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Methane photochemistry: A brief review in the frame of a new experimental program of Titan's atmosphere simulations

C. Romanzin [a,*], M.-C. Gazeau [a], Y. Bénilan [a], E. Hébrard [a], A. Jolly [a], F. Raulin [a], S. Boyé-Péronne [b], S. Douin [b], D. Gauyacq [b]

[a] *Laboratoire Interuniversitaire des Systèmes Atmosphériques, Universités Paris 12 & 7 – 61, av. du G^al de Gaulle, 94010 Créteil Cedex, France*
[b] *Laboratoire de Photo-Physique Moléculaire, Université Paris 11 – bât. 210, 91405 Orsay Cedex, France*

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Abstract

As methane is the main precursor of Titan's chemistry, its photolytic behaviour is of great importance for the understanding of Titan's atmospheric system. Thus, the main purpose of this paper is to present a critical review about available laboratory methane photolysis results. The way these results are further exploited in photochemical models of Titan's atmosphere is also discussed, as those models may lead to different and sometimes contradictory conclusions. Following this literature discussions, pertinent aspects of a new experimental project for a re-examination of methane photochemistry in the frame of new Titan's atmospheric simulations are also described.

Keywords: Methane photolysis; Titan; Atmosphere; Photochemical models; Atmospheric simulations

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1. Introduction

Titan is the only satellite in the solar system that presents a dense atmosphere. Essentially composed of nitrogen and a few percentage of methane, its compostion also reveals the existence of a complex organic chemistry leading to the formation of numerous nitriles and hydrocarbon molecules among which key compounds for prebiotic chemistry such as hydrogen cyanide.

The chemical evolution of its atmosphere is essentially driven by the photolysis and the electron impact dissociation of nitrogen and methane molecules. So, a good understanding of those primary processes is decisive to succeed in modeling satisfactorily the chemical processes taking place in Titan's atmospheric system.

In this paper, our interest will focus exclusively on the methane photolytic decomposition. A critical review about methane photolysis at Lyman-α (121.6 nm) will be presented first and followed by a discussion on the way methane photodissociation is described in photochemical models. To conclude, new experimental approaches currently developed in our labs and dedicated to the exploration of methane photochemistry will be described.

2. CH_4 photolysis

The electronic absorption spectrum of methane lies in the vacuum ultraviolet (VUV) region at wavelengths shorter than 140 nm, thus Lyman-α is the most intense incident radiation susceptible to be absorbed by methane in the high atmosphere. Therefore experimental photodissociation data at this wavelength are essential for studies aiming at a good atmospheric representative-

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[*] Corresponding author. Tel.: +33 145 171 537.
E-mail address: romanzin@lisa.univ-paris12.fr (C. Romanzin).

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ness. For this reason, our remarks will concern dissociation by 10.2 eV (Lyman-α) photons or close to only. Actually, the following paragraphs consist of a compilation and analysis of different results obtained by various workers, in order to determine and classify the different photolytic decomposition pathways of methane in the Lyman-α wavelength region. The electronic transition expected for such an energy is $^1T_2 \leftarrow {}^1A_1$ that corresponds to the $3sa_1 \leftarrow 1t_2$ electron promotion. The energetically allowed channels accessible with 10.2 eV photons are listed in Table 1. Among those channels, two possibilities can be ruled out since they are precluded because of spin conservation. Thus, seven possibilities remained to be considered.

2.1. Experiments in photolysis cells

In most experiments that have been performed in photolysis cells, a krypton lamp has been used as the light source (Milligan and Jacox, 1967; Laufer and McNesby, 1968; Hellner and Vermeil, 1970; Gorden and Ausloos, 1967; Hellner et al., 1971; Rebbert and Ausloos, 1972/73). The cell filled either with pure CH_4 or CD_4 or with CH_4–CD_4 mixtures is thus irradiated by the Kr resonance line at 123.6 nm. This emission corresponds to an energy of 10.0 eV. Other deuterated compounds have been used by some authors (Mahan and Mandal, 1962; Milligan and Jacox, 1967). The conclusions on primary decomposition processes are based mainly on results obtained from analysis of stable end-products by means of chromatography or/and mass spectrometry. Several outstanding points concerning the different fragmentation pathways can be distinguished from those studies.

Table 1
Energetically allowed channels at 10.2 eV (adapted from Cook et al. (2001))

CH_4 + hν → …	**thermodynamic thresholds (eV)**	**ΔE (eV)**	**reaction n°**
CH_3 (X^2A_2”) + H	4.47	5.73	**J_1**
CH_2 (X^3B_1) + H_2	4.62	5.58	▨
CH_2 (a^1A_1) + H_2	5.01	5.19	**J_{2a}**
CH_2 (b^1B_1) + H_2	6.04	4.16	**J_{2b}**
CH_2 (X^3B_1) + 2H	9.14	1.06	**J_3**
CH_2 (a^1A_1) + 2H	9.53	0.67	**J_4**
CH ($X^2\Pi$) + H + H_2	9.06	1.14	**J_5**
C (^3P) + 2H_2	8.01	2.19	▨
C (^1D) + 2H_2	9.27	0.93	**J_6**

Shaded areas indicate that the decomposition pathway considered is not spin conserving. Note that in the text any reference to (J_2) must be understood as (J_{2a} + J_{2b}).

2.1.1. Methylene photofragment, CH_2

Most of the first studies mentioned CH_2 as a major product. Mahan and Mandal (1962) have indeed suggested that elimination of molecular hydrogen via (J_2) was the most important primary photochemical process, even though they admitted that it was not the only one. Gorden and Ausloos (1967) study strengthened this hypothesis, also supported by further arguments established by Laufer and McNesby (1968). These latter succeeded in determining the total quantum yield of molecular hydrogen formation, Φ_{H_2}, and, the percentage of H_2 directly formed by molecular elimination, $^{mol}\Phi_{H_2}$. According to their results: $\Phi_{H_2} = 0.74$ and about 73% of the total molecular hydrogen detected is derived from direct elimination. One can then estimate $^{mol}\Phi_{H_2} = 0.58$ thus reinforcing the probability for (J_2) and (J_5) to occur. So, (J_2) and hence CH_2 seem to prevail on other channels and photofragments as it has been underlined by Slanger and Black (1982) (see Table 2). However, the conclusions of Braun and colleagues (1967) about the predominance of (J_2) are opposite. In their opinion, this fragmentation is the less probable unlike (J_5) whose non-negligible role has been put forward too by Hellner and Vermeil (1970).

2.1.2. Methylidyne photofragment, CH

Different works have pointed out the presence of CH in methane photolysis experiments. Braun et al. (1966), in an attempt to investigate the processes taking place in the VUV flash photolysis have been the first to detect CH radical directly via its $C^2\Sigma^+ - X^2\Pi$ and $A^2\Delta - X^2\Pi$ transitions in absorption. They could not conclude on its origin but they suggested that it was produced in a larger amount than CH_2. Gorden and Ausloos (1967) added that the primary dissociation channel (J_5) must be responsible for a significant fraction of CH radicals rather than a secondary fragmentation of CH_2 (Eq. (1)) and CH_3 radicals (Eq. (2)):

$$CH_2^{**} \to CH + H, \tag{1}$$

$$CH_3^{**} \to CH + H_2, \tag{2}$$

However this hypothesis of a subsequent fragmentation of methylene radicals leading to methylidyne (Eq. (1)) has been suggested by Laufer and McNesby (1968) as an additional way to produce CH according to the excess energy for (J_2) (see Table 1). Finally, the importance of CH among all the photofragments has been evaluated by Rebbert and Ausloos (1972/73) who measured $\Phi_{CH} = 0.059$. This low value is in agreement with the low probability of (J_5) suggested by Slanger and Black (1982) (see Table 2).

Table 2
Relative contributions of the CH_4 dissociation product channels after photoexcitation in the Lyman-α wavelength region

	Φ_H[a]	Φ_{H2}[b]	J_1	J_{2a}	J_{2b}	J_3	J_4	J_5
Slanger and Black, 1982	1.16	/	– –	+		+		–
Mordaunt et al., 1993[†] ***scenario 1***	1.0	0.24	0.51	0.24	/	0.05 + *0.20*		0.00 + *0.00*
Mordaunt et al., 1993[†] ***scenario 2***	1.0	0.51	0.49	0.00	/	∼0 + *∼0*		0.28 + *0.23*
Heck et al., 1996	(0.77)	0.33	0.66	0.22	/	∼0		0.11
Brownsword et al., 1997	0.47	0.60	0.38	0.52	/	0.01		0.08
Wang et al., 2000	(0.47)	0.654	0.291	0.584	/	/	0.055	0.07

Shaded line indicates that the experiment has been performed in collisional conditions unlike the others and is just mentioned for comparison.

[a] The values for Φ_H correspond to experimental determinations except when the figures are between brackets, then it corresponds to $(J_1) + 2(J_3) + 2(J_4) + (J_5)$.

[b] The values for Φ_{H2} correspond only to $(J_{2a}) + (J_5)$ and not to an experimental determination.

[†] The figures in italic correspond to: $CH_4 + h\nu \rightarrow CH_3^{**} + H \rightarrow {}^{3,1}CH_2 + 2H$ for (J_3) and (J_4), and to: $CH_4 + h\nu \rightarrow CH_3^{**} + H \rightarrow CH + H_2 + H$ for (J_5). These sequential contributions must be added to the direct contributions.

Considering those results, it appears that even though CH must be present, its origin is ambiguous. The problem is to know whether CH is formed by a primary process (J_5) or by a subsequent unimolecular decay of another photofragment like CH_2 and/or CH_3. However, if we sum Φ_{CH} and Φ_{CH_3} (see next paragraph), it appears that those fragments can account only for 16% of the total branching ratio, so that CH_2 must be predominant.

2.1.3. Methyl photofragment, CH_3

Braun et al. (1967) were the first to propose a primary dissociation scheme where (J_1) was the second most probable dissociation channel, making CH_3 the most abundant primary fragment after CH. This was supported by ab initio calculations from Karplus and Bersohn (1969) who pointed out that a C_{3v} deformation type would lead to the fragmentation pathway (J_1). Nevertheless, the evolution of CH_3 radicals is very uncertain since the energy in excess, released in the fragmentation after Lyman-α photolysis, is quite important (see Table 1). Thus, Ausloos and colleagues (Gorden and Ausloos, 1967; Rebbert and Ausloos, 1972/73) evoked the possibility of a secondary fragmentation leading to the production of CH radicals (Eq. (2)), whereas Laufer and McNesby (1968) suggested that it could lead to CH_2 (Eq. (3)).

$$CH_3^{**} \rightarrow CH_2 + H, \tag{3}$$

Few years later, Hellner and Vermeil (1970) evaluated the quantum yield for the CH_3 radical production, Φ_{CH_3}, and found it to be negligible ($\Phi_{CH_3} = 0.1$), in agreement with Lindholm's (1970) calculations which estimated the formation of methyl radical as highly improbable on the basis of symmetry considerations. Further results (Hellner et al., 1971; Slanger and Black, 1982), confirmed the low probability for (J_1) to occur.

To complete this review on methane photodecomposition, one must not forget to quote the determination of the atomic hydrogen quantum yield, Φ_H, by Slanger and Black (1982) at Lyman-α. They found $\Phi_H = 1.16$ and reached the conclusion that atomic hydrogen is essentially formed following (J_3) and (J_4) channels. It is noticeable too, that Braun et al. (1967) and Rebbert and Ausloos (1972/73) have been the only ones to take (J_6) into consideration, others considering this channel as unlikely to occur.

As a conclusion, one must keep in mind that the results discussed above were determined in collisional conditions and by means of correlations between stable end-products and supposed primary processes. One might then have some doubts about the primary nature of the probed processes because a significant part of information is lost due to collisional effects. Nevertheless, these were the only data available when the first models of Titan's atmosphere were created (see Section 3 for more details).

2.2. Collision free experiments

To solve the problems concerning the nature of the probed processes and improve our knowledge about methane VUV photodissociation, further experiments have been carried out. They consisted of irradiations of pure CH_4 and/or pure CD_4 at Lyman-α performed in collision free conditions. In most cases, methane was introduced in the photolysis zone of the experimental device through a jet. The primary processes were probed directly by detection of primary photofragments with techniques such as time of flight spectroscopy (TOF) and Doppler line profile measurements.

Mordaunt and colleagues (1993) have been the first to investigate methane photolysis in the conditions described above. They measured and analysed the kinetic energy distribution of atomic hydrogen formed during photodissociation (see Table 1 for the corresponding channels). They observed two populations of hydrogen atoms: a fast one and a slow one. According to them, the fast channel corresponds to hydrogen atoms formed concomitantly with $CH_3(X^2A_2'')(J_1)$, whereas the slow H atoms are formed via three body fragmentation processes such as (J_3), (J_4) and (J_5) (see Table 1 for the corresponding excess energy). They also suggested that a fraction of these slow atoms comes from a subsequent decay of CH_3^{**} radicals. The same observation concerning the energetic distinction between H atoms has also been reported by Heck and coworkers (1996). They evaluated that the fast channel accounts for 87% of the total H atoms and considered secondary fragmentation (Eq. (3)) and contribution from (J_5), (J_3) and (J_4) as responsible for the remaining 13%. In addition, they examined the H_2 distribution after absorption of two UV photons in the 210–230 nm range. They found a bimodal distribution and suggested that the fast H_2 comes from (J_2) dissociation pathway, whereas the slow ones might be formed through (J_5) and by secondary fragmentation of CH_3^{**} (Eq. (2)). A more recent study by Wang and Liu (1998) confirmed the existence of two kinds of H atoms distinguishable according to the fragmentation processes implied in their formation, but these latter did not conclude on the concerted or sequential character of those dissociations. Nevertheless they discussed about the radiationless pathways involved in (J_1) fragmentation.

In order to better understand this photolytic behaviour, Mebel and colleagues (1997) have carried out a comprehensive theoretical study on ($^1T_2$) and ($^3T_2$) excited states of methane. They discussed on the different dissociation pathways and, according to their results, formation of fast H atoms and of $CH_3(X^2A_2'')$ could be explained either by an internal conversion or by an intersystem crossing process. Cook and colleagues (2001) performed complementary ab initio calculations in which they described the possible fragmentation pathways from a mechanistic and dynamic point of view. They also carried out an experimental study and their general conclusions strengthened Wang and Liu's remarks (1998).

With the development of experimental setups adequate to work in collision free conditions, new determinations of atomic hydrogen quantum yields have become possible. In fact, it was another outstanding point of Mordaunt and co-workers (1993) study: they found $\Phi_H = 1.0^{+0.6}_{-0.4}$, in accordance with Slanger and Black's (1982) previous value (Φ_H = 1.16). But, the reinvestigation of the atomic hydrogen quantum yield by Brownsword et al. (1997), performed in very similar conditions, led to a much smaller value than the one reported by Mordaunt et al. (1993): $\Phi_H = 0.47 \pm 0.11$. To explain this difference, Brownsword et al. (1997) attributed a larger importance to (J_2) channel leading exclusively to H_2 than Mordaunt et al. (1993) did (see Table 2).

Finally, considering former and new data acquired by means of these comprehensive studies, several authors proposed some photodissociation schemes which are summarized in Table 2. Mordaunt and colleagues (1993) proposed two scenarios to rationalize the photolytic decomposition they observed, the distinguishing features between the two scenarios being the needed activation energy and the symmetry of the transition state. In scenario 1, CH_3^{**} leads exclusively to the formation of CH_2 radicals (Eq (3)), while in scenario 2 it leads both to CH and CH_2 radicals, (Eqs. (2) and (3)). But, independently from the chosen scenario, it appears that the simple C–H bond-breaking process (J_1) is the predominant channel. Anyway, these scenarios are limiting cases, it means that the real situation should be somewhere in between the two cases. The same remark applies for the values reported by Heck et al. (1996). In fact, they have just established proportionality relations between the different channels where (J_1) largely prevails, thus the set of branching ratios presented in Table 2 has been crudely stated without considering any contributions from (J_3) and (J_4) channels. Brownsword et al. (1997) combined their new Φ_H value with available literature ones to determine the relative contributions of the different channels to methane photodissociation and concluded that (J_2) and (J_1) play the major roles in the fragmentation process. But the most complete determination of quantum yields until now has been performed by Wang and co-workers (2000). By means of multiple experiments, the authors succeeded in drawing up a whole set of branching ratios. In addition, they brought experimental evidence that CH_2 is formed in the (a^1A_1) state, thus confirming earlier theoretical (Karplus and Bersohn, 1969; Lee and Janoschek, 1979) and experimental (Masanet and Vermeil, 1975; Lee and Chiang, 1983) studies.

Several features can be discussed from previous results. It appears that whereas the fragmentation following the (J_1) pathway was first believed as unlikely, new experimental data revealed that it is in fact one of the two main decomposition processes with (J_2) whose importance was already shown in former studies. Concerning methylidyne radical, its presence is not questioned but its weak abundance, already noticed by Rebbert and Ausloos (1972/73), tends to be confirmed by the different values found for (J_5) branching ratio. Another issue is the evolution of methyl radicals since their secondary fragmentation is often presented as an alternative source for CH and CH_2 radicals. This sequential decomposition of methane makes its photolysis even more complex to understand because it becomes difficult to really identify the primary products. Both primary and sequential processes are important and should be taken into account for a realistic simulation of Titan's atmosphere. So far, the only consensus established on methane photodissociation at Lyman-α concerns the electronic state in which methylene fragments are produced. Indeed, several studies, Masanet and Vermeil (1975), Lee and Chiang (1983), Wang et al. (2000), clearly concluded that CH_2 is formed in the (a^1A_1) state. We can also point out that there are few experimental data deduced from the direct analysis of hydrocarbon fragments. The main reason is that the detection is quite complex but it may be a complementary way to fully understand methane VUV photolysis.

3. Photochemical models

Numerous theoretical models have been built to explain and predict the chemical evolution of species in methane-rich atmospheres. All these models consider a straightforward photochemical scheme initiated by methane photolysis followed by radical–radical and radical–molecule reactions that eventually lead to the formation of complex hydrocarbons. This paragraph illustrates how the knowledge of the possible photofragment branching ratios has influenced the description of CH_4 chemistry in models. We will focus our review on photochemical models of Titan's atmosphere. For the first time, we give a compilation of all determined profiles of computed mixing ratios as a function of altitude (Fig. 1). Then, we will be able, on one hand, to comment on how the theoretical data obtained by the available photochemical models fit the observations (ISO data for hydrocarbons, Coustenis et al., 2003) and, on the other hand, to compare the output of models themselves.

A model for Jupiter's atmosphere, mainly composed of hydrogen and a few percentage of methane, has been first developed by Strobel (1969) and adapted few years later to simulate Titan's atmosphere (Strobel, 1974). Allen et al. (1980) updated the chemical part of this first model with the inclusion of the catalytic dissociation of CH_4 by C_2H_2 and the formation of polyynes as the precursory molecules for the haze layer on Titan. In the light of the scientific findings from the Voyager mission, in particular the predominance of nitrogen, Strobel (1982) constructed an updated model for hydrocarbons taking into account, for the first time, the photochemistry of N_2. Those early models, are incomplete because of the fact that methane chemistry was still poorly documented. For this reason $^1CH_2$ radical was considered as the main product of the methane photolysis at Lyman-α.

A year later, a one dimensional (1D) model of Titan's atmosphere was published (Yung et al., 1984). On the basis of a compilation of experimental studies on methane photolysis at Lyman-α (among others: Laufer and McNesby, 1968; Rebbert and Ausloos, 1972/73; Slanger and Black, 1982), these authors have adopted a scheme leading to $^1CH_2$, $^3CH_2$ and CH fragments with respective branching ratios of 0.41, 0.51 and 0.08. The branch (J_1) ($CH_4 + h\nu \rightarrow CH_3 + H$) was, consequently, considered as negligible. For the first time, the photochemistry of simple molecules containing carbon, hydrogen, nitrogen and oxygen atoms has been investigated using updated chemical schemes and new estimates of a number of key rate coefficients. Proper exospheric boundary conditions, vertical transport and condensation processes at the tropopause have been incorporated into the model. Starting with N_2, CH_4 and H_2O, and including interactions with ultraviolet sunlight, energetic electrons, and cosmic rays, the vertical profiles of the abundance of all the minor compounds detected by Voyager have been calculated. The authors have then compared the calculated profiles with the observed mixing ratios (UVS, IRIS and radio-occultation data of Voyager 1 and 2 missions) and have concluded that, except for C_2H_4, CH_3C_2H, C_3H_8 and C_4H_2, their model successfully accounts for all the species.

Nevertheless, the scheme for methane photolysis used by Yung et al. (1984) has been ruled out by the experimental study of Mordaunt et al. (1993). As detailed in Section 2.2, these authors have proposed two schemes which differ in the importance of CH_2 versus CH formation, CH_3 being given in both cases as the main fragment formed from the 121.6 nm dissociation of CH_4. This prediction that methylene radical can be expected as the major product has repercussions on models of the outer planets and Titan's atmospheres. In the case of the Saturn's satellite, the new scheme for methane where CH_3 production dominates has been adopted. Toublanc et al. (1995) built a photochemical model of Titan's atmosphere whose main objective was to improve the fit of the data obtained by new evaluations of Voyager spectra (Coustenis et al., 1989, 1991) and new observations from Earth (Tanguy et al., 1990). Despite many other improvements, in particular concerning the radiative transfer in the atmosphere, the model was not able to explain the mixing ratios observed for C_2H_4, CH_3C_2H and C_4H_2 compounds.

An other photochemical model was developed by Lara et al. (1996). This model makes use of the second scheme for methane photolysis proposed by Mordaunt et al. (1993) as well as many updated reaction rates. Moreover, it includes a more realistic treatment of physical processes that are supposed to occur in the atmosphere (condensation processes at the tropopause, deposition of water in the atmosphere from meteoritic ablation, and dissociation of N_2 by EUV wavelengths ($\lambda < 80$ nm) and by galactic cosmic rays impacts). Most species, except C_3H_n hydrocarbons, are reasonably well reproduced, since their mixing ratios fall within the error bars of Voyager observations.

In 1996, Romani re-examined the available experimental studies on methane photolysis at Lyman-α. Setting arbitrarily the (J_5) branching ratio to zero, this author proposed a scheme quite similar to the second branching ratio scheme of Mordaunt et al. (1993) ($q(J_1) = 0.41$, $q(J_2) = 0.38$, $q(J_3) = 0.093$, $q(J_4) = 0.10$) (Table 3). Nevertheless, this result was questioned by Smith and Raulin (1999) theoretical work. Indeed, these authors, took into account the most recent measurements

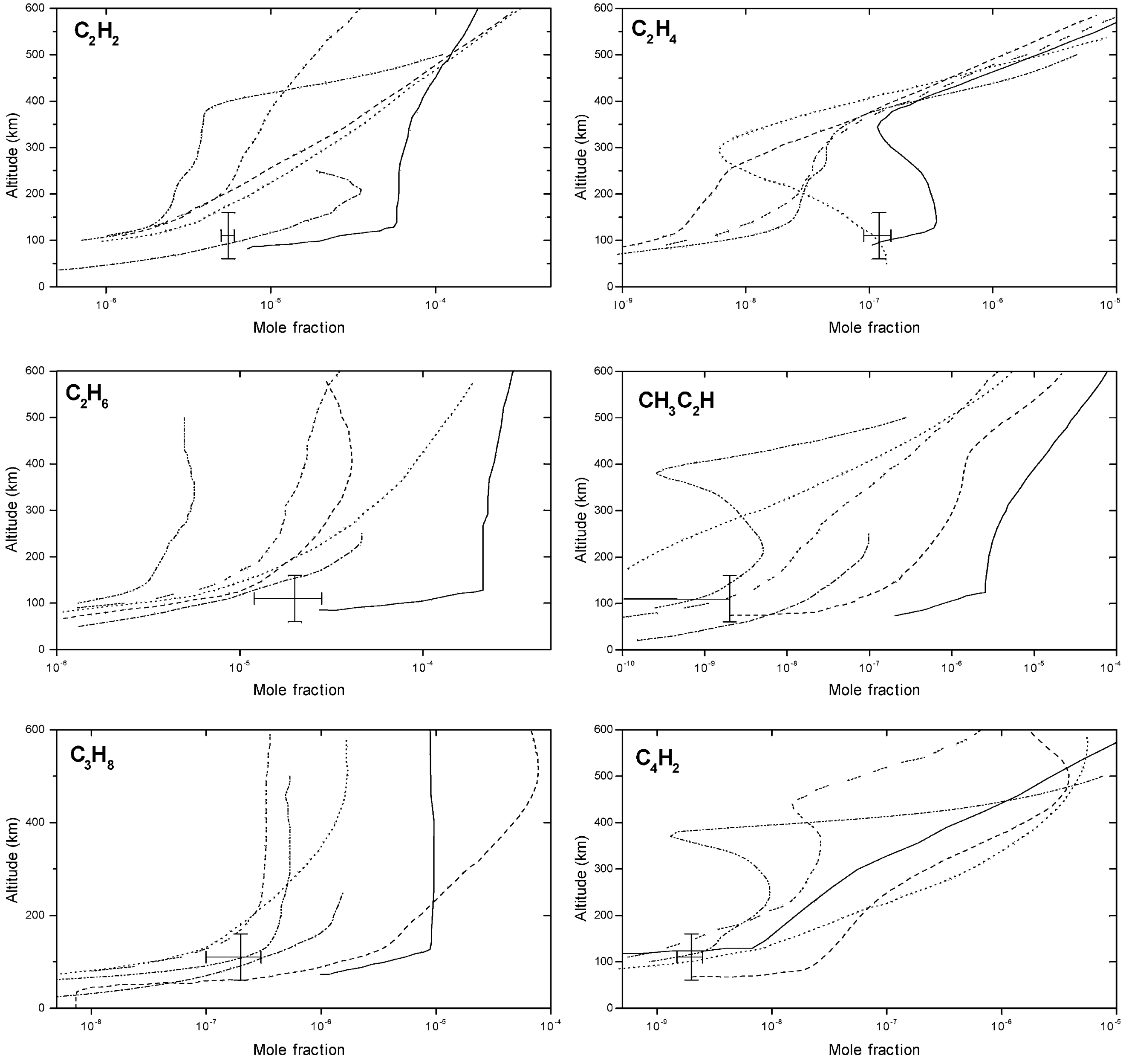

Fig. 1. Hydrocarbon abundances from various photochemical models. All panels shown in this figure include six different profiles with the associated labels: Yung et al. (1984) (solid line), Toublanc et al. (1995) (dashed line), Lara et al. (1996) (dotted line), Dire (2000) (dot dashed line), Lebonnois et al. (2001) (double dot dashed line) and Wilson and Atreya (2004) (dot segmented line). Reticles represent the stratospheric ISO observations including error bars in abundance and altitude (Coustenis et al., 2003).

Table 3
Theoretical determinations of branching ratio scheme compared to the experimental ones

	J_1	J_2	J_3	J_4	J_5	Comments
Romani (1996)	0.41	0.28	0.00	0.21	0.10	cf. Mordaunt et al. (1993)
Smith and Raulin (1999)	0.41	0.53	0.00	0.00	0.06	cf. Brownsword et al. (1997)

of H atoms and H_2 yields in the photolysis of methane (Heck et al., 1996: $q(J_1) = 0.66$, $q(J_2) = 0.22$, $q(J_5) = 0.11$; Brownsword et al., 1997: $\Phi(\mathrm{H}) = 0.47 \pm 11$) and provided new quantum yields for the five pathways ($q(J_1) = 0.41$, $q(J_2) = 0.38$, $q(J_3) = 0.093$, $q(J_4) = 0.10$). The latter are in good agreement with Brownsword et al. (1997) experimental results (Table 3). Because of these contradictory results both schemes have been tested in the first 2D latitude–altitude photochemical and transport model developed by Lebonnois et al. (2001). This model has been built in order to investigate seasonal variations of the composition of Titan's low stratosphere. It uses an updated photochemistry based on Toublanc et al. (1995) original work but without oxygen compounds. Whatever scheme is used (Mordaunt et al., 1993 or Smith and Raulin, 1999), the model gives similar results except in the very high atmosphere. The latitudinal variations of most species observed by Voyager 1 are well fitted, nevertheless, discrepancies are observed for ethylene C_2H_4, cyanoacetylene (HC_3N), diacetylene (C_4H_2) and cyanogene (C_2N_2) and are attributed to problems in the chemical scheme.

The methane photolytic scheme chosen by Dire for his 2D model (Dire, 2000) is based on the experimental work provided by Heck et al. (1996). Although mixing ratios derived from this model for ethane and propane agree with Voyager IRIS data, the model overestimates the abundances of acetylene (C_2H_2) and ethylene (C_2H_4) and, moreover, of diacetylene (C_4H_2). The author could not explain which parameter (dynamics, photochemical or diffusion) used in the model was responsible for these discrepancies, except for acetylene and ethylene for which the absence of a chemical reaction may explain the retrieved high mixing ratios.

As the most recent studies have not answered the issue of methane photolytic product yields at Lyman-α, Wilson and Atreya (2000) have used a 1D photochemical model with updated chemistry to investigate the significance of these quantum yield schemes on the hydrocarbon chemistry of Titan's atmosphere. Thanks to sensitivity studies, these authors have demonstrated that no discrimination between schemes is possible by just fitting the observations. Indeed, abundances of simple hydrocarbons such as acetylene (C_2H_2) and ethylene (C_2H_4), at the observed altitudes, are not sensitive to the choice of methane photolysis scheme. Only C_3 molecules abundances show substantial changes in their abundances especially C_3H_6 and CH_3C_2H whose changes are even surpassing observational uncertainties. The authors have concluded that the differences in the abundances among previous photochemical models are mainly due to the chemistry and the chosen eddy diffusion profiles, and not to the methane photolysis scheme. Another issue of Wilson and Atreya's paper (2000) is that their nominal scheme (Romani, 1996) provides an intermediate profile among the tested schemes (Mordaunt et al., 1993; Smith and Raulin, 1999). That is the reason why their latest Titan's 1D photochemical model (Wilson and Atreya, 2004) is based on this scheme instead of the one of Brownsword et al. (1997) even though the latter has been confirmed by the most recent and forefront experiment performed by Wang et al. (2000). Finally, with an improved description of the chemistry (extensive treatment of dissociation processes from solar photons and electrons) and the physics (parametrization of processes including cosmic rays, electron impacts and opacity provided by fractal haze particles) and with an appropriate eddy diffusion profile, this model leads to an improved but not fully satisfactory fit with observational data over previous Titan's photochemical models.

In conclusion of this overview of Titan's photochemical models, we can only agree with Lee et al. (2000) that "a rigourous test of the theory of hydrocarbon photochemistry, and a systematic comparison between these models using a consistent set of photochemical reactions applied to all of the atmosphere of the outer solar system is still lacking". Furthermore, we have seen that none of these models have provided a satisfactory explanation for the mixing ratios of the whole set of observed compounds, and in particular the hydrocarbons reported in Fig. 1.

To go further in the knowledge of Titan chemistry, sensibility studies are currently performed at LISA in order to point out its key parameters (Hébrard et al., 2005).

4. New experiments at LISA and LPPM

Our teams (LISA and LPPM) are currently developing new experimental projects dedicated to re-examine methane photochemistry. With that goal, we are carrying out two kinds of photolysis experiments in static conditions and in a gas flow system.

4.1. Static experiments

Classic photolysis experiments in closed cell are performed simultaneously with theoretical models. The experimental results are compared with the data obtained with a 0D model using the reaction pathway parameters (rate coefficients, branching ratios, photolysis frequencies, etc.) adapted to the considered perfectly known physical experimental conditions, namely pressure and temperature. Such a method allows to test the accuracy of the chemical scheme used. In the case of methane photochemistry studies, CH_4, placed in a cell at a pressure of one to few tens of millibars, is photolysed at Lyman-α delivered by an enclosed gas resonance light source filled with an H_2/He mixture. The evolution of the irradiated gas mixture is analyzed by IRTF spectrometry and the stable end-products are quantified. The chemical evolution of the system is then compared with the 0D model that uses a complete description of the CH_4 dissociation scheme involved (including secondary reactions) (Hébrard et al., 2005). Thus, static experiments can be a very powerful tool to highlight weaknesses in the description of the chemistry in photochemical models. From our point of view, comparison between models and experiments is an appropriate way to improve our understanding of chemical systems, and more accurate chemical schemes can be developed through coupling these approaches. However, one has to be aware that this objective can only be reached if experiments are performed in such conditions that wall-effects (Smith et al., 1999) and leaks (Vuitton, 2002) are avoided.

4.2. Flow experiments

The flow experiments are an alternative to those performed in photolysis cell as they minimize experimental artefacts evoked above. They differ also from non-collisional condition experiments (Section 2.2) as they allow a chemical evolution of the system. Indeed, flow experiments carried out in a laser photolysis reactor and using Cavity Ring Down Spectroscopy (CRDS) as detection technique, makes the measure of absolute concentrations of reactive species within an evolving system possible (Berden et al., 2000). CRDS is an absorption spectroscopy technique in which an increased decay rate of laser intensity within a stable optical cavity is induced by the presence of absorbing compounds within this cavity (O'Keefe and Deacon, 1988; Zalicki and Zare, 1995). This way, by scanning the wavelength of the probe laser, one can obtain absorption spectra inasmuch as one of the target compounds exhibits a transition in the scanned spectral region. At a given wavelength, corresponding to an absorption feature of one of the compounds, kinetic measurements (concentration versus time) can also be done by collecting the data for a range of delay intervals (typically 0–1000 μs) between the photolysis and probe laser pulses (Atkinson and Hudgens, 1997). Currently, experiments are performed in order to probe and compare the CH fragment production (through its $A \leftarrow X$ transition at 431 nm) from two energetically equivalent photolysis processes, i.e., a single photon process at 121.6 nm (Lyman-α), and a two-photon process at 248 nm.

5. Conclusion

Despite the fact that methane photolysis has been the subject of many theoretical and experimental studies, a complete understanding of the process has not been achieved yet. As we have shown, the available literature provides contradictory values for the branching ratios of the various possible CH_4 photolysis pathways at Lyman-α.

Photochemical models of Titan's atmosphere have been built using alternatively the most recent methane photodissociation scheme proposed by experimentalists or theoreticians, but none of those models have given satisfactory fits for the whole set of observed compounds. Indeed, a comprehensive description of the hydrocarbon photochemistry is still a great challenge. Sensitivity studies on the choice of methane photolysis scheme done by Wilson and Atreya (2000) have shown that no observational constraints are able to discriminate between those schemes. The reason is that the chemical system is very complex and discrepancies between observational and theoretical data cannot be attributed to the very primary step of the process.

As reported above, different schemes for the methane photolysis have been adopted to fit the available observations of Titan. However, continuous effort in conducting laboratory measurements under conditions applicable to Titan's atmosphere (especially low temperature and low pressure measurements) is still necessary. Thus, experiments should be performed in order to test, on one hand, the reliability of the description of critical reaction pathways and, on the other hand, the accuracy of kinetic parameters (absorption cross-sections, quantum yields and rate constants).

A more accurate chemical scheme could be then developed by coupling theoretical and experimental approaches. For example, following the photochemical evolution of a simple gas mixture can provide quantitative data which can be directly used to test a restricted part of the chemical scheme used in photochemical models. This is the method we use in order to determine the relative contributions of the different channels to methane photodissociation. In parallel, we are working on the direct detection and quantification of fragments issued from methane photolysis at Lyman-α and 248 nm by laser CRDS spectroscopy techniques (see Section 4.2.).

These studies are the first step of a new program named SETUP (a french acronym for Experimental and Theoretical Simulations Useful for Planetology), that couples laboratory experiments and theoretical studies in order to refine the theoretical description of the processes involved in Titan's atmosphere. The experimental device, currently under development, consists of a reactor where the initial gas mixture, representative of the main composition of the atmosphere: CH_4/N_2 (2/100), will be submitted simultaneously, for the first time, to both major energy sources that are responsible for the chemical evolution of Titan's atmosphere: electrons and photons. Cold plasma and UV irradiation (248 nm) will be respectively used to dissociate N_2 and CH_4 (by a two-photon mechanism). Time-resolved analysis of the resulting gas sample will be done by means of spectroscopic methods.

This work should provide adequate kinetic data and appropriate reaction pathways in order to improve models and therefore to enhance our knowledge of Titan complex atmospheric chemistry.

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