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## Highlights

- Updated versions of GEISA 2015 and HITRAN 2016 line lists are validated using terrestrial solar occultation spectra from ACE-FTS.
- Spectroscopic parameters for CO<sub>2</sub> and H<sub>2</sub>O are improved in both line lists.
- The primary difference we observe between the two line lists comes from O<sub>3</sub> absorption features near 3850 cm<sup>-1</sup> and from several CH<sub>4</sub> absorption lines in the regions 2800-3200 cm<sup>-1</sup> and 4000-4300 cm<sup>-1</sup>.

# Validation of the HITRAN 2016 and GEISA 2015 line lists using ACE-FTS solar occultation observations

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## Abstract

The ExoMars Trace Gas Orbiter (TGO) began its nominal science phase at Mars in April 2018, following releases of editions to two major spectroscopic line lists: GEISA 2015 (Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information), and HITRAN 2016 (High Resolution Transmission). This work evaluates both line lists over the spectral region between 2325–4350 cm<sup>-1</sup> using terrestrial solar occultation observations made by the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS). This spectral region is targeted on Mars by two complementary solar occultation instruments on TGO that will monitor temperature and pressure, aerosols,

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the abundance of CO<sub>2</sub>, CO, H<sub>2</sub>O, HDO, CH<sub>4</sub>, and other undetected trace gases. Major updates to GEISA 2015 and HITRAN 2016, with respect to previous editions, have been focused on CO<sub>2</sub> absorption features in support of Earth-observing missions to monitor greenhouse. Since CO<sub>2</sub> is the dominant absorber on Mars, making up 96.5% of the atmosphere, validating the updated line lists is critically important before their deployment for ExoMars. We report that updated CO<sub>2</sub> parameters make significant improvements to spectral fits made when using both line lists. Several updates to H<sub>2</sub>O lines in both line lists also show improvement. The primary difference we observe between the two line lists comes from O<sub>3</sub> absorption features near 3850 cm<sup>-1</sup> and from several CH<sub>4</sub> absorption lines in the regions 2800–3200 cm<sup>-1</sup> and 4000–4300 cm<sup>-1</sup>. Because of these differences, we find that using HITRAN 2016 tends to result in better spectral fits, especially below 30 km, than using GEISA 2015 in this spectral region. Differences are strongly reduced with increasing altitude (> 40 km) as pressure and gas abundance falls off. It was also discovered that several new errors in both new editions of GEISA and HITRAN were introduced since the HITRAN 2012.

*Keywords:* ACE-FTS, HITRAN, GEISA, ExoMars, line-list

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## 1. Introduction

New editions of two major spectroscopic line lists have been recently released: Gestion et Etude des Informations Spectroscopiques Atmosphériques: Management and Study of Atmospheric Spectroscopic Information (GEISA) in 2015 (Jacquinet-Husson et al., 2016); and High Resolution Transmission (HITRAN) in 2016 (Gordon et al., 2017). Here, we present a comparison

7 of spectral fits to solar occultation measurements of the Earth’s atmosphere  
8 made by the Canadian Space Agency’s (CSA’s) Atmospheric Chemistry Ex-  
9 periment (ACE) Fourier transform spectrometer (FTS) using both line lists.  
10 This work was motivated by the arrival of the European Space Agency (ESA)  
11 and Roscosmos’ ExoMars Trace Gas Orbiter (TGO) at Mars in October 2016.  
12 The TGO carries two infrared remote sensing instrument suites, the Atmo-  
13 spheric Chemistry Suite (ACS) (Korablev et al., 2018) and the Nadir and  
14 Occultation for Mars Discovery (NOMAD) (Vandaele et al., 2018). Both  
15 instrument suites carry channels dedicated to making solar occultation ob-  
16 servations at Mars in the infrared wavenumber range of 2325–4350  $\text{cm}^{-1}$ .

17 The controversial observation of methane ( $\text{CH}_4$ ) in the Martian atmo-  
18 sphere (Formisano et al., 2004; Krasnopolsky et al., 2004; Mumma et al.,  
19 2009; Webster et al., 2015, 2018; Giuranna et al., 2019) is one of the key mo-  
20 tivations of the ExoMars mission (Zurek et al., 2011; Vandaele et al., 2015;  
21 Korablev et al., 2018). NOMAD and ACS will search for  $\text{CH}_4$  by making  
22 solar occultation observations of its  $\nu_2$  vibration-rotation band centred near  
23 3000  $\text{cm}^{-1}$ , which hosts the strongest absorption features available to both  
24 instruments. A key benefit of searching for  $\text{CH}_4$  in this region is that it is  
25 relatively clear of interfering absorption lines from  $\text{CO}_2$ . There is a recently-  
26 observed, weak vibration-rotation band of carbon dioxide ( $\text{CO}_2$ ) that overlaps  
27  $\text{CH}_4$  in this region (Bertaux et al., 2008; Villanueva et al., 2008) and one of  
28 our specific objectives was to evaluate its spectroscopic parameters in GEISA  
29 2015 and HITRAN 2016.

30 ACS and NOMAD will also make detailed measurements of water vapour  
31 ( $\text{H}_2\text{O}$ ), having the capability of distinguishing isotopologues. The ratio of

32 HDO to H<sub>2</sub>O has been used as a critical indicator of the Martian climate in  
33 the ancient past (e.g., Encrenaz et al., 2018; Krasnopolsky, 2015). The rela-  
34 tive abundance of HDO on Mars is enriched relative to Earth, which supports  
35 mechanisms for hydrogen escape from the atmosphere, which are preferential  
36 towards the lighter isotope (Clarke et al., 2017). ACS and NOMAD will be  
37 able measure the vertical structure of H<sub>2</sub>O isotopologues, and monitor their  
38 ratios seasonally, spatially, and vertically.

39 In support of the study of Earth’s contemporary climate, and the carbon  
40 cycle, with the Orbiting Carbon Observatory (OCO-2) (Crisp et al., 2004,  
41 2017), the Greenhouse gases Observing SATellite (GOSAT) (Yokota et al.,  
42 2009), and the Total Carbon Column Observing Network (TCCON) (Wunch  
43 et al., 2011), a large effort has been undertaken to refine and reduce the un-  
44 certainty of the spectroscopic parameters of CO<sub>2</sub>. While the surface pressure  
45 of Mars is only between 550–720 Pa, roughly 0.5–0.7% of Earth’s, the vol-  
46 ume mixing ratio of CO<sub>2</sub> is 0.965, or 2400 times that on Earth (400 ppmv).  
47 Therefore, CO<sub>2</sub> absorption lines in Mars solar occultation spectra will be  
48 deeper and broader than for spectra recorded at Earth, and small changes in  
49 the spectroscopic parameters may have a large impact on trace gas retrievals  
50 made at Mars.

51 Our goal was to evaluate the new CO<sub>2</sub>, H<sub>2</sub>O, and CH<sub>4</sub> parameters by  
52 looking at whether their impact when fitting terrestrial spectra was positive  
53 or negative. We have performed spectral fitting for 125 sets of ACE-FTS  
54 occultation spectra (resolution of 0.02 cm<sup>-1</sup>) over 50 spectral windows cover-  
55 ing the spectral range of 2430–4450 cm<sup>-1</sup> using the HITRAN 2012, HITRAN  
56 2016, and GEISA 2015 line lists.

57 HITRAN 2016 and GEISA 2015 are compilations of data sources, many  
58 of which are shared. One of our most important results is that the updated  
59 CO<sub>2</sub> parameters for some of the stronger vibration-rotation bands, especially  
60 those centred at 3550 cm<sup>-1</sup> result in strongly improved spectral fits when  
61 using either HITRAN 2016 or GEISA 2015. However, we have also found  
62 that there are large differences in the spectroscopic parameters of ozone (O<sub>3</sub>),  
63 CH<sub>4</sub>, and H<sub>2</sub>O between the two data sets, and that using HITRAN 2016 leads  
64 to improved spectral fits compared to GEISA 2015. This result is significant  
65 since methane is one of the strongest absorbers in the Earth's atmosphere,  
66 and is one of the most variable gases. Methane is of key importance for TGO,  
67 as ACS and NOMAD both aspire to make its irregular and controversial  
68 detection in the Martian atmosphere definitive. However, at this time no  
69 methane features have been observed at Mars by TGO instruments (Korablev  
70 et al., 2019).

71 While individual contributions to the line lists are validated, they are  
72 often done in laboratory settings, observing controlled gas samples, rather  
73 than with observations of an atmosphere (e.g., Jacquinet-Husson et al., 2016;  
74 Gordon et al., 2017, and references therein). Bailey (2009) previously made  
75 a direct comparison between H<sub>2</sub>O transitions in older versions of GEISA and  
76 HITRAN, and qualitatively showed their differences using modelled spectra  
77 for Venus at high temperatures and above 4000 cm<sup>-1</sup>. A comprehensive vali-  
78 dation of the GEISA line list was done using TCCON and the Infrared Atmo-  
79 spheric Sounding Interferometer (IASI) (Clerbaux et al., 2009) by Armante  
80 et al. (2016). They describe a technique used to determine whether spec-  
81 troscopic parameters should be used to update the GEISA database based

82 on comparisons of computed spectra to observations. They specifically show  
83 H<sub>2</sub>O and HDO in the ExoMars region of interest and highlight improvements  
84 since GEISA 2011. They also compare CH<sub>4</sub> lines above 6000 cm<sup>-1</sup> to HI-  
85 TRAN 2012 and note an improvement to the residuals. This method was  
86 used in the compilation of GEISA 2015 (Jacquinet-Husson et al., 2016).

87 A comprehensive validation of the HITRAN 2012 line list was undertaken  
88 by Toon et al. (2016) using the MkIV balloon-borne FTS (Toon, 1991). They  
89 divided the spectral region between 670–5620 cm<sup>-1</sup> into fitting windows and  
90 quantitatively evaluated the best-fit residuals across the spectral range and  
91 with altitude for several versions of HITRAN released since 2000. They  
92 noted specific errors in the data base, where improvements were made, and  
93 where previous versions performed better. Their work was influential on the  
94 compilation of the latest version of HITRAN evaluated here (Gordon et al.,  
95 2017). Updates to Toon et al. (2016) are included in Toon (2019) and include  
96 evaluation of HITRAN 2016 and the TCCON internal line list, validation  
97 with laboratory spectra, and a specific analysis of CO<sub>2</sub> features. This work  
98 follows Toon et al. (2016) by using a similar quantitative evaluation technique  
99 and covering part of the same spectral region.

## 100 **2. HITRAN 2016**

101 The HITRAN (high-resolution transmission molecular absorption) database  
102 was first compiled for the Air Force Geophysics Laboratory (AFGL) by Mc-  
103 Clatchey et al. (1973) and major updated editions have been released on a  
104 four year cycle since 1992 (Rothman et al., 1992). The 2016 version of the HI-  
105 TRAN database (Gordon et al., 2017) describes changes made since the 2012



106 edition (Rothman et al., 2013). Among the most significant additions to the  
107 database have been the inclusion of spectroscopic parameters for collision-  
108 induced broadening from non-nitrogen based atmospheres and for non-Voigt  
109 line profiles (Wilzewski et al., 2016). The need for line broadening param-  
110 eters in atmospheres primarily composed of gases other than  $N_2$  has been  
111 motivated by extra-terrestrial spectroscopic applications, *e.g.*, Mars, which  
112 is 96%  $CO_2$ . HITRAN 2016 includes a sparse set of broadening parameters  
113 for atmospheres composed of  $H_2$ , He, or  $CO_2$  for a subset of gases that in-  
114 cludes CO, OCS,  $SO_2$ ,  $NH_3$ , HF and HCl, which are all sought at Mars by  
115 the ExoMars TGO. For very high-resolution applications, HITRAN 2016 also  
116 includes parameters for the speed-dependent Voigt, Galatry, and Hartman-  
117 Tran line shapes. These are again only available for a subset of wavenumbers  
118 and only for  $H_2O$ , CO,  $H_2$ ,  $O_2$ ,  $N_2O$ , HF and HCl. Because of the complexity  
119 of the newly included parameters, newly-developed online tools are now used  
120 to create user-defined database versions. The 2016 version also expands the  
121 list of available molecules with the addition of  $C_2N_2$  and  $COCl_2$ . While the  
122 number of additional lines, and the number of lines for which more accurate  
123 measurements have been made, is vast, we will primarily focus on key species  
124 relevant to Earth and Mars:  $CO_2$ ,  $H_2O$  and  $CH_4$ .

125 For  $CO_2$ , Gordon et al. (2017) identifies the imperative for high-accuracy  
126 spectroscopic parameters driven by GOSAT, OCO-2, TCCON, and others,  
127 and identifies validated improvements between the 2008 and 2012 versions of  
128 the HITRAN database (Toon et al., 2016). The 2012 version of the database  
129 was largely built on theoretical fits of the effective Hamiltonian or effective  
130 dipole moments, compiled as the CDS-296 database (Tashkun et al., 2015),

131 supplemented by higher-accuracy experimental measurements made by Toth  
132 et al. (2007, 2008a,b). The line intensity calculations in CDS-296 have  
133 high uncertainties ( $\sim 20\%$ ) and two new sets of theoretical computation have  
134 been produced: the Ames list (Huang et al., 2014) and the UCL-IAO list  
135 (Zak et al., 2016). These have been extensively validated experimentally,  
136 and Gordon et al. (2017) refers to 14 such studies that show that the UCL-  
137 IAO list tends to be more accurate, and that the uncertainties for the 2016  
138 version of HITRAN can be pushed down to the order of 0.5%. However, the  
139 majority of the experimental work focuses on important CO<sub>2</sub> bands for Earth  
140 observation (*e.g.*, for OCO-2) that lie outside the range of high-resolution  
141 solar occultation experiments on TGO, above 5000 cm<sup>-1</sup> (near 1.6 and 2  $\mu\text{m}$ ).  
142 Only laboratory measurements presented in Lyulin et al. (2012) and Durrý  
143 et al. (2010) cover the 2300–4400 cm<sup>-1</sup> range, and the latter only does so near  
144 3730 cm<sup>-1</sup>. The 2016 HITRAN line list for CO<sub>2</sub> between 2300–4400 cm<sup>-1</sup> is  
145 a combination of CDS-296 theoretical calculations (Tashkun et al., 2015),  
146 UCL-IAO or Ames theoretical calculations where better or newly available  
147 (Huang et al., 2014; Zak et al., 2016), and laboratory measurements where  
148 available and with low enough uncertainty (*e.g.*, Toth et al., 2008b; Durrý  
149 et al., 2010; Lyulin et al., 2012).

150 For H<sub>2</sub>O, the HITRAN 2012 line list was made up of *ab initio* calculations  
151 that comprised the BT2 line list (Barber et al., 2006), with updates, where  
152 available, from calculations using a more accurate method (Lodi et al., 2011;  
153 Lodi and Tennyson, 2012). Newer calculations using the methodology of Lodi  
154 and Tennyson (2012) have been made as part of an effort by the International  
155 Union of Pure and Applied Chemistry (IUPAC) task group (Tennyson et al.,

156 2009, and references therein). The new calculations have been validated  
157 experimentally by Birk et al. (2017) and the results have been used to update  
158 both the IUPAC database and the HITRAN line list. Extensive laboratory  
159 measurements have also been made for the German Aerospace Agency (DLR)  
160 in the spectral range between 1850–4000  $\text{cm}^{-1}$  by Loos et al. (2017a,b). When  
161 available, these replace the calculated line strengths of IUPAC and Lodi and  
162 Tennyson (2012).

163 The  $\text{CH}_4$  data in HITRAN 2012 was comprised of the data set described  
164 in Brown et al. (2013), which was a combination of theoretical calculations  
165 and experimental measurements. This data set replaced over 70% of the  
166 HITRAN 2008 line list for  $\text{CH}_4$  (Rothman et al., 2009). However, analysis  
167 of high-resolution solar occultation measurements in the Earth’s atmosphere  
168 made by the MkIV interferometer (Toon, 1991) determined that there were  
169 still several errors and omissions in the HITRAN 2012  $\text{CH}_4$  data (Toon et al.,  
170 2016), especially in the spectral region of the  $\nu_2$  transition critical to Exo-  
171 Mars, near 3000  $\text{cm}^{-1}$ . Errors that were identified were replaced by either  
172 the HITRAN 2008 values, or computations made by Tyuterev et al. (2013).  
173 Several laboratory studies have been recently undertaken, but the results  
174 have not yet been incorporated into the HITRAN line list, but an update to  
175 the 2016 edition is expected in the interim (Gordon et al., 2017).

### 176 **3. GEISA 2015**

177 The GEISA line list was first compiled in the early 1970s at the Labora-  
178 toire de Météorologie Dynamique (LMD) to support their radiative transfer  
179 investigations (Chédin et al., 1982). Key motivations for the compilation

180 were to include new gases important for planetary atmospheric applications,  
181 and to co-develop software tools to easily use the database. One distin-  
182 guishing feature is to treat certain isotopologues with distinct symmetries as  
183 independent species (such as HDO for H<sub>2</sub>O and CH<sub>3</sub>D for CH<sub>4</sub>) (Jacquinet-  
184 Husson et al., 2016). Comparing the available gases in current versions of  
185 GEISA and HITRAN, GeH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>3</sub>H<sub>4</sub>, and C<sub>6</sub>H<sub>6</sub> are unique to GEISA,  
186 while HOBr, O, H<sub>2</sub>, and CS are unique to HITRAN. There are also several  
187 minor isotopologues of trace gases unique to both. Updates to GEISA are  
188 made after evaluating the relevance of new data, the efficiency of including  
189 it, and after undergoing a validation process as described in Armante et al.  
190 (2016).

191 For CO<sub>2</sub>, the GEISA 2011 database was replaced by the CDS-296  
192 database (Tashkun et al., 2015). CDS-296 is also the primary source of  
193 CO<sub>2</sub> parameters in the 2016 edition of HITRAN. GEISA also contains three  
194 isotopologues not contained in CDS-296 from laboratory measurements  
195 by Jacquemart et al. (2012); Lyulin et al. (2012) (and others at higher  
196 wavenumbers than 4400 cm<sup>-1</sup>).

197 Extensive updates to H<sub>2</sub>O were made empirically for GEISA 2015 by  
198 a consortium of eight laboratories, nearly tripling the number of available  
199 lines since the 2011 edition. In the spectral region of interest to ExoMars  
200 (~2300–4400 cm<sup>-1</sup>), these measurements were made by the Laboratoire  
201 Inter-Universitaire des Systèmes Atmosphériques (LISA), the Institute of At-  
202 mospheric Optics (IAO), and University College, London (Jacquinet-Husson  
203 et al., 2016). Updates to H<sub>2</sub><sup>16</sup>O come from (Coudert et al., 2014), and updates  
204 for H<sub>2</sub><sup>17</sup>O and H<sub>2</sub><sup>18</sup>O come from Lodi et al. (2011); Lodi and Tennyson (2012)

205 and the IUPAC efforts, which is the same source as for HITRAN 2016. These  
206 were supplemented or updated by measurements made by Coudert and Che-  
207 lin (2016). GEISA 2015 also newly includes lines for two isotopologues of  
208 D<sub>2</sub>O not included in HITRAN.

209 Updates to CH<sub>4</sub> in this spectral range mainly come from the work of  
210 Niederer et al. (2013); Nikitin et al. (2013) which use the same methodology  
211 as Brown et al. (2013) (HITRAN 2012). The validation work of Armante  
212 et al. (2016) showed some imprecision in the new parameters, resulting in  
213 some CH<sub>4</sub> lines from GEISA 2011 being retained.

#### 214 **4. Methodology**

215 In this study, we break the wavenumber range of the ExoMars solar occul-  
216 tation spectrometers up into discrete fitting windows and analyze terrestrial  
217 solar occultation spectra recorded by ACE-FTS using the Jet Propulsion  
218 Laboratory Gas Fitting (GFIT or GGG) software suite. 125 occultations  
219 were analyzed. During an occultation, a series of observations of the sun  
220 are made while the limb of the atmosphere lies between the solar disk and  
221 the instrument. For each window, residuals were computed for each altitude  
222 level. The means of the residuals were taken at levels of equal pressure, and  
223 the root-mean-square (RMS) and standard deviation ( $\sigma$ ) were computed for  
224 each fitting window. The means of the residuals were taken, rather than  
225 computing the residuals of mean spectra, due to variations in line depths be-  
226 tween occultations, especially for CH<sub>4</sub> lines. In general, the lower the results  
227 RMS of the mean residuals is, the more accurate the spectroscopic parame-  
228 ters used in the fitting are. This methodology is very similar to that used by

229 Toon et al. (2016) who analyzed MkIV spectra.

230 ACE-FTS is a compact, double-pass interferometer with a spectral res-  
231 olution of  $0.02 \text{ cm}^{-1}$  and a spectral range of  $750\text{--}4400 \text{ cm}^{-1}$ . It has been  
232 operating continuously in low-Earth orbit since 2003. The 125 ACE-FTS  
233 occultations analyzed were recorded between 2004 and 2012 and are unre-  
234 stricted in longitude and season. Most observations are at high latitudes  
235 due to the ACE orbit (650 km with an inclination of  $74^\circ$ ). A sequence of  
236 measurements is made with an observation every 1–6.5 km, and on aver-  
237 age every 4 km. Two detectors provide an simultaneous spectral range of  
238  $750\text{--}4400 \text{ cm}^{-1}$  (Bernath et al., 2005).

239 Spectral fitting in this study was done with GGG, which is also being  
240 used to analyze solar occultation observations made by ACS on ExoMars.  
241 GGG is developed from early Occultation Display Spectra (ODS) used by  
242 the ATMOS FTS that flew on the space shuttle (Norton and Rinsland, 1991;  
243 Irion et al., 2002). It is a robust software suite adaptable for solar occultations  
244 (Toon, 1991; Toon et al., 2016; Olsen et al., 2015), ground based observations  
245 (Wunch et al., 2011), or laboratory measurements. For each altitude and  
246 each fitting window, GGG computes a spectrum from a set of parameters  
247 that include the calculated optical path, vertical profiles of pressure and  
248 temperature, and *a priori* gas volume mixing ratio (VMR) vertical profiles.  
249 GGG then performs non-linear least squares fitting to adjust VMR scaling  
250 factors (as well as other optional parameters such as continuum level and  
251 frequency shift) to obtain a best fit. Retrieved VMR vertical profiles can be  
252 obtained by inverting the matrix of VMR scale factors for each target gas at  
253 each altitude, with the matrix of slant paths (Sen et al., 1996; Wunch et al.,

254 2011).

255 *A priori* temperature, pressure, and specific humidity vertical profiles  
256 were derived from National Centers for Environmental Prediction (NCEP)  
257 reanalysis data (Kalnay et al., 1996) up to 40 km. The US standard atmo-  
258 sphere was used above 40 km.

For this work, we consider the fitting residuals for each window and focus on three pressure levels where we take the means of the residuals: 0.052, 0.0029, and 0.00023 atm, corresponding to 20,40 and 60 km respectively. For each occultation, fitting was performed at all altitudes and in all spectral windows. The closest altitude level to the predetermined pressure levels was identified. The residuals were computed for each window and the RMS and standard deviation were computed from the residual as:

$$\begin{aligned} \text{RMS}^2 &= \sum x_i^2/N, \\ \sigma^2 &= \sum (x_i - \bar{x})^2/(N - 1), \end{aligned} \quad (1)$$

259 where  $N$  is the number of spectral points,  $x_i$  is the residual value at the  
260  $i^{\text{th}}$  spectral point, and  $\bar{x}$  is the mean of the residual. In general, for this  
261 application  $\bar{x} \sim 0$  and  $\text{RMS}^2 \sim \sigma^2$ . For strong deviations between the  
262 computed and observed spectra,  $\sigma^2$  will reflect the magnitude of deviations  
263 from the mean of the residuals, while the RMS will reflect the deviation from  
264 zero, which is the expected outcome for a good fit. Therefore, the presented  
265 results will use the RMS values.

266 The fitting windows used are given in Tables 1 and 2, and panel a in  
267 Figure 1 shows their distribution over a sample of ACE-FTS solar occultation  
268 transmission spectrum. Panels b–e in Figure 1 illustrate the locations and

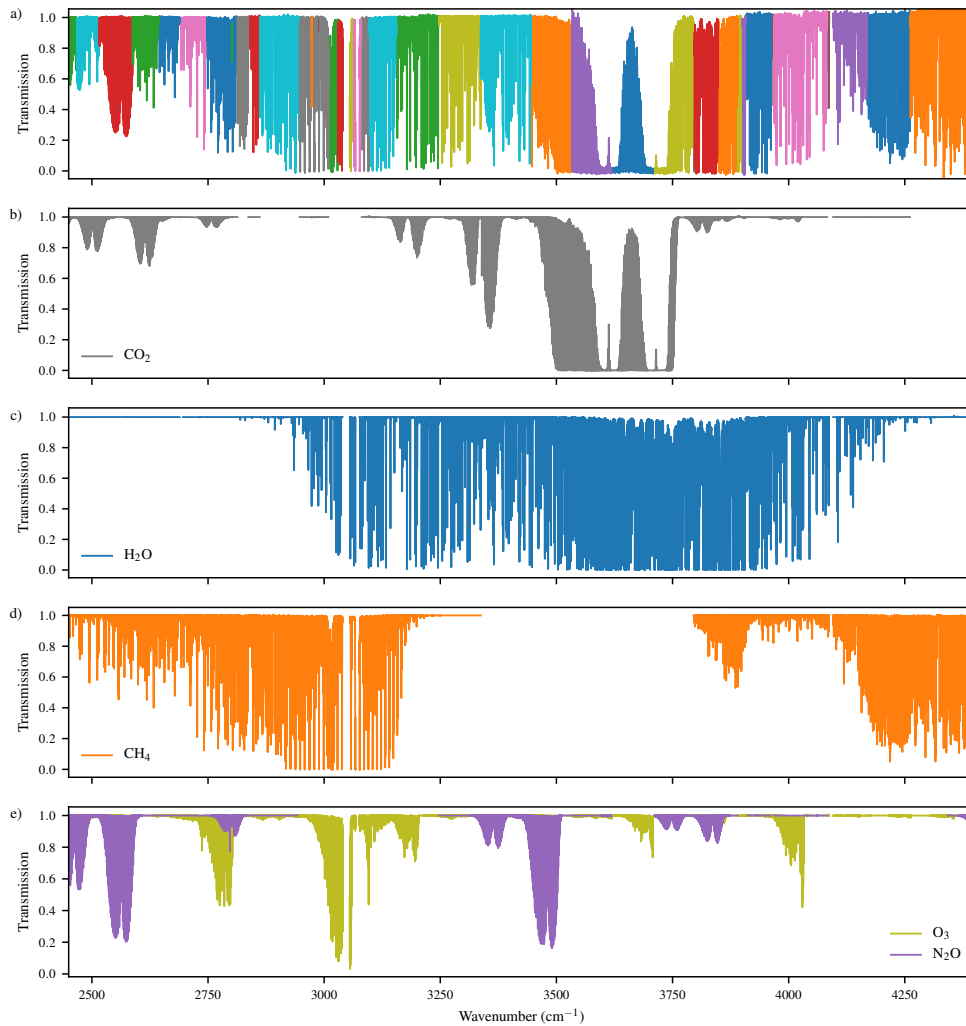


Figure 1: A look at ACE-FTS observations in the ExoMars spectral region of interest: a) mean ACE-FTS spectra at the 0.052 atm pressure level (near 20 km), the colours indicate different fitting windows; b) contributions from CO<sub>2</sub>; c) contributions from H<sub>2</sub>O; d) contributions from CH<sub>4</sub>; e) contributions from O<sub>3</sub> and N<sub>2</sub>O.

269 magnitudes of absorption features due to major gas species in the Earth's



270 atmosphere: CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, O<sub>3</sub>, and N<sub>2</sub>O.

## 271 5. Results

272 We begin with an overview of the differences between the HITRAN 2016  
273 and GEISA 2015 line lists in the ExoMars spectral region of interest, 2325–  
274 4350 cm<sup>-1</sup>. Figure 2 shows mean ACE-FTS spectra averaged at three differ-  
275 ent pressure levels corresponding to approximately 20, 40, and 60 km tan-  
276 gent altitudes. Each primary panel, for each pressure level, shows the mean  
277 ACE-FTS spectra, averaged over 125 occultations, for each fitting window  
278 (Figure 2 does not show continuous ACE-FTS spectra). Shown over top of  
279 the mean ACE-FTS spectra, is the mean of the calculated best fits for each  
280 window when using the HITRAN 2016 line list (as an example). It is im-  
281 portant to note that the noise level of the ACE-FTS spectra is not constant  
282 with wavenumber (Boone et al., 2005), and the noise can be seen increasing  
283 towards higher wavenumbers in Figure 2, even after averaging the ACE-FTS  
284 spectra.

285 The secondary panels in Figure 2 show the mean residuals for each fitting  
286 window at each pressure level. Shown are mean residuals when fitting with  
287 HITRAN 2012, GEISA 2015, and HITRAN 2016. HITRAN 2012 tends to  
288 have the largest numbers of errors and both newer line lists improve upon  
289 it. The most significant errors are in the CO<sub>2</sub> band centred at 3508 cm<sup>-1</sup>,  
290 which were corrected in the 2016 edition (and not present in GEISA 2015).  
291 Difficulty in fitting strong CO<sub>2</sub> lines in the region between 3500–3600 cm<sup>-1</sup>  
292 persists when using all three line lists, but this is also due to a strong increase  
293 in detector noise in that region, visible in the mean spectra, especially at the

Table 1: List of spectral fitting windows used to evaluate the HITRAN 2016 and GEISA 2015 line lists with ACE-FTS solar occultation observations of the Earth’s atmosphere. Given for each fitting window are: centre wavenumber, window width, and gases fit in the window.

Centre $\tilde{\nu}$ ( $\text{cm}^{-1}$ )	Width ( $\text{cm}^{-1}$ )	Gases fit
2455.5	25.9	CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O, N <sub>2</sub> O, O <sub>3</sub>
2491.5	47.9	CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O, N <sub>2</sub> O, O <sub>3</sub>
2551.55	71.35	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub>
2615.74	56.2	CO <sub>2</sub> , CH <sub>4</sub> , H <sub>2</sub> O, N <sub>2</sub> O, O <sub>3</sub> , HCl, C <sub>2</sub> H <sub>6</sub>
2666.6	44.76	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , HCl, C <sub>2</sub> H <sub>6</sub>
2689.8	0.62	HDO, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub>
2692.76	0.55	HDO, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub>
2708.17	0.54	HDO, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub>
2722.25	52.0	CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , H <sub>2</sub> O, N <sub>2</sub> O, O <sub>3</sub> , HCl, HDO
2780.74	65.15	CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , H <sub>2</sub> O, N <sub>2</sub> O, O <sub>3</sub> , HCl, HDO
2801.6	0.49	HDO, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub>
2825.0	22.95	H <sub>2</sub> O, O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , HDO, HCl
2849.15	24.55	HDO, CO <sub>2</sub> , H <sub>2</sub> O, CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , O <sub>3</sub> , N <sub>2</sub> O, HCl
2904.43	85.10	H <sub>2</sub> O, O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , HDO, HCl, NO <sub>2</sub> , OCS
2973.65	1.21	C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub> , H <sub>2</sub> O, CH <sub>4</sub> , O <sub>3</sub>
2978.2	62.0	CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , H <sub>2</sub> O, O <sub>3</sub> , HCl, HDO
2983.49	0.78	C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub> , O <sub>3</sub> , CH <sub>4</sub>
2986.74	0.58	C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub> , O <sub>3</sub>
2989.98	0.80	C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub> , O <sub>3</sub> , CH <sub>4</sub>
2993.52	1.23	C <sub>2</sub> H <sub>6</sub> , CO <sub>2</sub> , O <sub>3</sub> , CH <sub>4</sub> , H <sub>2</sub> O
3022.13	18.14	CH <sub>4</sub> , H <sub>2</sub> O, C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , O <sub>3</sub> , HCl
3035.08	9.2	CH <sub>4</sub> , H <sub>2</sub> O, C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , O <sub>3</sub>
3057.72	5.1	CH <sub>4</sub> , H <sub>2</sub> O, O <sub>3</sub>
3065.86	3.35	CH <sub>4</sub> , H <sub>2</sub> O, O <sub>3</sub>
3077.36	2.54	CH <sub>4</sub> , H <sub>2</sub> O, O <sub>3</sub>

Table 2: List of spectral fitting windows used to evaluate the HITRAN 2016 and GEISA 2015 line lists with ACE-FTS solar occultation observations of the Earth’s atmosphere. Given for each fitting window are: centre wavenumber, window width, and gases fit in the window.

Centre $\tilde{\nu}$ ( $\text{cm}^{-1}$ )	Width ( $\text{cm}^{-1}$ )	Gases fit
3089.75	17.5	CH <sub>4</sub> , H <sub>2</sub> O, C <sub>2</sub> H <sub>6</sub> , C <sub>2</sub> H <sub>4</sub> , CO <sub>2</sub> , O <sub>3</sub>
3126.65	58.0	CO <sub>2</sub> , CH <sub>4</sub> , C <sub>2</sub> H <sub>4</sub> , H <sub>2</sub> O, O <sub>3</sub> , HDO
3202.0	90.0	H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub> , HCN
3292.0	90.0	H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub> , HCN, N <sub>2</sub> O
3391.15	108.6	CO <sub>2</sub> , H <sub>2</sub> O, C <sub>2</sub> H <sub>2</sub> , NH <sub>3</sub> , HCN, N <sub>2</sub> O, O <sub>3</sub> , HDO
3489.0	86.0	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O
3577.0	86.0	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, HNO <sub>3</sub> , HDO
3665.0	86.0	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, HNO <sub>3</sub> , HDO
3753.0	86.0	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, HF, HDO
3798.8	7.46	H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub>
3822.5	51.0	CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub> O, O <sub>3</sub> , CH <sub>4</sub> , HF, HDO
3869.14	42.0	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , HF, HDO
3895.36	10.18	H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub>
3903.93	6.17	H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub>
3936.15	58.0	CO <sub>2</sub> , H <sub>2</sub> O, N <sub>2</sub> O, O <sub>3</sub> , CH <sub>4</sub> , HF, HDO
3967.79	2.0	H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub>
4026.0	114.0	H <sub>2</sub> O, CO <sub>2</sub> , O <sub>3</sub> , N <sub>2</sub> O, CH <sub>4</sub> , HF, CO
4085.69	3.4	HDO, CO, H <sub>2</sub> O, O <sub>3</sub> , CH <sub>4</sub>
4115.21	5.62	HDO, CO, O <sub>3</sub> , CH <sub>4</sub>
4128.34	9.53	HDO, CO, H <sub>2</sub> O, O <sub>3</sub> , CH <sub>4</sub>
4132.1	72.5	CO, H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub>
4214.2	94.1	CO, H <sub>2</sub> O, CO <sub>2</sub> , CH <sub>4</sub> , O <sub>3</sub>
4300.4	76.6	CO, H <sub>2</sub> O, CH <sub>4</sub> , O <sub>3</sub>
4377.0	75.4	H <sub>2</sub> O, O <sub>3</sub> , CH <sub>4</sub> , N <sub>2</sub> O, CO
4436.2	42.6	CO <sub>2</sub> , H <sub>2</sub> O, CH <sub>4</sub>

294 lowest pressure level.

295 In general, HITRAN 2016 performs better than GEISA 2015, and larger  
296 mean residuals are seen in Figure 2. The largest differences are observed the  
297 lowest pressure levels, while both line lists perform similarly at higher tan-  
298 gent altitudes. This suggests that the errors are related to either increased  
299 pressure and pressure broadening at lower altitudes, or (and) that the mag-  
300 nitude of the errors are related to line depth, and that when the line depths  
301 are small, the errors are less than the instrument noise. When CH<sub>4</sub> or CO<sub>2</sub>  
302 lines are saturated, the residuals show the negative impact of untreated line  
303 mixing, which was not implemented in this spectral region for this study, but  
304 is available in GGG (Mendonca et al., 2016). Key areas that GEISA 2015  
305 has difficulty with relative to HITRAN 2016 are between 2700–3200 cm<sup>-1</sup>,  
306 when strong CH<sub>4</sub> lines absorb totally, between 4100–4300 cm<sup>-1</sup>, where errors  
307 are related to O<sub>3</sub> lines and also CH<sub>4</sub> lines (shown in the following section).  
308 These are also errors near 3800 cm<sup>-1</sup> related to H<sub>2</sub>O. Fitting the strong CO<sub>2</sub>  
309 lines between 3500–3700 cm<sup>-1</sup> is challenging for GGG using any line list,  
310 as shown in Figure 2, especially the middle pressure level. The  $\nu_1$  band of  
311 HNO<sub>3</sub> is located in this region which is significant at 20 km.

312 At lower wavenumbers, where detector noise is lowest, there are system-  
313 atic features observable in the mean residuals when using either line list.  
314 Near 2550 cm<sup>-1</sup>, this is related to line widths in an N<sub>2</sub>O absorption band.  
315 Near 2650 cm<sup>-1</sup>, there is an observed absorption band of HNO<sub>3</sub> that is not  
316 included in either line list. Several HNO<sub>3</sub> bands are observable in ACE-FTS  
317 spectra that are not contained in the HITRAN or GEISA line lists. Weaker  
318 bands result in an apparent baseline curvature, while stronger bands show

319 a distinct vibration-rotation band structure in the residuals. Examples are  
320 shown in the following section.

321 Figure 3 shows the mean RMS for each fitting window, at each pressure  
322 level. The RMS was computed for each ACE-FTS occultation in a given  
323 window, and shown are the means of the RMS values, with the standard  
324 deviation of the mean. At the highest pressure level (top panel, near 60 km),  
325 all three line lists perform similarly. In the middle pressure level, near 40 km,  
326 we observe strong increases in the mean RMS values, and their uncertainties,  
327 where line depths extend beyond 50%, just above  $3500\text{ cm}^{-1}$  due to  $\text{CO}_2$ ,  
328 and near  $3000\text{ cm}^{-1}$  due to  $\text{CH}_4$ . At the lowest pressure level, the RMS  
329 uncertainties increase strongly for all windows, and the differences between  
330 line lists become most apparent. At this level, we see deviations between  
331 HITRAN 2012 and 2016, at the same locations observed in Figure 2. This  
332 analysis also supports the observations made from Figure 2 regarding GEISA  
333 2015. Specific examples and windows are explored in the following section.

## 334 6. Specific examples

### 335 6.1. $2440 - 2660\text{ cm}^{-1}$ : $\text{N}_2\text{O}$ and $\text{HNO}_3$

336 The spectral region between  $2440 - 2660\text{ cm}^{-1}$  was covered by four broad  
337 fitting windows centred at  $2455.5$ ,  $2491.5$ ,  $2551.55$ , and  $2615.74\text{ cm}^{-1}$ . This  
338 region is characterized primarily by the  $P$  and  $R$  branches of two vibration-  
339 rotation bands of  $\text{N}_2\text{O}$ , centred near  $2462$  and  $2562\text{ cm}^{-1}$ , and two vibration-  
340 rotation bands of  $\text{CO}_2$ , centred near  $2501$  and  $2614\text{ cm}^{-1}$ . For these bands, all  
341 three spectroscopic line lists perform similarly. In the  $2491.5\text{ cm}^{-1}$  window,  
342 small, but visible, improvements are apparent where  $\text{CO}_2$  lines are present in

343 the two updated editions of the line lists when compared to HITRAN 2012.

344 Both the GEISA 2015 and HITRAN 2016 line lists perform almost equiv-  
345 alently in this region. However, there are apparent problems in the fitting,  
346 and these problems persist in both data sets. At the lower pressure level, the  
347 N<sub>2</sub>O fits produce large mean residuals whose shape is indicative of errors in  
348 line width. These errors do not persist at the higher pressure levels and are  
349 likely due to errors in the broadening parameters in the line lists. The mean  
350 ACE-FTS spectra and mean residuals for the 2551.55 cm<sup>-1</sup> window, which  
351 are shown in Figure 4. The lines in this window are mainly due to N<sub>2</sub>O, with  
352 some CH<sub>4</sub> lines throughout, and the edge of an *R* branch of CO<sub>2</sub> on the left  
353 side.

354 Figure 5 shows the same information as Figure 4, but for the 2615.74 cm<sup>-1</sup>  
355 window. Again, both the GEISA 2015 and HITRAN 2016 line lists perform  
356 equivalently, and, again, there are systematic differences between the obser-  
357 vations and the computed spectra. These differences are due to HNO<sub>3</sub> lines  
358 not included in either line list. The broad curvature of the baseline in the  
359 residuals is due to a weaker band, while the distinct peaks to the right side  
360 of Figure 4 are the *P* branch of a stronger HNO<sub>3</sub> vibration-rotation band.  
361 There is a corresponding *R* branch in the adjacent 2666.6 cm<sup>-1</sup> window. The  
362 feature of another weak HNO<sub>3</sub> band is also present in the 2491.5 cm<sup>-1</sup> win-  
363 dow, and stronger missing lines are seen in the 2978.2 cm<sup>-1</sup> window, between  
364 2985–3010 cm<sup>-1</sup>, and in the 3391.15 cm<sup>-1</sup> window, between 3390–3415 cm<sup>-1</sup>.  
365 That these are due to HNO<sub>3</sub> is verified by measurements made for the line list  
366 distributed by the Pacific Northwest National Laboratory (PNNL) (Sharpe  
367 et al., 2004; Johnson et al., 2010). Supplementary HNO<sub>3</sub> line lists are used

368 for ACE-FTS and TCCON retrievals.

369 *6.2. 2660 – 3440 cm<sup>-1</sup>: CH<sub>4</sub>*

370 This wavenumber region is characterized by strong CH<sub>4</sub> absorption fea-  
371 tures, but also contains important bands of O<sub>3</sub>, N<sub>2</sub>O and CO<sub>2</sub>. This region  
372 was covered by several narrow windows and 12 wide windows ranging in  
373 width between 18–108 cm<sup>-1</sup>. The first window centred at 2722.25 cm<sup>-1</sup> fea-  
374 tures three strong CH<sub>4</sub> lines, and many associated weaker lines, and there are  
375 significant residual errors about each due to unaccounted line mixing. Toon  
376 et al. (2016) pointed out a positional error in a CH<sub>4</sub> line at 2742.3 cm<sup>-1</sup>  
377 that was introduced into HITRAN 2012 after the 2008 version. This error  
378 is present in GEISA 2015 and HITRAN 2016, and is shown in Figure 6a.  
379 While positive changes have been made to the HITRAN 2016 line list, cor-  
380 recting the positional error, strong residual features remain, but these are  
381 most likely due to unaccounted line mixing for such strong lines fit at a low  
382 altitude. This window also features several weak O<sub>3</sub> lines that are well fit by  
383 both line lists, except a small region around 2705–2710 cm<sup>-1</sup> where fitting  
384 with GEISA 2015 results in larger mean residuals than fitting with HITRAN  
385 2016, on the order of 0.005.

386 The window centred at 2780.74 cm<sup>-1</sup> contains weaker CH<sub>4</sub> lines and a  
387 large O<sub>3</sub> band. Both line lists perform similarly here, but there is what  
388 appears to be a single missing line in the GEISA 2015 list. This is an ozone  
389 line at 2773.15 cm<sup>-1</sup> that is not missing, but has an error in line strength,  
390 shown in Figure 6b. Toon et al. (2016) pointed out an error in position in an  
391 O<sub>3</sub> resonance transition at 2761.42 cm<sup>-1</sup> that is seen in HITRAN 2012 and  
392 GEISA 2015, but has been corrected in HITRAN 2016. However, there are

393 new O<sub>3</sub> positional errors at 2763.86 and 2798.0 cm<sup>-1</sup> in the HITRAN 2016  
394 line list that were not present in HITRAN 2012.

395 The fitting window centred at 2825.0 cm<sup>-1</sup> presents one of the largest dis-  
396 crepancies between HITRAN 2016 and GEISA 2015. The mean ACE-FTS  
397 spectra and mean residuals when fitting with the three line lists are shown in  
398 Figure 7 for the lowest pressure level. These discrepancies are characteristic  
399 of the strong CH<sub>4</sub> lines throughout this region, and the systematic differenti-  
400 ation between fitting results using the two line lists is seen in Figure 3. There  
401 is little difference between the two versions of HITRAN, and both result in  
402 mean residual errors on the order of ±0.01 about strong CH<sub>4</sub> lines. In sev-  
403 eral positions, however, when fitting with GEISA 2015, these residuals can  
404 be twice as large.

405 Windows centred at 2849.15, 2904.43, 2978.2 cm, and 3126.65<sup>-1</sup> are sim-  
406 ilar to those preceding, predominantly featuring strong CH<sub>4</sub> lines, with line  
407 mixing errors apparent in the mean residuals when using either line list, but  
408 the largest residuals are found when using GEISA 2015. In the 2978.2 cm<sup>-1</sup>  
409 window, there are several saturated (at low altitude) CH<sub>4</sub> lines, and the be-  
410 ginning of a broad, strong band of O<sub>3</sub> lines, but also a set of HNO<sub>3</sub> lines that  
411 are missing in both line lists.

412 The 3022.13 cm<sup>-1</sup> window contains a mixture of strong O<sub>3</sub> and CH<sub>4</sub>  
413 lines. There is an opaque region about 5 cm<sup>-1</sup> wide at the lower pressure  
414 level, which is the *Q*-branch of this CH<sub>4</sub> band. This feature is critically  
415 important for ExoMars, as it is the strongest and broadest *CH*<sub>4</sub> feature in  
416 the available wavenumber range, and where the ExoMars instruments will  
417 focus their search for a CH<sub>4</sub> signature. Mean residuals on the right side of



418 the  $Q$ -branch ( $3018\text{ cm}^{-1}$ ) are nearly equivalent when using GEISA 2015 or  
419 HITRAN 2016. On the left side ( $3015\text{ cm}^{-1}$ ), mean residuals when using  
420 GEISA 2015 are larger than when using HITRAN 2016 by 0.01–0.02. Most  
421 of the fitting differences in this region can be attributed to  $\text{CH}_4$ , but there is  
422 also a weaker  $\text{HCl}$  line at  $3014.4\text{ cm}^{-1}$  that contributes to these differences.  
423 Note that the residuals for both line lists are significant ( $\sim 0.002$ ) even at  
424 the highest pressure level (near 60 km), where line depths are much weaker  
425 and only extend to 0.9. Of particular interest to ExoMars is the recently  
426 observed, weak  $\text{CO}_2$  band centred near  $3000\text{ cm}^{-1}$  that overlaps with these  
427 strong  $\text{CH}_4$  features (Bertaux et al., 2008; Villanueva et al., 2008). This  
428 band is not visible in terrestrial solar occultation observations, its lines are  
429 too weak relative to the abundant absorption features of  $\text{CH}_4$  and  $\text{O}_3$ .

430 Figure 8 shows the mean spectra and mean residuals for fitting window  
431  $3089.75\text{ cm}^{-1}$ . This region contains a set of three  $\text{CH}_4$  lines near  $3090\text{ cm}^{-1}$   
432 that are poorly fit with either line list. When using HITRAN 2012 and  
433 HITRAN 2016, the magnitude of the mean residuals is 0.04, which is on the  
434 order of the line mixing errors seen when fitting stronger lines. When using  
435 GEISA 2015, the mean residuals are 50% larger. Figure 8 also shows a pair  
436 of saturated  $\text{CH}_4$  lines, and fitting errors characteristic of such lines.

437 The window centred at  $3126.65\text{ cm}^{-1}$  has some of the strongest  $\text{CH}_4$  lines,  
438 and, therefore, the largest residuals. GEISA 2015 and HITRAN 2016 perform  
439 similarly here. The window centred at  $3202.0\text{ cm}^{-1}$  contains the right edge of  
440  $\text{CH}_4\ \nu_2$  band. At higher wavenumbers,  $\text{H}_2\text{O}$  absorption becomes dominant.  
441 This window also features overlapping  $\text{CO}_2$  and  $\text{O}_3$  bands, the edge of the  
442 strong  $\text{CH}_4$  band, and several water vapour lines. The  $3292.0\text{ cm}^{-1}$  window

443 contains H<sub>2</sub>O and CO<sub>2</sub> lines, with an H<sub>2</sub>O line strength error at 3254.15 cm<sup>-1</sup>  
444 that has been reduced between HITRAN 2012 and HITRAN 2016, but is  
445 still significant in both HITRAN 2016 and GEISA 2015. This window con-  
446 tains several other H<sub>2</sub>O lines where significant improvements were made to  
447 both line lists since HITRAN 2012 (e.g., at 3273.4 and 3276.5 cm<sup>-1</sup>). The  
448 3391.15 cm<sup>-1</sup> window is similar, but hosts another set of HNO<sub>3</sub> lines missing  
449 from both line lists. There is also an H<sub>2</sub>O line strength error at 3367.65 cm<sup>-1</sup>  
450 in both GEISA 2015 and HITRAN 2016 that was not significant in HITRAN  
451 2012.

### 452 6.3. 3440 – 3770 cm<sup>-1</sup>: CO<sub>2</sub>

453 This region was covered by five wide windows centred at 3391.15, 3489.0,  
454 3577.0, 3665.0, and 3753.0 cm<sup>-1</sup>. These windows cover the strongest CO<sub>2</sub>  
455 vibration-rotation bands observed by the ExoMars instruments. Throughout  
456 this region, there are only small differences between fits using GEISA 2015  
457 and HITRAN 2016. However, there are significant improvements to several  
458 lines throughout since HITRAN 2012. Figure 9 shows the mean spectra and  
459 residuals for the window centred at 3489.0 cm<sup>-1</sup>, where the most dramatic  
460 improvement is seen. The spectroscopic parameters for an entire band have  
461 been updated, resulting in significant improvements to fitting.

### 462 6.4. 3770 – 4080 cm<sup>-1</sup>: H<sub>2</sub>O

463 This spectral region, covered by four broad fitting windows centred at  
464 3822.5, 3869.14, 3936.15, and 4026.0 cm<sup>-1</sup>, features the strongest set of water  
465 vapour lines in the ExoMars region of interest. It is in this region where we  
466 again find that spectral fitting with the HITRAN 2016 results in smaller

467 residuals than when using GEISA 2015, as seen in Figure 3. Figure 10  
468 shows the window centred at  $3869.14\text{ cm}^{-1}$ . The primary features are broad,  
469 saturated  $\text{H}_2\text{O}$  lines, but there are also many smaller  $\text{CH}_4$  and  $\text{N}_2\text{O}$  lines,  
470 and many very weak lines from  $\text{CO}_2$  and  $\text{O}_3$ . The lines where fitting with  
471 GEISA 2015 resulted in systematic residual errors are largely attributable  
472 to weaker  $\text{O}_3$  lines. Similar behaviour is seen in the window centred at  
473  $3822.5\text{ cm}^{-1}$ , where several  $\text{O}_3$  lines are not contained in GEISA 2015. Note  
474 the marked improvement in the strong  $\text{H}_2\text{O}$  line between HITRAN 2012 and  
475 the newer line lists near  $3886\text{ cm}^{-1}$ , as shown in Figure 6c, but clearly visible  
476 in Figure 10.

477 The two windows at  $3936.15$  and  $4026.0\text{ cm}^{-1}$  show improvements over  
478 the previous two windows when comparing GEISA 2015 and HITRAN 2016.  
479 The  $3936.15\text{ cm}^{-1}$  window contains a portion of an  $\text{O}_3$  *P*-branch. Significant  
480 residuals when using GEISA 2015 are from widely spaced  $\text{CH}_4$  lines (e.g., at  
481  $3912.15$ ,  $3914.6$ , and  $3914.9\text{ cm}^{-1}$ ), rather than  $\text{O}_3$ . Two of these features  
482 near  $3914.6\text{ cm}^{-1}$  are shown in Figure 6d. There is an  $\text{H}_2\text{O}$  line strength  
483 error in the HITRAN 2016 line list at  $3925.15\text{ cm}^{-1}$  that was not present  
484 in HITRAN 2012, nor GEISA 2015. The  $4026.0\text{ cm}^{-1}$  window hosts an  $\text{O}_3$   
485 band, for which all line lists have difficulty accurately fitting over the region  
486 of the *Q*-branch. The  $\text{O}_3$  band in this region is much better characterized by  
487 GEISA 2015 than that covered by the  $3822.5$  and  $3869.14\text{ cm}^{-1}$  windows, but  
488 there remain small discrepancies in some minor  $\text{CH}_4$  lines, especially towards  
489 the right edge of the window at  $4080.65$  and  $4082.8\text{ cm}^{-1}$ .

490 6.5. 4080 – 4420  $\text{cm}^{-1}$ :  $\text{CH}_4$

491 Above 4100  $\text{cm}^{-1}$ , the ACE-FTS noise increases, as can be seen in Fig-  
492 ure 2, and it becomes difficult to evaluate the line lists further. This region  
493 is characterized by a decreasing density of  $\text{H}_2\text{O}$  lines, increasingly stronger,  
494 and more dense  $\text{CH}_4$  absorption features, and a band of broadly spaced CO  
495 lines. We evaluated five wide fitting windows in this region centred at 4132.1,  
496 4214.2, 4300.4, 4377.0, and 4436.2  $\text{cm}^{-1}$ . At 4115.65  $\text{cm}^{-1}$ , a  $\text{CH}_4$  line miss-  
497 ing in HITRAN 2012, as identified by Toon et al. (2016), was added (also  
498 included in GEISA 2015). There are  $\text{CH}_4$  line strength errors in the GEISA  
499 2015 line list at 4133.35  $\text{cm}^{-1}$  and 4103.2  $\text{cm}^{-1}$  that result in mean residuals  
500 on the order of 0.1 at lower pressure levels. The latter is also apparent in  
501 HITRAN 2016, despite not being present in HITRAN 2012.

502 As shown in Figure 3, the mean RMS values dramatically increase in this  
503 spectral region for all evaluated line lists. At the lowest pressure level, fitting  
504 with HITRAN 2016 results in the smallest residuals and the lowest mean  
505 RMS values. It must be noted that the magnitude of the difference between  
506 results using HITRAN 2016 and GEISA 2015 is on the order of the difference  
507 between changing pressure levels, and that is only  $\sim 1/5$  of the magnitude  
508 of the mean RMS. Therefore, errors due to differences in the spectroscopic  
509 parameters are much, much smaller than the noise level of the instrument in  
510 this region.

511 The window centred at 4214.2  $\text{cm}^{-1}$  features the most dramatic difference  
512 between fitting using GEISA 2015 and fitting using HITRAN 2016. Mean  
513 residuals with magnitudes greater than 0.1 come from several  $\text{CH}_4$  lines near  
514 4208, 4229, and 4255  $\text{cm}^{-1}$ .

## 515 7. Conclusions

516 This study was motivated by the release of two new editions of spectro-  
517 scopic line lists, the 2015 version of GEISA and the 2016 version of HITRAN,  
518 and the launch and arrival of the ExoMars Trace Gas Orbiter as Mars,  
519 equipped with two suits of spectroscopic instruments dedicated to charac-  
520 terizing the Martian atmosphere. The largest efforts made recently towards  
521 updating infrared spectroscopic databases has been in support of terrestrial  
522 greenhouse gas observatories such as OCO-2, GOSAT, and TCCON. Since  
523 the Martian atmosphere is composed of 96.5% CO<sub>2</sub>, these updates are very  
524 significant for the ExoMars mission. Our objective was to validate the two  
525 line lists in the range of 2325–4350 cm<sup>-1</sup> by examining spectral fitting results  
526 for terrestrial solar occultation observations made by ACE-FTS.

527 This work follows that of Toon et al. (2016) who compared different  
528 versions of HITRAN, up to the 2012 release, in the spectral range of 670–  
529 5620 cm<sup>-1</sup> using the solar occultation measurements made by the MkIV FTS.  
530 They identified several errors in HITRAN 2012, some persisting from previ-  
531 ous releases, and others newly introduced. The analysis in Toon et al. (2016)  
532 is expanded in Toon (2019), which includes a detailed analysis of HITRAN  
533 2016 using laboratory and solar occultation spectra. Because spectroscopic  
534 parameters taken from previous HITRAN versions for some gases in some  
535 spectral regions perform better, and because HITRAN may be incomplete  
536 in some spectral regions (*e.g.*, HNO<sub>3</sub>), the TCCON and GGG development  
537 teams maintain a custom line list, as do other spectroscopic analysis teams,  
538 such as ACE-FTS.

539 The 2016 edition of the HITRAN line list addressed several errors identi-

540 fied in the 2012 edition by Toon et al. (2016), such as the positional error in an  
541 O<sub>3</sub> resonance transition at 2761.42 cm<sup>-1</sup> (still persists in GEISA 2015). We  
542 have observed, however, a few minor errors introduced into HITRAN 2016  
543 since the 2012 edition, such as the H<sub>2</sub>O line strength errors at 3367.65 cm<sup>-1</sup>  
544 (also in GEISA 2015) and 3925.15 cm<sup>-1</sup>.

545 For ExoMars, the gases of primary interest are CO<sub>2</sub>, H<sub>2</sub>O, CO, and CH<sub>4</sub>.  
546 Changes to line position and strength have been made to CO<sub>2</sub> lines across  
547 our spectral region. For terrestrial spectra, the strongest improvements seen  
548 in fitting coincide with the strongest absorption features, and the greatest  
549 improvement is seen between 3470–3530 cm<sup>-1</sup> for both GEISA 2015 and  
550 HITRAN 2016. In no region were increased residuals seen for CO<sub>2</sub> lines  
551 when using the updated line list editions when compared to HITRAN 2012.  
552 In the terrestrial observations, we also observe significant improvements to a  
553 subset of H<sub>2</sub>O lines, especially at higher wavenumbers, such as near 3093.7  
554 or 3885.5 cm<sup>-1</sup>. With the exception of individual CH<sub>4</sub> line errors, little  
555 difference is observed in the CH<sub>4</sub> or CO transitions in this spectral region  
556 between HITRAN 2012 and 2016.

557 Of key interest to us was the CO<sub>2</sub> vibration-rotation band centred at  
558 2982 cm<sup>-1</sup> and partially overlapping the critically important CH<sub>4</sub>  $\nu_2$  band.  
559 When comparing synthetic spectra generated with HITRAN 2016 or GEISA  
560 2015, significant differences in these lines are seen. This band is absent from  
561 GEISA 2015, but present in HITRAN 2012 and 2016. The lines included in  
562 HITRAN 2016 have significantly increased line strengths relative to HITRAN  
563 2012. Unfortunately, in terrestrial observations, these lines are too weak  
564 relative to interfering species, especially CH<sub>4</sub>, and noise. It is not observed

565 in the ACE-FTS spectra examined here above background noise levels, so  
566 residuals between spectral fits using HITRAN 2012 and 2016 have not been  
567 compared.

568 A critical difference between the application of spectroscopic calculations  
569 for Earth and Mars is that because the Martian atmosphere is predom-  
570 inantly CO<sub>2</sub> rather than N<sub>2</sub>, the collision-induced broadening parameters  
571 computed for HITRAN and GEISA will not be applicable to the Martian at-  
572 mosphere. There is ongoing work to determine spectroscopic parameters for  
573 a CO<sub>2</sub>-rich atmosphere: *e.g.*, Gamache et al. (2016); Devi et al. (2017) for wa-  
574 ter vapour; and Li et al. (2015) for CO. However, this study does not attempt  
575 to validate these parameters, nor does it evaluate the CO<sub>2</sub> self-broadening  
576 parameters.

577 When comparing the 2015 version of the GEISA line list to the latest,  
578 2016, release of HITRAN, we observe that lower RMS values are found for  
579 residuals from the majority of the spectral windows between 2325–4350 cm<sup>-1</sup>  
580 used here. We find that these are primarily due to differences in line strength  
581 or position for strong O<sub>3</sub> and CH<sub>4</sub> lines. There are some minor errors in  
582 specific lines noted as well.

583 We were surprised to find a large number of O<sub>3</sub> lines missing from GEISA  
584 2015 in the 3830–3870 cm<sup>-1</sup> region that were present in HITRAN 2012.  
585 The primary source of O<sub>3</sub> lines both HITRAN 2016 and GEISA 2015 is  
586 the Spectroscopy and Molecular Properties of Ozone (S&MPO) informa-  
587 tion system (Babikov et al., 2014) maintained by Reims University and the  
588 Institute of Atmospheric Optics (Tomsk). For GEISA 2015, new measure-  
589 ments of lines around this region were made at Reims University by Barbe

590 et al. (1997, 2012), but those lines precisely between 3830–3870  $\text{cm}^{-1}$  are at-  
591 tributed to a private communication from Barbe (2011).  $\text{O}_3$  line parameters  
592 in HITRAN 2016 are also included in the S&MPO database. In the region  
593 3623–4229  $\text{cm}^{-1}$ , HITRAN also includes an updated hot band from Barbe  
594 et al. (2013).

595 Our analysis fit the hydrogen halides HCl (between 2600–3050  $\text{cm}^{-1}$ )  
596 and HF (between 3700–4100  $\text{cm}^{-1}$ ). Parameters for these gases were not  
597 updated in the 2011 or 2015 editions of GEISA, but new calculations were  
598 implemented in the 2012 edition of HITRAN (Li et al., 2013). The result is  
599 differences in line position when performing spectral fitting with HITRAN  
600 2016 or GEISA 2015. Mean differences are very small relative to the noise  
601 of the ACE-FTS observations, less than 1%, with HITRAN 2016 performing  
602 slightly better at these line locations (*e.g.*, 2925.9  $\text{cm}^{-1}$  or 2944.93  $\text{cm}^{-1}$  for  
603 HCl, and 3877.7  $\text{cm}^{-1}$  or 3920.3  $\text{cm}^{-1}$  for HF).

604 In conclusion, we have noted consistent improvement in both line lists  
605 since HITRAN 2012, have noted errors and deficiencies in both line lists  
606 where found, and we hope that the collaborations in charge of both line  
607 lists will find this analysis useful when compiling the next release. However,  
608 for the purposes of the ExoMars TGO ACS and NOMAD instruments, we  
609 recommend HITRAN 2016 for use. HITRAN 2016 shows marked improve-  
610 ment over HITRAN 2012 in  $\text{CO}_2$  and  $\text{H}_2\text{O}$  transitions (as does GEISA 2015).  
611 GEISA 2015 currently produces larger residuals for strong  $\text{CH}_4$  lines that are  
612 critical for ExoMars, while an important  $\text{CO}_2$  band centred at 2982  $\text{cm}^{-1}$  has  
613 not yet been introduced.



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619 and the spectroscopy in the target region was provided by CDB and GCT.  
620 The HITRAN line list is hosted by the Harvard-Smithsonian Center for As-  
621 trophysics under the continued direction of Dr Laurence S. Rothman ([hi-](http://hitran.org)  
622 [tran.org](http://hitran.org)). The GEISA line list is compiled by the Atmospheric Radiation  
623 Analysis group at LMD and hosted by the Institut Pierre Simon Laplace ([cds-](http://cds-)  
624 [espri.ipsl.upmc.fr/GEISA/geisa\\_raie\\_2015.php](http://espri.ipsl.upmc.fr/GEISA/geisa_raie_2015.php)). Tools hosted by the Earth  
625 Observation Data Group were used to reformat the GEISA 2015 line list into  
626 the format of the HITRAN line list ([eodg.atm.ox.ac.uk/RFM/geihit.html](http://eodg.atm.ox.ac.uk/RFM/geihit.html)).  
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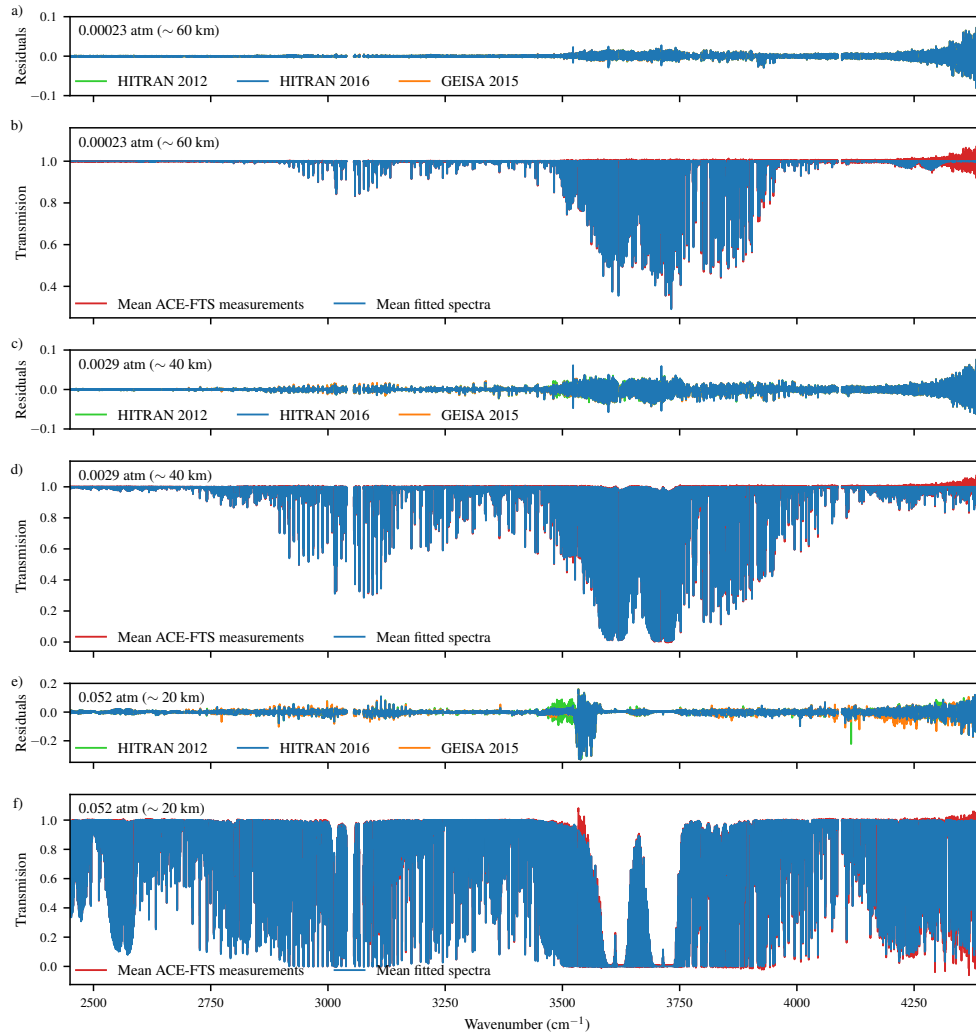


Figure 2: Mean ACE-FTS spectra, mean best-fit computed spectra, and mean residuals for each fitting window. Mean residuals are shown using HITRAN 2012 (green), HITRAN 2016 (blue) and GEISA 2015 (orange). Mean fitted spectra are shown only for when using HITRAN 2016. a) mean residuals from 0.00023 atm ( $\sim 60$  km), b) mean spectra and mean fits from 0.00023 atm, c) mean residuals from 0.0029 atm ( $\sim 40$  km), d) mean spectra and mean fits from 0.0029 atm, e) mean residuals from 0.052 atm ( $\sim 20$  km), f) mean spectra and mean fits from 0.052 atm.

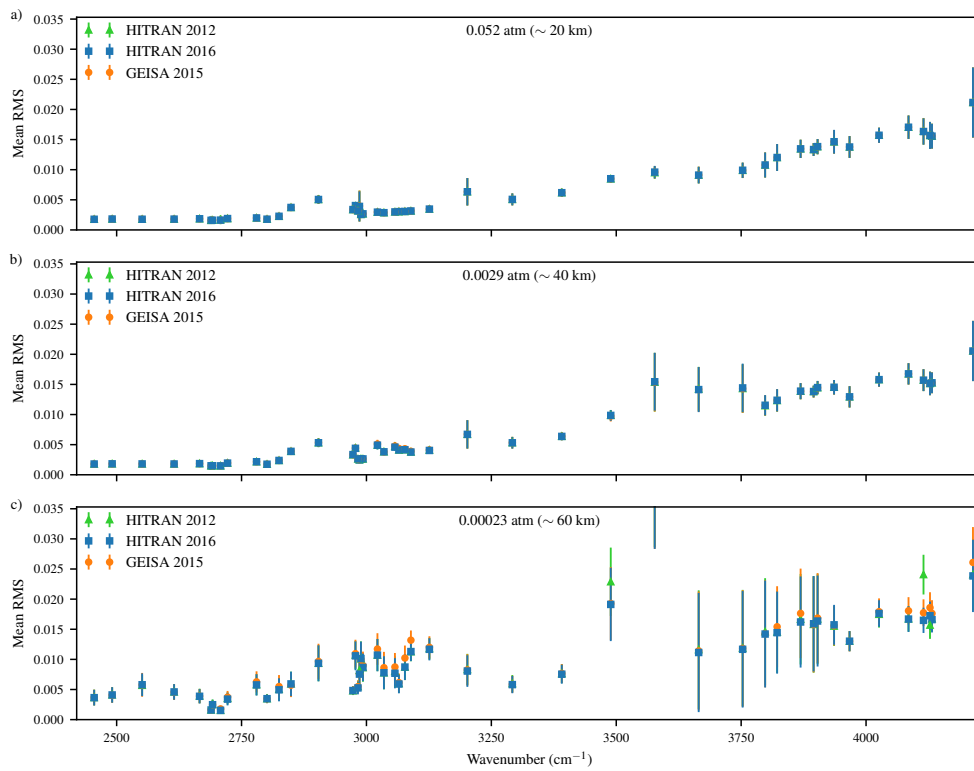


Figure 3: Mean RMS values computes for each fitting window when using each HITRAN 2012, HITRAN 2016, and GEISA 2015 at three pressure levels: a) 0.00023 atm ( $\sim 60$  km), b) 0.0029 atm ( $\sim 40$  km), c) 0.052 atm ( $\sim 20$  km).

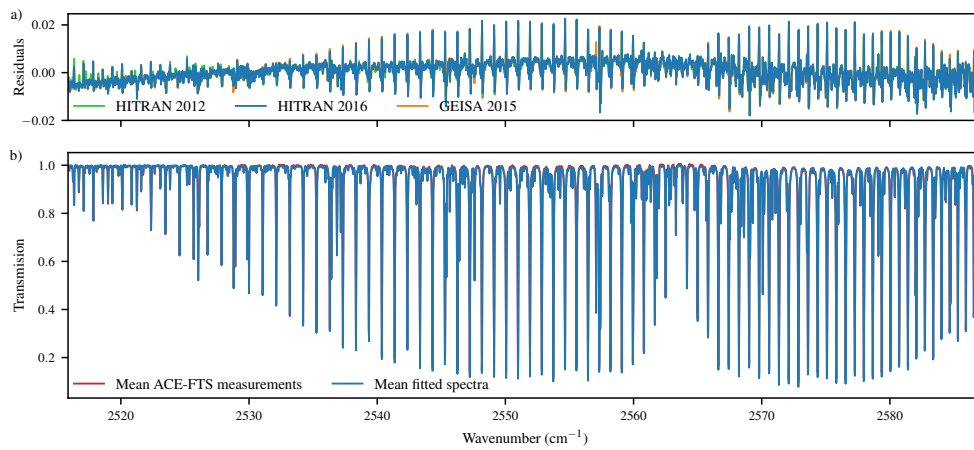


Figure 4: a) Mean residuals for the 2551.55 cm<sup>-1</sup> window at 0.052 atm (~ 20 km) with HITRAN 2012, HITRAN 2016, and GEISA 2015. b) Mean measured ACE-FTS spectrum and mean computed spectrum (for HITRAN 2016). The primary features in this window are N<sub>2</sub>O lines and the residuals correspond to the N<sub>2</sub>O lines.

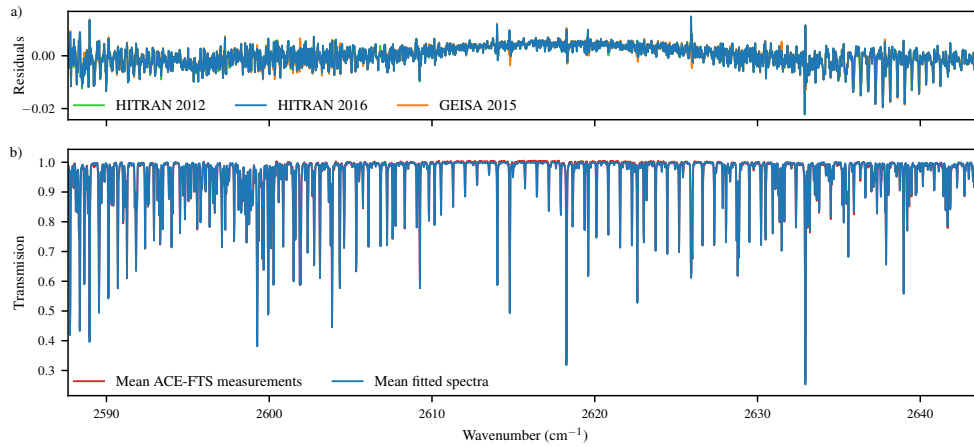


Figure 5: a) Mean residuals for the  $2615.74 \text{ cm}^{-1}$  window at  $0.052 \text{ atm}$  ( $\sim 20 \text{ km}$ ) with HITRAN 2012, HITRAN 2016, and GEISA 2015. b) Mean measured ACE-FTS spectrum and mean computed spectrum (for HITRAN 2016). The main features are from  $\text{N}_2\text{O}$  towards the left edge, a  $\text{CO}_2$  band across the entire window, and several strong  $\text{CH}_4$  lines. The residuals are due to  $\text{HNO}_3$ .

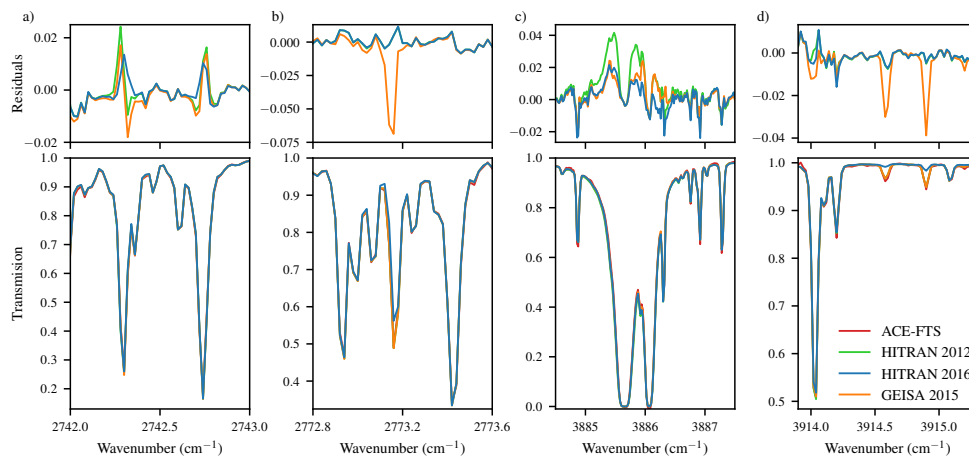


Figure 6: Zoom of the residuals and mean spectra (as in Figures 4 and 5) where errors are present, for the windows: a)  $2722.25 \text{ cm}^{-1}$ , b)  $2780.74 \text{ cm}^{-1}$ , c)  $3869.14 \text{ cm}^{-1}$ , d)  $3936.15 \text{ cm}^{-1}$ .

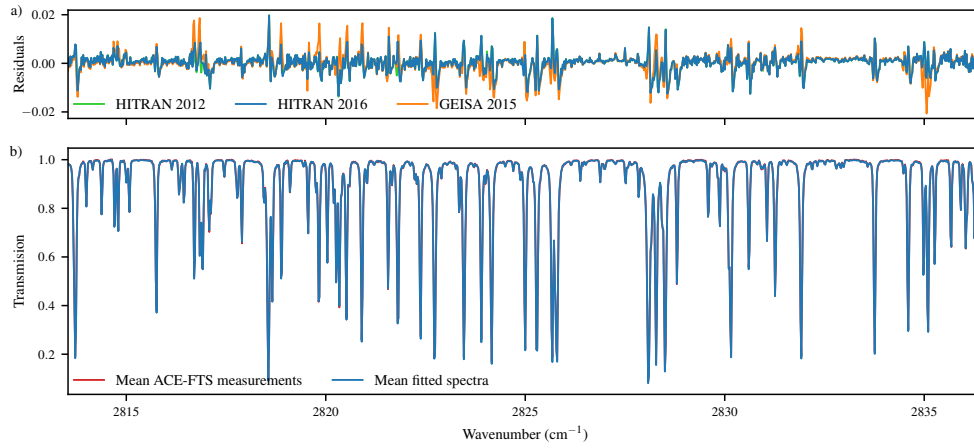


Figure 7: a) Mean residuals for the  $2825.0 \text{ cm}^{-1}$  window at  $0.052 \text{ atm}$  ( $\sim 20 \text{ km}$ ) with HITRAN 2012, HITRAN 2016, and GEISA 2015. b) Mean measured ACE-FTS spectrum and mean computed spectrum (for HITRAN 2016). Features are primarily  $\text{CH}_4$  lines.

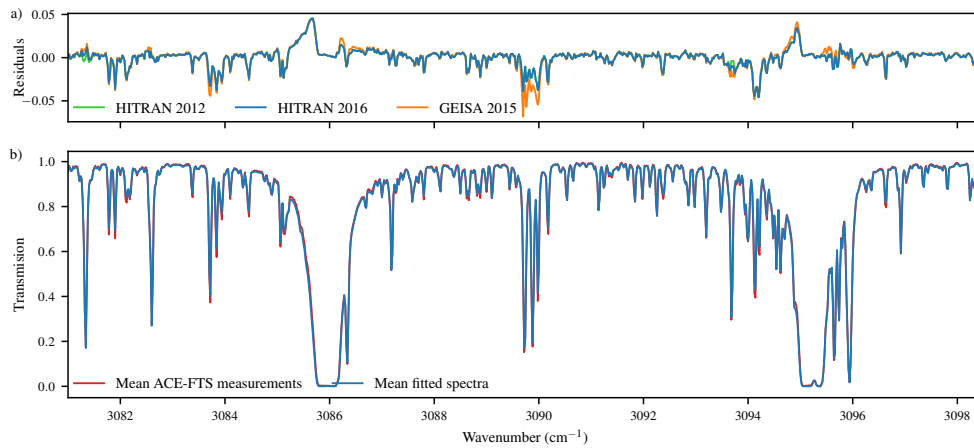


Figure 8: a) Mean residuals for the  $3089.75 \text{ cm}^{-1}$  window at  $0.052 \text{ atm}$  ( $\sim 20 \text{ km}$ ) with HITRAN 2012, HITRAN 2016, and GEISA 2015. b) Mean measured ACE-FTS spectrum and mean computed spectrum (for HITRAN 2016). Absorption are due to, in order of prominence,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_3$ . Large residuals near  $3090 \text{ cm}^{-1}$  are from  $\text{CH}_4$  lines.

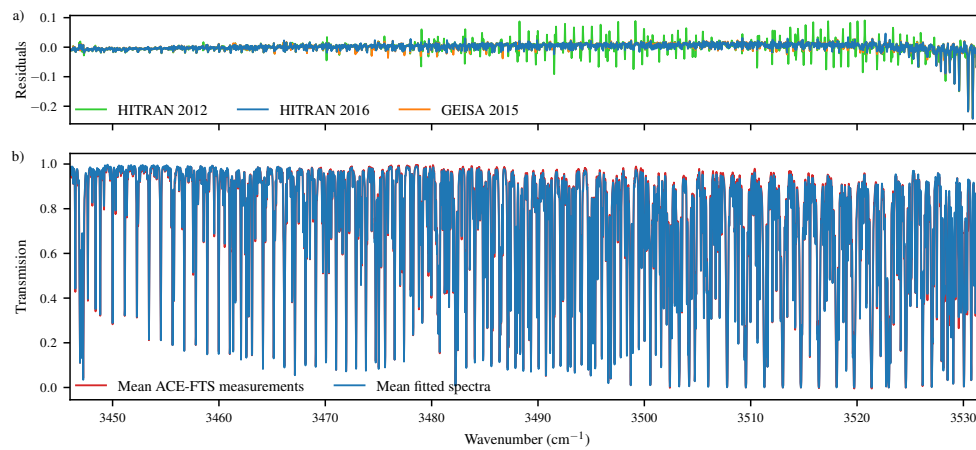


Figure 9: a) Mean residuals for the  $3489.0 \text{ cm}^{-1}$  window at  $0.052 \text{ atm}$  ( $\sim 20 \text{ km}$ ) with HITRAN 2012, HITRAN 2016, and GEISA 2015. b) Mean measured ACE-FTS spectrum and mean computed spectrum (for HITRAN 2016). The primary features are an  $\text{N}_2\text{O}$  band on the left side,  $\text{CO}_2$  bands on the right, and several  $\text{H}_2\text{O}$  lines. The strong residuals are due to  $\text{CO}_2$  when using the HITRAN 2012 line list.

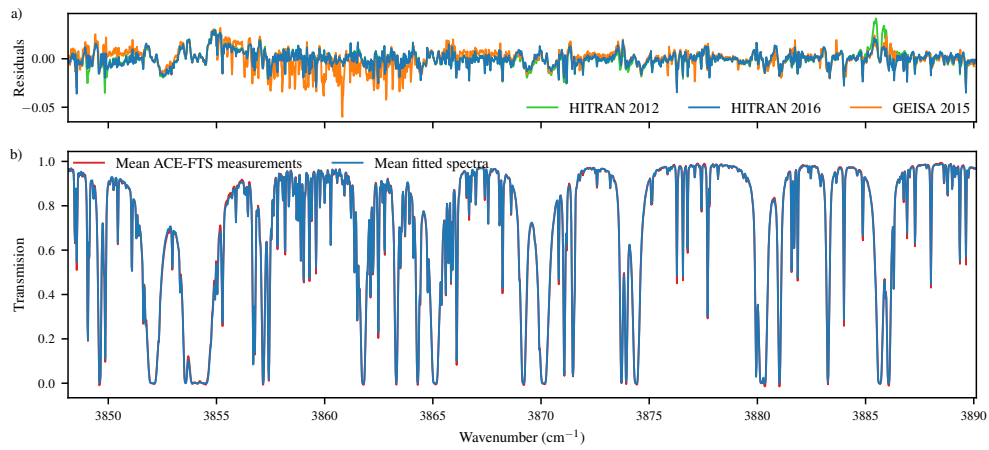


Figure 10: a) Mean residuals for the  $3869.14 \text{ cm}^{-1}$  window at  $0.052 \text{ atm}$  ( $\sim 20 \text{ km}$ ) with HITRAN 2012, HITRAN 2016, and GEISA 2015. b) Mean measured ACE-FTS spectrum and mean computed spectrum (for HITRAN 2016). The primary features are  $\text{H}_2\text{O}$  lines. The strong residuals near  $3860 \text{ cm}^{-1}$  are due to  $\text{O}_3$  when using GEISA 2015. Those near  $3886 \text{ cm}^{-1}$  are due to  $\text{H}_2\text{O}$  and are shown in Figure 6c.