Characterization of a precise phase-reading, CO$_2$ laser-based photoacoustic spectrometer

V. Slezak$^1$, A. Peuriot$^1$, N. Zajarevich$^1$, M. González$^2$ and G. Santiago$^2$

$^1$ CEILAP (CITEFA-CONICET), Juan B. de La Salle 4397, 1603 Buenos Aires, Argentina
$^2$ Laboratorio Láser, Facultad de Ingeniería, UBA, Paseo Colón 850, 1063 Buenos Aires, Argentina

E-mail: vslezak@citefa.gov.ar

Abstract. We present a simple resonant photoacoustic (PA) setup based on a modulated CW CO$_2$ laser and a synchronic detection system that acquires the signal and the reference through the sound card of a PC. The precise phase reading of this system allows detecting the delay of the signal coming from the excited CO$_2$ molecules immersed in air and, with an adequate processing, the environmental abundance of this gas, closely related to global warming, can be determined.

1. Introduction
The photoacoustic (PA) spectroscopy based on tunable light sources like CO [1] or CO$_2$ [2] lasers is a powerful tool which allows analyzing multicomponent samples [3]. Many polyatomic molecules show characteristic absorption bands within the emission range of the CO$_2$ laser (the so-called *finger print* region). Therefore, a compact and simple setup based on this type of source seems adequate for application in many areas, like pollution control (global warming), industrial environment (semiconductors), health (ammonia in breath gases) and agriculture (ethylene as growing hormone in vegetables). The samples resulting from almost all these processes always contain great amounts of carbon dioxide and water, which are also detectable with a CO$_2$ laser and, as a result, therefore are usually considered as undesirable interferences. In this paper we show the development of a resonant PA setup based on a simple home-made CO$_2$ laser that processes the microphone signal digitized by a PC sound-card through a specific program that carries out synchronous detection with the reference signal taken from the modulated laser output. This way, the system allows an accurate phase reading and the delay of the signal coming from CO$_2$ in presence of air [2] is precisely determined. The device is adequate to analyze mixtures containing CO$_2$, skipping any previous filtering.

2. Modelling of the photoacoustic signal phase
We will first analyze the phase of a photoacoustic (PA) signal induced by a CO$_2$ laser on a gas mixture that contains the carbon dioxide, a relevant molecule in biological and environmental processes.

It is known that, if low absorption is assumed, the model that describes the PA signal is a simple set of linear equations on the various concentrations. This linear system is obtained by recording the PA signal $S_i$ at different wavelengths $\lambda_i$, carefully chosen as to excite each of the $N$ species.
If we consider each PA signal as a phasor whose phase, relative to the laser excitation, is $\theta_i$, we can compute the in-phase component as:

$$ S_i \cos \theta_i = K_d P_0 \sum_{j=1}^{N} \sigma_{ij} C_j \cos \theta_j \quad i \geq j $$

where $K_d$ is the setup constant, $P_0$ the laser power at wavelength $i$, $C_j$ the volume concentration of the species $j$, $\sigma_{ij}$ the effective absorption cross section and $\theta_j$ the phase of species $j$ at wavelength $\lambda_j$.

When fast relaxation of absorbed light is ensured $\theta_j$ is almost zero. However, if CO$_2$ and N$_2$ are present, the Fermi coupling between the 001 level of CO$_2$ and the first excited vibrational state of N$_2$, determines an intermolecular energy exchange that reduces the heating rate. This process is referred as “kinetic cooling” [4] and the associated photoacoustic signal shows a noticeable phase shift compared to a substance that relaxes fast.

Meyer and co-workers [2] developed a simplified model that describes the energy exchange between the different vibrational levels of the H$_2$O, O$_2$, CO$_2$ and N$_2$ molecules (figure 1), and assigns a characteristic time $\tau$ computed as:

$$ \frac{1}{\tau} = k_1 C_{H_2O} + k_2 C_{O_2} + \frac{C_{CO_2}}{C_{N_2}} \left[ k_3 C_{N_2} + k_4 C_{O_2} + k_5 C_{CO_2} \right] $$

(2)

where $k_1$, $k_2$, $k_3$, $k_4$ and $k_5$ are the rate constants, in units of m$^3$/s, of the main V-V processes between the different species in the atmosphere.

Frequently, the photoacoustic signal contains an undesirable term due to window heating or scattering synchronic with the laser, at frequency $\omega$. These processes behave as another heat source of the form $H_b \exp(i \omega t + \phi)$ that generates a background signal whose phase $\theta$, relative to the laser is given by:

$$ \theta = \arctan \left( \frac{H_b \sin \phi + \sigma_{CO_2} C_{CO_2} \Psi \hbar \tilde{v}_{N_2} c / \omega \tau}{\sigma_{CO_2} C_{CO_2} \Psi \hbar \tilde{v}_{N_2} c \left( \frac{\tilde{v}_i}{\tilde{v}_{N_2}} - 1 \right) + H_b \cos \phi} \right) $$

(3)

where $\Psi$ is the photon flux, $\tilde{v}_i$ the laser wave number, $\tilde{v}_{N_2}$ the associated with the first excited vibrational state of N$_2$, $\hbar$ Planck’s constant and $c$ the speed of light. Equation (3) assumes $\omega \tau \gg 1$, a condition satisfied at audio frequencies and CO$_2$ concentration from 300 to 3000 ppmV.

Keeping to the same assumption, the in-phase component of the PA signal reduces to:

$$ S_i \cos \theta_i = K_d P_0 \sum_{j=1}^{N} C_j \sigma_{ij} \left( \frac{\tilde{v}_i}{\tilde{v}_{N_2}} - 1 \right) C_{CO_2} \sigma_{CO_2} + S_b \cos \phi $$

(4)

From equations (3) and (4) we appreciate the relevance of accurately determining the phase whenever N$_2$ and CO$_2$ are present in the measured gas sample.

3. Experimental setup

The resonant PA setup is based on a home-made tunable CW CO$_2$ laser and an aluminum longitudinal cell with quarter wavelength buffers and an electret microphone (Knowles, EK3132) attached to the cell’s wall at its midpoint (figure 2). It was used in a non-flowing way, and excited at the resonance of the second longitudinal mode, around 2230 Hz (setup constant $\sim 15$ V cm/W, determined from ethylene-air mixtures).
While attempting to determine the phase with a lock-in amplifier, we resorted to a reference given by the chopper that modulated the laser. However, this reference was not satisfactory for the laser beam did not maintain a stable position relative to the chopper. This inconvenience was particularly noticeable after tuning the laser to a new wavelength. This way, we decided to use a pyroelectric detector (Molectron, J3-05), placed behind the cell, to generate the reference signal and to use it as a normalizing tool. Nevertheless, this change did not suffice our requirements for the detector’s output showed a rather long risetime that varied with the laser power. Since the lock-in amplifier has a fixed trigger point, the mentioned variations of the reference signal determined false phase shifts. As an example, we have measured changes of up to 20 degrees when the laser power varied 50%.

Finally we employed another scheme of synchronic detection based on a PC sound card [5]. The algorithm computes the phase in a robust way, immune to changes of the reference signal.

Due to different delays, the system shows an offset phase $\theta_0$ that was determined by using an ethylene-air mixture. Since ethylene relaxes very fast [6], the expected phase at resonance was zero and the measured value is the offset.

Having calibrated the setup, we carried out a series of scans at different frequencies and fitted the measured values of phase to the expected function associated with a simple resonance at $f_0$:

$$\theta = \theta_0 - \arctan \left( \frac{f^2 - f_0^2}{f \cdot \Delta f} \right)$$

where $\Delta f$ is the full width at half height of the power resonance profile. Following the same idea, we fitted the amplitude readings to a Lorentzian profile to find the maximum amplitude with high precision.

4. Results

We performed a series of PA measurements of CO$_2$-air mixtures at the 10P(14) line. In figure 3a we plot the computed CO$_2$ concentration (using equation 4) versus the known value. The slope is 0.92 and the coefficient of determination $R^2=0.996$.

In figure 3b, we show the measured phase and the value returned by equation (3). Several measurements of pure air revealed a value $\varphi=80\pm3$ degrees. The value of $H_b$ was adjusted as to obtain the best fit.

The same way, we measured water vapor-air mixtures, using the 10R(20) line, and analyzed the records with the aid of equation (1) assuming fast relaxation ($\theta_i=0$). In this case we obtained a coefficient $R^2=0.995$. From the measured slope, and considering the setup constant, we computed an absorption cross section of water of $29.2 \times 10^{-24}$ cm$^2$ (at 296 K), a value similar to the one reported in reference [7].
We have used this photoacoustic setup for measuring CO₂ concentration in urban air. Owing to the rather small PA signal, it was necessary to take into account the background signal in amplitude and phase. In addition, we had to consider the strong temperature dependence of the effective absorption cross section of CO₂. We present the results in table 1 with an estimated error of about 10%.

| T [ºC] | H [%] | Relative humidity | H₂O [%] | Calculated | Measured | CO₂ [ppmV] |
|-------|------|-------------------|--------|------------|----------|------------|
| 25.8  | 47   | 1.6               | 0.971  | 366        |
| 20.5  | 43   | 1                 | 0.561  | 320        |
| 28    | 40   | 1.5               | 0.813  | 350        |

Our measurements bring values within the range of other registers gathered in the last years. The content of water vapor we obtained was below the one indicated by a hygrometer; the difference may be caused by adsorption processes [8] since water is a highly polar molecule.

In summary, the satisfactory tests we have carried out show this simple and compact setup is suitable for monitoring atmospheric components.

Acknowledgments
This research has been supported by the grants PICT 25469 (FONCyT), UBACYT I805 (UBA) and institutional funds from CITEFA, Argentina.

References
[1] Bernegger S and Sigrist M W 1990 Infrared Phys. 30 375
[2] Meyer P L and Sigrist M W 1990 Rev. Sci.Instrum. 61 1779
[3] Sigrist M W 1994 Air Monitoring by Spectroscopic Techniques (Chemical Analysis vol 127) ed M W Sigrist (New York: John Wiley & Sons) chapter 4 pp 163–238
[4] Wood A D, Camac M and Gerry E T 1971 Appl. Opt. 10 1877
[5] González M, Santiago G, Slezak V and Peuriot A 2007 Rev. Sci. Instrum. 78 055108
[6] Petcucescu A, Hall B, Fraenzle R, Phillips S and Lueptow R 2006 J. Acoust. Soc. Am. 120 1779
[7] Hinderling J, Sigrist M W and Kneubuehl F K 1987 Infrared Phys. 27 63
[8] Melander N and Henningsen J 1999 Proc. 10th Int. Conf. on Photoacoustic and Photothermal Phenomena (Rome) vol 463 pp 78–80