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Resonant photoacoustic detection of trace gas with DFB diode laser

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Abstract

A resonant photoacoustic detection system based on a low-power distributed feedback diode laser is developed. This sensor has been applied to the detection of acetylene (C_2H_2) using a specifically designed photoacoustic cell operating on its second longitudinal mode. The minimum detectable limit of about 10 parts-per-million volume (SNR = 1) is achieved with an average laser power of 3.5 mW at atmospheric pressure, and an integration time constant of 3 ms; thus, the minimum detectable absorption coefficient normalised by power and bandwidth is $4.0 \times 10^{-8}\, W\, cm^{-1}/\sqrt{Hz}$. The optimum operating pressure buffered with N_2 is also investigated. The realisation of our system is described and experimental results are compared with different modulation techniques and other results reported in the literature. A number of issues arising from the conventional use of mechanical chopping of the beam can be effectively suppressed in wavelength modulation PA spectroscopy (WM-PAS) and second harmonic detection.
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1. Introduction

With the rapid development of industrialisation, the monitoring and analysis of pollutants has become an essential environmental, chemical and industrial issue. There are numerous ways to undertake this monitoring, and different analytical techniques may be employed to accomplish it. One of these techniques is infrared laser photoacoustic spectroscopy (PAS), which offers stability, sensitivity, selectivity and a wide dynamic range. PAS is a calorimetric spectroscopy technique based on the photoacoustic effect, which relies upon the production of acoustic waves by the absorption of light. Since its discovery by Bell in 1880 [1,2], it has gradually improved in utility with the gradual improvement in PAS theory and the great progress in the properties of suitable light sources, sound transducers and highly sensitive detectors.

In the case of resonant PAS, the signal, which arises from the excitation of acoustic resonances in a closed or open cavity, is acquired by a lock-in amplifier that is locked to the frequency of the mechanical chopper used to amplitude modulate the light. This detection technique offers a high signal-to-noise ratio (SNR) but the sensitivity of trace gas detection may be limited by background signals because of periodic heating of the windows, cell walls and mechanical instability of the chopper. Recently, tunable laser diodes, room temperature operating DFB diode lasers, have been developed, offering fast response, narrow linewidth, continuous tunability, compact size, cost-effectivesss, and easy wavelength modulation, and have become widely used in PAS [3,4].

As is well known, the use of wavelength modulation PAS (WM-PAS) as a "zero-baseline" spectral technique (since absence of target molecules should not generate any signal) can effectively eliminate background PA signals arising from the windows and walls, which often limit the sensitivity of the PA detection system. In WM-PAS the laser frequency is modulated with f, but the PA signals are analysed at the frequency $2f$ (second harmonic detection). This can reduce the effect of these background noises on the detection sensitivity [5–7]. For WMS, the laser

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frequency is described by

$$v(t) = v_0 + \delta v \cos(\omega t), \tag{1}$$

where $v(t)$ is the instantaneous frequency of the laser, v_0 is the laser's centre frequency, δv is the modulation amplitude and ω is the sinusoidal modulation frequency [8]. The intensity $I(v)$ of the radiation can be expressed as a cosine Fourier series

$$I(v,t) = \sum_{n=0}^{\infty} A_n(v) \cos(n\omega t). \tag{2}$$

The individual harmonic components A_n (for $n > 0$) can be measured with a lock-in amplifier. In general, there are two main broadening mechanisms, Doppler broadening and collision broadening. At low pressure the dominant broadening mechanism is the Doppler broadening, which can be described by a Gaussian line shape. At high pressure, collision broadening is dominant. The absorption line is then of the normalised Lorentzian shape, which can be expressed as

$$\chi_L(v) = \frac{1}{\pi} \frac{\gamma_L}{(v - v_0)^2 + \gamma_L^2}, \tag{3}$$

$$\gamma_L = \gamma_{L,0}(p/p_0)(T_0/T)^{1/2}. \tag{4}$$

Here γ_L is the half-width of colliding broadening. v_0 is the central frequency of absorption line, $\gamma_{L,0}$ is the half-width of colliding broadening under the standard atmospheric pressure (T_0, p_0).

The second harmonic signal of a Lorentizian line shape function is

$$S_L^2(v) = -\eta \frac{I_0 S \rho L \gamma_L}{2\pi} \left(\frac{\gamma_L^2 - 3(v - v_0)^2}{((v - v_0)^2 + \gamma_L^2)^3} \right) \delta^2 v. \tag{5}$$

More details of WMS can be found in Refs. [9,10].

Acetylene is a well-known industrial gas. It is the lowest molecular weight analog of the class of neutral organic acetylenic compounds. This substance is also known as ethyne. Acetylene is a gas that forms highly explosive mixtures in air across a broad range of concentrations. The lower explosive limit is 2.5% in air (National Fire Protection Association, 1997). Moreover, as a characteristic gas, acetylene is usually analysed in dissolved gas-in-oil analysis to diagnose the potential inner faults of power transformers [11]. Due to the high risk of flammability and explosivity, the monitoring and analysis of acetylene at low concentration has become an essential environmental and industrial issue.

In the present work, a portable, low cost, simple, highly sensitive photoacoustic detection system based on diode laser modulation spectroscopy was developed for detection of C_2H_2. A near-infrared distributed-feedback (DFB) laser diode at 1.51 μm is used in order to excite the R25 rotational line of the vibrational C_2H_2 transition (absorp-

tion line $v = 6608.5124\,\text{cm}^{-1}$ and intensity $S = 1.414\text{E}-21\,\text{cm}^{-1}/(\text{molecule\,cm}^{-2})$), which was selected for the experiment on the basis of laser availability. The realisation of our system is described and experimental results are compared with different modulation techniques and other results reported in the literatures.

2. Theory of PAS

The detailed theory of the generation and detection of the PA signal in a cylindrical cell has been described elsewhere [12–15]. In brief, PAS is an absorption-based optical technique that involves absorption of the laser radiation (modulated or pulsed) at a wavelength that overlaps with an absorption feature of molecules of interest. During the nonradiative collosional relaxation processes, the absorbed radiation energy of the excited molecules is converted into periodic local heating at the modulation frequency. A standing pressure wave is produced within the photoacoustic cell that can be detected with commercial microphones and the lock-in technique. The PA signal, S, in volts, can be described as

$$S = S_m P C_{cell} N_{tot} c_m \sigma, \tag{6}$$

where the microphone sensitivity, S_m, is in units of millivolts per Pascal (mV/Pa); the laser optical power, P is in Watts (W); the PA cell response constant, C_{cell}, has units of Pascal per inverse centimetres per Watt (Pa/cm^{-1} W), N_{tot} is the total number density of molecules (molecule/cm^3), and coefficients c_m and σ are the concentration and absorption cross-section of the analyte, respectively. The PA signal is therefore proportional to the incident laser power and the concentration of the absorbing molecules. The PA cell constant, C_{cell}, is a scaling factor depending on the PA cell geometry, on the modulation frequency and on measurement conditions. It is usually determined experimentally from measurements with a gas of known absorption and certified concentration. When the laser modulation frequency coincides with a resonant frequency of the acoustic resonator, stronger PA signal will be achieved due to resonant buildup of the sound in the cavity. The cell constant is given in this case by

$$C_{cell} = \frac{Q_j(\gamma - 1)I_j L_c}{\omega_j V_c} p_j(r_M, \omega_j), \tag{7}$$

where Q_j is the quality factor of the acoustic resonance, usually defined as the ratio between the resonant frequency f_i and the frequency bandwidth at $1/\sqrt{2}$ of the maximum of the resonant profile, $Q_j = f_j/\Delta f_{1/\sqrt{2}}$, typically between 10 and 50 for the longitudinal resonators, but can be as high as 10^3 for spherical cavities [16]. W is the ratio of the specific heat at constant pressure and constant volume, ω_j the angular resonance frequency, V_c the cell volume, L_c the cell length, $p_j(r_M, \omega_j)$ the value of the normalised acoustic mode at the position r_M of the microphone and I_j is the overlap integral between the laser beam distribution $g(r)$

and the acoustic mode of the cavity:

$$I_j = \frac{1}{L_c} \int_V dV g(r) p_j \times (r, \omega_j). \tag{8}$$

In a cylindrical resonator, every mode j is characterised by three numbers $j = (n, m, k)$, corresponding to radial, azimuthal and longitudinal contributions to the given mode, respectively. The frequency of the jth eigenmode can be determined from the relationship

$$f_j = f_{nmk} = \frac{\omega_j}{2\pi} = \frac{c}{2} \sqrt{\left(\frac{\alpha_{mn}}{R}\right)^2 + \left(\frac{k}{L_{\text{eff}}}\right)^2}, \tag{9}$$

where c is the sound velocity in the medium, α_{mn} is the nth zero of the first derivative of the mth Bessel function divided by π, L_{eff} is the effective length of the resonator, differs from the geometrical length L of the resonator due to boundary effects at the resonator ends [17]

$$L_{\text{eff}} = L + \frac{16}{\pi} R. \tag{10}$$

In order to reach a good sensitivity, the PA cell must be optimised to increase the magnitude of cell constant. For a given molecular absorption feature and laser, the only way of improving the sensitivity is to increase the PA cell constant and reduce the background noises. For diode laser based PA spectrometer, longitudinal resonators may offer the best potential to achieve a high cell constant. One of the efficient techniques to reduce the background noises is WMS.

3. Experimental arrangement

The experimental arrangement is briefly presented in Fig. 1. A room-temperature single mode DFB diode laser emitting at 1511 nm is used as the PA excitation source. The laser is fibre-coupled, with the output from the distal
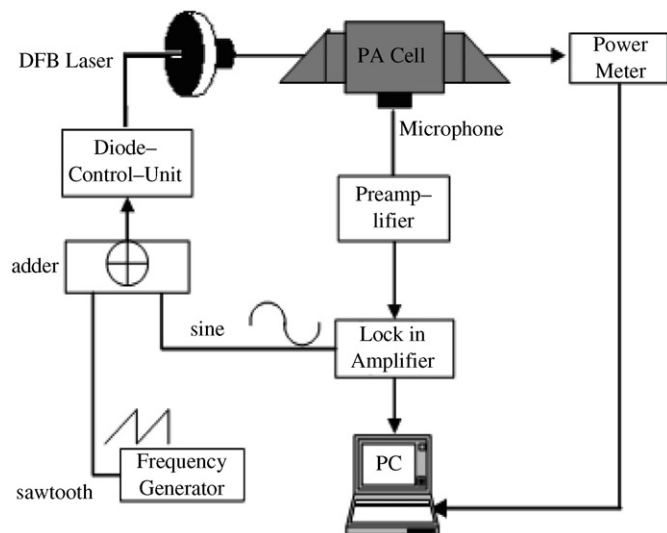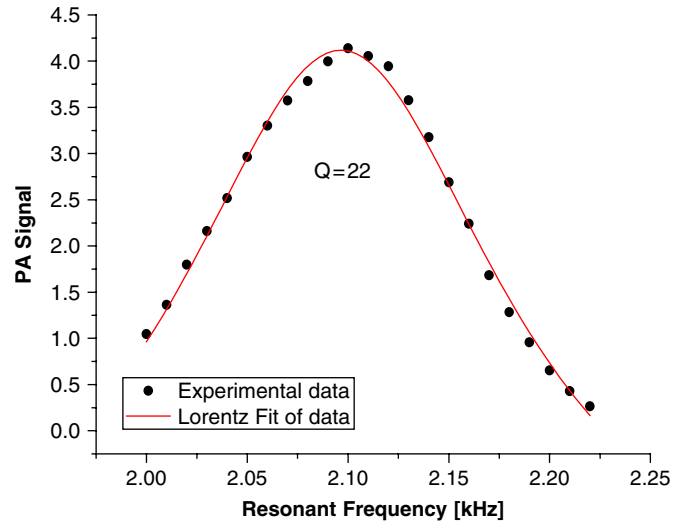

Fig. 2. Second longitudinal acoustic resonance of our PA cell at 2.1 kHz. Circles are experimental points and the curve is the result of a fit by a Lorentzian distribution. The quality factor $Q = 22$.

end collimated such that its optical axis is aligned with the cylindrical cavity axis. The excited acoustic wave was detected with a miniature electret microphone located at the centre of the resonator, i.e. at the maximum of the acoustic standing wave, and phase-sensitively measured using a lock-in amplifier before pre-amplification. The transmitted light power was simultaneously monitored with a power metre. The whole experiments were computer program-controlled and the spectra were measured using both internal frequency modulation of the laser and external amplitude modulation (AM) by a mechanical chopper (EG&G, Mode 197). All the modulated signals were demodulated using an analog lock-in amplifier (Stanford Research Systems, Mode SR830).

The laser diode is an InGaAs DFB diode which is temperature and current controlled by a commercial diode laser controller (ILX Lightwave LDX-3724, current stability $\approx 0.005\%$, temperature stability $\approx 0.01\%$). The usual technique of wavelength tuning is achieved by applying a current variation to the diode laser. The dependence of the wavelength variation upon the applied current is assumed to be linear, as stated by the manufacturer. The amplitude of the current ramp was approximately 40 mA to tune the wavelength across the whole absorption. In order to obtain WM a small sine wave modulation was added to the ramp.

The PA system is based on a longitudinal resonator. The stainless steel PA cell consisting of two buffer volumes (about half the length of the resonator) sealed with Brewster-angled windows and a central cylindrical acoustic resonator ($L = 15$ cm, $R = 1.5$ cm) is designed to operate in the second longitudinal resonance at approximately 2.1 kHz with a quality factor, Q, of approximately 22. The Brewster windows are made of SiO_2 with a thickness of 3 mm.

Fig. 1. Experimental arrangement for the photoacoustic measurements with WM.

A home-made waveform synthesizer was designed that combined a triangle wave from function generator (for sweeping the laser's wavelength across the acetylene transition), a sine wave from lock-in amplifier (for modulating the laser) and bias voltages for controlling the laser wavelength via the nominal diode temperature and injection current. At a bias of 70 mA and an operational temperature of 44.1 °C, the laser has a mean unmodulated output power of 3.5 mW. The laser was scanned across the transition at approximate 0.8 Hz. The laser's wavelength was modulated at 1.05 kHz, such that the 2f signal overlapped with the acoustic resonance. The magnitude of the sinusoidal voltage was adjusted during the experiment to give the largest demodulated signal. The microphone signal, amplified by a factor of 100 (EG&G, Model 5113) with a bandpass filter set at 30–30 kHz, was sent to lock-in amplifier, and ultimately acquired by the LabWindows/CVI controlled data gathering and processing system with a sampling frequency and total number of samples of 20 kHz and 8192, respectively.

The entire system of measurements was carried out in the nonflow-through arrangement, where the PA cell was filled with the measured gas. The different mixtures were laboratory-prepared. In order to obtain homogeneous mixture, C_2H_2 and the buffer gas N_2 were always mixed before the measurements.

4. Results and discussion

The frequency response of the PA cell has been investigated around 2.1 kHz at room temperature and standard atmospheric pressure, as shown in Fig. 2. 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 $Q = 22$ with a FWHM of 0.095 kHz.

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 [18]. Therefore, the optimum operating pressure has to be determined for each gas and even for each selected transition. At atmospheric pressure, pressure broadening seriously limits the sensitivity. The microphone response is also an important factor as it is known to work poorly at lower pressure. 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. Considering N_2 gas molecule, the major element of the practical air and probably have a positive molecular relaxation effects, so the whole work has been performed with N_2 as buffer gas under laboratory
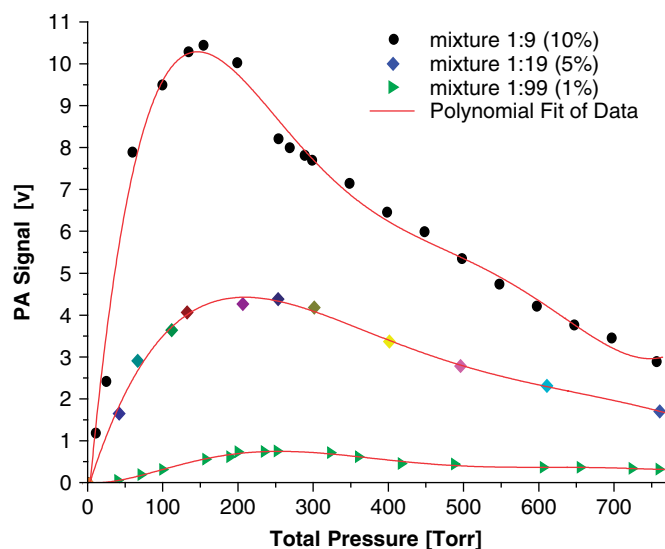

Fig. 3. Dependence of the PA signal on the total gas pressure in the PA cell for the R25 rotational line of C_2H_2 (6608.5124 cm^{-1}).

conditions. The quality factor Q decreases with pressure approximately as a power function. Experimentally we have found that the optimal pressure condition is almost irrespective the mixture ratios, so three kinds of different mixtures (1:9, 1:19, 1:99 v/v) of C_2H_2 with N_2 were only represented in Fig. 3. Some conclusions and explanations are made as follows: at the beginning the PA signal intensity is increasing continuously, because the higher the buffer gas pressure, the more intense the collosional relaxation processes [19,20]. Whereas, later, the PA signal intensity is gradually attenuate perhaps owing to the pressure dependence of the microphone sensitivity and the Q-factor [21]. The optimum signal (largest acoustic response) was found at a pressure of near 200 Torr. This issue will be further investigated in recent work.

Although it was necessary to find the optimal total pressure for routine measurements, especially for the requirement of high sensitivity. However, the practical applications are usually at atmospheric pressure for facility, such as monitoring of industrial environment, so the current measurements were all made at 1 atm. Using this PA cell we simultaneously measure the absorption spectrum of C_2H_2 with both WM and AM modulation technique. Both modulation techniques combined with phase-sensitive detection were employed to eliminate noises and provide a much better SNR than direct absorption. WM was achieved by adding a sinusoidal small amplitude current, with a half resonance frequency of the resonator, to the DC driving current of the laser. The modulation current was adjusted to make the laser line sweep across the characteristic absorption line of the gas molecules. Thus, the PA signal generated by line absorption in the gas appears at the frequency 2f. Usually, in addition to excitation of the gas molecules, the modulated laser beam may also generate PA background signal in the windows
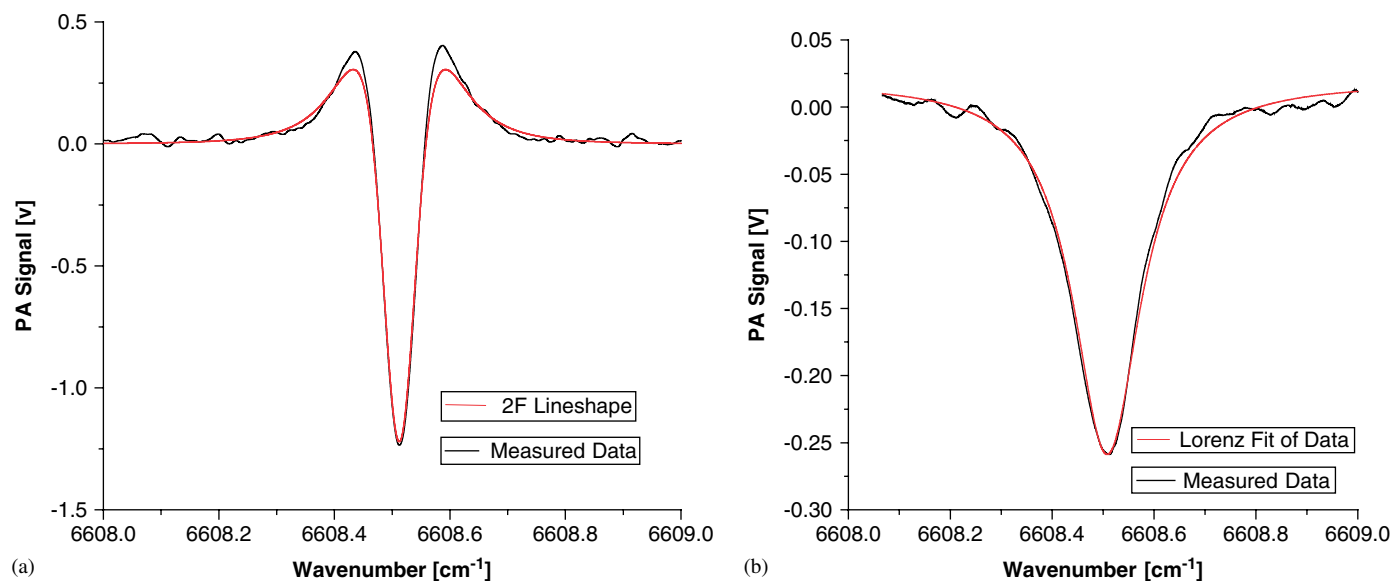
Fig. 4. Measured PA spectra of 1‰ C_2H_2 buffered with N_2 at atmospheric pressure, and fitting results: (a) WM—sensitivity 500 μv—time constant 3 ms, modulation frequency $f = 1.05$ kHz, (b) AM—sensitivity 500 μv—time constant 10 ms, modulation frequency $f = 2.1$ kHz.

and cell walls. However, the background effects that may appear are generated at f and, therefore, are not present in the PA signal at $2f$. This is a particular advantage of WM over AM. The sample concentration in the PA cell is 1‰ acetylene buffered with N_2 at a total pressure of 1 atm. Fig. 4a and b. gives an example of the measured PA spectra and the results of fitting. It was obviously found that the SNR is much better in MW than AM. To the best of our knowledge, windows and cell walls absorption is wavelength independent and can be effectively filtered out in WM, and the disturbance of mechanical noise and frequency stability of chopper can also be effectively avoided. Corresponding to Ref. [22], the calculated SNR is approximately 100 for WM modulation, this SNR indicates that the noise-limited minimal detection limit for this sensor is about 10 ppm v of acetylene, thus the minimum detectable absorption coefficient normalised by power and bandwidth is 4.0×10^{-8} W cm$^{-1}/\sqrt{Hz}$. However, when the PA system is operated under the optimal pressure condition, the detection sensitivity can be improved approximately by one order of magnitude. In spectroscopic measurements, the stability of the system is an important issue. One way to characterise the stability is to measure the "Allan variance" of the signal [23], which was originally introduced for determining frequency stability but can also be used for spectroscopic instruments [24]. The reliability of this sensor has been guaranteed through comparing with cavity enhanced absorption spectroscopy (CEAS) in our laboratory [25]. These matters will be discussed in a forthcoming article.

However, the sensitivity of this technique is power dependent (since the magnitude of the PA signal scales with the incident laser power). Taking into account the lower diode laser power, our results overall are in good agreement compared with similar works. In Ref. [26], the detection limit of 300 ppm v for C_2H_2 is reported at a pressure of 120 Torr (largest response) with almost the same other experimental conditions other than the resonator. In contrast to the results presented in Ref. [27] it should be mentioned that Hornberger et al. have combined the photoacoustics with a multipass configuration (the number of reflection is 50), and the NaCl–OH$^-$ colour centre laser power at 1.5 μm is 250 mW, and the results obtained are also in the optimal pressure region. Moreover, Michael E. Webber et al. have achieved 2.6 ppb with diode laser at 1.53 μm of 500 mW by using near-infrared fibre-amplifier and with a double-pass configuration [28]. Comparing different resonators, the Helmholtz resonator has the advantages of using cells of small volumes with low resonance frequency, and it has the best potential to increase the SNR by using differential scheme and multi-pass configuration [29]. This type of resonator consists of two volumes connected by a capillary, one for the detection of the laser-induced PA signal, while the other is for the detection of the background acoustic noise. The multi-pass differential Helmholtz Resonator will permit one to increase the PA signal as well as to reduce the background noise, even in the flowing mode. The performance of our PA sensing system is satisfying from comparative results for a low-power near-IR diode laser. However, the sensitivity needs further improvement for practical applications, such as atmospheric and environmental chemistry, spectral analysis and trace gas detection.

5. Conclusions

A low cost, simple, highly sensitive PA detection system based on near-IR diode laser and resonant PA cell is

reported. The WM technique combined with second harmonic detection can be used to eliminate background drift and signal fluctuations. The achieved sensitivity is 10 ppm v for acetylene detection at room temperature and standard atmospheric pressure. However, when the PA system is operated under the optimal pressure condition, the detection sensitivity can be improved approximately by one order of magnitude. The system performance is below expectation for the moment, as a result of some high electric noise level and insufficient laser power. It seems likely that further increases in sensitivity could be achieved by protecting the PA cell from external acoustic and electric interferences. A higher SNR may also be obtained by adding several microphones inside the resonator. Other ways of achieving high sensitivity are the combination of the photoacoustic with a multi-pass configuration and differential Helmholtz resonator [29–33]. The sensitivity can also be improved by increasing the laser power using a high-powered fibre amplifier in the near infrared for low-power DFB diode laser [28]. These improvements should allow us to increase significantly the system performance. These methods will all be considered for improving the sensitivity of our PA system in the future work. It was also show that the present system can be used to detect trace gases in a continuous flow. The described scheme is widely applicable to trace other gases representing interest in studies of atmospheric and environmental chemistry, spectral analysis, as well as industrial process monitoring. Our systems still contain expensive and voluminous equipments, which were used for this test; but a special circuitry may replace the lock-in amplifier and preamplifier for amplifying and processing. With these modifications the system could be made more portable and economic.

Acknowledgements

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