

# A Direct Detection of CO<sub>2</sub> in Sealed-off CO<sub>2</sub> Discharge Tube by Optoacoustic Effect

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A simple analytical method that allows direct monitoring of small amount of CO<sub>2</sub> in a CO<sub>2</sub> discharge tube which utilizes the optoacoustic detection technique is described. The dependence of the optoacoustic signal on the mole fraction of CO<sub>2</sub> was shown that the system responded linearly to the amount of CO<sub>2</sub> present in the miniature discharge cavity equipped with Cu electrodes. It was also found that fraction of dissociated CO<sub>2</sub> varied from 14 to 37% of the initial concentration which depended on the current and the pressure in the tube. This simple and easy detection method has proven to possess the practical advantages over the conventional systems for the study of CO<sub>2</sub> laser electrodes.

## Introduction

Since the discovery of a CO<sub>2</sub> laser by Patel<sup>1</sup>, wide areas with significant applications have been found for a sealed-off CO<sub>2</sub> laser such as military, medical, industrial, and instrumentation and scientific markets.<sup>2</sup> In a CO<sub>2</sub> laser cavity, carbon dioxide is dissociated into carbon monoxide and oxygen by the electrical discharge during the operation.<sup>3</sup> Since the output power of the laser is directly proportional to the CO<sub>2</sub> gas remaining after such electrical discharge, monitoring the concentration of CO<sub>2</sub> in the laser cavity is the essential feature for investigating the characteristics of laser electrodes and enhancing the performance of the lasers.

Many studies have been reported concerning analysis of the gas mixtures in the CO<sub>2</sub> laser plasma by using various methods such as a gas chromatography,<sup>4</sup> infrared spectroscopy,<sup>5</sup> and mass spectroscopy.<sup>6</sup> The practical difficulty in the use of these detection methods is that the sensitivity of the conventional IR spectroscopy is too low to detect small quantities of CO<sub>2</sub> present in the cavity (typically 50-150  $\mu$ g or 2.5-7.5 ppm). In GC or GC/MS detection, the striking difference in pressure between a laser tube and a chromatograph can easily produce errors during the sampling and injection of gas mixtures from the cavity into a column. Several sophisticated and specific experimental designs have been utilized to overcome these drawbacks.<sup>4-6</sup> Furthermore, since both the GC and mass techniques are destructive methods, the sample cannot be recovered and the monitoring of the concentration changes of the gas mixture can not be carried out continuously.

The optoacoustic effect in the gas phase is most frequently produced by the infrared radiation with IR active gas medium. The sensitivity of the optoacoustic detection has proven to be so high that wide applications of this effect have been made in pollution detection,<sup>7</sup> trace detection,<sup>8</sup> and high resolution spectroscopy.<sup>9</sup> Recently, a photoacoustic monitoring of absorbance changes in a reaction has been reported, which showed a significant improvement in the detection over the conventional spectrophotometric detection enabling it to be used when the absorbance changes are on the order of only 10<sup>-4</sup> unit.<sup>10</sup> In this report, by using the optoacoustic

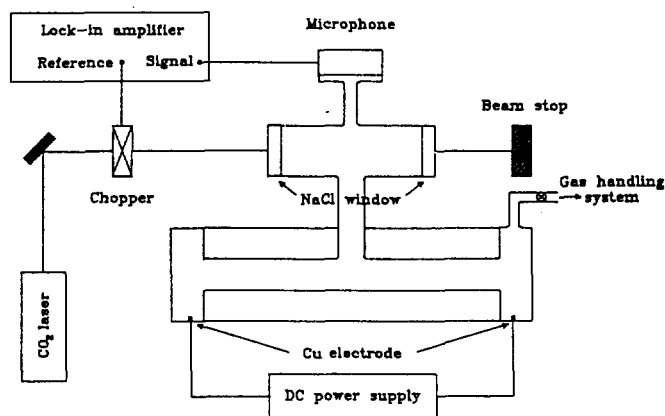
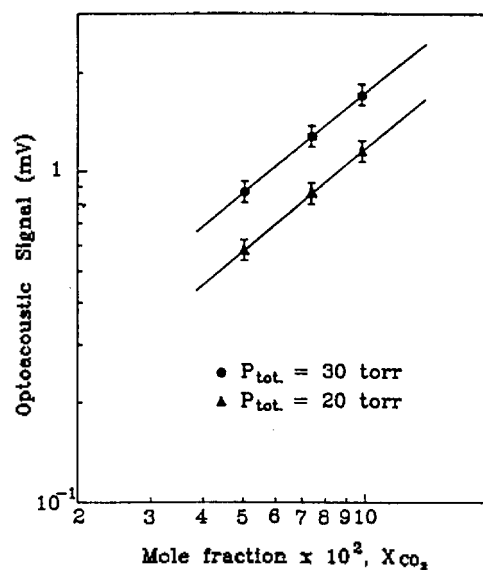


Figure 1. Schematic diagram of experimental set up for the optoacoustic detection of CO<sub>2</sub>.

spectroscopy, a relatively simple and direct experimental method is demonstrated to analyze the changes in the CO<sub>2</sub> concentration in the CO<sub>2</sub> discharge tube.

## Experimental

A schematic diagram of experimental setup used in this study for the optoacoustic detection is shown in Figure 1. The pyrex glass cell consisted of two volumes is connected by an adjoining tube. The first is the discharge chamber, which includes a coolant jacket and the gas reservoir, where two Cu electrodes with the distance of 10 cm are mounted in the central discharge tube. The other part is the acoustic cell, in which NaCl windows form the ends of the cell. The total gas volume in this system is approximately 20 cm<sup>3</sup>. An electret microphone with a built-in FET preamplifier is placed at the end of the acoustic chamber attached to the discharge tube. The output beam of cw CO<sub>2</sub> laser (Synrad Model 48-1-115) operating at multilines of 10.6  $\mu$ m is modulated at 35 Hz by a light chopper. When the laser beam is directed into the acoustic cell, the excitation of CO<sub>2</sub> by the IR radiation produces an optoacoustic effect. The optoacoustic signals from the microphone are then detected by



**Figure 2.** Optoacoustic signal dependence of the mole fraction of  $CO_2$ .

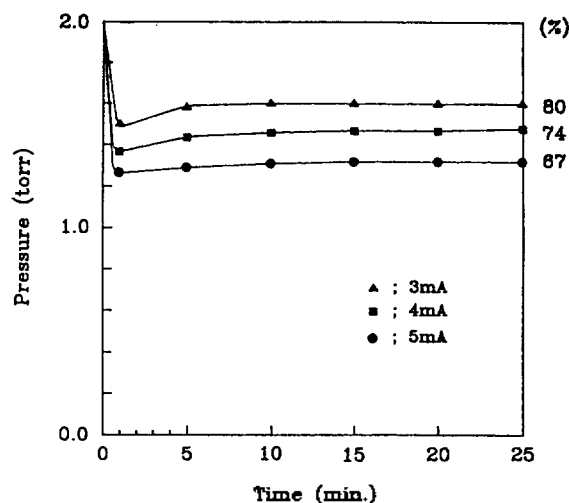
a lock-in amplifier (EG&G PARC Model 5210) with the time constant set at 300 ms.

Several gas mixtures are purchased and analyzed by a gas chromatography prior to use. The composition of the mixed gases is varied according to the ratios of  $CO_2 : CO : N_2 : He = 1-x : x : 1 : 8$ , where  $x=0, 0.25$  and  $0.5$ . Total pressure inside the chamber is kept within the ranges of 5 to 40 torr giving rise to the partial pressure of  $CO_2$  to be between 0.25 and 4 torr. Initially, the calibration of the optoacoustic signal is carried out with fixed total pressure in the cell and the laser power. As shown in Figure 2, the signal dependence on the mole fraction of  $CO_2$  is found that the system responds linearly to the amount of  $CO_2$  present in the cavity even at different total pressure of the mixed gas.

## Results and Discussion

In order to investigate the dissociation characteristics of  $CO_2$  in the tube, the optoacoustic measurements were conducted by applying dc discharge current between two Cu electrodes. The optoacoustic signals, indicating the changes of  $CO_2$  concentration, were monitored as a function of time during the electrical discharge in the sealed-off cavity. Figure 3 displays the variation in partial pressure of  $CO_2$  recorded from the optoacoustic signal with respect to the discharge time for three different discharge currents with the total pressure inside the tube fixed at 20 torr. Note that the concentration of  $CO_2$  is changed dramatically within 1 min after the discharge started and then nearly unchanged. The absence of data points before 1 min of discharge time was mainly due to the fact that the action of the discharge was found to be unstable, causing the fluctuation of signals. However, considerable decrease of optoacoustic signals was easily observed during that period.

Similar results were obtained where the different total pressures varying from 5 to 40 torr were used. It gives rise to the fraction of dissociated  $CO_2$  in the range of 14% and 37%, which depends on the current and the pressure, of



**Figure 3.** Change of  $CO_2$  concentration with respect to the discharge time in the cavity for different DC currents ( $\triangle$ ; 3 mA,  $\square$ ; 4 mA,  $\circ$ ; 5 mA). The total pressure inside the tube was 20 torr and DC voltage of 2.0 KV was applied to the Cu electrodes.

the initial concentration. It can be seen from the Figure 3 that the amount of  $CO_2$  dissociation is increased as the discharge current is increased. However, any simple relationship between the discharge current and the fraction of  $CO_2$  dissociated could not be obtained, which was beyond the scope of this experiment. These results are in good agreement with those of others where complex and sophisticated experimental designs were utilized in conjunction with the conventional techniques.<sup>6,11-13</sup>

Since our experimental setup did not achieve the optimum condition of a real laser system, no further attempts were made to investigate the performance characteristics of the  $CO_2$  laser. However, from the relatively simple experiment with a miniature discharge tube in this report, the practical advantages of this method over the conventional techniques are clear in that it possesses the capability for simple and direct detection of  $CO_2$  in the laser discharge cavity. A more comprehensive study on the characteristics of catalytic electrodes including perovskite oxides are in progress in conjunction with this optoacoustic detection method. Consequently, it appears that this optoacoustic monitoring method may find its great application to the study for the dissociation mechanism of  $CO_2$  along with the characterization of electrodes for further improvements of the sealed-off  $CO_2$  laser.

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## Optical Third-Harmonic Generation of Poly (2-Bromo-1,4-phenylenevinylene)

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Weakly electron withdrawing bromine substituted poly (2-bromo-1,4-phenylenevinylene) (PBrPV) was synthesized through water-soluble precursor method. The linear and nonlinear optical properties of PBrPV were compared with those of poly (1,4-phenylenevinylene) (PPV). The third-order nonlinear optical susceptibility,  $\chi^{(3)}$ , was measured by using third-harmonic generation (THG) technique at 1907 nm, fundamental wavelength. The calculated  $\chi^{(3)}$  values of PPV and PBrPV were  $3 \times 10^{-12}$  esu and  $2 \times 10^{-12}$  esu, respectively.

### Introduction

For realization of optical processing systems, the development of highly efficient optical nonlinear materials is expected. Some organic materials have good potential for nonlinear optical devices because of their large optical nonlinearity, very fast response time and low absorption loss as compared with inorganic semiconducting materials.<sup>1</sup> In particular, organic thin films which exhibit third-order optical nonlinearity have many useful applications in integrated optics such as optical bistability, optical switching and optical data processing. For these nonlinear optical materials, easy processibility such as thin-film preparation is needed for optical device application.<sup>2</sup> Among nonlinear organic materials, delocalized  $\pi$ -conjugated polymers are expected to possess extremely large third-order nonlinear susceptibilities.<sup>3</sup> Recently, conducting polymers have been a special interest to many investigators because of their possibility as a nonlinear optical material.<sup>4</sup> They usually possess delocalized  $\pi$ -conjugated systems toward their chain directions. For example, polyacetylene has been reported to show the third-order nonlinear optical susceptibility,  $\chi^{(3)}$  of  $1 \times 10^{-10}$  esu near the resonant condition which is almost the same as the well known third-order nonlinear optical organic polymer, p-toluenesulfonate (PTS) polydiacetylene.<sup>5</sup> Usually conducting polymers are in

crystalline states and they are difficult to process because of their nonfusibility and insolubility in almost all solvents. So, amorphous polymers with good processibility are expected to be good material as nonlinear optical media. Poly (p-phenylenevinylene) (PPV) is one of the examples that have been reported as amorphous optical polymers.<sup>6-8</sup> High molecular weight films of PPV can be prepared from a processible precursor polymer through relatively simple reactions. PPV has been reported to show third-order nonlinear susceptibility,  $\chi^{(3)}$  of  $7.8 \times 10^{-12}$  esu at 1.85  $\mu\text{m}$ .<sup>9</sup> Among the derivatized PPV structures, Kaino *et al.* investigated the poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMPV), which has a narrower band gap compared to PPV.<sup>10</sup> This reduction of band gap is attributed to the electron-donating character of the methoxy groups.  $\chi^{(3)}$  value of PDMPV was evaluated to be  $5.4 \times 10^{-11}$  esu at 1.85  $\mu\text{m}$  wavelength. The authors have examined the optical nonlinearity of poly(2-methoxy-1,4-phenylenevinylene) (PMPV) thin film as one of the easily processed  $\pi$ -conjugated polymers. The  $\chi^{(3)}$  of the PMPV was revealed to be  $7.9 \times 10^{-10}$  esu at 602 nm by using degenerate four-wave mixing technique.<sup>11,12</sup> In this paper, we report the influence of electron withdrawing substituent to third-harmonic generation. For this purpose, bromine atom as an electron acceptor was attached to the phenylene ring in PPV. Poly(2-bromo-1,4-phenylenevinylene) (PBrPV) was synthesized through water soluble precursor polymer and third-order nonlinear optical susceptibility was measured. The synthetic route and the structure of PBrPV are shown below.

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