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**Pressure Line Broadening and Shifting of Water Vapor Overtones**

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## Abstract

Some absorption lines of water vapor in the region around  $12100\text{ cm}^{-1}$  have been examined by using a diode laser spectrometer. The employed sources are double heterostructure AlGaAs diode lasers operating in *free-running* mode. The resolving power ( $\sim 10^7$ ) of the spectrometer permits the observation of the absorption features with a precision of less than  $0.01\text{ cm}^{-1}$ . Wavelength modulation spectroscopy along with the 2<sup>nd</sup> harmonic detection technique have been adopted in order to maximize the signal to noise ratio and to extract the necessary informations either on the line-width and on the line position for each resonance. The instrumental effects and the amplitude modulation always present with these sources have been taken into account. Collisional broadening and shifting coefficients have been measured at room temperature.

## Introduction

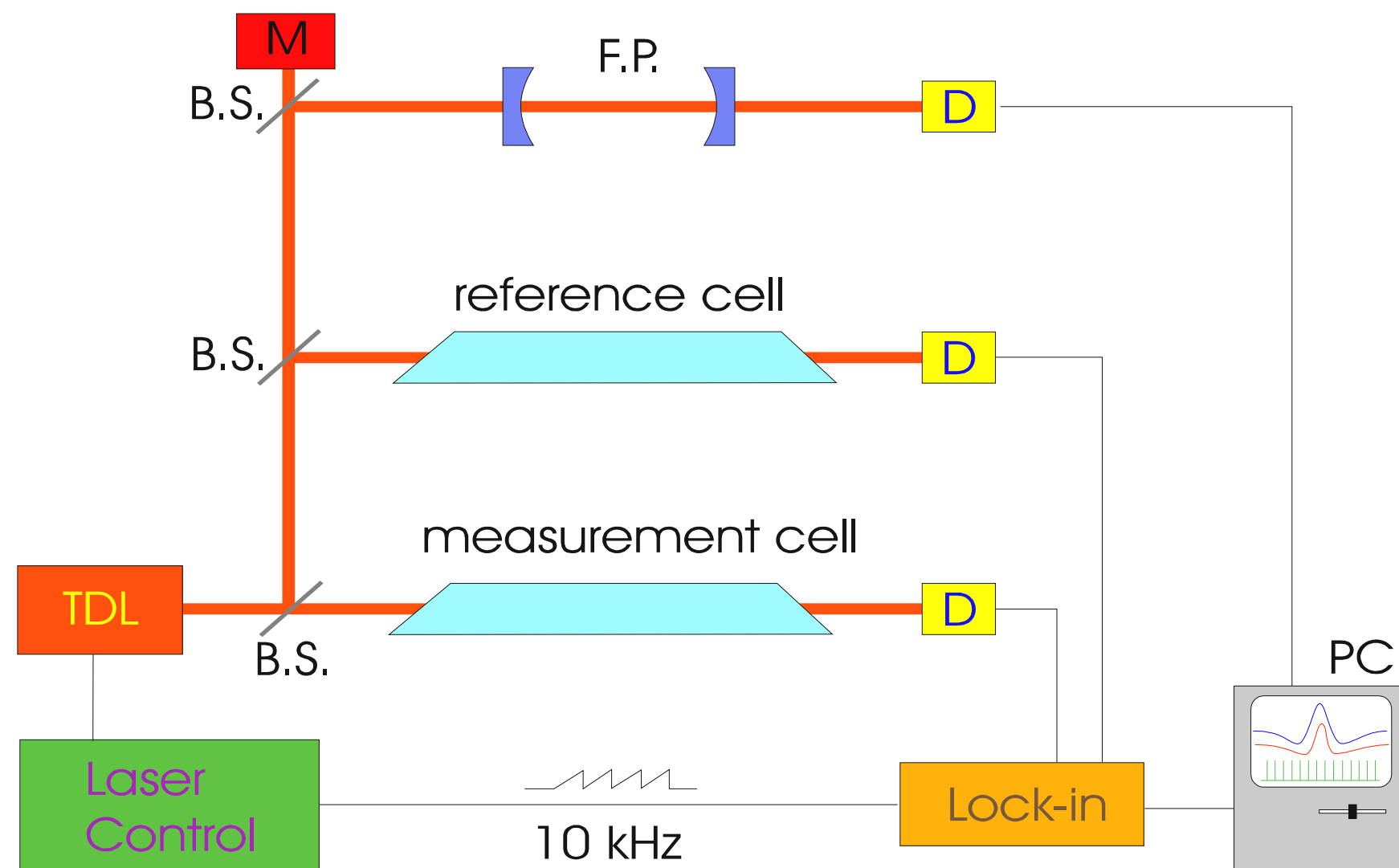
The availability of tunable laser sources, like commercial diode lasers (DLs), increased the interest on the spectroscopy of overtone and combination of ro-vibrational bands in the visible and in the NIR. DLs are suitable radiation sources for high resolution spectroscopy and in particular for the study of the optical resonances of many molecules, like  $\text{CH}_4$ <sup>1</sup>,  $\text{C}_2\text{H}_2$ <sup>2</sup>,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ <sup>3</sup>,  $\text{HCl}$ <sup>4</sup>,  $\text{HCN}$ ,  $\text{HF}$ ,  $\text{NH}_3$ <sup>5</sup>,  $\text{NO}_2$ <sup>6</sup>,  $\text{O}_2$ <sup>7</sup>, etc.. They can be easily modulated through their injection current, allowing the use of frequency modulation (FM) techniques.

When the amplitude of the FM is chosen much lower than the resonance line-width, the FM spectroscopy is usually called wavelength modulation (WM) spectroscopy. Here we apply the WM spectroscopy to water vapor in order to determine the line-shape parameters.

## Experimental set-up

The DL source is driven by a stabilized low-noise current supply. Its temperature is monitored within 0.002 K by a high-stability controller. The wavelength scan is obtained by adding a low frequency ( $\sim 1\text{ Hz}$ ) sawtooth signal to the driving current. The collimated DL radiation is splitted in three different beams, which go through a confocal Fabry-Perot interferometer, for marking the frequency, and through two different glass cells containing the sample

gas: one at a constant pressure as reference, and the other at progressively increased pressure. The transmitted radiation is collected by silicon photodiodes and the resulting signals are simultaneously acquired by a desk-top computer. For the harmonic detection a sinusoidal modulation current (at  $\sim 10$  kHz) is mixed to the diode laser injection current: the signals transmitted through the two cells are sent to a lock-in amplifier to extract the desired harmonic component.



**Fig. 1.** Sketch of the experimental apparatus for the WM spectroscopy. D: photodiode; B.S.: beam splitter; F.P.: Fabry-Perot interferometer; TDL: tunable diode laser; M: monochromator; PC: desk-top computer.

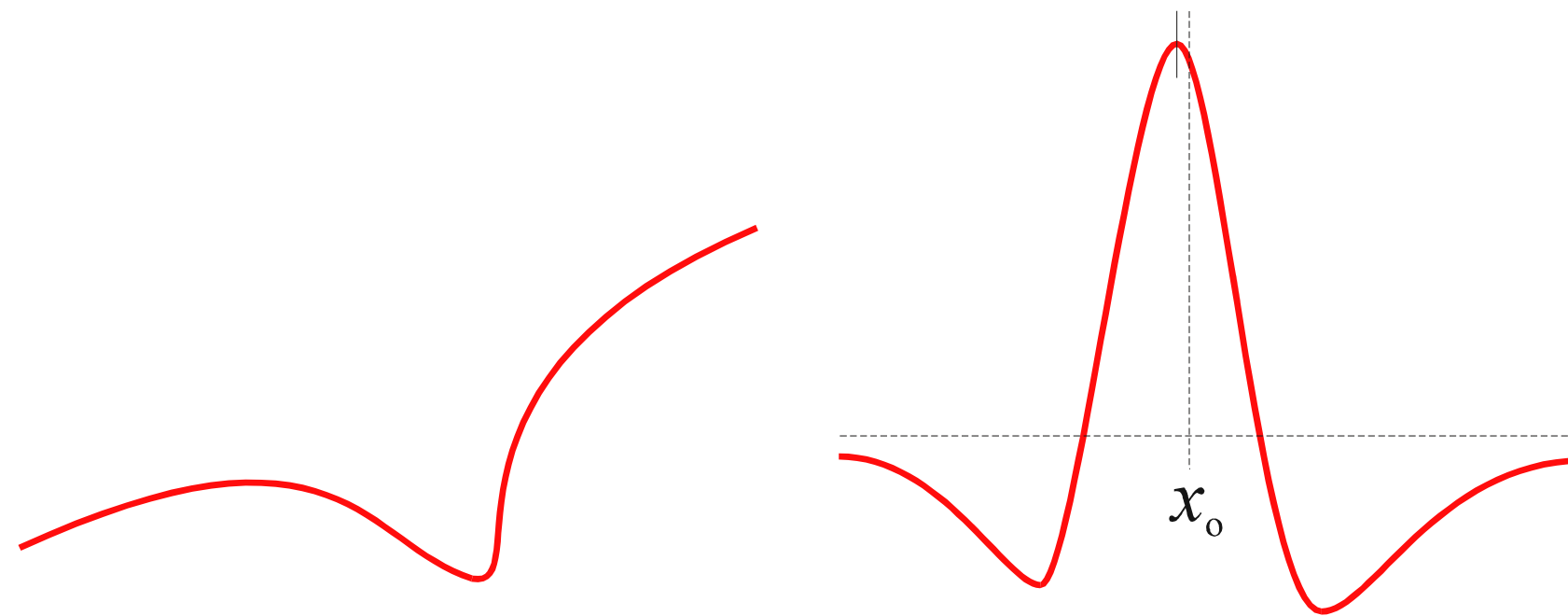
## Frequency modulation technique

When FM is used, the emission frequency  $\bar{\nu}$  of the DL is sinusoidally modulated via the injection current,

$$\nu = \bar{\nu} + m \cos 2\pi\nu_m t;$$

and the  $n$ -th harmonic component of the transmitted signal is detected by a lock-in amplifier at a reference frequency  $n\nu_m$ , multiple of the modulation frequency. When the amplitude  $m$  of the modulation is small compared to the width of the absorption line, the  $n$ -th harmonic component is proportional to the  $n$ -th derivative of the transmitted signal. In particular we detected the second harmonic component ( $2f$  detection).

The presence of a residual amplitude modulation (RAM) when modulating the DL emission frequency, even if it is relatively small, gives a sloping background in the direct absorption (DA) signal, and an asymmetry in the  $2f$  signal. As shown in Fig. 2, the center of the line does not match the maximum of the  $2f$  signal. The displacement is proportional to the slope of the emission profile as well as to the width of the line. This issue is of capital importance for what concerns the pressure induced shift since the apparent displacement of the center is proportional to the pressure. Let us analyze it in detail.



**Fig. 2.** DA (left) and 2<sup>nd</sup> harmonic WM signal (right) as detected by the DL spectrometer.

Generally the intensity of the radiation transmitted through a sample can be written as the product of the incoming intensity  $I_0(\nu)$  and the transmittance  $T(\nu)$ , where  $\nu$  is the distance from the central frequency of the line:

$$I(\nu) = I_0(\nu)T(\nu).$$

Let us assume a laser emission profile varying linearly with the frequency:

$$I_0(\nu) = \bar{I}_0(1 + s\nu),$$

where  $\bar{I}_0$  is the intensity at  $\nu = 0$  and  $s$  is the fractional variation per frequency unit. Hence the second derivative of the transmitted power is:

$$I''(\nu) = \bar{I}_0(1 + s\nu)T'' + 2s\bar{I}_0T'. \quad (1)$$

The apparent displacement of the center depends on the slope  $s$  of the profile and on the width  $\gamma_L$  of the line. By increasing the pressure, the width becomes larger and an apparent shift of the center occurs. This is proportional to the pressure in a way very similar to the *real* pressure induced shift. Let us write the transmittance in the weak absorption approximation:

$$T(\nu) = 1 - Sx \frac{\gamma_L}{\pi} \frac{1}{\nu^2 + \gamma_L^2} \quad (2)$$

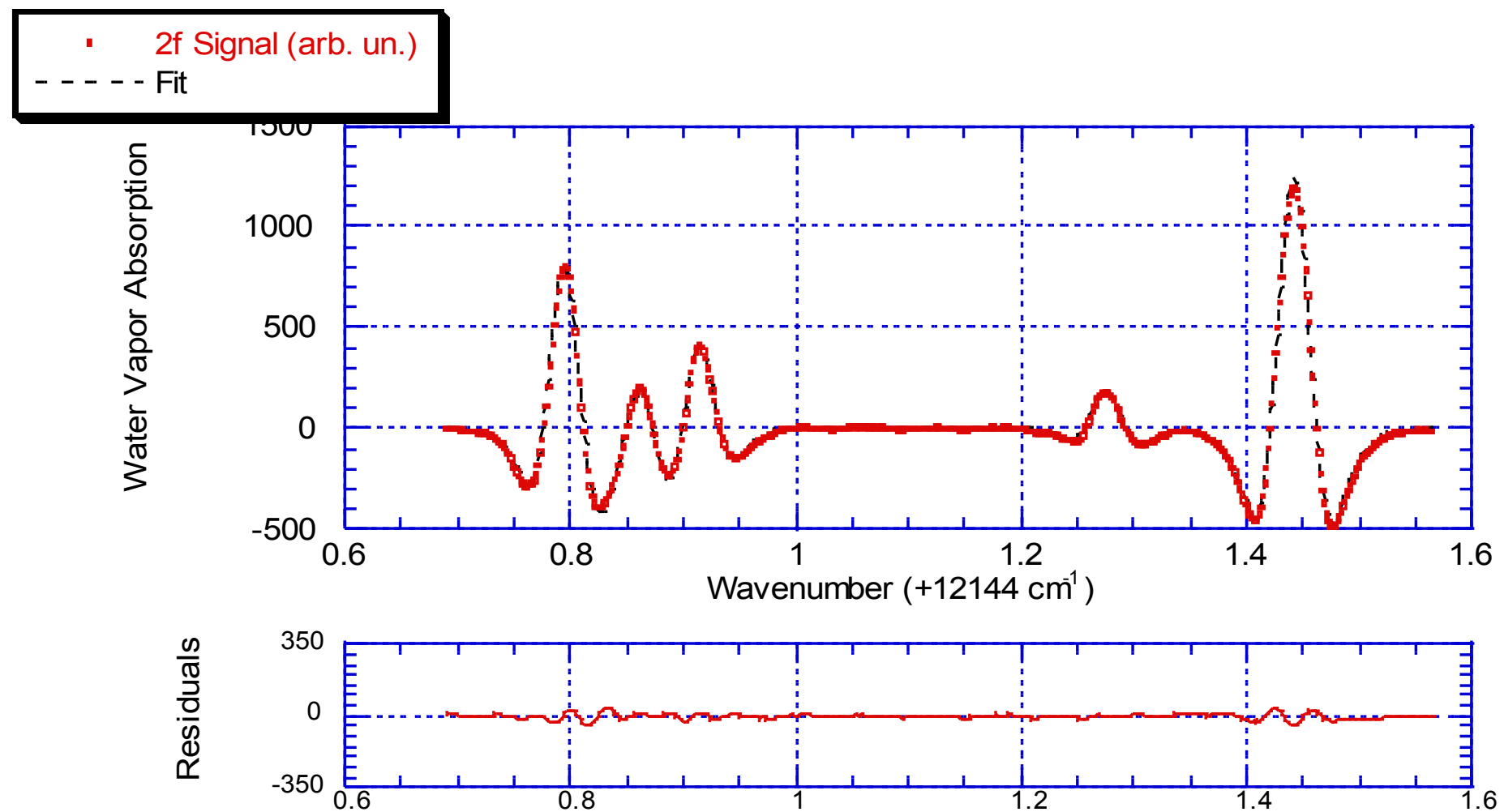
where a Lorentzian shape of the absorption line has been adopted,  $S$  is the line strength and  $x$  is the optical density. To get the shifting of the maximum of the  $2f$  signal, we expand the second derivative of Eq.(2) around  $\nu = 0$ :

$$\nu_{max} = \frac{1}{4} \gamma_L \left( \xi - \frac{5}{16} \xi^3 + \dots \right)$$

where  $\xi = s\gamma_L$ .

Putting  $\xi = 0.1$ ,  $\nu_{max}/\gamma_L = 1/4\xi \cong 0.025$ , so the displacement can be of the same order of magnitude of the pressure induced shift. Thus, if the maximum of the second derivative signal is used to determine the center of the line, it occurs an error that is proportional to the width, giving an incorrect contribution to the measurement of the pressure-shift coefficient. A refined knowledge of the lineshape parameters is obtained by fitting the second derivative signal. Nevertheless in the fit procedure one can be inclined to use simply the 2<sup>nd</sup> derivative of the

absorption function  $T''$ , multiplying it by a sloping linear function to match the asymmetry of the experimental signal – this is equivalent to consider only the first term of the right side of Eq.(1). Although at a first sight the result of the fit could seem qualitatively satisfactory, the resulting parameters are incorrect: the position of the center of the line will be again strongly affected by the pseudo-shift. The only choice for the fitting function is Eq. (1).



**Fig. 3.** Water vapor spectrum around  $12145 \text{ cm}^{-1}$  ( $\sim 823 \text{ nm}$ ) as revealed *in-phase* onto the 2<sup>nd</sup> harmonic at room temperature (RT) along with the best fit and its residuals. The  $\text{H}_2\text{O}$  pressure was 20 Torr. The acquisition time constant was 12.5 ms. All the features are the second derivatives of the absorptions as got by the WM spectrometer and their intensities and positions agree with what reported in HITRAN database<sup>8</sup>:  $12144.795$ ,  $12144.862$ ,  $12144.915$ ,  $12145.279$ ,  $12145.444 \text{ cm}^{-1}$  respectively.

## Experimental results

An example of spectrum obtained by using the DL spectrometer is shown in Fig. 3, where the second derivative of a small portion of the water vapor overtone band at around 823 nm is displayed with the best fit.

The measured line broadening and shifting coefficients related to three different buffer gases are listed in the following table. For convenience, the rotational quantum assignments are given for each line and the air-broadening coefficients from HITRAN database<sup>8</sup> ( $\gamma_{\text{air}}^{\text{Hitran}}$ ) are shown for comparison. HITRAN has a complete set of air-broadening coefficients for these lines, which has been got from a literature survey. All the errors are computed for 3 standard deviations ( $\sigma$ ); J' stands for upper rotational state, while J'' for the lower.

Water vapor collisional-broadening FWHM and shifting coefficients at RT.

Wavenumber cm <sup>-1</sup>	Rot. Transition J' <sub>Ka' Kc'</sub> ← J'' <sub>Ka'' Kc''</sub>	$\gamma_{\text{air}}$ MHz/Torr	$\gamma_{\text{H}_2}$ MHz/Torr	$\gamma_{\text{He}}$ MHz/Torr	$\gamma_{\text{air}}^{\text{Hitran}}$ MHz/Torr	$S_{\text{air}}$ MHz/Torr	$S_{\text{H}_2}$ MHz/Torr	$S_{\text{He}}$ MHz/Torr
12014.146	5 <sub>15</sub> - 6 <sub>16</sub>	6.2 ± 0.1	4.7 ± 0.2	1.9 ± 0.1	6.50	-0.8 ± 0.1	-0.9 ± 0.1	0.1 ± 0.1
12037.515	4 <sub>04</sub> - 5 <sub>05</sub>	7.0 ± 0.1	5.8 ± 0.2	1.9 ± 0.2	7.38	-0.8 ± 0.1	-0.9 ± 0.1	0.0 ± 0.1
12038.657	4 <sub>14</sub> - 5 <sub>15</sub>	6.9 ± 0.1	5.3 ± 0.1	1.6 ± 0.1	6.14	-0.8 ± 0.1	-1.0 ± 0.1	0.0 ± 0.1
12052.819	3 <sub>31</sub> - 4 <sub>32</sub>	6.5 ± 0.3	5.3 ± 0.3	2.7 ± 0.5	6.63	-0.7 ± 0.1	-0.6 ± 0.1	0.3 ± 0.1
12053.370	3 <sub>22</sub> - 4 <sub>23</sub>	7.0 ± 0.2	6.2 ± 0.3	1.9 ± 0.1	7.32	-0.4 ± 0.1	-0.7 ± 0.1	0.1 ± 0.1
12060.108	3 <sub>03</sub> - 4 <sub>04</sub>	8.3 ± 0.4	6.8 ± 0.1	2.0 ± 0.1	7.69	-0.6 ± 0.1	-0.8 ± 0.1	0.1 ± 0.1
12082.223	2 <sub>02</sub> - 3 <sub>03</sub>	7.7 ± 0.1	6.6 ± 0.3	1.9 ± 0.1	8.13	-0.5 ± 0.2	-0.6 ± 0.1	-0.1 ± 0.1
12098.170	1 <sub>10</sub> - 2 <sub>11</sub>	7.2 ± 0.2	6.9 ± 0.1	1.8 ± 0.1	8.13	-0.5 ± 0.1	-0.6 ± 0.2	0.0 ± 0.1
12103.674	1 <sub>01</sub> - 2 <sub>02</sub>	6.7 ± 0.2	6.7 ± 0.2	1.6 ± 0.1	8.59	-0.8 ± 0.1	-0.8 ± 0.1	-0.1 ± 0.1
12113.883	3 <sub>13</sub> - 3 <sub>12</sub>	8.1 ± 0.3	8.0 ± 0.2	2.0 ± 0.1	8.03	-0.4 ± 0.1	-0.6 ± 0.1	0.1 ± 0.1
12136.517	5 <sub>33</sub> - 5 <sub>32</sub>	4.4 ± 0.1	4.2 ± 0.1	1.6 ± 0.1	6.77	-0.7 ± 0.1	-1.1 ± 0.1	0.0 ± 0.1
12153.702	3 <sub>21</sub> - 3 <sub>22</sub>	6.5 ± 0.1	6.2 ± 0.1	1.7 ± 0.1	7.43	-0.1 ± 0.2	-0.7 ± 0.1	0.1 ± 0.1
12156.208	1 <sub>10</sub> - 1 <sub>11</sub>	6.4 ± 0.2	7.3 ± 0.1	1.8 ± 0.1	8.21	0.0 ± 0.1	-0.4 ± 0.1	0.3 ± 0.1
12159.813	4 <sub>22</sub> - 4 <sub>23</sub>	7.0 ± 0.2	5.9 ± 0.1	1.7 ± 0.1	6.57	-0.4 ± 0.1	-0.3 ± 0.1	0.0 ± 0.1

The correct assignments of the lines have been extracted from HITRAN database; they all belong to the vibrational transition (2,1,1) ← (0,0,0)

For the 12053.370 cm<sup>-1</sup> line we got also the N<sub>2</sub>-broadening and -shifting coefficients:

$$\gamma_{\text{N}_2} = (7.8 \pm 0.4) \text{ MHz/Torr} \quad S_{\text{N}_2} = (-0.5 \pm 0.1) \text{ MHz/Torr.}$$

By remembering that for this line  $\gamma_{\text{air}} = (7.0 \pm 0.2) \text{ MHz/Torr}$ , we have:

$$\gamma_{\text{air}}/\gamma_{\text{N}_2} = (0.9 \pm 0.2),$$

within  $3\sigma$ , which agrees with what reported in literature<sup>9</sup>.

For the 12014.146 and the 12052.819 cm<sup>-1</sup> lines the broadening and shifting coefficients have been measured by adopting a heavier noble gas too, neon; the two sets of results are very similar:

$$\gamma_{\text{Ne}} = (1.4 \pm 0.2) \text{ MHz/Torr}, \quad S_{\text{Ne}} = (-0.1 \pm 0.1) \text{ MHz/Torr},$$

and

$$\gamma_{\text{Ne}} = (1.4 \pm 0.1) \text{ MHz/Torr}, \quad S_{\text{Ne}} = (-0.2 \pm 0.1) \text{ MHz/Torr};$$

respectively.



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