strength; K, rotational quantum number; T, temperature; τ_{col}, time between two collisions; τ, lifetime of the excited state; and r, coordinate along the radius of the jet.

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THERMICALLY NONEQUILIBRIUM IONIZATION IN A CO_2:N_2:He MIXTURE

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UDC 537.521

The results of measuring the electron density in a supersonic stream of a laser-active mixture are given.

The development of laser technology and of nonequilibrium plasma chemistry is stimulating interest in the problem of obtaining a volumetric discharge in a dense molecular gas. As is well known, the uniform ignition of a discharge proves possible only with the application of special procedures, the most important of which is an increase in the initial level of electron density in the discharge gap through preliminary ionization of the gas. One of the interesting and, evidently, promising methods of uniform preionization of large volumes of dense gases in rapid-flow laser systems is thermally nonequilibrinm ionization [1, 2]. Such a method can be realized by heating and adiabatic cooling of the gas in a time less than the relaxation time of vibrational states of diatomic molecules (CO, N_2).

The electron densities recorded in experiments with a stream stagnation temperature $T_0 \approx 2000°K$, $P_0 \approx 15$ atm, and a nozzle Mach number $M = 4$ were $n_e \approx 10^{10}$-10^{11} cm^{-3}, which exceeds the value of n_e calculated by Saha's method for equilibrium conditions by several orders of magnitude [3]. The degrees of ionization attained made it possible to ignite an externally maintained discharge in a supersonic stream of nitrogen [4], through which one can effectively increase the energy stored in vibrational degrees of freedom of the molecules of laser-active media.

The mechanisms of nonequilibrium ionization proposed up to now, although they allow one to conclude that vibrationally excited molecules have a decisive influence on ionization processes, cannot explain the entire collection of experimental data available [5, 6]. The theoretical description of processes of nonequilibrium ionization in the case of a CO_2:N_2:He laser-active medium, of practical importance, is a still more difficult and, to a certain extent, indeterminate problem. Experiments acquire special importance here.

In the paper we give the results of research on the influence of carbon dioxide on the electron density in a supersonic stream of vibrationally excited nitrogen. We give the results

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of measurements of n_e in a CO_2:N_2:He laser mixture heated in a shock tube and expanding in a supersonic nozzle, as well as in a stream formed by supersonic mixing of N_2 and a CO_2 + He mixture. Measurements of electron density in the forechamber of a supersonic nozzle are reported and questions connected with the processes responsible for nonequilibrium ionization in laser-active media are discussed.

The measurement procedure and the installation on which the research was done are similar to those described in [4]. A shock tube with a nozzle on the end was used to heat the gas. The plane supersonic nozzle was made of plastic, the profiled part of which changed into a channel of rectangular cross section. The upper and lower walls of the channel expanded with an aperture half-angle of 2°. Electrodes with a length of 5 cm along the stream and a width of 10 cm were mounted in them at a distance of 20 cm from the critical cross section of the nozzle. The distance between the electrodes was 4 cm. The Mach number in the measurement region was M = 5 and the stream stagnation pressure was P_0 = 12-14 atm. A pulsed voltage with an amplitude of up to 2 kV was applied to the electrodes for a time of no more than 0.5 μsec.

To measure n_e behind the reflected shock wave in the nozzle forechamber we set up round electrodes with a diameter d = 18 mm, spaced 0.5 cm apart. They were inserted in a direction perpendicular to the motion of the shock wave front. The electron density was measured by applying a voltage pulse with an amplitube of up to 10 kV to the electrodes. We determined n_e from the current of the pulsed, externally maintained discharge,

$$n_e = I/v_e eS,$$

where S is the area of the electrodes. The current and voltage on the discharge gap were recorded with an OK-17 oscillograph.

The volt–ampere characteristic curves of current were taken in the experiments to determine the cathode voltage drop and the voltage range in which an externally maintained discharge is realized. A typical volt–ampere characteristic curve in a supersonic nitrogen stream is given in Fig. 1. As can be seen from the figure, the dependence of the current on the voltage has a form typical for the current of an externally maintained discharge, with clearly expressed characteristic sections: the space-charge-limited current at low voltages (AB), the saturation current (BC), and the current with ionization enhancement (CD).

When carbon dioxide was added to the nitrogen, the form of the dependence of the current on the applied voltage did not change. But the amount of current recorded decreased with an increase in the CO_2 concentration. A current was not recorded in "pure" carbon dioxide (the sensitivity of the recording system was I ≈ 1 mA, which corresponds to $n_e \approx 10^7$ cm^{-3}). The electron density in N_2 and a CO_2 + N_2 mixture was calculated for a ratio of electric field strength to particle number $E/N = 3 \cdot 10^{-16}$ V/cm^2. The velocities of electron drift were taken from [7]. The field strength in the discharge gap was determined from the relation $E = (U_0 - U_c)/d$, where U_c is the cathode voltage drop (U_c = 500 V; see Fig. 1). In Fig. 2 we give the electron density n_e as a function of the carbon dioxide concentration in the CO_2:N_2 mixture. It is seen from the figure that the addition of carbon dioxide to the nitrogen in the amounts typical for CO_2 lasers (5-15%) leads to a decrease in electron density by no more than 50%. This allows us to concude, in particular, that if nitrogen molecules with high vibrationally excited levels take part in the ionization reaction, then despite the energy exchange between nitrogen and CO_2, a sufficient number of highly excited nitrogen molecules remain in the mixture for ionization.

Measurements of n_e were made in a laser mixture CO_2:N_2:He = 1:5:4 at T_0 = 1300-2100°K. The electron density was measured both in a mixture mixed in advance and in a stream formed by supersonic mixing of N_2 and a CO_2 + He mixture. Synchronization of the start of formation of the CO_2 + He stream with the start of N_2 outflow was accomplished using a high-speed magnetic valve. The time of actuation of the valve was less than 0.5 msec. The Mach number of the nitrogen stream in the injection region was M = 3. As can be seen from Fig. 3, for the same stream stagnation temperatures the electron density in the mixing variant considerably exceeds the corresponding values of n_e in the regime with a premixed mixture. At $T_0 \approx 1900$°K, in particular, the values of n_e differ by an order of magnitude.

Such a difference is evidently due to the fact that with mixing of CO_2 + He in the supercritical part of the nozzle, processes of deactivation of nitrogen by carbon dioxide are considerably decreased. As is well known, nitrogen has an extremely long time of vibrational relaxation while a CO_2:N_2:He mixture relaxes considerably faster, which leads to lower values of

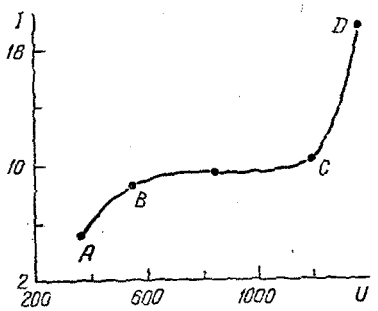

Fig. 1

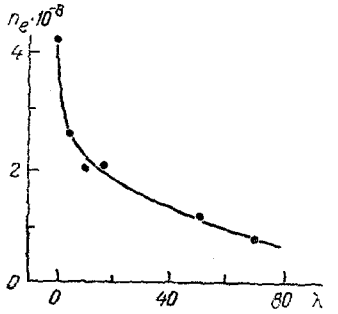

Fig. 2

Fig. 1. Typical volt–ampere characteristic curve of current in nitrogen (M = 5, P_0 = 1.3 MPa, T_0 = 1900°K). U, V; I, mA.

Fig. 2. Electron density as a function of carbon dioxide concentration in a mixture with nitrogen (M = 5, P_0 = 1.3 MPa, T_0 = 1900°K). n_e, cm^{-3}; λ is the CO_2 content in percent.

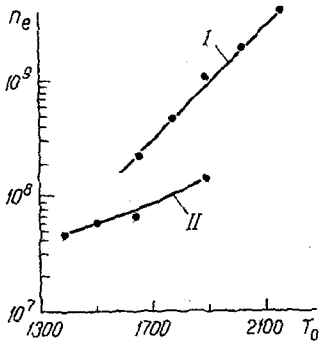

Fig. 3

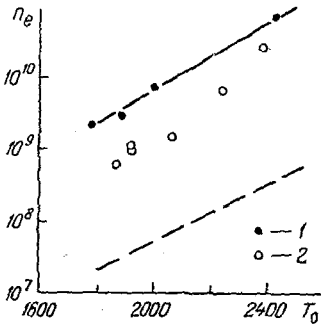

Fig. 4

Fig. 3. Electron density in a supersonic stream of a CO_2:N_2:He mixture as a function of the temperature in the forechamber (P_0 = 1.2 MPa, M = 5, CO_2:N_2:He = 1:5:4 mixture): I) measurements in the mixing regime; II) in a premixed mixture. T_0, °K.

Fig. 4. Electron density in nitrogen as a function of gas temperature in the forechamber (P_0 = 1.2 MPa): 1) measurements in the nozzle forechamber; 2) in the supersonic stream.

the vibrational temperature. In a regime with mixing, more efficient freezing in of the vibrational energy of nitrogen is achieved, which ultimately leads to higher electron densities.

The experiments on measuring the electron density in the forechamber of the supersonic nozzle, confirming the nonequilibrium character of the ionization processes in supersonic streams of vibrationally excited molecules, are of fundamental importance.

In Fig. 4 we give the results of measurements of n_e in nitrogen for the forechamber and in the stream beyond the nozzle. The measured values were compared with those calculated from the Saha formula. Here we allowed for the fact that, according to numerous literature data, such as [8, 9], in the working volume of an experimental installation (shock tube) the natural content of easily ionized impurities is $\delta_{Na} \simeq 1\text{–}3 \cdot 10^{-5}$%.

The emission of the sodium D line was also recorded in our experiments. The radiation was recorded with a photomultiplier through an interference filter.

We calculated n_e from a formula allowing for ionization of the impurity contained in the gas [10]. The solid line corresponds to the calculated value of n_e. During expansion of the gas in the nozzle, the particle density decreases and, in the absence of channels of loss and creation, the initial values of n_e must decrease to the values lying on the dashed line. As can be seen from Fig. 4, the measured electron densities in a supersonic nitrogen stream are considerably higher than the equilibrium values, i.e., processes increasing the degree of ionization occur during gas expansion in the nozzle. A full understanding of the essence of

the phenomenon taking place requires not only detailed information about the kinetics of the individual collisional and radiative processes occurring with ions, electrons, and neutral particles, but also certain assumptions about the energy distribution of the active and excited molecules. Our information about these processes is confined, in the best case, to knowledge of the rates of certain reactions, and these rates were usually measured for individual reactions under conditions far from the conditions occurring in the experiments.

Attention should be drawn to the following two important facts, however. First, intense energy exchange exists between electrons and vibrationally excited molecules, resulting in the fact that the electron temperature is closely connected with the vibrational temperature of these molecules [11]. Therefore, the electron temperature in the nozzle corresponds to the frozen-in vibrational temperature of nitrogen, considerably exceeding the translational temperature.

Second, the nonresonance interaction of excited nitrogen with sodium atoms leads to the appearance of atoms with excited electron levels [12].

Since the ionization cross section of excited particles is considerably larger than the ionization cross section of particles in the ground state, ionization processes with their participation evidently contribute to the formation of the superequilibrium electron density. Thus, it is possible for the following ionization processes to occur in expanding streams of vibrationally excited nitrogen:

$$\mathrm{Na}(3^2\mathrm{S}) + e \rightarrow \mathrm{Na} + 2e,$$
$$\mathrm{Na}(3^2\mathrm{P}) + \mathrm{Na}(3^2\mathrm{P}) \rightarrow \mathrm{Na}_2 + e,$$
$$\mathrm{Na}(3^2\mathrm{P}) + e \rightarrow \mathrm{Na} + 2e.$$

An experimental confirmation of the fact that the presence of sodium atoms causes ionization effects on the order of those recorded is a twofold increase in the signal upon the addition of salt (NaCl) to the low-pressure chamber of the shock tube. We note that if we formally apply the Saha equation [10] to calculate the electron density in the measurement region in the channel beyond the nozzle, taking $T = T_e = T_v$, we obtain sufficiently good agreement with the experimental data (see Fig. 4).

Measurements of the electron density were also made for argon. The recorded values of n_e coincided with the equilibrium values to within the experimental errors, which confirms the determining role of vibrationally excited molecules in ionization processes under nonequilibrium conditions.

Thus, our experiments showed that during expansion in a supersonic nozzle, a laser-active medium not only possesses amplifying properties but also is in nonequilibrium ionization. The degrees of ionization attained in this case are sufficient for the ignition and stabilization of a volumetric discharge in a supersonic stream.

NOTATION

n_e, electron density; I, current; v_e, electron drift velocity; e, charge of an electron; M, Mach number; P_0, stagnation pressure; T_0, stagnation temperature; T_e, electron temperature; T_v, vibrational temperature; E, field strength; N, number of gas particles; δ_{Na}, percentage content of sodium.

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MEASUREMENT OF OXYGEN RECOMBINATION RATE CONSTANTS BY THE PIEZOELECTRIC METHOD

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The piezoelectric method is used to measure pressure in a gas flow within a nozzle, measurement results are compared with calculation, and values of the oxygen atom recombination rate constant are obtained for the temperature range 1680-3250°K.

Calculation of parameters of hypersonic air coolant flows requires consideration of "reverse" processes – atomic recombination rates, molecular deactivation – and thus knowledge of the corresponding rate constants for such processes. However, at present such processes have been studied much more poorly than the corresponding forward ones. The goal of the present study was the measurement of oxygen recombination rates in a hypersonic cooling flow by recording pressure on the lateral walls of a planar wedge-shaped nozzle. This approach is based on the fact that in contrast to shock waves, where the density is the sensitive parameter of the kinetics, in a cooling hypersonic flow the pressure is the sensitive parameter.

Data available in the literature on the recombination rate constant k_r for the reaction $O + O + M \rightarrow O_2 + M$ are not numerous and vary amongst themselves by more than an order of magnitude. The analysis performed, for example, in review [1] concluded that it was impossible to recommend any value of k_r and proposed (for the range $T > 2000°K$) that for the case $M = O_2$ recalculation from the values of the rate constant for oxygen dissociation should be used. (The recombination rate constant k_r is then determined from the kinetic equation $d[O_2]/dt = k_r[O]^2[M]$, where $[O_2]$, $[O]$, and $[M]$ are the concentrations of O_2 molecules, oxygen atoms O, and particles M, which latter play the role of third bodies in the recombination process.)

The experiments were performed in a shock tube with internal diameter of 49.3 cm. The gas (pure oxygen) was heated first in an incident, then a reflected shock wave to a state of partial dissociation, then escaped through a planar wedge-shaped nozzle, with an included angle of 15°, critical section height of 4 mm, and curved confusor section 8 mm in radius. Pressure sensors were installed on the face wall ahead of the nozzle entrance, allowing study of the characteristics of the gas heated by the reflected wave. Additional piezosensors were placed at distances of 46, 76, and 126 mm from the critical section [2].

The velocity of the incident shock wave was measured by film (thermal) sensors. The working material used was oxygen, heated in a reflected shock wave to a pressure of 8-33 atm and temperature of 3670-4470°K. This corresponds to an initial oxygen dissociation of 25-44%. Experimental conditions are presented in Table 1.

The nozzle and entire measurement complex were located near the tube face at a distance of 11.5 m from the high pressure chamber. The method for performing experiments in such a shock tube with nozzle is described in detail in [3]. The piezoelectric sensors used were precalibrated by pressure measurements in an incident shock wave with known equilibrium pa-

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