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The Detectability Limit of Organic Molecules within Mars South Polar Laboratory Analogues

J. D. Campbell^{1,2}, **B. Schmitt**³, **O. Brissaud**³, **J-P. Muller**¹

¹ Imaging Group, Mullard Space Science Laboratory, Department of Space and Climate Physics, University College London (UCL), Holmbury St. Mary, RH5 6NT, UK

² now at Dept. of Earth Sciences, University of Oxford, OX1 3AN, UK

³ Université Grenoble Alpes, CNRS, Institut de Planétologie et d'Astrophysique de Grenoble, France

Corresponding author: Jacqueline D. Campbell (jacqueline.campbell@earth.ox.ac.uk)

Key Points:

- A new spectrum diagnostic of Polycyclic Aromatic Hydrocarbons (PAHs) pertinent to Mars has been produced
- The detectability limit of PAHs in Mars South Pole analogues has been established
- The evolution of the spectra of PAHs in Mars South Pole analogues as ice sublimates under emulated Martian conditions has been recorded

20 **Abstract**

21 A series of laboratory experiments was carried out in order to generate a diagnostic spectrum for
22 Polycyclic Aromatic Hydrocarbons (PAHs) of astrobiological interest in the context of the
23 Martian South Polar Residual Cap (SPRC), to establish PAH spectral features more easily
24 detectable in CO₂ ice (mixed with small amounts of H₂O ice) than the previously reported
25 absorption feature at 3.29 μm in order to constrain their detectability limit. There is currently no
26 existing literature on PAH detection within SPRC features, making this work novel and
27 impactful given the recent discovery of a possible subglacial lake beneath the Martian South
28 Pole. Although they have been detected in Martian meteorites, PAHs have not been detected yet
29 on Mars, possibly due to the deleterious effects of ultraviolet radiation on the surface of the
30 planet. SPRC features may provide protection to fragile molecules, and this work seeks to
31 provide laboratory data to improve interpretation of orbital remote sensing spectroscopic
32 imaging data. We also ascertain the effect of CO₂ ice sublimation on organic spectra, as well as
33 provide PAH reference spectra in mixtures relevant to Mars. A detectability limit of ~0.04% has
34 been recorded for observing PAHs in CO₂ ice using laboratory instrument parameters emulating
35 those of the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM), with new
36 spectral slope features revealed between 0.7 and 1.1 μm, and absorption features at 1.14 and,
37 most sensitively, at 1.685 μm. Mars regolith analogue mixed with a concentration of 1.5% PAHs
38 resulted in no discernible organic spectral features. These detectability limits measured in the
39 laboratory are discussed and extrapolated to the effective conditions on the Mars South Polar
40 Cap in terms of dust and water ice abundance and CO₂ ice grain size for both the main perennial
41 cap and the H₂O ice-dust sublimation lag deposit.

42 **Plain Language Summary**

43 Carbon molecule chains, or organics, are considered important in the search for life, as all life
44 that we know of on Earth is made from carbon. A particular type of organic, PAHs, that are
45 really common on Earth and throughout space, have never been found on Mars and it is likely
46 they are broken down too quickly on the Martian surface by the Sun's radiation to be discovered
47 using space satellites. However, some areas of Mars move and change, and expose dust. One
48 such area is the Martian South Polar Cap. This study uses laboratory experiments to simulate
49 expected conditions on the Mars South Pole, and mix PAHs with ices, then look at them using
50 instruments similar to those on satellites orbiting Mars to find out how much PAH material
51 would have to be in the ice to be able to detect it. These experiments allowed us to create a
52 spectrum that can be used to help to identify different materials. We have found that you can
53 observe features of PAHs at 1.685 and 1.14 μm in the spectra when there is 0.1% or more PAH
54 in a carbon dioxide ice sample, but it was not possible to see 1.5% of PAH in a sample of dust
55 similar to the dust on the surface of Mars.

56 **1 Introduction**

57 Our neighbouring planet, Mars, has increasingly been the target of scientific exploration and of
58 particular interest are its geological history, current environmental conditions, and perhaps most
59 importantly, its potential as a host for extraterrestrial life (Fairén et al., 2010). The polar caps of
60 Mars have more recently emerged as an area of scientific interest due to their abundance of water
61 ice and their dynamic nature, especially with the discovery of a possible stable body of liquid
62 water beneath the Martian South Pole (Orosei et al., 2018). The Martian North and South Pole

63 have permanent ice caps that expand throughout their respective winters, and maintain residual
64 caps in the summer. The North Polar Cap (NPC) is composed almost entirely of water ice, while
65 the longer, colder winter in the higher altitude southern hemisphere means that the central part of
66 the South Polar Cap (SPC) is covered by a permanent layer of CO₂ ice (Byrne, 2009), up to 10
67 metres thick, underlain, and surrounded by, water ice layers known as Polar Layered Deposits
68 (PLD; Piqueux et al., 2008).

69 Seasonal cycles of sublimation and deposition of CO₂ ice on the SPC are responsible for the
70 formation of ‘Swiss Cheese Terrain’ (SCT). This unique cryomorphology manifests as flat-
71 topped mesas with flat floored, quasi-circular depressions that form patterns resembling
72 Emmental Swiss Cheese (Malin et al., 2001). This terrain forms by preferential and progressive
73 sublimation and erosion of the walls of the depressions, at a typical speed of 3 metres per Mars
74 year. The reason these SCT sublimations features are of interest to this study is because of the
75 exposure of dust previously shielded within the SPC (Jian et al., 2009). The exposed dust that
76 has been concentrated by CO₂ ice sublimation may be a candidate site for the detection of a class
77 of organic molecules, Polycyclic Aromatic Hydrocarbons (PAHs), that may have been protected
78 from the Sun’s radiation within the SPC. If PAH is dispersed in the ice instead of being
79 associated with the dust, it will also be concentrated at the surface with the dust as the ice
80 sublimates away leaving any particles behind.

81 Work was previously carried out in order to look for PAH signatures on the thin, dust-covered
82 rims of SCT to no avail (Campbell et al., 2018) using the well-known PAH diagnostic absorption
83 feature at 3.29 μm (Allamandola, 2011), but no signs of PAHs were found. However, this strong
84 band is situated in the high wavelength wing of the very strong 3.1 μm band of water ice and may
85 thus be hidden in places where abundant water ice is present, such as on SPC margins (Douté et
86 al. 2007) and rim scarps (Campbell et al., 2018). It may be also hidden by the wide hydration
87 bands of minerals (adsorbed and structural water) that can extend up to 4 μm and may even be
88 saturated in some cases.

89 The aims of the experiments carried out and reported here were to generate a diagnostic near-
90 infrared spectrum for PAHs of astrobiological interest in the context of the Martian South Pole.
91 We emulate the parameters of the CRISM instrument’s Full Resolution Targeted (FRT) \sim 18
92 m/pixel mode to constrain the detectability limit of PAHs in CO₂ ice to establish the
93 characteristics of PAH spectral features at wavelengths other than the absorption feature at 3.29
94 μm , where they might be easier to discern against the CO₂ and H₂O ice spectrum. In addition, we
95 discuss how the detectability of these bands is affected by the presence of dust.

96 1.1 Polycyclic Aromatic Hydrocarbons

97 PAHs are a group of chemical compounds consisting of benzene rings of carbon with hydrogen.
98 In its NPAH form, nitrogen can be substituted for carbon atoms in the aromatic ring (Tang,
99 2018). PAHs occur not only on Earth, but throughout the universe. They have been found to
100 coalesce in space within dust clouds (Mulas et al., 2005), and are thought to account for up to
101 20% of total cosmic carbon (Allamandola, 2011).

102 PAHs frozen within ice particles in dense molecular clouds in space undergo processing by
103 ultraviolet light and cosmic rays to produce more complex species (Dartnell et al., 2012). PAHs

104 can also arise and increase in abundance through the irradiation of complex polymeric organic
105 material such as those found in carbonaceous meteorites (Thompson et al., 2020). A recent
106 paper on the Mukundpura carbonaceous chondrite meteorite found in India measured 500ppm
107 PAH (Kalpana et al., 2021). PAHs eventually rain down on primordial planets directly from
108 planetary accretion discs, or are delivered on comets and meteorites (Allamandola, 2011).
109 Therefore, PAHs should be present, or should have been present in the past, on all planetary
110 bodies in the solar system (Dullemond et al., 2007). PAHs have been detected on the surfaces of
111 Saturnian icy moons and comets (Cruikshank et al., 2008, 2014; Lopez-Puertas et al., 2013; Li,
112 2008) and have been measured in other carbonaceous chondrites meteorites at the level of a few
113 ppm (Becker et al. 1997).

114 The delivery of complex organic compounds to planets via bolide impact is a very important
115 concept in astrobiology, and could be instrumental in explaining abiogenesis (the origin of life).
116 Carbon's propensity to catenate (form long chains), and the carbon-based nature of all life on
117 Earth, means that the presence of carbon compounds is considered an essential component of any
118 potentially habitable environment (Plaxco and Gross, 2011). PAHs are sought after on many
119 solar system bodies in the search for the origin of life, but are conspicuously missing on Mars
120 (Benner et al., 2000). The discovery of PAHs on Mars would tell us that these organics could
121 survive in oxidizing environments receiving high levels of UV radiation, and may have
122 accumulated in the past when Mars had warmer and wetter conditions favourable to the
123 emergence of life.

124 1.2. PAHs on Mars

125 The detection of organics has been a primary objective of orbiters and landers since the Viking
126 missions (Klein, 1978). Despite apparent negative results for the detection of extant life by the
127 Viking landers in the 1970s, which searched for traces of biologically important compounds
128 (Klein, 1978; Schuerger and Clark, 2008), perchlorates were discovered by the 2008 Phoenix
129 lander (Hecht et al., 2009). More recently, organics were discovered by the Sample Analysis at
130 Mars (SAM) instrument on NASA's 2012 rover mission, Mars Science Laboratory (Freissinet et
131 al., 2015), known as "Curiosity". Perhaps of even more interest, is the re-analysis of the 1976
132 Viking Lander data by Navarro-Gonzalez et al. (2010) using modern laboratory techniques
133 suggested that there were both perchlorates and organic carbon present at the Viking Lander
134 sample sites, although they were not identified at the time. To date, no PAHs have been found on
135 Mars, but concentrations of about 1ppm of PAH have been found in Martian meteorites with
136 potential extraterrestrial origin (McKay et al. 1996, Becker et al., 1997; Botta and Bada, 2002).
137 A study by Dartnell et al. (2012) found that PAHs might be afforded protection from the effects
138 of UV radiation and oxidization within the subsurface of Mars, within rock, or in permanently
139 shadowed areas. Ice can also provide a barrier to deep UV solar radiation (Vincent, 1998;

140 Cockell et al., 2000), resulting in partial shielding and allowing organic compounds to become
141 more complex (Herbst and van Dishoek, 2009; Oberg et al., 2009).

142 **2 Laboratory Analysis**

143 2.1 Instruments

144 2.1.1. Laboratory Analysis

145 The site of the experiments was the Cold Surfaces Spectroscopy Facility ([https://cold-](https://cold-spectro.sshade.eu)
146 [spectro.sshade.eu](https://cold-spectro.sshade.eu)) at the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) in
147 France and has facilities for in-situ formation of ices, and cold rooms capable of keeping samples
148 up to -40°C to allow stable thermal conditions during preparation of icy materials for
149 experiments. This allows analysis of samples in the cryogenic CarboN-IR environmental cell,
150 which can maintain cold temperatures and low gas pressures, using the SHINE
151 (SpectropHotometer with variable INcidence and EMergence) instrument to record reflectance
152 spectra in visible and near-mid infrared wavelengths.

153 2.1.2. Spectro-gonio radiometer

154 The SHINE spectro-gonio radiometer was developed at IPAG, and is designed to measure
155 bidirectional reflectance and polarisation distribution functions of planetary material, enabling
156 the production of accurate datasets to help describe surface composition, roughness and texture
157 (Brissaud et al., 2004). In particular, the SHINE spectro-gonio radiometer is able to characterise
158 the light scattering properties of snows of various grain-size, compactness and surface roughness
159 at different stages of metamorphism. The instrument is able to measure from $0.35\text{-}4.80\ \mu\text{m}$, with
160 spectral resolution of between $6\text{-}40\ \text{nm}$, dependent on wavelength (ibid).

161 SHINE can be used in conjunction with the CarboN-IR environmental cell to analyse materials at
162 low temperatures.

163

164 2.1.3. CarboN-IR Environmental Cell

165 The CarboN-IR environmental cell system ([https://cold-spectro.sshade.eu/carbo-nir-simulation-](https://cold-spectro.sshade.eu/carbo-nir-simulation-chamber)
166 [chamber](https://cold-spectro.sshade.eu/carbo-nir-simulation-chamber)) allows for the study of planetary material samples in stable conditions. It can cool the
167 sample down to -210°C within an isothermal copper cell that can maintain a stable gas pressure
168 in thermodynamic equilibrium with the sample at the same temperature. The chamber is
169 designed to enable visible and near-IR monitoring throughout the physical evolution of ice
170 samples thanks to sapphire windows (Grisolle 2013).

171 **3 Methods**

172 The concept of this work is to produce empirical experimental data to support the interpretation
173 of data from orbital observations of the Martian SPC, namely the Compact Reconnaissance
174 Imaging Spectrometer for Mars (CRISM) on board NASA's Mars Reconnaissance Orbiter

175 (MRO), which has a surface spatial resolution of around ~18m/pixel (Murchie et al., 2007), with
176 a spectral resolution of ~6 nm.

177 3.1. Instrument parameters

178 The CRISM instrument has a resolution, of 9-19 nm full width at half maximum (FWHM) with
179 6.55 nm sampling over the 0.36-3.92 μm range (Murchie et al., 2007) In order to get a spectral
180 resolution as close as possible to CRISM, we recorded spectra over the 0.7-3.6 μm spectral range
181 using SHINE with a fixed slit of 1.5 mm, leading to 9-19 nm spectral resolution, and sampled
182 every 10 nm (except for the first experiment sampled at 20 nm). To complete a full reflectance
183 spectrum at this resolution took > 2.5 hours, so in order to effectively reduce the time between
184 two spectra, especially during ice sublimation, in many instances multiple shorter spectra at
185 wavelengths of interest were taken. The SHINE angular parameters used were fixed incidence
186 angle = 0° , and observation angle = 20° , optimized for the CarboN-IR cell. This is comparable
187 with a median phase angle of 0-30 $^\circ$ for CRISM (Ceamanos et al., 2013).

188 3.2. Sample Preparation

189 Three samples were analysed for various ratios of PAHs mixed with CO₂ ice and two with finely
190 ground Martian simulant JSC-Mars 1 (Allen et al., 1998). Much of the existing literature on
191 PAHs found on icy moons and comets references the laboratory spectra recorded by Colangeli et
192 al., (1992), which is pertinent to PAHs of astrophysical interest, rather than astrobiological, or
193 specifically Martian. The six PAH species analysed by Colangeli et al., (1992) were benzene,
194 chrysene, triphenylene, perylene, benzo [a] pyrene, pentacene and coronene. While chrysene and
195 perylene have been found in Martian meteorites (Becker et al., 1997) and phenanthrene, pyrene,
196 chrysene, perylene or benzopyrene and anthanthracene were found by McKay et al. (1996) the
197 remaining four types of PAH have never been detected in Martian material. Therefore, we
198 analysed our own mixture of PAHs based on those identified by McKay et al. (1996) in the
199 ALH84001 and EETA79001 Martian meteorites but absent from Colangeli's analysis. The PAHs
200 used were an existing mixture of anthracene (C₁₄H₁₀), phenanthrene-d10 (C₁₄D₁₀), and pyrene
201 (C₁₆H₁₀) in raw form, obtained from Sigma-Aldrich (www.sigmaaldrich.com), in a 300 mg
202 sample of equal parts of each PAH species. We will not discuss in this paper the bands due to or
203 modified by the deuterated species as they do not contribute to PAH spectral features of interest.

204 In studies of Saturnian moons Iapetus and Phoebe (Cruikshank et al., 2008), the amount of PAHs
205 detected on the surface was 10^{-4} to 10^{-3} g/cm³ (0.01-0.1 %) so the first sample used 0.10 % PAH
206 followed by 0.54 % and 0.67 % weight fractions for our three PAH samples mixed with CO₂ ice
207 in order to allow the detection limit to be determined by plotting band depth as a function of
208 concentration. The percentage amounts of PAH in CO₂ ice were difficult to fix precisely because
209 some CO₂ ice sublimated during the process of mixing the materials, but they were precisely
210 measured when the sample holder was filled with the prepared mixture, just before their
211 introduction into the cell (see below). Increases in the amount of PAH for Samples 2 and 3 were
212 chosen based on how well we could see the PAH features in Sample 1.

213 CO₂ ice was obtained from liquid decompression with a commercial device SnowPack©. This
214 produces a granular snowpack of 312.5 cm³ composed of small CO₂ ice grains. The average size
215 of the grains, 150 μm , was estimated by measuring the true surface of the grains observed with a

216 binocular microscope (Philippe et al. 2016). Part of the CO₂ ice snow pack was then manually
217 crushed, weighed, and a known mass of PAH powder was added and thoroughly mixed in a
218 stainless-steel container pre-cooled with liquid nitrogen to limit CO₂ ice sublimation. The cell,
219 also pre-cooled at -196°C, was filled up to its rim with the mixture (slightly compressed) and
220 weighed before rapid installation inside the pre-cooled CarboN-IR environment chamber (-100
221 °C). The Martian South Pole's lowest temperatures can reach -153 °C and never exceeds -60 °C
222 with the spring/summer temperatures for the SPC typically ranging between -80 and -100 °C
223 (Smith, 2004); hence the choice to keep the environmental cell at the lower spring/summer
224 temperature. The sapphire windows of the cryogenic chamber and of the external chamber were
225 then successively closed and air was completely evacuated from both volumes by pumping using
226 a detailed protocol developed to avoid frost condensation on the windows.

227 The grain sizes of our CO₂ ice samples are much smaller than what is generally observed on
228 Mars South Polar Cap where CO₂ ice tends to have very coarse centimeter sized grains, generally
229 in the form of compact slab (Douté et al. 2007). However, a major decrease in grain size, down
230 to the millimeter, occurs after equinox (Langevin et al. 2007) and corresponds to the large
231 increase of albedo observed over the perennial cap during its sublimation phase. The grains in our
232 samples are typically 5-10 times smaller than during the polar cap sublimation phase of interest.
233 However, preparing such coarse grained CO₂ ice grains is a quite complex process and takes
234 several weeks and was not possible given the experimental constraints (Philippe, 2016). But, as
235 we will discuss later, using smaller grains may put stronger or weaker constraints on the
236 detectability of PAHs, depending where their bands are situated relative to the CO₂ ice bands.

237 In addition, we measured one mixture of 1.5% PAH combined with a fine fraction (<25µm) of
238 JSC-Mars 1 Mars simulant as well as this dust alone, as a reference.

239 The sample holder is 4.5 cm in diameter and 2 cm deep and has a total volume of 31.8 cm³.
240 Knowing the mass of the sample, measured just after filling the holder, and the density of bulk
241 CO₂ ice (1.562 g.cm⁻³) allowed to estimate the initial density and porosity of the sample, which
242 is simply the fraction of the volume of the sample holder not occupied by CO₂ ice.

243 The percentage of H₂O ice mixed in the CO₂ snow was estimated (with uncertainty +/-20%) by
244 comparison of its 1.5 µm band depth with that of the nearby CO₂ bands (at 1.435 and 1.58 µm)
245 and relative to the spectra of a series of CO₂:H₂O ice mixtures previously measured and
246 modelled (Philippe 2016). The mass fraction of H₂O ice in our samples is mostly of the order of
247 the maximum values determined for the South Polar Cap, 0.08-0.12% (Douté et al. 2007) except
248 in one case (~0.20%) where it exceeds these limits.

249 3.3. Experiment Protocol

250 After introduction of the sample holder containing the PAH-CO₂ ice mixture into the CarboN-IR
251 cell and throughout the experiments, the cell and sample holder temperatures were kept at -
252 100°C. Following initial measurements of the samples, sublimation experiments were conducted
253 by pumping the CO₂ gas into the cell to monitor spectral and detection limit changes with
254 sublimation. Bidirectional reflectance spectra (at single geometry) on both full Vis-NIR and

255 partial spectral ranges were recorded regularly during the sublimation experiment to reflect
 256 regions of interest for later comparison to observational results from orbital sensors.

257 **4 Results**

258 4.1. Preliminary Measurements

259 A first guess of the detectability limit for PAHs in CO₂ ice was established with reference to
 260 levels detected on other planetary bodies such as Iapetus, 10⁻⁴ to 10⁻³ g/cm³ (Cruikshank et al.,
 261 2008). This was then tested at room temperature with a ~1% mix of PAH mixture with a
 262 transparent powder (alumine) in order to estimate the minimum amount of PAH required for
 263 detection within CO₂ ice but outside its absorption bands. From this preliminary experiment, an
 264 approximate detection limit of about 0.1% by weight was determined. This experiment also
 265 allowed us to define spectral ranges and resolution needed to detect the PAH mixture without
 266 interference from CO₂ ice spectra.

267 A spectrum of the ‘pure’ PAH mixture was also measured between 0.4 and 4.7 μm (at 20 nm
 268 sampling) as a reference (grey line in Figure 1). The positions and intensities of the bands are
 269 consistent with the reflectance spectra measured at higher spectral resolution up to 2.5 μm for
 270 our three PAHs by Izawa et al. (2014), except the 2.24 μm band which is much stronger in our
 271 PAH mixture spectrum.

272 Table 1 shows the details of the three CO₂ ice samples discussed in the subsequent sections.

273

274

Table 1: Sample Details

Sample No.	Sample 1	Sample 2	Sample 3
CO₂ Mass in g	31	23.5	30
PAH Mass in mg	32.7	158.1	161.6
Weight percentage of PAH to CO₂ in %	0.10	0.67	0.54
Weight percentage of H₂O to CO₂ in %	~0.12	~0.2	0.08
Weight fraction of PAH relative to H₂O	~0.8	~3.3	6.75
Density in g/cm³	0.98	0.74	0.94
Porosity in %	38.5	52	40

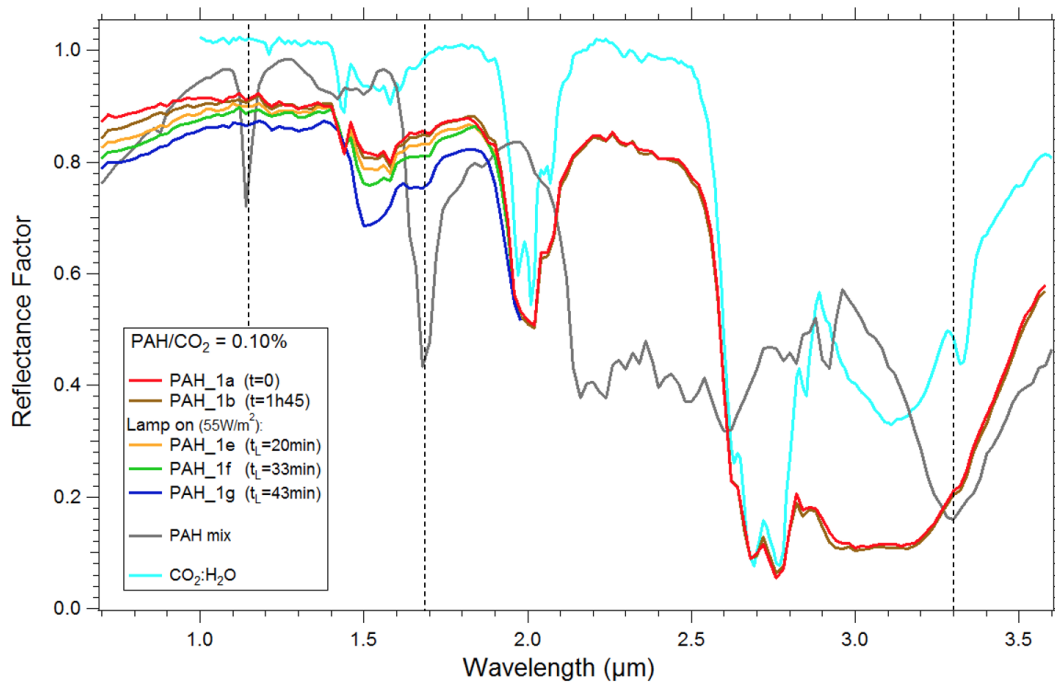
275

276 4.2. PAH/CO₂ = 0.1% - Sample 1

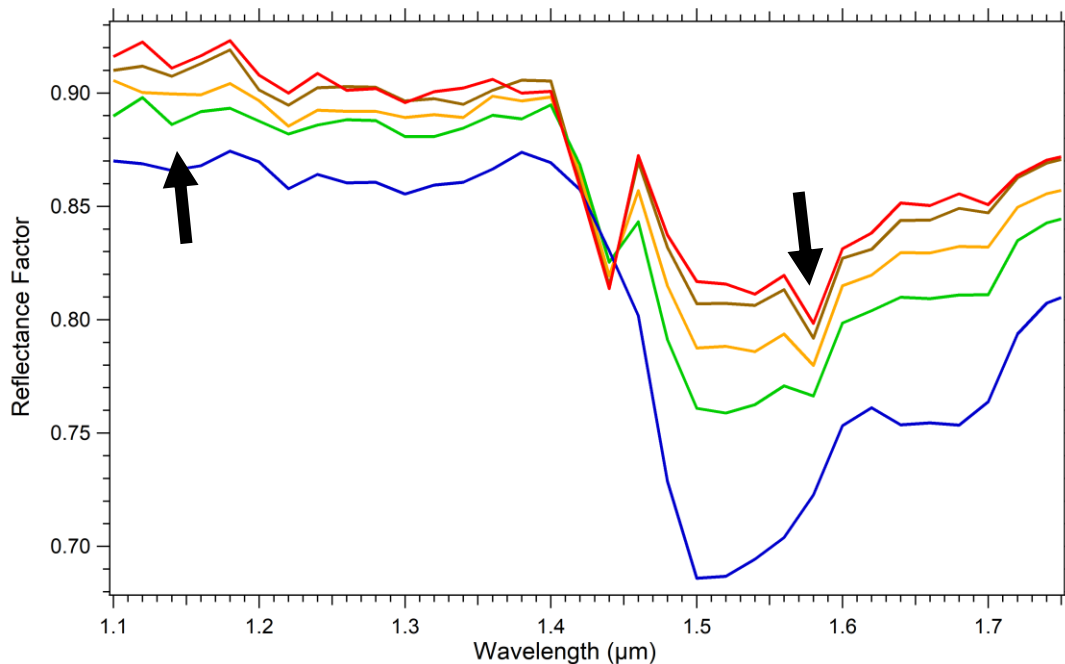
277 For the first PAH+CO₂ ice sample, an amount of PAH comparable to our pre-estimated detection
 278 limit, 0.1%, was used. During this experiment the speed with which the interior chamber was
 279 pumped out from the ambient air resulted in water frost particles condensing on the surface of
 280 the sample being blown onto the inside of the window, and could not be removed (in the
 281 subsequent experiments this was done more slowly and with additional heating of the window to

282 avoid this problem) meaning that water contamination at the surface of CO₂ ice may be stronger
283 in sample 1.

284 Two spectra were obtained from 0.4-3.6 μm with spectral sampling of 20 nm. As the vacuum
285 was very stable, to aid sublimation, a lamp was used to heat the sample surface, at 27 cm
286 distance from the window, resulting in 70W/m² equivalent to Mars at noon at 70° lat, achieving
287 a sample sublimation of ~3 mm between two spectra. Upon examination of these spectra it was
288 clear that the PAH feature at 3.29 μm is not observed on the side of the strong and broad 3.1 μm
289 water ice band (the small shoulder at 3.32 μm is due to CO₂ ice), and so the following spectra
290 were taken only between 0.6 and 2.0 μm at 20 nm sampling. Fig. 1 shows the results.



291



292

293 *Figure 1: Top: Spectra from sample 1, 0.10% PAH in CO₂ ice (with small amount of H₂O ice ~0.12%) at -100°C during*
 294 *progressive sublimation of CO₂ (PAH_1a to 1g). Black, dotted vertical lines indicate the main infrared PAH absorption features.*
 295 *The sublimation was first free (1a, 1b) then triggered by illumination with a lamp (55W/m² at sample surface): 1e-1g. The*
 296 *spectrum of the PAH mix and of CO₂ ice (with small amount of H₂O ice ~0.075%) are also shown for reference. Note the*
 297 *increasing slope below 1.1 μm and the bands at the limit of detection at 1.14 and 1.685 μm. Bottom: Detail of PAH absorption*
 298 *features indicated by black arrows*

299 It is clear over time, the overall reflectance of the spectra (PAH1a-1g) decreases as the CO₂ ice
300 sublimates, and the slope increases between 0.7 and 1.1 μm. This is likely to be associated with
301 the steep slope in the corresponding pure PAH mixture spectrum (black line) as sublimation
302 increased the ratio of PAH/CO₂ ice and probably concentrated the PAH at the surface of the
303 sample. We also notice that the water ice feature dominating around 1.52μm increases with
304 sublimation, as the tiny frost particles present at very low level (~0.12%) in CO₂ ice are also
305 segregated at the surface during sample sublimation (Philippe, 2016). A subtle absorption feature
306 with a band depth of about 0.6% is visible in the PAH 1a-1g series of spectra corresponding with
307 the pure PAH feature at 1.14 μm, with another weak feature visible at 1.68 μm (band depth ~
308 1%). This latter band strongly increases in intensity during CO₂ sublimation and reaches an
309 estimated depth of about 3% in the remaining PAH-H₂O ice lag deposit, but at this spectral
310 sampling it is difficult to separate it from the 1.645μm band of H₂O ice. It would seem that the
311 initial 0.10% PAH/CO₂ ice ratio is actually close to the detectability limit at this spectral
312 resolution and sampling, and subsequent experiments used a higher initial ratio and a two times
313 better spectral sampling to confirm the detection of the PAH bands.

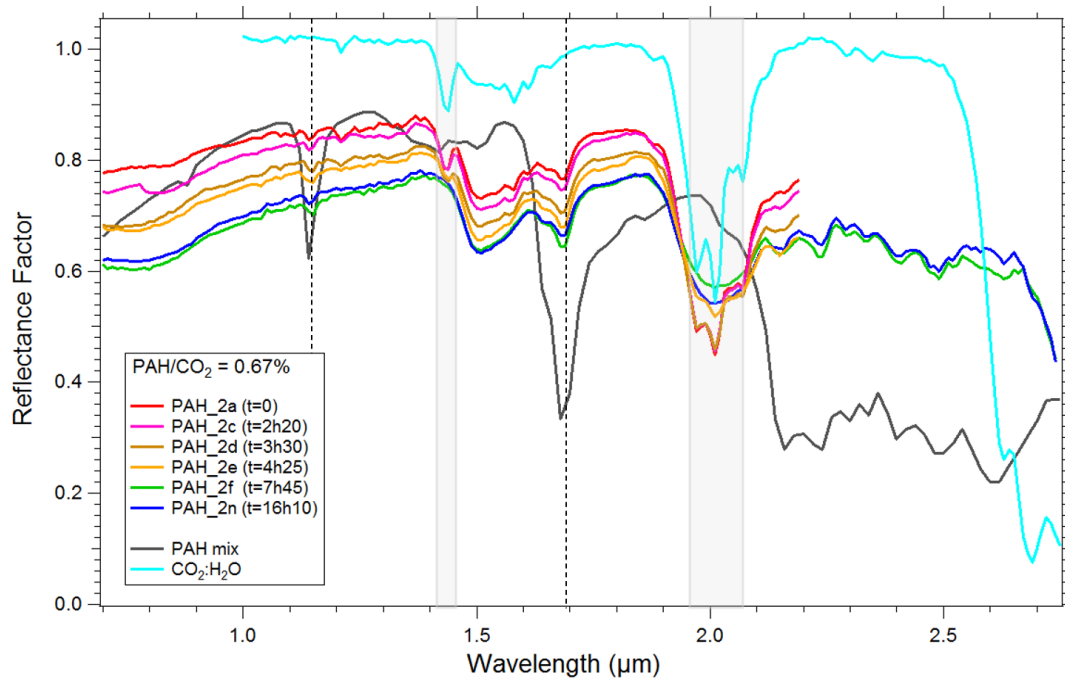
314 4.3. PAH/CO₂ = 0.67% - Sample 2

315 For this second experiment, more care was taken to limit frost condensation at the surface of the
316 CO₂ ice sample during transfer to the CarboN-IR cell and the ambient air was pumped more
317 slowly to avoid window condensation or frost particles blown on it, but this was not successful
318 as the water ice bands are about 2 times more intense than in Sample 1 with an estimated amount
319 of H₂O ice of about 0.2%.

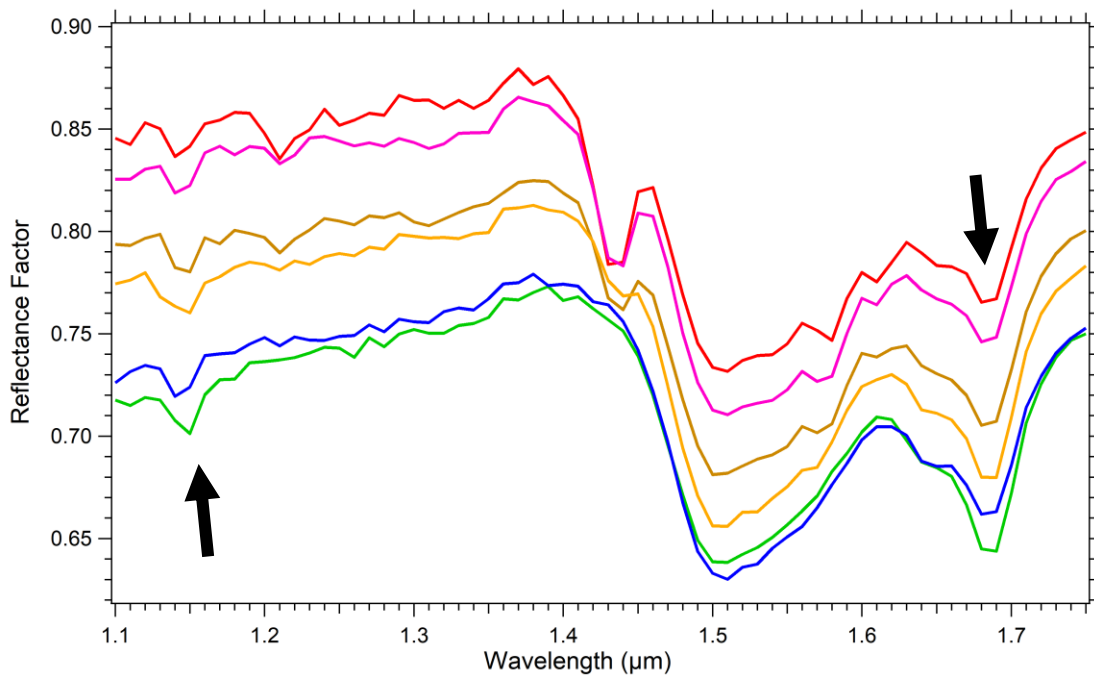
320 A higher spectral sampling, 10 nm, was used, meaning it took longer to obtain spectra, so a
321 spectral range of 0.7-2.2 μm was chosen to obtain multiple spectra to observe the evolution of
322 the features at 1.14 and 1.685 μm for the first 4 spectra (PAH2a-PAH2d) during the sublimating
323 sequence. This limitation of the spectral range did not limit this study as CRISM spectra below
324 2.5 μm are the most useful for this work due to the interference of strong atmospheric water and
325 ices features at 2.7-3.3 μm on Mars and because only the lower wavelength PAH features are
326 detected against a background of CO₂ ice. There was a small leak in the cell, increasing
327 sublimation rate, so the lamp was not used for sample 2 to reduce the sublimation rate of CO₂.
328 The spectral range was then increased to 0.7-2.75 μm and left to run overnight, resulting in total
329 of 6 spectra, shown in Fig. 2.

330

331



332



333

334 *Figure 2: Top: Spectra from sample 2, 0.67% PAH in CO_2 ice (with small amount of H_2O ice ~0.2%) at -100°C during*
 335 *progressive sublimation of CO_2 (PAH_2a to 2n). Black, dotted vertical lines indicate the main infrared PAH absorption features,*
 336 *transparent grey boxes indicate transforming CO_2 ice absorption features. The sublimation was free until the complete*
 337 *disappearance of CO_2 ice. The spectrum of the PAH mix and of CO_2 ice (with small amount of H_2O ice ~0.075%) are also shown*
 338 *for reference. Note the increasing slope below 1.1 μm and the bands clearly appearing at 1.14 and 1.685 μm , but also in the 2.1-*
 339 *2.6 μm range. Bottom: Detail of PAH absorption features indicated by black arrows*

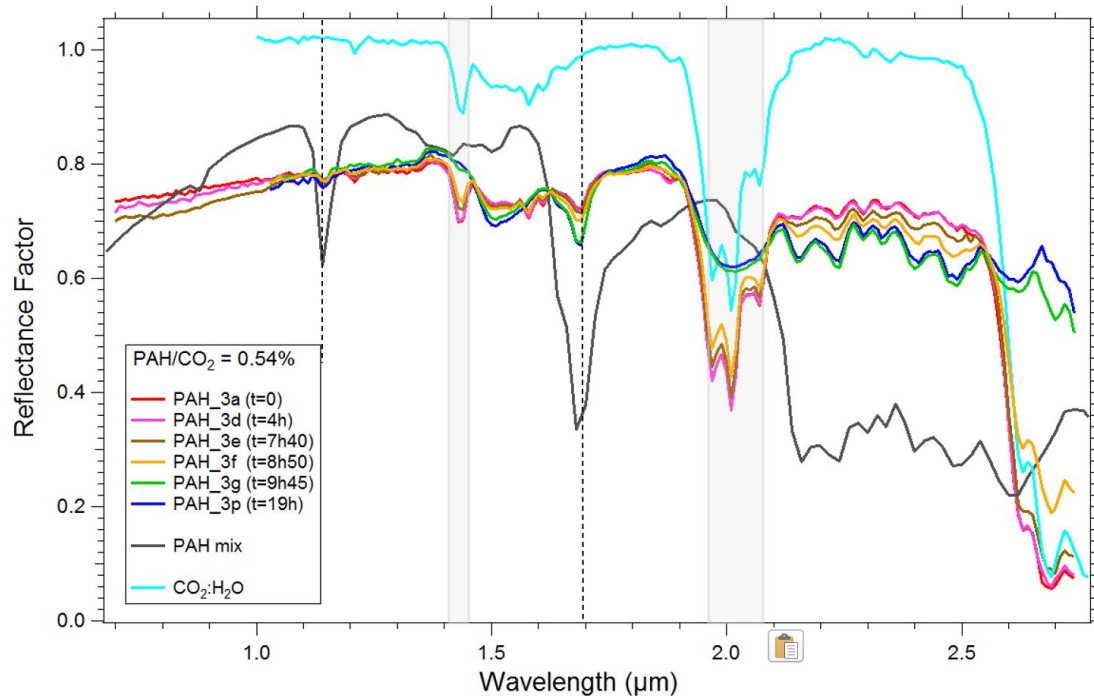
340 With the increased amount of PAH in the ice, the absorption features at 1.14 and 1.685 μm (band
341 depths of 2% and 7% in the mixture, respectively) are now clearly visible throughout all
342 PAH/CO₂ ice spectra, as well as the slope at 0.7-1.1 μm . In the extended spectra PAH2e-PAH2p,
343 there are also corresponding features visible at 2.15, 2.24, 2.29, 2.33, 2.41, 2.49 and 2.62 μm in
344 pure PAH and PAH/CO₂ ice spectra. It is also clear that with the increased initial amount of
345 H₂O ice in this sample (~0.2%, instead of ~0.12% in Sample 1) the CO₂ ice absorption feature at
346 1.435 μm and its triplet features around 2 μm become more rapidly dominated by the strong
347 and broad 1.5 and 2 μm absorption bands of water ice, as CO₂ ice sublimates. When all the CO₂
348 ice has sublimated, leaving only a thin deposit (~170 μm) of water ice-dust mixture, the intensity
349 of both the 1.14 and 1.685 μm bands have increased by about 70%, and then started to decrease
350 slowly while the H₂O ice band was stable.

351

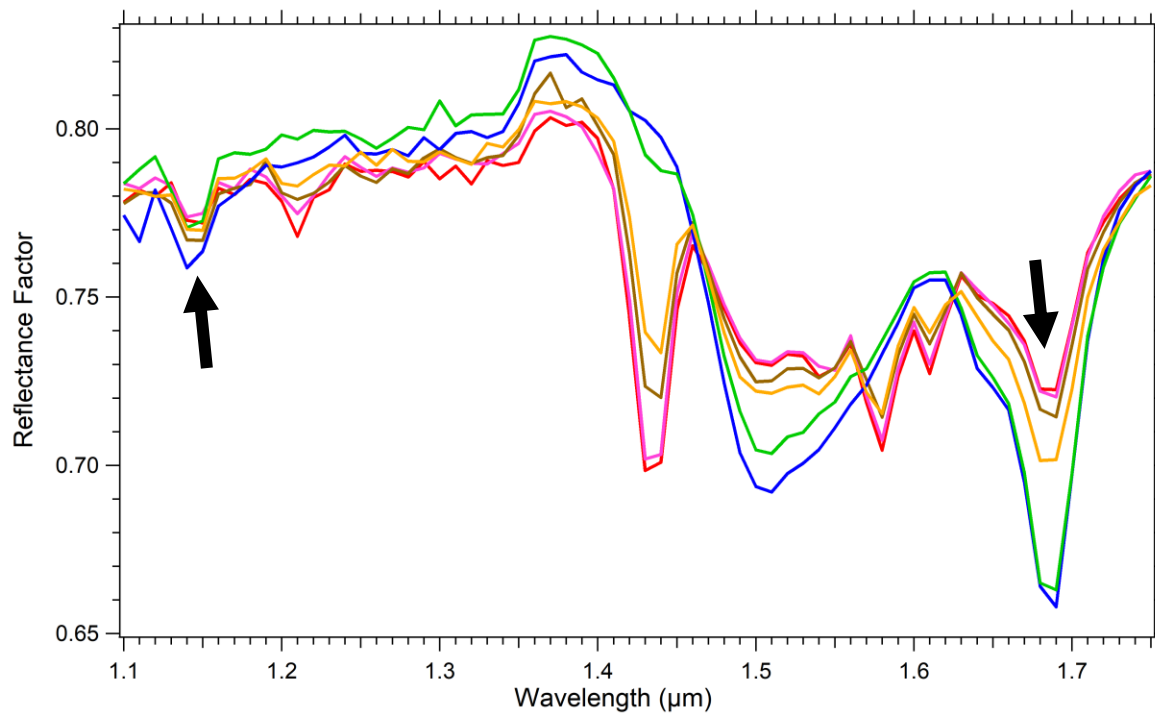
352 4.4. PAH/CO₂ = 0.54% - Sample 3

353 For this experiment a spectral range of 0.4 -2.75 μm was chosen with resolution of 10nm. Details
354 of sample 3 are shown in table 1. This time with an improved preparation protocol we succeeded
355 in efficiently suppressing any additional condensation of frost at the surface of the CO₂ ice, and
356 the water ice content (0.08%) is now similar to what was previously achieved for pure CO₂ ice,
357 as witnessed by the almost identical ratio between the 1.52 μm band of H₂O and 1.435 μm band
358 of CO₂ ice in the initial spectrum 3a (Figure 3).

359 Sixteen spectra were taken throughout the day and overnight during the sublimation sequence.
360 As with experiment 1, the vacuum was very stable, and slow sublimation occurred, resulting in
361 fairly homogenous spectra. Results are shown in Fig. 3.



362



363

364 *Figure 3: Top: Spectra from sample 3, 0.54% PAH in CO₂ ice (with small amount of H₂O ice ~0.08%) at -100°C during*
 365 *progressive sublimation of CO₂ (PAH_3a to 3p). Black, dotted vertical lines indicate the main infrared PAH absorption features,*
 366 *transparent grey boxes indicate CO₂ ice absorption features mentioned in the text. The sublimation was free until complete*
 367 *disappearance of CO₂ ice. The spectrum of the PAH mix and of CO₂ ice (with small amount of H₂O ice ~0.075%) are also shown*
 368 *for reference. Note the increasing slope below 1.1 μm and the bands clearly appearing at 1.14 and 1.685 μm, but also in the 2.1-*
 369 *2.6 μm range. Bottom: Detail of PAH absorption features indicated by black arrows.*

370

371 With 0.54% PAH, the features at 1.14, 1.685, 2.15, 2.24, 2.41, 2.49 and 2.62 μm are visible as
 372 with sample 2. With these higher signal-to-noise spectra, it is also possible to better observe the
 373 replicated PAH features at 2.29 and 2.33 μm , with the PAH/CO₂ ice mixture between 2.1 and
 374 2.5 μm closely mirroring the shape of the spectrum for pure PAH mixture. The change in the
 375 slope at 0.7-1.1 μm is also clear but unfortunately was not monitored until the end of the
 376 experiment. Again as with Sample 2, the CO₂ ice absorption feature at 1.435 μm becomes muted
 377 with sublimation, but the triplet feature at ~ 2 μm is less affected in the first stages of sublimation
 378 with an initial ‘contamination’ of only 0.08% water ice, as was the case with the small amount
 379 of H₂O ice in Sample 1. During CO₂ sublimation, the intensity of the 1.14 μm band increased by
 380 about 50%, and that of the 1.685 μm by a factor of 2.3 when only a H₂O ice-dust sublimation
 381 residue remained at the bottom of the sample holder (only about 120 μm thick). Other bands,
 382 such as those of 1.155 μm and 2.49 μm , increased by an even greater proportion.

383

384 4.5. PAH/dust = 1.52% and dust - Samples 4 and 5

385 A final experiment, with two spectra ranging from 0.4-3.9 μm at a resolution of 10nm, was taken
 386 of the PAH mixture in Mars simulant JSC Mars-1, weathered volcanic ash from Hawaii (Allen et
 387 al., 1998), as well as a pure dust spectrum for reference (Figure 4). The JSC Mars-1 regolith
 388 simulant was previously ground and sieved below 25 μm to simulate Martian atmospheric dust.
 389 Sample details are shown in Table 2.

390

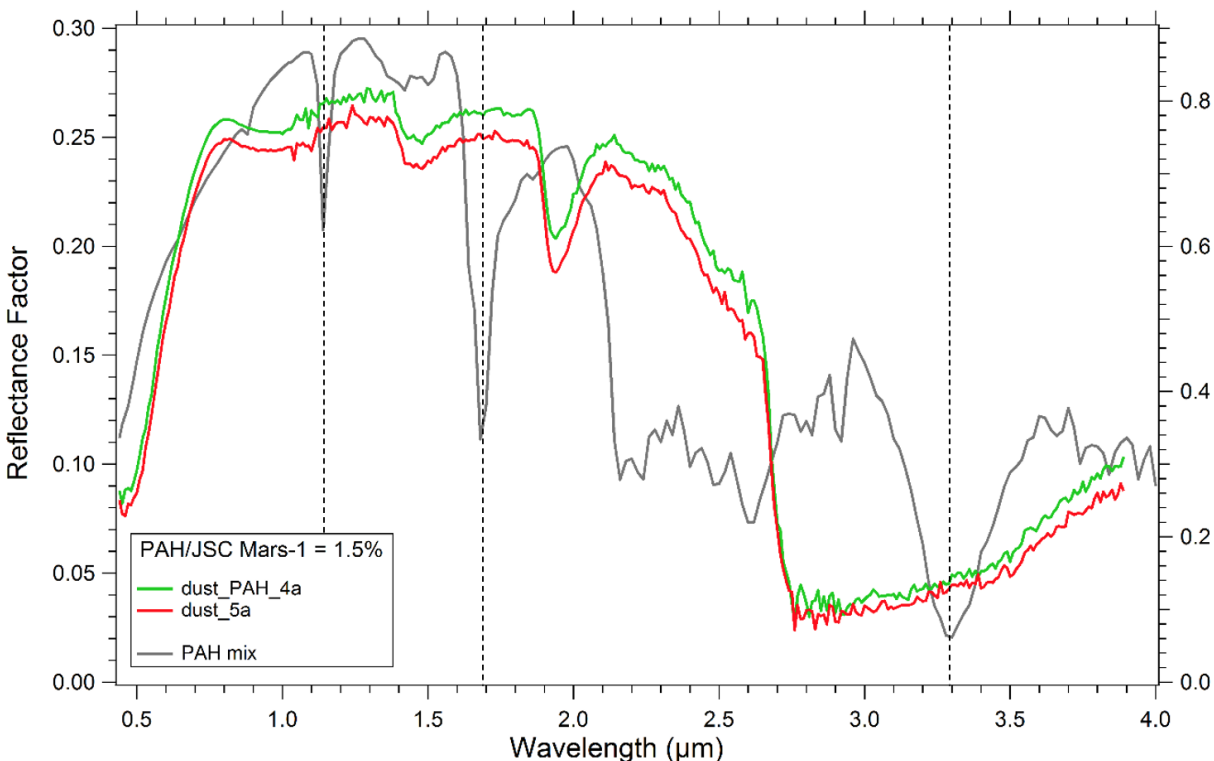
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392

Table 2: Details of Samples 4 and 5

Sample Description	Sample 4 : PAH/ JSC Mars-1 Dust Mix	Sample 5: JSC Mars-1 Dust
Dust Mass in g	7.7	15.4
PAH Mass in mg	117	-
Weight percentage of PAH to dust in %	1.52	-
Density in g/cm ³	1.895	1.91
Porosity in %	48.1	49.3

393



394
 395 *Figure 4: Spectra from samples 4 and 5, 1.52% PAH in JSC Mars-1 (dust_PAH_4a), and JSC Mars-1 (dust_5a) at room*
 396 *temperature. Black, dotted vertical lines indicate the main infrared PAH absorption features. The spectrum of the PAH mix is*
 397 *also shown for reference (right scale). Note that no sign of increase of slope below 1.1 μm and no bands are detected at 1.14,*
 398 *1.685 μm, nor at 3.29 μm,*

399 Despite PAH particles being clearly visible in the physical sample, and the ratio of PAH to
 400 substrate being 2.5 to 3 times higher than in ice samples 2 and 3, (1.52% compared to 0.67% and
 401 0.54%), no spectral features of PAHs were detectable in the dust spectrum.

402 Other than the pure dust sample being slightly lower in overall reflectance, there is no observable
 403 difference in spectra between pure dust and PAH/dust mix. This is most likely because of the
 404 relative opacity of dust compared with CO₂ ice, its continuum reflectance being three times
 405 lower. If PAHs are not discernible in Martian dust at concentrations an order of magnitude
 406 higher than that detected on Iapetus, it is likely to be an extremely limiting factor in detecting
 407 PAHs on the SPRC if any potential PAHs are mixed with dust and not in pure form. No known
 408 segregation process can concentrate PAH in dust as is the case with PAH/CO₂ ice mixtures. In
 409 order to ascertain whether PAHs in small amounts of dust are detectable when mixed in CO₂ ice,
 410 further experiments will need to be carried out to better emulate the scarp wall dust deposits in
 411 SCT. However, with our current set of experiments, it is already possible to make some

412 extrapolations on the detectability of PAH in materials with different compositions encountered
413 on the South polar cap and in the water ice-dust lag deposits at its margins.

414 **5 Discussion**

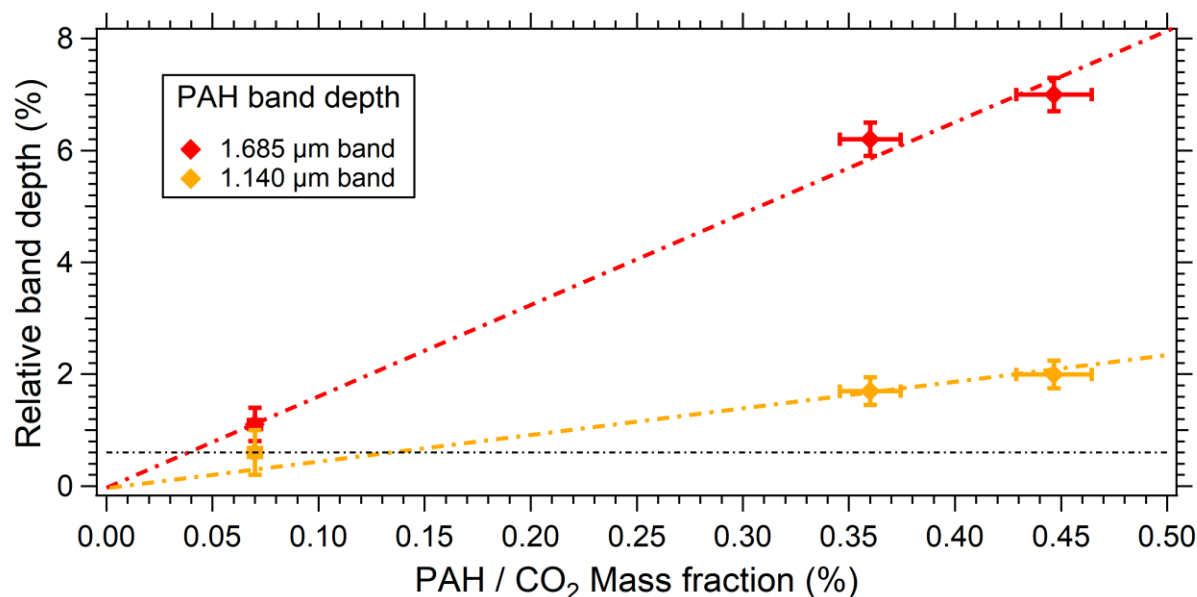
415 The results of these novel experiments are extremely useful to allow a future new analysis of
416 orbital observations from the CRISM instrument on Mars Reconnaissance Orbiter, and establish
417 a detection limit for PAHs in CO₂ ice and in H₂O ice-dust lag deposits, not only at the poles, but
418 in shadowed regions elsewhere, in sub-surface ice that may be sampled during future exploration
419 missions as well as on icy bodies. In addition, we ascertained the limitations of observing PAHs
420 directly in ‘dry’ Martian regolith, a first step towards establishing the detectability of PAH in the
421 regolith of other planets. This study also provides more relevant bi-directional reflectance data in
422 the near-infrared range on diagnostic PAH signatures of astrobiological importance to Mars, that
423 are pertinent to planetary ices, as most previous literature, except Izawa et al. (2014), used mid-
424 infrared transmission data from the 1990s which is more relevant to interstellar dust cloud PAH
425 detection.

426 PAHs are extremely important to theories of abiogenesis, and while their presence is
427 ubiquitous in space, their detection on planetary bodies remains a major objective in planetary
428 science. The attempt to detect them on Mars is worthwhile given the recent discoveries of other
429 organic compounds and subterranean lakes (Freissinet et al., 2015; Ojha et al., 2015; Orosei et
430 al., 2018).

431 In the spectrum of our mixture of three PAHs the strong 1.685 μm band is the first overtone
432 ($2\nu_{\text{CH}}$) of the fundamental aromatic symmetric C-H stretch modes (ν_{CH}) occurring at ~3.29 μm.
433 From the position of these two bands, we deduce that the 1.14 μm band is the second overtone
434 ($3\nu_{\text{CH}}$) of these modes, and the weak band at 0.88 μm is the third overtone ($4\nu_{\text{CH}}$) (Izawa et al.
435 2014). The other bands between 2.1 and 2.9 μm are mostly combination bands between these
436 stretching modes and various types of aromatic C=C deformation modes and C-H stretching and
437 bending modes. Due to the use of phenanthrene-d10 in our sample there are also additional bands
438 at 2.24 and 1.50 μm due to the first and second overtone of the fundamental C-D stretch modes.
439 Weaker bands between 1.30 and 1.55 μm are higher order combinations (Izawa et al. 2014). In
440 our discussion we will only consider the 1.14 and 2.685 μm C-H stretch overtone bands.

441 **5.1 Detectability of PAH in CO₂ ice**

442 We have shown that the most interesting and sensitive signature of PAH for detection on the
443 Mars residual CO₂ ice cap is this $2\nu_{\text{CH}}$ band at 1.685 μm, well outside the CO₂ ice bands and the
444 strongest H₂O ice bands (Figure 6). The only band that can slightly interfere with this PAH band
445 is the 1.645 μm band of water ice, which is seen in our spectra as a weak shoulder on the low
446 wavelength side of the PAH band (see e.g. Figure 2). However, it is shifted to lower
447 wavelengths by 0.04 μm, well above the resolution of all current and future near-infrared
448 spectrometers. We found that even with more than 0.1% water in CO₂ ice, which is rarely the
449 case in the very dry southern hemisphere (Douté et al. 2007 found 0.02-0.12% H₂O in CO₂ ice),
450 this ice band did not preclude the detection of PAH homogeneously mixed at levels below 0.1%
451 in CO₂ ice.



452

453 *Figure 5: Relative band depth of the 1.14 and 1.685 μm bands of PAH versus the mass fraction of PAH (contributing to these*
 454 *aromatic C-H stretching bands) of the initial homogeneous mixture in CO₂ ice at -100°C. The horizontal line represents a band*
 455 *depth detection level of 0.6% (at 3σ with S/N=450-500).*

456 In order to better assess the detectability level of this band and the 1.14 μm one for PAH
 457 homogeneously mixed with CO₂ ice (before any sublimation), we have plotted in Figure 5 the
 458 initial relative band depth of both bands versus the mass fraction of PAH containing C-H bonds
 459 (removing phenanthrene-d10 which did not contribute to these bands). Assuming the pre-flight
 460 SNR value of 450-500 around 1.14 and 1.68 μm given for CRISM (Murchie et al., 2007, Fig.
 461 33b), the detection level of these bands in an observed spectrum with reflectance close to 1 (as
 462 for CO₂ ice) is for a band depth of 0.6% relative to the nearby continuum (i.e. for a 3σ detection
 463 level, horizontal dotted line in figure 5). The detectability of the 1.685 μm band of PAH well
 464 mixed in fine grained CO₂ ice (D ~150 μm) is thus at about 0.04% PAH weight fraction, and that
 465 of the 1.14 μm at about 0.13%. The detection level for the 1.685 μm band should be only slightly
 466 affected at the lower temperature of the SPC (~-150°C), whereas the 1.645 μm H₂O band gets
 467 stronger and shifts slightly towards the PAH band (see Fig 2 of Grundy and Schmitt, 1997;
 468 1998). The 1.14 μm band is weaker but, on the other hand, absorbs at a wavelength without CO₂
 469 absorption and between two much weaker water ice bands.

470 The slope between 0.7 and 1.1 μm, and the absorption features in the 2.1-2.5 μm range may also
 471 provide additional clues to confirm detection. The visible slope of PAH occurs in a range of full
 472 transparency of both ices, but it cannot be used as a detection criteria as it may be confused with
 473 the slope induced by a small amount of contaminating reddish dust. The bands between 2.1 and
 474 2.5 μm are also mostly outside any strong CO₂ absorption and are clearly observed in most of
 475 our spectra, down to a PAH abundance at 0.1% level, despite a larger abundance of H₂O ice in
 476 our samples compared to the Mars South Polar Cap. However, the two generally weak CO₂ ice

477 bands at 2.295 and 2.35 μm may become much stronger in some situations (larger grain size, see
478 e.g. Douté et al. 2007; Langevin et al. 2007) and strongly interfere with this set of PAH bands.

479 On the other hand, the ‘classical’ strong 3.29 μm fundamental band of PAH interferes with the
480 relatively strong 3.32 μm band of CO_2 ice but is also buried in the wing of the strong water ice
481 band at 3.1 μm which can saturate even with a very small amount ($\ll 0.1\%$) of H_2O trapped in
482 CO_2 ice (see e.g. Figure 1). Similarly, when mixed with martian soil this band falls in the wing of
483 the very strong band of both structural and adsorbed H_2O . This 3.29 μm band thus cannot be
484 used to detect PAH in reflectance spectra of icy surfaces.

485 An important point to consider here is the difference in CO_2 ice grain sizes between our samples
486 ($\sim 150 \mu\text{m}$) and the perennial cap: from several centimetres (clear compact slab) decreasing down
487 to a few millimeters during sublimation in spring (Langevin et al. 2006, Douté et al. 2007).
488 Larger grains increase the intensity of the CO_2 absorption bands and can efficiently hide any
489 other signatures there on in their wings, but on the other hand, such large grains allow light to
490 penetrate and probe much deeper in the wavelength ranges outside the relatively narrow CO_2
491 bands. In particular, the 1.685 μm PAH band is situated at a wavelength where the absorption
492 coefficient of CO_2 is extremely low ($< 3 \cdot 10^{-4} \text{ cm}^{-1}$; Quirico and Schmitt 2004, Hansen 2005). So
493 it is anticipated from radiative transfer considerations that the detection level of this PAH band
494 should be largely improved in such coarse grained or slab ice, possibly down to the 0.01% level.
495 The main limitation will come from the abundance of water ice which has an absorption
496 coefficient around 10 cm^{-1} at 1.685 μm (in the wing of the 1.645 μm H_2O band) for pure ice
497 (Grundy and Schmitt, 1997; 1998), i.e. about 4 orders of magnitude above that of CO_2 ice. A
498 water ice abundance above a few percent should preclude the detection of trace amounts of PAH
499 at this wavelength. On the other hand the 1.14 μm band is situated at a wavelength of minimum
500 absorption of H_2O ice ($\sim 5 \cdot 10^{-2} \text{ cm}^{-1}$) and may be a better probe where H_2O ice is moderately
501 abundant.

502 Also, as CO_2 ice sublimates, the PAH contained in the sublimated layers segregates at its surface
503 together with H_2O ice and its band depth progressively increases by a factor which depends on
504 the initial amount of H_2O ice. This increase is only by a factor of 1.55 when the $\text{H}_2\text{O}/\text{CO}_2$ ratio is
505 large, as for sample 2 (0.20%), but can reach a factor of 2.3 when this ratio is small, as for
506 sample 3 (0.08%). So the ‘visibility’ of PAH is increased by the CO_2 sublimation only until a
507 mix of PAH and H_2O ice remains. On Mars the accumulation factor of PAH at the surface (at the
508 same initial concentration) will be larger as the thickness of sublimated CO_2 is more than an
509 order of magnitude larger than for our sample (2 cm).

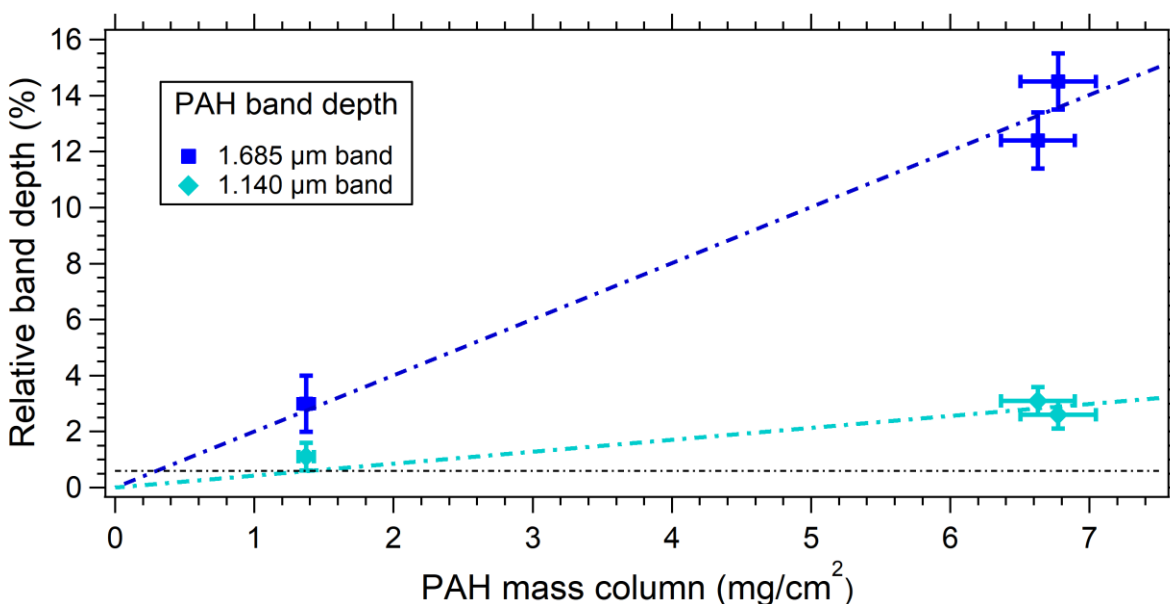
510

511 5.2 Detectability in the PAH- H_2O ice lag deposit

512 Another important result is that for all our samples, the PAH bands are still observed in the H_2O -
513 PAH mixture left over after complete sublimation of the CO_2 ice, and with an increased intensity
514 despite the relatively high initial content in H_2O ice (0.08-0.20%) relative to the Mars South
515 Polar Cap. Our three resulting sublimation lag deposits have $\text{H}_2\text{O}/\text{PAH}$ ratios ranging from 15 to
516 120% (see Table 1) and display very clear and strong PAH bands at all wavelengths for Samples
517 2 and 3 (Figures 2 and 3). Even for Sample 1, where H_2O ice dominates the composition of the

518 mixture, the 1.685 μm is easily detectable, although blended with the 1.645 μm H₂O band (but
 519 the sampling was only 20 nm for this sample) which now has a similar intensity (see the blue
 520 curve in figure 1). Its relative band depth is about 3%. So PAH may still be detectable in the lag
 521 deposit, as a shoulder $\sim 1\%$ deep on the side of the 1.645 μm band, if the initial weight abundance
 522 of PAH relative to H₂O ice is more than about 25% (~ 3 times less than for Sample 1). Given the
 523 average concentration of 0.02-0.04% for H₂O ice in CO₂ ice determined for the dry ice-rich
 524 terrains (Douté et al. 2007) at $L_s \sim 140^\circ$, we can still expect to be able to detect PAH mixed with
 525 pure H₂O ice in the sublimation lag deposit when PAH is present in the initial CO₂ ice down to a
 526 concentration as low as 0.005-0.01%.

527 In our experiment, we did not find a good correlation between the PAH band depths and the
 528 PAH/H₂O ice weight ratio, but rather some correlation with the PAH mass column in the sample
 529 (Figure 6). This is probably due to the fact that this lag deposit is very thin (65-170 μm ,
 530 assuming a porosity of 50%) and thus probably still optically thin in these bands. In our
 531 experiments a mass column of 0.3 mg/cm^2 may be derived as the 0.6% band depth detection
 532 level (for CRISM SNR, see 5.1) for PAH in PAH-H₂O mixtures. However, for optically thick
 533 water ice deposits, as on Mars, this may be underestimated. These estimates call for future
 534 experiments to measure the actual level of detectability of PAH mixed with water ice.



535
 536 *Figure 6: Relative band depth of the 1.14 and 1.685 μm bands of PAH versus the mass column of PAH (contributing to these*
 537 *aromatic C-H stretching bands) in the PAH-H₂O ice sublimation lag deposit. The horizontal line represents a band depth*
 538 *detection level of 0.6% (at 3σ with $S/N=450-500$).*

539 5.3 Effect of dust on the detectability of PAH

540 As we already saw with our single experiment of PAH-dust mixture, the limitation on the
 541 detectability of PAH is also strongly constrained by the amount of dust present in the ice. Indeed
 542 the martian dust aerosol particles that are mixed with CO₂ ice have strong absorption coefficients
 543 over all the near infrared range (in the range 30-120 cm^{-1} @ 1.14 μm , 50-180 cm^{-1} @ 1.685 μm

544 and increasingly larger above; Douté et al., 2007), so one to three orders of magnitude larger
545 than for H₂O ice and four to six orders larger than for CO₂ ice at the wavelengths of these PAH
546 absorptions. Furthermore, aeolian dust has a much smaller grain size (<10 μm) and therefore, in
547 addition to strongly absorbing light, it will scatter it efficiently and reduce the probed depth. The
548 non-detection of 1.5% PAH in a fine fraction (< 25 μm) of JSCMars-1 analogue is most likely an
549 underestimate of the detection limit of PAHs in dust.

550 On Mars a small amount of dust is mixed with CO₂ ice on the South Polar Cap. Its concentration
551 has been estimated in the 0.02-0.14% range with a dust/H₂O ratio ranging between 0.5 and 4 in
552 the CO₂ ice-rich terrains (Douté et al. 2007). These authors also derived very similar dust/H₂O
553 ratios for the water ice-rich terrains on the margins of the cap, as expected after sublimation of
554 the CO₂ ice.

555 Considering the similarity in absorption coefficient between dust and the strong absorption peak
556 at 2 μm of H₂O ice (~100 cm⁻¹), a high abundance of dust (~0.14%) mixed with CO₂ ice will
557 certainly cancel the positive effect of larger CO₂ grain size and limit the detectability of PAH to
558 a higher level than our measured value of 0.06%, possibly closer to 1%. The reflectance of such
559 types of dusty CO₂ ice is only slightly larger (by ~30%) than for the surrounding ‘dry’ terrains
560 (Douté et al. 2007). So penetration of light is already quite limited. But if dust is present in lower
561 amounts (~0.02-0.04%, reflectance almost twice that of dust) the penetration depth of light in
562 slab CO₂ ice should allow a lower detection limit for PAHs.

563 In the PAH-H₂O-dust sublimation lag deposit a similar degradation of the detection level should
564 occur depending on the dust/ H₂O ratio. If it is at its lower limit (~0.3) the effect should be
565 mostly to reduce the reflectance in the continuum absorption and thus reduce the detectability of
566 the 1.14 μm band and significantly affect the visible slope, but this will only partly reduce the
567 relative band depth of the 1.685 μm band. For higher concentrations of dust relative to both CO₂
568 and H₂O ice, its effect is likely to strongly reduce the detection level of PAH, possibly up to ~1%
569 for the largest observed dust/H₂O ratio ~4 (Douté et al. 2007).

570 All these results and rough estimates based on relative values of absorption coefficients call for
571 experiments to directly measure the detectability of PAHs in mixtures of PAH/dust/H₂O ice
572 dispersed in small amounts in slab CO₂ ice and as sublimation lags in order to better assess both
573 the boosting effect of large CO₂ grain size and the deleterious effects of dust. Radiative transfer
574 models may also help us to understand the detection limits both in experiments and in
575 observations.

576 5.4 Extrapolation to other PAHs

577 Another important question now arises about the wider applicability of our experiments with a
578 selection of only three of the simplest PAHs in comparison to other more complex molecules in
579 this family.

580 It is established that in PAHs the symmetric C-H stretching modes are of two types (for ‘bay’
581 and ‘non-bay’ hydrogen atoms; Baushlischer et al; 2009) but are non-specific of the particular
582 PAH molecule (which show only slight wavelength shifts). They occur in all the members of this
583 family but in different proportions depending on the compactness of the PAH, the ‘non-bay H

584 being generally dominant (100% in anthracene and pyrene, 80% in phenanthrene). For the
585 fundamental stretching modes, the two bands occur respectively in the 3.205-3.23 μm (bay H)
586 and 3.23-3.28 μm (non-bay H) ranges for the gas phase, and slightly shifted to higher
587 wavelength in the condensed phase. Accordingly, from a study of the visible-near-infrared
588 reflectance spectra of 47 simple and substituted PAHs in the solid state, Izawa et al. (2014)
589 showed that the overtone bands have mostly one major band (as we observed too) and their
590 positions are relatively well constrained in a narrow range: 1.138-1.150 μm for $3\nu_{\text{CH}}$ and 1.673-
591 1.690 μm for $2\nu_{\text{CH}}$ mode, with a small shoulder in the range 1.645-1.650 μm .

592 Depending on the exact PAH or mixture, its detectability from the $2\nu_{\text{CH}}$ 1.685 μm band may
593 therefore be only slightly decreased if the band shifts to the lower limit of its wavelength range
594 (more interference with the 1.645 μm H_2O ice band) but will increase if its peak shifts away
595 from this band. For the $3\nu_{\text{CH}}$ band, no effect on detectability is expected as there is no interfering
596 band nearby. All these shifts have no effects for the detectability in dust as the aeolian dust
597 spectrum display no features in these ranges having a quite flat spectrum.

598 Another factor that may affect detectability (by weight %) is the H/C ratio of the molecule or the
599 PAH mixture. In our mixture this ratio is relatively low (0.45) due to the use of one deuterated
600 molecule. It is similar to the values for larger compact PAH molecules, e.g. 0.5 for coronene
601 ($\text{C}_{24}\text{H}_{12}$), and lower than for the small PAHs found in Martian meteorites (Becker et al., 1997):
602 0.6 for chrysene ($\text{C}_{18}\text{H}_{12}$), 0.625 for pyrene ($\text{C}_{16}\text{H}_{10}$), 0.67 for perylene ($\text{C}_{20}\text{H}_{12}$) and 0.71 for
603 both anthracene and phenanthrene ($\text{C}_{14}\text{H}_{10}$). But these differences are quite small compared to the
604 previously discussed radiative transfer effects controlling the detectability of PAHs.

605 Only if some aromatic $\text{C}=\text{C}$ bonds in the PAH material are eliminated, either by substitution (by
606 oxygen atoms, OH, CH_3 , ...) or by hydrogenation, will the number of aromatic C-H stretching
607 modes decrease, and consequently the strength of both the 1.14 and 1.685 μm bands. In the last
608 case (H_n -PAHs) new, intrinsically stronger, aliphatic C-H stretching modes will appear at higher
609 wavelength, shifted by +0.10-0.26 μm for the fundamental modes (Sandford et al. 2013) and thus
610 by about +0.05-0.13 μm for the first overtone, and + 0.03-0.09 μm for the the second, as
611 observed by Izawa et al. (2014). Their first overtone will be easier to observe as it will shift
612 towards the minimum absorption between the 1.645 μm and the broad 2- μm water ice bands, but
613 it will be the reverse for the second overtone as it will shift in the wing towards the peak
614 absorption of the 1.26 μm H_2O band. However, this particular family of PAH molecules has not
615 been studied in our experiments.

616 **6 Conclusions**

617
618 To summarise: a detectability limit of $\sim 0.04\%$ has been established for observing PAH features
619 in sublimating CO_2 ice but this detection limit may drop by a large factor (to $\sim 0.01\%$) in coarse
620 grained ice if the amount of dust is at its lowest values ($\sim 0.02\%$) measured on the South Polar
621 Cap. On the other hand, even at its maximum detected concentration in CO_2 ice ($\sim 0.12\%$), water
622 ice should have only a limited effect on the detectability of PAHs.

623
624 Similarly in the PAH- H_2O -dust lag deposits observed on the SPC margins and rim scarps the
625 amount of dust is the main factor that may strongly limit the detectability of PAH (up to only 1%

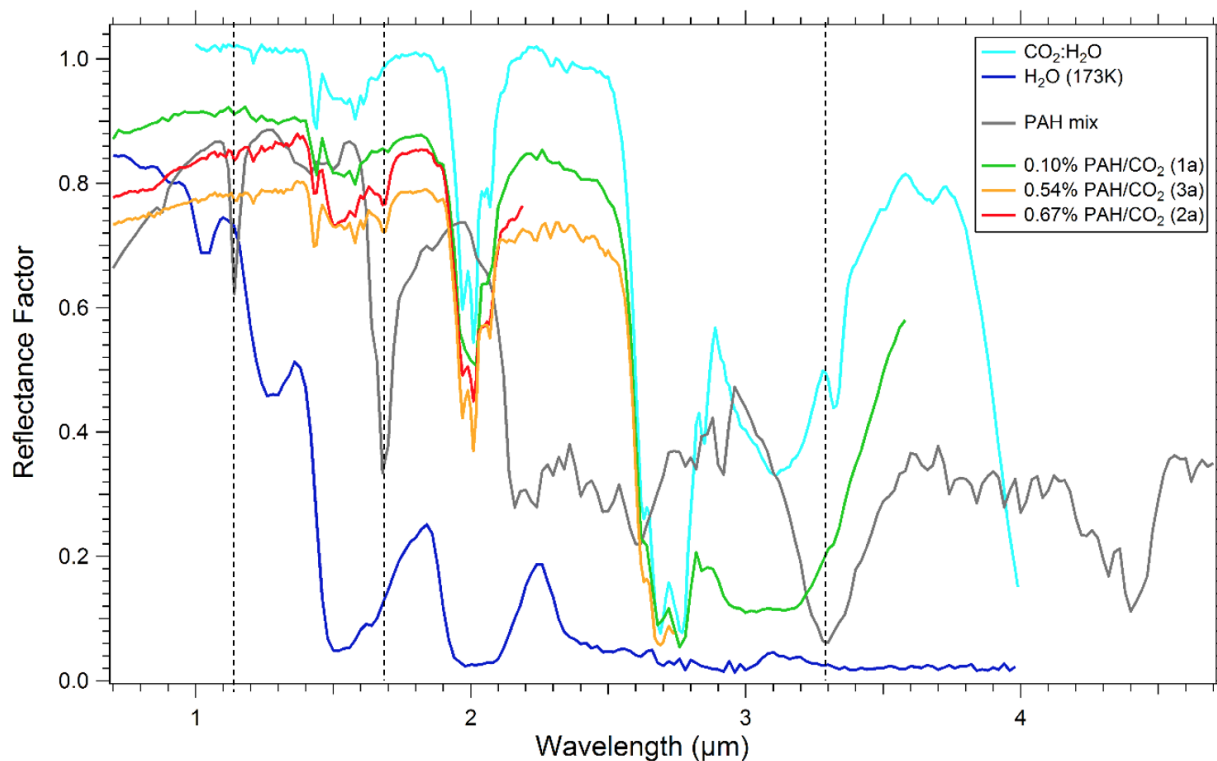
626 in the original CO₂ ice) while in dust-poor PAH-H₂O lag deposits PAHs can be detected when
 627 the PAH/H₂O ice ratio is larger than 25%, i.e. for initial PAH concentration in CO₂ ice in the
 628 range 0.01-0.05 %.

629
 630 These detectability limits are roughly applicable to most types of C_nH_n PAHs as the two
 631 diagnostic bands only slightly change in position and specific band strength among this PAH
 632 family. If other PAH families (substituted, hydrogenated...) are present on Mars or other icy
 633 bodies, then specific studies of their mixtures with CO₂ or H₂O ice and dust should be performed
 634 to assess their detection limits in specific environments.

635
 636 The detectability levels achievable in the near-infrared in favorable conditions on Mars are thus
 637 of the same order than the amount detected on other planetary bodies, i.e., 10⁻⁴ to 10⁻³ g/cm³
 638 (Cruikshank et al., 2008). One particular advantage of the near infrared bands may be that they
 639 allow us to probe deeper into the surface (up to few millimeters or centimeters for clear CO₂ ice
 640 slab) than just the very first microns seen by the 3.29 μm PAH band.

641
 642 When future space observations of the SPC are recorded at higher spectral resolution & sampling
 643 than our measurements (19 nm/10 nm) the better separation between the relatively narrow 1.685
 644 μm PAH band and the 1.645 μm H₂O ice band will further improve the PAH detectability.

645
 646



647
 648 *Figure 7: Spectra from three initial samples (1a, 2a, 3a) with varying amount of PAH in CO₂ ice (with small amount of H₂O ice*
 649 *~0.08-0.2%) compared to the spectrum of the PAH mix and with those of CO₂ ice (with ~0.075% H₂O ice) and pure H₂O ice at*
 650 *173K (Philippe 2016). Black, dotted vertical lines indicate the main infrared PAH absorption features.*

651 Analysis of Mars spectra and computer modelling will be carried out in future to apply the
652 empirical laboratory results to CRISM observations, and further laboratory work is planned to
653 obtain PAH spectra pertinent to non-polar regions of Mars. Detectability of PAHs in pure and
654 'contaminated' water ice has far reaching consequences for other planetary bodies such as
655 comets, Europa, Enceladus and Titan, the study of which would greatly benefit from being able
656 to discriminate the effects of PAH and ice on spectra, and comparison with PAH libraries.

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