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Stringent upper limit of CH₄ on Mars based on SOFIA/EXES observation

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Abstract

Discovery of CH₄ in the Martian atmosphere has led to much discussion since it could be a signature of biological/geological activities on Mars. However, the presence of CH₄ and its temporal and spatial variations are still under discussion because of the large uncertainties embedded in the previous observations. We performed sensitive measurements of Martian CH₄ by using the Echelon-Cross-Echelle Spectrograph (EXES) onboard the Stratospheric Observatory for Infrared Astronomy (SOFIA) on 16 March 2016, which corresponds to summer ($L_s = 123.2^\circ$) in the northern hemisphere on Mars. The high altitude of SOFIA (~13.7 km) enables us to significantly reduce the effects of terrestrial atmosphere. Thanks to this, SOFIA/EXES improves the chance to detect Martian CH₄ lines because it reduces the impact of telluric CH₄ on Martian CH₄, and allows us to use CH₄ lines in the 7.5 μm band which has less contamination. However, our results show no unambiguous detection of Martian CH₄. The Martian disk was spatially resolved into 3 x 3 areas, and the upper limits on the CH₄ volume mixing ratio range from 1 to 6 ppb. These results emphasize that release of CH₄ on Mars is sporadic and/or localized if the process is present.

35 1. Introduction

36 The presence of CH₄ in the Martian atmosphere has led to much discussion since it could be a
37 signature of on-going and/or past biological/geological activities on Mars (e.g., Atreya et al., 2007).
38 In 2004, the first detection of CH₄ on Mars was reported from the observations by the Planetary
39 Fourier Spectrometer (PFS) onboard the Mars Express (MEx) spacecraft (Formisano et al., 2004).
40 The mean abundance of CH₄ was found to be ~ 10 ppb. In the same year, detection of CH₄ was
41 also reported by ground-based observations with the Canada-France-Hawaii Telescope (CFHT) /
42 Fourier Transform Spectrometer (FTS) (Krasnopolsky et al., 2004). These discoveries of CH₄ on
43 Mars were remarkable because its source could be either biological activity (e.g., subsurface
44 micro-organisms) and/or hydrothermal activity (e.g., serpentinization) (Atreya et al., 2007).
45 Identification of the source of CH₄ is very valuable for advancing not only planetary science but
46 also future life explorations on Mars.

47 After 2004, Martian CH₄ has been investigated with remote-sensing observations by four groups,
48 two from spacecraft-borne observations (Geminale et al., 2008; Geminale et al., 2011; Fonti and
49 Marzo, 2010), and two from ground-based observations (Mumma et al., 2009; Krasnopolsky,
50 2012; Villanueva et al., 2013). The spacecraft-born PFS measurements showed the variations of
51 CH₄ amounts depending on season, location, and local time on Mars (Geminale et al., 2008;
52 Geminale et al., 2011). In particular, an enhancement of CH₄ (~60 ppb) over the north polar cap
53 during the northern summer was reported, which implied the possible presence of a CH₄ reservoir
54 associated with the polar cap (Geminale et al., 2011). In contrast, Fonti and Marzo (2010) analyzed
55 the data obtained with another spacecraft-born instrument (Thermal Emission Spectrometer (TES)
56 onboard Mars Global Surveyor (MGS)) and found substantially different spatial and seasonal
57 distributions, with peak abundance near 70 ppb over low-latitudes (Tharsis, Arabia Terra, and
58 Elysium). Meanwhile, the other two groups investigated CH₄ on Mars using high-resolution,
59 infrared spectrographs on ground-based facilities. Mumma et al. (2009) found extended plumes of
60 CH₄ (~ 40 ppb) during the northern summer over low-latitude regions (Terra Sabae, Nill Fossae,
61 and Syrtis Major) from IRTF/CSHELL observations performed in 2003. However, the same group
62 reported no detection of CH₄ during their follow-up observations in 2006, 2009, and 2010
63 (Villanueva et al., 2013). They derived an upper limit of 7 ppb from those non-detection
64 observations, which is generally smaller than the seasonal variations reported by the
65 spacecraft-borne measurements groups. By contrast, Krasnopolsky (2012) claimed the detection of
66 CH₄ (0-20 ppb) over Valles Marines using ground-based IRTF/CSHELL observations performed
67 in late January 2006, just 28 days after Villanueva et al. (2013) observations, where no CH₄ had
68 been observed over the same region (upper limit 7.8 ppb).

69 In short, these remote-sensing observations suggest a significant variability of CH₄ in space and
70 time. From these observations, the lifetime of CH₄ in the Martian atmosphere is estimated to be on
71 order of days to weeks. In contrast, the standard photochemical models showed that the lifetime of
72 CH₄ in the Martian atmosphere is about 300-600 years (Lefevre and Forget, 2009), and, as a
73 consequence, CH₄ should be uniformly distributed in the atmosphere. This discrepancy between
74 the observed variability and the model prediction has led to much debate on the reliability of the
75 previous remote-sensing observations. The reason behind such a debate is that the detected signal
76 of CH₄ is very weak and the observations had a large uncertainty because of contamination of
77 terrestrial lines and the need for a high signal-to-noise ratio. The previous ground-based
78 observations used lines in the P-branch or R-branch of 3.3 μm band. The widths of these lines (half
79 width at half maximum (HWHM)) are about 0.006 cm⁻¹, which is 5-10 times narrower than the
80 spectral resolutions of CSHELL, NIRSPEC and CRIRES. In addition, the terrestrial atmosphere
81 hampers the observation due to telluric CH₄ and its isotopes; their contribution to the observed
82 spectrum must be separated from the Martian CH₄ contribution to the spectrum. Zahnle et al.
83 (2010) pointed out that contamination from telluric ¹³CH₄ lines would be fatal in this aspect, being
84 10-50 times stronger than the Martian CH₄ lines (see **Fig. 1**). On the other hand, spacecraft-born
85 observations (i.e., MGS/TES and MEx/PFS) are free from such contamination of the terrestrial
86 atmosphere. However, their spectral resolutions are not enough for an unambiguous identification
87 of CH₄. Even at the highest spectral resolution of PFS (~1.3 cm⁻¹) and even the fact that PFS
88 observes the strongest lines of the Q-branch of 3.3 μm band, the absorption depth of 10 ppb of CH₄
89 yields only about 1 percent of the continuum emission, which is difficult to be distinguished from
90 side lobes caused by strong solar lines. The spectral resolution of the TES instrument is ~5 times
91 worse than that of PFS. Indeed, Fonti et al. (2015) carefully revisited their previous results from
92 the MGS/TES measurements, and concluded that they are either not able to be confirmed or
93 refuted.

94 Very recently, in-situ observations of CH₄ on Mars were performed by the Tunable Laser
95 Spectrometer (TLS) onboard Curiosity rover (Webster et al., 2013; Webster et al., 2015). TLS
96 detected CH₄ signal and showed strong variability of the amount (0-9 ppb). However, since TLS
97 can measure CH₄ variation only on the Gale crater (which is the landing site of the rover), sensitive
98 remote-sensing observation is still important to search for the source. Moreover, note that because
99 there is residual terrestrial CH₄ gas in the foreoptics chamber of the TLS instrument (Webster et al.,
100 2015), there is a debate on the reliability of this detection. Thus, it is still indispensable to confirm
101 the presence of CH₄ on Mars.

102 The Echelon-Cross-Echelle Spectrograph (EXES) onboard the Stratospheric Observatory for

103 Infrared Astronomy (SOFIA) has unique capabilities to perform a sensitive search for CH₄ from
104 Earth. Through the entire spectral range, the strongest CH₄ lines are located at 3.3 μm and 7.5 μm.
105 **Fig. 1** shows the terrestrial and Martian spectra around the CH₄ lines at 3038.498 cm⁻¹ (3.291 μm)
106 and 1327.0742 cm⁻¹ (7.535 μm), that are simulated for the IRTF/CSHELL and SOFIA/EXES
107 observations, respectively (note that the terrestrial transmittances shown in **Fig. 1** are calculated for
108 the best and worst airmass conditions of Mauna Kea and SOFIA observations, respectively). As
109 shown in **Fig. 1**, one of the advantages of the 7.5 μm band is less contamination of minor terrestrial
110 lines such as ¹³CH₄ or O₃ even though the intrinsic intensities of the CH₄ lines at 3.3 μm and 7.5
111 μm are comparable. However, observations of Martian CH₄ using this band are impossible from
112 ground-based observatories because of terrestrial CH₄. Encrenaz et al. (2005) attempted to search
113 for CH₄ on Mars using IRTF/TEXES in the mid-infrared spectral range, however, they could not
114 use the strongest lines because of the deep terrestrial CH₄ absorption. This imposed a limitation on
115 their data (derived upper limits were 20 ppb in the morning side and 70 ppb in the evening side).
116 The situation changes drastically for SOFIA thanks to the higher altitude (~13.7 km). With SOFIA,
117 Martian CH₄ lines at the 7.5 μm band can be measured in the wing of the terrestrial lines, which
118 makes this air-borne facility quite unique compared to any other ground-based facilities including
119 those located at the summit (~4 km in the altitude) of Mauna Kea. In order to detect the narrow
120 Martian CH₄ lines located at the wings of the deep terrestrial line, high spectral resolution is
121 essential. The EXES instrument realizes high spectral resolution of ~90,000, and it largely
122 improves the chances to detect CH₄ lines although the Martian lines are not fully resolved.
123 SOFIA/EXES can provide a few or several times better signals of Martian CH₄ than those by
124 previous ground-based observations with less contamination of the minor telluric lines. Moreover,
125 EXES has an additional advantage that we can measure multiple CH₄ lines simultaneously, which
126 allows us to improve the accuracy of the CH₄ retrieval.

127 In this study, we describe the results of our sensitive search of CH₄ on Mars using SOFIA/EXES.
128 The details of the SOFIA/EXES observations and data analysis are described in Section 2 and 3,
129 respectively. The observational results are discussed in Section 4.

130

131 **2. Observations**

132 SOFIA is an airborne observatory consisting of a specially modified Boeing 747SP with a 2.7
133 m diameter telescope flying at altitudes as high as 13.7 km (Young et al., 2012). EXES is an
134 infrared grating spectrograph onboard the SOFIA telescope. It is derived from the Texas Echelon
135 Cross Echelle Spectrograph (TEXES) instrument in operation at NASA IRTF and Gemini-North
136 (Lacy et al. 2002). EXES operates in the spectral ranges between 4.5 and 28.3 μm (350–2220 cm⁻¹),

137 with high spectral resolution mode ($R=50,000-100,000$), medium resolution mode ($R=5,000-$
138 $20,000$), and low resolution mode ($R=1,000-3,000$). The instrument is equipped with a $1024 \times$
139 1024 Si:As detector array. The high-resolution mode is provided by a steeply blazed aluminum
140 reflection grating used as an echelon, associated with an echelle grating to cross-disperse the
141 spectrum (Richter et al. 2010).

142 Our observations using SOFIA/EXES were performed on 16 March 2016 (see Table 1). The
143 observations were performed when SOFIA was flying at 13.7 km. The observed season on Mars
144 corresponds to summer ($L_s = 123.2^\circ$) in the northern hemisphere. The diameter of Mars was about
145 10 arcsec. The Doppler shift between Mars and Earth was -16.2 km/s. During the observation, the
146 longitude of the sub-earth and sub-solar points varied from 247°W to 253°W , and from 213°W to
147 220°W , respectively. The latitude of these points was 7.7°N (sub-earth) and 21.1°N (sub-solar).
148 For our search of CH_4 on Mars, we selected the $1326-1338 \text{ cm}^{-1}$ ($7.47 - 7.54 \mu\text{m}$) interval
149 considering the availability of multiple strong CH_4 lines, and used the high-spectral resolution
150 mode to improve the possibility of detecting the narrow Martian lines. The narrowest slit-width
151 (1.44 arcsec) was used to maximize the spectral resolving power that provided an instrumental
152 resolving power of $\sim 90,000$. The slit length is $10.69''$ (0.18 arcsec/pix), which is comparable to the
153 diameter of Mars ($\sim 10''$). **Fig. 2** illustrates the configuration of the slit positions. The slit was
154 oriented at a position angle of 260° . As shown in **Fig. 2**, we observed the planet at three separate
155 slit positions: which we called center, right, and left of the Martian disk. For the right and left
156 positions, the center of the slit was offset by $2.5''$ perpendicular to the slit angle. At each slit
157 position, we observed Mars for several minutes to reach the signal to noise ratio of more than ~ 200
158 with respect to the continuum emission. We nodded the telescope observing Mars and sky in A and
159 B positions, respectively, with a motion of 20 arcsec perpendicular to the slit. Subtraction of (A-B)
160 removes the telluric emissions and other background emission. In addition, we observed *alpha Lyr*
161 as a telluric calibration star.

162 An example of the spectrum measured with EXES is shown in **Fig. 3**. We recorded 17 different
163 spectral orders, covering $1326.57 - 1338.66 \text{ cm}^{-1}$. We selected this wavelength region based on the
164 expected strengths of Martian CH_4 lines and the terrestrial atmosphere from SOFIA. The spectral
165 coverage of EXES allows us to observe not only CH_4 but also H_2O , HDO, and CO_2 lines. The
166 spatial resolution of SOFIA at the time of the observations was roughly 3 arcsec. This corresponds
167 to a latitudinal/longitudinal resolution of about $\pm 27^\circ$ (~ 2000 km in the horizontal scale) at the
168 sub-Earth point.

169
170

171 3. Data analysis

172 3.1. Extraction of the Martian features

173 We searched for CH₄ on Mars using multiple lines. As shown in **Fig. 3**, there are 11 strong CH₄
174 absorption lines in the selected spectral range. We confined our analysis to three lines that have no
175 contamination from other lines (i.e., terrestrial CH₄ and H₂O, and Martian CO₂ and H₂O lines) and
176 stronger intensities than the other CH₄ lines. **Table 2** describes the CH₄ lines used for this analysis.
177 The line parameters were obtained from the HITRAN 2012 database (Rothman et al., 2013).

178 In order to increase the signal to noise ratio, the measured spectra were binned over 15 pixels
179 (~2.7") along the slit which binning size is determined from the spatial resolution of the telescope.
180 As a consequence, 3 averaged spectra were obtained for each slit position (see **Fig. 2**). The Martian
181 CH₄ lines should appear on the wings of the deep terrestrial lines. **Fig. 4a** shows an example of an
182 averaged EXES spectra around the CH₄ line at 1327.074219 cm⁻¹. As shown in **Fig. 4a**, the
183 terrestrial and Martian CH₄ lines were clearly separated. Then, the absorption feature of Martian
184 CH₄ lines were examined by fitting a local continuum level around the CH₄ lines. This local
185 continuum was determined by fitting the averaged spectra with a cubic polynomial for the spectral
186 interval of 25 points centered at the Martian CH₄ lines. The fitting did not include 17 center points
187 where Martian CH₄ is expected. **Fig. 4b** shows an example of the local continuum determined by
188 the cubic polynomial fit. The Martian CH₄ lines were extracted by obtaining the deviation of the
189 observed spectrum from the local continuum, and then they were compared with synthetic spectra
190 calculated by radiative transfer model.

191

192 3.2. Modeling of synthetic spectra

193 We performed radiative transfer calculations to evaluate (the upper limit on) CH₄ abundances in
194 the extracted Martian features. We used a fast and accurate radiative transfer model that includes
195 multiple scattering effects (Ignatiev et al., 2005). The calculation was performed in the spectral
196 ranges between 1325 and 1340 cm⁻¹. Dust, water ice clouds, CO₂ gas, and CH₄ gas absorption were
197 taken into account in the calculation. The vertical domain in the modeled Mars atmosphere was
198 represented by 80 layers which covers altitudes from the surface to 80 km with uniform thickness
199 of 1 km. The absorption coefficients of CO₂ and CH₄ gases were calculated based on the
200 line-by-line method with a spectral sampling of 0.00025 cm⁻¹ (about 1/60 of the spectral resolution
201 of the measurements) using the HITRAN 2012 database (Rothman et al., 2013). For the line shape
202 function, a Voigt function was adopted (Kuntz, 1997; Ruyten, 2004). The single scattering optical
203 properties of dust and water ice clouds were calculated with the Mie-theory (Wiscombe, 1980) and
204 then integrated with the modified gamma distribution (Kleinbohl et al., 2009). The refractive

205 indices of dust and water ice were from the works by Wolf and Clancy (2003) and Warren (1984),
206 respectively.

207 Geometry and orbital parameters during the observations such as emission angles, latitude, and
208 longitude of Mars were obtained from the NASA-JPL ephemeris generator
209 (<http://ssd.jpl.nasa.gov/horizons.cgi>). Based on that, we computed the synthetic spectra over the
210 Martian disk with an interval of 0.25 arcsec. Surface temperatures and vertical profiles of
211 temperature, pressure, dust, water ice clouds, and CO₂ volume mixing ratio were extracted from
212 the Mars Climate database (MCD) ver 5.2 for the each spatial point over the Martian disk (Millour
213 et al., 2015). In order to take into account the spatial resolution of the observations, the calculated
214 synthetic spectra were synthesized with a two-dimensional Gaussian function with a full width at
215 half maximum (FWHM) of 3 arcsec. The synthesized spectra were averaged over the expected slit
216 position to be compared with the measured spectra. The averaged synthetic spectra were finally
217 convolved in a wavelength domain with another Gaussian function that corresponds to the spectral
218 resolution of EXES (R=90,000; ~9 pixels).

219

220 3.3. Validation of the data reduction methodology

221 To check the validity of the extraction method and calculation of synthetic spectra, the
222 algorithm was applied to Martian CO₂ lines as well. For this purpose, a weak CO₂ isotope (638)
223 line at 1326.75438 cm⁻¹ and CO₂ isotope (628) line at 1327.917522 cm⁻¹ were selected. The line
224 intensity of the CO₂ (638) line is 9.662 x 10⁻²⁷ cm at 296 K with an uncertainty range between 2 %
225 and 5 %, and that of the CO₂ (628) line is 1.883 x 10⁻²⁶ cm with an uncertainty range being more
226 than 20 % (Rothman et al., 2013). **Fig. 5** shows examples of the extraction of these CO₂ lines by
227 using the local continuum determined by the cubic polynomial fit, and their comparison with the
228 synthetic spectra calculated by our radiative transfer model. The Martian CO₂ (638) line yields
229 about 10 % of absorption depth respect to the continuum emission, while the CO₂ (628) line does a
230 few percent of absorption because the Lower-state energy E'' of the CO₂ (628) line ($E'' =$
231 1052.7719 cm⁻¹) is larger than that of CO₂ (638) line ($E'' = 170.0769$ cm⁻¹). The extracted spectral
232 features of the Martian CO₂ lines show a good agreement with the synthetic spectra (note that the
233 volume mixing ratio of CO₂ considered in the synthetic spectra is the one extracted from MCD,
234 and the isotopic ratio of CO₂ is the terrestrial one included in HITRAN 2013).

235

236 3.4. Retrieval of CH₄ mixing ratio

237 The synthetic spectra were calculated for CH₄ volume mixing ratios ranging from 0 ppb to 50
238 ppb with intervals of 1 ppb, and the best-fit CH₄ mixing ratio was determined by minimizing the

239 cost function C . The cost function was defined as

$$240 \quad C = \sum (Y_{obs} - Y_{model})^2,$$

241 where $Y_{model}(x)$ is transmittance of synthetic spectra which is the synthetic spectra with CH₄
 242 divided by the one without CH₄, and Y_{obs} is transmittance of the EXES spectra which is the original
 243 SOFIA spectra divided by continuum simulated via Cubic polynomial fitting (as described in 3.1).
 244 The cost functions were calculated using the spectral interval of 25 points centered at the Martian
 245 CH₄ lines. The retrievals were performed independently for each line of the selected three CH₄
 246 lines. **Fig. 4c** shows an example of the comparison between the transmittance of the EXES spectra
 247 and synthetic ones.

248 The uncertainty in the retrieved CH₄ mixing ratio were carefully estimated via statistics using
 249 simulated EXES spectra and the following steps:

250 • Simulated EXES spectra in the relevant spectral region were calculated using the spectral
 251 resolution and sampling of the actual measurements considering the US standard earth
 252 atmosphere above 14 km with the airmass set to match the actual observation condition. Mars
 253 atmospheric absorption due to CO₂ gas is also included in this simulated spectra. Instrumental
 254 noise was input to the simulated EXES spectra. The instrumental noise were defined by

$$255 \quad Noise = \sqrt{\frac{C}{N}} \times \xi,$$

256 where N is the number of spectral points (i.e., 25) and ξ is a random number following a Gaussian
 257 distribution ($\sigma=1$). The first value in the equation represents the standard deviation between the
 258 best-fit model and the measured EXES spectra. To initialize the random number, a total of 100
 259 different "seed" values were used (i.e., we have different 100 noise patterns in total).

260 • Martian CH₄ absorptions were additionally included to the simulated EXES spectra. CH₄ volume
 261 mixing ratios from 0 to 30 ppb with intervals of 1 ppb were considered (i.e., 3100 simulated
 262 EXES spectra were obtained in the end).

263 • The CH₄ retrieval algorithm, which we used for the data analysis of the real measurement data,
 264 was applied to these simulated EXES spectra in a similar way. Such retrieval tests provide an
 265 estimate on the accuracy of the retrieved CH₄ mixing ratios. **Fig. 4d** shows an example of our
 266 retrieval test.

267 After the uncertainties were evaluated for the results of each CH₄ line, the CH₄ mixing ratios and
 268 their 3σ confidences were calculated by the weighted averages using the ones retrieved from three
 269 CH₄ lines independently (see Section 3 of Aoki et al., 2015).

270

271

272 4. Results and Discussions

273 **Table 3** summarizes the CH₄ volume mixing ratios independently retrieved from the selected
274 CH₄ lines, their weighted averages, and the corresponding locations (latitude and longitude) and
275 local times. The results from three lines were all consistent within 3σ . As shown in **Table 3**, there
276 are no definitive detections of CH₄. The upper limits range from 1 to 6 ppb, which are more
277 stringent than those by the previous remote-sensing observations.

278 The SOFIA/EXES observation covers Nili Fossae and Syrtis Major (10°S-30°N, 300-330°W)
279 where Mumma et al. (2009) had reported the presence of extended plumes of CH₄ (~ 40 ppb). The
280 observing season of this study is almost the same with those Mumma et al. (2009) although the
281 Martian Year is different (their IRTF/CSHELL observation was performed at $L_s=122^\circ$ in MY 26;
282 the SOFIA/EXES observation at $L_s=123^\circ$ in MY 33). As roughly half of the field of view of an
283 averaged SOFIA/EXES spectrum corresponds to the signal from Nili Fossae and Syrtis Major, our
284 measurement are capable of detecting such a CH₄ plume if it exists. However, the results show that
285 the CH₄ mixing ratio of 2 ± 4 ppb for the location covering Nili Fossae and Syrtis Major.
286 Non-detection of such a plume by SOFIA/EXES indicates that the release of CH₄ is very unlikely
287 an annual event.

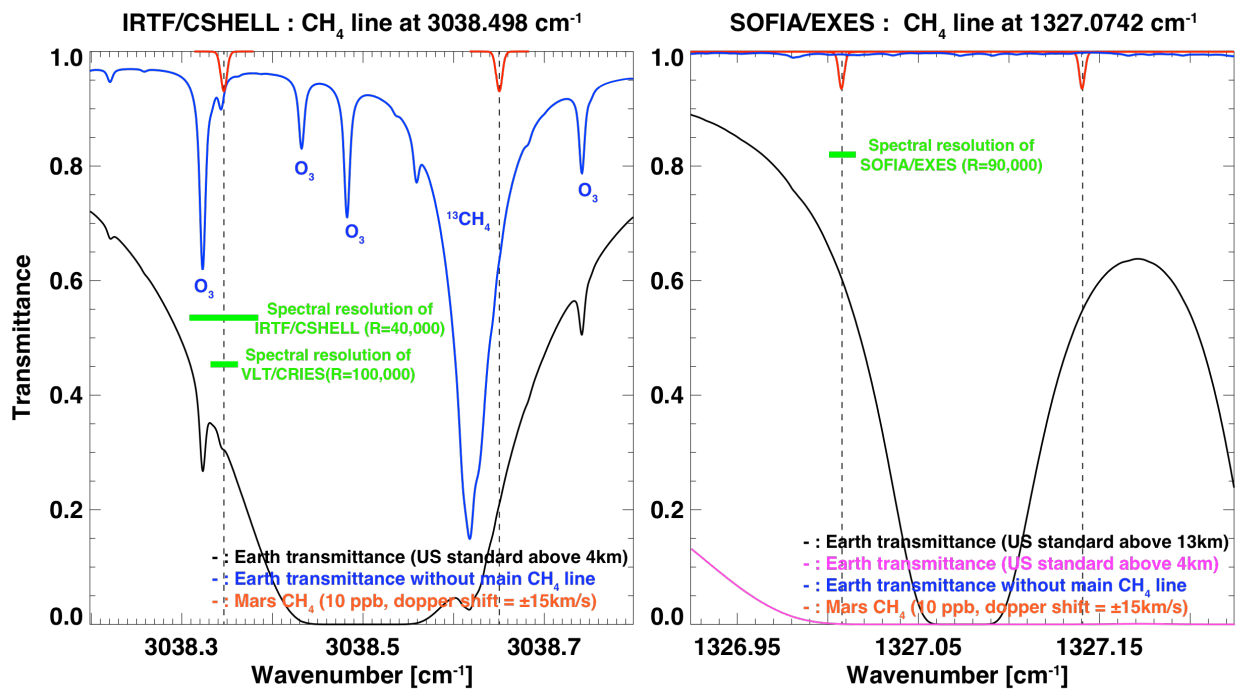
288 Fries et al. (2016) recently proposed a candidate of the CH₄ enhancement. The hypothesis is that
289 carbonaceous material is deposited into the Martian atmosphere in meteor showers and then
290 ambient UV generates CH₄ from that. Indeed, the CH₄ plume reported by Mumma et al. (2009)
291 was measured only a couple of days after a Mars encounter with the orbit of comet C/2007 H₂
292 Skiff. However, Roos-Serote et al. (2016) argued that there is no correlation between high
293 atmospheric CH₄ abundance and the occurrence of meteor showers after considering a full set of
294 CH₄ observations including new Curiosity/TLS observations and all the predicted meteor shower
295 events. The comet Skiff encountered Mars again on 8 March 2016, which is just 8 days before we
296 performed our observations with SOFIA/EXES. The non-detections of such CH₄ plumes by
297 SOFIA/EXES support the argument that the meteor shower does not likely produce high CH₄
298 abundances in the Mars atmosphere.

299 The SOFIA/EXES observation also covers Gale Crater (Latitude=4.5°S, Longitude=137°E)
300 where Curiosity/TLS has been measuring CH₄ abundances. TLS revealed that background level of
301 CH₄ mixing ratio over Gale Crater is 0.69 ± 0.25 ppb, and detected higher amount of CH₄ mixing
302 ratio (5-9 ppb) at $L_s=336.5^\circ$ in MY 31 and $L_s=55^\circ$ - 82° in MY 32 (Webster et al., 2015). However,
303 in MY 33, TLS does not detect such high amounts of CH₄ till $L_s=94.2^\circ$ (Roos-serote et al., 2016).
304 Our results show that the CH₄ mixing ratio covering Gale Crater is 1 ± 1 ppb, 0 ± 3 ppb, and 0 ± 1
305 ppb. The upper limits are larger than the TLS-reported background level but less than the high

306 value. The SOFIA/EXES observation was carried out at $L_s=123.2^\circ$ in MY 33, which is out of the
 307 seasonal range of high CH_4 abundance observed by TLS. One possible explanation for this
 308 non-detection of CH_4 by SOFIA/EXES could be due to strong temporal variation.

309 SOFIA/EXES is probably the most accurate remote-sensing facility for detecting CH_4 from
 310 Earth. However, our result did not show unambiguous detection of CH_4 . Non-detection of CH_4
 311 could be due to its strong temporal variation similar to what Curiosity/TLS has been measuring
 312 over Gale crater, or localized spatial distribution. Our results emphasize that release of CH_4 on
 313 Mars is sporadic and/or localized if the process is present.

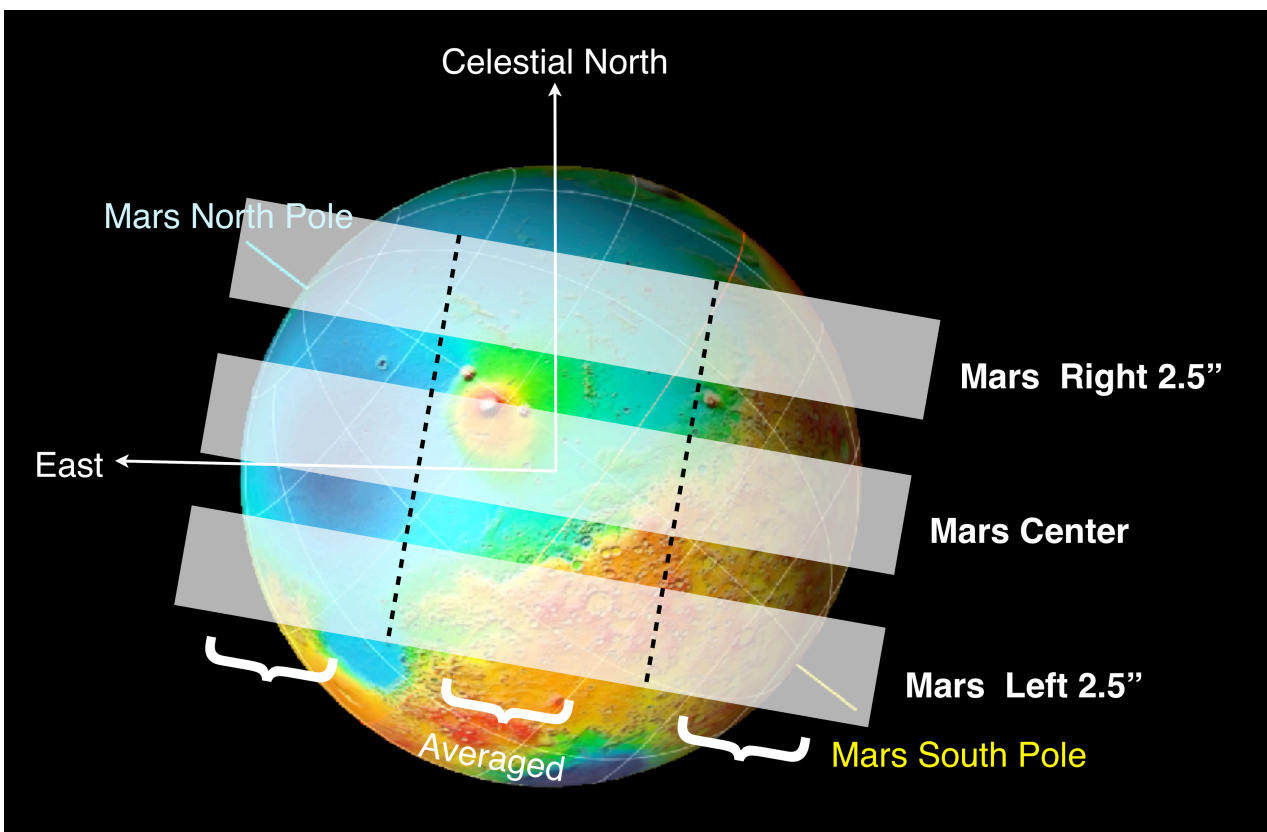
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315 **Figures and Tables**

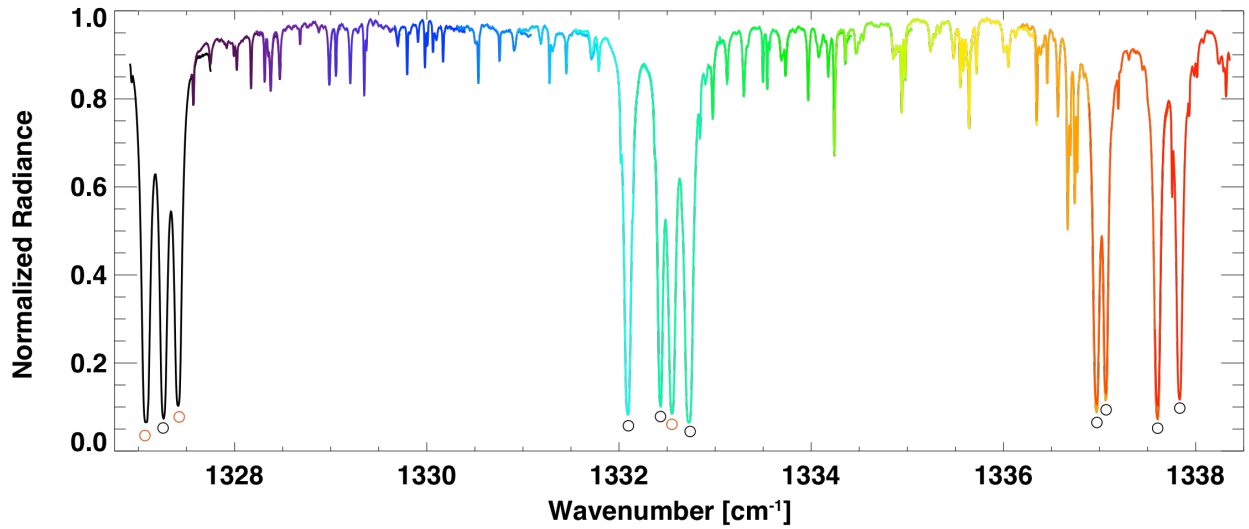
316

317 **Figure 1:** Synthetic spectra around the CH_4 line at 3038.498 cm^{-1} (left) and at 1327.0742 cm^{-1}
 318 (right). The former spectral region was used for the previous observations performed by
 319 IRTF/CSHELL, Keck/NIRSPEC, and VLT/CRIRES (e.g., Mumma et al., 2009; Villanueva et al.,
 320 2013), and the latter one was used for the SOFIA/EXES observations. The black and blue curves in
 321 the left figure represent the transmittance with/without the main CH_4 line due to terrestrial
 322 atmosphere calculated from US standard atmosphere above 4 km (which is the altitude of Mauna
 323 Kea Observatory) with airmass = 1.4 (which is the minimum airmass during the observation on 20
 324 March 2003 by Mumma et al. (2009)). The black and blue curves in the right figure are the
 325 transmittances calculated from US standard atmosphere above 14 km (which is the altitude of
 326 SOFIA) with airmass = 2.0 (which is the maximum airmass during our observation on 16 March

327 2016). The purple curve shown in the right figure is the same as black one but from US standard
 328 atmosphere above 4 km. The red curves shown in both figures are transmittance due to 10 ppb of
 329 Martian CH₄ with the Doppler shift between Mars and Earth being ± 15 km/s. The green bars
 330 shown in the left and right figures represent the spectral resolutions of IRTF/CSHELL and
 331 VLT/CRIRES, and that of SOFIA/EXES, respectively.
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 334 **Figure 2:** Geometry of the Mars observations taken by SOFIA/EXES. The instrument slit was
 335 oriented at a position angle of 260°. The slit is indicated as white boxes, and were put at the three
 336 separate slit positions: 'Mars Center', 'Mars Right 2.5', and 'Mars Left 2.5'. For the center position,
 337 the slit was placed over the sub-Earth point. For the right and left positions, we offset the center of
 338 the slit to 2.5" perpendicular to the slit angle. In this analysis, the measured spectra were binned
 339 over 15 pixels (~2.7") along the slit in order to increase the signal to noise ratio. As a consequence,
 340 3 averaged spectra were obtained for each slit position.
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343 **Figure 3:** Example of a Mars spectrum obtained by SOFIA/EXES, spatially integrated over the slit.

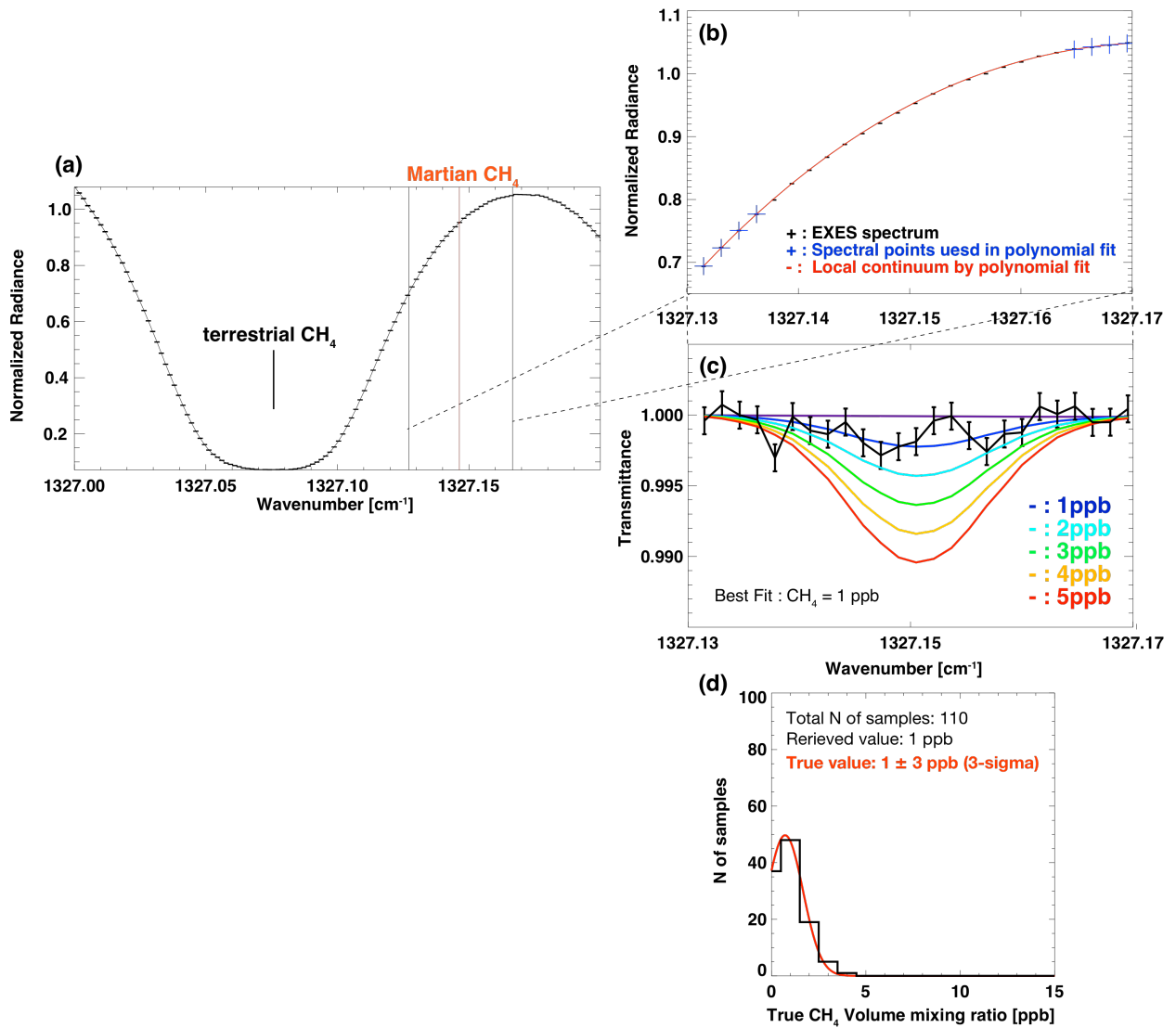
344 Differences in colors show the 17 spectral orders. The spectrum was observed on 16 March 2016

345 with 9 minutes integration. Circular symbols represent the strong terrestrial CH₄ lines. The red

346 ones are the CH₄ lines that are used in this analysis. The other lines visible in this spectrum are

347 H₂O, HDO, CO₂ (628), and CO₂ (638).

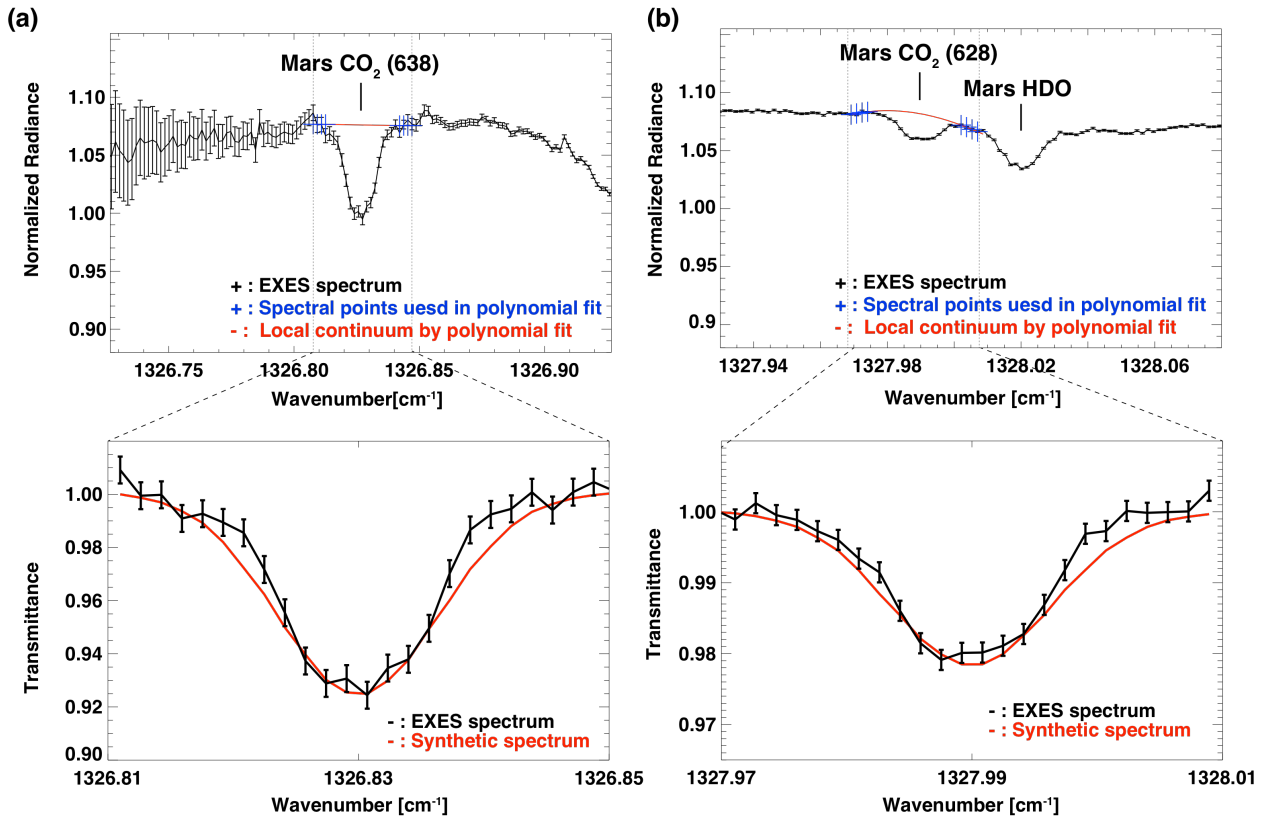
348



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350 **Figure 4:** An example of data analysis. **(a)** The black curve shows the averaged EXES spectrum in
 351 the spectral range between 1327.0 and 1327.2 cm^{-1} . The slit position is "Mars Center #1", and the
 352 mean Latitude, Longitude, and Local time of the averaged spectrum are 40°N, 113°E, and 12h,
 353 respectively. The strong absorption due the terrestrial CH_4 is visible at 1327.074219 cm^{-1} . The red
 354 vertical bar shows the expected spectral position of the Martian CH_4 line shifted due to Doppler
 355 velocity between Earth and Mars. The black bars represent the spectral range which was used for
 356 retrieval of CH_4 mixing ratio on Mars. **(b)** The black points are the same EXES spectrum as shown
 357 in (a) but focused around the expected Martian CH_4 lines. The red curve shows the local
 358 continuum established by the cubic polynomial fit. The blue points represent the spectral points
 359 used to perform the cubic polynomial fit. **(c)** The black curve shows the transmittance spectrum
 360 due to Mars atmosphere that is the EXES spectrum divided by the local continuum. The color
 361 curves are the synthetic transmittances with various mixing ratio of the Martian CH_4 (blue: 1 ppb,

362 light blue: 2 ppb, green: 3 ppb, orange: 4 ppb, red: 5 ppb) that is the synthetic spectrum with the
 363 Martian CH_4 divided by the one without the Martian CH_4 . The one with 1 ppb of CH_4 mixing ratio
 364 (the blue one) provides the minimum cost function (i.e., the best-fit synthetic spectrum). **(d)**
 365 Histogram of true CH_4 mixing ratio when the retrieved CH_4 mixing ratio is 1 ppb. The histogram is
 366 obtained from the retrieval test using simulated EXES spectra (see Section 3.4). The uncertainty of
 367 this retrieval is estimated to be 3 ppb (3σ) from the histogram.
 368



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 370 **Figure 5:** Examples of extraction of the Martian CO_2 lines and their comparison with the synthetic
 371 spectra calculated by our radiative transfer codes. Those of CO_2 (638) line at $1326.75438 \text{ cm}^{-1}$ and
 372 CO_2 (628) line at $1327.917522 \text{ cm}^{-1}$ are shown in Fig. (a) and (b), respectively. The positions of
 373 these lines are shifted due to the Doppler velocity between Mars and Earth. The black curves
 374 shown in the upper panels are the averaged EXES spectrum. The slit position is "Mars Center #1",
 375 and the mean Latitude, Longitude, and Local time of the averaged spectrum are 17°S , 179°E , and
 376 16h , respectively. In the upper panel of fig. (b), an absorption band due Martian HDO is also
 377 visible. Note that error values in the left wing of the Martian CO_2 (638) line are relatively high
 378 because they are close to the edge of the slit. The red curves and blue points in the upper panels
 379 show the local continuums established by the cubic polynomial fit and the spectral points used to
 380 perform the cubic polynomial fit, respectively. In the lower panels, the black curves represent the

381 transmittance spectra due to Mars atmosphere that are the EXES spectrum divided by the local
 382 continuum. The red curves are the synthetic transmittances. The extracted spectral features of the
 383 Martian CO₂ lines show a good agreement with the synthetic spectra.

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385 **Table 1** Overview of the SOFIA/EXES observations.

Date and time (UT)	<i>Ls</i> (°)	MY	Doppler shift (km/s)	Diameter of Mars (")	Aircraft Altitude (km)	Silt positions and integration times (min)	Sub Earth longitude (°W)	Spectral range (cm ⁻¹)
16/March/2016 9:59–10:32	123.2	33	-16.2	10	13.7	Mars Center #1: 9 Mars Center #2: 6 Mars Left 2.5": 9 Mars Right 2.5": 9	247-253	1326.57 -1338.66

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387 **Table 2** Parameters of CH₄ lines used in this study. The values are taken from the HITRAN 2012
 388 spectroscopic database (Rothman et al., 2013).

Wavenumber [cm ⁻¹]	Intensity [cm] (for 296 K)	Lower state Energy [cm ⁻¹]
1327.074219	9.631E-20	62.8781
1327.409783	5.781E-20	62.8757
1332.546743	5.732E-20	104.7746

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404 **Table 3** CH₄ mixing ratio on Mars retrieved from the SOFIA/EXES observation. Note that EXES
 405 spectra were spatially binned over ~ 2.7 arcsec, which corresponds latitudinal/longitudinal
 406 resolution of about $\pm 27^\circ$ at the sub-Earth point.

Slit position	Lat ($^\circ$)	East Lon ($^\circ$)	LT	CH ₄ Volume mixing ratio (3σ)			
				1327.0742 cm ⁻¹	1327.4098 cm ⁻¹	1332.5467 cm ⁻¹	Weighted average
Mars Center #1	-17	179	16	3 \pm 5 ppb	1 \pm 4 ppb	0 \pm 14 ppb	2 \pm 3 ppb
Mars Center #1	13	149	14	0 \pm 2 ppb	1 \pm 2 ppb	4 \pm 6 ppb	1 \pm 1 ppb
Mars Center #1	40	113	12	1 \pm 3 ppb	1 \pm 5 ppb	0 \pm 7 ppb	1 \pm 2 ppb
Mars Left	-42	155	15	0 \pm 9 ppb	0 \pm 6 ppb	0 \pm 14 ppb	0 \pm 4 ppb
Mars Left	-8	123	13	0 \pm 7 ppb	0 \pm 3 ppb	3 \pm 12 ppb	0 \pm 3 ppb
Mars Left	13	90	11	4 \pm 6 ppb	0 \pm 5 ppb	5 \pm 14 ppb	2 \pm 4 ppb
Mars Right	0	192	18	5 \pm 6 ppb	0 \pm 2 ppb	0 \pm 2 ppb	0 \pm 2 ppb
Mars Right	30	171	16	0 \pm 2 ppb	2 \pm 4 ppb	0 \pm 9 ppb	0 \pm 2 ppb
Mars Right	56	126	13	0 \pm 2 ppb	0 \pm 3 ppb	1 \pm 3 ppb	0 \pm 1 ppb
Mars Center #2	-17	172	16	2 \pm 5 ppb	0 \pm 5 ppb	0 \pm 8 ppb	1 \pm 3 ppb
Mars Center #2	13	143	14	0 \pm 3 ppb	0 \pm 2 ppb	3 \pm 7 ppb	0 \pm 1 ppb
Mars Center #2	40	107	12	0 \pm 4 ppb	5 \pm 8 ppb	0 \pm 5 ppb	1 \pm 3 ppb

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