A Direct Detection of CO_2 in Sealed-off CO_2 Discharge Tube by Optoacoustic Effect

Sung-Ho Kim, Joong-Gill Choi*, and Ung-In Cho***

***Department of Chemistry, Soonchunhyang University, Asan, Chungnam 337-880*
**Department of Chemistry, Yonsei University, Shinchon, Seoul 120-749*
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A simple analytical method that allows direct monitoring of small amount of CO_2 in a CO_2 discharge tube which utilizes the optoacoustic detection technique is described. The dependence of the optoacoustic signal on the mole fraction of CO_2 was shown that the system responded linearly to the amount of CO_2 present in the miniature discharge cavity equipped with Cu electrodes. It was also found that fraction of dissociated CO_2 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_2 laser electrodes.

Introduction

Since the discovery of a CO_2 laser by Patel[1], wide areas with significant applications have been found for a sealed-off CO_2 laser such as military, medical, industrial, and instrumentation and scientific markets.[2] In a CO_2 laser cavity, carbon dioxide is dissociated into carbon monoxide and oxygen by the electrical discharge during the operation.[3] Since the output power of the laser is directly proportional to the CO_2 gas remaining after such electrical discharge, monitoring the concentration of CO_2 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_2 laser plasma by using various methods such as a gas chromatography,[4] infrared spectroscopy,[5] and mass spectroscopy.[6] 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_2 present in the cavity (typically 50-150 μg 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.[4-6] 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,[7] trace detection,[8] and high resolution spectroscopy.[9] 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^{-4} unit.[10] In this report, by using the optoacoustic spectroscopy, a relatively simple and direct experimental method is demonstrated to analyze the changes in the CO_2 concentration in the CO_2 discharge tube.

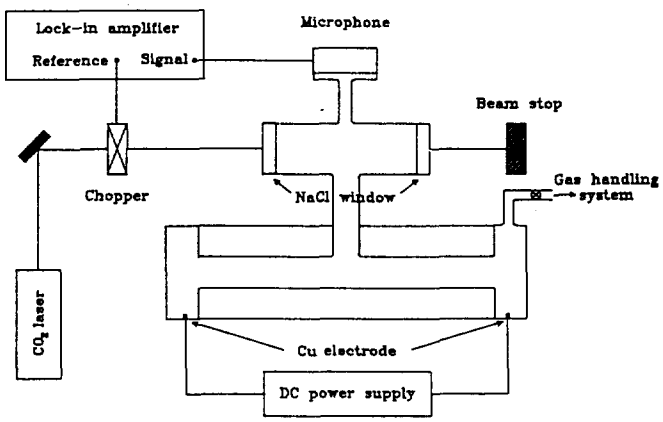

Figure 1. Schematic diagram of experimental set up for the optoacoustic detection of CO_2.

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 reservior, 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^3. An electret microphone with a built-in FET preamplifier is placed at the end of the acoustic chamber attached to the discharge tube. The ouput beam of cw CO_2 laser (Synrad Model 48-1-115) operating at multilines of 10.6 μm is modulated at 35 Hz by a light chopper. When the laser beam is directed into the acoustic cell, the excitation of CO_2 by the IR radiation produces an optoacoustic effect. The optoacoustic signals from the microphone are then detected by

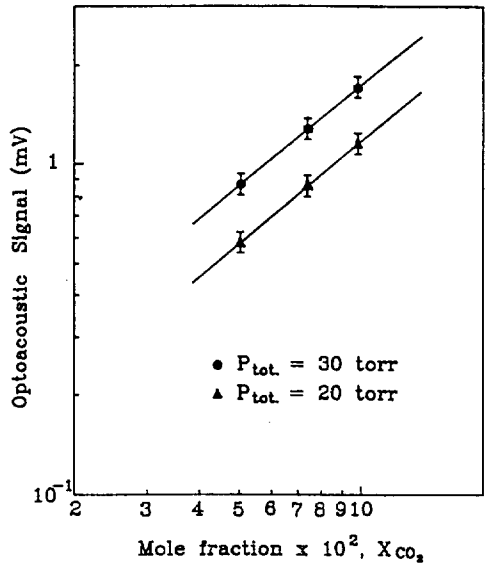

Figure 2. Optoacoustic signal dependence of the mole fraction of CO_2.

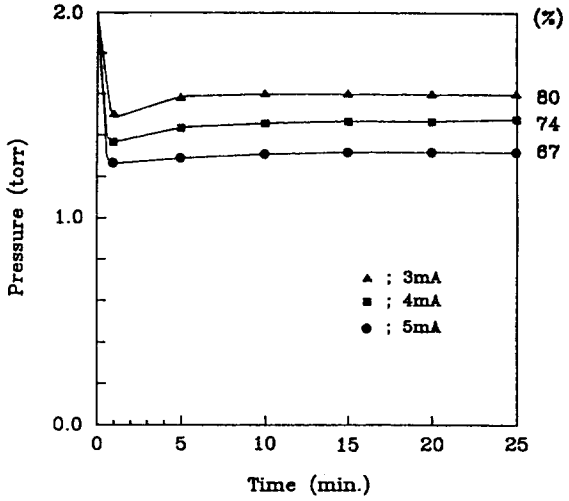

Figure 3. Change of CO_2 concentration with respect to the discharge time in the cavity for different DC currents (◈; 3 mA, ◇; 4 mA, ◈; 5 mA). The total pressure inside the tube was 20 torr and DC voltage of 2.0 KV was applied to the Cu electrodes.

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

Several gas mixtures are purchased and anlyzed 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 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 conjuction with the conventional techniques.[6,11-13]

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 conjuction 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)

Do-Hoon Hwang, Jeong-Ik Lee, Minyung Lee†, and Hong-Ku Shim

Department of Chemistry, Korea Advanced Institute of Science and Technology, Taejon 305-701
†Optics Laboratory, Korea Research Institute of Standards and Science, Taejon 305-606
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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 3×10^{-12} esu and 2×10^{-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.[1] 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.[2] Among nonlinear organic materials, delocalized π-conjugated polymers are expected to possess extremely large third-order nonlinear susceptibilities.[3] Recently, conducting polymers have been a special interest to many investigators because of their possibility as a nonlinear optical material.[4] They usually possess delocalized π-conjugated systems toward their chain directions. For example, polyacetylene has been reported to show the third-order nonlinear optical susceptibility, $\chi^{(3)}$ of 1×10^{-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.[5] Usually conducting polymers are in crystalline states and they are diffcult 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.[6-8] 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 7.8×10^{-12} esu at 1.85 μm.[9] 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.[10] 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 5.4×10^{-11} esu at 1.85 μm wavelength. The authors have examined the optical nonlinearity of poly(2-methoxy-1,4-phenylenevinylene) (PMPV) thin film as one of the easily processed π-conjugated polymers. The $\chi^{(3)}$ of the PMPV was revealed to be 7.9×10^{-10} esu at 602 nm by using degenerate four-wave mixing technique.[11,12] 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.

†Present address: Department of Chemistry, Ewha Womans University, Seoul 120-750, Korea