MEASUREMENT OF THE PROBABILITY OF THE TRANSITION P20 (00^01-10^00) IN CO_2 AND IMPACT BROADENING IN COLLISIONS WITH CO_2, N_2, AND He

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We measured the dependence of the absorption coefficient on the pressure for the vibrational–rotational transition P20 (00^01-10^00) in CO_2 using a CO_2 laser as a light source. We consider the question of the systematic error due to the contribution of impact broadening, when finding the probability from the experimental absorption. The refined value of the transition probability $A^{00^01,19}_{10^00,20} = 0.169$ sec^{-1}. We obtain the values of the impact half-widths for collisions of the type CO_2-CO_2, CO_2-N_2, CO_2-He, the values of which at J =300°K are respectively 3.28, 2.74, and 2.27 MHz/torr.

1. Certain Properties of Inverted Medium. A characteristic of an inverted medium is the difference between the populations of the work levels. This characteristic is usually expressed in terms of the signal gain

$$\alpha_0 = \frac{\lambda^2}{8\pi} S(\nu_0) A_{vJ}^{v'J'} \left[n_{v'J'} - n_{vJ} \frac{g_{v'J'}}{g_{vJ}} \right] \tag{1.1}$$

As applied to a molecular medium, the indices v' and J' characterize the vibrational and rotational levels of the upper state, and v and J do the same for the lower state. Accordingly, $g_{v'J'}/g_{vJ}$ is the ratio of the statistical weights. In the case of transitions along the P branch, which will be investigated from now on, we have

$$\frac{g_{v'J'}}{g_{vJ}} = \frac{2J-1}{2J+1}$$

Since the density of the inverted population is proportional to $[S(\nu_0)\ A_{vJ}^{v'J'}]^{-1}$, the accuracy with which the inversion can be measured is determined by the extent to which the probabilities of spontaneous emission $A_{vJ}^{v'J'}$ and the form factor $S(\nu_0)$ at the center of the line are known. At low pressures, when impact broadening can be neglected, we have

$$S(\nu_0) = S_D(\nu_0) = \frac{1}{\Delta\nu_D}\sqrt{\frac{\ln 2}{\pi}} \tag{1.2}$$

At high pressures, in practice at

$$\frac{\Delta\nu_L}{\Delta\nu_D} = \frac{\delta^0\nu_L}{\Delta\nu_D} p > 4$$

Here $\delta^0\nu_L$ is the impact half-width referred to unit pressure

$$S(\nu_0) = S_L(\nu_0) = 1/\pi\delta^0\nu_L p \tag{1.3}$$

In the general case, the form factor is given by

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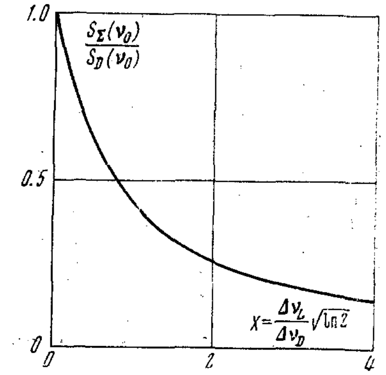

Fig. 1

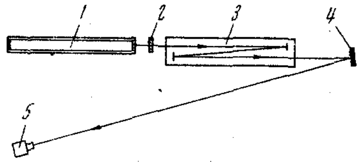

Fig. 2

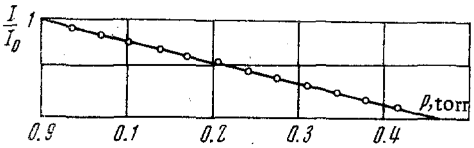

Fig. 3

$$S(\nu_0) = S_\Sigma(\nu_0) = \eta(p)\frac{1}{\Delta\nu_D}\sqrt{\frac{\ln 2}{\pi}} \tag{1.4}$$

The dependence of $\eta(p) = S_\Sigma/S_D$ on $(\Delta\nu_L/\Delta\nu_D)\sqrt{\ln 2}$ is shown in Fig. 1. At a fixed temperature of the medium, the quantity η becomes a function of the impact half-width. It is therefore necessary to find $A_{VJ}^{V'J'}$ and $\delta^0\nu_L$.

There are published values of the probability of spontaneous emission $A_{VJ}^{V'J'}$ for the molecule CO_2. The scatter of the corresponding data is quite large. The values of the quantity $A_{10^00.20}^{00^01.19}$ for the molecule CO_2 lie in the interval from 0.32 sec^{-1} [1] to 0.1 sec^{-1} [2].

In [3] the probabilities of the transition were determined in terms of the integral absorption coefficient

$$\int k_\nu d\nu = \frac{C}{8\pi\nu^2} n_{vJ} A_{vJ}^{v'J'} \frac{g_{v'J'}}{g_{vJ}}\left[1-\exp\left(-\frac{h\nu}{kT}\right)\right] \approx \frac{c}{8\pi\nu^2} n_{vJ} A_{vJ}^{v'J'} \frac{g_{v'J'}}{g_{vJ}} \tag{1.5}$$

As applied to the CO_2 molecule, the most exact is the method in which the radiation source is a CO_2 laser operating on one rotational transition [4]. If a monochromatic radiation source is used, the absorption coefficient (at the center of the line) is given by

$$K_0 = -\frac{1}{l}\ln\frac{I}{I_0} = S(\nu_0)\int K_\nu d\nu \tag{1.6}$$

where I_0 is the incident radiation power and I is the radiation power passing a path l in the medium. Experiment aimed at finding $A_{VJ}^{V'J'}$ reduces to a measurement of the transparency I/I_0 at the center of the absorption line in the region of low pressures, followed by drawing a tangent to the curve $\ln I/I_0 = f(p)$. The results of the measurements of the probabilities of the transition by this method are given in [4, 5]. Drawing a tangent to the experimental points can lead to appreciable systematic errors, inasmuch as at pressures on the order to several torr it is impossible to neglect the contribution of the impact broadening to the form factor of the line. The systematic error is given by

$$\frac{\Delta A_{vJ}^{v'J'}}{A_{vJ}^{v'J'}} \approx 2\sqrt{\frac{\ln 2}{\pi}}\frac{\delta^0\nu_L}{\Delta\nu_D}p$$

and reaches ~25% at p ~2 torr.

2. Measurement of the Probability of the P20 Transition of the CO_2 Molecule. Measurements of the transmission were carried out in the present study in the regions p < 0.5 torr. The experimental setup is shown in Fig. 2. The radiation source was a stabilized CO_2 laser 1 (length 200 cm, inside diameter of discharge tube 13 mm). The laser resonator was made up of a spherical mirror (R = 10 m) and a plane-parallel germanium plate. After considerable attenuation with filter 2, the radiation was introduced into the absorbing cell, in the form of a three-pass cell 3 with path length l = 677 cm. The cell was evacuated beforehand, and the gas was then admitted into it slowly with the aid of a precision leak valve. The pressure in the cell was measured with a calibrated radiation vacuum meter, the signal from which, after amplification with an electrometric amplifier, was fed to the horizontal input of an x-y recorder ("Climatic"

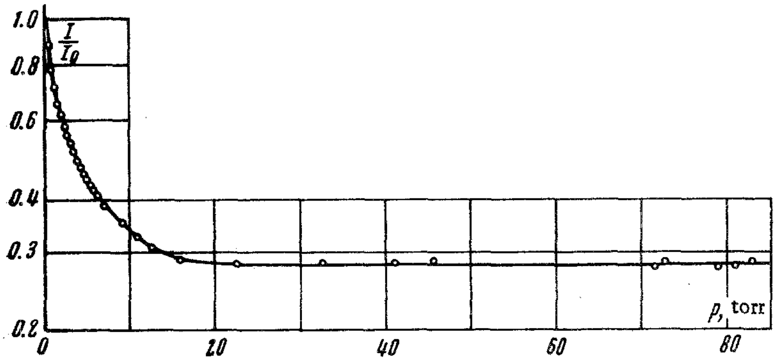

Fig. 4

TABLE 1

Authors	[7]	[8]	[4]	Present work
$A^{00^01,19}_{10^00,20}$ sec^{-1}	0.213±11%	0.192±3.6%	0.164±5%	0.169±3%

TABLE 2

Authors	[4]	Result of Kostokovskii [4]	[7]	[6]	Present work
$\delta^{\circ}\nu_{CO_2-CO_2}$ MHz/torr	3.19±(>5%)	3.32±7%	3.12±10%	5.2±3%	3.28±4%

M-100). The pressure registration system insured good linearity up to p ≈7 torr. A signal proportional to I/I_0 was simultaneously applied to the vertical input of the x-y recorder from a detector 5 (Ge−Au).

The reflecting echelette grating 4 (50 lines/mm) served to identify the P20 transition, on which all the experiments were performed. The distance from the grating to the detector was 8 m. The apparatus errors consisted of $\Delta p/p = 0.4\%$ in the $\Delta T/T = 0.07\%$. The nonlinearity of the registration system was ~0.1%.

The experiments were performed in the temperature interval 283-293.5°K, but all the experimental data were recalculated to 330°K.

Owingto the high laser stability, we were able to perform the measurements in the pressure region $p < 0.5$ torr (see Fig. 3). Before each cycle of measurement, the laser was tuned to the maximum power by means of translational motion of a germanium plate. Such tuning ensured coincidence of the generation frequency with the cener of the absorptional line. Each point is the result of averaging over 40 experimental curves. The P20 transition probability calculated from the slope of the tangent is given in Table 1, which indicates the most reliable data by other authors obtained for the same transition.

In [7] the laser operated simultaneously on three transitions (P18, P20, P22).

3. Impact Broadening by CO_2-CO_2 Collisions. In the case of large pressures, when the contributions of the Doppler broadening can be neglected, the absorption collision at the light center is determined by expression (1.6) with form factor (1.3).

The experiment reduced to a registration of the relative transparency of the medium I/I_0, but since the pressure was varied in the region $p \leqslant 100$ torr, a standard monovacuummeter was used to monitor it at $p > 7$ torr.

Figure 4 shows the complete experimental transmission curve of the cell as a function of the pressure. (The results were recalculated to 300°K.) The value of $\delta^0\nu_L$ calculated from the transmission at the plateau of the curve is given in Table 2.

TABLE 3

Authors	[7]	[8]	Present work
$\delta^0\nu_{CO_2-N_2}$ MHz/torr	$3.12 \pm 10\%$	—	$2.74 \pm 7\%$
$\delta^0\nu_{CO_2-He}$ MHz/torr	$2.38 \pm 10\%$	—	$2.27 \pm 7\%$
$\frac{\delta^0\nu_{CO_2-N_2}}{\delta^0\nu_{CO_2-CO_2}}$	$1 \pm 20\%$	$0.75 \pm 4\%$	$0.84 \pm 11\%$
$\frac{\delta^0\nu_{CO_2-He}}{\delta^0\nu_{CO_2-CO_2}}$	$0.76 \pm 20\%$	$0.59 \pm 4\%$	$0.69 \pm 11\%$

The results of all the measurements, with the exception of [5], are in good agreement with one another.

4. Broadening by CO_2-N_2 and CO_2-He Collisions. In the present paper we determined the impact half-widths for CO_2-N_2 and CO_2-He collisions of the P20 transition. To obtain the correct results, it is important that the mixture be homogeneous. The gases were mixed in our experiment in a separate chamber, with the aid of a high-power fan that was turned on for a few minutes. The mixture prepared in this manner was admitted into the working cell. After numerous repetitions of the experiment, the partial composition of the mixture was maintained constant ($p_{CO_2}/p_X = 1$).

The half-width reduced to 1 atm, in the case of broadening by an extraneous gas, is given by the relation

$$\delta^0\nu_{CO_2-X} = -\frac{P_{CO_2}}{P_X}\left[\frac{l\int k_\nu d\nu}{P_{CO_2}\pi\cdot\ln I/I_0} + \delta^0\nu_{CO_2-CO_2}\right] \quad (4.1)$$

Here $\delta^0\nu_{CO_2-CO_2}$ and $\delta^0\nu_{CO_2-X}$ are in $cm^{-1}\cdot atm^{-1}$. It follows from (4.1) that $\delta^0\nu_{CO_2-X}$ is determined with the lowest accuracy, since the error in the determination of the half-width includes also errors in the determination of the transition probability and $\delta^0\nu_{CO_2-CO_2}$.

Table 3 includes results pertaining to the broadening by nitrogen and helium, obtained in [7, 8] and in the present experiments. All the quantities are given for K=300°K. When account is taken of the experimental errors, the data in Table 3 agree with one another. A slight discrepancy, exceeding the limits of errors, occurs when the value $\delta\nu_{CO_2-He}/\delta\nu_{CO_2-CO_2}$ obtained in [8] and in the present paper are compared. The reason for the discrepancy is not clear.

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