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Magdalena Konefal, Samir Kassi, Didier Mondelain, Alain Campargue. High sensitivity spectroscopy of the O₂ band at 1.27 μm : (I) Pure O₂ line parameters above 7920 cm^{-1} . *Journal of Quantitative Spectroscopy and Radiative Transfer*, 2019, 362, pp.106653. 10.1016/j.jqsrt.2019.106653. hal-02328762

HAL Id: hal-02328762

<https://hal.science/hal-02328762>

Submitted on 21 Dec 2021

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4 High sensitivity spectroscopy of the O_2 band at $1.27\mu\text{m}$:
5 (I) Pure O_2 line parameters above 7920 cm^{-1} .
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35 **Keywords:**

36 Oxygen band at $1.27\mu\text{m}$, Spectral line shapes and intensities; Multispectrumline profile fitting; Cavity
37 ring-down spectroscopy; Absolute frequency measurements; Speed-Dependent Nelkin-Ghatak profile.
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47

48

Abstract

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The atmospheric band of O_2 near $1.27 \mu m$ plays an important role in determining the sounded air mass from ground or space borne atmospheric spectra. This band consists of narrow absorption lines of the $a^1\Delta_g - X^3\Sigma_g^-(0 - 0)$ transitions superimposed to a much broader collision-induced absorption structure. The present contribution is part of a long standing project aiming to improve different aspects of the spectroscopy of this band by highly sensitive cavity ring down spectroscopy (CRDS).

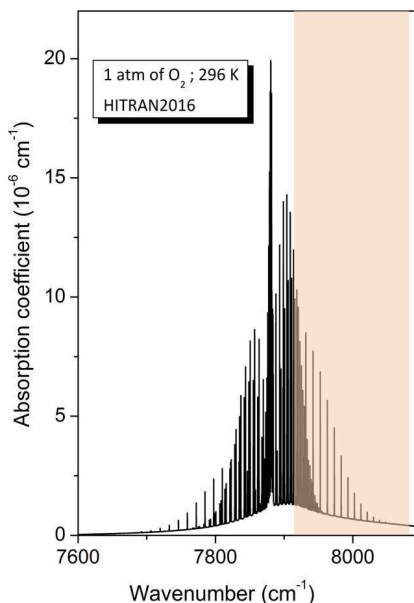
In the present contribution, low pressure (5 and 10 Torr) spectra of pure O_2 were recorded with unprecedented sensitivity in the $7920-8085 \text{ cm}^{-1}$ interval (noise equivalent absorption, α_{min} , on the order of 10^{-12} cm^{-1}) using an external cavity diode laser. About 170 lines including electric quadrupole transitions were accurately measured. The weakest lines have intensity on the order of $10^{-30} \text{ cm}^2/\text{molecule}$. The coupling of the CRDS spectrometer with a self-referenced frequency comb allows an important gain on the accuracy of the line center determination. Detailed line profile analysis using the quadratic Speed-Dependent Nelkin-Ghatak profile was performed for a series of twelve lines recorded for pressures up to 150 Torr. In particular, the very weak self-pressure shifts (on the order of $10^{-3} \text{ cm}^{-1}/\text{atm}$) could be determined for the first time. Line intensities with uncertainty of 1 % are reported for lines with intensity larger than $10^{-28} \text{ cm}^2/\text{molecule}$. Accurate spectroscopic parameters of the $a^1\Delta_g(v = 0)$ upper level were fitted to the zero-pressure line centers. An *rms* value of 108 kHz ($3.6 \times 10^{-6} \text{ cm}^{-1}$) is achieved for the (meas.-calc.) differences of the $^{16}O_2 a^1\Delta_g(v = 0)$ upper level ($J_{max} = 37$). Significant deviations compared to the HITRAN database are discussed.

67 **1.Introduction**

68 Being a symmetric diatomic molecule, the $^{16}O_2$ oxygen molecule has no dipolar electric moment
69 and thus no electric dipole-allowed vibrational bands. Weak magnetic dipolar transitions are observable in
70 the ground electronic state. They manifest as a fine-structure Q -type branch near 60 GHz as well as a
71 rotational R -type branch in the far infrared and in the region of the (1-0) fundamental vibrational band
72 near $6.5\mu\text{m}$. The oxygen spectrum shows a few electronic bands in the near infrared and visible which are
73 of particular importance for a number of atmospheric applications. The strongest transitions belong to the
74 well-known $b^1\Sigma_g^+ - X^3\Sigma_g^-(0 - 0)$ A-band near 760 nm which is about 100 times stronger than the
75 $a^1\Delta_g - X^3\Sigma_g^-(0 - 0)$ band near $1.27\mu\text{m}$ considered in this work. Note that electric dipole (E1)
76 transitions are forbidden for these two electronic bands too, as the involved electronic levels have all
77 gerade symmetry. The 760 nm A-band and the $1.27\mu\text{m}$ band are thus formed by relatively weak magnetic
78 dipole (M1) transitions and extremely weak electric quadrupole transitions (E2).

79 As the mixing ratio of oxygen is constant in the Earth's atmosphere, these two bands are valuable
80 to determine the air mass along the line of sight from ground [1] or space borne atmospheric spectra [2, 3].
81 In particular, the $1.27\mu\text{m}$ band is used by the Total Carbon Column Observing Network (TCCON) for
82 ground-based air mass determination [4, 5, 6]. The A-band and the $1.27\mu\text{m}$ band were selected by the
83 French space agency, CNES, for the satellite mission MicroCarb [7], dedicated to the accurate
84 determination of column integrated concentrations of CO_2 that should be launched by 2021. The targeted
85 accuracy on the column-averaged CO_2 mole fraction (better than 1 ppm or 0.3 % in relative) requires an
86 accurate derivation of the dry air column from the O_2 column using a constant volume mixing ratio of
87 0.2095 [8]. Compared to the A-band, the spectral proximity to the used $1.6\mu\text{m}$ CO_2 absorption band is an
88 advantage to reduce the uncertainties linked to the correction of surface pressure and aerosol scattering
89 effects [2]. Furthermore, the $1.27\mu\text{m}$ band has the advantage of having less saturated lines compared to the
90 stronger A-band.

91 **Fig. 1** presents a spectrum of the $1.27\mu\text{m}$ band for a pressure of 1 atm of oxygen computed using
92 the HITRAN2016 spectroscopic database [9]. In addition to the M1 and E2 rovibronic absorption lines,
93 the O_2 absorption bands include a broad continuum, namely the collision induced absorption (CIA)
94 continuum due to short-lived collisional O_2-O_2 (and O_2-N_2 in air) complexes. While, lines absorption is
95 proportional to the O_2 density, the self- and foreign components of the CIA are proportional to the squared
96 O_2 density and to the product of O_2 and N_2 densities, respectively. Note that the relative contribution of the
97 CIA and of the lines varies with the considered band [10]. In particular, the CIA of the $1.27\mu\text{m}$ band is
98 much stronger than that of the A-band [9, 11]. The resulting difference in pressure dependence of the O_2
99 absorption bands has been proposed as a mean to monitor O_2 in the atmosphere of exoplanets [12].



100
 101 **Fig. 1**
 102 Simulation of the absorption spectrum of oxygen at 1 atm and 296 K in the region of the $1.27\ \mu m$ band.
 103 (The HITRAN2016 values of the line parameters and of the CIA were used for the simulation). The $7920-$
 104 $8085\ cm^{-1}$ highlighted region is studied in this work while CRDS analysis of the lower range ($7658-7917$
 105 cm^{-1}) was reported in [13, 14].
 106

107 The present work is part of a project dedicated to a better characterization of the absorption lines
 108 and of the CIA of the $1.27\ \mu m$ O_2 band in order to fulfill demanding requests for atmospheric applications,
 109 in particular for the above mentioned MicroCarb mission. We have recently applied the highly sensitive
 110 cavity ring down spectroscopy (CRDS) technique to accurately determine the room temperature CIA
 111 binary coefficients from low density spectra (0.36 to 0.85 amagat) of pure oxygen and an O_2/N_2 mixture at
 112 room temperature, over the wide $7513-8466\ cm^{-1}$ region [15]. Although more accurate, the obtained
 113 binary coefficients were found in agreement with previous measurements by Maté *et al.* using high
 114 pressure Fourier transform spectroscopy (FTS) [16]. As concerned absorption lines, the most sensitive
 115 previous measurements of pure O_2 spectra were obtained by CRDS a few years ago [13, 17]. In particular,
 116 previous identification of E2 quadrupole lines in atmospheric solar spectra acquired with a ground based
 117 Fourier transform spectrometer (FTS) was confirmed in the laboratory by CRDS and the obtained
 118 quantitative intensity information was used as input data for calculation of a complete list of E2 transitions
 119 [17]. A systematic CRDS investigation was performed in the $7658-7917\ cm^{-1}$ region for “natural” and ^{18}O
 120 and ^{17}O highly enriched oxygen revealing not only the E2 transitions but also the M1 (1-1) hot band and
 121 new high rotational transitions of the (0-0) band of the five most abundant oxygen isotopologues ($^{16}O_2$,
 122 $^{16}O^{18}O$, $^{18}O_2$, $^{16}O^{17}O$, $^{17}O^{18}O$ and $^{17}O_2$) [13, 14]. These measurements combined with microwave and
 123 Raman data available in the literature allowed improving the determination of the spectroscopic constants

124 for the $X^3\Sigma_g^-$ and $a^1\Delta_g$ states [13, 14].

125 Interestingly, the line profiles of low rotational transitions of the ^{17}O -containing isotopologues were
126 observed to be importantly broadened in the room temperature spectra (recorded with a few tens Torr
127 pressure) [13]. This effect is related to the non-zero nuclear spin of the ^{17}O nucleus ($I= 5/2$) resulting in
128 significant nuclear-spin orbit hyperfine (hf) splitting of the upper energy levels. CRDS recordings with a
129 cryogenic cell at 80 K allows for a significantly better resolution of the hf structure [18]. The rotational
130 and hf spectroscopic parameters derived from these measurements and literature data, allowed for a very
131 good reproduction of the spectra including the hf multiplets [14].

132 These previous CRDS studies of pure O_2 spectra were thus mostly dedicated to weak lines and new
133 observations with marginal impact for atmospheric simulations. More important are the line parameters
134 (position, intensity and broadening coefficients) of the relatively strong M1 transitions which remain
135 insufficiently characterized. For instance, line intensities retrieved from previous FTS works with long
136 path absorption cell [19] are provided with a typical 10 % error bar in the current edition of the HITRAN
137 database [9]. Indeed, due to the weak absorption of the considered band (line intensities are less than
138 1×10^{-25} cm/molecule), the derivation of precise line parameters from FTS spectra is very challenging.
139 Previous FTS line shape studies [19-21] were all limited to the standard Voigt profile analysis. As
140 concerned pressure line shifts, only an upper limit of the pressure line shift could be estimated from FTS
141 spectra up to 3 bar [22]. Conversely, the line profiles of the (stronger) A-band transitions have been
142 recently the subject of important efforts in support of the OCO-2 mission, using both FTS and CRDS (see
143 [23] and references quoted therein). Note that in its present version, the HITRAN2016 database provides
144 for the $1.27\mu\text{m}$ band, line profile parameters transferred from ...the A-band [4, 24].

145 In the present contribution, we use an improved CRDS setup to investigate at very high sensitivity
146 the high energy region above 7920 cm^{-1} , which was not studied in our previous CRDS studies (see **Fig. 1**).
147 While a series of fibered distributed feedback (DFB) lasers were previously used as light source below
148 7920 cm^{-1} [13, 14], an external cavity diode laser (ECDL) is adopted in the present work for a more
149 efficient light injection into the CRDS cell. In addition, following previous works, ([25, 26]), the CRD
150 spectrometer is coupled to a self-referenced frequency comb (SRFC) providing accurate frequency value
151 for each ring down event. As a result, a gain in sensitivity of more than one order of magnitude (noise
152 equivalent absorption $\alpha_{\text{min}}\sim 10^{-12}\text{ cm}^{-1}$) is achieved leading to better quality line profile determination and
153 allowing for low pressure recordings at a few Torr, valuable for an accurate determination of the zero-
154 pressure line centers and of the line intensities.

155 Series of spectra of pure O_2 were recorded in view of the determination of the center, intensities,
156 self-pressure shifts and self-broadening parameters. A continuous spectrum recording with natural oxygen
157 over the 7920 - 8085 cm^{-1} interval was performed for pressure values of 5.0 and 10.0 Torr, leading to the

158 observation of more than 160 lines of the $^{16}O_2$, $^{16}O^{18}O$ and $^{16}O^{17}O$ isotopologues in normal isotopic
159 abundance. In spite of the low pressure of the recordings, the measured line profiles exhibit clear
160 deviations from the standard Voigt profile. In order to determine the best suited line profile, a detailed line
161 profile analysis was undertaken for twelve selected lines recorded for a series of pressures up to 150 Torr.
162 Using a multispectra treatment (see [27, 28]) a satisfactory reproduction of the series of recordings was
163 achieved with the quadratic speed-dependent Nelkin-Ghatak profile (qSDNGP). As a result, an empirical
164 dependence of the qSDNGP parameters *versus* the upper rotational quantum number was determined from
165 the twelve lines. Then, the resulting qSDNGP profile with constrained profile parameters was used to
166 determine the line centers and line intensities of all the lines of the 5 and 10 Torr spectra. In the
167 Discussion section, the obtained results, in particular position and intensities, are compared to literature
168 values. Accurate spectroscopic constants of the $a^1\Delta_g(v=0)$ upper level of $^{16}O_2$ and $^{16}O^{18}O$ are
169 determined from a fit of the zero-pressure line centers, providing accurate line positions not only in the
170 considered spectral region but for the whole absorption band.

171 The experimental setup and the performances achieved are described in the next Section. The line
172 profile analyses using the speed-dependent Nelkin-Ghatak profile is presented in Section 3. The obtained
173 results are discussed and compared with literature in Section 4 before the concluding remarks (Section 5).

174 **2. CRDS recordings**

175 *2.1. Spectra acquisition*

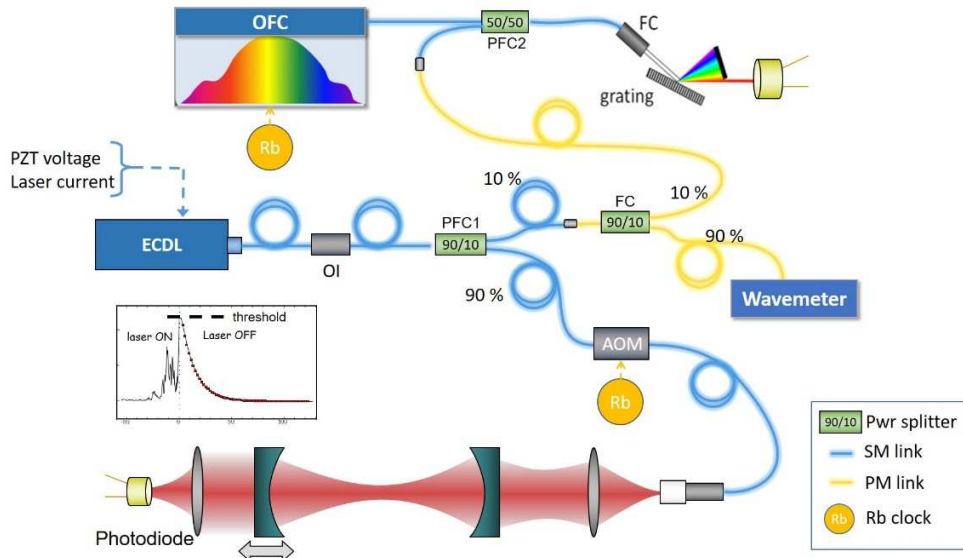
176 Except the use of an external cavity diode laser (ECDL) rather than a distributed feedback (DFB)
177 laser diode, the optical setup is mostly similar to those described in Refs. [29-32]. A sketch of the
178 experimental arrangement is presented in **Fig. 2**. The “on the fly” measurement of the laser frequency
179 values associated to each ring down event by coupling with a self-referenced OFC was first implemented
180 in Refs. [33-35].

181 The CRD system, except the laser source, was installed in a protective Plexiglas enclosure. The
182 stainless steel gas cell was covered with a tube of insulation foam. Its temperature was monitored with a
183 PT 1000 resistive probe (class Y, ± 0.15 K accuracy at room temperature) and an analog temperature
184 sensor (TSic 501, IST-AG, ± 0.1 K accuracy) both fixed on the cell surface. In order to limit the amount of
185 desorbed water vapor in the CRDS cell, the spectra were recorded in flow regime. The flow (not
186 monitored) was adjusted to roughly 5 sccm with a downstream manual needle valve. Controlling an
187 upstream solenoid valve, the pressure was actively PI regulated using either a 10 Torr or 1000 Torr
188 capacitance gauge (MKS Baratron, 0.15% accuracy of the reading) according the total pressure. The
189 regulation noise was 20 ppm at 10 Torr.

190 The ECDL light is first sent into a polarization maintained fiber coupler (PFC, 90/10), which directs
191 about 10% of the emitted light to a frequency measurement setup and the remaining 90% into a fibered

192 acousto-optic modulator (AOM) driven at RF frequency f_{AOM} , inserted before the 1.4-meter-long high-
 193 finesse cavity (HFC) ($F \approx 130,000$). The AOM, used on its order +1, interrupts the excitation once
 194 resonance with one of its longitudinal modes is achieved, leading to a ring down (RD) event. Each RD is
 195 detected with an InGaAs photodiode. Similarly to our previous realization [36], the resonance is sought by
 196 adjusting the length of the cavity over $\lambda/2$ with a piezo-electric tube (PZT_C) that hosts the output mirror. A
 197 fast modulation (50 Hz) spanning 5% of the cavity free spectral range (FSR) is superimposed to the PZT_C
 198 control voltage, which is slowly (1s full span) ramped over an FSR until a first RD event occurs. It is then
 199 locked to this position using a Proportional Integral (PI) locking software procedure that acts on the offset
 200 voltage, until enough RD events are recorded.

201



202

203 **Fig. 2**

204 Scheme of the CRD spectrometer coupled with the self-referenced optical frequency comb (OFC). The
 205 different components include an external cavity diode laser (ECDL), an optical isolator (OI), a fiber
 206 coupler (FC), two polarization maintained fiber couplers (PFC1,2), the OFC and acousto-optic modulator
 207 (AOM) referenced to a GPS referenced rubidium (Rb) clock.

208

209 The absolute ECDL emission frequency f_{ECDL} is determined from:

$$210 \quad f_{ECDL} = f_{CEO} + n f_{rep} \pm f_{BN} \quad (1)$$

211 Where the repetition rate f_{rep} and the carrier-envelope offset frequency f_{CEO} are locked to 250 MHz
 212 and 20 MHz, respectively, with a relative uncertainty of 10^{-11} . The number n of the tooth with which the
 213 ECDL is beating is deduced from the ECDL emission frequency measured by a Fizeau wavemeter (High
 214 Finesse WS-U-30 IR). The 5 MHz resolution and 20 MHz accuracy of this instrument are sufficient to
 215 determine unambiguously n as two consecutive teeth are separated by 250 MHz. The beat-note (BN)
 216 signal was recorded with a fast ADC (250 MHz sampling rate), and the peak frequency f_{BN} was obtained

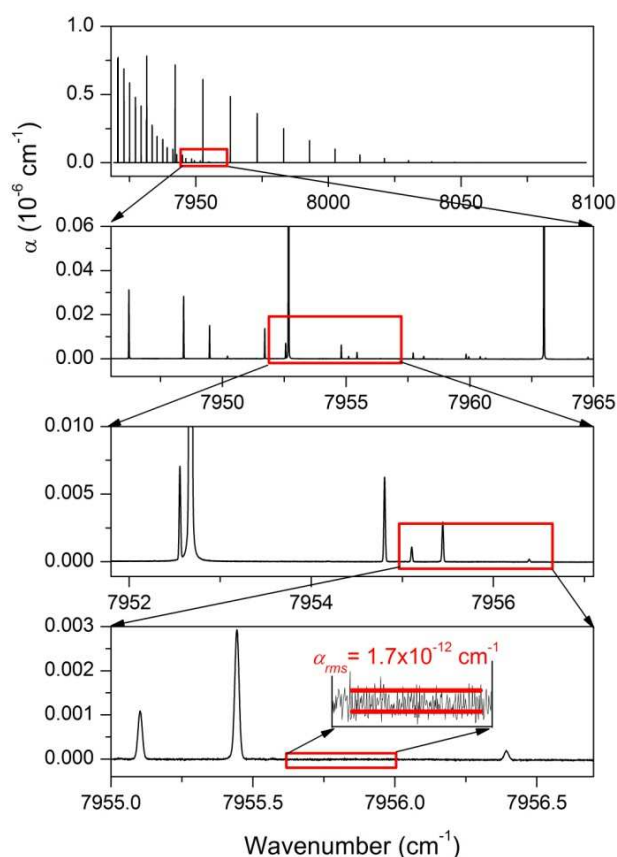
217 after Fourier transform (with a 7 kHz resolution) of the acquired signal. This beat note frequency, f_{BN} ,
218 provided with a refresh rate of one thousand times per second, was used to act on the ECDL frequency
219 with a PI software procedure, to stabilize its emission frequency to a given BN frequency set-point. This
220 mechanism ensured laser emission frequency stabilization to 300 kHz rms corresponding to the
221 uncertainty on the absolute laser emission frequency. The beat-note sign is deduced according to the
222 proximity of the absolute frequency to the wavemeter raw value. Note that the OFC-RF electronics, ADC
223 clock and AOM frequency synthesizer were referenced to a GPS referenced 10 MHz rubidium clock.

224 Because of the AOM, the high-finesse cavity excitation optical frequency is:

$$225 \quad f_{Exp} = f_{ECDL} + f_{AOM} \quad (2)$$

226 The ECDL (from Toptica) was tuned by acting on its internal grating angular position and the laser
227 chip current, in an electronically-controlled laser-current-feed-forward scheme. The grating angular
228 position can be roughly set with an external step motor and finely adjusted with an internal piezo electric
229 element (PZT_L). The ECDL has a mode-hop-free tuning range limited to 0.8 cm^{-1} obtained with a linear
230 scan of the PZT_L voltage over about 80% of its full range capability. Broadband spectra were therefore
231 obtained by concatenation of series of slightly overlapping individual narrow spectra. During automatic
232 broadband acquisition, the laser frequency was iteratively stepped by about 0.5 cm^{-1} , by acting on the
233 grating with the step motor. A mode-hop-free scanning situation was then automatically sought by
234 adjusting the PZT_L ramp offset over successive fast (1s) test scans. The instantaneous laser frequency and
235 the Fizeau wavemeter raw signals were used as mode hop free and monomode emission criterion,
236 respectively. Once the optimal PZT_L voltage offset was determined, a 10 minutes long, $\sim 60 \text{ MHz}$ step by
237 step scan was started. After each frequency jump, the laser was actively locked using the refreshed BN
238 frequency as a reference, until 40 RDs ($\sim 80 \text{ Hz}$ repetition rate) were acquired. The lock was then released
239 in order to allow for to a new step. Instead of forcing the BN set-points to pre-defined frequencies, we
240 preferred to set it to its effective value, 100 ms after the jump.

241 Two different RD averaging scheme were used. For broadband scans, the single laser frequency RD
242 dataset were averaged “on the fly”, together with the BN frequency in order to generate small size
243 individual spectra. Occasionally, when the BN frequency was too close from the 0 or 125 MHz limit, its
244 sign could not be determined. These spectral points were then rejected. In the case of individual high
245 resolution recordings dedicated to line profile analysis, every single RD event was recorded together with
246 experimental parameters, including BN, instantaneous raw wavelength, cell pressure, cell temperature and
247 ECDL scan parameters, leading to heavy data files. The benefit was that the post-processing of RD event
248 and BN packets was lossless. In addition, we could verify that the BN - thus the laser frequency - was
249 steady during each acquisition step and that RD events statistics was regular.



250

251 **Fig. 3**

252 CRDS spectrum of O_2 between 7919.8 and 8085.3 cm^{-1} at 10 Torr . The successive enlargements illustrate
 253 the sensitivity and high dynamical range of the recordings: absorption coefficients are determined from a
 254 value close to 10^{-6} cm^{-1} down to the noise level of about $1.7\times 10^{-12}\text{ cm}^{-1}$.
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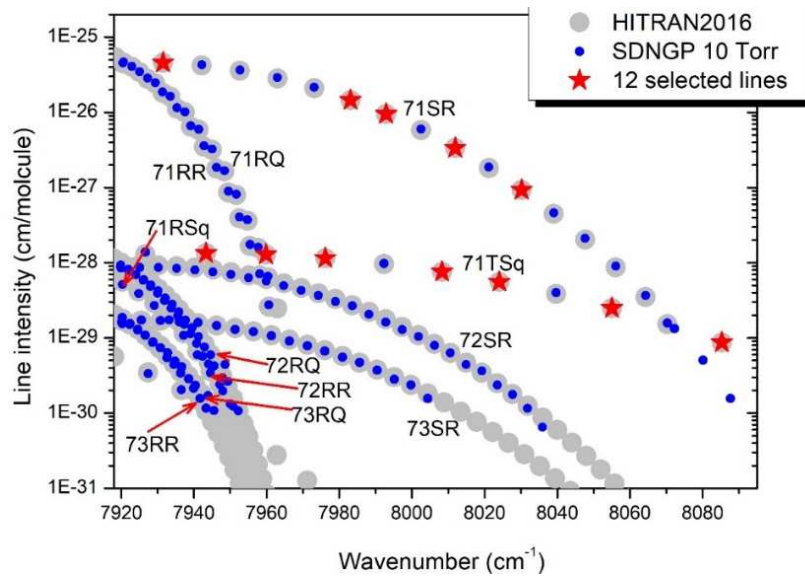
256 As mentioned above, the following analysis is based on two series of recordings with pure oxygen
 257 (AlphaGaz2 from Air Liquide, purity $\geq 99.9995\%$):

258 (i) Two wide spectra covering continuously the entire $7920\text{--}8085\text{ cm}^{-1}$ region with pressure values
 259 of 5.0 and 10.0 Torr . During the 5 Torr spectrum measurements, the cell temperature fluctuated between
 260 294.33 and 295.89 K and during the 10 Torr spectrum measurements between 294.34 and 295.38 K . The
 261 pressure stability was at the level $6\times 10^{-4}\text{ Torr}$ for both recordings.

262 (ii) Series of spectra at different pressures were recorded over a 0.78 cm^{-1} interval around 12 lines
 263 selected for a detailed line profile analysis. In general, the pressure range was $5\text{--}150\text{ Torr}$ with, in
 264 principle, four additional intermediate pressure values ($10, 50, 75, 100\text{ Torr}$). The temperature stability is
 265 at the level of from 0.025 to 0.07 K , except for the $S7R8$ line for which variations up to 0.11 K (due to an air
 266 conditioning problem) are noted. The pressure stability is from about 10^{-4} Torr for the lowest measured
 267 pressures to $2\times 10^{-2}\text{ Torr}$ for spectra at 150 Torr .

268 In all the recordings, the sampling step was chosen to be about $6\times 10^{-4}\text{ cm}^{-1}$ to be compared to a
 269 Doppler line width of about $8.5\times 10^{-3}\text{ cm}^{-1}$ (HWHM). The number of RD events averaged for each spectral
 270 point was 40 or 100 for broadband spectra. In the case of the line profile study, the number of RD (with a
 271 minimum value of 40) was increased on the line profile in order to achieve a similar noise level on the line
 272 and on the nearby baseline. **Fig. 3** illustrates the sensitivity and high dynamical range on the intensity
 273 scale of the 10.0 Torr spectrum. The noise equivalent absorption evaluated as the *rms* of the baseline
 274 fluctuations is around $2\times 10^{-12}\text{ cm}^{-1}$.

275 *2.2. Overview of the observations*



276 **Fig. 4**
 277 Overview of the $a^1\Delta_g-X^3\Sigma_g^-$ line listas provided by HITRAN2016 (full grey dots) [9] in the 7920-8075
 278 cm^{-1} region for oxygen in natural abundance. The lines measured by CRDS at 10 Torr (SDNGP fit, blue
 279 dots) and the 12 lines selected for multi-pressure recordings (red stars) are indicated. Following HITRAN
 280 notation, the $^{16}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}^{17}\text{O}$ lines are labeled 71, 72 and 73, respectively (The 71RS and 71TS
 281 branches correspond to quadrupolar electric transitions (q)).
 282
 283

284 Let us recall that each rotational level (N) of the ground $X^3\Sigma_g^-$ state of O_2 splits into three spin-
 285 components as the O_2 molecule has two unpaired electrons with parallel spin which sum up to the total
 286 electron spin $S=1$. It leads to a triplet multiplicity with total angular momentum $J= N-1, N$ or $N+1$. In the
 287 $a^1\Delta_g$ electronic excited state, the total electron spin is equal to 0 and the N value corresponds to J . Note
 288 that for the $^{16}\text{O}_2$ main isotopologue, only odd rotational levels exist in the ground state. The magnetic
 289 dipole (M1) transitions follow the $\Delta J= 0, \pm 1$ selection rule leading to the observation of nine $\Delta N(N)\Delta J(J)$
 290 branches: $[OP, PP, QP]$, $[PQ, QQ, RQ]$ and $[QR, RR, SR]$ corresponding to $\Delta J= -1, 0$ and $+1$, respectively
 291 (see Fig. 4 of [17]). Electric quadrupole (E2) transitions follow the $\Delta J= 0, \pm 1, \pm 2$ selection rule, which
 292 leads to 15 possible branches, but the $\Delta J= 0, \pm 1$ E2 lines coincide with the much stronger M1 lines and

293 cannot be separated. Therefore, only the $[NO,OO,PO]$ and $[RS, SS, TS]$ branches with $\Delta J= -2$ and $+2$,
 294 respectively, are measurable. In fact, no E2 transitions belonging to the OO and SS branches were detected
 295 so far.

296
 297 **Table 1**
 298 Overview of the assignments of the CRDS observations of the $a^1\Delta_g-X^3\Sigma_g^-$ transitions of O_2 in the 7919.8
 299 -8085.3 cm^{-1} range. For each branch, the range of J values corresponding to the measured transitions is
 300 given.
 301

Branch ^a	¹⁶ O ₂	¹⁶ O ¹⁸ O	¹⁶ O ¹⁷ O
S($N=J-1$)R($N=J$) <i>d</i>	$6 \leq J \leq 42$	$6 \leq J \leq 31$	$6 \leq J \leq 23$
R($N=J$)R ($N=J$) <i>d</i>	$15 \leq J \leq 37$	$14 \leq J \leq 31$	$14 \leq J \leq 26$
R($N=J-1$)Q($N=J$) <i>d</i>	$14 \leq J \leq 36$	$14 \leq J \leq 32$	$14 \leq J \leq 26$
T($N=J-1$)S($N=J$) <i>q</i>	$4 \leq J \leq 24$		
R($N=J$)S($N=J-1$) <i>q</i>	$13 \leq J \leq 27$		
Nb of lines	65^b	62	40

302
 303 *Notes:*
 304 ^a The notations *d* and *q* correspond to magnetic dipole (M1) and electric quadrupole (E2) transitions, respectively.
 305 Strictly speaking, *d* branches include a small contribution due to E2 transitions (see Text).
 306 ^b Including three lines of the (1-1) hot band and three lines not included in HITRAN2016 (S37R38, S39R40 and
 307 S41R42).

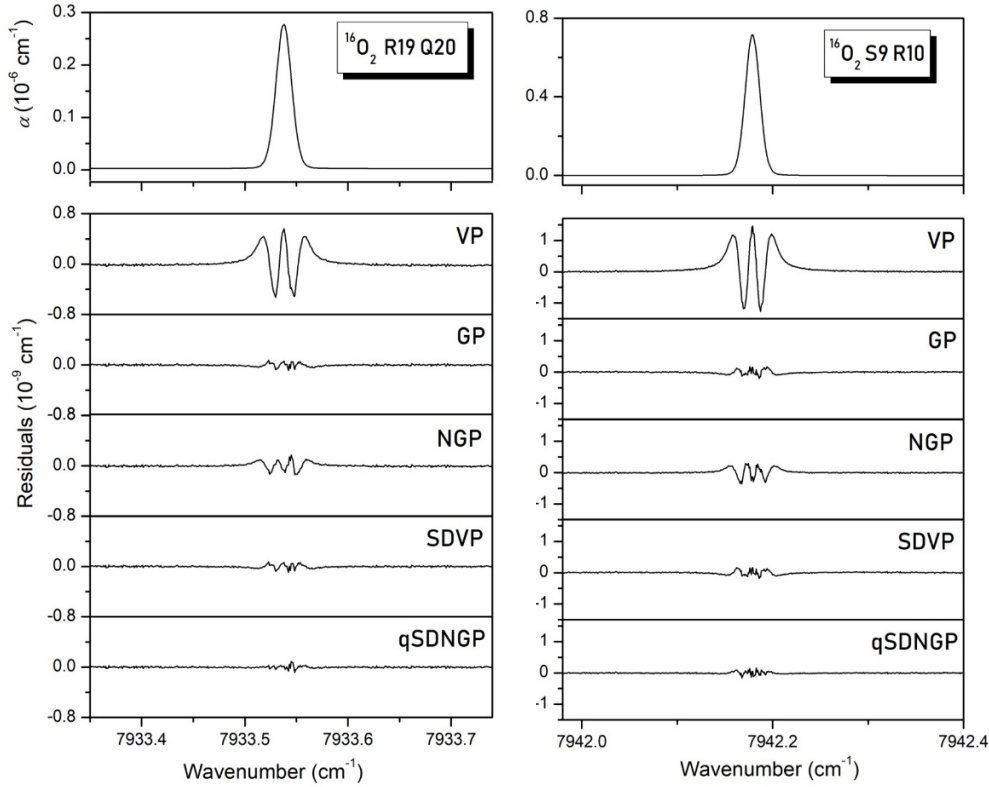
308 The assignment of the O_2 lines by comparison to the HITRAN2016 (calculated) line list was
 309 straightforward (see **Fig. 3**). Overall, 65, 62 and 40 transitions of the ¹⁶O₂, ¹⁶O¹⁸O and ¹⁶O¹⁷O
 310 isotopologues in natural isotopic abundance (0.99526 , 3.99×10^{-3} , 7.4×10^{-4} respectively) were identified
 311 (see **Table 1**). The ¹⁶O₂ transitions include nineteen E2 transitions of the *RS* and *TS* branches and three
 312 transitions of the (1-1) hot band. Note that in spite of the relatively low pressure values of the recordings,
 313 lines with intensity on the order of 1×10^{-30} cm/molecule could be measured. The HITRAN list includes
 314 lines with intensity down to 10^{-31} cm/molecule. Nevertheless, the S37R38, S39R40 and S41R42 lines
 315 around 8080 cm^{-1} with intensity larger than 10^{-30} cm/molecule were detected while they are absent in the
 316 HITRAN list, probably due to a high J value cut-off.

317 **3. Line profile analysis**

318 *3.1. Voigt profile*

319 In a first step, we considered separately the 5 and 10 Torr spectra and constructed the corresponding
 320 line lists assuming the usual Voigt profile (VP) for the line shape as this profile remains the most
 321 commonly used. The spectra were fitted using a homemade multi-line fitting program written in
 322 LabVIEW and C++. The Doppler width was fixed to the theoretical value calculated according to the
 323 temperature value and the isotopologue mass. The line intensity was then converted to the 296 K reference

324 temperature according to the lower state energy value and partition functions provided by the
 325 HITRAN2016 list [9].



326

327 **Fig. 5**
 328 Example of fit residuals of two $^{16}\text{O}_2$ lines at 10 Torr for different line profiles.
 329

330 A VP list of 167 and 164 lines was retrieved from the spectra at 10 and 5 Torr, respectively. The
 331 two lists including line position, line intensity and collisional width values are provided as Supplementary
 332 Material. Let us underline that the two fits were performed independently and the obtained line positions
 333 are thus including the pressure shift at measurement pressure. As illustrated in **Fig. 5**, the VP is not
 334 sufficient to reproduce the line profiles at 5 and 10 Torr and a more sophisticated line shape is required.
 335 The VP residuals exhibit a W shape which is the usual signature of collisional narrowing effects. Indeed,
 336 most of the residuals vanish by using a Galatry profile (GP) [37] or a Nelkin-Ghatak profile (NGP) [38,
 337 39] which accounts for the collisional narrowing assuming a soft-and hard-collision model, respectively.
 338 The residuals obtained with a Speed-Dependent Voigt Profile (SDVP) [40] and a quadratic Speed-
 339 Dependent NGP (qSDNGP) [41, 42] are also displayed in **Fig. 5**. Interestingly, the GP and SDVP fit
 340 residuals are similar in spite of different fitted parameters. NGP gives twice larger residuals than GP while
 341 the set of fitted parameters is identical. Although showing significant deviations up to one or two orders of

342 magnitude above the noise level, the qSDNGP allows the best line shape reproduction. Both the speed
 343 dependence of pressure broadening and shifting and the collisional narrowing (in the hard collision model)
 344 parameters are adjusted in the qSDNGP. It is worth noting that while the VP residuals are large, they do
 345 not show clear asymmetry and thus the fitted values of the VP and qSDNGP line centers are expected to
 346 be close (see Section 4). Note that the qSDNGP with a correlation parameter, known as the Hartmann-
 347 Tran profile (HTP), is the profile recommended for future implementation in spectroscopic databases [43].

348 In summary, the qSDNGP is found to be the most suitable profile to reproduce the recorded spectra.
 349 Nevertheless, considering the small pressure difference, the two available recordings at 5.0 and 10.0 Torr
 350 are sometimes insufficient to retrieve physically meaningful values of the seven qSDNGP parameters
 351 required to be fitted for each line. This is why we undertook a detailed line profile study of a selected set
 352 of lines over a larger pressure range in order to determine more reliable values of the line parameters (*e.g.*
 353 pressure shift). From this selected set of qSDNGP parameters, empirical dependence *versus* the rotational
 354 quantum number will be determined and used as constraints for a qSDNGP fit of all the lines observed in
 355 the spectra at 5.0 and 10.0 Torr.

356 3.2 Multi-pressure analysis of the selected lines

357 Five M1 lines of the SR branch and seven E2 lines of the TS branch of $^{16}O_2$ with J values ranging
 358 from 5 to 27 were chosen for recordings with pressures up to 150 Torr. They are listed in **Table 2** and
 359 highlighted on **Fig. 4**. The absence of overlapping with nearby lines (in particular due to water vapor
 360 present as an impurity), the range of J values and the intensity were used as criteria for the selection. In
 361 addition to the Doppler width (Γ_D), pressure broadening (Γ_0) and pressure-shift (Δ_0) parameters which are
 362 common to all the profiles, the qSDNG parameters include the quadratic speed dependence of the pressure
 363 width and shift (Γ_2 and Δ_2) and the Dicke narrowing parameter (ν_{vc}) [44]. A multispectrum fitting procedure
 364 in which parameters for lines recorded at different pressures are simultaneously adjusted, was used to
 365 retrieve the ($\nu_0, S_{296K}, \Gamma_0, \Delta_0, \Gamma_2, \Delta_2, \nu_{vc}$) parameters of the considered lines. The multispectrum fitting of
 366 high S/N spectra recorded in an appropriately large dynamic pressure range helps reducing the correlation
 367 between the fitted parameters *e.g.* between Γ_2 and ν_{vc} . The used fitting code is a homemade program
 368 written in LabVIEW and C++. The fitting procedure, based on the Minuit2 routine from CERN,
 369 minimizes the residuals *rms* of all fitted multi-pressure spectra.

370 An example of residuals obtained using a multispectrum fit with the Voigt, NG and qSDNG
 371 profiles is shown in **Fig. 6** for the S19R20 line recorded at seven pressures between 5 and 150 Torr. The
 372 clear asymmetry of the NGP residuals, increasing with pressure, is a manifestation of speed-dependent
 373 effects which are well accounted for by the qSDNGP.

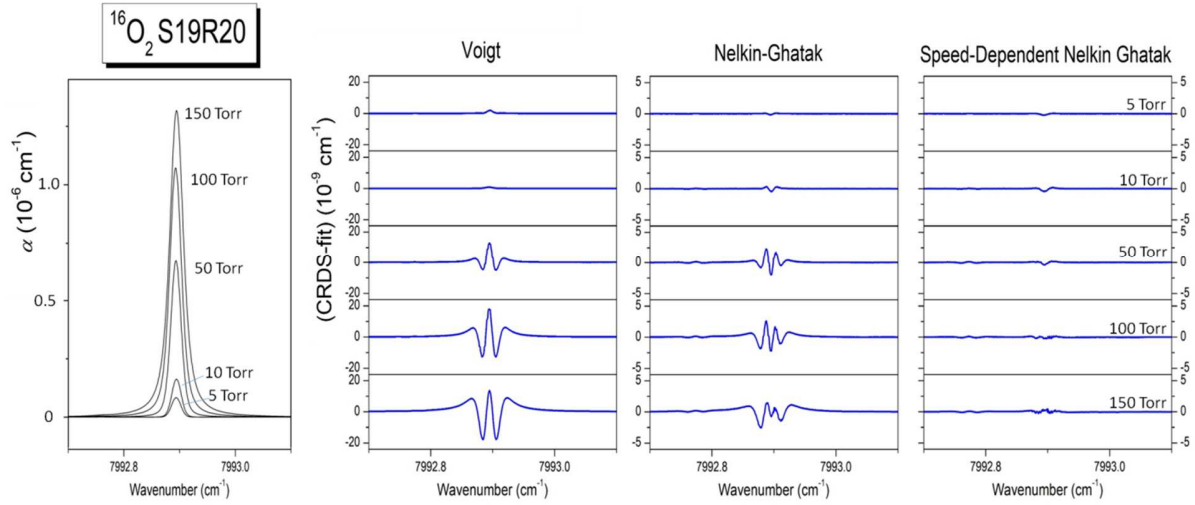


Fig. 6

Spectra of the S19R20 line of $^{16}\text{O}_2$ for a series of pressure between 5 and 150 Torr and corresponding residuals obtained by a multispectrum fit using Voigt, Nelkin-Ghatak and quadratic speed-dependent Nelkin-Ghatak profiles. Note that the absorption spectrum is plotted in 10^{-6} cm^{-1} unit while residuals are plotted in 10^{-9} cm^{-1} unit and that a different ordinate scale is used for the Voigt profile. The asymmetry of the NGP residuals shows the importance of speed-dependent effects.

The fitted values of the multispectrum qSDNGP parameters of the selected lines are given in **Table**

2.

The used multispectrum fitting program did not provide statistical error bar on the fitted values of the different parameters. In order to estimate the fitting error on the zero-pressure positions, we performed independent fit of each spectrum with free position and the $(S_{296\text{K}}, T_0, \Gamma_2, \Delta_2, \nu_{\text{vc}})$ set of parameters fixed to the values of **Table 2**. As an illustration of the consistency of the treatment, **Fig. 7** (left panel) shows the pressure dependence of the retrieved pressure shifts for the five selected SR lines. The error bars on the zero-pressure position included in **Table 2** correspond to the statistical error obtained from a linear regression *versus* pressure. Their values range between 16 kHz and 1.2 MHz (less than 50 kHz for the five SR lines).

A similar procedure was followed for the line intensities: all parameters, except $S_{296\text{K}}$, being fixed to their value of **Table 2**, the intensity value was fitted for each spectrum. The intensity error bars given in **Table 2** correspond to the standard deviation of retrieved intensities. The agreement of the intensity values retrieved at different pressures is at the 1% level (**Fig. 7**, right panel), except for the 5% excess of a few measurements of the S7R8 line (related to an air conditioning problem).

399 **Table 2**

400 Parameters derived for the twelve $^{16}O_2$ lines in the SR (dipolar) and TS (quadrupolar) branches analyzed using a multi-pressure fit.

401

<i>Line</i>	ν_0 (cm $^{-1}$)	S_{296K} (cm/molecule)	Γ_0 cm $^{-1}$ Torr $^{-1}$)	Δ_0 (cm $^{-1}$ Torr $^{-1}$)	Γ_2 (cm $^{-1}$ Torr $^{-1}$)	Δ_2 (cm $^{-1}$ Torr $^{-1}$)	ν_{vc} (cm $^{-1}$ Torr $^{-1}$)	<i>P</i> range (Torr)
S7R8	7931.51032391(54)	4.672(17)E-26	6.46E-5	2.55E-7	5.40E-6	6.49E-8	3.10E-6	5-40
S17R18	7983.1113247(18)	1.4991(17)E-26	5.69E-5	-6.34E-7	4.92E-6	2.15E-7	3.37E-6	5-150
S19R20	7992.8979892(12)	9.7701(77)E-27	5.47E-5	-8.09E-7	3.18E-6	2.22E-7	7.40E-6	5-150
S23R24	8011.9166511(14)	3.4530(43)E-27	5.12E-5	-1.11E-6	5.14E-6	2.25E-7	3.70E-6	5-150
S27R28	8030.1754833(17)	9.582(12)E-28	4.72E-5	-1.43E-6	5.36E-6	2.57E-7	3.91E-6	5-160
T5S6	7943.3447493(35)	1.3339(35)E-28	6.43E-5	8.96E-7	1.00E-7	2.59E-7	9.45E-6	5-50
T7S8	7959.8467071(35)	1.2755(56)E-28	6.34E-5	9.14E-7	5.41E-7	3.47E-7	1.11E-5	5-150
T9S10	7976.1717370(47)	1.1628(14)E-28	6.17E-5	6.91E-7	3.14E-7	4.52E-7	1.15E-5	5-150
T13S14	8008.2845747(59)	7.669(21)E-29	5.85E-5	-3.63E-8	4.13E-7	5.49E-8	1.21E-5	5-150
T15S16	8024.066710(24)	5.688(12)E-29	5.66E-5	-5.31E-8	3.80E-7	1.88E-7	1.15E-5	5-150
T19S20	8055.065516(24)	2.5522(37)E-29	5.25E-5	-1.05E-7	4.27E-7	2.61E-7	1.15E-5	5-150
T23 S24	8085.282656(42)	8.910(57)E-30	4.69E-5	-4.13E-7	1.80E-7	3.43E-7	9.18E-6	5-150

402

403 *Note*

404 *The uncertainty on the zero-pressure line positions (ν_0) and on the line intensities (S_{296K}) are given in the unit of the last quoted digit and corresponds to*
 405 *statistical errors (1σ) (see Text).*

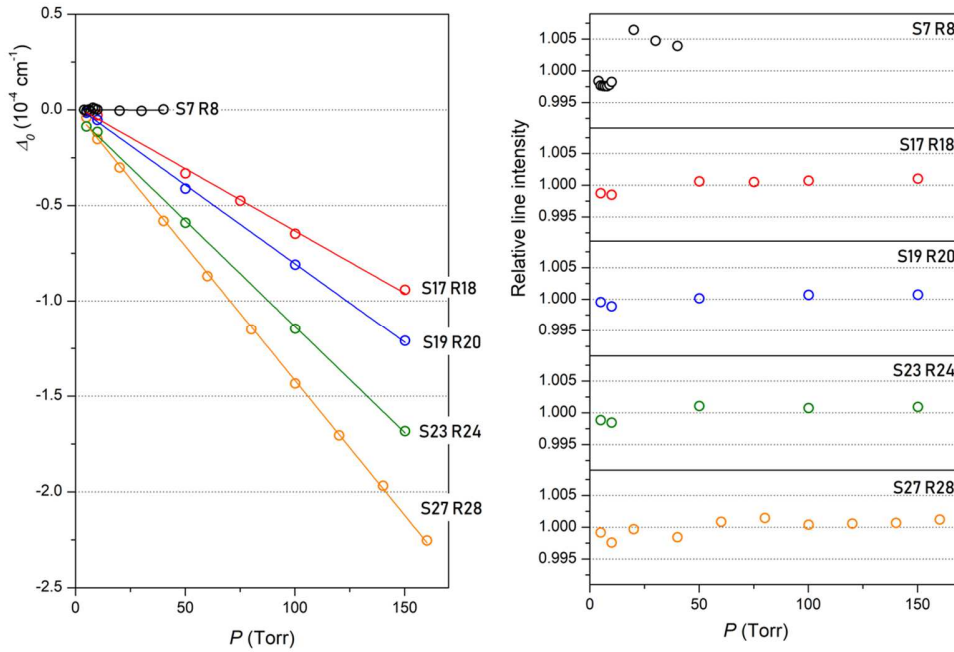
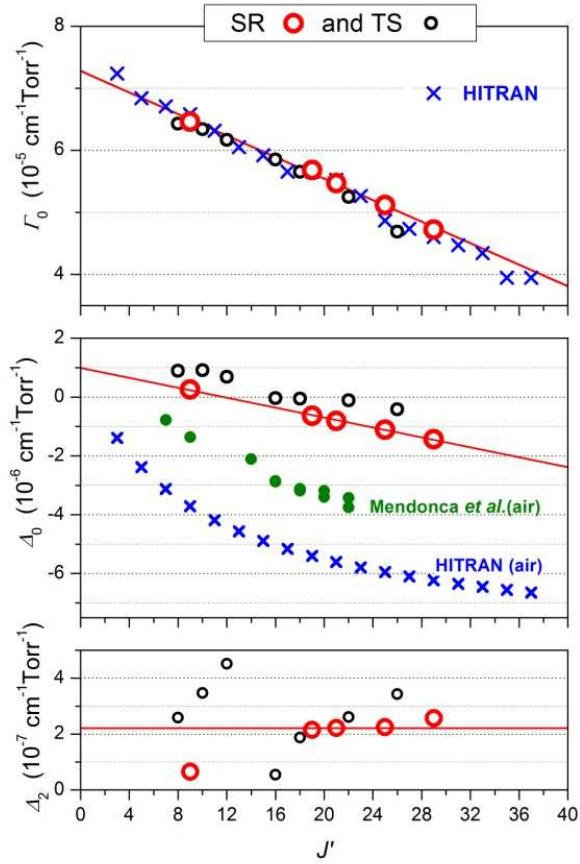


Fig. 7

Pressure dependence of the position shifts (Δ_0) and of the line intensities ($S_{296\text{K}}$) obtained by the qSDNGP multispectrum fit for the five SR lines selected.

The J' dependence of the Γ_0 , Δ_0 and Δ_2 line-shape parameters of the twelve selected lines is presented in **Fig. 8**. The pressure-shift and pressure-broadening parameters show a mostly linear J' dependence for J' between 8 and 37. The Γ_2 parameter is known to be strongly correlated with the Dicke narrowing parameter (ν_{vc}) [45, 46] which leads to a large dispersion of values in particular for the weaker TS E2 lines. This correlation is illustrated by the ν_{vc} values obtained for S17R18 and S19R20 which differ by a factor of 2 and seem anticorrelated with Γ_2 values (see **Table 2**). Thus the physical significance of ν_{vc} and Γ_2 parameters as obtained in our treatment is probably limited.

The strongest SR lines were mainly used to fix the empirical J' dependence of the line-shape parameters required for the treatment of all the lines observed in the spectra at 5 and 10 Torr. As a result, the following empirical expressions were obtained (all values in $\text{cm}^{-1}\text{Torr}^{-1}$): $\Gamma_0 = 7.28 \times 10^{-5} - 8.67 \times 10^{-7} J'$, $\Delta_0 = 9.93 \times 10^{-7} - 8.44 \times 10^{-8} J'$, $\Delta_2 = 2.21 \times 10^{-7}$, $\Gamma_2 = 5.30 \times 10^{-6}$, $\nu_{\text{vc}} = 3.53 \times 10^{-6}$. The empirical J dependence of Γ_0 , Δ_0 and Δ_2 are plotted in **Fig. 8** (red solid lines).



423 **Fig. 8**
 424 Dependence of the multi-pressure qSDNGP fitted values of Γ_0 , Δ_0 and Δ_2 of the five SR and seven TS
 425 lines *versus* the upper total angular momentum, J' (red and black open circles, respectively). Values
 426 provided in HITRAN2016 and by Mendonca *et al.* [6] are included for comparison (red crosses and green
 427 full circles, respectively). Note that the displayed Δ_0 pressure shifts are the air-pressure shifts for
 428 HITRAN2016 and Mendonca *et al.* The red lines correspond to the empirical laws used as constraints in
 429 the treatment of the global spectra at 5 and 10 Torr.
 430
 431

432 Constraining the line shape profile according to these empirical laws, the qSDNGP zero-pressure
 433 positions and line intensities were determined from independent fit of the lines observed at 5 and 10 Torr.
 434 The $^{16}O_2$ empirical laws were also adopted for the $^{16}O^{18}O$ and $^{16}O^{17}O$ isotopologues. As all the observed
 435 $^{16}O^{17}O$ transitions have $J' > 7$, their hyperfine structure has a marginal impact on the room temperature line
 436 profile [14]. The obtained qSDNGP lists at 5 and 10 Torr are included in the same Supplementary
 437 Material as the VP line lists.

438 A conservative 500 kHz accuracy is estimated for the zero-pressure line positions of isolated lines
 439 with intensity larger than 10^{-28} cm/molecule. Only a rough estimation can be provided for the accuracy of
 440 our intensity values of our two global qSDNGP lists. In addition to the pressure (0.25%) and temperature
 441 uncertainties (0.15 K), biases due to the choice of the line profile must be considered. Our results were

442 obtained from spectra recorded with a maximum pressure of 150 Torr. The use of relatively small pressure
 443 values helps to minimize biases related to the profile. As a test of our intensity values, we considered the
 444 S27R28 line of the main isotopologue with intensity of 9.28×10^{-28} cm/molecule which was recorded at
 445 500 Torr. Its line intensity at 500 Torr was obtained using the above empirical laws on the line parameters
 446 derived in the 0-150 Torr range. Small but significant residuals were obtained from the fit revealing some
 447 deviations from the empirical laws. Nevertheless, the line intensity was found to deviate by no more than
 448 0.24 % from its low pressure value. Note that the consistency of the intensity values derived from spectra
 449 at different pressures is at the 0.1 % level for four of the five lines displayed in **Fig. 7**. Overall, a 1 %
 450 uncertainty seems to be a reasonable estimate of the total error on the reported intensities for the lines with
 451 intensities larger than 10^{-28} cm/molecule.

452 **4. Discussion. Comparison with literature.**

453 *4.1. Line positions*

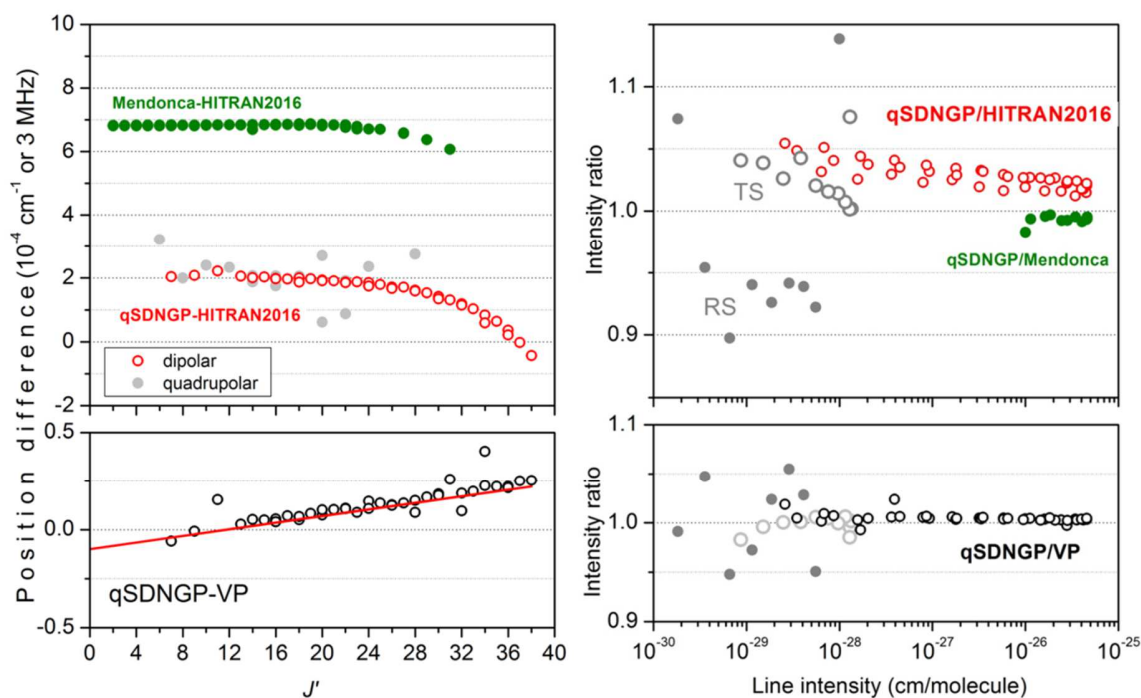
454 We recall that contrary to the qSDNGP positions which are empirically corrected from the pressure
 455 shifts, the VP positions of our global lists were obtained from independent fits (Section 3.1) and thus
 456 include the pressure shifts at 5 or 10 Torr. The (qSDNGP-VP) position differences at 10 Torr plotted
 457 *versus J'* in **Fig. 9** illustrate thus the pressure shifts at 10 Torr. The observed linear increase of the
 458 deviations for J' values up to 40 coincides and thus validates the empirical linear law determined above
 459 from five SR lines (red line in **Fig. 9**).

460 **Fig. 9** includes a comparison to the HITRAN2016 line positions. The HITRAN line positions of the
 461 $a^1\Delta_g - X^3\Sigma_g^-(0 - 0)$ band of $^{16}O_2$ were calculated by difference of the energy levels of
 462 $a^1\Delta_g(0)$ and $X^3\Sigma_g^-(0)$ states obtained by Yu *et al.* [47] from an isotopically invariant Dunham fit of all
 463 the O_2 transitions available in the literature. Only three experimental sources of $a^1\Delta_g - X^3\Sigma_g^-(0 - 0)$ line
 464 positions were available and used by Yu *et al.*: FTS values measured in emission by Amiot and Vergès
 465 [48], FTS absorption values obtained with long path absorption and pressure up to 1.06 bar by Cheah *et al.*
 466 [21] and our CRDS results obtained at a pressure of 50 Torr [13]. Overall, a reasonable agreement is
 467 obtained between the HITRAN2016 positions and the present accurate measurements, HITRAN
 468 deviations decreasing from about to 2×10^{-4} cm $^{-1}$ (6 MHz) for low J' values to a practically zero value
 469 around $J'= 36$. Nevertheless, for most of the lines, the deviations exceed the 10^{-4} cm $^{-1}$ error bar attached to
 470 HITRAN positions. Let us mention that the calculated transition frequencies reported in [13] are larger
 471 than HITRAN values by 2.5×10^{-4} cm $^{-1}$ leading to a consistency at the 5×10^{-5} cm $^{-1}$ level with present
 472 measurements.

473 In their paper, Mendonca *et al.* [6] indicated that their line positions originate from [13] but our
 474 comparison shows that they are larger by a mostly constant value of 4.3×10^{-4} cm $^{-1}$ compared to the

475 calculated values included in [13] ($+6.8\times 10^{-4}\text{ cm}^{-1}$ compared to HITRAN). It leads to differences between
 476 $5\times 10^{-4}\text{ cm}^{-1}$ and $7\times 10^{-4}\text{ cm}^{-1}$, compared to the present values (see Fig. 9).

477



478 **Fig. 9**
 479 Position differences *versus* the upper rotational quantum numbers and intensity ratios *versus* the CRDS
 480 line positions
 481 *Upper panels:* Comparison to HITRAN2016 data (mostly from [4], see Text) and Mendonca *et al.* [6].
 482 Grey symbols correspond to electric quadrupolar transitions.
 483 *Lower panels:* Comparison between our qSDNGP and VP line lists at 10 Torr. The deviation of the
 484 positions values increasing with J' measures the pressure shift at 10 Torr (see Text).
 485
 486

487 The HTRAN line positions of the $^{16}\text{O}^{18}\text{O}$ isotopologue were calculated in [14] using spectroscopic
 488 constants derived from a global fit of CRDS line positions measured from isotopically enriched spectra
 489 and microwave [49] and Raman measurements. Again, a satisfactory agreement is achieved, maximum
 490 deviations being limited to a few 10^{-4} cm^{-1} for the highest J' values which correspond to extremely weak
 491 lines (intensity below $10^{-29}\text{ cm/molecule}$). The average value of the deviations is only $-5.4\times 10^{-5}\text{ cm}^{-1}$ (-1.6
 492 MHz) while the $^{16}\text{O}^{18}\text{O}$ line intensities in natural O_2 are less than $10^{-28}\text{ cm/molecule}$).

493 4.2. Spectroscopic constants of the $a^1\Delta_g(0)$ upper state

494 The zero-pressure qSDNGP line positions were used to determine the spectroscopic constants of the
 495 $a^1\Delta_g(0)$ upper state of the $^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ isotopologues. The qSDNGP position values at 5 and 10 Torr
 496 were used to generate a single recommended list provided as Supplementary Material. The averaged
 497 position values were adopted except for the weakest lines where the 10 Torr value was preferred. The

498 experimental values of the upper energy level value were calculated by adding the ground state (GS)
 499 energy levels of Ref. [47] and fitted using the usual expression:

$$500 \quad F(J') = E + BJ'(J' + 1) - D[J'(J' + 1)]^2 + H[J'(J' + 1)]^3, \quad (1)$$

501 Where E is the energy term value, B is the rotational constant, D and H are the first- and second-
 502 order centrifugal distortion terms, respectively.

503 The obtained spectroscopic constants are presented in **Table 3** and the detailed lists and results of
 504 the fit are provided as a Supplementary Material. By excluding a number of less accurately determined
 505 values, a (meas.-calc.) *rms* value of 108 kHz ($\approx 3.6 \times 10^{-6} \text{ cm}^{-1}$) is achieved for $^{16}\text{O}_2$ with J' values between
 506 7 and 38. As a result of larger error bars on the positions of the weak $^{16}\text{O}^{18}\text{O}$ lines, the corresponding *rms*
 507 value is about a factor of ten larger (1.23 MHz). In addition, the obtained H value seems to be too large
 508 compared to that of the main isotopologue and that obtained in [14] from a larger data set.

509 **Table 3**
 510 Spectroscopic constants of the $\nu=0$ level of the $a^1\Delta_g$ state.

	$^{16}\text{O}_2$		$^{16}\text{O}^{18}\text{O}$	
	This work	Microwave. [49]	This work	Microwave [49]
E	7883.5107617(30)		7885.545863(38)	
B	1.417839009(16)	1.417839 0445(27)	1.33913386(32)	1.339135 0746(75)
D	$5.102390(25) \times 10^{-6}$	$5.102338(85) \times 10^{-6}$	$4.54680(76) \times 10^{-6}$	4.55084(22)
H	$-2.297(11) \times 10^{-12}$	$-2.295(58) \times 10^{-12}$	$-4.35(50) \times 10^{-12}$	
nb of lines	37/62	19	31/62	10
$J'_{min} - J'_{max}$	7-38	2-31	7-31	2-19
<i>rms</i>	$3.6 \times 10^{-6} \text{ cm}^{-1}$ (~108 kHz)	$1.03 \times 10^{-6} \text{ cm}^{-1}$ (31 kHz)	$4.1 \times 10^{-5} \text{ cm}^{-1}$ (1.23 MHz)	$1.40 \times 10^{-6} \text{ cm}^{-1}$ (42 kHz)

511
 512 It is interesting to discuss the obtained parameters in relation of the results reported in [49] from
 513 microwave measurements of rotational lines in the $\nu=0$ level of the $a^1\Delta_g$ state for various
 514 O_2 isotopologues. Drouin *et al.* [49] reported independent isotope fit parameters for six isotopologues, in
 515 particular $^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ (see **Table 3**). Due to the higher precision of the microwave measurements,
 516 smaller standard deviations are achieved but the overall agreement is very satisfactory. These microwave
 517 data were considered in [47] to determine the energy levels of the $\nu=0$ level of the $a^1\Delta_g$ state, used to
 518 compute the HITRAN line positions. Apart from the constant shift between our positions and HITRAN
 519 values (**Fig. 9**), the deviation observed for high J values might be related to the fact that the microwave
 520 measurements were limited to maximum J values of 31 while our input data set extends up to 38.

521 Note that the achieved *rms* of the fits is significantly smaller than the uncertainty on the GS
 522 energy levels used to compute our upper state energy levels (up to around 10^{-4} cm^{-1} for the $J=38$ levels of
 523 $^{16}\text{O}_2$ [47]). The derived constants have then an effective character and will be possibly refined when the
 524 accuracy of the GS levels will be improved. The present measurements limited to the high energy region

525 of the band do not allow for a sufficient number of GS combination relations to improve the GS
 526 spectroscopic constants. Nevertheless, this goal should become achievable when the spectrum of the entire
 527 band will have been recorded.

528 *4.3. Line intensities*

529 The HITRAN2016 line intensities have different sources: (i) M1 line intensities are calculated
 530 values obtained by Orr-Ewing on the basis of FTS intensities measured in [19] completed by values
 531 obtained by Mackie using a global intensity model for the very weak lines [50], (ii) quadrupolar line
 532 strength were calculated in [51], (iii) for the minor isotopologues, calculated values from [14] and [50] are
 533 used.

534 The qSDNGP/HITRAN2016 intensity ratios presented in **Fig. 9**, show that HITRAN intensities of
 535 the $^{16}O_2$ M1 lines are underestimated by about 2 % for the strongest lines and up to 5% for the weakest
 536 measured lines. As concerned TS and RS quadrupole lines, a good agreement is noted for the TS lines. A
 537 systematic overestimation of the HITRAN RS line intensities by about 8 % is apparent but should be
 538 confirmed as all the considered RS line are extremely weak (intensity smaller than 5×10^{-29} cm/molecule).

539 **Fig. 9** includes the comparison with the very recent work by Mendonca *et al.* [6] obtained by line-
 540 by-line SDVP fitting of air-broadened CRDS spectra. A multispectrum treatment was applied to spectra
 541 acquired at pressure of 495, 742.5.0 and 982.6 Torr. A very good agreement (better than 1 %) is noted
 542 between the intensity values derived by Mendonca *et al.* and our values.

543 *4.4. Line profile parameters*

544 As mentioned above, previous line profile studies of the $a^1\Delta_g-X^3\Sigma_g^-$ band in pure O_2 are scarce
 545 (see **Table 4**) and were performed by FTS using a Voigt profile. The value of the self-broadening
 546 parameter (Γ_0) reported in [20, 21] are overestimated. The most complete FTS study of the line-
 547 broadening was performed by Newman *et al.* [19] and includes the determination of the temperature
 548 exponent from spectra recorded at 294, 243 and 200 K for N'' values up to 23. The empirical law
 549 estimated from their results at 294 K shows a good agreement with our results (see **Table 4**).

550 **Table 4**

551 Comparison to literature values of the self-broadening (Γ_0) and self-pressure shift (Δ_0) of the $a^1\Delta_g-X^3\Sigma_g^-$
 552 O_2 band.

	Γ_0 (cm ⁻¹ Torr ⁻¹)	Δ_0 (cm ⁻¹ Torr ⁻¹)
Lafferty1998 [20]	$1.37(10)\times 10^{-4}$	
Cheah2000 [21]	$1.03(7)\times 10^{-4}$	$-4.6(2.1)\times 10^{-7}$
Hill2003 [22]		$ \Delta_0 < 2.6\times 10^{-6}$
Newman2000 [19]	$7.5\times 10^{-5}-1.05\times 10^{-7}N''^a$	
<i>This work</i>	$7.28\times 10^{-5}-8.67\times 10^{-7}J^b$	$9.93\times 10^{-7}-8.44\times 10^{-8}J^b$

553 *Note*

554 ^a Empirical expression estimated from Fig. 5 of [19].

555 ^b See Section 3.2 and Fig. 8

556 Two sources are used in HITRAN2016 for the self-collisional broadening values of the the $1.27\mu m$
 557 band under study. Both are related to the A-band: (i) Brown and Plymate performed a series of FTS
 558 recordings with pure O_2 and air and determine the corresponding broadening coefficients [24], (ii)
 559 Washenfelder *et al.* [4], increased by 1.5% the values from Yang *et al.* [52] to better reproduce their FTS
 560 atmospheric spectra of the $1.27\mu m$ O_2 band. While self-collisional broadening coefficients were
 561 determined in [24], atmospheric spectra provided information about air-collisional broadening coefficients
 562 and it is unclear how the air-coefficients of Ref. [4] were converted to self-collisional broadening
 563 coefficients in HITRAN2016. Nevertheless, in the case of the A-band, the differences between self- and
 564 air-broadening coefficients are small [23] and according to the FTS study of the $1.27\mu m$ band by
 565 Newman *et al.* “The effects of pressure broadening of lines by N_2 are indistinguishable from those for pure
 566 O_2 at the same temperature and pressure” [19]. The comparison of HITRAN values to our values included
 567 in **Fig. 8** shows a very good agreement, thus indicating that the broadening coefficients in the A-band and
 568 in the $1.27\mu m$ band are very close.

569 The self-pressure shift is very small in the considered band (about one order of magnitude smaller
 570 than in the A-band [23]) and thus difficult to measure: Δ_0 decreases from $+1\times 10^{-6}$ to -2×10^{-6} $cm^{-1}Torr^{-1}$
 571 when J' increases from 0 to 35 (see **Fig. 8**). Only an upper limit of its magnitude (2.6×10^{-6} $cm^{-1}Torr^{-1}$)
 572 could be reported from FTS recordings with O_2 pressures up to 3 atm [22]. From recordings at 1.06 bar,
 573 Cheah *et al.* retrieved a very approximate constant value ($-4.6(2.1)\times 10^{-7}cm^{-1}Torr^{-1}$ [21]) which is
 574 reasonable when compared to our measurements.

575 Self-pressure shifts are not included in the HITRAN database. We have included in **Fig. 8** the
 576 HITRAN values of the air-pressure shifts values taken from [4] and thus relative to the A-band. The
 577 magnitude of our self-pressure shifts in the $1.27\mu m$ band is considerably smaller. The values reported by
 578 Mendonca *et al.* [6] from air-broadened CRDS spectra in the same $1.27\mu m$ band have also a much larger
 579 amplitude. Although the values of Mendonca *et al.* were obtained from spectra recorded at much higher
 580 pressure than ours and analyzed with a different line profile (SDVP against qSPNGP), the most probable
 581 explanation of the observed differences between self- and air-shifts values in the $1.27\mu m$ band is that the
 582 O_2 -shifts have a significantly smaller amplitude than the N_2 shifts. This is indeed what was evidenced in
 583 the A-band (see Fig. 11 in [23]).

584 **5. Concluding remarks**

585 The first profile analysis of lines of the O_2 $a^1\Delta_g - X^3\Sigma_g^-(0-0)$ band in pure O_2 has been
 586 performed by CRDS coupled to a self-referenced frequency comb. The sensitivity of the recordings ($\alpha_{min}\sim$
 587 $10^{-12}cm^{-1}$), have allowed using low pressure values and thus reducing the impact of the line profile on the
 588 determination of the zero-pressure line center and of the line intensities. In particular line mixing effects
 589 are negligible at the pressure of the recordings. Important deviations from the standard Voigt profile are

590 evidenced even for pressure values limited to a few Torr. The quadratic Speed-Dependent Nelkin-Ghatak
591 profile was found to allow a satisfactory reproduction of the observed profiles. Overall, about 167 lines
592 including electric quadrupole transitions with intensity as 10^{-30} cm/molecule were measured in the high
593 energy part of the band accessible with the ECDL at disposal (7920-8085 cm^{-1} interval). A conservative
594 500 kHz accuracy is estimated for the zero-pressure line positions of isolated lines with intensity larger
595 than 10^{-28} cm/molecule. The small self-pressure shifts of the line centers are reported for the first time. The
596 spectroscopic constants of the $a^1\Delta_g(0)$ upper state of the $^{16}\text{O}_2$ and $^{16}\text{O}^{18}\text{O}$ isotopologues were determined
597 from a fit of the zero-pressure qSDNGP line positions. A standard deviation of 108 kHz (3.6×10^{-6} cm^{-1})
598 was achieved by using 37 line centers of $^{16}\text{O}_2$ corresponding to J values between 7 and 38. Taking into
599 account that the values of the ground state energy levels are not known with such accuracy [47], the full
600 spectral coverage of the considered O_2 band with similar accuracy will probably allow improving not only
601 the $a^1\Delta_g(0)$ upper state constants but also the $X^3\Sigma_g^-(0)$ GS constants.

602 Most of the measured line positions show deviations exceeding the 10^{-4} cm^{-1} error bar attached to
603 HITRAN positions. As concerned line intensities, HITRAN values are found to be underestimated by 2-4
604 % compared to our values.

605 The next step of our CRDS study of this band will be to extend the study to the low energy region
606 using a different CRDS spectrometer. The use of two different CRDS setups will allow checking the
607 consistency of the claimed accuracy of the line position (estimated to be 500 kHz in the present work). A
608 global intensity modeling including the different branches of magnetic dipole and electric quadrupole
609 transitions will be then undertaken. Additional laboratory work is still required to fulfill the needs for
610 remote sensing applications. It concerns in particular the air-broadened profiles, the temperature
611 dependence of the line profile parameters (and of the CIA) and line mixing effects which have an
612 important impact at atmospheric pressures remain to be characterized in particular in the region of the Q
613 branch.

614
615 **Acknowledgements**

616 M. K acknowledges financial support from the French Embassy in Poland. This work was
617 performed in the frame of the LabexOSUG@2020 (ANR10 LABX56). A partial support from CNES is
618 acknowledged. We are grateful to the reviewers for their useful and constructive suggestions.

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