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

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ABSTRACT

A new wavelength-dependent model for CH_4 photolysis branching ratios is proposed, based on the values measured recently by Gans et al. (Gans, B. et al. [2011]. Phys. Chem. Chem. Phys. 13, 8140–8152). We quantify the impact of this representation on the predictions of a photochemical model of Titan's atmosphere, on their precision, and compare to earlier representations. Although the observed effects on the mole fraction of the species are small (never larger than 50%), it is possible to draw some recommendations for further studies: (i) the Ly-α branching ratios of Wang et al. (Wang, J.H. et al. [2000]. J. Chem. Phys. 113, 4146–4152) used in recent models overestimate the CH_2:CH_3 ratio, a factor to which a lot of species are sensitive; (ii) the description of out-of-Ly-α branching ratios by the "100% CH_3" scenario has to be avoided, as it can bias significantly the mole fractions of some important species (C_3H_8); and (iii) complementary experimental data in the 130–140 nm range would be useful to constrain the models in the Ly-α deprived 500–700 km altitude range.

1. Introduction

Titan, the largest satellite in the kronian system, has a massive atmosphere of 1.5 bar at the surface, extending up to about 1500 km of altitude. Methane is its second most abundant constituent after nitrogen and participates for about 2–10% of the total composition depending on the altitude (Hébrard et al., 2007).

With such a massive and extended atmosphere, the radiative budget of Titan's atmosphere is complex, controlled by a progressive and selective absorption of the solar spectrum from the top of the atmosphere down to the surface by nitrogen and methane, but also by minor compounds produced by atmospheric photochemistry. Actually the combined photochemistry coupling nitrogen and methane systems leads to the production of heavier volatile organic species, but also to nitrogen-rich solid organic aerosols with a strong prebiotic interest starting from the upper layers of Titan's atmosphere (Waite et al., 2007).

The photolysis of methane is one of the central primary processes initiating the unique radical and ion chemistry network of "Titan's organic factory" (Atreya, 2007). Its influence on Titan's atmospheric chemical species has been quantified in the global sensitivity study led in Hébrard et al. (2009). This work shows that methane photolysis is a key process at altitudes as low as 600 km, with an increasing weight in the upper atmosphere.

Methane photolysis in the upper layers of the atmosphere is mainly driven by the Ly-α wavelength (121.6 nm), for which experimental fragmentation probabilities are available. However, this predominance disappears below ~700 km, and the evolution of the methane fragmentation pattern with wavelength can affect the photochemistry occurring at various altitudes in Titan's atmosphere. The variation of the branching ratios among the products of methane photolysis at other wavelengths than Ly-α is mostly unexplored, and recent results by Gans et al. (2011) shed a new light on this topic.

To assess the influence of the values of these branching ratios in a photochemical model of Titan's atmosphere, a local sensitivity study was performed by Wilson and Atreya (2000) for hydrocarbon species. Varying methane photodissociation branching ratios sequentially at Ly-α and in the rest of the spectral range, they found a significant effect of the Ly-α branching ratios for heavier species (containing more than two carbon atoms). But, the effect of non-Ly-α branching ratios was found to be small, modifying at most C_2H_6 density by 65%. In this study however, Ly-α remains the main contribution to methane photolysis down to 600 km.

The aim of the present article is to quantify the impact of the new measurements of methane photolysis branching ratios by Gans et al. (2011) on the predictions of a photochemical model of Titan's atmosphere, and on their precision. In the next section,

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we review the existing experimental data on the VUV fragmentation of methane, their implementation in recent photochemical models, and the expected contribution of non-Ly-α wavelengths to Titan's photochemistry. In Section 3, we develop a wavelength-dependent model for methane photolysis branching ratios, building on recent developments in the probabilistic representation of uncertain branching ratios (Plessis et al., 2010, 2011). This model is then implemented in a 1D photochemical model of Titan's atmosphere and used for a comparison of the predicted densities of minor chemicals with those produced by the dichotomous Ly-α/non-Ly-α representation. The results are presented and discussed in Section 4. We conclude by providing insights for the impact of the present wavelength-dependent model in other, non-Ly-α dominated, radiation fields (synchrotron, intergalactic, etc.). Motivated data needs for Titan's atmosphere modeling are also presented.

2. VUV photolysis of methane: data and models

We review in this section the existing data on the photodissociation of methane on the experimental side, notably recent data for a non-Ly-α wavelength. Next, we consider the status of the implementation of the photolysis branching ratios data in photochemical models of Titan's upper atmosphere.

2.1. Review of the experimental and theoretical data

Photodissociation of methane has long provided serious challenges both to theory and experiments. One of the first factors which make the quantitative description of methane photolysis challenging is that several energetically allowed fragmentation channels are open, following excitation at the VUV wavelengths. The seven spin-allowed and thermodynamically-open dissociation channels at the Ly-α wavelength (λ = 121.6 nm = 10.2 eV) are listed in Table 1.

On the experimental side, the challenge comes from the difficulty of quantitatively probing the fragments such as CH_2 and CH_3. If we consider only collision-free experimental studies on the photodissociation of methane, several earlier studies have been performed, particularly at Ly-α, all of them being mainly focused on the H atom fragment detection. Mordaunt et al. (1993) estimated the quantum yield for the H atom, $\Phi(H) = 1.0 \pm 0.5$. Soon after, Brownsword et al. (1997) reinvestigated the Ly-α photolysis of methane and found a much smaller value for the H quantum yield, $\Phi(H) = 0.47 \pm 0.11$. The H/D atom kinetic energy distribution after photodissociation of methane and its deuterated isotopomers, was revisited by Wang and Liu (1998) and Wang et al. (2000). A more recent work on the H atom detection by laser induced fluorescence led to a still different value for the H atom quantum yield ($\Phi(H) = 0.31 \pm 0.05$) (Park et al., 2008), which did not help to clarify the landscape of methane photolysis. Lately, Zhang et al. (2010) performed high resolution H atom Rydberg tagging time-of-flight spectra following the photolysis of methane at wavelengths between 128 and 130 nm. They interpreted their data by inferring very highly rotationally excited CH_3 fragments. Nevertheless, their fragment internal energy analysis in terms of pure rotational excitation is questionable and should deserve a more careful simulation of the internal energy distribution.

On the theoretical side, a complete quantitative description would imply to follow the seven aforementioned channels through adiabatic and non-adiabatic trajectories on the 9-dimensional potential energy surfaces (PES). Unfortunately, these calculations have not been performed yet. MRCI and EOM-CCSD approaches were used by Mebel et al. (1997) and gave the first evidence of local minima in the S_1 first excited surface of the 3s $^1T_2$ state of CH_4. This work was completed by *ab initio* calculations performed by Cook et al. (2001), who studied other regions of this S_1 surface but none of these studies could extract possible pathways, either adiabatic or non-adiabatic, leading to methane dissociation. Later, Van Harrevelt (2006) presented a study based on MR-SDCI calculations allowing to explore possible non-adiabatic pathways towards methane dissociation. He found that some of the minima previously calculated by Mebel et al. (1997) were in fact saddle points. He found the occurrence of conical intersection between the S_1 and the S_0 surfaces which would possibly lead to the formation of $CH_3(X)$ and $CH_2(a)$, in addition to the allowed dissociation into $CH_2(X)$ on the S_1 PES. Furthermore, he calculated the absorption cross section by MCTDH for excitation energies between 9 and 11 eV (137.8–112.7 nm). Then, by deconvolving the calculated absorption cross section by a semi-classical method, he could extract the contributions of the three Jahn–Teller distorted components of the S_1 state reached by VUV absorption (Van Harrevelt, 2007) (Fig. 1). The only available complete calculation of the dissociation pathways, via Trajectory Surface Hopping classical trajectory calculations, has been proposed by Lodriguito et al. (2009), but with much less accurate potential energy surfaces. These authors could derive branching ratios for methane photolysis which, according to them, "unexpectedly" fitted the experimental

Table 1
New branching ratios for methane photolysis channels at 121.6 nm and 118.2 nm with 1σ standard uncertainties (Gans et al., 2011).

	Dissociation channel	Notation in models	Branching ratio at 121.6 nm	Branching ratio at 118.2 nm
(1)	$CH_3(X^2A_2'') + H$	CH_3	$\Phi(1) = 0.42 \pm 0.05$	$\Phi(1) = 0.26 \pm 0.04$
(2)	$CH_2(a^1A_1) + H_2$	$^1CH_2$	$\Phi(2) = 0.48 \pm 0.05$	$\Phi(2) + \Phi(3) = 0.17 \pm 0.05$
(3)	$CH_2(a^1A_1) + 2H$		$\Phi(3) \approx 0$	
(4)	$CH_2(b^1B_1) + H_2$	–	$\Phi(4) \approx 0$[a]	$\Phi(4) \approx 0$[a]
(5)	$CH_2(X^3B_1) + 2H$	$^3CH_2$	$\Phi(5) = 0.03 \pm 0.08$	$\Phi(5) = 0.48 \pm 0.06$
(6)	$CH(X^2\Pi) + H + H_2$	CH	$\Phi(6) = 0.071$[b]	$\Phi(6) = 0.097$[b]
(7)	$C(^1D) + 2H_2$	–	$\Phi(7) = 0 \pm 0.006$	$\Phi(7) = 0 \pm 0.006$

[a] From Lee and Chiang (1983).
[b] Interpolated from Rebbert and Ausloos (1972/73).

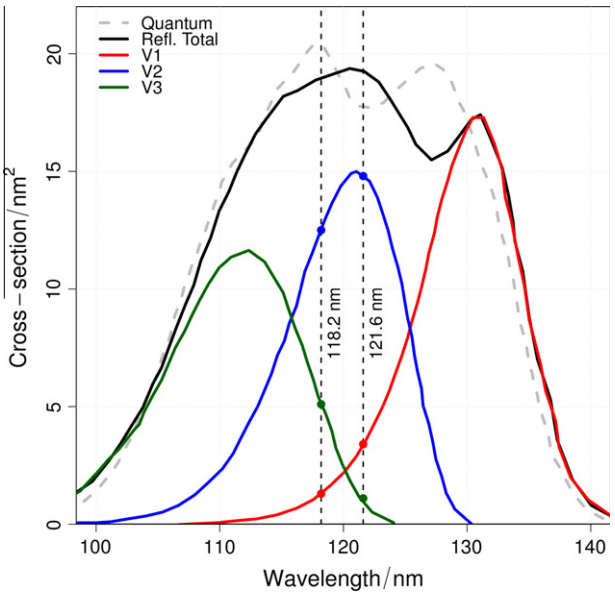

Fig. 1. Decomposition of the methane absorption cross-section into 3 bands according to Van Harrevelt (2007) (see text for details). This model could qualitatively explain the measured difference between the branching ratios at 118.2 and 121.6 nm (Section 2.2), and hints at a smooth variation of branching ratios with wavelength, as used in the proposed wavelength-dependent model (Section 3).