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## ABSTRACT

A model of repetitively pulsed low-pressure CO<sub>2</sub> discharges is developed. In the framework of this model, plasma characteristics (electric field, electron density, gas temperature, and vibrational temperature of the asymmetric mode) are calculated both during the pulses and in the afterglow periods. The CO<sub>2</sub> conversion factor in repetitively pulsed discharges is calculated. Results of computation of plasma parameters and of the conversion factor agree with available experimental data.

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In recent years, various aspects of plasma technologies for CO<sub>2</sub> conversion have attracted great attention.<sup>1–3</sup> A number of works on the conversion efficiency in various kinds of gas discharges have been performed. Among them, low-pressure CO<sub>2</sub> discharges are actively studied using both experimental and computational methods. In particular, parameters of repetitively pulsed discharges at low pressures have been measured.<sup>4,5</sup> Obtained experimental information has been used in computations<sup>6–8</sup> aimed at validation of kinetic schemes. In these computations, some key discharge characteristics, such as the gas temperature dependence on time, were taken from experiments. For deeper insight into the processes governing the discharge dynamics, it is helpful to calculate the whole set of plasma characteristics self-consistently.

In this work, based on the approach previously elaborated for simulation of stationary discharges,<sup>9</sup> a model of non-stationary regimes is developed. Calculations of characteristics of repetitively pulsed discharges for conditions of experiments<sup>4,5</sup> are performed. Obtained plasma parameters and the CO<sub>2</sub> conversion factor are compared with experimental data.

Low-pressure CO<sub>2</sub> discharges in long tubes, supplied by repetitive voltage pulses with on time  $\tau_{\text{on}}$  and off time  $\tau_{\text{off}}$  of millisecond range durations, are considered. The electric current  $I$  during the pulses is taken independent of time. In considered conditions, the balance of charged species in the discharge is governed by their production in electron–molecule collisions and loss due to ambipolar diffusion to the tube walls. The time required for establishing the balance of production and loss of charged species, in considered conditions being around or smaller than 0.1 ms, is much shorter than the current pulse

duration and than the time scales of variation of other plasma parameters: gas temperature, electric field, etc. It allows to consider the balance of charged species in quasi-stationary approximation. The stationary balance in low-pressure discharges is described by the Schottky equation:<sup>10</sup>

$$K_i n = \frac{D_a}{\Lambda^2}, \quad \Lambda = R/2.4, \quad (1)$$

where  $K_i$  is the ionization rate constant,  $n$  is the number density of molecules,  $R$  is the inner tube radius, and  $D_a$  is the coefficient of ambipolar diffusion [applicability of Eq. (1) in the considered conditions is discussed in Ref. 9]. Equation (1) gives the reduced electric field  $E/n$  vs the product  $nR$ . Note that in pulsed regimes, the gas density varies in time, due to gas heating (at constant pressure) during the current pulses and cooling between the pulses.

The dependence of gas temperature  $T$  on time  $t$  during the pulse is given by the following equation:

$$nC_p \frac{\partial T}{\partial t} = \eta j E + \frac{1}{r} \frac{\partial}{\partial r} \left( \chi r \frac{\partial T}{\partial r} \right). \quad (2)$$

where  $C_p$  is the heat capacity at constant pressure,  $\chi$  is the thermal conductivity,  $j(r)$  is the current density, and  $\eta$  is the fraction of total energy input transferred to gas heating. Solution of Eq. (2) in stationary case, for the parabolic radial profile of current density  $j(r) = j(0) (1 - r^2/R^2)$ , with  $j(0) = 2I/(\pi R^2)$  (see Ref. 9), and thermal conductivity proportional to the temperature,  $\chi = aT$ , gives expression for the temperature  $T_0$  at the axis<sup>9</sup>

$$T_0^2 = T_w^2 + 3\eta IE/4\pi a \quad (3)$$

(here  $T_w$  is the wall temperature, taken equal to 300 K). Equation (3) allows to estimate approximately the magnitude of the last term in Eq. (2), describing heat losses. The rate of heat losses is taken the same as that corresponding (for given  $T_0$ ) to stationary value. This approach results in an equation for the axial gas temperature,

$$nC_p \frac{dT_0}{dt} = \frac{2}{\pi R^2} \eta IE - \frac{8a(T_0^2 - T_w^2)}{3R^2}. \quad (4)$$

At evaluation of fraction  $\eta$ , it is assumed, as in Ref. 9, that the energy going to gas heating equals the total input energy less that transferred to the walls or emitted spontaneously by vibrationally excited molecules of the asymmetric mode and that spent on dissociation through electronically excited states,

$$\eta = 1 - gC_{\text{vib}} - C_{\text{dis}}, \quad C_{\text{vib}} = \frac{E_V K_{\text{vib}}}{eV_e E/n}, \quad C_{\text{dis}} = \frac{E_D K_{\text{dis}}}{eV_e E/n}. \quad (5)$$

where  $V_e$  is the drift velocity of electrons,  $K_{\text{vib}}$  and  $K_{\text{dis}}$  are the rate constants of vibrational excitation of the asymmetric mode and of dissociation by electron impact, respectively,  $E_V = 0.29$  eV is the vibrational quantum of the asymmetric mode,  $E_D = 5.52$  eV is the bond  $\text{CO}_2$  dissociation energy, and  $g$  is the fraction of energy of the asymmetric mode lost due to the transfer of vibrationally excited molecules to the walls or due to radiative decay,

$$g = \frac{\tau_w^{-1} + A_r}{K_q n + \tau_w^{-1} + A_r}, \quad (6)$$

where  $K_q$  is the rate constant of quenching of excited molecules  $\text{CO}_2(001)$  in collisions with unexcited molecules,  $\tau_w^{-1}$  is the rate of losses of species  $\text{CO}_2(001)$  at the tube walls, and  $A_r$  is the rate of their radiative decay.

Evaluation of the vibrational temperature  $T_V$  of the asymmetric mode at the axis is based on the balance equation for the number density  $n_v$  of excited molecules  $\text{CO}_2(001)$ ,

$$\frac{dz_v}{dt} = K_{\text{vib}} n_e - K_q n(z_v - z_T) - (\tau_w^{-1} + A_r) z_v, \quad (7)$$

where  $z_v = n_v/n = \exp(-E_V/kT_V)$  and  $z_T = \exp(-E_V/kT_0)$ . The rate of losses of vibrationally excited molecules at the walls is evaluated as

$$\tau_w = \frac{R^2}{6D} + \frac{R(2 - \gamma)}{\gamma V_{th}}, \quad (8)$$

where  $D$  is the diffusion coefficient of  $\text{CO}_2$  molecules,  $V_{th}$  is their thermal speed, and  $\gamma$  is the accommodation coefficient. The axial density of electrons is evaluated as  $n_e = 2I/(\pi R^2 e V_e)$ .

Equations (4) and (7) give  $T_0$  and  $T_V$  vs time during discharge pulses. Between the pulses,  $T_0$  is calculated using the following equation:

$$nC_p \frac{dT_0}{dt} = E_V n(z_v - z_T) K_q n(1 - g) - 8a(T_0^2 - T_w^2)/3R^2. \quad (9)$$

The first term in the right-hand side of Eq. (9) describes gas heating due to relaxation of vibrational energy [note that in considered conditions of relatively low  $T_V$ , the effect of this term on solution of Eq. (9) is quite weak]. Between the pulses,  $T_V$  is obtained using Eq. (7) with the first term in the right-hand side taken zero.

Kinetic and transport coefficients involved in equations presented above are taken from experiments or calculated with BOLSIG+ code<sup>11</sup> (using Phelps set of cross sections). For heat capacity, approximation of the data presented in Ref. 12 is taken  $C_p = 37.2 + 0.033(T_0 - 300)$  J/K/mol; the values and expressions for all other parameters are taken the same as in Ref. 9.

Calculations have been performed for conditions of experiment:<sup>5</sup> the inner tube radius  $R = 1$  cm, pulse duration  $\tau_{\text{on}} = 5$  ms, interval between the pulses  $\tau_{\text{off}} = 10$  ms, pressures 1 and 5 Torr, and discharge currents 20 and 50 mA. Initial values of the gas and vibrational temperatures are taken equal to 300 K. After two-three on-off periods, obtained temporal profiles of plasma parameters cease to change from period to period. Calculated profiles shown in the figures below correspond to the fifth pulse (to the stage when variation of the plasma parameters from pulse to pulse is negligibly small).

In Fig. 1, calculated and measured profiles of the temperatures  $T_0$  and  $T_V$  are given at pressure 1 Torr ( $T_0$  values<sup>5</sup> obtained using Raman spectroscopy are shown). For both currents,  $T_0$  approaches rather quickly a maximum value at the discharge stage and quickly restores initial value in the afterglow. Evaluation of the loss terms in Eq. (7) shows that in these conditions, a quenching of vibrationally excited molecules occurs mainly at the tube walls (as in stationary discharges at this pressure<sup>9</sup>). Considerable vibrational-translation nonequilibrium holds during the whole relaxation period.

Figure 2 shows profiles of  $T_0$  and  $T_V$  at 5 Torr. In this case,  $T_0$  increases during the whole discharge pulse and decreases in the afterglow to values exceeding 300 K;  $T_V$  in the afterglow relaxes quickly to the gas temperature.

Note that estimates of  $T_V$  are lower than the measured values, the difference increasing with the growth of current (similarly to estimates<sup>9</sup> for stationary regimes). A possible reason is the transfer to the  $\text{CO}_2$  asymmetric mode of vibrational energy of CO molecules produced due to  $\text{CO}_2$  conversion. The role of this process, not accounted in our calculations (considering only processes in pure  $\text{CO}_2$ ), increases with the growth of current and, hence, of CO content.

Figure 3 shows variation of the reduced field  $E/n$  and the number density of electrons  $n_e$  at the axis during the discharge pulse. (As described above, the stage of fast increase in  $n_e$  at the beginning of current pulse is replaced with stepwise growth to the quasi-stationary value.) The reduced field, being a decreasing function of  $nR$ , increases with time because of a decrease in the density  $n$ . Variation of  $n_e$  with time is weak.

In considered current and pressure ranges, dominating dissociation channel in repetitively pulsed discharges is, like in stationary discharges, the reaction  $\text{CO}_2 + e \rightarrow \text{CO} + \text{O} + e$ . In this case,  $\text{CO}_2$  conversion can be evaluated in terms of the  $G$ -value—the number of produced CO molecules per unit of input energy (typically per 100 eV), which is given by the following expression:<sup>9,13</sup>

$$G = \frac{K_{\text{dis}}}{eV_e E/n}. \quad (10)$$

In stationary discharges, the number  $\phi_{\text{CO}}$  of CO molecules produced per second is given by the relation  $\phi_{\text{CO}} = GW$ , where  $W = IEL$  is the discharge power (here  $L$  is the gap length).<sup>9</sup> In repetitively pulsed regimes, both  $G$  and  $E$  vary during the pulse. In this case,  $\phi_{\text{CO}}$  is evaluated by averaging over the on-off period,

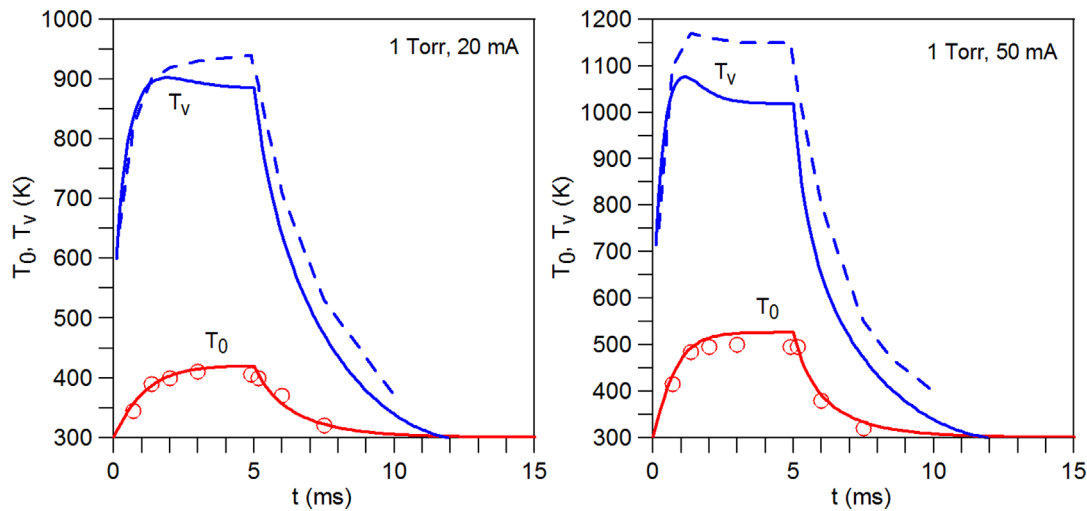


FIG. 1. Gas and vibrational temperatures at the axis vs time, at pressure 1 Torr, for currents 20 mA (left) and 50 mA (right). Points and dashed lines—experiment<sup>5</sup> and solid lines—calculation.

$$\phi_{\text{CO}} = IL \int_0^{\tau_{\text{on}}} G E dt / (\tau_{\text{on}} + \tau_{\text{off}}). \quad (11)$$

The molar fraction  $X_{\text{CO}}$  of CO molecules in the mixture is given by the ratio of  $\phi_{\text{CO}}$  to the gas flow rate  $\phi$  (in molecules per second). If  $X_{\text{CO}}$  is not small, a decrease in molar fraction  $X_{\text{CO}_2}$  of  $\text{CO}_2$  molecules due to conversion should be taken into account, by multiplying  $\phi_{\text{CO}}$  by  $X_{\text{CO}_2}$ , which results in  $X_{\text{CO}} = X_{\text{CO}_2} \phi_{\text{CO}} / \phi$ . The conversion factor, defined as  $\alpha = X_{\text{CO}} / (X_{\text{CO}_2} + X_{\text{CO}})$ , is given by the following expression:

$$\alpha = \frac{\phi_{\text{CO}}}{\phi + \phi_{\text{CO}}}. \quad (12)$$

Table I presents the values  $\alpha_{\text{calc}}$  of conversion factor, calculated, using obtained values of  $G$  and  $E$  vs time, for conditions of experiment:<sup>5</sup>  $L = 17$  cm and  $\Phi = 7.4$  sccm. The values  $\alpha_{\text{exp}}$  measured in Ref. 5 (Raman mean values) are also given. The character of variation of  $\alpha_{\text{calc}}$  with current and pressure is similar to that obtained in the experiment. Estimates of conversion factor for most of considered cases are rather close to measured data.

The model of repetitively pulsed discharges in low-pressure  $\text{CO}_2$  described above calculates self-consistently all plasma parameters (electric field, number density of electrons, gas temperature, and vibrational temperature of the asymmetric mode) vs time during both the discharge pulse and the afterglow. Knowledge of these parameters allows us to evaluate the  $\text{CO}_2$  conversion factor in repetitively pulsed discharges.

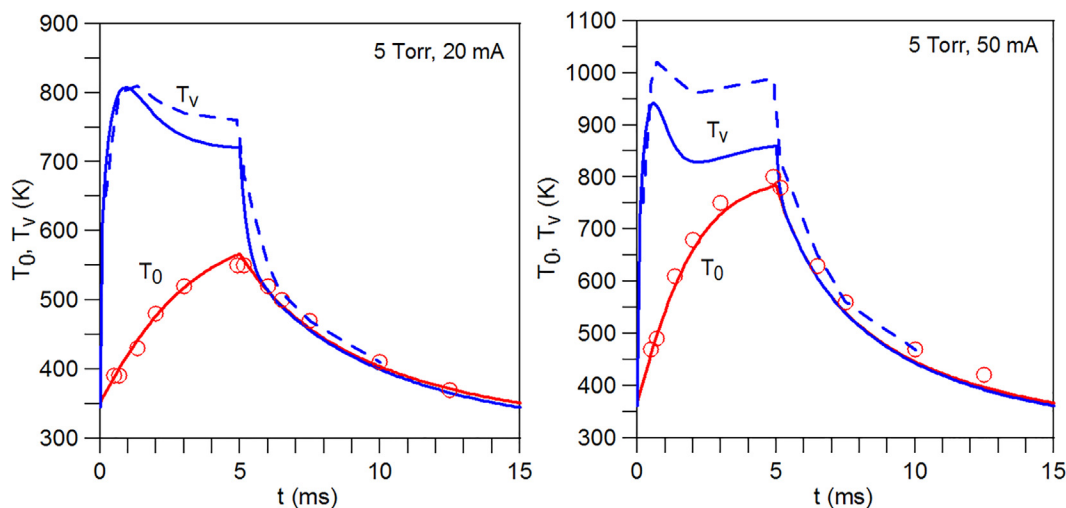


FIG. 2. Gas and vibrational temperatures at the axis vs time, at pressure 5 Torr, for currents 20 mA (left) and 50 mA (right). Points and dashed lines—experiment<sup>5</sup> and solid lines—calculation.

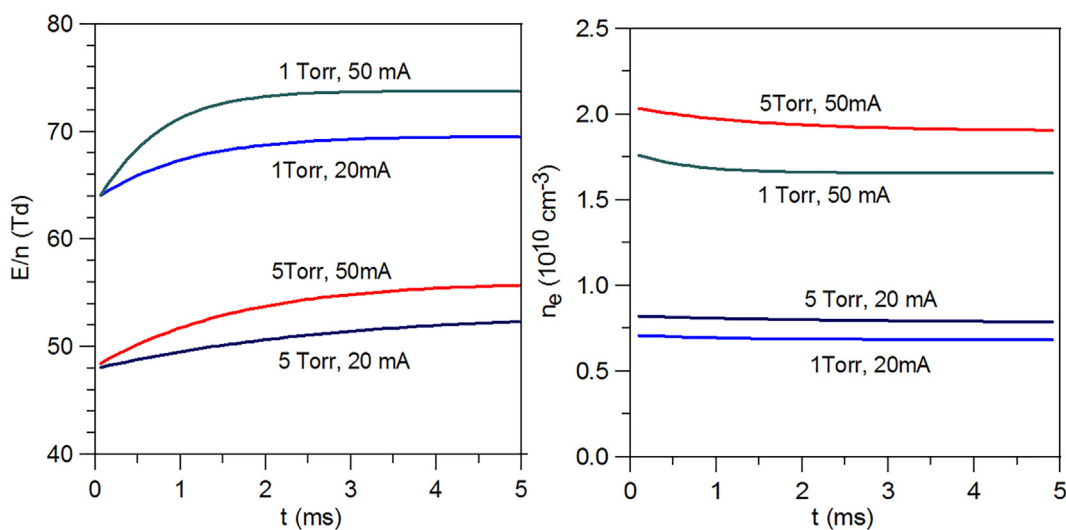


FIG. 3. Reduced electric field (left) and electron number density (right) at the axis vs time during current pulse for various pressures and currents.

TABLE I. Measured and calculated values of the conversion factor.

Pressure (Torr)	Current (mA)	$\alpha_{\text{exp}}$	$\alpha_{\text{calc}}$
1	20	0.08	0.055
5	20	0.085	0.07
1	50	0.12	0.12
5	50	0.16	0.15

Obtained estimates for the conversion factor at various pressures and currents are in reasonable agreement with measured data.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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