Photoacoustic spectroscopy of CO\textsubscript{2} laser in the detection of gaseous molecules

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Abstract. The detection of trace gases is very important for a variety of applications, including the monitoring of atmospheric pollutants, industrial process control, measuring air quality in workplaces, research into fruits physiological processes and medical diagnosis of diseases through the analysis of exhaled gases. The implementation of these and many other applications requiring gas sensors able to meet high sensitivity and selectivity. In this work, a photoacoustic laser spectrometer with CO\textsubscript{2} emission in the infrared range and a resonant photoacoustic cell was used. We obtain the resonance frequency of 2.4 kHz to photoacoustic cell, was estimated detection limit of the spectrometer for molecules of ethylene (C\textsubscript{2}H\textsubscript{4}), 16 ppbV and ammonia (NH\textsubscript{3}) 42 ppbV.

1. Introduction

Over the years, humanity has seen the effects caused by air pollution on both human health and the environment. There are two branches of scientific and technological research generated by this problem that involves environmental sustainability and today, is closely related to development. One is the advance in studies and mitigation of impacts caused by certain gaseous species on health and the environment. The other is to develop new technologies to detect and quantify emissions of greenhouse gases in different environments [1-12].

Ethylene gas (C\textsubscript{2}H\textsubscript{4}) is a volatile organic compound (VOC) generated mainly in the exhaust of automotive engines powered by fossil fuels and ethanol [13-19]. Ethylene gas is a precursor of tropospheric ozone (O\textsubscript{3}) from the reaction with nitrogen oxide (NO) and oxygen (O\textsubscript{2}) in the presence of sunlight. Tropospheric ozone is one of the main compounds of photochemical smog that has direct implications on human health [20]. One of the expected effects after exposure to ozone is reduced resistance to infectious diseases due to destruction of lung tissue. It is believed that chronic exposure to high levels of urban ozone leads to premature aging of lung tissues. At the molecular level, ozone readily attacks substances containing in its structure C = C bonds, such as those found in lung tissue [21-23]. Brazilian law does not regulate the emission of ethylene in the vehicle generating strategies to mitigate the difficulties of tropospheric ozone. The ammonia gas (NH\textsubscript{3}) is used in various applications as a source of nitrogen in fertilizer

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manufacturing, neutralizing agent in the oil industry and as a refrigerant in industrial systems because of its high cooling power and low potential for stratospheric ozone depletion makes this gas suitable for use in large industrial refrigeration machinery, thus avoiding the use of organic compounds chlorofluorocarbons (CFCs) [24]. Indoors, the biggest problem of ammonia to man is caused by leaks in refrigeration systems, which can pose dangers to workers from the site. However, a positive fact to be mentioned is that even in the ammonia concentrations in the range of tens of ppmV, produces an extremely unpleasant odor, facilitating their detection [25]. The threshold value of ammonia that a person can be exposed for 8 h daily work without causing damage to health is 30 ppmV [24]. Often there is loss of specific sensitivity of smell after some time spent in an environment contaminated by ammonia, it becomes necessary to vent these sites. Another problem that occurs indoors is related to the extensive breeding of animals [26-28], which is usually done in a given space, confining many animals. As the feces and urine are sources of ammonia, this can result in high concentrations of the compound that interferes in the health of animals and may cause injury to the owners [24]. As the impacts of emissions of gaseous pollutants are increasingly notorious, the environmental laws tend to be more prescriptive and restrictive. Thus, the study of new tools for the detection of gaseous molecules is of great importance for the development of future societies.

Currently there are several methods used for trace gases detection. Among them, non-spectroscopic methods such as gas chromatography, flame ionization detectors (FID) and spectroscopic methods such as differential optical absorption spectroscopy (DOAS), light detection and ranging (LIDAR), photoacoustic spectroscopy (PAS) and absorption spectroscopy in the infrared by Fourier transform (FTIR) [1-12]. The techniques should have high selectivity is necessary to distinguish the gas species present in a multicomponent gas mixture, such as air and high sensitivity is essential to detect very low concentrations of substances. A large dynamic range is important to monitor the gas components at high and low concentrations with the same instrument. In addition, a good time resolution ensures the possibility of on-line analyses controlled by the computer. Photoacoustic spectroscopy has consolidated one of the most sensitive and versatile in the monitoring of gases. Detection limits in the bands of part per billion by volume (ppbV, \(10^{-9}\)) and part per trillion (pptV, \(10^{-12}\)), added the relative experimental simplicity, good selectivity, fast and non-destructive character of the sample are some aspects that make photoacoustic spectroscopy a great tool for the detection of trace gases.

2. Metodology

In conventional absorption spectroscopy, the absorption of the radiation power transmitted through the sample is measured. On the contrary, in photoacoustic spectroscopy, the absorbed power is determined directly via its heat and hence the sound produced in the sample. The figure 1 shows the experimental setup. Actually, several laser-based methods have been reported because they are much more sensitive, as photoacoustic and cavity-ring-down spectroscopy [29-30]. Photoacoustic spectroscopic methods offer important advantages in pollutant gas monitoring. This technique is based on pressure changes in the sample, which is induced by rovibrational excitation of molecules and, subsequent, relaxation by collisions (heat). The pressure change is detected by one or more microphones placed inside a resonator pipe of a resonant photoacoustic cell through which, the air sample containing the molecules under consideration was flown. An acoustic signal is produced at the resonance frequency of about 2,400 Hz of our resonant cell, by a chopper modulation of the excitation laser beam. The resonance frequency value corresponds to the first longitudinal vibration mode. Our photoacoustic resonator is 67 mm long and has 18 mm of diameter. The figure 2 shown the design of the resonant photoacoustic cell used in this work.
The acoustic signal is detected by a microphone that generates an electric signal. This electric signal is pre-amplified and then detected by a lock-in amplifier (Stanford SR850) with time constant of 300 ms. The lock-in response is registered in a microcomputer. A continuous wave CO₂ infrared laser (Synrad 6500), tuneable over about 80 different lines between 9.2 and 10.6 μm, with a power of 1.9W at the emission line 10P(14) (949.5 cm⁻¹) for detection of ethylene and 10P(34) (931.0 cm⁻¹) to ammonia was employed as the excitation source. At this power level, saturation effects of the photoacoustic signal were not observed. These lines can be swept by a step motor controlled by a microcomputer. Within this spectral region, many small molecules show a unique fingerprint. The photoacoustic instrument used in this work has been developed for gas detection at small concentrations. All the measurements and the sample collection were made at room temperature.

For measurements with multicomponents samples the analysis of these samples can be made for a number of \( n \) different species, rather than just one. This was accomplished by measuring the photoacoustic (PA) signal \( S_i \) at a set of wavelengths \( \lambda_i \) (\( i = 1, 2 \ldots m \)) chosen on the basis of the absorption spectra of the individual components to be detected. These individual absorption spectra were obtained from the HITRAN-PC database, [31] which calculates the...
absorption cross sections ($\sigma$) of a given molecule at different wave numbers $k_i = 1/\lambda_i$ in a given interval. Thus, the expression used to determine the concentrations of a given component in the multicomponent gas mixture is:

$$S_{\lambda_i} = S_i = CP_i N_{\text{tot}} \sum_{j=1}^{n} c_j \sigma_{ij}$$

with $i = 1, 2, \ldots, m; j = 1, 2, \ldots, n$ and $m > n$. Here, $P_i = P(\lambda_i)$ represents the laser power at wavelength $\lambda_i$ and $c_j$ is the concentration of the gas component $j$ with absorption cross section $\sigma_{ij}$ at $\lambda_i$. $N_{\text{tot}}$ is the total number density of molecules in the mixture and was considered to be typically $\sim 10^{19}$ cm$^{-3}$ [32]. The absorption cross section $\sigma_{ij}$ is related to the photoacoustic generation efficiency of each gas component for each CO$_2$ laser line. The sum is taken over the $n$ components present in the sample. The constant $C$ is the so-called cell constant and it depends, as well as the detection sensitivity, on the cell geometry, the microphone response and on the nature of the acoustic mode [32-33]. The expression used to determine the concentrations of a given component in single component samples:

$$S_i = CP_i N_{\text{tot}} c_i \sigma_i$$

The $C$ constant value was then obtained from the eq. (2), which yielded 40.2 V.cm/W. The unity of the cell coupling constant was furnished by the manufacturer of our photoacoustic cell (Prof. Markus W. Sigrist).

3. Results and Discussions

Figure 3 shows a graph of the resonant frequency of the photoacoustic cell for different concentrations of ethylene. You can see that the frequency does not vary significantly with the concentration of gas. Analyzing the results we found that the frequency 2.400 Hz optimizes the operation of the photoacoustic cell becoming standard frequency for the operation of the used cell. It is often possible to perform outside of the resonant frequency of the cell but the detection limit is strongly affected. Dilutions were made of ethylene in nitrogen and ammonia nitrogen. As nitrogen does not absorb infrared radiation in the range used in the experiment were obtained from various concentrations. Thus it was possible to estimate the lower limit of detection for these two gases (Figure 4 and 5). The ethylene (1.1ppmV), ammonia (5 ppmV) and nitrogen (Pure) gases were calibrated and purchased in the White Martins and all measurements were performed with the sample under continuous flow of 5 L/h.

Using different concentrations of ethylene were variations in frequency modulation laser (1.0 to 3.5 kHz), thereby obtaining the resonant frequency of the photoacoustic cell, ie the frequency that optimizes the functioning of the cell (Figure 3).
Figure 3. Resonance curve showing the photoacoustic signal variation with the chopper modulation frequency and concentrations of the ethylene.

Figure 4 shows the calibration curve of the photoacoustic spectrometer for different concentrations of ethylene diluted in nitrogen. A lower detection limit of 16 ppbV was obtained for this gas.

Figure 4. Calibration curve for ethylene (detection limit)
Figure 5 shows the calibration curve of the photoacoustic spectrometer for different concentrations of ammonia diluted in nitrogen. A lower detection limit of 42 ppbV was obtained for this gas.

![Calibration curve for ammonia (detection limit)](image)

Due to the behavior of the photoacoustic signal is linear with the concentration of the sample, we can extend this linearity to hundreds of ppmV though without the optical saturation effect, which damages the linearity of the photoacoustic system.

4. Conclusions

Serious impacts on the environment and human health are associated with the presence of greenhouse gases in the atmosphere. For a better understanding of the environmental impacts and to the development of predictive models for the scenarios of air pollution, it is necessary the knowledge of chemical species involved and their spatial and temporal distributions in the atmosphere. Thus, photoacoustic spectroscopy is extremely important for the identification and determination of concentrations of gases, and has applications such as process control of industrial emissions, physiological studies on plants and fruits, certification of gas, medical diagnostics through analysis of exhaled air since it allows the temporal monitoring the gas concentrations [34]. As the various gaseous pollutants are present at different concentrations in the atmosphere, monitoring of these gases represent a scientific and technical challenge. In this study we observed that the laser photoacoustic spectroscopy was able to measure CO₂ concentrations at trace levels up to hundreds of ppmV ethylene and ammonia. The results demonstrated that photoacoustic spectroscopy is a very important tool for sensitive and selective detection of these molecules with minimum detectable concentration of dozens of ppbV.

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