INVESTIGATION OF THE SPECTRAL PARAMETERS OF THE VIBRATIONAL-ROTATIONAL LINES OF THE ν_1 BAND OF SO_2

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The CO_2 Laser absorption spectra of sulphur dioxide and a sulphur dioxide air mixture have been measured. The obtained results are used to correct the intensities and halfwidths of four SO_2 absorption lines.

Sulphur dioxide is a gaseous component of the atmosphere, whose content varies from 10^{-3} to 10 ppm depending on the presence of local sources. The low-frequency wing of the rotational-vibrational SO_2 band φ_1 (with center near 1151 cm^{-1}) appears to be in the 8–13 μm atmospheric transparency window, and this makes it necessary to take into account the effect of this band on the attenuation of the radiation of lasers operating in this spectral region.

Experimental results which relate to the absorption of CO_2-laser radiation by sulphur dioxide are not many. For example, the absorption coefficients of an SO_2-air mixture were derived in Ref. 1 at an SO_2 partial pressure of 0.94 atm and a total pressure of the mixture of 1 atm. The absorption coefficients of the SO_2-air mixture can be calculated employing the spectral parameters of absorption lines given in Ref. 2, but the accuracy of the calculation for laser radiation is often low. Recently, by means of a diode laser, the frequencies of numerous SO_2 absorption lines, which coincide with or approximate various CO_2-laser lines, were measured.[3] An exact knowledge of the location of the absorption and generation lines in the spectrum makes it possible to calculate the spectral parameters of the vibrational-rotational lines in using a technique based on an analysis of the dependence of the absorption coefficient on the gas pressure at the frequency of the laser line.

Measured results of absorption coefficients of SO_2 and SO_2-air mixtures at the frequencies of the CO_2-laser generation lines in the 9.4 μm region at SO_2 pressures 0.1–40 Torr and air pressures of 0–1 atm at room temperature, using a spectral complex consisting of a tunable CO_2-laser, a system for creating model media, a cell, and an amplifier-recording system with a microcomputer, are given below (see Fig. 1).

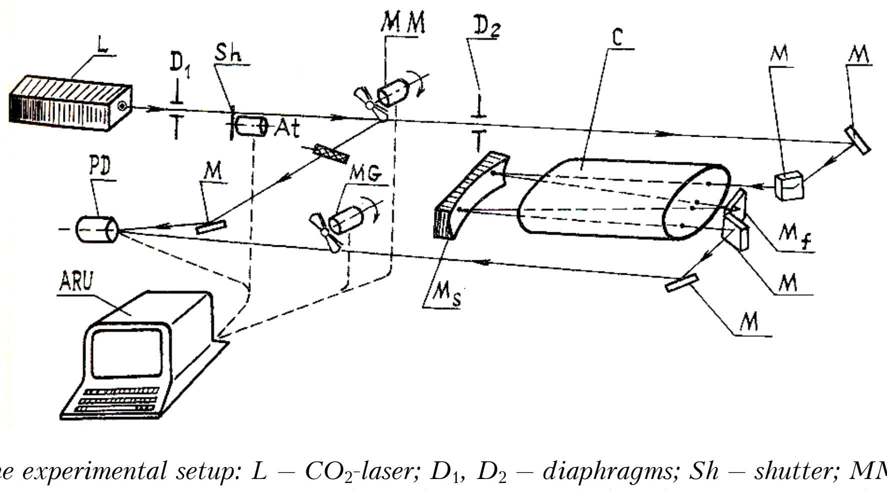

FIG. 1. The experimental setup: L – CO_2-laser; D_1, D_2 – diaphragms; Sh – shutter; MM – mirror modulator; At – attenuator; MG – mechanical gate; PD – photodetector; C – replaceable cell; Ms – mirror (spherical); Mf – mirror (flat); Mr – mirrors (rotational); ARU – the amplifier-recording block with computer.

The tunable CO_2-laser is mounted on an invar rod frame according to the Yakobi scheme[4] and operates in the single-mode single-frequency regime. Tuning of the radiation wavelength is carried out without changing the resonator parameters by displacing a screen with a diaphragm in the laser generation spectral scanning plane. The construction of the gas-discharge tube makes it possible to replace the working mixtures and to use carbon dioxide isotopes. The laser is powered by an IP-06 stabilized source. The active frequency stabilization provides frequency stability of the order of 10^{-7}, which for a resonator length of 265 cm corresponds to a spectral width of the generation line of $1.5 \cdot 10^{-5}$ cm^{-1}.

The setup is based on the two-beam scheme. Modulated by a shutter with a frequency of 1000 Hz, the CO_2-laser beam is directed to the liquid-nitrogen cooled photodetector (the photoresistance is based on gold-doped germanium) by means of a channel switch (mirror modulator), alternately passing through the "measuring" channel (outside the cell). The mechanical gate intercepts both beams for the "zero-line" registration. The attenuator, made of a fine-mesh grid, serves for intensity matching in both channels. A spherical and a flat mirror provide fourfold transmission of the radiation through the cell. Replaceable cells, from 3 to 55 cm long, are made of quartz glass with KPS-5 or NaCl windows and can be heated or cooled by hot or cold air (nitrogen), fed to the cell jacket. The cell temperature is automatically maintained in the range 40–50°C by means of a thermostat, which contains temperature sensors, an electronic thermometer, and a temperature controller. The system for creating model media is made of glass and allows one to bleed in mixtures of predetermined composition into the cells and to control the gas pressure in the cells by means of the VIT-2P and VDG-1 vacuum gauges and a PPR-2M monometer.

The electrical signal from the photodetector is amplified by a narrow-band amplifier with a synchronous detector, the reference voltage for which is taken from the shutter. Operation of the experimental setup during the measurements is controlled by an Elektronika D3-28 microcomputer. The microcomputer, through the interface unit, collects the information from the digital voltmeter and outputs the results to the digital printer and also commutates the measurements in the channels by means of the control unit and auxiliary devices. The computer program provides for protection of the stored data from errors, their filtration, and the accumulation of information up to a predetermined signal-noise ratio. After completing the cycle of measurements the values of the partial and total pressures in the cell, the transmittance values, the absorption coefficients and their standard deviations are output to the printer.

The random error of the measurements of the absorption coefficient, conditioned substantially by the errors of the vacuum gauges (1–4%), stands at 3–8% for the transmittance interval 0.2–0.8 and 10–15% for transmittance greater than 0.8.

The center of the sulphur dioxide absorption band is shifted toward the shortwave region of the atmospheric transmittance window, and the measurements were carried out in the short-wave region of the atmospheric transmittance window, and the measurements were carried out in the shortwave *R*-branch of the CO_2-laser generation spectrum.

Comparison of the measured results for the mixture SO_2-air with the calculations (using the data of Ref. 2) shows that at pressures greater than 70–50 Torr the calculations and the experiment agree to within 10–20%. As the pressure decreases, substantial differences are observed for a number of lines, especially noticeable in the pressure range below 40 Torr. The foregoing is illustrated by Figs. 2 and 3, where the absorption coefficients for the CO_2-laser lines R-26 and R-14 at different partial (P_1) and total (P_2) pressures are given. The observed facts are evidently associated with the fact that the vibrational-rotational SO_2 lines are located at a distance of 0.001–0.01 cm^{-1} from each other; as is shown in Figs. 2 and 3 (fragments of the SO_2 spectrum), the linear spectrum (at low pressures) turns into a quasicontinuous one (at high pressures). In this case individual errors in assigning the parameters of the absorption lines do not exert a substantial effect on it.

Figures 2 and 3 show that the form of the dependence of the absorption coefficient on the pressure is different at different distances between the absorption and generation lines. Such relations make it possible to specify the parameters of the absorption lines in the case in which the generation and absorption lines closely coincide (this condition is practically fulfilled for all of the examined lines) and in the case in which the latter is isolated. This is realized in practice for only a few pairs of lines and, as a rule, at low pressures, when the total coefficient in the wing of neighboring lines is small.

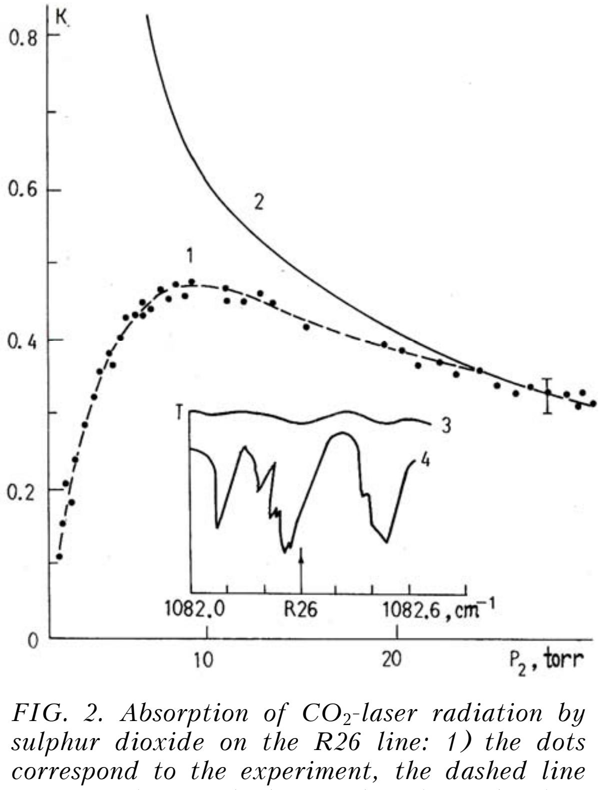

FIG. 2. Absorption of CO_2-laser radiation by sulphur dioxide on the R26 line: 1) the dots correspond to the experiment, the dashed line corresponds to calculations based on the data from Table 1; 2) calculations based on Ref. 2; 3) the spectrum of the SO_2 mixture at a total pressure of 1 atm; 4) the SO_2 -spectrum at a pressure of 25 Torr.

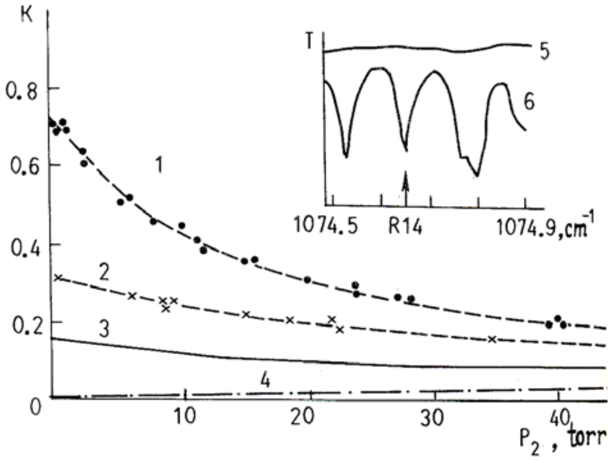

FIG. 3. The absorption of CO_2-laser radiation by sulphur dioxide in air on the R14 line: 1 and 2) the dots and crosses correspond to the experiment at $P_1 = 3$ Torr and $P_1 = 10$ Torr, respectively. The dashed lines correspond to calculations based on Table I; 3) calculations based on Ref. 2 at $P_1 = 10$ Torr; 4) contribution of the wings; 5) the spectrum of the SO mixture at a total pressure of 1 atm; 6D SO_2 -spectrum at a pressure of 40 Torr.

The spectral parameters of four SO_2 absorption lines were obtained during experiments in using standard methods of minimization of the rms deviation between the experimental data and the calculation of the absorption coefficient based on the Voigt contour of the absorption line, taking into account the shift of the line center:

$$K = 2S_{\gamma}\pi^{-3/2}\int_{-\infty}^{\infty}\frac{\exp(-t^2)dt}{(\nu-\nu_0-\Delta-t\gamma_0/\sqrt{\ln 2}\,)^2+\gamma^2}.$$

where $\gamma = \alpha_1 P_1 + \alpha_2 P_2$, $\Delta = \beta_1 P_1 + \beta_2 P_2$, and $t = u(\nu_0 - \Delta)/c$.

Here S is the intensity, $cm^{-2} \cdot atm^{-1}$; ν and ν_0 are the frequencies of the laser and absorption lines, cm^{-1}; γ_0 is the Doppler halfwidth, cm^{-1}; γ is the Lorentz halfwidth, cm^{-1}; Δ is the line shift, cm^{-1}; α_1 and α_2 are the self-broadening and broadening coefficients, respectively, $cm^{-1} \cdot atm^{-1}$; β_1 and β_2 are the self-shift and shift coefficients, respectively, $cm^{-1} \cdot atm^{-1}$; $P1$ and P_2 are the partial pressures of SO_2 and the buffer gas, respectively, atm; u is the velocity of the motion of the molecule in the direction of the observer; and c is the velocity of light.

The total contribution of the wings of the neighboring lines (0.1-5%) was calculated accordance with the data[2] at $\alpha_1 = 0.4$ cm^{-1} atm^{-1}. Obtained during the experiments, spectral parameters of SO_2-lines are given in Table I, and the calculations with them are shown in Figs. 2 and 3 (dashed lines). The data from Ref. 2 are given in the table for comparison. For lines $30_{14,16}$—$31_{15,17}$ and $18_{16,16}$—$19_{17,3}$ intensities of lines agree well. Because of the high values of the absorption coefficients in the wings of the neighboring lines, it was not possible to determine the α_2 values for these lines accurately (estimates of ranges for are given In Table I).

TABLE I. Characteristics of SO_2 absorption Lines

SO_2 line	CO_2 laser line	ν_0, sm^{-1}	$\Delta\nu \cdot 10^4$, sm^{-1}	$S \cdot 10^4$ $sm^{-2} \cdot atm^{-1}$	α_1, $sm^{-1} \cdot atm^{-1}$	α_2, $sm^{-1} \cdot atm^{-1}$	References
$18_{16.16}$-$19_{17.3}$	R0	1084.6661*	310	120	0.40	0.06-0,13	our data
		1084.6658	306	130	-	0.11	Ref. 2
$30_{14.16}$-$31_{15.17}$	R6	1082.2932*	30	77	0.33	0.06-0,13	our data
		1082.2959	3	81	-	0.11	Ref. 2
$36_{15.21}$-$37_{16.22}$	R4	1074.6457*	4	13	0.09	0.035	our data
		1074.6479	18	37	-	0.11	Ref. 2
$37_{12.26}$-$38_{13.25}$	R8	1083.4793*	5	25	0.14	0.048	our data
		1083.4810	22	62	-	0.11	Ref. 2

* Ref. 3.

Noteworthy are the results obtained for the vibrational-rotational lines $36_{15.21}$—$37_{16.22}$ and $37_{12.26}$—$38_{13.25}$; the line intensities and halfwidths are almost three times less than in Ref. 2. Since the absorption is practically resonant for both lines ($\Delta\nu > 5 \cdot 10^{-4}$ cm^{-1}), line center shifts, as the processing of the experimental data shows, do not appear, and the ratio (0.02) of the halfwidth of the laser line to the Doppler one does not limit the application of Bouguer's law, a possible cause of the underestimates of S and γ might be the differences in the methods for determining the spectral parameters (for $\nu - \nu_0 < \gamma_L$ the absorption coefficient is proportional to S/γ_L, and the variation of the contour parameters (see the formula) is such that it is possible to obtain only the correct relation between the intensity and the halfwidth). Indeed, if the halfwidths α_1 and α_2 are multiplied by the ratio S[2]/S [our data], which equals 3 for the line $36_{15,21}$–$37_{16,22}$ and 2.5 for the line $37_{12,26}$–$38_{13,25}$ (assuming the data from Ref. 2 to be accurate), then the values of α_1 and α_2 are 0.27 and 1.105 cm^{-1} atm^{-1} for the first line and 0.12 cm^{-1} atm^{-1} for the second one; these results agree well with the data for the two other lines given in Table I.

Thus, the results of the experimental investigations of the dependence of the absorption coefficients of SO_2 and SO_2-air mixtures permit one to come to the following conclusion: the experimentally obtained values of the intensities and the broadening coefficients agree well with the atlas data[2]; the value of the self-broadening coefficient α_1 lies in the range 0.27–0.4 cm^{-1} atm^{-1}. The spectral parameters contained in Ref. 2 might be employed for the calculation of the absorption coefficients of SO_2-air mixtures in the near-earth layer at total pressure of 300–760 Torr. Higher altitudes and, correspondingly, lower pressures require a refinement of the parameters, especially the positions of the SO_2 line centers.

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