

# Associative ionization of diatomic molecules during adiabatic expansion in supersonic flow

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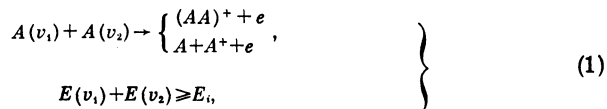
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Associative ionization of the  $N_2$  and  $CO$  molecules was investigated experimentally and theoretically under conditions of adiabatic cooling of a gas heated by a shock wave. It was found that in a wide range of conditions the contribution of the associative ionization processes exceeded greatly (by several orders of magnitude) the thermal ionization contribution.

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## INTRODUCTION

Ionization processes in molecular gases play an important role in the investigations relating to the design of high-power gas lasers, as well as in plasma chemistry, high-temperature gasdynamics, and physics of the atmosphere. Ionization by electron impact and photoionization have now been thoroughly studied and are used widely in experiments involving non-self-sustaining discharges in molecular gases.<sup>1</sup> It has been suggested<sup>2</sup> that there may be an ionization channel in gases involving collisions of vibrationally excited molecules in accordance with the following scheme



where  $A(v)$  is a molecule in the  $v$ -th vibrational state of energy  $E(v)$ ;  $E_i$  is the ionization energy;  $AA^+$  and  $A^+$  are the complex and simple ions of the molecule  $A$ .

Recombination, which is the reverse of the reaction (1), plays an important role in the electron balance of a gas-discharge plasma and has been investigated thoroughly by experimental methods.<sup>3</sup> Studies of the forward reaction (1) under electric discharge conditions present considerable difficulties due to the complexity and variety of plasmachemical reactions resulting in the ionization of molecules, so that it is not possible to separate experimentally the reaction (1) from the large number of possible ionization channels. An alternate method for investigating associative ionization is to determine the conductivity of a molecular gas under conditions of strong vibrational excitation in the absence of other sources of charged particles. These conditions are easily attained during adiabatic expansion of molecular gases in supersonic flow. The strong dependence of the vibrational-translational ( $V-T$ ) relaxation time on the gas temperature has the result that the vibrational energy in a supersonic stream of this kind is considerably greater than the energy of the translational and rotational degrees of freedom. Since adiabatic expansion results in a strong cooling of a gas, the thermal ionization process is then negligible and the reaction (1) is the only possible source of electrons.

The first experimental investigations of the associative ionization of nitrogen during adiabatic expansion in

a supersonic nozzle were reported by us in an earlier paper<sup>4</sup> and the results confirmed the existence of the associative ionization of the vibrationally excited molecules and its high efficiency. We shall report a systematic investigation of the reaction (1) in carbon monoxide and nitrogen streams. The results will be compared with the published experimental data on gas-discharge plasmas in  $N_2$  and  $CO$ .

## THEORETICAL BASIS OF THE METHOD

The processes of associative ionization of diatomic molecules are dominated by the energy of the vibrational degrees of freedom. For example, the reaction (1) in molecular nitrogen may involve only particles which are located no lower than at the 32-nd vibrational energy level. Since the population of such levels is negligible even at temperatures of several thousand degrees, one can investigate reactions of the (1) type only under strongly nonequilibrium conditions. In our investigations such conditions were established by adiabatic expansion in a supersonic nozzle of a gas previously heated and compressed by a shock wave. Vibrational relaxation in supersonic nozzles has already been investigated in detail both experimentally and theoretically (for a review see Ref. 5).

One of the results of our investigations was the determination of the role of anharmonicity of the molecular vibrations in the processes of relaxation and redistribution of energy between the vibrational levels. It was found that the experimentally observed difference between the vibrational relaxation times measured behind the front of a shock wave and in an adiabatically expanding stream is due to a relatively high population of the upper vibrational levels of the molecules, resulting from the vibrational-vibrational ( $V-V$ ) exchange processes under conditions when the difference between the vibrational  $T_v$  and translational  $T$  temperatures is typical of the nozzle experiments. The anharmonicity of the vibration in the  $T_v \gg T$  case has the effect that the rate of direct  $V-V$  processes, representing exchange of a larger for a smaller vibrational quantum, is greater than the rate of the reverse processes involving acquisition from the thermal reservoir of an energy equal to the anharmonicity energy. This produces a nonequilibrium non-Boltzmann distribution of the molecules between the vibrational levels. The function  $f(v)$  de-

scribing the distribution of the molecules between the vibrational levels under conditions of adiabatic expansion in a nozzle will be derived using a theory developed in Ref. 6. The theory is based on the procedure of transforming a set of quantum vibrational numbers  $v$  into a continuous variable in the kinetic equations.

The system of kinetic equations which then describes the evolution of the distribution function  $f(v)$  reduces to one differential equation analogous to the Fokker-Planck equation in the diffusion approximation. An analysis of this equation in the case of an abrupt contribution of an energy  $\varepsilon_0$  to the vibrational degrees of freedom shows that at high vibrational levels the distribution function  $f(v)$  is of the form<sup>6</sup>

$$\left. \begin{aligned} f(v) &= \frac{(\nu/4, \varepsilon_0)^{1/4}}{(v+1)^{1/2} \tau_{V-T}^{3/4}} - \frac{1}{2\tau}; \\ \tau &= \int_0^v \nu dt, \quad f > 0, \end{aligned} \right\} \quad (2)$$

where  $\nu$  is the effective  $V-V$  exchange frequency. Since the process of adiabatic expansion in a nozzle under "frozen" flow conditions, when the vibrational energy is not converted into heat and is simply redistributed between the various vibrational states, is fully analogous to the case of pulsed excitation of lower vibrational levels, the solution (2) should apply also in the case of expansion. Then, the energy  $\varepsilon_0$  is equal to the frozen store of the vibrational energy, which can be found from

$$u \frac{\partial \varepsilon(x)}{\partial x} \Big|_x = \frac{\varepsilon(x^*)}{\tau_{V-T}(x^*)}, \quad (3)$$

where  $\varepsilon(x)$  and  $\tau_{V-T}(x)$  are, respectively, the equilibrium vibrational energy and the  $V-T$  relaxation time, corresponding to the gas parameters in a section  $x$  in the nozzle;  $u$  is the stream velocity;  $x^*$  is the coordinate of the cross section where the freeze-in occurs. In the case of the stream parameters typical of gas-dynamic lasers, the value of  $x^*$  is practically identical with the coordinate of the throat section. The relaxation time  $\tau$  in Eq. (2), representing the number of the effective  $V-V$  exchange processes, depends on the shape of the supersonic nozzle used in adiabatic expansion and it is given by the expression

$$\tau = \int_{x^*}^x \frac{\nu}{u} dx.$$

It follows from Eq. (2) that a vibrational state  $v$  can be filled only if  $\tau$  exceeds  $\tau = (v+1)^2/12\varepsilon_0$ , so that a suitable selection of the shape of the nozzle can ensure considerable populations of higher vibrational levels. For example, in the case of  $N_2$  and a nozzle of the kind used in experimental investigations (see the description of the apparatus below), when the initial parameters of the gas are  $P_0 = 10$  atm and  $T_0 = 2500^\circ$  K and the expansion corresponds to a Mach number  $M = 6$  in the stream, it follows from Eq. (2) that  $f(32) \approx 10^{-4}$ .

If we know the distribution function  $f(v)$ , we can determine the rate of rise of the number of electrons in a stream due to the associative ionization reaction (1):

$$q_{v-i} = N^2 \left[ \int_{v=0}^{v^{**}} f(v) dv \right]^2 K, \quad (4)$$

where  $N$  is the density of the gas;  $K$  is the rate constant of the process (1);  $v_0$  is defined by the expression  $E(v_0) = E_i/2$ ;  $v^{**}$  is the vibrational quantum number at which the rates of the  $V-V$  and  $V-T$  processes become equal. The value of  $K$  is estimated in Ref. 2 from an analysis of the experimental data on a glow discharge in nitrogen and it is reported there that  $K \approx 3.5 \exp(-1160/T) \times 10^{-15}$  cm<sup>3</sup>/sec. When this constant is used for the stream described above, it readily follows from Eq. (4) that if  $(v^{**} - v_0) \approx 10$ , then  $q_{v-i} \approx 10^{12}$  cm<sup>-3</sup> · sec<sup>-1</sup>.

The density of electrons in a stream is determined by the net effect of a source described by Eq. (4) and a sink representing the recombination and trapping processes. When these processes are allowed for, the degree of ionization of a gas  $\alpha$  can be described by the following equation

$$u \partial \alpha / \partial x = q_{v-i} N^{-1} - \gamma \alpha - \beta \alpha^2 N, \quad (5)$$

where  $\gamma$  and  $\beta$  are, respectively, the trapping and bulk recombination coefficients.

The quantities  $\gamma$  and  $\beta$  in Eq. (5) are affected strongly by the presence of impurities in a gas and by the nature of the molecular ions produced by the reaction (1). For example, in the adiabatic expansion of nitrogen the constants  $\beta$  for the  $N_2^+$  and  $N_4^+$  ions differ by an order of magnitude, and the presence of electronegative impurities in a gas [ $O_2$ , CN, Fe(CO)<sub>5</sub>] can alter by several orders of magnitude the value of the coefficient  $\gamma$ . Therefore, Eq. (5) should be analyzed allowing for specific experimental conditions. Simple estimates show that all the electron-loss mechanisms occurring in a characteristic time of  $\sim 10^{-4}$  sec can be ignored in the case of a pure nitrogen stream. Then, Eq. (5) readily gives

$$\alpha \approx \int_{x^*}^x \frac{q_{v-i} N^{-1}}{u} dx. \quad (6)$$

Estimates obtained from Eq. (6) for the above flow parameters yield  $\alpha \approx 10^{-9}$  and  $n_e \approx 10^8$  cm<sup>-3</sup>, which are many orders of magnitude higher than the equilibrium values even for the gas in the forechamber. Since there are no sufficiently accurate methods for determining the electron densities as low as  $\sim 10^8$  cm<sup>-3</sup>, an experimental confirmation of the effects of associative ionization can be provided using a simple estimate of  $n_e$  deduced from the conductivity of a gas in a static electric field  $E_0$ . The restrictions on the value of  $E_0$  then reduce to a simple requirement that the impact ionization processes should not occur in a gas during the measurement time. This requirement is satisfied when the value of the parameter  $E_0/N$  governing the electron energy is less than  $10^{-15}$  V · cm<sup>2</sup>, so that for the above parameters of a nitrogen stream we have  $E_0 \leq 100$  V/cm.

## DESCRIPTION OF THE APPARATUS

Pulsed gasdynamic apparatus for investigating quasi-steady streams in vibrational nonequilibrium was described in Refs. 7 and 8. Adiabatic compression of a gas to a pressure of 3–30 atm and a temperature of  $(1-6) \times 10^3$  °K was produced by a shock tube with a square (5 × 5 cm) channel cross section. A shock wave was generated by filling the high-pressure chamber with

a driver gas (helium or hydrogen) and then breaking a partition made up of a set of lavsan polyester films. The time taken to establish a quasisteady flow through the nozzle at the initial pressures of the investigated gas (nitrogen, carbon monoxide) of 0.03–0.1 atm in the shock tube channel amounted to 0.1–0.2 msec and the time for quasisteady outflow of a heated plug was 0.5–1 msec. The section with the nozzle was separated from the main shock tube channel by a thin copper diaphragm with incisions and it was evacuated; this ensured rapid formation of the stream and increased greatly the duration of the quasisteady phase of the flow.<sup>7</sup>

The initial temperature and pressure of the heated gas (before the flow) were determined from the equilibrium shock adiabat using the measured velocity of the incident shock wave.

The construction and parameters of the nozzle array were similar to those of a nozzle used earlier to study gasdynamic lasers.<sup>8</sup> The height of the throat cross section was 0.55 mm, the ratio of the areas of the exit and throat cross sections was  $A/A^* = 52$ , and the Mach number of the stream at the exit from the nozzle was  $M = 6$ . The nozzle had a two-dimensional profile with the maximum expansion angle (Prandtl–Meyer angle) and a sharp edge 5-cm long in the throat cross section, where it changed to a channel of constant cross section. This nozzle ensured the fastest fall of the translational temperature along the axis of the nozzle without disturbing the homogeneity of the stream, i.e., it ensured the highest efficiency of freezing-in the vibrational energy.

The walls of the channel with the constant cross section were made of a fabric based laminated plastic (textolite), in which copper electrodes with the diameter of 1 cm were embedded flush with the walls (Fig. 1). The conductivity of the plasma was determined by recording the nonself-sustaining current when a voltage of  $\sim 100$  V was applied to the discharge gap. Electrostatic effects gave rise to a stray signal on the screen of an oscilloscope even in the absence of any voltage on the electrodes. This stray signal was measured using an identical pair of electrodes and, in the system employed, it represented  $10^{-2}$ – $10^{-1}$  of the measured value. Typical oscillograms of the current and the current-

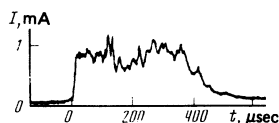
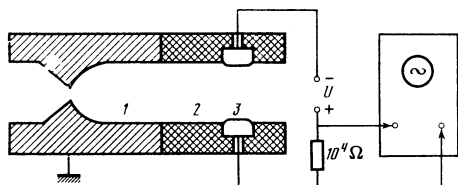


FIG. 1. Schematic representation of the apparatus and a typical oscillogram of the current: 1) profiled metal nozzle; 2) channel of constant cross section made of insulating material; 3) measuring electrodes.

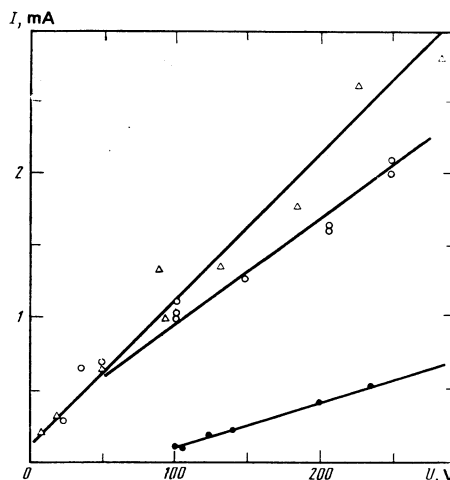


FIG. 2. Dependences of the current between the electrodes on the applied voltage obtained for initial temperatures of  $4000 \pm 150^\circ\text{K}$  ( $\Delta$ ),  $2250 \pm 100^\circ\text{K}$  ( $\bullet$ ),  $2800 \pm 150^\circ\text{K}$  ( $\circ$ ), and for initial pressures  $10 \pm 1$  atm ( $\Delta$ ),  $7 \pm 1$  atm ( $\bullet$ ),  $9 \pm 1$  atm ( $\circ$ ). Positions of measuring electrodes 8 cm ( $\Delta$ ,  $\bullet$ ) and 14 cm ( $\circ$ ) from the throat section. Gas in the forechamber:  $\text{N}_2$  ( $\Delta$ ,  $\bullet$ ) and  $\text{CO}$  ( $\circ$ ).

voltage characteristics are plotted in Figs. 1 and 2.

The velocity of the gas stream at the measurement point was about  $2 \times 10^5$  cm/sec, whereas the drift velocity of electrons under the experimental conditions was considerably higher:  $(2-4) \times 10^6$  cm/sec. Since the drift velocity of ions was considerably less, the density of electrons in a stream could be estimated from

$$n_e = \frac{I/S}{ev_{de}(E/N)}, \quad (7)$$

where the values of  $v_{de}(E/N)$  for nitrogen and carbon monoxide were determined from the results of Refs. 9 and 10.

In estimating  $n_e$  from Eq. (7), we ignored the inhomogeneity of the field between the electrodes and the influence of charge separation on this field. Since the field inhomogeneity resulted in an overestimate of the electron density calculated from Eq. (7) by a factor not exceeding 2–3, and charge separation should reduce the electron density (possibly by a considerable amount), one could assume that the values of  $n_e$  deduced from Eq. (7) were overestimated by a factor not exceeding 2–3.

## DISCUSSION OF RESULTS

We used the above method to determine  $n_e$  in adiabatically expanding  $\text{N}_2$  and  $\text{CO}$  streams, and to record the current-voltage characteristics (Figs. 2–4). The current-voltage characteristics of the gases obeyed Ohm's law (Fig. 2), demonstrating the validity of Eq. (7) under our experimental conditions. We also found the dependences of the electron density  $n_e$  on the initial temperature of the gas (Figs. 3a and 3b). For the flow of nitrogen from the above nozzle (Fig. 3a) the experimental dependence  $n_e(T_0)$  could be approximated satisfactorily by the Arrhenius law  $n_e \propto \exp(-\bar{E}/T_0)$ , where the effective "activation energy" was  $\bar{E} \approx 1$  eV.

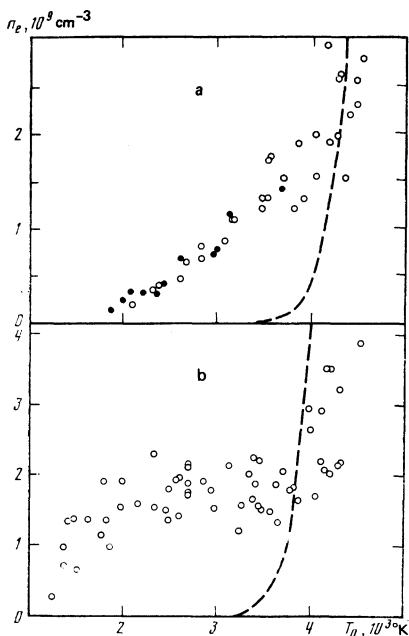


FIG. 3. Dependences of the electron density  $n_e$  on the initial temperature of nitrogen (a) and carbon monoxide (b) at initial pressures  $8.5 \pm 1$  atm (a) and  $9.5 \pm 1$  atm (b), under an applied voltage of 100 V. Measuring electrodes located at distances 14 cm (○) and 8 cm (●) from the nozzle throat. The dashed curves represent the temperature dependences calculated for a thermally ionized forechamber gas using the Saha formula.

The gas temperature in the measurement section was  $T \approx 0.1T_0$ , i.e., an analysis of the ionization process at this temperature allowed us to estimate the effective activation energy as  $E_c \approx 0.1$  eV. This was in good agreement with the dependence  $n_e(T_0)$  obtained from Eqs. (4) and (6), whereas according to the estimates of Ref. 2 the rate constant of the associative ionization of Eq. (1), reduced to the gas temperature  $T$ , should have the form  $K \propto \exp(-0.1 \text{ eV}/T)$  for nitrogen. We compared the experimental values of  $n_e$  with those calculated from the Saha formula for the initial temperature of the gas and assuming that its density was equal to that in the measurement cross section (Fig. 3a). The agreement between the experimental results and those calculated for equilibrium conditions obtained for the gas temperatures  $T_0 \approx 4000^\circ \text{ K}$  indicated that the contribution of electron-loss processes was small throughout the hydrodynamic channel, in agreement with the results reported in Refs. 11 and 12.

An analysis of the temperature dependence  $n_e(T_0)$  in the carbon monoxide case (Fig. 3b) showed that, in contrast to nitrogen, there was no pronounced exponential law and the electron density reached saturation at  $T \approx 2000^\circ \text{ K}$  changing to an exponential dependence of the Saha type at  $T \approx 4000^\circ \text{ K}$ .

It is clear from Fig. 3b that the electron density at  $T_0 \approx 4000^\circ \text{ K}$  was less than the equilibrium value, indicating the existence of an electron-loss channel during expansion. The existence at high values of  $T_0$  of a region with an exponential rise of  $n_e$  indicated that the main electron-loss mechanism was trapping, because

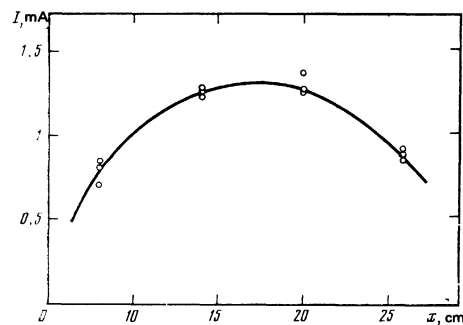


FIG. 4. Dependence of the current between the electrodes in a carbon monoxide stream on the distance between the measurement and throat cross sections under a voltage of 100 V. Initial temperature  $2800 \pm 150^\circ \text{ K}$ , initial pressure  $10 \pm 1$  atm.

the bulk recombination would have resulted in a weak dependence of  $n_e$  on  $T_0$ . The conclusion of the predominance of trapping during flow of carbon monoxide was confirmed by the results of an analysis of the dependence  $n_e(x)$  shown in Fig. 4. Since the value of  $n_e$  fell approximately twofold when the coordinate of the measurement cross section was changed from 17 to 27 cm, in the case of electron loss mainly by bulk recombination the value of  $\beta$  would have been  $\beta > 2 \times 10^{-5} \text{ cm}^3/\text{sec}$ , considerably higher than the values of  $\beta$  known for  $\text{CO}^+$  and  $\text{C}_2\text{O}_2^+$ . It was pointed out in Ref. 13 that if CO contains even a small amount of  $\text{Fe}(\text{CO})_5$ , which usually accumulates in carbon monoxide stored in metal cylinders and is characterized by  $\gamma \approx 10^{-9} \text{ cm}^3/\text{sec}$ , may favor strong trapping of electrons. If we assume that in our case the loss of electrons is due to this mechanism, the concentration of  $\text{Fe}(\text{CO})_5$  can be estimated to be  $\eta > 10^{-4}$ .

An increase in the initial pressure of carbon monoxide was found to increase monotonically the electron density in a supersonic stream. For example, when the initial temperature was  $2600^\circ \text{ K}$ , the value of  $n_e$  measured at a distance of 14 cm from the critical cross section changed from  $1.8 \times 10^8$  to  $4.76 \times 10^9 \text{ cm}^{-3}$  when the initial pressure rose from 2.5 to 22.5 atm.

Estimates of the populations of the vibrational levels with the number  $v_0 \sim 29$  obtained from Eq. (2) for CO gave negative values of  $f(v_0)$ . This indicated that the rates of the  $V-V$  processes under our experimental conditions were slight and that an "excitation wave" described by Eq. (2) did not ensure excitation of the vibrational levels of numbers  $v \sim v_0$  in the measurement cross section. However, the experimentally determined relatively high electron density indicated the existence of a nonequilibrium ionization process.

This discrepancy could be due to the approximate nature of the analytic theory,<sup>6</sup> inaccuracy of the selected  $V-V$  exchange constants, or other ionization sources in a stream associated with vibrationally excited CO molecules (for example, the processes associated with presence of foreign impurities in the stream). A series of control experiments consisted in forcing into the gas in the nozzle cross section beyond the throat, i.e., into the stream of carbon monoxide with a lower translational temperature, a small amount of molecular hydro-

gen favoring strong  $V-T$  relaxation of the CO molecules. This resulted in practically complete absence of charged particles from the stream in question, which was convincing evidence that the vibrationally excited CO molecules participated in the ionization processes. The measurement method was tested and the influence of the thermal ionization effects was estimated by measuring the electron density in Ar, Xe, and O<sub>2</sub> with the same initial parameters. No electric current which might indicate electron densities of  $10^7$  cm<sup>-3</sup> or higher was recorded within the sensitivity limits of the method.

Thus, the superequilibrium density of thermally excited and frozen-in vibrational states of the molecular gas could find extensive applications in many practical problems in molecular and laser physics, such as preionization of a medium in an electric-discharge continuous-flow laser, additional electric "excitation" in gasdynamic and chemical lasers, diagnostics of energy losses in gasdynamic lasers due to redistribution of the energy between the upper vibrational levels; formation of electronic and molecular beams utilizing the gasdynamic methods, etc. Moreover, allowance for this ionization mechanism in a relaxing gas may be very important in the description of the phenomena in hypersonic hydrodynamics and plasma chemistry (such as the appearance of anomalously high electron densities in a stream during flow past other bodies at the velocities encountered in space, the influence of electrons, ions, and molecules with a high level of vibrational excitation on the course of chemical and plasmachemical reactions, etc.).

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