Self-, N$_2$- and O$_2$-broadening coefficients for the $^{12}C^{16}O_2$ transitions near-IR measured by a diode laser photoacoustic spectrometer

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ABSTRACT

Using a high-resolution tunable diode laser photoacoustic spectrometer, self-, N$_2$ and O$_2$ pressure broadening coefficients for the first 11 transitions of $^{12}C^{16}O_2$ in the R branch of the $(30012) \leftarrow (00001)$ overtone band at the 6348 cm^{-1} have been revisited at room temperature ($\sim$298 K). Air-broadening parameters have also been calculated from the N$_2$ and O$_2$ measurements. The dependence of the broadening on rotational quantum number m is discussed. The recorded lineshapes are fitted with standard Voigt line profiles in order to determine the collisional broadening coefficients of carbon dioxide transitions. The results are compared to our previous measurements and to the values reported in the HITRAN04 database and by other research group with a different spectroscopic technique.

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1. Introduction

It is well known that carbon dioxide (CO$_2$) has been recognized as the principal anthropogenic driver of climate change. Since the beginning of industrial age, the CO$_2$ concentrations have increased by 25% from approximately 280–370 ppmv nowadays. The infrared absorption spectroscopy of carbon dioxide is of great interest for many important applications, like for instance, combustion, biological processes and planetary atmospheres. Thus, it has stimulated a great deal of spectroscopical studies on its ro-vibrational bands in the IR (4000–10000 cm^{-1}) range, particularly, in the near infrared (NIR) spectral range, ro-vibrational bands of CO$_2$ are suitable for the monitoring of atmospheric carbon dioxide by absorption spectroscopy from satellite [1–3], ground-based [4] or balloon platforms [5,6]. Accurate measurements of line parameters such as position, intensity, pressure broadening and shift are needed to interpret the remote sensing data. Many spectroscopic techniques, such as Fourier Transform Infrared Spectroscopy [7], tunable diode laser absorption spectroscopy [8], photoacoustic spectroscopy [9], cavity ring-down spectroscopy or cavity enhanced absorption spectroscopy [10,11] have already been proposed to perform this task. In comparison with other spectroscopic techniques based on direct absorption, PA spectrometers 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.

Although, the accurate broadening parameters of CO$_2$ are essential for remote sensing as pointed out recently by Miller et al. [12], only a few papers, to our knowledge, have been published for the measurements of the foreign gas effect on this specific band. In our previous study [13], we have constructed a newly designed near-infrared (NIR) diode laser photoacoustic spectrometer, the precise line parameters (i.e., line positions and air-, Ar-broadening parameters) have been determined for 11 transitions of $^{12}C^{16}O_2$ with quantum number m from 0 to 20 in the R branch of the $(30012) \leftarrow (00001)$ band centered at 6348 cm^{-1} [13]. In the present study, we have measured the self-, N$_2$- and O$_2$-broadening effect for these 11 transitions. The broadening parameters for air are also calculated from the measured N$_2$ and O$_2$ parameters assuming binary collisions and a 79/21 percent atmospheric ratio of N$_2$ to O$_2$ [14]. A detailed comparison of our data with previous measurements and the HITRAN04 database [17] is presented, and possible causes of uncertainties and discrepancies are also discussed.

2. Experimental procedure

Since the photoacoustic effect was discovered by A.G. Bell in 1880, it has been widely applied to spectroscopy. Fig. 1 shows our experimental setup. The details of the experiment are similar to those previously reported [13]. A single-mode InGaAsP DFB tunable diode-laser (NTT Electronics Corporation) lasing in the region from 1571.3 up to 1575.3 nm was used as the radiation source, which only covers the spectral range of the first eleven lines of the R branch of the $(30012) \leftarrow (00001)$ band of CO$_2$. The laser wavelength is temperature-stabilized by commercial diode laser

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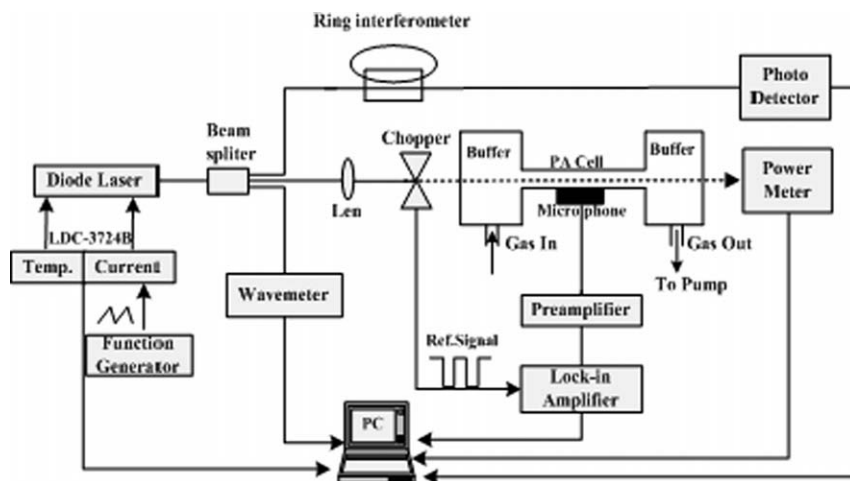
Fig. 1. Schematic diagram of the PAS experimental setup.

controller (ILX Lightwave LDC-3724B) and is driven by a low noise current supply. A low frequency ramp at 1 Hz from a function generator is used to scan the laser diode over the selected absorption lines by modulation of the driving current. The laser beam is coupled into 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 mechanically modulated by a chopper (EG& G Model 197) at the first longitudinal mode of the PA cell. A ring interferometer (RI) with a free spectral range (FSR) of 0.00625 cm^{-1} 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.

The digitized signal from the lock-in amplifier (Stanford Research Systems, SR830) was stored and processed by personal computer (PC). With the aid of a computer controlled by LabWindows/CVI (National Instruments)-based software, the spectrometer automatically performs the tasks including the laser frequency scan and monitor, the acquisition of digitized PA signal, and the spectral data processing.

We have checked the apparatus function of the spectrometer by recording low pressure PA spectra, and proved it was negligible. In these conditions the lineshape could be fitted by a simple Gaussian curve having a Doppler width in good agreement with the theoretical value. The carbon dioxide in natural abundance was purchased from Nanjing Special Gas with the stated purity with a stated purity of 99.99%. The pressures are measured with an uncertainty of 0.4%. Further details about the experimental apparatus, gas sample pressures and gas sample temperatures monitoring, calibration procedures and experimental precautions taken to minimize systematic errors have been discussed else where [15,16]. The pressure broadening coefficients were measured several times for each buffer gas in order to minimize various errors. Typically, 10 spectral scans (corresponding to ~10 s data acquisition time) were averaged for each measurement in order to improve the SNR (signal to noise ratio). All measurements were done at room temperature (~298 K). To retrieve the line parameters we apply a nonlinear least-squares fit to the measured PA spectra using a Voigt profile for the modelling of the lineshape. The fitting procedure has also been described detailedly in our previous studies [15,16].

One example of recorded PA spectrum and its fitting with a Voigt profile for the transition of CO_2 between 6358.4 and 6359 cm^{-1} is presented in Fig. 2. The recorded transition spectrum in this region shows that the weakest transition at 6358.845 cm^{-1}, the SNR is close to 3, and by considering the reported linestrength of ~2.886×10^{-26} cm/molecule [17], it turns out that our spectrometer can detect minimum absorption linestrength $S_{min} \approx 1.0 \times 10^{-26}$ cm/molecule under these experimental conditions.

3. Spectrometer characterization

3.1. Response of the PA cell

It is well known that the PA cell is the key cell of a photoacoustic system, which is directly related to the system sensitivity. An improved PA cell used in this work is made of aluminum material with a central cylindrical resonator (diameter Ø = 6 mm, length L = 100 mm) and two buffer volumes acting as acoustic filters. The typical frequency response of the PA cell has been investigated around 1.5 kHz at room temperature and standard atmospheric pressure, as shown in Fig. 3. Circles are experimental points and the curve is the result of a fit by a Lorentzian distribution, from the figure we can obtain the quality factor Q = 28, and the optimal resonant frequency f = 1458 Hz, which is corresponding to the first longitudinal mode of the PA cell by theoretic calculation.

The PA signal is directly proportional to the PA cell's quality factor Q and the molecular absorption and also depends on the vibrational–translational relaxation rate of the target transition. Therefore the optimum operating pressure has to be determined. As we all know, at atmospheric pressure, pressure broadening seriously limits the detection sensitivity. The microphone response is also an important factor as it is known to work poorly at lower pressure. Fig. 4 shows the PA signal intensity as function of the total gas (pure CO_2) pressure in the PA cell. The best performance (largest acoustic response) of our system was found for a total pressure of near 125 Torr (1 Torr = 133.3 Pa). In fact, the laser optical energy absorbed by the molecules is not directly measured, but is determined indirectly by means of collosional relaxation processes, which is the acoustic wave generated in the sample due to its thermal expansion. The conversion from optical to thermal energy therefore depends on some physico-thermal properties of the sample, not only on the analysed species, but also mainly on the buffer gas. Consequently, molecular relaxation of the excited rovibrational energy into sample heating is a key step in the generation of the PA signal.