

Diode laser spectroscopy of oxygen electronic band at 760 nm

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Summary. — Collisional broadening and shift coefficients have been obtained by analyzing the line shapes of oxygen absorptions in the 760 nm electronic band. By using a diode laser spectrometer with commercially available heterostructure $\text{Al}_x\text{Ga}_{1-x}\text{As}$ diode lasers operating in “free-running mode”, line shape parameters have been collected at room temperature by varying the gas pressure. A systematic study has been carried on seven absorption lines by scanning the diode laser emission wavelength around the gas resonances. The weak absorption lines have been detected by using the wavelength modulation (WM) spectroscopy technique with 2^{nd} harmonic detection.

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1. – Introduction.

The double heterostructure diode lasers (DLs) have become the cheapest monochromatic sources in the field of the atomic and molecular spectroscopy. Commercially available AlGaAs and InGaAlP DLs emissions can be easily tuned and scanned around most of the ro-vibrational overtone or electronic absorptions of molecules like CH₄, C₂H₂, C₂H₄, HCl, HCN, HF, H₂O, NH₃, NO₂, O₂, O₃, etc.. Unfortunately these transition lines are weak and therefore noise-reduction techniques must be used.

The frequency modulation (FM) technique [1] can be applied to DLs by playing with their injection current. When the frequency of the modulation is chosen much lower than the resonance line-width, the FM spectroscopy is usually called wavelength modulation (WM) spectroscopy. Overtone absorption resonances have been successfully observed by using AlGaAs diode lasers with WM spectroscopy and harmonic detection techniques [2, 3].

Unfortunately a change in the injection current causes a variation of the emission power, inducing a typical sloping background in the transmitted signal, therefore, besides a FM, one has to deal with an unavoidable amplitude modulation. This brings to an asymmetry of the collected shapes that must be properly taken into account to avoid systematic errors when analyzing the data.

In this work we show an example of utilization of these type of sources in accurate molecular spectroscopy by using the WM technique. In particular we focalize our attention on the measurement of collisional broadened and shifted ¹⁶O₂

absorption lines in the atmospheric A band [4], namely the lines belonging to the electronic transition $b^1\Sigma_g^+ \leftarrow X^3\Sigma_g^-$ (vibrational transition $0 - 0$).

The knowledge of the pressure induced broadening and shift coefficients can be important in the atmospheric analysis, especially for constructing spectroscopical maps of the planets. Moreover, the knowledge of these parameters is important also to better understand the intermolecular interactions.

The oxygen weak lines belonging to the A band have been observed in the past by conventional absorption spectroscopy in the earth atmosphere by using telescopes and the sun as light source [5], and more recently by diode laser spectroscopy [6] in laboratory frames.

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 such as the electric dipole forbidden ones which this paper is concerning of. Since a diode laser apparatus is much cheaper than either the dye laser based one and the high resolution Fourier transform spectrometer, in practice it enables any research laboratory to do high resolution spectroscopy.

2. – Experimental apparatus.

As stated previously, WM spectroscopy techniques have been adopted here for pressure broadening and shift measurements. The experimental apparatus for the WM technique is shown in fig. 1. For this experiment the SHARP DL mod. LT030MD has been utilized as source. This type of DL has single modes both transversely and longitudinally. The current is driven by a stabilized low-noise cur-

rent generator, which permits also the scan of the emission wavelength by mixing to the driving current an attenuated low frequency ($\sim 1\text{Hz}$) sawtooth signal. The DL is temperature regulated within 0.002 K by a Peltier junction driven by a high stability temperature controller. The diode laser emission wavelength shows a strong, even if linear, temperature dependence ($\sim 0.2\text{ nm/K}$); therefore one of the major requirements, when using these sources for spectroscopy, is the very good temperature stabilization. The mode hops are the major DL drawback in free-running mode, which is the simplest and cheapest way to operate. The current dependence for small variations can be considered linear too, with a dependence of about 0.01 nm/mA . The measurement cell used in this work is a Pyrex cylindrical cell, 1 m long and 5 cm in diameter. The laser probe passes three times through this cell to reach a path-length of 3 m . A confocal 5 cm Fabry-Perot interferometer is adopted to mark the frequency scan and to check the goodness of the DL emission. A 350 mm focal length monochromator is employed for the rough wavelength reading. For the line-shift measurements, the fixed pressure oxygen reference is a 3 m air-path, keeping into account that the atmospheric oxygen partial pressure is 160 Torr . Silicon photodiodes collect the transmitted signals. For the “in-phase” detection a sinusoidal modulation at a frequency of 10 KHz is added to the DL injection current. The transmitted power is collected by the photodiodes and sent to single channel lock-in amplifiers in order to extract the second harmonic signals. The resulting second derivative of the absorption feature has a very good signal to noise (S/N) ratio and a flat baseline.

3. – Experimental results.

Since the LT030MD emission wavelength is around 755 nm at 25°C, we were obliged to warm it up to 45°C in order to observe the oxygen absorption lines of the $b^1\Sigma_g^+(\nu' = 0) \leftarrow X^3\Sigma_g^-(\nu'' = 0)$ electronic transition band at 760 nm. These are weak as they are forbidden by the electric dipole transition selection rules. We got the lines assignments from the work of Babcock and Herzberg [5], and the wavelengths at 21°C are obtained by using the index of refraction of the air as calculated by Edlén [7]. A small portion of the molecular spectra is visible in fig. 2. The amplitude modulation, which is associated with the emission frequency modulation, results in a sloping background of the direct absorption signal and in an asymmetry of the 2^{nd} derivative shape when collecting the 2^{nd} harmonic signal; this explain the strong asymmetry visible in this figure.

A list of the observed O₂ absorption lines at atmospheric pressure and room temperature (RT) is reported in Table I. When working in free-running mode, the resolving power of the diode laser spectrometer is about 10^7 ; this and the high sensitivity permits to observe weak lines as the ones shown in fig. 3. Here the second derivative signal of the absorption features of the R R(19) and R R(17) oxygen absorption lines are well resolved. By using the proper fit function and algorithm, we obtained for the peak distance: $\Delta\nu' = (6.4 \pm 0.1) \text{ cm}^{-1}$, in agreement to $\Delta\nu' = 6.3 \text{ cm}^{-1}$ obtained from Hitran database [8].

3.1. Signal analysis. – A correct line shape analysis is important when studying the pressure broadening and shift of the absorption features. For the line-shift

measurements a specific study has been developed in our previous work [9]. Briefly, the radiation $I(\nu)$ transmitted through an absorbing gas sample can be described by the Lambert-Beer equation:

$$(1) \quad I(\nu) = I_o(\nu) \exp[-\alpha(\nu)x],$$

where $I_o(\nu)$ is the incoming radiation intensity at frequency ν , 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 case of weak absorptions [$\alpha(\nu)x \ll 1$], that is always verified in our case, eq. (1) can be approximated by:

$$(2) \quad I(\nu) \simeq I_o(\nu)[1 - \alpha(\nu)x].$$

Describing $\alpha(\nu)$ by a function that takes into account the contribution of the Doppler broadening and the collisional (pressure) broadening, one must adopt the Voigt function, a convolution of the Lorentz and the Gauss curves, given by:

$$(3) \quad f(\nu) = \int_{-\infty}^{+\infty} \frac{\exp[-(t - \nu_o)^2(\Gamma_G^2 \ln 2)]}{(t - \nu)^2 + \Gamma_L^2} dt,$$

where ν_o is the gas resonance frequency, Γ_G and Γ_L are the gaussian and lorentzian full width at half the maximum (FWHM) respectively. By Revealing onto the 2nd harmonic component in order to increase the S/N, one has to deal with the 2nd derivative of the transmitted signal, therefore if we assume that the laser emission intensity varies linearly with the frequency, i.e. the injection current, we put:

$$(4) \quad I_o(\nu) = \bar{I}_o[1 + s(\nu - \bar{\nu})],$$

where $\bar{\nu}$ is the beginning of the frequency sweep, s is the fractional change in the background and \bar{I}_o is the background intensity at $\nu = \bar{\nu}$. Then the 2nd derivative of

the total signal will be:

$$(5) \quad I''(\nu) = -\bar{I}_0 x [(1 + s\nu)\alpha''(\nu) + 2s\alpha'(\nu)],$$

where $\alpha'(\nu)$ and $\alpha''(\nu)$ are the first and the second derivatives of the absorption function. In the following, in order to get all the line shape parameters, we used this function within the computer program “LINEFIT” [10].

3.2. Pressure broadening and shift. – Pressure broadenings and shift in nitrogen (γ_{N_2} , S_{N_2}), and the self broadening and self shift (γ_0 , S_0) coefficients have been measured at room temperature for the more intense oxygen lines; the results are shown in Table II. For the $^RQ(15)$ we measured also the broadening coefficients in helium.

A work on the oxygen A band has been carried out by Ritter and Wilkerson [11] by using a tunable dye laser along with a multipass White cell to reach a path length of 80 m. They got a list of self and air broadening coefficients. For the self broadening of the $^RQ(7)$, $^RR(11)$ and $^RR(13)$ lines there is an agreement with our results within the errors, but in the others there is a difference up to 30%. The main origin of this difference is presumably coming from the pressure narrowing (Dicke effect) they took into account to explain a deviation from the Voigt line shape observed in their measurements. By adopting a fit function that takes into account the narrowing, they found a reduction of the fit residuals. Indeed we did not observe any appreciable deviation from the standard convolution of gaussian and lorentzian line shape in the pressure range we used in our experiments (40 – 400 Torr). Ray and Ghosh [12, 13] measured the pressure broadening coefficients in

the same spectral range by considering a Dicke narrowing too. Again their results are larger than ours. In any case our measurements are affected by a bigger error ought to the smaller optical path-length. By a multipass cell, which we are currently working on, a much better S/N can be obtained by the diode laser spectrometer too, and therefore a considerable error reduction and a higher sensitivity can be achieved. Self and N₂-broadening coefficients have also been obtained by Corsi [14], and by de Angelis et al. [15] in the same band at different gas temperatures, but for absorption lines different from ours, therefore no comparison can be done.

Our results show that the shift effect is about an order of magnitude smaller than the broadening, but it is still well observed. For the ^RR(11) line the pressure shift measurement results are shown in fig. 4, which shows a certain negative slope of the data. Also the work of Phillips and Hamilton [16] deals with the pressure shift measurements of the atmospheric oxygen A band. As ours, their measurements always give negative shift coefficients, but ours are about as half as theirs. In spite of the measurements errors, a trend of the coefficients with the rotational quantum number N can be seen from the collected data, even if barely: the smaller is N, the smaller is the shift, as they observed too. In any case our results often show larger coefficients for N₂ than for self broadening and shift.

4. – Conclusions.

By using the diode laser in “free running” mode a very fine molecular spectroscopy has been performed. Some weak oxygen absorptions belonging to the atmospheric A band have been collected and specific line shape measurements per-

formed. Pressure broadening and shift have been measured at room temperature through a few meters of path-length. The pressure shift coefficients always show a negative value. Care has been put in correctly analyzing the absorption data, taking into account the amplitude modulation that comes with the frequency modulation of these sources.

The excellent resolving power of the spectroscopic apparatus potentially permits to discriminate different gases in a complex atmosphere, with response times of a few hundreds of milliseconds. Sensitivity of some tens of ppm per meter of optical path has also been obtained with the more intense oxygen absorption lines.

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Figure captions

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

Fig. 2. – Second derivative of the oxygen spectrum around 759.6 nm. The more intense line is the $^RQ(19)$. On the left the $^RR(21)$ and on the right the $^RR(23)$ line are visible. The measurement has been done at room temperature with an oxygen pressure of 20 Torr, through a path-length of 3 m and with a time constant of 2.5 ms.

Fig. 3. – Two very close weak absorption lines at 13158.67 cm^{-1} $^RR(19)$, and 13158.74 cm^{-1} $^RR(17)$ (little squares) at atmospheric pressure and room temperature in a path-length of 3 m, along with the best fit (solid line). The lock-in time constant was 4 ms. The peaks distance has been measured to be $(6.4 \pm 0.1)\text{ cm}^{-1}$.

Fig. 4. – Difference of the position of the absorption lines collected in the measurement and reference cells as function of the pressure for the $^RR(11)$ transition. The values of the pressure are those of the oxygen gas in the measurement cell. The negative slope is evident.

TABLE I. – List of observed oxygen absorption lines belonging to the atmospheric A band [5]. The wavelengths are in air, at atmospheric pressure, and at $T = 293$ K.

Wavelength (nm)	Classification	Wavenumber (cm^{-1})
759.528	$RQ(21)$	13162.53
759.581	$RR(23)$	13161.60
759.627	$RQ(19)$	13160.81
759.655	$RR(21)$	13160.33
759.746	$RQ(17)$	13158.74 ^a
759.750	$RR(19)$	13158.67 ^a
759.869	$RR(17)$	13156.61
759.890	$RQ(15)$	13156.27
760.011	$RR(15)$	13154.16
760.054	$RQ(13)$	13153.42
760.174	$RR(13)$	13151.34
760.241	$RQ(11)$	13150.19
760.360	$RR(11)$	13148.12
760.681	$RQ(7)$	13142.57
761.210	$RQ(3)$	13133.43
761.324	$RR(3)$	13131.48
761.510	$RQ(1)$	13128.26
763.221	$PP(7)$	13098.83

^a The correct wavenumbers of these lines have been extracted from the Hitran database [8].

TABLE II. – List of observed oxygen line broadening (γ) and shift (S) coefficients.

$\nu' = 13142.57 \text{ cm}^{-1} \quad {}^R\text{Q}(7)$	$\nu' = 13148.12 \text{ cm}^{-1} \quad {}^R\text{R}(11)$
$\gamma_0 = (3.8 \pm 0.2) \text{ MHz/Torr}$	$\gamma_0 = (3.6 \pm 0.2) \text{ MHz/Torr}$
$\gamma_{N_2} = (4.1 \pm 0.1) \text{ MHz/Torr}$	$\gamma_{N_2} = (3.1 \pm 0.1) \text{ MHz/Torr}$
$S_0 = (-0.2 \pm 0.1) \text{ MHz/Torr}$	$S_0 = (-0.2 \pm 0.2) \text{ MHz/Torr}$
$S_{N_2} = (-0.3 \pm 0.1) \text{ MHz/Torr}$	$S_{N_2} = (-0.3 \pm 0.1) \text{ MHz/Torr}$
$\nu' = 13153.42 \text{ cm}^{-1} \quad {}^R\text{Q}(13)$	$\nu' = 13151.34 \text{ cm}^{-1} \quad {}^R\text{R}(13)$
$\gamma_0 = (2.5 \pm 0.2) \text{ MHz/Torr}$	$\gamma_0 = (3.6 \pm 0.2) \text{ MHz/Torr}$
$\gamma_{N_2} = (3.0 \pm 0.2) \text{ MHz/Torr}$	$\gamma_{N_2} = (3.3 \pm 0.1) \text{ MHz/Torr}$
$S_0 = (-0.2 \pm 0.1) \text{ MHz/Torr}$	$S_0 = (-0.2 \pm 0.1) \text{ MHz/Torr}$
$S_{N_2} = (-0.3 \pm 0.1) \text{ MHz/Torr}$	$S_{N_2} = (-0.3 \pm 0.1) \text{ MHz/Torr}$
$\nu' = 13156.27 \text{ cm}^{-1} \quad {}^R\text{Q}(15)$	$\nu' = 13154.16 \text{ cm}^{-1} \quad {}^R\text{R}(15)$
$\gamma_0 = (3.2 \pm 0.1) \text{ MHz/Torr}$	$\gamma_0 = (2.8 \pm 0.1) \text{ MHz/Torr}$
$\gamma_{N_2} = (3.3 \pm 0.1) \text{ MHz/Torr}$	$\gamma_{N_2} = (3.0 \pm 0.1) \text{ MHz/Torr}$
$\gamma_{He} = (2.9 \pm 0.1) \text{ MHz/Torr}$	
$S_0 = (-0.3 \pm 0.1) \text{ MHz/Torr}$	$S_0 = (-0.4 \pm 0.1) \text{ MHz/Torr}$
$S_{N_2} = (-0.4 \pm 0.1) \text{ MHz/Torr}$	$S_{N_2} = (-0.4 \pm 0.2) \text{ MHz/Torr}$
$\nu' = 13160.81 \text{ cm}^{-1} \quad {}^R\text{Q}(19)$	
$\gamma_0 = (2.9 \pm 0.1) \text{ MHz/Torr}$	
$\gamma_{N_2} = (2.7 \pm 0.2) \text{ MHz/Torr}$	
$S_0 = (-0.3 \pm 0.1) \text{ MHz/Torr}$	
$S_{N_2} = (-0.4 \pm 0.1) \text{ MHz/Torr}$	







