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G. A. Postema<sup>a</sup>; S. v. Heusden<sup>a</sup>

<sup>a</sup> Philips Research Laboratories, Eindhoven, The Netherlands

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# Infrared Emission of Air Pollutants Induced by a CO<sub>2</sub> Laser

G. A. POSTEMA and S. v. HEUSDEN

*Philips Research Laboratories, Eindhoven, The Netherlands*

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**KEY WORDS:** CO<sub>2</sub> laser; air pollutants; infrared emission; sulphur hexa fluoride.

A possible method for the measurement of air pollutants is described. It is based on infrared emission from gases at specific wavelengths induced by a CO<sub>2</sub> laser. The emission level can be increased by adding a sensitizing gas (e.g. SF<sub>6</sub>) to the sample gas. Although the mechanism of the emission is not fully understood experimental data indicate that the emission is of thermal origin. Spectra of some air polluting gases are included in this paper.

In 1966 Bordé *et al.*<sup>1,2</sup> and later Ronn<sup>3</sup> and Robinson and co-workers<sup>4-6</sup> reported on infrared emission by gases when they were irradiated by a 40-W cw CO<sub>2</sub> laser. The wavelengths of the emission spectra coincided with the wavelength of the infrared absorption spectra and differed from the wavelength of the exciting laser beam. The emission is specific to the gas and therefore the gas can be identified.

In the experiments described in the present paper the beam of a 55-W CO<sub>2</sub> laser was focussed by a concave mirror to a diameter of about 1 mm in front of the entrance slit of a monochromator (Jarrell-Ash 0.5 m). A schematic diagram of the experimental arrangement is given in Figure 1. A Golay detector (SP 50 Pye-Unicam) and a mechanical chopper (SP 52 Pye-Unicam) at a frequency of 11 Hz were used in conjunction with a synchronous amplifier (SP 51 Pye-Unicam).

Air polluting gases such as SO<sub>2</sub>, CO, NO and NO<sub>2</sub> were added to a nitrogen flow of 60 l/hr and emission was observed with a focussed laser beam. A minimum laser power is required in order to observe emission; below 20 W no emission could be observed.

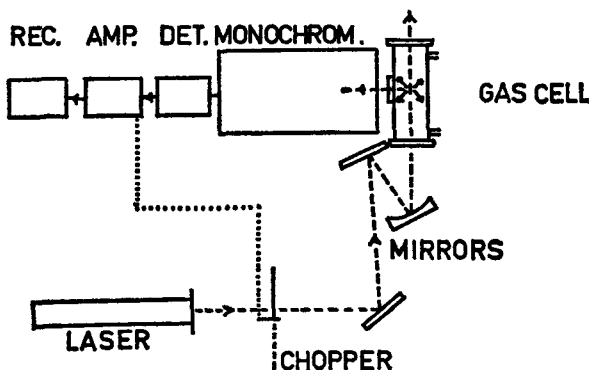


FIGURE 1 Schematic diagram of experimental arrangement.

It is known that  $\text{SF}_6$  is a good absorber of the  $\text{CO}_2$  laser radiation. Bailey *et al.*<sup>7</sup> indicated in 1971 that the intensity of the emission of gases as  $\text{CO}$ , among others, could be increased considerably by adding some  $\text{SF}_6$ ,  $\text{CO}_2$  or  $\text{C}_2\text{H}_4$  to the gas flow. The signal did not depend strongly on the  $\text{SF}_6$  concentration: from 0.05% to 0.2% no change in emission signal was observed.

Table I presents the relative intensity of the emission of the gases and the wavelength of the emission peak. Peak heights of the emission are compared to the peak height of the  $\text{SO}_2$  emission at 7.26 micron (resolution 394 Å;  $\text{SF}_6$  concentration 0.1%; time constant 10 sec). The emission peaks of  $\text{CO}$ ,  $\text{NO}_2$  and  $\text{SO}_2$  are given in Figures 2, 3 and 4. It was possible to detect a

TABLE I  
Relative intensity of the emission peaks  
of several gases with respect to  $\text{SO}_2$

| Gas           | Relative intensity | Emission wavelength (micron) |
|---------------|--------------------|------------------------------|
| $\text{SO}_2$ | 1                  | 7.26                         |
| $\text{CO}$   | 0.6                | 4.56                         |
| $\text{CO}_2$ | 5                  | 4.37                         |
| $\text{NO}$   | 0.3                | 5.30                         |
| $\text{NO}_2$ | 5                  | 6.30                         |
| $\text{O}_3$  | 0                  | —                            |
| $\text{SF}_6$ | —                  | 5.93                         |

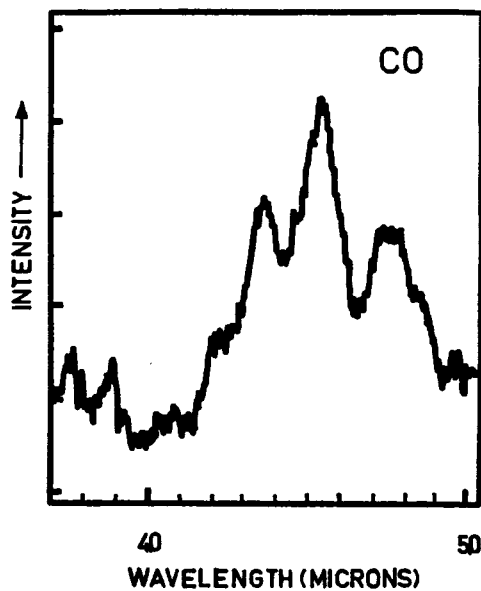


FIGURE 2 Emission spectrum of CO. [CO] = 2000 ppm. Time constant = 10 sec.

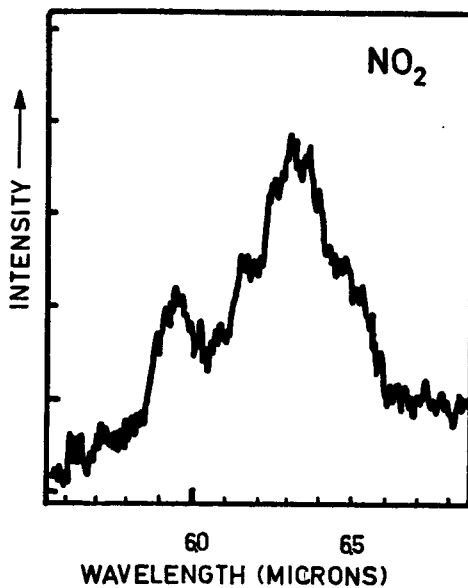


FIGURE 3 Emission spectrum of NO<sub>2</sub>. [NO<sub>2</sub>] = 200 ppm. Time constant = 10 sec.

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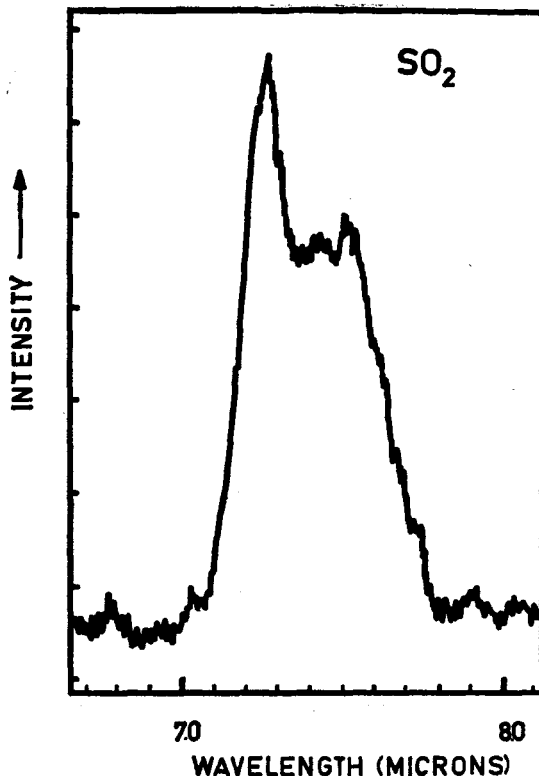


FIGURE 4 Emission spectrum of  $\text{SO}_2$ .  $[\text{SO}_2] = 2000$  ppm. Time constant = 10 sec.

sulphur dioxide concentration of 20 ppm with a time constant of 40 sec and a signal-to-noise ratio of 4.

During the experiments a delay time of about 15 msec was observed between the emitted infrared radiation and the scattered laser light (Figure 5). During the experiments pressure variations with the same frequency as the chopped laser beam were observed in the gas cell.

These two observations suggest that the emission is of thermal origin. The delay time was demonstrated in a modified set-up where the emitted radiation was detected directly with an InSb detector (RPY 77, Mullard; rise time 100 nsec) and the mechanical chopper was replaced by an electronic modulator coupled to the laser. A second detector (CdHgTe, 77°K, S.A.T.) was placed in the laser beam after the gas cell. The signals of both detectors were fed to an oscilloscope and recorded with a video recorder (Philips EL 3402)

in order to have slow-motion pictures of the fast-changing signals. Square-wave laser pulses of 10 msec and of 100 msec duration each with repetition times of 1 sec were applied. The signals of both detectors are presented in Figure 6. It can be seen that the signal due to emission rises slowly. At the end of the laser pulse the emission signal falls slowly. At shorter pulses the emission signal is lower. These observations support the assumption that the emission is mainly thermal.

The method looks promising for the measurement of common air pollutants, such as  $\text{SO}_2$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$  and  $\text{CO}_2$ .

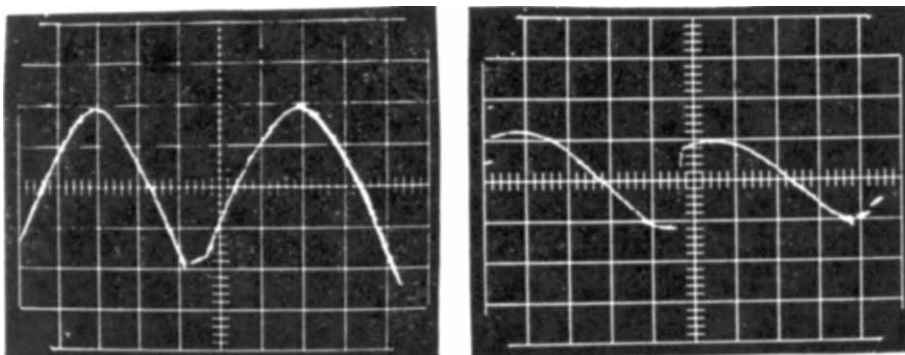


FIGURE 5a Direct detector signal due to emission of acetone with optimal adjustment of the phase of the chopper blades (x-axis: 10 msec/cm).

FIGURE 5b Direct detector signal due to scattered radiation of the laser beam with the same chopper phase as under a (x-axis: 10 msec/cm).

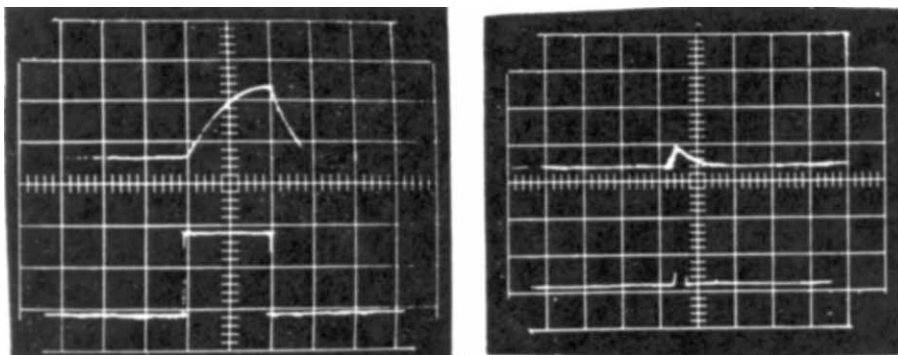


FIGURE 6a Emission signal compared to the laser pulse signal (pulse duration 100 msec).

FIGURE 6b Same as 6a but with a laser pulse of 10 msec.

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