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J. Mouzay, K. Henry, I. Couturier-Tamburelli, G. Danger, N. Piétri, et al.. Photochemistry of benzene (C₆H₆) hydrogen cyanide (HCN) co-condensed ices part 1: A source of solid-state production of volatile nitrile compounds in Titan's stratosphere. *Icarus*, 2021, 368, pp.114595. 10.1016/j.icarus.2021.114595 . hal-03330139

HAL Id: hal-03330139

<https://hal.science/hal-03330139>

Submitted on 2 Aug 2023

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1 **Photochemistry of benzene (C₆H₆) hydrogen cyanide (HCN) co-condensed ices part 1: a**
2 **source of solid-state production of volatile nitrile compounds in Titan's stratosphere**

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10

11 **Abstract**

12 Since 2015, during northern spring, a massive “noxious” stratospheric cloud has been
13 detected at 250 km of altitude at the south pole of Titan, which persisted until the last targeted
14 Cassini's flybys in July 2016. Its chemical composition seems to be the result of a co-
15 condensation process of benzene and hydrogen cyanide in a 4:1 mixing ratio. Since, its
16 altitude of detection allows to undergo long-UV solar radiations known to trigger
17 photochemical aging processes, we experimentally simulated its evolution under
18 stratospheric-like radiation conditions. The ice photo-processing ($\lambda > 200$ nm) led to the
19 detection of nitriles by infrared spectroscopy such as acetonitrile (CH₃CN), benzonitrile
20 (C₆H₅CN) as well as a partial identification of propionitrile (CH₃CH₂CN) and acrylonitrile
21 (C₂H₃CN). Gas chromatography coupled to mass spectrometry (GC-MS) analyses of the
22 volatile fraction released in the gas phase during the warming of the photo-processed ice have
23 been confirmed by previous assignments and provided the detection of several other
24 hydrocarbons ranging from C₃ to C₈. These experimental results are of prime interest in the
25 context of the future Dragonfly mission. They provide a list of nitrile derivatives that can be
26 produced from this stratospheric cloud. Indeed, they may contribute at the end to the organic
27 layer that recovers Titan's surface and would be analyzed by the mass spectrometer (Dra-MS)
28 of this space mission.

29

30 **Introduction**

31 Titan, Saturn's largest moon, has been probed for more than thirteen years by *Cassini-*
32 *Huygens* space mission, with a hundred of targeted flybys. So far, Titan is the only satellite in

33 the solar system to possess a dense atmosphere highly reductive with a complex chemistry
34 due to its N₂ and CH₄ composition, which ratio varies over the altitude (Niemann et al. 2010).
35 In the upper part of the atmosphere, high energetic particles (electrons coming from Saturn's
36 magnetosphere, X-rays, solar photons, ...)(Coates et al. 2009; Galand et al. 2010; Waite et al.
37 2007; Yung et al. 1984) lead to the photo-dissociation of these main atmospheric constituents
38 resulting in the formation of complex organic compounds (Coustenis et al., 2007; Cui et al.,
39 2009; Imanaka & Smith, 2007; Magee et al., 2009; Samuelson et al., 1997; Waite et al.,
40 2007). Since the first flyby of Titan by *Voyager 1*, numerous gaseous species are present in
41 the surrounding gas phase (Coustenis et al. 1999; Hanel et al. 1981; Kunde et al. 1981;
42 Samuelson et al. 1997), including hydrogen cyanide (HCN) (Coustenis et al. 2007; Hanel et
43 al. 1981). Later, Composite Infrared Spectrometer instrument (CIRS) and Ion and Neutral
44 Mass Spectrometer (INMS) of the Huygens probe extended of the molecules detected in the
45 gas phase, and determined their relative abundance over the atmosphere (Coustenis et al.
46 2007; Cui et al. 2009; Koskinen et al. 2011). It was the case for benzene (C₆H₆) which was
47 detected by ISO (Coustenis et al. 2003) and confirmed by Cassini CIRS/Huygens INMS
48 (Coustenis et al. 2007; Waite et al. 2005).

49

50 At lower altitude, the decreasing stratospheric temperature profile allows organics to
51 condense (Anderson et al., 2018, 2016; De Kok et al., 2007; Griffith et al., 2006; Khanna et
52 al., 1987; Lavvas et al., 2011; Mayo & Samuelson, 2005; Samuelson et al., 2007, 1997;
53 Samuelson & Mayo, 1991), resulting in the formation of ice particles (Lavvas et al. 2011,
54 2010). In this atmospheric region, the temperature variation lead to a chemical
55 complexification of solid particles, which result from a coating with successive ice layers
56 (Anderson et al., 2016). Theoretical models of the cloud microphysics and radiative transfer
57 models have then established condensation profiles of gaseous molecules in the Titan's
58 stratosphere for different seasons and regions (Anderson et al. 2018; Barth 2017; Lavvas et al.
59 2011). Besides, Cassini-Huygens space mission highlighted the formation of massive
60 stratospheric ice clouds at low altitudes by ISS and CIRS instruments, at the southern pole,
61 due to exceptional climatic conditions. Indeed, two years after the northern spring equinox in
62 2009, Titan's meridional circulation has been reversed. This inversion had the consequence of
63 increasing the mixing ratios of trace organics in the southern hemisphere following a drastic
64 cooling, with temperatures dropping under 120 K in the stratosphere at an altitude of 250
65 km(Achterberg et al. 2014; Coustenis et al. 2016). Vinatier et al. have shown that the 682 cm⁻¹

66 signature, observed below 300 km since 2013, is attributed for a part to the CH bending mode
67 of benzene (C₆H₆) ice. More recently, in the same region during the late southern fall in 2015,
68 Anderson et al. (2017) reported the detection of a massive cloud around 250 km of altitude
69 with a 220 cm⁻¹ far-infrared signature. This feature may result from the simultaneous
70 condensation of benzene and hydrogen cyanide in a 4:1 ratio (Anderson et al. 2017, 2018).

71

72 FUV photons (Gudipati et al., 2013; Lavvas et al., 2008; Wilson, 2004) that reach the
73 stratosphere can trigger photochemical reactions at these altitudes, representing the main
74 process for the loss of molecules in this atmospheric layer. Besides, at 220 nm, the solar flux
75 is estimated to be 1 x 10¹⁰ photons.cm⁻².s⁻¹ at 200 km competing the one obtained at shorter
76 wavelength in the highest atmospheric layers, which induces a complex gas-phase chemistry
77 (Gudipati et al., 2013). This solar flux can also participate to the photochemical aging of
78 Titan's stratospheric ice particles (Anderson et al. 2016). Anderson et al. (2016) showed also
79 that the interaction of FUV solar photons with ice particles of HC₃N and HCN, like those
80 detected in a northern stratospheric cloud, could lead to the solid-state formation of
81 dicyanoacetylene (C₄N₂). The quantities of this photo-product were similar to those detected
82 in the stratosphere. These observations led Anderson et al. (2016) to conclude that solid-phase
83 C₄N₂ can be synthesized via a surface reactivity rather than a condensation at the surface of
84 aerosols. Therefore, the photochemical evolution of Titan's stratospheric ice clouds could
85 partially contribute to a change in chemical composition of the atmosphere. To account for
86 these observations, we can rely on experimental simulations of FUV photolysis. These were
87 carried out either on pure nitriles ices, i.e., hydrogen cyanide (HCN), acrylonitrile (C₃H₃N),
88 propionitrile (C₃H₅N), cyanoacetylene (HC₃N), dicyanoacetylene (C₄N₂) (Couturier-
89 Tamburelli et al., 2018a, 2018b, 2014; Gudipati et al., 2013) or on pure hydrocarbons ices
90 with acetylene (C₂H₂) (Abplanalp et al. 2019) and benzene (C₆H₆) (Mouzay et al. 2021a).
91 Moreover, with the help of GC-MS analyses, the formation of several kinds of volatile
92 hydrocarbons, in particular aromatic derivatives such as toluene, ethylbenzene, xylenes and
93 styrene were identified from the photochemistry of pure benzene ices under conditions
94 relevant with Titan's stratospheric chemistry (Mouzay et al. 2021a,b). The formation of
95 volatile nitrogen compounds was also identified by infrared spectroscopy (Toumi et al., 2016)
96 and mass spectrometry (Couturier-Tamburelli et al. 2018b, Fleury et al. 2019) following the
97 exposure of pure nitrile ices to FUV radiations, compatible with those reaching the
98 stratosphere,. Except the experimental study of Pola et al. (2011) which emphasized, by GC-

99 MS analyses, the formation of nitriles derivatives from the photolysis ($\lambda = 248$ nm) of a
100 gaseous C_6H_6/CH_3CN mixture, no other experiment was performed to understand the
101 nitrogen-bearing species possibly generated from the photochemistry of $C_6H_6:HCN$ ices in
102 relevant Titan conditions. The resulting photoproducts could then sublime enriching the gas
103 phase, depending on the climatic conditions (if this HASP cloud is long-lived and in a steady
104 state). Therefore, several experiments demonstrated the formation of diversified organics
105 (hydrocarbons, aromatics, nitriles or amines) from $N_2:CH_4$ gas mixtures (Coll et al. 1999;
106 Gautier et al. 2011; Hörst et al. 2018; Ramírez et al. 2005, 2001; Tran et al. 2005) in
107 conditions simulating the photochemistry occurring from the stratopause to the highest
108 atmospheric layers. However, the photochemistry of $C_6H_6:HCN$ ices, relevant for Titan's
109 stratospheric cloud chemistry is still lacking.

110 .

111 In this work, the role of the photochemical evolution of $C_6H_6:HCN$ co-condensed ices
112 is investigated in the energetic conditions of Titan's stratosphere. We particularly focus on the
113 solid-state formation of volatile photo-products. Different ratios of $C_6H_6:HCN$ ices were
114 irradiated in low temperature conditions, and their evolution was monitored by IR
115 spectroscopy. The released compounds in the gas phase during the photo-processed ice
116 warming were recovered and analyzed by gas chromatography coupled to mass spectrometry
117 (GC-MS). These experiments allowed to determine if from such ices the low-energetic solar
118 conditions of the stratosphere can lead to the formation of nitrogen derivative photo-products,
119 from such ices.

120

121 1. Methods

122 1.1. Setup and formation of $C_6H_6:HCN$ co-condensed ices

123 The description of the experimental setup, AHIIA, used for these experiments is
124 detailed elsewhere (Abou Mrad, 2014). Gaseous benzene (for HPLC, assay $\geq 99.9\%$, from
125 Sigma-Aldrich) was purified by several degassing steps with the help of nitrogen baths. HCN
126 is synthesized by the thermal reaction of potassium cyanide (KCN) and an excess of stearic
127 acid $CH_3(CH_2)_{16}COOH$ in a primary pumped vacuum line, as described in Gerakines et al.
128 (2004). Benzene and hydrogen cyanide 4:1; 1:1 and 1:4 mixes have been prepared in a 1L-
129 glass line. Gas mixtures were deposited on a polished copper surface, which temperature was
130 controlled between 70 K to 300 K with a closed-cycle helium refrigerator and maintained

131 using a model 21 CTI cold head cryostat, a resistive heater, and a Lakeshore 331 temperature
132 controller, within a high vacuum chamber (10^{-8} mbar). Each deposited gas sample
133 corresponded to a quantity of about 20 μmol . The quantity of sample deposited was chosen to
134 obtain an intensity inferior of 1 a. u. on IR spectra. The IR spectra were recorded in reflection-
135 absorption mode in the mid-infrared region between 4000 and 600 cm^{-1} using a Bruker Tensor
136 27 Fourier transform infrared spectrometer with a DTGS detector. Each spectrum was
137 averaged over 100 scans during photolysis experiments with a resolution of 1 cm^{-1} , except for
138 the background averaged over 300 scans with the same resolution (Butsher et al. 2015).

139 Each co-condensed ice was deposited at 70 K, annealed to 105 K and followed by a cooling
140 down to 70 K in order to increase the crystallization of C_6H_6 while preventing the desorption
141 of both C_6H_6 and HCN (cf. supplementary information figure S1). Sublimation was supposed
142 to occur at any temperature in a high vacuum chamber as compounds of the ice are in
143 equilibrium with their vapor phase. Therefore, at 10^{-8} mbar in the chamber, this vapor can be
144 continuously pumped, gradually causing the ice to sublimate. However, the lower is the
145 temperature, the slower is the process. We have chosen to perform the experiments at 70 K,
146 since a benzene/HCN ice starts to sublimate around 80 K in our experimental conditions (cf.
147 supplementary information figure S1). Furthermore, this temperature provides trapping a
148 maximum of photoproducts in the ice allowing their identifications. A drawback of this
149 protocol is that some clusters of benzene or HCN can be formed during this protocol. (Hodyss
150 et al. 2008, Lignell and Gudipati 2015) during the annealing to 105 K.

151 Photolysis was performed using an Oriel 500 W high-pressure mercury lamp ($\lambda=200\text{-}2500$
152 nm with discrete Hg lines in the UV-Vis region between 200 and 600 nm, where most of the
153 photon flux (2.34×10^{16} photon. $\text{cm}^{-2}.\text{s}^{-1}$, ~ 13 mW. cm^{-2}) resides (Mouzay et al. 2021a, b) . The
154 duration of the photolysis was chosen at 48 hrs to simulate a short sedimentation period of the
155 co-condensed ices compatible with those expected in Titan's stratosphere (Gudipati et al.
156 2013). Moreover, using both a 1-D microphysical model (Lavvas, 2010, 2011) and a general
157 circulation model (GCM) including microphysics aerosols (Larson et al. 2014), the residence
158 time of aerosol in the Titan atmosphere has been estimated to be 395 Titanian years.
159 According to the model of Larson et al., aerosols are supposed to spend most of their time in
160 the lower atmosphere.

161

162 Considering a solar flux of $\sim 10^{14}$ photons.cm⁻².s⁻¹ at 100 km on Titan (Gudipati et al. 2013),
163 the photons flux of the UV source employed is therefore 234 times more important than the
164 one reaching the Titan's lower stratosphere. Consequently, 2 days of photolysis in **the**
165 laboratory correspond to 468 days or 1.3 years on Titan which become 2.6 years by
166 considering Titan's exposure to the sun during the day and the night. Furthermore, two other
167 mandatory criteria related to experimental feasibility and chemical considerations have also
168 led us to choose such a duration of irradiation: 1) because of benzene's weak electronic
169 absorption at these wavelengths, the duration must be sufficiently long to observe spectral
170 modifications using a low sensitivity in situ technique, i.e., IR spectroscopy: 2) to obtain only
171 the formation of primary products.

172 After irradiation, the vacuum chamber was isolated from the pumping, and ice samples were
173 warmed up to 300 K with the cryogenic system switched-off. Before this warming up, argon
174 was added in the chamber to reach a total pressure of ~ 5 mbar (Abou Mrad et al. 2020) which
175 optimizes the transfer of **volatile organic compounds (VOC)** from the chamber towards the
176 pre-concentration loop. No modification on the photo-processed ice was observed with IR
177 spectroscopy after Ar addition. The species sublimating from the ice were trapped over 16 h
178 in a pre-concentration loop cooled in liquid nitrogen (77 K). This loop is part of the interface,
179 named VAHIA (Volatile Analyses from the Heating of Interstellar/cometary Ice Analogs)
180 which connects vacuum chamber and GC-MS instrument. A detailed description of the
181 interface is reported elsewhere (Abou Mrad et al. 2014, 2020). Subsequently, the pre-
182 concentration loop was warmed **and helium** was added into the loop to reach a total pressure
183 of 200 mbar which facilitates the sample transfer to the injection unit of the GC-MS (Abou
184 Mrad et al. 2016, 2020). The injection unit ensures the online injection of the sample through
185 a specific gas **injection loop** (500 μ L) to the injector of the GC-MS instrument as described in
186 the next section.

187

188 *1.2.GC-MS conditions for sample analysis*

189 The GC-MS analyses were performed on a ThermoFisher Trace 1310 gas
190 chromatograph coupled to a ThermoFisher ITQ 900 MS ion trap, which has been modified for
191 gaseous sample injection. A detailed description of the setup is described elsewhere (Abou
192 Mrad et al. 2014). A volume of 500 μ L of samples was injected into a split/splitless (SSL)
193 injector kept at 300°C operating in split mode with a ratio of 10. The GC-MS injection loop

194 for gaseous samples is maintained at 110°C. Analytes were separated on a Rxi®-624Sil MS
195 (60m x 0.25mm i.d. x 0.25 µm film thickness), using helium as carrier gas with a constant
196 flow rate of 1 mL.min⁻¹. The initial temperature of the column was set at 45°C and hold for 3
197 min, followed by an increase of 5°C.min⁻¹ to 150°C and then by 20°C.min⁻¹ to 220°C hold for
198 2 min. The transfer line to the mass spectrometer was set to 250°C. The ion source
199 temperature was set to 250°C and the maximum ion time in the trap is of 25 ms. The ion trap
200 mass spectrometer worked with electronic impact as ionization mode (ionization energy of
201 70eV). The signal was collected with a full scan mode in the 15-300 u. mass range and a scan
202 event time of 0.16 s. For these analyses, the GC has been modified with the implementation of
203 a MicroJet Cryo-Trap MJT-1035E from Frontier Laboratories LTD on a Restek Rxi guard
204 column (20cm x 0.25 mm i.d.) to enhance detection sensitivity as well as chromatographic
205 resolution (Abou Mrad et al. 2020).

206 *1.3.GC-MS peak identification methodology*

207 The identification of VOC was performed by comparing retention time and mass
208 spectrum of the sample chromatographic peaks with the ones of analytical standards which
209 include hydrocarbons, aromatics and nitriles derivatives. Standards were pre-concentrated in
210 the loop of the VAHIA interface with the exact same protocol (Abou Mrad et al. 2014) than
211 the one used to recover VOC from irradiated ices. The confirmation of identifications of
212 hydrocarbon compounds was performed by comparing the mass spectrum of peaks detected
213 from the ¹²C₆H₆:HCN experiment with the ones detected in a ¹²C₆H₆ experiment, already
214 confirmed with ¹³C₆H₆ isotopic experiment (Mouzay et al. 2021b). For nitrogen compounds,
215 we performed a C₆H₆:HCN¹⁵ experiment. Hence, in this last experiment, fragment that
216 contain *x* N atom(s) will shift from *x* mass unity allowing to assess the number of nitrogen
217 atom constituting the considered molecule.

218

219 **I. Spectroscopic properties of C₆H₆:HCN ices**

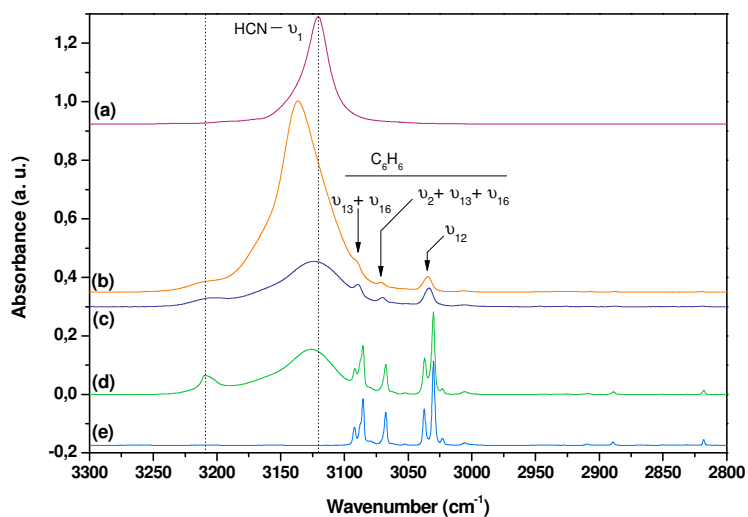
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221 The interaction of benzene with hydrogen cyanide was studied theoretically (Mateus et
222 al. 2011) and showed that linear or cyclic aggregates could be formed between benzene and
223 hydrogen cyanide molecules (benzene:nHCN with n ≤ 4). However, no spectroscopic
224 information relative to these aggregates has been reported, to our knowledge. Therefore, to
225 simulate different condensation scenarios that may occur in Titan's atmosphere depending on

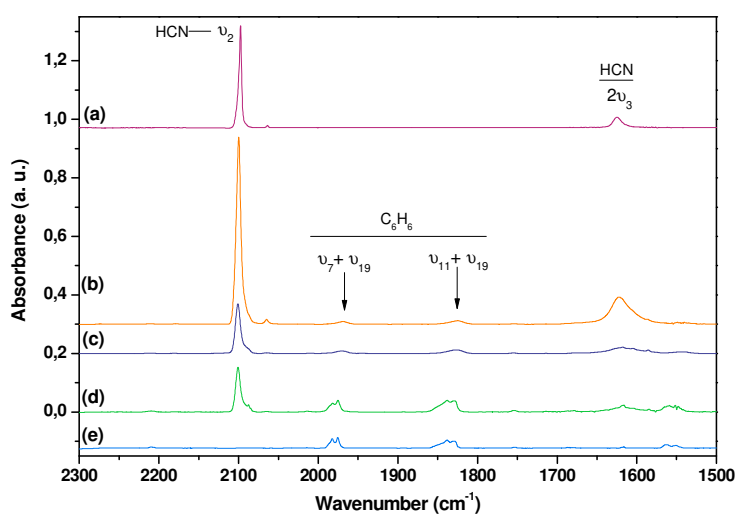
226 the climatic conditions, we considered **benzene/HCN ice ratios**. Afterwards, the considered
227 **benzene (C₆H₆)/HCN** ice will be designated by its mixing ratio (1:1, 1:4 and 4:1) The gaseous
228 mixture C₆H₆:HCN **has been** deposited at 70 K **to prevent desorption of benzene and HCN at**
229 **higher deposition temperatures. After the** deposition a rapid annealing at 105 K **was**
230 **performed in order to maximize the crystalline state of the benzene in the ice. A cooling down**
231 **to 70 K was then performed to limit the HCN desorption** In figure 1, the infrared spectra of
232 C₆H₆:HCN ices in the 1:4, 1:1 and 4:1 ratios were compared to pure C₆H₆ and HCN ices,
233 deposited with the exact same methodology. The $\nu_2 + \nu_{13} + \nu_{16}$ IR feature (which shape is not
234 affected by the change of chemical environment) of benzene were normalized from the
235 spectrum of the 1:4 ratio to the one of the 1:1 ratio. Similarly, the ν_1 IR feature of HCN in the
236 4:1 ratio was normalized to the one of the 1:1 ratio. Except a slight shift of band frequencies,
237 due to the presence of HCN, the shape of benzene features in the 4:1 mix is similar to the one
238 observed with the crystalline C₆H₆ ice (Mouzay et al. 2021a). Indeed, benzene is present in a
239 crystalline form in this 4:1 ratio whereas in the 1:1 and 1:4 mixes, the benzene is amorphous.
240 Hence, the increase of the HCN proportion in the mixtures induced a loss of organization of
241 the benzene network preventing its crystallization. The complexation between C₆H₆ and HCN
242 molecules also induces a shift of the ν_1 HCN mode toward high frequencies with respect to
243 the same ν_{CH} absorption band of the HCN monomer. This shift can be up to 16 cm⁻¹ in the
244 1:4 mixtures. Finally, we observe an additional band peaking is observed between 3200 and
245 3210 cm⁻¹. This band is not observed in the infrared spectrum of monomers and its position
246 depend on the C₆H₆ and HCN ratios. This band is characteristic of aggregates formation
247 between C₆H₆ and HCN. Wavenumbers of benzene and hydrogen cyanide vibrational modes
248 in each ice ratio are listed in table 1.

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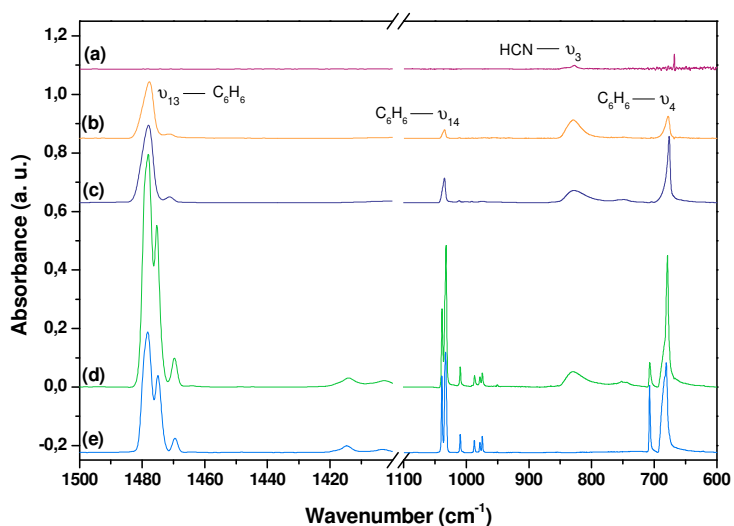
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254 Figure 1 – Enlarged regions of IR spectra of ices deposited at 70 K annealed to 105 K and
 255 followed by a cooling down to 70 K: (a) pure crystalline HCN ice; C₆H₆:HCN co-condensed
 256 (b) ratio 1:4, (c) ratio 1:1, (d) ratio 4:1 ; (e) pure crystalline benzene ice

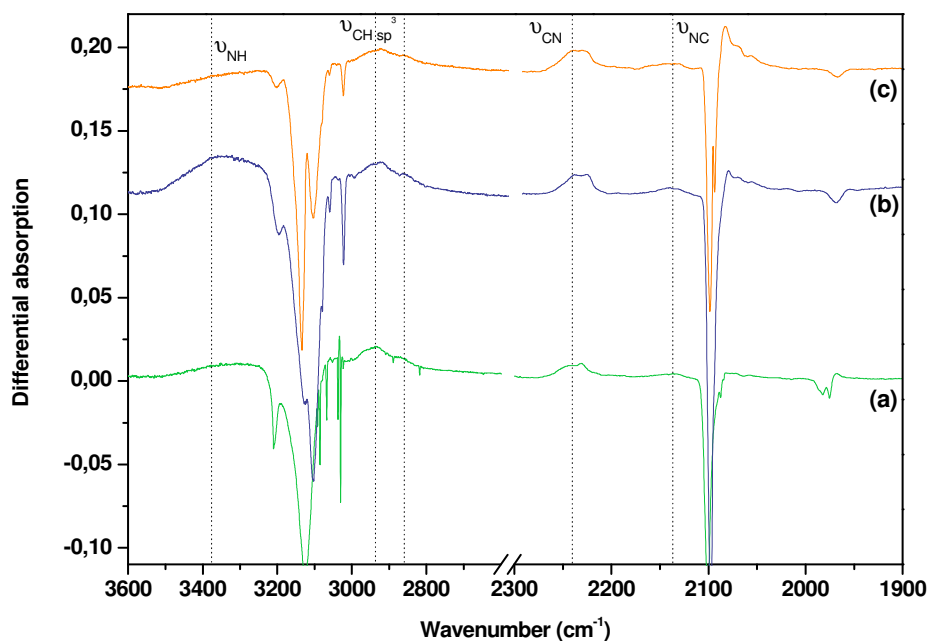
257 **II. Investigating C₆H₆:HCN ices photochemistry under long-UV photons**

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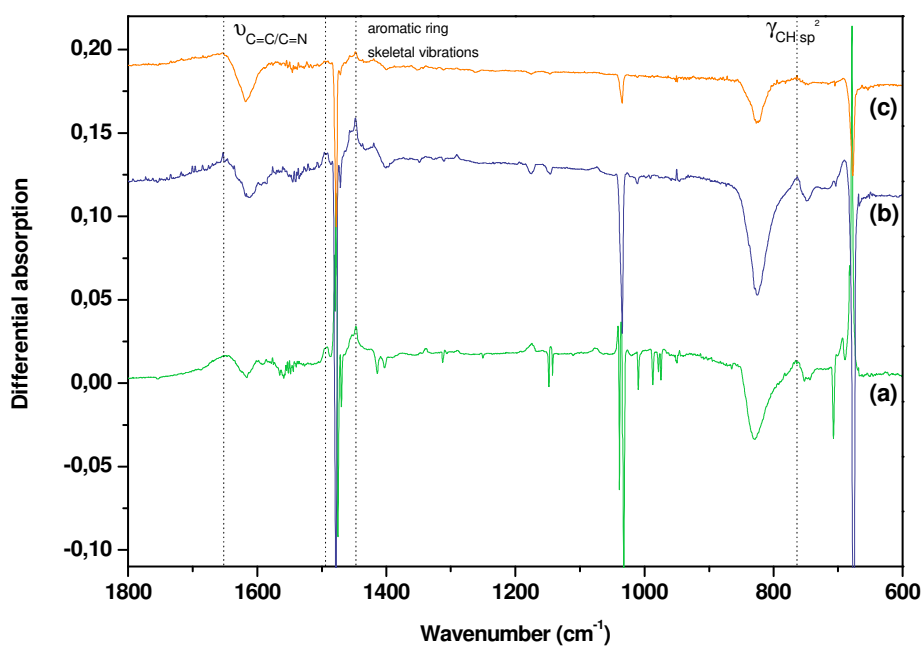
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The photochemistry of pure benzene or pure hydrogen cyanide ices in Titan's stratospheric-like conditions showed (Couturier-Tamburelli et al. 2018a, Mouzay et al. 2021a,b) that crystalline HCN ice is not photo-chemically active under mercury lamp radiations. Benzene ice demonstrated a weak photo-degradation rate, explained by the weak absorption of benzene in this wavelength range corresponding to singlet-singlet absorption ($^1B_{2u} \leftarrow ^1A_{1g}$) or singlet-triplet absorptions ($^3E_{1u} \leftarrow ^1A_{1g}$, $^3B_{2u} \leftarrow ^1A_{1g}$) (Dawes et al. 2017).

To simulate the solar photons reaching Titan's stratosphere (Gudipati et al., 2013; Lavvas et al., 2008; Wilson, 2004), each C₆H₆:HCN ice was irradiated with a mercury lamp. Whatever the considered ratio, results are similar. Consequently, we focused on C₆H₆:HCN 4:1 ice since its composition simulates that of Titan's High Altitude Stratospheric Polar (HASP) cloud. Ices were irradiated during 48 hrs at 70 K after the annealing to 105 K. During the photolysis, a depletion of infrared bands of benzene and hydrogen cyanide infrared absorption bands are observed, visualized through negative bands on the subtraction spectra (figure 2). While a pure ice of HCN is not reactive in these conditions (Couturier-Tamburelli et al. 2018a), in the case of benzene/HCN ice, HCN reacts with photo chemically-activated benzene to form new nitrogen-bearing compounds. Furthermore, with the photolysis of the 4:1 ice, a photo-reactivity similar to that of pure benzene ice is observed (Mouzay et al. 2021a). Indeed, characteristic bands of benzene polymers are observed, as well as increase of amorphous benzene ones demonstrating an amorphization of the ice during the photolysis (cf. figure 3). Finally, the absorption bands observed at 1341, 1078, 946, 898, 783 and 627 cm⁻¹ coming from direct benzene photolysis could be assigned to fulvene molecule, one of benzene's valence isomers (Mouzay et al., 2021a, c) cf. figure 4).



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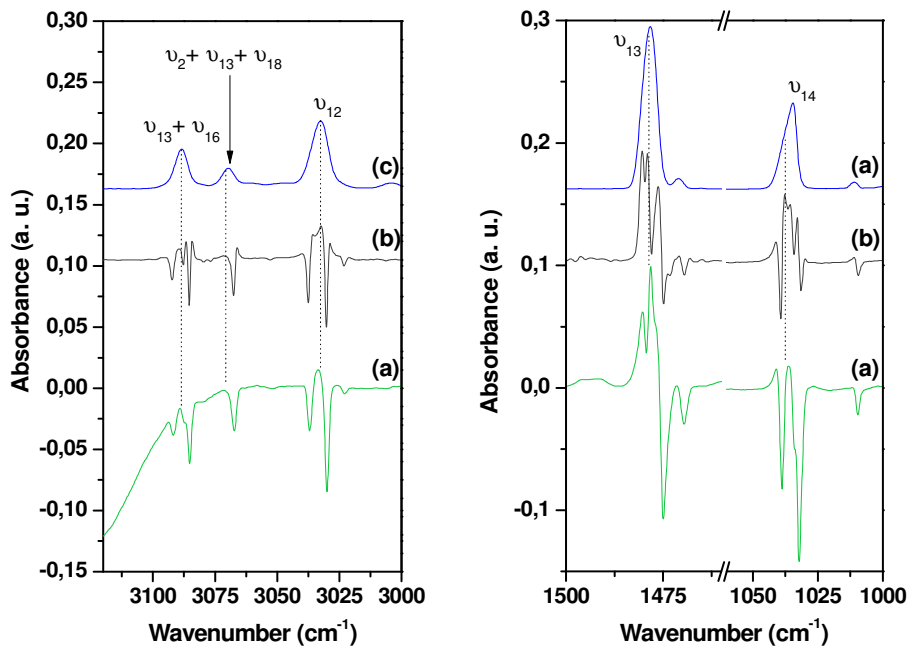


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284 Figure 2 - FTIR difference spectra (after - before photolysis **with the mercury lamp**)
 285 highlighting the formation of photoproducts from C₆H₆:HCN co-condensed ices at 70K : (a)
 286 ratio 4:1 ; (b) ratio 1:1 ; (c) ratio 1:4. Dot lines correspond to common newly produced
 287 structures.

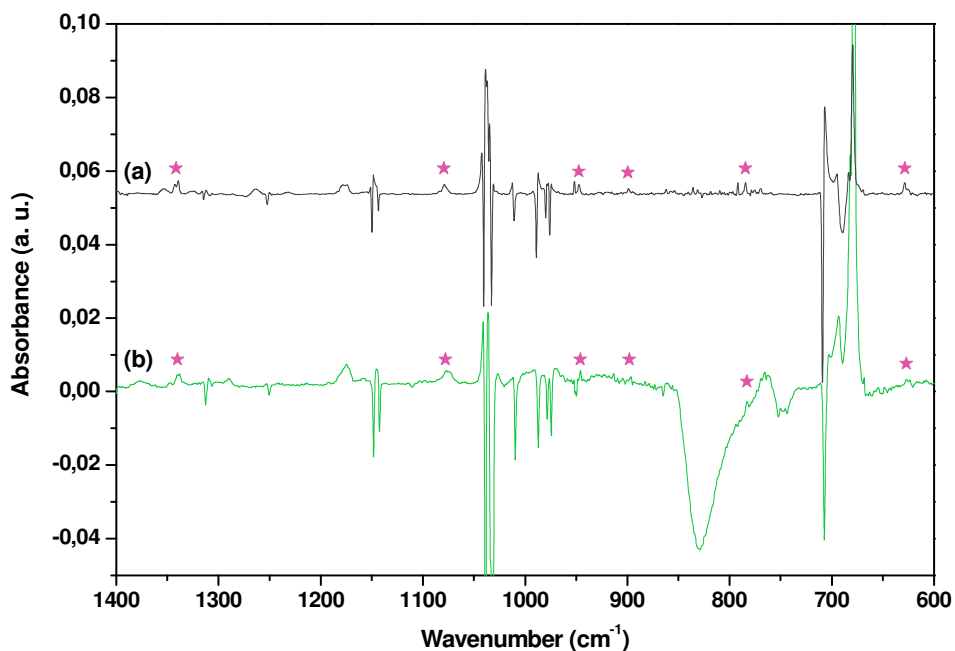
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291 Figure 3 – Comparison of the FTIR difference spectrum after-before irradiation (with the
 292 mercury lamp, 70 K) of a co-condensed ice $C_6H_6:HCN$ 4:1 (a) and a pure benzene ice (b) with
 293 the FTIR spectrum of a an amorphous benzene ice (50 K, c)
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296 Figure 4 – Comparison of the FTIR difference spectrum after-before irradiation (with the
 297 mercury lamp, 70 K) of a pure benzene ice (a) and a $C_6H_6:HCN$ 4:1 ice (b) on which the
 298 absorption bands assigned to fulvene are identified by stars
 299

300

2.1. Identification of chemical functions produced by photolysis

The decrease of benzene and hydrogen cyanide observed in infrared spectroscopy during the photolysis is accompanied by the apparition of new infrared features as displayed in figures 2, 3 and 4. Frequencies and assignments of the new spectral features are reported in table 2.

The peaks observed between 3000 and 2800 cm^{-1} are assigned to νCH aliphatic stretching modes. In all ices, a common maximum is observed at ~ 2966 and 2936 cm^{-1} , assigned to νCH_3 and νCH_2 asymmetric stretching modes (Imanaka et al. 2004; Sciamma-O'Brien et al. 2017). The shoulder at 2877 cm^{-1} , also common to all ratios can be assigned to νCH_3 symmetric stretching modes (Sciamma-O'Brien et al. 2017). The νCH aromatic stretching modes are not observed around 3100 cm^{-1} because of benzene absorption bands that mask this spectral region (figure 2).

In other spectral regions new absorption bands are observed, which confirms the formation of structures possessing aliphatic and/or aromatic CH groups. Indeed, peaks observed at 1447 cm^{-1} and 1453 cm^{-1} (figure 2) could both correspond to either skeletal vibration of an aromatic ring or a $-\text{CH}_3$ antisymmetric bending mode or $-\text{CH}_2$ scissor in-plane bending of aliphatic/aromatic structures (Sciamma-O'Brien et al. 2017). In all ice ratios, there is a 763 cm^{-1} peak that can be attributed to a sp^2 aromatic CH out-of-plane bending (quartet) (Carpentier et al. 2012).

The presence of nitrogenous functions can be assigned to two different bands of infrared spectra. The first bands at 3379 cm^{-1} observed in the 1:1 mix, and presumed in the others, would involve compounds with amine functions, corresponding either to $-\text{NH}_2$ asymmetric or to $-\text{NH}$ stretching modes (Imanaka et al. 2004). The second band around 2240 cm^{-1} , with two shoulders (located at 2244 and 2231 cm^{-1}), highlights the formation of nitrile functions. These features can be assigned to $-\text{C}\equiv\text{N}$ stretching modes of aliphatic and aromatic nitriles respectively (Carrasco et al. 2018; Sciamma-O'Brien et al. 2017). At lower frequencies, the growth of the broad band near 2145 cm^{-1} is characteristic of isonitrile functions (Carrasco et al. 2018). Shouldered to the infrared feature of the νCN stretching mode of HCN, a new band increases around 2085 cm^{-1} in the three ices. As already observed in the case of HCN adsorbed on HC_3N photolysis, this band can be assigned to the formation of cyano-based polymeric material (Couturier-Tamburelli et al. 2018a). In addition, the common band around

333 1650 cm^{-1} in the three mixes can be assigned to $\nu\text{C}=\text{C}$ stretching mode of alkene/aromatic
334 structures or $\nu\text{C}=\text{N}$ from imines derivatives (Sciamma-O'-Brian et al. 2017).

335 2.2. Identification of nitriles derivatives compounds

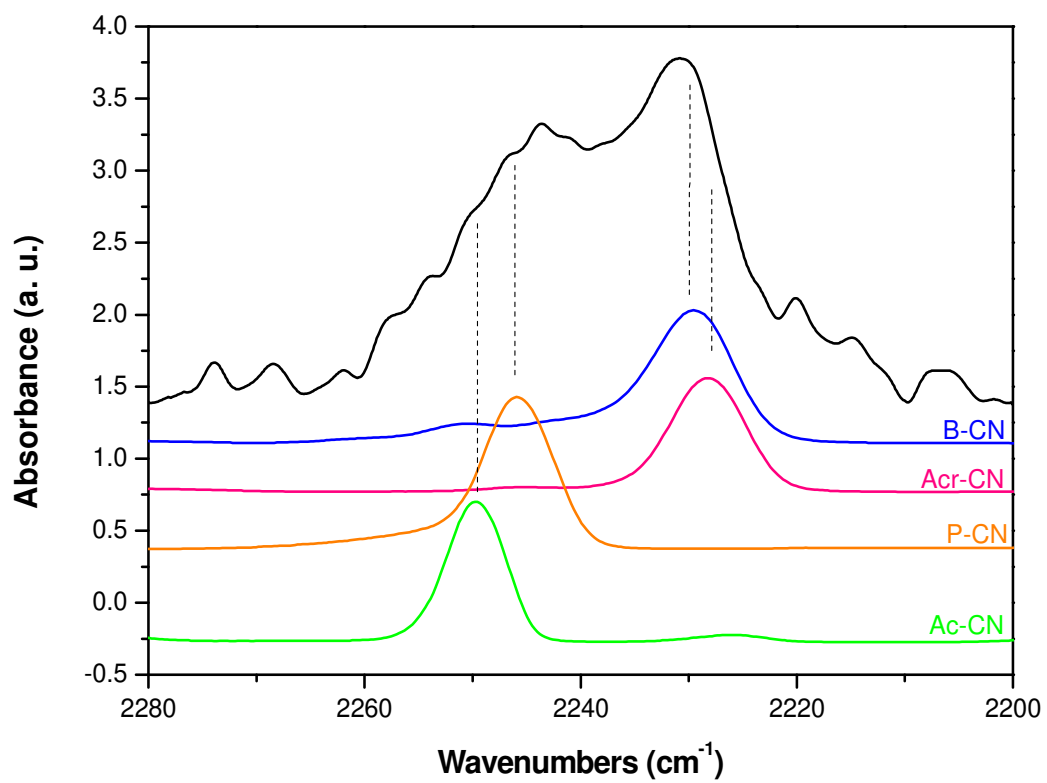
336

337 The analysis of infrared spectra recorded during the photolysis of $\text{C}_6\text{H}_6:\text{HCN}$ ices **show**
338 the formation of nitriles (aromatic and aliphatic) **due to the appearance** of a broad band
339 between 2270 and 2210 cm^{-1} , characteristic of **an** overlap of several absorption bands.

340 Acetonitrile, propionitrile, acrylonitrile and benzonitrile **are** specifically targeted because
341 they have been detected in Titan's atmosphere, except for benzonitrile which formation **is**
342 only foresee by photochemical models (Loison et al. 2019). However, its detection would be
343 the evidence of the chemical reaction between C_6H_6 and HCN in photolyzed ices. The
344 comparison of the infrared spectra resulting from each of these targeted molecules with the
345 difference spectrum after-before irradiation of the $\text{C}_6\text{H}_6:\text{HCN}$ 4:1 ice is displayed in figure 5.
346 Infrared spectra **related to the $\nu\text{C}\equiv\text{N}$ stretching mode dominated** nitrile ices. Hence, if these
347 nitriles are formed during the photo-processing of these ices, the intensity of the $\nu\text{C}\equiv\text{N}$ mode
348 will be the most intense among the other modes. It is important to highlight that other nitriles
349 derivatives, which are unknown yet, **could** be formed and **could** contribute to the spectral
350 feature displayed in figure 5. Frequencies of **reference spectra of** nitrile derivatives are also
351 reported in table 3 and compared to the ones produced during the photo-processing of the
352 $\text{C}_6\text{H}_6:\text{HCN}$ 4:1 ice.

353 The photo-produced absorption bands at 1491, 1447 and 1289 cm^{-1} are in good agreement
354 with the ones of the IR spectrum of **a benzonitrile ice. Other spectral features of photo-**
355 **produced could correspond to those of solid benzonitrile.** However, they are located in
356 spectral regions that reflect the polymerization of benzene, so their assignment is therefore not
357 possible. **Other bands are also observed and do not correspond to the ones of benzonitrile,** as
358 reported in table 3, indicating the formation of other nitrogen-bearing derivatives. Indeed, all
359 the absorption bands of acetonitrile were observed especially the one at 1452 cm^{-1} which
360 cannot be attributed to any of the three previous nitriles mentioned. However, below 1700 cm^{-1} ,
361 acrylonitrile and propionitrile possess few spectral features that present weak intensities.
362 Moreover, the figure 5 suggests that the contribution of acrylonitrile is weak from the
363 subtraction spectrum obtained after photolysis. Its comparison with the ones of propionitrile
364 and acrylonitrile **shows** a good correlation but does not allow to unambiguously confirm their
365 formation during the photolysis process.

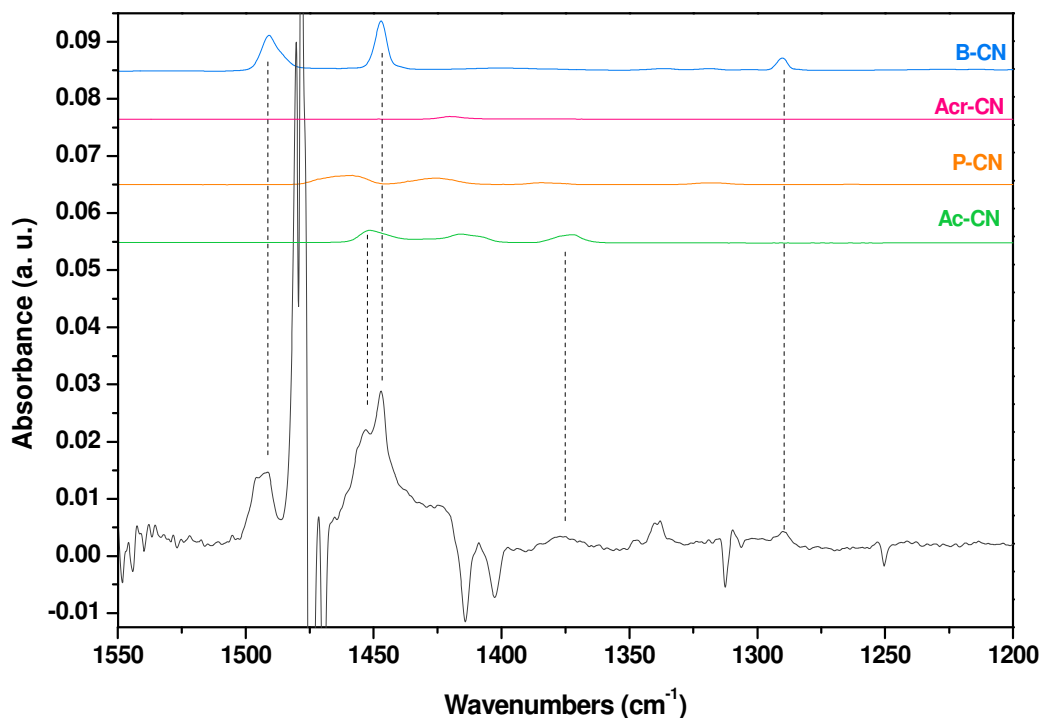
366



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371 Figure 5 - Comparison between FTIR difference spectrum (after - before photolysis with
 372 mercury lamp) (multiplied by a factor 4) from C₆H₆:HCN 4:1 co-condensed ice at 70 K
 373 (black) and the infrared spectra of solid acetonitrile (Ac-CN, green), propionitrile (P-CN,
 374 orange), acrylonitrile (Acr-CN, pink) and benzonitrile (B-CN, blue).

375

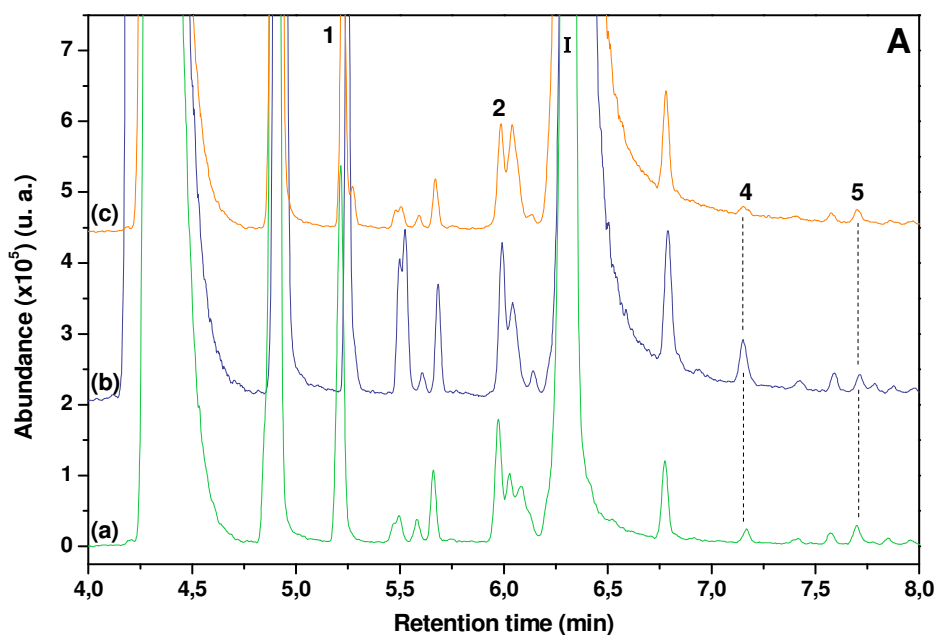
376 III. Identification of volatile organic compounds by GC-MS analyses

377

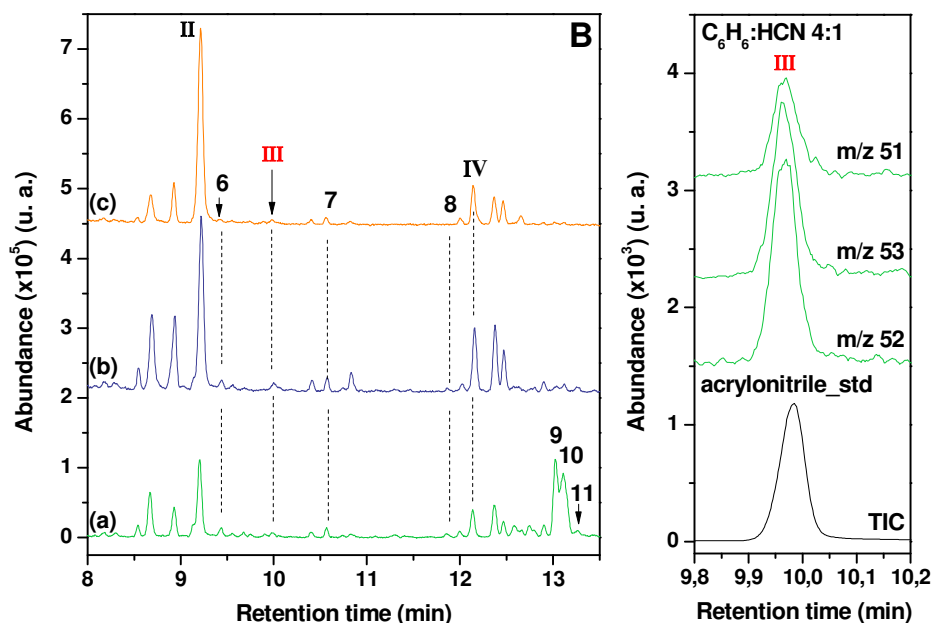
378 To obtain a better identification of volatile organic compounds (VOC) formed during
 379 photolysis experiments, the C₆H₆:HCN ices were warmed up to 300 K to trap and identify by
 380 VOC GC-MS. Unfortunately, we cannot rule out that during the annealing, other products
 381 than those formed in the solid phase during the photolysis process may be formed. However,
 382 the chromatographic experiments should allow us to confirm the formation of products
 383 identified by IR spectroscopy and to determine if these products are identical in the three ice
 384 ratio. The three TIC (Total Ion Current) chromatograms (figure 6) correspond to the three
 385 experiments, the ratio 4:1, 1:1 and 1:4 of C₆H₆:HCN ices, submitted to long-UV radiations
 386 and subsequently warmed. The identification of the VOC are realized thanks to the injection
 387 of standards in the same analytical conditions used for the analyzes of the gas phase of photo-
 388 processed C₆H₆:HCN ices. Three parameters from the TIC chromatograms allow the
 389 identification of organic compounds which are the concordance of retention times, mass
 390 fragmentation patterns as well as the presence of a mass shift related to the number of

391 nitrogen atoms in the N¹⁵ experiments. The identification of hydrocarbons is based on the
392 comparison with the GC-MS analyses of the photo-processing of pure benzene (^{12/13}C₆H₆)
393 ices (Mouzay et al., 2021b).

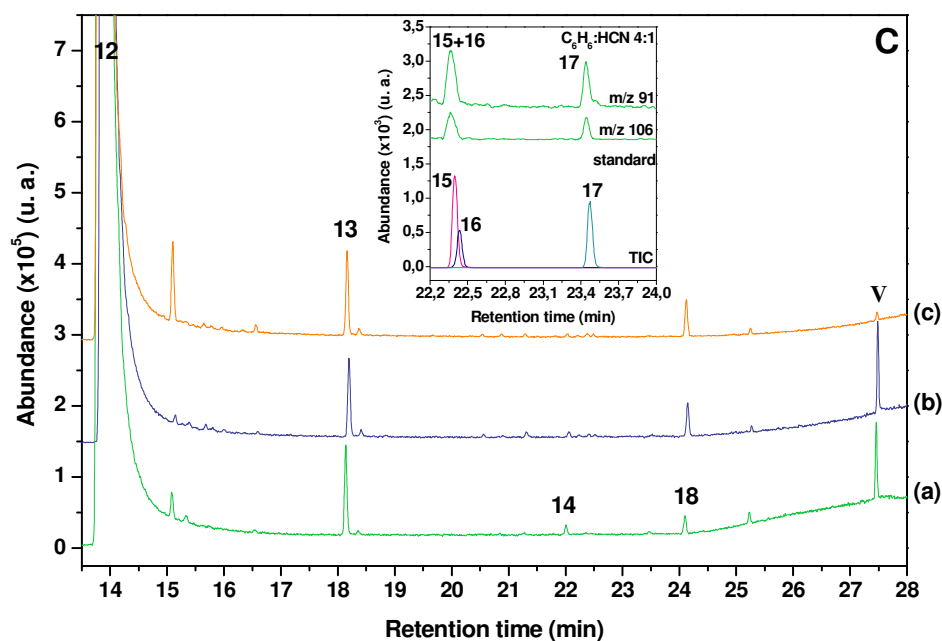
394 The peaks labelled from I to V correspond respectively to hydrogen cyanide, acetonitrile,
395 propionitrile, acrylonitrile and benzonitrile which confirm their identification obtained with
396 infrared spectroscopy after the photolysis process (cf. figures S2-S5, supplementary
397 information). Hydrocarbons already detected in the gas phase after the photoprocessing of a
398 pure benzene ice (Mouzay et al. 2021b) are also identified in the gas phase of C₆H₆:HCN ices
399 (labels 1-18). In relation to the IR spectra recorded during the photolysis experiment (cf.
400 figure 2), absorption bands, observed after the photo-processing of C₆H₆:HCN ices at 1447
401 and 1453 cm⁻¹ could be attributed to the formation of these volatile aromatic derivatives
402 (νC=C stretching modes), based on Sciamma O'Brien et al.'s work (2017).



403



404



405

406 Figure 6 - (A-B-C) TIC GC-MS chromatograms of the gas phases released during the
 407 warming-up of photo-processed **with mercury lamp** $C_6H_6:HCN$ co-condensed ices in a ratio
 408 4:1 (a), 1:1 (b) and 1:4 (c). The enlarged part (B) displays the ion extracted chromatogram of
 409 the three most intense fragment of acrylonitrile (bottom part) compared to the TIC
 410 chromatogram of the corresponding standard (top part). The enlarged part (C) displays the ion
 411 extracted chromatogram of the two most intense fragments of xylene isomers (top part) and
 412 are compare to the TIC chromatogram of the corresponding standard (bottom part) o-xylene,
 413 m-xylene and p-xylene. The peak at 22.4 min (15+16) corresponds to the co-elution of m- and
 414 p-xylene.

415

416

417 Discussion and conclusion

418 The formation and the composition of Titan's stratospheric ice clouds are **the result of**
419 **complex processes** within the framework of observations performed on the solar system's
420 bodies. Many works inferred the presence of nitrile species like HCN, HC₃N, CH₃CN, in the
421 upper atmosphere which diffuse to lower altitudes, while they are submitted to long-UV
422 photons. **These molecules potentially lead to the formation of aerosols by condensation**
423 **(Sciamma O'Brien et al.'s work 2017)**. Anderson et al (2017) reported the detection of
424 massive cloud around 250 km of altitude. Experimental simulation indicates that the CIRS-
425 detected HASP cloud's chemical composition is consistent with a C₆H₆:HCN ice containing ~
426 approximately 80% C₆H₆ and 20% HCN (Anderson et al 2017).

427 In this work, we aimed to simulate the photochemical aging in the stratosphere of benzene
428 condensed simultaneously with hydrogen cyanide. From the results obtained after the
429 photolysis of C₆H₆:HCN **ices**, at 70 K, with a **mercury** lamp, dynamic organic chemistry has
430 been demonstrated. Thanks to IR spectroscopy, **we identified in solid phase** benzonitrile and
431 acetonitrile and **we proposed as tentative attempt** propionitrile and acrylonitrile **molecules**.
432 Through the identification of these nitrile derivatives, we demonstrated a solid-state
433 consumption pathway relevant for Titan's stratospheric chemistry, triggered by the
434 photochemical activation of C₆H₆. These results demonstrated the possibility of a solid-state
435 formation pathway of nitrile derivatives from the photo-processing of different C₆H₆:HCN
436 ices and by extension from the CIRS-HASP cloud. As first mentioned theoretically by
437 Anderson et al. (2016), stratospheric clouds could thus participate to the formation of complex
438 molecules referring to this experimental work. **Of course, the results obtain in this study must**
439 **be taken cautiously because we simulate a simplified thin cloud exposed during 2.6 years**
440 **while the timescale on Titan are higher. Moreover, the thickness of the cloud is not taken into**
441 **account in our experimental work and the photochemical reactivity studied can only affect the**
442 **first layers of the cloud. We have also to take in mind that the surface of the cloud is regularly**
443 **renewed so that molecules detected here might be formed in different quantities on Titan.**

444 The temperature of Titan's stratosphere varies from 70 to 190 K at 79°S in July 2015
445 (Anderson et al 2018). To take into account the warming-up of the stratosphere reported by
446 Coustennis et al. (2019) in the region in which the HASP cloud has been detected, we
447 performed a slow warming-up of the irradiated ices, formed by co-condensation processes. **Of**
448 **course, because of our experimental constraints, the warming is performed up to room**
449 **temperature which is much higher than those reached in the Titan atmosphere** Hence, this step

450 allows to determine the role of the UV-Vis radiations-induced photochemical aging in the
451 **potential** formation of volatile photo-products in Titan's stratosphere. From the GC-MS
452 analyses performed on the volatile fraction that has sublimated from these photo-processed
453 ices, we **confirmed** the formation of acrylonitrile (Cui et al. 2009; Lellouch et al. 2010; Magee
454 et al. 2009) and acetonitrile (Cui et al. 2009) which have been detected in gas phase in
455 Titan's stratosphere. Mixing ratio of acetonitrile has been estimated to be 10^{-8} at 200 km
456 (Nixon et al. 2010 against 10^{-9} for acrylonitrile and propionitrile (Cordiner et al. 2015; Marten
457 2002; Palmer et al. 2017). In addition, we have **identified** benzonitrile that has not been
458 detected yet in Titan's atmosphere by IR spectroscopy (VIMS/CIRS instruments) or mass
459 spectrometry (INMS instrument). Its only astrophysical detection to date has taken place in
460 the interstellar medium (McGuire et al. 2018). In the stratosphere (around 200 km) according
461 to the photochemical model (radiative transfer) developed by Loison et al. (2019),
462 benzonitrile formation could result from the direct bimolecular reaction involving CN radical
463 with benzene. Therefore, this production in the lower atmospheric layers is weak since CN are
464 very efficiently consumed through reactions with CH_4 . Despite a strong dipole moment, its
465 weak abundance at these altitudes will make the benzonitrile detection difficult (Loison et al.
466 2019). In addition, hydrocarbons coming from the photo-degradation of benzene have been
467 detected and their production rates seem to be affected by the mixing ratio of the initial ice.
468 An exhaustive analysis of this effect will require additional experiments and will be
469 investigated in the future. However, our laboratory experiments demonstrate for the first time
470 that the massive HASP icy cloud's chemical composition could potentially be a source of a
471 rich production of this aromatic nitrile, among other nitriles derivatives or hydrocarbons.
472 **These molecules** might be released in gas phase in the stratosphere, when changing season
473 occurs, as observed at the south pole (Coustenis et al. 2019). These organics will probably
474 diffuse towards lower altitudes until they reach the surface. Hence, this work demonstrates the
475 importance of laboratory experiments to prepare future space missions, in particular the
476 Dragonfly space mission dedicated to the analysis of the organic layer that recovers Titan's
477 lakes and ground. It provides a list of molecules that may be detected during this future
478 mission. Moreover, the results brought by this experimental work could supply motivating
479 elements for future space missions dedicated in part to the specific study of the chemistry of
480 stratospheric clouds, as reported by Nixon et al. (2020).

481

482 **Acknowledgements**

483 This work has been funded by the French national program “PNP”, Programme de Physique
484 et Chimie du Milieu Interstellaire (PCMI, INSU), and the Centre National d’Etudes Spatiales
485 (CNES, exobiology program). It was also supported by the French Agence Nationale de la
486 Recherche (VAHIIA grant ANR-12-JS08-0001 and RAHIA_SSOM grant ANR-16-CE29-
487 0015).

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585

Table 1

586

Positions, assignments and band strength of infrared absorption bands of C₆H₆ and HCN in the co-condensed ices at 70 K after annealed to 105 K

Assignments [a, b]		Wavenumbers (cm ⁻¹)					
		This work			Mouzay et al. (2021a)		This work
		C ₆ H ₆ :HCN 4:1	C ₆ H ₆ :HCN 1:1	C ₆ H ₆ :HCN 1:4	Pure C ₆ H ₆ ice (70 K after annealing)	Pure C ₆ H ₆ ice (amorphous)	Pure HCN ice (70 K after annealing)
C ₆ H ₆	v ₁₃ + v ₁₆ , e _{1u} CH aromatic stretching	3092 3086	3089	3090	3091 3084	3088	-
	v ₂ + v ₁₆ + v ₁₈ , e _{1u}	3068	3070	3071	3067	3070	-
	v ₁₂ , e _{1u}	3037 3030	3034	3035	3036 3029	3032	-
	v ₁₃ , e _{1u} C=C aromatic stretching	1478 1475	1478	1478	1477 1474	1477	-
	v ₁₄ , e _{1u} C-H in-plane bending	1039 1032	1034	1035	1038 1032	1034	-
	v ₄ , a _{2u} C-H out of plane bending	679	676	678	680	674	-
	HCN	v ₁ , Σ ⁺ , CH stretching	3126	3124	3137	-	-
v ₂ , Σ ⁺ , C≡N stretching		2101	2101	2100	-	-	2097
2v ₃ , π		1616	1618	1622	-	-	1625
v ₃ , π, CH bending		829	828	828	-	-	826
C ₆ H ₆ :HCN	C _{sp} H stretching	3210	3202	3202	-	-	-

587 [a] Bertie & Keefe, 2004; Mair & Hornig, 1949 ; [b] Bernstein et al. 1997; Gerakines et al. 2004

Table 2
Positions, assignments of new infrared absorption bands obtained during the photolysis at 70 K of C₆H₆:HCN mixes ($\lambda > 230\text{nm}$)

		Wavenumbers (cm ⁻¹)			References	
		This work				
Assignments	C ₆ H ₆ :HCN 4:1	C ₆ H ₆ :HCN 1:1	C ₆ H ₆ :HCN 1:4			
592	Refere					
593	nces					
		asymmetric stretching -NH ₂ /-NH- stretching	3353	3379	3355	a
594	[a]	asymmetric stretching CH ₃	2966	2966	2966	a, b
595	Imanak	asymmetric stretching CH ₂	2936	2936	2935	a, b
596	a et al.	symmetric stretching CH ₃	2877	2877	2877	a, b
597	2004 ;	-C≡N stretching (aliphatic nitriles)	2244	2244	2246	a, c, d
598	[b]	-C≡N stretching (aromatic nitriles)	2231	2232	2237	a, d
599	Sciamm	-N≡C stretching (aliphatic isonitriles)	2143	2146	2140	c, d
600	a-					
601	O'Brien	C=C stretching (alkene/aromatics)/C=N stretching				
602	et al.	(imines)	1653	1653	1653	b
603	2017 ;	C=C stretching (alkene/aromatics)/	1600-1565	1598-1550	1590-1550	
604	[c]	aromatic ring skeletal vibration	1491	1491	1491	b, e
605	Carrasc	aromatic ring skeletal vibration and -CH ₃ (as) bending/-				
606	o et al.	CH ₂ scissor in plane bending (alkane/aliphatic and	1453	1457	1457	b, e
607	2018 ;	aromatic)				
608	[d]					
609	Mutsuk	aromatic ring skeletal vibration and -CH ₃ (as) bending/-				
610	ura &	CH ₂ scissor in plane bending (alkane/aliphatic and	1447	1448	1447	b
611	Akita	aromatic)				
612	1999 ;	ν C-N stretching (aromatic amines)	1289	1290	-	b
613	[e]	in plane bending =CH (alkene/aromatic)/ ν C-N	1073	1073	-	b
614	Strazzul	out of plane bending -CH sp ² (aromatic)	798-754	798-754	-	b, e
615	la &					
616	Barata					

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Table 3

Experimental new infrared bands obtained during the photolysis of C₆H₆:HCN (4:1) mix compared with those of nitriles ice recorded at 70 K

Acetonitrile	Propionitrile	Acrylonitrile	Benzonitrile	C₆H₆:HCN
CH₃CN	C₂H₅CN	C₂H₃CN	C₆H₅CN	4:1
	2952			2966
2940				2936
	2890			2877
2248	2245			2278-2212
		2227	2231	
			1598	
			1582	1600-1565
			1572	
			1489	1491
1452	1460*			1453
			1445	1447
	1425			1424
1415*		1413*		
	1316*			
			1289	1289
			1192*	
			1178*	
			1161*	
	1074		1072	1073
1037*			1026*	
	1003*	976*		
916				
771	782	759	758	795-754

* absorption bands masked by the IR features of benzene.

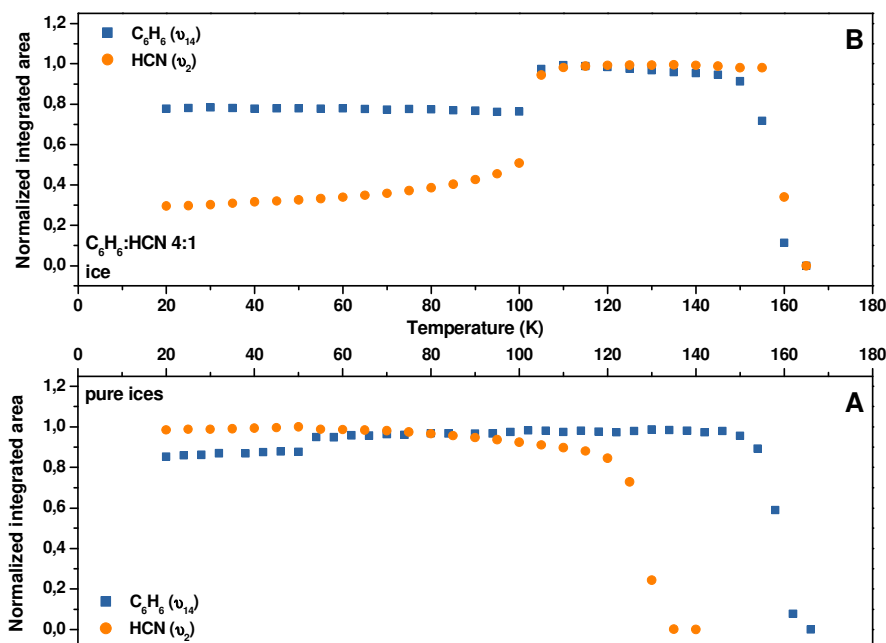
Table 4 – List of volatile photoproducts identified by GC-MS - coming from the photo-processing of co-condensed ices C₆H₆:HCN 4:1/1:1/1:4 at 70 K subsequently warmed-up to 300 K. The comparison with identifications reported in the literature is also mentioned.

Products identified		Peak identification	Identification	Detected in laboratory experiments	
				High altitude conditions	Low altitude conditions
C3	propene (C ₃ H ₆)	1	NIST	b,f,c,d,e,f	g, i
C4	but-2-ene (C ₄ H ₈)	2	NIST	a,b,c,e	g
	but-1-en-3-yne (C ₄ H ₄)	3	NIST	b,c,e	g
	diacetylene (C ₄ H ₂)	4	NIST	c,e	g, i
C5	pentane (C ₅ H ₁₂)	5	standard	a,b,c,d,f	g
	2-methyl-buta-1.3-diene (C ₅ H ₈)	6	NIST	no	g
C6	hexane (C ₆ H ₁₄)	7	standard	a,b,c	g
	methylcyclopentane (C ₆ H ₁₂)	8	NIST	no	g
	fulvene ? (C ₆ H ₆)	9	NIST	no	no
	C ₆ H ₆ isomer	10	NIST	no	no
	cyclohexane (C ₆ H ₁₂)	11	standard	no	g
	benzene (C ₆ H ₆)	12	standard	c	g
C7	toluene (C ₇ H ₈)	13	standard	c,e	g
C8	ethylbenzene (C ₈ H ₁₀)	14	standard	no	g
	m-xylene (C ₈ H ₁₀)	15+16	standard	no	g
	p-xylene (C ₈ H ₁₀)		standard	no	g
	o-xylene (C ₈ H ₁₀)	17	standard	no	g
	styrene (C ₈ H ₈)	18	standard	no	g,h
C1	hydrogen cyanide (HCN)	I	standard	a,b,c,d,e,f	i,j
C2	acetonitrile (CH ₃ CN)	II	standard	a,b,c,d,e,f	h,i,i
C3	propionitrile (C ₂ H ₅ CN)	III	standard	a,b,c,d,e	h,i
	acrylonitrile (C ₂ H ₃ CN)	IV	standard	a,b,c,d,e	i,j
C7	benzonitrile (C ₆ H ₅ CN)	V	standard	no	no

References : [a] Coll et al. 1999 ; [b] Ramírez et al. 2005, 2001 ; [c] Navarro-González et al. 2001 ; [d] Gautier et al. 2011; [e] Torokova et al. 2015 ; [f] anaka & Smith, 2010 ; [g] Tran et al. 2005; [h] Jacovi et al. 2010 ; [i] Hörst et al. 2018; [j] Clarke 2000

1 **Supplementary material**

2



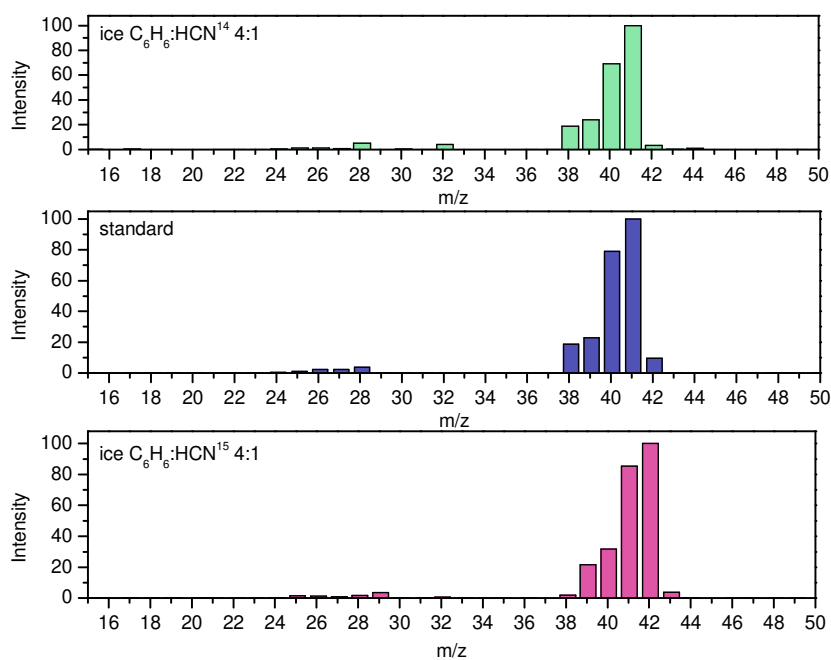
3

4 Figure S1 - Comparison of the evolution of the normalized integrated areas of the IR absorption bands
 5 related to benzene ν_{14} and HCN ν_2 vibrational modes in: (A) in pure ices and (B) in a C_6H_6 :HCN co-
 6 condensed ice (4:1 ratio), as a function of temperature ($\beta = 1 \text{ K}\cdot\text{min}^{-1}$). Each of these ices was initially
 7 deposited at 20 K and then warmed-up until complete desorption visualized by the total disappearance of
 8 their spectral features from the IR spectra recorded regularly during this step. In the case of pure ices,
 9 desorption of HCN begins as early as 80 K, while that of benzene is observed from 130 K (A). In the case
 10 of the C_6H_6 :HCN co-condensed ice (B), the sublimation of benzene, started from 110 K, leads to that of
 11 HCN at 150 K. It should also be noted that the crystallization temperature is modified by this interaction
 12 as the transition from an amorphous to a crystalline phase is observed simultaneously for C_6H_6 and HCN
 13 between 100 and 105 K, against $\sim 55 \text{ K}$ for C_6H_6 in a pure ice.

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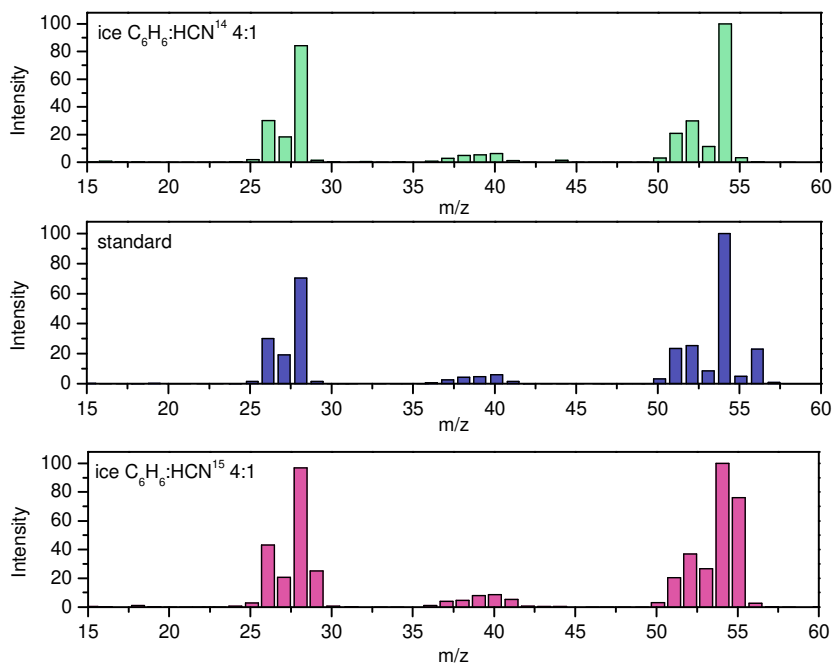
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18 Figure S2 - Mass spectra of acetonitrile (peak II) from C₆H₆:HCN¹⁴ 4:1 ice (top, green), standard
 19 (middle, blue) and C₆H₆:HCN¹⁵ 4:1 ice (bottom, pink)

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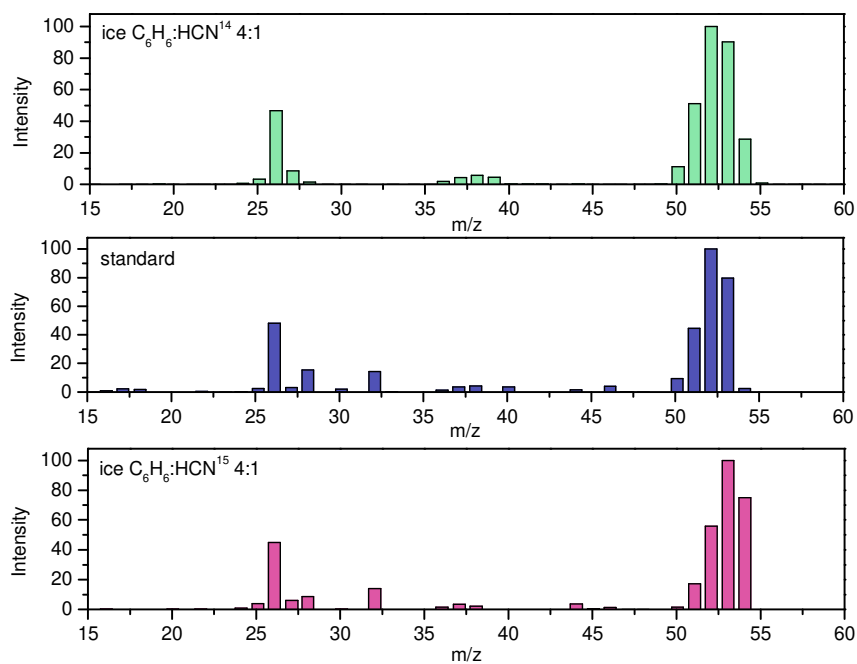


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22 Figure S3 - Mass spectra of propionitrile (peak III) from C₆H₆:HCN¹⁴ 4:1 ice (top, green), standard
 23 (middle, blue) and C₆H₆:HCN¹⁵ 4:1 ice (bottom, pink)

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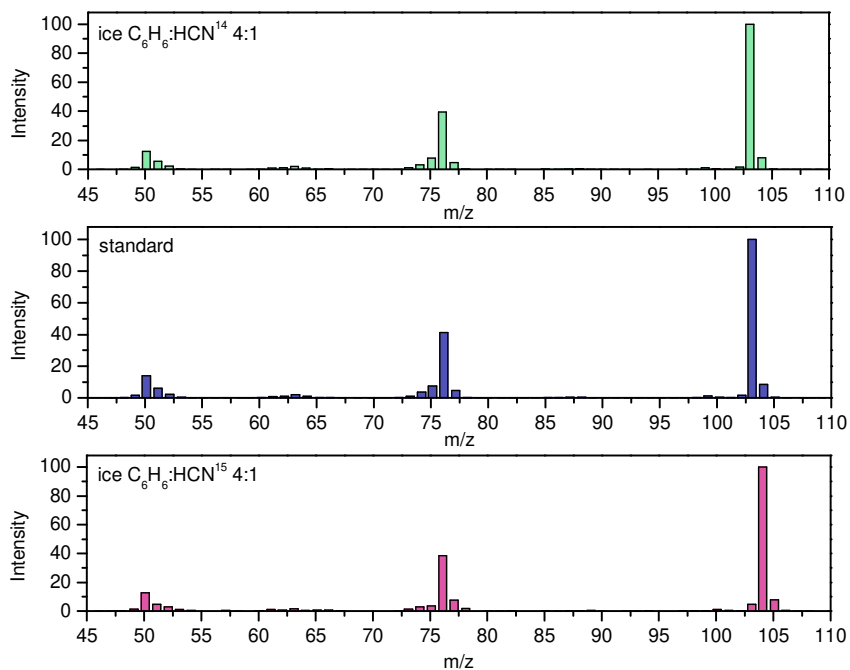
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27 Figure S4 - Mass spectra of acrylonitrile (peak IV) from C₆H₆:HCN¹⁴ 4:1 ice (top, green), standard
 28 (middle, blue) and C₆H₆:HCN¹⁵ 4:1 ice (bottom, pink)

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31 Figure S5 - Mass spectra of benzonitrile (peak V) from C₆H₆:HCN¹⁴ 4:1 ice (top, green), standard
 32 (middle, blue) and C₆H₆:HCN¹⁵ 4:1 ice (bottom, pink)