

## MEASUREMENTS OF THE NH<sub>3</sub> AND SO<sub>2</sub> ABSORPTION COEFFICIENTS AT THE CO<sub>2</sub>-LASER LINES

A.A. Adamenkov, Yu.N. Bulkin, Yu.N. Kolobyanin, and E.A. Kudryashov

*Russian Federal Nuclear Physics Center  
at the All-Russian Scientific-Research Institute of Experimental Physics  
Received May 31, 1994*

*This paper describes an automated test stand used for investigation of laser radiation absorption by atmospheric pollutant gases. The absorption coefficients of ammonia and sulphur dioxide have been measured at the CO<sub>2</sub>-laser lines that are most strongly absorbed. It is shown that two lines from the sequential band (00021-10011) are suitable for ammonia detection.*

### 1. INTRODUCTION

Ammonia (NH<sub>3</sub>) and sulfur dioxide (SO<sub>2</sub>) are the most widespread atmospheric pollutants. These gases accompany industrial production and play an important role in acid rain formation. Therefore, continuous monitoring of the content of NH<sub>3</sub> and SO<sub>2</sub> in the atmosphere has acquired particular importance. One of the most sensitive methods which allows the determination of harmful pollutant concentration at the level of maximum permissible concentration (MPC) and even lower is the laser method.<sup>1</sup> A CO<sub>2</sub> laser tunable in the range 9–11 μm, whose radiation is absorbed by NH<sub>3</sub> and SO<sub>2</sub>, is suitable for this purpose. To measure concentration of these pollutants in the case of CO<sub>2</sub>-laser sounding of the atmosphere, one should know the NH<sub>3</sub> and SO<sub>2</sub> absorption coefficients at different wavelengths.

There are many papers concerned with the CO<sub>2</sub>-laser radiation absorption by ammonia (see, e.g., Refs. 2, 3, and 4). In the aforementioned papers the spread of experimental values of the absorption coefficients at individual CO<sub>2</sub>-laser lines attains 30%. Therefore, it becomes actual to carry out some additional experiments to update the database on ammonia absorption in the spectral range 9–11 μm. It should be noted that by now the NH<sub>3</sub> absorption coefficients were measured within the traditional CO<sub>2</sub>-laser bands (00011–10001, 00011–10002).

At the same time it is of practical interest to study the NH<sub>3</sub> absorption at the lines from the sequential bands (00021–10011 and 00021–10012) since at these lines the atmospheric CO<sub>2</sub> absorption is almost two orders of magnitude smaller than that in the region of traditional CO<sub>2</sub>-laser bands. The SO<sub>2</sub> absorption was experimentally studied only in Ref. 3 where the absorption coefficients of chemically pure SO<sub>2</sub> at the lines 9R(8)–9R(30) from the traditional CO<sub>2</sub>-laser band (00011–10002) were determined. For gas analysis such information is insufficient since broadening of spectral SO<sub>2</sub> lines by the principal atmospheric constituents, N<sub>2</sub> and O<sub>2</sub>, may differ from self-broadening.

In this paper we give experimental values of the absorption coefficients of mixtures of NH<sub>3</sub> with N<sub>2</sub> and SO<sub>2</sub> with N<sub>2</sub> at the lines from traditional (00011–10001, 00011–10002) and sequential (00021–10011) CO<sub>2</sub>-laser bands that are most strongly absorbed.

### 2. EXPERIMENTAL SETUP AND MEASUREMENT PROCEDURE

The NH<sub>3</sub> and SO<sub>2</sub> absorption coefficients were investigated on a special stand (Fig. 1). The frequency- and power-controlled automated tunable CO<sub>2</sub> laser 1, operating in traditional and nontraditional spectral ranges (in particular, at the lines from the sequential bands), was used as a radiation source. A feature of this laser was an automatically tuned lasing line. At the laser output the beam was split into reference and sounding beams with the beam-splitting semi-transparent plate 2 fabricated of NaCl. The reference beam was directed to the panoramic spectrograph 3 to control the radiation wavelength. The panoramic spectrograph is an optical system consisting of spherical mirrors, a diffraction grating, and a thermal screen. Using the mirror modulator 4 rotating at a frequency of ≈ 10 Hz, the sounding beam was directed to the meter of input signal power 5 during the first half-period of rotation, and during the second half-period, after passage through the measuring cell 7, it was fed into the power meter of output signal 6. The PM-4 pyroelectric detectors that recorded the radiation from special scatterers were used as power meters. It allowed the increase of measurement accuracy for weak fluctuations of the laser directional pattern caused by rotation of the diffraction grating. The signals from pyroelectric sensors were amplified to ≈ 5 V and were fed into the personal computer 9 for further processing with the help of the 12-bit ADC 8. A glass tube 150 cm long and with inner diameter of 3 cm with NaCl end windows was used as a measuring cell. The vacuum post 10 was used to evacuate the cell down to a pressure of ≈ 10<sup>-4</sup> atm and to fill it with the mixture under study to an accuracy of 10<sup>-3</sup> atm. All measurements were carried out at atmospheric pressure. The gas temperature was taken to be equal to the temperature

of the cell wall and was measured with the thermometer 11 graduated to 0.1 K. During the measurements the wall temperature was 291.3 K.

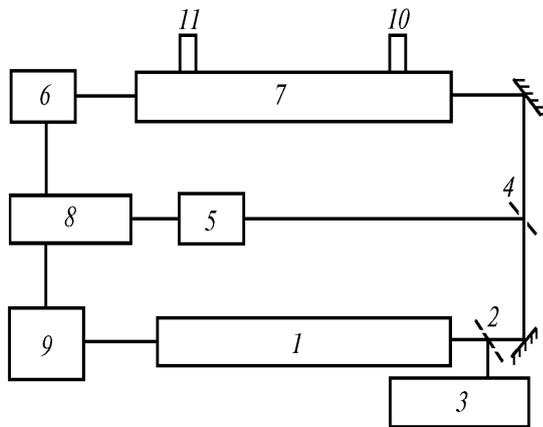


FIG. 1.

A mixture of  $(1.8 \pm 0.1) \times 10^{-2}\%$   $\text{NH}_3$  with pure  $\text{N}_2$  was used to study the ammonia absorption. A standard reference mixture of  $(10.0 \pm 0.2)\%$   $\text{SO}_2$  with pure  $\text{N}_2$  prepared at the Kiev Institute of Analytical Instrument Manufacture was used for studying the  $\text{SO}_2$  absorption.

The measurement procedure was as follows. First for calibration the cell was filled with chemically pure nitrogen at a pressure of 1 atm through a multilayer filter gauze with a mesh size of  $\approx 3 \mu\text{m}$ . That allowed us to clean the gas from possible fine particles and to decrease radiation scattering during its passage through the cell. For calibration, we measured the ratio of the input to output signals in the cell  $A_{1j}$  at the  $\text{CO}_2$ -laser lines chosen beforehand, which was then written into the PC database. After calibration, the cell was evacuated and then filled with the mixture under study. Then the ratio of input to output signals  $A_{2j}$  was recorded at the same laser lines. The absorption coefficient was found from the expression

$$K_j = (1/PL) \ln(A_{1j}/A_{2j}), \quad (1)$$

where  $j$  is the serial number of the corresponding  $\text{CO}_2$ -laser line,  $P$  is the partial pressure of the investigated gas, and  $L$  is the cell length. Apart from evacuation and filling of the cell with gas, the measurements (including line-by-line tuning of the laser) were automated. The obtained absorption coefficients were displayed on the PC. The measurement error was determined from 10 runs of experiments using the standard procedure.<sup>5</sup>

### 3. MEASUREMENT RESULTS

The results of measurements of the  $\text{NH}_3$  and  $\text{SO}_2$  absorption coefficients are listed in Tables I and II together with the experimental results from Refs. 2, 3, and 4. As follows from the results presented in Table I, the  $\text{NH}_3$  absorption coefficients obtained at the traditional laser lines are in good agreement with the results of the other works. Only at the  $9R(30)$  line the value of the absorption coefficient being equal to  $73.1 \text{ atm}^{-1}\text{cm}^{-1}$  exceeds the analogous values reported in Refs. 2 and 4 by about 20%; however, it practically

coincides with the calculated value  $72.2 \text{ atm}^{-1}\text{cm}^{-1}$  reported in Ref. 6. It should be noted that in the present paper the ammonia absorption at the  $10PS(31)$  and  $10PS(33)$  lines from the sequential band (00021–10011) of  $\text{CO}_2$  laser is likely to be studied for the first time. The absorption coefficients were  $30.2$  and  $17.0 \text{ atm}^{-1}\text{cm}^{-1}$ , respectively. If we take into account that radiation absorption in the sequential band (00021–10011) spectrum by atmospheric  $\text{CO}_2$  is almost two orders of magnitude smaller than that in the spectrum of traditional bands, the lines  $10PS(31)$  and  $10PS(33)$  are of practical interest for remote sounding of the atmosphere.

TABLE I. Experimental values of the  $\text{NH}_3$  absorption coefficients at the  $\text{CO}_2$ -laser lines.

Frequency, $\text{cm}^{-1}$	$\text{CO}_2$ -laser line	$K$ , $\text{atm}^{-1}\text{cm}^{-1}$			
		Ref. 2	Ref. 3	Ref. 4	Present work
929.8285	$10PS^*(33)$	—	—	—	$17.0 \pm 1.2$
931.0014	$10P(34)$	—	13.4	14.0	$13.7 \pm 1.1$
931.7562	$10PS(31)$	—	—	—	$30.2 \pm 2.1$
932.9604	$10P(32)$	13.0	15.8	13.7	$13.9 \pm 1.1$
964.7689	$10R(4)$	—	—	11.0	$9.6 \pm 1.0$
966.2503	$10R(6)$	—	32.5	26.3	$25.4 \pm 1.6$
967.7072	$10R(8)$	—	25.8	20.5	$21.4 \pm 1.5$
1075.9878	$9R(16)$	—	13.3	11.2	$13.2 \pm 1.1$
1084.6351	$9R(30)$	60.0	—	56.2	$73.2 \pm 5.2$

\*S denotes lines from the sequential band (00021–10011).

TABLE II. Experimental values of the  $\text{SO}_2$  absorption coefficients at the  $\text{CO}_2$ -laser lines.

Frequency, $\text{cm}^{-1}$	$\text{CO}_2$ -laser line	$K$ , $\text{atm}^{-1}\text{cm}^{-1}$	
		Ref. 3	Present work
1069.0141	$9R(6)$	—	$0.039 \pm 0.004$
1070.4623	$9R(8)$	0.036	$0.041 \pm 0.004$
1071.8838	$9R(10)$	0.044	$0.036 \pm 0.004$
1073.2785	$9R(12)$	0.048	$0.045 \pm 0.004$
1074.6465	$9R(14)$	0.054	$0.052 \pm 0.004$
1075.9878	$9R(16)$	0.056	$0.056 \pm 0.004$
1077.3025	$9R(18)$	0.068	$0.066 \pm 0.004$
1078.5906	$9R(20)$	0.088	$0.077 \pm 0.004$
1079.8523	$9R(22)$	0.72	$0.073 \pm 0.004$
1081.0874	$9R(24)$	0.090	$0.087 \pm 0.005$
1082.2962	$9R(26)$	0.105	$0.109 \pm 0.005$
1083.4787	$9R(28)$	0.092	$0.103 \pm 0.005$
1084.6351	$9R(30)$	0.110	$0.114 \pm 0.005$
1085.7564	$9R(32)$	—	$0.110 \pm 0.005$
1086.8697	$9R(34)$	—	$0.107 \pm 0.005$
1087.9483	$9R(36)$	—	$0.127 \pm 0.005$
1089.0011	$9R(38)$	—	$0.143 \pm 0.006$
1090.0283	$9R(40)$	—	$0.149 \pm 0.006$
1091.0301	$9R(42)$	—	$0.131 \pm 0.006$

As seen from the results listed in Table II, the obtained values of the  $\text{SO}_2$  absorption coefficients at the  $9R(8)$  and  $9R(30)$  lines are in good agreement with those reported in Ref. 3. It enables us to assume that the coefficients of broadening of  $\text{SO}_2$  spectral lines by  $\text{SO}_2$  and  $\text{N}_2$  are close in values, since in Ref. 3, in contrast to the present paper, a mixture of 95%  $\text{SO}_2$  with 5%  $\text{N}_2$  was

investigated. The experimental values of the  $\text{SO}_2$  absorption at the far lines  $9R(32)$ – $9R(42)$  of  $\text{CO}_2$  laser listed in Table II exceed  $0.1 \text{ atm}^{-1}\text{cm}^{-1}$ . The maximum absorption coefficient being equal to  $0.149 \text{ atm}^{-1}\text{cm}^{-1}$  was obtained at the  $9R(40)$  line. This value is 40% larger than that at the  $9R(26)$  line usually used in the measurements, suggesting that the  $9R(40)$  line may be used for remote sounding of the atmosphere.

#### 4. CONCLUSION

In the present paper we have described the computer-controlled experimental automated stand that provides efficient and highly accurate study of absorption by atmospheric pollutants in traditional and nontraditional spectral ranges of  $\text{CO}_2$ -laser generation. To illustrate the capabilities of the stand, we have determined the  $\text{NH}_3$  and  $\text{SO}_2$  absorption coefficients at the  $\text{CO}_2$ -laser lines that are most strongly absorbed. The obtained  $\text{NH}_3$  and  $\text{SO}_2$  absorption coefficients at the traditional laser lines agree with the results of the other works within the experimental error.

It has been shown that for ammonia in the sequential band (00021–10011) of  $\text{CO}_2$ -laser generation

there exist lines [ $10PS(31)$  and  $10PS(33)$ ] the absorption at which is sufficiently strong. These lines are of practical importance for measuring  $\text{NH}_3$  concentration in the presence of atmospheric  $\text{CO}_2$ . The obtained experimental values of the  $\text{SO}_2$  absorption coefficients at the far lines  $9R(36)$ – $9R(42)$  from the traditional band (00011–10002) of the  $\text{CO}_2$ -laser generation exceed the absorption coefficient at the  $9R(26)$  line usually used for gas analysis.

#### REFERENCES

1. P.L. Meyer and M.W. Sigrist, *Rev. Sci. Instrum.* **61**, No. 7, 1779–1807 (1990).
2. A.P. Force, D.K. Killinger, W.F. De Feo, and N. Menyuk, *Appl. Opt.* **24**, No. 17, 2837–2841 (1985).
3. A. Mayer, J. Comera, H. Charpentier, and C. Jaussaud, *Appl. Opt.* **17**, No. 3, 391–393 (1978).
4. R.J. Brewer and C.W. Bruce, *Appl. Opt.* **17**, No. 23, 3746–3749 (1978).
5. J. Taylor, *Introduction into the Theory of Errors* [Russian translation] (Mir, Moscow, 1985), 272 pp.
6. O.K. Voitsekhovskaya, S.V. Kuznetsov, S.V. Sapozhnikov, N.N. Trifonova, and M.P. Cherkasov, *Atm. Opt.* **4**, No. 9, 669–673 (1991).