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MEASUREMENT OF THE TIME OF VIBRATIONAL RELAXATION OF THE 00^01 *LEVEL OF THE* CO_2 *MOLECULE*

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We measured the time of collision relaxation of the vibrational level 00^01 of the CO_2 molecule in pure CO_2 and in mixtures with nitrogen, helium, and water vapor at 300° K, using the phase method. The results are compared with the data by others and are in good agreement with them.

1. INTRODUCTION

A number of recent papers have been devoted to the vibrational relaxation of CO_2 from the upper laser level 00^01. The phase method recently proposed in[1] was used to measure the times of vibrational relaxation of CO_2 in pure CO_2 at T = 300° K; these times agree with the data obtained by the method of pulsed excitation[2,3] and by the method of amplifying laser radiation in the afterglow[4], and deviate from the data obtained by the "spectrophone" method[5]. It is of interest to employ the phase method to determine the relaxation time of the 00^01 level of the CO_2 molecule in gas mixtures used in CO_2 lasers. It should be noted that it is necessary here to interpret suitably the experimental results.

We present here a detailed analysis of the phase method of measuring the time of vibrational relaxation of CO_2 in a gas mixture, and report the measurements made in the case of CO_2 relaxation in pure CO_2 and in CO_2 mixed with N_2, ^4He, H_2O at 300° K.

2. ANALYSIS OF THE PHASE METHOD OF MEASURING THE TIME OF VIBRATIONAL RELAXATION OF CO_2 MIXED WITH N_2

In the investigation, by the phase method, of the time of vibrational relaxation of CO_2 in a gas mixture, the most thorough analysis is required for the processes that determine the behavior of the population of the 00^01 level of the CO_2 molecules mixed with N_2, since the lower vibrational level v = 1 of the N_2 molecule is practically at resonance ($\Delta E = 18\ cm^{-1}$) with the 00^01 level of CO_2. In this case there is a rather extensive group of reactions:

$$CO_2(00^0 1) + CO_2(00^0 0) \rightarrow \begin{array}{l} \nearrow CO_2(nm^l0) + CO_2(00^0 0) + \Delta E_1 \\ \rightarrow CO_2(nm^l0) + CO_2(n_1m_1^{l_1}0) + \Delta E_2, \\ \searrow 2\,CO_2(00^0 0) + \Delta E_3 \end{array} \qquad (1)$$

$$CO_2(00^01) + CO_2(nm^l0) \rightarrow CO_2(nm^l0) + CO_2(n_1m_1^l,0) + \Delta E_4, \qquad (2)$$

$$CO_2(00^01) + N_2(v=0) \rightarrow CO_2(nm^l0) + N_2(v=0) + \Delta E_1, \qquad (3)$$

$$CO_2(00^01) + N_2(v=0) \rightleftarrows CO_2(00^00) + N_2(v=1) \pm \Delta E_5, \qquad (4)$$

$$CO_2(00^00) + N_2(v=1) \rightarrow CO_2(nm^l0) + N_2(v=0) + \Delta E_6, \qquad (5)$$

$$N_2(v=1) + N_2(v=0) \rightarrow 2N_2(v=0) + \Delta E_7. \qquad (6)$$

Let us consider now a certain volume of gas containing a mixture of CO_2 and N_2. If there is a driving force that propels the CO_2 molecules from the 10^00 level (their number is denoted by CO_2^0) to the 00^01 level, then the equations for the change of the number of CO_2 molecules excited at the 00^01 level (which we designate CO_2^*) and the molecules of N_2 at the level v = 1 (N_2^*) are

$$d(CO_2^*)\,/\,dt = a(CO_2^*) + b(N_2^*) + ce^{-i\omega t}, \qquad (7)$$

$$d(N_2^*)\,/\,dt = e(N_2^*) + d(CO_2^*), \qquad (8)$$

where $a = -[k_1(CO_2^0) + k_2(CO_2) + k_3(N_2) + k_4(N_2)]$, $b = k_{-4}(CO_2^0)$, $e = -[k_{-4}(CO_2^0) + k_5(CO_2^0) + k_6(N_2)]$, $d = k_4(N_2)$, c is a constant that depends on the population of the 10^00 level, the absorption coefficient of the 10.6-μ radiation and the intensity of this radiation; ω is the frequency of the driving force; $k_1, k_2, \ldots$ are the constants of the reactions (1)–(6) in cm^3/sec), and k_4 and k_{-4} pertain to the direct and the inverse reactions.

If it is assumed that the deviation of the level populations from the equilibrium Boltzmann distribution is small, then a, b, e, and d can be regarded as constants, and the system (7) and (8) takes the form

$$d\Delta_1\,/\,dt = \Delta_1 a + \Delta_2 b + ce^{-i\omega t}, \qquad (9)$$

$$d\Delta_2\,/\,dt = \Delta_2 e + \Delta_1 d, \qquad (10)$$

where Δ_1 and Δ_2 are the non-equilibrium increments to the Boltzmann populations $(CO_2^*)_B$ and $(N_2^*)_B$.

Solving the system (9) and (10), we obtain the following expression for Δ_1:

$$\Delta_1 = De^{-i(\omega t - \varphi)},$$

where D is a constant that depends on a, b, e, and d; φ is the phase shift, determined from

$$\operatorname{tg}\varphi = \omega\frac{bd + (e^2 + \omega^2)}{ebd - a(e^2 + \omega^2)}. \qquad (11)$$

Since φ is determined by coefficients consisting of combinations of reaction-rate constants, then the influence of the individual processes on the phase shift φ is differently manifested at different values of ω.

Let us estimate the rates of the reactions (1)–(6), using the values of the constants k_1, k_3, k_4, k_{-4}, and k_6 given in[3]. We consider by way of an example a mixture with $CO_2 : N_2 = 1 : 1$ at T = 300°K and P = 100 Torr. The total rate W_1 of the reaction (1) is

$$W_1 = (CO_2^*)\, k'_1 (P_{CO_2^0}) = (CO_2^*)\, k'_1 P X_{CO_2} \frac{1}{Q_{CO_2}}.$$

Here $P^0_{CO_2}$ is the pressure of the CO_2 molecules in the ground state, in Torr, P is the total pressure of the mixture, X_{CO_2} is the molar fraction of CO_2, Q_{CO_2} is the vibrational partition function of the CO_2 molecule, and $k_1 = 3.5 \times 10^2$ Torr^{-1} sec^{-1} from[3]. Then $W_1 = 1.6 \times 10^4 (CO_2^*)$ cm^{-3} sec^{-1}.

We can estimate analogously the remaining reaction rates: $W_2(\max) = 6.6 \cdot 10^2 (CO_2^*)$ cm^{-3} · sec^{-1}, $W_3 = 5.3 \cdot 10^3 (CO_2^*)$ cm^{-3} · sec^{-1}, $W_4 = 9.5 \cdot 10^5 (CO_2^*)$ cm^{-3} · sec^{-1}, $W_5 = 8.8 \cdot 10^5 (N_2^*)$ cm^{-3} · sec^{-1}, $W_6 = 6.5 \cdot 10^{-2} (N_2^*)$ cm^{-3} · sec^{-1}. Having at our disposal the rates of all the reactions, we can easily obtain the values of the coefficients a, b, e, and d in (7) and (8):

$$a = -9.6 \cdot 10^5 \text{ sec}^{-1}, \quad b = 8.8 \cdot 10^5 \text{ sec}^{-1},$$
$$e = -8.7 \cdot 10^5 \text{ sec}^{-1}, \quad d = 9.5 \cdot 10^5 \text{ sec}^{-1}.$$

Let us estimate the value of tan φ (11) at different frequencies ω. At $\omega \ll 10^6$ sec^{-1} (and correspondingly $\omega/2\pi \ll 160$ kHz), we can neglect ω^2 compared with e^2, and then

$$\operatorname{tg}\varphi = \frac{bd + e^2}{ebd - ae^2}\,\omega. \tag{12}$$

For $\omega \gg 1.4 \times 10^6$ sec^{-1} (corresponding to $\omega/2\pi \gg 200$ kHz) we have

$$\operatorname{tg}\varphi = -\omega / a. \tag{13}$$

Since the predominant term in the coefficient a is $k_4(N_2)$, we have at high frequencies ($\omega/2\pi \gg 200$ kHz) in this case tan $\varphi \approx \omega\tau_4 / X_{N_2}$, where τ_4 is the characteristic time of exchange of quanta between the level 00^01 of the CO_2 molecule and the level v = 1 of the N_2 molecule, and X_{N_2} is the molar fraction of N_2 in the mixture.

Accordingly, for a mixture with $CO_2 : N_2 = 1 : 10$ we obtain expression (12) at $\omega/2\pi \ll 25$ kHz and (13) at $\omega/2\pi \gg 90$ kHz.

If we retain from the entire set of reactions only (1) and (3)–(5), which have the largest rates, then expression (12) for $\omega/2\pi \ll 25$ kHz can be reduced to the form

$$\operatorname{tg}\varphi = \frac{\omega}{P}\left[\frac{X_{CO_2} + X_{N_2} k_4'/k_{-4}'}{k_1' X_{CO_2}^2 + X_{N_2} X_{CO_2} (k_3' + k_5' k_4'/k_{-4}')}\right], \tag{14}$$

where P is the pressure of the investigated gas [Torr], k′ is the constant of the reaction rate (Torr^{-1} sec^{-1}) and X is the molar fraction of the gas. Thus, by experimentally measuring the phase shift φ, we can obtain from (14), at a definite frequency ω, information concerning the processes that influence the population of the 00^01 level.

In the present investigation, the driving-force frequency was $\omega/2\pi \sim (0.5–3)$ kHz, so that the results for $CO_2 : N_2$ were reduced in accordance with formula (14). In the case of the CO_2-He and CO_2-H_2O mixtures, the processes leading to the change of the population of the level 00^01 are nonresonant and the recalculation for the binary mixture is carried out in accordance with the formula

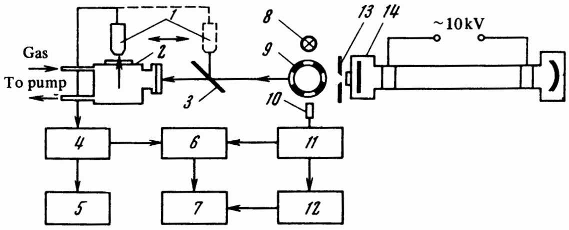
$$\operatorname{tg}\varphi = \frac{\omega}{P}\,\frac{1}{k'_{CO_2-CO_2} X_{CO_2} + (1 - X_{CO_2})\, k'_{CO_2-x}}, \tag{15}$$

where x denotes the gas in which the CO_2 relaxes.

3. EXPERIMENTAL SETUP AND PROCEDURE

The experiment was performed with a setup developed by Konyukhov and co-workers, in accordance with a procedure proposed by them in[1]. In our investigation this setup was modernized and its final variant is shown in the figure. The main units are: a CO_2 laser with a power output on the order of 10 W at $\lambda \approx 10.6\ \mu$, a Ge + Au radiation receiver with threshold sensitivity 2.2×10^{-10} W/Hz$^{1/2}$, a working cell placed in a thermostat, and a phase-measuring network.

The modulated CO_2-laser radiation in the (00^01–10^00) band of CO_2 was absorbed in the cell with the investigated CO_2 (pure or mixed with other gases) and excited the 00^01 vibrational level of CO_2. The radiation intensity at $\lambda \approx 4.3\ \mu$ from this level changes periodically at the same modulation frequency, but with a phase shift relative to the modulated laser radiation. By measuring this shift, it is easy to obtain from (14) the constant of the reaction rate k_{CO_2-x}. We note that at a laser output power on the order of 10 W, the deviation of the CO_2 population at the 00^01 level from equilibrium is small and the relation (14) is valid under the conditions of our experiment. All the investigations were performed in specially dried gases of special purity. To prevent entrance of random impurities, all the measurements were made with the investigated gas flowing through the cell at a low rate. The temperature of the gas inside the cell varied through ±2°C, which did not affect the measured relaxation time within the limits of the permissible measurement error. We measured the time of vibrational relaxation of CO_2 in pure CO_2 and in CO_2 mixed with N_2, ^{4}He and H_2O at T = 300°K. The CO_2 content in the mixtures with N_2 and He was ~ 9%; the $CO_2 : H_2O$ mixture contained 5×10^3 ppm of H_2O. The pressure of the investigated gas in the cell ranged from 20 to 350 Torr.



Block diagram of setup: 1–Ge:Au receiver, 2–cell, 3–mirror, 4–U2-6 amplifier, 5–41-5 frequency meter, 6–K3-2 synchronous detector, 7–F2-1 phase meter, 8–incandescent lamp, 9–shutter, 10–FD-3 photodiode, 11–U2-6 amplifier, 12–phase shifter, 13–slit, 14–CO_2 laser.

4. RESULTS

The measurement results are presented in the form of the reaction-rate constants $[k_{CO_2-x}]$ = sec^{-1} Torr^{-1} in the table. The table also lists the data published in the periodic literature. It is seen from the table that our results are in good agreement with the data obtained by the pulsed excitation method[3]. Measurements performed with the aid of a "spectrophone"[5,6] give values $k_{CO_2-CO_2}$ that differ by an approximate factor 1.5. The results of[6] are in better agreement with our data, but

$k_{CO_2-CO_2}$	$k_{CO_2-N_2}$	k_{CO_2-He}	$k_{CO_2-H_2O}$	Reference
411 ± 14	—	—	—	[1]
385 ± 40	—	—	—	[2]
350 ± 9	106 ± 8	84 ± 6	$(2.4 \pm 0.9) \cdot 10^4$	[3]
385	—	—	—	[4]
188 ± 13	—	—	—	[5]
321 ± 72	—	—	—	[6]
—	185	—	—	[7]
—	—	—	$(3.1 \pm 0.2) \cdot 10^4$	[8]
—	—	—	$2.8 \cdot 10^4$	[9]
354 ± 14	145 ± 20	87 ± 15	$(1.7 \pm 0.9) \cdot 10^4$	Our data

it should be noted that in this case $k_{CO_2-CO_2}$ is subject to a considerable error. The "spectrophone" method was used to measure $k_{CO_2-N_2}$ in[7]. Some discrepancy in the value of $k_{CO_2-CO_2}$ obtained in[1] by an analogous method should be attributed mostly to uncontrollable H_2O impurities. In our experiments, the H_2O content in the gas mixtures was less than 100 ppm and, according to simple calculations, had no influence on the measured reaction-rate constant within the limits of the permissible measurement errors. It is of interest to note that our results are in satisfactory agreement with the data obtained by the method of amplification of laser emission in the afterglow[4]. Within the limits of error, our measurements coincide with the values of $k_{CO_2-H_2O}$ obtained in[3,8,9] by the pulsed excitation method.

The good agreement between the values of $k_{CO_2-CO_2}$ and k_{CO_2-X} obtained by the phase method and the values obtained in[3,4,8,9] indicates that the phase method of measurements is reliable.

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[1] V. K. Konyukhov, V. V. Korogod, and V. I. Tikhonov, Zh. prikl. spektr. 10, 252 (1969).

[2] L. O. Hocker, M. A. Kovacs, C. K. Rhodes, G. W. Flynn, and A. Javan, Phys. Rev. Lett., 17, 233, 1966.

[3] C. B. Moore, R. E. Wood, Bei-Lok Hu, J. T. Yardley, J. Chem. Phys., 46, 4222, 1967.

[4] P. K. Cheo, J. Appl. Phys., 38, 3563, 1967.

[5] T. L. Cottrell, J. M. Macfarlane, A. W. Read, and A. H. Young, Trans. Farad. Soc., 62, 2655, 1966.

[6] P. V. Slobodskaya, Opt. spektr. 22, 29 (1967).

[7] T. L. Cottrell, J. M. Macfarlane, and A. W. Read, Trans. Farad. Soc., 63, 2093, 1967.

[8] D. E. Heller and C. B. Moore, J. Chem. Phys., to be published, 1970.

[9] W. A. Rosser, Jr., and E. T. Gerry, J. Chem. Phys. 51, 2286, 1969.

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