RECOMBINATION RADIATION FROM A NONEQUILIBRIUM JET OF DISSOCIATED CARBON DIOXIDE

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We have investigated experimentally the emission properties of the CO_2 ($^1B_2 \to X^1\Sigma_g{}^+$) recombination band in a nonequilibrium (oscillating) jet of a 20% CO_2 + 89% Ar mixture in the range of stagnation temperatures from 2600 K to 4600 K. We have determined the basic characteristics of the mechanism underlying the formation of the distribution function of optically active molecules by analyzing curves of the population of various energy states of electron-excited $CO_2(^1B_2)$ molecules as functions of the translational and vibrational temperatures of the flow and the concentrations of dissociation products CO and O. We show that the spectral distribution of the intensities of recombination radiation from CO_2 in the investigated range of regimes can be described on the assumption of equilibrium between the distribution of optically active molecules and the total energy of the reagents in two-particle $CO(^1\Sigma, v) + O(^3P)$ recombination.

An experimental study of the depletion of highly excited states in dissociating carbon dioxide gas has been reported previously [1, 2]. Our present objective is to investigate experimentally the reverse of the process discussed in [1, 2], i.e., the overpopulation of electron-excited states of CO_2 during nonequilibrium recombination in a supersonic jet.

It should be noted that the loss of equilibrium in the population of highly excited molecular states in a chemically reacting gas is a fairly general phenomenon. The simplest mechanism characterizing the balance of populations of states energetically close to the barriers of the dissociation reaction include activation–quenching processes

$$AB + M \rightleftarrows AB^* + M \tag{I}$$

and dissociation–recombination processes involving active particles

$$AB^* \rightleftarrows A + B \tag{II}$$

In cases where the rates of processes II are greater than the rates of processes I, the variation of the populations of the active molecules AB* reflect the variation of the concentration of the dissociated particles, i.e., the depletion of highly excited states AB* is observed prior to the stabilization of equilibrium dissociation, and their overpopulation is observed in nonequilibrium recombination.

One of the most typical manifestations of such overpopulation is recombination radiation, which occurs when the content of dissociated components in the reacting gas is well above the equilibrium level. In carbon dioxide gas such radiation is attributed to radiation transition from the $CO_2(^1B_2)$ electron-excited state to the $CO_2(X^1\Sigma_g{}^+)$ ground state. Here the total intensity of recombination radiation from CO_2 is determined by the total population of the ($^1B_2$) level, and its spectral distribution is determined by the partial distribution function of optically active $CO_2(^1B_2)$ particles among the vibrational states. The total recombination rate constants, which determine the relationship between the population of optically active molecules and the concentration of recombining particles, and the spectral distributions of the recombination radiation have been measured both at room temperatures [3, 4] and at high temperatures [5, 6]. The total radiation recombination rate constant in the process

$$CO + O\,(^3P) \to CO_2\,(^1B_2) \to CO_2\,(X^1\Sigma) + h\nu \tag{III}$$

is given as follows in [6]:

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$$K_{rr} = 1.13\cdot10^{-18}\exp(-1960/T)\ \mathrm{cm^3\cdot sec^{-1}}; \quad (1)$$

this expression describes the experimental data in the temperature range from 1300 K to 2700 K. The authors of [6] also not that the extrapolation of Eq. (1) to room temperature yields good agreement with Pravilov's data [3].

The spectra distribution of the recombination radiation at room temperatures has a maximum in the vicinity of 400 nm and extends from 300 nm to 700 nm. When the temperature is elevated to 2700 K, the maximum shifts to 300 nm, possibly on account of filling of the excited vibrational levels of the $^1B_2$ state. In the selective recombination process CO + O(^{1}D) [4] the high $^1B_2$ vibrational levels become populated directly, a fact that is mirrored in the large shift of the radiation spectrum toward short wavelengths (the maximum occurring in the vicinity of 250 nm). It is therefore clear that the recombination conditions have a fundamental influence on the recombination radiation spectrum,and the detailed analysis of their interrelationship requires comprehensive investigation of the mechanism underlying the formation of the distribution function of optically active molecules. In general, this mechanism comprises a very complicated superposition of different recombination–dissociation channels

$$CO\ (v) + O\ (^3P) \rightleftarrows CO_2\ (^1B_2,\ v') \quad (IV)$$

$$CO\ (v) + O\ (^1D) \rightleftarrows CO_2\ (^1B_2,\ v'') \quad (V)$$

(processes of quenching and thermal activation of active particles

$$CO_2\ (^1B_2,\ v) + M \rightleftarrows CO_2\ (X^1\Sigma_g^+) + M \quad (VI)$$

process of intramolecular and intermolecular vibration–vibration energy transfer

$$CO_2\ (^1B_2,\ v^1)\ [+M\cdot(v')] \rightleftarrows CO_2\ (^1B_2,\ v'')\ [+M\ (v'')], \quad (VII)$$

and intramolecular (spontaneous and collisional) conversion and emission processes.

Data on the rates and relative efficiencies of these processes under various recombination conditions are nonexistent in the literature. Measurements in a thermal-equilibrium gas are insufficient for the acquisition of such data; what is needed are investigations for various relations between the vibrational and transnational energies of the system and under various conditions of electron excitation of the reagents the details are given in [2, 4]). The present study represents one step in this direction.

MULTICHANNEL SPECTROSCOPIC MEASUREMENTS IN SHOCK-HEATED FLOWS

The intensities of recombination radiation in various spectral intervals are measured under the conditions of a vibrational-nonequilibrium flow of dissociated CO_2 gas. A wide range of variation of the temperature and pressure of the flow over wide ranges makes it possible to achieve substantial variations of the reagent concentrations, the degree of vibrational nonequilibrium of the flow, and the efficiencies of the various collision processes IV-VII.

The investigations are carried out on an apparatus [7] that combines a shock tube with a two-dimensional vacuum chamber (with walls separated by a distance l = 45 mm). A shock wave is reflected from the end of the tube, and a supersonic jet begins to flow into the vacuum chamber through a slit orifice of half-height h_* = 1 mm cut in the end. The shock tube and the vacuum chamber have CaF_2 windows, which are washed prior to each experiment. The apparatus is evacuated to a pressure $\sim 1.3\cdot10^{-1}$ Pa. Impurities are purged from the mixture by two-stage freeze-out in liquid nitrogen.

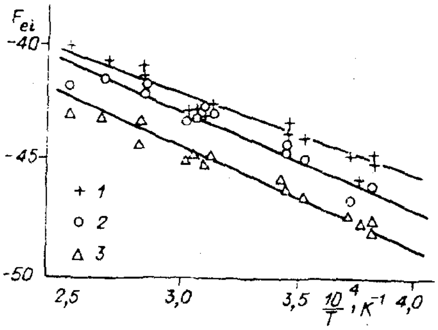

Fig. 1

The most important phase of the study is the measurement of the emission characteristics of supersonic jets of dissociated CO_2 in several narrow spectral intervals of the $CO_2(^1B_2 \rightarrow X^1\Sigma_g{}^+)$ recombination band. The maximum information is obtained using interference filters at $\lambda_1 = 285 \pm 7$ nm, $\lambda_2 = 353 \pm 3.5$ nm, and $\lambda_3 = 488 \pm 1.5$ nm. An additional series of experiments is also carried out to measure the emission properties of the flow at $\lambda_4 = 308 \pm 1.8$ nm. All the experimental series are accompanied by emission–absorption measurements in the infrared range of the spectrum in the CO_2 2.7-μm (mixed modes $\nu_1\nu_3$) and $\nu_2\nu_3$ and 4.3-μm (antisymmetric mode ν_3) band or in the CO 4.7-μm band.

The emission spectrum of CO_2 has an unresolved structure in this range, making it impossible to identify the specific vibrational–rotational levels responsible for emission and absorption in the transmission bands of the light filters.

The analysis of the emission measurements requires reliable data on the absorption coefficients in the separate spectral intervals. Special series of measurements are performed for this purpose under conditions of complete thermodynamic equilibrium behind the reflected shock waves in the shock tube. The velocity of the incident shock wave is measured along three baselines within 1% error limits. The equilibrium parameters and the composition of the gas behind the reflected shock wave are determined from calculations [8, 9] and from the equilibrium constant [10]. The transition from reactive to absolute measurements is achieved by means of a standard TRU 1300-2350 tungsten filament lamp and "black body" (for the IR spectrum) and Lyumen (for ultraviolet measurements) sources calibrated from the lamp. In the determination of the effective optical transition cross sections σ_i in the designated spectral bands $\lambda_i \pm \Delta\lambda_i$, the optical transition at the wavelength λ_i is identified (in view of the nonresolution of the vibrational–rotational structure of the band) with fixed energy states of the CO_2 molecule: the upper state ε_{i2} (term $^1B_2$) and the lower state ε_{i1} (term $X^1\Sigma$). Then in the presence of an optically thin layer, in accordance with Beer's law

$$I_{ei} = \text{const} - \sigma_i n_i^* l \tag{2}$$

and the Boltzmann distribution

$$n_i^* = (n/Z)\exp\left(-\frac{\varepsilon_{i2}}{kT}\right), \tag{3}$$

where

$$Z = \left(1 - \exp\left(-\frac{1997^{-1}}{T}\right)\right)\left(1 - \exp\left(-\frac{960}{T}\right)\right)^{-2}\left(1 - \exp\left(-\frac{3380}{T}\right)\right)^{-1},$$

the function $F_{ei} = f(1/T)$

$$F_{ei} = \ln\left(\frac{ZI_{ei}}{I_L nl}\right) - \frac{hc}{\lambda_i kT_L} = \ln\sigma_i - \frac{\varepsilon_{i2}}{kT} \tag{4}$$

must have a linear form [11] and can be used to determine empirical values of σ_i, ε_{i2}, and $\varepsilon_{i1} = \varepsilon_{i2} - hc/\lambda_i$. In relation (2)-(4) I_{ei} denotes the experimental amplitudes of the emission signals,

$$I_L = \text{const} - \exp\left(-\frac{he}{\lambda_i kT_L}\right)$$

TABLE 1

i	λ_i, nm	σ_i, cm^2	$\varepsilon_{2,i}$, eV	$\varepsilon_{1,i}$, eV	Symbol No. in Fig. 1
1	285	$7,42 \cdot 10^{-15}$	7,15	2,78	1
2	353	$7,82 \cdot 10^{-15}$	6,63	3,11	2
3	488	$5,66 \cdot 10^{-15}$	5,86	3,32	3

is the amplitude of the radiation from the standard source, which is maintained at the same temperature $T_L = 2340$ K in all the experimental series, n is the total concentration of CO_2 in the mixture, Z is the vibrational partition function (the partition function of the state $^1B_2$ is assumed to be close to that of the ground state of CO_2), and l is the path length in the investigate gas. Fig. 1 shows the results of such calibration measurements in the temperature range from 2600 K to 4000 K. The values obtained for σ_i and ε_i are given in Table 1.

It is important to note that the values of σ_i and ε_i determined in the present study are considerably higher than the corresponding values obtained previously for the temperature range 1700-3000 K [1, 11]. Considering also the reported [1] substantial reduction in the effective values of σ_i and ε_i at temperatures below 1500 K, we can conclude that the postulated existence of a fixed transition $\varepsilon_{i2} \to \varepsilon_{i1}$ having an effective cross section σ_i and governing the optical properties of the CO_2 recombination band over a wide range of temperatures, is not entirely justified. The same conclusion is drawn from an attempt to fit data [1, 11, 12] on the effective energies and cross sections in selected narrow spectral intervals to the spectral distributions obtained for CO_2 recombination radiation at lower temperatures [3, 6]. Nonetheless, allowing for the fact that $T_{equi} = 2600$-4000 K the results of the present study are adequately described by the functions (4) with the parameters σ_i and ε_i given in Table 1, we have attempted to use these functions to analyze the emission measurements in nonequilibrium jets. In so doing, we recognize that such processing of the experimental data is justified only so long as the vibrational distribution of optically active molecules does not deviate too far from the range of values of T_{equi} in which σ_i and ε_i have been measured.

The measurements in shock-heated jets span the ranges of stagnation temperatures 2600-4600 K and stagnation pressures $(0.4\text{-}3.5) \cdot 10^6$ Pa. All the measurements are carried out in a 20% CO_2 + 80% Ar mixture. The equilibrium concentration of CO_2 prior to the initiation of jet flow varies from $8 \cdot 10^{15}$ cm^{-3} to $1.6 \cdot 10^{19}$ cm^{-3}, and the equilibrium concentrations of the dissociation products CO and O vary from $5 \cdot 10^{15}$ cm^{-3} to $1 \cdot 10^{18}$ cm^{-3}. The relaxation time to the equilibrium parameters behind the reflected shock wave at the end of the tube varies from 200 μsec in the lowest-temperature regimes to 10 μsec in the highest-temperature regimes [13].

The transit time of the gas from the rest state in the shock tube to the investigated point $x = 8h_*$ on the jet axis varies from 5-6 μsec to ~ 4 μsec.

An abrupt drop in the rates of the total recombination processes with decreasing temperature and density in the expanding jet flow makes it reasonable to assume that the composition of the stabilized gas prior to flow in the shock tube is constant under these conditions. Given this assumption, the values of the steady-flow parameters on the jet axis are described by quasi-one-dimensional equations for isentropic flow from a cylindrical source:

$$\frac{\gamma}{\gamma - 1} \frac{R}{\mu} T + \frac{u^2}{2} = \frac{\gamma}{\gamma - 1} \frac{R}{\mu} T_* + \frac{u_*^2}{2}, \qquad (5)$$
$$\rho u x = \rho_* u_* h_*, \quad T \rho^{1-\gamma} = T_* \rho_*^{1-\gamma}.$$

Here T_*, ρ_*, and u_* are the temperature, density, and velocity of the flow in the critical cross section of the nozzle, $T_* = 2T_0/(\gamma + 1)$, and γ is the effective adiabatic exponent of the mixture ($\gamma = 1.45$).

Figure 2 shows typical oscillograms of the emission signals in different spectral intervals at the point $x = 8h_*$ on the jet axis. The initial part of the IR signals has an emission peak associated with passage through the unsteady zone of the jet [7], followed by an interval of smooth decrease of the signals, indicating the dissociation of CO_2 in the shock tube. This stage of the flow is characterized by a smooth increase of the recombination radiation signals because of the increasing reagent concentrations. All the signals then acquire a steady zone, which is dictated by relaxation to the equilibrium parameters before entry into the nozzle and is disrupted by the disturbance of the state of the gas at the end of the tube. The scope of our work includes an analysis of this steady flow stage, in which the macroscopic flow parameters admit the simplest interpretation.

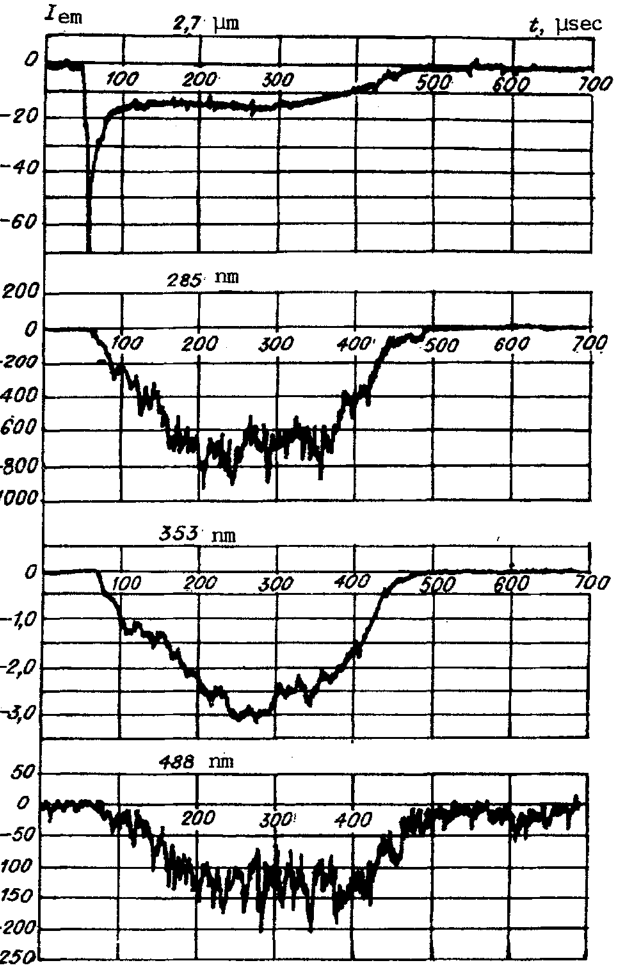

Fig. 2

ANALYSIS OF THE MECHANISMS OF FILLING OF OPTICALLY ACTIVE STATES

The populations of various energy states of the optically active term $^1B_2$ are determined on the basis of the emission measurements in the CO_2 recombination band in conjunction with the values obtained for the effective transition cross sections (see Table 1). However, since the designated states constitute only a small fraction of the possible excited states of chemically active CO_2^* molecules, all subsequent consideration will include, in one form or another, the assumption that the vibrational levels of electron-excited $CO_2(^1B_2)$ molecules have smooth, continuous population distributions. The first step of our analysis is the purely formal representation

$$\frac{n_i^*}{n_j^*} = \exp\left(-\frac{\varepsilon_{2,i}-\varepsilon_{2,j}}{kT_{V,k}^*}\right),$$

where the parameter $T_{V,k}^*$ (the so-called $i \rightleftarrows j$ transition temperature) is to be regarded merely as a convenient way of writing the population ratio, and not as proof of the existence of a Boltzmann population distribution.

Examples of such an analysis of the transition temperatures $T_{V,1}^* = (\varepsilon_{2,2} - \varepsilon_{2,1})/(k \ln(n_1^*/n_2^*))$ and $T_{V,2}^* = (\varepsilon_{2,3} - \varepsilon_{2,2})/(k \ln(n_2^*/n_3^*))$ are compared in Fig. 3 with the results of measurements of the vibrational temperatures T_V of the CO_2 ground state. (The procedure used to determine the vibrational temperatures in shock-heated CO_2 jets from mission–absorption measurements in IR bands is described in detail in [7, 14].) Our attention is called not only to the high level of the transition temperatures, but also to the significant growth in the relative population of the highest states as the flow temperature and the concentrations of dissociated particles increase. On the other hand, the ratio of the populations of the lowest vibrational levels of the term $^1B_2$ (according to previous data [14], the zero vibrational level of the term $^1B_2$ corresponds to $\varepsilon_{2,0} \approx 5.7$ eV) yields a transition temperature $T_{V,2}^*$ only slightly higher than the vibrational temperature of non-electron-excited CO_2 molecules.

The accelerated rise of the vibrational temperature of the CO_2 ground state relative to the gasdynamic flow parameters (the dashed line in Fig. 3 represents the local transnational temperature of the flow T_T) is associated with a specific aspect of

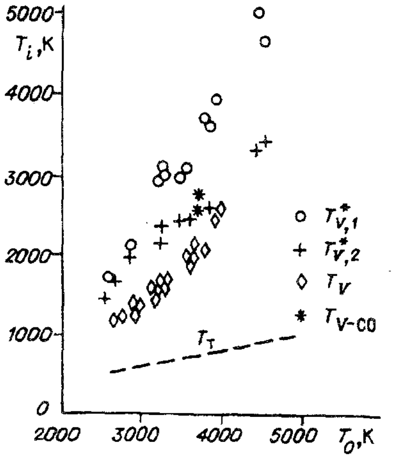

Fig. 3

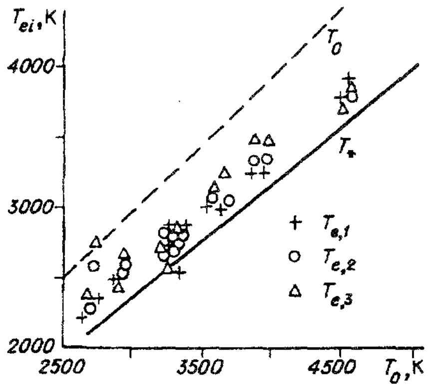

Fig. 4

the reported experiments: the stagnation pressure decreases with increasing temperature. The degree of nonequilibrium of the vibrational degrees of freedom in the investigated flow regimes is in good agreement with previous experiments and calculations [7, 14]. The vibrational temperatures of CO, determined in a small series of experiments involving emission–absorption measurements in a 4.7-μm band, are found to be 300-500 K higher than the vibrational temperatures of CO_2, i.e., very close in order of magnitude to the temperature $T_{V,2}{}^*$ at which the lower vibrational levels of electron-excited molecules are populated. Assuming that these values of $T_{V,2}$ characterize the total vibrational distribution of the $CO_2(^1B_2)$ state and using the Boltzmann equation (3) in the form

$$n_i^* = \frac{n}{Z\,(T^*_{V,2})}\exp\left(-\frac{\varepsilon_{2,i}}{kT_{e,i}}\right), \tag{6}$$

we attempt to find the total temperature at which the state $^1B_2$ is populated relative to unexcited molecules. Figure 4 shows the resulting data on the population temperature of various energy levels of the $^1B_2$ state at various jet stagnation temperatures. Two facts stand out: First, the values obtained for the temperatures $T_{e,i}$ are much higher than the vibrational temperatures T_V of the ground term; second – and of utmost importance – they are extremely close to one another. It is also clearly perceived that the variations of the temperatures $T_{e,i}$ are linearly related to the variations of the thermodynamic temperatures of the flow, and their values lie in the interval between the stagnation temperature T_0 and the critical temperate T_* of the jet.

Proceeding to the possible mechanisms by which the observed distribution functions of optically active molecules are formed, as a first step we need to consider a pure deactivation mechanism, which precludes the influence of recombination processes. Indeed, if we assume that all the populations of electron-excited molecules are frozen even in the subsonic section of the nozzle, this could account for the equality of the population temperatures of different states and their linear relation to the thermodynamic temperature of the flow. However, such an explanation spawns a great many contradictions. First, the rate constants of the quenching of electron-excited molecules are known to be rather high (usually at least 10^{-11}-10^{-12} $cm^3 \cdot sec^{-1}$). In particular, according to published data [1, 2, 4], the quenching of $CO_2(^1B_2)$ molecules can take place under our stated conditions with a frequency of 10^6 sec^{-1}, and their spontaneous dissociation must take place approximately an order of magnitude faster in this case. Second, even if this is not so and the total frequency of deactivation and dissociation of optically active particles does not exceed 10^5 sec^{-1} under our conditions (this rate is at least necessary for the observed freezing of T_{ei} to occur), it is most peculiar that this rate changes extremely little over a wide range of variation of the composition (the concentration of atomic oxygen, e.g., ranges from 10^{15} to 10^{18} cm^{-3} in our work), temperature, and density of the gas, establishing a constant ratio

$$\beta \equiv \frac{T_{ei}}{T_0} \approx 0{,}84 - 0{,}87. \tag{7}$$

Third, and lastly, experiments performed at close temperatures and at various pressures have shown that not only does a decrease in pressure lead to earlier freezing of T_{ei} at a higher level, but also, conversely, the ratio of the population of active particles n_i^* to the completely frozen-in value $n_i^*(T_0)$ decreases approximately linearly with the pressure (see Table 2). Similarly, the ratio of n_i^* to the product of the concentrations of recombining CO and O particles decreases with decreasing

TABLE 1

T_0, K	P_0, Pa	$\frac{n_1^*}{n_1^*(T_0)}$	$\frac{n_1^*}{[CO][O]}$, cm^3	$\frac{n_2^*}{n_2^*(T_0)}$	$\frac{n_2^*}{[CO][O]}$, cm^3	$\frac{n_3^*}{n_3^*(T_0)}$	$\frac{n_3^*}{[CO][O]}$, cm^3
3306	$16{,}5 \cdot 10^5$	$2{,}40 \cdot 10^{-2}$	$1{,}78 \cdot 10^{-31}$	$2{,}86 \cdot 10^{-2}$	$1{,}08 \cdot 10^{-30}$	—	—
3264	$16{,}1 \cdot 10^5$	$2{,}35 \cdot 10^{-2}$	$1{,}62 \cdot 10^{-31}$	$3{,}12 \cdot 10^{-2}$	$1{,}12 \cdot 10^{-30}$	$9{,}33 \cdot 10^{-2}$	$6{,}61 \cdot 10^{-29}$
3280	$16{,}3 \cdot 10^5$	$2{,}04 \cdot 10^{-2}$	$1{,}20 \cdot 10^{-31}$	$1{,}94 \cdot 10^{-2}$	$8{,}67 \cdot 10^{-31}$	$7{,}96 \cdot 10^{-2}$	$3{,}50 \cdot 10^{-29}$
3289	$16{,}5 \cdot 10^5$	$2{,}13 \cdot 10^{-2}$	$1{,}36 \cdot 10^{-31}$	—	—	$6{,}11 \cdot 10^{-2}$	$4{,}15 \cdot 10^{-29}$
3184	$12{,}4 \cdot 10^5$	$1{,}33 \cdot 10^{-2}$	$1{,}06 \cdot 10^{-31}$	$1{,}38 \cdot 10^{-2}$	$5{,}93 \cdot 10^{-31}$	$3{,}26 \cdot 10^{-2}$	$2{,}40 \cdot 10^{-29}$
3234	$12{,}2 \cdot 10^5$	$1{,}56 \cdot 10^{-2}$	$1{,}11 \cdot 10^{-31}$	$1{,}37 \cdot 10^{-2}$	$5{,}87 \cdot 10^{-31}$	$8{,}4 \cdot 10^{-3}$	$1{,}32 \cdot 10^{-29}$

pressure, lending further support to the collision recombination mechanism of evolution of the populations of optically active molecules.

We begin with the elementary recombination mechanism involving quasiequilibrium in reaction IV, which is understood to mean, more precisely, the two-stage process

$$CO\,(v) + O\,(^3P) \rightleftarrows CO_2\,(^3B_2) \rightleftarrows CO_2\,(^1B_2) \qquad \text{(IX)}$$

Assuming that all other processes (vibrational relaxation, electron relaxation, and energy exchange with other excited particles) are much slower and do not disrupt the equilibrium in reaction IX, we must set the energy of the newly formed active particles equal to the total energy of the reagents, i.e., their mutual kinetic energy and CO vibrational energy. This energy plus the recombination energy [5.45 eV for CO + O(^{3}P)] is then equal to the total energy of active molecules relative to the CO_2 ground state; the total energy is described phenomenologically for all the detected states by Boltzmann distributions with the temperatures T_{ei} (6). Since the values are approximately equal, in order of magnitude, to the sum of $T_V(CO)$ and T_T, it is possible in principle to consider two limiting mechanisms of conversion of the total energy of the generated quasimolecules into energy of the optically active mode of electron-excited $CO_2(^1B_2)$ particles: 1) All the vibrational energy is concentrated directly in the optically active mode; 2) the conversion process $CO_2(^1B_2) \rightarrow CO_2(^3B_2)$ (the longest stage of reaction IX) is paralleled by intense VV exchange

$$CO_2\,(^3B_2,\, 0,\, 0,\, v_3) \rightarrow CO_2\,(^1B_2,\, v_1,\, v_2,\, v_3),$$

(in which all vibrational states of the term $CO_2(^1B_2)$ are filled uniformly. The second mechanism, which postulates, as in [15], that the times of redistribution of vibrational energy of highly excited molecules are much shorter than the characteristic time constants of spontaneous dissociation, seems preferable to us for the added reason that the excitation of asymmetrical vibrations $CO_2(^3B_2, v_3)$ is most probable in the "fusion" CO + O, and all appearances indicate that the optically active mode comprises deformation vibrations $CO_2(^1B_2, v_1)$ [16, 17].

Based on this assumption, the populations n_i^* of optically active states are related to the total dependence of the density n^* of electron-excited molecules through the Boltzmann equation in the form

$$n_i^* = \frac{n^*}{Z\,(T_{V,2}^*)} \exp\left(\frac{-\Delta\varepsilon_{2,i}}{kT_{V,2}^*}\right), \qquad (8)$$

where $T_{V,2}^*$ and $\Delta\varepsilon_{2i} = \varepsilon_{2i} - \varepsilon_0$ are the temperature and relative energy of vibrationally excited states of active molecules (ε_0 is the energy of the ground vibrational level of the distribution of active molecules).

The total population of electron-excited molecules, in turn, can be related to the CO and O concentrations by the following equation if quasiequilibrium is assumed in reaction IX:

$$K_g n^* = K_r[CO][O].$$

Here K_g is the frequency of spontaneous dissociation of CO_2^* quasimolecules, and K_r is the two-frequency recombination rate constant.

Consequently, the populations of the designated states n_i^* in the experiments can be related to the concentration of the reagents CO and O and the vibrational distribution of electron-excited CO_2^* molecules by the equation

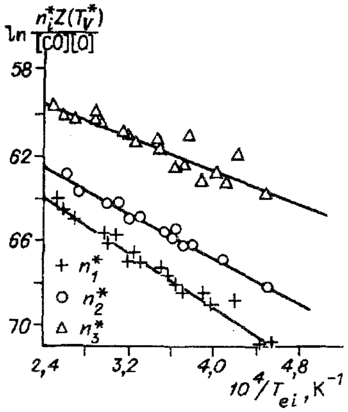

Fig. 5

$$n_i^* = \frac{K_0}{Z(T_{V2}^*)} [CO][O] \exp\left(-\frac{\Delta\varepsilon_{2i}}{kT_V^*}\right) \tag{9}$$

($K_0 = K_r/K_g$ is the equilibrium constant of reaction IX).

On the other hand, the equilibrium constant of the total reaction

$$CO_2 \rightleftarrows CO + O$$

has been approximated in [2] according to data from [10] by an analytical expression of the form

$$\frac{[CO_2]}{[CO]\,[O]} = A \exp\frac{D}{T} = 1{,}19\cdot 10^{-26} \exp\frac{61\,350}{T}\ (\mathrm{cm}^3).$$

This relation between the concentrations is achieved in a shock tube prior to the initiation of flow at the stagnation temperature T_0. During expansion, in view of the constant chemical composition of the gas, the variations of all the concentrations are governed by the decrease in the density. This decrease, expressed as a ratio and calculated from the system of equations (5), has the following value at some distance from the nozzle orifice:

$$\frac{\rho^*}{\rho_0} = \delta \approx 4{,}7\cdot 10^{-2}.$$

Consequently, the relation between the CO_2 concentration and the concentration of dissociation products CO and O is given by the equation

$$n = A\delta [CO]\,[O] \exp\frac{D}{T_0}. \tag{10}$$

Combining Eq. (10) with Eqs. (6) and (7), we have

$$n_i^* = \frac{A}{Z(T_V^*)} [CO]\,[O]\,\delta \exp\frac{\varepsilon_{2i} - \beta D}{T_{ei}}. \tag{11}$$

Clearly, we have obtained a relation that very closely resembles Eq. (9) corresponding to the above-formulated elementary mechanism of formation of the distribution function of optically active molecules. Experimental data on the populations of the energy states n_1^*, n_2^*, and n_3^* (see Table 1), plotted in coordinates $\ln \frac{n_i^* Z(T_V^*)}{[CO]\,[O]} = f\left(\frac{1}{T_{ei}}\right)$, are compared in Fig. 5 with the values calculated according to Eq. (11).

The agreement between the experimental points and the calculations not only confirms the validity of the postulated mechanism, but also enables us to refine some of its quantitative characteristics. For example, we can assume that the equilibrium constant K_0 of reaction IX coincides with the coefficient A of the exponential function in process II. A comparison of the remaining terms in Eqs. (9) and (11) then makes it possible to determine the effective value of ε_0 in Eq. (8). This value, averaged over all the experimental results, is

$$\varepsilon_0 = 5.66 \pm 0.08 \text{ eV},$$

which agrees quite well with previous data [3, 17] for the zero energy level of $^1B_2$.

Summarizing the results, we conclude that the spectral distribution of the intensity of recombination radiation from carbon dioxide gas in a vibrationally nonequilibrium supersonic jet of dissociated CO_2 is described by process of recombination and spontaneous dissociation of active molecules, whose vibrational distribution is in equilibrium with the recombining particles.

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