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The O₂ far-infrared absorption spectrum between 50 and 170 cm⁻¹

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47 **Abstract**
48 The oxygen absorption spectrum in the 50-170 cm⁻¹ spectral range is studied at the AILES beam
49 line of the SOLEIL synchrotron with a Fourier transform spectrometer equipped with a 151-m multipass
50 gas cell. The spectrum recorded at room temperature (23.15°C) with a pressure of 19.76 Torr is formed by
51 weak pure rotational magnetic dipole transitions. Line parameters of 26 lines are derived and compared to
52 literature values. In particular, measured line intensities confirm the 45 years-old previous values reported
53 by Boreiko *et al.* (J. Quant. Spectrosc. Radiat. Transfer 32 (1984)109-117). The agreement with HITRAN
54 intensities (within 1 % level for the strongest lines) indicates that the 20 % HITRAN error bar could be
55 reduced.

56 **1. Introduction**

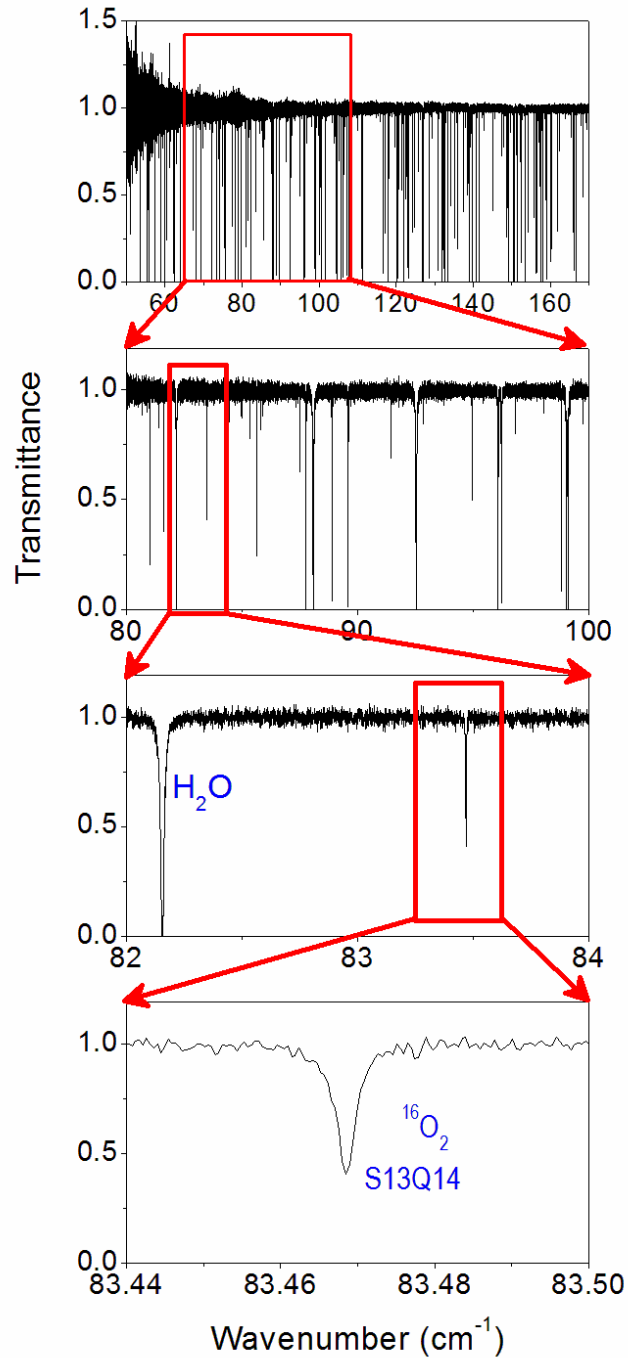
57 Being a homonuclear diatomic molecule, the ¹⁶O₂ oxygen molecule has no dipolar electric moment
 58 and thus no electric dipole-allowed rotational or vibrational bands. However, in the ground $X^3\Sigma_g^-$ state,
 59 two electron spins remain unpaired ($S=1$) which gives rise to a magnetic dipole moment. Weak magnetic
 60 dipolar transitions are thus observable in the ground electronic state as a fine-structure consisting of a Q -
 61 type branch near 60 GHz and a single line at about 119 GHz as well as the presently studied rotational R -
 62 type branch in the far infrared. The fine structure lines have been used by microwave radiometry for the
 63 atmosphere remote sensing for a long time [1]. The use of additional channels operating at the frequency of
 64 the rotational line near 425 GHz allow increasing accuracy of temperature and humidity profiles retrieval
 65 together with a better spatial resolution [2,3]. Corresponding instruments were developed [4] and
 66 considered for several missions such as the EU Geostationary Observatory for Microwave Atmospheric
 67 Sounding (GOMAS), the Geosynchronous Microwave (GEM) Sounder/Imager Observation System
 68 proposed by USA, the Chinese geostationary orbit meteorological Fengyun satellites, etc.

69 As a result of the **three electron spin-components** ($S=1$), each rotational level (N) of the ground
 70 $X^3\Sigma_g^-$ state splits **into three components**. It leads to a triplet multiplicity with total angular momentum $J=$
 71 $N-1, N$ or $N+1$. Note that for the symmetric ¹⁶O₂ main isotopologue, only odd rotational levels exist in the
 72 ground state. The studied rotational magnetic dipole (M1) transitions follow thus the $\Delta N= +2, \Delta J= 0, +1$
 73 selection rules leading to the observation of only two $\Delta N(N)\Delta J(J)$ branches: SQ and SR , respectively. Note
 74 that the $SQ(J), SR(J)$ and $SR(J-1)$ lines have relative intensities of about 1, 0.3 and 0.2, respectively.

75 **2. Experiment**

76 The present recordings were performed during a measurement campaign at SOLEIL synchrotron
 77 devoted to the study of the H₂O-O₂ (and H₂O-N₂) foreign continuum of water vapor. The experimental set
 78 up is very similar to that previously used to study the far-infrared self-continuum of water vapor [5,6].

79 The spectrum was recorded at a pressure of 19.76 Torr measured with a Pfeiffer 100 mbar full range
 80 (stated uncertainty of 0.25% of the reading) using the standard mode of the synchrotron radiation and a
 81 multipass cell. The total absorption path length equals 151.75 ± 1.5 m corresponding to 60 passes between
 82 mirrors separated by 2.52 m and 0.5 m of space between windows. We recorded the spectrum using the
 83 FTIR Bruker IFS 125 spectrometer of the AILES beamline. The resolution (defined as $0.9/\text{MOPD}$ where
 84 MOPD is the maximum optical path difference) was set to 0.00102 cm^{-1} and no apodization of the
 85 interferogram was used (boxcar option of the Bruker software). A total of 290 interferograms were co-
 86 added. An overview of the transmittance spectrum is displayed on the upper panel of **Fig. 1**. Due to the
 87 very high intensity of the water lines in the region, the spectrum is dominated by water absorption present
 88 as an impurity (the relative water concentration was estimated to be 40 ppm, see below). Successive
 89 zooms are applied in **Fig.1** to show one of the strongest observed O₂ lines near 83.5 cm^{-1} (S13Q14).



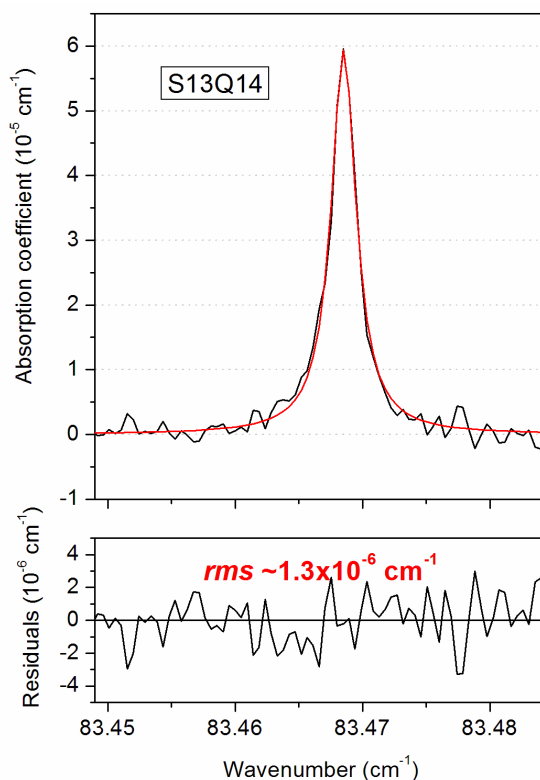
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Fig. 1

Room temperature FTS absorption spectrum of oxygen ($P=19.76$ Torr) recorded at SOLEIL synchrotron between 50 and 170 cm^{-1} . The spectrum is dominated by lines due to water present as an impurity with 40 ppm relative concentration. The last zoom shows the S13Q14 line of $^{16}O_2$ at 83.47 cm^{-1} .

96 3. Spectra analysis and results

97 The line parameters retrieval was performed using a homemade multiline fitting program in
 98 LabVIEW. In our pressure conditions, the pressure broadening (about 10^{-3} cm⁻¹ HWHM at 19.76 Torr [7])
 99 gives the dominant contribution to the line profile width. The contributions of the Doppler broadening (on
 100 the order of 10^{-4} cm⁻¹ near 100 cm⁻¹) and of the apparatus function (about 3.5×10^{-4} cm⁻¹ HWHM) are
 101 smaller. The FTS spectrum was fitted over a spectral interval around each O₂ line, using a Voigt line
 102 profile for the O₂ and the water interfering lines. The line position, line area and Lorentzian width were
 103 adjusted for each line. **Fig. 2** shows the achieved line profile reproduction in the case of the isolated
 104 S13Q14 line. The residuals are at the noise level and correspond to a noise equivalent absorption on the
 105 order of 10^{-6} cm⁻¹. The relative concentration of water due to desorption from the cell walls was estimated
 106 to be about 40 ppm with a considerable H₂¹⁸O enrichment resulting from previous measurements of the
 107 self-continuum of water vapor with a sample highly enriched in ¹⁸O [6].



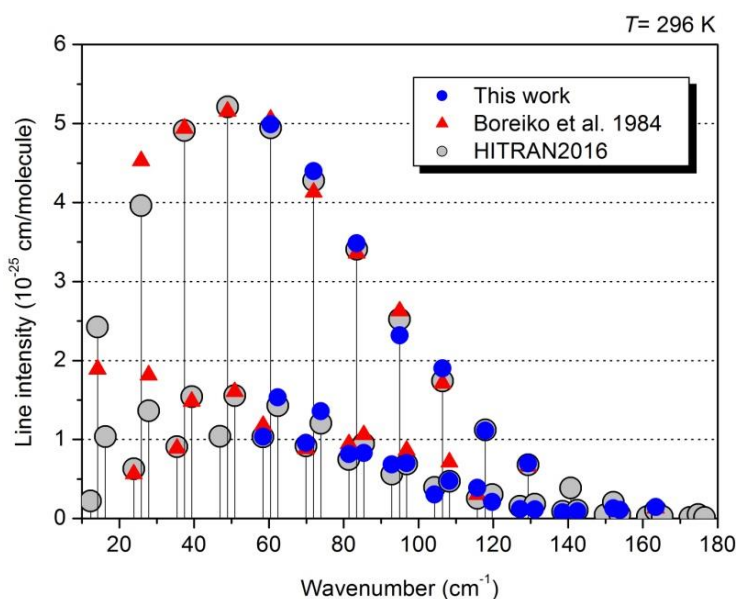
108
 109 **Fig. 2**
 110 Line profile fit of the S13Q14 line using a Voigt line shape and corresponding (obs.- calc.)
 111 residuals.
 112

113 As a result, a list of twenty-six ¹⁶O₂ lines with intensity ranging between 7.8×10^{-27} and 5.0×10^{-25}
 114 cm/molecule was obtained (see **Table 1**). The list covers the S9R9-S25R26 and S9Q10-S27Q28 ranges of
 115 the SR and SQ branches (see **Fig. 3**).

Transition	Position (cm ⁻¹)	Intensity at 296 K (cm/molecule)
S9R9	58.4153(4)	1.0(4)E-25
S9Q10	60.45547(7)	5.0(3)E-25
S9R10	62.3772(2)	1.5(5)E-25
S11R11	69.9077(2)	1.0(3)E-25
S11Q12	71.96900(7)	4.4(3)E-25
S11R12	73.8694(2)	1.4(2)E-25
S13R13	81.3866(3)	8(7)E-26
S13Q14	83.46851(5)	3.5(2)E-25
S13R14	85.3487(2)	8(3)E-26
S15R15	92.8514(3)	7(1)E-26
S15Q16	94.95289(6)	2.3(1)E-25
S15R16	96.8136(1)	7(1)E-26
S17R17	104.3007(8)	3(3)E-26
S17Q18	106.42091(7)	1.9(1)E-25
S17R18	108.2629(2)	5(2)E-26
S19R19	115.7317(4)	4(2)E-26
S19Q20	117.8708(1)	1.1(1)E-25
S19R20	119.6943(1)	2.1(9)E-26
S21R21	127.1435(3)	1.2(5)E-26
S21Q22	129.3011(1)	7.0(7)E-26
S21R22	131.1068(2)	1.1(5)E-26
S23R23	138.5347(3)	8(4)E-27
S23R24	142.4977(3)	9(5)E-27
S25Q26	152.0961(6)	1.0(7)E-26
S25R26	153.8655(7)	1.1(6)E-26
S27Q28	163.457(1)	1.0(7)E-26

116 **Table 1**

117 List of the rotational lines of ¹⁶O₂ measured by FTS between 50 and 170 cm⁻¹.



118 **Fig. 3**

119 Overview of the rotational magnetic dipole transitions of ¹⁶O₂ between 10 and 180 cm⁻¹: line lists
 120 provided by HITRAN2016 [7] (open grey circles), measured by Boreiko *et al.* [9] (red triangles) and
 121 measured in the present work (blue circles).
 122
 123

124 4. Comparison to literature

125 The HITRAN positions of the considered lines were calculated by difference of the ground state
126 energy levels obtained by Yu *et al.* [8] from an isotopically invariant Dunham fit of all the O₂ transitions
127 available in the literature, in particular highly accurate microwave measurements. HITRAN line positions
128 are provided with 10⁻⁶ and 10⁻⁵ cm⁻¹ accuracy for positions below and above 90 cm⁻¹, respectively.
129 Although agreeing with HITRAN values, our line positions determined with an accuracy no better than
130 5×10⁻⁵ cm⁻¹ are insufficient to improve the accuracy of HITRAN positions.

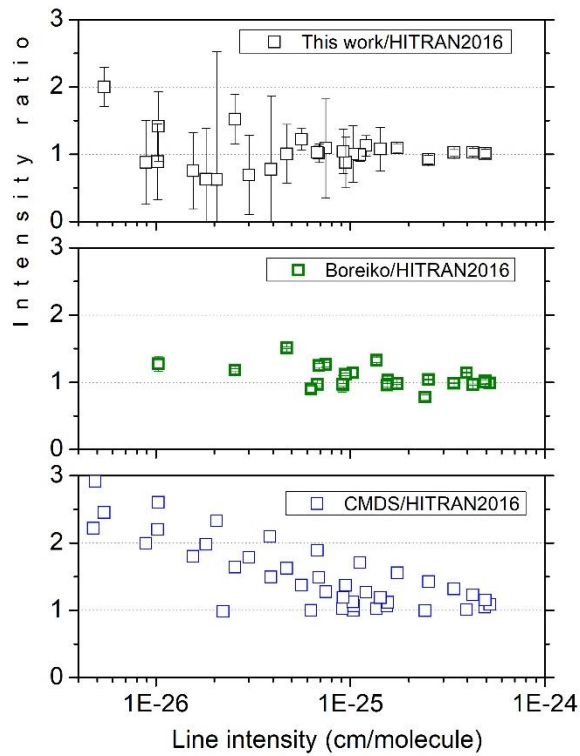
131 To the best of our knowledge, the most recent laboratory measurement of the considered rotational
132 lines was reported by Boreiko *et al.* in 1984 [9]. These authors used a high pressure Hg arc source, a
133 multipass White cell providing a 45.1 path length and performed FTS recordings with a spectral resolution
134 of 0.07 cm⁻¹, for a series of pressures ranging between 52 and 672 Torr. Their measurements of 23 lines
135 extend down to 14 cm⁻¹ but only one line was reported above 130 cm⁻¹ (see **Fig. 3**). Particular care was
136 devoted to the intensities determination from the proportionality factor between the equivalent widths of
137 the lines and the recording pressures [9]. As a result the (statistical) error bars attached to the measured
138 intensities are small, on the order of 1 %.

139 Although showing a dispersion larger than 1 %, the intensity comparison between HITRAN values
140 and the values reported by Boreiko *et al.* is on average very good (see **Fig. 4**, upper panels). The HITRAN
141 intensity values were calculated by Mackie using a global intensity model [7]. We do not know if the
142 measurements of Ref. [9] were used to scale the calculated values but the agreement is excellent.

143 Our intensity values derived from a single FTS spectrum recorded with a ten times better spectral
144 resolution and a smaller pressure fully confirm the intensity results by Boreiko *et al.* In spite of larger
145 statistical error bars, the overall agreement with HITRAN for the lines with intensity larger than 10⁻²⁵
146 cm/molecule is similar or even better than that obtained with the values of Boreiko *et al.* (see **Fig. 3**).
147 HITRAN intensity values are provided with 20 % error bar. The overall agreement indicates that HITRAN
148 error bars are largely overestimated and could be reduced to 2% at least for the strongest lines. Note that a
149 similar situation was found for the first rotational triplet. Measurements of the S1R1 and S1Q2 lines at
150 368 and 425 GHz, respectively, in pure oxygen and in air by resonator technique at room temperature and
151 atmospheric pressure were performed with a statistical uncertainty of about 5% but the measured values
152 agree with HITRAN within 1-3% [10].

153 The GEISA database [11], the Cologne Database for Molecular Spectroscopy (CDMS) [12,13,14]
154 and the catalogue elaborated at Jet Propulsion Laboratory (JPL) [15] provide alternative line lists for the
155 considered transitions. The GEISA and JPL intensities coincide with HITRAN values. **Fig. 4** includes a
156 comparison of the HITRAN values to the CDMS intensities. While the lowest *J* transitions have CDMS
157 intensities coinciding to HITRAN values, the highest *J* transitions (*J* ~ 30) have an intensity

158 overestimated by a factor of more than two. The intensity adjustment applied to JPL intensities in
 159 March 2014 is intended to be applied to the CDMS catalogue in the near future.



160
 161 **Fig. 4**
 162 Comparison to HITRAN values of the intensities the $^{16}O_2$ lines between 10 and 180 cm^{-1} from
 163 different sources: present measurements (open squares), measurements by Boreiko *et al.* [9] (open green
 164 squares), provided by CDMS [12,13, 14] (blue open squares).

165
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