AMMONIA AND ETHYLENE MEASUREMENTS IN PURE NITROGEN

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The present manuscript describes a sensitive system based upon photoacoustic spectroscopy technology used in the detection of trace gases at very low concentrations. The detection of gases is very important for a variety of applications, including medical diagnosis of diseases with the analysis of exhaled gases, the atmospheric pollutants assessment or analysis of physiological processes at fruits and vegetables. To fulfill the above applications and many others requiring gas detector able to have high sensitivity and selectivity. In this work, was used an infrared photoacoustic spectroscopy able to measure concentration dependent response for ethylene molecules and for ammonia molecules.

Key words: nitrogen, ammonia molecules, ethylene molecules, CO$_2$ laser photoacoustic spectroscopy.

1. INTRODUCTION

Ammonia gas is found in trace quantities in the atmosphere, being produced from the putrefaction of nitrogenous animal and vegetable matter. Ammonia and ammonium salts are also found in small quantities in rainwater. The kidneys secrete ammonia to neutralize excess acid. Ammonium salts are found distributed through fertile soil and in seawater [1].

Ethylene gas is a volatile organic compound generated mainly in the exhaust of automotive engines powered by fossil fuels and ethanol. Ethylene gas is a precursor of tropospheric ozone from the reaction with nitrogen oxide and oxygen in the presence of sunlight. Tropospheric ozone is one of the main compounds of photochemical smog that has direct implications on human health. 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 [1].

The study of new tools for the detection of gaseous molecules is of great importance for the development of future societies.

Ideally, a sensing tool has to meet important features such as high sensitivity and selectivity, high accuracy and precision, large dynamic range, multicomponent capability, none or only minor sample preparation, good temporal resolution, versatility, reliability, ease of use, and robustness. Spectroscopic systems including differential optical absorption spectroscopy, Fourier-transform infrared spectrometers, light detection and ranging (Lidar) systems. Although there is no ideal instrument that would fulfill all the requirements mentioned above, the sensing techniques based on photoacoustic principles offers some important advantages in different applications such as: continuous, sensitive (down to ppb – $10^{-9}$ or even sub-ppb concentrations), specific and near real time monitoring of numerous gases [2–4].

The success of the photoacoustic based trace gas sensing techniques crucially depends on the availability and the performance of the tunable laser source and of the detection scheme employed. Lasers offer the advantage of high spectral power density owing to their intrinsic narrow linewidth in the range of MHz. Since the laser linewidth is usually much smaller than the molecular absorption linewidth, it is not an important issue in most measurements.

In this context, we utilized CO$_2$ laser photoacoustic spectroscopy method to measure the minimum detectable concentrations for ammonia and ethylene molecules in pure nitrogen.

2. METHOD

The CO$_2$ laser photoacoustic spectroscopy used for the gas content measurement and presented in this report is schematically shown in Fig. 1 and described also in other works by [2–26]. In brief, photoacoustic spectroscopy utilizes a line-tunable CO$_2$ laser and a photoacoustic cell, where the gas is analyzed. In photoacoustic spectroscopy, the absorbed power is determined directly via its heat and hence the sound produced in the sample.

The experimental setup consists of a homebuilt, line-tunable and frequency stabilized CO$_2$ laser. This laser, emitting radiation in the 9.2–10.8 µm infrared region on 55 different vibrational-rotational lines, has a maximum power of 6.5 W on the 10P(20) line [5–8].

Our laser beam was modulated by a high quality, low vibration noise and variable speed (4–4000 Hz) mechanical chopper model DigiRad C-980 or C-995 (30 aperture blade), operated at the appropriate resonant frequency of the cell (564 Hz).
We used a dual-phase, digital lock-in amplifier Stanford Research Systems model SR 830 with the following characteristics: full scale sensitivity, 2 nV–1 V; input noise, 6 nV (rms)/√Hz at 1 kHz; dynamic reserve, greater than 100 dB; frequency range, 1 mHz–102 kHz; time constants, 10 μs–30 s, or up to 30000 s.

The photoacoustic cell has a total volume of approximately 1.0 dm³ and it is made of stainless steel and Teflon to reduce the out gassing problems. The photoacoustic cell consists of an acoustic resonator tube, windows, gas inlets and outlets, microphones and an acoustic filter to suppress the window noise. The photoacoustic cell windows are made of ZnSe and positioned at Brewster angle to their mounts. The resonant conditions are obtained as longitudinal standing waves in an open tube (excited in its first longitudinal mode). To achieve a larger signal, we chose a long absorption path length ~300 mm and an inner diameter of the pipe of 7 mm. The fundamental longitudinal wave, therefore, has a nominal wavelength of 600 mm and a resonance frequency of 564 Hz.

The two buffer volumes placed near the Brewster windows have a length of 75 mm and a diameter of 57 mm. The inner wall of the stainless steel resonator tube is highly polished. It is centered inside the outer stainless steel tube with Teflon spacers. A massive spacer is positioned at one end to prevent bypassing of gas in the flow system; the other is partially open to avoid the formation of closed volumes. Gas is admitted and exhausted through two ports located near the ends of the resonator tube. The perturbation of the acoustic resonator amplitude by the gas...
flow noise is thus minimized. The acoustic waves generated in the photoacoustic cell are detected by four Knowles electrets miniature microphones (sensitivity 20 mV/Pa each) in series, mounted flush with the wall. They are situated at the loops of the standing wave pattern, at an angle of 90° to one another. The electrical output from these microphones is summed and the signal is selectively amplified by the lock-in amplifier [5–20].

We used a modular software architecture (Keithley TestPoint software) aimed at controlling the experiments, collecting data, and preprocessing information. It helps to automate the process of collecting and processing the experimental results. The software transfers powermeter readings, normalizes data, and automatically stores files. It allows the user to record parameters such as the photoacoustic cell responsivity (a constant used to normalize raw data), gas absorption coefficient, number of averaged samples at every measurement point, sample acquisition rate, and the total number of measurement points. This software interfaces the lock-in amplifier, the chopper, the laser powermeter and the gas flowmeter. It allows the user to set or read input data and instantaneous values for the photoacoustic voltage, average laser power after chopper, and trace gas concentration [20–26].

Of great significance in these determinations is the gas handling system due to its role in ensuring gas purity in the photoacoustic cell. It can be used to pump out the cell, to introduce the sample gas in the photoacoustic cell at a controlled flow rate, and monitor the total and partial pressures of gas mixtures. Also, the gas handling system can perform several functions without necessitating any disconnections [26].

CO$_2$ laser photoacoustic spectroscopy performs well in terms of sensitive and selective detection of trace gas and it allows near on-line measurements.

3. RESULTS

Figure 2 shows a graph of the resonant frequency of the photoacoustic cell (as a function of laser beam chopping frequency).

The acoustic resonator is characterized by the quality factor ($Q$), which is defined as the ratio of the resonance frequency to the frequency bandwidth between half power points. The amplitude of the microphone signal is $1/\sqrt{2}$ of the maximum amplitude at these points, because the energy of the standing wave is proportional to the square of the induced pressure.

The quality factor was measured by filling the photoacoustic cell with 1 ppmV of ethylene buffered in nitrogen at a total pressure of 1 atm and by tuning the modulation frequency in 10 Hz increments (2 Hz increments near the top of the
curve) across the resonance profile to estimate the half width, as described above.

For this photoacoustic cell, the profile width at half intensity was 35 Hz, yielding a quality factor $Q = 16.1$ at a resonance frequency $f = 564$ Hz.

Figure 2 – Resonance curve of the photoacoustic cell.

Figure 3 shows the calibration measurements (concentration dependent response) for ammonia experimentally determined using commercially prepared, certified gas mixtures containing 10 ppmV ammonia diluted in pure nitrogen.

Figure 3 – Calibration curve for ammonia.
Figure 4 shows the calibration measurements (concentration dependent response) for ethylene, experimentally determined using commercially prepared, certified gas mixtures containing 0.96 ppmV ethylene diluted in pure nitrogen.

For calibration we examined this reference mixture at a total pressure of approximately 1013 mbar and a temperature of 23 °C, using the commonly accepted values: 30.4 cm⁻¹atm⁻¹ (for ethylene) and 57 cm⁻¹atm⁻¹ (for ammonia).

4. CONCLUSIONS

CO₂ laser photoacoustic spectroscopy technique is very important for the identification and determination of concentrations of trace gases, and has many applications like medical diagnosis of diseases with the analysis of exhaled gases, the atmospheric pollutants assessment or analysis of physiological processes at fruits and vegetables [1–26].

As the gases are present at different concentrations in the exhaled breath, or in the atmosphere or in fruits and vegetables, monitoring of these gases represent a scientific and technical challenge.

The results demonstrate that CO₂ laser photoacoustic spectroscopy is an important tool for sensitive and selective detection of ammonia and ethylene molecules.
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