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1 A methodology to construct a reduced chemical scheme 2 for 2D-3D photochemical models: Application to Saturn

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8 **Abstract**

We present a methodology to build a reduced chemical scheme adapted to the study of hydrocarbons in the atmospheres of giant planets and Titan. As an example, we have built a reduced chemical scheme, containing only 25 compounds and 46 reactions (including photolysis), which is well adapted to compute the abundance of the main hydrocarbons observed so far in the atmosphere of Saturn (CH_3 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , $\text{CH}_3\text{C}_2\text{H}$, C_3H_8 and C_4H_2). This scheme gives similar results, within the error bars of the model, as a 1D photochemical model using an initial chemical scheme containing 90 compounds and more than 600 reactions. As a consequence, such a methodology can be used to build a reduced scheme well adapted to future 2D (or 3D) photochemical models and GCMs.

9 *Key words:* Saturn, Photochemistry, Hydrocarbons, 2D photochemical
10 models

11 **1. Introduction**

12 Recent Cassini and ground-based observations (Greathouse et al. 2005, Howett
13 et al. 2007, Fouchet et al. 2008, Guerlet et al. 2009, Hesman et al. 2009, Guerlet
14 et al. 2010) and observations gathered in the framework of the Herschel Guar-
15 anteed Time Key Program "Water and related chemistry in the Solar System"
16 (Hartogh et al., 2009) give unprecedented data on the structure and the compo-
17 sition of Saturn's atmosphere as a function of latitude and time. Interpretation

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of these data requires adapted models like general circulation model and 2D/3D photochemical models which are currently lacking. One limitation to the development of 2D/3D photochemical models is the complexity of the chemical scheme (large number of compounds and reactions) required to study the evolution of hydrocarbons, which are the main trace species of the stratosphere. In typical 1D photochemical models, the number of species can reach 100 and there are more than 500 reactions. In fact, the aim of 1D modeling is to complete the chemical scheme as much as possible in order to have the best description of chemical processes occurring in the atmosphere and explain how light and heavy molecules are produced. In 2D/3D modeling, it is not possible for the time being to include such a large chemical scheme due to computational time limitations. As a consequence, it is important to determine a reduced chemical scheme, which is known to be representative of the main atmospheric chemical processes. The problem is then to create such a reduced chemical scheme which would be simple enough to be usable for 2D/3D models and whose results would remain valid.

In the present paper, we present a methodology to build a reduced chemical scheme validated to study the production of the main hydrocarbons in the stratosphere of Saturn. In section 2, we present the photochemical model, including the background atmosphere, the initial chemical scheme and the method used to study the propagation of uncertainties in the model. Mole fraction profiles and their uncertainties are presented in section 3 and compared to recent CIRS observations. The methodology used to build a reduced chemical scheme is presented in section 4, the result is given in section 5 and discussed in section 6.

2. Photochemical model

2.1. Atmospheric model

Our 1D photochemical model uses a fixed background atmosphere with fixed boundary conditions (no evolution with latitude and time). The temperature

profile presented in Fig. 1 has been synthesized by combining two different observations. At pressure levels greater than 10^{-5} mbar, we used the temperature profile derived from Cassini/CIRS data corresponding to a planetographic latitude of 20° S (data provided by S. Guerlet), which is the latitude around which the subsolar point was located at the time these data have been collected (in 2006). Details of the temperature profile retrieval can be found in Fouchet et al. (2008) and Guerlet et al. (2009). At pressure levels lower than 10^{-5} mbar, we used data derived from Smith et al. (1983). A subjective extrapolation is done to connect the two points ($p = 10^{-5}$ mbar, $T = 140$ K) and ($p = 10^{-7}$ mbar, $T = 420$ K).

We used a non-uniform altitude grid with 124 levels from -184 km (pressure level $p \approx 10^4$ mbar) to 1580 km ($p \approx 10^{-7}$ mbar). The altitude reference ($z = 0$) corresponds to $p = 1$ bar. Two consecutive levels (z and $z + \Delta z$) are separated by a distance smaller than $H(z)/5$, where $H(z)$ is the atmospheric scale height at altitude z .

We summarize hereafter the boundary conditions of the model. At the lower boundary, we set the mole fraction of H_2 , He, CH_4 and CO respectively to $y_{H_2} = 0.86$, $y_{He} = 0.135$ (Conrath and Gautier, 2000), $y_{CH_4} = 4.5 \cdot 10^{-3}$ (Flasar et al. 2005, Fletcher et al. 2009) and $y_{CO} = 5.0 \cdot 10^{-10}$ (Cavalié et al., 2009). All other compounds have a flux given by the maximum diffusion velocity $v = -K/H$ where K is the eddy diffusion coefficient and H the atmospheric scale height at the lower boundary. At the upper boundary, zero fluxes were assumed for all the species except for atomic hydrogen and for some oxygen compounds (CO, CO_2 and H_2O). H atoms are produced by photochemical processes at higher altitudes in the thermosphere. We assumed a fixed downward flux for atomic hydrogen at the upper boundary equal to $\Phi_H = -1.0 \times 10^8 \text{ cm}^{-2} \cdot \text{s}^{-1}$ following the work of Moses et al. (2005). The photochemical model results are not particularly sensitive to this value. The external source of oxygen in the atmosphere of Saturn could be in the form of infalling interplanetary dust particles (IDP), ring and/or satellite material, or large comets. Recent submillimetric observations favor a cometary origin for CO in the stratosphere of Saturn (Cavalié et al.,

Figure 1: Temperature profile (in K) of Saturn's atmosphere adopted in the present photo-chemical model as a function of pressure p (in mbar). This atmospheric structure is inferred from two sources. From the bottom up to $p \approx 10^{-5}$ mbar: recent CIRS data (Fouchet et al., 2008) corresponding to a planetographic latitude of 20° S. For $p < 10^{-5}$ mbar: extrapolation using data from Smith et al. (1983).

2010). The abundance levels at which H_2O has been observed in the stratosphere of Saturn implies that the source of H_2O is more likely to be a steady source with an origin local to the Saturn system because of transport and condensation issues (Moses et al., 2005). This is reinforced by the recent observation of active plumes emanating from the south pole of Enceladus suggesting that this small moon is likely to be the principal source of neutrals in Saturn's magnetosphere (Smith et al., 2010). The source of H_2O should be soon definitely established from Herschel observations (Hartogh et al., 2009). In the present model, we used a simplified parametrization of the external input of oxygen compounds. The external oxygen is assumed to be released in the upper atmosphere in the form of CO , H_2O and CO_2 with the following flux: $\Phi_{\text{CO}} = 1.5 \cdot 10^6 \text{ cm}^{-2} \cdot \text{s}^{-1}$, $\Phi_{\text{H}_2\text{O}} = 1.5 \cdot 10^6 \text{ cm}^{-2} \cdot \text{s}^{-1}$ and $\Phi_{\text{CO}_2} = 7.5 \cdot 10^4 \text{ cm}^{-2} \cdot \text{s}^{-1}$ (Moses et al. 2000,

90 Cavalié et al. 2009).

91 The eddy diffusion coefficient $K(z)$ (in $\text{cm}^2\cdot\text{s}^{-1}$) is presented in Fig. 2. This
 92 coefficient, together with the methane mole fraction at the lower boundary,
 93 gives a satisfactory profile of methane in comparison with Voyager/UVS and
 94 Cassini/CIRS data (Fig. 3).

Figure 2: Eddy diffusion coefficient (solid line) and molecular diffusion coefficient of CH_4 (dashed line) (expressed in $\text{cm}^2\cdot\text{s}^{-1}$) as a function of pressure (mbar). The methane homopause is located around 10^{-5} mbar in agreement with Smith et al. (1983).

95 2.2. Chemical model

96 In the present study, we used the review of the hydrocarbon chemistry at
 97 low temperature described in Hébrard et al. (2006) and Hébrard et al. (2009) for
 98 Titan's atmosphere. The initial chemical scheme, associated rate constants and
 99 uncertainty factors of reaction rates have been extracted from these two papers.
 100 The chemical scheme includes 90 compounds (H, H_2 , He, hydrocarbons and
 101 oxygen compounds), 549 reactions and 59 photodissociation processes. The list
 102 of reactions can also be provided upon request and will soon be included in the

103 KIDA database (<http://kida.obs.u-bordeaux1.fr/>). The photodissociation rates
 104 have been computed with a mean zenith angle obtained from a subsolar point
 105 located at 20°S a solar declination equal to -20° . Their uncertainty factors
 106 have been set to $F_J = 1.5$ (Dobrijevic and Parisot, 1998).

107 2.3. Uncertainty propagation

108 The overall precision of photochemical models is highly sensitive to the un-
 109 certainties in the rate coefficients used in the chemical scheme. Since the conti-
 110 nuity equations are non-linear and strongly coupled, it is necessary to use global
 111 sensitivity methods to study how these uncertainties propagate in the photo-
 112 chemical model (Dobrijevic et al., 2010b). The present model is similar to the
 113 model used in Dobrijevic et al. (2010a). We used a Monte-Carlo approach to
 114 generate 500 profiles as a function of altitude. This number is a good com-
 115 promise between the computation time and the statistical significance of the
 116 distributions.

117 3. 1D photochemical model results

118 Figs. 3, 4 and 5 present, for each compound of interest, the 500 profiles
 119 generated by our Monte-Carlo procedure and the initial profile. Initial pro-
 120 files (black solid lines) correspond to profiles obtained with the initial chemical
 121 scheme and the nominal values of chemical rate constants. The type of distrib-
 122 ution of mole fractions depends on the compound and can vary with altitudes:
 123 distributions are not always normal or log-normal. In this case, quantiles are
 124 useful measures to represent the distributions. Figures show the 5th and 15th
 125 20-quantiles and the 1st and 19th 20-quantiles, which give the intervals contain-
 126 ing respectively 50% and 90% of the profiles. Uncertainty on the CH_4 profile
 127 (due to uncertainties on reaction rate coefficients) is very low, much lower than
 128 the uncertainties of observations, because the CH_4 profile is mainly controlled
 129 by the eddy diffusion coefficient. On the contrary, uncertainties on other profiles
 130 derived from the model are much greater than those of observations, especially
 131 for C_3 and C_4 compounds.

132 The aim of the present study is to present a methodology to derive a very
 133 reduced chemical scheme, not to compare our model to all the previous obser-
 134 vations (taken at different times with different techniques and different spatial
 135 resolutions). In order to validate our initial scheme and our 1D photochemical
 136 model, we restrict the comparisons with recent data that correspond to the same
 137 latitude (around 20° S) and epoch (2006). In particular, the set of data pub-
 138 lished by Guerlet et al. (2009) and Guerlet et al. (2010) gives the opportunity
 139 to compare our model with consistent data acquired by the same instrument
 140 and analyzed with the same procedure.

141 Taking uncertainties into account, our model is in relatively good agreement
 142 with CIRS observations at the subsolar point. All the observational data are
 143 within the 1st and 19th 20-quantiles of our model. This shows that chemical
 144 processes included in the initial chemical scheme and physical processes im-
 145 plemented in the model are representative of the main processes that govern
 146 the composition of Saturn's stratosphere. To go deeper into the comparison of
 147 the model with CIRS data, it would be necessary to compare synthetic spec-
 148 tra generated from our Monte-Carlo profiles with the CIRS spectra. Such a
 149 work deserves a dedicated study. The aim here is not to adjust some model
 150 parameters to have a perfect agreement between the model and observations (if
 151 possible), but only to have a good agreement to construct a reliable reduced
 152 chemical scheme.

153 4. Reduction methodology

154 How to reduce a chemical scheme? A reduced chemical scheme is built by
 155 removing a set of reactions from the initial chemical scheme. Using this reduced
 156 chemical scheme, our 1D photochemical model should give results in agreement
 157 with the ones obtained with the initial chemical scheme. This agreement de-
 158 pends on a given criterion. Typically, the new results should remain close to a
 159 reference. Two reference results are then conceivable: results from a reference
 160 model and results from observations. Ideally, observations should be used as

161 a reference but we see in figures 3, 4 and 5 that error bars of the model are
162 greater than the error bars of observations. For this reason, a reference model
163 has been preferred to a reference set of observables. The reference model is
164 our 1D photochemical model that includes uncertainties propagation of rate
165 constants.

166 Since only a few compounds have been observed to date and only a part
167 of the atmosphere can be probed by various instruments, we have decided to
168 limit the criterion presented above to a given list of compounds and we focus our
169 study in the part of the atmosphere which lies between the 1 bar and 10^{-5} mbar
170 pressure levels. The list of compounds corresponds to the ones that have been
171 already detected in the atmosphere: CH_3 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , $\text{CH}_3\text{C}_2\text{H}$,
172 C_3H_8 and C_4H_2 (with the exception of C_6H_6 for reasons detailed below).

173 The strength of the relationship between outputs (mole fractions) and in-
174 puts (rate constants) can be evaluated by Rank Correlation Coefficients (RCCs)
175 in the presence of non-linearity in the model. RCCs convert a nonlinear but
176 monotonic relationship into a linear relationship by replacing the values of the
177 sampled inputs/outputs by their respective ranks. These correlation coefficients
178 can vary between -1 and 1; a positive value means that both correlated para-
179 meters increase or decrease simultaneously. In the presence of nonlinear but
180 monotonic correlations, this simple procedure improves the resolution of sensi-
181 tivity analysis (Helton et al., 2006).

182 In practice, RCCs are calculated using the logarithm of mole fractions and
183 rate constants. Rate constants with low RCCs (in absolute value) have weak
184 influence on the uncertainty of the mole fraction of a given compound. Removing
185 these reactions will have very little influence on the results of the model. This
186 means that below a given threshold (a given value of RCC), all the reactions can
187 be removed. The lower the RCC threshold, the greater the number of reactions
188 and compounds that remain in the reduced chemical scheme. Our criterion to
189 validate a reduced chemical scheme was the reproduction of a reference model
190 within a certain confidence interval. The confidence interval may be given by the
191 5th and 15th 20-quantiles or the 1st and 19th 20-quantiles for instance (this is

an arbitrary choice). The profiles of each target molecule should stay within the confidence interval to consider the current reduced scheme as suitable. In the following, the confidence interval is given by the 1st and 19th 20-quantiles in the part of the atmosphere where the compounds are observed. The determination of an optimal RCC threshold (which would give the most satisfactory reduced scheme) is an empirically iterative procedure that can be tiresome since the new reduced chemical scheme must be tested for each value of the RCC threshold. A slight modification of this threshold can add or remove a few reactions in the reduced chemical scheme. We have noticed, moreover, that the number of runs in the Monte Carlo procedure can affect this "optimal threshold". As a consequence, in order to limit the number of runs and tests, we did not make an exhaustive study to search for the "optimal RCC threshold".

The RCCs between mole fractions and rate constants combine the information of the main influent pathways in the chemical scheme, weighted by their uncertainties. A first attempt has been made using the RCCs computed with the 500 mole fraction profiles and the corresponding rate constants presented previously. One limitation with this method, as stated by Carrasco et al. (2008), is that uncertainty factors of some rate coefficients are very important, which increase the intrinsic importance of some reactions. This methodology is well adapted to derive the key reactions of the chemical scheme (Dobrijevic et al., 2010b), but not to construct a reduced scheme. For instance, we were not able to find an interesting reduced scheme for C_3H_4 and C_4H_2 . Too many compounds and reactions were necessary to produce vertical profiles in agreement with the reference model for these two compounds. This explains also why we did not include C_6H_6 in our model. The other reason is that the chemistry of C_4 , C_5 and C_6 compounds is not well known. In particular, many reactions and compounds are lacking in the initial chemical scheme (see for instance Dobrijevic and Dutour 2007). Consequently, we consider that it is not pertinent to search for a reduced scheme that matches the vertical profile of C_6H_6 .

In a second attempt, we set all the uncertainty factors to a given value F . Carrasco et al. (2008) stated that the value of F does not change significantly

the reduced schemes. We chose $F = 1.5$ for all photodissociation processes and reactions. We have generated 500 profiles using a Monte-Carlo procedure and then computed the RCCs for all the compounds we were interested in and all the reaction rates. After a few attempts, we set the RCCs threshold to 0.2. This led us to a reduced scheme with 33 compounds and 54 reactions (including photolysis). Four compounds of this scheme were not produced (they appeared only as a reactant) and thus were removed from the scheme. Thirteen compounds did not appear as a reactant, but only as a product. Some of these sink compounds were relatively abundant (compared to the compounds of interest) and were then removed, as well as their corresponding reactions. It was not possible to remove all the sinks because too many reactions were concerned. However, sink compounds with low mole fractions do not alter the abundance of main compounds. In the end, the reduced chemical scheme contains only 25 compounds and 46 reactions (including 18 photodissociations) listed in tables 1 and 2. As a result, we have reduced the number of compounds by 72%, the number of reactions by 92% and the computation time by a factor 100.

Table 1: List of the 25 compounds of the reduced chemical scheme

He ; H ; H ₂
CH ; C ; ¹ CH ₂ ; CH ₃ ; CH ₄
C ₂ ; C ₂ H ; C ₂ H ₂ ; C ₂ H ₃ ; C ₂ H ₅ ; C ₂ H ₄ ; C ₂ H ₆
C ₃ H ₃ ; CH ₃ C ₂ H ; C ₃ H ₅ ; C ₃ H ₆ ; C ₃ H ₈ ;
C ₄ H ₃ ; C ₄ H ₂ ; C ₄ H ₆ ; C ₄ H ₄ ;
C ₆ H ₄

5. Photochemical model results with the reduced chemical scheme

In order to be valid, the reduced scheme must be in agreement with the reference model. So, the steady state abundances of the main compounds computed using the reduced scheme were compared to the reference model in figures 6, 7 and 8. For all the compounds, the agreement is very good: profiles lie between the 5th and 15th 20-quantiles in the middle atmosphere (especially where the compounds have been observed, typically between 10 mbar and 10^{-2} mbar).

Table 2: Reduced chemical scheme: Photolysis reactions (R1 to R18) and chemical reactions (R19 to R46). Rate constants, cross sections, photolysis rates and uncertainty factors are given in Hébrard et al. (2006) and Hébrard et al. (2009).

R1	$\text{H}_2 + h\nu \rightarrow \text{H} + \text{H}$	R19	$\text{H} + \text{CH} \rightarrow \text{C} + \text{H}_2$
R2	$\text{CH}_4 + h\nu \rightarrow \text{CH}_3 + \text{H}$	R20	$\text{H} + \text{C}_2\text{H}_3 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$
R3	$\text{CH}_4 + h\nu \rightarrow {}^1\text{CH}_2 + \text{H}_2$	R21	$\text{H} + \text{C}_2\text{H}_5 \rightarrow \text{CH}_3 + \text{CH}_3$
R4	$\text{CH}_4 + h\nu \rightarrow \text{CH} + \text{H}_2 + \text{H}$	R22	$\text{H} + \text{C}_3\text{H}_5 \rightarrow \text{CH}_3\text{C}_2\text{H} + \text{H}_2$
R5	$\text{CH}_3 + h\nu \rightarrow {}^1\text{CH}_2 + \text{H}$	R23	$\text{C} + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_3 + \text{H}$
R6	$\text{C}_2\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H} + \text{H}$	R24	$\text{C} + \text{CH}_3\text{C}_2\text{H} \rightarrow \text{C}_4\text{H}_3 + \text{H}$
R7	$\text{C}_2\text{H}_4 + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{H}_2$	R25	$\text{CH} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \text{H}$
R8	$\text{C}_2\text{H}_4 + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{H} + \text{H}$	R26	${}^1\text{CH}_2 + \text{H}_2 \rightarrow \text{CH}_3 + \text{H}$
R9	$\text{C}_2\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$	R27	${}^1\text{CH}_2 + \text{CH}_4 \rightarrow \text{CH}_3 + \text{CH}_3$
R10	$\text{C}_2\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{H} + \text{H}$	R28	${}^1\text{CH}_2 + \text{C}_2\text{H}_5 \rightarrow \text{C}_3\text{H}_6 + \text{H}$
R11	$\text{C}_2\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{H}_2$	R29	$\text{C}_2\text{H} + \text{H}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}$
R12	$\text{CH}_3\text{C}_2\text{H} + h\nu \rightarrow \text{C}_3\text{H}_3 + \text{H}$	R30	$\text{C}_2\text{H} + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{CH}_3$
R13	$\text{C}_3\text{H}_8 + h\nu \rightarrow \text{C}_3\text{H}_6 + \text{H}_2$	R31	$\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H}$
R14	$\text{C}_4\text{H}_2 + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{C}_2$	R32	$\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$
R15	$\text{C}_4\text{H}_4 + h\nu \rightarrow \text{C}_4\text{H}_2 + \text{H}_2$	R33	$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_4$
R16	$\text{C}_3\text{H}_6 + h\nu \rightarrow \text{C}_3\text{H}_5 + \text{H}$	R34	$\text{C}_2\text{H}_3 + \text{C}_4\text{H}_2 \rightarrow \text{C}_6\text{H}_4 + \text{H}$
R17	$\text{C}_4\text{H}_6 + h\nu \rightarrow \text{C}_4\text{H}_4 + \text{H}_2$	R35	$\text{H} + \text{CH}_3 + \text{M} \rightarrow \text{CH}_4 + \text{M}$
R18	$\text{C}_4\text{H}_6 + h\nu \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_2$	R36	$\text{H} + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{C}_2\text{H}_3 + \text{M}$
		R37	$\text{H} + \text{C}_2\text{H}_3 + \text{M} \rightarrow \text{C}_2\text{H}_4 + \text{M}$
		R38	$\text{H} + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_2\text{H}_5 + \text{M}$
		R39	$\text{H} + \text{C}_3\text{H}_3 + \text{M} \rightarrow \text{CH}_3\text{C}_2\text{H} + \text{M}$
		R40	$\text{H} + \text{CH}_3\text{C}_2\text{H} + \text{M} \rightarrow \text{CH}_3 + \text{C}_2\text{H}_2 + \text{M}$
		R41	$\text{H} + \text{CH}_3\text{C}_2\text{H} + \text{M} \rightarrow \text{C}_3\text{H}_5 + \text{M}$
		R42	$\text{H} + \text{C}_3\text{H}_5 + \text{M} \rightarrow \text{C}_3\text{H}_6 + \text{M}$
		R43	$\text{CH}_3 + \text{CH}_3 + \text{M} \rightarrow \text{C}_2\text{H}_6 + \text{M}$
		R44	$\text{CH}_3 + \text{C}_2\text{H}_5 + \text{M} \rightarrow \text{C}_3\text{H}_8 + \text{M}$
		R45	$\text{CH}_3 + \text{C}_3\text{H}_3 + \text{M} \rightarrow \text{C}_4\text{H}_6 + \text{M}$
		R46	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$

Fig. 9 shows that the agreement for C_4H_2 between the reduced model and the reference model is limited to pressure levels lower than about 10^{-3} mbar. The mole fraction of $\text{CH}_3\text{C}_2\text{H}$ (Fig. 8) obtained with the reduced model is not in agreement with the initial model for pressure levels greater than about 10 mbar. So, the reduced chemical scheme proposed here is not perfect since it does not produce profiles of $\text{CH}_3\text{C}_2\text{H}$ and C_4H_2 that are reliable in the whole part of the atmosphere studied here. Since high pressure and low pressure levels are poorly constrained by observations, this discrepancy seems acceptable. If necessary, it is of course possible to improve the situation by lowering the RCC threshold. This would lead to a less reduced chemical scheme.

6. Discussion

How to use this reduced scheme? A priori, the chemical scheme provided here should be used with the same rate constants as the ones we used (see Hébrard et al. 2006; Hébrard et al. 2009). However, if the initial chemical scheme have to be changed (because some rate coefficients or uncertainty factors have to be up-

dated or some reactions have to be added), it is necessary to redo the procedure presented in this paper to build a new reduced scheme. In particular, J. Moses pointed out (personal communication) that the rate coefficient of reaction R34 might be overestimated (and that our uncertainty factor is underestimated). A particular attention might be paid on this reaction in a future update of the chemical scheme. Also, the methodology presented here gives a reduced scheme with several sink compounds (with no destruction mechanisms). Although we have eliminated most of these compounds, it is not possible to eliminate all the reactions that involve sink compounds without changing significantly the results. As a consequence, users of 2D/3D photochemical models should take care of the presence of sink compounds by adding appropriate destruction mechanisms.

Is the reduced scheme suitable for other latitudes? The aim of this reduced scheme is to be used in 2D/3D photochemical models. In order to test the validity of our reduced chemical scheme, we have made a comparison of the model results derived from the initial chemical scheme and the reduced chemical scheme at different latitudes. Our reference model corresponds to the subsolar point at 20° S. We have tested 2 other latitudes: 60° S and 40° S. For these tests, only the solar zenith angle has been changed (we used the same temperature profile). For all compounds, the behavior of the model is the same whatever the chemical scheme used. An example is shown in Fig. 10 for C_3H_8 . Other compounds are even less affected by variation of the solar zenith angle. To be fully satisfying, the validation should take into account the fact that temperature profiles also vary with latitudes. For instance, Cassini data show that the temperature profile measured at 60° S is about 10 K higher than at 20° S (Guerlet et al., 2009). It would be interesting to study how uncertainties of rate constants propagate in the photochemical model when considering different temperature profiles and solar zenith angles. One limitation we see is that many reaction rates have no temperature dependence in our initial chemical scheme (because this temperature dependence is not known). It is essential to have a good description of the chemistry as a function of temperature to see a possible variation of error bars of the model as a function of latitude. To do that, it would be necessary to

improve our chemical scheme in order to estimate the temperature dependence of many reaction rates and to estimate their uncertainty factors. This kind of work is beyond the scope of the present study.

Can we find a minimal chemical scheme? The reduced chemical scheme presented here is not a minimal chemical scheme. To obtain a minimal scheme from the reduced one, we might remove some additional reactions depending on their RCCs. We could first remove one reaction at a time and check sequentially the 46 reactions of the reduced scheme. If a reaction could be removed, then we could try to remove another reaction and repeat this procedure as long as the model results would be in agreement with the reference model. However, in such a non-linear system, different sequences of removal might give different results. As a consequence, a great number of runs are necessary to achieve this task. Actually, since the initial chemical scheme is expected to be updated frequently, we find it useless to try to find a minimal chemical scheme.

7. Conclusion

One major step in the development of 2D and 3D photochemical models is to determine a chemical scheme that is both simple (i.e. it contains a small number of compounds and reactions) and valid (i.e. the results of the model are in agreement with a reference model). In the present paper, we have presented a methodology to build a reduced chemical scheme. The reference model is a 1D photochemical model that includes uncertainties of rate coefficients. The screening of the chemical scheme is based on the correlations between outputs of the model (mole fractions) and the inputs (rate coefficients). This methodology is quite similar to the one used to determine key reactions of a photochemical model (Dobrijevic et al., 2010a). We found a reduced chemical scheme where about 70% of the compounds and 90% of the reactions have been removed from the initial chemical scheme.

It is not guaranteed that the reduced chemical scheme derived here for Saturn is well adapted for other giant planets and Titan. As a consequence, this work

should be done again for other planets to check this specific point. Also, this work should be done again if the reference chemical scheme is different from the one used in the present study.

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Figure 3: Model. Gray solid lines: Abundance profiles of CH_4 and C_2H_2 obtained after 500 runs. Black solid line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution. CH_4 observations. Lower atmosphere: CIRS Cassini data (Flasar et al., 2005; Fletcher et al., 2009). Upper atmosphere: UVS Voyager data from Festou and Atreya (1982) (triangle) and Smith et al. (1983) (diamond). C_2H_2 observations. Bold solid line: CIRS Cassini observations and $1-\sigma$ uncertainties at 20° S (Guerlet et al., 2009, 2010). Diamond: sub-solar IRTF data (Greathouse et al., 2005). Triangle: sub-solar CIRS Cassini data (Howett et al., 2007). Square: sub-solar CIRS Cassini data (Hesman et al., 2009).

Figure 4: **Model**. Gray solid lines: Abundance profiles of C_2H_6 and CH_3C_2H obtained after 500 runs. Black solid line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution. C_2H_6 observations. Bold solid line: CIRS Cassini observations and $1-\sigma$ uncertainties at 20° S (Guerlet et al., 2009, 2010). Diamond: sub-solar IRTF data (Greathouse et al., 2005). Triangle: sub-solar CIRS Cassini data (Howett et al., 2007). Square: sub-solar CIRS Cassini data (Hesman et al., 2009). C_3H_4 observation. Bold solid line: CIRS Cassini observations and $1-\sigma$ uncertainties at 20° S (Guerlet et al., 2009, 2010).

Figure 5: Model. Gray solid lines: Abundance profiles of C_3H_8 and C_4H_2 obtained after 500 runs. Black solid line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution. Gray dotted line: 100% saturation profile. C_3H_8 and C_4H_2 observations. Bold solid line: CIRS Cassini observations and $1-\sigma$ uncertainties at 20° S (Guerlet et al., 2009, 2010). Square: IRTF data at -20° planetocentric latitude (Greathouse et al., 2006)

Figure 6: Red line: Abundance profiles of CH_3 and C_2H_2 with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution.

Figure 7: Red line: Abundance profiles of C_2H_4 and C_2H_6 with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution.

Figure 8: Red line: Abundance profiles of $\text{CH}_3\text{C}_2\text{H}$ and C_3H_8 with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution.

Figure 9: Red line: Abundance profiles of C_4H_2 with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution.

Figure 10: Abundance profiles of C_3H_8 for different latitudes. Black lines: Initial chemical scheme. Gray lines: Reduced chemical scheme. The mean solar zenith angle corresponding to 20° S, 40° S and 60° S are respectively 51°, 54° and 63°.

- > This study concerns photochemistry of hydrocarbons in the atmosphere of Saturn.
- > We present a methodology to derive a very reduced chemical scheme that can be used in future 2D (or 3D) photochemical models.
- > Our reduced scheme of 25 compounds and 46 reactions gives similar results, within the error bars of the model, than a 1D photochemical model.