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PULSED LASER PHOTOACOUSTIC SPECTROSCOPY OF GASES

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Abstract Pulsed laser photoacoustic spectrometer based on CO₂ laser excitation is reported. Advantage has been taken of the temporal resolution of the gas absorption signal relative to that of the background. Detection sensitivity of 1.5 ppbv ethylene ($4.9 \times 10^{-8} \text{ cm}^{-1}$) is achieved.

Background Information

Pulsed laser excitation is an alternative experimental approach to photoacoustic spectroscopy and detection, relative to modulated cw lasers. The technique provides temporal resolution of the photoacoustic signal (vs. phase resolution in modulated cw technique), which makes it feasible to separate the molecular gas absorption signal from the background window and cell wall absorption. Since the sensitivity of the photoacoustic detection is mainly limited by the magnitude of the background signal, rejection of a large portion of it by temporal resolution leads to a high signal/noise ratio [1-2].

The specific experimental technique and the corresponding detection sensitivity was demonstrated previously by investigating the detection of SO₂ in the UV [1]. The simpler of the two systems investigated was based on the fixed frequency XeCl excimer laser (laser wavelength: 308 nm) and was found to have the sensitivity limit of 2ppbv of SO₂. Better matching of the excitation wavelength with a SO₂ absorption line was achieved with our second system based on a continuously tunable frequency doubled pulsed dye laser operating at 300.05 nm. This system achieved the detection limit of 0.2ppbv of SO₂, corresponding to the absorption coefficient of $2.9 \times 10^{-9} \text{ cm}^{-1}$. Linear dependence of the photoacoustic signal on SO₂ concentration was established for at least 5 orders of magnitude. Photoacoustic detection of gaseous formic and acetic acids in the UV was subsequently demonstrated with a similar experimental setup [2].

Since the middle IR region contains a wealth of absorption lines of many gases of interest, especially for pollution monitoring, a study was initiated to explore the potentials of pulsed IR photoacoustic spectroscopy. This paper reports the results of investigation of detection sensitivity and the influence of some interfering species.

Experimental Apparatus

The experimental apparatus (Fig.1) uses a line tunable TEA pulsed CO₂ laser (Tachisto 215G) adjusted to deliver 100 mJ per pulse in the TEM₀₀ mode. Nominal laser pulse repetition frequency is 1 Hz. Laser output energy is monitored by a pyroelectric joulemeter (Gen-Tec ED-200). Computer controlled laser wavelength tuning is also available [3]. The photoacoustic cell is of cylindrical shape (25 cm long, 2.7cm inside diameter), closed with Brewster angle windows. The cell contains an extension

Fig.1. Experimental arrangement: PL-pulsed CO₂ laser; WL-wavelength positioning system; GS-gas sampling system; SA-spectrum analyzer; MIC-microphone; JM-joulemeter; WFM-digital waveform recorder; COMP-computer.

opposite to the microphone to avoid the interference of the acoustic wave reflected from the cell wall [1]. A condenser microphone (Bruel and Kjaer 4166 with 2619 pre-amplifier) is used to monitor the acoustic signal.

Both the acoustic waveform and the laser excitation energy are digitized by a waveform recorder (Keithley/MetraByte PCIP-Scope plug-in board). Data acquisition and processing is performed by a personal computer (IBM PC compatible). Acoustic waveforms can be either on-line analyzed or stored for subsequent analysis. The analysis includes the calculation of the photoacoustic signal amplitude and its normalization to the laser excitation energy.

The gas sampling system is based on two-stage dilution of accurately measured, higher concentration gas mixture. Certified gas mixture (Matheson Gas Products), independently calibrated by gas chromatography/mass spectrometry is used as the starting gas mixture which is subsequently diluted to produce lower concentrations varying over more than three orders of magnitude.

Experimental Results and Discussion

The sensitivity of the pulsed laser photoacoustic apparatus is investigated by using ethylene (C₂H₄) as the target gas. Ethylene gas mixtures are convenient to work with and its absorption coefficients at CO₂ laser wavelengths are well known [4]. Calibrated mixture of 13 ppmv ethylene in synthetic air is diluted to the required concentration levels by the gas sampling system. Waveform of the pulsed photoacoustic signal for ethylene is presented on Fig.2 (solid line). Subsequent peaks on the acoustic waveform (not presented on Fig.2) also exist, resulting from the cell window (and to a lesser extent, wall) absorption. Amplitude of the gas molecular signal is measured and normalized to the laser excitation energy. Resulting quantity is proportional to the gas absorbance. For detection sensitivity studies with ethylene, 10P(14) CO₂ laser line with the highest ethylene absorption coefficient [4] is used. Excitation energy of 100 mJ per pulse is found to be appropriate, still avoiding optical saturation. The dependence of the photoacoustic amplitude on ethylene concentration is presented on Fig.3. 100 laser pulses are averaged for each concentration on Fig.3. The detection limit of the apparatus, defined as the absorbing gas concentration which corresponds to the signal to noise ratio equal to unity, is found by extrapolation from the data on Fig.3. In this way, the detection limit is found to correspond to 1.5 ppbv of ethylene, which results in the minimum detectable absorption coefficient of $4.9 \times 10^{-8} \text{ cm}^{-1}$. This detection sensitivity compares favorably with the sensitivity of modulated cw technique [5]. It should be noticed that a larger number of averaged pulses than the one currently used (100) would increase the detection sensitivity correspondingly.

Atmospheric trace gas detection, however, is in practice typically limited by interferences from other atmospheric constituents than the one being measured.

Fig.2. Photoacoustic signal waveforms - ethylene: (1)-619ppbv, (2)-227ppbv, (3)-84ppbv; carbon dioxide: (4)-292ppmv, (5)-440ppmv, (6)-880ppmv.

Fig.3. Dependence of the photoacoustic signal on ethylene concentration.

The role of carbon dioxide (CO_2) in this process is of special interest, because of the effect of kinetic cooling, resulting in an inverse photoacoustic signal [6]. In order to investigate this effect with pulsed CO_2 laser excitation, the photoacoustic signal from CO_2 in synthetic air (N_2/O_2) is measured at 10P(14) line (Fig.2, dashed line). Experiments performed with real atmospheric samples containing both CO_2 and water vapor, did not reveal inverse signals, since the conditions for kinetic cooling are not fulfilled [6]. Experiments to further quantify the CO_2 and water vapor interference with short pulse excitation are underway.

Conclusions

From the application point of view, pulsed photoacoustic apparatus is potentially advantageous over the modulated cw one. To obtain the same sensitivity, modulated cw excitation is usually enhanced by either optical multipassing the excitation beam through the sample cell or by using acoustically resonant operation, or both. The acoustically nonresonant mode of operation of the pulsed technique is certainly advantageous for the field use. Compact pulsed CO_2 lasers needed for this application are technologically completely feasible. The inherent simplicity of design, together with the measured level of performance, makes pulsed photoacoustic spectrometer a strong candidate for the development of a photoacoustic trace level monitor of gases for field use.

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