

Experimental simulation of Titan's stratospheric photochemistry: benzene (C₆H₆) ices

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Abstract

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Key points: Titan, benzene ice, photochemistry

Abstract

We performed laboratory experiments to the photochemical evolution induced by long-UV radiations of benzene ices in Titan's atmosphere. The aim of this study was to investigate if photo-processed benzene ices could lead to the formation of aerosols analog to the ones observed in Titan's stratosphere. Prior to that, spectroscopic properties of amorphous and crystalline benzene ices were studied as a function of the temperature, using infrared spectroscopy. UV photolysis experiments ($\lambda > 230\text{nm}$) of benzene ices lead to the formation of volatile photo-products of which fulvene is identified and of a residue, dominated by νCH IR features which demonstrate that pure aromatic-based polymeric structures are not sufficient to explain the composition of Titan's haze layer present in the stratosphere. However, we provide a characterization of long-UV-induced benzene-containing aerosols analogs, which will contribute to Titan's surface organics layer which is of prime interest in the context of the future Dragonfly space mission.

Plain Language Summary

Titan, often compared to the early Earth is the only moon in the solar system to have a dense atmosphere mainly composed of nitrogen and methane. In the upper part of the atmosphere ($>1000\text{ km}$), UV photons, photoelectrons, energetic ions and magnetospheric electrons induce the dissociation and the ionization of N_2 and methane. These reactions lead to the formation of complex organic molecules including hydrocarbons as benzene and aerosols of the high atmosphere (an organic haze responsible of Titan's brownish color), which are submitted to different UV radiation classes depending of the altitude. Therefore, during their sedimentation to the surface, these organic photoproducts are known to be modified. Once the tropopause reached, molecules like C_6H_6 condense and evolve under long UV radiations to contribute to aerosol formation.

Introduction

Ended in September 2017, Cassini-Huygens space mission permitted a wide exploration of the atmosphere of Saturn's largest moon, Titan and brought much information on its chemical composition (A. Coustenis et al., 2010; Vinatier et al., 2010). However, lots of data related to Titan's haze still remains to be analyzed, in particular, spectroscopic ones. The interpretation of data coming from Cassini's observations, Voyager and ground-based ones have nevertheless permit to put in evidence hundreds of complex organic compounds such as hydrocarbons [ethane (C_2H_6), acetylene (C_2H_2), ethylene (C_2H_4), methylacetylene (C_3H_4), propane (C_3H_8), propene (C_3H_6), diacetylene (C_4H_2)], nitriles [hydrogen cyanide (HCN), cyanoacetylene (HC_3N) and cyanogen (C_2N_2)] (Coustenis et al., 2007; Hanel et al., 1981; Kunde et al., 1981; Nixon et al., 2013)... and aerosols as end products which form haze layers (Wilson & Atreya, 2003) in the atmosphere. All these organic particulates/molecules have been produced by the dissociation and ionization of the main atmospheric constituents, N_2 and CH_4 (Lavvas et al., 2013; Liang et al., 2007; Waite et al., 2007). Based on their photochemistry, theoretical models predict the formation of simple molecules and that of benzene, one of the most complex molecule observed up to now (Krasnopolsky, 2014; Vuitton et al., 2006; Wilson & Atreya, 2003; Yung et al., 1984).

Detected for the first time by ISO (Athena Coustenis et al., 2003), the presence of benzene vapor in Titan's atmosphere has been confirmed by the Cassini Composite Infrared Spectrometer (CIRS) and the Cassini Ion and Neutral Mass Spectrometer (INMS) from Cassini mission (Athena Coustenis et al., 2003, 2007; Waite et al., 2007). *In situ* measurements performed over the altitude allowed to determine benzene mixing ratio (Coustenis et al., 2007; Cui et al., 2009; Koskinen et al., 2011). It decreases with the altitude indicating a high altitude production and a low altitude sink (Vuitton et al., 2008; Waite et al., 2007; Wilson & Atreya, 2004; Yoon et al., 2014) which is partially explained by condensation process as it is the main loss process of organics in Titan's atmosphere (Anderson C. M. et al., 2016; Anderson et al., 2018; De Kok et al., 2007; C. A. Griffith et al., 2006; Khanna et al., 1987; P. Lavvas et al., 2011; Mayo & Samuelson, 2005; R. E. Samuelson et al., 1997; Robert E. Samuelson et al., 2007; Robert E. Samuelson & A. Mayo, 1991) Indeed, vapor condensation of organics occurs in the lower part of the stratosphere where the temperature diminishes, at an altitude which depends, for a given compound, on several parameters such as its saturation vapor pressure and abundance or the local temperature, resulting in the formation of microscopic icy particles or aerosols (Lavvas et al., 2010, 2011). Using cloud microphysics and radiative transfer models, different groups (Barth, 2017; P. Lavvas et al., 2011) published the condensation profile and cloud formation of the different gaseous species present in the stratosphere. They both proposed the

72 condensation of benzene around 85km for temperature of about 130 K from their models based on the
73 temperature profile measured during the descent of Huygens in the atmosphere (Fulchignoni et al., 2005)
74 and vapor abundances measured at north latitudes (Coustenis et al., 2010; Vinatier et al., 2015). However,
75 seasonal dynamics can perturb ices formation such as vertical dramatic cooling episodes
76

77 Benzene is a particularly important molecule because it is suspected to have a key role in the formation of
78 polycyclic aromatic hydrocarbons (PAHs), polyphenyls or polycyclic aromatic heterocycles (PANHs) or
79 even aerosols at high altitude, e.g. (Delitsky & McKay, 2010; Gautier et al., 2017; S Lebonnois, 2002;
80 Mahjoub et al., 2016; Waite et al., 2007). In fact, Vuitton et al. (2008) have suggested that benzene is
81 formed in the highest atmospheric layers (>900 km) from ion molecule reactions and diffuses downward
82 where it induces under photolysis the formation of phenyl radicals ($C_6H_5^\bullet$) known to be at the origin of a
83 rich production of aromatics. A recent study has upgraded benzene photochemical reactions network,
84 highlighting the importance of neutral and ionic reactions for the production of aromatic species such as
85 toluene ($C_6H_5CH_3$) or ethylbenzene ($C_6H_5C_2H_5$) (Loison et al., 2019). In addition, some studies have been
86 performed to investigate the influence of C_6H_6 in Titan's aerosol production either theoretically (Delitsky
87 & McKay, 2010; P. Lavvas et al., 2011; Sébastien Lebonnois, 2005) or experimentally (Gautier et al.,
88 2017; Sciamma-O'Brien et al., 2014, 2017; Sebree et al., 2014; Trainer et al., 2013; Yoon et al., 2014) by
89 incorporation of benzene in a N_2/CH_4 mixture using discharged plasmas or far-UV radiations. Hence, the
90 role of gas phase benzene photolysis in Titan's atmosphere is well documented while the one that it could
91 playing the stratosphere in the aerosol production has not yet been investigated experimentally to our
92 knowledge. Previous experimental works have focused on understanding the long-UV solar photons-
93 induced aging process of nitriles ices formed under stratospheric-like conditions in laboratory (Couturier-
94 Tamburelli et al., 2015a, 2018; Gudipati et al., 2013). The authors demonstrated the formation of
95 polymeric residues which infrared features correspond, for most of them, to the ones observed by CIRS
96 and VIMS instruments of the aerosols layer present in the stratosphere of Titan. However, no study has
97 been performed on the fate of hydrocarbon ices at these altitudes. As benzene is expected to condense
98 below 100 km, that are altitudes mainly crossed by solar UV photons $\lambda > 230$ nm (Gudipati et al., 2013;
99 Lavvas et al., 2008; Wilson, 2004), understanding the evolution of pure benzene ices submitted to low-
100 energy photons is essential to identify subsequently its contribution to the formation of aerosols that will
101 participate to the organic layer that recovers Titan's surface. Therefore, in this work, we conducted
102 laboratory experiments to perform the photolysis of pure benzene ices, under photons at $\lambda > 230$ nm in
103 order to help to understand the composition of photo-produced aerosols in the stratosphere. In particular,
104 we want to highlight the role of benzene ices photolysis in the production of stratospheric aerosols by

comparing our spectroscopic data with the ones of the stratospheric aerosol layer acquired by VIMS instrument, before this episode of exceptional climatic conditions.

Experimental Details

Benzene (for HPLC, assay $\geq 99.9\%$, from Sigma-Aldrich) was used after purification by vacuum distillation by several freeze-pump-thaw steps with the help of several liquid nitrogen baths. As well, the absence of impurities (H_2O , CO_2) in each benzene ice film deposited is checked by IR spectroscopy. No trace of H_2O or CO_2 is observed in our experiments. Benzene was deposited from a glass-line on a gold-plated surface, which temperature was controlled between 16K to 300K with a closed-cycle helium refrigerator and maintained using a model 21 CTI cold head cryostat, a resistive heater and a Lakeshore 331 temperature controller, within a high vacuum chamber (10^{-8} mbar). Each deposited ice sample corresponds to a quantity of about 20 μmol of benzene. Samples were warmed-up with a heating rate between 0,5 and 2 $\text{K}\cdot\text{min}^{-1}$. The IR spectra were recorded in reflection-absorption mode in the mid-infrared region between 4000 and 600 cm^{-1} using a Bruker Tensor 27 Fourier transform infrared spectrometer with DTGS detector (Butscher et al., 2015). Each spectrum was averaged over 100 scans during photolysis experiment and over 500 scans for the vibrational analysis of the photopolymer, with a resolution of 1 cm^{-1} , except for the background averaged over 300 scans with the same resolution.

Photolysis experiments have been performed using an Oriel 500W high-pressure mercury lamp ($\lambda=200\text{--}2500$ nm) with discrete Hg lines in the UV-Vis region between 200 and 600 nm, where most of the photon flux of 2.34×10^{16} $\text{photon}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ (~ 13 $\text{mW}\cdot\text{cm}^{-2}$) resides. The photolysis time (48 hours) was chosen according to three criteria: 1) the duration must correspond to a period of time in which benzene ices were detected in the stratosphere (here, considering a solar flux of $\sim 10^{14}$ $\text{photons}\cdot\text{cm}^{-2}\cdot\text{s}^{-1}$ at 200 km on Titan, it corresponds to 468 days (1.3 year) on Titan) 2) due to the weak electronic absorption of benzene at these wavelengths, the duration must be sufficiently long to observe spectral modification using a low-sensitivity *in situ* technique, i.e., IR spectroscopy and 3) to obtain only the formation of primary products.

We performed two different experiments: the first one fairly reproduces the condensation sequence of ices in Titan's stratosphere, i.e. vapor benzene was deposited on the sample holder kept at 130K. This temperature was maintained at 130 K in order to obtain the crystalline phase for few hours and then cooled down to 70 K to prevent any desorption of benzene. The second experiment consisted in depositing vapor benzene at 70 K and was then followed by an annealing to 130K before to cool down at 70K. These two experiments have been done in order to see if any differences are observed in the crystallization process on the infrared spectrum.

Sublimation is supposed to happen at any temperature in a high vacuum chamber because when an ice is formed, it is in equilibrium with the vapor phase. Since the chamber has turbo pumps, that vapor can continuously be pumped away, causing the ice to sublime more and more over time. Nevertheless, this is a slow process at lower temperatures and this phenomenon is negligible at 70K, a temperature corresponding to the lowest one reached in the Titan stratosphere. Furthermore, this choice of this temperature is all the more judicious than we want to study nextly co-condensed ices with different molecules i.e. HCN which starts sublimation at around 80 K under our experimental conditions. In both experiments, benzene is crystal prior to the photolysis step and the irradiation of icy benzene leads to the same photo-chemical activity of this molecule in our experimental conditions. Likewise, this temperature is sufficiently low to trap in the ice the volatile photo-produced fraction that will be characterized in a future work. In these conditions of temperature (70 K), the subsequent benzene loss rate will only be attributed to photochemical processes avoiding any other competitive pathway as sublimation. The evolution of the solid samples was monitored by *in situ* infrared spectroscopy. After irradiation, ice samples are warmed-up to 300 K with the cryogenic system switched-off in order to sublime the volatiles photo-produced. The refractory organic residue is retained on the surface of the substrate.

I. Benzene ice

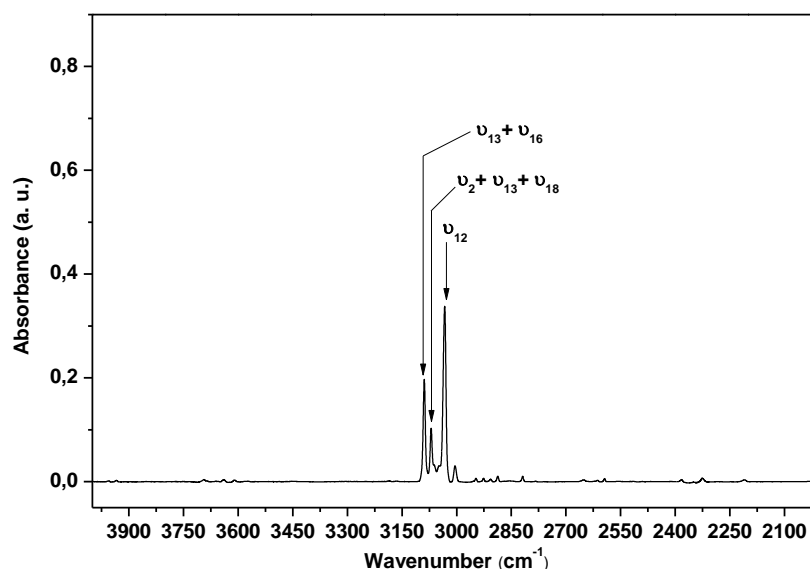
As the infrared data are poorly documented in the literature, it is necessary to study the thermal evolution of benzene in our experimental conditions to determine the evolution of the shape of its spectral features and its desorption/condensation temperature.

X-ray analysis supplemented by Fourier transform methods showed benzene crystal structure as orthorhombic, with four molecules per unit (Bacon G. E. et al., 1964; Cox et al., 1958), which crystallographic parameters have also been determined. In this configuration, benzene molecules pack together like sheets of six-toothed gear wheels (Cox, 1958; Cox et al., 1958). First member of aromatic ring family, benzene belongs to D_{6h} group and possesses 30 normal vibrational modes. Only two of them, namely A_{2u} (non-degenerate) and E_{1u} (degenerate), are infrared-active. However, physical state of benzene can induce the activation of other vibrational modes (Halford & Schaeffer, 1946; Hollenberg & Dows, 1962), in particular for crystalline benzene, explained by the development of intramolecular forces. Solid benzene ice infrared spectrum was first studied by Halford and Schaeffer (1946) in amorphous phase and then by numerous teams (Hollenberg & Dows, 1962; Mair & Hornig, 1949; Strazzulla & Baratta, 1991) as a crystal. As we intent, in this study, to contribute to the interpretation of the VIMS-measured infrared spectra of aerosols present in Titan's stratosphere, we have chosen to focus on the six

most intense absorption bands, the others being assigned to combination modes and/or harmonics, already detailed elsewhere (Bertie & Keefe, 2004; Mair & Hornig, 1949). Here, we present a study of pure solid benzene infrared spectrum in both amorphous and crystalline phase along with the vibrational assignments using Herzberg notation (Herzberg, 1945).

1. Amorphous pure benzene ice at 16 K

The infrared spectrum of amorphous benzene deposited at 16 K is shown in figure 1. Wavenumbers of amorphous/crystalline benzene fundamental and combination modes of this work, along with their assignment (Bertie and Keefe, 2004; Mair and Hornig, 1949, Herzberg, 1945), are listed in table 1. Intense absorption bands are observed below 1500 cm^{-1} . First, with the most intense one at 1478 cm^{-1} corresponding to $\nu\text{C}=\text{C}$ asymmetric stretching mode (ν_{13}), followed by the infrared feature of two other fundamental vibrational modes at 1035 cm^{-1} (ν_{14}) and at 674 cm^{-1} (ν_4) assigned to δCH in-plane bending mode and γCH out of plane bending mode respectively. Another prominent absorption band characteristic of aromatic molecules, associated to νCH stretching mode (ν_{12}), is located at 3033 cm^{-1} . The most intense combination modes are attributed to $\nu_2 + \nu_{13} + \nu_{18}$ and $\nu_{13} + \nu_{16}$ at 3070 and 3089 cm^{-1} respectively.



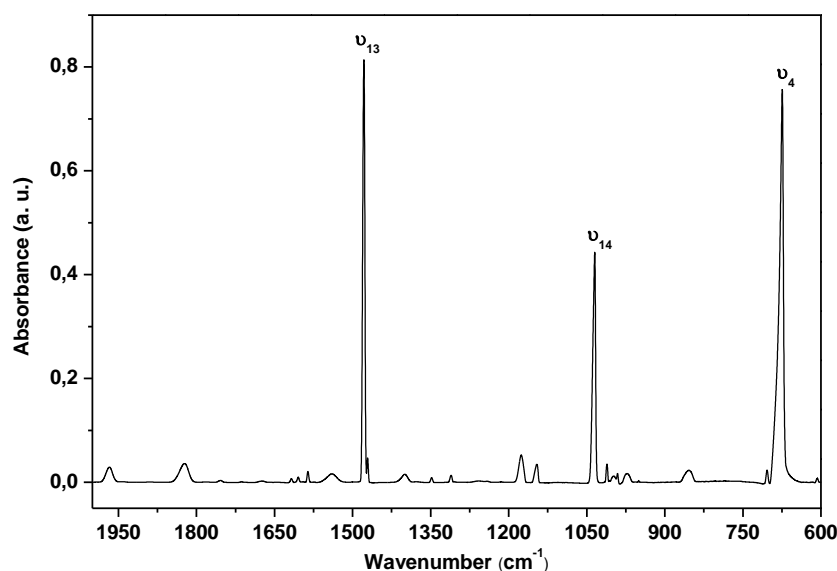


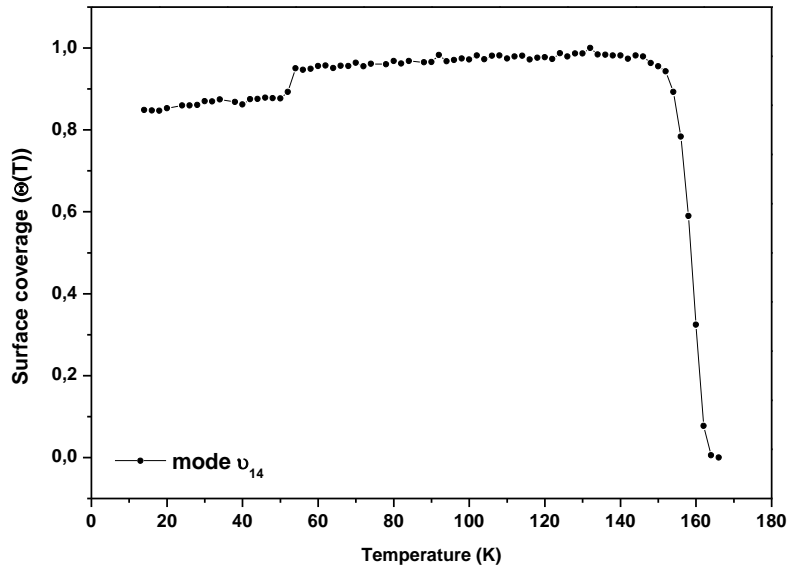
Figure 1 - Infrared spectrum of amorphous benzene deposited at 16 K in the 4000-600 cm^{-1} region; small bands on the spectrum correspond to harmonics or combination modes

2. Influence of the temperature on pure benzene ices: identification of phase transition and desorption processes

As the thermal evolution of solid benzene is rarely (Hollenberg & Dows, 1962; Ishii et al., 1996; Mair & Hornig, 1949) documented in the literature, we propose here to study the influence of the temperature on the position and the shape of its infrared absorption bands. To monitor its phase transition by infrared spectroscopy, as previously described in the literature (Fraser et al., 2001; Koehler, 2001; Toumi et al., 2016), benzene ice was deposited at 16 K and then warmed up to 300 K with several heating rates (from 0,5 to 2 $\text{K} \cdot \text{min}^{-1}$). Figure 2 presents the integrated normalized absorbance of C_6H_6 ν_{14} modes over the temperature and figure 3 shows the infrared spectra of benzene as an amorphous ice and a crystalline one (cf. table 1). Its crystallization is observed around 55 K which is consistent with works published earlier (Ishii et al., 1996; Dawes et al., 2017). Once the crystallization step has been initiated, C_6H_6 pure ice spectra shows significant changes involving mainly the shift and the split of most of infrared absorption bands which become thinner. Above 3000 cm^{-1} , absorption bands corresponding to ν_{12} and $\nu_{13} + \nu_{16}$ modes are split into two bands whereas $\nu_2 + \nu_{13} + \nu_{18}$ one keeps the same shape, becoming thinner with respect to the amorphous ice. The main band of ν_{13} mode infrared signal is also split into two bands as well as the ν_{14} mode infrared feature. Besides, shape modifications of this last vibrational mode as a function of the temperature has already been put forward earlier (Swenson et al., 1959). The ν_4 mode is shifted to higher frequencies but its shape looks almost identical. From 70 K to 130 K, there are only slight shifts ($< 1 \text{ cm}^{-1}$) towards higher frequencies for the vibrational modes above 1440 cm^{-1} and to lower frequencies for the others along with bands intensity variations for all these modes. We observed a

213 maximal crystallization around 130 K in our experiment. Above 165 K, all the molecules desorb, and we
 214 did not obtain any residue from pure C₆H₆ ice sublimation at room temperature.

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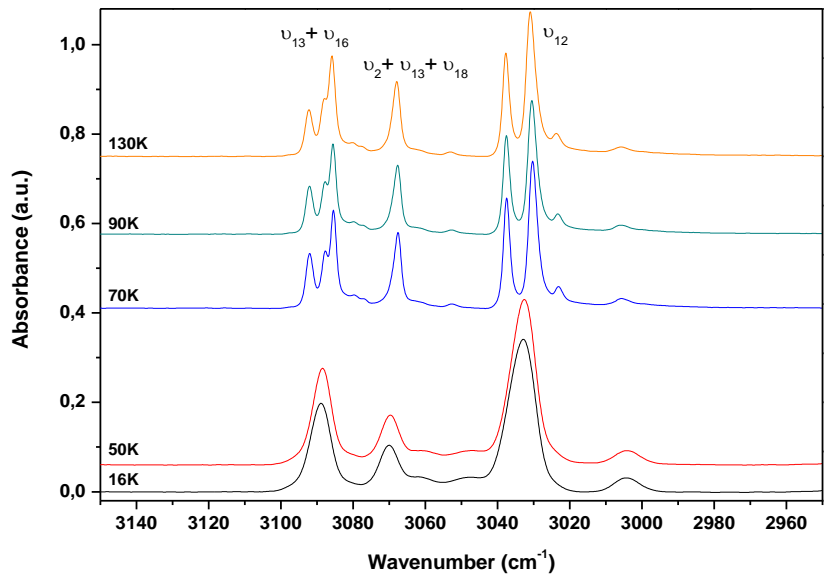


216

217

218 Figure 2 - Integrated normalized absorbance of C₆H₆ ν₁₄ modes with temperature (1.2 K.min⁻¹)
 219 determined by FTIR spectroscopy

220



221

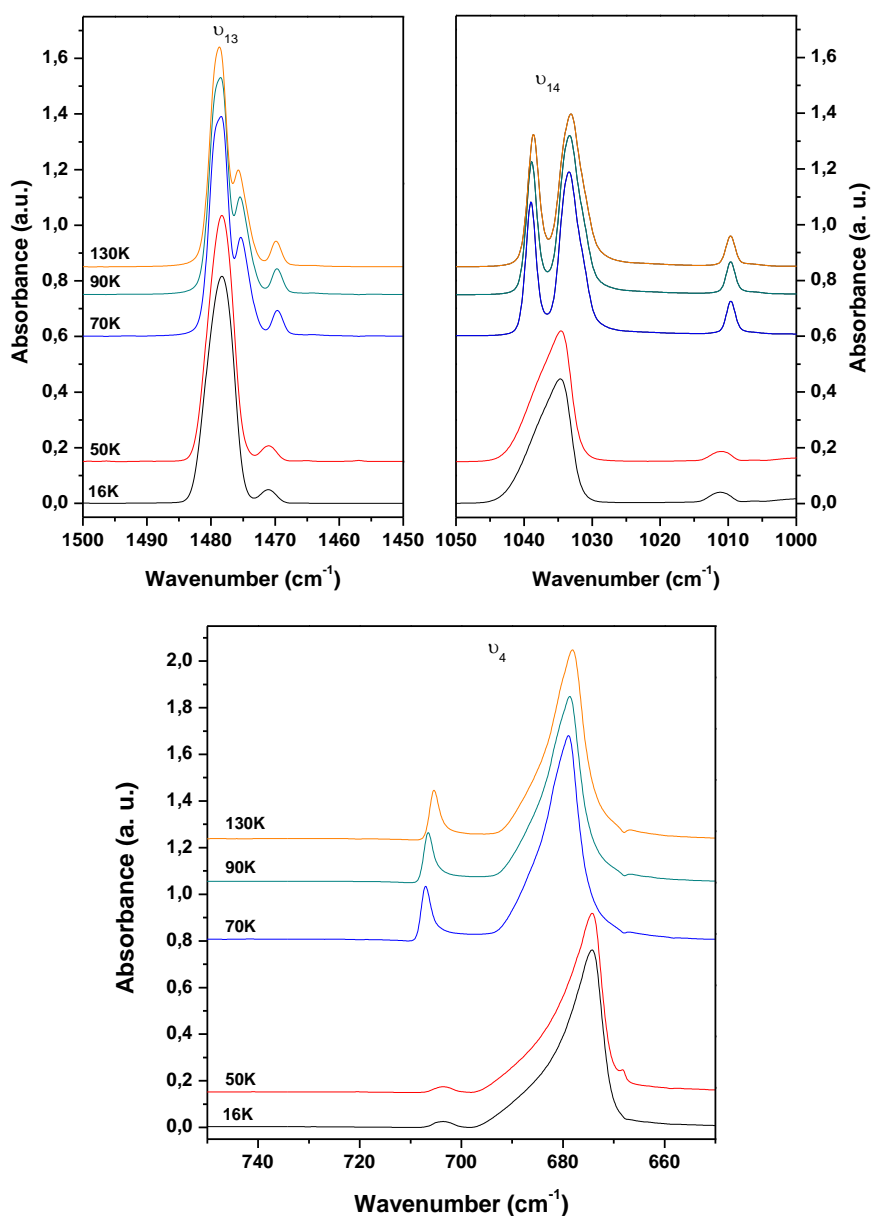


Figure 3 - Infrared spectra of C₆H₆ (amorphous ice) (16 K, 50 K) and (crystalline ice) (70 K, 90 K, 130 K)

II. Simulating long-UV-induced aging of benzene icy clouds in Titan's stratosphere like conditions

1. UV absorption of benzene and dissociative pathways

Several electronic absorption spectra of benzene in both liquid and gaseous phase have been published in the 200-300 nm range (Pantos et al., 1978; Suto et al., 1992). Recently, Dawes et al. (2017) published both amorphous and crystalline solid benzene UV spectrum under vacuum, compared to the one obtained from the gas phase. Whatever the considered phase, benzene electronic spectrum shows small absorption bands above 230 nm; however when we perform irradiation at $\lambda > 230$ nm we are going

235 to irradiate through either singlet-singlet absorption ($^1B_{2u} \leftarrow ^1A_{1g}$) or singlet-triplet absorptions ($^3E_{1u} \leftarrow$
236 $^1A_{1g}$, $^3B_{2u} \leftarrow ^1A_{1g}$) (Dawes et al. 2017).

237 Most of laboratory experiments interested in the photochemical behavior of benzene are carried out
238 using lasers leading to the formation of a solid polymer (Nakashima & Yoshihara, 1982) and C_6H_6
239 valence isomers (Griffith et al., 1975; Yokoyama et al., 1990). These later have also been formed during
240 the photolysis of benzene in cryogenic matrices at low temperature (Johnstone and Sodeau, 1991;
241 Ruiterkamp et al., 2005; Toh et al., 2015, Mouzay et al., submitted). Fulvene, benzvalene and Dewar
242 benzene are produced in argon or nitrogen matrix, when benzene is photolyzed at 253.7 nm or $\lambda > 230$ nm.
243 Their theoretical infrared spectra, obtained by DFT calculations, are already known (Wheless et al.,
244 1995; Zhou & Liu, 1997).

245 The photolysis of adsorbed benzene at 105 K under KrF laser ($\lambda = 248$ nm) demonstrates several
246 dissociative pathways ; one or two 248 nm photons absorption induces the breaking of the CH bond
247 causing the release of H° and $C_6H_5^\circ$, only three-photons excitation triggers the aromatic ring opening
248 through the detection of C_2H_4 and C_2H_2 fragments by mass spectrometry (Varakin, 2018). Besides, Yoon
249 et al. (2014) have suggested that $C_6H_5^\circ$ and H° fragments, also produced at shorter wavelengths
250 ($\lambda = 193$ nm), lead to the formation of aerosols.

251

252 **2. Simulation of benzene photochemical aging at its condensation altitude**

253 In order to understand the photochemical evolution undergone by stratospheric benzene condensates,
254 pure benzene ices were irradiated at $\lambda > 230$ nm, which simulate solar photons that cross the stratosphere.
255 During the photolysis, benzene absorption bands decrease, as displayed in figure 4. The evolution of most
256 of benzene vibrational modes as a function of time cannot be fitted by any-order kinetic rate, because of
257 new spectral features growing at their edge. However, combination mode $\nu_2 + \nu_{13} + \nu_{18}$ peaking at 3068 cm^{-1}
258 1 makes an exception to these observations and its evolution over time can be fitted by a first-order kinetic
259 rate, as shown in figure 5, and gives a kinetic constant of $(6.4 \pm 0.5) \cdot 10^{-4} \text{ min}^{-1}$. As the photon flux of our
260 lamp is about $2.34 \times 10^{16} \text{ photon.cm}^{-2}.\text{s}^{-1}$, the corresponding photo-dissociation cross-section is estimated
261 to be $4.6 \times 10^{-22} \text{ photons.cm}^{-2}$. This value of benzene photo-dissociation cross-section is probably a
262 consequence of radical recombinations and slow diffusion processes, etc... Indeed, at low temperature,
263 the mobility of molecules and heavy radicals is low while H° radicals can locally diffuse through
264 benzene's ice bulk.

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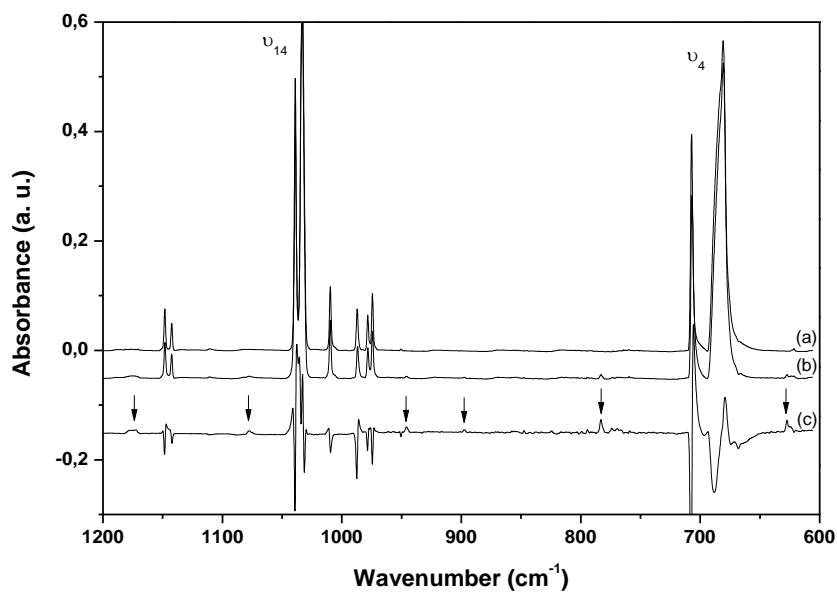
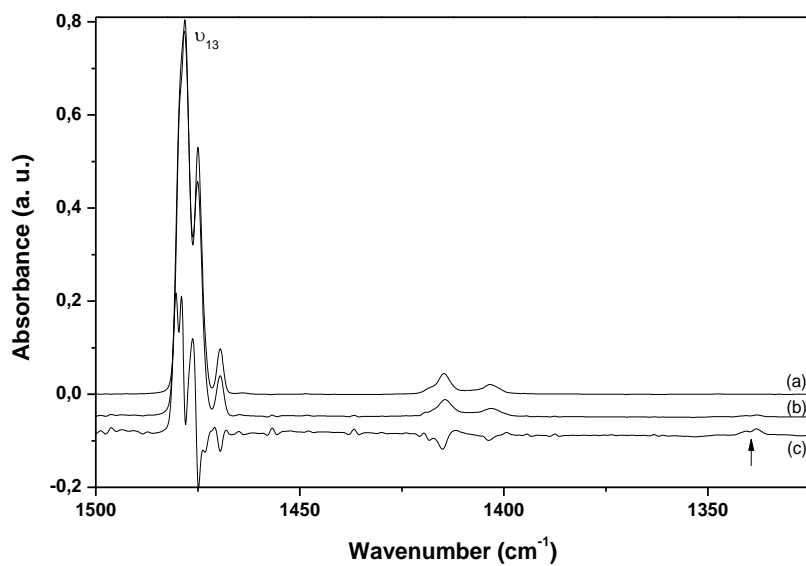
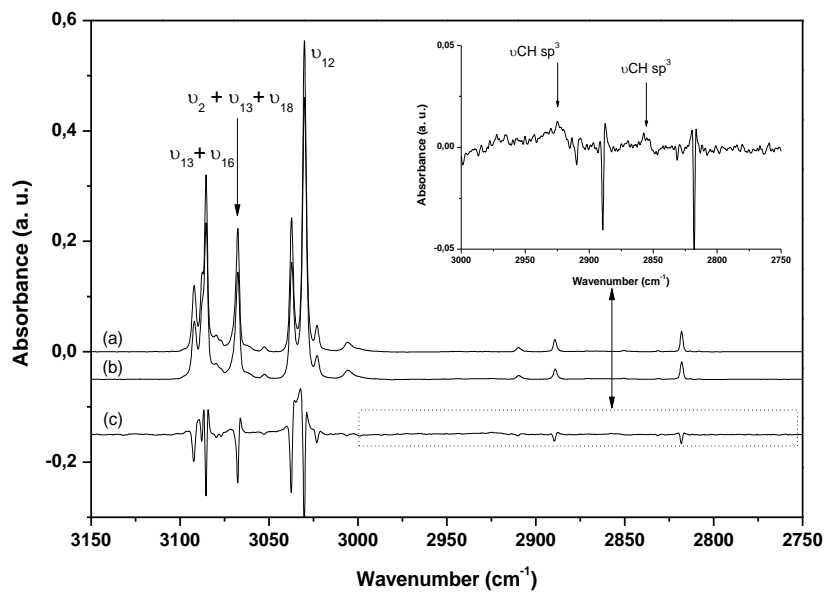


Figure 4 - FTIR spectra of C_6H_6 at 70K : (a)/(b) before/after 2880 min of irradiation ($\lambda > 230\text{nm}$) and (c) subtraction spectrum multiplied by a factor of 3. Arrows highlight the new spectral features photo-produced corresponding to fulvene isomer.

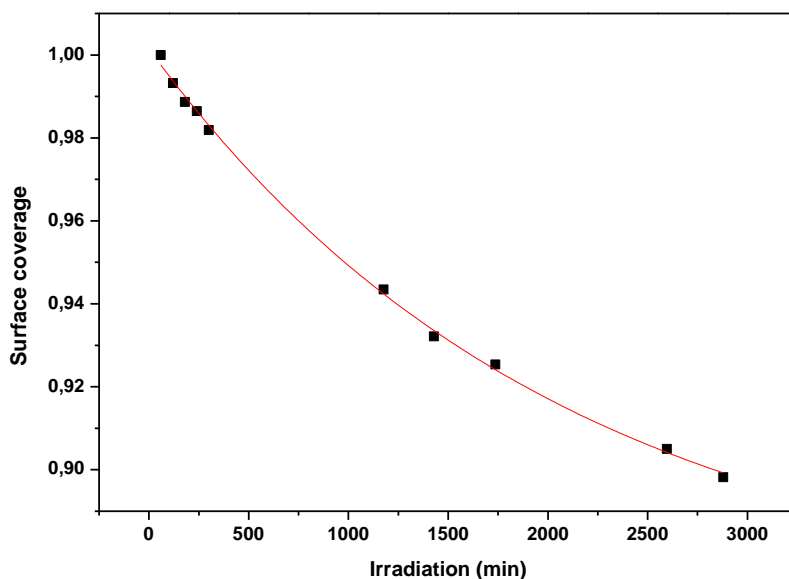


Figure 5 - Evolution of surface coverage of benzene $\nu_2 + \nu_{13} + \nu_{18}$ combination mode during UV irradiation at 70K. The decrease is fitted by a single exponential decay.

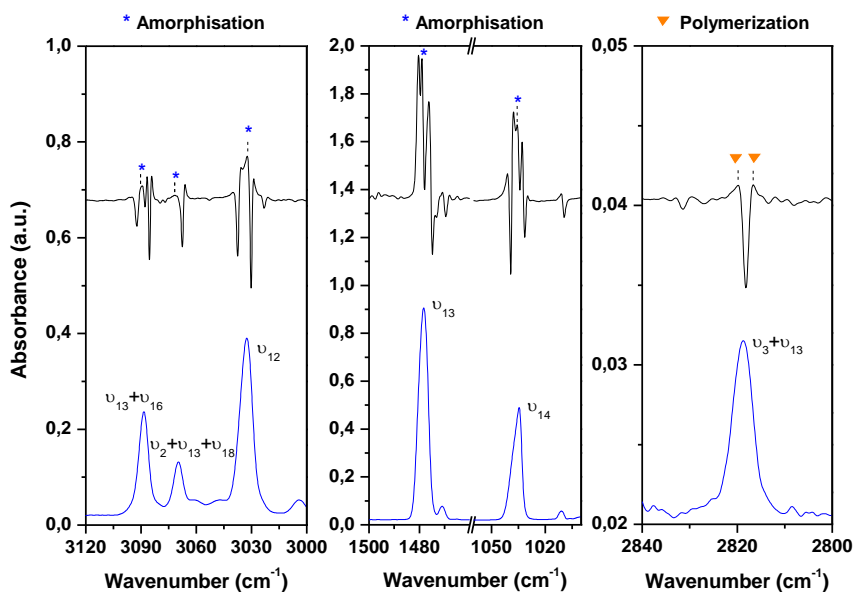


Figure 6 - Comparison of the difference FTIR spectrum after-before UV irradiation of a benzene ice (70 K, top) with the one of amorphous benzene ice (50 K, bottom), in different spectral regions. Peaks marked with asterisks correspond to amorphous benzene features. The right part highlights the features characteristic of polymerization, marked with triangles.

After 2880 min of irradiation, 14 ± 5 % of C_6H_6 is consumed. The infrared features that grow at the edge of benzene absorption bands can be assigned to two different mechanisms: amorphization or

polymerization. Figure 6 compares the subtraction infrared spectrum of the benzene ice after-before UV photolysis with the one of amorphous benzene ice (50 K). The peaks marked with asterisks, on the left side of the figure, correspond to amorphous benzene features while the ones, marked with triangles, on the right side, are characteristic of the formation of polymeric material, as it has already been highlighted by Couturier-Tamburelli et al. (2015, 2018), in the case of HC₅N or HC₃N photolysis.

In addition to these two pathways, we observed the formation of new absorption bands, which frequencies are listed in table 2. The weak bands at 2930 and 2855 cm⁻¹ indicate the formation of aliphatic compounds, corresponding respectively to a CH₂ asymmetric and symmetric stretching mode (Carpentier et al., 2012; Imanaka et al., 2004; Sciamma-O'Brien et al., 2017). Several absorption bands below 1400 cm⁻¹ are found at 1341, 1338, 1078, 946, 898, 783 and 627 cm⁻¹. These frequencies are compared, in table 2, to the ones of solid state and *in situ* matrix-produced fulvene (5-methylenecyclopenta-1,3-diene), one of benzene valence isomers. The formation of fulvene was identified during UV photolysis ($\lambda > 230$ nm) of matrix-isolated benzene (Table 2). The sublimation of nitrogen matrix after the irradiation leads to the spectroscopic characterization of solid fulvene. The comparison of these new absorption bands frequencies with those obtained after nitrogen matrix sublimation confirms the formation of fulvene in C₆H₆ irradiated ices.

3. Infrared characterization of benzene aerosols

At the end of the photolysis experiment, we performed a warming-up to allow non-irradiated benzene monomers as well as volatile photoproducts, such as fulvene, to be released as gases. This step allows to characterize *in situ* the refractory polymer produced by photochemistry. In our experimental conditions, a little amount of non-volatile residue was observed after the warming-up. The residue obtained corresponds to an organic material that can be used as a reference spectrum to more easily identify the changes in the residue which will soon be obtained by introducing HCN into our mixture. It has a brownish color, reminiscent of Titan's haze, and is soluble in dichloromethane, as laboratory analogs of high-altitude produced aerosols soluble in methanol, another polar solvent (Carrasco et al., 2009).

The infrared spectrum of the benzene residue is presented in figure 7 and shows the presence of a broad and well-structured band in the 3350-2750 cm⁻¹ region, along with a band at 1404 cm⁻¹ that could be assigned to semi-circle stretching of aromatics rings (Larkin, 2011). The greater intensities are observed for the peaks located above 3000 cm⁻¹ corresponding to ν CH sp² stretching modes by comparison with the peaks below 3000 cm⁻¹, assigned to ν CH sp³ stretching modes. As this cluster is the result of the overlap of several absorption bands, a deconvolution into gaussian components was realized

to characterize each of them, as presented in figure 8. Their respective assignments are reported in table 3. During fitting process, we set positions as free parameters, as processed in previous studies (Carrasco et al., 2018). Taking into account previous works concerning both the influence of benzene in the chemical composition of tholins (Sciamma-O'Brien et al., 2017) and the spectroscopic characterization of hydrogenated amorphous carbon-based structures (Dartois et al., 2004), only two vibrational modes are exclusive to this study, the others being common to the studies cited above.

Gaussian component at 3213 cm^{-1} could be assigned to CH stretching modes from conjugated alkynes derivatives which could explain the frequency shift towards lower energies with respect to the one observed in alkyne functions (Larkin, 2011). The intense 3144 cm^{-1} peak could result from a CH sp^2 stretching mode from a derivative/substituted polyphenyl compound (Ghanem et al., 1987). Aromatic and vinylic $-\text{CH}_2$ asymmetric stretching modes are centered at 3086 cm^{-1} (Sciamma-O'Brien et al., 2017) while CH stretching modes from aromatic/alkene family are found at 3060 , 3031 and 2999 cm^{-1} (Sciamma-O'Brien et al., 2017). By means of previous studies (Imanaka et al., 2004; Quirico et al., 2008; Sciamma-O'Brien et al., 2017), $-\text{CH}_3$ asymmetric and symmetric stretching modes are assigned to gaussian component at 2964 and 2863 cm^{-1} respectively against 2930 and 2829 cm^{-1} for $-\text{CH}_2$ group (Larkin, 2011). A last peak has been found at 2894 cm^{-1} which could be assigned either to $\text{sp}^3\text{ vCH}$ stretching mode or to $-\text{CH}_2$ Fermi resonance (Carpentier et al., 2012) or asymmetric $-\text{CH}_2$ wing mode (Dartois et al., 2004). Besides, this last vibrational mode presents its symmetric counterpart at 2800 cm^{-1} (Dartois et al., 2004).

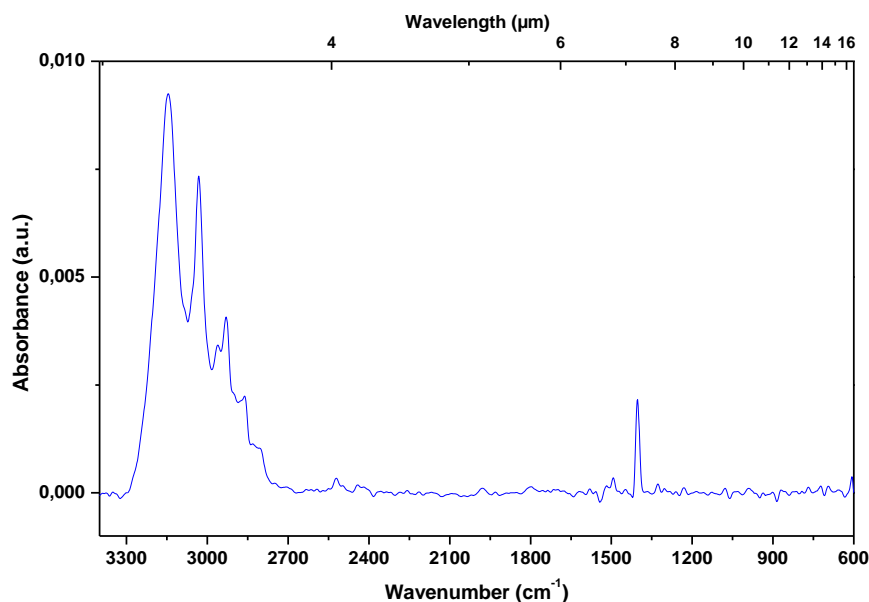


Figure 7 - FTIR spectra recorded at 300K of C_6H_6 residue produced by UV radiations ($\lambda > 230\text{ nm}$) at 70K and warmed-up to 300K

Discussion

Vapor condensation of benzene in Titan's stratosphere, modeled in different works, leads to the formation of icy particles which formation altitude depends on climatic conditions as well as abundances. Based on different models, the condensation of benzene is expected at 85 km for a temperature of about 130 K (Barth, 2017; P. Lavvas et al., 2011). At these altitudes, ices can evolve according two main pathways; the first one consists in the adsorption of condensable species and the second one is triggered by photochemical reactions induced by long-UV solar photons. For benzene, which is a key molecule at high altitude in the formation of both complex organics and aerosols that recover Titan's surface, none of these processes have been experimentally investigated in stratospheric-like conditions. Hence, the role played by benzene ices in this part of the atmosphere has not been clearly identified so far. In this work, we have shown the photochemical activity of icy benzene under long-UV radiations ($\lambda > 230$ nm) which results in the formation of volatiles photoproducts, in particular the fulvene detected by IR spectroscopy, and a refractory material, i.e. the laboratory equivalent of Titan's aerosols. At 70 K, it takes 48 hrs to lose almost 14 ± 5 % of benzene in our experiment. However, as the solar flux reaching Titan's stratosphere is around 10^{14} photon.cm⁻².s⁻¹, the same depletion rate for benzene will be achieved after 1.5 earth year on Titan. Even if we present the photochemistry of benzene at lower temperature (70 K) than the one at which it is expected to condensed, our results demonstrate a low dissociation rate of benzene in the stratosphere's condition. Hence, most of the benzene ice would not be modified by the surrounding solar UV photons that penetrate the stratosphere. With small increasing temperatures, all photo-produced volatiles species and that of benzene undergo thermal desorption leaving only benzene photopolymer in solid state, depending on the season in Titan's atmosphere.

The formation of aerosols produced by the photochemistry of gas phase benzene under more energetic conditions relevant for simulating the chemistry occurring at higher altitudes in Titan's atmosphere, has been experimentally investigated in other groups (Gautier et al., 2017; Sciamma-O'Brien et al., 2017; Trainer et al., 2013). Our experimental spectrum of the benzene residue is compared to the IR spectra of aerosols generated by N₂:C₆H₆ gas mixture submitted to UV radiations (Gautier et al., 2017) (top, blue) or by a N₂:CH₄:C₆H₆ gas mixture in a cold plasma discharge (Sciamma-O'Brien et al., 2017). We also compared it with observational data of Titan's atmosphere at ~ 200 km supplied by VIMS (Lowest altitude where a well-resolved spectrum is observed) (Bellucci et al., 2009; Carrasco et al., 2018; Kim et al., 2011) spectrometer, as presented in figure 8. In their work, Kim et al. retrieve the detailed spectral

feature using a radiative transfer program including absorption and scattering by haze particles. The spectral features of the haze retrieved from the VIMS data at various altitudes are similar to each other, indicating relatively uniform spectral properties of the haze with altitude. The observations were carried out on January 15, 2006 during the solar egress at 71°S (Bellucci et al., 2009).

As observed on figure 8, it is in the spectral region characteristic of aromatic structures that we have found major discrepancies. Indeed, the most intense band observed at 3144 cm^{-1} in our residue matches only with the very small VIMS observed-spectral signature of stratospheric aerosols, in terms of position but not in intensity. On the other hand, our deconvoluted bands at 3086, 3060, 3031 and 2999 cm^{-1} are common to the ones observed in these other laboratory-produced aerosols and on the VIMS data. Their relative intensities correspond rather well to the ones observed in the other aerosols. In particular, the greatest intensities observed for these bands mimic the ones observed in the aerosols produced from the $\text{N}_2:\text{CH}_4:\text{C}_6\text{H}_6$ gas mixture

In addition, from 3000 to 2850 cm^{-1} , we found a similar shape of the spectra indicating that similar aliphatic structures obtained in all the laboratory experiments are in good agreement with those of the Titan's haze. However, the intensity relatives to these aliphatic structures are obtained in smaller quantities than the aromatics in our residue compared to other experimental data and the observation. Nevertheless, these relative proportions are close to those produced in the cold plasma discharge. As a consequence, the polymeric structure that has been produced under the exposure of a benzene ice to long-UV radiations may present similar aromatic/aliphatic groups in terms of structures and proportions with the aerosols generated by plasma discharge at higher altitudes in the atmosphere. So, the residue formation is probably wavelengths dependent.

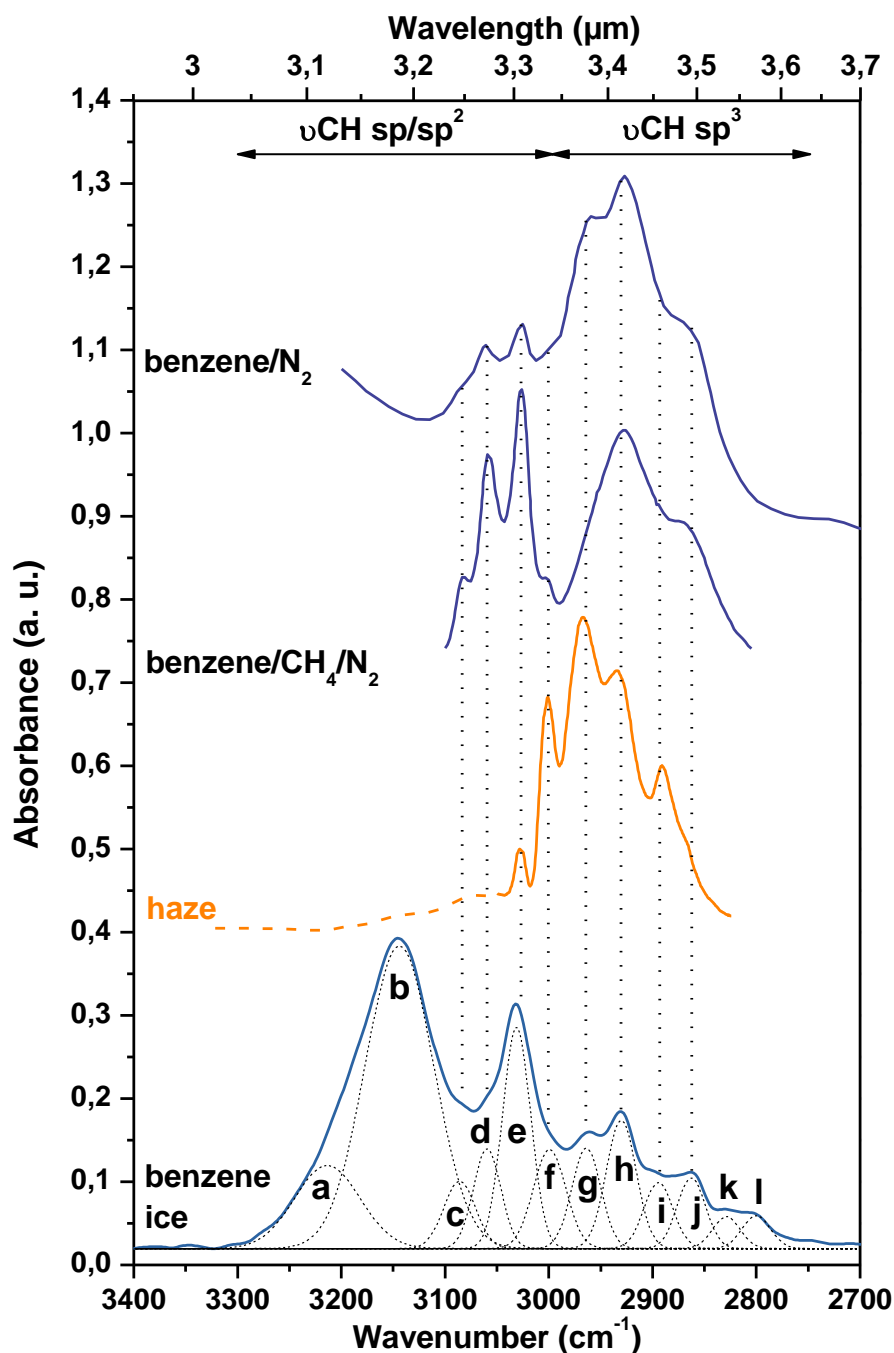


Figure 8 - Deconvoluted infrared spectrum of benzene residue (bottom, blue line) produced by photochemistry ($\lambda > 230$ nm) and subsequent warm-up to room temperature are compared to VIMS solar occultation spectrum at altitude 203 km (Bellucci et al., 2009; Kim et al., 2011) (orange solid line was processed by Carrasco et al. (2018) from Kim et al. (2011) between 3050 and 2825 cm^{-1} and orange dashed line corresponds to Titan's haze spectra from Kim et al. (2011) above 3050 cm^{-1}). As well, this experimental spectrum is compared to the IR spectra of aerosols generated by a $\text{N}_2:\text{C}_6\text{H}_6$ gas mixture submitted to UV radiations (Gautier et al., 2017) (top, blue) or by a $\text{N}_2:\text{CH}_4:\text{C}_6\text{H}_6$ gas mixture in a cold plasma discharge (Sciamma-O'Brien et al., 2017). For the interpretation of the legend, the reader must refer to the web version of this article.

However, several deconvoluted absorption bands of the benzene residue, namely at 3213, 2829 and 2800 cm^{-1} are not observed among the infrared features of Titan's haze observed in the stratosphere. Thereby, pure benzene aerosols are not sufficient to explain the composition of Titan's haze. In our study, the benzene residue formed in our experiments results from photo-processed ices without considering further aging processes such as the one induced by the accretion of condensates at their surface. Besides, Courtin et al. (2015) demonstrate the coating of condensates below 300 km to induce the depletion of the ratio between aromatics and aliphatics. In addition, experimental works performed by Couturier-Tamburelli et al. (2018) highlighted a possibility of photo-insertion of hydrogen atoms in a nitrile-based residue coated with icy HCN. Therefore, it will be of interest to investigate the coating effects on the spectral features assigned to -CH stretching modes of benzene residues. However, if the 3144 cm^{-1} absorption band, characteristic of benzene photochemistry, is normalized on the intensity of the corresponding band from VIMS observations, we can assume that benzene aerosols contribution is very little in Titan's atmosphere at the time at which the measure was performed. It demonstrates that other kinds of aerosols, present in the stratosphere, explain the large intensity of aliphatic CH contributions. In fact, this residue is produced by photo-processed hydrogen carbonaceous -based ices while in Titan's stratosphere, the haze probed by Cassini VIMS spectrometers results from the complex photochemistry of hydrocarbons and nitriles. Nevertheless, these preliminary laboratory experiments constitute a first step in understanding the role played by benzene ices in the formation of gaseous species and aerosols in the stratosphere that will subsequently be transported to the surface. It will then allow to experimentally simulate a more complex benzene-containing cloud to better understand their photochemical evolution at these altitudes as well as their contribution to the surface organic layer.

Conclusion

To understand the fate of benzene ices in Titan's stratosphere; we turned to laboratory experiments to simulate its photochemical evolution triggered by long-UV radiations ($\lambda > 230\text{nm}$). Our results demonstrate a photochemical activity of benzene which leads to the formation of volatile photo-products in particular, the fulvene, as well as a solid polymer, i.e. laboratory analog of benzene aerosols. Its spectroscopic characterization highlights a good correlation with VIMS observations for the positions of most of the deconvoluted absorption bands, which does not hold for the relative intensities of CH sp^2/sp^3 ratio obtained in benzene photopolymer. Therefore, pure aromatic-based aerosols are not sufficient to explain the composition of Titan's haze. However, this study also helps to establish comparisons with the changes that may be observed when benzene is co-condensed with another molecule like HCN. Indeed,

these aerosols could contribute to the organic material present on Titan's surface which will be investigated by the future Dragonfly space mission.

Keywords : Titan, Atmosphere ; Benzene ; Ices, IR spectroscopy ; Clouds, UV photochemistry

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Table 1
Positions, assignments and band strength of the most intense infrared absorption bands of icy C₆H₆ at different temperatures

Assignments (Herzberg, 1945)	Band strength (cm.molecules ⁻¹)			Wavenumbers (cm ⁻¹)	
	This work	Di Lonardo et al., (1999)	Bertie and Keefe, (1994)	This work	
	T=70 K crystalline ice	gas	liquid	T=16 K amorphous ice	T=70 K after 130 K crystalline ice
$\nu_{16} + \nu_{13}, e_{1u}$	1.3x 10 ⁻¹⁸	1.1 x 10 ⁻¹⁷		3089	3092 3085
$\nu_2 + \nu_{18} + \nu_{16}, e_{1u}$	4.1 x 10 ⁻¹⁹	-	3.30 x 10 ⁻¹⁸	3070	3068
ν_{12}, e_{1u} CH aromatic stretching	2.2x 10 ⁻¹⁸	-		3033	3038 3030
ν_{13}, e_{1u} C=C aromatic stretching	2.7 x 10 ⁻¹⁸	2.3 x 10 ⁻¹⁸	1.4 x 10 ⁻¹⁸	1478	1478 1475
ν_{12}, e_{1u} C-H in-plane bending	6.0 x 10 ⁻¹⁹	1.4 x 10 ⁻¹⁸	9.4 x 10 ⁻¹⁸	1035	1039 1033
ν_4, a_{2u} C-H out of plane bending	7.5x 10 ⁻¹⁹	1.0 x 10 ⁻¹⁷	7.7 x 10 ⁻¹⁸	674	679

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Table 2

Positions and assignments of new infrared absorption bands obtained during the photolysis at 70K of C₆H₆ ice ($\lambda > 230\text{nm}$), compared to the infrared features of fulvene in solid state and in cryogenic matrices

Wavenumbers (cm ⁻¹)	Wavelengths (μm)	Assignments	Attempt of assignment	Solid fulvene bands (cm ⁻¹)		Matrix-isolated fulvene bands (cm ⁻¹)	
				After irradiation of benzene ice (this work)	After sublimation of nitrogen matrix	N ₂	Ar ^e
2930	3.41	asymmetric stretching CH ₂ ^{a,b}	Residue aliphatic groups ?	-	-	-	-
2855	3.5	symmetric stretching CH ₂ ^c	Residue aliphatic groups ?	-	-	-	-
1341 1338	7.46 7.47	in-plane bending CH ^d	fulvene	1339	1339	1343.6	1342.8
1078	9.28	in-plane bending CH/C-C-C in-plane bending ^d	fulvene	1076	1076	1080.7	1081.1
946	10.6	ring in-plane deformation + C-C stretching ^d / out-of-plane bending CH ^d	fulvene	939	939	932.4	926.3
898	11.1	ring in-plane deformation/C-C stretching ^d	fulvene?	896	896	894.0	894.5
783	12.8	out-of-plane bending CH ^d	fulvene	778	778	773.0	770.6
627	15.9	out-of-plane bending aromatic CH ₂ ^d	fulvene	622	622	617.8	616.3

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Notes :

- ^a (Imanaka et al., 2004)
^b (Sciamma-O'Brien et al., 2017)
^c (Carpentier et al., 2012)
^d (Wheeless et al., 1995)
^e (Johnstone and Sodeau, 1991)

Table 3
Deconvoluted infrared absorption bands of C₆H₆ residue in the 3150-2750 cm⁻¹ region

Label	Wavenumbers (cm ⁻¹)	Wavelengths (μm)	Assignments
a	3213	3,12	sp -CH stretching (conjugated alkyne ?) ^d
b	3144	3,18	sp ² -CH stretching (derivative/substituted polyphenyl ?) ^e
c	3086	3,24	sp ² asymmetric -CH ₂ stretching (aromatic/alkene) ^{b, c}
d	3060	3,26	sp ² -CH stretching (aromatic) ^b
e	3031	3,30	sp ² -CH stretching (aromatic) ^b
f	2999	3,33	sp ² -CH stretching (aromatic/alkene) ^b
g	2964	3,37	sp ³ asymmetric CH ₃ stretching (alkane/aliphatic) ^{a, b}
h	2930	3,41	sp ³ asymmetric CH ₂ stretching (alkane/aliphatic) ^{a, b}
i	2894	3,46	sp ³ -CH stretching ^f / -CH ₂ Fermi resonance ^f / sp ² asymmetric CH ₂ wing ^c
j	2863	3,49	sp ³ symmetric CH ₃ stretching (alkane/aliphatic) ^b
k	2829	3,53	sp ³ symmetric CH ₂ stretching (alkane/aliphatic) ^d
l	2800	3,57	sp ² symmetric CH ₂ wing ^c

Notes :

^a (Imanaka et al., 2004)

^b (Sciamma-O'Brien et al., 2017)

^c (Dartois et al., 2004)

^d (Larkin, 2011)

^e (Ghanem et al., 1987)

^f (Carpentier et al., 2012)