

Water vapor overtones pressure line broadening and shifting measurements

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Abstract. By using a spectrometer having as source a commercial etherostructure $\text{Al}_x\text{Ga}_{1-x}\text{As}$ diode laser operating in “free-running mode”, line shape parameters of some water vapor ro-vibrational overtones at 820–830 nm have been measured at room temperature. These weak absorption lines have been detected by using the wavelength modulation spectroscopy technique with second-harmonic detection. The broadening and shifting coefficients have been obtained by fitting the collected second-harmonic absorption features while varying the pressure of different foreign gases.

PACS. 33.70.Jg Line and band widths, shapes, and shifts – 33.20.Ea Infrared spectra – 07.57.Ty Infrared spectrometers, auxiliary equipment, and techniques

1 Introduction

As an important atmospheric constituent and a generally relevant pointer for checking combustion and propulsion processes, the water vapor molecule has been extensively studied. Specifically, the absorptions in the NIR and IR spectra have been detected by means of non monochromatic as well as by monochromatic spectroscopic sources. In particular, as the double heterostructure diode lasers became a cheap and easy-to-handle sources, they gained more room in the field of atomic and molecular spectroscopy.

The room-temperature-operated AlGaAs and AlGaInP diode lasers (DLs) emissions can be easily tuned and scanned around most of the ro-vibrational overtone transitions of molecules like CH_4 , C_2H_2 , C_2H_4 , HCl , HCN , HF , H_2O , NH_3 , NO_2 , O_2 , O_3 , etc. Unfortunately the overtone line strengths are usually weak and therefore noise-reduction techniques must be used.

The frequency modulation (FM) technique [1] can be applied to DLs by modulating their injection current. 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. Overtone resonances have been successfully observed by using AlGaAs diode lasers with WM spectroscopy and harmonic detection techniques [2–4].

Unfortunately a change in the injection current of the DLs causes a variation of the emission power, inducing a typical sloping background; therefore an amplitude modulation (AM) comes always with FM. This induces an asymmetry of the collected shapes that, to avoid

systematic errors, must be properly taken into account in the data analysis.

This work shows an example of utilization of these sources in high resolution molecular spectroscopy by using the WM technique. Here the main issue is the measurement of collisional broadened and shifted H_2O absorption lines centered at 823 nm, belonging to the combination overtone vibrational transitions $2\nu_1 + \nu_2 + \nu_3$ from the ground state, where ν_1 is the symmetrical stretching, ν_2 is the bending, and ν_3 is the antisymmetrical stretching vibrational mode.

These weak lines have been observed in the past by conventional absorption spectroscopy in the earth atmosphere by the use of telescopes and the sun as light source [5], and more recently by Fourier transform [6] and by diode laser [7] spectrometers in laboratory frames.

The use of the WM technique applied to coherent sources like DLs permits to reach good sensitivities per unit of optical path-length even for very weak lines like those considered in this paper.

2 Experimental apparatus

The experimental apparatus adopted in this work for the WM spectroscopy is shown in Figure 1. For this experiment the HITACHI DL Mod. HL8311G has been adopted as source. This type of CW laser has a single transverse and longitudinal mode and an emission power of 15 mW when operating at a 70 mA injection current. The current was driven by a stabilized low-noise current generator, which permitted also the scan of the emission wavelength by mixing to the driving current an attenuated low frequency (~ 1 Hz) sawtooth signal.

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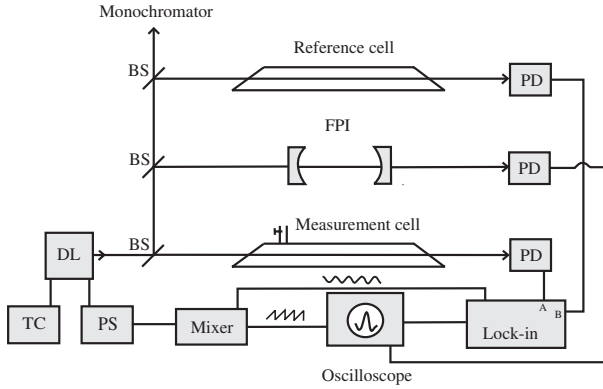


Fig. 1. Outline of the experimental apparatus. DL: diode laser; BS: beam splitter; PD: photodiode; FPI: Fabry-Perot interferometer; TC: temperature controller; PS: power supply.

The DL was temperature controlled within $0.002\text{ }^{\circ}\text{C}$ during the whole measurement procedure by a high-stability temperature controller. In fact, the temperature dependence of the diode lasers emission wavelength is critical but linear ($\sim 0.2\text{ nm}/^{\circ}\text{C}$), therefore one of the major requirements for using these sources is the very good temperature stabilization. The current dependence for small current variations can be considered linear too, with a dependence of $\sim 0.01\text{ nm}/\text{mA}$. By using DL in free-running mode, as in this case, mode hops permit only a partial coverage of the nominal diode laser operating spectral range, but this choice is the simplest and the most economical. The measurement cell employed in this work was a 1 m long glass cylindrical cell, with a diameter of 5 cm and with two Brewster angle glass windows. The laser probe passed five times through this cell to reach a path-length of 5 m. A confocal 5 cm Fabry-Perot interferometer was adopted to linearize the scan of the diode laser over the scan range and to check the laser emission mode. A 0.35 m monochromator was employed for the rough wavelength reading. For the line-shift measurements, a reference cell equal to the measurement one was kept at fixed saturated water vapor pressure at room temperature (RT) ($P_{\text{sat}} \simeq 20\text{ torr @ } RT$) with an optical path-length of 5 m too. For the “in-phase” detection a sinusoidal modulation at a frequency of 3–4 kHz was added to the DL injection current. The transmittance was collected by silicon photodiodes and sent to two lock-in amplifiers to extract the second harmonic signals. By this way a good signal-to-noise ratio (S/N) has been obtained, typically ranging from ~ 3 to ~ 30 , depending of the gas pressure. The detectors have not been oriented for a normal incidence of the laser beam, in order to avoid any feedback from their windows to the laser, that could greatly increase the noise.

3 Experimental details and results

The DL HL8311G emits at 830 nm at RT . Around this wavelength many water vapor overtone absorption lines can be observed. Spectral lines could be detected down to 820 nm by cooling the DL to some degrees below $0\text{ }^{\circ}\text{C}$.

These lines belong to the vibrational transitions bands $(2, 1, 1) \leftarrow (0, 0, 0)$, the strongest, or $(3, 1, 0) \leftarrow (0, 0, 0)$, $(1, 3, 1) \leftarrow (0, 0, 0)$, as well as $(1, 1, 2) \leftarrow (0, 0, 0)$ the weakest. We focalized our attention to the $(2, 1, 1)$ and the collisional broadening and shifting coefficients have been obtained for its 14 absorption resonances. The measurement and reference cells were evacuated down to some tens of mtorr by a rotary pump, then a small quantity of distilled water has been let in and an equilibrium vapor pressure has been settled. After this operation the reference cell has been sealed in order to maintain this equilibrium condition. Once an absorption line is found to be intense and well isolated from the others, the foreign gas was admitted in the measurement cell with a progression of some tens of torr per time from about 20 to 400 torr. The stability of the water vapor partial pressure was guaranteed within the experiment by controlling the drop of the pressure at the beginning of each measurement run. Usually an experiment lasted from 20 to 30 minutes and during this time the maximum drop caused by wall adsorption has been measured to be 2 torr. This is compatible with what observed by others in different measurement cells [8].

The two lock-in amplifiers collected the second derivative signals both from the measurements and reference cells, and sent them to a computer to fit and extract the typical line-shape and position parameters for each H_2O absorption line. The right algorithm for obtaining this has been developed specifically for this purpose [9] and tested previously with a similar spectroscopy work on oxygen [4] in the weak absorption limit, for which the Lambert–Beer equation can be written:

$$I(\nu) \simeq I_0(\nu)[1 - \alpha(\nu)x],$$

where $I(\nu)$ is the transmitted radiation intensity at frequency ν , $I_0(\nu)$ is the incoming intensity, x is the optical density, that is the product of the density of the gas by the radiation path-length, $\alpha(\nu)$ is the absorption coefficient. In substance the fit program describes the absorption feature by a Voigt function superimposed to a sloping background coming from the AM. In fact, as stated previously, when we swept the DL laser wavelength around the chosen resonance by the DL current, we swept also the laser intensity, and this results in an asymmetric line shape. The Full Width at Half the Maximum (FWHM) of the Lorentzian component of the Voigt (I) profile, which originates from the molecular collision processes, has been systematically collected at various pressure values, and within the errors we did not observe any deviation from the linearity of the behavior of $\Gamma(p)$ that could justify a Dicke narrowing [7] in this range of pressure.

In Figure 2a portion of the spectrum analyzed in this work is shown. The second derivatives of five water vapor lines are visible in a range spanning 1 cm^{-1} without any laser mode hop. According to HITRAN database [11], all the lines belong to the $(2, 1, 1) \leftarrow (0, 0, 0)$ transition. Their positions agree with the ones listed by HITRAN within 0.01 cm^{-1} . The high S/N ratio is remarkable.

In Figure 3 there is an example of FWHM air-broadening measurements of one water vapor absorption

Table 1. List of measured water vapor FWHM absorption lines broadening parameters at *RT*.

Wavenu. (cm ⁻¹)	Rot.Tr. (^a)	γ_{air} (MHz/torr)	γ_{H_2} (MHz/torr)	γ_{He} (MHz/torr)	$\gamma_{\text{air}}^{\text{Hitran}}$ (MHz/torr)
12 014.146	5 ₁₅ - 6 ₁₆	6.2 ± 0.1	4.7 ± 0.2	1.9 ± 0.1	6.50
12 037.515	4 ₀₄ - 5 ₀₅	7.0 ± 0.1	5.8 ± 0.2	1.9 ± 0.2	7.38
12 038.657	4 ₁₄ - 5 ₁₅	6.9 ± 0.1	5.3 ± 0.1	1.6 ± 0.1	6.14
12 052.819	3 ₃₁ - 4 ₃₂	6.5 ± 0.3	5.3 ± 0.3	2.7 ± 0.5	6.63
12 053.370	3 ₂₂ - 4 ₂₃	7.0 ± 0.2	6.2 ± 0.3	1.9 ± 0.1	7.32
12 060.108	3 ₀₃ - 4 ₀₄	8.3 ± 0.4	6.8 ± 0.1	2.0 ± 0.1	7.69
12 082.223	2 ₀₂ - 3 ₀₃	7.7 ± 0.1	6.6 ± 0.3	1.9 ± 0.1	8.13
12 098.170	1 ₁₀ - 2 ₁₁	7.2 ± 0.2	6.9 ± 0.1	1.8 ± 0.1	8.13
12 103.674	1 ₀₁ - 2 ₀₂	6.7 ± 0.2	6.7 ± 0.2	1.6 ± 0.1	8.59
12 113.883	3 ₁₃ - 3 ₁₂	8.1 ± 0.3	8.0 ± 0.2	2.0 ± 0.1	8.03
12 136.517	5 ₃₃ - 5 ₃₂	4.4 ± 0.1	4.2 ± 0.1	1.6 ± 0.1	6.77
12 153.702	3 ₂₁ - 3 ₂₂	6.5 ± 0.1	6.2 ± 0.1	1.7 ± 0.1	7.43
12 156.208	1 ₁₀ - 1 ₁₁	6.4 ± 0.2	7.3 ± 0.1	1.8 ± 0.1	8.21
12 159.813	4 ₂₂ - 4 ₂₃	7.0 ± 0.2	5.9 ± 0.1	1.7 ± 0.1	6.57

The correct assignments of these lines have been extracted from the HITRAN database [11]; they all belong to the vibrational transition (2, 1, 1) ← (0, 0, 0).

^a $J'_{K'_a K'_c} \leftarrow J''_{K''_a K''_c}$, where ' stands for "upper" state, and '' for "lower" state.

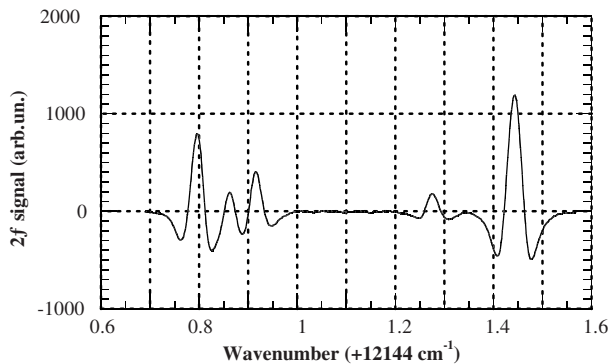


Fig. 2. Water vapor spectrum around 12145 cm⁻¹. All the features are the second derivatives of the absorptions as got by the WM spectrometer and their intensities and positions agree with what reported by HITRAN database: 12 144.795, 12 144.862, 12 144.915, 12 145.279, 12 145.444 cm⁻¹, respectively. The lock-in amplifier time constant was 12.5 ms. The H₂O pressure was the vapor pressure at *RT*, that is ~ 20 torr.

line (12 082.223 cm⁻¹) obtained by varying the air pressure in the measurement cell at *RT*.

The measured absorption line broadening are listed in Table 1, where the results related to three buffer gases are shown. For convenience, the rotational quantum assignments are given for each line and the air-broadening coefficients extracted from HITRAN database ($\gamma_{\text{air}}^{\text{Hitran}}$) are shown. All the errors are computed for 3 standard deviations (σ), J' stands for upper rotational state, while J'' for the lower. HITRAN database has a complete set of air-broadening coefficients for these lines, which has been got from a literature survey. In a comparison, our coefficients agree with them only in some case, but in many cases are different, even if they are of the same order of magnitude.

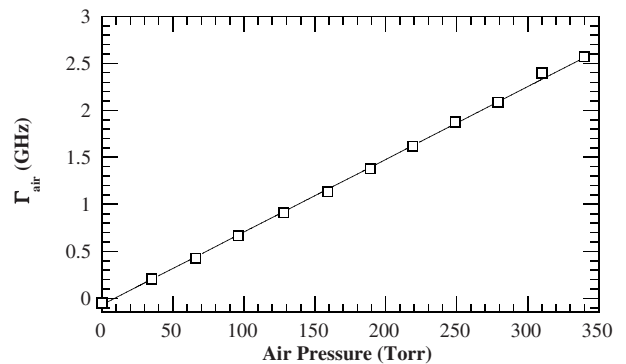


Fig. 3. Plot of the Lorentzian FWHM measurements (Γ_{air}) as varying the air pressure at *RT*. The absorption line is the 12 082.223 cm⁻¹. The best linear fit is shown. The maximum errors are within the squares symbols dimensions.

In Figure 4 the air-shifting of the 12 082.223 cm⁻¹ line is displayed as a function of the total pressure in the cell. In spite of the big errors the negative slope is evident.

In Table 2 the line shifting parameters are shown for the same buffer gases. All the results are obtained at room temperature. The shifting coefficients got by Ponsardin *et al.* [10] are in agreement with these, but they observed the lines lying below 820 nm, limit that our spectrometer could not reach by the diode lasers available in our laboratory.

Most of the He-shifting parameters are so weak to be virtually zero for this apparatus, while two of them (12 052.819, 12 156.208) are certainly positive.

For checking the rule $\gamma_{\text{air}} = 0.9\gamma_{\text{N}_2}$ found in literature [12], also the N₂-broadening has been measured

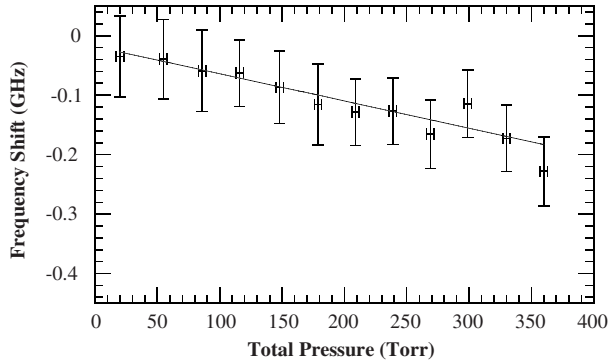


Fig. 4. Shifting of the position of the absorption line collected in the measurement and reference cells as the air pressure is increased for the $12082.223 \text{ cm}^{-1}$ line. The pressure is the total pressure in the measurement cell. The best linear fit is shown.

Table 2. List of measured water vapor absorption line shifting parameters at *RT*.

Wavenumber (cm^{-1})	S_{air} MHz/torr	S_{H_2} MHz/torr	S_{He} MHz/torr
12014.146	-0.8 ± 0.1	-0.9 ± 0.1	0.1 ± 0.1
12037.515	-0.8 ± 0.1	-0.9 ± 0.1	0.0 ± 0.1
12038.657	-0.8 ± 0.1	-1.0 ± 0.1	0.0 ± 0.1
12052.819	-0.7 ± 0.1	-0.6 ± 0.1	0.3 ± 0.1
12053.370	-0.4 ± 0.1	-0.7 ± 0.1	0.1 ± 0.1
12060.108	-0.6 ± 0.1	-0.8 ± 0.1	0.1 ± 0.1
12082.223	-0.5 ± 0.2	-0.6 ± 0.1	-0.1 ± 0.1
12098.170	-0.5 ± 0.1	-0.6 ± 0.2	0.0 ± 0.1
12103.674	-0.8 ± 0.1	-0.8 ± 0.1	-0.1 ± 0.1
12113.883	-0.4 ± 0.1	-0.6 ± 0.1	0.1 ± 0.1
12136.517	-0.7 ± 0.1	-1.1 ± 0.1	0.0 ± 0.1
12153.702	-0.1 ± 0.2	-0.7 ± 0.1	0.1 ± 0.1
12156.208	0.0 ± 0.1	-0.4 ± 0.1	0.3 ± 0.1
12159.813	-0.4 ± 0.1	-0.3 ± 0.1	0.0 ± 0.1

for the $12053.370 \text{ cm}^{-1}$ line along with the shift:

$$\begin{aligned}\gamma_{\text{N}_2} &= 7.8 \pm 0.4 \text{ MHz/torr} \\ S_{\text{N}_2} &= -0.5 \pm 0.1 \text{ MHz/torr}.\end{aligned}$$

By remembering that for this line

$$\gamma_{\text{air}} = 7.0 \pm 0.2 \text{ MHz/torr},$$

we got:

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

within 3σ .

For the $12014.146 \text{ cm}^{-1}$ and the $12052.819 \text{ cm}^{-1}$ lines the broadening and shifting coefficients have been measured also by adopting a heavier noble gas, neon; the two sets of results are very similar:

$$\begin{aligned}\gamma_{\text{Ne}} &= 1.4 \pm 0.2 \text{ MHz/torr} \\ S_{\text{Ne}} &= -0.1 \pm 0.1 \text{ MHz/torr};\end{aligned}$$

and

$$\begin{aligned}\gamma_{\text{Ne}} &= 1.4 \pm 0.1 \text{ MHz/torr} \\ S_{\text{Ne}} &= -0.2 \pm 0.1 \text{ MHz/torr};\end{aligned}$$

respectively.

4 Conclusions

45 collisional broadening and 45 shifting coefficients by different perturber gases have been measured at *RT* for the water vapor combination overtone transitions located around 12100 cm^{-1} . An AlGaAs diode laser based spectrometer has been employed for this purpose with the simplest configuration, that is the “free-running” mode. The results are similar to what reported in literature by using more expensive systems, even if the signal to noise ratio is lower. By the aid of a multipass measurement cell it is virtually possible to increase such a ratio and to compete with the traditional spectroscopy techniques. A sole wavelength-modulated diode laser permitted the detection of 14 water vapor absorption lines by changing its temperature from -3 to $37 \text{ }^\circ\text{C}$. The sensitivity of this diode laser spectroscope showed to be of the order of some tens of ppm per meter of optical path length when applied to this water vapor absorptions.

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