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High-resolution investigation of the weak $\nu_1 + 3\nu_2^1 - \nu_2^1 + \nu_3$ band of CO_2 around 2 μm

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Abstract. Fundamental spectroscopical parameters of the weak $\nu_1 + 3\nu_2^1 - \nu_2^1 + \nu_3$ band of CO_2 are reported using a high-resolution, direct-absorption spectrometer, based on a distributed feed-back diode laser emitting at 2 μm. Line intensities and self-broadening coefficients have been measured for the first time with high accuracy, for nine lines of the R branch, from R(44) up to R(59). Comparison with available data has been made, and a generally good agreement has been found.

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Carbon dioxide continues to stimulate interest to the spectroscopical community, for its relevant role in many areas of physics, chemistry, geology, medicine, and biology. In many applications, such as environmental monitoring and medical diagnostics, a very precise determination of the concentration of CO_2 or of its isotopic species is required. For such purposes, the intense fundamental vibrational bands in the mid-infrared would be the most indicative for a spectroscopic monitoring, but unfortunately they fall outside the emission region of simple emitting devices, such as room-temperature diode lasers. Recently, weaker bands in the 1.5–2 μm range have been investigated for an accurate monitoring of CO_2 concentrations, and in particular the $\nu_1 + 2\nu_2^0 + \nu_3$ combination band around 2 μm is very promising [1–3], since it is the strongest band reached by room-temperature DFB diode lasers, less than 3000 times weaker than the ν_3 at 4.3 μm. The knowledge of spectroscopic parameters, such as line intensities, pressure broadening and shift coefficients is of fundamental importance for an accurate determination of gas concentrations, and indeed high-resolution measurements have been performed recently with diode lasers on the strongest bands in the near-infrared [3–7], to confirm previous data acquired mainly with Fourier transform spectrometers (FTS) [8–16]. At the level of precision required by most applications, even very weak hot-bands buried below the strong lines can play a relevant role in the determination of the gas density from lineshape measurement, but unfortunately there are not many experimental data available for such bands, since FTS cannot be used when much stronger overlapping bands are present. As a matter of fact, all the present data for the weak bands in the neighbouring of the $\nu_1 + 2\nu_2^0 + \nu_3$ band have been calculated [16]. In addition, we note that these weak bands can be used as sensitivity markers in high-accuracy CO_2 spectrometers [2], and also for this application an accurate knowledge of their intensity is needed. In this work, we present high-resolution measurements, performed with a diode laser spectrometer, of line intensity and self-broadening coefficients for some lines of the $\nu_1 + 3\nu_2^1 - \nu_2^1 + \nu_3$ hot-band of CO_2 at 2 μm, in coincidence with the strongest lines of the $\nu_1 + 2\nu_2^0 + \nu_3$. Although the investigated lines are even 1000 times weaker than the neighbouring intense transitions, by means of an accurate lineshape analysis we have been able to determine the spectroscopical parameters with an uncertainty lower than that reported for band calculations.

1 Experimental setup

The diode laser used was an InGaAs/InP DFB diode laser (Sensor Unlimited SU-2000), emitting up to 7 mW of single-mode radiation, with less than 20 MHz linewidth, tunable in a range of approximately 15 cm^{-1} around 2 μm. The laser radiation was collimated by a lens and after passing through an optical isolator (−35 dB) was split in two beams: the first beam went through the cell containing CO_2, while the second one was sent through a 25-cm-long confocal Fabry–Pérot interferometer, whose free spectral range had been measured to be 299 ± 1 MHz, to mark the frequency scale. The absorption cell was an astigmatic multipass Herriot cell (New Focus 5611), with a measured total length of 1850 ± 40 cm in 91 passes. The detailed apparatus is described elsewhere [6, 7].

The analysis of the data has been made with the help of the LINEFIT 2.0 software package [17]. The absorption profile was fitted assuming Voigt profiles for the lineshapes, whatever the pressure. To measure the lineshape of the weak lines in the presence of much stronger absorption features, we have recorded two sets of waveforms in two different ways. In the first case, the laser frequency sweep was wide enough to encompass two adjacent lines of the strong $\nu_1 + 2\nu_2^0 + \nu_3$ band. The number of acquired points was 2500, and all the lines included in the acquisition were fitted at the same time. The pressure was varied in the range 10–30 Torr.

In the second case, a much narrower frequency sweep was used, encompassing only one line of the $\nu_1+3\nu_2^1-\nu_2^1+\nu_3$ band. In this case the contribution to the absorption due to the neighbouring strong lines has been approximated with a second-order polynomial. The pressure was in the range 30–100 Torr. For the measurement of line strengths the two sets of data have been mixed, yelding the same results. On the contrary, for the self-broadening, only the data taken with narrow frequency sweeps have been used.

2 Results and discussion

The spectral range covered by the diode laser includes nine lines of the band $\nu_1+3\nu_2^1-\nu_2^1+\nu_3$ of $^{12}CO_2$, from the R(44) up to the R(59). For all these lines we measured the intensity, whereas the self-broadening coefficient has been measured for all lines but R(57). This is due to the fact that the much stronger line R(30), belonging to the band $\nu_1+2\nu_2^0+\nu_3$, lies very close to this, and at the relatively high pressures required for self-broadening measurements the overlap reduces the accuracy of the parameter.

2.1 Line intensity

In order to determine the line intensity S, as we always have a significant line overlap, we have reconstructed the line profiles from the parameters derived from the fit procedure, and then we have integrated them in order to determine the total absorbance. We have repeated this procedure at different pressures to get an improvement in the accuracy. The integral area per unit pressure was successively divided by the length L of the absorption path, and by the Loschmidts' number $N_L(T)$, at the temperature T of the gas. The error bars reported in Fig. 1 are mainly determined by uncertainties in the normalization and in the pressure.

The room temperature has been monitored to be stable during each series within 1 °C, even if it varied for different series from 20 °C up to 23 °C. However, for a correct comparison with available data, all the line intensities have been referred to $T = 296$ K. The total error on the final value of S has been estimated to be within 5%, which is essentially due to the statistical spread and reproducibility of the result for different series. The resulting values of S are listed in Table 1, whereas in Fig. 2 they are plotted along with the corresponding values from HITRAN database. Our values for S are from 5% to 15% smaller than the HITRAN ones; we note anyway that the two sets of data are in relatively good agreement, if we consider the uncertainty on the HITRAN data, which is given at the 5%–10% level.

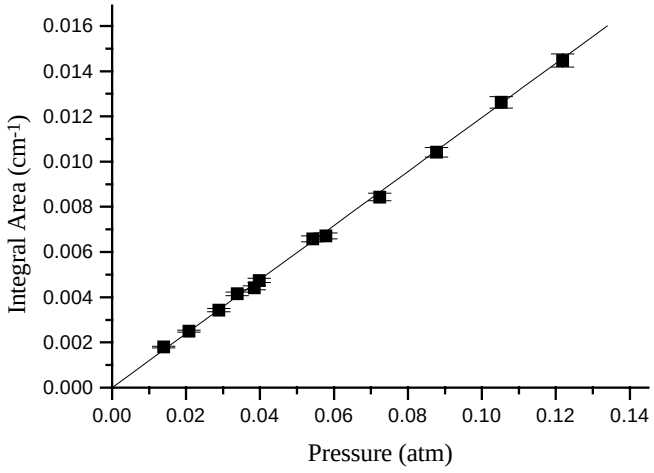

Fig. 1. Intensity values of line R(44) as a function of pressure

Table 1. Measured line intensity S of the investigated lines of the $\nu_1+3\nu_2^1-\nu_2^1+\nu_3$ band of CO_2

J	ν_o^a /cm^{-1}	S_{exp} / $\times 10^{-24}$ cm/mol	S^a
44	4994.05835	4.41 (9)	4.64
47	4994.31835	2.74 (5)	2.95
50	4996.90866	1.54 (8)	1.78
52	4997.80765	1.17 (3)	1.25
53	4996.75170	0.94 (3)	1.05
54	4998.68105	0.79 (2)	0.866
55	4997.50441	0.62 (1)	0.72
57	4998.22792	0.47 (4)	0.49
59	4998.92226	0.25 (2)	0.323

[a] From HITRAN database

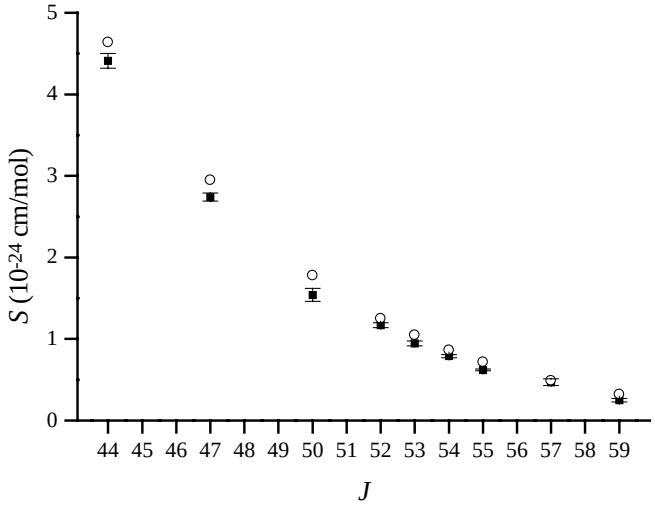

Fig. 2. Comparison between experimental (■) and HITRAN (○) strenght values

2.2 Broadening

The Lorentzian halfwidth γ_L is assumed to vary linearly as a function of the pressure p,

$$\gamma_L = a_s p\,, \tag{1}$$

where a_s is the self-broadening coefficient.

We therefore measured the Lorentzian halfwidth at different pressures, and then we fitted it according to the law of (1), in order to extract the coefficient a_s. The error for a single measurement of the width has been assumed to be 10 MHz or the error coming out from the fit procedure, whichever is the larger. The errors for the broadening coefficients reported in Table 2 are twice the standard deviation coming

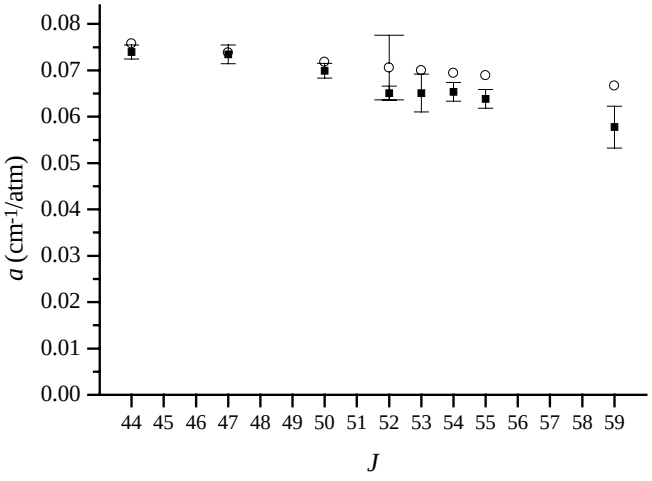

Fig. 3. Comparison between experimental (■) and HITRAN (○) self-broadening coefficients

Table 2. Measured self-broadening a_s coefficients for eight lines of the $\nu_1+3\nu_2^1-\nu_2^1+\nu_3$ band of CO_2

J	a_s(exp) /cm^{-1}/atm	a_s (HITRAN)
44	0.0740 (15)	0.0758
47	0.0735 (20)	0.0738
50	0.0700 (20)	0.0718
52	0.0651 (15)	0.0706
53	0.0651 (40)	0.0700
54	0.0654 (20)	0.0694
55	0.0638 (20)	0.0689
59	0.0578 (45)	0.0667

from the linear fit of the data, according to (1). The results are summarized in Table 2. Also the measured values for the self-broadening can be compared to the values given by HITRAN in Fig. 3: the experimental values are generally smaller, and the discrepancy is increasing with the angular momentum J. Once more, the two sets are in accordance when the uncertainty on HITRAN data (10%–20%) is considered.

3 Conclusion

By using a DFB diode laser we demonstrated the possibility of performing accurate lineshape measurements on a weak band of CO_2 in the presence of a much stronger absorption band. As a result, we measured fundamental spectroscopical parameters for nine ro-vibrational transition lines of the weak $\nu_1+3\nu_2^1-\nu_2^1+\nu_3$ combination band at 2 μm. Line intensities and self-broadening coefficients have been measured with a precision higher than that typical of FT spectrometers or band calculations, which have been previously used to retrieve such kind of data in this band. A comparison has been made with data from the HITRAN database, and a generally good agreement has been found both for intensities and for self-broadening coefficients. Since our measurements provided a reduction of the uncertainties by at least a factor of two, the values we give can be used for future refinement of band calculations [16]. The investigated lines can now be used also as accurate intensity references to calibrate high-sensitivity spectrometers for CO_2 monitoring, working on the strong $\nu_1+2\nu_2^0+\nu_3$ band.

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References

1. G. Modugno, C. Corsi, M. Gabrysch, F. Marin, M. Inguscio: Appl. Phys. B **67**, 289 (1998)
2. P. Werle, R. Mücke, F. D'Amato, T. Lancia: Appl. Phys. B **67**, 307 (1998)
3. R.M. Mihalcea, M.E. Webber, D.S. Baer, R.K. Hanson, G.S. Feller, W.B. Chapman: Appl. Phys. B **67**, 283 (1998)
4. F. Thibault, J. Boissoles, R. Le Doucen, J.P. Bouanich, P. Arcas, C. Boulet: J. Chem. Phys. **96**, 4945 (1992)
5. R.M. Mihalcea, D.S. Baer, R.K. Hanson: Appl. Opt. **36**, 8745 (1997)
6. M. De Rosa, C. Corsi, M. Gabrysch, F. D'Amato: J. Quant. Spectrosc. Radiat. Transfer **61**, 97 (1998)
7. C. Corsi, F. D'Amato, M. De Rosa, G. Modugno: Eur. Phys. J. D, **6**, 327 (1999)
8. K.P. Vasilevskii, L.E. Danilochkina, V.A. Kazbanov: Opt. Spectrosc. **38**, 499 (1975)
9. F.P.J. Valero, C.B. Suárez, R.B. Boese: J. Quant. Spectrosc. Radiat. Transfer **23**, 337 (1980)
10. E. Arié, N. Lacome, P. Arcas, A. Levy: Appl. Opt. **25**, 2584 (1986)
11. J.W.C. Johns: J. Mol. Spectrosc. **125**, 442 (1987)
12. L. Rosenmann, M.Y. Perrin, J. Taine: J. Chem. Phys. **88**, 2995 (1988)
13. V. Dana, A. Valentin, A. Hamdouni, L.S. Rothman: Appl. Opt. **28**, 2562 (1989)
14. C.B. Suárez, F.P.J. Valero: J. Molec. Specrosc. **140**, 407 (1990)
15. M. Hammerich, L. Vildrik-Sørensen, H. de Vries, J. Henningsen: Appl. Phys. B **53**, 170 (1991)
16. L.S. Rothman, R.L. Hawkins, R.B. Wattson, R.R. Gamache: J. Quant. Spectrosc. Radiat. Transfer **48**, 537 (1992)
17. F. D'Amato, A. Ciucci: ENEA Report, RT/INN/94/01 (1994)