

The absorption spectrum of nitrous oxide between 7647 and 7918 cm–1 $\,$

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1 2	The absorption spectrum of nitrous oxide between 7647 and 7918 ${ m cm}^{-1}$	
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44 45

Abstract

We revisit the room temperature absorption spectrum of natural nitrous oxide recorded by 46 high sensitivity cavity ring down spectroscopy between 7647 and 7918 cm⁻¹ (1.31–1.26 µm) reported 47 48 by Liu et al. (doi: 10.1016/j.jms.2011.03.025). In this previous analysis, 2272 transitions could be as-49 signed in the region and no intensity information was provided. In the present work, on the basis of 50 improved predictions of the effective operator models, the assignments could be extended to more 51 than 3200 transitions and, more importantly, line intensities are provided for all the transitions. The assigned transitions belong to 49 bands of the ${}^{14}N_2{}^{16}O$, ${}^{14}N^{15}N^{16}O$, ${}^{15}N^{14}N^{16}O$, ${}^{14}N_2{}^{18}O$, and ${}^{14}N_2{}^{17}O$ iso-52 53 topologues, 16 being newly assigned. All the identified bands correspond to the ΔP = 14 series of transitions, except for four ΔP = 12 and two ΔP = 13 bands of the ¹⁴N₂¹⁶O isotopologue (P= 2 V_1 + V_2 +4 V_3 54 55 is the polyad number where $V_{i=}$ 1-3 are the vibrational quantum numbers). For comparison, the 56 HITRAN2020 database includes only the v_1+3v_3 band of the main isotopologue and a number of calculated line parameters for the fourth minor isotopologue, ${}^{14}N_2{}^{18}O$. 57

The band-by-band analysis provides accurate spectroscopic parameters of 46 bands from a fit of the measured line positions. Nine resonance perturbations were identified including a few extra lines for two ${}^{14}N_{2}{}^{16}O$ bands. The interaction mechanisms and the perturbers were assigned on the basis of the effective Hamiltonian models.

62 The comparison with current spectroscopic databases (HITRAN, HITEMP, NOSD) is discussed. 63 All show significant deviations compared to the reported results (*e.g.* for ΔP = 13 band intensities). 64 The reported results will be thus valuable to more accurately account for the absorption of nitrous 65 oxide in the region.

66 **1. Introduction**

67 Nitrous oxide is a powerful greenhouse gas with a warming effect power about 300 times 68 stronger than carbon dioxide. Its atmospheric concentration of about 330 ppb is increasing at a rate 69 of about 1 ppb/year. The atmospheric importance of N_2O makes an accurate characterization of its 70 absorption spectrum suitable. We are involved in a long-term project aiming at a study of the high 71 sensitivity absorption spectrum of nitrous oxide by cavity ring down spectroscopy (CRDS) in the near-72 infrared. Fig. 1 presents an overview of the spectral intervals studied by CRDS within the last fifteen 73 years. Overall, the 5696-8630 cm⁻¹ range was continuously covered by CRDS [1-11]. The HITEMP [12] and HITRAN2020 [13] lists of ¹⁴N₂¹⁶O are included in the plot. The HITRAN list corresponds to an 74 intensity cut off of 2×10⁻²⁵ cm/molecule at 296 K *i.e.* about 4 orders of magnitude above the CRDS 75 76 detectivity threshold. The HITEMP line list for N₂O is a mixture of the NOSD-1000 [21] and 77 HITRAN2016 [22] data. The NOSD-1000 list is a calculated line list with positions obtained using an 78 effective Hamiltonian (EH) model with parameters fitted on experimental positions [14] and 79 intensities computed from effective dipole moments (EDM) with parameters fitted on measured line 80 intensities [15]. In the studied regions, the CRDS studies provide the main source of line positions 81 used to refine the parameters of the EH models. As concerns line intensity calculations, they require 82 a set of EDM parameters for each ΔP value ($P = 2V_1 + V_2 + 4V_3$ is the polyad number where $V_i = 1-3$ are 83 the vibrational quantum numbers). We have highlighted in Fig. 1, the transitions for which intensity 84 information was retrieved from the CRDS spectra. Line intensities were obtained for only part of the 85 recorded CRDS spectra which makes some sets of EDM inaccurate or incomplete and leads to strong 86 deviations between the HITEMP line list and the recorded CRDS spectra (see e.g. Ref. [10].

In the present work, we reconsider the spectral region between 7647 and 7918 cm⁻¹, first 87 88 analyzed by Liu et al. [7] in 2011. In that work, 2272 transitions could be assigned but no intensity 89 information was provided. Here, using the same spectra, line intensities are systematically retrieved. 90 We have included in the lower panel of Fig. 1 a review of the intensity information available in the 91 literature in the considered region. It is limited to two studies by Fourier transform spectroscopy 92 (FTS) by Daumont et al. [15] and Toth [16]. The former is the more sensitive. It was performed with an absorption path length of 48.26 m and corresponds to a detectivity threshold of about 10⁻²⁶ 93 cm/molecule, to be compared to a 10^{-29} cm/molecule value for the weakest lines measured by CRDS. 94

95 This paper is organized as follows. The experimental setup and the construction of the 96 measured lists are briefly described in Section 2. In Section 3, we present the spectra analysis by 97 comparison with the effective operator predictions which added about 900 new rovibrational 98 assignment transitions compared to Ref. [7]. The band-by-band fitting of the G_v , B_v . D_v , and H_v band 99 parameters and identification of resonance perturbations are presented in Section 4 before the 100 discussion of the comparison with current spectroscopic databases (Section 5).



101

102 Fig. 1.

103 Overview of various line lists of ${}^{14}N_2{}^{16}O$ between 5500 and 9000 cm⁻¹

104 *Upper panel:* HITEMP and HITRAN2020 line lists (grey and green symbols, respectively). The 105 range of previous CRDS investigations is indicated: (a): 5696- 5910 cm⁻¹ [1], (b) 5905-7066 cm⁻¹ [2-4], 106 (c) 6950-7653 cm⁻¹ [5,6], (d) 7647-7918 cm⁻¹ [7], (e):7915-8334 cm⁻¹ [8,9], (f): 8320-8622 cm⁻¹ [10,11] 107 and this work. Red circles correspond to CRDS intensities previously reported.

Lower panel: Enlargement of the (d) region corresponding to the range of the present study.
 FTS line lists of Refs. [15,16] (magenta and blue dots, respectively) and the present CRDS list (red circles) are superimposed to the HITEMP list [12] (grey).

112 **2.** Experimental details and line list construction

113 The description of the CRDS recordings is presented in Refs. [7,17] and not repeated here. 114 Ten fibered distributed feed-back (DFB) diode lasers were used as light sources in order to cover continuously the 7647-7918 cm⁻¹ region, except for an inaccessible gap between 7896.87 and 7901.17 115 116 cm⁻¹. Two series of spectra were recorded at a temperature of 293 K, for pressure values of 1 and 10 117 Torr. The 1 Torr spectra cover the low energy range (7647-7818.5 cm⁻¹) while the high energy region (7715-7918 cm⁻¹) corresponding to weaker absorption were recorded at 10 Torr. The typical value of 118 the noise equivalent absorption coefficient was $\alpha_{min} \sim 1 \times 10^{-10}$ cm⁻¹ (see Fig. 2 of Ref. [7]). The wave-119 120 number scale of the spectra was calibrated with the help of a lambdameter and accurate reference line positions of H₂O (present as an impurity) taken from the HITRAN database [13]. Each spectral 121 interval corresponding to the tuning range of one DFB laser diode (~20 cm⁻¹) was calibrated inde-122 123 pendently [7]. As indicated in Ref. [7], the maximum differences between line positions measured on 124 the overlapping part of two successive spectra are less than of 2×10^{-3} cm⁻¹ which leads to the 1×10^{-3} 125 cm⁻¹ average uncertainty value. Nevertheless, for the highest interval (7901-7918 cm⁻¹), the frequen-126 cy calibration could not be checked in Ref. [7] by comparison with the nearby intervals. Here, by 127 comparison with the line positions from Ref. [8] above 7915 cm⁻¹, we found that the frequency calibration of Ref. [7] for the 7901-7918 cm⁻¹ interval has to be corrected by decreasing the wavenumber 128 129 scale by 0.0025 cm⁻¹ (this correction was validated by lower state combination relations performed 130 during the band-by-band analysis).



131 132

132 Fig. 2

133 Overview of the N₂O line list including the measurements at 1 and 10 Torr (black and red circles) and

134 their averaged values (blue circles).

136 The line centers and intensities were determined using an interactive least squares multi-line 137 fitting program assuming a Voigt function for the line profile The accuracy of the measured line in-138 tensities is about 3% or better for most lines and up to 20% for the weakest or strongly blended lines. 139 The complete line lists retrieved from the 1 Torr and 10 Torr spectra consist of 2185 and 2591 140 lines, respectively. In order to generate a single line list, in the overlapping part of the 1 and 10 Torr recordings (7715-7818.5 cm⁻¹), line parameters were averaged for the lines with intensity in the 10⁻²⁷ 141 - 2×10⁻²⁵ cm/molecule range and for the weakest and strongest lines, the 10 Torr and 1 Torr line 142 143 parameters were retained.

Overall, the global line list includes about 4100 entries. Lines due to water vapor, present as an impurity (73 and 38 lines at 1 and 10 Torr, respectively) were identified using the HITRAN line list [13] and removed from the list. The overview of the ${}^{14}N_{2}{}^{16}O$ line list obtained at the final stage of the assignment process (see below), is presented in **Fig. 2** with distinct colors according to the origin of the line parameters.

3. Rovibrational analysis

151 Overall, 3219 lines belonging to 49 bands of ${}^{14}N_2{}^{16}O$, ${}^{14}N{}^{15}N{}^{16}O$, ${}^{15}N{}^{14}N{}^{16}O$, ${}^{14}N_2{}^{18}O$, and 152 ${}^{14}N_2{}^{17}O$ were identified. Except for four ΔP = 12 bands and two ΔP = 13 bands of the ${}^{14}N_2{}^{16}O$ isoto-153 pologue, all the bands belong to the ΔP = 14 series of transitions. **Fig. 3** compares the CRDS observa-154 tions of the five N₂O isotopologues with the corresponding predictions of the respective effective 155 operator models. The assignments were carried out based on the predictions of the global effective 156 Hamiltonian models.

157 For ¹⁴N₂¹⁶O, we used the non-polyad EH model [14]. In this model the eigenstates of the EH 158 are not localized within a polyad. This means that all ΔP series of the transition intensities must be 159 fitted with a single set of effective dipole moment parameters. This non-polyad EDM model is a gen-160 eralization of the polyad EDM model which was used to fit the N₂O intensities so far (see e.g. [15]). 161 The non-polyad EDM model of the line intensities will be presented in a separated publication. For 162 other isotopologues, the polyad EH models [9,18] were used with a set of EH parameters refined using new line positions from Refs. [11,14,15,18]. For ¹⁴N₂¹⁷O line positions, we refitted data pre-163 164 sented in Ref. [19] using measurements from Refs. [1,3,7,8].

165 In our region, all the observed bands of the minor isotopologues belong to the ΔP = 14 series 166 of transitions. For each minor isotopologue, the corresponding EDM parameters were fitted to the 167 measured intensities reported in [8] and then used to predict the line intensities.

168 **Table 1**

169 Comparison of the number of transitions and bands for the different N_2O isotopologues reported in 170 Ref. [7] and obtained by CRDS in this work in the 7647–7918 cm⁻¹ region.

171

Isotopologue	Abundance [13]	Number of transitions ^a	Number of bands ^a
¹⁴ N ₂ ¹⁶ O	0.990333	2451(1746)	36(24)
¹⁴ N ¹⁵ N ¹⁶ O	3.64093×10 ⁻³	151(89)	3(2)
¹⁵ N ¹⁴ N ¹⁶ O	3.64093×10 ⁻³	291(167)	5(3)
¹⁴ N ₂ ¹⁸ O	1.98582×10 ⁻³	268(210)	4(3)
¹⁴ N ₂ ¹⁷ O	3.69280×10^{-4}	58(60)	1(1)
Total		3219(2272)	49(33)

172

173 Note
 174 ^a Numbers given within parentheses correspond to Ref. [7].

175

470

176**Table 1** compares the number of lines and bands identified in this work to our previous177analysis of the same spectra in Ref. [7]. Compared to Ref. [7], 950 transitions are newly assigned and178sixteen of the 49 bands are new (12, 1, 2 and 1 for ${}^{14}N_2{}^{16}O$, ${}^{14}N^{15}N^{16}O$, ${}^{15}N^{14}N^{16}O$, and ${}^{14}N_2{}^{18}O$, respec-179tively). Note that the rotational structure of 23 of the bands identified extends below or above the180studied 7647–7918 cm⁻¹ region. In the following band-by-band analysis, the dataset of these bands181will be complemented with measurements from Ref. [5] or Ref. [8] in the 6950-7653 cm⁻¹ and 7915-

182 8334 cm⁻¹ regions, respectively (see Fig. 1). Overall, twelve bands (8, 1, 2 and 1 for ${}^{14}N_2{}^{16}O$, ${}^{14}N^{15}N^{16}O$, 183 ${}^{15}N^{14}N^{16}O$, and ${}^{14}N_2{}^{18}O$, respectively) and four sub-bands of ${}^{14}N_2{}^{16}O$ are newly measured. They are 184 marked with "N" in Table 2.





186 Fig. 3

187 Overview comparison between the transitions of ${}^{14}N_2{}^{16}O$ (446), ${}^{14}N^{15}N^{16}O$ (456), ${}^{15}N^{14}N^{16}O$ (546), 188 ${}^{14}N_2{}^{18}O$ (448), and ${}^{14}N_2{}^{17}O$ (447) assigned between 7647 and 7918 cm⁻¹ (right panels) and the 189 corresponding spectra predicted in the frame of the effective operator approach (left panels).

190The experimental line list, provided as Supplementary Material, includes the experimental191and EH calculated positions and intensities for each line, together with corresponding rovibrational192assignments and the measured line positions from Ref. [7] for comparison. Compared to Ref. [7], the193transition dataset has been extended by about 950 new assignments and thus the fraction of194unassigned lines is significantly reduced. About 230 and 570 lines at 1 and 10 Torr, respectively, are

195 left unassigned in the 7647-7918 cm⁻¹ region. Most of them are very weak and not organized in
196 regular series.

- 197 **4. Band-by-band analysis**
- 198 *4.1. Band parameter fits*

199 In the case of unperturbed bands, the rotational analysis was performed using the standard200 equation for the vibration–rotation energy levels:

201

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

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

204 The spectroscopic parameters of the different upper states were fitted to the measured 205 transition wavenumbers with lower state constants constrained to the values obtained by Toth 206 [16,20]. Different sets of parameters were fitted for the e and f levels as the e and f sub bands may 207 be perturbed in a different way (see below). In the case of upper states observed through different 208 bands and branches, a global fit was performed in order to provide a unique set of parameters for 209 each upper state. The detailed results of the band-by-band fit of the spectroscopic parameters are 210 provided as Supplementary Material. Note that the rotational structure of 23 bands extend below or above the studied 7647–7918 cm⁻¹ region under study. The line position dataset of these bands was 211 212 complemented with measurements from Ref. [5] and Ref. [8] in the 6950-7653 cm⁻¹ and 7915-8334 213 cm⁻¹ regions, respectively (see **Fig. 1**). The added lines are tagged with their source in the fit results 214 provided as Supplementary Material.

The retrieved constants of the upper states are listed in **Table 2**. The bands are ordered according to their band centers. Due to the reduced input data set (see Table 2 for details), for three very weak ${}^{14}N_{2}{}^{16}O$ hot bands, we give only the band center provided by the global effective Hamiltonian. The typical *rms* values of the fits are on the order of 1×10^{-3} cm⁻¹, which is consistent with our claimed accuracy on the line positions.

4.2. Local perturbations

Among the 49 analyzed bands, nine local perturbations were evidenced. The interaction mechanism, the perturber state and the *J* value of the angular momentum quantum number corresponding to the energy crossing was identified on the basis of the EH predictions (see **Table 3**).

225 Table 3

- 226 Local resonance interactions identified in the N₂O bands studied between 7647 and 7918 cm⁻¹
- 227

Isotopologue	Affected bands	Interacting states	J _{cross}	Interaction mechanism	Ref. ^a	
	2003e-1000e	$(1607) \leftrightarrow (1606)$	32	Intranolyad anharmonic	[7]	
	0802e-0200e		52	intrapolyad annarmonic	[7]	
	2003e-0200e	$(16\ 0\ 7) \leftrightarrow (16\ 0\ 6)$	32	Intrapolyad anharmonic	ΤW	
	1223e–0220e	(16 2 7) (15 1 12)	<i>e</i> : 32	Internetived Corielis	[7]	
¹⁴ N ¹⁶ O	1223f–0220f	$(1027) \leftarrow (15115)$	<i>f</i> : 32	interpolyad corions	[7]	
	3112e-0110e		<i>e</i> : 46	Intropolyad apparmania	[8]	
	3112f-0110f	$(15 1 7) \leftrightarrow (15 1 8)$	<i>f</i> : 40	intrapolyau annarmonic		
	22020 02000	$(16\ 0\ 10) \leftrightarrow (16\ 2\ 16)$	26	Intrapolyad anharmonic + I-type	[8]	
	52028-02008	$(16\ 0\ 10) \leftrightarrow (16\ 0\ 9)$	49	Intrapolyad anharmonic	TW	
	3202e-1000e	$(16\ 0\ 10) \leftrightarrow (16\ 2\ 16)$	26	Intrapolyad anharmonic +/-type	TW	
¹⁴ N ¹⁵ N ¹⁶ O	2202e-0000e	$(14\ 0\ 8) \leftrightarrow (14\ 2\ 12)$	34	Intrapolyad anharmonic + I-type	TW	
¹⁵ N ¹⁴ N ¹⁶ O	20020 00000	$(14\ 0\ 8) \leftrightarrow (14\ 2\ 11)$	48	Intrapolyad anharmonic + <i>I</i> -type	[8]	
N-N-0	5002e-0000e	$(14\ 0\ 8) \leftrightarrow (14\ 0\ 6)$	35	Intrapolyad anharmonic	[8]	
¹⁴ N ₂ ¹⁷ O	1003-0000	$(1403) \leftrightarrow (1402)$	70	Intrapolyad anharmonic	[7]	

228 229

230

Note ^{*a*} First report of the considered perturbation.

231 232 The (15 1 7) state (3112 in normal mode notation) is connected to the (15 1 8) state by an 233 intrapolyad anharmonic interaction which induces an intensity transfer around the energy crossing at 234 J= 46 and J= 40 for e and f sublevels, respectively. The 3112-0110 perturbed band is centered near 235 7970.4 cm⁻¹, thus above the spectral region under study. Most of the band was analyzed in Ref. [8] 236 where the perturbation and the interaction mechanism were identified. Here, we observed part of 237 the P-branch and we could newly identify 33 and 18 lines for e and f sublevels, respectively. A total of 238 9 extra lines could be assigned for the 3112e-0110e band around the J crossing value of 46, including 239 some taken in the unassigned line list of Ref. [8]. The line parameters of these extra lines are includ-240 ed in the Supplementary Material. The residuals between the measured line positions of the 3112-241 0110 band and those calculated by using the spectroscopic constants of **Table 2** are presented in **Fig.** 242 4.

243 Similarly, most of the rotational structure of the perturbed 3202-0200 band centered near 7940.1cm⁻¹ is located above our region and the perturbation was first evidenced in Ref. [8]. The 244 245 3202e upper state [(16 0 10) in cluster labelling notation] is in resonance anharmonic + l-type interac-246 tion with the (16 2 16) state around the energy crossing at J = 26. Due to intensity transfers, 6 extra 247 lines around the crossing value J= 26 were identified in this work, one of them was assigned by using 248 the unassigned line list of Ref. [8]. Also, another local perturbation affects the (16 0 10) state around 249 J=49. It is due to an intrapolyad anharmonic interaction with the (16 0 9) state. Fig. 4 includes the 250 plot of the deviations between the measured values of transition wavenumbers of the 3202e-0200e

band at 7940.2 cm⁻¹ and the corresponding values calculated using the spectroscopic constants of

252 Table 2.

253



254 255 Fig. 4

Energy differences between the measured values and the values calculated using the spectroscopic parameters of Table 2, for the upper levels of two ${}^{14}N_2{}^{16}O$ bands affected by local perturbations. For each J_{upper} value, the values corresponding to the R(J_{upper} -1) (dots) and P(J_{upper} + 1) (open circles) are plotted. The two considered bands have their center located above the presently studied region (7647-7918 cm⁻¹) and only part of the Pbranches was observed. The remaining part of the rotational structure was observed in Karlovets et al. [8] and is included in the plots.

262 Left panels

263 3112-0110 band at 7970.4 cm⁻¹. The (15 1 7) upper state is perturbed by an intrapolyad anharmonic interaction 264 with the (15 1 8) state (energy crossing at *e*: *J*= 46; *f*: *J*= 40).

265 Right panel

2663202e-0200e band at 7940.1 cm⁻¹. The (16 0 10) upper state is perturbed by an intrapolyad anharmonic +/-type267interaction with the (16 2 16) state (energy crossing at J = 26) and by an intrapolyad anharmonic interaction268with the (16 0 9) state (energy crossing at J = 49).

```
270 In the case of {}^{14}N^{15}N^{16}O isotopologue, only the 2202e-0000e was found strongly perturbed.
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- 271 The interaction mechanism is presently identified as an intrapolyad anharmonic + *l*-type interaction
- between the (14 0 5) bright state and the (14 2 12) dark states with an energy crossing at J= 34. Fig. 5
- 273 illustrates the effect of the resonance interaction. The perturbation induces a shift of the line posi-
- tions up to 0.02 cm⁻¹ around the energy crossing at J= 34.



275 276 Fig. 5

Position differences between the measured line positions of the 2202e-0000e band ($^{14}N^{15}N^{16}O$) at 7880.386 cm⁻¹ and the calculated ones using the spectroscopic parameters of Table 2. For each J_{upper} value, the values corresponding to the R(J_{upper} -1) (red circles) and P(J_{upper} + 1) (blue circles) are plotted. The (14 0 5) upper state is perturbed by an interpolyad anharmonic +*I*-type interaction with the (14 2 12) state (energy crossing at J = 34).

282

Several occurrences of intrapolyad interaction were already evidenced for the ${}^{15}N^{14}N^{16}O$ [8] and ${}^{14}N_2{}^{17}O$ [7] isotopologues. In particular, the upper state of the v₁ + 3v₃ band of ${}^{14}N_2{}^{17}O$ isotopologue is perturbed by an anharmonic interaction with the (14 0 2) state around the energy crossing at *J* = 70. The 3002e-0000e band of ${}^{15}N^{14}N^{16}O$ is perturbed by an anharmonic and an anharmonic +*I*-type interaction at *J* = 35 and *J*= 48, respectively.

288

5. Comparison with the calculated line lists

As detailed above, our assignments rely on improved predictions of the spectrum of the various N₂O isotopologues in the frame of the effective operator approach. Below, we first compare the observations to these (unpublished) predictions and then present the comparison to the available databases, namely HITRAN2020 [13], Nitrous Oxide Spectroscopy Databank (NOSD) [21] and HITEMP [12].

- 294
- 295

296 5.1. Present predictions

297 Fig. 6 and Fig. 7 show an overview comparison between the observations and the predictions 298 presently used for the spectrum analysis, for the line positions and line intensities, respectively. 299 Overall, the agreement is satisfactory for line positions with deviations less than 0.02 cm⁻¹ for the 300 various isotopologues. This was expected as the line position measurements of Ref. [7] are part of 301 the input data used to refine the used EH parameters. Nevertheless, significant differences are ob-302 served with deviation values depending on the vibrational bands. The largest disagreements, on the order of 0.04 cm⁻¹, are noted for the newly assigned 1113-0110 band of ¹⁴N₂¹⁸O. For the main 303 304 isotopologue, deviations with clear rotational dependence are noted for the 3820e-0220e band. This 305 is probably related to the fact that the 3820e upper state is perturbed by an interpolyad Coriolis in-306 teraction with the 5510e state. The crossing point is around J= 26. The corresponding interaction 307 term (ΔV_1 = -2, ΔV_2 = 3, ΔI_2 = 1, ΔV_3 = 0) was accounted in our global fit *via* the main Coriolis parameter, 308 only. The observed deviations indicate that the main term is not sufficient. In the next EH fits of ¹⁴N₂¹⁶O line positions, additional parameters will be added to better account for this Coriolis cou-309 310 pling.

The measured ¹⁴N₂¹⁶O line intensities are in reasonable agreement with the values predicted 311 312 by the effective operator model (upper panel of Fig. 7) but important deviations are noted for some 313 bands (note the logarithmic scale adopted for the ratios). As a rule, the deviations are due to under-314 estimated calculated values due to some missing or inaccurate EDM parameters. For instance, the 315 largest discrepancies (more than a factor 10) concern the 3311-0000 and 4111-0000 bands belonging 316 to the ΔP = 13 series. These are the first ΔP = 13 bands observed with Δv_3 = 1. Thus, the EDM parame-317 ters needed to model the intensities of such bands are unknown and the intensity values cannot be 318 predicted accurately.

319 As concerns minor isotopologues (lower panel of Fig. 7), it is worth underlying that the exper-320 imental values should be taken with cautious as they rely on the (reasonable) assumption that the 321 used sample has a natural isotopic abundance. Nevertheless, we can insure that, for a given 322 isotopologue, the band-by-band change of the ratios is due to the calculations. For instance, the average ratios of the different ¹⁴N₂¹⁸O bands show large variations with a more than one order under-323 324 estimation of the calculated intensity values for the 3002-0000 band. This band (as all those of the 325 minor isotopologues in the region) belong to the ΔP = 14 series of transitions. The 3002-0000 band is 326 a ΔP = 14 band with Δv_3 = 2. There are two bands of this series (ΔP = 14 and Δv_3 = 2) previously measured, namely the cold 2202e-0000e band [8] and the hot band 2312e/f-0110e/f [9]. The main EDM 327 parameter M_{222} (see Ref. [23] for M parameter notation) responsible for the calculated intensities of 328 329 this series was fitted to these measurements. In this work, the intensities of two other bands of this 330 series were measured (3002e-0000e and 0602e-0000e). The EDM parameters which govern their

intensities, namely M_{302} and M_{060} were not previously determined leading to strong underestimations of the predicted intensities.



333 334 Fig. 6

- Position differences between the measured and predicted values for the various N_2O isotopologues contributing to the spectrum in the 7647 - 7918 cm⁻¹ spectral region.
- 337



- 338 339
- Fig. 7 340 Intensity ratios of the measured N₂O line intensities to those predicted by EDM the effective opera-341 tor model in the 7647 - 7918 cm⁻¹ spectral region. Note the logarithmic scale adopted for the ordi-
- 342 nate scale.
- *Upper panel:* Main isotopologue, ${}^{14}N_2{}^{16}O$. The values corresponding to $\Delta P = 12$, 13 and 14 are plotted 343
- 344 with different colors,
- Lower panel: Minor isotopologues: ¹⁴N¹⁵N¹⁶O, ¹⁵N¹⁴N¹⁶O, ¹⁴N₂¹⁸O, and ¹⁴N₂¹⁷O. All transitions belong to 345 346 the ΔP = 14 band series.
- 347

348 5.2. HITRAN2020, NOSD-1000 and HITEMP

As illustrated in **Fig. 1**, the HITRAN2020 line list [13] is limited to the 90 strongest transitions of the v_1+3v_3 band of the main isotopologue. The source of the HITRAN line parameters in our region is the database constructed by Toth from FTS spectra (although the HITRAN database gives as source "R.A. Toth, Jet Propulsion Laboratory, Linelist of N₂O parameters from 500 to 7500 cm⁻¹, private communication" which is outside our region...).

The NOSD-1000 line list of ${}^{14}N_2{}^{16}O$ is a high temperature line list calculated in 2016 within the effective operator approach [21]. Its intensity cutoff is 10^{-25} cm/molecule at 1000 K. The HITEMP N₂O line list [12] was constructed in 2019 by merging three NOSD line lists at 296, 500 and 1000 K (of ${}^{14}N_2{}^{16}O$) in order to make the list applicable over the 296-1000 K range (it thus includes the NOSD-1000 list). The HITEMP list reproduces HITRAN for the minor isotopologues.



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Differences between the measured position values of ¹⁴N₂¹⁶O and the corresponding values provided by the HITRAN2020 [13], NOSD-1000 [21] and HITEMP [12] spectroscopic databases (blue open circles, red open circles and black dots, respectively), in the 7647 - 7918 cm⁻¹ spectral region.

Fig. 8 and Fig. 9 show an overview comparison between the observations and the various databases for positions and intensities, respectively. As expected, the literature databases (all calculated) show more important deviations from the measurements than the refined calculated line lists used for the above assignments. Roughly, a gain by one order of magnitude has been achieved on the position values compared to HITEMP2019. As for line intensities, deviations are similar to those of the present predictions, with significant underestimation of HITEMP intensities for a number of

- bands. Note that the 3311-0000 and 4111-0000 bands belonging to the ΔP = 13 series which show the
- 372 largest deviations compared to the present predictions are absent in the HITEMP database.
- 373



374 375 **Fig. 9**

Intensity ratios of the measured ¹⁴N₂¹⁶O line intensities to the predicted values provided by the
 HITRAN2020 [13], NOSD-1000 [21] and HITEMP [12] spectroscopic databases (blue open circles, red
 open circles and black dots, respectively), in the 7647 - 7918 cm⁻¹ spectral region.

379

380 6. Conclusion

The characterization of the absorption spectrum of nitrous oxide has been significantly improved between 7647 and 7918 cm⁻¹ by (*i*) the systematic retrieval of the line intensities, (*ii*) the extension of the rovibrational assignments (about 950 assignments added to the 2272 previously reported from the same spectra in Ref. [7]), (*iii*) the detailed analysis of a number of local rovibrational perturbations.

The reported observations will help to improve the N₂O line lists in the spectroscopic databases in terms of completeness and accuracy. In particular, in the considered region, the HITRAN list includes only about 90 transitions of the v_1+3v_3 band for the main isotopologue while 2451 transitions of 36 bands have been identified in the present work. As concerns the NOSD-1000 [21] and HITEMP [12] line lists calculated in the frame of the effective operator approach, part of the positions and intensities deviate significantly from the observations. This is due to the lack of previous experimental data which prevented the determination of some relevant EH or EDM parameters. 393 Due to the existence of interpolyad couplings in N₂O, a non-polyad effective Hamiltonian model has been recently elaborated for ${}^{14}N_2{}^{16}O$ [14]. For consistency, a non-polyad effective dipole 394 395 moment model is under construction. A single set of effective dipole moment parameters for all ΔP 396 series will be determined from a global fit of the transition intensities available in the literature. In 397 this context, together with previous sets of line intensities measured by CRDS (see Fig. 1), the inten-398 sity information obtained in this work will bring strong constraints to the non-polyad EDM parame-399 ters. Let us mention that in the future, intensity information will be completed from a systematic intensity retrieval from the CRDS spectra in the5905-7647 cm⁻¹ region [intervals (b) and (c) in **Fig. 1**]. 400

401

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410		References
411	1.	Bertin T, Mondelain D, Karlovets EV, Kassi S, Perevalov VI, Campargue A. High sensitivity cavi-
412		ty ring down spectroscopy of N_2O near 1.74 $\mu m.$ J Quant Spectrosc Radiat Transf
413		2019;229:40–9. doi: 10.1016/j.jqsrt.2019.02.011.
414	2.	Liu AW, Kassi S, Perevalov VI, Tashkun SA, Campargue A. High sensitivity CW-cavity ring down
415		spectroscopy of N_2O near 1.5 μm (II). J Mol Spectrosc 2007:244;48-62. doi:
416		10.1016/j.jms.2007.05.010.
417	3.	Liu AW, Kassi S, Malara P, Romanini D, Perevalov VI, Tashkun SA, Hu SM, Campargue A. High
418		sensitivity CW-cavity ring down spectroscopy of N_2O near 1.5 μm (I). J Mol Spectrosc
419		2007:244;33-47. doi: 10.1016/j.jms.2006.03.007.
420	4.	Liu AW, Kassi S, Perevalov VI, Hu SM, Campargue A. High sensitivity CW-cavity ring down
421		spectroscopy of N_2O near 1.5 μm (III). J Mol Spectrosc 2009;254:20–7. doi:
422		10.1016/j.jqsrt.2019.02.011.
423	5.	Lu Y, Mondelain D, Liu AW, Perevalov VI, Kassi S, Campargue A. High Sensitivity CW-Cavity
424		Ring Down Spectroscopy of N ₂ O between 6950 and 7653 cm ⁻¹ (1.44-1.31 μ m): I. Line posi-
425		tions. J Quant Spectrosc Radiat Transfer 2012;113:749-62. doi: 10.1016/j.jqsrt.2012.03.005.
426	6.	Karlovets EV, Lu Y, Mondelain D, Kassi S, Campargue, Tashkun SA, Perevalov VI, High sensitiv-
427		ity CW-Cavity Ring Down Spectroscopy of N ₂ O between 6950 and 7653 cm ^{-1} (1.44–1.31 µm):
428		II. Line intensities. J Quant Spectrosc Radiat Transfer 2013;117:81-7. doi:
429		10.1016/j.jqsrt.2012.11.003.
430	7.	Liu AW, Kassi S, Perevalov VI, Tashkun SA, Campargue A. High sensitivity CW-cavity ring down
431		spectroscopy of N ₂ O near 1.28 µm. J Mol Spectrosc 2011:267;191-9.
432		doi:10.1016/j.jms.2011.03.025.
433	8.	Karlovets EV, Campargue A, Kassi S, Perevalov VI, Tashkun SA. High sensitivity Cavity Ring
434		Down Spectroscopy of N ₂ O near 1.22 µm: (I) Rovibrational assignments and band-by-band
435		analysis. J Quant Spectrosc Radiat Transfer 2016;169:36-48. doi:
436		10.1016/j.jqsrt.2019.02.011.
437	9.	Tashkun SA, Perevalov VI, Karlovets EV, Kassi S, Campargue A. High sensitivity Cavity Ring
438		Down Spectroscopy of N ₂ O near 1.22 μ m: (II) ¹⁴ N ₂ ¹⁶ O line intensity modeling and global fit of
439		¹⁴ N ₂ ¹⁸ O line positions. J Quant Spectrosc Radiat Transfer 2016;176:62–69. doi:
440		10.1016/j.jqsrt.2016.02.020.
441	10.	Karlovets EV, Kassi S, Tashkun SA, Campargue A. The absorption spectrum of nitrous oxide
442		between 8325 and 8622 cm ⁻¹ J Quant Spectrosc Radiat Transf 2021;262:107508. doi:
443		10.1016/j.jqsrt.2021.107508.
444	11.	Karlovets EV, Tashkun SA, Kassi S, Campargue A. An improved analysis of the N ₂ O absorption
445		spectrum in the 1.18 µm window. J Quant Spectrosc Radiat Transf 2022;278:108003. doi:
446		10.1016/j.jqsrt.2021.108003.
447	12.	Hargreaves RJ, Gordon IE, Rothman LS, Tashkun SA, Perevalov VI, Lukashevskaya AA, et al.
448		Spectroscopic line parameters of NO, NO ₂ , and N ₂ O for the HITEMP database. J Quant
449		Spectrosc Radiat Transfer 2019;232:35–53. doi:10.1016/j.jqsrt.2019.04.040.
450	13.	Gordon IE, Rothman LS, Hargreaves RJ, Hashemi R, Karlovets EV, Skinner FM, Conway EK, et
451		al. The HITRAN2020 molecular spectroscopic database. J Quant Spectrosc Radiat Transf,
452		2022;277:107949. doi: 10.1016/j.jqsrt.2021.107949.
453	14.	Tashkun SA. Global modeling of the ¹⁴ N ₂ ¹⁶ O line positions within the framework of the non-
454		polyad model of effective Hamiltonian. J Quant Spectrosc Radiat Transf 2019;231:88-101,
455		doi: 10.1016/j.jgsrt.2019.04.023.
456	15.	Daumont L, Van der Auwera J, Teffo JL, Perevalov VI, Tashkun SA. Line intensity
457		measurements in ${}^{14}N_2{}^{16}O$ and their treatment using the effective dipole moment approach.
458		II. The 5400-11000 cm ⁻¹ region. J Quant Spectrosc Radiat Transfer 2007;104:342–56. doi:
459		10.1016/j.jqsrt.20 06.09.004.
460	16.	Toth RA. Line positions and strengths of N ₂ O between 3515 and 7800 cm ⁻¹ . J Mol Spectrosc
461		1999;197:158–87. doi: 10.1006/jmsp.1999.7907.

- 462 17. Macko P, Romanini D, Mikhailenko SN, Naumenko OV, Kassi S, Jenouvrier A, Tyuterev VG,
 463 Campargue A. High sensitivity CW-cavity ring down spectroscopy of water in the region of
 464 the 1.5 μm atmospheric window. J Mol Spectrosc 2004;227(1):90–108. doi:
 465 10.1016/j.jms.2004.05.020.
- Tashkun SA, Perevalov VI, Kochanov RV, Liu AW, Hu SM. Global fitting of ¹⁴N¹⁵N¹⁶O and ¹⁵N¹⁴N¹⁶O vibrational-rotational line positions using the effective Hamiltonian approach. J Quant Spectrosc Radiat Transf 2010;111(9):1089–105. doi: 10.1016/j.jqsrt.2010.01.010.
- 469
 19. Vlasova AV, Perevalov BV, Tashkun SA, Perevalov VI. Global fittings of the line positions of
 470
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- 47120. TothRA.Linelistof N_2O parametersfrom500to7500cm^{-1}.472http://mark4sun.jpl.nasa.gov/n2o.html
- 473 21. Tashkun SA, Perevalov VI, Lavrentieva NN. NOSD-1000, the high-temperature nitrous oxide
 474 spectroscopic databank. J Quant Spectrosc Radiat Transfer 2016;177:43–8.
 475 <u>https://doi.org/10.1016/j.jqsrt.2015.11.014</u>.
- 476 22. Gordon IE, Rothman LS, Hill C, Kochanov RV, Tan Y, Bernath PF, et al. The HITRAN2016
 477 molecular spectroscopic database. J Quant Spectrosc Radiat Transf 2017;203:3–69. doi: 478 10.1016/j.jqsrt.2017.06.038.
- 479 23. Lyulin OM, Perevalov VI, Teffo JL, Effective Dipole Moment and Band Intensities of Nitrous
 480 Oxide, J. Mol. Spectrosc. 1995;174:566–80. <u>https://doi.org/10.1006/jmsp.1995.0023</u>)

Band ^a	$(P I_2 i)^b$	ΔG_{v}^{c}	Gv	B _v	$D_v \times 10^7$	$H_{v} \times 10^{12}$	RMS ^d	N_{fit}/N_{obs}^{e}	J _{max P/Q/R} f	ΔP^{g}	Note ^{<i>h</i>}
¹⁴ N ₂ ¹⁶ O											
3600e-0000e	(12.0.16)	7640 47399(11)	7640 47399(11)	0 41184936(35)	-8 50(28)	8 782(61)	0.49	137/147	P57/R57	12	1
4400e-0000e ^ĸ	(12 0 10)	/040.4/333(11)	/040.4/333(11)	0.41104550(55)	0.50(20)	0.702(01)	0.45	137/147	137/137	12	-
2113e-1110e	(1717)	7657.000257(60)	9537.26849(60)	0.4055439(43)	0.423(52)		0.94	12/21	P17/R27	14	1
2113f-1110f	(1/1/)	7657.00026(80)	9537.26832(80)	0.406515(20)	-9.6(10)		0.84	11/16	P14/R23	14	1
1004e-0001e	(18 0 4)	7664.81052(47)	9888.56729(47)	0.4033368(29)	1.629(35)		0.88	22/27	P29/R28	14	1
0203e-0000e	(14 0 1)	7665.273385(68)	7665.273385(68)	0.40978312(18)	2.5006(10)	3.320(16)	0.49	197/200	P72/R63	14	1
0223e-0000e	(14 2 1)	7673.63782(50)	7673.63783(50)	0.4099796(10)	1.1509(58)	-3.593(92)	0.71	66/85	P65/R52	14	1
1333e-0330e		7674.09763(15)	9441.01001(15)	0.40909338(39)	1.5836(19)		0.68	80/90	P50/R44	14	1
1333f-0330f N	(17 3 3)	7674 00929(20)	0441 01052(20)	0 40000061(06)	1 5424/57)		0.75	23/25	P24/R41	14	
1333f-0330e N		7074.09828(50)	9441.01032(30)	0.40909001(90)	1.3424(37)		0.75	3/5	Q11	14	
3710e-0110e			0766 70770/11)	0 41090205(69)	0.0007/90)	E 70/24)	0.50	101/117	P52/R41	12	1
3710e-0110f N	(13 1 16)	/0//.51591(14)	8266.28378(14)	0.41080395(08)	0.9997(80)	5.79(24)	0.59	1/2	Q02	12	
3710f-0110f		7677.51574(14)	8266.28361(14)	0.41338803(60)	0.3976(61)	3.70(16)	0.68	121/130	P54/R44	12	1
1512e-0110e N	(15 1 2)	7678.870122 [/]	8268.46690 ^m					/9	P24/R36	14	
1512f-0110f N	(15 1 2)	7678.870106	8268.47233 ^m					/14	P27/R29	14	
2003e-1000e	(16 0 7)	7691.58483(11)	0076 40017(11)		1 (707/45)	2 20/10)	0.72	40/60	P30/R48	14	2
2003e-0200e	(16 0 7)	7808.35587(11)	8976.48817(11)	0.40513544(55)	1.6707(45)	2.39(10)	10) 0.73	96/168	P59/R51	14	1,3
3820e-0220e N	(11210)	7705.61362(63)	8883.35829(63)	0.4124361(32)	2.694(34)	-	0.80	19/24	P33/R29	12	
3820f-0220f N	(14 2 16)	7705.61272(50)	8883.35739(50)	0.4124294(25)	0.889(25)	-	0.60	15/20	P31/R30	12	
1203e-0200e	(16 0 4)	7708.908827(93)	8877.041127(93)	0.40796933(32)	2.4131(24)	2.896(50)	0.59	172/181	P62/R56	14	1
1223e-0220e		7710 77475(00)		0 40007001(40)	1 2020(22)	1 750/57)	0.55	79/167	P48/R62	14	1,4
1223e-0220f N	(1(2)2)	//10.//4/5(99)	8888.51942 (99)	0.40837821(48)	1.2025(32)	-1.759(57)	0.55	11/15	Q20	14	
1223f-0220f	20f (1623)			0 40007451(00)	1 0025(40)	2 51/11)	0.00	103/174	P57/R54	14	1,4
1223f-0220e N		//10.//505(13)	8888.51972(13)	0.40837451(60)	1.8035(49)	2.51(11)	0.00	4/5	Q17	14	
4111e-0000e	(12.1.10)	7715.06542(45)	7715.06542(45)	0.41075365(92)	1.9302(36)		0.67	20/26	P13/R48	13	
4111f-0000e	(13 1 10)	7715.06296(63)	7715.06296(63)	0.4125991(27)	1.959(21)		0.67	11/15	Q34	13	
0602e-0000e	(1402)			0 41 47 42 40 (02)	C 2C05(07)	46 12/20)	0.57	F0/C0	D41/D40	14	
3002e-0000e ^{<i>k</i>}	(14 0 2)	//22.58/30(1/)	//22.58/30(1/)	0.41474349(83)	0.2095(97)	40.13(29)	0.57	58/68	P41/K48	14	
4600e-0200e N	(14 0 20)	7738.47827(78)	8906.61057(78)	0.4113308(77)	-0.83(15)		0.89	11/14	P22/R21	12	
1113e-0110e	(15 1 2)	7747 02054/04	9225 706410/0A	0 40710700/22	17150(14)	0 122/22)	0.49	176/198	P67/R67	14	1
1113e-0110f	(12 1 2)	1141.02034(84)	0555.790410(84)	0.40719799(23)	1./159(14)	0.122(23)	0.40	26/31	Q40	14	

Table 2. Spectroscopic parameters (in cm⁻¹) for the different bands of N₂O isotopologues assigned in the CRDS spectrum between 7647 and 7918 cm⁻¹.

1113f-0110f		7747 020142(01)	0225 70(012/01)	0.40004222/20)	1 7020(11)	0.220(1.0)	0.49	177/198	P70/R68	14	1
1113f-0110e	-	//4/.028142(81)	8335.796012(81)	0.40804222(20)	1.7030(11)	0.339(16)	0.48	34/35	Q40	14	
0912e-0310e N	(17110)	7765.798975	9661.79043 ^m					/21	P37	14	
0912f-0310f N	(17110)	7765.799826	9661.79502 ^m					/13	P28	14	
1003e-0000e	(14 0 3)	7782.661469(83)	7782.661469(83)	0.40682441(14)	1.7052(56)	0.1833(61)	0.43	124/128	P75/R82	14	
0822e-0220e	(16.2.5)	7799.82850(25)	8977.57317(25)	0.4130224(10)	- 1.064(98)	-35.08(25)	0.66	55/60	P40/R51	14	
0822f-0220f	(1025)	7799.82956(20)	8977.57423(20)	0.41302649(83)	2.5672(86)	2.59(23)	0.56	56/59	P40/R50	14	
0802e-0200e 0802e-0000e ^k	(16 0 6)	7800.70549(27)	8968.83779(27)	0.4128192(12)	5.577(11)	30.28(29)	0.73	40/69	P41/R52	14	2
3311e-0000e 3310e-0000e ^k	(13 1 12)	7817.83164(20)	7817.83164(20)	0.40971292(74)	1.2793(45)		0.68	39/49	P17/R42	13	
3311f-0000e		7817.83240(30)	7817.83240(30)	0.4113001(11)	0.9355(74)		0.68	32/36	Q41	13	
0712e-0110e 2312e–0110e ^k		7836.25583(15)	8425.02371(15)	0.41147721(61)	2.5344(53)	3.75(12)	0.75	91/97	P55/R57	14	
0712e-0110f N								15/19	Q27	14	
0712f-0110f 2312f–0110f ^k	- (15 1 5)	7836.25541(13)	8425.02328(13)	0.41365611(27)	2.7122(10)		0.71	86/93	P45/R56	14	
0712f-0110e N								12/13	Q25	14	
1403e-0001e N	(1808)	7855.8086(11)	10079.5654(11)	0.4060705(45)	2.129(39)		0.83	11/20	P30/R31	14	
2202e-0000e	(14 0 5)	7874.15546(12)	7874.15546(12)	0.41216104(40)	3.7169(29)	11.964(50)	0.58	96/107	P60/R66	14	
0622e-0000e 2220e-0000e ^k	(14 2 4)	7884.02171(44)	7884.02171(44)	0.4124230(10)	0.3705(64)	-12.22(11)	0.63	51/65	P61/R58	14	
4112e-1110e N		7903.51036(44)	9783.77610(44)	0.4074211(17)	1.996 (13)		0.81	30/35	P36/R24	14	
4112f-1110f N	(1/111)	7903.50935(58)	9783.77509(44)	0.4091909(19)	2.014(17)		0.67	21/31	P34/R22	14	
3312e-0310e	(17.1.10)	7911.90362(27)	9660.96885(27)	0.4094902(14)	1.977(12)		0.72	28/31	P08/R33	14	5
3312f-0310f	(1/110)	7911.90528(38)	9660.97044(38)	0.4117341(31)	1.137(20)		0.80	7/37	P07/R05	14	5
0912e-0310e N	(1716)	7911.906629 [/]	9515.68961 ^m					/18	P37	14	
0912f-0310f N	(1710)	7911.905789 [/]	9515.69535 ^m					/9	P28	14	
3332f-0330f	(17 2 0)	7016 00502(24)	0692 00720(24)	0 4112721/15)	1 729/21)	11 25(21)	0.62	31/34	P33/R44	14	5
3332f-0330e	(1/ 5 0)	7910.99502(24)	5065.90759(24)	0.4113/31(13)	1.720(21)	11.33(21)	0.05	6/6	Q11	14	5
4002e-1000e	(16 0 11)	7934.15251(18)	9219.05585(18)	0.40751321(64)	2.3439(51)	2.40(11)	0.73	79/93	P54/R60	14	5
3222e-0220e		7943.49717(19)	9121.24184(19)	0.41072577(84)	0.5451(68)		0.71	50/62	P36/R37	14	5
3222f-0220f	(16 2 8)	70/2 /0750/27)	0121 24226/22	0.4107222(15)	2 (11/22)	9.27(01)	0.50	34/34	P36/R40	14	5
3222f-0220e		7943.49739(27)	9121.24220(27)	0.410/322(13)	2.041(22)	5.27(51)	0.39	7/8	Q11	14	5
3112e-0110e	(15 1 8)	7970.41297(18)	8559.18084(18)	0.4093019(11)	2.4733(60)	7.420(93)	0.71	37/113	P69/R56	14	5,6

3112e-0110f								14/15	Q19	14	5
3112f-0110f	1	7070 41214(47)		0.4100471/42	2.4706(60)	F 71(11)	0.50	33/94	P65/R66	14	5,6
3112f-0110e		/9/0.41314(17)	8559.18101(17)	0.4109471(13)	2.4786(68)	5.71(11)	0.58	10/13	Q18	14	5
3002e-0000e	(14 0 8)	7998.6264(62)	7998.6264(62)	0.4094239(29)	2.1128(32)		0.90	15/20	P78	14	5
3202e-0200e	(16 0 10)	7940.09975(21)	0100 22205(21)	0 4102225(21)	4 4 4 7 (2 2)	05 ((12)	0.70	36/95	P52/R41	14	5,7,8
3202e-1000e	(16 0 10)	7823.41971(21)	9108.32305(21)	0.4103225(21)	4.447(32)	85.6(13)	0.78	16/42	P25/R33	14	9
				¹⁴ N ¹⁵ N ¹⁶ O							
1003e-0000e	(14 0 3)	7650.753893(96)	7650.753893(96)	0.40710138(21)	1.73037(77)		0.60	127/142	P58/R54	14	1
1512e-0110e N	(1 - 1 -)	7853.58564(74)	8429.01929(74)	0.4094226(51)	2.140(72)		0.87	18/23	P26/R25	14	
1512f-0110f N	(1515)	7853.58373(70)	8429.01738(70)	0.4111180(41)	2.207(47)		0.79	17/23	P28/R27	14	
2202e-0000e	(14 0 8)	7880.38631(18)	7880.38631(18)	0.4097635(11)	2.829(14)	13.31(49)	0.59	42/61	P48/R28	14	10
				¹⁵ N ¹⁴ N ¹⁶ O							
1113e-0110e	(15 1 2)	7667.80653(31)	8253.11865(31)	0.39349566(98)	1.5853(54)		0.78	40/58	P44/R27	14	1
1113f-0110f	(15 1 3)	7667.80403(26)	8253.11615(26)	0.3943259(12)	1.946(11)		0.88	48/63	P36/R25	14	1
1003e-0000e	(14 0 3)	7702.499365(77)	7702.499365(77)	0.39310842(28)	1.5827(22)	0.444(45)	0.51	169/177	P62/R59	14	1
2202e-0000e N	(14 0 5)	7799.40281(30)	7799.40281(30)	0.3981881(14)	3.152(17)	7.41(53)	0.74	45/53	P36/R46	14	
3112e-0110e N	(15 1 0)	7890.93194(63)	8476.24406(63)	0.3956738(88)	3.71(30)		0.76	25/28	P27/R25	14	
3112f-0110f N	(15 1 8)	7890.93088(80)	8476.24300(80)	0.397278(12)	6.75(50)		0.76	19/23	P24/R22	14	
3002e-0000e	(14 0 8)	7918.58234(32)	7918.58234(32)	0.3957901(22)	2.635(14)	8.73(25)	0.83	32/124	P56/R58	14	1,5,11
				¹⁴ N ₂ ¹⁸ O							
1113e-0110e N	(15 1 2)	7687.32065(48)	8271.54531(48)	0.3847327(27)	1.435(26)		0.71	13/21	R30	14	
1113f-0110f N	(15 1 5)	7687.32155(63)	8271.54621(63)	0.3855560(34)	1.282(36)		0.78	13/17	R29	14	
1003e-0000e	(14 0 3)	7718.947472(91)	7718.947472(91)	0.38434145(32)	1.4612(26)	0.599(55)	0.54	176/185	P57/R58	14	1
0602e-0000e	(14 0 2)	7704 88604(20)	7704 88604(20)	0 2007/000(0E)	2 9195(06)	E 92(26)	0.62	52/57		11	
1402e-0000e ^{<i>k</i>}		7794.88004(20)	7794.88004(20)	0.38874088(93)	2.8183(90)	5.82(20)	0.02	52/57	F45/K30	14	
3002e-0000e	(14 0 8)	7894.89002(17)	7894.89002(17)	0.38625655(66)	2.0672(57)	3.07(13)	0.64	75/80	P56/R46	14	
	-			¹⁴ N ₂ ¹⁷ O							
1003e-0000e	(14 0 3)	7749.64347(21)	7749.64347(21)	0.3949679(17)	1.683(20)	3.77(63)	0.67	38/58	P40/R44	14	12

Notes

The confidence interval (1SD) is in the units of the last quoted digit.

 ${}^{a}V_{1}V_{2}I_{2}V_{3}$ correspond to the maximum value of the modulo of the expansion coefficients of the eigenfunction. V_{2} is given between parenthesis when it is larger than 10. b Cluster labelling notation: ($P=2V_{1}+V_{2}+4V_{3}$, I_{2} , i), i is the order number within the cluster increasing with the energy. ${}^{c}\Delta G_{v}=G_{v}^{''}-G_{v}^{''}$ is the band center. d Root Mean Square of the (Obs.-Calc.) differences of the position values (10⁻³ cm⁻¹).

^e N_{fit} is the total number of transitions included in the fit; N_{obs} is the total number of measured transitions of the considered band. ^f Observed branch with the maximum value of the total angular momentum quantum number of the input data. ^g $\Delta P = P' - P''$, where P' and P'' are the upper and lower polyads. ^h Notes:

1- The line positions were included in the fit from Ref. [5];

2- Intrapolyad anharmonic resonance (16 0 7) \leftrightarrow (16 0 6) (J_{cross} =32);

3- Intrapolyad anharmonic resonance $(1607) \leftrightarrow (1606) (J_{cross}=32);$

4 -Interpolyad Coriolis resonance (16 2 7) \leftrightarrow (15 1 13) (J_{cross} = e: 32, J_{cross} = f: 32);

5- The line positions were included in the fit from Ref. [8];

6- Intrapolyad anharmonic resonance (15 1 7) \leftrightarrow (15 1 8) (J_{cross} = e: 46, J_{cross} = f: 40);

7- Intrapolyad anharmonic +*I*-type resonance (16 0 10)↔(16 2 16) (J_{cross} =26);

8- Intrapolyad anharmonic (16 0 10) \leftrightarrow (16 0 9) (J_{cross} =49);

9- Intrapolyad anharmonic +/-type (16 0 10) \leftrightarrow (16 2 16) (J_{cross} =26);

10- Intrapolyad anharmonic resonance +/-type (14 0 5) \leftrightarrow (14 2 12) (J_{cross} =34);

11- Intrapolyad anharmonic resonance (14 0 7) \leftrightarrow (14 0 6) (J_{cross} =35);

Intrapolyad anharmonic +/-type resonance (14 0 7) \leftrightarrow (14 2 11) (J_{cross} =48);

12- Intrapolyad anharmonic resonance (14 0 3) \leftrightarrow (14 0 2) (J_{cross} =70);

^{*k*} Band name as presented in Ref. [7];

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<sup>1</sup> Band center as provided by the global effective Hamiltonian.
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^{*m*} Vibrational term value as provided by the global effective Hamiltonian.