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5	www.elsevier.com/locate/				ww.elsevier.com/locate/jqsrt
7	Diode laser overtone spectroscopy of CO_2 at 780 nm				
9					
11	A. Lucchesini [*] , S. Gozzini Istituto per i Processi Chimico-Fisici del CNR, Area della Ricerca, Department of Physics, Via G. Moruzzi, 1, I-56124 Pisa, Italy				
13					
10		Received 14 Jur	ne 2004; accepted 8 March 2	2005	
15					
17	Abstract			0	
19	Overtone absorption	lines of ${}^{12}C^{16}O_2$ have	ve been examined by u	sing a tunab	le diode laser (TDL)
21	spectrometer in the re double heterostructure	gion around 12770 cn InGaAlAs TDLs og	n^{-1} . The spectrometer sperating in the "free-ru	sources are c nning" mode	ommercially available e, which allowed the
23	detection of the line positions within 0.01 cm ⁻¹ . The observed carbon dioxide absorption lines belong to the $v_1 + 3v_3$ ro-vibrational band with rotational quantum number J up to 48. The minimum absorbance				
25	cross section of the ord © 2005 Published by E	er of $\simeq 1 \times 10^{-27} \text{ cm}^2/$ Elsevier Ltd.	molecule.	veakest lines	naving the absorption

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Keywords: Carbon dioxide; Overtone absorption spectroscopy; Tunable diode-laser spectrometer

³¹ 1. Introduction

Carbon dioxide is one of the most investigated molecules especially since it has been recognized as one of the main sources on the green house effect that is responsible of the global earth warming up. From the chemical-physical view point it is a good sample for the right interpretation of the classical and quantum mechanical behavior of a linear and symmetric molecule. The CO₂ overtones resonances have been observed in the Venus planet and in particular they have been detected more than 70 years ago [1] in the near infrared (NIR) spectrum; since then

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- 1 they have been analyzed in laboratory by more and more sophisticated spectroscopic apparatus. starting from classical monochromator, long absorption path lengths and photographic systems
- 3 [2], later by the photoacoustic detection technique [3] and then by the intra cavity laser absorption spectroscopy (ICLAS) technique [4] that increased the signal to noise ratio (S/N) and permitted
- 5 more and more precise measurements and spectroscopic predictions [5]. In this case powerful and expensive laser-based systems have been used to reveal and elaborate the acquired data.
- 7 Here we present a spectroscopic work based on the less expensive semiconductor diode lasers (DLs), the commercially available ones, that are radiation sources still suitable for high resolution
- 9 spectroscopy even in the "free-running" regime, that is without any external optical and electrical feedback. DLs have been successfully utilized to study the optical resonances of molecules, like
- CH₄[6], C₂H₂[7], C₂H₄[8–10], CHF₃[11], CO [12], CO₂[13,14], HF [15], HCl [16], H₂O [17], H₂S 11 [14], HCN [18], NH₃ [10], NO [19], NO₂ [20,21], O₂ [22], etc.; still this list does not pretend to be
- 13 exhaustive for the increasing utilization of this type of sources. In order to be used in the frequency modulation (FM) technique they can be easily modulated through their injection
- 15 current, and when the value of the frequency is chosen much lower than the resonance line-width, the FM spectroscopy is usually called "wavelength modulation spectroscopy" (WMS). In this
- work we apply the WMS and the second harmonic detection techniques to the carbon dioxide 17 absorptions around 780 nm, where the ${}^{12}C^{16}O_2$ ro-vibrational transitions from the fundamental energy level to $(10^{0}5)_{1}$ lie.
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23

2. Experimental setup

Fig. 1 shows the experimental setup used for the WMS. The source is a Fabry–Perot type 25 semiconductor laser SHARP Mod. LT024MD that emits a 40 mW single mode at 780 nm without any external optical feedback, i.e. it is said to operate in *free-running* mode. It is driven by a 27 stabilized low-noise current supply. Its temperature is monitored by a high-stability controller $(\Delta T = 0.01 \text{ K} \text{ within } 1 \text{ h})$. The temperature control of the DL is very important as its emission 29 wavelength is a linear function of the temperature ($\approx 0.1 \text{ nm/K}$) but with periodical mode hops. The wavelength scan is obtained by adding a low frequency ($\sim 1 \text{ Hz}$) sawtooth signal to the driving 31 current. The wavelength dependence on the current is linear ($\approx 0.01 \text{ nm/mA}$) for small current variations and is a critical parameter for free-running DL spectroscopy (usual current amplitude 33 values $\sim 10-100$ mA). The collimated DL radiation is split in different beams, which go through a confocal 5cm Fabry-Perot interferometer to check the frequency sweep and the laser emission 35 mode, and through two Herriott type 43 cm multipass cells by SIT S.r.l., each one giving 30 m path length, one containing the sample gas and the other containing water vapor for checking 37 whether the obtained absorption features come from H_2O . Finally the laser beam passes through the iodine reference cell for the precise wavenumber measurements. This cell is a closed Pyrex 39 glass cell that is warmed up to 340-345 K in order to have enough I₂ vapor pressure for a good S/ N ratio. The transmitted radiations are collected by silicon photodiodes and the resulting signals 41 are simultaneously acquired by a desk-top computer. A 35cm focal length monochromator is employed for the rough wavelength reading ($\Delta \lambda \simeq 0.01$ nm). A sinusoidal current is mixed to the

43 diode laser injection current for the harmonic detection: the signals transmitted through the cells are sent to the lock-in amplifiers to extract the desired harmonic components. An optical insulator

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Fig. 1. Outline of the experimental apparatus. BS: beam splitter; D: photodiode; F.-P.: Fabry–Perot interferometer; M: monochromator; OI: optical insulator; TDL: tunable diode laser; PC: desk-top computer.

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is put in front of the DL in order to avoid the "feedback noise" due to the reflections coming from
the various optical elements along the beam path. The carbon dioxide gas was supplied by Praxair
Inc. with the following characteristics: grade 4.8 (99.998%),
CO<0.5 ppm, H₂O<3 ppm, N₂<10 ppm, O₂<2 ppm,total hydrocarbons <4 ppm.

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3. Frequency modulation

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

$$I(v) = I_0(v)\tau(v).$$
⁽¹⁾

The transmittance can be described by the Lambert–Beer equation:

$$\tau(v) = e^{-\sigma(v)z},\tag{2}$$

where $z = \rho l$ is the column amount (in molecule cm⁻²), i.e. the product of the absorbing species number density ρ (in molecule cm⁻³) and the optical path *l* (in cm) of the radiation through the sample; the absorption cross section $\sigma(v)$ is expressed in cm²/molecule. In case of small optical

depths $[\sigma(v)z \ll 1]$, that is always verified in our case, Eq. (2) can be approximated by 41

$$\tau(v) \simeq 1 - \sigma(v) z \,. \tag{3}$$

43 $\sigma(v)$ takes into account the shape of the absorption line: Gaussian for Doppler broadening and Lorentzian for collisional (pressure) broadening.

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When FM is used, the emission frequency of the DL is sinusoidally modulated at frequency $v_m = \omega_m/(2\pi)$ via the injection current,

$$v = \bar{v} + a \cos \omega_{\rm m} t. \tag{4}$$

5 If the DL emission frequency \bar{v} is swept over an interval across the chosen transition, one gets a signal that depends on both the line shape and the modulation parameters. Since it is an even function of the time, it can be written as a cosine Fourier series,

$$\tau(\bar{v} + a \cos \omega_{\rm m} t) = \sum_{n=0}^{\infty} H_n(\bar{v}, a) \cos n\omega_{\rm m} t, \tag{5}$$

where $H_n(\bar{v})$ is the *n*th harmonic component of the modulated signal. By demodulating the signal with a lock-in amplifier at a multiple nv_m (n = 1, 2, ...) of the modulation frequency, an output signal that is proportional to the *n*th component $H_n(\bar{v})$ is collected. When the amplitude *a* is chosen smaller than the width of the transition line, the *n*th Fourier component is proportional to the *n*-order derivative of the original signal,

$$H_n(\bar{v}, a) = \frac{2^{1-n}}{n!} \left. a^n \frac{d^n \tau(v)}{dv^n} \right|_{v=\bar{v}}, \quad n \ge 1.$$
(6)

¹⁹ During our work usually we detected the second harmonic component (2f detection), which ²¹ enhances the S/N ratio and reduces to zero the unwanted background.

23 3.1. High modulation regime

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In order to improve the signal to noise ratio a larger value of the modulation amplitude is used, but when the amplitude *a* is increased, the derivative approximation of Eq. (6) fails, and the *n*th harmonic component $H_n(v, a)$ is generally given as [23]

29
$$H_n(v,a) = \frac{2}{\pi} \int_0^{\pi} \tau(v + a \cos \theta) \cos n\theta \,\mathrm{d}\theta.$$
(7)

31 The analytical evaluation of this integral is not always possible. Arndt [24] and Wahlquist [25] derived the analytical form for the harmonic components H_n for a Lorentzian absorption

function. Reid and Labrie [26] have found an excellent agreement between the theoretical expression of Eq. (7) and the experimental 2f line shape for different values of modulation

35 amplitude and for various absorption functions. An expression for the nth harmonic component can be obtained by inverting Eq. (5):

$$H_n(x,m) = \varepsilon_n i^n \int_{-\infty}^{+\infty} \hat{\tau}(\omega) J_n(m\omega) e^{i\omega x} d\omega, \qquad (8)$$

where

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$$\hat{\tau}(\omega) = \frac{1}{2\pi} \int \tau(x) e^{-i\omega x} dx$$
(9)

is the Fourier transform of the transmittance profile; $x = v/\Gamma$ and $m = a/\Gamma$ are respectively the

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1 frequency and the amplitude of the modulation, normalized to the line-width; J_n is the *n*th order Bessel function; $\varepsilon_0 = 1$, $\varepsilon_n = 2$ (n = 1, 2, ...) and *i* is the imaginary unit.

3 Let us assume for simplicity a Lorentzian absorption line-shape centered at v = 0 and halfwidth at half the maximum (HWHM) Γ_L : this is acceptable when collisional broadening 5 dominates as it mostly happens in our case. Then the cross section coefficient will be

7
$$\sigma_{\rm L}(x,m) \propto \frac{1}{1 + (x + m\cos\omega t)^2}.$$
 (10)

⁹ By referring to the works of Arndt and Wahlquist we recalculated the second Fourier component of the cross section coefficient by putting n = 2

13
$$H_2(x,m) = -\frac{1}{m^2} \left[\frac{\{[(1-ix)^2 + m^2]^{1/2} - (1-ix)\}^2}{[(1-ix)^2 + m^2]^{1/2}} + c.c. \right]$$
(11)

15 and by eliminating the imaginary part:

17
$$H_2(x,m) = \frac{2}{m^2} - \frac{2^{1/2}}{m^2}$$

19

$$\times \frac{\frac{1}{2[(M^{2} + 4x^{2})^{1/2} + 1 - x^{2}][(M^{2} + 4x^{2})^{1/2} + M]^{1/2} + |x|[(M^{2} + 4x^{2})^{1/2} - M]^{1/2}}{(M^{2} + 4x^{2})^{1/2}},$$
21
(12)

23 where

25

$$M = 1 - x^2 + m^2.$$

In order to obtain the line position parameters with as maximum accuracy as possible by the WMS technique, we used this function opportunely normalized to fit all the 2*f* spectroscopy observed features. The adopted fit procedure uses a standard non-linear least square method. The optimum S/N ratio has been obtained when the modulation index m = 2.2 - 2.3 in accordance to what stated in the literature [24,26].

It can be observed that Eq. (12) is different from the one shown by Reid and Labrie (Eq. (13) in Ref. [26]) and indeed by using the one or the other in the fit procedure the results are not substantially different. In any case Eq. (12) has been checked to be the right expression of the 2nd harmonic component.

35

37 4. Experimental results

Up to 50 absorption lines have been observed and their position measured within 0.01 cm⁻¹ by the comparison with a very precisely known I₂ absorption spectrum [27] and the aid of a I₂
 reference cell. Table 1 shows the results with the wavenumbers in vacuum. The listed wavelengths

- are in air at 294 K and have been deduced by using the index of refraction formula from the work
- 43 of Edlén [28]. The line positions correspond almost perfectly within the errors to the calculated ones by Campargue and colleagues [5].

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1	Table	1
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List of the observed CO₂ absorption lines

J	λ at 294 K (nm)	$R(J) (\mathrm{cm}^{-1})$	λ at 294 K (nm)	$P(J) (\mathrm{cm}^{-1})$
0	782.539	12775.47		
2	782.453	12776.88	782.682	12773.14
4	782.374	12778.16	782.787	12771.42
6	782.304	12779.31	782.901	12769.57
8	782.242	12780.33	783.022	12767.60
10	782.186	12781.24	783.150	12 765.51
12	782.138	12782.02	783.286	12 763.29
14	782.098	12782.67	783.430	12 760.95
16	782.067	12783.19	783.581	12 758.48
18	782.042	12783.60	783.740	12755.89
20	782.025	12783.87	783.908	12753.17
22	782.015	12784.03	784.082	12750.33
24	782.014	12784.05	784.265	12747.36
26	782.020	12783.95	784.455	12744.27
28	782.034	12783.73	784.653	12741.05
30	782.056	12783.37	784.859	12737.71
32	782.084	12782.90	785.072	12734.25
34	782.120	12782.31	785.294	12730.66
36	782.165	12781.58	785.523	12726.95
38	782.217	12 780.74	785.760	12723.11
40	782.271	12779.77	786.004	12719.15
42	782.343	12778.67	786.257	12715.06
44	782.418	12777.45	786.517	12710.86
46	782.500	12776.11	786.785	12 706.53
48	782.589	12774.65	787.061	12 702.08

The maximum error is $0.01 \,\mathrm{cm}^{-1}$.

29

An example of a 2f spectrum in the region of the R branch turning point is shown in Fig. 2. The folding in the *J* sequence is due to the decrease of the rotational constant *B'* with the vibrational excitation. All the line positions have been extracted and identified within 0.01 cm^{-1} by using a non-linear fit procedure that uses Eq. (12).

Ought to the derivative spectroscopy method and the high modulation amplitude adopted here it is difficult to obtain absolute intensity measurements directly from the 2*f* signals. We tried to measure the absolute transmission values by using the direct absorption (DA) technique at room

37 temperature with the same long path-length as the WMS one and with a CO_2 pressure around 95–100 Torr that gives the best signal. The maximum absorption cross sections obtained in this

39 way are shown in the following Table 2. For the weakest absorptions the S/N ratio was so poor that we can assert only roughly the order of magnitude of σ_{max} . It is the case of R(0), R(46) and

41 R(48) were $\sigma_{\text{max}} \approx 1 \times 10^{-27} \text{ cm}^2/\text{molecule}$. Some intensity values are missing because in those cases it was impossible to give reliable and reproducible results by this technique.

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Fig. 2. Second derivative signal of the carbon dioxide transmission spectrum around 782 nm obtained by WMS with 10 Hz bandwidth at $p_{CO_2} = 91$ Torr and room temperature. The transitions are identified by their rotational quantum number.

19	Table 2
	List of the measured maximum CO ₂ absorption cross sections σ_{max}

J	R(J) (cm ⁻¹)	$\sigma_{\rm max}~(10^{-26}{\rm cm}^2/{\rm molecule})$	$P(J) ({\rm cm}^{-1})$	$\sigma_{\rm max}~(10^{-26}{\rm cm}^2/{\rm molecule})$
0	12775.47	0.1		
2	12776.88	1.3 ± 0.3	12773.14	1.0 ± 0.3
4	12778.16	0.6 ± 0.3	12771.42	1.0 ± 0.3
6	12779.31	2.3 ± 0.2	12769.57	2.0 ± 0.2
8	12780.33	3.6 ± 0.2	12767.60	2.6 ± 0.2
10	12781.24	3.5 ± 0.2	12765.51	2.6 ± 0.2
12	12782.02	4.6 ± 0.1	12763.29	4.5 ± 0.1
14	12782.67	4.8 ± 0.1	12760.95	4.1 ± 0.1
16	12783.19	6.1 ± 0.1	12758.48	5.1 ± 0.1
18	12783.60	4.8 ± 0.1	12755.89	3.5 ± 0.2
20	12783.87	4.9 ± 0.1	12753.17	0.7 ± 0.2
22			12750.33	0.5 ± 0.3
24			12747.36	0.4 ± 0.3
26			12744.27	3.0 ± 0.2
28	12783.73	3.5 ± 0.2	12741.05	1.8 ± 0.2
30	12783.37	3.1 ± 0.2	12737.71	3.6 ± 0.2
32	12782.90	1.9 ± 0.2	12734.25	1.8 ± 0.2
34	12782.31	2.0 ± 0.2	12730.66	1.6 ± 0.3
36	12781.58	2.1 ± 0.2	12726.95	1.2 ± 0.3
38	12780.74	1.3 ± 0.3	12723.11	1.0 ± 0.3
40	12779.77	2.3 ± 0.2	12719.15	0.8 ± 0.2
42	12778.67	1.1 ± 0.3	12715.06	0.7 ± 0.2
44	12777.45	1.1 ± 0.3	12710.86	0.5 ± 0.3
46	12776.11	0.1	12706.53	0.4 ± 0.3
48	12774.65	0.1		

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1 4.1. Determination of the band parameters

To calculate the B_ν, D_ν rotational parameters and v₀ band origin we calculated the combination differences R(J - 1) - P(J + 1) = Δ₂F''(J) and the sum R(J) + P(J) [29] from our measurements.
 In fact

7 $\Delta_2 F''(J) = (4B'' - 6D'') \left(J + \frac{1}{2}\right) - 8D'' \left(J + \frac{1}{2}\right)^3$ (13)

9 but usually $D''/B'' \approx 10^{-6}$, therefore Eq. (13) can be written as

$$\Delta_2 F''(J) = 4B''\left(J + \frac{1}{2}\right) - 8D''\left(J + \frac{1}{2}\right)^3.$$
(14)

¹³ Therefore from the linear regression fit of $\Delta_2 F''(J)/(J+\frac{1}{2})$ vs. $(J+\frac{1}{2})^2$ shown in Fig. 3 it comes out

$$B_{000} = (0.39016 \pm 0.00005) \,\mathrm{cm}^{-1}$$

17 and

11

19 $D_{000} = (1.2 \pm 0.2) \times 10^{-7} \,\mathrm{cm}^{-1}$

which better the results obtained by Herzberg in 1953 [2] on an average of many polyads.

21 Moreover

23
$$R(J) + P(J) = 2v_0 + (2B' - 4D') + 2(B' - B'' - 6D')J(J + 1) - 2(D' - D'')J^2(J + 1)^2,$$
25 (15)

which, by the previous consideration and taking into account that $D' \simeq D''$, where " stands for the lower and ' for the upper state, becomes

$$R(J) + P(J) = 2v_0 + 2B' + 2(B' - B'')J(J + 1).$$
(16)



Fig. 3. Plot of $\Delta_2 F''(J)/(J+\frac{1}{2})$ vs. $(J+\frac{1}{2})^2$ along with the best linear fit.

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Fig. 4. Plot of R(J) + P(J) vs. J(J + 1) along with the best linear fit. The measurement errors are within the empty dots.

17

In Fig. 4 R(J) + P(J) as a function of J(J + 1) is shown with the best linear fit. The almost perfect linearity is remarkable (linear regression coefficient r = 0.99978). From the intercept and the angular coefficient and by using the B' value obtained previously we get

21

23

25

$$B_{10^05} = (0.37453 \pm 0.00005) \,\mathrm{cm}^{-1}$$

and

$$v_0 = (12774\ 715 \pm 0\ 002)$$
 cm

The B_{000} , D_{000} and $B_{10^{0}5}$ parameters match the ones obtained in the work of Campargue and colleagues [5] within the errors.

31

33 **5.** Conclusion

By diode laser WM spectroscopy and by the aid of a 30 m total path-length multipass Herriott type cell, 50 ${}^{12}C^{16}O_2$ absorption lines have been detected around 12 770 cm⁻¹ and their positions measured within 0.01 cm⁻¹. They belong to the combination overtone $v_1 + 5v_3$ ro-vibrational

band with rotational quantum numbers J up to 48. The absolute line positions have been obtained

- 39 by comparison with a reference I₂ absorption cell and the utilization of a very precise atlas. The maximum absorption cross section of the observed lines ranges between 1×10^{-27} and $5 \times$
- 41 10^{-26} cm²/molecule at room temperature. Care has been put in the fit of the absorption features by taking into account the distortion caused by the high modulation amplitude adopted with the
- 43 WM technique. On the base of these measurements, the B_{ν} , D_{ν} rotational parameters and the ν_0 band origin have been obtained.

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- / suggestion
- 9

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