)} CH + H_2 + H \end{cases}$$

where the $B_i(\lambda)$ and $B_{ii}(\lambda)$ are uncertain wavelength-dependent probabilities.

In order to generate random samples of wavelength-dependent branching ratios, we followed a procedure based on interpolation in logratio space of random samples generated at the measurement wavelengths, using Dirichlet-based distributions [4]. A set of curves is displayed in Fig. 1.

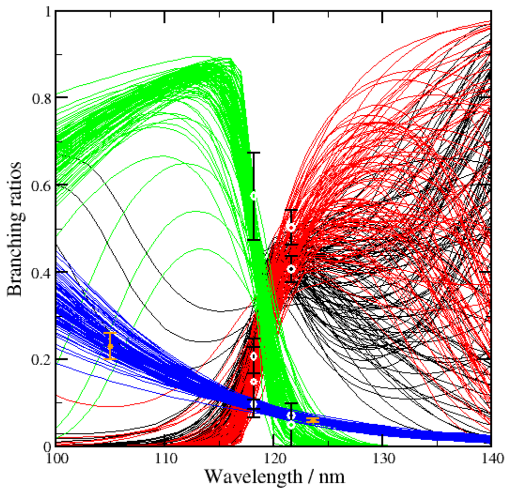

Figure 1: Sample of extrapolated branching ratios. The experimental data are figured as bullets with 95% uncertainty bars: (blue) b_{CH}; (green) $b_{CH_2(X)}$; (red) $b_{CH_2(a)}$; (black) b_{CH_3}

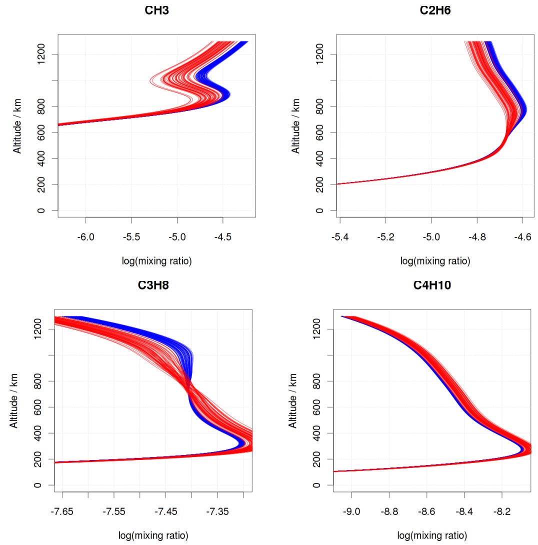

Figure 2: Samples of altitude-dependent mixing ratios for a few species for both scenarii: (blue) scenario 1; (red) scenario 2.

3 Titan's photochemistry

In the present version of the 1D IPSL photochemical model [7], there is no discrimination between electronic states of CH_2. They were consequently aggregated, resulting in the reduced set of branching ratios $\{b_{CH}, b_{CH_2}, b_{CH_3}\}$.

Two scenarii were considered and compared:

• Scenario 1: the "standard" model: $b_{CH_3} \equiv 1$ outside of Ly-α;

• Scenario 2: as defined in section 2.

For each scenario, a sample of 60 values of the branching ratios was generated and used as input of the photochemistry code. The stationnary mixing ratios of all species in the model were inspected, and the corresponding uncertainty factors were estimated from the sample of output profiles.

The mean values of most species are notably changed, and, as expected, uncertainty factors are also larger for most species in scenario 2 (Fig. 2).

4 Conclusion

This study confirms that accutate data on the photolysis of methane at Ly-α constrain strongly photochemical model of Titan.

We expect that the non-Lyα branching ratios will have a stronger impact for other photon fields, as in the interstellar medium or some experimental setups. For such cases, there is an obvious need of accurate *ab initio* calculations and additional non-Lyα branching ratios measurements.

In any case, modelers should avoid the "$b_{CH_3} \equiv 1$ outside of Ly-α" scenario, which has no experimental support.

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