THE GAS TEMPERATURE IN MICROWAVE DISCHARGE AT
PLASMOCHEMICAL DISSOCIATION OF CARBON DIOXIDE

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ABSTRACT

Local measurements of neutral gas temperatures of CO₂ non-equilibrium plasma in microwave discharge at a moderate pressures P=40 - 100 Torr and specific energy input J=1-10 J/cm³ were carried out. Interpolated data obtained by spectroscopic and thermoelectric couple techniques appear to give results coincident within the experimental error.

1. INTRODUCTION

Researches of the carbon dioxide dissociation in microwave moderate pressure gas discharges (P=100 Torr) (1,2) has demonstrated high productivity and energetic efficiency of dissociation process.

High efficiency (up to 80%) and discharge diagnostic research results (1-5) testify to a nonequilibrium dissociation mechanism of CO₂ molecule at excitation its vibrational degrees of freedom. In a marked unhomogeneous microwave discharge two zones are conventionally distinguished. A "passive" high temperature central quasi-equilibrium zone unattained by the gas mainstream, and an "active" peripheral nonequilibrium zone penetrated by the gas mainflow in which vibrational-translational nonequilibrium (Tᵥ > Tₒ) is observed.

A theoretical analysis of carbon dioxide dissociation shows that its highest efficiency is achieved through asymmetric vibrational mode (0₀₀) excitation. It is noted that this vibrational mode excitation in a low and moderate pressure plasma is valid at E/N = (1-3)·10⁻¹⁰ V/cm² (1,2) (here E - is electric field, N - is gas density), which realizes under optimum experimental conditions (2-5) at P=100 Torr, J=5 J/cm³.

The efficiency of CO₂ dissociation in nonequilibrium plasma (80% for presonic flow moderate pressure gas discharges and 90-95% for supersonic flow gas discharges) has been proved by now (1,2). However, the choice of conditions for CO₂ dissociation has not been optimized yet.

So, the problem of nonequilibrium plasmochemical discharges researches is formulated as follows: determination of the
distribution functions of plasma components on different degrees of freedom with space resolution. In this paper the problem is developed in respect to translational movement of heavy particles of plasma.

2. EXPERIMENTAL

The paper gives the results of neutral gas temperature measurements in nonequilibrium plasma in stationary microwave moderate pressure discharges in the optimal regimes of CO₂ plasmochemical dissociation:

$$CO_2 \rightarrow CO + 1/2O_2; \quad H=2.9 \text{ eV/mol CO}_2.$$  \hspace{1cm} (1)

The experimental setup is presented in Fig.1. The microwave power input with amplitude $W_0=2$ kW and frequency $f=2400$ MHz was transferred from the generator to a rectangular waveguide of 90x45 mm cross section. The quartz tube with an inner diameter of 20 mm was as plasmochemical reactor and perpendicularly crossed the wide wall of the waveguide. The power input into the discharge $W_d$ was measured by the calorimetric load placed at the end of the waveguide. The specific energy input varied in the range of $J=1-10$ J/cm². The gas stream former in the upper part of the reactor with the construction differ from the one used by (1-3) provided tangential gas flow into the reactor which eventually made the discharge stationary and the quartz tube walls thermally insulated. It should be noted that the tangential turning of the gas flow determines the nature of the discharge glowing: nearly all along the reactor the axis and the wall zones are respectively
characterized by low and high gas density.

3. RESULTS

The distribution of carbon monoxide on rotational levels in electronically-excited state CO($B'$, $^1Σ^+$, $v'$ = 0) was considered. The measurements of intensity distribution (0-1) vibronic band of the CO Angstrom system ($B'$, $^1Σ^+$ $→$ $A'$, $^1Π$ transition) were taken both laterally and above the discharge tube.

The spectroscopic set up used provided reliable resolution of the Q and R branches of the rotational structure. The dia-

![Graph](image)

**Fig. 2.** The dependence of $\ln(\text{const} \cdot I_{k'k''}/S_{k'k''})$ values on $F(k')$ for CO($B'$, $^1Σ^+$, $v'$ = 0) on Q (a) and R (b) branches (0-1) vibronic band of the Angstrom system.
fragments placed in front of the discharge provided local measurements.

CO molecule rotational distributions both on the discharge axis and in the boundary region 4 mm off the discharge axis were determined. The results obtained from the measurements on the boundary region 4 mm off the discharge axis are plotted in Fig. 2. The dependences of \( \ln(\text{const} \, I_{k',k''}/S_{k',k''}) \) values on rotational levels energies \( F(k') \) are shown (here \( I_{k',k''} \) - is the line intensity of the given rovibronic transition, \( S_{k',k''} \) - is the Honl-London factors, \( k' \) and \( k'' \) - are rotational quantum numbers for upper and lower states of the radiative transition respectively). The dependences for \( Q \) and \( R \) branches are plotted separately. The experimental conditions are as follows: pressure \( P = 70 \text{ Torr} \), power input \( W_d = 0.96 \text{ KW} \), \( \text{CO}_2 \) expenditure \( Q = 0.14 \text{ l/s} \). Observed from Fig. 2 near to linear dependences of \( \ln(\text{const} \, I_{k',k''}/S_{k',k''}) \) on \( F(k') \) testify to Boltzmann distribution of the CO molecule on rotational levels. It consequently allows to define the rotational temperature terms.

The rotational temperature is often equated to gas temperature. However the experiments (6,7) show that this statement, especially for nonequilibrium low pressure plasma, is not always satisfied. In general it is unnecessary to know the mechanisms of rovibronic states excitation. When, for example, excitation by heavy particles collisions take place, than the error in gas temperature derived from rovibronic molecular spectra may be of the order of magnitude of value (6,7). The details of identification of rotational and gas temperatures are discussed in (7). Therefore shall analyse only our experimental data.

Firstly, in CO gas discharge, the metastable states due to low concentrations play a minor role than, for instance, in \( \text{N}_2 \) gas discharges. The low concentrations of the metastable particles are caused by their radiative decay and rapid destruction at colliding with \( \text{CO}_2 \), CO and \( \text{O}_2 \) molecules (8). This has been experimentally proved with relating to CO electronically-excited states in \( \text{CO}_2 \) discharges. Moreover, other authors (8,9) showed that in carbon dioxide discharges the CO(\( a^3 \Pi \)) and CO (\( B^1 \Sigma^+ \)) electronic states are mainly populated by a direct electron impact from the ground electronic state CO(\( X^1 \Sigma^+ \)).

Secondly, in conditions of our experiments (at \( P \approx 100 \text{ Torr} \)) the radiative lifetime of the CO molecules in \( B^1 \Sigma^+ \)excited state considerably exceeds the CO molecular rotational relaxation time (10). This fact also testify to a possible identifying the rotational temperatures and neutral gas temperatures. Thus in the conditions of our experiments the identifying of rotational temperatures with gas temperatures is correct.

For gas temperature measurements in the dark zones of the plasmachemical reactor volume two types of thermoelectric couples were used.

Fig. 3 illustrates the results on spatial distribution of gas temperatures in a plasmachemical reactor at \( P = 70 \text{ Torr}, W_d = 0.96 \text{ KW}, Q = 0.14 \text{ l/s} \) at the tangential turning of the gas flow into the discharge tube. To analyse the dependences represented on Fig. 3 the plasmachemical reactor should be divided
into a number of sections (see Fig. 3).

The gas is heated in the microwave power input section(2), nevertheless due to thermal conductivity and reverse convection flows, high temperatures (700–1700 K) are already observed in section(1).

A strong tangential turning of the gas flow in section(2) evidently results in minimum gas density and, consequently, it is the discharge axis that maximum temperatures occurs. The boundary layer temperature measurements in section(2) do not depend on the side of the microwave power input. This fact is explained by intense convection heat exchange of these discharge zones. At the same time the quartz tube wall temperature on the side by the microwave power input is $\approx 800$ K, which is usually $\approx 100$ K higher than the wall temperature measured on the opposite side. Both certain microwave power absorption by the quartz tube surface and preferential gas heating near this surface are responsible.

Decreasing temperatures in the axis of the reactor and increasing temperatures in the boundary layer observed in section(3) are caused by thermal conductivity of the heated gas and convectional flows. The latter increase as the tangential component of the flow rate gradually decreases.

Complete gas mixing, and consequently, temperature equating in the radial direction occurs at the gas flow output from the quartz tube into section(4). Here gas temperatures decrease approximately to $\approx 1400$ K. Gas flow to section(5) causes a sudden drop of the temperature up to $\approx 1100$ K which remains radially homogeneous. It is due to the large volume of section (5), as considerable heat is carried away by the reactor walls.

Gas temperature determining in the reactor dependent on the discharge parameters was also carried out. Fig. 4 illustrates gas temperature dependence on gas expenditure $Q$ at constant power input into the discharge $W_d=0.96$ KW. It should be noted that in Fig. 4 a pressure scale was plotted as along with ex-
Fig. 4. Variation of gas temperatures on CO$_2$ expenditure Q (pressure P) at constant energy input; 1 and 2 are dependencies for the discharge zone 4 mm off axis on the side of microwave power input and opposite it.

Expenditure Q variation, gas pressure P also changed. Curves 1 and 2 correspond to the measurements the boundary layer of section(2) 4 mm off the discharge axis. Curve 1 refers to the discharge zone closest to the microwave power input and curve 2 - with the discharge zone furthest to it. One can easily see that as gas expenditure Q (and pressure P) increases gas temperature fall and attain a stationary level at Q = 0.16 l/s (P = 90 Torr). The dependences may be qualitatively explained in the following way: at pressure P = 90 Torr, the magnitude $E/N = (2-3) \cdot 10^{-16} \text{V cm}^2$ (5) which as has been mentioned corresponds to preferential asymmetric vibrational mode of CO$_2$ excitation, i.e. to optimal conditions of CO$_2$ dissociation through vibrational excitation. Decreasing gas expenditures (pressures) should eventually result in increased $E/N$ of the discharge (5). It causes a higher relative part of CO$_2$ electronically-excited states, which ultimately result in higher gas heating due to E-T relaxation processes.

The differences of the curves 1 and 2 can be also qualitatively explained. At lower Q gas in the boundary layer closest to the microwave power input heats more (curve 1) than in the part furthest to the power input (curve 2). At higher gas expenditure the curves are brought together and at Q = 0.16 l/s, the temperatures tend to coincide within the experimental error due to more effective gas mixing at higher gas expenditures.

So, experiments like these confirm the fact that optimal CO$_2$ dissociation regimes in nonequilibrium plasmochemical dis-
charges are characterised by minimal neutral gas temperatures. They also implicitly confirm (2-5) that with a minor discharge tube diameter CO₂ dissociation efficiency occurs at a higher energy input (the specific energy input at Q=0.16 1/s and W₀= 0.96 KW is J=6 J/cm³). Our experimental data cannot serve as a proof of this fact as CO₂ dissociation efficiency was not measured directly, besides a waveguide of a different cross section than in (2-5) was used. Nevertheless, all the above experimental data directly or implicitly confirm the existing point of view of the CO₂ optimal dissociation mechanism.

REFERENCES

(9) E.A. Trubachev, Proceedings of P.N. Lebedev Physical Institute, 102, 3 (1977).