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The absorption spectrum of nitrous oxide between 7647 and 7918 cm⁻¹

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Abstract

We revisit the room temperature absorption spectrum of natural nitrous oxide recorded by high sensitivity cavity ring down spectroscopy between 7647 and 7918 cm^{-1} (1.31–1.26 μm) reported by Liu et al. (doi: 10.1016/j.jms.2011.03.025). In this previous analysis, 2272 transitions could be assigned in the region and no intensity information was provided. In the present work, on the basis of improved predictions of the effective operator models, the assignments could be extended to more than 3200 transitions and, more importantly, line intensities are provided for all the transitions. The assigned transitions belong to 49 bands of the $^{14}\text{N}_2^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$, and $^{14}\text{N}_2^{17}\text{O}$ isotopologues, 16 being newly assigned. All the identified bands correspond to the $\Delta P=14$ series of transitions, except for four $\Delta P=12$ and two $\Delta P=13$ bands of the $^{14}\text{N}_2^{16}\text{O}$ isotopologue ($P=2V_1+V_2+4V_3$ is the polyad number where $V_i=1-3$ are the vibrational quantum numbers). For comparison, the HITRAN2020 database includes only the $\nu_1+3\nu_3$ band of the main isotopologue and a number of calculated line parameters for the fourth minor isotopologue, $^{14}\text{N}_2^{18}\text{O}$.

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 $^{14}\text{N}_2^{16}\text{O}$ bands. The interaction mechanisms and the perturbations were assigned on the basis of the effective Hamiltonian models.

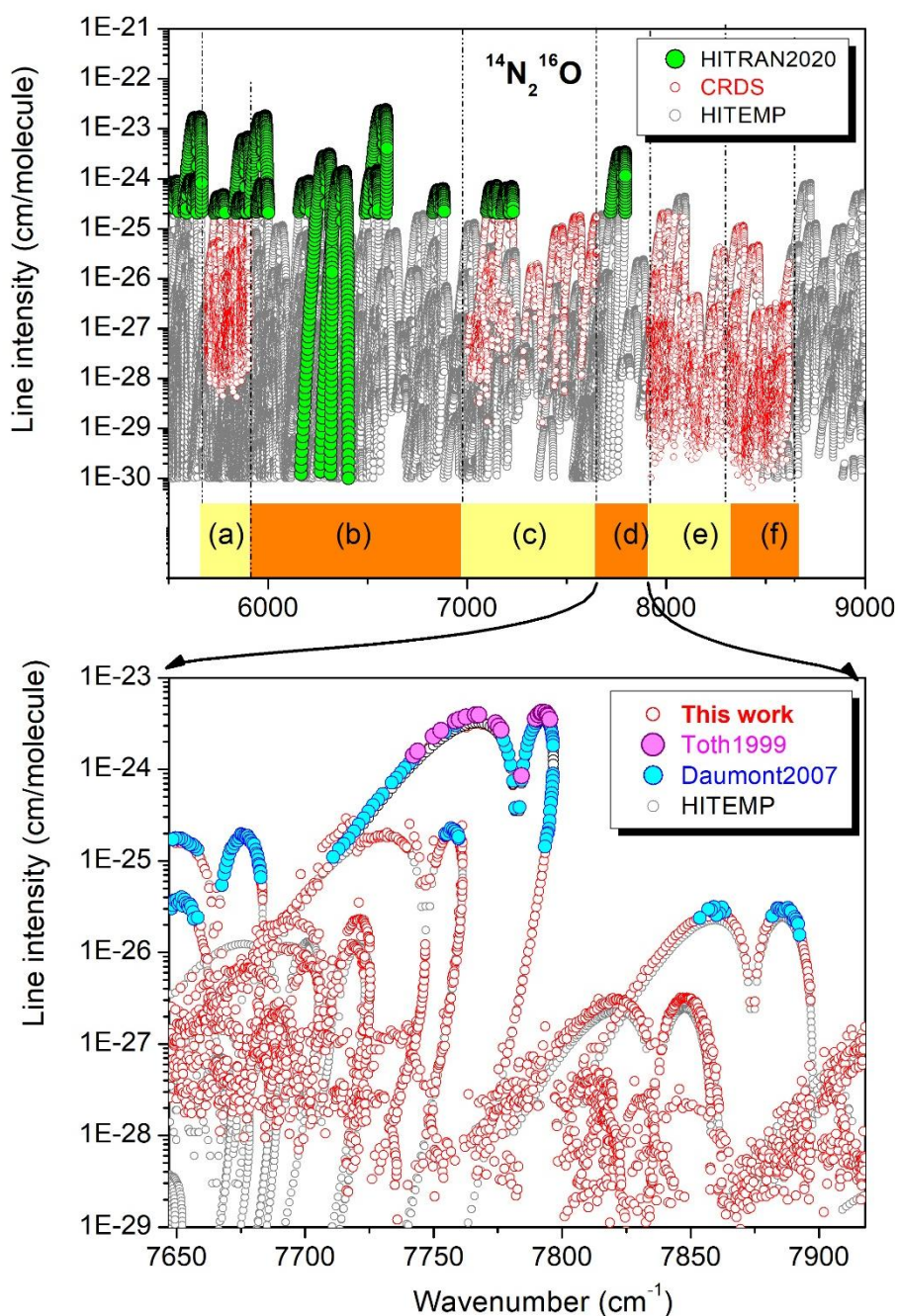
The comparison with current spectroscopic databases (HITRAN, HITEMP, NOSD) is discussed. All show significant deviations compared to the reported results (*e.g.* for $\Delta P=13$ band intensities). The reported results will be thus valuable to more accurately account for the absorption of nitrous oxide 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 N₂O 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]
74 and HITRAN2020 [13] lists of ¹⁴N₂¹⁶O are included in the plot. The HITRAN list corresponds to an
75 intensity cut off of 2×10⁻²⁵ cm/molecule at 296 K *i.e.* about 4 orders of magnitude above the CRDS
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 $V_j=1-3$ 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]).

87 In the present work, we reconsider the spectral region between 7647 and 7918 cm⁻¹, first
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
93 an absorption path length of 48.26 m and corresponds to a detectivity threshold of about 10⁻²⁶
94 cm/molecule, to be compared to a 10⁻²⁹ cm/molecule value for the weakest lines measured by CRDS.

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.**

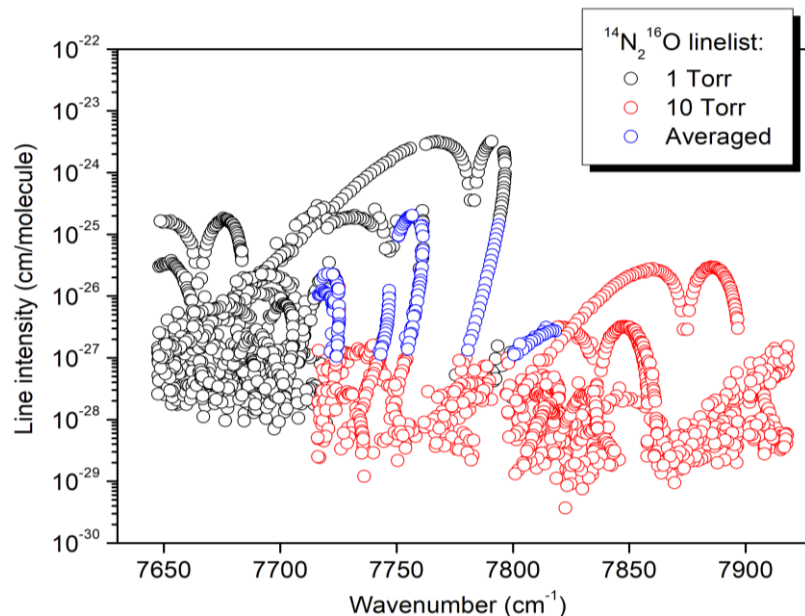
103 Overview of various line lists of $^{14}\text{N}_2^{16}\text{O}$ between 5500 and 9000 cm^{-1}

104 *Upper panel:* 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.

108 *Lower panel:* Enlargement of the (d) region corresponding to the range of the present study.
 109 FTS line lists of Refs. [15,16] (magenta and blue dots, respectively) and the present CRDS list (red
 110 circles) are superimposed to the HITEMP list [12] (grey).
 111

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 con-
115 tinuously the 7647-7918 cm^{-1} region, except for an inaccessible gap between 7896.87 and 7901.17
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
118 (7715-7918 cm^{-1}) corresponding to weaker absorption were recorded at 10 Torr. The typical value of
119 the noise equivalent absorption coefficient was $\alpha_{min} \sim 1 \times 10^{-10} \text{ cm}^{-1}$ (see Fig. 2 of Ref. [7]). The wave-
120 number scale of the spectra was calibrated with the help of a lambdameter and accurate reference
121 line positions of H_2O (present as an impurity) taken from the HITRAN database [13]. Each spectral
122 interval corresponding to the tuning range of one DFB laser diode ($\sim 20 \text{ cm}^{-1}$) was calibrated inde-
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 $2 \times 10^{-3} \text{ cm}^{-1}$ 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 cali-
128 bration of Ref. [7] for the 7901-7918 cm^{-1} interval has to be corrected by decreasing the wavenumber
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 **Fig. 2**
132 Overview of the N_2O line list including the measurements at 1 and 10 Torr (black and red circles) and
133 their averaged values (blue circles).
134
135

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
141 recordings (7715-7818.5 cm⁻¹), line parameters were averaged for the lines with intensity in the 10⁻²⁷
142 - 2×10⁻²⁵ cm/molecule range and for the weakest and strongest lines, the 10 Torr and 1 Torr line
143 parameters were retained.

144 Overall, the global line list includes about 4100 entries. Lines due to water vapor, present as
145 an impurity (73 and 38 lines at 1 and 10 Torr, respectively) were identified using the HITRAN line list
146 [13] and removed from the list. The overview of the ¹⁴N₂¹⁶O line list obtained at the final stage of the
147 assignment process (see below), is presented in **Fig. 2** with distinct colors according to the origin of
148 the line parameters.

149

150 **3. Rovibrational analysis**

151 Overall, 3219 lines belonging to 49 bands of $^{14}\text{N}_2^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$, and
 152 $^{14}\text{N}_2^{17}\text{O}$ were identified. Except for four $\Delta P= 12$ bands and two $\Delta P= 13$ bands of the $^{14}\text{N}_2^{16}\text{O}$ iso-
 153 tologue, all the bands belong to the $\Delta P= 14$ series of transitions. **Fig. 3** compares the CRDS observa-
 154 tions of the five N_2O 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 $^{14}\text{N}_2^{16}\text{O}$, 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 N_2O 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
 163 using new line positions from Refs. [11,14,15,18]. For $^{14}\text{N}_2^{17}\text{O}$ line positions, we refitted data pre-
 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 $\Delta P= 14$ 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

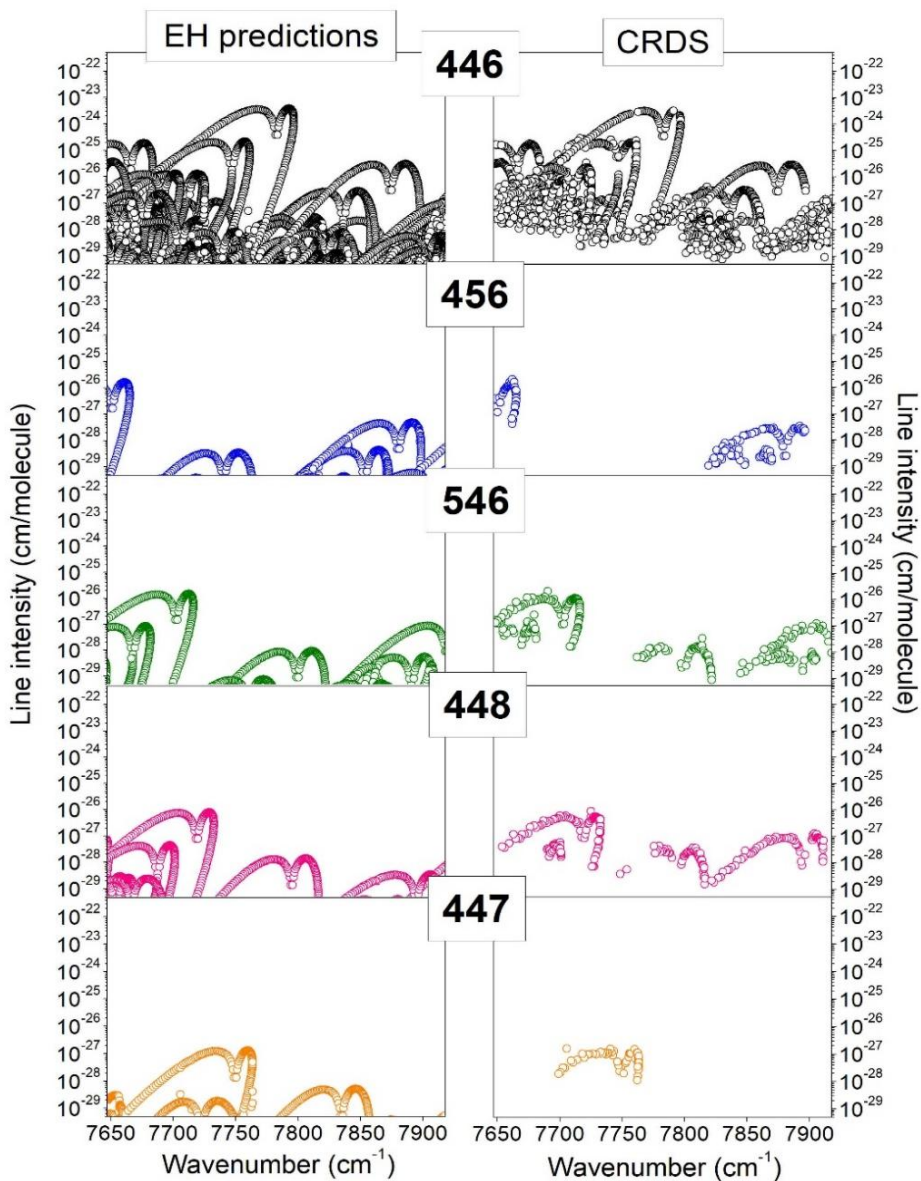
Isotopologue	Abundance [13]	Number of transitions ^a	Number of bands ^a
$^{14}\text{N}_2^{16}\text{O}$	0.990333	2451(1746)	36(24)
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$	3.64093×10^{-3}	151(89)	3(2)
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$	3.64093×10^{-3}	291(167)	5(3)
$^{14}\text{N}_2^{18}\text{O}$	1.98582×10^{-3}	268(210)	4(3)
$^{14}\text{N}_2^{17}\text{O}$	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

176 **Table 1** compares the number of lines and bands identified in this work to our previous
 177 analysis of the same spectra in Ref. [7]. Compared to Ref. [7], 950 transitions are newly assigned and
 178 sixteen of the 49 bands are new (12, 1, 2 and 1 for $^{14}\text{N}_2^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, and $^{14}\text{N}_2^{18}\text{O}$, respec-
 179 tively). Note that the rotational structure of 23 of the bands identified extends below or above the
 180 studied 7647–7918 cm^{-1} region. In the following band-by-band analysis, the dataset of these bands
 181 will 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 $^{14}\text{N}_2^{16}\text{O}$, $^{14}\text{N}^{15}\text{N}^{16}\text{O}$,
 183 $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, and $^{14}\text{N}_2^{18}\text{O}$, respectively) and four sub-bands of $^{14}\text{N}_2^{16}\text{O}$ are newly measured. They are
 184 marked with “N” in Table 2.



185
 186 **Fig. 3**
 187 Overview comparison between the transitions of $^{14}\text{N}_2^{16}\text{O}$ (446), $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ (456), $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ (546),
 188 $^{14}\text{N}_2^{18}\text{O}$ (448), and $^{14}\text{N}_2^{17}\text{O}$ (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).

190 The experimental line list, provided as Supplementary Material, includes the experimental
 191 and EH calculated positions and intensities for each line, together with corresponding rovibrational
 192 assignments and the measured line positions from Ref. [7] for comparison. Compared to Ref. [7], the
 193 transition dataset has been extended by about 950 new assignments and thus the fraction of
 194 unassigned 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 standard
200 equation for the vibration–rotation energy levels:

$$201 F_v(J) = G_v + B_v J(J + 1) - D_v J^2(J + 1)^2 + H_v J^3(J + 1)^3 \quad (1)$$

202 where G_v is the vibrational term value, B_v is the rotational constant, D_v and H_v are the centrifugal
203 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
211 above the studied 7647–7918 cm⁻¹ region under study. The line position dataset of these bands was
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.

215 The retrieved constants of the upper states are listed in **Table 2**. The bands are ordered ac-
216 cording to their band centers. Due to the reduced input data set (see Table 2 for details), for three
217 very weak ¹⁴N₂¹⁶O hot bands, we give only the band center provided by the global effective Hamilto-
218 nian. The typical *rms* values of the fits are on the order of 1×10^{-3} cm⁻¹, which is consistent with our
219 claimed accuracy on the line positions.

220 *4.2. Local perturbations*

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

224

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
¹⁴ N ₂ ¹⁶ O	2003e-1000e 0802e-0200e	(16 0 7) ↔ (16 0 6)	32	Intrapolyad anharmonic	[7]
	2003e-0200e	(16 0 7) ↔ (16 0 6)	32	Intrapolyad anharmonic	TW
	1223e-0220e 1223f-0220f	(16 2 7) ↔ (15 1 13)	<i>e</i> : 32 <i>f</i> : 32	Interpolyad Coriolis	[7]
	3112e-0110e 3112f-0110f	(15 1 7) ↔ (15 1 8)	<i>e</i> : 46 <i>f</i> : 40	Intrapolyad anharmonic	[8]
	3202e-0200e	(16 0 10) ↔ (16 2 16) (16 0 10) ↔ (16 0 9)	26 49	Intrapolyad anharmonic + <i>l</i> -type Intrapolyad anharmonic	[8] TW
	3202e-1000e	(16 0 10) ↔ (16 2 16)	26	Intrapolyad anharmonic + <i>l</i> -type	TW
¹⁴ N ¹⁵ N ¹⁶ O	2202e-0000e	(14 0 8) ↔ (14 2 12)	34	Intrapolyad anharmonic + <i>l</i> -type	TW
¹⁵ N ¹⁴ N ¹⁶ O	3002e-0000e	(14 0 8) ↔ (14 2 11)	48	Intrapolyad anharmonic + <i>l</i> -type	[8]
		(14 0 8) ↔ (14 0 6)	35	Intrapolyad anharmonic	[8]
¹⁴ N ₂ ¹⁷ O	1003-0000	(14 0 3) ↔ (14 0 2)	70	Intrapolyad anharmonic	[7]

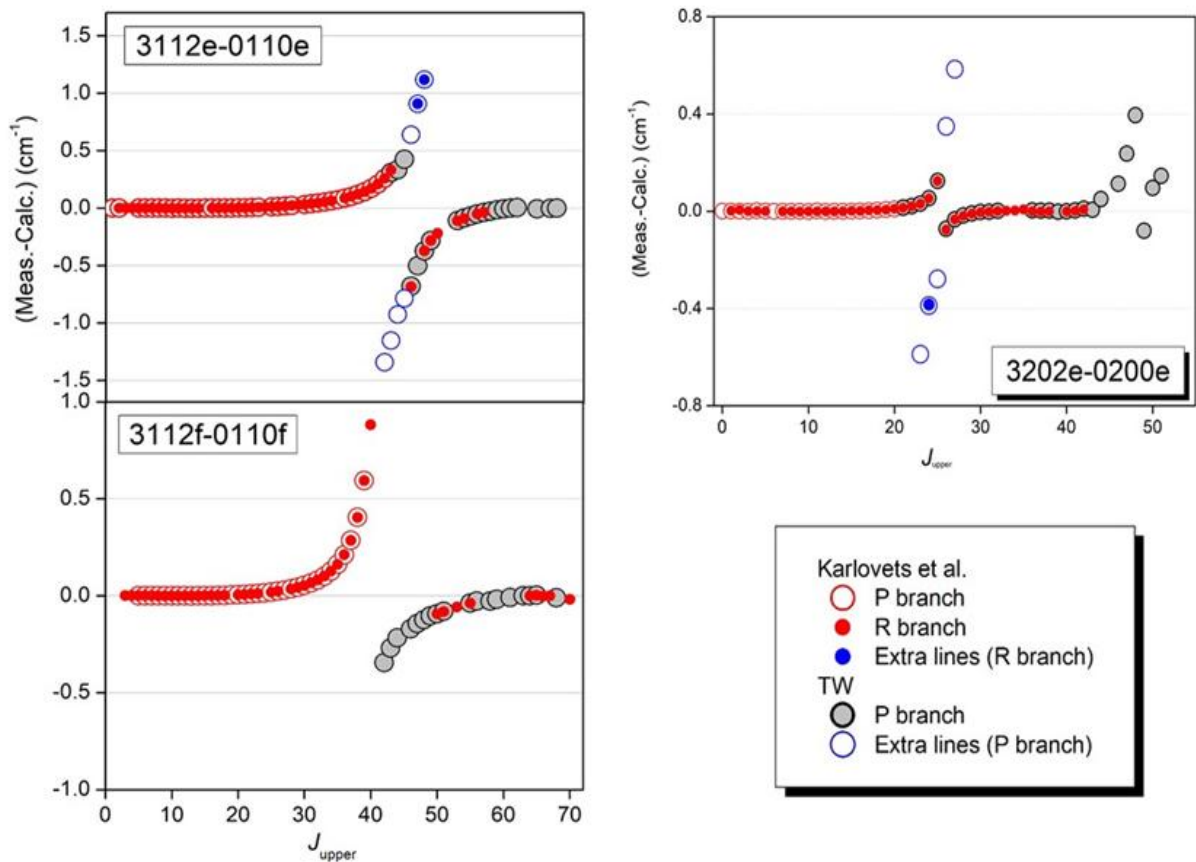
228
 229 *Note*

230 ^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
 244 7940.1cm⁻¹ is located above our region and the perturbation was first evidenced in Ref. [8]. The
 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

251 band at 7940.2 cm^{-1} and the corresponding values calculated using the spectroscopic constants of
 252 **Table 2**.
 253

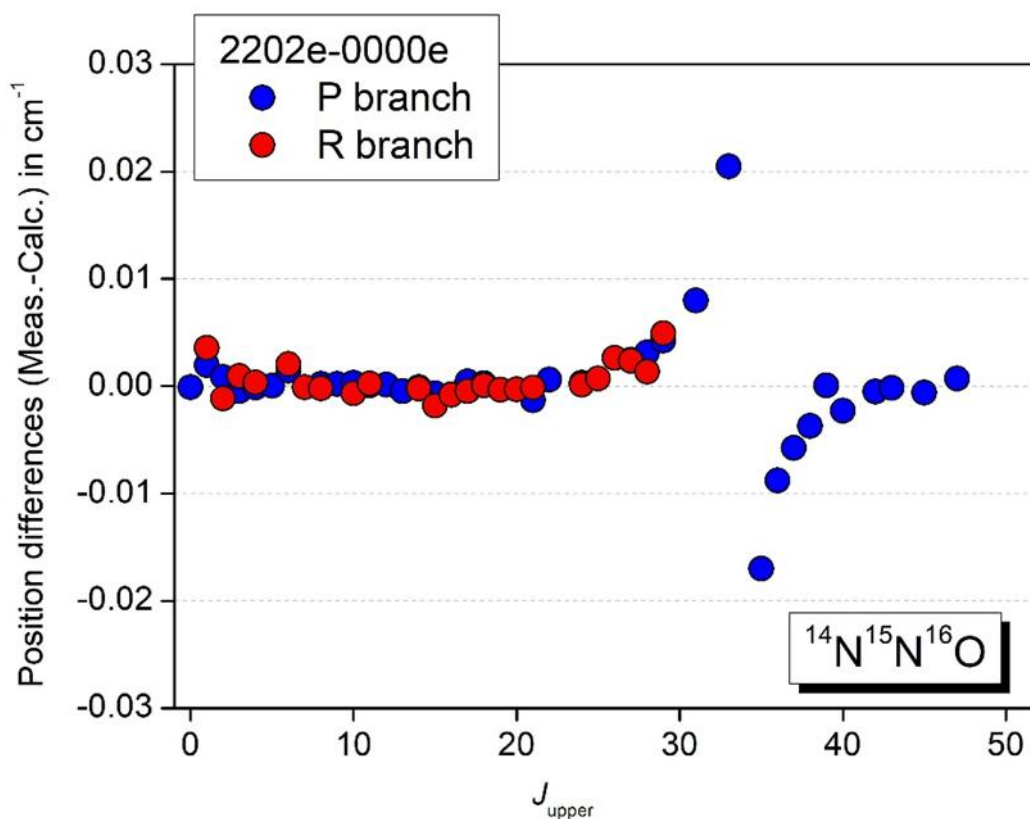


254 **Fig. 4**
 255 Energy differences between the measured values and the values calculated using the spectroscopic parameters
 256 of Table 2, for the upper levels of two $^{14}\text{N}_2^{16}\text{O}$ bands affected by local perturbations. For each J_{upper} value, the
 257 values corresponding to the $R(J_{\text{upper}} - 1)$ (dots) and $P(J_{\text{upper}} + 1)$ (open circles) are plotted. The two considered
 258 bands have their center located above the presently studied region ($7647\text{--}7918\text{ cm}^{-1}$) and only part of the P-
 259 branches was observed. The remaining part of the rotational structure was observed in Karlovets et al. [8] and
 260 is included in the plots.
 261

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*
 266 3202e-0200e band at 7940.1 cm^{-1} . The $(16\ 0\ 10)$ upper state is perturbed by an intrapolyad anharmonic $+l$ -type
 267 interaction with the $(16\ 2\ 16)$ state (energy crossing at $J=26$) and by an intrapolyad anharmonic interaction
 268 with the $(16\ 0\ 9)$ state (energy crossing at $J=49$).

269
 270 In the case of $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ isotopologue, only the 2202e-0000e was found strongly perturbed.
 271 The interaction mechanism is presently identified as an intrapolyad anharmonic $+l$ -type interaction
 272 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-
 274 tions up to 0.02 cm^{-1} around the energy crossing at $J=34$.



275
 276 **Fig. 5**
 277 Position differences between the measured line positions of the 2202e-0000e band ($^{14}\text{N}^{15}\text{N}^{16}\text{O}$) at
 278 7880.386 cm^{-1} and the calculated ones using the spectroscopic parameters of Table 2. For each J_{upper}
 279 value, the values corresponding to the $\text{R}(J_{\text{upper}} - 1)$ (red circles) and $\text{P}(J_{\text{upper}} + 1)$ (blue circles) are plot-
 280 ted. The $(14\ 0\ 5)$ upper state is perturbed by an interpolyad anharmonic $+/-$ -type interaction with the
 281 $(14\ 2\ 12)$ state (energy crossing at $J = 34$).
 282

283 Several occurrences of intrapolyad interaction were already evidenced for the $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ [8]
 284 and $^{14}\text{N}_2^{17}\text{O}$ [7] isotopologues. In particular, the upper state of the $\nu_1 + 3\nu_3$ band of $^{14}\text{N}_2^{17}\text{O}$
 285 isotopologue is perturbed by an anharmonic interaction with the $(14\ 0\ 2)$ state around the energy
 286 crossing at $J = 70$. The 3002e-0000e band of $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ is perturbed by an anharmonic and an anhar-
 287 monic $+/-$ -type interaction at $J = 35$ and $J = 48$, respectively.

288 5. Comparison with the calculated line lists

289 As detailed above, our assignments rely on improved predictions of the spectrum of the vari-
 290 ous N_2O isotopologues in the frame of the effective operator approach. Below, we first compare the
 291 observations to these (unpublished) predictions and then present the comparison to the available
 292 databases, namely HITRAN2020 [13], Nitrous Oxide Spectroscopy Databank (NOSD) [21] and HITEMP
 293 [12].
 294
 295

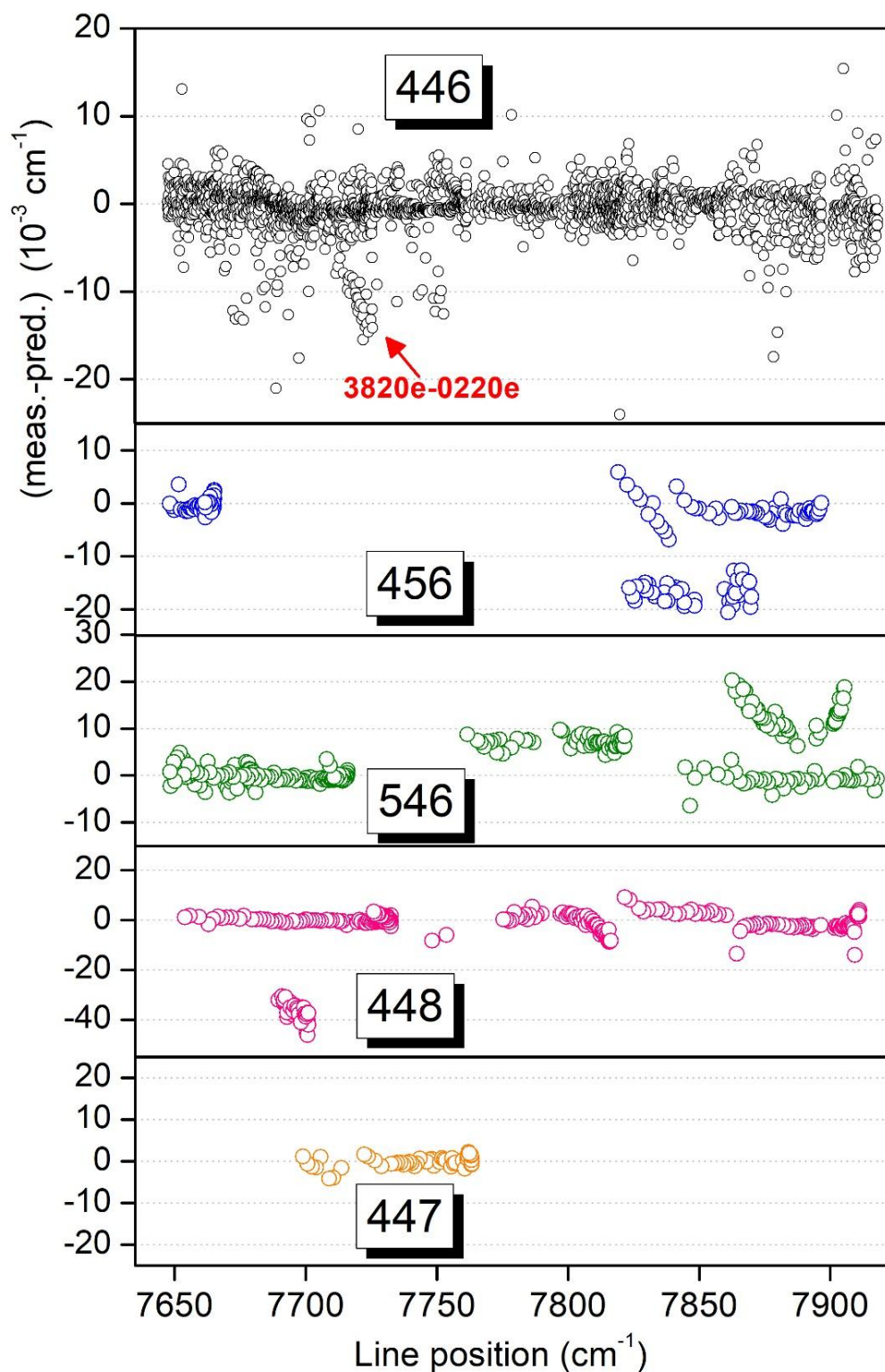
296 5.1. Present predictions

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
303 order of 0.04 cm^{-1} , are noted for the newly assigned 1113-0110 band of $^{14}\text{N}_2^{18}\text{O}$. For the main
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 ($\Delta V_1=-2$, $\Delta V_2=3$, $\Delta I_2=1$, $\Delta V_3=0$) 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
309 $^{14}\text{N}_2^{16}\text{O}$ line positions, additional parameters will be added to better account for this Coriolis cou-
310 pling.

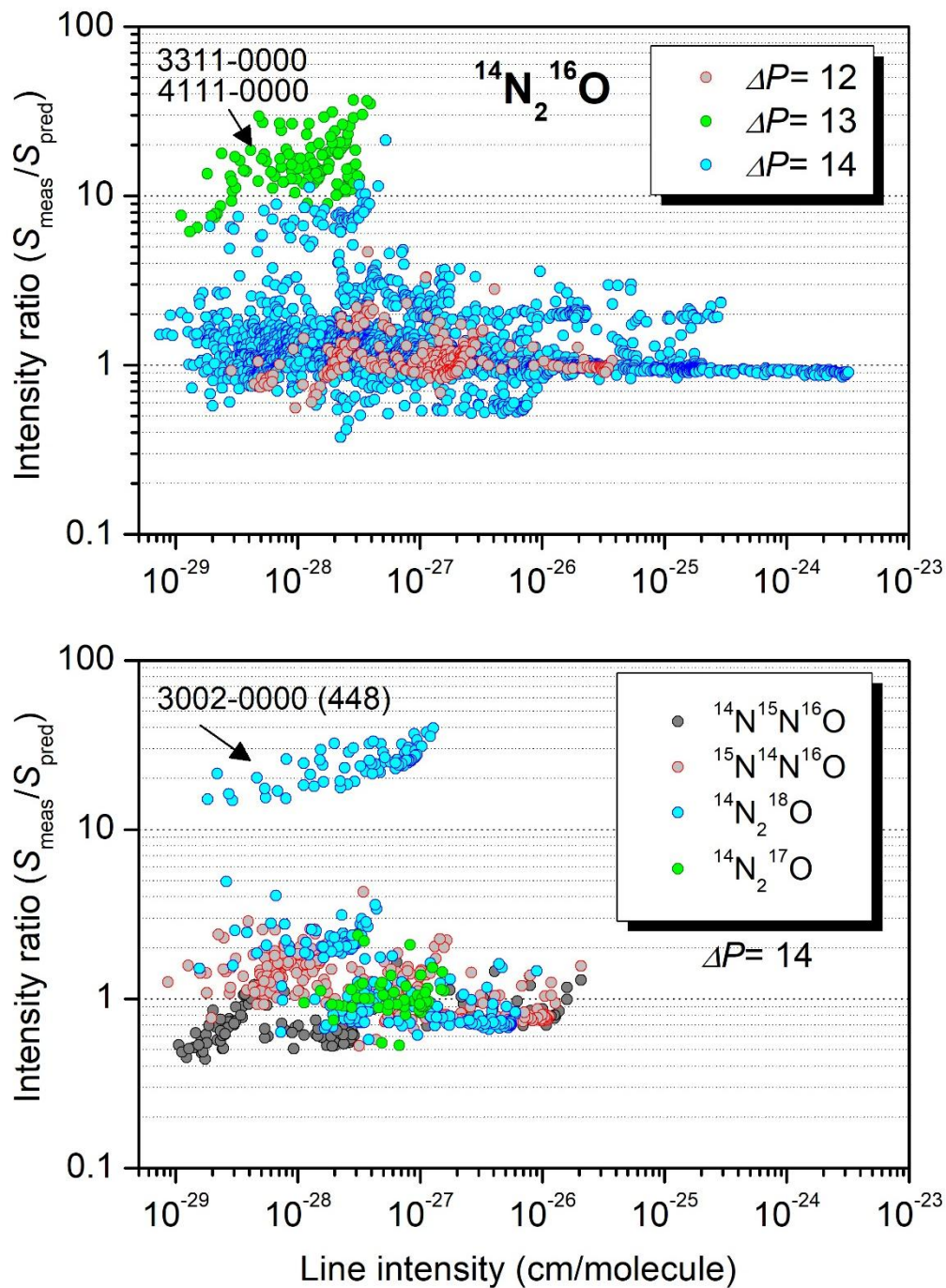
311 The measured $^{14}\text{N}_2^{16}\text{O}$ line intensities are in reasonable agreement with the values predicted
312 by the effective operator model (upper panel of **Fig. 7**) but important deviations are noted for some
313 bands (note the logarithmic scale adopted for the ratios). As a rule, 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 $\Delta P=13$ series. These are the first $\Delta P=13$ bands observed with $\Delta v_3=1$. Thus, the EDM param-
317 eters 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 av-
323 erage ratios of the different $^{14}\text{N}_2^{18}\text{O}$ bands show large variations with a more than one order under-
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 $\Delta P=14$ series of transitions. The 3002-0000 band is
326 a $\Delta P=14$ band with $\Delta v_3=2$. There are two bands of this series ($\Delta P=14$ and $\Delta v_3=2$) previously meas-
327 ured, namely the cold 2202e-0000e band [8] and the hot band 2312e/f-0110e/f [9]. The main EDM
328 parameter M_{222} (see Ref. [23] for M parameter notation) responsible for the calculated intensities of
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

331 intensities, namely M_{302} and M_{060} were not previously determined leading to strong underestima-
332 tions of the predicted intensities.



333 **Fig. 6**
334 Position differences between the measured and predicted values for the various N_2O isotopologues
335 contributing to the spectrum in the $7647 - 7918 \text{ cm}^{-1}$ spectral region.
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Fig. 7

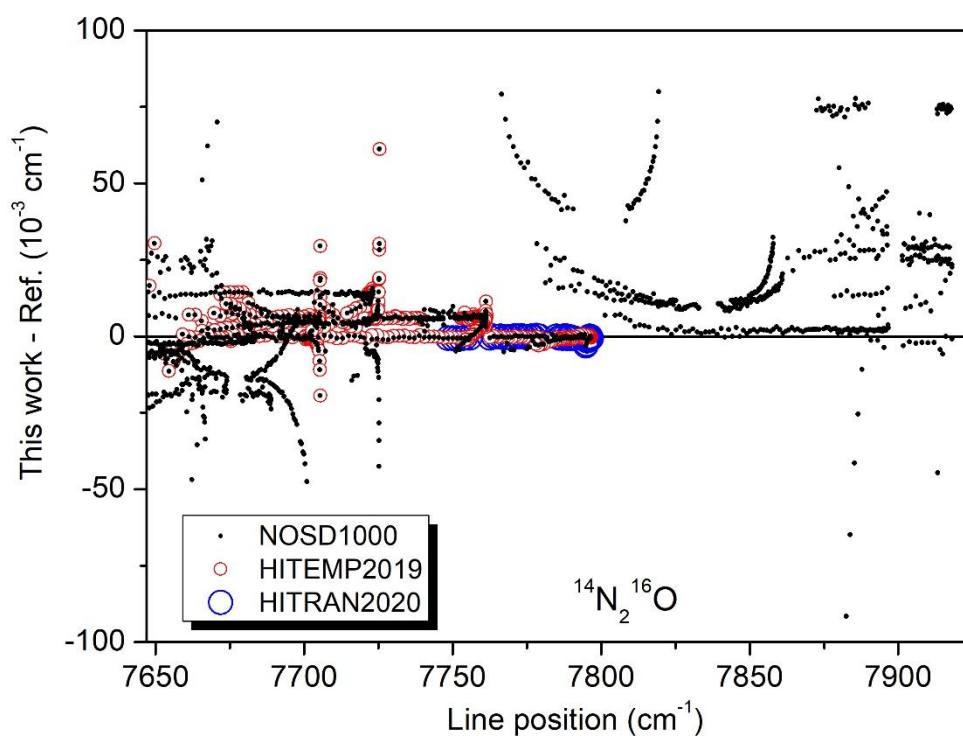
Intensity ratios of the measured N_2O line intensities to those predicted by EDM the effective operator model in the $7647 - 7918 \text{ cm}^{-1}$ spectral region. Note the logarithmic scale adopted for the ordinate scale.

Upper panel: Main isotopologue, $^{14}\text{N}_2^{16}\text{O}$. The values corresponding to $\Delta P = 12, 13$ and 14 are plotted with different colors,

Lower panel: Minor isotopologues: $^{14}\text{N}^{15}\text{N}^{16}\text{O}$, $^{15}\text{N}^{14}\text{N}^{16}\text{O}$, $^{14}\text{N}_2^{18}\text{O}$, and $^{14}\text{N}_2^{17}\text{O}$. All transitions belong to the $\Delta P = 14$ band series.

349 As illustrated in **Fig. 1**, the HITRAN2020 line list [13] is limited to the 90 strongest transitions of
 350 the $\nu_1+3\nu_3$ band of the main isotopologue. The source of the HITRAN line parameters in our region is
 351 the database constructed by Toth from FTS spectra (although the HITRAN database gives as source
 352 “R.A. Toth, Jet Propulsion Laboratory, Linelist of N_2O parameters from 500 to 7500 cm^{-1} , private
 353 communication” which is outside our region...).

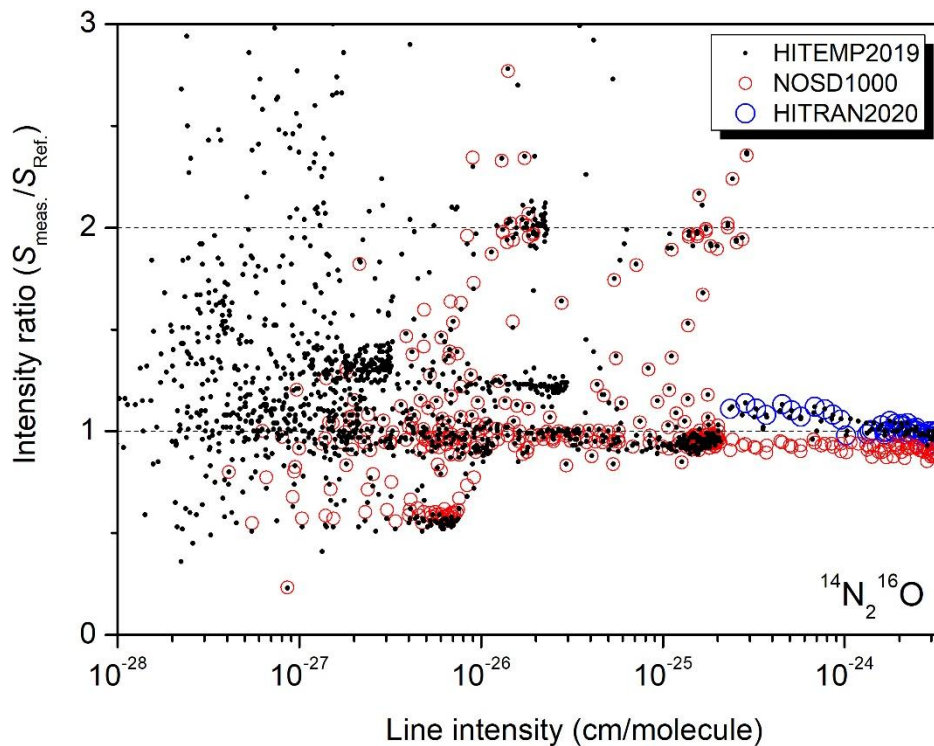
354 The NOSD-1000 line list of $^{14}\text{N}_2^{16}\text{O}$ is a high temperature line list calculated in 2016 within the
 355 effective operator approach [21]. Its intensity cutoff is 10^{-25} cm/molecule at 1000 K. The HITEMP N_2O
 356 line list [12] was constructed in 2019 by merging three NOSD line lists at 296, 500 and 1000 K (of
 357 $^{14}\text{N}_2^{16}\text{O}$) in order to make the list applicable over the 296-1000 K range (it thus includes the NOSD-
 358 1000 list). The HITEMP list reproduces HITRAN for the minor isotopologues.



359 **Fig. 8**
 360 Differences between the measured position values of $^{14}\text{N}_2^{16}\text{O}$ and the corresponding values provided
 361 by the HITRAN2020 [13], NOSD-1000 [21] and HITEMP [12] spectroscopic databases (blue open cir-
 362 cles, red open circles and black dots, respectively), in the 7647 - 7918 cm^{-1} spectral region.
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365 **Fig. 8** and **Fig. 9** show an overview comparison between the observations and the various da-
 366 tabases for positions and intensities, respectively. As expected, the literature databases (all calculat-
 367 ed) show more important deviations from the measurements than the refined calculated line lists
 368 used for the above assignments. Roughly, a gain by one order of magnitude has been achieved on
 369 the position values compared to HITEMP2019. As for line intensities, deviations are similar to those
 370 of the present predictions, with significant underestimation of HITEMP intensities for a number of

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



374 **Fig. 9**
375 Intensity ratios of the measured $^{14}\text{N}_2^{16}\text{O}$ line intensities to the predicted values provided by the
376 HITRAN2020 [13], NOSD-1000 [21] and HITEMP [12] spectroscopic databases (blue open circles, red
377 open circles and black dots, respectively), in the 7647 - 7918 cm^{-1} spectral region.
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380 6. Conclusion

381 The characterization of the absorption spectrum of nitrous oxide has been significantly im-
382 proved between 7647 and 7918 cm^{-1} by (i) the systematic retrieval of the line intensities, (ii) the ex-
383 tension of the rovibrational assignments (about 950 assignments added to the 2272 previously re-
384 ported from the same spectra in Ref. [7]), (iii) the detailed analysis of a number of local rovibrational
385 perturbations.

386 The reported observations will help to improve the N_2O line lists in the spectroscopic data-
387 bases in terms of completeness and accuracy. In particular, in the considered region, the HITRAN list
388 includes only about 90 transitions of the $\nu_1+3\nu_3$ band for the main isotopologue while 2451 transi-
389 tions of 36 bands have been identified in the present work. As concerns the NOSD-1000 [21] and
390 HITEMP [12] line lists calculated in the frame of the effective operator approach, part of the positions
391 and intensities deviate significantly from the observations. This is due to the lack of previous experi-
392 mental data which prevented the determination of some relevant EH or EDM parameters.

393 Due to the existence of interpolyad couplings in N_2O , a non-polyad effective Hamiltonian
394 model has been recently elaborated for $^{14}\text{N}_2^{16}\text{O}$ [14]. For consistency, a non-polyad effective dipole
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
400 intensity retrieval from the CRDS spectra in the $5905\text{-}7647\text{ cm}^{-1}$ region [intervals (b) and (c) in **Fig. 1**].

401

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409 research project.

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Table 2. Spectroscopic parameters (in cm^{-1}) for the different bands of N_2O isotopologues assigned in the CRDS spectrum between 7647 and 7918 cm^{-1} .

Band ^a	$(P\ l_2\ i)^b$	ΔG_v^c	G_v	B_v	$D_v \times 10^7$	$H_v \times 10^{12}$	RMS ^d	$N_{\text{fit}}/N_{\text{obs}}^e$	$J_{\text{max P/Q/R}}^f$	ΔP^g	Note ^h
¹⁴ N ₂ ¹⁶ O											
3600e-0000e 4400e-0000e ^k	(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
2113e-1110e	(17 1 7)	7657.000257(60)	9537.26849(60)	0.4055439(43)	0.423(52)		0.94	12/21	P17/R27	14	1
2113f-1110f		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	(17 3 3)	7674.09763(15)	9441.01001(15)	0.40909338(39)	1.5836(19)		0.68	80/90	P50/R44	14	1
1333f-0330f N		7674.09828(30)	9441.01052(30)	0.40909061(96)	1.5424(57)		0.75	23/25	P24/R41	14	
1333f-0330e N									3/5	Q11	14
3710e-0110e	(13 1 16)	7677.51591(14)	8266.28378(14)	0.41080395(68)	0.9997(80)	5.79(24)	0.59	101/117	P52/R41	12	1
3710e-0110f N								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 ^l	8268.46690 ^m					/9	P24/R36	14	
1512f-0110f N		7678.870106 ^l	8268.47233 ^m					/14	P27/R29	14	
2003e-1000e	(16 0 7)	7691.58483(11)	8976.48817(11)	0.40513544(55)	1.6707(45)	2.39(10)	0.73	40/60	P30/R48	14	2
2003e-0200e	(16 0 7)	7808.35587(11)						96/168	P59/R51	14	1,3
3820e-0220e N	(14 2 16)	7705.61362(63)	8883.35829(63)	0.4124361(32)	2.694(34)	-	0.80	19/24	P33/R29	12	
3820f-0220f N		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	(16 2 3)	7710.77475(99)	8888.51942 (99)	0.40837821(48)	1.2625(32)	-1.759(57)	0.55	79/167	P48/R62	14	1,4
1223e-0220f N								11/15	Q20	14	
1223f-0220f		7710.77505(13)	8888.51972(13)	0.40837451(60)	1.8035(49)	2.51(11)	0.66	103/174	P57/R54	14	1,4
1223f-0220e N								4/5	Q17	14	
4111e-0000e	(13 1 10)	7715.06542(45)	7715.06542(45)	0.41075365(92)	1.9302(36)		0.67	20/26	P13/R48	13	
4111f-0000e		7715.06296(63)	7715.06296(63)	0.4125991(27)	1.959(21)		0.67	11/15	Q34	13	
0602e-0000e 3002e-0000e ^k	(14 0 2)	7722.58736(17)	7722.58736(17)	0.41474349(83)	6.2695(97)	46.13(29)	0.57	58/68	P41/R48	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 3)	7747.02854(84)	8335.796410(84)	0.40719799(23)	1.7159(14)	0.122(23)	0.48	176/198	P67/R67	14	1
1113e-0110f								26/31	Q40	14	

1113f-0110f		7747.028142(81)	8335.796012(81)	0.40804222(20)	1.7030(11)	0.339(16)	0.48	177/198	P70/R68	14	1
1113f-0110e								34/35	Q40	14	
0912e-0310e N	(17 1 10)	7765.798975 ^l	9661.79043 ^m					/21	P37	14	
0912f-0310f N		7765.799826 ^l	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		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	(15 1 5)	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		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	(18 0 8)	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	(17 1 11)	7903.51036(44)	9783.77610(44)	0.4074211(17)	1.996 (13)		0.81	30/35	P36/R24	14	
4112f-1110f N		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		7911.90528(38)	9660.97044(38)	0.4117341(31)	1.137(20)		0.80	7/37	P07/R05	14	5
0912e-0310e N	(17 1 6)	7911.906629 ^l	9515.68961 ^m					/18	P37	14	
0912f-0310f N		7911.905789 ^l	9515.69535 ^m					/9	P28	14	
3332f-0330f	(17 3 8)	7916.99502(24)	9683.90739(24)	0.4113731(15)	1.728(21)	11.35(21)	0.63	31/34	P33/R44	14	5
3332f-0330e								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	(16 2 8)	7943.49717(19)	9121.24184(19)	0.41072577(84)	0.5451(68)		0.71	50/62	P36/R37	14	5
3222f-0220f		7943.49759(27)	9121.24226(27)	0.4107322(15)	2.041(22)	9.27(91)	0.59	34/34	P36/R40	14	5
3222f-0220e								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

3112e-0110f								14/15	Q19	14	5
3112f-0110f								33/94	P65/R66	14	5,6
3112f-0110e		7970.41314(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)						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
$^{14}\text{N}^{15}\text{N}^{16}\text{O}$											
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	(15 1 5)	7853.58564(74)	8429.01929(74)	0.4094226(51)	2.140(72)		0.87	18/23	P26/R25	14	
1512f-0110f N		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
$^{15}\text{N}^{14}\text{N}^{16}\text{O}$											
1113e-0110e	(15 1 3)	7667.80653(31)	8253.11865(31)	0.39349566(98)	1.5853(54)		0.78	40/58	P44/R27	14	1
1113f-0110f		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 8)	7890.93194(63)	8476.24406(63)	0.3956738(88)	3.71(30)		0.76	25/28	P27/R25	14	
3112f-0110f N		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
$^{14}\text{N}_2^{18}\text{O}$											
1113e-0110e N	(15 1 3)	7687.32065(48)	8271.54531(48)	0.3847327(27)	1.435(26)		0.71	13/21	R30	14	
1113f-0110f N		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 1402e-0000e ^k	(14 0 2)	7794.88604(20)	7794.88604(20)	0.38874088(95)	2.8185(96)	5.82(26)	0.62	52/57	P43/R50	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	
$^{14}\text{N}_2^{17}\text{O}$											
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 (16 0 7) \leftrightarrow (16 0 6) ($J_{cross}=32$);
- 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 +/-type resonance (16 0 10) \leftrightarrow (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];

^l Band center as provided by the global effective Hamiltonian.

^m Vibrational term value as provided by the global effective Hamiltonian.