

**Supporting Information**

**for**

**Laboratory studies of molecular growth in the Titan ionosphere**

Roland Thissen (1), Veronique Vuitton\* (1), Panayotis Lavvas (2), Joel Lemaire (3), Christophe Dehon (3), Odile Dutuit (1), Mark A. Smith (2,4), Stefano Turchini (5), Daniele Catone (5), Roger V. Yelle (1,2), Pascal Pernot (3), Arpad Somogyi (4), and Marcello Coreno (6).

- (1) Laboratoire de Planétologie de Grenoble, CNRS, Université J. Fourier, UMR 5109, Grenoble, France,
- (2) Lunar and Planetary Laboratory, University of Arizona, Tucson, USA,
- (3) Laboratoire de Chimie Physique, CNRS, Université Paris-Sud, UMR 8000, Orsay, France,
- (4) Department of Chemistry and Biochemistry, University of Arizona, Tucson, USA,
- (5) CNR-ISM, Roma, Italy,
- (6) CNR-IMIP & INFM-TASC, Elettra Sincrotrone, Trieste, Italy,

*Corresponding author address:*

Laboratoire de Planétologie de Grenoble  
Bâtiment D de Physique - BP 53  
38041 Grenoble cedex  
tel +33 (0)4 76 63 52 78 / fax +33 (0)4 76 51 41 46  
[veronique.vuitton@obs.ujf-grenoble.fr](mailto:veronique.vuitton@obs.ujf-grenoble.fr)

**TABLE S1: Relative Intensities of the Four Major Ions Present in the Mass Spectrum of CCl<sub>4</sub>.**

m/z	ion	relative intensity	
		reference <sup>a</sup>	measured <sup>b</sup>
116.91	C <sup>35</sup> Cl <sub>3</sub> <sup>+</sup>	1000	1000
118.90	C <sup>35</sup> Cl <sub>2</sub> <sup>37</sup> Cl <sup>+</sup>	958	963±33
120.90	C <sup>35</sup> Cl <sup>37</sup> Cl <sub>2</sub> <sup>+</sup>	306	229±15
122.90	C <sup>37</sup> Cl <sub>3</sub> <sup>+</sup>	33	no signal

<sup>a</sup> The reference intensities are combinations of the natural isotopic abundances. <sup>b</sup>

The measured intensities were obtained with an electron energy of 70 eV and an electron pulse time of 71 ms, corresponding to the maximum number of CCl<sub>3</sub><sup>+</sup> ions in the FT-ICR cell.

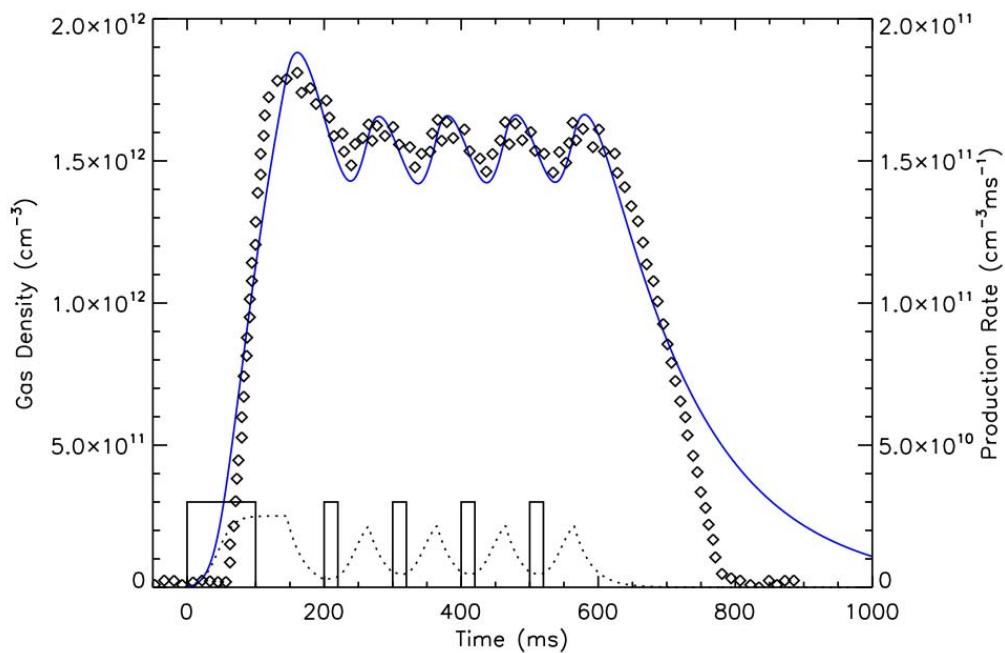
**TABLE S2: Principal Production and Loss Reactions for the Ions Detected Experimentally.**

reactions	k $\text{cm}^3 \text{ s}^{-1}$	R#
$\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3$	$1.1 \times 10^{-9}$	$k_1$
$\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2$	$1.1 \times 10^{-9}$	$k_2$
$\text{CH}_2^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4^+ + \text{H}_2$	$9.1 \times 10^{-10}$	$k_3$
$\text{N}_2^+ + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{N}_2 + \text{H}$	$9.8 \times 10^{-10}$	$k_4$
$\text{N}_2^+ + \text{CH}_4 \rightarrow \text{CH}_2^+ + \text{N}_2 + \text{H}_2$	$1.0 \times 10^{-10}$	$k_5$
$\text{N}_2^+ + \text{CH}_4 \rightarrow \text{N}_2\text{H}^+ + \text{CH}_3$	$5.7 \times 10^{-11}$	$k_6$
$\text{N}_2\text{H}^+ + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{N}_2$	$8.9 \times 10^{-10}$	$k_7$
$\text{C}_2\text{H}_5^+ + \text{HCN} \rightarrow \text{HCNH}^+ + \text{C}_2\text{H}_4$	$2.7 \times 10^{-9}$	$k_8$
$\text{C}_2\text{H}_5^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{C}_2\text{H}_4$	$2.1 \times 10^{-9}$	$k_9$
$\text{HCNH}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{HCN}$	$2.3 \times 10^{-9}$	$k_{10}$
$\text{N}^+ + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{NH}$	$5.8 \times 10^{-10}$	$k_{11}$
$\text{N}^+ + \text{CH}_4 \rightarrow \text{HCNH}^+ + \text{H}_2$	$4.1 \times 10^{-10}$	$k_{12}$
$\text{CH}_5^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_3^+ + \text{CH}_4$	$1.5 \times 10^{-9}$	$k_{13}$
$\text{C}_2\text{H}_3^+ + \text{CH}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}_2$	$1.9 \times 10^{-10}$	$k_{14}$
$\text{C}_3\text{H}_5^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_5\text{H}_5^+ + \text{H}_2$	$3.8 \times 10^{-10}$	$k_{15}$
$\text{C}_2\text{H}_4^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{CH}_3$	$3.8 \times 10^{-10}$	$k_{16}$
$\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_3\text{H}_3^+ + \text{CH}_4$	$6.5 \times 10^{-10}$	$k_{17}$
$\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_5^+ + \text{H}_2$	$6.8 \times 10^{-11}$	$k_{18}$

$\text{N}_2^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2^+ + \text{N}_2$	$3.8 \times 10^{-10}$	$k_{19}$
$\text{C}_2\text{H}_2^+ + \text{CH}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{H}$	$7.0 \times 10^{-10}$	$k_{20}$
$\text{C}_2\text{H}_4^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{CH}_3$	$7.0 \times 10^{-10}$	$k_{21}$
$\text{N}_2^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_3^+ + \text{N}_2 + \text{H}$	$8.6 \times 10^{-10}$	$k_{22}$
$\text{C}_2\text{H}_3^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_2$	$8.2 \times 10^{-10}$	$k_{23}$
$\text{CH}_5^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{CH}_4$	$1.5 \times 10^{-9}$	$k_{24}$
$\text{C}_2\text{H}_5^+ + \text{C}_2\text{H}_4 \rightarrow \text{C}_3\text{H}_5^+ + \text{CH}_4$	$3.6 \times 10^{-10}$	$k_{25}$
$\text{CH}_5^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CH}_4$	$3.7 \times 10^{-9}$	$k_{26}$
$\text{C}_2\text{H}_5^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{C}_2\text{H}_4$	$1.9 \times 10^{-9}$	$k_{27}$
$\text{H}_3\text{O}^+ + \text{HCN} \rightarrow \text{HCNH}^+ + \text{H}_2\text{O}$	$3.8 \times 10^{-9}$	$k_{28}$
$\text{N}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{N}_2$	$1.9 \times 10^{-9}$	$k_{29}$
$\text{H}_2\text{O}^+ + \text{CH}_4 \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3$	$1.1 \times 10^{-9}$	$k_{30}$
$\text{H}_2\text{O}^+ + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H}_2^+ + \text{H}_2\text{O}$	$1.9 \times 10^{-9}$	$k_{31}$

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**Figure S1.** Comparison between the measured (symbols) and simulated (solid line) gas density variation with time for a 100 ms primary gas pulse followed by 4 secondary gas pulses of 20 ms each every 100 ms. The pulse sequence is presented by the boxes in the lower part, while the production rate necessary to provide the simulated density is presented with the dotted lines. The maximum density corresponds to a pressure in the apparatus of  $7.5 \times 10^{-5}$  mbar.



**Figure S2.** Variation of Elettra photon flux with photon energy (solid line) and the flux variation eventually applied in the model calculations after inclusion of saturation effects in the ion trapping efficiency (plus symbols).

