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Collisional Broadening and Shift of Acetylene and Oxygen Overtones

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Abstract

Overtone absorption lines of acetylene and oxygen around 12000 and 13000 cm^{-1} have been examined by the use of tunable diode lasers and the wavelength modulation spectroscopy with 2nd harmonic detection technique. The collisional broadening and shift coefficients have been obtained. The correct interpretation of the absorption features when detecting the second harmonic signal in the presence of a sloping background is discussed.

Introduction

Overtone and combination of ro-vibrational bands in the visible and in the infrared have been studied more than sixty years ago. The availability of tunable laser sources, like commercial diode lasers (DL), increased the interest on the spectroscopy of such bands. DLs are suitable radiation sources for high resolution spectroscopy and in particular for the study of the line-shape of molecular transitions in the NIR of many molecules, like CH_4[1], C_2H_2[2], CO_2, H_2O[3], Hcl[4], HCN, HF, NH_3[5], NO_2[6], O_2, etc.. They can be easily modulated, allowing the use of frequency modulation (FM) techniques, which permit the detection of the weak overtone and combination ro-vibrational bands in the near-infrared region. 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. In particular we focalize our attention to acetylene and oxygen as we studied the possibility to correctly determine the line-shape parameters, when the WM tecnique is used.

When the injection current of a DL changes, along with the variation of the frequency, a simultaneous variation of the intensity of the emitted radiation occurs. This results in an asymmetry of the detected signal which must be kept into account for a correct determination of the line position and of the shift-coefficient.

Experimental set-up

The experimental apparatus for the diode laser spectroscopy is shown in Fig. 1.

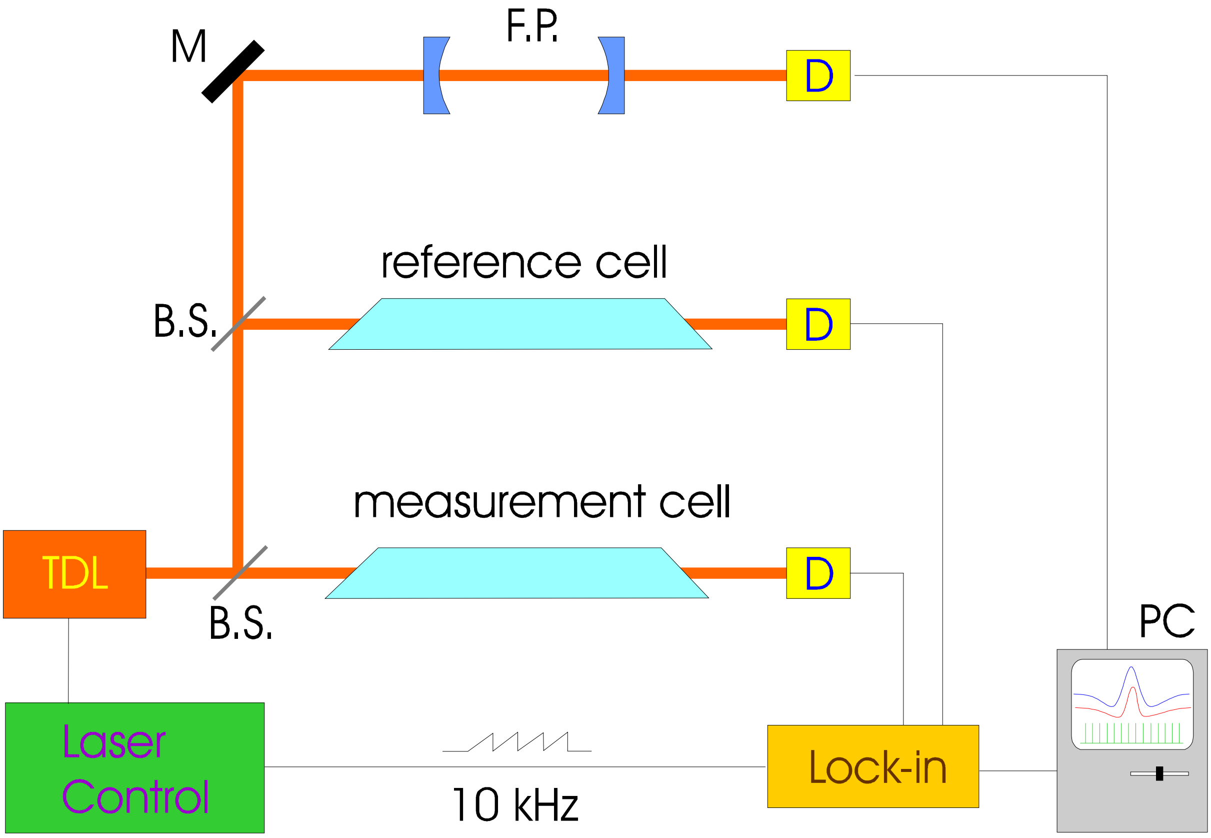

Fig. 1 Sketch of the experimental apparatus for the WM spectroscopy. D: photodiode; BS: beam splitter; FP: Fabry-Perot interferometer; TDL: tunable diode laser; M: monochromator; PC: desk-top computer

The radiation is emitted by a AlGaAs diode laser which is driven by a stabilized low-noise current supply and it is temperture controlled within 0.002 K by a high-stability temperature controller. The wavelength scan is obtained adding to the driving current a low frequency (~1 Hz) sawtooth signal. The radiation is splitted in three different beams, which go respectively through a confocal Fabry-Perot interferometer, which marks the relative frequency scale, and two different cells containing the sample gas: the first one is kept at constant pressure and is used as reference for the line position, while in the second cell the pressure is successively increased. The transmitted radiation is then collected by three photodiode and the resulting signals are simultaneously acquired by a personal computer. For the harmonic detection a sinusoidal modulation current (at ~ 10 kHz) is mixed to the diode laser injection current. The transmittance signals from the two cells are sent to a lock-in amplifier to extract the desired harmonic component. The acquired data are then analysed using LINEFIT 2.0, a software package for the reduction of spectroscopical data, released by D'Amato[7] and one of the authors (A. C.). The software has been properly modified to fit the harmonic detected signals.

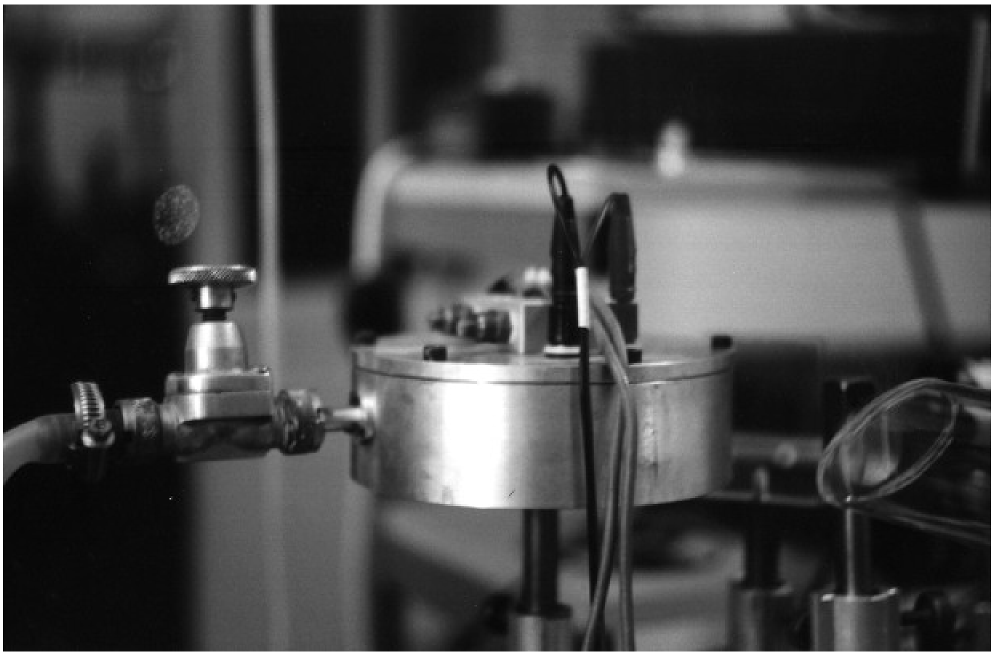

Fig. 2 DL source holder that has been utilized in the spectrometer. The aluminum can hosts the laser and the termo-couple that mantains fixed the DL temperature. In order to better control the temperature and eventually to go below 0°C, a rotary pump vacuum can be made inside.

Frequency modulation technique

When FM is used, the emission frequency $\bar{\nu}$ of the TDL is sinusoidally modulated by varying the injection current,

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

the frequency $\bar{\nu}$ is slowly scanned across the transition and the *n*-th harmonic component of the transmitted is detected with 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 transmission signal (derivative spectroscopy). In particular we detected the second harmonic component (2*f* detection).

The presence of a residual amplitude modulation (RAM) when modulating the emission frequency of a DL, even if relatively small, gives a sloping background in the direct absorption (DA) signal, and in an asymmetry in the 2*f* signal. As shown in Fig. 3, the center of the line does not coincide with the maximum of the 2*f* signal, which is apparently displaced. Such displacement is proportional to the slope of the emission profile as well as to the width of the line. This last feature is of capital importance for what concerns pressure induced shift. The apparent displacement of the center seems to be proportional to the pressure, and if this apparent shift is not correctly considered, the determination of the pressure induced shift coefficient may be wrong.

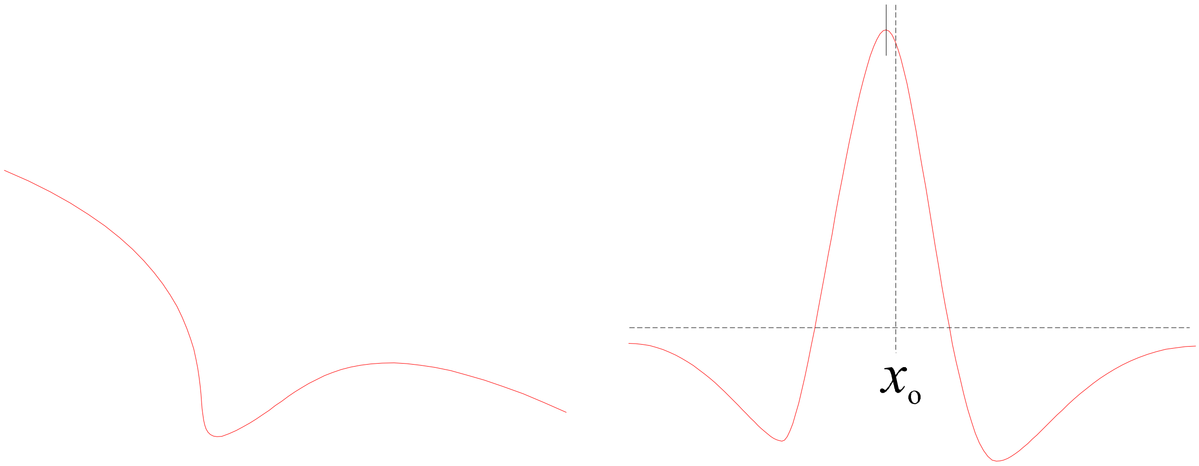

Fig. 3 DA (left) and 2nd harmonic WM signal (right) as detected by the DL spectrometer.

Derivative spectroscopy limit

In a rather general way, the intensity of the radiation transmitted through a sample can be written as the product

$$I(\nu) = I_o(\nu)\,T(\nu)$$

of the incoming intensity $I_o(\nu)$ and the transmittance $T(\nu)$ (or spectral transmission), where ν is the distance from the central frequency of the line. We assume a laser emission profile varying linearly with the frequency: $I_o(\nu) = \bar{I}_o(1 + s\nu)$, where $\bar{I}_o$ is the intensity at ν_o and s is the fractional variation per frequency unit. Hence the second derivative of the transmitted power is

$$I''(\nu) = \bar{I}_o\,(1 + s\nu)\,T'' + 2s\bar{I}_o T'\ . \tag{1}$$

The apparent displacement of the center depends on the the slope s of the profile and on the width γ_L of the transition line. As the pressure increases, the width of the line becames larger, because of the pressure broadening., then an apparent displacement of the center due to the linear background occurs and seems to be proportional to the pressure, in a way similar to the *real* pressure induced shift. If this apparent shift is not correctly considered the measure of the pressure induced line-shift will be wrong.

Let us consider a Lorentzian shape of the absorption line. In the weak absorption approximation the transmittance is

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

Its second derivative can be easily expanded around $\nu = 0$ to get the dispalcement of the maximum of the 2*f* signal from the center of the line:

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

where $\xi = s\gamma_L$. This 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, a systematic error can occur, which is proportional to the width. It can give an additional incorrect contribution to the measurement of the pressure-shift coefficient. A more refined knowledge of the lineshape parameters can be obtained fitting the second derivative signal. Nevertheless, when fitting the experimental data, one can be inclined to use simply the 2nd derivative of the absorption function T'', multiplying it by a sloping linear function in order to match the asymmetry of the experimental signal – this is equivalent to consider only the first term of the r.h.s. of Eq. (1). Although at a first sight the result of the fit could seem qualitatively satisfactory, the resulting parameters cold be incorrect. In particular the position of the center of the line will be strongly affected by the pseudo-shift. The only choice for the fitting function is Eq. (1).

Experimental results

Many acetylene and oxygen absorption lines have been observed.

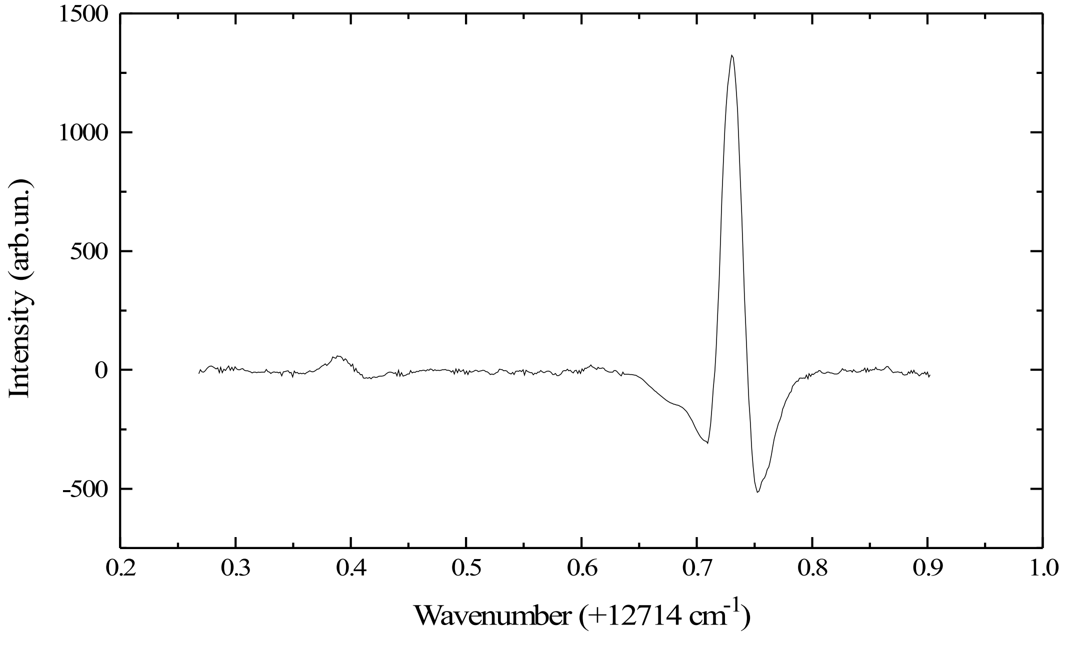

Fig. 4 Two acetylene absorption lines observed by WM spectroscopy and 2nd harmonic detection technique when the gas pressure was 38 Torr. The more intense is located at 12714.73 cm^{-1} (ν_1+3ν_3, R21, 786.273 nm @ 15ºC). The other, whose origin is suggested in the text, has its minimum at 12714.39 cm^{-1} (786.294 nm @ 15ºC). The lock-in time constant was 12.5 ms.

Two acetylene resonances are shown in Fig. 4, where near a well know C_2H_2 line (R21, 12714.73 cm^{-1},$\nu_1+3\nu_3$ band,) a small one is present, whose origin is still unknown. This could be a rotational line splitting of the R21 by a local perturber via a Coriolis interaction[8].

As already mentioned, it is the amplitude variation of the laser emission that causes the strong asymmetry in the 2nd derivative signal visible in the figure.

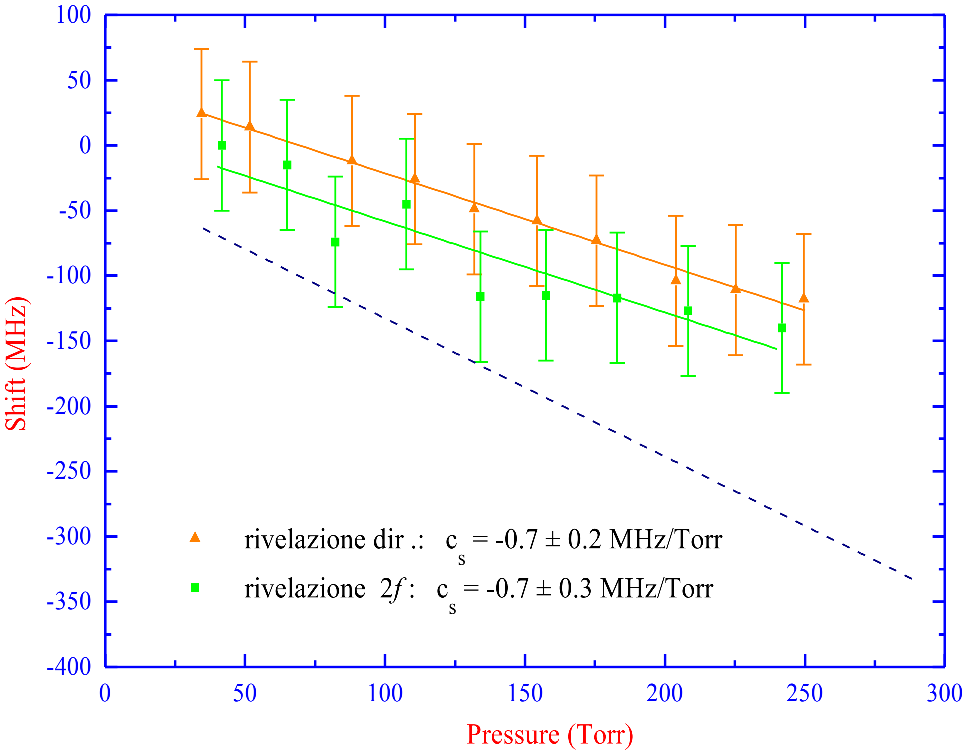

Fig. 5 Shift measurements data related to the acetylene R21 absortion line. The triangles refer to the DA measurements, while the squares are the 2nd harmonic data. The dashed lline shows what it is got by fitting the 2nd harmonic results by the wrong function.

Fig. 5 shows the results concerning the measurements of pressure induced shift for the acetylene transition R(21) of the band $\nu_1+3\nu_3$. The absorption intensity was strong enough to be detected directly, the condition of small absorption approximation being still satisfied. Then both the direct absorption signals and the second derivative (2*f*) signals were acquired and successively fitted. The 2*f* signals have been fitted both with the total second derivative function and with the second derivative of the absorption, multiplied by an *ad hoc* linear ramp. The lineshape parameters obtained in the first case agree very well with the ones from the fitting of the DA signals and the values of the shift-coefficients are equal; while in the last case, the value of the shift-coefficient comes to be appreciably different.

Large modulation amplitude

Sometimes a larger value of the modulation amplitude is required to improve the signal to noise ratio (S/N). When the amplitude *m* of the modulation is incresed the derivative spectroscopy approximation fails, and the n-th harmonic compnent $H_n(\nu,m)$ is generally given as

$$H_n(\nu,m) = \frac{2}{\pi}\int_0^{\pi} \alpha(\nu + m\cos\vartheta)\cos n\vartheta \, d\vartheta$$

where α is absorption function. The analytical evaluation of this integrals is not always possible. Arndt[9] and Wahlquist[10] derived the analytical form for the harmonic components $H_n(\nu,m)$ for a Lorentzian absorption function α, while for Gaussian or Voigt absorption function numerical methods must be adopted. Reid and Labrie[11] have found an excellent agreement between the theoretical expression and the experimental $2f$ lineshape, for different values of modulation amplitude and for different absorption function.

It is not possible to get an analytical expression for a Voigt function, nevertheless it is possible to write down an analytical expression for the second harmonic component of the Martin and Puerta approximation[12], which takes into account the laser emission profile too. Such expression has been used in a properly designed fit routine for LINEFIT 2.0.

Hence, for the same transition line, we acquired the second harmonic signal, at different values of the pressure and for three different values of the modulation amplitude. These signals have been successively fitted and the results for the self broadening and shift are shown in Fig. 6.

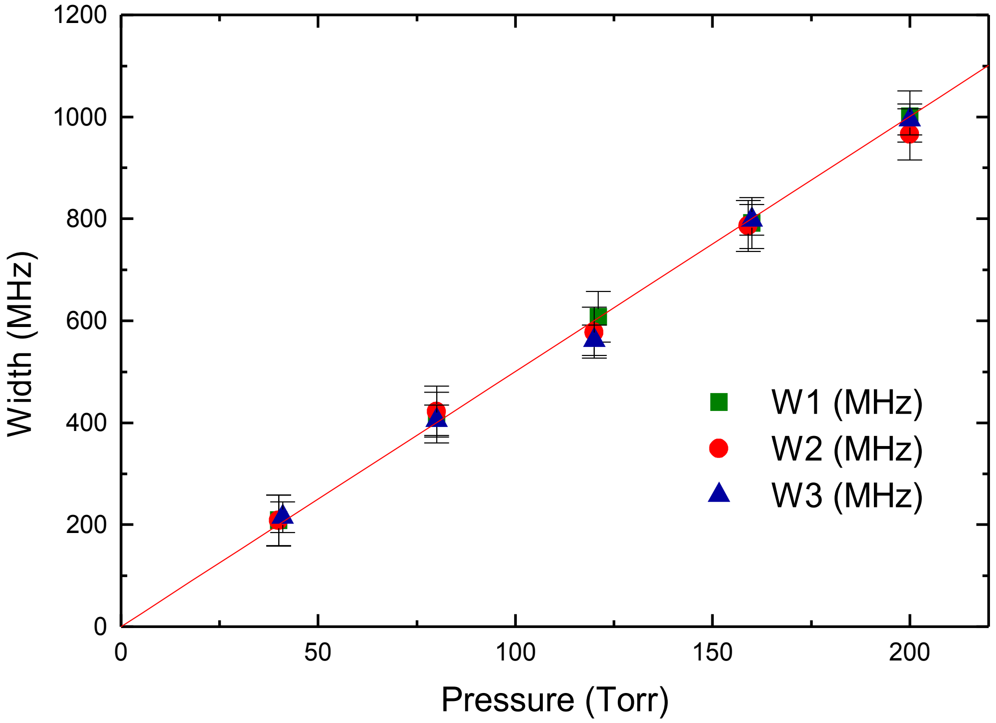

Fig. 6 Results of the shift measurements and fit in three different conditions of modulation: the squares are the results got with modulation amplitude ~200 MHz (well below the line-width ~1 GHz); the circles refer to amplitude ~1.5 GHz; the triangles refer to amplitude ~3 GHz.

The results are in pretty good agreement within the errors. It has been noted that for larger amplitude, the effect of the sloping background is reduced. This can be qualitatively explained by considering that the additional modulation broadening is constant for a fixed modulation amplitude, and in the case of high modulation its contribution is bigger than the Lorentzian (pressure) one.

For the 12692.67 (R7) and 12703.31 cm^{-1} (R13) lines of the $\nu_1+3\nu_3$ acetylene band the self-broadening coefficients are:

$$\gamma_{self(R7)} = (9.4 \pm 0.6)\ \mathrm{MHz/Torr}$$
$$\gamma_{self(R13)} = (12.4 \pm 0.6)\ \mathrm{MHz/Torr.}$$

Measurements on the 11765.60 cm-1 (P7)line, belonging to the $2\nu_1+\nu_2+\nu_3$ band give:

$$\gamma_{self(P7)} = (13.2 \pm 0.6)\ \mathrm{MHz/Torr.}$$

Table I. Collisional-broadening coefficients obtained for the 12706.36 cm^{-1} ($\nu_1+3\nu_3$, R15) acetylene line.

γ_{He}	γ_{H_2}	γ_{air}	γ_{self}
(3.7 ± 0.2) MHz/Torr	(6.6 ± 0.1) MHz/Torr	(5.8 ± 0.1) MHz/Torr	(11.0 ± 0.1) MHz/Torr

Table II. Collisional-broadening coefficients obtained for the 12688.71 cm^{-1} ($\nu_1+3\nu_3$, R5) acetylene line.

γ_{H_2}	γ_{air}	γ_{self}
(8.3 ± 0.3) MHz/Torr	(8.1 ± 0.1) MHz/Torr	(13.5 ± 0.1) MHz/Torr

Self-collisional shift of some acetylene lines has been measured, the coefficients for R7, R13, 12652.52 (P9) and 12649.82 cm^{-1} (P10) on the of the $\nu_1+3\nu_3$ band being respectively:

$$S_{R13} = (-0.7 \pm 0.4)\ \mathrm{MHz/Torr}$$
$$S_{R7} = (-1.0 \pm 0.1)\ \mathrm{MHz/Torr}$$
$$S_{P9} = (-0.6 \pm 0.1)\ \mathrm{MHz/Torr}$$
$$S_{P10} = (-0.5 \pm 0.1)\ \mathrm{MHz/Torr}$$
$$S_{R21} = (-0.7 \pm 0.2)\ \mathrm{MHz/Torr}$$

Pressure-broadening and shift for the new absorption line at 12714.39 cm^{-1} give respectively:

$$\gamma_{self} = (12 \pm 1)\ \mathrm{MHz/Torr}; \qquad S = (-0.8 \pm 0.5)\ \mathrm{MHz/Torr.}$$

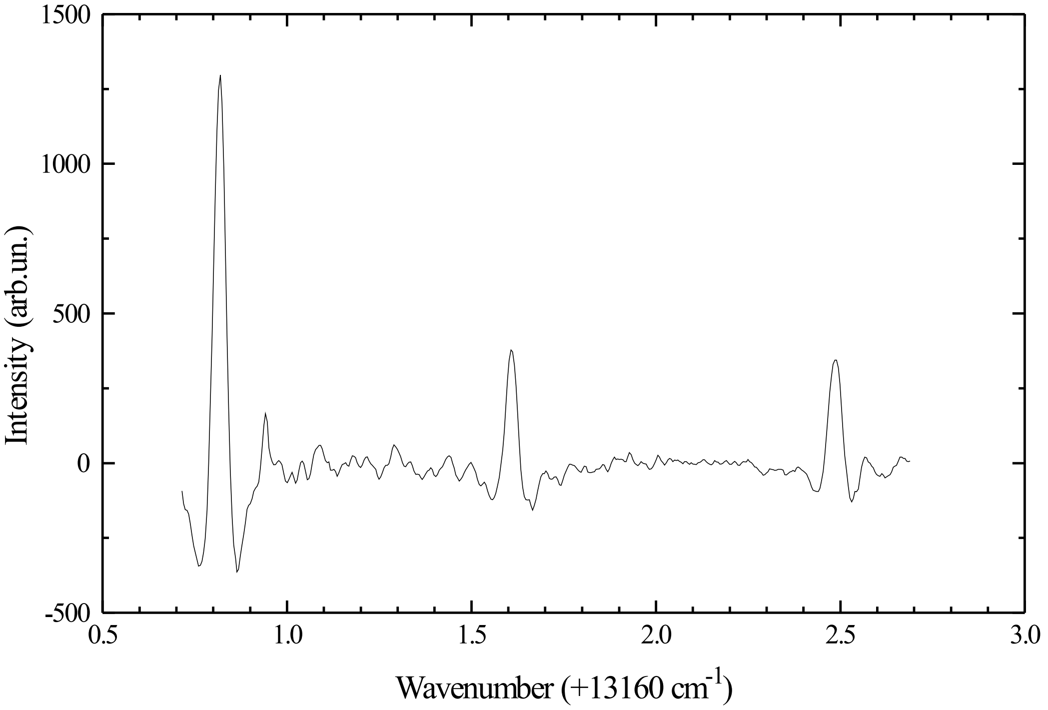

Fig. 7 Oxygen spectrum around 13160 cm^{-1} (~760 nm) as revealed *in-phase* onto the 2nd harmonic. This measurement has been obtained in a path-length of ~6 m in air. The lock-in time constant was 4 ms.

An example of spectrum as revealed by our DL spectrometer is shown in Fig. 7, where the second detivative of a small portion of the electronic $b^1\Sigma^+_g \leftarrow X^3\Sigma^-_g$ transitions is displayed. The self- , N_2- and He-broadening coefficients at room temperature are listed in Table III.

Table III. Collisional-broadening coefficients obtained for the 13156.27 cm^{-1} $(b^1\Sigma^+_g \leftarrow X^3\Sigma^-_g)$ oxygen line.

γ_{He}	γ_{N_2}	γ_{self}
(2.9 ± 0.1) MHz/Torr	(3.4 ± 0.1) MHz/Torr	(3.2 ± 0.1) MHz/Torr

The pressure shift coefficient for such a line gives:

$$S_{self} = (-0.3 \pm 0.1)\ \text{MHz/Torr}.$$

Summary and Conclusions

By using the DLs and WM spectroscopy overtone absorption lines of acetylene and oxygen have been examined. It has been possible to reveal weak absorptions and also to make specific line-shape measurements under different environmental conditions. Care has been put in correctly analyzing the absorption data, removing the amplitude modulation that comes with the frequency modulation of these sources. DLs as spectroscopic sources are compact, easy operational, and cheap. Compared to the more expensive dye lasers, they show much less noise and better long-time stability. Moreover the resolving power of the spectrometer (~10^7 in free running mode) permits to discriminate different gases in a complex atmosphere.

[1] A. Lucchesini, I. Longo, C. Gabbanini, S. Gozzini, L. Moi, *Appl. Opt.* **32**, 5211 (1993)

[2] A. Lucchesini, M. De Rosa, D. Pelliccia, A. Ciucci, C. Gabbanini, S. Gozzini, *Appl. Phys. B*, to be published

[3] A. Lucchesini, L. DellÕAmico, I. Longo, C. Gabbanini, S. Gozzini, L. Moi, *Nuovo Cimento D* **13**, 677 (1991)

[4] K.V. Reddy, *J. Mol. Spectrosc.* **82**, 127 (1980)

[5] A. Lucchesini, D. Pelliccia, C. Gabbanini, S. Gozzini and I. Longo, *Nuovo Cimento D* **16**, 117 (1994)

[6] W. Lenth and M. Gehrtz, *Appl. Phys. Lett.* **47**, 1263 (1985)

[7] D'Amato and A. Ciucci, "LINEFIT 2.0, a Software for Reduction of Spectroscopical Data", *ENEA Report* RT/INN/94/1 (1994)

[8] B.C. Smith and J.S. Winn, *J. Chem. Phys.* **94**, 4120 (1991)

[9] Arndt, *J. Appl. Phys.* **36**, 2522 (1965)

[10] Wahlquist, *J. Chem. Phys. B* **35**, 1708 (1961)

[11] Reid and D. Labrie, *Appl. Phys. B* **26**, 203 (1981)

[12] Martin and J. Puerta, *Appl. Optics* **20**, 259 (1981); —, *Appl. Optics* **20**, 3923 (1981)