QUASIEQUILIBRIUM MODEL OF THE KINETICS OF COUPLED MODES OF CO_2 MOLECULES

R. Sh. Islamov

UDC 539.196.5

The correct allowance for the influence of anharmonicity in the vibrational spectrum of CO_2 on the level distribution of molecules under nonequilibrium conditions, when the vibrational temperature departs significantly from the gas temperature, has become especially urgent in connection with obtaining generation on a number of long-wavelength transitions of CO_2 molecules [1, 2]. The shifts in the levels of coupled modes (symmetric and deformation) are due mainly to Fermi resonance and can reach a considerable value, comparable with the gas temperature even for low levels. In [3] the main features of the quasi-steady level distribution of coupled modes were clarified within the framework of the Treanor model of vibrational kinetics. The influence of the ascending flux of quanta, excited by VV exchange under nonequilibrium conditions, on the vibrational distribution was considered in [4-6]. In the present paper we propose a quasiequilibrium model of CO_2 kinetics, obtained without presuming quasi-steadiness of the ascending flux of quanta, and making it possible, in contrast to [3-6] to describe the dynamics of the variation of the distribution of molecules among multiplets as a result of processes of VV exchange and VT relaxation between multiplets, with allowance for possible processes of pumping by outside sources. With a Boltzmann population distribution within the multiplets, having the translational temperature of the gas, the problem of studying relaxation in coupled modes is reduced to the equations for an effective anharmonic oscillator with levels corresponding to the multiplets of CO_2 molecules. In this case the levels of the effective oscillator are degenerate with a multiplicity equal to the number of levels in the corresponding multiplet, and they have an anharmonicity constant dependent on the gas temperature. The population distribution of the effective oscillator can be studied by methods developed for the investigation of a one-mode anharmonic oscillator. The proposed quasiequilibrium model was used for a numerical calculations of the temporal evolution of the distribution function of CO_2 molecules over the levels of coupled modes under the conditions of an extremely maintained discharge.

1. Quasiequilibrium Model of the Vibrational Kinetics of CO_2 Molecules

The system of kinetic equations for the populations of individual levels of CO_2 molecules has the form [7]

$$\frac{dy_n}{dt} = -\sum_M \sum_{m=1}^{n-1} k_{nm}(M)\frac{p}{y_\Sigma} y_M\left(g_m y_n - g_n y_m \exp\left(-\frac{E_n - E_m}{T}\right)\right) + \sum_M \sum_{m=n+1}^{N} k_{mn}(M)\frac{p}{y_\Sigma} y_M\Bigl(g_n y_m - g_m y_n \tag{1.1}$$
$$\exp\left(-\frac{E_m - E_n}{T}\right)\Bigr) - \sum_{s=1}^{N-1}\sum_{q=s+1}^{N}\sum_{m=1}^{n-1} k_{nm}^{sq}\frac{p}{y_\Sigma}\left(g_q g_m y_s y_n - g_s g_n y_q y_m \exp\left(-\frac{E_s + E_n - E_q - E_m}{T}\right)\right)$$
$$+ \sum_{s=1}^{N-1}\sum_{q=s+1}^{N}\sum_{m=n+1}^{N} k_{mn}^{sq}\frac{p}{y_\Sigma}\left(g_q g_n y_s y_m - g_s g_m y_q y_n \exp\left(-\frac{E_s + E_m - E_q - E_n}{T}\right)\right),$$

where N is the number of levels taken into account; y_M is the molar-mass concentration of the M-th component of the mixture (CO_2, Ar, etc.); y_n is the molar-mass concentration of CO_2 molecules at the n-th level with an energy E_n and a multiplicity of degeneracy g_n; y_Σ is the total molar-mass concentration of the mixture; $k_{nm}(M)$ and k_{nm}^{sq} are the rate constants of the processes of VT relaxation and VV exchange; p and T are the gas pressure and temperature.

Moscow. Translated from Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, No. 3, pp. 16-22, May-June, 1986. Original article March 15, 1985.

0021-8944/86/2703-0329$12.50

A direct solution of the system (1.1) for a large number of levels requires considerable outlays of machine time, owing to the necessity of allowing for many individual processes. The presence of the multiplet structure of the levels of coupled modes of CO_2 molecules, with levels rather close in energy (in comparison with a quantum of deformation vibration, $\nu_2 = 667\ cm^{-1}$), leads to the fact that the rates of nonresonance VV exchange and VT transitions within the multiplets prove to be considerably higher than the rates of the corresponding VV transitions between neighboring multiplets. Therefore, an equilibrium distribution of the levels in a multiplet is established considerably faster than the equilibrium distribution of the multiplets is formed, and for a number of conditions it is reasonable to take it as a Boltzmann distribution with the translational temperature of the gas [7]. In the latter case, the problem of vibrational relaxation in coupled modes under highly nonequilibrium conditions is reduced to the equations for the populations of the levels of an effective anharmonic oscillator with the position E_I of the I-th level given by the relation

$$E_I = -T \ln\left[\sum_{n\in I} g_n \exp(-E_n/T) \Big/ \sum_{n\in I} g_n\right], \tag{1.2}$$

and the multiplicity G_I of degeneracy of the I-th level equal to the number of levels in the I-th multiplet:

$$G_I = \sum_{n\in I} g_n.$$

With such a choice of E_I, the Boltzmann population distribution of the levels of the I-th multiplet is written as

$$y_n = Y_I g_n \exp\left(-\frac{E_n - E_I}{T}\right), \quad n \in I, \tag{1.3}$$

where the reduced (to a unit statistical weight) population Y_I of a level of the effective oscillator is taken as equal to the average population of levels of the I-th multiplet:

$$Y_I = \sum_{n\in I} y_n \Big/ \sum_{n\in I} g_n.$$

Both the average energy ε_I of levels in the I-th multiplet and the position E_I of the effective I-th level are determined by the gas temperature. There is a connection between them:

$$\varepsilon_I \equiv \sum_{n\in I} y_n E_n \Big/ \sum_{n\in I} y_n = \frac{d(E_I/T)}{d(1/T)}.$$

In the present work the energy shift of the levels was calculated, just as in [3], in the first order of perturbation theory, neglecting anharmonic terms differing from the Fermi-resonance terms. This makes it possible to calculate the position E_I of the effective level, coinciding with that calculated on the basis of energy levels from [8] to within a fraction of a percent. The values of $\Delta E_I = I\nu_2 - E_I$ for the lower levels of the effective oscillator are given in Fig. 1 for T = 100, 200, and 300°K (lines 1-3). Using Eq. (1.3) and the detailed kinetic equations (1.1), we can find that the effective oscillator introduced is described by the kinetic equations

$$\begin{aligned} G_I \frac{dY_I}{dt} = {} & -\sum_M K_I(M) \frac{p}{y_\Sigma} y_M \left(Y_I - Y_{I-1} \exp\left(-\frac{E_J - E_{I-1}}{T}\right)\right) + \sum_M K_{I+1}(M) \frac{p}{y_\Sigma} y_M \left(Y_{I+1} - Y_I \exp\left(-\frac{E_{I+1} - E_I}{T}\right)\right) - \\ & - \sum_{J=0}^{I_0-1} K_{I,I-1}^{J,J+1} \frac{p}{y_\Sigma} \left(Y_J Y_I - Y_{J+1} Y_{I-1} \exp\left(-\frac{E_J + E_I - E_{J+1} - E_{I-1}}{T}\right)\right) \\ & + \sum_{J=0}^{I_0-1} K_{I+1,I}^{J,J+1} \frac{p}{y_\Sigma} \left(Y_J Y_{I+1} - Y_{J+1} Y_I \exp\left(-\frac{E_J + E_{I+1} - E_{J+1} - E_I}{T}\right)\right)\Bigr), \end{aligned} \tag{1.4}$$

where the effective rate constants of VT relaxation and VV exchange are determined through the detailed constants of the corresponding processes:

$$K_I(M) = \sum_{n\in I} \sum_{m\in I-1} k_{nm}(M) g_n g_m \exp\left(-\frac{E_n - E_I}{T}\right); \tag{1.5}$$

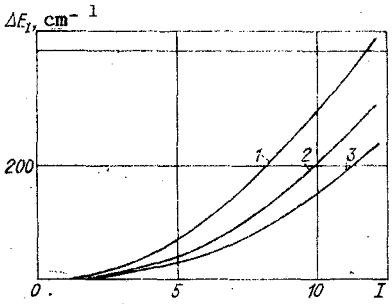

Fig. 1

$$K_{I,I-1}^{J,J+1} = \sum_{s\in J} \sum_{q\in J+1} \sum_{n\in I} \sum_{m\in I-1} k_{nm}^{sq} g_s g_n g_q g_m \exp\left(-\frac{E_n + E_s - E_I - E_J}{T}\right) \tag{1.6}$$

(I_0 is the number of the highest multiplet taken into account). The energy level of the effective oscillator is degenerate with multiplicity [3]

$$G_I = \begin{cases} (I+2)^2/4 & \text{for even } I, \\ (I+1)(I+3)/4 & \text{for odd } I. \end{cases}$$

Because of the smallness of the matrix elements for transitions on two or more quanta, only one-quantum processes of VT relaxation and VV exchange are retained in (1.4).

The constants of VT relaxation and VV exchange appearing in Eqs. (1.5) and (1.6) can be assigned with a relatively low degree of accuracy at present. Therefore, along with detailed calculations of Eqs. (1.5) and (1.6), approximate methods of estimating them can also be of interest.

From the theory of vibrational relaxation (e.g., [9]) it is known that for both VT and VV processes the rate constants are proportional to the square of the matrix element L_{mn} of the interaction operator and the adiabaticity function $F_M(\Delta E)$, dependent on the energy defect of the process, the temperature, and the parameters of the colliding molecules,

$$k_{nm}(M) = k_M F_M (E_n - E_m) \frac{L_{nm}}{\sigma_{nm}},$$

$$k_{nm}^{sq} = k_{CO_2} F_{CO_2} (E_s + E_n - E_q - E_m) \frac{L_{nm}}{\sigma_{nm}} \frac{L_{sq}}{\sigma_{sq}},$$

where k_M are the rate constants of relaxation of the deformation mode in a collision with the M-th component of the mixture; $\sigma_{nm} = 2$ if $g_n = g_m = 2$ and $\sigma_{nm} = 1$ if $g_n = 1$ or $g_m = 1$.

The adiabaticity function calculated in accordance with theory is usually in poor agreement with experimental data. The role of this defect of the theory can be weakened by drawing upon experimental results to a large degree. In [7] an adiabaticity function was used (obtained in [10] on the basis of very general assumptions) in which the dependence on the energy defect is determined from the condition of consistency with experimental data in processes with small [experiments on determining the constant $k_{10^00-02^00}(M)$] and large (measurements of the rate constant k_M of relaxation of the deformation mode) energy defects. For the squares of the matrix elements of the transitions it is characteristic that they comprise a significant amount only for transitions with an energy approximately equal to a quantum of the deformation vibration. By virtue of the rather weak dependence of the adiabaticity function on the energy defect for relaxation processes in coupled modes, this allows us to simplify the calculation of $K_I(M)$ and $K_{I,I-1}^{J,J+1}$:

$$K_I(M) \simeq k_M \Phi_{I,\ I-1},$$

$$K_{I,I-1}^{J,J+1} \simeq k_{10}^{01} \Phi_{I,I-1} \Phi_{J,J+1} \exp\left(\frac{E_I + E_J - E_{I-1} - E_{J+1}}{2T}\right),$$

$$\Phi_{I,I\pm1} = 2\sum_{n\in I}\sum_{m\in I\pm1} L_{nm}\exp\left(-\frac{E_n - E_I}{T}\right).$$

Using (1.2), we obtain

$$\Phi_{I,I-1} \simeq Q_I \equiv 2\sum_{n\in I}\sum_{m\in I-1} L_{nm}.$$

A numerical test shows that this estimate is sufficiently precise. For $\Phi_{7,6}$, for example, the error is only 0.4% at T = 300°K and increases somewhat at low temperatures, reached 3.4% at T = 50°K.

For the squares of the matrix element L_{nm} of a harmonic oscillator we have

$$\sum_{n\in I+1} L_{ns} - \sum_{m\in I-1} L_{sm} = g_s, \quad s\in I. \tag{1.7}$$

Allowance for mixing of the wave functions of multiplet levels due to Fermi resonance does not alter the correctness of Eq. (1.7), and summing it for all levels of the I-th multiplet, we have

$$Q_{I+1} = Q_I + 2G_I$$

and hence, in accordance with [5],

$$Q_I = \begin{cases} I(I+2)(2I+5)/12 & \text{for even} \quad I, \\ (I+1)(I+3)(2I+1)/12 & \text{for odd} \quad I. \end{cases}$$

Thus, we can write

$$K_I(M) \simeq k_M Q_I; \tag{1.8}$$

$$K_{I,I-1}^{J,J+1} \simeq k_{10}^{01} Q_I Q_{J+1} \exp\left(\frac{E_I + E_J - E_{I-1} - E_{J+1}}{2T}\right). \tag{1.9}$$

A numerical test shows the sufficiently high accuracy of these simplifications. For example, the error in determining $K_7(CO_2)$ and $K_7(Ar)$ from Eq. (1.8) is about 10% at T = 180°K.

From the kinetic equation (1.4) we get the equation for energy relaxation under highly nonequilibrium conditions,

$$\frac{d(E^1 + E^2)}{dt} = -\sum_{I=1}^{\infty}\left(\sum_M K_I(M)\frac{p}{y_\Sigma}y_M\right)\left(Y_I - Y_{I-1}\exp\left(-\frac{E_I - E_{I-1}}{T}\right)\right) \times$$
$$\times (\varepsilon_I - \varepsilon_{I-1}) - \sum_{I=1}^{\infty}\sum_{J=0}^{\infty} K_{I,I-1}^{J,J+1}\frac{p}{y_\Sigma} Y_I Y_J (\varepsilon_I - \varepsilon_{I-1} + \varepsilon_J - \varepsilon_{J+1}),$$

where E^1 and E^2 are the energies of the symmetric and deformation modes. The equation usually used,

$$\frac{d(E^1 + E^2)}{dt} \simeq -\left(\sum_M k_M \frac{p}{y_\Sigma} y_M\right)\left(1 - \exp\left(-\frac{\nu_2}{T}\right)\right)(E^2 - E_T^2),$$

is obtained if the approximations $\varepsilon_I - \varepsilon_{I-1} \simeq \nu_2$, $E_I - E_{I-1} \simeq \nu_2$ (in which case $E^2 \simeq \sum_{I=1}^{\infty} Q_I Y_I \nu_2$) and (1.8) are used.

2. Temporal Evolution of the Distribution Function of Average Level Populations of Multiplets of Coupled Modes of CO_2

It is characteristic for the CO_2 molecule that levels of low and very high multiplets are excited under the conditions of a gas discharge [11]. Therefore, in solving the kinetic equations (1.4), we take into account the processes of excitation of vibrational levels by electron impact from the ground level and underlying levels in all multiplets up to the 17th.

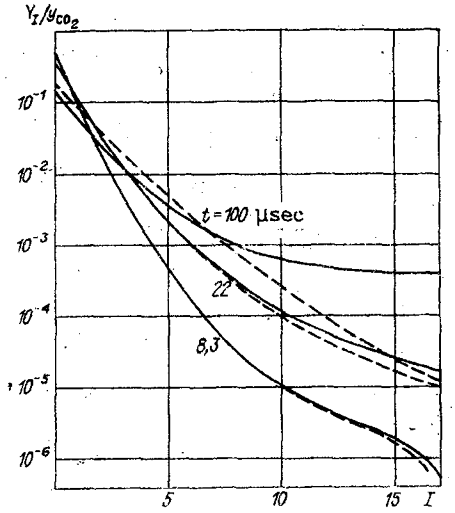

Fig. 2

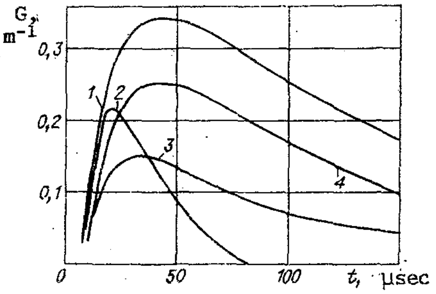

Fig. 3

The method of calculating the kinetic coefficients and electron energy balance in mixtures of vibrationally excited CO_2 with inert gases, and the results of calculations for the CO_2:Ar = 1:9 mixture considered below, are given in [12]. The constants of VT relaxation and VV exchange were calculated from the approximate equations (1.8) and (1.9). Along with the balance equations for the populations of vibrational levels, we solved the equation for the gas temperature with allowance for heating in processes of VT relaxation and VV exchange, as well as due to elastic losses in collisions of electrons with molecules and atoms and in the excitation of rotational levels of molecules.

The temporal evolution of the distribution function of the average level populations of multiplets of CO_2 molecules in a CO_2:Ar = 1:9 mixture at $p = 1.33 \cdot 10^4$ Pa and an initial temperature of 100°K for a pumping level w = 1500 W/cm^3 and with a ratio $N = 1 \cdot 10^{-16}$ V·cm^2 of the electric field strength E to the density of neutral particles is shown by solid lines in Fig. 2. Such conditions can occur during adiabatic cooling in supersonic nozzles. In the calculations it was assumed that the energy expended on the excitation of the asymmetric mode is not able to relax in the times under consideration.

The levels of the high multiplets may overlap. In those cases when they have the same symmetry (this is possible from the 12-14th multiplets), combined states are formed because of anharmonicity, and the direct relaxation of the energy of an upper multiplet into a lower one through these states becomes possible. Such a relaxation channel in high multiplets can be very efficient and fully compensate for the inflow of quanta due to the VV current and electron pumping. One must estimate to what degree the VVT channel of current relaxation affects the level populations of the multiplets. For this purpose we calculated the evolution of the distribution function of the average populations of multiplet levels of CO_2 molecules with time under the condition that quanta reaching the levels of the 17th multiplet in processes of VV exchange or as a result of electron pumping are removed from the system through rapid VT relaxation (see Fig. 2, dashed lines).

For the conditions under consideration, VVT relaxation can markedly affect the populations of upper multiplets over times $t \gtrsim 8$ μsec. The difference is essentially determined by the additional heating of the gas. The populations of the lower multiplets depend relatively little on the VVT relaxation channel. Nevertheless, it can be reflected noticeably in the amplification ratio for long-wavelength transitions of CO_2 molecules. The dynamics of the amplification ratio of the Q branch of the 03^10—10^00 transition with a wavelength of 18.4 μm is shown in Fig. 3 (curve 1). The introduction of VVT relaxation decreases the amplification ratio and shortens the time in which the amplification exceeds the threshold level (curve 2). For comparison, we also present the influence of water vapor (curve 3, CO_2:Ar:H_2O = 0.1:0.8998:0.0002 mixture) and the sensitivity to the fraction η of the energy going directly into heat in the discharge (curve 4, η = 10%; for the other curves η = 0.6%).

LITERATURE CITED

1. A. A. Vedeneev, A. Yu. Volkov, et al., "A gas-dynamic laser with thermal pumping on transitions between deformation and symmetric modes of CO_2," Pis'ma Zh. Tekh. Fiz., 4, No. 11 (1978).

2. D. G. Bakanov, A. A. Infirmovskaya, et al., "Generation in the 16.8-17.2 μm wavelength range in a gas-dynamic CO_2 laser," Pis'ma Zh. Tekh. Fiz., 7, No. 13 (1981).
3. A. A. Likal'ter, "Relaxation of the symmetric mode of vibrations of the CO_2 molecule," Zh. Prikl. Mekh. Tekh. Fiz., No. 3 (1975).
4. V. K. Konyukhov and V. N. Faizulaev, "Influence of the current of quanta on the vibrational distribution and relaxation of the energy of anharmonic oscillators," Kratk. Soobshch. Fiz., No. 8 (1981).
5. A. A. Likal'ter, "Vibrational kinetics of CO_2 under strong excitation of Fermi-resonance modes," Teplofiz. Vys. Temp., 20, No. 4 (1982).
6. V. N. Faizulaev, "Influence of the current of quanta on the relaxation of coupled modes of CO_2 molecules," Zh. Prikl. Mekh. Tekh. Fiz., No. 6 (1982).
7. R. Sh. Islamov, Yu. B. Konev, N. I. Lipatov, and P. P. Pashinin, "Theoretical investigation of the characteristics of amplification and generation between levels of symmetric and deformation modes of CO_2 molecules during adiabatic expansion of heated mixtures containing argon in supersonic nozzles," Preprint No. 113, Fiz. Inst. Akad. Nauk SSSR, Moscow (1982).
8. L. S. Rothman and W. S. Benedict, "Infrared energy levels and intensities of carbon dioxide," Appl. Opt., 17, No. 16 (1978).
9. E. E. Nikitin, Theory of Elementary Atomic—Molecular Processes in Gases [in Russian], Khimiya, Moscow (1970).
10. I. Procaccia and R. D. Levine, "Vibrational energy transfer in molecular collisions: an information theoretic analysis and synthesis," J. Chem. Phys., 63, No. 10 (1975).
11. M. J. W. Boness and G. J. Schulz, "Vibrational excitation in CO_2 via the 3.8-eV resonance," Phys. Rev. A, 9, No. 5 (1974).
12. R. Sh. Islamov and Yu. B. Konev, "Discharge plasma kinetical coefficients calculations for mixture of vibrationally excited CO_2 with inert gases," in: Proceedings of the 15th International Conference on Phenomena in Ionized Gases, Contributed Papers, Part 1 (1981).