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M. Dobrijevic, T. Cavalié, F. Billebaud. A methodology to construct a reduced chemical scheme for 2D-3D photochemical models: Application to Saturn. *Icarus*, 2011, 10.1016/j.icarus.2011.04.027 . hal-00768791

**HAL Id: hal-00768791**

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Submitted on 24 Dec 2012

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## Accepted Manuscript

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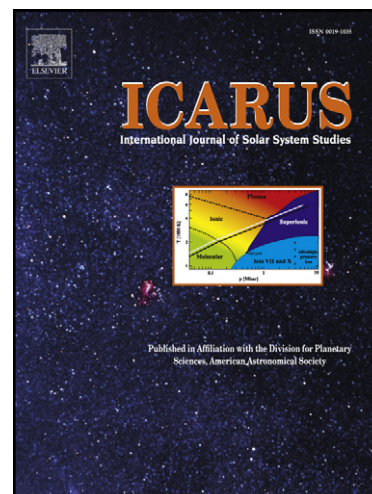
PII: S0019-1035(11)00163-1  
DOI: [10.1016/j.icarus.2011.04.027](https://doi.org/10.1016/j.icarus.2011.04.027)  
Reference: YICAR 9805

To appear in: *Icarus*

Received Date: 6 January 2011  
Revised Date: 27 April 2011  
Accepted Date: 30 April 2011

Please cite this article as: Dobrijevic, M., Cavalié, T., Billebaud, F., A methodology to construct a reduced chemical scheme for 2D-3D photochemical models: Application to Saturn, *Icarus* (2011), doi: [10.1016/j.icarus.2011.04.027](https://doi.org/10.1016/j.icarus.2011.04.027)

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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 ( $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{C}_2\text{H}$ ,  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_2$ ). 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

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

34 In the present paper, we present a methodology to build a reduced chemi-  
35 cal scheme validated to study the production of the main hydrocarbons in the  
36 stratosphere of Saturn. In section 2, we present the photochemical model, in-  
37 cluding the background atmosphere, the initial chemical scheme and the method  
38 used to study the propagation of uncertainties in the model. Mole fraction pro-  
39 files and their uncertainties are presented in section 3 and compared to recent  
40 CIRS observations. The methodology used to build a reduced chemical scheme  
41 is presented in section 4, the result is given in section 5 and discussed in section  
42 6.

## 43 **2. Photochemical model**

### 44 *2.1. Atmospheric model*

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

47 profile presented in Fig. 1 has been synthesized by combining two different  
 48 observations. At pressure levels greater than  $10^{-5}$  mbar, we used the tempera-  
 49 ture profile derived from Cassini/CIRS data corresponding to a planetographic  
 50 latitude of  $20^\circ$  S (data provided by S. Guerlet), which is the latitude around  
 51 which the subsolar point was located at the time these data have been col-  
 52 lected (in 2006). Details of the temperature profile retrieval can be found in  
 53 Fouchet et al. (2008) and Guerlet et al. (2009). At pressure levels lower than  
 54  $10^{-5}$  mbar, we used data derived from Smith et al. (1983). A subjective ex-  
 55 trapolation is done to connect the two points ( $p = 10^{-5}$  mbar,  $T = 140$  K) and  
 56 ( $p = 10^{-7}$  mbar,  $T = 420$  K).

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

62 We summarize hereafter the boundary conditions of the model. At the lower  
 63 boundary, we set the mole fraction of  $\text{H}_2$ , He,  $\text{CH}_4$  and CO respectively to  $y_{\text{H}_2} =$   
 64  $0.86$ ,  $y_{\text{He}} = 0.135$  (Conrath and Gautier, 2000),  $y_{\text{CH}_4} = 4.5 \cdot 10^{-3}$  (Flasar et al.  
 65 2005, Fletcher et al. 2009) and  $y_{\text{CO}} = 5.0 \cdot 10^{-10}$  (Cavalié et al., 2009). All other  
 66 compounds have a flux given by the maximum diffusion velocity  $v = -K/H$   
 67 where  $K$  is the eddy diffusion coefficient and  $H$  the atmospheric scale height at  
 68 the lower boundary. At the upper boundary, zero fluxes were assumed for all the  
 69 species except for atomic hydrogen and for some oxygen compounds ( $\text{CO}$ ,  $\text{CO}_2$   
 70 and  $\text{H}_2\text{O}$ ). H atoms are produced by photochemical processes at higher altitudes  
 71 in the thermosphere. We assumed a fixed downward flux for atomic hydrogen  
 72 at the upper boundary equal to  $\Phi_{\text{H}} = -1.0 \times 10^8 \text{ cm}^{-2} \cdot \text{s}^{-1}$  following the work  
 73 of Moses et al. (2005). The photochemical model results are not particularly  
 74 sensitive to this value. The external source of oxygen in the atmosphere of  
 75 Saturn could be in the form of infalling interplanetary dust particles (IDP), ring  
 76 and/or satellite material, or large comets. Recent submillimetric observations  
 77 favor a cometary origin for CO in the stratosphere of Saturn (Cavalié et al.,

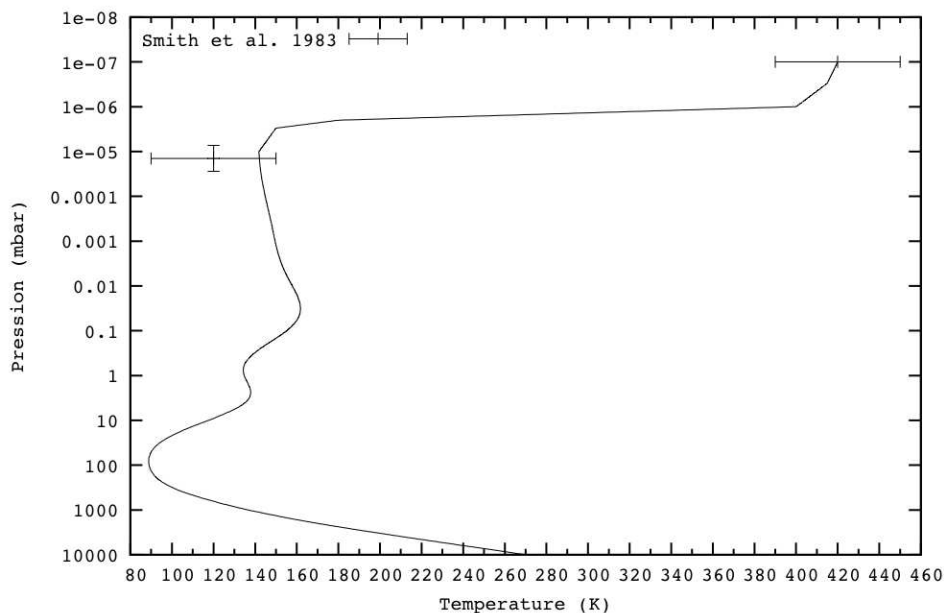


Figure 1: Temperature profile (in K) of Saturn's atmosphere adopted in the present photochemical model as a function of pressure  $p$  (in mbar). This atmospheric structure is inferred from two sources. From the bottom up to  $p \approx 10^{-5}$  mbar: recent CIRS data (Fouchet et al., 2008) corresponding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

2010). The abundance levels at which  $\text{H}_2\text{O}$  has been observed in the stratosphere  
of Saturn implies that the source of  $\text{H}_2\text{O}$  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  $\text{H}_2\text{O}$  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  $\text{CO}$ ,  $\text{H}_2\text{O}$  and  $\text{CO}_2$  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).

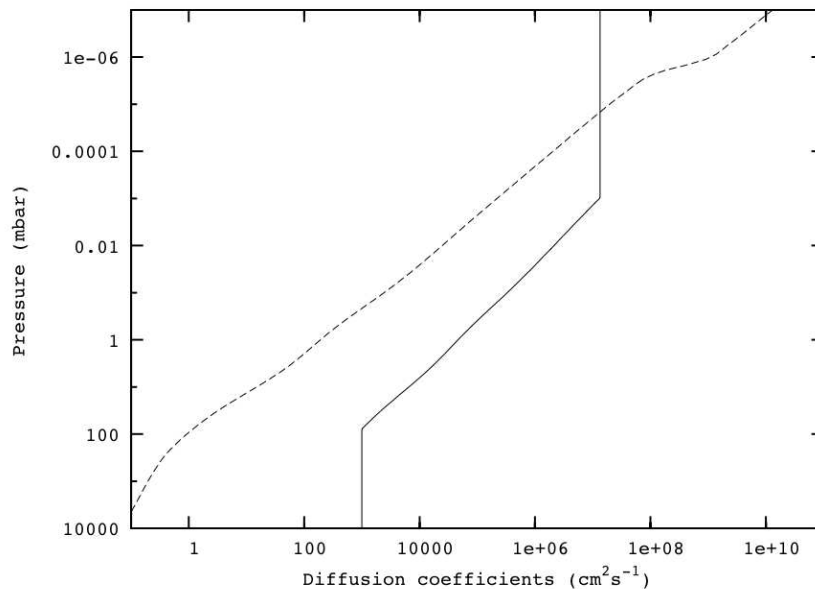


Figure 2: Eddy diffusion coefficient (solid line) and molecular diffusion coefficient of  $\text{CH}_4$  (dashed line) (expressed in  $\text{cm}^2\cdot\text{s}^{-1}$ ) as a function of pressure (mbar). The methane homopause is located around  $10^{-5}$  mbar in agreement with Smith et al. (1983).

## 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,  $\text{H}_2$ , 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  $-20^\circ$ . 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<sub>4</sub> profile  
127 (due to uncertainties on reaction rate coefficients) is very low, much lower than  
128 the uncertainties of observations, because the CH<sub>4</sub> 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<sub>3</sub> and C<sub>4</sub> 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:  $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{C}_2\text{H}$ ,  
172  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_2$  (with the exception of  $\text{C}_6\text{H}_6$  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

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

204 The RCCs between mole fractions and rate constants combine the information  
205 of the main influent pathways in the chemical scheme, weighted by their  
206 uncertainties. A first attempt has been made using the RCCs computed with  
207 the 500 mole fraction profiles and the corresponding rate constants presented  
208 previously. One limitation with this method, as stated by Carrasco et al. (2008),  
209 is that uncertainty factors of some rate coefficients are very important, which  
210 increase the intrinsic importance of some reactions. This methodology is well  
211 adapted to derive the key reactions of the chemical scheme (Dobrijevic et al.,  
212 2010b), but not to construct a reduced scheme. For instance, we were not able to  
213 find an interesting reduced scheme for  $C_3H_4$  and  $C_4H_2$ . Too many compounds  
214 and reactions were necessary to produce vertical profiles in agreement with the  
215 reference model for these two compounds. This explains also why we did not  
216 include  $C_6H_6$  in our model. The other reason is that the chemistry of  $C_4$ ,  $C_5$   
217 and  $C_6$  compounds is not well known. In particular, many reactions and com-  
218 pounds are lacking in the initial chemical scheme (see for instance Dobrijevic  
219 and Dutour 2007). Consequently, we consider that it is not pertinent to search  
220 for a reduced scheme that matches the vertical profile of  $C_6H_6$ .

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

223 the reduced schemes. We chose  $F = 1.5$  for all photodissociation processes  
 224 and reactions. We have generated 500 profiles using a Monte-Carlo procedure  
 225 and then computed the RCCs for all the compounds we were interested in  
 226 and all the reaction rates. After a few attempts, we set the RCCs threshold  
 227 to 0.2. This led us to a reduced scheme with 33 compounds and 54 reactions  
 228 (including photolysis). Four compounds of this scheme were not produced (they  
 229 appeared only as a reactant) and thus were removed from the scheme. Thirteen  
 230 compounds did not appear as a reactant, but only as a product. Some of  
 231 these sink compounds were relatively abundant (compared to the compounds of  
 232 interest) and were then removed, as well as their corresponding reactions. It was  
 233 not possible to remove all the sinks because too many reactions were concerned.  
 234 However, sink compounds with low mole fractions do not alter the abundance  
 235 of main compounds. In the end, the reduced chemical scheme contains only 25  
 236 compounds and 46 reactions (including 18 photodissociations) listed in tables  
 237 1 and 2. As a result, we have reduced the number of compounds by 72%, the  
 238 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 <sub>2</sub>
CH ; C ; <sup>1</sup> CH <sub>2</sub> ; CH <sub>3</sub> ; CH <sub>4</sub>
C <sub>2</sub> ; C <sub>2</sub> H ; C <sub>2</sub> H <sub>2</sub> ; C <sub>2</sub> H <sub>3</sub> ; C <sub>2</sub> H <sub>5</sub> ; C <sub>2</sub> H <sub>4</sub> ; C <sub>2</sub> H <sub>6</sub>
C <sub>3</sub> H <sub>3</sub> ; CH <sub>3</sub> C <sub>2</sub> H ; C <sub>3</sub> H <sub>5</sub> ; C <sub>3</sub> H <sub>6</sub> ; C <sub>3</sub> H <sub>8</sub> ;
C <sub>4</sub> H <sub>3</sub> ; C <sub>4</sub> H <sub>2</sub> ; C <sub>4</sub> H <sub>6</sub> ; C <sub>4</sub> H <sub>4</sub> ;
C <sub>6</sub> H <sub>4</sub>

## 239 5. Photochemical model results with the reduced chemical scheme

240 In order to be valid, the reduced scheme must be in agreement with the refer-  
 241 ence model. So, the steady state abundances of the main compounds computed  
 242 using the reduced scheme were compared to the reference model in figures 6, 7  
 243 and 8. For all the compounds, the agreement is very good: profiles lie between  
 244 the 5th and 15th 20-quantiles in the middle atmosphere (especially where the  
 245 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	$\text{C}_4\text{H}_{10} + h\nu \rightarrow \text{C}_2\text{H}_2 + \text{C}_2$	R32	$\text{C}_2\text{H}_3 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4 + \text{H}$
R15	$\text{C}_4\text{H}_8 + h\nu \rightarrow \text{C}_4\text{H}_2 + \text{H}_2$	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  $\text{C}_4\text{H}_2$  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  $\text{C}_4\text{H}_2$  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-

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

272 Is the reduced scheme suitable for other latitudes? The aim of this reduced  
273 scheme is to be used in 2D/3D photochemical models. In order to test the valid-  
274 ity of our reduced chemical scheme, we have made a comparison of the model re-  
275 sults derived from the initial chemical scheme and the reduced chemical scheme  
276 at different latitudes. Our reference model corresponds to the subsolar point at  
277  $20^\circ$  S. We have tested 2 other latitudes:  $60^\circ$ S and  $40^\circ$ S. For these tests, only  
278 the solar zenith angle has been changed (we used the same temperature profile).  
279 For all compounds, the behavior of the model is the same whatever the chemical  
280 scheme used. An example is shown in Fig. 10 for  $C_3H_8$ . Other compounds are  
281 even less affected by variation of the solar zenith angle. To be fully satisfying,  
282 the validation should take into account the fact that temperature profiles also  
283 vary with latitudes. For instance, Cassini data show that the temperature pro-  
284 file measured at  $60^\circ$ S is about 10 K higher than at  $20^\circ$ S (Guerlet et al., 2009).  
285 It would be interesting to study how uncertainties of rate constants propagate  
286 in the photochemical model when considering different temperature profiles and  
287 solar zenith angles. One limitation we see is that many reaction rates have no  
288 temperature dependence in our initial chemical scheme (because this tempera-  
289 ture dependence is not known). It is essential to have a good description of the  
290 chemistry as a function of temperature to see a possible variation of error bars  
291 of the model as a function of latitude. To do that, it would be necessary to

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

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

## 306 7. Conclusion

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

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

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

#### 324 *Acknowledgements*

325 T. Cavalié wishes to acknowledge for funding from the Centre National  
326 d'Études Spatiales (CNES).

#### 327 **References**

328 Carrasco, N., Plessis, S., Dobrijevic, M., Pernot, P., 2008. Toward a Reduction of  
329 the Bimolecular Reaction Model for Titan's Ionosphere. *International Journal*  
330 *of Chemical Kinetics* 40 (11), 699–709.

331 Cavalié, T., Billebaud, F., Dobrijevic, M., Fouchet, T., Lellouch, E., Encrenaz,  
332 T., Brillet, J., Moriarty-Schieven, G. H., Wouterloot, J. G. A., Hartogh, P.,  
333 2009. First observation of CO at 345 GHz in the atmosphere of Saturn with  
334 the JCMT: New constraints on its origin. *Icarus* 203, 531–540.

335 Cavalié, T., Hartogh, P., Billebaud, F., Dobrijevic, M., Fouchet, T., Lellouch,  
336 E., Encrenaz, T., Brillet, J., Moriarty-Schieven, G. H., 2010. A cometary  
337 origin for CO in the stratosphere of Saturn? *Astronomy and Astrophysics*  
338 510, A88.

339 Conrath, B. J., Gautier, D., 2000. Saturn Helium Abundance: A Reanalysis of  
340 Voyager Measurements. *Icarus* 144, 124–134.

341 Dobrijevic, M., Cavalié, T., Hébrard, E., Billebaud, F., Hersant, F., Selsis, F.,  
342 2010a. Key reactions in the photochemistry of hydrocarbons in Neptune's  
343 stratosphere. *Planetary and Space Science* 58, 1555–1566.

344 Dobrijevic, M., Dutour, I., 2007. The distribution of hydrocarbons in Titan's  
345 atmosphere: An evolutionary algorithm-based model. *Planetary and Space*  
346 *Science* 55, 2128–2136.



- 347 Dobrijevic, M., Hébrard, E., Plessis, S., Carrasco, N., Pernot, P., Bruno-Claeys,  
348 M., 2010b. Comparison of methods for the determination of key reactions  
349 in chemical systems: Application to Titan's atmosphere. *Advances in Space*  
350 *Research* 45, 77–91.
- 351 Dobrijevic, M., Parisot, J. P., 1998. Effect of chemical kinetics uncertainties on  
352 hydrocarbon production in the stratosphere of Neptune. *Planetary and Space*  
353 *Science* 46, 491–505.
- 354 Festou, M. C., Atreya, S. K., 1982. Voyager ultraviolet stellar occultation mea-  
355 surements of the composition and thermal profiles of the Saturnian upper  
356 atmosphere. *Geophysical Research Letters* 9, 1147–1150.
- 357 Flasar, F. M., Achterberg, R. K., Conrath, B. J., Pearl, J. C., Bjoraker, G. L.,  
358 Jennings, D. E., Romani, P. N., Simon-Miller, A. A., Kunde, V. G., Nixon,  
359 C. A., Bézard, B., Orton, G. S., Spilker, L. J., Spencer, J. R., Irwin, P. G. J.,  
360 Teanby, N. A., Owen, T. C., Brasunas, J., Segura, M. E., Carlson, R. C.,  
361 Mamoutkine, A., Gierasch, P. J., Schinder, P. J., Showalter, M. R., Ferrari, C.,  
362 Barucci, A., Courtin, R., Coustenis, A., Fouchet, T., Gautier, D., Lellouch, E.,  
363 Marten, A., Prangé, R., Strobel, D. F., Calcutt, S. B., Read, P. L., Taylor,  
364 F. W., Bowles, N., Samuelson, R. E., Abbas, M. M., Raulin, F., Ade, P.,  
365 Edgington, S., Pilorz, S., Wallis, B., Wishnow, E. H., 2005. Temperatures,  
366 Winds, and Composition in the Saturnian System. *Science* 307, 1247–1251.
- 367 Fletcher, L. N., Orton, G. S., Teanby, N. A., Irwin, P. G. J., Bjoraker, G. L.,  
368 2009. Methane and its isotopologues on Saturn from Cassini/CIRS observa-  
369 tions. *Icarus* 199, 351–367.
- 370 Fouchet, T., Guerlet, S., Strobel, D. F., Simon-Miller, A. A., Bézard, B., Flasar,  
371 F. M., 2008. An equatorial oscillation in Saturn's middle atmosphere. *Nature*  
372 453, 200–202.
- 373 Greathouse, T. K., Lacy, J. H., Bézard, B., Moses, J. I., Griffith, C. A., Richter,  
374 M. J., 2005. Meridional variations of temperature,  $C_2H_2$  and  $C_2H_6$  abun-

- 375 dances in Saturn's stratosphere at southern summer solstice. *Icarus* 177, 18–  
376 31.
- 377 Greathouse, T. K., Lacy, J. H., Bézard, B., Moses, J. I., Richter, M. J., Knez,  
378 C., 2006. The first detection of propane on Saturn. *Icarus* 181, 266–271.
- 379 Guerlet, S., Fouchet, T., Bézard, B., Moses, J. I., Fletcher, L. N., Simon-Miller,  
380 A. A., Michael Flasar, F., 2010. Meridional distribution of  $\text{CH}_3\text{C}_2\text{H}$  and  
381  $\text{C}_4\text{H}_2$  in Saturn's stratosphere from CIRS/Cassini limb and nadir observa-  
382 tions. *Icarus* 209, 682–695.
- 383 Guerlet, S., Fouchet, T., Bézard, B., Simon-Miller, A. A., Michael Flasar, F.,  
384 2009. Vertical and meridional distribution of ethane, acetylene and propane  
385 in Saturn's stratosphere from CIRS/Cassini limb observations. *Icarus* 203,  
386 214–232.
- 387 Hartogh, P., Lellouch, E., Crovisier, J., Banaszkiewicz, M., Bensch, F., Bergin,  
388 E. A., Billebaud, F., Biver, N., Blake, G. A., Blecka, M. I., Blommaert, J.,  
389 Bockelée-Morvan, D., Cavalié, T., Cernicharo, J., Courtin, R., Davis, G.,  
390 Decin, L., Encrenaz, P., Encrenaz, T., González, A., de Graauw, T., Hut-  
391 semékers, D., Jarchow, C., Jehin, E., Kidger, M., Küppers, M., de Lange, A.,  
392 Lara, L., Lis, D. C., Lorente, R., Manfroid, J., Medvedev, A. S., Moreno, R.,  
393 Naylor, D. A., Orton, G., Portyankina, G., Rengel, M., Sagawa, H., Sánchez-  
394 Portal, M., Schieder, R., Sidher, S., Stam, D., Swinyard, B., Szutowicz, S.,  
395 Thomas, N., Thornhill, G., Vandenbussche, B., Verdugo, E., Waelkens, C.,  
396 Walker, H., 2009. Water and related chemistry in the solar system. A guar-  
397 anteed time key programme for Herschel. *Planetary and Space Science* 57,  
398 1596–1606.
- 399 Hébrard, E., Dobrijevic, M., Bénilan, Y., Raulin, F., 2006. Photochemical ki-  
400 netics uncertainties in modeling Titan's atmosphere: a review. *Journal of*  
401 *Photochemistry and Photobiology C: Photochemistry Reviews* 7, 211–230.
- 402 Hébrard, E., Dobrijevic, M., Pernot, P., Carrasco, N., Bergeat, A., Hickson,  
403 K. M., Canosa, A., Le Picard, S. D., Sims, I. R., 2009. How Measurements

- 404 of Rate Coefficients at Low Temperature Increase the Predictivity of Pho-  
405 tochemical Models of Titan's Atmosphere. *Journal of Physical Chemistry*  
406 113 (42), 11227–11237.
- 407 Helton, J., Johnson, J., Sallaberry, C., Storlie, C., 2006. Survey of sampling-  
408 based methods for uncertainty and sensitivity analysis. *Reliability Engineer-*  
409 *ing and System Safety* 91, 1175–1209.
- 410 Hesman, B. E., Jennings, D. E., Sada, P. V., Bjoraker, G. L., Achterberg, R. K.,  
411 Simon-Miller, A. A., Anderson, C. M., Boyle, R. J., Nixon, C. A., Fletcher,  
412 L. N., McCabe, G. H., 2009. Saturn's latitudinal C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> abundance  
413 profiles from Cassini/CIRS and ground-based observations. *Icarus* 202, 249–  
414 259.
- 415 Howett, C. J. A., Irwin, P. G. J., Teanby, N. A., Simon-Miller, A., Calcutt,  
416 S. B., Fletcher, L. N., de Kok, R., 2007. Meridional variations in stratospheric  
417 acetylene and ethane in the southern hemisphere of the saturnian atmosphere  
418 as determined from Cassini/CIRS measurements. *Icarus* 190, 556–572.
- 419 Moses, J. I., Fouchet, T., Bézard, B., Gladstone, G. R., Lellouch, E., Feuchtgru-  
420 ber, H., 2005. Photochemistry and diffusion in Jupiter's stratosphere: Con-  
421 straints from ISO observations and comparisons with other giant planets.  
422 *Journal of Geophysical Research (Planets)* 110 (E8), E08001.
- 423 Moses, J. I., Lellouch, E., Bézard, B., Gladstone, G. R., Feuchtgruber, H., Allen,  
424 M., 2000. Photochemistry of Saturn's Atmosphere. II. Effects of an Influx of  
425 External Oxygen. *Icarus* 145, 166–202.
- 426 Smith, G. R., Shemansky, D. E., Holberg, J. B., Broadfoot, A. L., Sandel, B. R.,  
427 McConnell, J. C., 1983. Saturn's upper atmosphere from the Voyager 2 EUV  
428 solar and stellar occultations. *Journal of Geophysical Research* 88, 8667–8678.
- 429 Smith, H. T., Johnson, R. E., Perry, M. E., Mitchell, D. G., McNutt, R. L.,  
430 Young, D. T., 2010. Enceladus plume variability and the neutral gas densities

431 in Saturn's magnetosphere. *Journal of Geophysical Research (Space Physics)*  
432 115 (A14), A10252.

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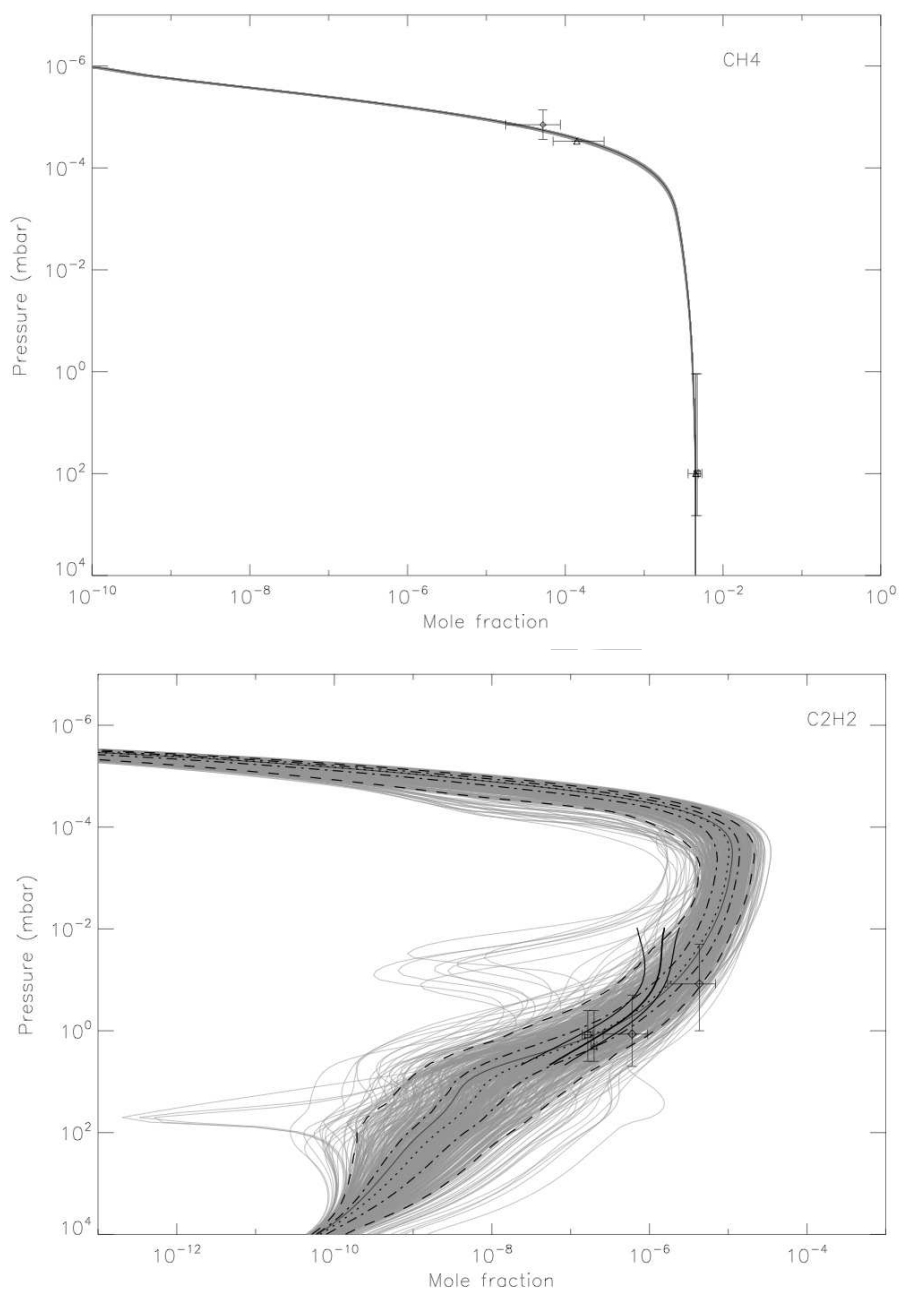


Figure 3: Model. Gray solid lines: Abundance profiles of CH<sub>4</sub> and C<sub>2</sub>H<sub>2</sub> obtained after 500 runs. Black solid line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution. CH<sub>4</sub> 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<sub>2</sub>H<sub>2</sub> 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).

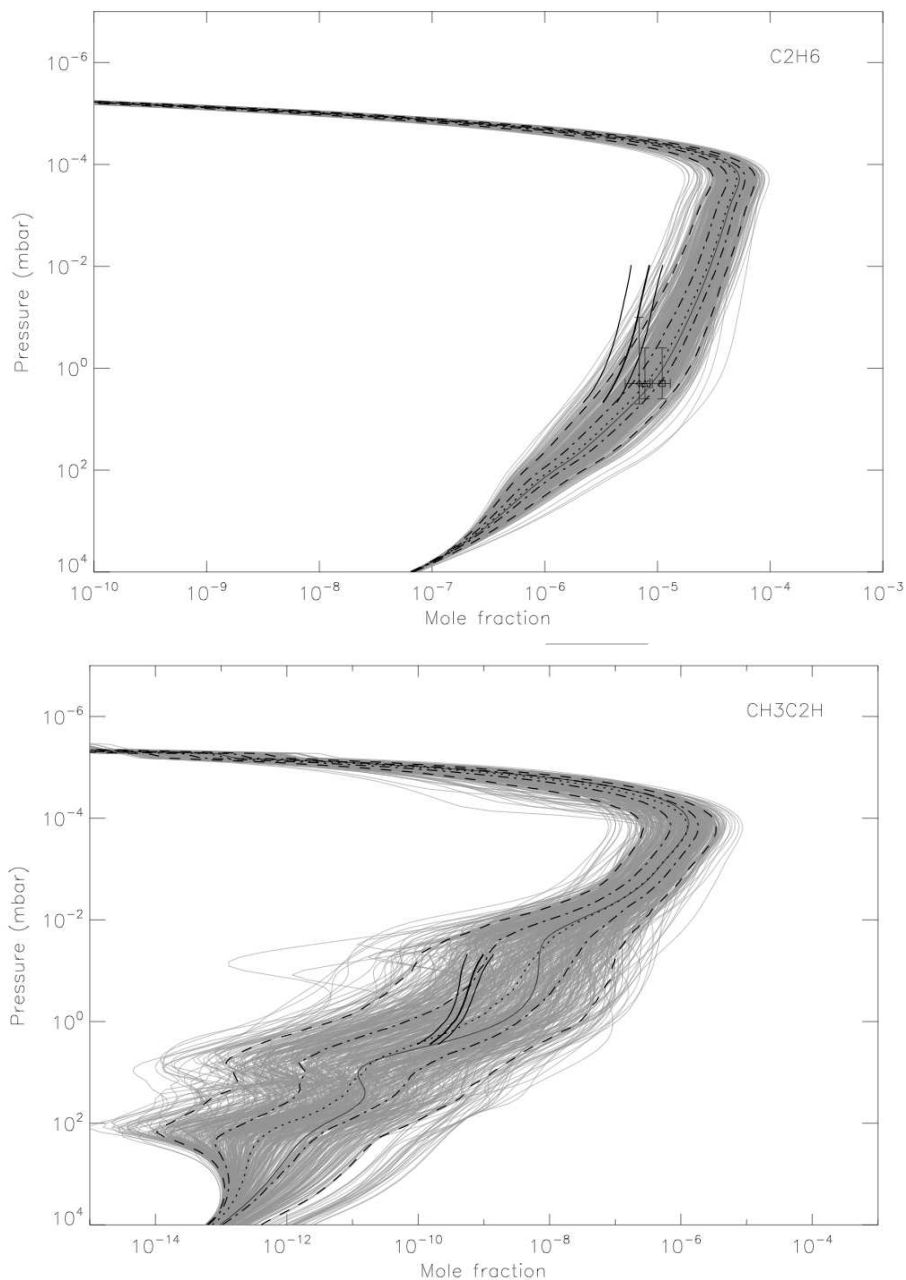


Figure 4: Model. Gray solid lines: Abundance profiles of  $C_2H_6$  and  $CH_3C_2H$  obtained after 500 runs. Black solid line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black 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  $20^\circ S$  (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  $20^\circ S$  (Guerlet et al., 2009, 2010).

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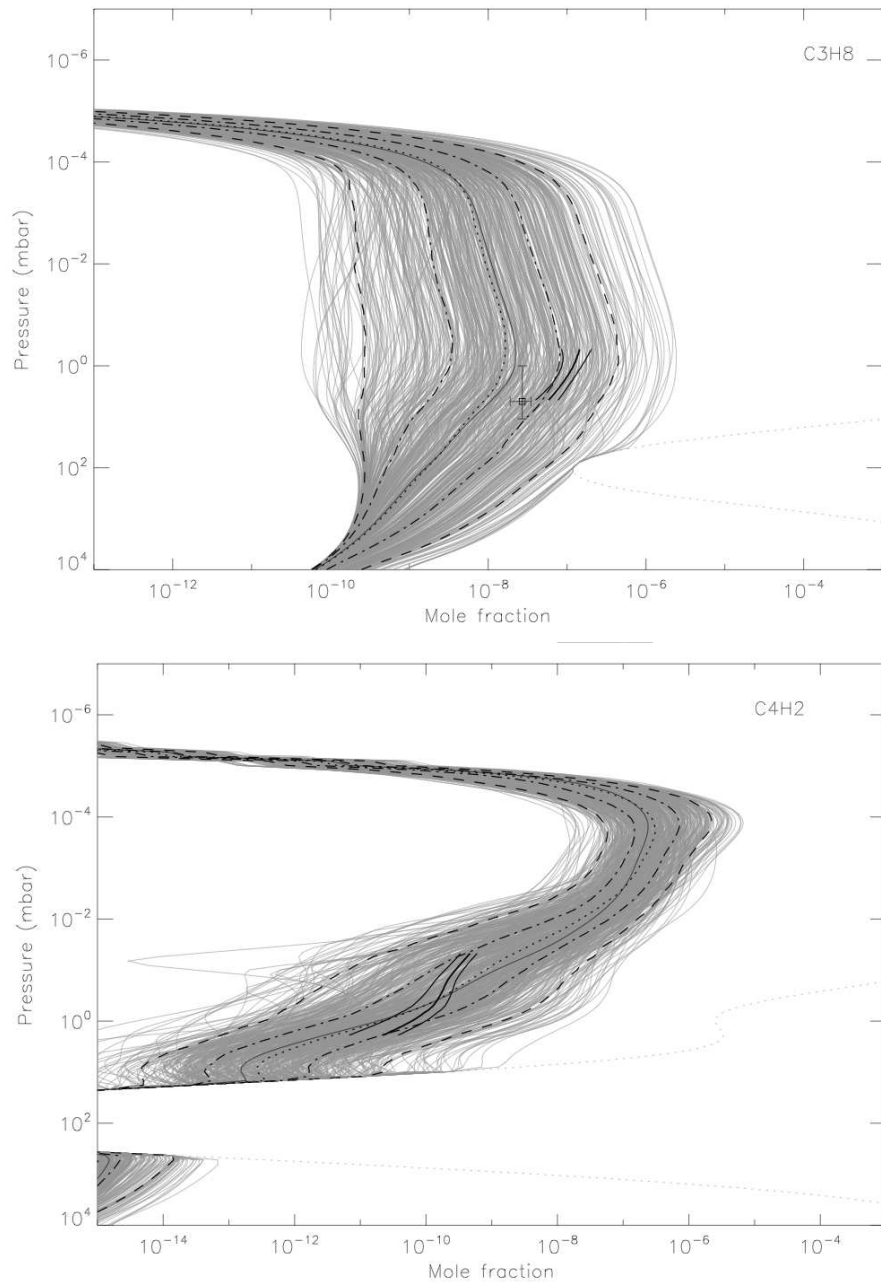


Figure 5: Model. Gray solid lines: Abundance profiles of  $C_3H_8$  and  $C_4H_2$  obtained after 500 runs. Black solid line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed 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  $20^\circ$  S (Guerlet et al., 2009, 2010). Square: IRTF data at  $-20^\circ$  planetocentric latitude (Greathouse et al., 2006)

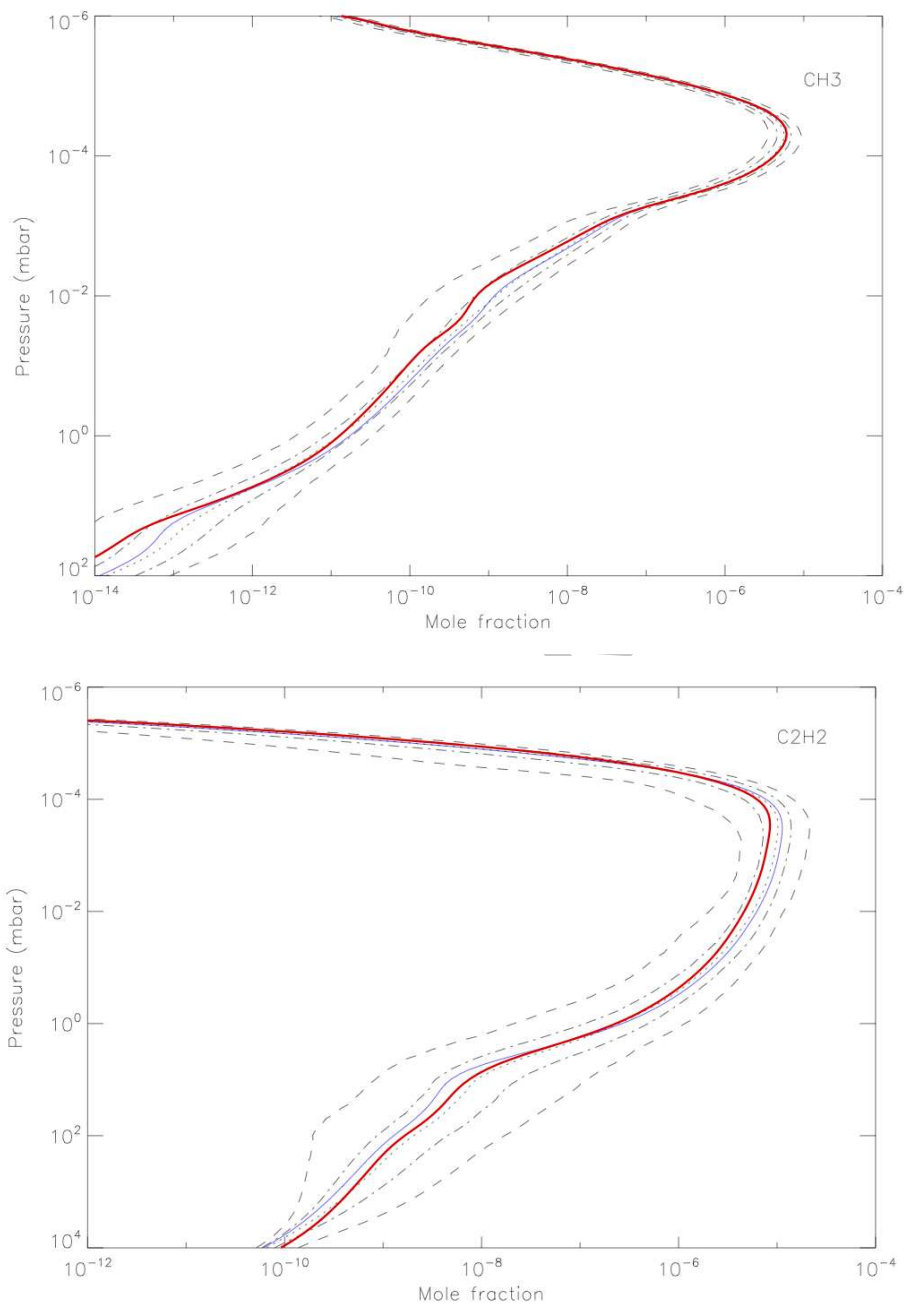


Figure 6: Red line: Abundance profiles of  $\text{CH}_3$  and  $\text{C}_2\text{H}_2$  with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution.



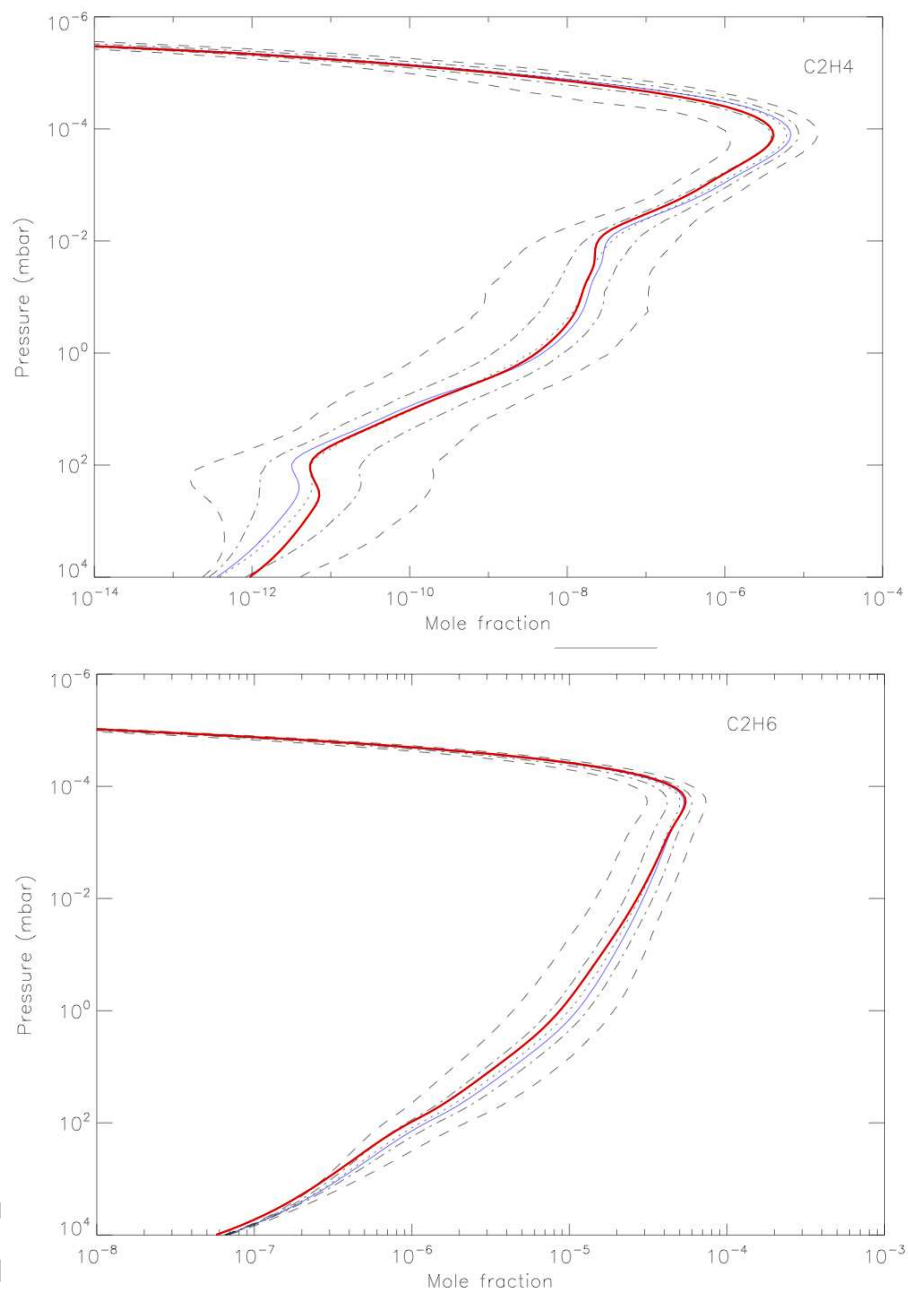


Figure 7: Red line: Abundance profiles of  $C_2H_4$  and  $C_2H_6$  with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: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

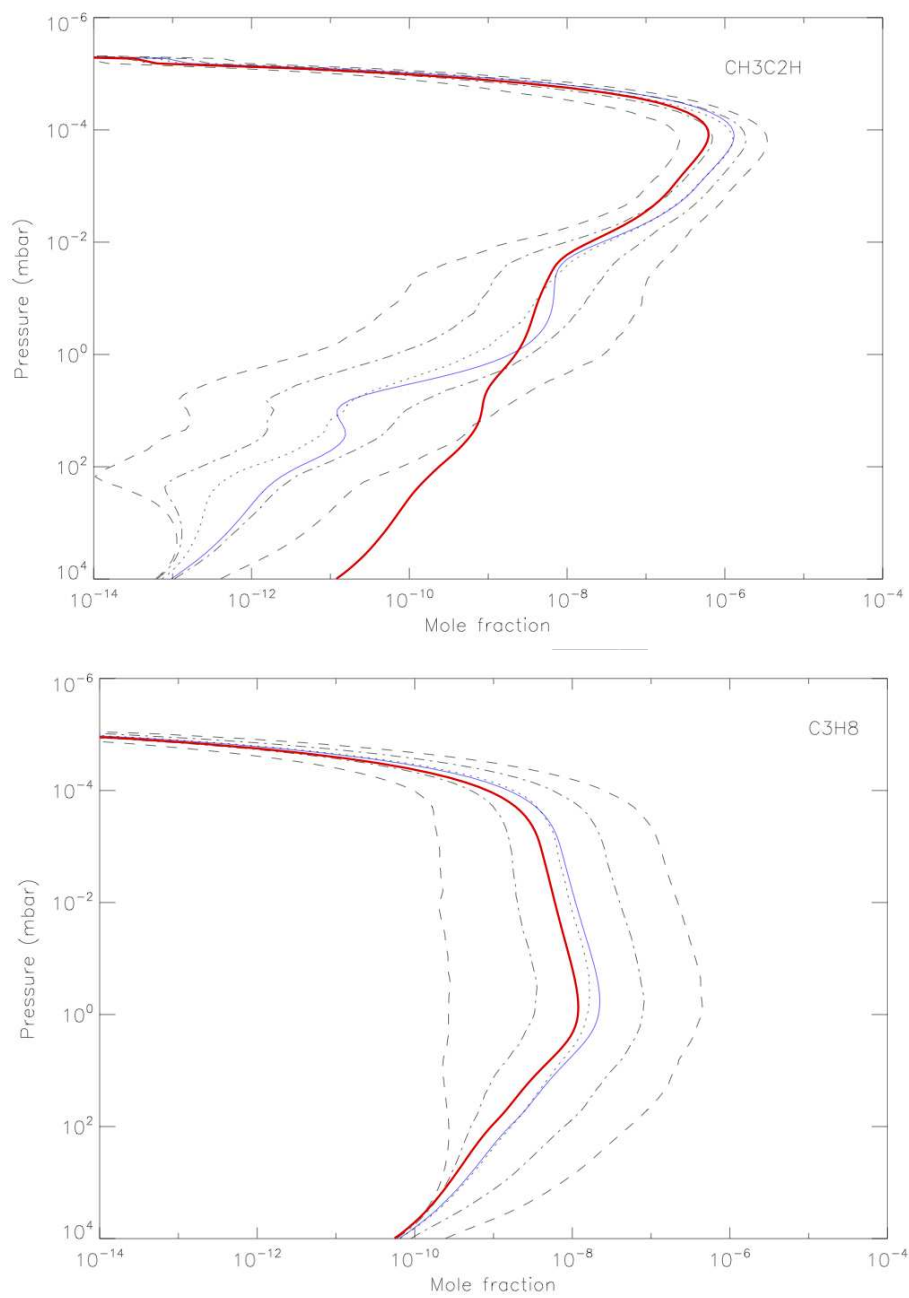


Figure 8: Red line: Abundance profiles of  $\text{CH}_3\text{C}_2\text{H}$  and  $\text{C}_3\text{H}_8$  with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th 20-quantiles of the distribution.

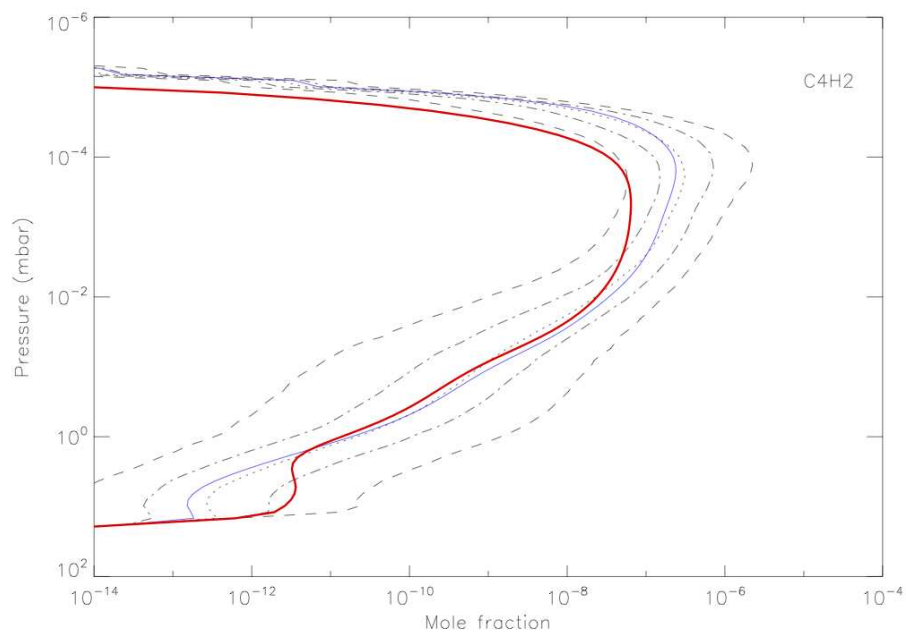


Figure 9: Red line: Abundance profiles of  $C_4H_2$  with the reduced chemical scheme. Blue line: initial profile obtained with the initial chemical scheme. Black dotted line: median profile. Black dashed-dotted lines: 5th and 15th 20-quantiles of the distribution. Black long-dashed lines: 1st and 19th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

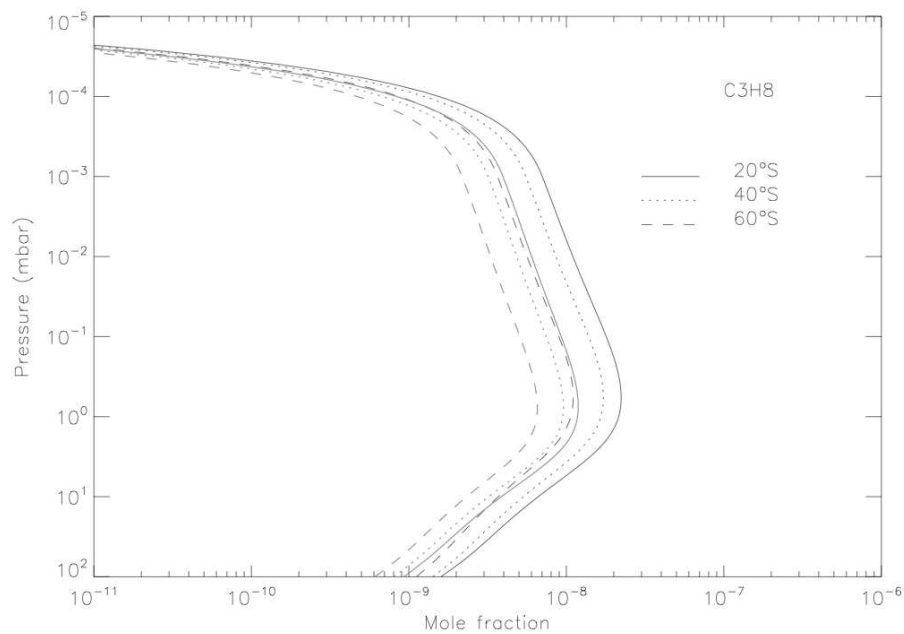


Figure 10: Abundance profiles of  $C_3H_8$  for different latitudes. Black lines: Initial chemical scheme. Gray lines: Reduced chemical scheme. The mean solar zenith angle corresponding to 20° S, 40° S and 60° S are respectively 51°, 54° and 63°.

- > 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.

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