Photoacoustic spectroscopy on gases with high pressure continuously tunable CO₂ laser

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Abstract: We present a novel photoacoustic detection system with a high pressure CO₂ laser as radiation source. The laser is continuously tunable across wavelength ranges from 13 cm⁻¹ to 18 cm⁻¹ wide. The narrow bandwidth of 0.017 cm⁻¹ allows to resolve any fine structure in the absorption spectra of trace gases at atmospheric pressure. The absorption spectra of four gases are reported, demonstrating the great potential improvement in detection selectivity.

1. INTRODUCTION

A mobile photoacoustic (PA) detection system using a conventional CO₂ laser as radiation source has been developed in our laboratory and successfully applied to air pollution monitoring [1]. The system exhibits an excellent detection sensitivity and a high selectivity, the latter being however limited by absorption interferences owing to the discrete tunability of the laser. The implementation of a high pressure CO₂ laser into a PA system is expected to provide a breakthrough in selectivity, since the overlapping of adjacent pressure-broadened transitions of the CO₂ molecules results in a continuous tunability of the laser for pressures above ca. 10 bars [2].

We have developed such a high pressure CO₂ laser which we now use as radiation source in a novel PA detection system.

2. EXPERIMENTAL SETUP

The high pressure CO₂ laser is schematically drawn at the bottom of Fig. 1. The pressure of the laser gas mixture is 11.5 bars [3]. The tuning of the laser is achieved by rotating the flat cavity mirror with a computer controlled DC motor. Continuous tunability has been achieved over ca. 16 cm⁻¹, 13 cm⁻¹, 16 cm⁻¹, and 18 cm⁻¹ in the 9R-, 9P-, 10R-, and 10P-branches, respectively, with pulse energies ranging from 10 mJ to 50 mJ. The pulse energy must be limited to avoid damage to the optical components. The pulse duration of ca. 80 ns is much shorter than the time constant for the vibrational to translational energy transfer in the mid infrared so that the processes of absorption and relaxation are well separated in time. Yet the pulse repetition rate of 200 mHz, limited by the discharge mechanism, precludes the use of resonance enhancement in the PA cell, which is detrimental to the sensitivity of the PA detection system. Despite the residual modulation in the gain curve of the laser at 11.5 bars, the direct measurement of the wavelength with a scanning monochromator (bandwidth: 0.09 cm⁻¹) shows a linear frequency tuning. The absence of mode pulling effects, due to the highly frequency-selective resonator configuration, permits an easy calibration of the laser wavelength [4].

The PA detection system is schematically shown in Fig. 1. The laser pulses are slightly focused into a non-resonant cylindrical stainless steel cell and directed to a pyroelectric detector for the measurement of the pulse energy while the PA signal is recorded by a miniature electret microphone (Knowles BT1751) at the center of the cell [4]. The pyroelectric detector can be removed for the direct measurement of the laser wavelength with a scanning monochromator.

The PA measurement on pure $^{12}\text{C}^{16}\text{O}_2$ at a reduced pressure of 85 mbar shown in Fig. 2 demonstrates the excellent wavelength resolution of the laser: the CO_2 absorption line is easily resolved despite an overall bandwidth of only ca. 0.034 cm^{-1} . Assuming a Lorentzian laser emission profile we estimate from the convolution with the Lorentzian absorption line profile a bandwidth of $0.017 \pm 0.003\text{ cm}^{-1}$. This corresponds to the ultimate wavelength resolution of the detection system. Such measurements on low-pressure CO_2 are used for the laser wavelength calibration: owing to the high-resolution wavelength tuning, the wavelength of the transitions can be determined to an accuracy of ca. $\pm 5 \times 10^{-4}\text{ cm}^{-1}$. The linear frequency tuning permits a linear interpolation for wavelengths between the transitions thereby providing a much higher accuracy than the direct measurement with the scanning monochromator.

3. RESULTS OF THE PA INVESTIGATIONS

The spectrum of multicomponent gas mixtures is the result of a linear superposition of the spectra of the individual compounds. Presently we have applied our novel PA system to the investigation of four trace gases of environmental concern: ethylene (C_2H_4), methanol (CH_3OH), ethanol ($\text{C}_2\text{H}_5\text{OH}$) and toluene (C_7H_8). Since the pulse energy varies from pulse to pulse and across the tuning range we first analyzed the energy dependence of the PA signal for a mixture of 101.8 ppm C_2H_4 buffered in 1 bar of non-absorbing synthetic air (80% N_2 , 20% O_2). At the 10P(14) laser transition the PA signal exhibits a strongly nonlinear energy dependence in contrast to the nearly linear behaviour at 10P(18) where the absorption is much smaller. We attribute the nonlinearity to the saturation of the strong transition of C_2H_4 at 10P(14). Consequently, care has to be taken for calibration measurements [4].

Furthermore, trace gas analysis is possible only if the calibration measurements are scalable to small concentrations. To address this issue the concentration dependence of the PA signal for C_2H_4 at 10P(14) and 10P(18) has been investigated. A gas mixing unit MKS 147C allowed us to vary the C_2H_4 concentration from the original 101.8 ppm down to 50 ppb. The PA signals at 10P(14) and 10P(18) shown in Fig. 3 are plotted as a function of the concentration for a pulse energy of 20 mJ. The regression lines with slope 1 in both cases demonstrate the linear dependence.

The absorption spectra of ethylene, methanol, ethanol and toluene at atmospheric pressure have been measured throughout the 9P branch as shown in Figs. 4 and 5. The substantial potential improvement in detection selectivity of the system using the continuously tunable CO_2 laser is evidenced by the vertical lines representing the accessible transitions of low pressure CO_2 lasers. The spectra have been measured with a wavelength resolution of $4 \times 10^{-2}\text{ cm}^{-1}$ which is enough to resolve the fine structure of the absorption spectra at atmospheric pressure. However, as illustrated in Fig. 5 the absorption spectra of various hydrocarbons can be quite similar, so that the measurements may have to be extended to the entire emission range of the laser in order to increase the selectivity. The detection sensitivity of the system is presently insufficient for investigations on ambient air. Yet the direct analysis of exhausts appears feasible. A new PA cell with an expected higher sensitivity is currently being developed.

4. CONCLUSION

A novel PA system with a continuously tunable CO_2 laser applied to the analysis of atmospheric compounds is presented. The absorption spectra of various gases at atmospheric pressure have been measured for the first time with such a scheme thereby demonstrating a great potential improvement in detection selectivity. Present work focuses on detailed analyses of multicomponent gas mixtures including further compounds of environmental concern such as benzene, isopentane, ozone and ammonia.

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Fig. 1. Experimental setup for PA studies with the high pressure CO₂ laser. PyD: pyroelectric detector

Fig. 2. Scan around the 10P(20) transition of pure CO₂ at 85 mbar. The curve is a Lorentzian fit with a FWHM of 0.034 cm⁻¹.

Fig. 3. Concentration dependence of the PA signal for ethylene at a total pressure of 1000 mbar. The lines are linear fits.

Fig. 4. Normalized PA spectrum of 101.8 ppm C_2H_4 (light line) and 15.9 ppm CH_3OH (solid line) buffered in 1 bar of synthetic air. The vertical lines indicate the emission lines of low pressure CO_2 lasers.

Fig. 5. Normalized PA spectrum of 20.8 ppm C_2H_5OH (solid line) and 101 ppm C_7H_8 (light line) buffered in 1 bar of synthetic air. The vertical lines indicate the emission lines of low pressure CO_2 lasers.