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Decomposition of carbon dioxide in a discharge maintained by continuous focused sub-terahetz radiation at atmospheric pressure

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For the first time, experiments were carried out on the decomposition of carbon dioxide in a plasma torch maintained by continuous focused gyrotron radiation with a frequency of 263 GHz in an argon flow at atmospheric pressure. It is shown that, despite the decrease in the electron density by a factor of 5, when 3% carbon dioxide is added to the plasma-forming gas, it is possible to achieve its degree of conversion of 22% due to the nonequilibrium nature of maintaining the discharge. Thus, the prospects of using high-power electromagnetic radiation in the subterahertz range for solving plasma-chemical problems of the decomposition of highly stable molecules have been demonstrated. Keywords: microwave discharge, nonequilibrium plasma, gyrotron, subterahertz radiation, CO_2 decomposition.

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The decomposition of carbon dioxide (CO_2) in various atmospheric-pressure discharges with subsequent conversion of reaction products is a topical problem in the field of low-temperature plasma physics [1,2]. The highest degrees of CO_2 conversion were achieved in non-equilibrium plasma of barrier and microwave discharges and in gliding arc discharges [1]. Microwave discharges are thought to be the most promising in terms of enhancing the degree of non-equilibrium of plasma. One of these approaches consists in raising the frequency of heating radiation. It was demonstrated in [3] that the use of microwave gyrotron radiation with a frequency of 24 GHz instead of common magnetron radiation allows one to produce strongly non-equilibrium plasma that provides a record-high degree of CO_2 conversion. In view of this, it appears important to study a gas discharge maintained by subterahertz radiation. Such studies have become possible only relatively recently when high-power subterahertz gyrotrons operating in continuous and pulsed modes were constructed [4]. In the submillimeter range, quasi-optical systems for electromagnetic radiation focusing allow one to localize the discharge within a region on the order of a wavelength in size, thus enhancing the specific energy deposition into plasma [5]. The electron density in such discharges is close to the critical one for a given heating field frequency, and the temperature characteristics of plasma have a substantially non-equilibrium distribution [6]. Unique plasma parameters of subterahertz discharges make them promising non-equilibrium media for modern plasma-chemical applications (especially those that require efficient disruption of molecules with a high interatomic binding energy [2]).

In the present study, we report the results of experiments on decomposition of carbon dioxide in a plasma torch maintained by continuous focused radiation with a frequency of 263 GHz in a gas flow under atmospheric pressure. The experimental setup is shown in Fig. 1. A gyrotron with an operating frequency of 263 GHz and a power up to 1.1 kW in the continuous mode was used as a source of subterahertz radiation [6].

A Gaussian linearly polarized subterahertz radiation beam was introduced through a polyethylene window into the gas discharge chamber, which was a 6-way vacuum cross with standard CF 250 flanges [7]. Electromagnetic radiation was focused with a parabolic mirror inside the chamber. The cross-section diameter of the quasi-optical beam at the waist was 1.2 mm, and the maximum power density was $20\,\mathrm{kW/cm^2}$. A metal tube with an outer diameter of 4 mm and an inner diameter of 3 mm was positioned at the beam waist. Plasma-forming gas was supplied via this tube toward the incident converging electromagnetic radiation. Argon mixed with hydrogen and carbon dioxide was used as the plasma-forming gas. Hydrogen was added in order to measure the electron density by examining the broadening of Balmer lines due to the linear Stark effect. The flow ratio of components of the plasma-forming mixture was adjusted experimentally with the use of gas flow regulators in such a way that a stable plasma torch was maintained in flows of both a binary mixture of Ar and H_2 and a ternary mixture of these gases with CO_2 within the probed heating power range. The argon flow was 30 l/min, and the flows of hydrogen and carbon dioxide were 1 l/min. Prior to experiments, the gas discharge chamber, which was connected to the ambient atmosphere via an exhaust tube, was filled with carbon dioxide.

A discharge was initiated in the plasma-forming mixture flow at the end of the metal gas inlet tube at a subterahertz radiation power in the chamber in the range of

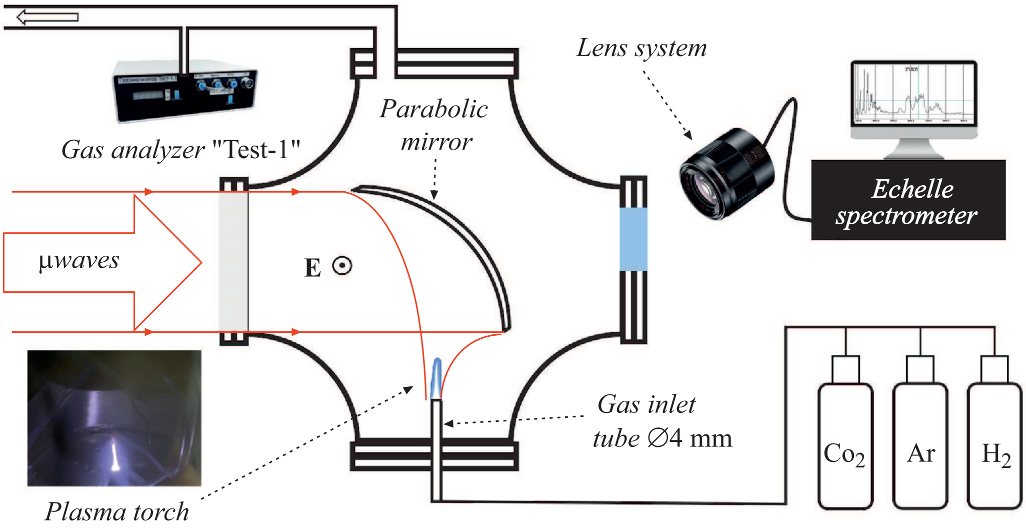

Figure 1. Diagram of the experimental setup.

600−1000 W and had the form of a plasma torch with its base bound to the tube end. The torch maintained in the flow of a binary mixture of argon and hydrogen was 2−2.5 cm in length. When the hydrogen flow was increased to 3 l/min, the shape and size of the discharge and the conditions under which it was maintained remained virtually unchanged. When carbon dioxide was added, the plasma torch immediately changed its color and became smaller (1−1.5 cm in length). Since the torch length is probably limited by the spatial distribution of the electric field intensity in the focused beam, the discharge persists in a region where the breakdown conditions are satisfied for the plasma-forming mixture (with its heating taken into account). The diameter of the plasma torch, the outline of which was assumed to be the boundary of visible plasma glow, was approximately equal to the gas inlet tube diameter. The maximum CO_2 flow with which the discharge could be maintained only at the maximum output radiation power was 1.5 l/min. A quartz window was located at one of the flanged ports of the gas discharge chamber. Optical emission spectra of the discharge were recorded through this window with an S150 duo portable dual-channel spectrometer. An echelle diffraction grating with a period of 75 lines/mm was mounted in one of the channels. This provided an opportunity to perform measurements in a narrow adjustable spectral region with a resolution up to 0.1 Åand an instrument function width up to 11 Å. The gas atmosphere composition in steady-state conditions was measured using a „Test-1“ gas analyzer with electrochemical (O_2), optical (CO_2, CO), and thermal conductivity (H_2) sensors. Control gas samples were collected in certain operation regimes and subjected to gas chromatography–mass spectrometry analysis. The key parameter quantifying the efficiency of reaction $CO_2 \rightarrow CO + 1/2\,O_2$ is conversion degree k [%] that characterizes the ratio of the number of disrupted molecules to their initial number and is given by

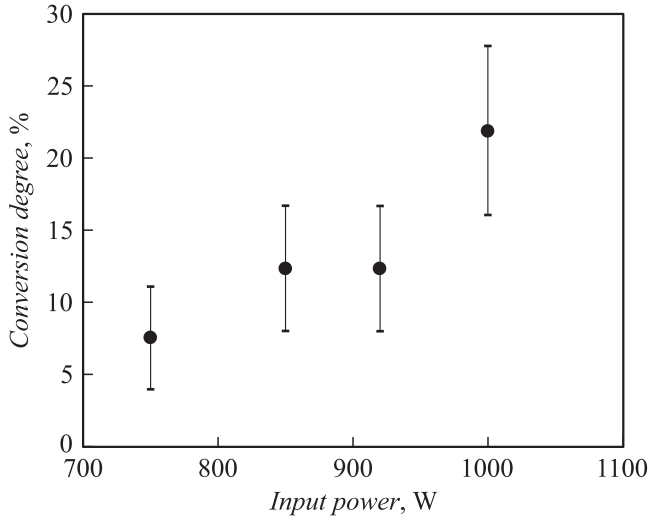

Figure 2. Dependence of the degree of conversion of carbon dioxide on the applied electromagnetic radiation power.

$$k_{CO_2}[\%] = \frac{CO_2(off) - CO_2(on)}{CO_2(off)},$$

where $CO_2(on)$ and $CO_2(off)$ are the concentrations of CO_2 during the discharge and without plasma, respectively.

Figure 2 presents the dependence of the degree of conversion of carbon dioxide on the applied electromagnetic radiation power. It can ben seen that the conversion degree in the implemented discharge regimes increases with radiation power and falls within the range from 7 to 22%. The obtained conversion degrees are among the highest of those reported for atmospheric-pressure discharges without catalysts [1,3]. However, the energy efficiency (the fraction of energy spent on CO_2 decomposition) is very low: 1−3%.

The achieved high degrees of conversion of carbon dioxide are attributable to the fact that plasma of the discharge maintained by continuous subterahertz radiation with a frequency of 263 GHz is strongly non-equilibrium and has a high density. It has been demonstrated earlier that the electron temperature in a subterahertz discharge of this type maintained in an argon flow in external air atmosphere is 1.5−1.7 eV, the gas temperature is 0.2 eV, and the electron density is several times higher than the critical one for the heating field frequency [7]. In order to estimate the influence of CO_2 added to the plasma-forming gas on the discharge plasma parameters, the electron density was determined by optical emission spectroscopy: the broadening of Balmer emission lines H_α and H_β relative to their natural profile in the Holtsmark field of ions due to the linear Stark effect was measured. The broadening of emission lines for hydrogen-like atoms is related directly to the density of plasma ions, which is equal to the electron density in singly ionized plasma [8].

Figure 3 shows the obtained dependences of the electron density in the plasma torch maintained by continuous subterahertz radiation on the applied power for two-component $(Ar + H_2)$ and three-component $(Ar + CO_2 + H_2)$ plasma-forming gas mixtures. It can be seen that the estimates based on the broadening of H_α and H_β hydrogen lines match within the measurement accuracy. The electron density was almost independent of the plasma heating power [7].

The electron density for the two-component gas mixture $(Ar{+}H_2)$ was $(2.5 \pm 0.5) \cdot 10^{15}\,\mathrm{cm}^{-3}$, which is approximately 3 times higher than the critical electron density for a heating field frequency of 263 GHz. This is typical of elevated-pressure microwave discharges [9]. The obtained estimate agrees with the values of electron density reported in [7], which were measured with a better accuracy, since the resolution of analyzed emission lines was higher.

It turned out that 3% of added CO_2 in the three-component plasma-forming gas mixture induced an approximately five-fold reduction in electron density, which was found to be within $(1-12) \cdot 10^{14}\,\mathrm{cm}^{-3}$. This may be attributed to the emergence of channels of electron loss in plasma due to sticking to atoms and molecules of the new plasma-forming mixture component. Since the diffusion electron loss and the recombination rate in atmospheric-pressure discharges are low [9], the electron density in steady-state conditions is specified either by the electrodynamic limit upon reaching the critical frequency of the heating field (as was the case in the discharge in an $Ar + H_2$ flow) or by the balance of ionization and electron loss rates. It is easy to demonstrate that, depending on the heating power, the ionization rate reaches $(5.6-8.4) \cdot 10^7\,\mathrm{s}^{-1}$, while the rate of electron sticking to O_2 molecules only (with sticking to CO and CO_2 neglected) varies with the degree of CO_2 conversion within the range from $2 \cdot 10^7$ to $6 \cdot 10^7\,\mathrm{s}^{-1}$ [10–12]. Since the rates of electron production and loss remain roughly balanced as the heating power increases, the electron density does not change, and this is what was observed experimentally. The electron density should grow if the heating power increases further, since the ionization rate will increase faster than the sticking rate. The growth will cease when the electron density reaches the critical value for the heating field frequency once again (this time at a higher degree of CO_2 conversion). This dynamics of plasma parameters in the examined discharge type confirms that high-power subterahertz radiation holds promise for production of non-equilibrium plasma media.

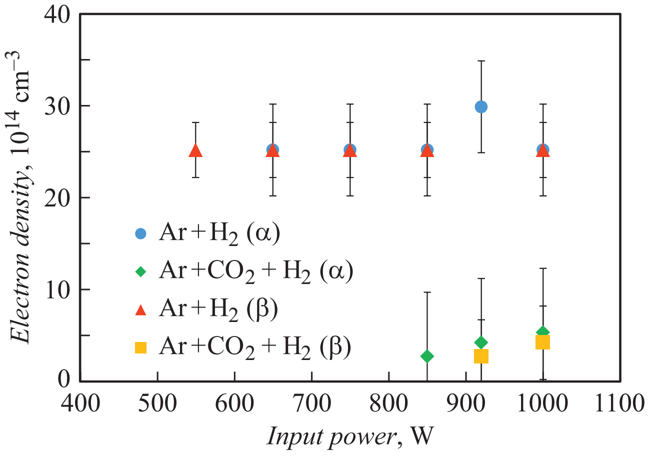

Figure 3. Dependences of the electron density in the plasma torch on the heating power for different compositions of the plasma-forming gas. Estimates based on the broadening of H_α and H_β lines.

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Conflict of interest

The authors declare that they have no conflict of interest.

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