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1 In situ Investigation of Neutrals Involved in the Formation of Titan Tholins

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34 **Abstract**

35

36 The Cassini Mission has greatly improved our understanding of the dynamics and chemical
37 processes occurring in Titan's atmosphere. It has also provided us with more insight into the
38 formation of the aerosols in the upper atmospheric layers.

39 However, the chemical composition and mechanisms leading to their formation were out of
40 reach for the instruments onboard Cassini. In this context, it is deemed necessary to apply and
41 exploit laboratory simulations to better understand the chemical reactivity occurring in the gas
42 phase of Titan-like conditions. In the present work, we report gas phase results obtained from a
43 plasma discharge simulating the chemical processes in Titan's ionosphere. We use the
44 PAMPRE cold dusty plasma experiment with an N₂-CH₄ gaseous mixture under controlled
45 pressure and gas influx. An internal cryogenic trap has been developed to accumulate the gas
46 products during their production and facilitate their detection. The cryogenic trap condenses the
47 gas-phase precursors while they are forming, so that aerosols are no longer observed during
48 the 2h plasma discharge. We focus mainly on neutral products NH₃, HCN, C₂H₂ and C₂H₄. The
49 latter are identified and quantified by *in situ* mass spectrometry and infrared spectroscopy. We
50 present here results from this experiment with mixing ratios of 90-10% and 99-1% N₂-CH₄,
51 covering the range of methane concentrations encountered in Titan's ionosphere. We also
52 detect *in situ* heavy molecules (C₇). In particular, we show the role of ethylene and other
53 volatiles as key solid-phase precursors.

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55 **Keywords:** Titan, Saturn; Atmospheres, chemistry; Plasma discharge; Experimental techniques

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64 I) Introduction

65

66 Titan is Saturn's largest moon and second largest in the Solar System after Ganymede.
67 It has a mean radius of 2,575 km. One major interest in Titan is its uniquely dense (a 1.5-bar
68 ground pressure) and extensive (~1,500 km) atmosphere, primarily made of N₂ and CH₄. In fact,
69 the extent of the atmosphere alone accounts for about 58% in size of Titan's radius. Titan's first
70 flyby by Pioneer 11 (1979) revealed the moon as being a faint brownish dot orbiting Saturn. The
71 subsequent Voyager 1 (1980), Voyager 2 (1981), Cassini (2004 - 2017) and Huygens (2005)
72 spacecraft have uncovered physicochemical processes unique in the solar system occurring
73 both in the atmosphere and surface. Early seminal studies (Khare and Sagan, 1973; Sagan,
74 1973; Hanel et al., 1981) showed that Titan's reducing atmosphere is also composed of
75 complex and heavy organic molecules and aerosols, their laboratory analogous counterparts
76 coined *tholins*. This chemistry is initiated at high altitudes and participates in the formation of
77 solid organic particles (Khare et al., 1981; Waite et al., 2007, and Hörst, 2017 for a more recent
78 and holistic review of Titan's atmospheric chemistry). At altitudes higher than 800 km, the
79 atmosphere is under the influence of energy deposition such as solar harsh ultraviolet (VUV)
80 radiation, solar X-rays, Saturn's magnetospheric energetic electrons and solar wind
81 (Krasnopolsky, 2009; Sittler et al., 2009). Cosmic dust input is also thought to chemically
82 interact with volatiles in the middle atmosphere (English et al., 1996; Frankland et al., 2016). To
83 wit, Titan is presumably one of the most chemically complex bodies in the solar system. Some
84 of the techniques used to better understand the processes occurring in Titan's atmosphere are
85 detailed hereafter.

86

87 Earth-based observations of Titan have been one way to determine the atmospheric
88 composition and structure, as well as surface and subsurface features. For example, direct
89 monitoring of seasonal tropospheric clouds from Earth-based observations helped us infer their
90 transient locations (Brown et al., 2002). Ground-based submillimeter observations were used to
91 infer the stratospheric composition with for example, the determination of hydrogen cyanide
92 (HCN) and acetonitrile (CH₃CN) mixing ratios (Tanguy et al., 1990; Bezdard and Paubert, 1993;
93 Hidayat et al., 1997), and with the rise of ground-based observation techniques such as the
94 Atacama Large Millimeter Array (ALMA) (Cordiner et al., 2014a, 2014b; Molter et al., 2016;
95 Serigano et al., 2016; Palmer et al., 2017). The use of other space-based telescopes such as
96 the Infrared Space Observatory (ISO) and the Herschel Space Observatory has additionally

97 provided information on the stratospheric composition and neutral abundances (Coustenis et al.,
98 2003; Courtin et al., 2011; Rengel et al., 2014). Early on, atmospheric studies brought by the
99 Voyager 1 mission were able to identify several organic molecules (Hanel et al., 1981; Kunde et
100 al., 1981; Maguire et al., 1981). Later, the Cassini-Huygens (NASA/ESA) mission provided us
101 with a more precise atmospheric characterization of the composition (Teanby et al., 2012;
102 Vinatier et al., 2015; Coustenis et al., 2016), wind (Flasar et al., 2005; Achterberg et al., 2011)
103 and upper atmosphere thermal profiles (e.g. Snowden et al., 2013), while the Huygens lander
104 (ESA) was able to provide insight on the *in situ* composition (Israel et al., 2005) and optical
105 properties of the aerosols (Doose et al., 2016). Cassini's Composite Infrared Spectrometer
106 (CIRS) limb spectral imaging (Vinatier et al., 2009) examined the role of volatiles in Titan's
107 chemistry and atmospheric dynamics. Many hydrocarbons and nitriles were shown to have wide
108 latitudinal variations of vertical mixing ratios (sometimes contradicting Global Circulation
109 Models, e.g. de Kok et al., 2014), emphasizing the importance of understanding the complex
110 coupling between gas phase chemistry and global dynamics. Both polar enrichments of nitriles
111 (e.g. Teanby et al., 2009) as well as the presence of heavy ions (Crary et al., 2009; Wellbrock et
112 al., 2013; Desai et al., 2017) have also been suggested to participate in Titan's aerosol
113 production. Thus, ground- and space-based observations have and will be especially important
114 in the post-Cassini era (Nixon et al., 2016).

115
116 Photochemical models have been complementarily used to predict the thermal,
117 compositional and structural evolution of Titan's atmospheric column (e.g. Atreya et al., 1978;
118 Carrasco et al., 2007, 2008). Furthermore, these models offer us testable hypotheses for
119 experiments and predictions for chemical pathways leading to the formation of aerosols (e.g.
120 Waite et al., 2007; Yelle et al., 2010).

121
122 Lastly, experimental techniques have also been used to simulate Titan's atmospheric
123 conditions (Khare et al., 1984; Sagan and Thompson, 1984; Pintassilgo et al., 1999; Cable et
124 al., 2012; Carrasco et al., 2013; Sciamma-O'Brien et al., 2015, Tigrine et al., 2016; Hörst et al.,
125 2018) and determine chemical mechanisms that are otherwise out of Cassini's reach. A wide
126 range of laboratory simulations have been used to complementarily investigate Titan's
127 atmospheric chemistry and different energy inputs (see Cable et al., 2012 for a thorough review
128 of these experiments). Typically in our lab, plasma discharges (Szopa et al., 2006; Sciamma-
129 O'Brien et al., 2010; Carrasco et al., 2012) or UV irradiation (Peng et al., 2013) have been used
130 to achieve Titan-like ionospheric conditions. In this context, it is deemed necessary to apply and

131 exploit such a technique to better understand the chemical reactivity occurring in Titan-like
132 upper atmospheric conditions. Hence, the gas phase which we know is key to the formation of
133 aerosols on Titan (Waite et al., 2007) is emphasized. Indeed, chemical precursors that are
134 present in the gas phase (Carrasco et al., 2012) follow certain chemical pathways that still need
135 to be investigated. For instance, Sciamma-O'Brien et al., 2010 showed how the production of
136 atomic hydrogen coming from CH₄ was anti-correlated with aerosol formation, by changing the
137 initial methane amount in the discharge. They argued that the presence of molecular and atomic
138 hydrogen in too large amounts in the gas mixture may have an inhibiting effect on the
139 polymerization reaction that produce the tholins.

140 To simulate the methane mixing ratios and energy conditions present in Titan's ionosphere, we
141 used the PAMPRE cold dusty plasma experiment (Szopa et al., 2006) with an N₂-CH₄ gas
142 mixture under controlled gas influx and pressure. Cold plasma discharges have been shown to
143 faithfully simulate the electron energy distribution of magnetospheric electrons and protons, and
144 UV irradiation deposited at Titan's atmosphere within a range of ~ 10 eV – 5 keV (Sittler et al.,
145 1983; Chang et al., 1991; Maurice et al., 1996; Brown et al., 2009; Johnson et al., 2016),
146 making them good laboratory analogs to simulate the ionospheric chemistry.

147
148 A first study (Gautier et al., 2011) dealt with the identification of gas products in the
149 PAMPRE reactor and used an external cold trap to study the gas phase. Analyses were made
150 by gas-chromatography coupled to mass spectrometry. More than 30 reaction products were
151 detected and a semi-quantitative study was performed on nitriles, the most abundant molecules
152 collected. However, one of the limitations to this technique is how the products are transported
153 *ex situ*, and may allow for loss or bias in their chemical reactivity and measurements. *In situ*
154 detections were then made by mass spectrometry with no cryogenic trapping (Carrasco et al.,
155 2012). Unfortunately, the only use of mass spectrometry prevented any univocal identification of
156 large organic molecules likely involved as precursors for aerosol formation. Since then, setup
157 improvements such as an internal cryogenic trap and infrared spectroscopy have been made in
158 order to study the gas phase *in situ* using these different complementary techniques. The
159 purpose of the cryotrap is to act as a cold finger enabling the volatiles to condensate and
160 preventing them from being evacuated from the chamber. This has allowed us to avoid any
161 volatile loss and to take on a quantitative approach on volatile products. Thus, to better
162 characterize the initial volatile products precursors to aerosols, we used a coupled analysis of
163 mass and infrared spectrometry. The presence of an internal cold trap made the condensation
164 of these volatiles possible, allowing for *in situ* measurements.

165

166 We will first describe our experimental chamber, which was designed to be relevant to simulate
167 Titan's ionosphere conditions. This was achieved by choosing methane concentrations
168 pertaining to those found in the upper atmosphere. Mass spectrometry results of volatiles at two
169 methane concentrations will be then presented, as well as their infrared spectroscopic analyses
170 with a quantitative approach taken on four major neutral volatiles (NH_3 , C_2H_2 , C_2H_4 and HCN)
171 acting as precursors to the formation of aerosols. Finally, we will discuss the discrepancies
172 between both methane conditions, as well as ethylene, ammonia and hydrogen cyanide
173 chemistry.

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175

176 **II) Experimental Setup**

177

178 ***2.1. The PAMPRE experiment and in situ cryogenic analysis***

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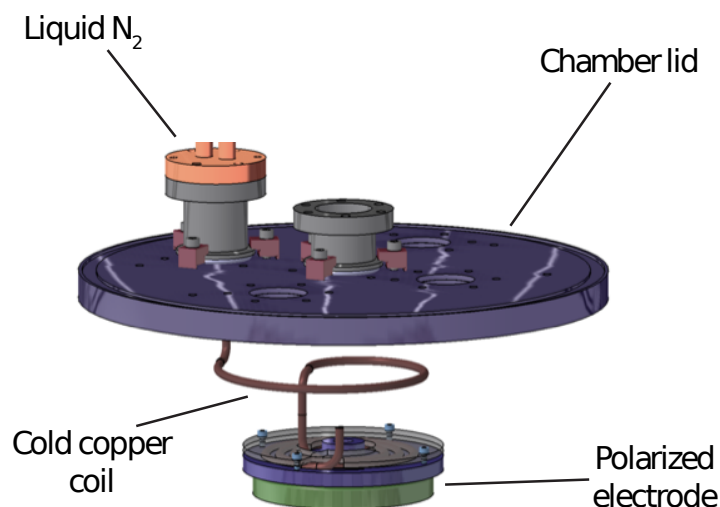
180 The PAMPRE cold plasma reactor used in this study aims, by design, at reproducing
181 exogenic energy sources, for example Saturn's magnetosphere particles, UV radiation, cosmic
182 rays and coronal processes impacting Titan's atmosphere (Szopa et al., 2006; Alcouffe et al.,
183 2010). The reactor delivers a capacitively coupled plasma discharge, produced by a 13.56 MHz
184 radiofrequency generator through a tuning match box. The gas influx is held constant and
185 monitored with mass flow controllers. The latter can tune an N_2 - CH_4 mixing ratio from 0% to
186 10% of CH_4 from highly pure N_2 (>99.999%) and 90-10% N_2 - CH_4 (>99.999%) bottles. An *in situ*
187 mass spectrometer (MS) and Fourier-Transform Infrared (FT-IR) spectrometer are also
188 integrated to the system.

189 To simulate Titan's atmospheric conditions, 90-10% and 99-1% N_2 - CH_4 ratios were considered.
190 Both correspond to a 55 sccm flow in standard conditions. Pressure gauges are set at 0.9 mbar
191 of constant pressure in the reactor while the plasma power is constant at 30W.

192

193 In order to detect, analyze and preserve all of the products during our experiments, we
194 need a trapping mechanism to capture these compounds, and thus prevent them from being
195 evacuated. Gautier et al. (2011) used an external cryogenic trap system, shaped as a cylindrical
196 coil, immersed in liquid nitrogen. Then, they isolated the coiled trap and analyzed the gas phase
197 *ex situ*. Here, the setup is different, and we believe more efficient as the trapping and
198 subsequent analyses are performed *in situ* and avoid any transfer line bias. Moreover, this

199 cryo-trap mainly traps the gas-phase chemistry in the preceding stages to the formation of solid
200 organic aerosols, preventing their production. In the absence of such a cryo-trap, the plasma is
201 dusty and several mg/h of solid particles are produced. As a result, this enables us to effectively
202 study in detail these gas-phase precursors of tholins, trapped and accumulated during a 2h
203 plasma discharge. Fig. 1 shows the 3D schematics of our cryogenic trap. An external liquid
204 nitrogen tank extends as a copper circuit into the chamber for cooling. This cooling circuit goes
205 through the upper lid of the chamber, and spirals down onto and lays flat on the polarized
206 electrode. This cooling system is semi-closed, in that the remaining liquid nitrogen is stored in
207 another container outside the reactor. The electrode temperature is controlled with a
208 temperature regulator (Cryo-Diffusion Pt100 probe) which controls the liquid nitrogen circulation
209 in the cooling circuit with a solenoid valve. The initial temperature is adjusted to $-180 \pm 2^\circ\text{C}$ prior
210 to the experiment.
211



212
213

214 **Fig. 1.** 3D schematics of the cryogenic trap. The cold trap goes through the top lid of the reactor and coils down into
215 the chamber, which is then in contact with the polarized electrode. The electrode is thus cooled to low-controlled
216 temperatures and the liquid nitrogen goes out through an exit system. This cryogenic trap enables the *in situ*
217 condensation of the produced volatiles within the plasma.

218

219 Using the cryogenic trap set at $T = -180 \pm 2$ °C, the protocol used was the following: The plasma
220 discharge and cooling system are turned on and the electrodes are kept for 2h at $T = -180$ °C.
221 The duration of the plasma discharge was chosen to trap and accumulate the gas phase
222 products, and improve their detection. The discharge reaches a steady state after a few
223 minutes, as shown in Alcouffe et al., (2010). A similar 2h trapping was previously performed in
224 Gautier et al., (2011) with an external cold trap, which was then analyzed by GC-MS. For
225 consistency, we have chosen the same discharge duration. During this time, the products
226 formed in the N_2 - CH_4 plasma are accumulated and adsorbed onto the chamber walls still at low-
227 controlled temperatures thanks to the cryogenic system. After 2h, the plasma is switched off, the
228 chamber is pumped down from 0.9 mbar to 10^{-4} mbar, and the cold trap is stopped. The volatile
229 products are gradually released under vacuum. We then proceed to do *in situ* gas phase
230 measurements as the chamber goes back to room temperature (Fig. 3). During this temperature
231 increase, it is possible that some additional neutral-neutral chemistry could occur. Our analytical
232 capacity enables us to address the most abundant and therefore stable molecules, which are
233 not expected to vary strongly apart from the sublimation process.

234

235 **2.2. Mass Spectrometry**

236

237 QMS quadrupole mass spectrometers were used (Pfeiffer and Hiden Analytics) for *in*
238 *situ* measurements inside the chamber. Once the neutral gas is ionized within the MS chamber
239 (SEM voltage of 1000V), each mass is collected by the detector. The MS samples near the
240 reactive plasma with a 0.8 mm-diameter capillary tube, long enough to keep a high-pressure
241 gradient between the MS and plasma chambers. Thus, an effective 10^{-5} - 10^{-6} mbar resident
242 pressure in the MS chamber is maintained throughout the experiment. This vacuum background
243 was thoroughly checked before each simulation. The experiments were done using a 1u
244 resolution, covering a 1-100 mass range, at a speed of 2s/mass with a channeltron-type
245 detection. Finally, a baseline noise filter was applied to each spectrum.

246

247 **2.3. Infrared Spectroscopy**

248

249 A ThermoFisher Nicolet 6700 Fourier Transform Infrared (FT-IR) spectrometer was used
250 for *in situ* analysis of the gas phase in transmission mode. The spectrometer uses a Mercury
251 Cadmium Telluride (MCT/A) high sensitivity detector with a KBr beamsplitter. During each

252 measurement, 500 scans were taken at a resolution of 1 cm^{-1} for $650\text{--}4000\text{ cm}^{-1}$ corresponding
253 to a short-wavelength mid-IR ($15.4\text{--}2.5\ \mu\text{m}$) range. The optical path length is 30 cm.
254

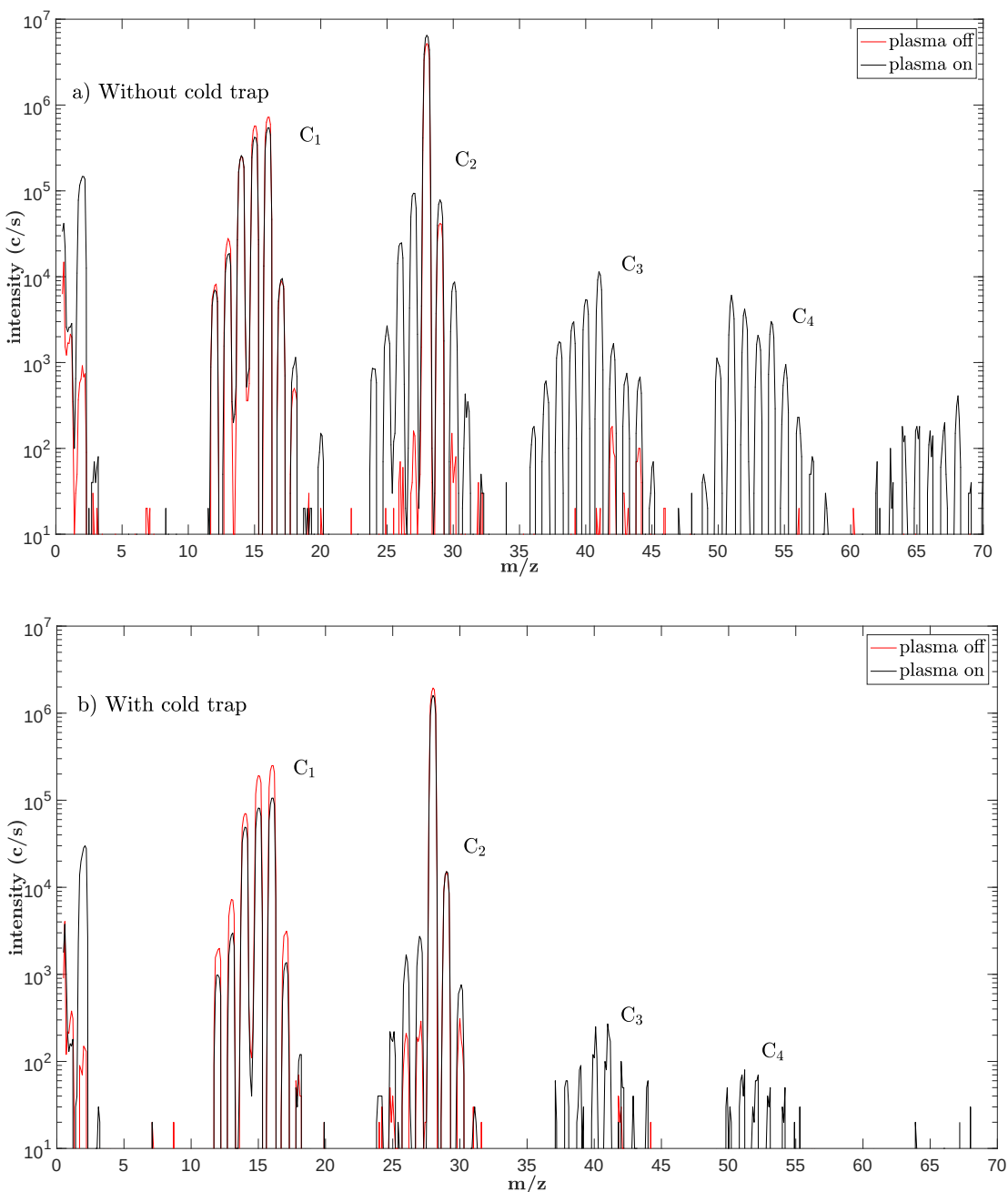
255 **III) Results**

256

257

258 We will now present results from two sets of experiments done at two initial methane
259 concentrations, 1% and 10% (three and two replicates, respectively), representative of the
260 methane concentration range found in Titan's ionosphere (Waite et al., 2005). The effect of the
261 cold trap on the plasma can be appreciated by comparing the mass spectra in the same
262 conditions with and without the cold trap (Fig. 2).

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Fig. 2. (a) Upper panel: No cryogenic trap. Mass spectra of a 90-10% N_2 - CH_4 mixture with plasma off (red) and plasma on (black). The consumption of methane at m/z 16 and its fragments m/z 15, 13, 12 is visible after the plasma is switched on. (b) Lower panel: With cold trap. Mass spectra of a 90-10% N_2 - CH_4 mixture with plasma off (red) and plasma on (black). The main products seen in the top plot (C_2 , C_3 and C_4) decrease by about two orders of magnitude in intensity in the bottom figure. This shows the efficient role of the cryotrap, which is to trap (albeit not completely here) the gas products formed in the plasma.

272
273 Fig. 2 shows two sets of N₂-CH₄ mass spectra, one (in red) taken before the plasma is switched
274 on, the other (in black) taken 5 min after plasma ignition, thus making sure methane dissociation
275 and the plasma have reached their equilibrium state (Sciamma-O'Brien et al., 2010; Alves et al.,
276 2012).

277 The m/z 29 and 30 peaks are the isotopic signatures of N₂.
278 Under usual conditions, without cold-trap, several mg/h of solid particles are produced in the
279 plasma volume in steady state conditions after the very first minutes of the discharge (Sciamma-
280 O'Brien et al., 2010). Now, with the cold-trap, solid particles are no longer produced even after a
281 2h plasma duration: the aerosol formation is prevented. So, we must investigate how far the
282 gas-phase chemistry goes in the presence of the cold trap. The plasma is out of
283 thermodynamical equilibrium and hosts fast ion-neutral reactions. If the entrapment is faster
284 than the chemistry, then the absence of aerosols might be explained by the fact that any
285 product larger than CH₄ would be removed from the reaction space. But, if the chemical kinetics
286 of the gas phase chemistry is competitive with the entrapment, then complex molecules are
287 produced before their entrapment on the cold reactor walls. In this case, the absence of
288 aerosols is caused by the low amount of gas-phase precursors in the discharge, thus preventing
289 the gas-to-solid conversion. The analysis of the mass spectra obtained *in situ* during the plasma
290 discharge with and without cold-trap (Fig. 2) informs us on this effect of the cold-trap on the gas-
291 phase chemistry.

292
293 The methane consumption can be estimated with m/z 15 and m/z 16 on Fig. 2 corresponding to
294 the CH₃⁺ and CH₄⁺ fragments. Following the method described in Sciamma-O'Brien et al., 2010,
295 we quantify the methane consumption with the CH₃⁺ (m/z 15) fragment at a pressure of 0.9
296 mbar. With the current cold trap setup, we found this consumption to be of 52% and 60% at
297 10% and 1% [CH₄]₀, respectively. Without the current cryotrap system, Sciamma-O'Brien et al.,
298 2010 found methane consumption efficiencies of 45% and 82% at 10% and 1% [CH₄]₀. The
299 behavior of methane consumption obtained with and without cold trap are comparable, even if
300 an effect of the different electrode temperature cannot be discarded.

301
302 In the following sections, we define C_n families as molecular classes using a C_xH_yN_z
303 nomenclature for N-bearing and hydrocarbon species, where x + z = n. As such, C_n blocks
304 detected using mass spectrometry can be traced, where n is related to the presence of heavy
305 aliphatic and N-bearing compounds.

306 In the C₁ block, in addition to the methane ion peaks, we can notice the signature of the residual
307 water of the mass spectrometer at m/z 17, 18. Other compounds due to the residual air in the
308 mass spectrometer can be seen at m/z 32 (O₂) and m/z 44 (CO₂).

309 The role of the cryotrap has a substantive effect on trapping organic volatile products. Heavy
310 compounds such as the C₄ block (Fig. 2a) vanish with the cold trap (Fig. 2b), despite similar
311 methane consumptions.

312 This shows the role of the cryo-trap, which is to efficiently condense and accumulate *in situ* the
313 organic products on the cold walls of the reactor instead of being evacuated out as volatiles
314 during the discharge.

315 Methane is consumed in similar quantities in the plasma discharge with and without the
316 cryotrap. Some large and complex molecules are still detected during the discharge by mass
317 spectrometry (Fig. 2b), up to the upper mass limits of our instrument (m/z 100) with the cold
318 trap, showing that the gas phase chemistry ensuring their formation is still occurring. Their
319 concentration in the gas phase is drastically reduced, by two orders of magnitude (Fig. 2b),
320 suggesting that they are efficiently trapped on the plasma walls while they are forming. The cold
321 trap does not prevent the formation of complex gas-phase molecules, but mainly blocks the gas-
322 to-solid conversion step. The cryogenic trap stops the gas-phase chemistry in the stage
323 preceding the formation of solid organic aerosols. It condenses the gas-phase precursors while
324 they are forming, and no aerosols are observed during the 2h plasma discharge.

325

326 **3.1 Release of volatiles back to room temperature**

327

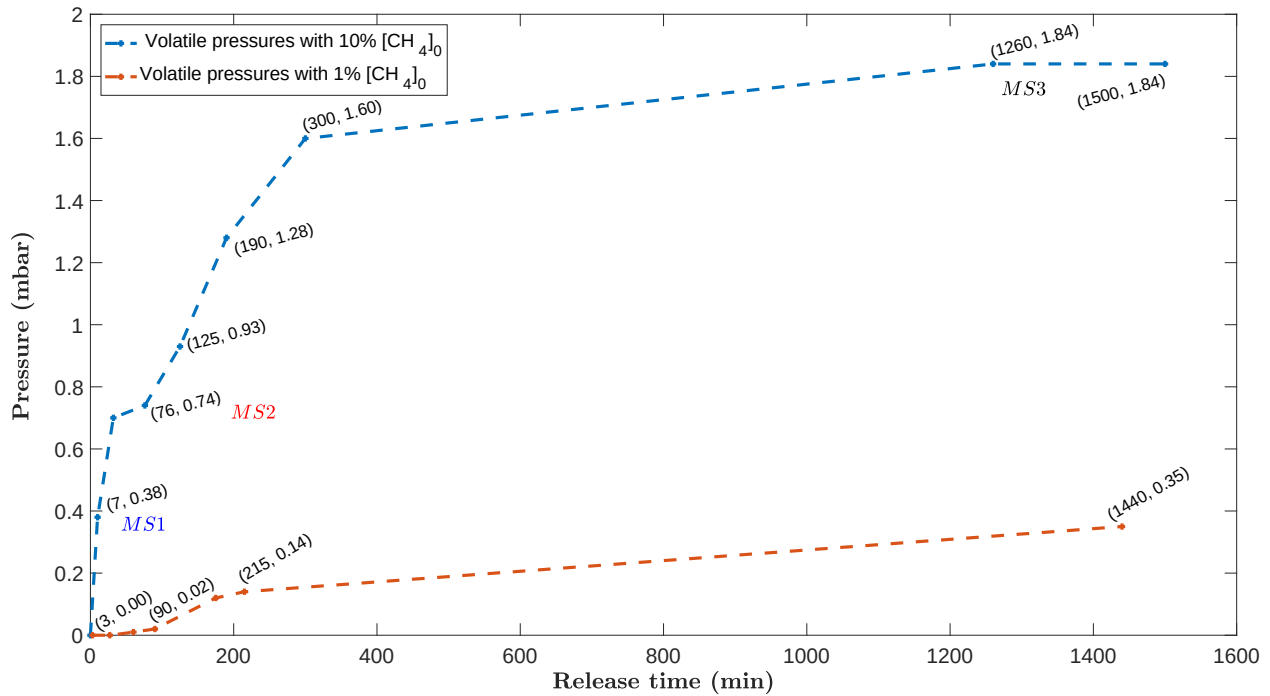
328 We leave the cold trap continuously on during a 2h plasma discharge. After 2h, the plasma and
329 cryo-trap are stopped, the chamber is pumped down to 10⁻⁴ mbar, isolated, and left to go back
330 to room temperature. Hence, all the species condensed on the cold walls are progressively
331 desorbed according to their vaporization temperatures and analyzed *in situ*. We define MS1,
332 MS2 and MS3 (Figures 3 and 4) as three mass spectra for 10% [CH₄]₀ taken at three different
333 pressures (~ 0.38, 0.74 and 1.84 mbar) and temperatures (-130°C, -79°C and +22°C) during
334 volatile release, respectively. The temperature heat-up rate initially increases relatively fast (~ 7
335 °C/min **between t = 0 min and the acquisition of the MS1 spectrum**), then decreases to ~ 0.3
336 °C/min near MS2 and finally reaches a temperature decrease rate of ~ 0.1 °C/min above -50°C
337 (MS3).

338 This desorption is recorded with a pressure gauge within the isolated chamber as the
339 temperature increases. Figure 3 (top) shows the pressure of the gas products being released

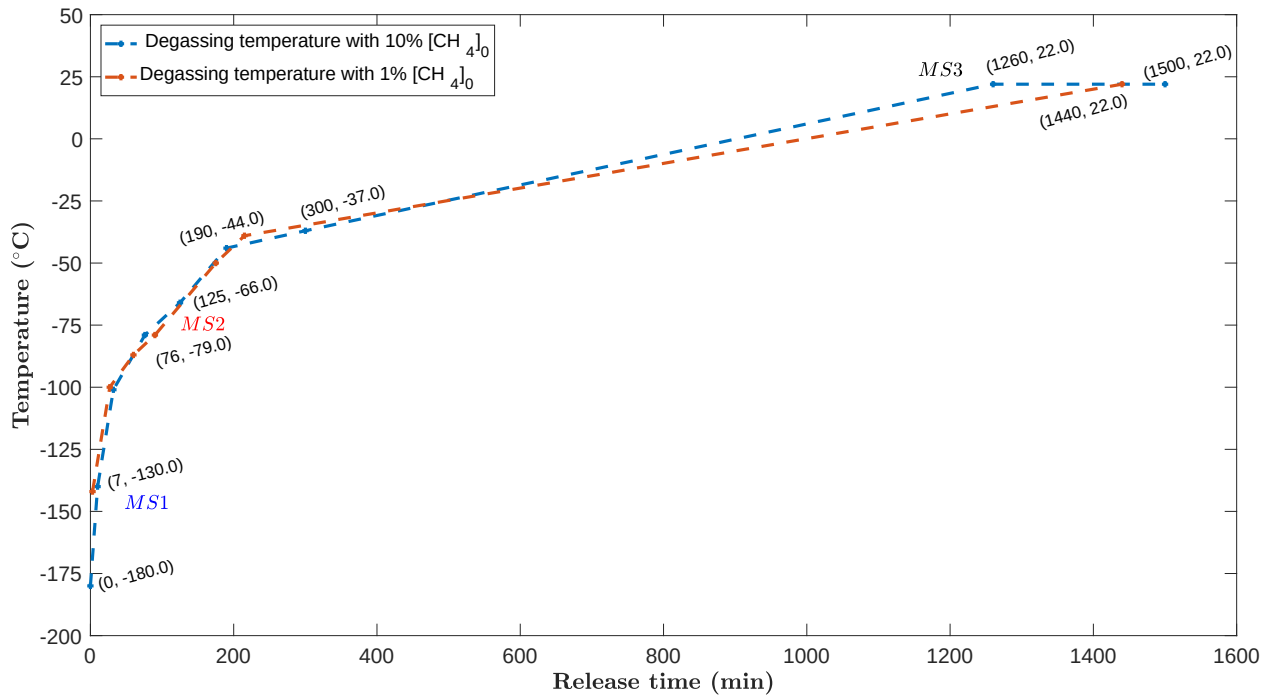
340 and the temperature of the electrode (bottom) according to time, both at $[\text{CH}_4]_0 = 10\%$ and
341 $[\text{CH}_4]_0 = 1\%$, in blue and red, respectively. Both pressures increase, owing to the volatiles
342 sublimating though in different behaviors. Most of the volatiles have been released at $\sim 6\text{h}$ of
343 release (Figure 3, top) and the curve starts to reach an asymptotic limit in the case of 10%
344 methane, (i) the release starts immediately with the temperature increase until 0.74 mbar at -
345 79°C where it reaches a small plateau, followed by (ii) a second volatile release starting at -75°C
346 with a sharp decrease in heating rate at 300 min until it (iii) reaches a second plateau at 1.84
347 mbar. On the other hand, products formed in $[\text{CH}_4]_0 = 1\%$ conditions have a different release
348 pattern. Notwithstanding the discrepancy in final pressure obtained (0.35 mbar, 5x less), the
349 products take a much longer time to be desorbed, the release starting at about 90 min with a
350 much smoother slope. Unlike at 10% methane, there is no plateau; the release of the volatiles is
351 continuous and in a rather limited pressure range.

352 These qualitative differences suggest, as a first approximation, different products in the two
353 methane conditions. In particular, all the products released at temperatures below -100°C at
354 10% methane are absent in the case of 1% methane. This means that these specific
355 compounds are not produced in significant amounts in the plasma discharge at 1% CH_4 .

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Fig. 3. (Top) Pressure evolution of the gas products according to degassing time in a 90-10% (blue) and 99-1% N₂-CH₄ (red) gas mixture. Labeled at each data point are the times and vessel pressures, respectively. The MS1 (-130°C, 0.38 mbar), MS2 (-79°C, 0.74 mbar), MS3 (+22°C, 1.84 mbar) color-coded labels correspond to the three spectra of Fig. 4 taken at their corresponding temperatures and pressures, underlying significant detections at 10% methane. (Bottom) Temperature evolution during degassing of the volatiles with the same color code for both mixing ratios.

365

366 3.1.1. Products released at temperatures below -100°C in the case of [CH₄]₀ = 10%,

367

368 We are first interested in the molecules released below -100°C in the case of [CH₄]₀ = 10%,
369 which are not produced (or at least not in detectable quantities) in [CH₄]₀ = 1%.

370 As a first qualitative guess, we use the Antoine Law (Mahjoub et al., 2014) Eq. (1) to calculate
371 the vapor pressure of C₂H₆, which, at -180°C, is slightly above the triple point of -183.15°C (Fray
372 and Schmitt, 2009). C₂H₆ is indeed one of four volatiles expected to be present our final gas
373 mixture (Gautier et al., 2011), along with C₂H₂, C₂H₄, and HCN. We use the A, B, C parameters
374 from the NIST database (Carruth and Kobayashi, 1973). The low temperature used in the
375 present study is at the edge of the validity range for C₂H₆. Nonetheless, we extend this law's
376 validity domain and assume it to be applicable to these low-temperature conditions and thus
377 must consider this calculation as a first approximation only. The vapor pressure is calculated at -
378 180°C.

$$\log_{10}(P_s) = A - \left(\frac{B}{T + C} \right) \quad (1)$$

379

380 For C₂H₆, we find P_s = 5.7 x 10² mbar. This vapor pressure combined with the fact that we are
381 slightly above the triple point of C₂H₆ near the liquid/vapor equilibrium, shows that this species
382 will hardly condense.

383 HCN, C₂H₂ and C₂H₄ all have their triple points (Fray and Schmitt, 2009) at temperatures higher
384 than -180°C. They are listed in Table 1. Fray and Schmitt, 2009 provided a review of vapor
385 pressure relations obtained empirically and theoretically for a wide variety of astrophysical ices.
386 They fitted polynomial expressions to extrapolate the sublimation pressures and used
387 theoretical and empirical interpolation relations to obtain the coefficients of the polynomials. The
388 polynomial expression from Fray and Schmitt, 2009 is given Equ. 2. The polynomials (Table 1)
389 are noted A_i and T_p are the corresponding temperatures, -180°C (93K) in our case. The
390 sublimation pressures (P_{sub}) are presented in Table 1.

391

392

$$\ln(P_{sub}) = A_0 + \sum_{i=1}^n \frac{A_i}{T_i} \quad (2)$$

394

395

396

	T_p (°C)	A_0	A_1	A_2	A_3	A_4	$P_{\text{Sub}} (-180^\circ\text{C})$ in mbar
HCN	-14.15	1.39×10^1	-3.62×10^3	-1.33×10^5	6.31×10^6	-1.13×10^8	1.69×10^{-12}
C_2H_2	-81.15	1.34×10^1	-2.54×10^3	0	0	0	9.48×10^{-4}
C_2H_4	-169.15	1.54×10^1	-2.21×10^3	-1.22×10^4	2.84×10^5	-2.20×10^6	1.3×10^3

398 **Table 1.** Vapor pressures P_{sub} (mbar) calculated at 93K (-180°C) for HCN, C_2H_2 and C_2H_4 . The T_p and A_i columns
399 correspond to the triple points and coefficients of the polynomials of extrapolations, respectively, as given by Fray
400 and Schmitt, 2009.

401
402 The larger values (Table 1) for the two C_2 hydrocarbons in comparison with HCN agree with a
403 first substantial release of the light C_2 hydrocarbons at temperatures below -100°C . HCN
404 contributes to the gas composition mainly in the second stage, for temperatures larger than -
405 80°C , because of its low vapor pressure at colder temperatures.

406 The absence of C_2 hydrocarbons in the case of $[\text{CH}_4]_0 = 1\%$ is in agreement with the ex-
407 *situ* analysis made in Gautier et al., (2011).

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410 3.1.2. Detections by mass spectrometry

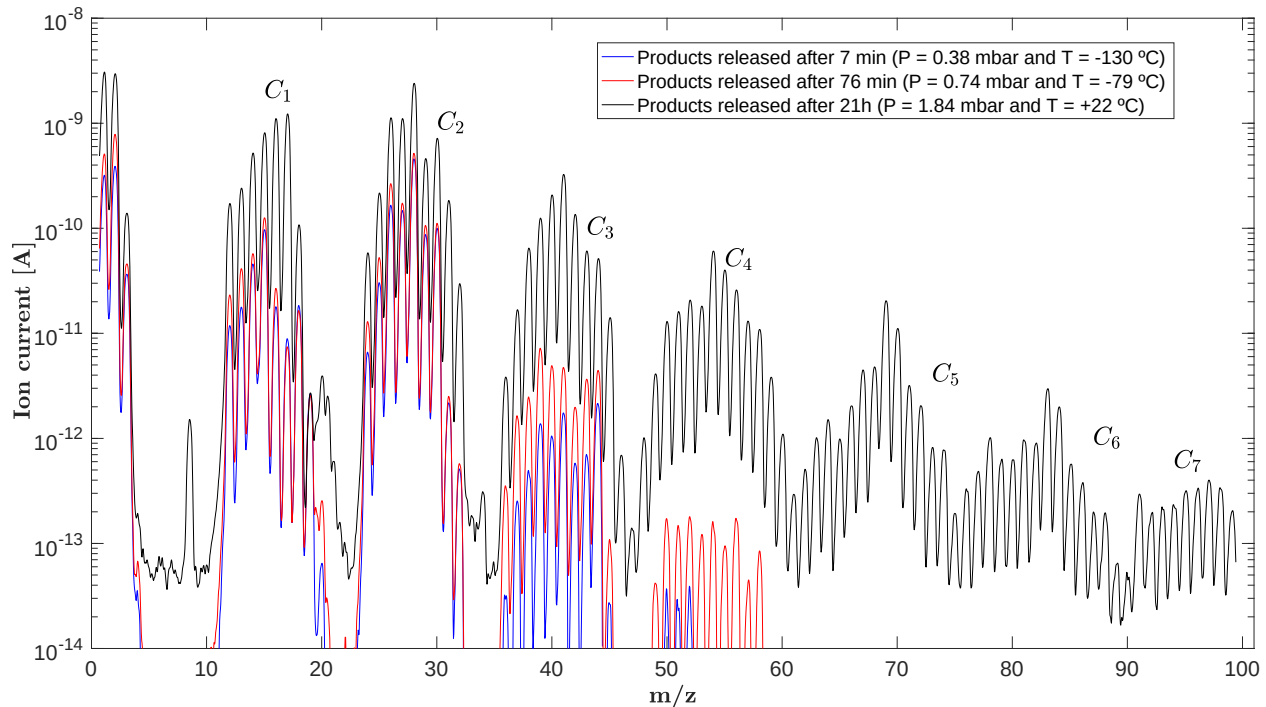
411
412 To go further in the analysis of the gas release, we monitored the gas phase composition by
413 mass spectrometry at three threshold moments *MS1*, *MS2*, *MS3* for 10% methane and only in
414 the final gas mixture for 1%.

415 In the case of 10% methane (Fig. 3 dashed blue line), the assigned *MS1*, *MS2* and *MS3* spectra
416 are defined as the T, P conditions of -130°C and 0.38 mbar, -79°C and 0.74 mbar and $+22^\circ\text{C}$
417 and 1.84 mbar of products formed, respectively. *MS1* is representative of the first release stage
418 occurring at temperatures lower than -100°C , *MS2* is on the pressure plateau beginning at -
419 100°C , and *MS3* corresponds to the final gas mixture obtained. For 1% methane conditions, we
420 will only focus on the last point, where a substantial volatile pressure was measured.

421
422 A first iteration at $[\text{CH}_4]_0 = 10\%$ was done. Mass spectra of the volatiles are shown Fig. 4. at
423 different stages in their release after the plasma discharge, namely *MS1*, *MS2* and *MS3*.

424

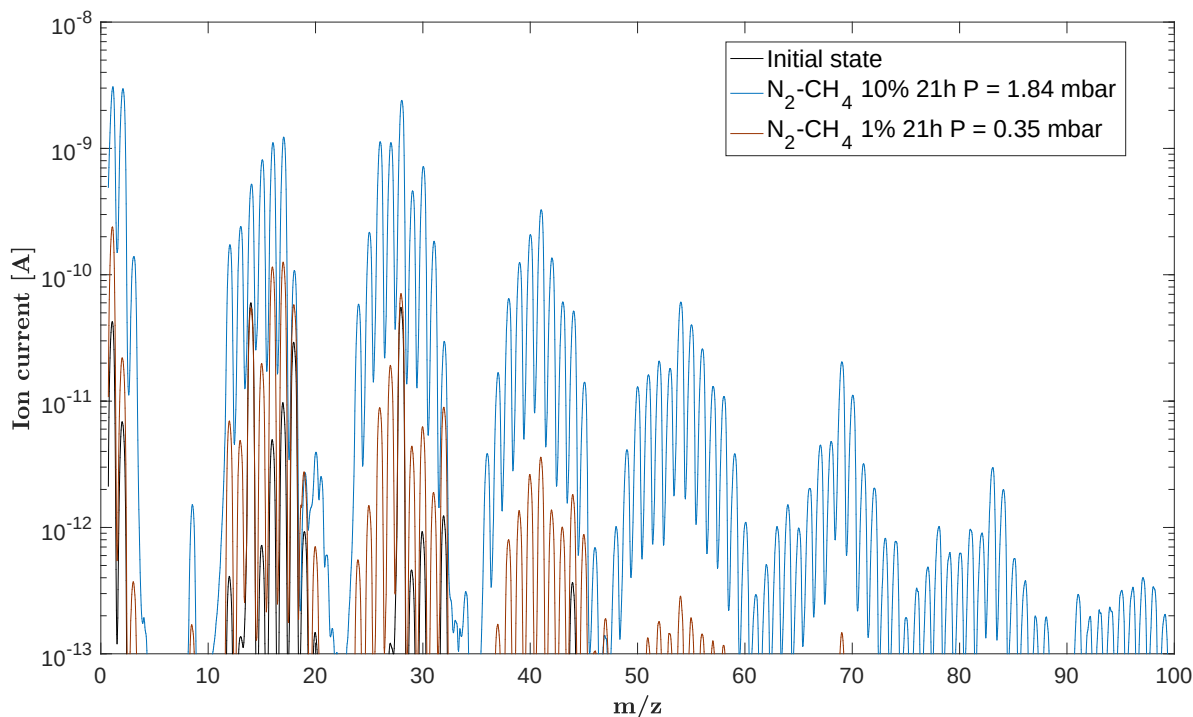
- 425 - *MS1*: 7min after stopping the cryogenic trap (blue line), C₁, C₂ and C₃ block species
426 have started to appear, with C₁ and C₂ (light volatiles of m/z < 30 amu) dominating
427 the spectrum. Masses 15 and 28 stand out for the C₁ and C₂ blocks, respectively.
428 Mass 28 cannot be attributed to N₂ as it was not trapped at -180°C during the
429 experiment. It can be attributed to ethylene C₂H₄ or ethane C₂H₆ as both molecules
430 are expected to be released at temperatures lower than -100°C and both have their
431 major fragment at m/z 28 according to the NIST database. However, the previous
432 ethane vapor pressure calculations and its triple point (Fray and Schmitt, 2009) show
433 that it could not condense. In these plasma conditions, it is risky to attribute m/z 29 to
434 methanimine (CH₂=NH) as the contribution of propane (C₃H₈) becomes non
435 negligible (Carrasco et al., 2012). m/z 29 corresponds indeed to the main peak in the
436 fragmentation pattern of C₃H₈. A few heavier volatiles in the C₃ and C₄ block are also
437 beginning to be detected. At m/z 44 we could also suspect the contribution of CO₂. A
438 blank mass spectrum of the mass spectrometer only has previously been measured
439 (Carrasco et al., 2012), showing the same intensity of 2 x 10⁻¹² A at m/z 44 as the
440 one seen in Fig. 4 (blue plot), at low temperature. It corresponds to the weak air
441 signature within the mass spectrometer at a vacuum limit of about 3 x 10⁻⁸ mbar.
442 Consequently, the contribution of CO₂ observed in the mass spectra of Fig. 4 at m/z
443 44 is minor inside the chamber among the released products and corresponds to the
444 residual air in the mass spectrometer itself.
- 445
- 446 - *MS2*: The main differences compared to *MS1* revolve around the C₃ and C₄ blocks
447 with the appearance of heavier hydrocarbons (red line, m/z > 50). Within the C₃
448 block, an important contribution appears at m/z 39, consistent with the cyclopropene
449 isomer C₃H₄. A significant increase is also observed at m/z 40 and 44 compatible
450 with the fragmentation pattern of propane C₃H₈ in the NIST database. No species
451 with masses higher than m/z 58 are detected yet.
- 452
- 453 - *MS3*: Remarkable changes occur at this final stage (black line), where many new
454 species stand out. In the C₁ block, m/z 17 (NH₃) strongly increases to become the
455 dominating C₁ compound.



456
 457 **Fig. 4.** Detection and evolution of several C_n blocks for $[CH_4]_0 = 10\%$. Plots marked in blue, red and black represent
 458 intermittent spectra taken 7 min, 76 min and 21h after commencing volatile release back to room temperature (*MS1*,
 459 *MS2* and *MS3*, respectively). The indicated temperatures correspond to those taken at the start of a mass scan. Note
 460 that during a scan acquisition (~ 200 s long), the temperature may change over $0.3\text{ }^\circ\text{C}$ to $23\text{ }^\circ\text{C}$ depending on the
 461 heating rates. The color code used here is the same as *MS1*, *MS2* and *MS3* of Fig. 3.

462
 463
 464 If we now compare the final stages obtained in the case of $[CH_4]_0 = 1\%$ and 10% on Fig. 3, the
 465 total pressure of volatiles obtained (0.35 mbar , blue line) is much less than in the case of $[CH_4]_0$
 466 $= 10\%$ (red). Fig. 5 shows a comparison of the final states at $[CH_4]_0 = 1\%$ (brown) and $[CH_4]_0 =$
 467 10% (blue), with the initial state (black), taken just before the volatile release at low-controlled
 468 temperature $T = -180^\circ\text{C}$. As expected from the lower final pressure, the mass spectrum is much
 469 less intense in the case of $[CH_4]_0 = 1\%$ than 10% . No signature is detected beyond the C_5 block
 470 for 1% whereas large intensities are found until the C_7 block in the case of 10% . However, the
 471 major peaks are the same in both cases. The C_1 block is dominated by $m/z\ 17$, accountable for
 472 ammonia. This important production, discussed in section 4.2, is a new result compared to the
 473 work by Gautier et al. (2011) and Carrasco et al. (2012). Indeed, as detailed in Carrasco et al.
 474 (2012), ammonia was hardly detectable with the analytical methods used in the two latter
 475 studies. The C_2 block has high peak intensities at $m/z\ 26, 27, 28, 30$ for $[CH_4]_0 = 10\%$ but the
 476 one at 28 stands out in both methane conditions, compatible with C_2H_4 or C_2H_6 . The C_3 block is

477 dominated by m/z 41, accountable for acetonitrile CH_3CN ; m/z 54 dominates C_4 , which could
478 correspond to butadiene C_4H_6 or $\text{C}_2\text{N}_2\text{H}_2$ (HCN dimer). For $[\text{CH}_4]_0 = 10\%$, the C_5 , C_6 and C_7
479 blocks are dominated by masses 69, 83 and 97, respectively. The odd masses predominantly
480 detected suggest a strong contribution of N-bearing molecules in both conditions.
481 The intensity evolution of m/z 17, 26, 27, 28 and 41 over time are shown Figure 11 in the
482 Supplementary Material.
483



484
485 **Fig. 5.** Three superimposed spectra at different $[\text{CH}_4]_0$ concentrations. In black, the initial mass spectrum taken
486 before release of the volatiles, still at low-controlled temperature (and representative of the blank of our mass
487 spectrometer). In blue and brown, the final state of volatiles at $[\text{CH}_4]_0 = 10\%$ after 21h and $[\text{CH}_4]_0 = 1\%$ after 21h of
488 release, respectively.

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491 **3.2 Monitoring and quantification using Mid-Infrared spectroscopy**

492
493 Alongside the neutral mass analysis, infrared spectra are simultaneously taken throughout the
494 release of the volatiles inside the chamber to provide quantification of these volatiles.
495 The measurement range is 650 cm^{-1} to 4000 cm^{-1} ($2.5\text{ }\mu\text{m}$ to $15.4\text{ }\mu\text{m}$) at a resolution of 1 cm^{-1}
496 during the release of the gas phase products analyzed *in situ*. Fig. 6 shows the spectra taken in

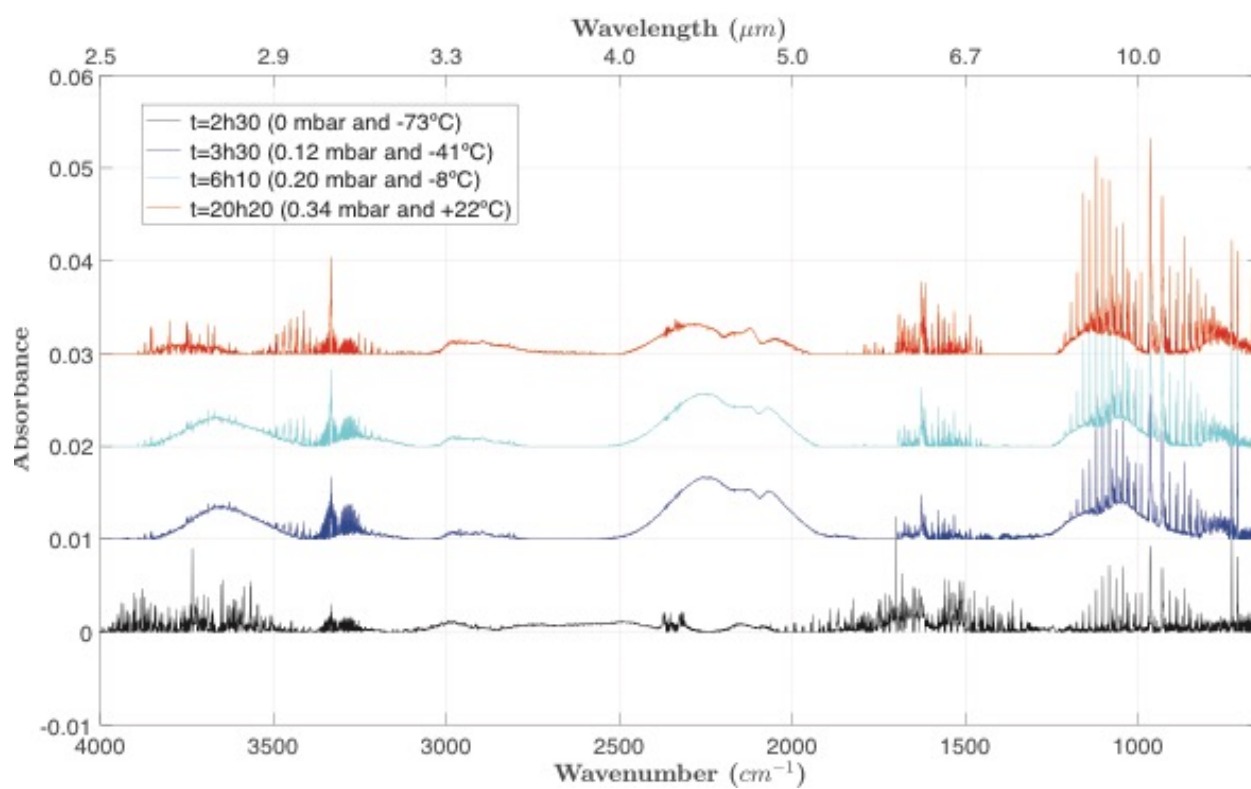
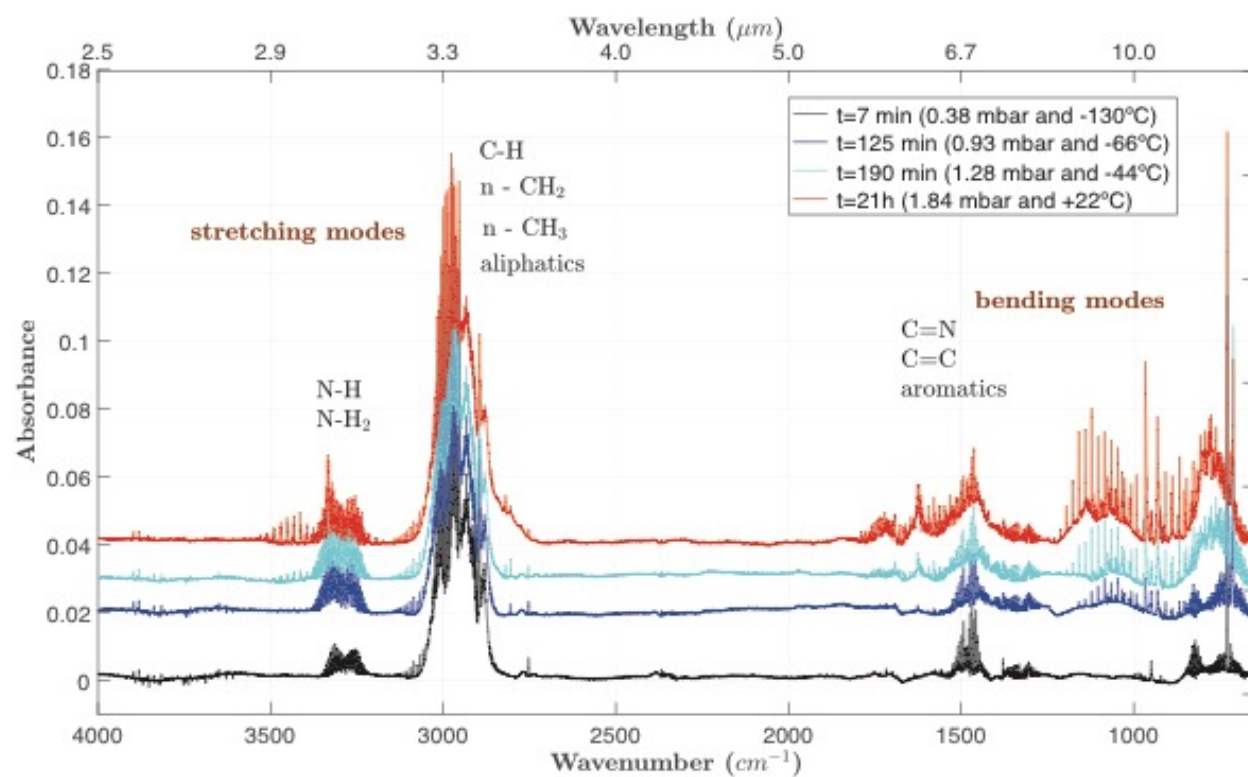
497 both initial methane conditions. The top plot was taken for a $[\text{CH}_4]_0 = 10\%$, the bottom at $[\text{CH}_4]_0$
498 $= 1\%$.

499 There is a clear discrepancy in the volatile products formed between the two conditions. $[\text{CH}_4]_0$
500 $= 10\%$ produces $-\text{CH}$ and $-\text{CH}_2$ compounds visible in the stretching mode region 3,000-3,500
501 cm^{-1} that are absent in the $[\text{CH}_4]_0 = 1\%$ case. Likewise, there is a relatively far greater
502 absorption of molecules bearing C=N and C=C bonds ($\sim 1,500 \text{ cm}^{-1}$) with $[\text{CH}_4]_0 = 10\%$. Fig. 6
503 (bottom) also has a large, broad absorption spread out over 2,000-2,500 cm^{-1} absent in the top
504 figure. These signatures could correspond to a scattering feature of solid grains in suspension
505 which could be the result of the released precursors reacting post-discharge. Furthermore, in
506 Sciamma-O'Brien et al. (2010), it had been shown that the gas to solid conversion yield was
507 more important in the case of the 1% experiment than in the 10% experiment, in agreement with
508 a higher amount of N-bearing gas phase products compared to hydrocarbons in the 1%
509 experiment. The present results are consistent with this previous study.

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515 **Fig. 6** FT-IR spectra of the volatiles taken after the 90-10% (top) and 99-1% (bottom) N₂-CH₄ plasma conditions,
 516 plotted with an arbitrary absorbance against a 650-4000 cm⁻¹ wavenumber range. The volatile density produced
 517 during the plasma discharge is being incrementally released and analyzed through IR spectroscopy. Top: Total gas
 518 pressures of 0.38 mbar (-130°C), 0.93 mbar (-66°C), 1.28 mbar (-44°C) and 1.84 mbar (+22°C) are shown in black,
 519 blue, cyan and red, respectively. Bottom: Total measured gas pressures of 0 mbar (-73°C), 0.12 mbar (-41°C), 0.20
 520 mbar (-8°C) and 0.34 mbar (+22°C) with the same color code. One clear difference is in the absence of any
 521 substantial aliphatic compounds (2800-3100 cm⁻¹) at [CH₄]₀ = 1% (bottom) that stand out at [CH₄]₀ = 10% (top).

522
 523
 524 Among all the signatures observed, we identified and calculated the concentrations of four
 525 volatiles as they are released in the chamber: NH₃, C₂H₂, C₂H₄, and HCN. These species are
 526 listed in Table 2. Ammonia (NH₃), acetylene (C₂H₂), hydrogen cyanide (HCN), ethylene (C₂H₄),
 527 are all species present at ionospheric and/or stratospheric altitudes on Titan, considered to be
 528 key in the formation of Titan's aerosols (Hanel et al., 1981; Kunde et al., 1981; Maguire et al.,
 529 1981; Wilson and Atreya, 2003, 2004) and formed in the upper atmosphere (Hörst, 2017).

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Selected species	C _x H _y N _z	Main absorption bands (cm ⁻¹)	Detected in Titan's atmosphere
Ammonia	NH ₃	962 (10.4 μm)	1, 4 (upper limit inferred)
Acetylene	C ₂ H ₂	729.25 (13.7 μm)	1, 2, 6
Hydrogen cyanide	HCN	712.3 (14.0 μm)	1, 5, 6, 7, 8
Ethylene	C ₂ H ₄	949.3 (10.5 μm)	1, 3

535
 536 **Table 2.** Four major volatile compounds detected and analyzed by infrared spectroscopy at [CH₄]₀ = 1% and [CH₄]₀ =
 537 10%. The main infrared absorption bands which were used for density calculations are also given. References
 538 are 1: Vinatier et al. (2007), 2: Cui et al. (2009), 3: Coustenis et al. (2007), 4: Nelson et al. (2009), 5: Paubert et
 539 al. (1984), 6: Teanby et al. (2007), 7: Moreno et al. (2015), 8: Molter et al. (2016). For more details on the
 540 bands and absorption cross-sections used for the molecular density calculations, the reader is referred to Table
 541 3 and Figures 9 and 10 of the Supplementary Material.

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To track the production and evolution with time/temperature of these four compounds, we used *in situ* infrared quantification. By using Beer-Lambert's Law (Eq. 3), we can calculate the concentration of any given gas phase product.

$$I_t = I_0 \times e^{-l.\sigma.N} \quad (3)$$

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I_t , I_0 and l are, respectively, the transmitted, incident intensities, optical path (cm) and σ the absorption cross-section ($\text{cm}^2.\text{molecule}^{-1}$) given by the Pacific Northwest National Lab (PNNL), University of Washington (Sharpe et al., 2004), GEISA (Armante et al., 2016) and ExoMol (Harris et al., 2006; Hill et al., 2013; Tennyson et al., 2016) databases. In addition, N is the molecular density (cm^{-3}). The absorption A is as follows:

$$A_{(\lambda)} = l \times \sigma_{(\lambda)} \times N \quad (4)$$

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Using the integrated experimental absorption A with the integrated database absorption cross-section σ between the two wavelengths λ_1 and λ_2 , (4) becomes:

$$\int_{\lambda_1}^{\lambda_2} A d\lambda = l \times N \times \int_{\lambda_1}^{\lambda_2} \sigma d\lambda \quad (5)$$

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558

So, we obtain the molecular number density N (molecules.cm^{-3}):

$$N = \frac{1}{l} \times \frac{\int_{\lambda_1}^{\lambda_2} A d\lambda}{\int_{\lambda_1}^{\lambda_2} \sigma d\lambda} \quad (6)$$

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Number densities are derived over a wavenumber range (see Table 3 of the Supplementary Material), covering the absorption band considered for each species.

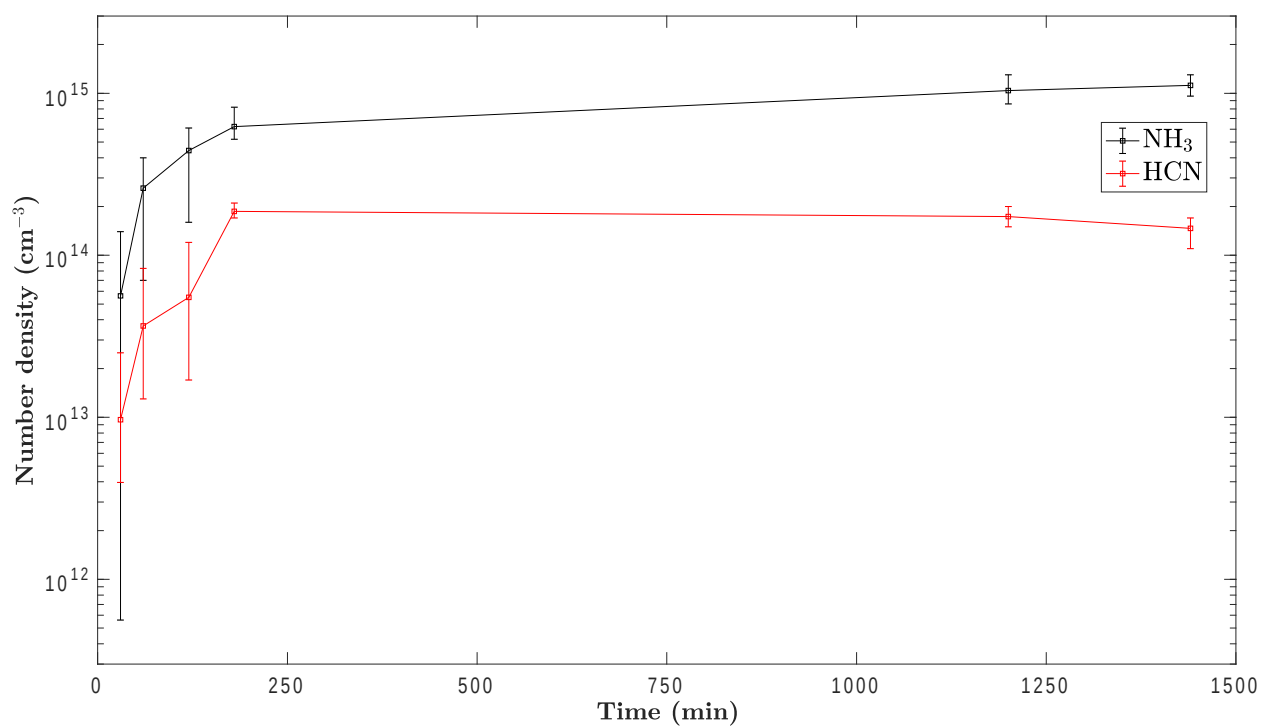
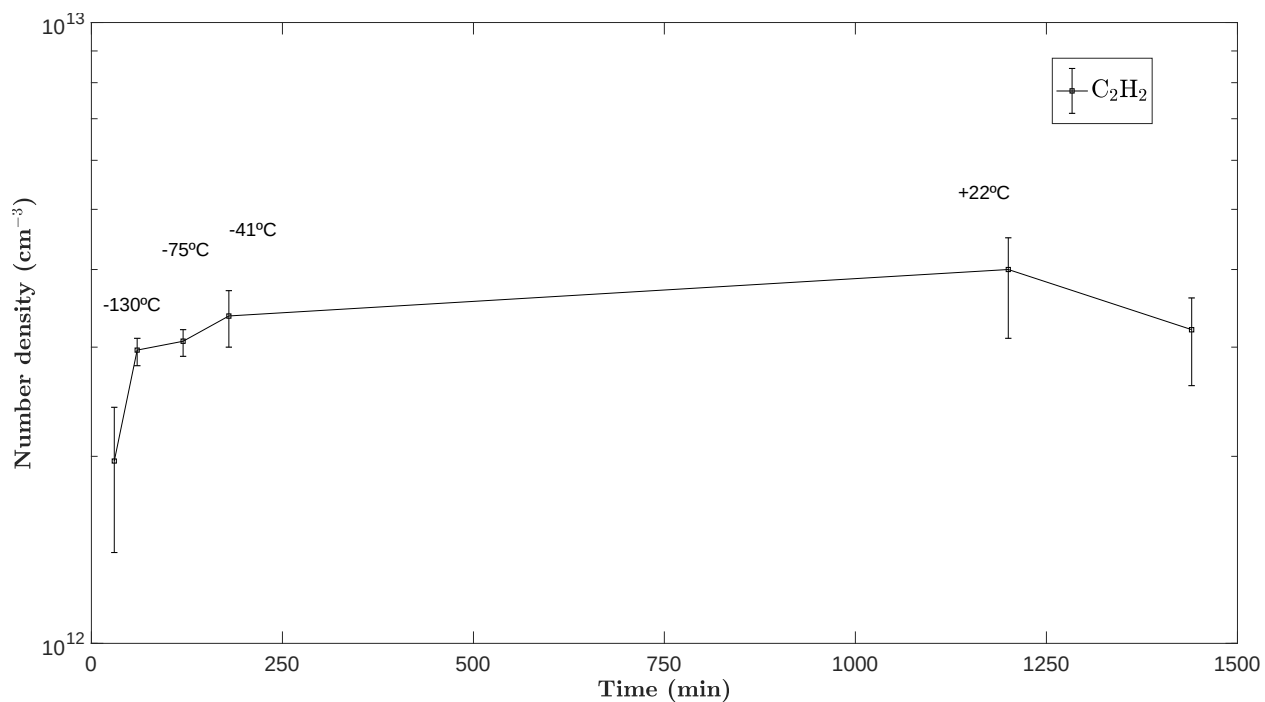
563 The main absorption band of each species was taken for all cases. The density results for both
564 conditions are shown Fig. 7 and Fig. 8. For the detailed number density calculation results and
565 data points used with the specific integration bands, the reader is invited to peruse the
566 Supplementary Material of the online version of this article.

567 The 962 cm^{-1} ($10.4\ \mu\text{m}$) NH_3 assigned band refers to the ν_2 N-H symmetric deformation. It is
568 part of the NH_3 doublet at 930 and 960 cm^{-1} , caused by the motion of nitrogen through the plane
569 of the three protons leading to an energy barrier. In the case of C_2H_2 , we used acetylene's
570 729.25 cm^{-1} frequency of oscillation ($13.7\ \mu\text{m}$). This band corresponds to the symmetric CH
571 bending mode ν_5 of every other C and H atom to its respective neighboring atom. For HCN, we
572 used the fundamental ν_2 bend frequency at 712 cm^{-1} ($14.0\ \mu\text{m}$); C_2H_4 the ν_7 CH_2 wag
573 deformation at 949 cm^{-1} ($10.5\ \mu\text{m}$). C_2H_4 centered at 950 cm^{-1} is surrounded by the NH_3 doublet
574 at 930 and 960 cm^{-1} . This absorption represents the fundamental absorption of ammonia's ν_2
575 normal vibrational mode. The motion of nitrogen through the plane of the three protons causes
576 this vibration with an energy barrier. For a summary on each band and frequency used, the
577 reader is referred to Table 3 of the Supplementary Material.

578
579 Molecular number densities at N_2/CH_4 : 99/1% are listed in Table T-4. The measurements taken
580 at t_{1-6} correspond approximately to 30 min, 60 min, 120 min, 180 min, 1200 min and 1440 min,
581 respectively. Three datasets were acquired after three experiments in the same initial
582 conditions. At this point, it is noteworthy to remember that t_0 represents the time when the
583 plasma conditions and cryo-trap cooling are ended (Fig. 3), and thus when the condensed
584 volatiles can effectively desorb from the chamber still under vacuum walls into the gas phase.

585 Overall, ammonia is the most dominant C_1 neutral ($\sim 1.1 \times 10^{15}\text{ cm}^{-3}$) produced at 1% CH_4 ,
586 confirming its high intensity at m/z 17 detected in mass spectrometry (Fig. 4). C_2H_2 and C_2H_4
587 also reached relatively high abundance $\sim 3.2 \times 10^{12}\text{ cm}^{-3}$ and $\sim 9.9 \times 10^{12}\text{ cm}^{-3}$, respectively.
588 These number densities correspond to the final measurements.

589



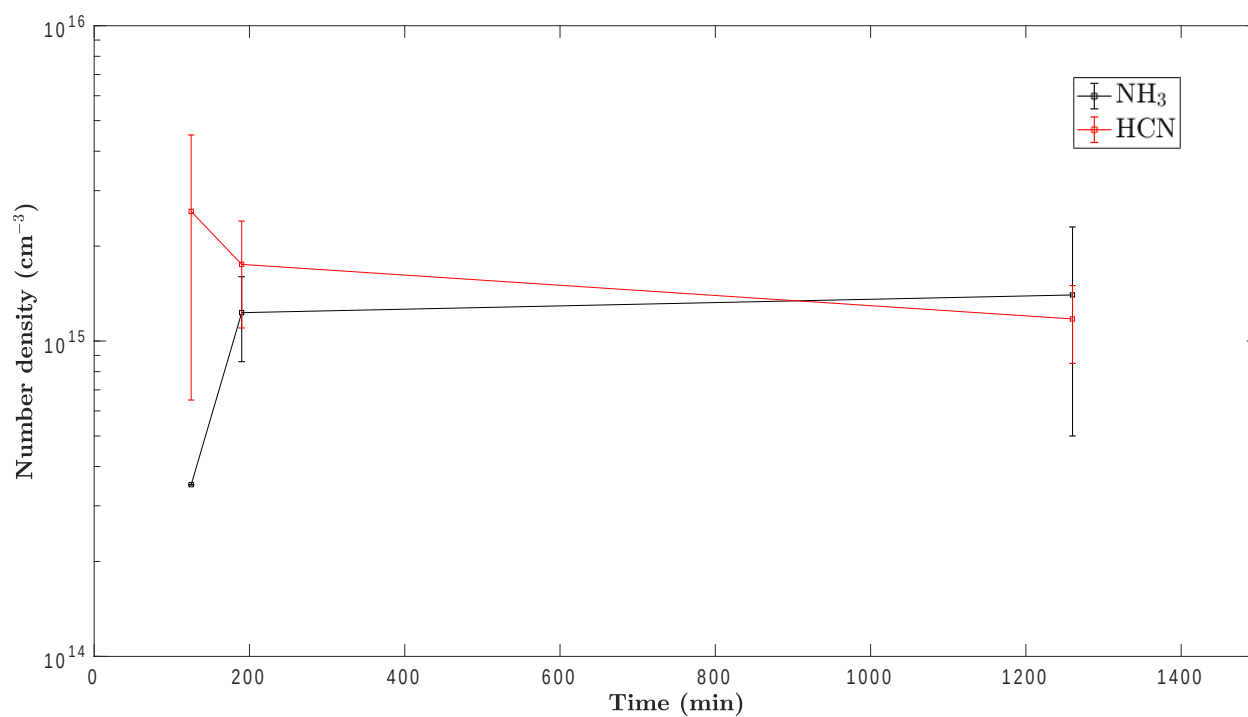
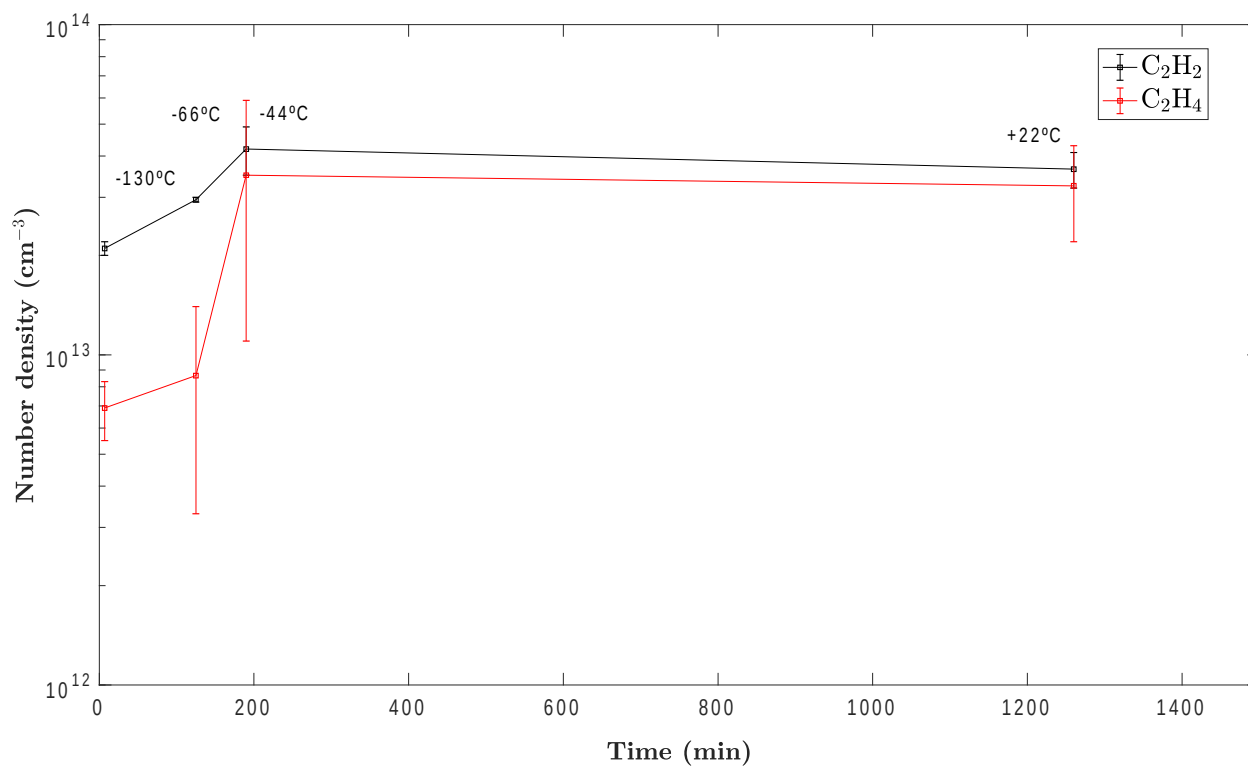
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Fig. 7. 1% methane conditions. Top: Molecular densities and average fitted kinetic profiles of C_2H_2 and C_2H_4 . Bottom: NH_3 and HCN . Approximate temperatures are also labeled over each data point. The error bars represent the dispersion of the data points for all three experiments (Table 4 and 5 of the online version of this article).

595 Fig. 8 shows the same kinetic profiles from a 10% methane initial gas mixture, with the
596 molecular densities listed in Table T-4. The C₂ species all reach concentrations at an order of
597 magnitude higher than those at 1%, correlating with the higher methane concentration initially
598 injected, which promotes the production of hydrocarbon species. C₂ species are thus strongly
599 favorably produced with increasing methane concentrations. This is especially notable with the
600 amount of HCN produced ($\sim 1.2 \times 10^{15} \text{ cm}^{-3}$) in the 10% [CH₄]₀ condition.

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Fig. 8. 10% methane conditions. Top: Molecular densities and average fitted kinetic profiles of C_2H_2 and C_2H_4 . Bottom: NH_3 and HCN . Approximate temperatures are also labeled over each data point. The error bars represent the dispersion of the data points for both experiments (Table 4 and 5 of the online version of this article).

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3.3 Methane consumption and hydrocarbon yield

With a 10% CH₄ mixing ratio, the condition with the most products, we consider the CH₄ consumption to provide yield estimates on the carbon conversion to hydrocarbon gas products. We note D as the total gas flow rate (N₂-CH₄) into the chamber in standard conditions. We first calculate the amount of CH₄ consumed in standard conditions (mg.h⁻¹), with $D = 55$ sccm. If n_{tot} is the total number of gas phase moles entering the reactor per second, the ideal gas law becomes:

$$\frac{dn_{tot}}{dt} = \frac{P_0}{R \times T_0} \times D \quad (7)$$

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With P_0 the gas pressure in Pa, R the ideal gas constant, T the absolute temperature (300 K), $dn_{tot}/dt = 2.22 \times 10^{19}$ molecules.s⁻¹. As seen previously, with a mixing ratio of $[CH_4]_0 = 10\%$, we find a CH₄ consumption of 52%. So,

$$\frac{dn_{CH_4cons}}{dt} = D_{CH_4} \times CH_{4cons} \times dn_{tot}/dt \quad (8)$$

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And the methane consumption rate is $dn_{CH_4cons}/dt = 1.15 \times 10^{18}$ molecules.s⁻¹. As the plasma runs for 2h, the total methane consumption is $n_{CH_4cons}(2h)/dt = 8.28 \times 10^{21}$ molecules. The total volume of the PAMPRE reactor is $\sim 28 \times 10^3$ cm³. Consequently, there is a CH₄ total consumption of about 2.9×10^{17} molecules.cm⁻³ over the 2h of the plasma discharge. With a calculated HCN total number of molecules of $\sim 1.2 \times 10^{15}$ cm⁻³, HCN accounts for $\sim 0.4\%$ of the carbon conversion from the consumed CH₄, while it is $\sim 0.3 \%$ and 0.2% for C₂H₂ and C₂H₄, respectively.

632 IV) Discussion

633

634 4.1 Volatile discrepancies at $[CH_4]_0 = 1\%$ and $[CH_4]_0 = 10\%$

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636 There are evident differences in the volatile products formed in both methane concentrations
637 used in this study (Fig. 3, Fig. 6, Tables T-3 and T-4 of the online version of this article). Despite
638 obtaining ~ 1.84 mbar solely in volatile products with 10% methane and ~ 0.35 mbar at 1%
639 methane, both spectra on Fig. 5 appear to qualitatively show the same nitrogen-bearing odd
640 mass compounds, albeit at different intensities. One major discrepancy though, lies in the
641 overwhelming amount of hydrocarbon species produced at 10% methane. The C_2 block is
642 dominated by the m/z 28 amu signal (Fig. 5), dominating the rest of the spectra, which
643 according to the NIST database, corresponds to ethylene and ethane's main fragment (this
644 mass cannot be linked to a release of N_2 , as the cryotrap temperatures were not cold enough to
645 trap any nitrogen during the experiment). However, the vapor pressure indicates that ethane is
646 difficult to trap, and so m/z 28 can be mainly attributed to C_2H_4 . Furthermore, the I_{30}/I_{28} ratio of
647 the absolute intensities in the mass spectra at m/z 30 and m/z 28 amu correspond to the ones
648 given by NIST, ~ 30 -35%. On Titan, short-lived species such as C_2H_4 remain tantalizing to
649 study, as they experience stratospheric dynamical processes with changing mixing ratios. By
650 preventing the condensation of N_2 , this study shows how m/z 28 may be attributed to C_2H_4 as
651 one of the most abundant hydrocarbons at 10% CH_4 .

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653

654 4.2 Ammonia

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656 Moreover, NH_3 stands out as being the most dominant N-bearing molecule in both $[CH_4]_0 =$
657 1% and $[CH_4]_0 = 10\%$ conditions, with final calculated concentrations of $\sim 1.1 \times 10^{15}$ and $\sim 1.4 \times$
658 10^{15} molecules. cm^{-3} , respectively.

659 Ammonia production was previously shown to be positively correlated with an increasing
660 methane concentration (Carrasco et al., 2012). However, the latter study did not consider
661 ammonia detection due to lack of a quantification approach as well as the m/z 17 H_2O fragment
662 contamination. NH_3 , as well as HCN, are nitrogen-bearing volatiles of utmost importance related
663 to prebiotic chemistry in reducing atmospheric environments. So, studying NH_3 in Titan's upper
664 atmosphere is crucial to understanding the chemical pathways leading to the formation of
665 aerosols and how it is incorporated in them. Cassini/INMS analyses of early Titan flybys (Vuitton

666 et al., 2007) first reported the presence of ammonia in the ionosphere, which was later more
667 robustly confirmed by Cui et al. (2009). Yelle et al. (2010), Carrasco et al. (2012), Loison et al.
668 (2015) discussed NH_3 chemical pathways. As such, the formation of ammonia in Titan's
669 atmosphere is still unclear, though it is thought to most likely involve methanimine CH_2NH which
670 itself acts as an important source for NH_2 radicals in plasma conditions, to eventually forming
671 NH_3 . An ionic characterization of pathways and reactions pertaining to ammonia production is
672 out of the scope of this paper.

673 Yelle et al. (2010) proposed an explanation for the production of NH_3 . Indeed, NH_3 is being
674 photochemically formed in the upper atmosphere and fed down into the stratosphere. While
675 photochemical models (Lara et al., 1996; Krasnopolsky, 2009) did not initially predict the
676 formation of NH_3 in the upper atmosphere, its production can be explained through ion reactions
677 (Yelle et al., 2010), by measuring the protonated ion NH_4^+ . Based on the long chain reaction
678 forming NH_3 detailed by Yelle et al. (2010) and its importance in our experimental results (major
679 nitrogen-bearing molecule), the contribution of nitrogen-bearing functional groups (e.g. amines,
680 nitriles or imine) or their contribution to eventually be incorporated into the organic aerosols
681 seems pertinent. This appears to be the case for NH_3 , being the main N-bearing compound. In
682 more advanced environments whether on Titan (Neish et al., 2009) or in the interstellar medium
683 (e.g. Largo et al., 2010), NH_3 remains an open and current topic to study prebiotic chemistry.

684

685 *4.3 C_2H_4 pathways to tholin formation*

686

687 The presence of ethylene in the ionosphere (Waite et al., 2007) and stratosphere (e.g.
688 Coustenis et al., 2007) is well established. However, similar to the other volatiles chosen in this
689 study, its influence and participation in tholin formation needs to be further investigated. The
690 relative concentration of C_2H_4 in Titan's atmospheric column is subject to distinct features. It
691 was first noted by Coustenis et al. (2007) and Vinatier et al. (2007) how the retrieved
692 stratospheric vertical abundances of C_2H_4 from Cassini/CIRS data showed both a unique
693 decrease in the mixing ratios towards high northern latitudes as well as being the only species
694 whose mixing ratio decreases with altitude at 15°S near the equator. Compared to other C_2
695 molecules (e.g. C_2H_2 , C_2H_6 , HCN), C_2H_4 is unique in that its mixing ratio decreases with altitude
696 at equatorial and northern polar latitudes. One hypothesis given by Vinatier et al. (2007) was
697 that C_2H_4 (along with C_4H_2 and $\text{CH}_3\text{C}_2\text{H}$), is subject to a photodissociative sink along with
698 equatorward transport from the winter polar vortex in the lower stratosphere and troposphere

699 (Crespin et al., 2005), essentially removing it away from the gaseous atmosphere. This sink
700 could eventually be the multiple haze layer.

701
702 As discussed previously and shown Fig. 5 and Table 5 (Supplementary Material), C₂H₄ is an
703 important C₂ compound in the 10% [CH₄]₀ mixture. Similar experiments (Gautier et al., 2014)
704 argued that (although in the absence of a cooling plasma system) tholins are formed with CH₂
705 patterns, coherent with C₂H₄ putatively acting as a strong gaseous precursor. This study comes
706 in agreement, at least on a tholin formation scale that C₂H₄ participates in their formation. This
707 experimental result also confirms that, if the stratospheric multiple haze layer is indeed the sink
708 to this molecule (Vinatier et al., 2007), the latter can easily take chemical pathways leading to
709 the formation of aerosols.

710 Pathways involving C₂H₄ (alongside C₂H₂) loss have been suggested by Yelle et al. (2010).
711 They proposed that C₂H₄ (and C₂H₂) reacts with NH radicals (Reaction 9) to produce heavier
712 nitrile molecules such as CH₃CN (Reaction 10) or the cyanomethylene radical HC₂N.

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715 The formation of NH radicals, reaction (9), occurs in ion chemistry conditions through
716 proton exchange, while these same radicals can then react with ethylene, reaction (10) in
717 neutral conditions. Given the large abundance of produced NH₃, it is possible that NH radicals
718 were formed and reacted with C₂H₄ during our 2h plasma, which incidentally is favorably
719 produced with increasing CH₄ concentration (Reaction 9).

720 Interestingly, C₂H₄ is implicated in NH₃ formation. According to Yelle et al. (2010),

721



722 Prior to this, the formation of the amino radical NH₂ involves ion chemistry, with the following
723 ion-neutral reaction:

724



725 Thus, C₂H₄ in our plasma may participate in the production of heavier nitrile species or
726 ammonia during the plasma discharge.

727

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729 *4.4 HCN production*

730

731 Hydrogen cyanide in Titan's atmosphere is well documented and known to be the most
732 abundant nitrile trace volatile (e.g. Kim et al., 2005; Vinatier et al., 2007), with high mixing ratios
733 at stratospheric altitudes in the northern polar regions.

734 HCN is also of prime importance in the search for prebiotic conditions in the solar system
735 and beyond (Oró, 1961) as well as being one of the precursors to amino acids and peptides
736 (Oró, 1961; Hörst et al., 2012; He and Smith, 2014; Rahm et al., 2016). In addition, the
737 chemistry of HCN mainly relies on its relatively high polarity and quite strong C≡N triple bond,
738 with a bond dissociation energy D(H-CN) of ~ 5.2 eV calculated by photodissociation and
739 photoionization models (Berkowitz, 1962; Davis and Okabe, 1968; Cicerone and Zellner, 1983).
740 Thus, making it a relatively stable molecule.

741 As shown Figs. 7 and 8, HCN is one of the most abundant products formed in both [CH₄]₀ = 1%
742 and [CH₄]₀ = 10% conditions, with ~ 1.5 x 10¹⁴ cm⁻³ and 1.2 x 10¹⁵ cm⁻³ on average,
743 respectively. Carbon yield calculations stresses the carbon conversion to HCN (~ 0.4%), while
744 other C₂ species all are favorably produced by an order of magnitude at 10% CH₄ than at 1%
745 CH₄.

746 HCN and HCN-based copolymers are also known to participate in the chemical growth
747 patterns of tholin formation (Pernot et al., 2010; Gautier et al., 2014) along with the CH₂
748 monomer, which is in agreement with the idea that haze forming acts as an HCN sink in the
749 stratosphere (McKay, 1996; Vinatier et al., 2007). This study seems to confirm the prevalent role
750 of HCN in the formation of tholins.

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754 V) Conclusions

755

756 The present study was aimed at expanding previous work focused on the volatile
757 production and their participation in tholin production using a cold dusty plasma experiment
758 (Gautier et al., 2011; Carrasco et al., 2012), but with one major twofold novelty (i) the ability to
759 trap these volatiles *in situ* within our plasma reactor with a new experimental setup at low-
760 controlled temperatures, and (ii) quantitatively analyze their formation using IR spectroscopy. It
761 is important to be cautious in interpreting these quantitative results, as three (T, P and t)
762 parameters change simultaneously during the sublimation phase entailing possible unsuspected
763 ice-volatile chemistry. The approach we took was solely focused on the gas phase. Indeed,
764 these volatiles, still poorly understood and which give Titan its unique nature of being one of the
765 most chemically complex bodies in the Solar System, act as substantial gas phase precursors
766 to the formation of Titan's organic aerosols populating its haze layers. Hence, simulating
767 ionosphere conditions is crucial in constraining the volatile population, its reactivity and potential
768 chemical pathways.

769

770 Major discrepancies exist between the two initial methane concentrations we used, 1%
771 and 10%, with many more hydrocarbons formed in the latter case (detection of C₇ species), but
772 with similar amounts of N-bearing species, only at different concentrations. Our results confirm
773 the important role of C₂ species in the tholin precursor volatile family (m/z 28 e.g.), as well as
774 that of NH₃. One of them, ethylene C₂H₄, being a relatively major C₂ hydrocarbons, might even
775 reveal an important “hub” role at least at 10% [CH₄]₀ through which specific chemical pathways
776 involving C₂H₄ are favored (see Section 4.3). The importance of C₂H₄ might also be relevant at
777 1% [CH₄]₀ although this is difficult to assess in this study due to the cryotrapping efficiency
778 which is not optimum at -180°C to quantify it, as suggested by the thermodynamical calculations
779 and mass spectra during the discharge. Eventually, tholins themselves may be benefitting from
780 the incorporation of C₂H₄, which itself stresses the value of considering a yet unaccomplished
781 fully-coupled ion and neutral chemistry study. This is out of the scope of this paper, as the cryo-
782 trap system prevents the formation of tholins. These experiments have also shown a strong
783 incorporation of carbon into HCN, along with NH₃ being a competitive product to HCN,
784 especially with a [CH₄]₀ = 1% (an order of magnitude more in final concentration).

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786 Future compelling work to expand this study might be to consider other molecular families
787 participating in the neutral reactivity, therefore increasing our knowledge of volatile chemistry

788 precursor to tholin production. In addition, adding selected volatiles such as HCN, an important
789 nitrile, in trace amounts into our gaseous mixture would improve the understanding of its
790 influence on the chemical reactivity in plasma conditions in future work. Moreover, predicting ion
791 densities and characterizing ion-neutral reactions in these conditions would be key to
792 understanding their incorporation into the solid phase and validating chemical pathways which
793 are still largely unknown in Titan ionosphere simulations. Perhaps most importantly, a fully-
794 coupled ion-neutral characterization would fundamentally bring credence to understanding the
795 complex organic realm encompassing Titan's gas phase chemistry.

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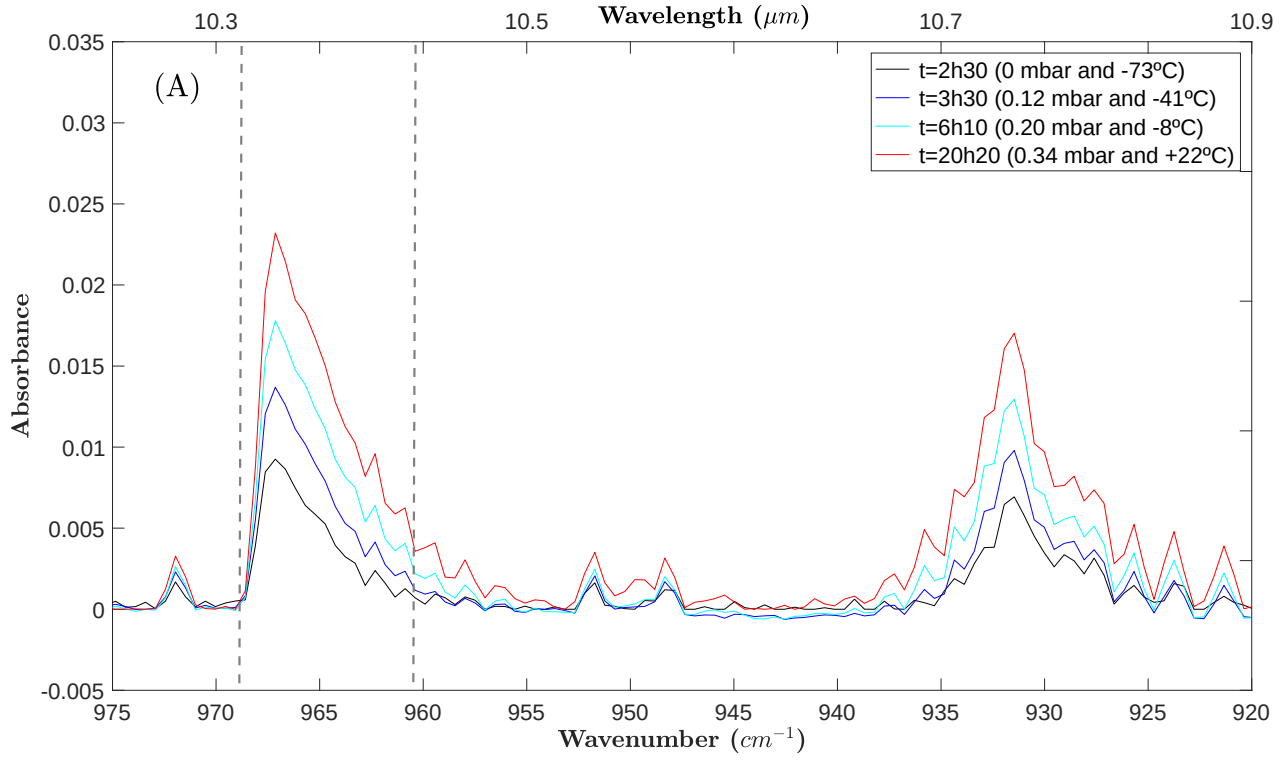
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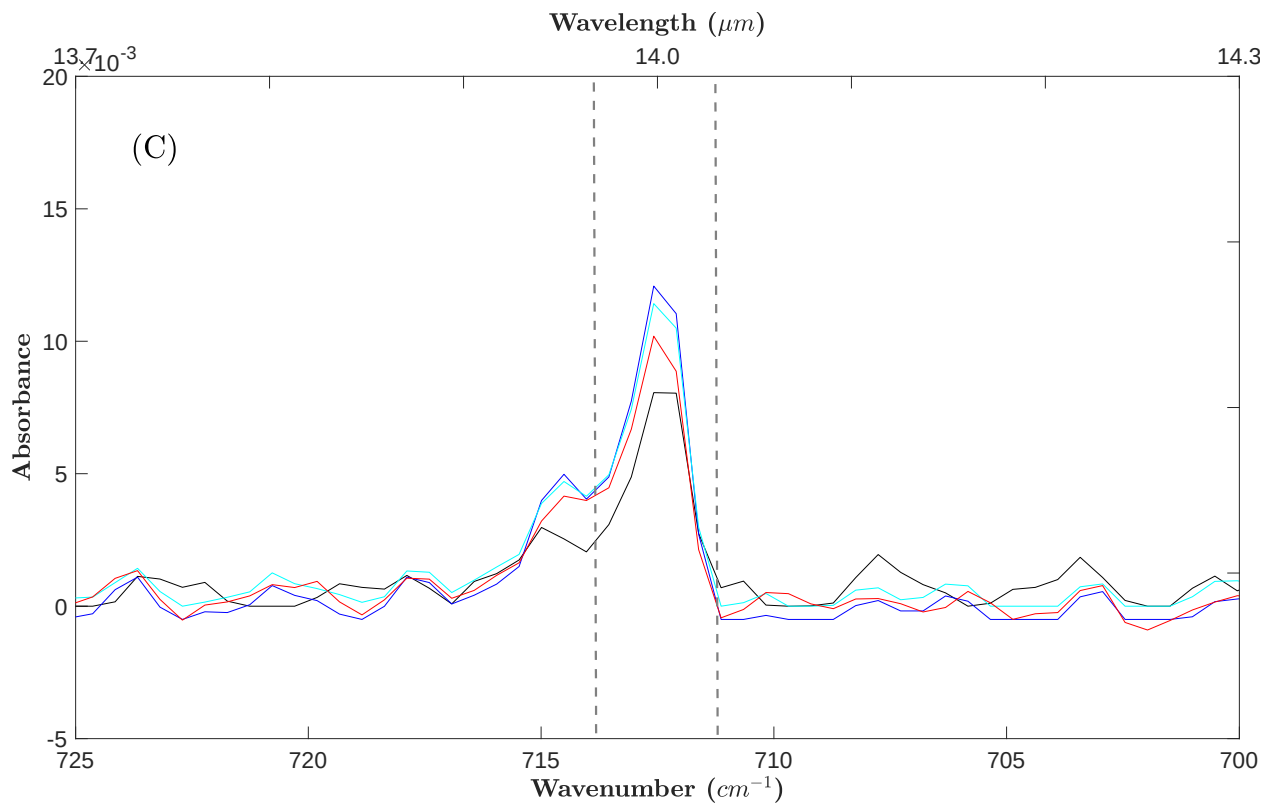
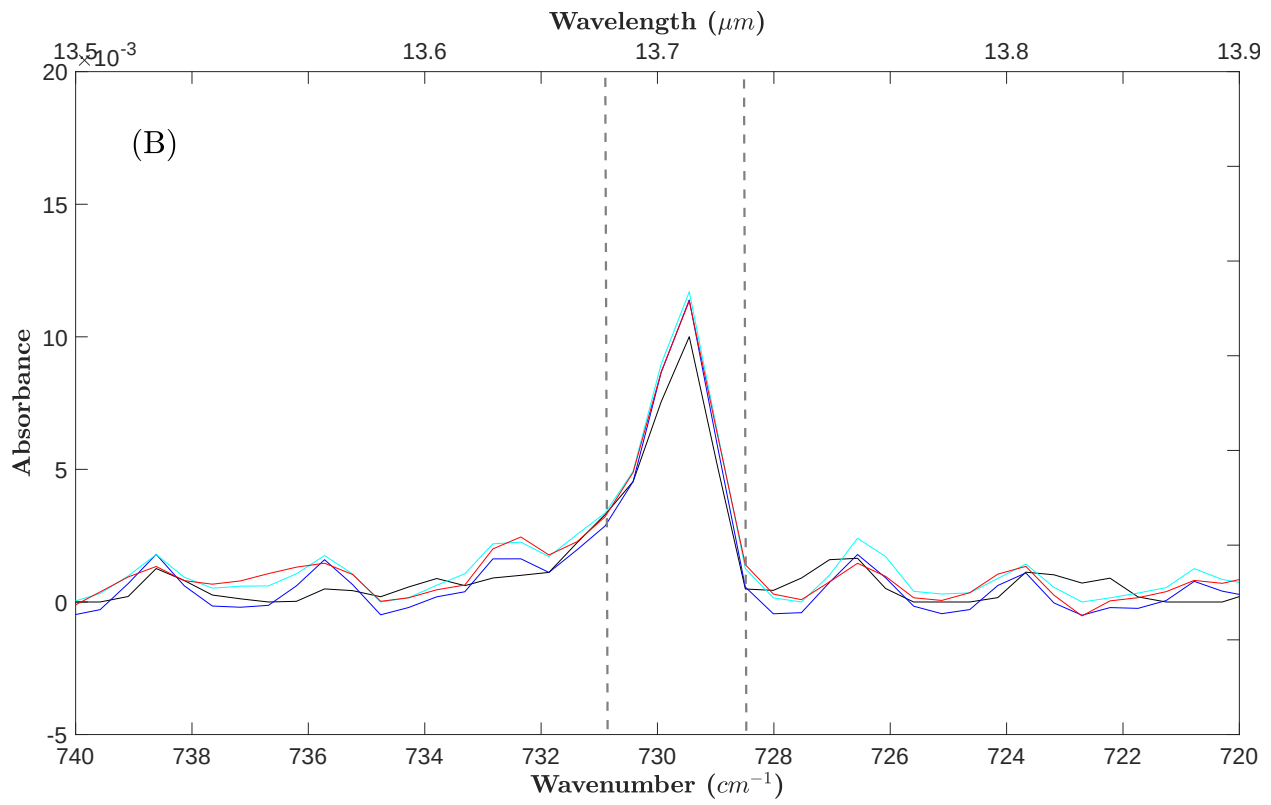
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Supplementary Material

1% CH₄





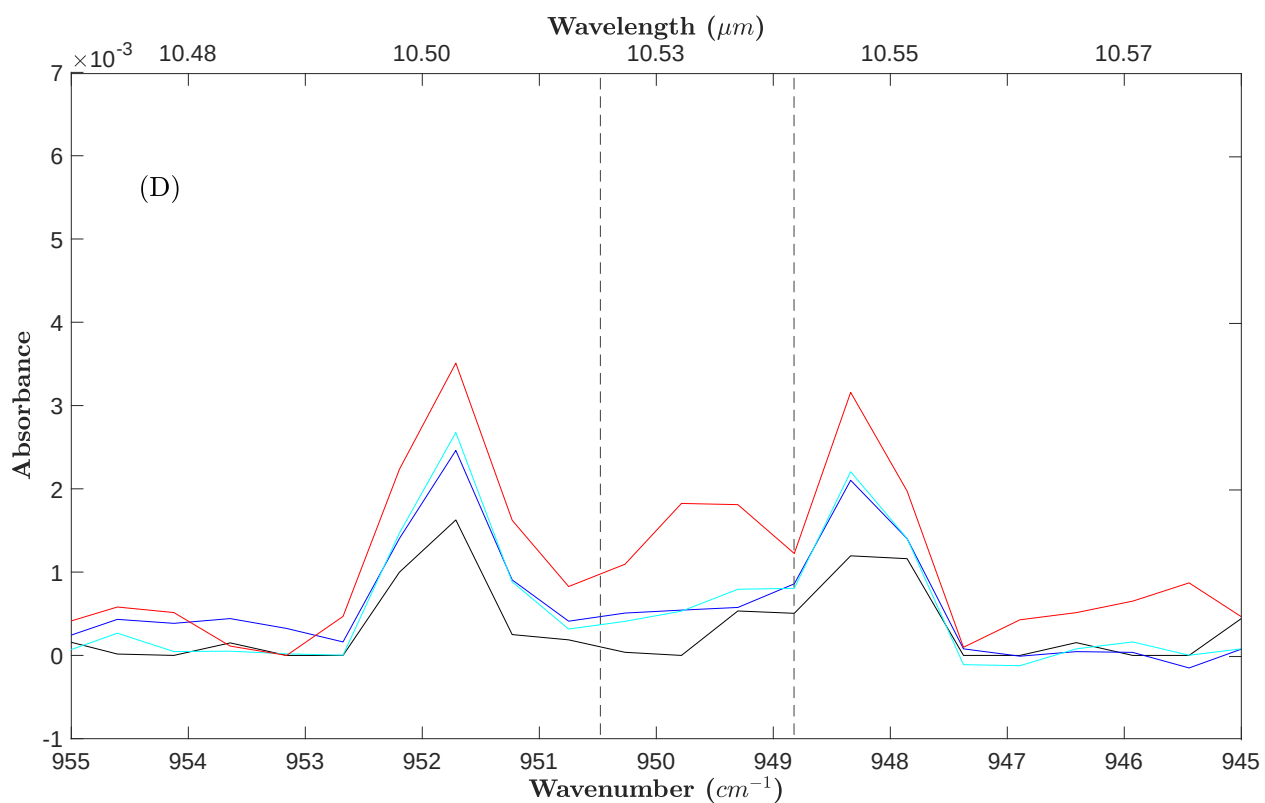
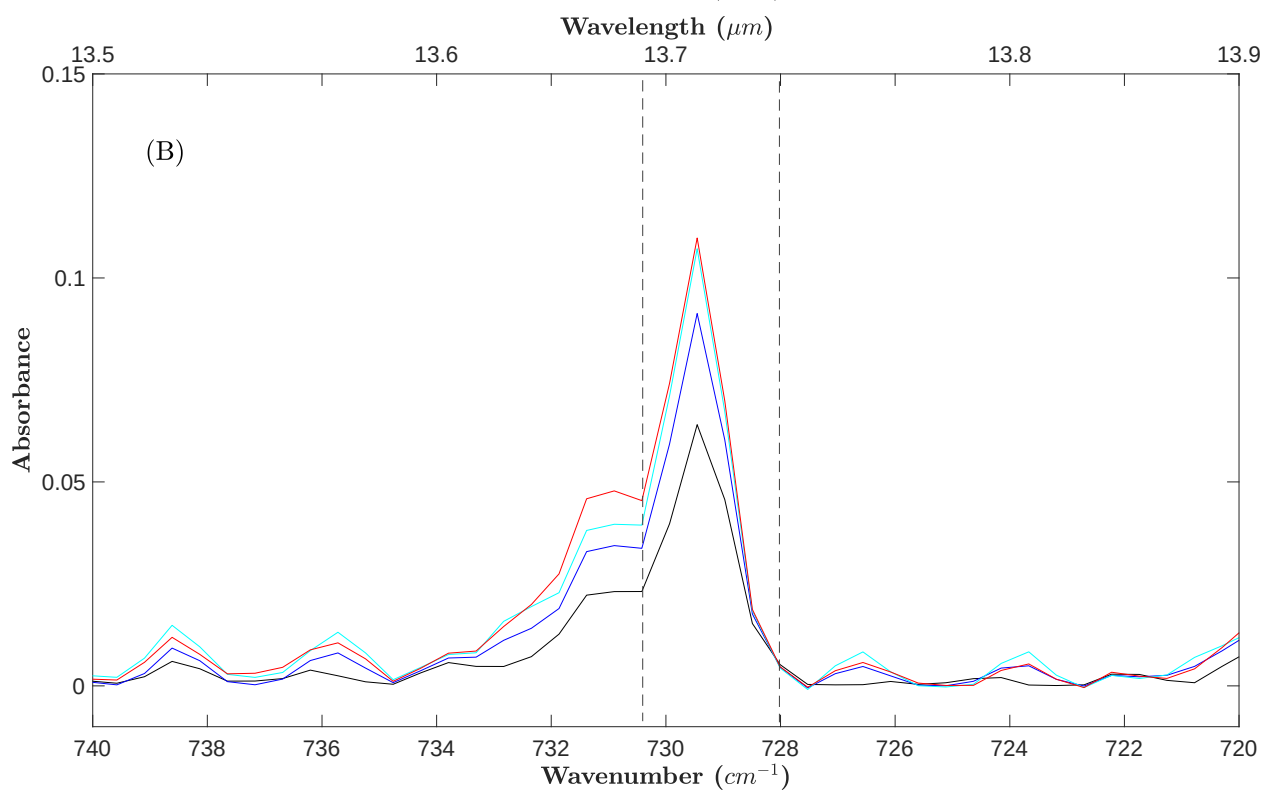
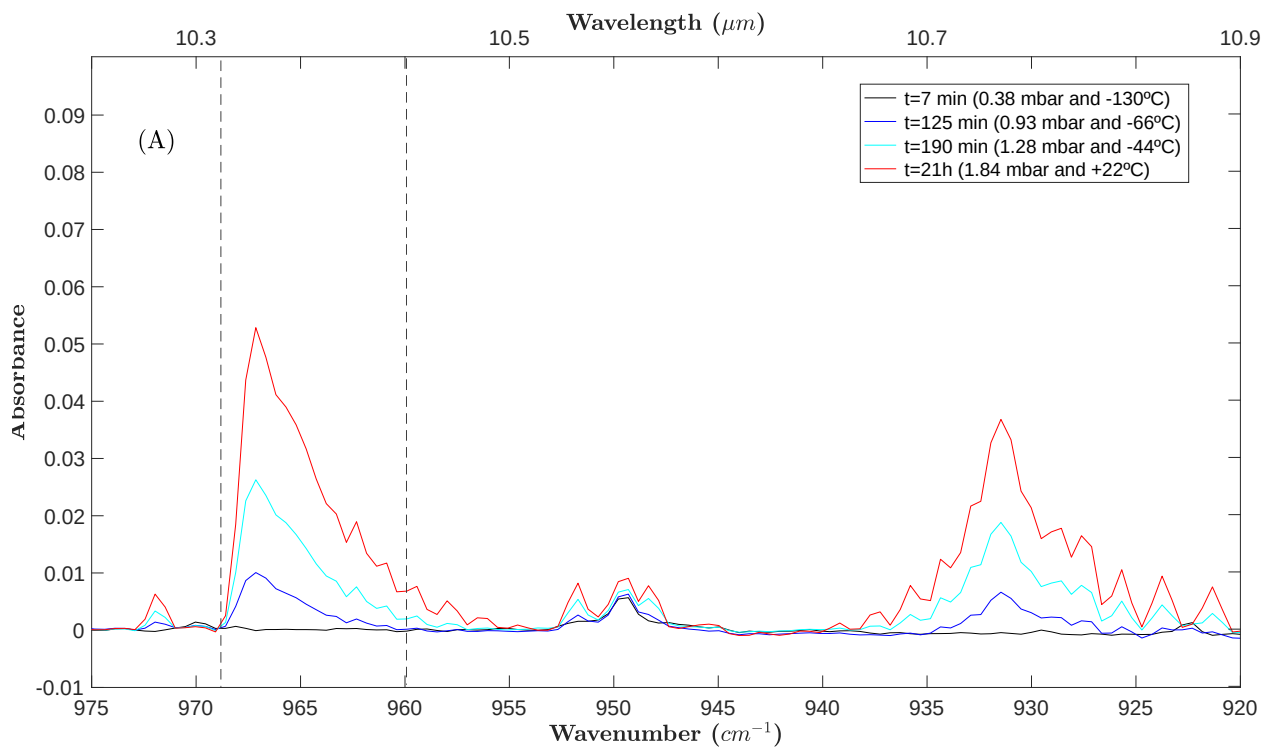


Fig. 9. $[\text{CH}_4]_0 = 1\%$. Main absorption bands of (A) NH_3 (930 cm^{-1} and 960 cm^{-1} doublet), (B) C_2H_2 (729.25 cm^{-1}), (C) HCN (713 cm^{-1}), (D) C_2H_4 (949.55 cm^{-1}). The color code is the same as in Figure 6. The vertical dashed gray lines correspond to the integration band used for the density calculations on either side of the absorption peaks.

10% CH₄



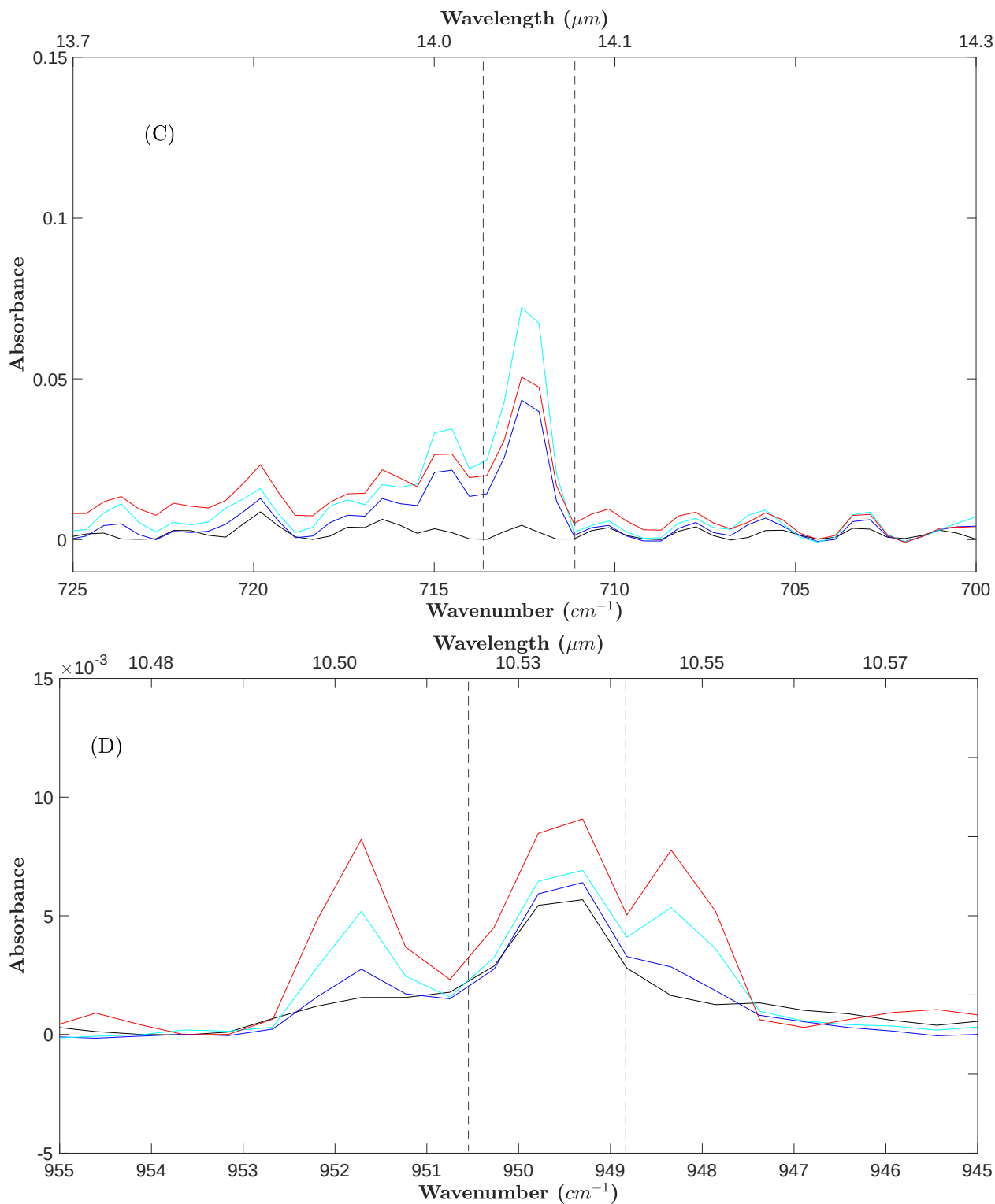


Fig. 10. $[\text{CH}_4]_0 = 10\%$. Main absorption bands of (A) NH_3 (930 cm^{-1} and 960 cm^{-1} doublet), (B) C_2H_2 (729.25 cm^{-1}), (C) HCN (713 cm^{-1}), (D) C_2H_4 (949.55 cm^{-1}). The color code is the same as in Figure 7. The vertical dashed gray lines correspond to the integration band used for the density calculations on either side of the absorption peaks.

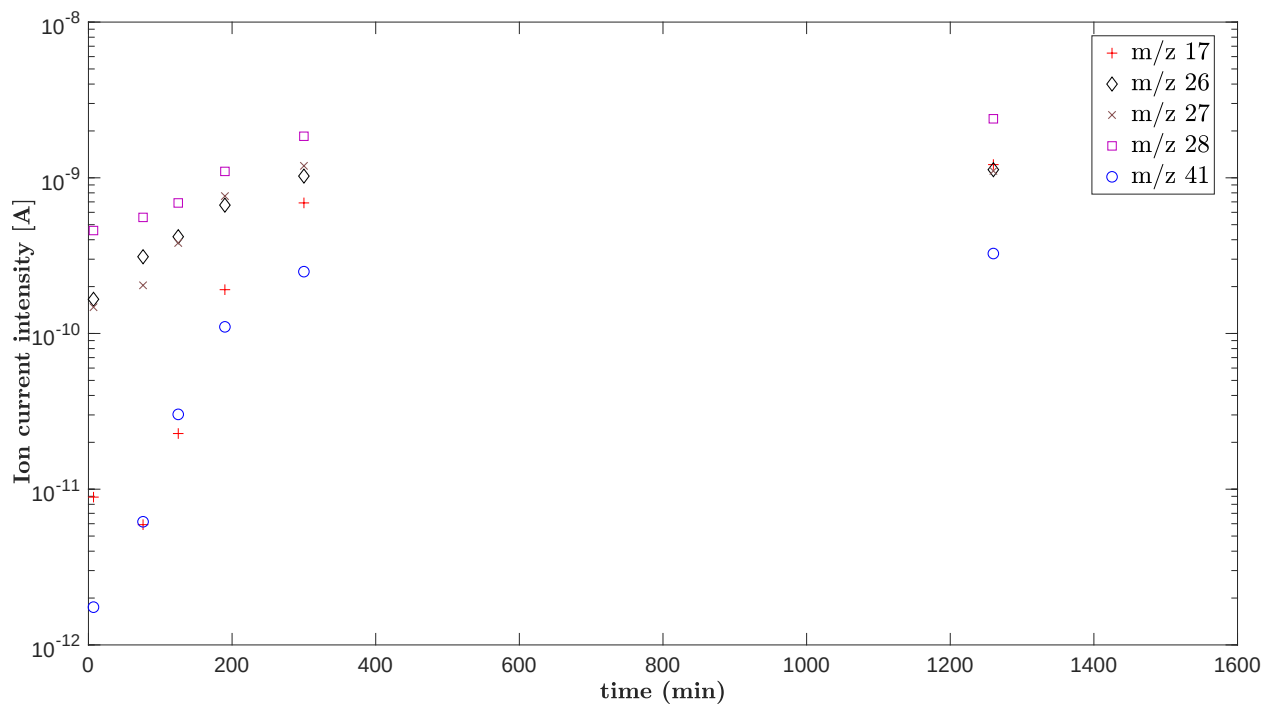


Fig. 11. Evolution of the intensities (same time scale as Figure 3) of selected species, NH_3 (m/z 17), C_2H_2 (m/z 26), HCN (m/z 27), C_2H_4 (m/z 28) and CH_3CN (m/z 41) over time.

Selected species	Fundamental frequency ¹	Main peak (cm ⁻¹)	FWHM (cm ⁻¹)	Integrated absorption cross-section σ (cm ² .molecule ⁻¹)
Ammonia	ν_2	965	± 4.0	4.04 x 10 ⁻¹⁸
Acetylene	ν_5	729.25	± 1.25	1.92 x 10 ⁻¹⁶
Hydrogen Cyanide	ν_2	712.3	± 1.2	4.09 x 10 ⁻¹⁸
Ethylene	ν_7	949.5	± 1.0	2.43 x 10 ⁻¹⁷

Table 3. IR peak locations, fundamental frequencies and integrated wavenumber ranges, absorption cross-sections (cm².molecule⁻¹) for each selected volatile, as analyzed in both methane conditions. For the calculation results (derived from Equ. 6), see the following Tables 4-5. ¹Sharpe et al., 2004 and <http://vpl.astro.washington.edu/spectra/allmoleculeslist.htm>

Time/Species	NH_3 (cm^{-3})			C_2H_2 (cm^{-3})			HCN (cm^{-3})			C_2H_4 (cm^{-3})		
\underline{T}_1	5.6 x 10^1 1	2.8 x 10^1 3	1.4 x 10^1 4	2.1 x 10^1 2	2.4 x 10^1 2	1.4 x 10^1 2	4.0 x 10^1 2	2.5 x 10^1 3	-	-	-	-
mean	5.6×10^{13}			2.0×10^{12}			9.7×10^{12}			-		
\underline{T}_2	7.0 x 10^1 3	3.1 x 10^1 4	4.0 x 10^1 4	3.1 x 10^1 2	3.0 x 10^1 2	2.8 x 10^1 2	1.3 x 10^1 3	8.3 x 10^1 3	1.4 x 10^1 3	-	-	-
mean	2.6×10^{14}			3.0×10^{12}			3.7×10^{13}			-		
\underline{T}_3	1.6 x 10^1 4	5.6 x 10^1 4	6.1 x 10^1 4	3.1 x 10^1 2	2.9 x 10^1 2	3.2 x 10^1 2	1.7 x 10^1 3	1.2 x 10^1 4	2.8 x 10^1 3	-	-	-
mean	4.4×10^{14}			3.1×10^{12}			5.5×10^{13}			-		
\underline{T}_4	5.2 x 10^1 4	5.3 x 10^1 4	8.2 x 10^1 4	3.7 x 10^1 2	3.0 x 10^1 2	3.4 x 10^1 2	2.1 x 10^1 4	1.8 x 10^1 4	1.7 x 10^1 4	-	-	-
mean	6.2×10^{14}			3.4×10^{12}			1.9×10^{14}			-		
T_5	9.6 x 10^1 4	8.6 x 10^1 4	1.3 x 10^1 5	4.4 x 10^1 2	3.1 x 10^1 2	4.5 x 10^1 2	2.0 x 10^1 4	1.5 x 10^1 4	1.7 x 10^1 4	-	-	-
mean	1.0×10^{15}			4.0×10^{12}			1.7×10^{14}			-		
T_6	9.6 x 10^1 4	1.3 x 10^1 5	1.1 x 10^1 5	3.4 x 10^1 2	3.6 x 10^1 2	2.6 x 10^1 2	1.7 x 10^1 4	1.6 x 10^1 4	1.1 x 10^1 4	-	-	-
mean	1.1×10^{15}			3.2×10^{12}			1.5×10^{14}			-		

Table 4. Calculated molecular densities from IR absorption at $[\text{CH}_4]_0 = 1\%$, for three different data sets. T_{1-6} correspond to measurements done at approximately 30 min (-130°C), 60 min (-85°C), 120 min (-70°C), 180 min (-41°C), 1200 min (+22°C) and 1440 min (+22°C), respectively. Each column corresponds to one experiment. Number density calculations are performed with the integrated absorption cross-section of the ExoMol or Hitran databases at the resolution of our experimental spectra (see Table 3). Blank boxes indicate the absence of the species where no number density was derived.

<u>Time/Species</u>	<u>NH₃ (cm⁻³)</u>		<u>C₂H₂ (cm⁻³)</u>		<u>HCN (cm⁻³)</u>		<u>C₂H₄ (cm⁻³)</u>	
<u>T₁</u>	-	-	2.0 x 10 ¹³	2.2 x 10 ¹³	-	-	8.3 x 10 ¹²	5.5 x 10 ¹²
mean	-		2.1 x 10 ¹³		-		6.9 x 10 ¹²	
<u>T₂</u>	3.5 x 10 ¹⁴	-	2.9 x 10 ¹³	3.0 x 10 ¹³	6.5 x 10 ¹⁴	4.5 x 10 ¹⁵	1.4 x 10 ¹³	3.3 x 10 ¹²
mean	3.5 x 10 ¹⁴		3.0 x 10 ¹³		2.6 x 10 ¹⁵		8.7 x 10 ¹²	
<u>T₃</u>	8.6 x 10 ¹⁴	1.6 x 10 ¹⁵	3.5 x 10 ¹³	4.9 x 10 ¹³	1.1 x 10 ¹⁵	2.4 x 10 ¹⁵	1.1 x 10 ¹³	5.9 x 10 ¹³
mean	1.2 x 10 ¹⁵		4.2 x 10 ¹³		1.8 x 10 ¹⁵		3.5 x 10 ¹³	
<u>T₄</u>	2.3 x 10 ¹⁵	5.0 x 10 ¹⁴	4.1 x 10 ¹³	3.2 x 10 ¹³	8.5 x 10 ¹⁴	1.5 x 10 ¹⁵	2.2 x 10 ¹³	4.3 x 10 ¹³
mean	1.4 x 10 ¹⁵		3.7 x 10 ¹³		1.2 x 10 ¹⁵		3.3 x 10 ¹³	

Table 5. Calculated molecular densities from IR absorption at $[\text{CH}_4]_0 = 10\%$, for two different data sets. T_{1-4} correspond to measurements done at approximately 7 min (-130°C), 125 min (-66°C), 190 min (-44°C) and 21h (+22°C), respectively. Each column corresponds to one experiment. Number density calculations are performed with the integrated absorption cross-section of the ExoMol or Hitran databases at the resolution of our experimental spectra (see Table 3). Blank boxes indicate the absence of the species where no number density was derived.