STUDY OF VIBRATIONAL DEACTIVATION OF MOLECULES OF CARBON DIOXIDE GAS DURING COOLING OF STREAM IN A SUPERSONIC NOZZLE

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The vibrational temperature of the antisymmetrical type of vibrations (ν_3) of the CO_2 molecule at the exit of a supersonic nozzle is measured in the present work using the method of recording the infrared emission. Freezing in of the ν_3-type vibrations was observed during the flow of undiluted carbon dioxide in a nozzle. In this case the vibrational temperature T_3 considerably exceeded the translational temperature. On the basis of a comparison of the experimental results with calculation it can be concluded that vibrational deactivation of CO_2 molecules occurs three to five times faster than the excitation of the vibrations during heating in a shock wave. All the experiments were conducted under the following conditions: maximum expansion of gas in nozzle $A/A_* = 115$, temperature range 1900-2400°K, pressure range 1-17.5 atm.

For calculations of the nonequilibrium flow of a relaxing gas in nozzles and jets it is necessary to know the energy exchange probabilities or the vibrational deactivation times. The main source of quantitative information on these parameters is experiment. Such experiments as a rule are conducted under conditions differing from the conditions under which processes occur in nozzles and jets: in the experiments either the excitation of the molecules in shock waves or the vibrational deactivation of the molecules after resonance laser excitation is studied. For diatomic molecules it is shown that the time τ of vibrational deactivation in cooling practically coincides with the time τ_* of vibrational excitation [1, 2]. The results of experiments on the measurement of τ in shock tube nozzles for the nitrogen molecule [3], where $\tau_*/\tau = 15$, proved to be erroneous [2]. The anharmonic effect suggested in [3] cannot explain the considerable difference between τ_* and τ [4]. Quantitative data on the kinetics of vibrational deactivation in cooling streams for triatomic molecules are practically absent. Experiments with laser excitation do not solve the problem since in this case the nature of the excitation differs considerably from thermal excitation and the distribution of the molecules by levels in the excitation deviates considerably from the Boltzmann distribution. The necessity exists for the direct measurement of the characteristics of the process of deactivation of the vibrations of triatomic molecules in a cooling stream. This pertains to the study of the processes in carbon dioxide, which is the principal component of the mixture used in powerful gasdynamic lasers.

In the present work an experimental study is conducted of the process of vibrational deactivation of molecules of carbon dioxide which escape from a nozzle mounted in the end of a shock tube. The vibrational temperature of the ν_3-type vibrations of CO_2 at the exit of the nozzle (by the method of recording the infrared emission), the initial gas pressure, and the velocity of the incident shock wave were measured in the experiments. The rest of the values were calculated on the assumption of one-dimensional flow of gas in the shock tube and nozzle.

1. The experiments on the study of the vibrational deactivation of carbon dioxide were conducted on a single-diaphragm shock tube of round cross section with an internal diameter of 50 mm. Hydrogen, helium, and argon or a mixture of these gases taken from standard cylinders were used in the high-pressure chamber 0.8 m long. The length of the low-pressure chamber was 4.5 m. A nozzle was mounted in the end of

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the low-pressure chamber and behind it was a reservoir with a volume of ~150 liters. The evacuation of the tube and reservoir was accomplished by a roughing pump to a residual pressure of $2 \cdot 10^{-2}$ mm Hg. Because of insufficient sealing the evacuation of the tube did not exceed $2 \cdot 10^{-3}$ mm Hg; the initial working gas pressure was above 10 mm Hg and the time of the experiment following evacuation of the tube did not exceed 5 min. The carbon dioxide studied was taken from standard cylinders and was dried in a special reservoir of silica gel where it was kept for three days, undergoing forced circulation.

To simplify the procedure of converting from measurements in the nozzle to calibration from the emission in the shock wave with the same recording system the nozzle was made in the form of a cylindrical insert in the shock tube in such a way that the installation of the nozzle left the recording system unchanged. The diaphragm in the end of the tube in front of the entry to the nozzle was absent. The necessary initial pressure p_0 at the entry and p_- at the exit from the nozzle was maintained through the increase in pressure p_5/p_1 in the reflection of the shock wave from the end of the tube and through additional continuous pumping of the experimental gas through the nozzle before the experiment.

For the control experiments a flat wedge-shaped nozzle with a total aperture angle of ~9° and an area ratio of $A/A_* = 16$ (A and A_* are the areas of the exit and critical cross sections of the nozzle) was used. The measurements showed that the flow of carbon dioxide gas in such a nozzle remains equilibrium in the range of gas temperatures in front of the nozzle entry of T_0 = 1500-2600°K and pressures p_0 = 2.5-27 atm. Here and later it was assumed that $T_0 = T_5$ and $p_0 = p_5$, i.e., the gas parameters behind the reflected shock wave coincided with the gas parameters in front of the nozzle entry, despite the "doubling" of the reflected shock wave which is significant in carbon dioxide. An axially symmetrical profiled nozzle with a deflection point in the region of the critical cross section was used to obtain the vibrationally frozen-in nonequilibrium flow of carbon dioxide. The diameter of the critical cross section in this nozzle was 2.34 mm, the initial total aperture angle was close to 60°, the nozzle length was 75 mm, and $A/A_* = 115$. The contour of the subsonic part of the nozzle consisted of a section of a circle with a radius equal to the diameter of the critical cross section.

A system consisting of a focusing mirror, a radiation receiver, a compatible electron cascade, and a recording oscillograph was set up to record the infrared emission of the carbon dioxide and to measure the vibrational temperature of the ν_3-type vibrations of CO_2 at the exit from the nozzle. The adjustment of the system and testing of the steadiness of the sensitivity and frequency characteristics of the recording channel were accomplished with the help of an auxiliary infrared source and light modulator. The resolving power of the recording channel was limited by the frequency characteristics of the electron amplifiers used and was ~20 μsec.

The spectral sensitivity of the photoreceiver used in the work extended from 2 to 8.5 μ. The bands corresponding to the vibrational transitions of the ν_3-type of CO_2 vibrations (antisymmetrical valence vibrations) with a center near 4.27 μ are the most intense in this region of the spectrum. The edge of this system of bands is located at ~4.17 μ and the long-wavelength boundary expands with temperature, extending into the wavelength region of 5 μ or more. The absence of a spectral instrument from the recording system was possible for the following reasons. The spectral intensity of the emission of a vibrationally nonequilibrium gas depends in a complicated way on the absolute values of and ratios between the translational, rotational, and vibrational temperatures and on the degree of breakdown of equilibrium in the gas [5]. This is connected with the fact that during the freezing in of the vibrational degrees of freedom of the molecules during the cooling of the gas the vibrational temperature can differ markedly from the translational and rotational temperatures. Therefore the width of each vibrational band in the spectrum can be much less than the width realized during total equilibrium. The integral emissivity (in the absence of reabsorption) does not depend on the degree of departure from equilibrium. Therefore in the present work the entire system of bands was recorded as a whole without spectral resolution.

The pressure of the experimental gas at the exit from the nozzle is low and the integral emission intensity of ν_3CO_2 was recorded with difficulty. The intensity of the other bands of CO_2 emission and of the overtones is much lower so that the necessity of using a spectral instrument to isolate the ν_3CO_2 emission disappears. The absence of reabsorption was determined by the low pressure of the emitting gas. Under these conditions the recorded radiation is proportional to the concentration n of carbon dioxide molecules and depends on the vibrational temperature of the ν_3-type CO_2 vibrations (we will designate it as T_3): $I = n\varphi(T_3)$. The value of the temperature factor $\varphi(T_3)$ was determined by direct calibration from the emission of the carbon dioxide behind the front of the incident shock wave. The carbon dioxide was diluted with argon to a considerable extent. This proved to be necessary to prevent the effect of reabsorption and to decrease the signal to the necessary level. The difference between the optical characteristics of the mixture CO_2 + Ar and undiluted carbon dioxide gas, connected with the difference in line broadening, plays an insignificant role under the conditions of these experiments since the unreabsorbed integral emission of the entire system of lines as a whole was recorded in the experiments. The absence of reabsorption was controlled in the experiments conducted at different pressures.

The emission signal of the gas behind the shock-wave front becomes practically constant after several dozen microseconds; this level was used for the calibration measurements. It was assumed that equilibrium ($T_3 = T$) is established in this case; the values of T and n were calculated from the measured V and p_1 using laws of conservation of the flows of mass, momentum, and energy.

In order to obtain the values of T_3 from the measured intensity at the exit from the nozzle it is necessary to know the concentration n of carbon dioxide molecules in this section of the flow. The ratio of gas densities at the exit and entrance of the nozzle depends weakly on the state of the working gas: the calculated gas density for nonequilibrium flow in a nozzle under the conditions being considered coincides with the equilibrium value to within 5%. Therefore the ratio of concentrations at the exit and entry of the nozzle which corresponds to stationary equilibrium flow and equals $1.93 \cdot 10^{-3}$ was used in the analysis of the results. By measuring the intensity of infrared emission of CO_2 molecules at the exit from the nozzle one can determine the vibrational temperature T_3 corresponding to the excitation of ν_3-type vibrations of CO_2.

2. Let us examine the flow of relaxing carbon dioxide gas in a nozzle. It is convenient to write the relaxation equations for the vibrational energy in accordance with the data on the kinetics of vibrational energy exchange in CO_2. It is assumed that each type of vibration can be considered as harmonic with a Boltzmann distribution of the molecules by levels, so that values of the T_i-vibrational temperature of the i-th type exist. Because of the Fermi resonance $T_1 = T_2$ (the indices here and later indicate the type of vibration of the CO_2 molecule). It is assumed that the energy exchange between the ν_1, ν_2, and ν_3 types of vibration proceeds through the channels (001) ⇌ (030) and (001) ⇌ (110) [6, 7] and that only the ν_2 type of vibration participates in the vibration–translation exchange. For the vibrational energy e_i, which is expressed through the average number of quanta in the given type of vibrations $e_i = [\exp(\theta_i/T_i) - 1]^{-1}$ (θ_i is the characteristic vibrational temperature), one can obtain the equation

$$\frac{de_2}{dt} = \nu p Q \varphi + \frac{p}{\tau}(e_2^\circ - e_2)], \quad \frac{de_3}{dt} = -pQ\varphi$$
$$\varphi = e_3(e_2 + 1)^3 - e_2^3(e_3 + 1)\exp[-(\theta_3 - 3\theta_2)/T] \tag{2.1}$$

where e_i° is the value of e_i when $T_i = T$, τ and Q are the vibration–translation relaxation time and the probability of energy exchange between the ν_1, ν_2, and ν_3 types of vibration, and ν is a constant factor which allows for the presence of two channels of such exchange. The value of ν depends on the ratio of probabilities of the processes (001) ⇌ (030) and (001) ⇌ (110) and on the value of e_2 and varies in the range from 0.5 to 1.5, i.e., $\nu \approx 1$. When $T_2 = T$ (the usual conditions for conducting experiments on the laser fluorescence of CO_2) the equation for e_3 is simplified to the linear equation

$$\frac{de_3}{dt} = pQ'(e_3^\circ - e_3), \qquad Q' = \frac{1 - \exp(-\theta_3/T)}{[1 - \exp(-\theta_2/T)]^3} \tag{2.2}$$

In the more general case of gas flow in a nozzle Eqs. (2.1) must be used. The kinetics of the vibrational relaxation of carbon dioxide examined in [8] is evidently extremely elaborate.

The purpose of the present investigation is the determination of the coefficients Q and τ which make it possible to solve the problem of the vibrational relaxation of carbon dioxide. The method of successive approximations was used for this. The search for the values of Q and τ began with the values Q° and τ° known from the literature and as a first approximation it was assumed that $Q = kQ^\circ$ and $\tau = r\tau^\circ$, where Q° and τ° depend on the translational temperature and the factors k and r are unknown. Such an approach makes it possible to take into account the temperature dependence of Q and τ on the basis of available information with the condition that the factors k and r depend little on T. To determine the value of τ° the values obtained in experiments with shock waves and summarized in the review [9] were used. These values are approximated by the temperature dependence $\log \tau^\circ$ (atm · sec) $= 17.42\, T^{-1/3} - 7.85$. The probability of occupation of the (001) level has been obtained in studies by the method of laser fluorescence in the temperature range of 300-1000°K. It was established in [10] that under these conditions the decay of the (001) level follows the linear equation (2.2); converting from Q' to Q, from [10] one can find Q° in the form of the dependence (dimensionality $\mathrm{atm}^{-1} \cdot \mathrm{sec}^{-1}$) $\log Q^\circ = 6.35 - 390/T$ for $T \geq 388^\circ$K and $Q^\circ = 2.2 \cdot 10^5$ for $T < 388^\circ$K. It is established in [11, 12] that in the region T = 800-1000° the results of [10] are incorrect (Q° grows more rapidly with an increase in temperature). For T = 1000° the value of Q° should be increased by 32%. Apparently the most reliable are the results of [13] obtained by the phase method with laser excitation of the (001) state of CO_2 in the range from 300 to 1000°K. Values of Q° according to [10] were used in the present work.

The equations of gasdynamics for a one-dimensional steady stream were used to solve the problem of the flow of a relaxing gas in a nozzle:

$$\rho u A = \mathrm{const}, \quad \rho u \frac{du}{dx} = -\frac{dp}{dx}, \quad \frac{d}{dx}\left(H + \frac{u^2}{2}\right) = 0, \quad p = \frac{\rho R T}{\mu} \tag{2.3}$$

$$H = \beta RT / \mu + \varepsilon \qquad (\beta = {}^7/_2)$$

$$\varepsilon = (R / \mu)\,(\theta_1 e_1 + 2\theta_2 e_2 + \theta_3 e_3)$$

Here ρ and u are the gas density and flow velocity, H is the enthalpy of a unit mass of gas, R is the universal gas constant, μ is the molecular weight, and ε is the vibrational energy. The singular point originating near the critical cross section was passed through by the method of a series expansion of the unknown variables analogous to [8]. The value of the flow rate $\rho u A$ of the gas was determined through trials. The flow rate for equilibrium flow was taken as the initial value.

The boundary layer arising at the walls of the nozzle was taken into account in the framework of a displacement model. The displacement thickness δ^* was determined from the empirical equation [14]

$$\delta^* / x = \varkappa\,(\rho^* u x / \mu^*)^{-\lambda}$$

where ρ^* and μ^* are the effective density and viscosity of the gas within the boundary layer and $\varkappa$ and λ are constant coefficients which depend on the configuration of the nozzle and the flow in the layer. The values of ρ^* and μ^* are determined for the temperature T^* corresponding to the effective enthalpy $h^* = H_0/4$ (Eckert's model). In the calculations it was assumed that $\varkappa = 0.49$ and $\lambda = 0.3$.

The calculated distributions of vibrational (T_2 and T_3) (curves 3-5) and translational temperatures (T) (curves 1 and 2) are presented in Fig. 1 for the flow of carbon dioxide in the supersonic nozzle used. Conditions at nozzle entry: $T_0 = 1500^\circ$K, $p_0 = 15$ atm. Solid lines: solutions without allowance for boundary layer; dashed lines: with allowance for boundary layer. It was assumed that $k = r = 1$ and $\nu = 1.5$. It is seen from the graph that at a distance of ~1 cm the decrease in vibrational energy of the carbon dioxide molecules ceases and the vibrational state is "frozen in." The transition to frozen-in flow corresponds to an increase in the area of the nozzle cross section of about 25 times compared with A_*. The effect of the viscosity of the gas on the flow parameters is not great.

When $k = r = 1$ (i.e., when the literature data on Q and τ are used) in undiluted carbon dioxide the values of T_2 and T_3 coincide, in contrast to the frozen-in flow of the mixtures $CO_2 + N_2 + He$ and $CO_2 + N_2 + H_2O$ in a gasdynamic laser [6, 8] where the processes of vibrational exchange promote the freezing in of the ν_3 state of CO_2 (exchange with N_2) and the deactivation of the ν_1 and ν_2 states of CO_2 (exchange with He and H_2O), i.e., they promote a considerable difference between T_2 and T_3. The coincidence of T_2 and T_3 in the process of cooling of undiluted carbon dioxide qualitatively corresponds to data concerning the single vibrational relaxation time τ in the excitation of carbon dioxide molecules in shock waves. With a decrease in the exchange probability for $(\nu_3) \rightleftharpoons (\nu_1, \nu_2)$ (a decrease in k) the temperature T_2 decreases and

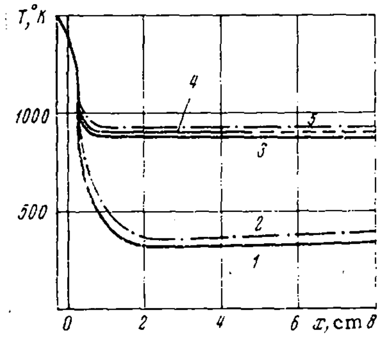

Fig. 1

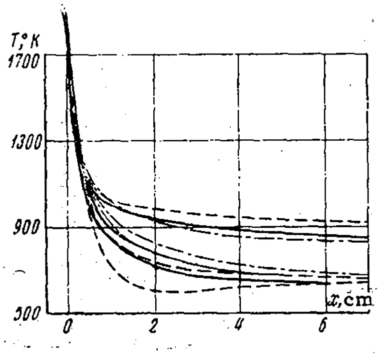

Fig. 2

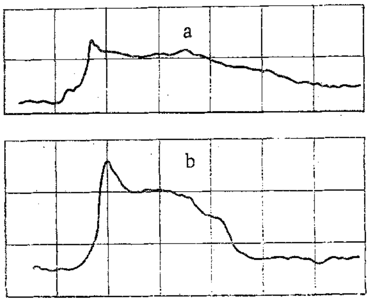

Fig. 3

TABLE 1. Experimental Results of Measurement of Vibrational Temperature T_3 at Exit from Supersonic Nozzle of Shock Tube

N	T_0, °K	p_0, atm	T_3, °K	T_+, °K
1	1930	17.3	730	624
2	1930	9.7	790	624
3	2090	11.1	820	691
4	1920	7.3	850	620
5	2200	17.4	870	736
6	2420	10.7	940	827
7	2050	8.1	960	674
8	2160	8.5	990	720
9	2000	5.2	1000	654
10	2030	4.3	1120	687
11	2060	3.9	1150	716
12	1930	2.0	1210	645
13	2430	1.9	1550	851
14	2420	1.5	1640	827
15	2420	1.0	1660	827

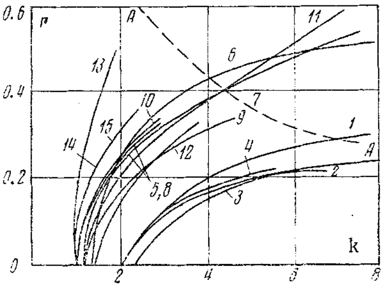

Fig. 4

approaches the translational temperature. The effect of a change in the parameter ν on the calculated results is insignificant, especially for small r.

The nozzle used in the experiments has a considerable aperture angle at the start of the supersonic section. In order to evaluate the applicability of the model of quasi-one-dimensional flow, control calculations of the effect of non-one-dimensionality were made. The flow in individual current tubes was calculated; the streamlines bounding them were taken from the results of a calculation for $\gamma = 1.2$ (γ is the ratio of specific heat capacities) carried out by U. G. Pirumov and É. A. Ashratov. The temperature distribution along the nozzle obtained from the calculation of the flow in individual streamtubes is presented in Fig. 2. The following were used in the calculation: $T_0 = 1930$°K, $p_0 = 17.3$ atm, $k = 1$, $r = 0.1$, $\nu = 1.5$. The greatest temperature differences are observed at the start of the supersonic region of flow. At the exit from the nozzle the difference between the calculated temperature averaged over the cross section (solid line) and the results for the central (dashed line) and peripheral streamtubes (dot-dash line) is dozens of degrees.

3. In the experiments conducted the initial pressure of the carbon dioxide in the shock tube varied in the range from 2 to 45 mm Hg and the velocity of the shock wave varied from 1.2 to 1.9 km/sec. Samples of the oscillograms of the infrared emission intensity at the exit from the nozzle are presented in Fig. 3. The initial conditions in front of the nozzle entry were: (a) $T_0 = 1870$°K, $p_0 = 3.4$ atm; (b) $T_0 = 2200$°K, $p_0 = 3.1$ atm. The time scale is 100 μsec per division. Two sections of increase in emission are seen on the oscillograph curves. The larger first increase is apparently connected with the effect of the radiation scattered from the walls of the nozzle before the arrival of the emitting gas into the field of view of the photoreceiver. Attempts to exclude the effect of scattered light (such as placing a large window transparent to infrared radiation in the wall of the nozzle opposite the receiver) were not able to get rid of it completely. Apparently the origin of the scattered light is connected with intense emission of the gas in front of the nozzle entry. The level of intensity of the scattered light (which was ~10-15% of the useful signal) was taken as the zero reference level. The next sharp increase in the signal is connected with the passage of a system of shock waves in the nozzle [15]; the duration of this maximum varied from 20 to 100 μsec in different experiments. After this the signal varied little with time. This level was identified with a quasistationary mode of outflow. Then the emission intensity decreased.

The vibrational temperature T_3 at the nozzle exit was calculated from the level of emission intensity in the quasistationary mode of flow. A summary of the results obtained is presented in Table 1, and the calculated values of T_+ corresponding to the equilibrium flow of carbon dioxide under the same initial conditions are given there for comparison. It is seen from the table that the flow of carbon dioxide in the experiments is vibrationally frozen in. The value of T_3 at the nozzle exit depends on the pressure. For example, for the same initial temperature $T_0 = 2420$°K the vibrational temperature falls from 1600 to 940°K upon an increase in pressure p from 1 to 10.7 atm.

The value T_3 was measured in the experiments, whereas the kinetics of the relaxation processes in carbon dioxide gas were determined by two values (τ and Q). Therefore some ratio between the values of τ and Q corresponds to each experimental value of T_3. For a more specific representation of the results of the work a curve was constructed in the plane of r and k for the parameters characterizing the deviation from the values of τ and Q known from the literature for each experiment (Fig. 4). Each point on such a curve corresponds to a numerical solution of the problem of the flow of relaxing carbon dioxide with the given initial conditions and the experimentally measured value of T_3 at the nozzle exit. The coordination of the values of r and k was conducted by the method of fitting to the experimental value of T_3 with an accuracy of 10°K. The numbers near the curves are the experiment numbers in Table 1.

The curves obtained in the rk plane form a bundle of lines emerging from the segment (1-1.4) on the abscissa (at r = 0) and directed toward higher values of k. The curvature of the lines increases with an increase in the initial pressure of the carbon dioxide; a slight decrease is noted in the curvature with an increase in temperature. The intersection of the bundle with the curve AA corresponds to realization of the condition $T_3 = T_2$ for the experiment. The 0k axis describes the flow when $T_2 = T$; the region between the 0k axis and the curve AA describes the flow when $T_2 < T_3$ and the region above the curve AA describes the flow when $T_2 > T_3$.

The temperature T_2 must be measured simultaneously in such experiments to obtain unambiguous results of the measurement of τ and Q. The results of the measurements presented in Fig. 4 make it possible to draw a number of important conclusions. The experiments conducted indicate that in the nonequilibrium cooling of carbon dioxide the vibrational deactivation time τ is several times lower than the time obtained by measurements in shock waves, while the probability Q for V−V exchange between the ν_3 and the ν_1 and ν_2 states of CO_2 can be higher than the probabilities obtained by the method of laser fluorescence. The nature of the curves presented in Fig. 4 is such that attempts to adopt as a basis one of the parameters known from the literature ($Q°$ or $\tau°$) leads to the result that the other parameter must be very small (τ) or very large (Q); the case k = r = 1, like the case k < 1, is not realized in these experiments.

Such a conclusion requires additional analysis: first, one must examine possible systematic errors in conducting the experiment and, second, one must allow for the errors in the values of $\tau°$ and $Q°$.

In the present work a number of factors must be regarded as sources of systematic errors: the nonideal and non-one-dimensional nature of the flow in the shock tube and nozzle, the inaccuracy in identifying the section of quasistationary flow in the nozzle, the effect of scattered light on the recorded intensity, the presence of impurities in the experimental gas, discordance between the rated data of the recording instrument and the true values and nonlinear distortions in the electronic circuits, and errors in the reference tables of thermodynamic data and in the subsequent calculations. One method of excluding part of the systematic errors is randomization, i.e., their conversion to random errors through a change in the experimental conditions. For this purpose work was conducted with a different recording instrument (photoreceiver, oscillograph) with the use of gas from different cylinders.

A part of the systematic errors can be estimated (such as the effect of nonlinear distortions in the electronic circuits). For a number of the errors one can indicate the nature of their effect on the result. For example, the scattered light at the nozzle exit can only increase the recorded signal. Therefore the conclusions of the present work relative to a decrease in the vibrational deactivation time τ in the cooling stream remain valid.

With respect to the errors in the values of $\tau°$ and $Q°$ we note the following. The value of $\tau°$ was studied under various conditions so that the systematic error in each individual work can be considered as excluded because of randomization. Assuming that the results of these works have the same weight one can estimate the random error in the measurement of $\tau°$, which is ~20% with a probability of 0.95. The random error in the measurement of $Q°$ is much less than the systematic differences between the results of different works and therefore it can be ignored in the present analysis (for example, the results in [13] were obtained by a statistical analysis of 216 measurements of $Q°$). Refinement of the values of $Q°$ obtained in [10] and used as the standard did not indicate their considerable increase in [12] (k = 1.32 at T = 1000°K) and led to a decrease in $Q°$ in [13] (k < 1).

Let us examine the causes which could result in a considerable acceleration in the processes of energy exchange in CO_2 in the present experiments. Some impurities (such as water vapor) could remain in the experimental gas after purification or enter the gas from the walls of the shock tube. Water vapor has a slight effect on the processes of vibrational exchange in CO_2 at temperatures above 600°K. With an increase in temperature the efficiencies of water and carbon dioxide molecules in the process of vibration–translation exchange become comparable. Therefore the role of impurities in the kinetics of the processes studied is apparently small. The importance of the impurities forming in the experimental gas grows with an increase in temperature [1]. Among the dissociation products of the CO_2 molecules oxygen atoms can make the greatest contribution to the kinetics of vibrational relaxation. At a pressure of 1 atm and a temperature of 2400°K carbon dioxide contains $\sim 0.1\%$ oxygen atoms. It follows from Fig. 4 that with an increase in the initial temperature to 2400°K the deactivation process occurs more slowly than at lower temperatures.

In the absence of the effect of impurities the reason for the observed acceleration of the vibrational deactivation of CO_2 may be connected with intramolecular processes. The failure to allow for anharmonicity, the isolation of individual channels of exchange, and the assumption that there is a Boltzmann distribution of the molecules by vibrational levels are simplifications without which the phenomenological description of the kinetics of vibrational relaxation is considerably complicated. A dependence of the parameters studied on the initial states and paths of relaxation of the system examined can arise as a result of such simplifications.

A comparison of the experimental results obtained with a calculation of the flow of relaxing carbon dioxide leads to the conclusion that when T = 730-1660°K deactivation by vibration–translation exchange in CO_2 occurs three to five times faster than the same process during heating in shock waves, and vibration–vibration exchange during deactivation of CO_2 in a supersonic stream is more probable than during deactivation after resonance laser excitation in a motionless gas.

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