Pressure-induced line broadening for the (30012)←(00001) band of CO_2 measured with tunable diode laser photoacoustic spectroscopy

J.S. Li[a],*, K. Liu[a], W.J. Zhang[a], W.D. Chen[b], X.M. Gao[a]

[a]Environmental Spectroscopy Laboratory, Anhui Institute of Optics & Fine Mechanics,
Chinese Academy of Sciences, Hefei 230031, People's Republic of China
[b]Laboratoire de Physicochimie de l'Atmosphère, Université du littoral Côte d'Opale, 145 AV. Maurice Schumann, 59140 Dunkerque, France

Abstract

Pressure-induced foreign-broadening lineshape parameters of the carbon dioxide rovibrational transitions belonging to the (30012)←(00001) overtone band near the 1.573 μm wavelength region are measured by using a tunable diode laser photoacoustic spectrometer. The spectroscopic analysis has concerned the first 11 lines of the R branch. For these lines, the air- and Ar-broadening coefficients are measured at room temperature (∼298 K). The measured broadening coefficients of all the transitions of $^{12}C^{16}O_2$ are compared with those given in the HITRAN04 database and former measurements with a different spectroscopic method. Agreements and discrepancies are underlined and briefly discussed. The recorded lineshapes are fitted with standard Voigt line profiles in order to determine the collisional broadening coefficient of carbon dioxide transitions.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: CO_2; Near-infrared spectra; Photoacoustic spectroscopy; Spectral lines parameters

1. Introduction

The study of the carbon dioxide molecule has always been of immense importance in atmospheric science, astrophysics, pollution control, remote sensing, etc. Carbon dioxide absorbs radiation in the terrestrial atmosphere and creates greenhouse warming of the Earth's surface. It has been suggested that this molecule is the second most important greenhouse gas after atmospheric water, and plays a non-negligible role in the global climate of the earth due to the increasing use of automobiles and human activity (in particular combustion). Many spectroscopic techniques, such as Fourier transform infrared spectroscopy (FTIRS), tunable diode laser absorption spectroscopy (TDLAS), photoacoustic (PA) spectroscopy, cavity ring-down spectroscopy (CRDS) or cavity-enhanced absorption spectroscopy, have already been proposed to detect this molecule during the last decades in order to better understand the physicochemical processes in planetary

atmospheres with particular regard to the Earth and its climate. In comparison with other spectroscopic techniques based on direct absorption [1–3], PA spectrometers [4,5] are very simple devices, compact and much less sensitive to the problems of interference fringes and optical misalignments, which are the main drawbacks of other spectroscopic techniques mentioned above. For atmospheric applications, near-infrared wavelengths are well-suited for these endeavors, but to achieve these goals a good knowledge of line parameters (i.e. positions, strengths and pressure-broadening coefficients) of the spectral lines is required to very high precision and accuracy. The spectral region covering the $(30012) \leftarrow (00001)$ band of CO_2 is suitable for remote and in situ sensing of carbon dioxide in the lower stratosphere.

Previously, the $(30012) \leftarrow (00001)$ band of CO_2 has been extensively measured for both the linestrength [6–14] and self-broadening [8–10,12,13,15]. In contrast, there are almost no air-broadened measurements for this band and only a handful of values computed from a combination of nitrogen and oxygen-broadening coefficients, and much less for inert gases. Rosa et al. [10] firstly reported self, foreign gas (N_2 and O_2) broadening and shifts for the most intense lines of the P branch of the $2v_1 + 2v_2 + v_3$ band of CO_2 around 1.573 µm by TDLAS; thus, the air-broadening coefficients were derived from a combination of nitrogen- and oxygen-broadening coefficients. Subsequently, Henningsen and Simonsen [9] determined the linestrengths, self-broadening coefficients and pressure shifts for the rotational transitions in the $(30012) \leftarrow (00001)$ band between P20 and R66. Recently, Devi et al. [16] presented the most extensive set of measurements to date for self- and air-broadening coefficients of a near-infrared band of CO_2 at room temperature with the McMath–Pierce Fourier transform spectrometer. More recently, Devi et al. [17] reported the line position, intensity and line shape parameters (Lorentz widths, pressure shifts, line mixing, speed dependence) for transitions of the $(30013) \leftarrow 00001$ band of CO_2 again. At the same time, Predoi-Cross et al. [18] also reported the line shape parameters (linestrengths, self-broadening coefficients, etc.) measurement and computations for self-broadened carbon dioxide transitions in the $(30012) \leftarrow (00001)$ and $(30013) \leftarrow (00001)$ bands using an FTS with a resolution of $0.008 \, cm^{-1}$. It is worth noting that Devi et al. [17] and Predoi-Cross et al. [18] are seeing line mixing in these transitions. To maximize the accuracies of the retrieved parameters, multispectrum fitting with speed-dependent line shapes and line mixing were used. Toth et al. [15] also saw it, but used the Voigt line shape in order to do more bands. Overall, the speed-dependent Voigt line shape-fitted broadening parameters are slightly higher than those obtained by a standard Voigt fit. The intensities are not changed much with the different shapes (0.5% or less), but the widths change by ~2%.

Since the atmospheric CO_2 collides not only with the principal constituents of the air (N_2 and O_2) but also with species present in much lower concentrations, studies of prototypical systems like CO_2–Ar are also of high importance. However, there are few measurements of CO_2 broadened by Ar in any band, especially in the near infrared. Furthermore, it has been observed experimentally [19] that the CO_2–Ar line pressure broadening is fairly similar to that in CO_2–N_2, for which a quantum description is not yet feasible. Thibault et al. [20] determined the line-broadening coefficients of CO_2–Ar in the fundamental v_3 band experimentally by FTIRS and theoretically via quantum-mechanical approaches as well as semiclassical methods for temperatures from 120 to 765 K. Alwahabi et al. [21] presented the measurements of collisional broadening coefficients for CO_2–Ar and CO_2–He binary mixtures using tunable single-mode laser radiation at 2 µm by polarization spectroscopy. Besides those mentioned in Refs. [20,21], Nakamichi et al. [22] recently reported the N_2-, O_2- and various inert gases-broadening of five transitions (R(0), P(8), P(16), P(26) and P(38)) in the $30013 \leftarrow 00001$ band by using CRDS within the temperature range 263–326 K.

In the present study, we have reinvestigated the $(30012) \leftarrow (00001)$ band of CO_2 using a high-resolution diode laser-based PA spectrometer. The foreign gases (dry air- and Ar-) broadening coefficients of 11 lines within the laser tunable range were obtained by modeling individually these spectral lines with the standard Voigt profile, which considers separately Doppler and collisional broadenings.

2. Experimental details

2.1. Spectrometer details

Fig. 1 shows the experimental setup of the PA spectrometer. A detailed description of this apparatus is given elsewhere [4,5], except for the excitation source and the PA cell. In the present study, a room-temperature
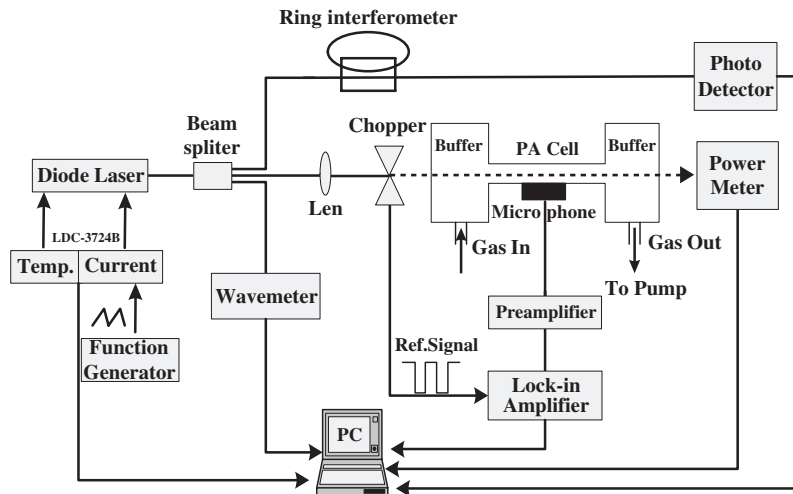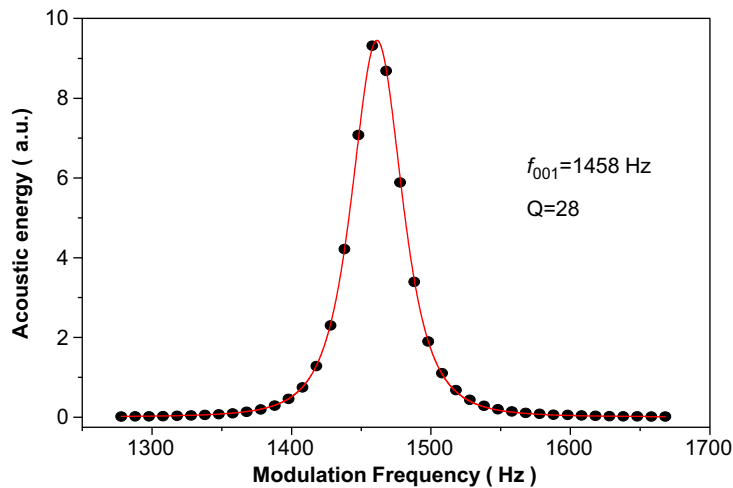
Fig. 1. Schematic diagram of the experimental setup.

Fig. 2. First longitudinal resonance of our PA cell at 1.458 kHz. Circles are experimental points and the curve is the result of a fit by a Lorentzian distribution. The quality factor $Q = 28$.

single-mode fiber-coupled near-infrared telecommunication distributed feedback (DFB) diode laser emitting near 1573 nm serves as the excitation source. The coarse wavelength tuning of the diode laser is achieved by changing the temperature of the base plate on which the diode laser is mounted, whereas for fine wavelength tuning we scan the drive current of the diode laser by applying a ramp voltage from a function generator. The typical tuning rates of the diode laser are ~0.02 cm^{-1}/mA and ~0.42 cm^{-1}/°C. The temperature and current were controlled by a commercial diode laser controller (ILX Lightwave LDC-3724B), with short-term (1 h) temperature stability <0.004 °C and long-term (24 h) temperature stability <0.01 °C. The diode laser power was temperature and current dependent, and the mean output power was about 4.0 mW. An improved PA cell was made of a central cylindrical resonator (aluminum: $\varnothing = 6$ mm, $l = 100$ mm) and two buffer volumes acting as acoustic filters. The acoustic resonator is operated in its first longitudinal mode at $f = 1.458$ kHz with a higher quality factor, as shown in Fig. 2.

The laser beam is coupled to a single-mode fiber optic cable using bulk optics. A 1×3 fiber splitter divides the laser output into three beams. The main beam (90% of the power) is collimated by a fiber collimator and directed to the PA cell containing pure CO_2 or mixture of CO_2 and different perturber gas at known
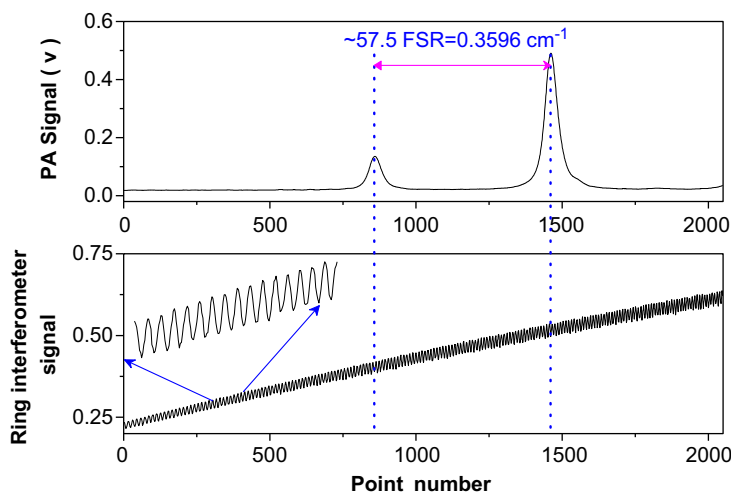
Fig. 3. From top to bottom: PA spectrum of CO_2 transitions at 6348.6239 and 6348.9834 cm^{-1}, and ring interferometer signal. The inset shows a segment of the ring interferometer signal.

temperature and pressure. To carry out phase-sensitive detection, the beam is mechanically modulated using a chopper in a 50/50 duty cycle at the first longitudinal resonant frequency of the PA cell. The PA cell is associated with a sensitive miniature electric microphone (Mode MA211, sensitivity: 50 mV/Pa). The main advantage for resonant operation is that the system's sensitivity can be effectively improved by amplifying the acoustic signal and reducing the sensitivity to $1/f$ noise. Simultaneously, the transmitted laser beam exiting the PA cell is detected by an optical power meter (Newport, Model 1830-C) to normalize the PA signal. A ring interferometer (RI) with a free spectral range (FSR) of 0.00625 cm^{-1} shown in Fig. 3 receives the secondary beam (8% of the power), which is monitored by a Ge photodetector (New Focus 2011) for wavelength calibration, and the remaining one is focused on the probe of a wavemeter (Burleigh, WA-1500-NIR, with an accuracy of about ± 0.001 cm^{-1}) to know the absolute wavelength.

A PC-based data-acquisition card was used to acquire the detected signals sampling at 20 kS/s with 12-bit resolution. A simultaneous TTL signal from the function generator is used to trigger the data-acquisition card to sample the experimental data. A GPIB card was also used with the computer to control the laser controller. With the aid of a computer controlled by LabWindows/CVI program, the sensor automatically performs the tasks including the laser frequency scan and monitor, the acquisition of digitized PA signal, and the spectral data processing.

The temperature and current are kept fixed at the transition and the diode drive current is ramped to record each individual transition at different perturber pressures. The lock-in time constant is kept fixed at 1 ms. Typically, 10 spectral scans with the laser-scanning rate of 1 Hz (corresponding to ∼10 s data acquisition time) were averaged for each measurement. In this process, we recorded and studied 11 rovibrational transitions of carbon dioxide in the coverage of the 6348–6363 cm^{-1} spectral region. All the measurements are carried out at room temperature (∼298 K).

2.2. Gas sample details

First, the PA cell was evacuated to the order of 10^{-4} Torr using a mechanical pump or a molecular pump. Then, the PA cell was filled with the natural abundance CO_2 gas of 99.99% purity. After recording every pure CO_2 spectra with a certain pressure, dry air (and filtered with a 1 μm-diameter filter) or argon gas with 99.999% purity is introduced as a perturber gas into the PA cell step-by-step and each perturber gas pressure-dependent measurement is conducted. For foreign broadening coefficient determination, the measurements were performed over five group pressure values. For each group, the pure CO_2 spectra were first recorded at a room temperature of ∼298 K, and then the perturber gas (dry air or argon gas) was added step-by-step with pressure change from 50 to 300 Torr; accordingly, the CO_2 spectra under different perturber pressures were

Table 1
Summary of experimental conditions of the $^{12}C^{16}O_2$ spectra analyzed in this work

CO$_2$ in air			CO$_2$ in Ar		
Temp (K)	CO$_2$ pressure (Torr)	Air pressure (Torr)	Temp (K)	CO$_2$ pressure (Torr)	Ar pressure (Torr)
298	50 ± 0.15	50 ± 0.22, 100 ± 0.21, 150 ± 0.23, 200 ± 0.18, 250 ± 0.22	298	60 ± 0.20	50 ± 0.20, 100 ± 0.23, 150 ± 0.25, 200 ± 0.18, 250 ± 0.21
298	55 ± 0.21	50 ± 0.23, 100 ± 0.24, 150 ± 0.26, 200 ± 0.23, 250 ± 0.25	298	65 ± 0.17	50 ± 0.21, 100 ± 0.26, 150 ± 0.25, 200 ± 0.28, 250 ± 0.20
298	65 ± 0.18	50 ± 0.21, 100 ± 0.24, 150 ± 0.16, 200 ± 0.27, 250 ± 0.23	298	70 ± 0.14	50 ± 0.23, 100 ± 0.23, 150 ± 0.26, 200 ± 0.27, 250 ± 0.25
298	75 ± 0.22	50 ± 0.22, 100 ± 0.23, 150 ± 0.21, 200 ± 0.25, 300 ± 0.21	298	75 ± 0.15	50 ± 0.25, 100 ± 0.23, 150 ± 0.22, 200 ± 0.26, 250 ± 0.21
298	85 ± 0.21	33 ± 0.22, 76 ± 0.24, 135 ± 0.26, 185 ± 0.18, 267 ± 0.25	298	80 ± 0.22	50 ± 0.20, 100 ± 0.22, 150 ± 0.24, 200 ± 0.27, 250 ± 0.22

also recorded. Before each measurement, the gas sample was allowed to stabilize thermally with enough time. The total sample pressures were known to be better than 0.4%. The experimental conditions of the CO$_2$ spectra analyzed in this work are summarized in Table 1. The system error was estimated to be better than 3%, based on uncertainties in the pressure, uncertainty of FSR of RI, the error of calibration of the PA cell, etc. Further details about the experimental apparatus, sample pressures and sample temperature monitoring, calibration procedures and experimental precautions taken to minimize systematic errors have been discussed elsewhere [2,3].

2.3. Retrieval details

The PA signal intensity, S, in volts, can be described as

$$S = S_m P_L C_{cell} \alpha, \tag{1}$$

where the microphone sensitivity, S_m, is in units of milli-volts per Pascal (mV/Pa); the laser optical power, P_L, is in watts (W); the PA cell response constant, C_{cell}, has units of Pascal per inverse centimeters per watt (Pa/cm W); and α is the absorption coefficient of the transition that is being interrogated, in inverse centimeters. The PA signal intensity is therefore proportional to the incident laser power and the concentration of the absorbing molecule. Thus, the PA detection method derives sensitivity benefit from the use of as much laser power as is available. The PA cell constant, C_{cell}, is a scaling factor depending on the PA cell geometry, on the modulation frequency and on measurement conditions (i.e. acoustical properties of the measured gas sample), and is usually achieved experimentally from measurements with a gas of known absorption and certified concentration.

For gaseous molecule absorption, the line shape function may be represented by a Lorentzian when only collisional effects are important, a Gaussian when the Doppler effect is dominant, or a Voigt function, where both effects are important. In many applications both Doppler and pressure broadening are considerable, and therefore a Voigt function is typically used to represent the line shape. Here, all the recorded spectra are fitted with standard Voigt line profiles in order to determine the collisional broadening coefficient of carbon dioxide transitions.

The experimental profile is fitted with a simulated curve by using a non-linear least-squares fitting program [2,3]. Fig. 4 represents the experimental line profile fitted with the Voigt function and residual for the transitions between 6353.8 and 6354.7 cm^{-1}. The recorded transition spectrum in this region (Fig. 4) shows the weakest transition at 6354.4215 cm^{-1} with an SNR of ~5. This transition has a reported linestrength ~4.404 × 10^{-26} cm/molecule [23]. As illustrated in the inset, a typical noise level of sensitivity α_{min} ~1.0 × 10^{-7} cm^{-1} was achieved with a laser radiation power less than 5 mW. As is well known, the sensitivity of this
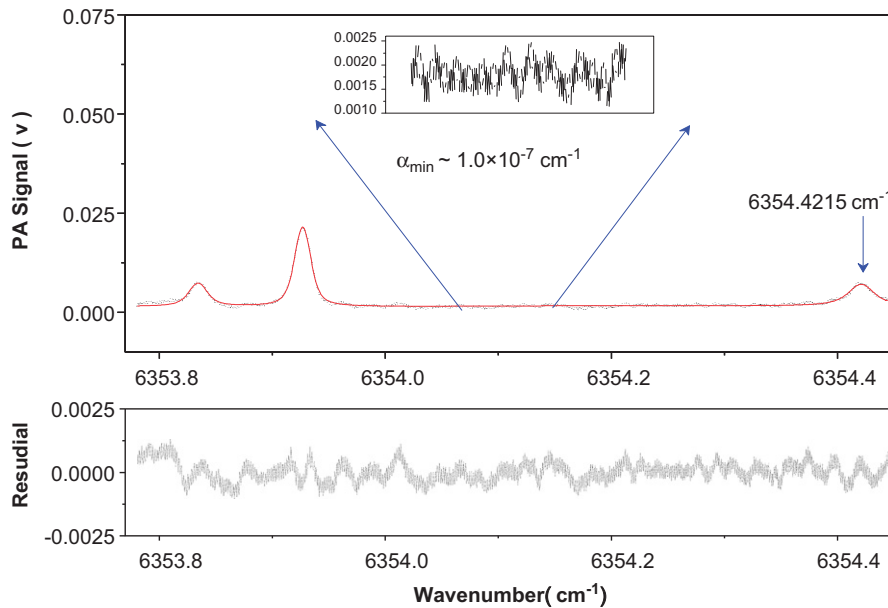
Fig. 4. Comparison between the experimental lineshape and the fit Voigt function for the CO_2 transitions between 6353.8 and $6354.7\,\mathrm{cm}^{-1}$ at $P_{CO_2} = 14.65\,\mathrm{Torr}$. The lower part shows the residual obtained from the least-square fitting.
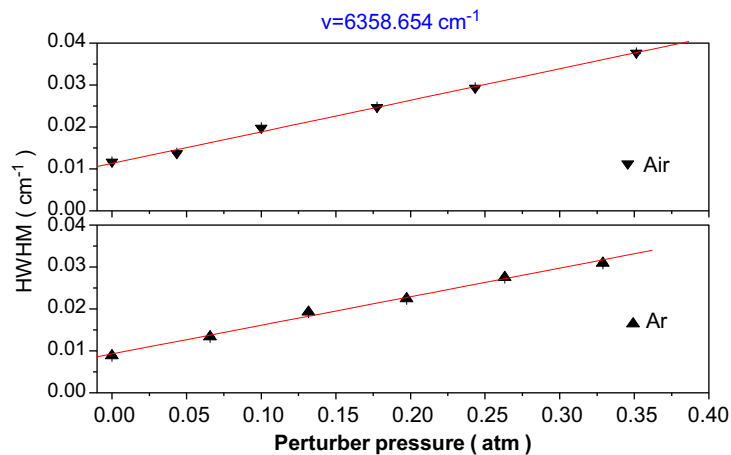

Fig. 5. Plot of collisional half-width at half-maximum vs. each perturber (air and Ar) pressure for CO_2 transition at $6358.654\,\mathrm{cm}^{-1}$. The straight line is the linear fit of the data points and the vertical bars are the error bars obtained from the non-linear least-squares fitting of the line profiles with Voigt lineshape functions. Where error bars are not visible, the measurement uncertainties are smaller than the size of the symbol used.

technique is power dependent (since the magnitude of the PA signal scales with the incident laser power). If higher laser output power can be achieved, the sensitivity will be further improved.

The data obtained for the half-width at half-maximum (HWHM) of the Lorentzian component are plotted as a function of perturber gas pressure. The slope of this graph gives the value of the collisional broadening coefficient ($\mathrm{cm}^{-1}\,\mathrm{atm}^{-1}$ at 298 K) for that particular transition. Fig. 5 shows an example of the Lorentzian HWHM against perturber gas (air and Ar) pressure for the transition at $6358.654\,\mathrm{cm}^{-1}$. In the fit, the amplitude, the Lorentz width, the line center frequency and the magnitude of the background are varied, while the Doppler width is maintained fixed at the theoretical value. The same procedure is also followed for the other transitions.
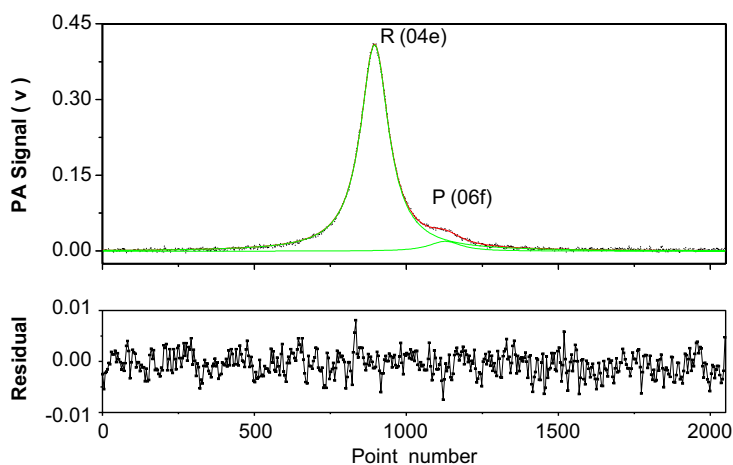
Fig. 6. The unresolved double lines profile for the R (04e) and P (06f) transitions of 60 Torr CO_2 broadened by 200 Torr of Ar at 298 K. The top panel shows the measured (in dotted line) and calculated (in solid line) line profiles with a multispectrum fitting program. The lower panel shows the corresponding fitting residuals.

The studied transitions are well resolved by the spectrometer and isolated, except the transitions of R(04e), R(06e), R(14e) and R(16e), which are unresolved with the transitions of P(04f), P(06f), R(02f) and R(04f), respectively, since pressure broadening is very serious at high pressure. For isolated transitions we used a single-line fitting program, while for unresolved lines a multispectrum fitting program was used. Additional details about the multispectrum fitting procedure are given in Refs. [2,3]. Fig. 6 shows an example of the measured CO_2 line profiles for P(04e) at 6351.640 cm^{-1} and P(06f) at 6351.506 cm^{-1}, which was broadened by 200 Torr of Ar. The Voigt line profile calculated with a multispectrum fitting program is also shown by the solid curve. Initially, we determined the line shape parameters of the transition at 6351.640 cm^{-1}, assuming very little influence of the neighboring transitions at 6351.506 cm^{-1} on its lineshape since the line strength of the former is almost 23.4 times greater than that of the latter. But single-spectrum fitting of this transition led to a greater value of broadening coefficients compared with the other transitions. Later, we used a multispectrum fitting program to fit these two transitions simultaneously to obtain broadening coefficients of both the transitions. The broadening coefficients for the transition at 6351.640 cm^{-1} are less than that obtained by the single-line fitting procedure. This indicates that the lineshape of the transition at 6351.640 cm^{-1} is indeed affected by that at 6351.506 cm^{-1}. The same procedure is also followed for the other three unresolved transitions.

3. Results and discussion

The whole tunable range of our diode laser has been found to extend from 1571.3 up to 1575.3 nm, which only comprises the first 11 lines of the R branch of the (30012)←(00001) band of CO_2. Although the range we studied contains some other lines belonging to other bands, and their positions can be confirmed by the wavemeter reading, we decided to neglect these weak lines except for transitions of P(04f), P(06f), R(02f) and R(04f) belonging to the (31112)←(01101) band, since they are very close to the transitions of R(04e), R(06e), R(14e) and R(16e) (see text). Therefore, foreign (air-, and Ar-) broadening has been measured only on the most intense lines, P(0)–P(20). The spectral parameters achieved in the present work are summarized in Table 2.

From the data reported herein, the results presented here on air broadening are smaller than the data from the HITRAN04 molecular database [23], and the discrepancies with our results for air broadening are less than 4%. Recent measurements on the carbon dioxide $(22^01)←(00^00)$ band by Henningsen et al. [9] and $(30^01)_{III}←(000)$ band by Pouchet et al. [24] show that systematic errors of several percents in the broadening coefficients can happen in the near-infrared by neglecting the Galatry collision-narrowing effect, where Voigt function fitting and diode laser absorption spectroscopy are used. Henningsen et al. [9] described that

Table 2
Measured air- and Ar- broadened coefficients (in cm^{-1}/atm at 298 K) for the $(30012) \leftarrow (00001)$ band of $^{12}C^{16}O_2$ at room temperature

Line	Position (cm^{-1})	Δv_{Air} (This work)	%unc.[a]	Δv_{Ar} (This work)	%unc.
R00e	6348.624	0.08991	0.085	0.08224	0.151
R02e	6350.147	0.0844	0.136	0.07827	0.094
R04e	6351.640	0.08499	0.17	0.07792	0.051
R06e	6353.103	0.07677	0.155	0.07048	0.188
R08e	6354.536	0.0755	0.182	0.06942	0.118
R10e	6355.939	0.07295	0.196	0.0645	0.199
R12e	6357.312	0.07467	0.199	0.06772	0.146
R14e	6358.654	0.07523	0.126	0.06821	0.362
R16e	6359.967	0.07106	0.114	0.0653	0.153
R18e	6361.250	0.06896	0.149	0.06222	0.085
R20e	6362.504	0.06923	0.175	0.05917	0.144

[a]The error corresponds to one standard deviation obtained by averaging the different measurements.

collisional narrowing must be considered at low pressures where the Doppler contribution is significant compared with the Lorentz width, while the effects of collisional narrowing could be neglected at higher pressure where the Doppler contribution is small compared with the Lorentz width. Fortunately, all the measurements in the present work are made at high pressure. In fact, we choose to apply only the Voigt profile since the result of the fitting was quite good. Fig. 7(a) compares the air-broadened width coefficients determined in the present work to the data given in the HITRAN04 database [23] as well as to those measured by Devi et al. [16,17] and Henningsen et al. [9]. It is clear that all the results exhibit similar m-dependences ($m = -J$ for P branch lines and $J + 1$ for R branch lines), but the HITRAN04 values are systematically higher than the present results by 3.3%. However, the results measured by Devi et al. are higher than the HITRAN04 values by $1.8 \pm 1.1\%$. Our values are very close to those of Henningsen et al. except for the R0 line (deviation reaches to -8.6%) within experimental measurement uncertainty. This good agreement may be attributed to the same line shape used for the line widths retrieval. Devi et al. [17] have found that the line-by-line Voigt profile retrievals systematically underestimate the self-broadening coefficients by $\sim 2.0\%$ while overestimating the intensities by $\sim 0.4\%$ compared with their constrained multispectrum/speed dependence with line-mixing retrievals. Moreover, Predoi-Cross et al. [18] also observed that the speed-dependent Voigt-fitted broadening parameters are slightly higher than those obtained by a Voigt fit.

Since argon gas is an inert perturber, the collisional broadening coefficients of the transitions of CO_2 obtained in this work are low compared with the air-broadening coefficients of the relative transitions. Fig. 7(b) compares the Ar-broadening coefficients determined in the present work to the results reported by Thibault et al. [20] and Nakamichi et al. [22] as well as to these data fitted to a rational expression, i.e. the 1,1-Padé approximant [22,25]:

$$\Delta v(m) = \frac{a + b|m|}{1 + c|m|}. \tag{2}$$

The coefficients a, b and c used for calculation in the present work, Thibault et al.'s, and Nakamichi et al.'s work are summarized in Table 3. Comparison to the measurements from Thibault et al. [20] shows that the mean deviation is less than 3% for low m values, whereas the deviation reaches 10% for high m values. However, comparison to the measurements from Nakamichi et al. [22] shows that the characteristic is almost contrary, the maximum deviation occurs at low m values, and they differ by as much as 12% from those determined in the present work.

4. Conclusion

A near-infrared DFB diode laser PA spectrometer was used to determine 11 CO_2 lines-broadening coefficients by air and argon in the $(30012) \leftarrow (00001)$ band near 1.573 μm. The spectral region ranging from
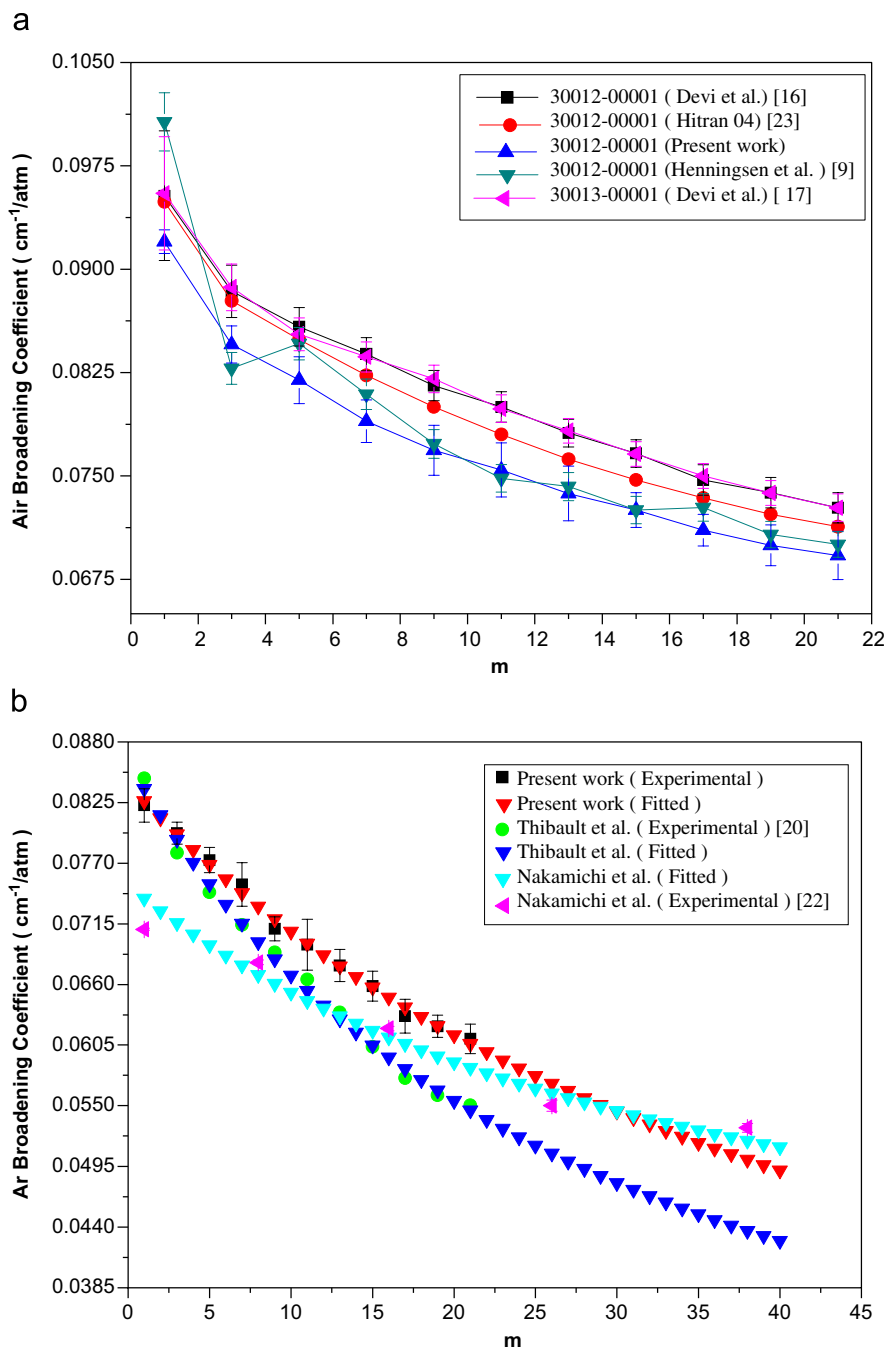
Fig. 7. The measured (a) air- and (b) Ar-broadened HWHM coefficients for the $(30012) \leftarrow (00001)$ band of $^{12}C^{16}O_2$ from this work are plotted vs. the quantum number m ($m = J + 1$ for R(J), $m = -J$ for P(J)) and compared with HITRAN04 database [23] as well as other measurements [9,16,17,20,22]. The errors correspond to one standard deviation obtained by averaging the different measurements. The measured Ar-broadened width coefficients are fitted to a rational expression, i.e. the 1,1-Padé approximant [22,25].

6348 to 6364 cm^{-1}, which is suitable for the in situ laser probing of CO_2 in the middle atmosphere, has been revisited. Our data have been compared with the data given by the HITRAN04 molecular database and former measurements, and some discrepancies have been found. Air-broadening coefficients were determined for 11 transitions and found to be from 3% to 4% lower than those in the HITRAN04 database, but very

Table 3
Parameters for the 1,1-Padé approximant in Eq. (2)

	a	b	c
Thibault et al. [20]	0.08628	0.00043	0.03553
Nakamichi et al. [22]	0.075	0.00079	0.027
Present work	0.08422	0.00018	0.0215

close to those of Henningsen et al. [9] within experimental measurement uncertainty. For Ar-broadening measurements, the difference is distinct between our results and those of Thibault et al. [20] and Nakamichi et al. [22]. From the results obtained in this study and from other measurements in the $(30012) \leftarrow (00001)$ overtone band, we feel that perhaps it may be needed to consider the effect of collisional narrowing in analyzing the high-resolution spectra. We strongly believe that the system can further be improved with higher sensitivity. We also believe that the reported detection scheme presented here will be helpful in spectroscopic sensing of atmospheric trace gases.

Acknowledgments

References

[1] Gao XM, Fan H, Huang T, et al. Natural gas pipeline leak detector based on NIR diode laser absorption spectroscopy. Spectrochim Acta Part A 2006;65:133–8.

[2] Deng LH, Gao XM, Cao ZS, et al. Empirical line intensities of methane at 1.51 μm. JQSRT 2007;103:402–10.

[3] Zhao WX, X Gao M, Deng LH, Huang T, Wu T, Zhang WJ. Absorption spectroscopy of formaldehyde at 1.573 μm. JQSRT 2007; 107: 331–9.

[4] Li JS, Gao XM, Li WZ, et al. Near-infrared diode laser wavelength modulation-based photoacoustic spectrometer. Spectrochim Acta Part A 2005;64:338–42.

[5] Li JS, Gao XM, Fang L, et al. Resonant photoacoustic detection of trace gas with DFB diode laser. Opt Laser Technol 2007;39:1144–9.

[6] Toth RA, Brown LR, Miller CE, Devi VM, Benner DC. Line strengths of $^{12}C^{16}O_2$: 4550–7000 cm^{-1}. J Mol Spectrosc 2006;239:22–42.

[7] Boudjaadar D, Mandin J-Y, Dana V, Picqué N, Guelachvili G. $^{12}C^{16}O_2$ line intensity measurements around 1.6 μm. J Mol Spectrosc 2006;236:158–67.

[8] Régalia-Jarlot L, Zeninari V, Parvitte B, Grossel A, Thomas X, von der Heyden P, et al. A complete study of the line intensities of four bands of CO_2 around 1.6 and 2.0 μm: a comparison between Fourier transform and diode laser measurements. JQSRT 2006;101:325–38.

[9] Henningsen J, Simonsen H. The $(22^01–00^00)$ band of CO_2 at 6348 cm^{-1}: linestrengths, broadening parameters, and pressure shift. J Mol Spectrosc 2000;203:16–27.

[10] De Rosa M, Corsi C, Gabrysch M, D'Amato F. Collisional broadening and shift of lines in the $2v_1 + 2v_2 + v_3$ band of CO_2. JQSRT 1999;61:97–104.

[11] Toth RA, Hunt RH, Plyler EK. Line intensities of the CO_2 Σ–Σ bands in the 1.43–1.65 μ region. J Mol Spectrosc 1971;38:107–17.

[12] Valero FPJ, Suarez CB. Measurement at different temperatures of absolute intensities, line half-widths, and broadening by Ar and N_2 for the $30^01_{II} \leftarrow 00^00$ band of CO_2. JQSRT 1978;19:579–90.

[13] Fukabori M, Aoki TA, Aoki TE, Ishida H, Watanabe T. Line parameter measurements of trace gases in the near infrared region. Adv Space Res 2000;25:985–8.

[14] Shao J, Gao XM, Zhang WJ, Yuan YQ, Yang Y, Pei SX. Highly sensitive tunable diode laser absorption spectroscopy of CO_2 around 1.57 μm. Chin Phys Lett 2005;22:57–60.

[15] Toth RA, Brown LR, Miller CE, Devi VM, Benner DC. Self-broadened widths and shifts of $^{12}C^{16}O_2$: 4750–7000 cm^{-1}. J Mol Spectrosc 2006;239:243–71.

[16] Devi VM, Benner DC, Brown LR, Miller CE, Toth RA. Line mixing and speed dependence in CO_2 at $6348\,cm^{-1}$: positions, intensities, and air- and self-broadening derived with constrained multispectrum analysis. J Mol Spectrosc 2007;242:90–117.

[17] Devi VM, Benner DC, Brown LR, Miller CE, Toth RA. Line mixing and speed dependence in CO_2 at $6227.9\,cm^{-1}$: constrained multispectrum analysis of intensities and line shapes in the $30013 \leftarrow 00001$ band. J Mol Spectrosc 2007;245:52–80.

[18] Predoi-Cross A, Unni AV, Liu W, Schofield I, Holladay C, McKellar ARW, et al. Line shape parameters measurement and computations for self-broadened carbon dioxide transitions in the $30012 \leftarrow 00001$ and $30013 \leftarrow 00001$ bands, line mixing and speed dependence. J Mol Spectrosc 2007;245:34–51.

[19] Margottin-Maclou M, Henry A, Valentin A. Line mixing in the Q branches of the $v_1 + v_2$ band of nitrous oxide and of the $(11^10)_I \leftarrow (02^20)$ band of carbon dioxide. J Chem Phys 1992;96:1715–23.

[20] Thibault F, Calil B, Buldyreva J, Chrysos M, Hartmann JM, Bouanich JP. Experimental and theoretical CO_2–Ar pressure-broadening cross sections and their temperature dependence. Phys Chem Chem Phys 2001;15:3924–33.

[21] Alwahabi ZT, Zetterberg J, Li ZS, et al. Measurements of collisional broadening coefficients by infrared polarization spectroscopy. Appl Spectrosc 2007;61:424–7.

[22] Nakamichi S, Kawaguchi Y, Fukuda H, Enami S, Hashimoto S, Kawasaki M, et al. Buffer-gas pressure broadening for the $(30^01)_{III} \leftarrow (0\,0\,0)$ band of CO_2 measured with continuous-wave cavity ring-down spectroscopy. Phys Chem Chem Phys 2006;8:364–8.

[23] Rothman LS, Jacquemart D, Barbe A, Chris Benner D, Birk M, Brown LR, et al. The HITRAN 2004 molecular spectroscopic database. JQSRT 2005;96:139–204.

[24] Pouchet J, Zéninari V, Parvitte B, Durry G. Diode laser spectroscopy of CO_2 in the $1.6\,\mu m$ region for the in situ sensing of the middle atmosphere. JQSRT 2004;83:619–28.

[25] Baker Jr GA. Essentials of Padé approximants. New York: Academic Press; 1975.