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FEATURES OF VIBRATIONAL RELAXATION OF THE SYSTEM OF LOW CO_2 MOLECULE LEVELS

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By using numerical computations and analytic solutions, the vibrational relaxation of the system of low CO_2 molecule levels is studied. The examination is on the basis of level-by-level kinetics in the range of initial pressures and translational temperatures characteristic for a number of experimental papers in which the rate of energy transfer between symmetric longitudinal and deformation vibrations was determined. The nonmonotonicity of the behavior of the vibrational level populations with time is clarified and the domains of their variation are indicated in which the determination of the energy transfer rate constant is possible in the individual relaxation channels.

1. Because of the strong Fermi resonance between symmetric and deformation vibrations of CO_2 molecules, the equidistance of the energetic spectrum already turns out to be spoiled for the lowest levels. This results in anharmony of the vibrations and is the reason for the high rate of vibrational exchange between the modes ν_1 and ν_2, where ν_1 is the notation of the symmetric valence, and ν_2 of the symmetric deformation vibrations. Experimental investigations have clarified the substantial spread (more than two orders of magnitude) in the magnitude of the rate constants for this exchange, as has repeatedly been mentioned in the literature (see [1], for example). Theoretical computations of the transfer rate on the basis of the Shvarts—Slavsky—Herzfeld theory [2, 3] result in large values. Computations on the basis of taking account of long-range attractive forces in the Born approximation [4] yield a value for the transition probability of the vibrational energy between the modes ν_1 and ν_2 that is an order greater than in [2]. High theoretical values of the transfer probabilities between the modes ν_1, ν_2 would seem to permit the assumption of local equilibrium between the symmetric and deformation vibrations. However, such low values of the probability of this transfer have been obtained in a number of experimental papers, that the assumption of local equilibrium must be rejected.

On the basis of processing a set of experimental papers, a set of energy transfer constants was proposed in [5] for a system of low CO_2 molecule levels. However, here assumptions were made which significantly simplified the relaxation process; for instance, it was assumed in advance that the exchange process between Fermi-perturbed levels proceeds at the highest rate. In order to eliminate a number of a priori assumptions about the kinetics of the exchange processes between the modes ν_1 and ν_2, computations of the populations of the individual vibrational levels of the CO_2 molecules were performed in this paper on the basis of level-by-level kinetics with all the fundamental relaxation channels taken into account and by using the theoretical values of the transition probabilities taken from [3, 4].

2. The scheme for the vibrational levels of the CO_2 molecule that are henceforth considered is represented in Fig. 1. The digit 1 denotes the energy level corresponding to double the value of the energy of the level 01^10, i.e., the level with the energy 1334.9 cm^{-1}, 2 is the level with mixed wave functions $(10^00,02^00)^{I}$ because of Fermi resonance (according to the terminology in [2]), and with the energy 1285.7 cm^{-1}, 3 is the level $(10^00,02^00)^{II}$

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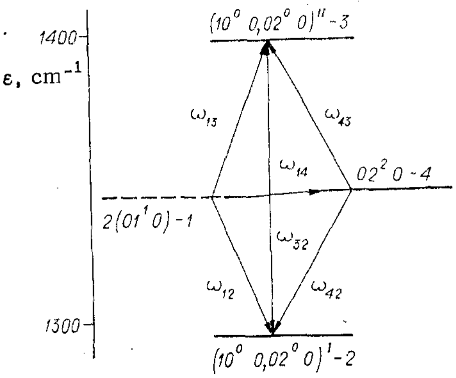

Fig. 1

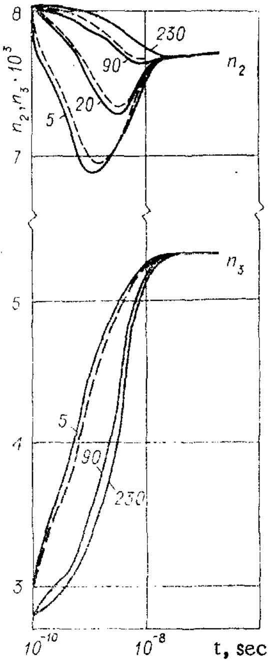

Fig. 2

with the energy 1388.5 cm^{-1}, and 4 is the level 02^20 with the energy 1335.8 cm^{-1}. Henceforth, we shall examine molecules in some quantum state $v_1v_2^lv_3$ as a separate species of gas. The CO$_2$ gas under consideration can be represented in the form of a mixture of gases between whose components the following reactions will occur:

$$(10^00,\ 02^00)^{\text{I}} + (00^00) \rightleftarrows (10^00,\ 02^00)^{\text{II}} + (00^00) - 102{,}8\ \text{cm}^{-1}; \tag{2.1}$$

$$(01^10) + (01^10) \rightleftarrows (10^00,\ 02^00)^{\text{II}} + (00^00) - 53{,}7\ \text{cm}^{-1}; \tag{2.2}$$

$$(02^20) + (00^00) \rightleftarrows (10^00,\ 02^00)^{\text{II}} + (00^00) - 52.7\,\text{cm}^{-1}; \tag{2.3}$$

$$(01^10) + (01^10) \rightleftarrows (02^20) + (00^00) - 1\ \text{cm}^{-1}; \tag{2.4}$$

$$(01^10) + (01^10) \rightleftarrows (10^00,\ 02^00)^{\text{I}} + (00^00) + 49{,}1\ \text{cm}^{-1}; \tag{2.5}$$

$$(02^20) + (00^00) \rightleftarrows (10^00,\ 02^00)^{\text{I}} + (00^00) + 50{,}1\ \text{cm}^{-1}. \tag{2.6}$$

We later examine experiments in which the change in the gain of a weak signal with wavelength 9.6 μm or 10.6 μm is fixed after one is saturated. For example, a pulse with wavelength 10.6 μm resulting in saturation of the transition 00°1-(10°0, 02°0)$^{\text{II}}$ was passed through a CO$_2$-filled absorption cell heated to 100°C in [6]. Consequently the population of the level (10°0, 02°0)$^{\text{II}}$ diminished and the vibrational relaxation process started, which then were determined by using the time behavior of a signal with the wavelength 9.6 μm. Since little energy is dissipated during perturbing radiation on the order of $2 \cdot 10^{-9}$ sec, the active degrees of freedom remain practically unchanged, and since the fast vibrational relaxation stage is quasiresonant in nature, then the translational temperature does not change during its course. The total store of vibrational CO$_2$ quanta at the initial moment does not change in this experiment, while only level 3 turns out to be depleted in the system of levels in Fig. 1, where it is depleted by the quantity $\alpha = n_3^b/n_3\ (t = 0) \leq 0.5$ (n_3^b is the Boltzmann population of the level (10°0, 02°0)$^{\text{II}}$ prior to inclusion of the perturbing radiation, normalized at the numerical density of the CO$_2$ gas).

Taking into account that the quantity n_3^b is of the order $2.8 \cdot 10^{-3}$ at T = 400°K, it can be expected that the total perturbation of the population of the CO$_2$ low-level system is not large in the first stage prior to the beginning of the vibrational translational relaxation, and the solution of the system of kinetic equations describing the vibrational—vibrational exchange is sought in a linear formulation [5, 7].

Therefore, the experiment [6] can be described by using the following model: A Boltzmann distribution over the vibrational—rotational levels exists in a system of low levels of CO$_2$ molecules that is not initially perturbed; a perturbation with the wavelength 10.6 μm instantaneously depletes the level (10°0, 02°0)$^{\text{II}}$ whereupon vibrational—vibrational relaxation starts, where the distribution over the rotational levels is again already a Boltzmann distribution.

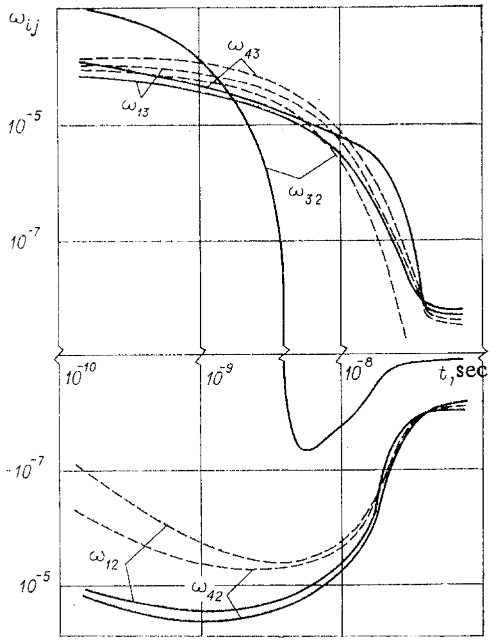

Fig. 3

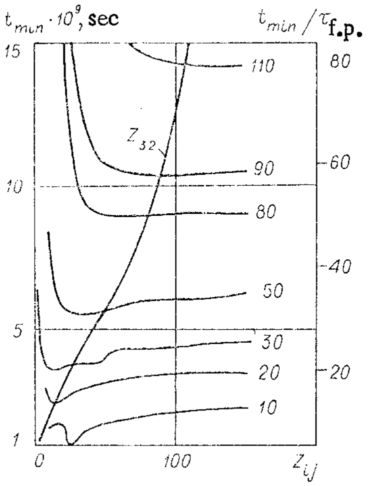

Fig. 4

3. The system of kinetic equations describing the vibrational relaxation process has the form

$$dn_0/d\bar{t} = -\omega_{12} - \omega_{13} - \omega_{14},\quad dn_1/d\bar{t} = 2\omega_{12} + 2\omega_{13} + 2\omega_{14},$$
$$dn_2/d\bar{t} = -\omega_{12} - \omega_{42} - \omega_{32},\quad dn_3/d\bar{t} = -\omega_{13} - \omega_{43} + \omega_{32},$$
$$dn_4/d\bar{t} = -\omega_{14} + \omega_{42} + \omega_{43}, \tag{3.1}$$

where n_0 is the normalized number density of the level (00°0), n_1 of the level (01^10), n_2 of the level $(10°0,\ 02°0)^{I}$, n_3 of the level $(10°0,\ 02°0)^{II}$, n_4 of the level (02^20), respectively:

$$\omega_{ij} = \frac{1}{Z_{ij}}\left[n_j n_k \frac{g_M g_i}{g_j g_k}\exp\left(\frac{\Delta\varepsilon_{ij}}{kT}\right) - n_M n_i\right];$$

g_i is the degree of degeneration of the level i, $1/Z_{ij} = P_{ij}$ is the transition probability from the level i to the level j, $\bar{t} = t/\tau_{f.p.}$; $\tau_{f.p.}$ is the free-path time.

We shall seek the solution of the system (3.1) in the form

$$n_i = n_i(t=0) + n_i',\ T = T_0 + T',\ \rho = \rho_0 + \rho'.$$

Here the energy conservation equation is converted to the form

$$\frac{T'}{T_0} = -\frac{2}{5}\frac{(\Theta_2 - 2\Theta_1)}{T_0}n_2' - \frac{2}{5}\frac{(\Theta_3 - 2\Theta_1)}{T_0}n_3' - \frac{(\Theta_4 - 2\Theta_1)}{T_0}n_4' \ll 1.$$

Since $T_0 = 400°K$, $\Theta_2 - 2\Theta_1 = -70.6°K$, $\Theta_3 - 2\Theta_1 = +76.8°K$, $\Theta_4 - 2\Theta_1 = +1.4°K$, then in a first approximation the temperature change can be neglected.

Using the first two integrals [7] of system (3.1) we reduce it to the form

$$\frac{dn_i'}{d\bar{t}} = \sum_{j=2}^{4} A_{ij} n_j' + A_i \quad (i = 2, 3, 4), \tag{3.2}$$

where $A_{ij} = A_{ij}(n_k^b, \alpha, Z_{ij})$, k = 0, 1, 2, 3, 4.

The solution of system (3.2) is the following

$$n_i' = \sum_{j=1}^{3} C_{ij}\exp z_i\bar{t} + C_{i4}, \tag{3.3}$$

where $C_{ij} = C_{ij}(n_0^b, n_i^b, \alpha, Z_{ij})$ (i, j = 1 − 4) $z_i = z(n_0^b, n_i^b, \alpha, Z_{ij})$.

The dashed lines in Fig. 2 are the solution of (3.3) for the levels $(10°0,\ 02°0)^{I}$ and $(10°0,\ 02°0)^{II}$, i.e., for the populations n_2 and n_3. The numbers denote the values of the

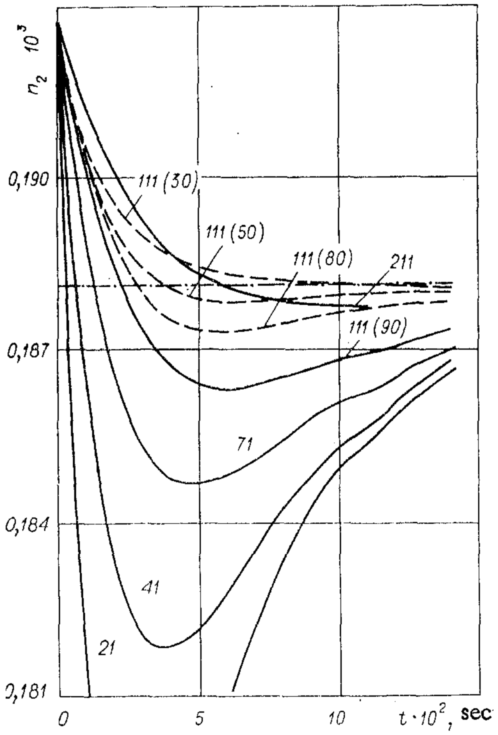

Fig. 5

collisional number Z_{32} [the inverse probability in collision for the transition between the levels $(10^{0}0, 02^{0}0)^{\mathrm{II}}$ and $(10^{0}0, 02^{0}0)^{\mathrm{I}}$]. The remaining collision numbers were taken from [3] or from [6], where they were refined. The initial temperature and pressure were the following: $T = 400$°K, $p = 10^5$ Pa. The quantity α was taken at 0.5. Results of numerical computations of system (3.1) by a Newton method by using an implicit scheme are presented by continuous curves. The good agreement is seen between the linearized and numerical solutions in a broad range of collision numbers, which permitted subsequent utilization of the analytic solution for variation of the parameters of the problem. The value of the number $Z_{32} = 90$ is in agreement with that recommended in [3] for $T = 400$°K, while $Z_{32} = 5$ is close to the values presented in [4]. The difference in evolution of the population n_2 for these two cases is seen in Fig. 2. In the case of [4], when the energy exchange between levels 2 and 3 proceeds with a very high probability, the curve describing the population n_2 has a deep minimum, while ahead of it there are approximately two domains with different slope, where the quantity $W = (1/n_2)dn_2/dt$ corresponding to the first of them, is an order of magnitude greater than the same quantity for the second section. For $Z_{32} = 90$ [3], the curve describing the change in $n_2(t)$ has a small minimum with gradual growth of W as it is approached. For high values of Z_{32} the magnitude of the minimum diminishes.

The behavior of the population $n_3(t)$ is monotonic in nature. For $Z_{32} = 5$ the curve n_3 has the value of the derivative $dn_3/dt \approx -dn_2/dt$ in the initial domain (this condition is not satisfied later). For $Z_{32} = 90$ this domain is very much smaller. As Z_{32} increases the form of the curves changes slightly.

Presented in Fig. 3 are results of numerical computations of the separate components of the equations for n_2 and n_3 for the system (3.1). The dashed curves correspond to a set of constants from [3], the continuous curves correspond to the same constants, with the exception of the value $Z_{32} = 5$. As is seen from Fig. 3, for $Z_{32} = 5$ $|\omega_{32}| \geq |\omega_{ij}|$ up to $t \sim 10^{-9}$ sec. Therefore, at the initial instant $dn_2/dt \approx -\omega_{32} \approx -dn_3/dt$, later this equality is spoiled.

For $Z_{32} = 90$ $\omega_{32} \sim \omega_{13} \sim \omega_{43}$, i.e., the relaxation of level 3 depends on the channels (2.1), (2.2), (2.3); relaxation of level 2 is described, as before, by the equation $dn_2/dt \approx -\omega_{32}$, and the number of vibrational quanta in the system of levels 2 and 3 is already not conserved since $\frac{d}{dt}(n_2 + n_3) \approx \omega_{13} + \omega_{43}$, but an approximate equality $n_3 + n_2/3 \approx$ const generally exists.

The presence of an extremum in the behavior of the gain coefficient of a weak signal with the wavelength 9.6 μm was noted in [6], which again corresponds to the behavior of the population 2. As has been shown above, the behavior of the population of the level (10°0, 02°0)^{I} has several sharply different domains even for small values of Z_{32}. The rate constant of the process (2.1) can here by determined only on the initial section of the curve n_2 and the process is not described by using a single-exponential function, as has been assumed in [6], but has the more complex nature of (3.3).

For large values of Z_{32} the behavior of the curve $n_2(t)$ depends on many parameters Z_{ij} and determination of the collision number Z_{32} is possible only indirectly at the time of reaching the minimum and at its depth.

4. We now examine how the depth of the minimum of the curve and the time of its attainment depend on the set of collision numbers Z_{ij}. The dependence of t_{min} on Z_{32} according to the analytic expression (3.3) is presented in Fig. 4. As is seen from Fig. 4, as Z_{32} grows the quantity t_{min} increases, where this growth is nonlinear. For instance, according to [6] the characteristic time of attenuation of the process (2.1) is determined to equal $4.4 \cdot 10^{-9}$ sec for $p_0 = 10^5$ Pa. According to Fig. 4, attainment of the minimum, which is considered the termination of the relaxation process in the channel (2.1) in [6], occurs in a time equal to 24 $\tau_{f.p.}$. This corresponds to the value $Z_{32} \approx 32$ on the curve in Fig. 4, which agrees with the deduction made in [5]. Also presented in Fig. 4 are values of t_{min} for variations in the number Z_{42} and for fixed values of all the other collision numbers Z_{ij} taken from [3]. The numbers to the right of the curves refer to the corresponding values of the number Z_{32}.

Variation of the numbers Z_{43}, Z_{12}, Z_{14}, Z_{13} showed that the strongest dependence of t_{min} exists on Z_{42}, Z_{43}, Z_{12} for small values. The quantity t_{min} is practically independent of the number Z_{14}, a dependence on the number Z_{13} is observed only for very small values.

A dependence of N_2 on t is presented in Fig. 5 for T = 300°K, p = 10^5 Pa, and $\alpha = 0.5$ for different values of Z_{32} in the form of continuous curves. The dashed curves correspond to a variation in the number Z_{12} whose values are indicated in the parentheses. As in the case T = 400°K, the curves describing the population $n_2(t)$ possess a minimum, but its magnitude is less both absolute and relative. As Z_{32} grows, t_{min} increases and the depth of the minimum decreases. As Z_{12} grows, the depth of the minimum starts to increase.

Such a tendency is conserved even for the variation of all the remaining numbers Z_{ij} except Z_{32}, for which the tendency is reversed, as already mentioned.

The graphs presented in Figs. 4 and 5 permit making certain deductions about the behavior of the population n_2 and the time to reach the minimum upon adding another gas, N_2 say, to the CO_2. Since the reactions (2.1), (2.3), (2.6) will proceed with approximately the same efficiency but the numerical density of the CO_2 molecules in the state 01^10 will drop, this will correspond to conservation of the numbers Z_{23}, Z_{43}, Z_{42} and increasing the numbers Z_{12}, Z_{13}, Z_{14}. For instance, the time to reach the minimum will vary here, but only because of mainly Z_{12}.

In conclusion, it must be noted that, as is seen from Fig. 2, large theoretical values of the transition probabilities between the levels (10°0, 02°0)^{I} and (10°0, 02°0)^{II}, i.e., small values of the numbers Z_{32}, do not denote a more rapid build-up of the local equilibrium between the levels mentioned. More likely, the converse, because of the involvement of several quantum levels in the exchange process, the process will proceed with a high vibration amplitude. For high values of $Z_{32} \sim 90$, the population of the level (10°0, 02°0)^{I} ceases to differ significantly from its quasiequilibrium value. For still higher values of $Z_{32} \sim 200$, the build-up time for the quasiequilibrium state is close to the value of the time corresponding to small values of Z_{32}. If Z_{32} is actually small, then the curve of the population of the level (10°0, 02°0)^{I} should have a domain with different slope. For instance, in experiments on the collapse of generation in [8], two domains with different slope were clarified. The rate constant of the first process corresponds to $Z_{32} \sim 8$ in a conversion of the experimental data in conformity with [5], which is in good agreement with theoretical data [4] but does not correspond to rotational relaxation as was assumed in [5], for which the magnitude of the number is $Z \sim 2$ [8]. The numerical modeling of the vibrational relaxation process performed above for CO_2 gas after it has passed through a powerful nanosecond pulse displays a nonmonotonic behavior of the change in population of the mixed level (10°0, 02°0)^{I} because of Fermi resonance. Only the initial section of the curve describing the change in the population of this level corresponds to the relaxation channel (2.1). If the initial system of constants [4] is taken, then the subsequent evolution of the population of the level $(10°0,\ 02°0)^{I}$ will depend simultaneously on both the relaxation over the channel (2.1) and relaxation over the channels (2.2), (2.3). If leakage of vibrational quanta occurs over channel (2.1), then filling the level $(10°0,\ 02°0)^{I}$ will occur over channels (2.2) and (2.3), which results in the long run in equilibrium of these oppositely directed processes and the achievement of the minimum on the curve $n_2(t)$.

The model used in this paper for vibrational relaxation certainly needs correction in order to take more complete account of the processes in the initial stage. The process of emptying the level $(10°0,\ 02°0)^{II}$ because of radiation, the process of rotational relaxation if it is also prolonged in nature, requires simultaneous examination in studying the vibrational relaxation between the levels $(10°0,\ 02°0)^{I}$ and $(10°0,\ 02°0)^{II}$.

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ENERGY ACCOMMODATION FOR GAS IONS ON A POLYCRYSTALLINE MATERIAL

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The interaction between a body and a low-density gas flow is largely characterized by the coefficients for the exchange of momentum and energy or the equivalent accommodation coefficients, the latter being used in determining convective heat fluxes and aerodynamic characteristics under free-molecular flow conditions, and they are important elements in the working relations no matter what the scheme used for the reflection of the gas atoms by the surface (specular-diffuse scattering, isolated reflection, Shamberg's model, Nochill's model, etc.).

The most detailed theoretical studies have been made of the interaction between gas atoms with clean crystalline structures. There are many papers on the simulation of collisions between atomic particles and surfaces, which give approximate analytic solutions characterizing the mechanisms for momentum and energy transfer from the gas atoms to ideal crystalline surfaces [1, 2].

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