KINETIC PROCESSES IN THE LOWER LEVELS OF THE CO$_2$ MOLECULE

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1. Detailed information on processes leading to relaxation of the level populations in the symmetric and bending modes of CO$_2$ molecules is important for the theoretical study of amplification and generation in long-wavelength transitions of CO$_2$, the generation of short pulses of radiation at 10.6 and 9.6 μm, and several other problems. The individual groups of levels in these modes are perturbed as a result of the Fermi resonance; hence, these are frequently called coupled modes. At the present time, calculating the rate constants for the numerous processes in the coupled-mode system cannot by itself pretend to yield quantitative results. There are a number of papers involving experimental research on the dynamics of the process by which equilibrium is established in the lower levels following a transient perturbation of the population in one of them [1-9]. In [1, 5, 6], following saturation of the transitions in either the 9.4- or 10.4-μm band by a short pulse, a change in the absorption coefficient was observed in the other of these bands; in [7], fluorescence was observed between wavelengths of 15.48 and 16.92 μm. In [2-4], the time required for generation in the 9.4- and 10.4-μm bands to cease after turning off the pump was measured. In [8], the absorption in the transitions of several bands in the 4.3-μm region was measured using a tunable probe laser; this allowed the dynamics of the populations of several lower levels to be studied directly. In [9], the excess population of several of the lower levels relative to the equilibrium value in two-photon Raman excitation of CO$_2$ was studied as a function of pressure.

The interpretation of the experimental results is complex and, in some cases, nonunique. For example, the experiments on the cessation of generation are complicated by nonlinear and threshold effects in the generation process and, in [4], by rotational relaxation effects. The possibility of two-photon interaction processes between the saturating and probe beams [10] could not be excluded in [1, 5]. It is important to emphasize that it is difficult to interpret the results in [1-7] directly; one result of this was that the measured time constants were converted into rate constants for the individual processes on insufficient grounds For the reasons just mentioned, there is a significant difference between the results of the various studies.

A method for calculating the amplification in transitions between coupled modes in CO$_2$ during the expansion of a heated gas based on solving a system of kinetic equations for the populations of all levels located below 5000 cm^{-1} was described in detail in [11]. The correlations between the rate constants for individual processes following from general theoretical considerations were used in this system of equations. This allows one to obtain a relation between the experimentally measured time constants for changes in the individual level populations and the rate constants for a large number of processes not directly measured. The purpose of the present work is to carry out a numerical analysis of the most important experimental research on the dynamics of the establishment of equilibrium in the lower levels of the CO$_2$ molecule in order to show that it is possible to interpret them in a unified fashio Moreover, the good agreement between calculation and experiment provides a good basis for the theoretical assumptions used in [11].

2. It is known from the theory of vibrational relaxation (see, for example, [12]) that the rate constants for VV and VT processes are proportional to the squares of the matrix elements for the operators describing the interactions which lead to the corresponding transitions, and the adiabatic functions which depend on the energy defect of the process, and the temperatures and parameters of the colliding molecules. Unlike the antisymmetric mode, the radiational transitions between the levels of the coupled modes are not strong and, following [10], it can be assumed that both the nearly resonant collisional processes between these modes and the nonresonant processes are the result of short-range forces which call off exponentially with distance, and that the contribution of the long-range multipole forces is

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TABLE 1

vlui	0001	1001	2002	2201	2001	3102	3301	3101
1001	p							
2002	0	$0{,}5p$						
2201	0	$2p$	p^2					
2001	0	$0{,}5p$	p^2	p^2				
3102	0	0	$1{,}46p$	$0{,}5p$	$0{,}04p$			
3301	0	0	0	$3p$	0	$1{,}5p^2$		
3101	0	0	$0{,}04p$	$0{,}5p$	$1{,}46p$	p^2	$1{,}5p^2$	
4003	0	0	0	0	0	$1{,}16p$	0	$0{,}01p$
4202	0	0	0	0	0	$2{,}48p$	$0{,}5p$	$0{,}02p$
4002	0	0	0	0	0	$0{,}33p$	0	$0{,}33p$
4401	0	0	0	0	0	0	$4p$	0
4201	0	0	0	0	0	$0{,}02p$	$0{,}5p$	$2{,}48p$
4001	0	0	0	0	0	$0{,}01p$	0	$1{,}16p$

considerably weaker. In this case, the matrix elements of the interaction operator are proportional to powers of a small parameter equal to the ratio of the amplitude of the oscillations to the range of the exponential potential, and the most probable type of transition between the levels of the coupled modes will be transitions with a change in vibratory momentum $|\Delta \ell| \leqq 2$ between levels that are close in energy; of the nonresonance transitions, those with a quantum-number change of 1 will be the most probable. Thus, the VV and VT processes between levels in the coupled modes,

$$\begin{gathered} CO_2(v_1 l_1 u_1 i) + CO_2(v_2 l_2 u_2 j) \to \\ \to CO_2(v_1+1,\ l_1 \pm 1,\ u_1 m) + CO_2(v_2 - 1,\ l_2 \pm 1,\ u_2 k); \end{gathered} \tag{2.1}$$

$$CO_2(vlui) + M \to CO_2(vluj) + M; \tag{2.2}$$

$$CO_2(vlui) + M \to CO_2(v,\ l \pm 2,\ uj) + M; \tag{2.3}$$

$$CO_2(vlui) + M \to CO_2(v-1,\ l \pm 1,\ uj) + M \tag{2.4}$$

and the VV and VT processes in which the antisymmetric mode takes part,

$$\begin{gathered} CO_2(v_1 l_1 u_1 i) + CO_2(v_2 l_2 u_2 j) \to \\ \to CO_2(v_1 l_1,\ u_1 - 1,\ i) + CO_2(v_2 l_2,\ u_2 + 1,\ j); \end{gathered} \tag{2.5}$$

$$CO_2(v_1 l_1 u i) + M \to CO_2(v_2 l_2,\ u - 1,\ j),\ u = 1, 2,\ |l_1 - l_2| \leqslant 1, \tag{2.6}$$

were taken into account in the kinetic equations for the level populations of the CO_2 molecule. In (2.1)-(2.6), we have designated the energy levels of the coupled modes using the quantum number of the bending mode v and the vibrational angular momentum ℓ in the group of levels that are similar in energy; levels with identical angular momentum are shifted by the Fermi resonance and form multiplets; i is the number of the level within the multiplet, beginning with the highest, and u is the quantum number for the antisymmetric mode.

The adiabaticity function calculated from the parameters of the colliding molecules is frequently in poor agreement with experimental data. It is possible to reduce the role of this defect in the theory by using experimental results extensively where possible. With this aim in view, an adiabaticity function which follows from very general theoretical ideas [13, 14] and depends mainly on the energy defect of the process ΔE,

$$F(M,\ \Delta E) = A(M,\ \Delta E/2kT)\exp(-\lambda_i(M)|\Delta E|),$$

was used: [$A(M, x) = (x^2/2)K_3(x)e^x$ in the case where M = Ar, He, and $A(M, x) = (x^3/8)K_3(x) \cdot e^x$ in the case where $M = CO_2$ and N_2; the $K_n(x)$ are modified Bessel functions of order n (i = 2 for the coupled modes and i = 3 for the antisymmetric mode)]. The rate constants for processes (2.1) and (2.2)-(2.4) were calculated using the equations

$$k(2.1) = \frac{k_2(CO_2)}{g_2(CO_2)} F(CO_2,\ \Delta E) \frac{L(v_1 l_1 u_1 i \to v_1 + 1,\ l_1 \pm 1,\ u_1 m)}{\sigma(l_1 \to l_1 \pm 1)} \frac{L(v_2 l_2 u_2 j \to v_2 - 1,\ l_2 \pm 1,\ u_2 k)}{\sigma(l_2 \to l_2 \pm 1)}, \tag{2.7}$$

and

$$k((2.2)-(2.4), M)=\frac{k_2(M)}{g_2(M)}F(M, \Delta E)\frac{L(v_1 l_1 ui \to v_2 l_2 uj)}{\sigma(l_1 \to l_2)}, \quad (2.8)$$

respectively, where $L(v_1 \ell_1 ui \to v_2 \ell uj)$ is the square of the interaction operator matrix element, $\sigma(\ell_1 \to \ell_2) = 1$ for $\ell_1 = 0$ or $\ell_2 = 0$ [otherwise, $\sigma(\ell_1 \to \ell_2) = 2$]. The parameters $\lambda_2(M)$ and $g_2(M)$ were determined in the following way: In the processes $CO_2(1101) + M \to CO_2(0001) + M$, we must obtain the rate constants $k_2(M)$ known from experiment (numerous experimental references and the approximate expressions used are given in [11]), and the calculation of the dynamics of the changes in the populations of the individual levels should yield the time constants measured in the experimental references (see, for example, [6]). The matrix elements were calculated using the wave functions for the states including the Fermi resonance. The squares of their relative values are given in Table 1, where p is a parameter equal to the square of the ratio of the amplitude of the oscillations in the bending mode to the range of the exponential potential and is defined as in [15].

We can now write the rate constants for the processes in (2.6) as follows:

$$k((2.6), M)=u\frac{k_3(M)}{g_3(M)}F(M, \Delta E).$$

The exponential factors $\lambda_3(M)$ can be calculated from the condition that they agree with the results in [15] at T = 300°K. Summing the rate constants for the processes (0011) → ($v\ell 0i$) over all channels should yield the experimentally determined rate constants for the relaxation of the antisymmetric mode, for which approximate expressions are given in [11]. From this, the normalization coefficients $g_3(M)$ were determined. The rate constants for processes (2.5) were given in the form

$$k(2.5) = 3.4\cdot 10^4 (u_2 + 1) u_1 (300/T)^{3/2}\ \text{sec}^{-1}\ \text{Pa}^{-1}.$$

3. Of the works on measuring the absorption in the 9.4-μm band after transmission of a saturating pulse in the 10.4-μm band, [6] should be singled out. In this work, a pulse of radiation 2 nsec in length in several rotational transitions in the 10.4-μm band (P12–P22) was passed through a cell containing a $CO_2/N_2/He$ mix with various concentration ratios at a temperature of 373°K, and the variation in the transmission coefficient in the P24 transition in the 9.4-μm band was observed. The short pulse duration allowed the vibrational relaxation processes in the lower levels to be separated from two-photon processes, rotational relaxation, and VV exchange in the asymmetric mode. Several stages in the absorption variation were identified as a result of the measurements: a brief decreasing-absorption stage with time constant τ which immediately followed the termination of the pulse and the end of rotational relaxation and VV-exchange in the antisymmetric mode, and a stage with a significantly slower increase in absorption. Jacobs, Pettipiece, and Thomas [6] reported that 1/τ depends on the partial pressures of the components and obtained values of $1/\tau_{CO_2} = (2.25 \pm 0.75)\cdot 10^3\ \text{sec}^{-1}\cdot\text{Pa}^{-1}$, $1/\tau_{N_2} = (2.25 \pm 0.75)\cdot 10^3\ \text{sec}^{-1}\cdot\text{Pa}^{-1}$, and $1/\tau_{He} = (0.6 \pm 0.2)\cdot 10^3\ \text{sec}^{-1}\cdot\text{Pa}^{-1}$. These frequencies were identified with the rate constants for the processes

$$CO_2(2002) + M \rightleftarrows CO_2(2001) + M. \quad (3.1)$$

The system of kinetic equations for the CO_2 level populations was solved with initial conditions corresponding to saturation of the 10.4-μm band in order to analyze this experiment. The variation in the transmission coefficient obtained as a result of the calculation for a CO_2 pressure of 6.6 kPa is shown in Fig. 1a. Rotational relaxation was not taken into ac-

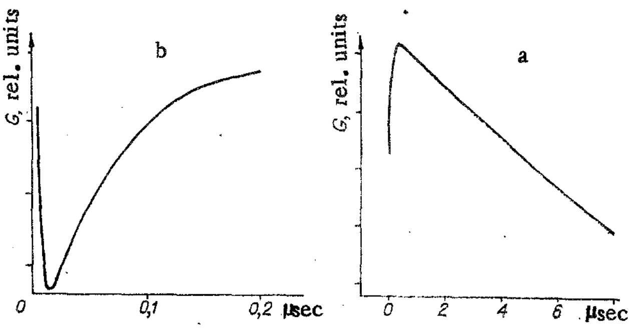

Fig. 1

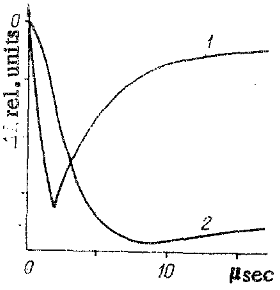

Fig. 2

count in the calculations; the decrease in the transmission in Fig. 1b can be explained by VV exchange in the antisymmetric mode. With the exception of this initial portion where the transmission is decreased, the dynamics of the transmission in the 9.4-μm band is described well by the expression

$$G(t) = A + B \exp(-t/\tau) + C \exp(-\alpha t), \tag{3.2}$$

in which the index α describes the increase in absorption a fairly long time after the saturating pulse. Using (3.2) to approximate the results of similar computations for $CO_2/N_2/He$ mixes of various composition, we obtain the values of the frequencies $1/\tau = pCO_2/\tau CO_2 + pN_2/\tau N_2 + pHe/\tau He$ recommended in [6] if the following rate constants are used for the reverse processes in (3.1): 360 $sec^{-1}\cdot Pa^{-1}$ for CO_2, 450 $sec^{-1}\cdot Pa^{-1}$ for nitrogen, and 100 $sec^{-1}\cdot Pa^{-1}$ for helium. Then the slow stage with the onset of absorption observed in [6] is obtained without using additional assumptions about the nature of the processes between the coupled-mode levels. The two-stage nature of the variation in absorption is determined by the entire set of processes in (2.1)-(2.3), and mainly by those involving the lower coupled-mode levels. The measured time constants cannot be assigned to any one of these processes.

Of course, a numerical result from just one experiment does not allow one to establish the extent to which the values given for the rate constants for processes (3.1) are reliable. They depend to a great extent on the way in which the rate constants for all of the processes in (2.1)-(2.3) are correlated. In this context, it is important to analyze other work as well.

In [7], a pulse of radiation 2 μsec in duration at 9.6 μm or 10.6 μm was transmitted through CO_2 at a pressure of 100 Pa and a temperature of 300°K. The fluorescence intensity was recorded over the 15.48-16.92-μm region, but the individual bands in this spectral region were not resolved. A rapid decrease in the fluorescence intensity was observed during the pulse at 9.6 μm because of the depopulation of level 2002; later, the initial state was restored – rapidly at first (with a time constant $1/\tau = (2.9 \pm 0.6)\cdot 10^3$ $sec^{-1}\cdot Pa^{-1}$, and then slowly. The fluorescence varied at characteristic frequencies greater than $75\cdot 10^3$ $sec^{-1}\cdot Pa^{-1}$ during the 10.6-μm pulse; following this, a weak, slow variation was observed. Huddleston and Weitz [7] proposed that the short time constant refers to processes similar to (3.1), while the longer time constant characterizes VV coupled-mode exchange.

The numerical modeling carried out above (which included all of the kinetic processes mentioned above), together with the radiational transition probabilities, completely explained the observed picture. The calculated variation of the fluorescence in the spectral region given in [7] for the transmission of a pulse at 9.6 and 10.6 μm is shown in Fig. 2 (curves 1 and 2, respectively). Quantitative agreement with the measured time constant for curve 1 is obtained for a rate constant of 390 $sec^{-1}\cdot Pa^{-1}$ for the reverse reaction in (3.1). A numerical analysis of the section of curve 2 immediately following the end of the pulse of radiation using the method of least squares indicated that it could not be approximated well by an exponential law, but that the characteristic time scale on which the fluorescence varied in this section is of order 10^4 $sec^{-1}\cdot Pa^{-1}$. On the whole, curve 2 is in qualitative agreement with experiment. Thus, it is not necessary to assume that the value of order $7.5\cdot 10^3$ $sec^{-1}\cdot Pa^{-1}$ refers to the processes in (3.1) while the value of order $3\cdot 10^3$ characterizes the VV coupled-mode exchange to explain the experimental results from the excitation of fluorescence by radiation at 9.6 and 10.6 μm. The authors themselves [7] came to the conclusion that, under their assumptions, it is difficult to explain the results of the experiment with excitation at 10.6 μm. Just as in [6], the measured time constants characterize the entire set of processes (2.1)-(2.3) involving the lower coupled-mode levels.

The influence of argon on the time constant of the variation in the fluorescence turned out to be weak all the way up to a partial pressure of 1.2 kPa for a fixed CO_2 pressure of 100 Pa. The calculations for a $CO_2:Ar = 0.75:8$ mix indicated that when a ratio of 0.07 is chosen for the rate constants in reactions (3.1) for argon and CO_2, the time constant changes by 19% compared with pure CO_2, which is within the limits of experimental error. It can hence be concluded that the ratio of the rate constants mentioned above for argon and CO_2 is no greater than 0.07.

In [9], the excess populations (relative to the equilibrium population at a temperature of 300°K) of several levels populated by collisions in the two-frequency excitation of states 2001 and 2002 were measured as a function of CO_2 pressure using active Raman-scattering spec-

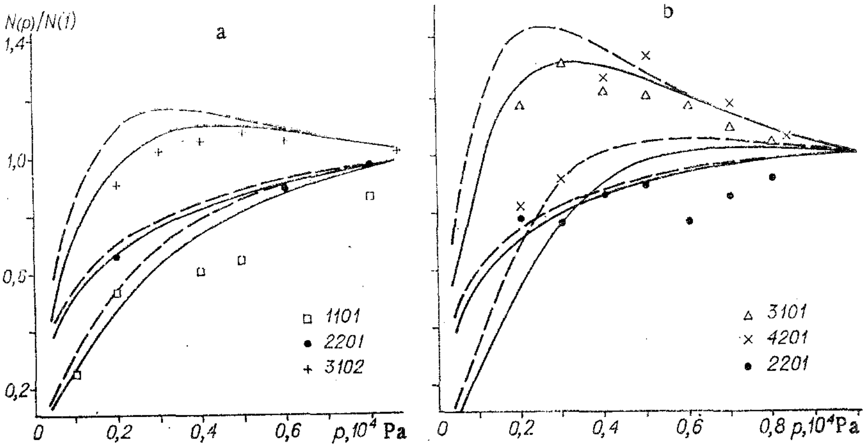

Fig. 3

TABLE 2

Rate constant	Process	[8] $T=280$ K	[6]* $T=373$ K	[7]* $T=300$ K	[9]* $T=300$ K	[10] $T=300$ K
k_0 ($sec^{-1} \cdot Pa$)	$(2001)+CO_2 \rightarrow$ $\rightarrow (2002)+CO_2$	360±60	360	390	315	550
k/k_0	$(2001)+CO_2 \rightarrow$ $\rightarrow (2201)+CO_2$	1,67	2,16	2,22	2,18	1,08
k/k_0	$(1101)+(1101) \rightarrow$ $\rightarrow (2001)+(0001)$	0,94	0,93	0,91	0,92	0,35
k/k_0	$(1101)+(1101) \rightarrow$ $\rightarrow (2201)+(0001)$	8,4	9,8	10,4	10	3,7

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*Results of the numerical analysis carried out in the present work.

TABLE 3

M	[8] $T=280$ K	[6]* $T=373$ K	[7]* $T=300$ K	[5] $T=400$ K	[16] $T=300$ K	[17] $T=300$ K
He	0,12	0,33	—	0,054	—	0,91
Ne	—	—	—	—	0,47	0,3
Ar	—	—	0,07	—	—	0,17
Kr	—	—	—	—	—	0,17
Xe	—	—	—	—	—	0,15
N_2	0,12	1,25	—	0,46	—	0,35

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*Results of the numerical analysis carried out in the present work.

troscopy. The method possesses high spectral resolution, and allows the populations of individual levels to be easily measured. However, the dynamics of the populations were not measured; because of this, only estimated values of the rate coefficients were given; in particular, the rate constant for process (3.1) was estimated to be less than 525 $sec^{-1} \cdot Pa^{-1}$. No signs that reactions of the type

$$(2001)+(2001) \rightarrow (4001)+(0001),\ (2002)+(2002) \rightarrow (4003)+(0001)$$

occur were observed in the experiments, even though they have small energy defects, and the concentration of excited molecules was sufficient for observing them. The fact that these processes are absent can be explained by the smallness of the corresponding matrix elements of the interaction operator, and indicates that we may restrict ourselves to only taking processes (2.1)-(2.3) into account in the calculations. The experimental data on the populations of several levels immediately allows not only the value of the rate constant for (3.1) to be estimated, but also allows conclusions about the ratios of the rate constants for the various processes to be made.

The calculated and experimental pressure dependences for the excess populations in two-frequency Raman excitation of levels, 2002 (a) and 2001 (b) are shown in Fig. 3. The calculated curves are for a time of 20 nsec and rectangular pump pulses which ensure, just as in the experiment, that the pump efficiency (per molecule) remains constant as the pressure varies. The dashed lines are the results of the calculation for rate constants of 390 $sec^{-1} \cdot Pa^{-1}$ for the reverse reaction in (3.1), and the solid lines are those for 315 $sec^{-1} \cdot Pa^{-1}$. In the latter case, the majority of the experimental and calculated results are in very good agreement. Thus, the ratios between the rates for processes (2.1)-(2.3) (which in fact determine the pressure dependence of the populations) allow us to describe correctly the population dynamics of multiplets with at least three quantum numbers. The reasons for the marked difference between the calculated and experimental results for the population of level 4201 remains unclear.

The ratio of the squares of the matrix elements of the first- and second-order terms in the expansion of the interaction potential in terms of the normal coordinate for the bending mode (the parameter p in Table 1) were determined from theoretical considerations [10, 15]. The effects of this parameter turn out to be weak because we have used experimental information on kinetic processes with large and small energy defects. Thus, a change by a factor of two in the value of p when analyzing the experiments in [7] led to a change of 5% in the rate constants for process (3.1), and the influence of this parameter on the calculated level populations in the experiments turned out to be even smaller in [9].

4. The rate constants for VV and VT processes in the system of lower levels of CO_2 were determined in [8]. The absorption in several ($v\ell uk$) → ($v\ell$, $u + 1$, k) transitions in the 4.3-μm region after restoration of the inversion in the 10.4-μm band with a short pulse of radiation was measured with the use of a tunable laser. The gas was excited in an electrical discharge. The rate constants were determined via a mathematical analysis of the dynamics of the populations of the 2001, 2002, 2001, and 1101 levels using a six-level model in which the 0011 and 0001 levels were also taken into account. A comparison of the results from [8] and the results of the analysis of experiments [6, 7, 9] carried out above, and the results of a calculation of the rate constants within the framework of the theory of vibrational relaxation under the action of the short-range forces [10] is shown in Table 2. Evidently, the rate constants obtained in [8] for the four processes involving CO_2 molecules and those obtained from the mathematical analysis [6, 7, 9] agree with one another to within 20%, which is less than the measurement errors. Thus, it can be concluded that the large scatter in the measured rate constants for the processes in the lower levels of the CO_2 molecule is due to the interpretation of the results, and not possible measurement errors.

At present, the information on the rate constants of processes (3.1) for collisions with other molecules and inert-gas atoms is extremely limited. The rate constants for the reverse processes in (3.1) for various collision partners, normalized to the corresponding rate constant for CO_2, are given in Table 3. For comparison, the results of research on the vibrational relaxation of N_2O molecules using a spectrophone [17] (rate constants for various collision partners normalized to the rate constant for N_2O) are given in the last column. The decrease in the rate constant with increasing mass of collision parter observed in [17] is in qualitative agreement with the Schwartz-Slavsky-Herzfeld theory, but is weaker. The picture should probably be similar for CO_2. From this point of view, the results for nitrogen in [8] are preferable to those in [6].

On the whole, results [6-9] and the analysis carried out above for these results lead us to recommend a rate constant of 360 $sec^{-1} \cdot Pa^{-1}$ for the process CO_2 (2001) + CO_2 → CO_2 (2002) + CO_2, and correlation of the rate constants of processes (2.1)-(2.3) as outlined in Eqs. (2.7) and (2.8) for detailed calculations of the level populations of CO_2 molecules.

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