Photochemical kinetics uncertainties in modeling Titan’s atmosphere: First consequences

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Abstract

Uncertainties carried by the different kinetic parameters included in photochemical models of planetary atmospheres have rarely been considered even if they are supposed to be contributing mostly to the inconsistencies between observations and computed predictions. In this paper, we report the first detailed analysis of the propagation of uncertainties carried by the reaction rate coefficients included in an up-to-date photochemical model of Titan’s atmosphere. Monte Carlo calculations performed on these reaction rate coefficients have been used to introduce their uncertainties and to investigate their significance on the photochemical modeling of Titan’s atmosphere. Crude approximations in the implemented physical processes have been adopted to limit the number of free parameters. This allows us to pinpoint specifically the importance of chemical processes uncertainties in Titan’s photochemical models and to evaluate their chemical robustness. First implications of this preliminary study related to purely chemical rate coefficient uncertainties are discussed. They are important enough to question indeed any comparisons between theoretical models with observations as well as any potential conclusions subsequently inferred. Since the latest missions, such as Cassini–Huygens, are likely to induce an ever-increasing interest for such kind of comparing studies, our conclusions show that it is crucial to reform the way we think of, and use, current photochemical models to understand the processes occurring in the atmospheres of the outer Solar System.

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1. Introduction

In any scientific experiment, rigorous evaluation of the uncertainty is crucial. It is equally true for modeling studies of planetary atmosphere if we are to place confidence in the predicted results. Photochemical models of the giant planets and their satellites are indeed particularly sensitive to the imprecision carried by their different kinetic parameters enclosed as the low-temperature processes they illustrate are still poorly constrained by laboratory evidence and often need to be evaluated and/or estimated. This imprecision is even supposed to be contributing mostly to the discrepancies between observations and computed predictions.

Photochemistry of Titan’s atmosphere has been arising in recent years, an ever-increasing interest explained by the manifold importance of its most abundant minor constituent and most important photochemically active species, methane (CH\textsubscript{4}). Driven by its photodissociation at Lyman \textit{x} generating highly reactive radical species associated to a dense background N\textsubscript{2} atmosphere, a complex and multiphasic organic chemistry is indeed flourishing, possibly even reminding of some processes of our prebiotic Earth’s environment (Raulin and Owen, 2002). Despite the quality of numerous investigations dedicated to the description of its atmosphere (Yung et al., 1984; Toublanc et al., 1995; Lara et al., 1996; Lebonnois et al., 2001; Wilson and Atreya, 2004), theoretical models have been unable to simultaneously fit the various observations. Not so long ago, Lebonnois et al. (2001) pointed out that these observed discrepancies may have to be attributed indeed
to problems in the adopted chemical scheme, which could be identified only by performing sensitivity studies.

Sensitivity studies applied on Titan’s atmosphere were first restricted to zero-dimensional (0D) box modeling of laboratory experiments concerning hydrocarbon photochemistry (Smith, 1999). Wilson and Atreya (2000) studies focused in particular on methane photolysis influence on hydrocarbon chemistry and are based on recent studies which have not fully resolved the issue of its different product yields at Lyman α (Mordaunt et al., 1993; Romani, 1996; Smith and Raulin, 1999). Their investigations establish that hydrocarbon abundances at altitudes of existing observations are not sensitive to the choice of methane photolysis scheme and conclude that an updated chemical scheme is mainly accountable for discrepancies between theoretical models and observations of Titan’s atmosphere. Even with its improved physical and chemical description—increasing the number of free parameters—and an appropriate eddy diffusion profile, the state-of-the-art Wilson and Atreya (2004) model leads to improved but not fully satisfactory fits with observational data. Lebonnois (2005) sensitivity studies, even if limited to benzene and aerosol production in Titan’s and Jupiter’s atmospheres, are found to be useful to bring more constraints on photochemical models and to locate difficulties in the chemical schemes. All parameters in photochemical models are interdependent and the system as a whole is strongly nonlinear. Thus, traditional sensitivity studies, by simply varying each parameter in turn, do not estimate the overall uncertainty in the computed results. For this reason, Monte Carlo approaches in which all chemical parameters are perturbed randomly a large number of times according to a pre-defined probability distribution, are useful to achieve this goal.

Such Monte Carlo inquiries on overall uncertainties estimation have already been devoted to the Earth’s atmosphere (Stolarski et al., 1978; Thompson and Stewart, 1991; Stewart and Thompson, 1996), hydrocarbon chemistry in Neptune’s atmosphere (Dobrijevic and Parisot, 1998) and Saturn’s atmosphere (Dobrijevic et al., 2003), astrochemistry (Vasyunin et al., 2004; Wakelam et al., 2005, 2006) and Titan’s ionospheric chemistry (Carrasco et al., 2007). Broadening the foremost Smith (1999) researches though restricted to 0D box approximations, Hébrard et al. (2005) preliminary sensitivity studies of the influence of photochemical parameter uncertainties on hydrocarbon neutral chemistry of Titan’s atmosphere, showed that uncertainties in computed hydrocarbon concentrations can be very significant and must be systematically investigated prior to any meaningful comparisons between modeled and observed abundances. Following Dobrijevic and Parisot (1998) and Smith (1999) conclusions, they suggested that uncertainties would be greater in one-dimensional (1D) models due to the possible propagation of uncertainties by vertical transport.

By reporting the study of the influence of purely chemical kinetics uncertainties on computed abundances in Titan’s atmosphere, such an extension to a 1D photochemical model fruitfully improves Hébrard et al. (2005) calculations by including transport processes, as well as nitrogen- and oxygen-containing species updated chemistries.

Uncertainty propagation of purely chemical reactions performed on Hébrard et al. (2006) updated model is applied here to the estimation of neutral abundances in Titan’s atmosphere. Hébrard et al. (2006) review provides moreover a detailed investigation of the photochemical sources of uncertainties in theoretical modeling and a better evaluation of these uncertainties at temperatures representative of Titan’s atmospheric conditions. In the following, our 1D photochemical model is briefly presented before the diverse sources of uncertainties carried by theoretical photochemical models are outlined and the general method used for their estimation are laid out. Consequences of the intrinsic imprecision of the chemical parameters on the specific case of Titan’s photochemistry are then laid out, confronted to available observations and discussed in the frame of Cassini–Huygens results.

### 2. Photochemical modeling of Titan’s atmosphere

Our primary objective was to build a simple and tractable 1D model amenable to chemical uncertainty analysis. Crude approximations in the implemented physical processes were inevitably adopted to limit the number of free parameters, which nevertheless allowed us to pinpoint specifically the importance of chemical process uncertainties in Titan’s photochemical models and to evaluate their chemical robustness. In our 1D photochemical model extending from Titan’s surface to 1300 km, abundances of any atmospheric species are governed by the altitude-dependent continuity–diffusion equation

$$\frac{d y_i}{dt} = P_i - y_i L_i - \frac{d y_i}{dz} - C_i, \quad (1)$$

where $y_i$ is the concentration of species $i$ (cm$^{-3}$), $P_i$ its chemical production (cm$^{-3}$ s$^{-1}$), $L_i$ its chemical loss rate (s$^{-1}$), $\Phi_i$ its vertical flux (cm$^{-2}$ s$^{-1}$) and $C_i$ its condensation factor. The coupled 1D time-dependent continuity equation was solved using the Crank–Nicholson numerical method for 260 atmospheric levels with a vertical resolution of 5 km. A detailed description of hydrocarbon, nitriles and oxygen coupled photochemistry, both vertical eddy and molecular diffusion, and radiative transport (including Rayleigh scattering by N$_2$ and aerosols absorption) were included. Calculations were performed for $-10.7°$S latitude and $-22.54°$ solar declination, conditions relevant to Huygens probe entry in Titan’s atmosphere on 14th January, 2005 for intended use of observational constraints. Our main goal was to study in what extent photochemical models are sensitive to the values of poorly known photochemical parameters. A fixed vertical structure, a fixed solar irradiance and a fixed eddy diffusion coefficient were used throughout our calculations in order
to focus exclusively on the chemistry issue in Titan’s atmosphere.

2.1. Physical inputs

Atmospheric parameter inputs (T, P, n) were taken from Yelle et al. (1997) recommended engineering model which have been used for all pre-landing studies related to the Huygens probe. No doubt remains that an updated model will be established in the future for use with the Huygens entry and descent performance validation activities, but these adopted parameters were, however, found to be in good agreement with their in situ measurements by the Huygens Atmospheric Structure Instrument (HASI) aboard the Huygens probe (Fulchignoni et al., 2005). An external water (H2O) flux equal to $5 \times 10^{10} \text{cm}^{-2} \text{s}^{-1}$ (Feuchtgruber et al., 1997) was adopted to account for the water influx arising from micrometeorites initiating oxygen chemistry in Titan’s atmosphere. We assumed a zero flux as an upper boundary condition for most other species, except for atomic hydrogen (H) and molecular nitrogen (N2), which were assumed to escape with velocities following Jean’s thermal escape mechanism, $v_{\text{th}} = 2.54 \times 10^{8}$ and $v_{\text{th}} = 5.90 \times 10^{4} \text{cm s}^{-1}$, without taking nonthermal escape processes into account despite recent developments on this matter (Yelle et al., 2006). At the lower boundary, nitrogen (N2) and methane (CH4) mole fractions were taken from Yelle et al. (1997) model and, respectively, set to 0.95 and $3.0 \times 10^{-2}$. The mole fraction of carbon monoxide (CO) at the surface was assumed to be fixed at $5.2 \times 10^{-5}$ on the basis of the Gurwell and Muhleman (2000) high resolution ground-based interferometric observations. Molecular hydrogen (H2) mole fraction was assumed to be fixed at $1.1 \times 10^{-3}$ following Samuelson et al. (1997).

Using a radiative transfer program adapted from Dobrijevic et al. (2003), the incident solar flux at every level in the atmosphere $F(\lambda, z)$ was calculated as a function of the diurnally averaged unattenuated solar flux at the top of the atmosphere $F_\infty(\lambda)$ (taken from Floyd et al., 1998). Molecular absorption, N2 Rayleigh scattering and absorption by the aerosols were considered in these calculations. Focusing only on the issue brought by the chemical uncertainties in the models, we chose to neglect aerosol diffusion to adopt the Yung et al. (1984) approximation concerning aerosol absorption.

Nitrile compounds formation is initiated in Titan’s reducing atmosphere by N2 dissociation, proceeding mostly through direct EUV photolysis and galactic cosmic ray (GCR) absorption (Lara et al., 1996). With their refined treatment of UV (80–100 nm), EUV (<80 nm), soft X-rays (<5 nm) and photoelectrons (<80 nm)-induced N2 dissociation, Lara et al. (1999) found the N(4D) and N(4S) total production rates to be very similar at all altitudes, although the partial contributions from solar radiation (>80 nm) and photoelectrons (<80 nm) are somewhat different. We therefore adopted an overall N2 + hv → N(4S) + N(4D) scheme. Cosmic ray-induced N2 dissociation at lower altitudes was treated using the simplified Lara et al. (1996) model, neglecting the entire cascading energy deposition developed by Capone et al. (1983). Effect of magnetospheric electrons was neglected in our simplified description of the N2 dissociation, as supported by Toub lanc et al. (1995).

Such temperature conditions exist in Titan’s lower stratosphere that many gaseous compounds become saturated. In a first approximation validated by Lara et al. (1996), compounds were assumed to condense out according to their own saturation vapour pressures. Saturation laws were taken from Sagan and Thompson (1984), Reid et al. (1988), Moses et al. (1992, 2000). The condensing compounds, namely CH4, C2H2, C2H4, C2H6, CH3C2H, C3H8, C4H2, C4H8, C4H10, HCN, HC3N, CH3CN, C2N2, C4N2, H2O and CO2, were then assumed to follow their saturation law below the condensation level, neither with any supersaturation nor was re-evaporation allowed.

Molecular diffusion coefficients are often provided as measurements of diffusivity in a two constituents medium. However, Titan’s atmosphere is not a binary mixture of gases, but is rather composed of many constituents. Lack of experimental measurements available for each parameter involved, however, compelled us to consider only its two most abundant species, CH4 and N2. Following the convenient method recommended by Fuller et al. (1966), the molecular diffusion coefficient $D_{ij}$ (in cm$^2$ s$^{-1}$) of species $i$ in species $j$ was taken as

$$D_{ij} = \frac{0.00143 T^{1.75}}{P M_i^{1/3} (\Sigma_i)^{1/3} + (\Sigma_j)^{1/3}}$$

where $P$ is the pressure in bar, $T$ the temperature in K, $M_j$ the reduced molecular mass in g mol$^{-1}$, $(\Sigma_i)$, and $(\Sigma_j)$ are calculated by summing the different atomic diffusion volumes of species $i$ and $j$, respectively (Reid et al., 1988). The molecular diffusion coefficient of component $i$ in Titan’s atmosphere considered here as a binary mixture $D_{i,j}(\text{CH}_4,\text{N}_2)$ (in cm$^2$ s$^{-1}$) was thus calculated following Blanc’s law (Blanc, 1908):

$$D_{i,j}(\text{CH}_4,\text{N}_2) = \left( \frac{\xi_{\text{CH}_4}}{D_{i,j}(\text{CH}_4)} + \frac{\xi_{\text{N}_2}}{D_{i,j}(\text{N}_2)} \right)^{-1},$$

where $\xi_{\text{CH}_4}$ and $\xi_{\text{N}_2}$ are the mole fractions of methane (CH4) and molecular nitrogen (N2), respectively. The eddy diffusion coefficient $K(z)$ (in cm$^2$ s$^{-1}$) usually acts as a free parameter that must be usually estimated to fit observations. Four different eddy diffusion coefficients were sensitivity tested: Hidayat et al. (1997) profile, inferring a low homopause level from their millimeter observations of HCN vertical profile in much of the lower regions of the atmosphere; Strobel et al. (1992) profile, inferring a higher homopause level around 1000 km from their analysis of Voyager UVS solar occultation and airglow data; Toublanc et al. (1995) profile, developing
their profile based on Toon et al. (1992) profile adapted to fit Tanguy et al. (1990) HCN distribution and Voyager UVS data for methane (CH₄); and, finally, our own processing of the ion–neutral mass spectrometer densities measurements aboard Cassini during Ta flyby (Waite et al., 2005), adequately fitting INMS data by assuming a constant value of 4.2 × 10⁶ cm² s⁻¹ above the homopause with an exponential decrease at lower altitudes to reach Yung et al. (1984) value on the surface. This approach allows our calculations to cover much of the eddy diffusion profiles suggested previously (see Fig. 1 and Wilson and Atreya (2004) for a complete review). Hidayat et al.’s (1997) and Strobel et al.’s (1992) profiles appear to be mean profiles compared to these various profiles, among them Toublanc et al.’s (1995) profile, or inferred from the latest INMS observations (Waite et al., 2005).

2.2. Photochemical scheme

Hébrard et al. (2006) chemical scheme is based upon updated chemical rate coefficients and cross-sections appropriate for the atmospheric conditions on Titan from up-to-date available literature. Our model thus calculated abundances for 127 different hydrocarbon, nitrile and oxygen species involved in 676 different chemical reactions and 69 photodissociation processes. Our selected wavelength range excluded any electronic impact-induced chemistry only effective at EUV wavelength.

Following Lara et al.’s (1996) conclusions according to which nitrogen- and oxygen-containing species chemistries in Titan’s atmosphere modeling is very dependent on the distribution of hydrocarbon compounds, whereas hydrocarbon chemistry is much less dependent on the distribution of nitrogen- and oxygen-containing species, Hébrard et al. (2006) focused while building their chemical scheme on the photochemical formation of C₂, C₃ and C₄ compounds in general, the aromatic compound C₆H₆ and polyynes up to C₈H₂. In order to focus specifically on the significance of gaseous phase chemical uncertainties, we chose not to detail the chemical transition from these simple molecules towards aerosol particle in the context of Titan’s atmosphere as investigated in Lebonnois et al. (2002). Formation of these larger molecules was thus considered only through the formation of a product species SOOT, in order to avoid any inconsistencies in carbon conservation. Moreover, many more species and reactions may exist than are explicitly considered in our chemical scheme, and that is already a source of systematic errors. They can tentatively be estimated by simply enumerating the different reactions according to the number of carbons in the parent compound, as described as crosses in Fig. 2. Despite the fairly limited number of species implemented in Hébrard et al. (2006) chemical scheme, the total number of reactions generated to describe
the full set of photochemical processes on Titan can be extremely large. According to Aumont et al. (2005), this total number of reactions may follow an exponential distribution, with a growth factor depending on the different functionalities considered in our reacting species. Fig. 2 states that even if our reactions involving the smallest species may be governed by such kind of exponential law (continuous line), there is, however, an obvious and deep lack of information regarding the larger species. For that matter, it may well be illusory to achieve an exhaustively detailed knowledge of such a complex photochemical system without the use of an implicit representation and chemical scheme generators (Dobrijevic and Dutour, 2006).

A major limitation in constructing accurate atmospheric models of the outer planets and their moons is the availability of low-temperature, low-pressure kinetic data. Indeed, most of the relevant experimental research has been motivated by the importance of hydrocarbon chemistry in combustion studies. The majority of published results describe therefore chemical systems different from the ones that can be found in the stratosphere of Titan, where appropriate conditions are \( T = 71-175 \) K, \( P < 0.2 \) Torr and \( \text{N}_2 \) as background atmosphere. Most photochemical reaction rate coefficients have indeed scarcely been determined in a temperature range representative of Titan’s atmosphere, and their extrapolation to such low temperatures is therefore uncertain. For many recombination reactions moreover, only the high pressure limiting rate constants are available and the buffer gases are almost never \( \text{N}_2 \) as it should be for simulating Titan’s chemistry. The identities of product species are finally rarely determined along with the measurements of kinetic rate constants nor are quantum yields for formation of neutral product species often reported when photodissociation cross-sections are published. Fortunately, literature, when available, sometimes offer estimates based on various chemical arguments. It is important, however, to keep in mind the natural tendency to use photochemical rate constants allowing the model to best match the data. For their review, Hébrard et al. (2006) paid therefore a particular attention to rely on the latest and/or more reliable experimental data available in the literature, insofar as conflicting conclusions had been raised previously. Their qualifying statements were reported as a way of testifying to some extent the overall uncertainties in their reaction model, and were used as they are in this paper.

3. Uncertainties and Monte Carlo simulation

3.1. Uncertainties in photochemical models

First of all, we assumed that the basic parameters of our photochemical model along with the reaction scheme are well known, implying that the background atmospheric model, the solar irradiation, and specially the eddy diffusion coefficient are all well constrained. The intrinsic imprecision carried by our photochemical model arises thus mostly from the uncertainties in the photochemical parameters used. We must emphasize that, in spite of being obviously restricted to crude physical approximations, this ideal case allowed us to evaluate the imprecision specifically generated by the photochemical kinetic data already implemented in our chosen chemical scheme.

3.1.1. Photodissociation rates uncertainty

Photodissociation rates \( J_i(z) \) (s\(^{-1}\)) at the altitude \( z \) of the different absorbing species \( i \) included in the model can be computed in the range of wavelength \([\lambda_1, \lambda_2] \) as

\[
J_i(z) = \sum_{j} \left( \int_{\lambda_1}^{\lambda_2} q_{ij}(\lambda) \sigma_i(\lambda) F(\lambda, z) \, d\lambda \right),
\]

which requires beforehand the determination of their absorption cross-sections \( \sigma_i(\lambda) \), their different photodissociation pathways \( j \) characterized by quantum yields \( q_{ij}(\lambda) \) and the incident solar UV flux at every level in the atmosphere \( F(\lambda, z) \) as well. Specific inaccuracies in both photoabsorption cross-sections and quantum yields determination as well as imprecision carried by incident solar flux calculations result then inevitably in uncertainties in photolysis rates \( J_i(z) \). Mainly because of the feedback between the abundances and the photodissociation processes in the actinic flux calculation, these uncertainties would be, however, difficult to evaluate without an extensive investigation beyond the frame of the present study. In order to focus specifically on the purely chemical sources of uncertainty, we chose indeed to make the assumption that the different photodissociation processes used in our model are quite well quantified. Effects of these specific uncertainties on computed abundances have yet to be investigated in a foregoing research. For the calculations considered in this paper, the photoabsorption cross-sections and quantum yields were incorporated at the lowest temperature available in a given wavelength range.

3.1.2. Reaction rates uncertainty estimation

Reaction rates and their uncertainties are supposed to be constrained within the temperature range of their experimental and/or theoretical determination, which is often not representative of Titan’s altitude-dependent temperatures. The UMIST99 database for astrochemistry\(^1\) (Le Teuff et al., 2000) provides such information, but for conditions representative of the interstellar medium and with a lower level of precision, as rate coefficients are classified in only four categories of precision: within 25%, 50%, 100% and 900%. NASA JPL panel data evaluation (Sander et al., 2003) or the International Union of Pure and Applied Chemistry (IUPAC) evaluation (Atkinson et al., 1999) are restricted to the 200–400 K temperature range, optimized as they are indeed for Earth chemistry (conditions and species). Baulch et al. (2005) latest critical evaluation of

\(^1\)http://www.udfa.net.
kinetic data is restricted for combustion modeling and thus only for temperature above 298 K. Extrapolating uncertainties at low temperatures is indeed another source of uncertainty.

As previously pointed out, Hébrard et al.’s (2006) review not only gave us the parameters to calculate the standard set of coefficients $k_i$ for bi- and trimolecular reactions at temperatures adapted for describing Titan’s atmosphere, but provided us moreover with some additional parameters quantifying their temperature-dependent uncertainties in the same representative range. Their estimate of the uncertainty of the reaction rate $k_i$ at any given temperature, $F_i(T)$, may be obtained from the following expression adapted from Sander et al. (2003):

$$F_i(T) = F_i(300 \text{ K}) e^{g_i(1/T-1/300)},$$  \hspace{1cm} (5)

where $F_i(300 \text{ K})$ is the uncertainty in the rate constant $k_i$ at $T = 300 \text{ K}$. $F_i = 1.25$ means a precision of $k_i$ within 25%, $F_i = 1.5$ within 50%, $F_i = 2$ within 100%, etc. The coefficient $g_i$ has been defined in Hébrard et al. (2006) evaluation for use with $F_i(300 \text{ K})$ in the above expression to obtain the rate constant uncertainty at different temperatures. Both uncertainty factors, $F_i(300 \text{ K})$ and $g_i$, do not necessarily result from a rigorous statistical analysis of the available data. Rather, they have been evaluated to construct the appropriate uncertainty factor, $F_i(T)$, following an approach based on the fact that rate constants are almost always known with a minimum uncertainty at room temperature, supposedly constant within the temperature range of experiments but not within the temperature range of interest to the study of planetary atmospheres.

More details on such adopted uncertainty limits, as a function of temperature, as inferred from Hébrard et al. (2006) review and implemented in our Monte Carlo study, can be found in their paper and will not be repeated here. Hébrard et al. (2006) paper display the whole set of adopted nominal reaction rates along with their uncertainty parameters. The adopted uncertainty factors at room temperature $F_i(300 \text{ K})$ range from 1.1 to 12 and their attached “uncertainty-extrapolating” coefficients $g_i$ from 30 to 600. These assigned uncertainties represent Hébrard et al. (2006) own subjective assessment we chose here to follow.

### 3.2. Monte Carlo method

To include these chemical kinetic uncertainties and investigating their effect on modeled abundances in Titan’s atmosphere, we implemented a Monte Carlo procedure developed by (Dobrijevic and Parisot, 1998; Dobrijevic et al., 2003) to study the gas-phase chemistry of the atmospheres of the giant planets (see Fig. 3). This method was itself adapted from earlier studies dedicated to terrestrial stratospheric chemistry (Stolarski et al., 1978; Thompson and Stewart, 1991; Stewart and Thompson, 1996) and subsequently applied to Titan (Smith et al., 1998; Hébrard et al., 2005) and the interstellar medium (Vasyunin et al., 2004; Wakelam et al., 2005, 2006).

We assumed that reaction rate coefficients $k_i$ could be considered as random variables, lognormally distributed over an uncertainty range centered on the recommended rate constant $k_{0i}$ (Stewart and Thompson, 1996) and generated as

$$\log(k_i) = \log(k_{0i}) + \epsilon_i \log(F_i),$$  \hspace{1cm} (6)

where $\epsilon_i$ is a random number normally distributed with null mean and unity standard deviation and $F_i$ is the temperature-dependent uncertainty factor attached to the $i$th reaction rate. Our approach implied that each reaction rate coefficient $k_i$ was perturbed randomly following a lognormal distribution with a standard deviation $\log(F_i)$. The probability to find $k_i$ between $k_{0i}/F_i$ and $k_{0i} \times F_i$ is

![Fig. 3. Schematic representation of the Monte Carlo method used to study the effect of chemical uncertainties on Titan’s atmosphere modeling (adapted from Dobrijevic et al., 2003).](image-url)
then 68.3%. Rate values greater than $2 \log(F_i)$ were, however, rejected in order to dismiss extreme values of $k_i$. We insured moreover that any randomized reaction rate coefficient generated could not be higher than reactive diffusion speed occurring in Titan’s atmosphere. Calculations based on mere kinetic theory of gases gives as an absolute limit rate in pure $N_2$ for the different temperatures considered (Hébrard, 2006):

$$k_0(z) = 5.19 \times 10^{-11} \sqrt{T(z)} \ \text{cm}^3 \ \text{molecules}^{-1} \ \text{s}^{-1}. \quad (7)$$

In practice, a steady-state can be reached because inputs (internal and external fluxes) are balancing losses (condensation, Jeans escape). For the nominal run, the continuity equations have been integrated long enough (3 Titan years = $3 \times 10^9$ s) to reach a steady-state. With each new set of rate coefficients, the continuity equations were then integrated to a given time (1 Titan year = $10^9$ s), arbitrarily chosen in order to insure calculations convergence towards near steady-state conditions in a decent computation time.

4. Results of uncertainties analysis and discussion

4.1. Uncertainties on abundances

Propagation of uncertainties in chemical rate coefficients on photochemical model results in Titan’s atmosphere is now examined in detail. Figs. 4–6 display the results for some of the major products of methane ($CH_4$)/nitrogen ($N_2$)/oxygenated compounds combined photochemistry in Titan’s atmosphere: methane ($CH_4$), acetylene ($C_2H_2$), ethylene ($C_2H_4$), ethane ($C_2H_6$), acetonitrile ($C_2H_5N$), cyanoacetylene ($C_2H_3N$), cyanoacetylene ($C_2H_3N$) and benzene ($C_6H_6$) for hydrocarbons; hydrogen cyanide (HCN), water (H$_2$O) and carbon dioxide (CO$_2$) for oxygenated compounds. Five hundred profiles were drawn for each altitude group with their associated standard deviation profiles. Each hundred profiles were drawn as a function of altitude along with their nominal profiles inferred from our photochemical model. Abundances retrieved by available observations are also indicated, and subsequently detailed.

We chose to display directly our computed raw distributions rather than the post-processed mean abundances profiles with their associated standard deviation profiles. In that case, most of the unsaturated compounds (acetylene, $C_2H_2$; ethylene, $C_2H_4$; acetonitrile, $C_2H_5N$ and cyanoacetylene, $C_2H_3N$) display a few outstanding profiles extending over several orders of magnitude. Any information carried by these outstanding profiles may be significantly representative of the robustness of our Titan’s atmospheric model. Deeply rooted in the photochemical scheme itself, they may very well be the signature of a change in qualitatively different chemical routes for different altitudes. Studies involving correlation tests between the different Monte Carlo sets are currently dedicated to this issue and more specifically to the understanding of the different chemical mechanisms occurring in Titan’s ionosphere (Carrasco et al., submitted to Icarus). Any statistical treatment would conceal part of this information. Dealing with these lone profiles when computing synthetic spectra, as described further below, would undoubtedly have a strong influence that may be minimized if not concealed by considering only a statistical plotting of the profiles. Moreover, many different criterions can be adopted for this statistical plotting (mean, median, mode, etc.) and to select one from another is already part of a subjective post-processing procedure we chose not to perform at this stage. Figs. 7 and 8 illustrate some of the limitations of this approach; computing 500 profiles appears to be barely sufficient for a complete statistical study, and results display different behaviors with the compound and the altitude considered. More specifically, any deep statistical analysis involving a ±σ criterion as described in Appendix A may prove to be deceiving. Ethane ($C_2H_6$) profiles distribution displays a difference between its nominal profile $y^0_i(z)$ and its mean profile $y_i(z)$ below 500 km whereas hydrogen cyanide (HCN) profiles distribution displays a similar difference above 500 km. Propane ($C_3H_8$) profiles distribution displays quasi-identical nominal and mean profiles except in the 600–900 km region whereas benzene ($C_6H_6$) never displays such particularity (see Fig. 7). The logarithms of the acetylene ($C_2H_2$) abundances at 1000 km are quasi-lognormally distributed whereas the logarithms of propane ($C_3H_8$) abundances at 600 km rather tends to exhibit a normal distribution (see Fig. 8). Thus, it appears difficult to use one unique criterion to define the error statistically for each compound at all altitudes when confronted to many different behaviors.

Table 1 summarizes however some statistical results obtained after the numerical treatment described in Appendix A. It displays the mean abundance $y_i(z)$ and its attached uncertainty factor $F_y(z)$ (linked to the ±σ profiles) for some of the most abundant neutrals at 200, 800 and 1200 km. As expected, methane ($CH_4$) is the major component, common to the three altitudes, but is also the most accurate component in our model, with a relative uncertainty $F_{CH_4}$ ranging from 0 at 200 km to 22% at 1200 km. Titan’s atmospheric model is relatively well constrained for methane ($CH_4$), insofar as we only considered purely chemical uncertainties, since it is largely inert and may be mainly distributed through diffusive processes. Numerous heavy species have a poorly known chemistry that induces inevitably large uncertainties in their densities. Most of their uncertainty factors range from 2 to 6 at all altitudes, reaching a value of about 40 for diacetylene ($C_4H_2$) and triacetylene ($C_6H_6$). This highlights the need for improving our knowledge about the reactivity and the formation processes of these compounds.

These results state nonetheless that computed abundance profiles are extremely affected by the uncertainties carried by the chemical reaction rates. The situation can be very different depending on the compound and altitude considered, and from one run to another, the slope of each
Fig. 4. Hydrocarbons abundance profiles as a function of altitude obtained after 500 runs using Hidayat et al. (1997) eddy diffusion profile. Different observed abundances have also been indicated with error bars in abundance and altitude. Boxes represent the Cassini CIRS observations Flasar et al. (2005), white triangular bars the Cassini UVIS observations Shemansky et al. (2005), white circled reticles the Cassini INMS observations Waite et al. (2005), black reticles the ISO observations Coustenis et al. (2003), horizontal lines the Vervack et al. (2004) reanalysis of Voyager UVS observations, black squared reticles the Voyager IRIS observations close to Titan’s equator Coustenis and Bézard, 1995. For C$_2$H$_6$, the white triangular reticles represent Livengood et al. (2002) IRHS-IRTF observations. For C$_3$H$_8$, the white diamond-shaped reticles represent the Roe et al. (2003) TEXES-IRTF observations.
Fig. 5. Nitriles abundance profiles as a function of altitude obtained after 500 runs using Hidayat et al. (1997) eddy diffusion profile. Different observed abundances have also been indicated with error bars in abundance and altitude. Boxes represent the Cassini CIRS observations Flasar et al. (2005), white triangle bars the Cassini UVIS observations Shemansky et al. (2005), black reticles the ISO observations Coustenis et al. (2003), horizontal lines the Vervack et al. (2004) re-analysis of Voyager UVS observations, black squared reticles the Voyager IRIS observations close to Titan’s equator Coustenis and Bezard (1995). For HCN and CH$_3$CN, the white squared bars show the Marten et al. (2002) and Tanguy et al. (1990) IRAM observations.

Fig. 6. Oxygenated compounds abundance profiles as a function of altitude obtained after 500 runs using Hidayat et al. (1997) eddy diffusion profile. Different observed abundances have also been indicated with error bars in abundance and altitude. Boxes represent the Cassini CIRS observations Flasar et al. (2005), black bars and black reticles the ISO observations Coustenis et al. (1998), black squares and black squared reticles the Voyager IRIS observations close to Titan’s equator Coustenis and Bezard (1995).
The abundance profile can be either pretty uniform or very altered. No correlation was found between abundances $y_i(z)$ and relative uncertainties $F_{y_i}(z)$, meaning that larger uncertainties cannot be assigned exclusively to minor compounds. Some tendencies related to the compound family can, however, be highlighted.

Globally, the heavier the compound gets, the lower its abundance is. For example, $y_{C_2H_2}(z) < y_{C_4H_2}(z) < y_{C_6H_2}(z)$.

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**Fig. 7.** Some hydrocarbons abundance nominal profiles $y_i(z)$ (thick line), mean profiles $\bar{y}_i(z)$ (thin line) and their attached standard deviation profiles (dashed lines), obtained after 500 runs, as a function of altitude using Hidayat et al. (1997) eddy diffusion profile.

**Fig. 8.** Distributions of acetylene ($C_2H_2$) and propane ($C_3H_8$) abundances, at 1000 and 600 km, respectively. (Left) Acetylene ($C_2H_2$) nominal value at 1000 km is closed but very different from the mean and median values. (Right) Propane ($C_3H_8$) nominal value at 600 km is closed to the median value and very different from the mean value.
Table 1
Mean abundances $y_i(z)$ and uncertainty factors $F_i(z)$ of the most abundant neutral compounds in Titan's atmosphere at 200, 800 and 1200 km using Hidayat et al. (1997) eddy diffusion profile

<table>
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<th>Compound</th>
<th>$y_i(z)$</th>
<th>$F_i(z)$</th>
<th>Compound</th>
<th>$y_i(z)$</th>
<th>$F_i(z)$</th>
<th>Compound</th>
<th>$y_i(z)$</th>
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Due to the possible propagation of uncertainties by vertical transport. Confronted to our own results, this statement seems to be somewhat revised since such obvious conclusions can hardly be inferred by comparisons between their 0D profiles and our own; vertical transport processes are clearly involved, but not in the same extent for all compounds and all altitudes.

Firstly, whereas 0D abundances for unsaturated hydrocarbons were fairly invariant in the high-altitude regions dominated mostly by methane photolysis ($>600$ km), 1D uncertainties profiles may be as globally extended in this same region for both saturated and unsaturated compounds. This effectively suggests that including vertical transport processes in our calculations indeed allowed the uncertainties to propagate towards higher altitudes. Secondly, 0D uncertainties were globally more important for both saturated and unsaturated hydrocarbons in the low-altitude low-temperature regions dominated by unsaturated compounds photolysis—and particularly acetylene (C$_2$H$_2$) photolysis ($<600$ km), where chemical uncertainties are indeed more important for all compounds. But 1D uncertainties may seem, however, much lower for both saturated and unsaturated compounds in this region, except for ethylene (C$_2$H$_4$) and diacetylene (C$_4$H$_2$). Of the entire set of compounds represented here, it appears that ethylene (C$_2$H$_4$) and diacetylene (C$_4$H$_2$) are the only ones barely or not reaching their saturation
vapour pressure in these low-altitude regions of the atmosphere. These specific compounds lack an important condensation loss factor normally assumed to dominate in these regions, forcing all the other compounds abundance profiles to follow the profiles associated with their own saturation vapour pressure. The occurrence of condensation for a compound $i$ seems to lessen its attached uncertainty factor $F_{yi}(z)$.

The still unresolved argument on methane photodissociation pathways at Lyman $z$ critically reviewed in Romanzin et al. (2005) and sensitivity-tested in Wilson and Atreya (2000) illustrates somewhat the importance of uncertainties carried by the photodissociation processes in Titan’s atmosphere. The feedback existing in the actinic flux $F(\lambda, z)$ calculation between the different abundances $y_{i}(z)$ and photodissociation processes $J_{i}(z)$ urged us unfortunately to focus specifically on the purely chemical sources of uncertainty in this preliminary study. Uncertainties on abundances $F_{yi}(z)$ calculated in its frame allow us from now on to evaluate more precisely the overall photodissociation process uncertainties $F_{Ji}(z)$ in order to investigate their specific effects. We should emphasize that only the implementation of the uncertainties propagated both by the purely chemical reactions and by these photodissociation processes would, however, account for overall uncertainties on neutral abundances.

4.2. Comparisons with available observations

In order to make comparisons with observations, we decided to use data provided by a whole set of observing techniques. We must emphasize on the limitations of these comparisons. These observations may indeed differ in date, resolution and technique and may even be often inconsistent with each other, but yet have been applied here to latitudes close to Huygens probe landing site when available. Abundances retrieved by the Cassini CIRS observations (Flasar et al., 2005), the Cassini UVIS observations (Shemansky et al., 2005), the Cassini INMS observations (Waite et al., 2005), the ISO observations (Coustenis et al., 2003), the Vervack et al. (2004) reanalysis of Voyager UVS observations, the Voyager IRIS observations close to Titan’s equator (Coustenis and Bézard, 1995), the Livengood et al. (2002) IRHS-IRTF observations, the Roe et al. (2003) TEXES-IRTF observations and the Marten et al. (2002) and Tanguy et al. (1990) IRAM observations have been indicated.

Moreover, we are not performing a “direct” comparison with raw observational data, as the values promoted by these observations were actually obtained through their preliminary implementations in photochemical models producing synthetic spectra, and then compared with observational spectra. Therefore, although we subsequently call them “observations”, their results are not “raw data” but model-dependent observing results (in the sense that the results depend on abundances retrieved from the photochemical models). Ideally, the best way to proceed would be to compute synthetic spectra with our 500 photochemical model run results, and then compare each of them with observational spectra. As noticed previously, profiles produced through the Monte Carlo procedure exhibit shapes that can strongly differ from one run to another, leading potentially to very different spectra in both intensity and width. As a matter of fact, this represents an enormous amount of work and computing time, which would specifically require further studies. Any forthcoming work would have to deal, however, with this computation of synthetic spectra in order to make more valuable comparisons. Within the present work, we restricted ourselves to such crude comparisons, bearing in mind the limitations of this procedure.

We can notice that the uncertainties on our computed profiles and observations overlap for most of our compounds. As we pointed out above, the underestimation of ethylene ($C_{2}H_{4}$) abundance by photochemical models is a recurrent problem whose obvious discrepancies with existing observations may be notably due to specific issues related to dynamics (Lebonnois, personal communication). More generally, we can expect the chosen constant solar irradiation geometry (and subsequent constant thermal structure) to induce some additional bias between mean computed abundances and the spatially and temporally resolved observations. Keeping in mind the limitations of a 1D photochemical model and taking the uncertainties on the computed mole fractions into account, we can acknowledge a good agreement between our modeling predictions and the different abundances inferred from the available observations, despite the crude approximations adopted. However, it certainly does not mean that the chemical scheme used in our photochemical model is perfect. It means that, under the present assumptions and chemical uncertainties, our chemical scheme is appropriate to explain the abundances of compounds detected in Titan’s atmosphere. It also means that according to such uncertainties, a few modifications in the chemical scheme (by taking different reaction rates found in the literature) could be done without changing this consistency with observations. For most of the compounds represented here, the chemistry-induced uncertainties on computed abundances are indeed much larger than the current estimated uncertainties on abundances inferred from observations, the worst case especially being diacetylene ($C_{4}H_{2}$). The main implication of this statement is that uncertainties on computed abundances might not constrain the chemical reaction schemes and physical parameters of Titan’s atmosphere as tightly as expected from illusive and crude comparison between modeled results and observations.

First, the propagation of rate coefficient uncertainties in Titan’s atmosphere lead to important uncertainties on production rates. Thus, appointing preponderant reaction pathways in Titan’s photochemical scheme—and consequently promoting specific experimental investigations—on the basis of production rates alone could be slanted without a complete sensitivity study taking into account
overall photochemical uncertainties and probabilities associated with each reaction rate.

Secondly, any conclusions concerning the relevance of some other processes (electron-impact and/or cosmic-ray depositions, aerosol opacities from fractal and/or Mie particles, heavy hydrocarbons and polynyes different polymerization pathways, etc.) need to take into account the overall chemistry uncertainty discussed in this paper. The effects of these different processes may be systematic and/or dominate the chemical processes but might as well induce differences in abundance profiles much smaller than overall differences due to purely chemical uncertainties (Wilson and Atreya, 2004; Lebonnois, 2005). The following sensitivity study on the eddy diffusion profile $K(z)$ illustrates the way such processes must be further investigated in the light of our findings in order to lead to truly useful conclusions.

4.3. Eddy diffusion coefficient

Dynamics play undoubtedly some role in the distribution of Titan’s constituents and the significance of some dynamical processes should be explored. Owing to the complexity involved in relating microscopic turbulent processes to macroscopic transport, the eddy diffusion coefficient $K(z)$ often acts in photochemical modeling of planetary atmospheres as a free parameter that must be estimated to match constituent observations. The inference of a consistent vertical profile for $K(z)$ for all species in 1D photochemical transport models is problematical, especially on Titan. It could be indicative that each constituent has a specific effective eddy diffusion coefficient based on its own chemistry or alternatively that we lack a complete understanding of the basic photochemistry in these atmospheres. This first evaluation of the chemical imprecision carried by 1D photochemical models of Titan’s atmosphere has thus been applied to the study of this issue (Figs. 9–13).

Considering the limitations of existing observations and the uncertainties in some physical parameters included in such photochemical models—such as aerosol opacity—Wilson and Atreya (2004) maintain that it is not possible to rule out the eventuality that the globally averaged distribution of Titan’s constituents may be accurately and simultaneously described with a single eddy diffusion profile. According to the results presented here, and following Dobrijevic et al. (2003), we think that chemical

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Fig. 9. Different methane ($\text{CH}_4$) abundance profiles as a function of altitude obtained after 500 runs using Hidayat et al. (1997) (top left), Strobel et al. (1992) (top right), Toublanc et al. (1995) (bottom left) and INMS-derived Waite et al. (2005) (bottom right) eddy diffusion profiles.
and physical parameters—and particularly this unique eddy diffusion coefficient $K(z)$—may not be constrained from observations as tightly as expected, since many profiles may give computed abundances in agreement with the whole set of observations used. Actually, the existence of uncertainties on the computed abundances induces inevitably an uncertainty on the eddy diffusion coefficient profile. Its evaluation is a very important task, but the amount of computer time needed to estimate it would be very significant and we chose not perform it. However, in order to illustrate this point, we tested the sensitivity of our computed abundances to the eddy diffusion coefficient $K(z)$ by running our Monte Carlo procedure with Hidayat et al. (1997), Strobel et al. (1992), Toublanc et al. (1995) and our own INMS-derived (Waite et al., 2005) eddy diffusion profiles. As outlined previously, we cover in this way much of the eddy diffusion profiles suggested previously (see Fig. 1). Several points worthy of discussion resulted from this sensitivity study to the eddy diffusion coefficient $K(z)$.

Practically, the eddy diffusion coefficient profile can be obtained from the adjustment of the computed abundances of a largely inert species to the observed values.

Due to its high abundance in Titan’s atmosphere, methane (CH$_4$) is widely considered as inert enough to be distributed mostly through diffusive processes (see Wilson and Atreya, 2004, Fig. 5a). Thus the methane distribution is thought to be adapted to be used as a proxy for the determination of the homopause level. Methane (CH$_4$) abundance profiles below 700 km do not seem indeed to be very sensitive to the chemical uncertainties propagated through our Monte Carlo simulations whatever the eddy diffusion profile is. They do however display huge variations at higher altitudes, especially when comparing between the two extreme Strobel et al. (1992) high homopause (1040 km) and Toublanc et al. (1995) low homopause (680 km) cases. Turbulent macroscopic transport of the neutral species in Titan’s high atmosphere does not seem so tightly constrained by the existing observations as previously advocated for. This conclusion could have a strong influence on the ion chemistry specific uncertainties in Titan’s ionosphere (Carrasco et al., submitted to Icarus).

In the lower atmosphere, chemistry plays a major role for most of the neutral species. However, since hydrogen cyanide (HCN) is mainly reacting in the upper atmosphere and transported down to lower altitudes, its chemical time

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Fig. 10. Different hydrogen cyanide (HCN) abundance profiles as a function of altitude obtained after 500 runs using Hidayat et al. (1997) (top left), Strobel et al. (1992) (top right), Toublanc et al. (1995) (bottom left) and INMS-derived Waite et al. (2005) (bottom right) eddy diffusion profiles.
constant should be much greater than the eddy diffusion time constant in much of the lower regions of Titan’s atmosphere (see Wilson and Atreya, 2004, Fig. 5b). Hydrogen cyanide (HCN) abundance profiles above 400 km do not seem indeed to be very sensitive to the chemical uncertainties propagated through our Monte Carlo simulations. This result confirms that HCN can be expected to be a good candidate for constraining theoretically the eddy diffusion profile $K(z)$ in the middle atmosphere [300 km—homopause] but not in the lower atmosphere, insofar as its observations match up, which is unfortunately far from obvious. Results concerning water ($H_2O$) tend to suggest that it would be a candidate as good as hydrogen cyanide (HCN) for constraining this same physical parameter in the middle atmosphere if not for its barely detectable low abundance and the fact that this abundance is strongly constrained by another not very well-known parameter, the external water flux $F_{ext}$. As stated before, any conclusion based on the largely inert and diffusively distributed methane ($CH_4$), hydrogen cyanide (HCN) and water ($H_2O$) distributions used as proxies for the determination of the homopause level would be hazardous this far, without an extensive analysis of overall photochemical uncertainties.

No correlations were found neither between abundances $y_i(z)$ and relative uncertainties $F_{yi}$ as several situations resulted from this sensitivity study to the eddy diffusion coefficient $K(z)$: almost identical uncertainties attached to different nominal abundance profiles (water, $H_2O$), quite different uncertainties attached to almost identical nominal abundance profiles (methane, $CH_4$), and highly different uncertainties attached to different nominal abundance profiles (diacetylene, $C_4H_2$, hydrogen cyanide, HCN or acetonitrile, $CH_3CN$). Diacetylene $C_4H_2$ modeled abundances are especially always consistent with existing observations whatever the eddy diffusion coefficient profile $K(z)$ is, which argues again for the difficulty to constrain such physical parameters from observations as tightly as expected previously.

Globally, a few modifications in the eddy diffusion coefficient $K(z)$ (by comparing Hidayat et al. (1997) and Strobel et al. (1992) mean profiles for example) do not change significantly the good agreement between our modeling predictions and the different abundances inferred...
from the available observations (except for ethylene, C\textsubscript{2}H\textsubscript{4}), despite the crude approximations adopted.

The following demonstration is aimed to illustrate how powerful the comparisons between theoretical models and observations may be when quantifying modeled uncertainties \( \Delta y_i(z) \) and acknowledging their importance. Despite every caution we outlined before, we nevertheless tried to single out the “best” eddy diffusion coefficient \( K(z) \) from fitting our Monte Carlo profiles to methane (CH\textsubscript{4}), hydrogen cyanide (HCN), water (H\textsubscript{2}O) and acetonitrile (HC\textsubscript{3}N) observations. Smith et al. (1982) and Vervack et al. (2004) methane (CH\textsubscript{4}) observations in the upper atmosphere, Hidayat et al. (1997) and Marten et al.’s (2002) hydrogen cyanide (HCN) observations and Coustenis et al. (1998) water (H\textsubscript{2}O) observations were used as guidelines. Toublanc et al. (1995) eddy diffusion profile and our INMS-derived profile Waite et al. (2005) seem to be the best-fit profiles among all the profiles tested. On the contrary, acetonitrile (CH\textsubscript{3}CN) observations are, however, best fitted with Hidayat et al. (1997) and Strobel et al. (1992) eddy diffusion profiles. According to our starting postulate that our reaction scheme is well known, any good description of light nitriles should lead to a good description of heavier nitriles and that is not the case; this postulate may thus be erroneous.

Conclusions such as the one above concerning nitriles chemistry will, however, remain chancy as long as a complete quantification of the uncertainties carried by the photodissociation rates \( \Delta J_i(z) \) is implemented in theoretical models.

5. Conclusion

We have reported in this paper the results of a 1D photochemical model of Titan’s neutral constituents based on an extensively updated chemistry focused on the representativeness of the photochemical rate coefficients and their uncertainties (Hébrard et al., 2006). Through a comprehensive cross-examination of extensive reaction rates database, the different chemical sources of uncertainties in photochemical models of Titan’s atmosphere and their precise evaluation were indeed reviewed at representative temperatures. By implementing them through a Monte Carlo procedure into our 1D photochemical model
of Titan’s atmosphere, we were able to assess their effect on the computed abundances of different compounds observed in this environment. These calculations are the first to establish that uncertainties related to purely chemical rate coefficients can be so significant on these computed concentrations to challenge any comparisons with observations and any potential conclusions subsequently inferred.

Taking these uncertainties into account, we may indeed be inclined to acknowledge at first a good agreement between our modeling predictions and the different abundances inferred from the available observations, this despite the crude approximations adopted (reduction of the actinic flux calculation, simplification of the cosmic rays deposition, omission of any electron-impact induced—i.e. ionospheric—chemistry, no adjustments in aerosol opacities) and without adjusting artificially any surface fluxes. The uncertainties on most of the computed abundances are, however, much larger than the estimated uncertainties on abundances gathered from observations. Sensitivity studies on methane (CH₄) abundance was not addressed in this paper but may well be investigated more thoroughly in future research, especially since the methane (CH₄) abundance recommended so far (Yelle et al., 1997) and used in this paper is quite different from the recent observed abundance (Flasar et al., 2005). However, we are not expecting to notice consequently any significant discrepancies with the general trends on overall uncertainties illustrated and discussed in this paper.

Photochemical models are supposedly useful to constrain the physical and chemical parameters of planetary atmospheres (molecular abundances, eddy diffusion coefficient, boundary conditions, chemical schemes, etc.). By including the uncertainties attached to chemical reaction rates in photochemical models, our results imply that these parameters might not be constrained as tightly as expected. The modification of the photochemical scheme (addition and/or modification of photochemical reaction rates, physical processes and approximations adopted) might give no conclusive results since large uncertainties of computed profiles may still be in agreement with the observed abundances. Several eddy diffusion profiles may even give satisfactory agreement with observations without changing this chemical scheme. In such a complex, heavily
coupled and nonlinear system as Titan’s photochemistry, to find a set of parameters improbably fitting observations is not an improvement per se. We showed that uncertainties-attached computed abundances can be satisfyingly consistent with observations without systematically implementing new elaborate physical and chemical processes; adding these new processes would not improve our theoretical model. Further studies should be preferably devoted to lower the uncertainty factors of computed abundances before adding new free parameters into theoretical models.

While focusing exclusively on the purely chemical sources of uncertainty, it is important to emphasize moreover that we most probably only estimated a lower limit of the uncertainty on the modeled abundance profiles since we did not consider the uncertainties attached specifically to the multiple photodissociation processes included in our model. Their extensive and precise evaluation and their effects on computed abundances are to be investigated in a foregoing research and to be coupled to the chemical uncertainties discussed in this paper. Only afterwards could photochemical models be truly compared with observations. The case for uncertainty analysis applied to Titan’s ionospheric chemistry must be outlined too. After testing both Yung et al. (1984) and Troublanc et al. (1995) neutral modeled predictions, Keller et al. (1998) concluded indeed that ion densities strongly depend on the neutral atmosphere. This important correlation between ion and neutral reactivity has been accounted for so far by both Banaszkiewicz et al. (2000) and Wilson and Atreya (2004) in developing ion–neutral coupled models. Our results, specially the one above 1000 km, could be implemented in such coupling to study the propagation of computed neutrals uncertainties on ion densities, and the contrary. Following Carrasco et al. (2007) procedure, global uncertainties significance on ionospheric chemistry could then be assessed by confronting simulated mass spectra to past and future INMS raw observational data (Carrasco et al., submitted to Icarus).

Although Titan’s chemical processes may be so complicated as to hinder any enhancements in elaborating a fully detailed chemical scheme, we advocate for substantial efforts in conducting laboratory experiments, especially at low temperatures, to improve our knowledge of chemical reaction rates by lowering their attached uncertainties $F_i(300 \text{ K})$ and $q_i$. Promoting such low-temperature kinetic studies would greatly assist in developing planetary atmospheric models that more accurately—and usefully—reproduce observations. Techniques to pinpoint specifically the parameters that are responsible for inducing the largest uncertainties (such as the one developed by Dobrjievic et al., 1995) would be an important pre-requisite for orienting such future laboratory investigations. It would allow eventually a more efficient use of photochemical modeling, whose results are already being confronted to the insights provided by the successful and ongoing Cassini—Huygens mission.

Appendix A. Calculation of the error

The computed abundance distribution ($y_i(z)$) is well fitted, for most compounds, by a lognormal function centered on the mean value $\log_{10}(y_i(z))$. We were therefore able to use the standard deviation $\sigma$ of $\log_{10}(y_i(z))$ distribution to evaluate the error $\Delta \log_{10}(y_i(z))$ or the uncertainty $F_{y_i}(z)$, defined by

$$\log_{10}(y_i(z)) = \log_{10}(y_i(z)) \pm \Delta \log_{10}(y_i(z)) = \log_{10}(y_i(z)) \pm \log_{10}(F_{y_i}(z)).$$  

(8)

There is a 68.3% probability of finding $\log_{10}(y_i(z))$ within $\log_{10}(y_i(z)) \pm \sigma$ with $\sigma = \log_{10}(F_{y_i}(z))$. We identified $[\log_{10}(y^\text{min}_i), \log_{10}(y^\text{max}_i)]$ as the smallest interval containing 68.3% of the curves. $y^\text{min}_i$ and $y^\text{max}_i$ can therefore be written as

$$y^\text{min}_i(z) = 10^{\log_{10}(y_i(z)) - \Delta \log_{10}(y_i(z))} = 10^{\log_{10}(y_i(z))} / F_{y_i}(z).$$  

(9)

and

$$y^\text{max}_i(z) = 10^{\log_{10}(y_i(z)) + \Delta \log_{10}(y_i(z))} = F_{y_i}(z) 	imes 10^{\log_{10}(y_i(z))}.$$  

(10)

The error is thus defined as

$$\sigma = \log_{10}(F_{y_i}(z)) = \frac{1}{2} (\log_{10}(y^\text{max}_i(z)) - \log_{10}(y^\text{min}_i(z))).$$  

(11)

$$10^\sigma = F_{y_i}(z) = \sqrt{y^\text{max}_i(z) / y^\text{min}_i(z)}.$$  

(12)

We define $y^\dagger_i(z)$ as the abundance associated to the mean value $\log_{10}(y_i(z))$,

$$y^\dagger_i(z) = 10^{\log_{10}(y_i(z))}.$$  

(13)

The error domain $[y^\dagger_i(z), y^\dagger_i(z)]$ is thus $[y^\dagger_i(z) \times F_{y_i}(z)]$ and we finally get

$$y^\dagger_i(z) = 10^{\log_{10}(y_i(z))} = \sqrt{y^\text{min}_i(z) \times y^\text{max}_i(z)}.$$  

(14)

In the present paper, results are given in terms of $y^\dagger_i(z)$ and $F_{y_i}(z)$. The previous equations allow to determine also $y^\text{min}_i(z)$ and $y^\text{max}_i(z)$.

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