1	The update of the line positions and intensities in the line list of carbon dioxide
2	for the HITRAN2020 spectroscopic database
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Abstract

43 This paper describes the updates of the line positions and intensities for the carbon 44 dioxide transitions in the 2020 edition of the HITRAN spectroscopic database. The new line list 45 for all 12 naturally abundant isotopologues of carbon dioxide replaces the previous one from the 46 HITRAN2016 edition. This update is primarily motivated by several issues related to deficient 47 HITRAN2016 line positions and intensities that have been identified from laboratory and 48 atmospheric spectra. Critical validation tests for the spectroscopic data were carried out to find 49 problems caused by inaccuracies in CO₂ line parameters. New sources of data were selected for 50 the bands that were deemed problematic in the HITRAN2016 edition. Extra care was taken to 51 retain the consistency in the data sources within the bands. The comparisons with the existing 52 theoretical and semi-empirical databases (including ExoMol, NASA Ames, and CDSD-296) and 53 with available experimental works were carried out. The HITRAN2020 database has been 54 extended by including additional CO_2 bands above 8000 cm⁻¹, and magnetic dipole lines of CO_2 55 were introduced in HITRAN for the first time by including the v_2+v_3 band in the 3.3-µm region. 56 Although the main topic of this article are line positions and intensities, for consistency a recent 57 algorithm for the line-shape parameters proposed in Hashemi et al. JQSRT (2020) was reapplied 58 (after minor revisions) to the line list.

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1. Introduction

61 A plethora of critical applications drives a constant demand for ever higher-quality 62 spectroscopic parameters of carbon dioxide (CO₂) transitions. Atmospheric CO₂ is the key 63 gaseous contributor to the greenhouse effect in the terrestrial atmosphere. Its continuous 64 increase in the atmosphere over the last two centuries from anthropogenic sources is considered 65 the principal driver of climate change. The Martian and Venusian (and those of many rocky 66 exoplanets) atmospheres consist mostly of carbon dioxide with mole fractions of over 95%. 67 Monitoring CO₂ is important in combustion. There are several satellite-based observatories, 68 including GOSAT[1-3], GOSAT-2 [4], OCO-2 [5,6], OCO-3 [7], MIPAS [8], and ACE [9], as well as 69 ground-based networks TCCON [10] and NDACC [11], monitoring atmospheric CO₂. Accurate 70 interpretation of the data from these missions is necessary to make informed decisions regarding

controlling the anthropogenic contribution to the greenhouse effect and, ultimately, climate change. All aforementioned CO_2 remote sensing activities depend on the reliability of the reference CO_2 spectroscopy.

74 The HITRAN molecular spectroscopic database is the widely recognized standard 75 providing the spectroscopic data for atmospheric applications. Among many other molecules, it 76 includes the necessary calculated and experimental parameters for all naturally abundant 77 isotopologues of carbon dioxide. The HITRAN2016 [12] CO₂ line list for 12 stable isotopologues 78 contains 559874 transitions. Most of the issues related to spectral completeness (at least below 79 8000 cm⁻¹) and insufficient accuracy of line parameters were resolved in HITRAN2016 [12]. 80 However, there is still a lot of room for improvement to meet the ever-increasing demands of the scientific community. Since the release of the HITRAN2016 database[12], many new 81 82 experimental and theoretical data have become available, and they can be used as sources for 83 improving line positions, line intensities, and line-shape parameters of CO₂. The HITRAN-related 84 updates, including the CO_2 -air and CO_2 - CO_2 line-shape parameters together with the speed 85 dependence of the broadening parameters, their temperature-dependent exponents, the full 86 and first-order line mixing, as well as their temperature dependencies have been published in 87 Hashemi et al. [13].

88 In the present work, we will mainly focus on the issues associated with deficiencies in line 89 positions and intensities in HITRAN2016. Most of these problematic cases have been identified 90 in laboratory and atmospheric spectra, mainly from the Kitt Peak National Observatory, MkIV 91 balloon, cavity ring down spectroscopy (CRDS) measurements, and the Total Carbon Column 92 Observing Network (TCCON) [10,14–16]. A general review of the CO_2 bands affected by these 93 issues was performed, and alternative sources of data for each CO₂ problematic band were 94 considered. Apart from new experimental data, the additional resources for improvements were 95 provided by two recent comprehensive CO₂ line lists, namely the 2019 version of the semiempirical CDSD-296 [17] list and the ExoMol variational nuclear motion line list [18], hereafter 96 97 referred to as UCL-4000. Using these spectroscopic data, we improved and extended the CO₂ line 98 lists for all 12 stable isotopologues of carbon dioxide.

99 The updates of the line positions, intensities, and line-shape parameters were 100 incorporated into the carbon dioxide line list of the 2020 edition of the HITRAN spectroscopic 101 database [16]. The remainder of this paper is organized as follows. In Section 2, we present an 102 overview of CO₂ line lists in the HITRAN2016, ExoMol, NASA Ames, and CDSD-296 spectroscopic 103 databases. In Section 3, we describe evaluations of the HITRAN CO₂ line list based on laboratory and atmospheric measurements between 670 and 8310 cm⁻¹. For wavenumbers below 8000 cm⁻¹ 104 105 ¹, we discuss line intensity updates to the HITRAN2016 line list for bands provided by the Carbon Dioxide Spectroscopic Databank (CDSD) based on global fits of semi-empirical models to 106 107 measurements and those obtained by the *ab initio* calculations of University College London 108 (UCL). In Section 4, we discuss new measurements with sub-percent relative uncertainty [19–22] 109 that were used to improve some CO₂ bands in the 1.4 to 2.1-µm region. In Section 5, we present new CO₂ bands above 8000 cm⁻¹ that have been included in the HITRAN2020 edition from the 110 latest high-temperature line list of the ExoMol [18] database (with appropriate cut-off) for the 111 main CO₂ isotopologue and the CRDS spectra [14] for the ¹⁶O¹²C¹⁸O isotopologue. The line 112 113 parameters of the v_2+v_3 magnetic dipole band of the ${}^{12}C^{16}O_2$ isotopologue, which have been 114 introduced into HITRAN for the first time, will be presented in Section 6. The revision, which updates the air- and self-broadened line-shape parameters of CO₂, described in Ref. [13], will be 115 116 discussed in Section 7. The presentation of the final version of the HITRAN2020 CO₂ line list will 117 be given in Section 8, followed by a closing discussion and conclusions in Section 9.

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2. Review of the current carbon dioxide line lists

The present section describes the status of the most currently used spectroscopic databases of carbon dioxide: HITRAN2016 [12], NASA Ames [23], and the recent ExoMol [18] and CDSD-296 [17] line lists. The laboratory and atmospheric spectra helped to expose several problems in the HITRAN2016 CO₂ line list occurring in various spectral regions (for more details, see Section 3). The CDSD-296, ExoMol, and NASA Ames line lists were used to update, extend or improve the line positions and intensities, including a number of problematic bands, resulting in the 2020 version of the HITRAN spectroscopic database [24].

127 The CO_2 line list for the 12 stable isotopologues in the 2016 version of HITRAN [12] 128 contained 559874 CO₂ transitions and covered the wavenumber range of 0.757-14075.298 cm⁻¹. The HITRAN2016 data for the ¹⁴C¹⁶O₂ radioactive isotopologue in HITRAN2016 were provided as 129 static files rather than through the relational database structure featured in HITRANonline [25]. 130 The HITRAN2016 carbon dioxide line list, below 8000 cm⁻¹, comprised CDSD line positions [26] 131 and *ab initio* line intensities from UCL [27-29] except for the bands that were identified as 132 "sensitive"[27], where CDSD (circa 2015) intensity values were preferred. Most of the line 133 parameters above 8000 cm⁻¹ were taken from the 2015 version of the CDSD-296 database [26]. 134 135 An extended and improved version of the CDSD for atmospheric applications (CDSD-296) was 136 published in 2019 [17]. This database contains a computed line list based on global modelling of 137 the line positions and intensities using the method of effective operators [30,31]. The global 138 model of the CO₂ absorption spectrum is a polyad model with a block diagonal structure, each polyad being characterized by the polyad number $P = 2V_1 + V_2 + 3V_3$ (where V_i are the vibrational 139 140 quantum numbers). For each CO₂ isotopologue, the effective Hamiltonians and effective dipole 141 moment parameters were fitted to measured line positions and intensities, respectively. More 142 than 530000 spectral lines for the 12 stable isotopologues of CO₂ covering the 345-14075 cm⁻¹ 143 spectral range were included in this database. The reference temperature is 296K, and the intensity cut-off is 10⁻³⁰ cm/molecule. A comparison between the line positions of common lines 144 145 from the HITRAN2016 and CDSD-296 [17] databases versus wavenumber in the 0-14075 cm⁻¹ 146 spectral region is presented in Fig. 1. This plot shows the good agreement between the line 147 positions from HITRAN2016 (mostly based on the previous CDSD version [26]) and those from 148 the new version of the CDSD-296 [17]. As a result, most of the line positions, as well as lower 149 state energies for the 12 CO₂ isotopologues between 345 and 14075 cm⁻¹ in HITRAN2020, have 150 been updated using the CDSD-296 [17] values. It should be noted that the slightly updated 151 version of the CDSD-296 database (uploaded at ftp.iao.ru as pub/CDSD-296/cdsd-152 296 version 1.rar) was used. This version differs from the CDSD-296 published in Tashkun et al. [17] in the following ways: (i) the ΔP = 6 region of the ¹⁶O¹²C¹⁸O isotopologue was recalculated 153 154 using the new set of effective dipole moment parameters; (ii) a total of 226 lines with vibrational 155 quantum number ΔI_2 =4 of the ¹²C¹⁶O₂, ¹³C¹⁶O₂, and ¹⁶O¹²C¹⁸O isotopologues were added. The

lower-state energies and the uncertainty codes were also transferred from the CDSD-296 line listto the HITRAN2020 line list.

158 The recent high-temperature line list from the ExoMol database (named UCL-4000) for the main isotopologue of CO₂ (¹²C¹⁶O₂) was published in Yurchenko et al. [15]. This line list 159 contains almost 2.5×10⁹ transitions involving about 3.5×10⁶ states. The wavenumber range of the 160 CO_2 list is from 0 to 20000 cm⁻¹ with the lower-state energies up to 16000 cm⁻¹ and J \leq 202. These 161 162 results were generated using UCL's ab initio dipole moment surface (DMS) [32] and the semi-163 empirical potential energy surface (PES) Ames-2 [22] with the variational program TROVE [33]. 164 The UCL-4000 line list was converted to HITRAN format and compared with the HITRAN2016 line list. As a result, more than 3600 spectral lines above 8000 cm⁻¹ were added to the HITRAN2020 165 166 spectroscopic database [24] (see Section 5).



Fig. 1. Differences between the line positions from the HITRAN2016 [12] and CDSD-296 [17] databases.
 The NASA Ames line lists for 13 CO₂ isotopologues were published by Huang et al. [23].
 They were computed at 296 K using the empirically refined Ames-2 potential energy surface and

pure *ab initio* DMS-2 dipole moment surface with $J \le 150$ and the lower-state energy up to 24000 cm⁻¹. Intensities of selected bands from this database were used for HITRAN2020 as described in Sections 2 and 5.

Critical validation tests of the available spectroscopic data were carried out using the existing theoretical and semi-empirical databases, including ExoMol, NASA Ames, and CDSD-296 [17,18,23] and with published experimental works [14,34–42]. Accordingly, the present work allowed revealing some problems with the HITRAN2016 CO₂ line list and thus allowed improving and extending the line lists for all 12 stable isotopologues in the final version of the HITRAN2020 CO₂ line list.

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3. Evaluation of the HITRAN CO₂ line lists by laboratory and atmospheric spectra

197 In this section, we present the general review of problematic bands identified in 198 laboratory and atmospheric spectra, mainly those obtained from the Kitt Peak National 199 Observatory, MkIV balloon, CRDS, and TCCON [10,14–16]. Most of the issues have been 200 associated with deficient line positions and intensities for which critical validation tests were 201 performed, and alternative sources of data for each problematic band were suggested.

202 Several CO₂ line lists, including HITRAN2008 [43], HITRAN2012 [44], and HITRAN2016 [12], 203 were evaluated by fitting laboratory (mainly Kitt Peak) and atmospheric solar absorption spectra 204 (MkIV and TCCON) between 670 and 8310 cm⁻¹ [15,16]. The studied region was divided into 205 several windows, most encompassing at least one complete CO₂ absorption band or a sub-206 branch. The GFIT spectral fitting algorithm [45] was used in all cases assuming a Voigt line profile 207 and no line mixing. The line lists were evaluated in terms of the RMS fitting residuals and the 208 window-to-window consistency of the retrieved gas amounts. There was no analysis of the 209 separate isotopologues. The results showed progressive overall RMS fit improvements through 210 the use of each successive HITRAN version. This analysis showed that the HITRAN2020 CO₂ line 211 list is substantially better than all previous HITRAN versions. In particular, in HITRAN2016, there 212 were a few regions where it is worse than a previous version in terms of RMS fitting residuals (around 1800 cm⁻¹, 4800 cm⁻¹, and 6400 cm⁻¹). As an example, **Fig. 2** shows the absolute RMS 213 214 residuals of the fits for 41 windows averaged over the 137 Kitt Peak and 12 JPL laboratory spectra

in the 670-8310 cm⁻¹ spectral region. The pressure range is from 0.013 kPa-93 kPa (0.1 Torr to 700 Torr) except for 2 Kitt Peak spectra (1.71 kPa and 1.89 kPa) covering 600-1400 cm⁻¹. However, in this plot, the HITRAN2020 line list gives worse fits in the 3730 cm⁻¹ window in Kitt Peak lab spectra than most previous line lists. This is due to the Self-Broadened Half-Widths (SBHWs) being too small in this region (the Kit Peak lab spectra include some with 200 Torr of pure CO₂). This SBHW issue has no effect on fits to atmospheric spectra.

The large discrepancies were also identified in the 4800 cm⁻¹ regions, where the 221 HITRAN2016 line list was worse than previous editions in terms of RMS fitting residuals. The same 222 223 situation in this region was observed in the MkIV balloon spectra (low pressure). The Kitt Peak 224 laboratory spectrum revealed rotationally-dependent errors at the 10-15% level in the *ab initio* intensities for the 40002-01101 band of the ¹²C¹⁶O₂ isotopologue. Fits to a Kitt Peak laboratory 225 spectrum in the 4800 cm⁻¹ region are presented in **Fig.3**. Also, it was shown that the scattering 226 227 factor of the 40002-01101 band is slightly elevated (1.4 to 1.7). In addition to that, for low J, 228 around J=1 to 3, there is a visible spike in the scatter factor, which suggests a J-localized 229 resonance. Indeed, by analyzing predictions within the effective operator model [30], it was 230 found that the 40002 and 21113 vibrational levels of the P= 8 polyads are interacting through a 231 Coriolis interaction. This interaction causes systematic problems with the *ab initio* intensities [27] 232 for the transitions involving either of these two vibrational states.



Fig. 2. The upper panel shows the absolute value of the mean *RMS* fit for 5 different CO₂ line lists: HIT2008:
HITRAN2008 [43]; HIT2012: HITRAN2012 [44], HIT2016: HITRAN2016[12], ATM2018: 523230 CO₂ lines
[15], HIT2020: HITRAN2020 [24]. The lower panel shows the differences from HITRAN2012 [44].



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- Fig.3. The fits to a Kitt Peak laboratory spectrum in the 4800 cm⁻¹ region using the HITRAN2016 linelist
 [12]. The positive residuals arise from the 40002-01101 band of the ¹²C¹⁶O₂ isotopologue.

For the HITRAN2016 CO₂ line list, there are 24 bands involving the 40002 and 21113 243 244 vibrational levels affected by Coriolis interaction. To quantify the impact of this perturbation on 245 intensities, validation tests for the 40002 - 01101, 21113 - 01101, and 21113 - 11102 bands of the ¹²C¹⁶O₂ isotopologue were carried out using the published experimental values [34,35] and 246 247 data from the various carbon dioxide spectroscopic databases [12,17,23] (Fig. 4). This comparison showed that the CDSD-296 line intensities [17] are preferable for the 40002 - 01101 and 21113 -248 249 11102 bands whereas, in the case of the 21113-01101 band, the *ab initio* intensities from NASA 250 Ames [23] are the best choice. However, because of the lack of measurements, we could not 251 make similar comparisons for the numerous remaining bands affected by these Coriolis 252 interactions. We hope that new experimental data will become available for further validation 253 tests of bands involving the 40002 and 21113 vibrational levels.

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278Fig.4. Ratio of the experimental line intensities of the 40002 - 01101, 21113 - 01101, and 21113 - 11102279bands (centers: 4808 cm⁻¹, 4809 cm⁻¹, and 3544 cm⁻¹, respectively) from Refs [34,35] to those from the280various CO_2 spectroscopic databases [12,17,23].

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In the 1800-2000 cm⁻¹ spectral region, CO₂ retrievals of mixing ratio based on the HITRAN2016 database produces CO₂ retrieved amounts that are 5% larger than those based on previous line lists. The VMR Scale Factors (VSF) obtained by averaging each retrieved singlespectrum VFS value over all 19 MkIV balloon spectra that were fitted for each window are plotted versus wavenumber in **Fig. 5**. The MkIV instrument simultaneously records the region 600 cm⁻¹ to 5650 cm⁻¹, so derived VSFs should have good window-to-window consistency. The upper circle
 indicates anomalously high HITRAN2016 values in the 1800-2000 cm⁻¹ spectral region,
 corroborating observation in laboratory spectra.

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Fig.5. The VMR Scale Factors (VSF) were obtained by averaging each retrieved single-spectrum VFS value
 over all 19 MkIV balloon spectra that were fitted for each window. The measured VSF values are plotted
 versus wavenumber. See the designations of the databases in the caption of Fig. 2.

297 It was found that the most significant deviations in this region correspond to the 11102 -298 00001 band near 1933 cm⁻¹. The 11101 - 00001 and 11102 - 00001 bands borrow intensities from 299 the strong 00011 - 00001 band via Coriolis interaction. It was shown in Ref. [17] that the ab initio 300 NASA Ames line intensities [23] for the 11101 - 00001 band deviate considerably from the 301 observations. A comparison of the 11102 - 00001 line intensities with the published measurements [36,37] and the different CO₂ databases [12,17,23] for the ¹²C¹⁶O₂, ¹³C¹⁶O₂, and 302 303 ¹⁶O¹²C¹⁸O isotopologues is presented in **Fig. 6**. Replacement of line intensities of the CO₂ bands 304 considered in the HITRAN2016 database with CDSD-296 [17] rectifies the above-mentioned discrepancy in the 1800-2000 cm⁻¹ region. For consistency, the line intensities of the 11101 -305 306 00001 band for other CO₂ isotopologues were also replaced by the intensities from the CDSD database in the HITRAN2020 line list. The 20003-01101 and 12202-01101 hot bands of ¹²C¹⁶O₂ 307

308 located near 1900 cm⁻¹ were also increased by 5% to match the ATM values [15]. The intensity 309 origin for these bands in HITRAN2016: 20003-01101 – UCL *ab initio* [27] and 12202-01101 – UCL 310 ab initio and CDSD2015 [26,27]. Also, the comparison of the ATM and CDSD2019 line intensities showed a deviation up to 30% for the 20003- 01101 band of the ¹²C¹⁶O₂ isotopologue. 311 312



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Fig. 6. The comparison of line intensities between the published measurements from Refs [36,37] and the different CO₂ databases [12,17,23] for the 11102-00001 bands of the ¹²C¹⁶O₂, ¹³C¹⁶O₂, and ¹⁶O¹²C¹⁸O 315 isotopologues with centers: 1933 cm⁻¹, 1897 cm⁻¹, and 1903 cm⁻¹, respectively. 316

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318 The TCCON observations considered here cover the 3950 to 9500 cm⁻¹ spectral region.

319 These measurements are made with a Fourier transform spectrometer with an InGaAs detector

and optical path difference (OPD) of 45 cm, corresponding to a resolution of 0.02 cm⁻¹. We use 320 321 the definition: resolution = 0.9/OPD, which is how the Bruker OPUS software defines it. This 322 assumes that the interferograms have been windowed with a Triangular, Happ-Genzel, or 323 Blackman-Harris apodization function. For a box-car apodization (i.e. no apodization), the 324 resolution would be 0.61/OPD. Use of the HITRAN2016 line lists reduces the CO₂ retrieved from 325 the 6220 and 6338 cm⁻¹ windows by 0.5% and 1.5%, respectively, by comparison to results obtained with the other line lists, thus introducing a new inconsistency of 1.5%. Retrieved VMR 326 327 Scale Factors (VSF) obtained by averaging single-spectrum based on fitting each spectral window 328 from the TCCON spectra are presented in Fig.7. This issue is associated with the 30012 - 00001 329 and 30013 - 00001 line parameters and is discussed in detail in Section 4.





Fig.7. Retrieved VMR Scale Factors (VSF) obtained by averaging single-spectrum based on fitting each
 spectral window from the TCCON spectra. Results are plotted versus wavenumber. See the designations
 of the databases in the caption of Fig. 2.

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The comparison of the fits to 136 Kitt Peak lab spectra with those modeled using the HITRAN2016 CO₂ line list shows large residuals in the 3500 and 4800 cm⁻¹ spectral windows due to inaccuracies of line positions of the 10012-0001, 20012-00001, and 20013-00001 bands of the ¹³C¹⁶O₂ isotopologue. The comparison showed that the HITRAN2012 [44] line positions for the 20012-00001 and 20013-00001 bands led to better residuals than those of the HITRAN2016 and CDSD-296 [17] databases. As a result, the line positions of the 20012 - 00001 and 20013 - 00001 bands of the ¹³C¹⁶O₂ isotopologue were replaced with the corresponding HITRAN2012 line positions in the HITRAN2020 CO_2 line list. In the case of the 10012-00001 band, we subtracted 0.0009 cm⁻¹ from the CDSD [17] line positions used for this band in HITRAN2020 to match the ATM values [15].

Also, inaccuracies in the positions of some ${}^{16}O^{12}C^{18}O$ lines of the 01121-01101 hot band (P13e, P14e, P14f, Q12f, Q13e, Q13f, R11e, R12e, and R12f) were evidenced in the HITRAN2016 line list between 4600 and 4625 cm⁻¹. This issue was identified by comparison with fits to Kitt Peak spectra and was solved by replacing the line positions with positions from the CDSD-296 database [17] in the HITRAN2020 CO₂ line list.

351 As mentioned above, below 8000 cm⁻¹, most line intensities in the HITRAN2016 database 352 came from the UCL-IAO line lists [27–29] which are based on *ab initio* calculations. Because of 353 excessive uncertainty in the *ab initio* line positions, the HITRAN2016 line list is, in general, a 354 combination of the CDSD- based line positions [26] and the UCL variational line intensities [27-355 29]. In the case of the so-called "sensitive bands" (as defined by Zak et al. [27-29]) ab initio 356 intensities were replaced with those from CDSD when available. This substitution resulted in 357 some cases where transitions in a given band would have intensities from both ab initio 358 calculations as well as those from CDSD. Although this approach was justified in many cases, a 359 number of inconsistencies in the rotational distribution of intensities in HITRAN2016 were revealed in CRDS spectra of ¹⁸O and ¹³C enriched and natural CO₂ near 1.74 μ m [39,40,46]. In 360 361 these works, the anomalies involve the perpendicular bands of the ΔP = 9 series of transitions. As 362 shown in Fig 8, the mixing of CDSD and UCL ab initio intensities for the 41104-00001 bands of $^{12}C^{16}O_2$ and $^{13}C^{16}O_2$ isotopologues leads to an apparent inconsistency in the rotational 363 364 dependence with substantial intensity variation between successive J values or even missing 365 transitions. A similar situation was found in the case of the 41104-00001 band of ¹⁶O¹²C¹⁸O 366 isotopologue (See Fig. 9). A comparison of the measurements from Refs [39,40,46] to various 367 carbon dioxide spectroscopic databases is presented in Fig. 10. As can be seen from this figure, 368 the NASA Ames intensity values for this band are all close to the experimental ones. As a result, for HITRAN2020, the NASA Ames intensities of the 41104-00001 bands of the ¹²C¹⁶O₂, ¹³C¹⁶O₂, 369 and ¹⁶O¹²C¹⁸O isotopologues were preferred to the mixed intensity values in the HITRAN2016 line 370 371 list.

372 Similar validation tests using the values available in the literature and from the different 373 CO₂ databases were carried out for other bands affected by the problem due to the mixing of 374 intensities of CDSD and *ab initio* origin in the HITRAN line list. These bands were systematically 375 searched (see Fig. 5 of Ref.[39]), and when problems were identified, alternative sources of data for each such band were suggested. For the $^{12}C^{16}O_2,\ ^{13}C^{16}O_2,\ ^{16}O^{12}C^{18}O,$ and $^{16}O^{13}C^{18}O$ 376 isotopologues, we present in Table 1 the set of bands that were checked and affected by this 377 378 issue along with the alternative intensity sources for these bands used in HITRAN2020. 379 The substitution of the suggested intensity sources for the bands presented in Table 1 was 380 performed for the corresponding bands of all the CO₂ isotopologues in HITRAN2020 where 381 experimental data exists. In the absence of experimental reference data, the replacement of the 382 intensity source was performed only for the corresponding band of the specific isotopologue. In the case of the 31104e-01101e and 11112e-11101e hot bands of the ${}^{16}O^{12}C^{18}O$ and ${}^{13}C^{16}O_2$ 383 384 isotopologues, respectively (see **Fig.11**), we cannot offer an alternative source for replacing the 385 mixed line intensities, since there is no experimental data to verify them. Nevertheless, we kept the HITRAN2016 line intensities for the 31114e-01101e band of ¹⁶O¹²C¹⁸O isotopologue in 386 387 HITRAN2020. In the future, we will consider using UCL ab initio [28] line intensities for this band. In the case of the 11112e-11101e hot band of the ¹³C¹⁶O₂ isotopologue, the UCL and CDSD-296 388 389 databases [17,27] give similar line intensities, although there is an inconsistency in the rotational 390 dependence with substantial intensity variation between successive J values of the P branch. 391 Validation of this band is a challenge for future experiments. It should also be noted that for the 21103-02201 band of the ¹²C¹⁶O₂ isotopologue in Table 1, the line intensity was updated only for 392 393 the R2e line from CDSD2015 [26] to UCL [27] in HITRAN2020. This is the reason why the source 394 of the line intensity remained the same as in HITRAN2016.

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Fig. 8. Comparison of the CRDS measurements (purple squares) of the 41104 - 00001 band of ¹³C¹⁶O₂ [46]
 and ¹⁶O¹²C¹⁸O [40] to various databases: HITRAN2016 [44], CDSD-296 (CDSD2015) [26], CDSD-296
 (CDSD2019) [17], UCL [27,28], and NASA Ames [23] line lists.



Fig.9. Overview comparison of the *Q*-branch of the 41104 - 00001 band $({}^{12}C^{16}O_2)$ [39] to the HITRAN2016[12], CDSD-296 (CDSD2015) [26], CDSD-296 (CDSD2019) [17], UCL [27] and NASA Ames [23] line lists. The lower panel highlights the *Q* branch where the HITRAN2016 list uses UCL and CDSD2015 as intensity sources for *J* below 50 and above 52, respectively, leading to the observed intensity jump between *Q*(50) and *Q*(52). The CRDS measurements [39] validate the NASA Ames intensity values which were taken as the unique source for HITRAN2020 of this band.

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420 **Table 1.** The bands for the ${}^{12}C^{16}O_2$, ${}^{13}C^{16}O_2$, ${}^{16}O^{12}C^{18}O$, and ${}^{16}O^{13}C^{18}O$ isotopologues where 421 intensities were from mixed sources in HITRAN2016 and the new sources of intensities chosen

422 for HITRAN2020.

Band	Band center	Intensi	ty origin	- Experimental works		
Dana	(cm ⁻¹)	HITRAN2016	HITRAN2020	Experimental works		
	¹² C ¹⁶ O ₂ isotopologue					
21103-02201	1846.33	[26,27]	[26,27]	-		
13302-02201	1907.85	[26,27]	[27]	-		
20002-01101	2003.76	[26,27]	[17]	[41]		
21102-10002	2054.72	[26,27]	[27,28]	-		
22201-11101	2120.50	[26,27]	[17]	[42]		
40002-21103	2295.65	[26,27]	[27]	-		
30004-01101	3125.10	[26,27]	[17]	[34]		
31104-10002	3131.52	[26,27]	[27]	-		
22203-01101	3156.20	[26,27]	[27]	-		
31103-10002	3306.48	[26,27]	[27]	-		
22202-01101	3342.10	[26,27]	[27]	-		
23302-02201	3344.01	[26,27]	[27]	-		
31102-10001	3365.31	[26,27]	[17]	[34]		
30002-01101	3398.45	[26,27]	[27]	-		
21101-00001	3501.45	[26,27]	[27]	-		
40002-11102	3544.64	[26,27]	[27]	-		
01121-10002	4031.07	[26,27]	[27]	-		
31104-00001	4416.15	[26,27]	[17]	[35]		
41103-10001	4613.12	[26,27]	[27]	-		
25501-02201	4696.61	[26,27]	[27]	-		
10021-01101	5346.31	[26,27]	[17]	[47]		
50006-01101	5572.65	[26,27]	[27]	-		
50005-01101	5768.12	[26,27]	[27]	[39]		
42204-01101	5805.64	[26,27]	[17]	[39]		
41104-00001	5830.79	[26,27]	[23]	[39]		
50004-01101	5920.94	[26,27]	[27]	-		
50003-01101	6057.89	[26,27]	[27]	[48]		

¹³ C ¹⁶ O ₂ isotopologue						
04421-01101	1946.12	[26,29]	[27,28]	-		
11112-11101	2110.13	[26,27]	[27]	-		
¹⁶ O ¹² C ¹⁸ O isotopologue						
31104-30004	616.12	[26,28]	[17,28]	-		
21101-10002	2195.21	[27,28]	[28]	-		
21101-00001	3454.63	[27,28]	[28]	-		
31104-01101	3677.44	[26,28]	[28]	-		
¹⁶ O ¹³ C ¹⁸ O isotopologue						
12202-01101	1856.75	[26,28]	[28]	-		



Fig.10. Ratios of the measured line intensities of the 41104 - 00001 band of the ${}^{12}C^{16}O_2$, ${}^{13}C^{16}O_2$ and ${}^{16}O^{12}C^{18}O$ [39,40,46] isotopologues to the HITRAN2016 [12], CDSD-296 (CDSD2019) [17], UCL [27,28] and NASA Ames [23] line lists.





Fig. 11. The 31104e-01101e and 11112e-11101e hot bands of ${}^{16}O^{12}C^{18}O$ (628) and ${}^{13}C^{16}O_2$ (636) isotopologues, respectively, having the mixed line intensities in the HITRAN2016 database [12].

4. New experimental data with sub-percent uncertainty

459 Accurate line parameters of the spectral lines are generally required for the most 460 demanding atmospheric applications. In particular, the accurate values of the line intensities with 461 uncertainties as low as 0.3%-0.5% [49] are necessary for forward models used in retrievals of CO₂ 462 concentrations from some remote sensing missions. A number of very accurate measurements 463 have become available after the release of HITRAN2016 in the NIR region: the most recent CRDS measurements from NIST [19,20] and FTS measurements from DLR reported in Birk et al. [22] 464 465 (with the corresponding measurements and line parameter database provided on Zenodo [21]). 466 The results obtained in these works were used to improve the HITRAN line intensities of the ¹²C¹⁶O₂ isotopologue. 467

468 The accurate CRDS line intensity measurements for the 3001i-00001 (i = 2-4) bands 469 reported by Long et al. [19] were used to refine the calculated HITRAN2016 CO_2 band intensities 470 near 1.6 μ m. This region is actively used for spectroscopic measurements of atmospheric CO₂ 471 concentrations. For instance, the 30013-00001 band is targeted by the OCO-2 and OCO-3 472 missions [5,7], while the 30012–00001 band is used for the LIDAR missions [50]. It was shown in 473 Ref. [19] that the band-integrated CRDS intensity measurements and the *ab initio* calculations 474 of Zak et al. [27] agree at the 0.06% level for the 30013–00001 and 30014–00001 bands, but 475 there is a systematic discrepancy of about 1.1% for the 30012–00001 band. We note that the 476 HITRAN2016 line intensities are from the *ab initio* UCL results [27], and they have relative 477 uncertainties < 2 % for the 30012 - 00001 and 30013 - 00001 bands and < 5 % for the 30014 -478 00001 band, respectively. In contrast, the current CO₂ spectroscopic databases [17,23] show a 479 significant spread in their line intensities at about or above 1%. Following these results [19], the 480 HITRAN2016 line intensities for the 3001*i*-00001 (*i*=2-4) bands were scaled to the recommended 481 band-dependent scaling constant factors, while preserving the original J-dependence of the ab 482 initio calculations. The comparison of the HITRAN2016 and HITRAN2020 line intensities of the 30012-00001 band of ¹²C¹⁶O₂ isotopologue to the experimental values reported in Long et al. [19] 483 484 is plotted in Fig.12.

485 Bruker IFS 125HR Fourier-transform spectrometer measurements have been conducted 486 at the German Aerospace Center (DLR) to measure pure carbon dioxide transmittance spectra in

487 the 6000–7000 cm⁻¹ spectral region, including the 30011 - 00001, 30012 - 00001, 30013 - 00001, 488 30014 - 00001, and 00031 - 00001 bands [22]. In this work, line intensity uncertainties of 0.15% 489 were reported. The scaling factor 1.0061 was used for the HITRAN2016 line intensities of the 30011 - 00001 band of the ¹²C¹⁶O₂ isotopologue to match with DLR measurements [22]. The 490 491 30013 - 00001 and 30014 - 00001 HITRAN2016 line intensities and NIST measurements were 492 found to be in good agreement with the DLR measurements. However, for the 30012 - 00001 493 band, the differences outside of the stated uncertainties with both NIST measurements and 494 HITRAN2016 were reported. The difference for the 30012-00001 band was 1.6%, whereas for 495 Long et al. [19] the difference was about 1%. It should be noted that these differences are outside 496 the stated uncertainty budget. In addition, the DLR data showed systematic differences of 497 relative line intensities to HITRAN2016 within the 3001*i*-00001 (*i*=2,3) bands on the order of 0.3%.

498 Regarding the line positions for the 3001i-00001 (i = 2-4) bands, they were replaced with 499 positions from the CDSD-296 database [17] in the HITRAN2020 line list (See Section 2 for details). 500 As an example, we will refer to two recent papers [51,52] that provide a comparison for line 501 positions of the 30012-00001 and 30013-00001 bands. These works confirm good agreement of 502 the line positions for the corresponding bands with an experimental measurement [53-58] and 503 the CDSD-296 [17] database. The comparison for the 30012-00001 line positions with the known 504 and most recent measurements [51,53-55] is given in Fig. 6 of Ref. [51], including CDSD-296 [17]. 505 This figure shows that the accurately measured line positions [51] to those from Refs [53-55] 506 agree reasonably well for the rotational quantum number *m* below -32. However, Fig.6 [51] does 507 not include the comparison with the recently measured P32 transition from Ref. [56] with the 508 120kHz uncertainty, but this position value equals 6319.195652 cm⁻¹ (fitted by Voigt profile) and 509 totally coincides with the position value of P32 transition from Ref. [51] used in Fig.6. Lamb dips 510 of the 30013-00001 line positions were accurately measured by a comb-locked cavity ring-down 511 spectrometer with an accuracy of a few kHz. Fig.5 in Ref. [52] shows the comparison of line 512 positions obtained in Ref. [52] and those reported by Long et al. [57] with Doppler-limited and by 513 Burkart et al. [58] with Doppler-free Lamb-dip measurements. The comparison with CDSD-296 514 [17] is also presented that agree very well with measurements with differences around 20 kHz 515 for $-44 \le m \le 43$, and the difference increases up to 4.6 MHz for J = 72.

In Fleurbaey et al. [20], it was shown that a constant scaling of 1.0069 ± 0.0002 of HITRAN2016 values in the 20013–00001 band of CO₂ near 2.06 µm is consistent with the experiment. Therefore, we have performed this scaling in HITRAN2020. In Refs [19,20], the reported relative uncertainty in intensity is better than 0.1%, thus the uncertainty code 8 (< 1%) for the line intensities was given for the corresponding bands in the HITRAN2020 line list.

In the HITRAN2016 edition, the line intensities of the 00031–00001 band of the ¹²C¹⁶O₂ 521 isotopologue near 1.4 µm used CDSD-296 [26] as an intensity source because this band was 522 identified as "sensitive" in the ab initio calculations [27]. The comparison of the CDSD line 523 524 intensities with the DLR measurements [20] showed rotationally-dependent deviations up to 4%. 525 To improve the 00031–00001 line intensities in the HITRAN2020 line list, we scaled the UCL line 526 intensities [27] by the factor of 1.1217 to match the line intensities reported by Birk et al. [22] 527 (See Fig. 12). It should be noted that two lines (P20 and R18) were absent in the UCL line list [27], 528 so that the intensities of these corresponding lines were updated from Birk et al. [22].

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Fig. 12. *Upper panel:* Comparison of the HITRAN2016 and HITRAN2020 line intensities of the 30012-00001 band of ${}^{12}C^{16}O_2$ isotopologue to the experimental values measured by Long et al. [19]. *Lower panel:* Comparison of the measured line intensities reported in Birk et al. [22] and the UCL intensities scaled by

the factor of 1.1217 for the 00031-00001 band of the ${}^{12}C^{16}O_2$ isotopologue. Scaled UCL intensities were

- adapted for HITRAN2020 in this band.
- 540

The weak 10032 - 10002 and 01131 - 01101 hot bands of the ${}^{12}C^{16}O_2$ isotopologue located near 6900 cm⁻¹ were also compared to the DLR measurements [22]. It was found that the HITRAN2016 line intensities of the 10032 - 10002 band should be scaled by a factor of 1.1346 while the line intensities of the 01131 - 01101 band having the intensity origin from CDSD-296K [26] should be scaled by a factor of 1.0022.

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5. New bands above 8000 cm⁻¹

The recent high-temperature ExoMol UCL-4000 line list containing almost 2.5×10⁹ 548 transitions at T=4000K for the ¹²C¹⁶O₂ isotopologue was published in Ref. [18]. To compare this 549 550 line list with HITRAN2016, we converted UCL-4000 to HITRAN format at 296 K and applied an intensity cut-off of 10⁻³⁰ cm/molecule using the ExoMol to HITRAN.py program downloaded 551 552 from http://exomol.com/software/[59]. This code transfers the position, intensity, Einstein A, 553 lower state energy, and upper/lower level statistical weights into the correct location for a 554 HITRAN default format ".par" file. It works by looking at the "trans" file to get the upper and 555 lower state ID. We edited this program to extract the m_1 , m_2 , l_2 , m_3 HITRAN quantum numbers 556 from the ExoMol files. In the case where the states were not assigned, the vibrational 557 assignments were replaced with "-2-2-2-20". When it was possible, we also performed additional assignments using the CDSD-296 [17] and Ames [23] databases. Fig. 13 gives an overview 558 comparison of the HITRAN2016 line list to the UCL-4000 line list for the ¹²C¹⁶O₂ isotopologue from 559 0 to 20000 cm⁻¹. It should be noted that the ¹²C¹⁶O₂ line list in HITRAN2016 was limited to the 560 spectral range 158.302 to 14075.298 cm¹. The new ¹²C¹⁶O₂ lines from the UCL-4000 line list, along 561 562 with data from the HITRAN2016 database, are shown in Fig.13. These UCL-4000 transitions are 563 highlighted in blue and located above 8000 cm⁻¹. Over 3600 spectral lines with line intensities from 1.8×10⁻²⁸ to 9.9×10⁻³⁰ cm/molecule from the UCL-4000 line list were included in the 564 565 HITRAN2020 spectroscopic database. The line positions in the UCL-4000 dataset [18] are 566 calculated from the energy levels derived from the HITRAN2016 database. Due to the diversity 567 of data in HITRAN some inconsistencies could occur when deriving upper state energy levels, 568 which could result in deviations. As a result, the UCL-4000 line list has an issue regarding the 569 matching of line positions. As an example, this case is shown in Fig. 14, where the comparison

570 of the line positions for the 50015 - 00001 and 60014 - 10002 bands of the ¹²C¹⁶O₂ isotopologue 571 is presented. We traced the source of the discrepancies in UCL-4000 to the procedure used to 572 substitute the variational (upper) state energies with the empirical values. The substituted 573 energies were taken from HITRAN2016, either as the lower state energy term values E" or as E'= 574 E''+v (where v is the transition wavenumber). The examples of these upper state energies, 575 including those shown in Fig. 14, were affected by the inconsistency of the original line positions 576 from different sources. Most of such inconsistency cases identified in the present analysis have 577 been improved in HITRAN2020 and will be propagated to UCL-4000 after the release of 578 HITRAN2020.



579

Fig. 13. Overview of the HITRAN2020 line list for principle isotopologue in the 0-20000 cm⁻¹ spectral
 region. Bands that also existed in HITRAN2016 [12] are shown in black and those added from ExoMol
 UCL-4000 [18] – in blue.



587

Fig. 14. Difference between the HITRAN2020 and ExoMol UCL-4000 line positions for the 50015 - 00001 and 60014 - 10002 bands of the ${}^{12}C^{16}O_2$ isotopologue.

588 The weak 30022 - 00001 and 30023 - 00001 bands of the ${}^{16}O^{12}C^{18}O$ isotopologue with 589 band centers as 8374.23 cm⁻¹ and 8497.45 cm⁻¹, respectively, were missing in the HITRAN2016 590 [12] and CDSD-296 [17] spectroscopic databases. These bands were assigned in the analysis of 591 CRDS spectra of natural CO₂ near 1.18 µm [14] and included in the new CO₂ line list. We also 592 calculated the energy levels (thereby obtaining line positions) for the 30022 - 00001 and 30023 -593 00001 bands of ${}^{16}O^{12}C^{18}O$ up to J_{max} =34 using the spectroscopic constants of the lower and upper 594 state obtained in Refs [14,60] and equation (1).

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$$F_{\nu}(J) = G_{\nu} + B_{\nu}J(J+1) - D_{\nu}J^{2}(J+1)^{2} + H_{\nu}J^{3}(J+1)^{3}$$
(1)

597 where G_v is the vibrational term value, B_v is the rotational constant, D_v and H_v are the centrifugal 598 distortion constants, *J* is the angular momentum quantum number.

599 Also, it was shown in Ref. [14] that the R-branch intensities of the very weak 00041 -01101 hot band of the ¹²C¹⁶O₂ isotopologue, which are missing in CDSD-296 [17], are in good 600 agreement with the NASA Ames intensities [23] while HITRAN2016 values were largely 601 602 overestimated. For the HITRAN2020 database, the line intensities of the 30022-00001, 30023-603 00001, and 00041-01101 bands were updated using the line intensities from NASA Ames [23]. 604 Fig.15 shows the good agreement between the CRDS line intensities from Ref. [14] and the 605 calculated values from the NASA Ames line list [23]. The uncertainty codes for line positions and 606 intensities were updated to 4 for these bands in the HITRAN2020 line list, corresponding to (\geq 0.0001 cm^{-1} and < 0.001 cm^{-1}) and ($\geq 10 \%$ and < 20 %), respectively. 607



Fig.15. Comparison CRDS [14] and NASA Ames [23] line intensities of the 30022 - 00001 and 30023 - 00001
 bands of the ¹⁶O¹²C¹⁸O isotopologue.

611

612 6. Addition of magnetic dipole band of ${}^{12}C^{16}O_2$ at 3.3 μ m

613 The HITRAN2020 database has been extended by including the 01111 - 00001 (v_2+v_3) magnetic dipole band of the principal isotopologue of carbon dioxide. These line parameters 614 615 were introduced into HITRAN for the first time; all previous editions of HITRAN provided only CO₂ 616 electric dipole transitions. Interestingly, the first observation of the v_2+v_3 band has been reported 617 at 3.3 µm in the atmosphere of Mars [61] by the ExoMars Trace Gas Orbiter ACS instrument [62]. 618 This band is forbidden as an electric dipole absorption. However, it is allowed through electric 619 quadrupole and the magnetic dipole mechanisms, which are typically much weaker than those 620 allowed through the electric dipole mechanism. The maximum line intensities in the 01111-

621 00001 band are on the order of 6×10⁻²⁸ cm/molecule. The detailed studies of this band providing 622 the selection rules for the vibration-rotation transitions are presented in Refs [61,63]. The 623 vibrational transition magnetic dipole moment of the 01111-00001 band was fitted to the line 624 intensities measured with a Bruker IFS 125 HR FTS and a 30 m base multipass gas cell of the V.E.Zuev Institute of Atmospheric Optics SB RAS [64]. The line positions and intensities of this 625 band were computed using the vibrational transition magnetic dipole moment and the set of the 626 effective Hamiltonian parameters reported by Majcherova et al. [65]. We included the calculated 627 line parameters up to J=64 of the 01111-00001 band of ¹²C¹⁶O₂ in the HITRAN2020 line list. The 628 calculated line intensities were consistent with an intensity cut-off 10⁻³⁰ cm/molecule at 296K. 629 630 The calculated line intensities agree well with the values measured independently by Optical-631 Feedback-Cavity Enhanced Absorption Spectroscopy (OFCEAS) in Fleurbaey et al. [66] for five R-632 branch lines of this band (R26-R32 and R36). An overview of the 01111-00001 magnetic dipole band of the main CO₂ isotopologue with band center 3004.012 cm⁻¹ is displayed in **Fig. 16**. The 633 634 corresponding uncertainty codes for the line positions and intensities were used for the 01111-635 00001 band of ${}^{12}C^{16}O_2$: code 4 (\geq 0.0001 and < 0.001) and code 4 (\geq 10 % and < 20 %), respectively. 636 It should be noted that to distinguish the magnetic dipole transitions in the traditional HITRAN ".par" format, the letter "m" was introduced into the quantum field dedicated to upper state 637 638 rotational ("local") quanta (see HITRAN2004 paper [67]).

639 We should also mention that in their OFCEAS study of the v_2+v_3 band, Fleurbaey et al. [66] 640 reported, together with the detection of the magnetic dipole lines the measurement of weaker 641 electric quadrupole of the same v_2+v_3 band. This detection was made possible by accurate ab *initio* predictions of the E2 line intensities ¹²C¹⁶O₂ in the 0-10000 cm⁻¹ range [68]. Overall, the *ab* 642 643 initio intensities of the very weak quadrupole lines are validated by these OFCEAS values (maximum line intensities on the order of 10⁻²⁸ cm/molecule). There is also evidence for these 644 645 quadrupole lines in the ACS Mars spectrum [68]. The weak electric quadrupole lines are not 646 included in the present version of the HITRAN database and will be considered for forthcoming 647 editions.



650

Fig. 16. The 01111-00001 magnetic dipole band of the main CO_2 isotopologue [64,66]. The band center of this band is 3004.012 cm⁻¹.

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7. The line-shape parameters for the HITRAN2020 CO₂ line list

655 A major update of the line-shape parameters of CO₂ broadened by air and CO₂ is described 656 in Ref. [13]; this involved both enhancing the HITRAN database and improving completeness. A 657 systematic extrapolation method was introduced for producing the air- and self- half width 658 (broadening) Voigt profile parameters for unmeasured transitions [69], based on the 659 measurements reported in Ref. [70]. The temperature-dependent exponents of the air- and self-660 broadening parameters were generated based on existing measurements and a semi-empirical 661 calculation method using the measurements given in Refs [71,72]. Air- and self-pressure shifts 662 for every line of CO₂ were calculated using the semi-empirical approach proposed by Hartmann 663 [72] and fits using carefully selected experimental data.

664 Besides providing the standard 160-character ".par" parameter, the HITRAN2020 665 database will include additional parameters for the speed-dependent Voigt (SDV) profile [73,74] 666 in a separate set. The list of the SDV parameters was provided in Table 1 of Ref. [13]. The air- and self-speed dependence of the broadening parameters with their temperature dependence will be added for all the lines of CO₂, and they can be downloaded using customized output format on <u>www.hitran.org</u>. One can also retrieve these parameters with the HITRAN Application Programming Interface (HAPI) [75] using the SDVoigt parameters group.

671 The CO_2 line-mixing package, developed by Lamouroux et al. [76], was updated using the 672 new spectroscopic parameters obtained in the present study and the parameters found in Ref. [13]. This package is available at HITRANonline and can be used to calculate the CO₂ absorption 673 674 coefficient accounting for the full line-mixing and the first-order line-mixing parameters. 675 Furthermore, as part of the HITRAN2020 extension, the first-order line-mixing parameters were 676 provided for every allowed transition of CO₂, and they can be accessed using a user-defined 677 format in HITRANonline. The new data were verified using different sets of laboratory spectra to 678 compare with the absorption coefficient calculated by the line-mixing package program. A 679 considerable improvement was achieved for the regions examined compared to HITRAN2016 (we 680 refer to figures 16-19 in Ref. [13]), which should be beneficial for the CO₂ retrieval missions such 681 as the OCO-2, ACE, and GOSAT.

682

8. Overview summary of the HITRAN2020 CO₂ line list

683 The HITRAN2020 line list for the twelve stable isotopic species of carbon dioxide contains 545084 transitions. It covers the spectral range from 0.757 cm⁻¹ to 19908.186 cm⁻¹ with $J \le 128$ 684 685 and with the lower-state energies up to 6533.030 cm⁻¹. Most of the line positions and their 686 corresponding lower state energies were replaced by using the CDSD-296 database [17]. For the 687 problematic line intensities identified in new laboratory and atmospheric spectra, critical 688 validation tests were performed to improve the accuracy of the CO₂ lists. The line-shape 689 parameters of CO₂ broadened by air and CO₂ were updated. A summary of the CO₂ line list in the 690 HITRAN2020 edition compared to the HITRAN2016 is given in **Table 2**. The HITRAN2020 carbon 691 dioxide line list generated in HITRAN format is available on the HITRANonline website 692 www.hitran.org and Supplementary material I of this paper. We also present the supplementary 693 "difference" file (Supplementary material II) that shows every parameter change for each 694 transition between HITRAN2016 and HITRAN2020. This will provide comprehensive information

on the changes made in this work, although it will not show the new bands. An overview of theline lists in HITRAN2020 and HITRAN2016 is plotted in Fig.17.

Also, it should be noted that the new version of the Total Internal Partition Sum (TIPS)
software was reported for 57 molecules, including the CO₂, in Ref. [77]. These data are provided
with HITRAN2020 and a new version of the TIPS code is available in both FORTRAN and python
languages.



701

702Fig. 17. An overview of the HITRAN2016 and HITRAN2020 line lists for the 12 stable CO2 isotopologues:703 ${}^{12}C^{16}O_2(626), {}^{13}C^{16}O_2(636), {}^{16}O^{12}C^{18}O(628), {}^{16}O^{12}C^{17}O(627), {}^{16}O^{13}C^{18}O(638), {}^{16}O^{13}C^{17}O(637), {}^{12}C^{18}O_2(828),$ 704 ${}^{18}O^{12}C^{17}O(827), {}^{12}C^{17}O_2(727), {}^{13}C^{18}O_2(838), {}^{18}O^{13}C^{17}O(837), {}^{13}C^{17}O_2(737)$ (The numbers in parentheses

705 are the AFGL shorthand code for the isotopologues).

706	Table 2. Comparison of HITRAN2020 and HITRAN2016 line lists for the 12 stable CO ₂ isotopologues
707	

Formula	AFGL	Abundanaa	HITRAN2016		HITRAN2020			
	code	Abundance	Number of lines	Spectral region (cm ⁻¹)	Q(296K)	Number of lines	Spectral region (cm ⁻¹)	Q(296K)
¹² C ¹⁶ O ₂	626	0.984204	173024	158.302-14075.298	286.094	174446	158.302-19908.186	286.094
¹³ C ¹⁶ O ₂	636	0.011057	70577	332.649-13734.963	576.644	69870	332.649-13734.963	576.644
¹⁶ O ¹² C ¹⁸ O	628	0.003947	127850	1.473-12677.181	607.713	122140	1.473-12677.182	607.713
¹⁶ O ¹² C ¹⁷ O	627	7.339890×10 ⁻⁴	77941	0.757-12726.562	3542.610	73942	0.757-12726.562	3542.610
¹⁶ O ¹³ C ¹⁸ O	638	4.434460×10 ⁻⁵	43782	2.945-9212.609	1225.270	41058	2.945-9212.608	1225.270
¹⁶ O ¹³ C ¹⁷ O	637	8.246230×10 ⁻⁶	25175	9.086-8061.741	7140.024	23607	9.086-8061.739	7140.024
¹² C ¹⁸ O ₂	828	3.957340×10 ⁻⁶	10522	482.813-8162.743	323.424	10498	482.814-8162.752	323.424
¹⁷ O ¹² C ¹⁸ O	728	1.471800×10 ⁻⁶	15878	491.181-8193.172	3766.044	14623	498.617-8193.172	3766.044
¹² C ¹⁷ O ₂	727	1.368470×10 ⁻⁷	6518	535.384-6932.693	10971.91	6493	535.384-6932.693	10971.91
¹³ C ¹⁸ O ₂	838	4.446000×10 ⁻⁸	2916	539.626-6686.983	652.242	2926	539.620-6686.983	652.242
¹⁸ O ¹³ C ¹⁷ O	837	1.653540×10 ⁻⁸	4190	549.473-4914.496	7593.900	3980	549.473-4914.496	7593.900
¹³ C ¹⁷ O ₂	737	1.537500×10 ⁻⁹	1501	575.853-3614.084	22129.96	1501	575.853-3614.084	22129.96
Total			559874			545084		

Note: AFGL code is the shorthand notation for the isotopologue, abundance is the terrestrial value assumed by HITRAN, and *Q*(296

710 K) is the partition sum at the reference temperature of 296 K.

9. Conclusion

713 This work presents an improved and extended version of the HITRAN2020 spectroscopic 714 database for the carbon dioxide molecule. The database includes updates of the line positions 715 and intensities described in this work, and line shape parameters (described in Hashemi et al. 716 [13]) for 12 stable CO₂ isotopologues. Critical validation tests for the spectroscopic data, including 717 the comparisons with the most advanced theoretical and semi-empirical databases [17,18,23,27] and accurate experimental measurements, were carried out. Evaluation of the HITRAN CO₂ line 718 lists by comparison to laboratory and atmospheric spectra below 8310 cm⁻¹ and the description 719 720 of the updates made for the bands having mixed CDSD and UCL-IAO line intensities in the 721 HITRAN2016 line list below 8000 cm⁻¹ are presented. Recent experimental measurements with 722 sub-percent uncertainty [19–22] were used to improve the CO_2 bands in the (1.4-2.1) μ m region. Several new CO₂ bands (more than 3600 transitions) above 8000 cm⁻¹ were added to the 723 HITRAN2020 edition from the new high-temperature UCL-4000 ¹²C¹⁶O₂ line list from the ExoMol 724 725 [18] database. Also, the updated CO₂ line list has been extended by including new experimentally 726 observed bands [14] corresponding to the ¹⁶O¹²C¹⁸O isotopologue. The magnetic dipole 01111-00001 band of the ¹²C¹⁶O₂ isotopologue in the 3.3 µm region was introduced into HITRAN for the 727 first time. Updated self- and air-broadened line shape parameters of CO₂, as described in Ref. 728 729 [13] and involved in the enhancement of the HITRAN databases, were also revised. These updates 730 of the CO₂ line parameters in HITRAN2020 are expected to have an important impact on the capabilities of current and future remote-sensing missions. The updated line lists for 12 CO₂ 731 732 isotopologues are available as Supplementary material of this paper or can be downloaded from 733 the HITRAN website (www.hitran.org).

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adequately specify the experimental procedure. Such identification is not intended to imply
 recommendation or endorsement by NIST, nor is it intended to imply that the materials or
 equipment identified are necessarily the best available for the purpose.

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