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Photolytic behaviour of methane at Lyman-α and 248 nm: Studies in the frame of a simulation program of Titan’s atmosphere (S.E.T.U.P.)

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Abstract

This paper first describes briefly some of the forefront global simulations of Titan’s atmosphere that have been carried out up to now. In these experiments, an initial gaseous mixture of N₂/CH₄ is submitted to a single energy source and the retrieved gas and/or solid phase(s) is/are analyzed by different techniques.

The second section presents a new simulation program, named S.E.T.U.P., currently under development in our laboratory. In this program, an original experimental device will be used to perform simulation experiments. The specificities of this device are also discussed in details in the second part. Indeed, it will allow:

(i) to improve the representativeness of such simulation experiments towards Titan’s atmospheric conditions. For the first time, the initial gas mixture will be submitted to both major energy sources that are responsible for the chemical evolution of Titan’s atmosphere: electrons and photons (248 nm).

(ii) to perform an in situ diagnostic by means of time resolved spectroscopy. Qualitative as well as quantitative analysis will be performed in order to investigate the chemical mechanisms involved in the evolution of the gaseous mixture.

In a third part, the paper reports some studies on the photolytic behaviour of methane at Lyman-α and at 248 nm. Indeed, such a work was necessary to validate the experimental device that will be used to carry out the Titan’s simulations in the S.E.T.U.P. program.

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Keywords: Photochemistry; Titan’s atmosphere; Experimental simulations; CRDS technique

1. Introduction

Due to its similarity with the primitive Earth, Titan, the largest moon of Saturn, is of main interest for exobiology. Indeed, both objects exhibit a dense atmosphere very rich in organic compounds and with a similar vertical atmospheric structure. Moreover, they both present a liquid phase on their surface, see Elachi et al. (2006) and Mitri et al. (2007) for recent detections on Titan. During their evolution, Titan and the Earth may have gone through the same processes: complex chemical reactions, precipitation, erosion, volcanism and meteoritic and cometary impacts (Raulin et al., 1994). Thus, studying Titan, where a primitive organic chemistry is still going on today, is a way to improve our knowledge of terrestrial prebiotic processes, and more generally, of the origin of the organic matter and its evolution in the solar system since its formation.

The whole set of data obtained from observations, theoretical modelling and laboratory experiments (Gazeau et al., 2000) are necessary to understand planetary atmospheres. The complex evolution of those environments can be simulated experimentally by submitting a given gas mixture to energy deposition under controlled conditions (Sagan et al., 1984). The study of the gaseous products can provide information on the nature and relative abundances of the minor trace species that are expected, given the main composition of the atmosphere. Such information can then be used as a precious guide for observa-
tonal campaigns and for theoretical modelling of the studied atmosphere. Indeed, experimental simulations can highlight weaknesses in photochemical models, for example, by showing the presence of a compound that has not been considered by the model. In that case, new pathways leading to the formation of this compound will have to be included in the model. The solid phase also generally formed during these experimental simulations provides good laboratory analogues of atmospheric aerosols. The latter are usually named “tholins”. The determination of their chemical composition, their physical and chemical properties (solubility, size of the particles, etc.) and their spectral characteristics (in a very wide range of wavelengths) is of prime importance. It is, so far, the only way to retrieve the information on atmospheric hazes that are necessary to develop models and interpret the optical data already available on the studied extraterrestrial atmospheres. Moreover, getting such analogues is useful for developing and calibrating instruments for in situ analysis.

2. The global simulation experiments of Titan’s atmosphere

During the last decades, numerous laboratory experiments have been performed with the goal to simulate Titan’s atmospheric chemical processes. In these experiments, initial gaseous mixtures representative of the main composition of Titan’s atmosphere, essentially N₂/CH₄, are submitted to different energy sources. Fig. 1 shows the estimation of the energy flux dissipated as the function of altitude for the main energy sources available in Titan’s atmosphere: solar ultraviolet radiation and energetic particles (galactic cosmic rays and Saturnian magnetospheric electrons).

Indeed, in the high atmosphere of Titan that is above the altitude of about 700 km, molecular nitrogen N₂ is dissociated by energetic photons (\( \lambda < 90 \) nm) into atomic nitrogen. Then, the latter diffuse to lower altitude where the available VUV photons (\( \lambda < 160 \) nm) dissociate methane. A complex chemistry, coupling hydrocarbons and nitrogen compounds (nitriles), is then initiated, leading finally to the production of aerosols in the stratosphere. In this region, the energy is deposited through energetic particles and photons belonging to the middle of the UV range (Fig. 1). Besides those external sources, a possible electrical activity (terrestrial lightning like discharges) is proposed (Ramirez et al., 2001).

In the first experimental simulations of Titan, photons were simulated by UV lamps (Gupta et al., 1981; Clarke et al., 2000) and the effects of cosmic rays and charged particles were reproduced by cold plasmas (Thompson et al., 1991; Coll et al., 1999), whereas lightnings were produced by electric discharges, sparks or laser-induced plasmas (Borucki et al., 1988; Scattergood et al., 1989; de Vanssay et al., 1995). Those experiments were open to criticism due to the presence of wall effects. Some recent simulation experiments have been improved by using flow systems. Such systems reproduce more accurately the chemistry. In particular, they allow to operate at low pressure, lower mixing ratio for trace constituents than in static system and within conditions always close to the initial conditions in terms of chemical composition without a too important contribution of the end-products into the system. Furthermore, flow systems allow to limit wall effects.

Recently, simulation experiments of Titan’s atmospheric chemistry have been carried out essentially in six laboratories all over the world.

In the Department of Chemistry at the Rensselaer Polytechnic Institute (Troy, New York, USA), Tran et al. (2003) and Ferris et al. (2005) performed Titan’s laboratory simulations using initial gas mixtures composed of N₂/CH₄ as well as various hydrocarbons, nitriles and/or carbon monoxide (CO) (98/2/few ppm) at a total pressure of about 900 mbar and at room temperature. The aim of their work was to simulate the action of long wavelength solar UV light on Titan’s atmosphere. Thus, a low-pressure mercury lamp with emissions at 185 and 254 nm was used. Such energy deposition is representative for Titan’s stratosphere, where UV photons at shorter wavelengths than 145 nm are no longer available. Both gas and solid phases were studied. The volatile products, collected in a cold trap after irradiation of the initial mixture in the flow reactor, were analyzed qualitatively and quantitatively by gas chromatography coupled with mass spectrometry (GC/MS). The solid products, which condensed on the quartz and gold-coated silicon plates placed in the flow reactor, were studied by UV to NIR absorption. The determination of their elemental composition was also performed as well as solubility studies.

In the laboratorio de Quimica de Plasmas y Estudios Planetarios of the Universidad Nacional Autonoma de Mexico (Mexico), Navarro-Gonzalez et al. (2001) used a static system (reactor 0.5 L) where the initial gas mixture N₂/CH₄ (90/10) at low pressure (~mbar) and ambient tem-
perature was submitted to corona discharges. The idea was to mimic the electrical activity within the tropospheric methane clouds (lightning) with the aim to determine if such energy could cause an additional chemistry in the gas phase. Comparison with other energy deposition was also discussed. Other experiments were performed in order to characterize Titan’s aerosols analogues in the spectroscopic point of view (determination of the complex refractive index) as developed in Ramirez et al. (2002).

In the Department of Chemistry and Lunar and Planetary Science Laboratory of the University of Arizona (Tucson, USA), the SETI Institute/NASA Ames Research Center (Moffett Field, USA), the Service d’Aéronomie (SA) of CNRS/IPSL/UVSQ (Verrières le Buisson, France) and the Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA) of CNRS/University Paris 12 & 7 (Créteil, France), the energy source used is a cold plasma-type discharge. The temperature of the neutral gas in such plasmas remains close to room temperature even when the electron temperature is extremely high. Such cold plasmas are thought to simulate accurately the irradiation by magnetospheric electrons and cosmic rays (Thompson et al., 1991). As described in the following paragraphs, among those laboratories, the first three are more concerned with the characterization of tholins whereas, in LISA, both solid and gas phase were investigated.

In the Department of Chemistry of the Lunar and Planetary Science Laboratory, Titan’s atmospheric simulations devoted to produce tholins were performed by Sarker et al. (2003). The tholins were then systematically analyzed by Fourier transform ion cyclotron resonance mass spectrometry. This work yielded insights on the mass distribution of tholins structure and relationships regarding the distribution of saturation and nitrogen function. Tholins composition were determined to be made of 340–780 Da molecular weight units (depending on the N2/CH4 ratio of the initial gas mixture) with C/N and C/H ratios of 1.83 and 0.73, respectively. The material turns out to be readily soluble in water. The aim of the work was to underline the role of tholins in a prebiotic chemistry occurring in Titan’s atmospheric system.

In the SETI Institute/NASA Ames Research Center, Imanaka et al. (2004) formed tholins from a N2/CH4 mixture (90/10) at low and room temperature (300 K) by means of an inductively coupled plasma. In the flow system they used, the pressure was varied from 0.1 to 10 mbar in order to test the influence of the pressure on tholins’ chemical and optical properties. Indeed, several kinds of tholins have been characterized by spectroscopic methods such as IR spectroscopy, UV, VIS/NIR spectroscopy, microprobe laser desorption/ionization mass spectrometry and Raman spectroscopy. As in Sarker’s work, information on tholins chemical composition was retrieved from their experiments. They found that tholins are essentially made of nitrogen containing polycyclic aromatic compounds in a matrix of carbon and nitrogen branched networks, or polymer-like branched chain structure terminated with –CH3, –NH2 and –C≡N with fewer aromatic compounds. The elemental analysis was also achieved in order to assess the nitrogen incorporation into tholins. The C/N ratio of 1.5–1.8 and the optical properties (k value at 0.5 µm of 0.031) determined for tholins formed at low pressure infer that they are good analogues of Titan’s haze.

At the S.A., Szopa et al. (2006) developed the PAMPRE experiment (French acronym for Aerosols Production in Microgravity by Reactive Plasma) dedicated to the study of tholins. In a static system, a capacitive coupled radiofrequency cold plasma is settled in a N2/CH4 mixture (up to 10% CH4) at 0.1–10 mbar and at room temperature (~300 K). Such a device allows the production of solid particles in levitation, thus preventing any wall effects and allowing the study of the formation and growth of the particles directly in the plasma. Another improvement claimed by the authors is that the energy deposited by the electrons in the plasma can be compared energetically with the solar spectrum. After the experiment, the produced dust is collected and characterized by several techniques: scanning electron microscopy coupled with electron diffusive spectroscopy, pyrolysis–gas chromatography–mass spectrometry. The tholins produced in these conditions tend to be good analogues of Titan’s aerosols as their morphology (quasi-spherical), size (ranging from 0.5 to 1.5 µm) and composition (C/N = 1.97, C/H = 0.75, presence of aromatic species and complex aliphatic molecules) are compatible with Titan’s aerosols data deduced from observations. The experimental device gives the opportunity to generate tholins in great amount and the aim of the work is to achieve the determination of their structure and optical properties as well as to understand the processes and mechanisms implied in their production and evolution.

At LISA, Coll et al. (1997) carried out Titan’s simulation experiments within conditions close to those of Titan’s atmosphere: cold plasma simulation system, low pressure and low temperature. A glow discharge was established in a flux (≈2 mbar of total pressure) with a mixture of N2/CH4 (98/2) which passed through a U-tube reactor immerged in a cryogenic fluid maintained at 100–150 K. Characterization of the tholins formed during the simulations has been performed carefully avoiding any contamination (Coll et al., 1999). In addition to the study of tholins, the mixture of gases was also analyzed: 44 hydrocarbons and 26 N-containing compounds were identified, including C2N2 which remained the last constituent of Titan’s atmosphere that had not been observed in previous simulation experiments. This discovery showed that the chosen experimental conditions represent Titan’s atmosphere quite accurately. The gas phase end products were analyzed by IRFTS (InfraRed Fourier Transform Spectroscopy) and GC–MS (Gas Chromatography and Mass Spectrometry) techniques. The lack of knowledge of the mechanisms leading to the formation of the products (gas and solid phases) has become a serious limit to the understanding of what is going on in the simulation experiments. Furthermore, the comparison between all simulation
experiments is nearly impossible because experimental conditions are too different: temperature, pressure, composition of the initial gas mixture, energy sources, duration of experiment, etc. That is the reason why, Bernard (2004) developed a dedicated kinetic model adapted to a new set of experimental simulations in order to determine the basic elementary mechanisms involved in the discharge. Such work required to get information on the gaseous stable molecules which were detected by IRTF as previously, as well as the transient species (radicals and ions) which were qualitatively determined by UV–visible emission spectroscopy. Indeed, UV–vis radiations emitted from the excited species (nitrogen, radicals, ions, etc.) formed inside the reactor were collected by an optical fibre connected to a UV spectrometer. The analysis in the 230- to 915-nm range was achieved by using a monochromator (THR Jobin-Yvon) of Czerny–Turner type with of focal length of 1.5 m and a resolving power of 20,000.

Experimental simulations have been carried out in order to retrieve relevant data concerning the gas (determination of minor compounds) and the solid phase (tholins’ physical and chemical characterization) and relevant information has been recovered. They were indeed often in good agreement with observational data (Coll et al., 1999). This kind of approach is thus fully justified for the study of Titan’s atmosphere and, more generally, extraterrestrial’s environments. The main concern of all authors has been to perform simulations in conditions as close as possible as the Titan’s real ones. Many improvements have been achieved in terms of experimental conditions such as pressure and temperature for instance. But up to now, only one energetic source has been used (photons or electrons). Moreover, little attention has been paid to the role of reactive intermediates in the evolution of gaseous simulation mixtures. They just have been once qualitatively detected in a recent work done by Bernard (Bernard, 2004). However, it is mandatory to analyze quantitatively both types of species – stable and reactive ones – to be able to understand the chemistry involved in such laboratory experiments. In order to do so, a new experimental program is being developed at LISA. This new experimental device will allow the deposit of both energy types and the quantitative analysis of the reaction products including transient reactive species. Details about this program are given in the next section.

3. A new step in terms of representativeness towards Titan’s conditions and understanding of Titan’s chemistry: the S.E.T.U.P. program

In order to go further in the representativeness of experimental simulations, we want now to consider simultaneously the contributions of electrons and photons, both responsible for the physical and chemical evolution of compounds in the atmosphere. This step will be achieved with the program S.E.T.U.P. (French acronym for Experimental and Theoretical Simulation Useful for Planetology studies). Future experiments will indeed be performed using an unique device. The latter consists of a reactor where the initial gas mixture will be exposed, for the first time, to both major energy sources that are responsible for the chemical evolution of Titan’s atmosphere (i.e. electrons and photons). As a result, the chemistry of nitrogen and the photochemistry of methane will be combined in simulation experiments. So far, in such experiments, the analysis was only performed on the resulting gas sample. From now on, time resolved analysis of intermediates species as well as primary products will be performed to determine the chemical mechanisms involved in the reactor.

The reactor (a double wall cylinder, made of Pyrex, whose length and diameter has still to be determined taking into account the velocity of gases and the kinetics of the reactions involved) will consist in two separate units (Fig. 2):

(i) The “plasma unit” where a cold plasma will be produced by means of two electrodes in order to dissociate the molecular nitrogen introduced with a controlled outflow upstream from the reactor.

(ii) The “photochemical unit” where the methane, introduced downstream from the plasma unit with a controlled outflow, will be photodissociated by means of UV radiation. A pulsed excimer laser, providing photons at 248 nm, will be used to dissociate methane via a multiphotonic absorption process.

Thanks to this configuration of the reactor, charged species and metastable compounds produced from nitrogen dissociation will already have vanished so that methane fragments will only interact with nitrogen atoms.

An in-situ quantitative analysis of the stable compounds as well as the short-lived intermediate species will be implemented on the reactor in order to investigate the chemical mechanisms involved. Cavity Ring Down Spectroscopy technique (Fig. 2) has been chosen since it allows to measure absolute concentrations of reactive species within an evolving scheme (Atkinson and Hudgens, 1997; Romanzin et al., 2006). Indeed, absorption can be derived from the increased decay rate of laser radiation within a stable optical cavity induced by absorbing compounds (see Wheeler et al., 1998 and O’Keefe and Deacon, 1988). Absorption spectra can thus be obtained by scanning the wavelength of the probe laser through the spectral region containing a transition of a target compound. At a given wavelength, corresponding to an absorption feature, 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.

Thanks to the use of the C.R.D.S. technique, we will be able to obtain quantitative measurements of crucial parameters (including kinetic ones) still poorly known concerning Titan’s chemistry. Following the methodology we adopted at several occasions (Smith et al., 1999; Vuitton et al., 2006), a theoretical study will be carried out additionally.
to this experimental work. A comprehensive chemical scheme will be adapted to the conditions of temperature, pressure and irradiation (pulsed laser) of our experiments and will be used in a Facsimile box model (Curtis, 1979). Thus we will be able to compare the theoretical chemical evolution of the gas mixture with our experimental data. Such comparison will allow to underline weaknesses in the chemical scheme used to describe the system: the relevance of given reaction pathways and the accuracy of the kinetic data used could be tested. This work will be a guide to determine the specific experiments to be undertaken in order to determine the missing kinetic data or to determine these parameters with greater precision in the correct range of temperatures and pressures. The next section describes preliminary results concerning the experimental development of the photochemical unit.

4. Validation of the photochemical unit: comparative studies of CH₄ photolysis at 121.6 and 248 nm

In Titan’s atmosphere, photolysis of methane mainly involves Lyman-α photons (121.6 nm ⇔ 10.2 eV). Such mechanism cannot be easily reproduced in the laboratory for several reasons: difficulty to work in the VUV range, traditional photochemical lamps unsuitable for high-speed kinetic studies, etc. Therefore, in our simulation experiments, a pulsed laser (KrF Excimer delivering photons at 248 nm ⇔ 5 eV) will be used to dissociate methane in the photochemical unit of the reactor. Thus, the first step of the S.E.T.U.P. program has been dedicated to comparative photolysis experiments of methane at 248 and 121.6 nm in order to establish the relevance of the chosen irradiation setup.

The first point we checked was the equivalence of methane photodissociation at 121.6 and 248 nm on an energetically point of view. As shown in Fig. 3, the electronic absorption spectrum of methane lies in the vacuum ultraviolet (VUV) region at wavelengths shorter than 140 nm. As a consequence, Lyman-α is the most intense radiation likely to be absorbed by methane in Titan’s high atmosphere. The different photolytic decomposition pathways of methane in the Lyman-α wavelength region are also displayed on Fig. 3. Absorption of 121.6 nm photons leads to methane dissociation by a single-photon absorption process. On the contrary, due to the negligible absorption of 248 nm photons, one can infer that no dissociation can occur with such an irradiation. Yet, by focusing the incident laser beam at 248 nm with a short focal lens, the energy is concentrated in a minimal volume. In such conditions, the energy density can become high enough so that non-linear multiphotonic processes can occur. The aim of the present study was to determine the number (n) of photons involved when methane is dissociated by a focused laser beam at 248 nm. In other words, (n) corresponds to the order of the multiphotonic process which is related to the multiphotonic dissociation efficiency (\(W\)) according to:

\[ W = \sigma_n F^n \]

where \(F\) is the photon flux (photons cm\(^{-2}\) s\(^{-1}\)) and \(\sigma_n\) the cross section for a \(n\)-photons process (cm\(^{-2}\) s\(^{-1}\)). Therefore, the log-log plot of the multiphotonic dissociation efficiency as the function of the photon flux gives the opportunity to determine the value of \(n\) as shown in Fig. 4. After a region where no dissociation occurs (the...
threshold of the multiphotonic process is not reached) and before a region where saturation is observed, a straight line with a slope equal to \( n \) is obtained.

4.1. Experimental

4.1.1. Methane photolysis

Pulsed source (248 nm): A KrF Excimer laser (TIU Laser) with a repetition rate of 10 Hz and a laser pulse duration of 20 ns has been used to dissociate methane by a multiphotonic process. The laser energy was varied from 20 to 130 mJ for 20 ns duration pulses. In this configuration, the flux (\( 10^{19} \) photons per second) is four orders of magnitude greater than the one obtained with classical UV-lamps. The beam was focused in the center of the cell with a lens of 17 cm focal length (original size 14 \( \times \) 5 mm).

Continuous source (121.6 nm): A lamp filled with a gas mixture (5.5 mbar \( \text{H}_2 \) (2%) in \( \text{He} (>99.99\% - \text{Linde Gas}) \) has been used to get a 121.6 nm emission (Lyman-\( \alpha \)). Discharge in the lamp is initiated with a Tesla coil and the gas is excited by a microwave generator (Somelec – France) delivering a power of 200 W at 2450 MHz. The pressure of the gas in the lamp has been settled at a level allowing to maintain a stable discharge. The window between the lamp and the reactor is made of \( \text{MgF}_2 \). The beam diameter is about 2 cm and the photon flux of the lamp, determined by an actinometrical method (Cottin et al., 2000 and references therein), was \( \Phi_{122 \, \text{nm}} \approx 2 \times 10^{15} \) photons s\(^{-1}\).

Photolysis cell: Methane photolysis has been carried out directly in the IRTF multi-reflection cell (2.6 l) with optical path ranges from 2.1 to 10.6 m.

4.1.2. Infrared Analysis

The analysis has been performed by using an infrared Fourier transform spectrometer (Bruker Equinox 55) in the 400- to 7000-cm\(^{-1}\) range and with a spectral resolution of 2 cm\(^{-1}\). The infrared bands of the different detected compounds (\( \text{CH}_4 \) (3019.5 cm\(^{-1}\)), \( \nu_5 \) band of \( \text{C}_2\text{H}_2 \) (729.1 cm\(^{-1}\)), etc.) have been modelled using data retrieved from the GEISA database (Jacquinet-Husson, 2005).

4.2. Study of the methane photolysis at 248 nm

The experimental determination of \( n \) have been performed according to the following procedure. Methane was irradiated at 248 nm within the experimental conditions described in the previous section. After the irradiation period of 2 h, the abundances of stable hydrocarbons formed consequently to the photolysis were determined by means of classical FTIR. spectroscopy. On the basis of our knowledge of the fragments accessible with an energy greater than 10 eV: \( \text{CH}_3, \text{CH}_2 \) and \( \text{CH} \) (see Table 1, adapted from Romanzin et al. (2005)), one can predict the formation of stable compounds like \( \text{C}_2\text{H}_2, \text{C}_2\text{H}_4 \) and \( \text{C}_3\text{H}_6 \), according to subsequent reactions such as:

\[
\begin{align*}
\text{CH} + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_4 + \text{H} \\
\text{CH}_2 + \text{CH}_2 & \rightarrow \text{C}_2\text{H}_2 + 2\text{H} \\
\text{CH}_2 + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_4 + \text{H} \\
\text{CH}_3 + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \\
\end{align*}
\]

Fig. 3. Absorption cross section of methane adapted from Mount et al. (1977) and different photolytic decomposition pathways in the vacuum ultraviolet (VUV) region figure derived from Cook et al. (2001) data.

Fig. 4. Theoretical log-log plot of the multiphotonic dissociation efficiency as a function of the photon flux.
So, the production of stable hydrocarbons reflects the efficiency of CH$_4$ dissociation into primary products. In this work, the amount of stable products formed consequently to methane photolysis, like acetylene (C$_2$H$_2$) has been assumed to be proportional to the dissociation efficiency $W$ so that:

\[
\frac{1}{2} \frac{\text{C}_2\text{H}_2}{\text{C}_138}/W = r_n \cdot F_n
\]

Two sets of methane irradiation experiments ($P = 250$ and $500$ mbar, respectively) have been performed with quantitative measurements of the C$_2$H$_2$ produced for different 248 nm photon fluxes. The results after two hours experiments are displayed in Fig. 5. It appears that the logarithm of the relative quantity of acetylene formed in our experiments is proportional to the logarithm of the laser flux deposited (varying in a wide range from $5 \times 10^27$ to $3 \times 10^28$ photons cm$^{-2}$ s$^{-1}$). The slope of 2.1 indicates that 248 nm photolysis of methane proceeds via a two-photons process within our experimental conditions. This result is important for our concern as it shows that the 248-nm photolysis of methane is efficient and energetically equivalent to the one photon process at 121.6 nm (respectively, $2 \times 5$ eV vs. 10.2 eV).

However, as both physical processes are different, the branching ratios for the CH$_3$, CH$_2$ and CH radicals production (and consequently the following photochemistry) could be different. That is the reason why we have performed methane irradiation at 121.6 nm in the same cell in order to test the influence of the radiation wavelength on the nature and the abundance of the products formed.

### 4.3. Study of the methane photolysis at 121.6 nm

Many studies have been carried out in order to determine and rank the different photolytic decomposition pathways of methane in the Lyman-$\alpha$ wavelength region. The energetically allowed channels accessible with 10.2 eV photons are listed in Table 1. As discussed in a previous publication (Romanzin et al., 2005), the available literature provides contradictory values for the branching ratios of the various possible CH$_4$ photolysis pathways at Lyman-$\alpha$ (Table 1). For example, the unique channel ($J_1$) leading to the release of a methyl radical (CH$_3$) concomitantly with an hydrogen atom ($J_1$) is given as the predominant one ($66\%$) in Heck et al. (1996) work whereas it accounts only for $29.1\%$ in Wang et al. (2000). These discrepancies reveal that there is still a strong need for a determination of fragments branching ratios resulting from methane’s dissociation at 121.6 nm. Of course, as no data are available at all, fragmentation pathways for methane’s dissociation at 248 nm should also be investigated.

Our concern here is to determine, on the basis of the products formed in both cases, whether the two-photons absorption at 248 nm leads to a methane fragmentation process different from the single photon absorption one at 121.6 nm. It is indeed, another point to check to establish the relevance of the chosen irradiation setup and take into account some possible differences. To achieve this,

<table>
<thead>
<tr>
<th>Channel</th>
<th>Reaction</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>J1</td>
<td>CH$_3$ (X$^2$A$_u^+$) + H</td>
<td>4.47</td>
</tr>
<tr>
<td>J2a</td>
<td>CH$_3$ (a$^1$A$_1$) + H$_2$</td>
<td>5.01</td>
</tr>
<tr>
<td>J2b</td>
<td>CH$_2$ (b$^1$B$_2$) + H$_2$</td>
<td>6.04</td>
</tr>
<tr>
<td>J3</td>
<td>CH$_2$ (X$^3$B$_1$) + 2H</td>
<td>9.14</td>
</tr>
<tr>
<td>J4</td>
<td>CH$_2$ (a$^1$A$_1$) + 2H</td>
<td>9.53</td>
</tr>
<tr>
<td>J5</td>
<td>CH (X$^1$X) + H + H$_2$</td>
<td>9.06</td>
</tr>
</tbody>
</table>

Table 1: Dissociation channels accessible with an energy of 10.2 eV (Lyman-$\alpha$ irradiation) and their relative contributions according to available literature data (Brownsword et al. (1997), Mordaunt et al. (1993), Heck et al. (1996), Wang et al. (2000) and Slanger and Black (1982))

One has to note that no data have been published so far concerning methane dissociation at 248 nm.

![Fig. 5. Log–log plot of the relative abundance of C$_2$H$_2$ formed after methane irradiation at 248 nm as a function of the photon flux delivered by the KrF photolysis laser.](image-url)
aim, irradiation experiments of methane at 121.6 and 248 nm have been performed in parallel. Experiments at 248 nm have been described in the previous section. They have permitted to validate the energetic equivalence of the 248 nm photolysis towards the 121.6 nm one but also, to identify the nature and abundances of the various resulting hydrocarbons. Thus, in order to compare with the ones resulting from Lyman-α methane photolysis, similar experiments have been performed by means of a H$_2$ photochemical lamp (see Section 4.1.1 for experimental details). They were carried out in the same photolysis cell but at lower pressure (10 mbar) because of the strong absorption cross-section of CH$_4$ at 121.6 nm. After irradiation, the resulting gas mixture was analyzed by means of FTIR spectroscopy as for the 248 nm photolysis experiments. The results obtained are discussed in the following paragraph.

### 4.4. Comparative study of the methane photolysis at 121.6 and 248 nm

As a matter of fact, the qualitative analysis has shown great differences between both processes as ethane (C$_2$H$_6$) is surprisingly only observed during the Lyman-α experiments. Furthermore, comparable amounts of acetylene (C$_2$H$_2$) and ethylene (C$_2$H$_4$) are formed in both experiments (Fig. 6) whereas the amount of deposited energy is tremendously different. Indeed, as mentioned previously, the photon flux of the two sources used in these experiments differ widely. Nevertheless, a direct comparison is not possible as the absorption cross-sections modulate these differences (2 x 10$^{-17}$ cm$^2$ at 121.6 nm (Vatsa and Volpp, 2001) and 2.7 x 10$^{-53}$ cm$^4$ s at 248 nm (Galasso, 1992). Moreover, one of the sources is pulsed whereas the other is continuous and the volume excited by the photons is not the same in the two experiments. At 248 nm, indeed, it restricts to the focal volume defined by the action of the lens on the laser beam. According to these considerations, it appears that a direct quantitative analysis is not obvious. The analysis of the stable products in the two experiments differs widely. Nevertheless, a direct comparison is not possible as the absorption cross-sections modulate these differences (2 x 10$^{-17}$ cm$^2$ at 121.6 nm (Vatsa and Volpp, 2001) and 2.7 x 10$^{-53}$ cm$^4$ s at 248 nm (Galasso, 1992). Moreover, one of the sources is pulsed whereas the other is continuous and the volume excited by the photons is not the same in the two experiments. At 248 nm, indeed, it restricts to the focal volume defined by the action of the lens on the laser beam. According to these considerations, it appears that a direct quantitative analysis is not obvious. The analysis of the stable products in the two experiments differs widely.

To go further in the interpretation of those results, theoretical developments are currently under progress as well as attempts to directly detect CH, CH$_2$ and CH$_3$ fragments resulting from CH$_4$ photolysis. These data are indeed determining for theoretical models. Moreover, experimental simulations to be carried out in the new S.E.T.U.P.’s experimental device (building up of the reactor and tests of the C.R.D.S. spectroscopic detection technique), a re-examination of methane photolysis has been undertaken. One has to note that the available literature provides contradictory results for the methane’s primary photolytic scheme at Lyman-α and that no studies have been undertaken yet to establish the different photolytic decomposition pathways of methane at 248 nm. Comparative methane photolysis experiments have thus been performed at both wavelengths (121.6 nm and 248 nm) by using a photochemical classic continuous lamp and an excimer pulsed laser, respectively. The analysis of the stable products by means of I.R. spectrometry has led us to conclude that the photodissociation processes are energetically equivalent (one-photon vs. two-photons, respectively) but that the photodissociation channels are probably different.

5. Conclusions

Laboratory experiments are required both for the development of models and the interpretation of observations. A lot of different experimental simulations of Titan’s atmosphere have been performed in order to achieve a better understanding of the chemistry going on this satellite. Among the different laboratories developing this kind of experimental approach, the L.I.S.A. is at the origin of a new and original simulation program called S.E.T.U.P. This latter will allow to improve the representativeness of the simulation experiments towards Titan’s atmospheric conditions and to give new insights into the chemical mechanisms involved. In parallel to the development of the new experimental device (building up of the reactor and tests of the C.R.D.S. spectroscopic detection technique), a re-examination of methane photolysis has been undertaken. One has to note that the available literature provides contradictory results for the methane’s primary photolytic scheme at Lyman-α and that no studies have been undertaken yet to establish the different photolytic decomposition pathways of methane at 248 nm. Comparative methane photolysis experiments have thus been performed at both wavelengths (121.6 nm and 248 nm) by using a photochemical classic continuous lamp and an excimer pulsed laser, respectively. The analysis of the stable products by means of I.R. spectrometry has led us to conclude that the photodissociation processes are energetically equivalent (one-photon vs. two-photons, respectively) but that the photodissociation channels are probably different. To go further in the interpretation of those results, theoretical developments are currently under progress as well as attempts to directly detect CH, CH$_2$ and CH$_3$ fragments resulting from CH$_4$ photolysis. These data are indeed determining for theoretical models. Moreover, experimental simulations to be carried out in the new S.E.T.U.P.’s experimental device will permit the determination of adequate kinetic data and the identification of critical reaction pathways. The knowledge of Titan’s complex atmospheric chemistry will therefore be improved.

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References
