## APPLIED PHYSICS

# **Electron-Impact Dissociation of CO<sub>2</sub> (a Review)**

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**Abstract**—Rate constant of electron-impact dissociation of  $CO_2$  in a direct-current atmospheric-pressure gas discharge is found based on detailed analysis and generalization of the results of calculations of the energy spectrum of electrons in gas discharges in pure carbon dioxide  $CO_2$  and  $CO_2$ -containing mixtures by using various models. It is demonstrated that collisions of  $CO_2$  molecules with electrons represent the dominant mechanism of decomposition of  $CO_2$  molecule at values of reduced electric field in the range from 55 to 100 Td. An expression governing the rate constant of the electron-impact dissociation of  $CO_2$  molecules as a function of reduced electric field is obtained.

**Keywords:** plasma, discharge in CO<sub>2</sub>, dissociation of CO<sub>2</sub>, dissociation rate constant, electron impact **DOI:** 10.1134/S1063780X22040092

## 1. INTRODUCTION

Current interest to analysis of gas discharges in carbon dioxide  $CO_2$  and  $CO_2$ -containing mixtures is caused by development and optimization of plasmachemical technologies for  $CO_2$  utilization [1]. The problem of  $CO_2$  utilization is related to a search for the type of an atmospheric-pressure gas discharge characterized by optimal conditions for  $CO_2$  dissociation [2–5].

One of the stages on the way to creation and optimization of plasma-chemical technologies consists in development of self-consistent collisional radiative models for multicomponent plasma in CO<sub>2</sub> and CO<sub>2</sub>containing mixtures [6-8]. Finding an electron energy distribution function (EEDF) is one of the important problems that can be solved by constructing such models. Knowledge of the EEDF is required for calculation of drift velocity  $v_{\rm dr}$ , the ratio of diffusion coefficient D and mobility  $\mu$  (D/ $\mu$ ), the total ionization coefficient  $\alpha_r/N$  for CO<sub>2</sub> molecule, temperature  $T_e$ (average energy  $\langle \varepsilon \rangle$ ) of electrons, along with the rate constants of plasma-chemical reactions and processes with participation of electrons and CO<sub>2</sub> molecules. It is well known [3, 9] that dissociation of CO<sub>2</sub> caused by electron-impact excitation of electronic states represents the dominant mechanism of decomposition of this molecule in gas discharges characterized by large magnitude of reduced electric field E/N, where N is the concentration of gas particles and E is the electric field strength.

The EEDF is calculated using a set of cross sections of electron interaction with the heavy compo-

nent of plasma. The set of cross sections represents a model representation of plasma processes affecting the EEDF. Development of models for studying the electron component (the EEDF and its principal moments) in gas discharges in pure CO<sub>2</sub> and CO<sub>2</sub>containing mixtures was discussed in reviews [10–14] along with studies [6-8, 15-43]. The electron component was studied in a barrier discharge (BD) [6], a pulsed discharge [7, 27], a combined discharge (pulsed discharge + direct-current gas discharge) [29], a high-frequency discharge [33], a plasma-beam discharge [20, 31, 35], a direct-current gas discharge (DCD) [12, 15–19, 21–24, 26–28, 30, 34, 36], and a microwave discharge (MD) [6, 8, 25, 30, 37]. Formation of a self-consistent set of cross sections and bulk physicochemical processes leading to CO<sub>2</sub> decomposition represent an important aspect of these studies.

Despite a large number of studies, many problems related to the electron component remain unsolved. The lack of a unified point of view regarding electronic configuration of excited states of  $CO_2$  and mechanisms of  $CO_2$  dissociation in gas discharges, along with the lack of experimental data on EEDF, cross sections and rate constants of processes, lead to ambiguous results of studies and reduce predictive capabilities of the models. It is impossible to give preference to any specific model. This creates difficulties in studies related to application of gas discharges for  $CO_2$  utilization. One of possible approaches for overcoming these difficulties is based on detailed analysis and generalization of the results obtained using different models proposed so far. In the present work, we describe such an approach aimed at determination of the rate constant of electron-impact dissociation of  $CO_2$ . The work includes analytical review of the methods of calculation and results of studies of the electron component in gas discharges in pure  $CO_2$  and  $CO_2$ -containing mixtures. Based on comparison of the models, we formulate a list of physicochemical processes playing an important role in  $CO_2$  dissociation.

## 2. KINETIC MODELS

This research was conducted based on values of rate constants of electron-impact  $CO_2$  dissociation obtained using known models of calculation of parameters of the electron component in gas discharges [41–43]. The rate constant was determined by applying the procedure described at the end of Section 3 with cross section adapted from [9, 14, 28, 35, 44–46].

Comparison of known models [6, 9, 12, 14, 15, 27, 28, 30, 34, 35, 38–46, 61, 70, 72–77, 79–84] allowed us to create Table 1 of bulk physicochemical processes involved in  $CO_2$  decomposition that are taken into account when calculating the EEFD. The component composition of chemical compounds in a gas discharge is rather complex even in the case of pure  $CO_2$ . It includes molecular ( $CO_2$ , CO,  $O_2$ , etc.), atomic

(C and O), and ionic ( $CO_2^+$ ,  $CO^+$ ,  $O^+$ , etc.) components. Only processes and reactions with participation of  $CO_2$  molecule and electron *e* as initial interacting particles were taken into account at the present stage of analysis. When creating the table, we used the notations for  $CO_2$  energy levels adapted from [14, 61, 72, 86-89]. The number of the process or reaction that was included in the model is presented in the first column. The second column contains the equation describing the process or reaction, the energy of the quantum level, and the threshold of the process or reaction ( $\epsilon$ ,  $\epsilon'$ ,  $\epsilon''$ ,  $\epsilon'''$ ,  $\epsilon_{HTC}$ ,  $\epsilon_{RB}$ ,  $\epsilon_{TC}$ ,  $\epsilon_{R}$ ,  $\epsilon_{KC}$ ,  $\epsilon_{SR}$ ,  $\epsilon_{BTC}$ ). Symbols J and J' denote quantum numbers of rotational energy levels of CO<sub>2</sub> molecule.  $v_1v_2^{l_2}v_3$  is the spectroscopic symbol of a vibrationally excited CO<sub>2</sub> molecule. Whole numbers  $v_1$ ,  $v_2$ , and  $v_3$  determine the values of vibrational levels corresponding to symmetric, deformation, and antisymmetric modes of the molecule. Number  $l_2$  is referred to as the vibrational angular momentum with respect to molecular axis. This number represents one of characteristics of deformation vibrations of the molecule. Symbols (...)', (...)", and (...)" correspond to vibrational levels of CO<sub>2</sub> molecule determined taking into account mode interaction as a result of Fermi resonance. Symbols Y,  $Y_{\rm e}$ , and  $Y_{\epsilon}$ ' denote electronic states of the molecule ( $Y_{\rm TC}$ ,  $Y_{\rm HTC}$ , and  $Y_{\rm BTC}$  correspond to triplet states,  $Y_{\rm R}$  and  $Y_{\rm RS}$  correspond to Rydberg states,  $Y_{\rm RB}$  corresponds to states responsible for the appearance of bands in the absorption spectrum of the molecule, and  $Y_{\rm KC}$  corresponds to a group of states with excitation thresholds in the vicinity of 12.75 eV). The third column represents references to studies [6, 9, 12, 14, 15, 27, 28, 30, 34, 35, 38–46, 61, 70, 72–77, 79–84] in which the models under consideration were discussed in detail. References to publications from which the values of cross sections for processes and reactions taken into account in the discussed models were adapted are provided in parentheses.

Various methods are used when studying the electron component in gas discharges containing CO<sub>2</sub>. In overwhelming majority of models [6–8, 12, 15–43], the electron component was studied using the method of two-term spherical harmonics expansion of the EEDF. The only exception is study [39] where the EEDF was analyzed using the Monte-Carlo method. In the present work, the energy spectrum of electrons was found in the two-term approximation of the EEDF spherical harmonics expansion [41–43]. This method is valid upon fulfillment of assumptions described in [11, 12, 28, 90, 91]. The validity of the two-term approximation of EEDF spherical harmonics expansion with respect to E/N was discussed in [11, 90, 92–98].

In the course of solving the kinetic equation governing the EEDF, elastic collisions accompanied by momentum transfer from electrons to CO<sub>2</sub> molecules are described in the diffusion approximation [41–43]. This approximation remains valid under the condition that the average energy of translational motion of particles in a gas discharge in CO<sub>2</sub> (at gas temperature  $T \le$ 2000–3000 K) is much lower than the corresponding energy of electrons (electron temperature  $T_e = 1-2 \text{ eV}$ ) [3, 88, 90, 99, 100].

Energy loss of electrons upon excitation of internal degrees of freedom of the  $CO_2$  molecule are taken into account in the integral describing inelastic collisions in terms of balance relations for energy-level populations [41–43]. Processes of electron-impact excitation and de-excitation of rotational levels of CO<sub>2</sub> molecule are an exception. Energy exchange between translational degrees of freedom of electrons and rotational degrees of freedom of CO<sub>2</sub> molecule can be described both in the diffusion approximation and in terms of balance relations for populations of rotational levels. The difference of energies corresponding to adjacent rotational levels of  $CO_2$  molecule is on the order of  $\sim k_B \times T_{rot}$ . Quantity  $T_{rot}$  is the rotational temperature that is approximately comparable to gas temperature T. The following relation is valid for the conditions of an atmospheric-pressure gas discharge:  $T_e \gg T_{rot}$ , T. The average translational energy of CO<sub>2</sub> molecules, along with the average energy stored in its rotational degrees of freedom, is higher that the difference of energies corresponding to adjacent rotational levels. Under these conditions, description of excitation and

No.	Process, quantum energy level, threshold (of process/reaction), eV	Models (cross section)			
Collision accompanied by momentum transfer from electron to CO <sub>2</sub> molecule					
1.0	$CO_2(00^00) + e \rightarrow CO_2(00^00) + e$	$ \begin{array}{l} [42]([42, 47]), [43]([7, 43]), [41]([41, 48]), \\ [39]([39]), [12]([49]), [38]([38]), [15]([50]), \\ [40]([40]), [27]([21]), [34]([21]), [35]([51]), \\ [30]([28]), [28]([16, 21, 52]) \end{array} $			
	Excitation of rotational levels of the ground state of carbon dioxide CO <sub>2</sub>				
2.0	$\operatorname{CO}_2(J') + e \to \operatorname{CO}_2(J'') + e, J' < J''$	[28, 35]([53]), [30](28), [42]([42, 47])			
	Dissociative attachment of electron to CO <sub>2</sub> molecule				
3.0	$CO_2(00^00) + e \rightarrow CO + O^-$ $\varepsilon = 3.3$	$ [28, 42]([42, 47, 54]), [43]([7, 43]), [41]([41, 55]), [39]([39]), [40]([40]), [15]([50]), \\ [38]([56]), [12]([49, 57]), [35]([58, 59]) \\ [27]((61)) $			
	$\varepsilon = 4.5$ and $8.2$				
	Electron-impact excitation of vibrations of c	carbon dioxide gas $CO_2$			
4.0	$CO_2(00^00) + e \rightarrow CO_2(01^10) + e$ $\varepsilon = 0.083$	$      \begin{bmatrix} 15 \\ (50 \\ ), [12] \\ (21, 49, 57 \\ ), [40] \\ (40) \\ (40) \\ (27) \\ (21) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (21, 42) \\ (43) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (21, 42) \\ (43) \\ (28) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (21, 42) \\ (23) \\ (28) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (21, 42) \\ (28) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (21, 42) \\ (28) \\ (28) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (21, 42) \\ (28) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (21, 42) \\ (28) \\ (28) \\ (28) \\ (28) \\ (28) \\ (28) \\ (28) \\ (21, 42) \\ (28) \\$			
5.0	$CO_2(00^00) + e \leftrightarrow CO_2(v_1v_2v_3) + e$ $\varepsilon = 0.167$	$ \begin{array}{c} [12]([21, 49, 57]), [40]([40]), [27]([21]), \\ [28]([62, 63]), [35]([28, 62]), [30]([28]), \\ [42]([21, 42]), [43]([21, 64, 65]), [41]([41]), \\ [39]([39]) \end{array} $			
5.1	$CO_2(00^00) + e \leftrightarrow CO_2(10^00 + 02^00) + e$ $\varepsilon = 0.167$	[38]([38])			
	$(02^{0}0 + 10^{0}0) = (02^{0}0 + 10^{0}0)' + (02^{0}0 + 10^{0}0)''$ $\epsilon' = 0.1595, \epsilon'' = 0.1723$	[61]			
5.2	$CO_2(00^00) + e \leftrightarrow CO_2(02^20) + e$ $\varepsilon = 0.1657$	[61]			
6.0	$CO_2(00^{0}0) + e \leftrightarrow CO_2(v_1v_2v_3) + e$ $\varepsilon = 0.291$	[12]([21, 49, 57]), [40]([40]), [27]([21]), [28]([62, 63]), [35]([28, 62]), [30]([28]), [42]([42, 54]), [38]([38]), [41]([41])			
6.1	$CO_2(00^00) + e \leftrightarrow CO_2(03^{1}0 + 11^{1}0) + e$ $\varepsilon = 0.291$	[43]([21, 43]), [39]([39])			
	$(03^{1}0 + 11^{1}0) = (03^{1}0 + 11^{1}0)' + (03^{1}0 + 11^{1}0)''$ $\varepsilon' = 0.2398, \varepsilon'' = 0.2577$	[61]			
6.2	$CO_2(00^00) + e \leftrightarrow CO_2(03^30) + e$ $\varepsilon = 0.2486$	[61]			
7.0	$CO_2(00^00) + e \leftrightarrow CO_2(00^01) + e$ $\varepsilon = 0.3$	$ \begin{array}{l} [15]([50]), [12]([21, 49, 57]), [40]([40]), \\ [27]([21]), [28]([62, 63]), [35]([28, 62]), \\ [30]([28]), [42]([21, 42]), [43]([21, 43]), \\ [41]([41]), [38]([38]), [39]([39]), [61] \end{array} $			
8.0	$CO_2(00^00) + e \leftrightarrow CO_2(v_1v_2v_3) + e$ $\varepsilon = 0.333 - 0.339$	$ \begin{array}{l} [12]([21, 49, 57]), [40]([40]), [28]([62, 63]), \\ [35]([28, 62]), [30]([28]), [42]([21, 42]), \\ [43]([21, 43, 64, 65]), [38]([38]), [41]([41]), \\ [39]([39]) \end{array} $			

**Table 1.** Chemical compounds and physicochemical processes with participation of  $CO_2$  molecules and electrons in a gas discharge

	Process quantum anarmy laval threshold	
No.	(of process/reaction), eV	Models (cross section)
	Electron-impact excitation of vibrations of c	arbon dioxide gas CO <sub>2</sub>
8.1	$CO_2(00^{0}0) + e \leftrightarrow CO_2(04^{0}0 + 12^{0}0 + 20^{0}0) + e$ $\varepsilon = 0.3301$	[61]
	$(04^{0}0 + 12^{0}0 + 20^{0}0) = (04^{0}0 + 12^{0}0 + 20^{0}0)' + (04^{0}0 + 12^{0}0 + 20^{0}0)'' + (04^{0}0 + 12^{0}0 + 20^{0}0)''' \epsilon' = 0.3162, \epsilon'' = 0.3314, \epsilon''' = 0.3471$	[61]
8.2	$CO_{2}(00^{0}0) + e \leftrightarrow CO_{2}(04^{2}0 + 12^{2}0) + e$ $\varepsilon = 0.3317$ $(04^{2}0 + 12^{2}0) = (04^{2}0 + 12^{2}0)' + (04^{2}0 + 12^{2}0)''$ $\varepsilon' = 0.3208, \varepsilon'' = 0.3426$	[61]
8.3	$CO_2(00^{0}0) + e \leftrightarrow CO_2(04^{4}0) + e$ $\varepsilon = 0.3317$	[61]
8.4	$CO_2(00^00) + e \leftrightarrow CO_2(01^{1}1) + e$ $\varepsilon = 0.3728$	[61]
9.0	$CO_2(00^00) + e \leftrightarrow CO_2(v_1v_2v_3) + e$ $\varepsilon = 0.416 - 0.422$	$ \begin{array}{l} [12]([21, 49, 57]), [40]([40]), [28]([62, 63]), \\ [35]([28, 62]), [30]([28]), [42]([21, 42]), \\ [38]([38]), [41]([41]), [39]([39]) \end{array} $
9.1	$CO_{2}(00^{0}0) + e \leftrightarrow CO_{2}(05^{1}0 + 13^{1}0 + 21^{1}0) + e$ $\varepsilon = 0.4146,$ $(05^{1}0 + 13^{1}0 + 21^{1}0) = (05^{1}0 + 13^{1}0 + 21^{1}0)' +$ $(05^{1}0 + 13^{1}0 + 21^{1}0)'' + (05^{1}0 + 13^{1}0 + 21^{1}0)''',$ $\varepsilon' = 0.3948, \ \varepsilon'' = 0.4144, \ \varepsilon''' 0.4346$	[61]
9.2	$CO_{2}(00^{0}0) + e \leftrightarrow CO_{2}(05^{3}0 + 13^{3}0) + e$ $\varepsilon = 0.4147,$ $(05^{3}0 + 13^{3}0) = (05^{3}0 + 13^{3}0)' + (05^{3}0 + 13^{3}0)''$ $\varepsilon' = 0.4022  \varepsilon'' = 0.4272$	[61]
9.3	$CO_2(00^00) + e \leftrightarrow CO_2(05^50) + e$ $\varepsilon = 0.4147$	[61]
9.4	$CO_2(00^{0}0) + e \leftrightarrow CO_2(05^{1}0 + 13^{1}0 + 21^{1}0 + 02^{0}1 + 10^{0}1) + e$	[43] ([21, 43, 64, 65])
10.0	$CO_2(00^00) + e \leftrightarrow CO_2(v_1v_2v_3) + e$ $\varepsilon = 0.5$	[15]([50]), [12]([21, 49, 57]), [28]([62, 63]), [35]([28, 62]), [30]([28]), [42]([42, 54]), [41]([41]), [38]([38]), [39]([39])
10.1	$CO_2(00^00) + e \leftrightarrow CO_2(06^{2}0 + 22^{2}0 + 14^{2}0) + e$ (06 <sup>2</sup> 0 + 22 <sup>2</sup> 0 + 14 <sup>2</sup> 0) = (06 <sup>2</sup> 0 + 22 <sup>2</sup> 0 + 14 <sup>2</sup> 0)' + (06 <sup>1</sup> 0 + 22 <sup>1</sup> 0 + 14 <sup>1</sup> 0)'' + (06 <sup>1</sup> 0 + 22 <sup>1</sup> 0 + 14 <sup>1</sup> 0)'''	[43]([1, 21, 43, 64, 65])
10.2	$CO_{2}(00^{0}0) + e \leftrightarrow CO_{2}(30^{0}0 + 22^{0}0 + 14^{0}0) + e$ (30 <sup>0</sup> 0 + 22 <sup>0</sup> 0 + 14 <sup>0</sup> 0) = (30 <sup>0</sup> 0 + 22 <sup>0</sup> 0 + 14 <sup>0</sup> 0)' + (30 <sup>0</sup> 0 + 22 <sup>0</sup> 0 + 14 <sup>0</sup> 0)'' + (30 <sup>0</sup> 0 + 22 <sup>0</sup> 0 + 14 <sup>0</sup> 0)'''	[43]([1, 21, 43, 64, 65])
10.3	$CO_2(00^00) + e \leftrightarrow CO_2(06^40 + 14^40) + e$ $(06^40 + 14^40) = (06^40 + 14^40)' + (06^40 + 14^40)''$	[61]
11.0	$CO_2(00^00) + e \leftrightarrow CO_2(\Sigma v_1 l^1 0, v_1 > 2) + e$ $\varepsilon = 2.5$	$ \begin{array}{l} [12]([21, 49]), [40]([40]), [27]([21]), [28]([62, \\ 63]), [42]([42]), [30]([28]), [35]([28, 62]), \\ [43]([1, 21, 43, 64, 65]), [41]([41]) \end{array} $
11.1	$CO_2(00^00) + e \leftrightarrow CO_2(v_1v_2v_3) + e$ $\varepsilon = 0.8 - 1.32$	[39] ([39])

No.	Process, quantum energy level, threshold (of process/reaction), eV	Models (cross section)
11.2	CO <sub>2</sub> (00 <sup>0</sup> 0) + e ↔ CO <sub>2</sub> (v <sub>1</sub> 0 <sup>0</sup> 0) + e v <sub>1</sub> = 4-8, ε = 1.72-2.2	[38] ([38])
11.3	CO <sub>2</sub> (00 <sup>0</sup> 0) + e ↔ CO <sub>2</sub> (v <sub>1</sub> 1 <sup>1</sup> 0) + e v <sub>1</sub> = 3−7, ε = 1.78−2.2	[38] ([38])
	Electron-impact ionization and photoioniz	ation of CO <sub>2</sub> molecule
12.0	$CO_2(00^00) + e \rightarrow \text{positive ions} + e + e$ $\epsilon = 13.773$	$ \begin{array}{l} [15]([50]), [12]([49, 66]), [40]([40]), [41]([41]), \\ [27]([21]), [28]([54, 62]), [30]([28]), [35]([66, \\ 67]), [42]([42, 47, 54]), [38]([66]), \\ [43]([14, 43]) \end{array} $
12.1	$CO_2(00^00) + e \rightarrow CO_2^+ (Y = X^2\Pi_g) + e + e$ $\varepsilon = 13.776$	[35]([14, 68]), [39]([39])
12.2	$CO_2(00^00) + e \rightarrow CO_2^+ (Y = A^2\Pi_u) + e + e$ $\varepsilon = 17.316$	[35]([14, 68]), [39]([39])
12.3	$CO_2(00^00) + e \rightarrow CO_2^+(Y = B^2 \Sigma_u^+) + e + e$ $\varepsilon = 18.076$	[35]([14, 68]), [39]([39])
12.4	$CO_2(00^00) + e \rightarrow CO_2^+(Y = C^2\Sigma_g^+) + e + e$ $\epsilon = 19.395$	[35]([14, 68]), [39]([39])
13.0	$CO_2(00^00) + hv \rightarrow \text{positive ions} + e$ $\epsilon = 13.773$	[38]([69]), [70]
13.1	$CO_2(00^{0}0) + hv \rightarrow CO_2^+(Y = X^2\Pi_g) + e$ $\varepsilon = 13.773$	[38]([69]), [70]
13.2	$CO_2(00^{0}0) + hv \rightarrow CO_2^+ (Y = A^2\Pi_u) + e$ $\varepsilon = 17.316$	[70]([70])
13.3	$CO_2(00^{0}0) + hv \rightarrow CO_2^+(Y = B^2 \Sigma_u^+) + e$ $\varepsilon = 18.076$	[70]([70])
13.4	$CO_2(00^{0}0) + hv \rightarrow CO_2^+ (Y = C^2 \Sigma_g^+) + e$ $\epsilon = 19.395$	[70]([70])
14.0	$CO_2(00^00) + e \rightarrow O^+ + \epsilon = 19.07$	[35]([20, 68]), [39]([39])
14.1	$CO_2(00^00) + e \rightarrow CO^+ + \epsilon = 19.47$	[35]([20, 68]), [39]([39])
14.2	$CO_2(00^00) + e \rightarrow C^+ + \epsilon = 27.82$	[35]([20, 68]), [39]([39])
14.3	$CO_2(00^00) + e \rightarrow O_2^+ + C + e + e$ $\varepsilon = 18.07$	[6]([21, 71])
14.4	$CO_2(00^00) + e \rightarrow CO(^1\Sigma^+) + O + e^+ + e$ $\epsilon = 19.07$	[38]([67])
14.5	$CO_2(00^{0}0) + e \rightarrow CO_2^{++} + e + e + e$ $\varepsilon = 37.6$	[39]([39]), [70]([70])
14.6	$CO_2(00^00) + e \to C^{++} + \varepsilon = 72$	[39]([39])
14.7	$CO_2(00^00) + e \to O^{++} + \varepsilon = 74$	[39]([39])
15.0	$CO_2(00^00) + hv \to CO^+ + \varepsilon = 19.5$	[38]([69])
15.1	$CO_2(00^00) + hv \to O^+ + \varepsilon = 9.1$	[38]([69])

No.	Process, quantum energy level, threshold (of process/reaction), eV	Models (cross section)
15.2	$CO_2(00^00) + hv \to C^+ + \varepsilon = 27.9$	[38]([69])
15.3	$CO_2(00^00) + hv \rightarrow CO_2^{++} + e + e$ $\varepsilon = 37.6$	[38]([69])
	Electron-impact excitation of electronic sta	ates of $CO_2$ molecule
16.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^3\Sigma_{\mu}^+, \varepsilon = 3.72 - 3.85$	[15]([50]), [40]([40]), [72, 73]
17.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e$	[72, 73]
	$Y_{\varepsilon} = {}^{3}\Delta_{u},  \varepsilon = 4.10,  Y_{\varepsilon} = {}^{3}\Sigma_{u}^{-},  \varepsilon = 4.47$	
17.1	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^3\Sigma_u^+,  \varepsilon = 4.89$	[14, 74]
17.2	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Delta_u, \varepsilon = 5.58$	[72–77]
17.3	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Sigma_u^-, \varepsilon = 6.53$	[14-74]
18.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{7.0}) + e$ $\varepsilon = 7.0$	[15]([50]), [40]([40]), [12]([49]), [41]([41]), [27]([21]), [42]([42, 78]), [43]([21, 43])
19.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{7,4}) + e Y = {}^{3}\Sigma_u^+, \varepsilon = 7.4$	[28, 30, 35]([28, 62])
20.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{8.0}) + e$ $\varepsilon = 8.0$	[42]([42, 78])
21.0	$CO_2(00_00) + e \rightarrow CO_2(Y_{\epsilon}) + e Y_{\epsilon} = {}^{3}\Sigma_{\mu}^{+}, \epsilon = 8.15$	[14]([14, 79])
22.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Delta_u, \varepsilon = 8.38 - 8.41$	[14]([14, 74, 80]), [28, 30, 35]([28, 62, 63])
23.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e$	[14, 81]
	$Y_{\varepsilon} = {}^{3}\Sigma_{u}^{+}, \varepsilon = 8.53, Y_{\varepsilon} = {}^{3}\Pi_{g}, \varepsilon = 8.73, Y_{\varepsilon} = {}^{3}\Delta_{u}, \varepsilon = 8.80$	
24.0	$\operatorname{CO}_2(00^00) + e \rightarrow \operatorname{CO}_2(Y_{\mathrm{HTC}}) + e \varepsilon_{\mathrm{HTC}} = 8.89$	[39]([39])
25.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Pi_{g}, \varepsilon = 8.93$	[14, 79]
26.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{9.0}) + e$ $\varepsilon = 9.0$	[42]([42, 78])
27.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{\epsilon}) + e Y = {}^{3}\Delta_u, \epsilon = 9.13,$	[14, 81]
	$Y = {}^{3}\Sigma^{-}, \epsilon = 9.19, Y = {}^{1}\Sigma^{-}, \epsilon = 9.27$	[14, 79]
28.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{9,3}) + e Y_{\epsilon} = {}^1\Pi_{e}, \epsilon = 9.3$	[28, 30, 35]([28]), [14, 74, 80]
29.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Delta_u, \varepsilon = 9.32$	[14, 79]
29.1	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e$	[14, 81]
	$Y_{\varepsilon} = {}^{3}\Sigma_{u}^{-}, \varepsilon = 9.73, Y_{\varepsilon} = {}^{1}\Sigma_{u}^{-}, \varepsilon = 9.73, Y_{\varepsilon} = {}^{1}\Delta_{u}, \varepsilon = 9.95$	
29.2	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Sigma_u^+, \varepsilon = 10.3$	[14, 80]
30.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{10.5}) + e$ $\varepsilon = 10.5$	$ \begin{array}{l} [40]([40]), [41]([41]), [12]([49]), [27]([21]), \\ [43]([14, 21]) \end{array} $
31.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{RB}) + e \varepsilon_{RB} = 10.7$	[39]([39])
32.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Sigma_u^+, \varepsilon = 11.0 - 11.08$	[28]([28]), [30, 35]([62, 63]), [14, 74, 79]
33.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{11.1}) + e$ $\varepsilon = 11.1$	[42]([42, 78])
34.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Pi_u, \varepsilon = 11.28$	[14, 80]

No.	Process, quantum energy level, threshold (of process/reaction), eV	Models (cross section)
35.0	$\mathrm{CO}_2(00^00) + e \rightarrow \mathrm{CO}_2(Y_{\mathrm{TC}}) + e$	[39]([39])
	$\varepsilon_{\rm TC} = 11.3,$	
	$Y_{\rm TC} = {}^3\Pi_u,  \varepsilon = 11.31$	[14, 79]
36.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y_{\varepsilon}) + e Y_{\varepsilon} = {}^1\Pi_u, \varepsilon = 11.39$	[14, 79]
37.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{11.9}) + e$ $\varepsilon = 11.9$	[42]([42, 78])
38.0	$CO_2(00^00) + e \rightarrow CO_2(Y_R) + e \varepsilon_R = 11.385 - 12.627$	[39]([39])
38.1	$CO_2(00^{0}0) + e \rightarrow CO_2(Y_{12,4}) + e$ $\varepsilon = 12.4$	[42]([42, 78])
39.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{KC}) + e$ $\varepsilon_{KC} = 12.75$	[39]([39])
40.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{SR}) + e \varepsilon_{SR} = 12.9 - 13.7$	[28, 30, 35]([28, 62, 63]), [39]([39])
41.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{17.3}) + e$ $\varepsilon = 17.3$	[42]([42, 78])
42.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{18.07}) + e$ $\epsilon = 18.07$	[42]([42, 78])
43.0	$CO_2(00^00) + e \rightarrow CO_2(Y_{BTC}) + e$ $\epsilon_{BTC} = 25.0$	[39]([39])
I	Electron-impact dissociation of C	O <sub>2</sub> molecule
50.0	$CO_2(00^00) + e \rightarrow CO_2(Y) + e \rightarrow CO + O + e$	[40, 43]([16, 21, 40, 45])
	$Y = {}^{1}\Sigma_{u}^{+}, {}^{3}\Pi_{u}, {}^{1}\Pi_{u}, \varepsilon = 10.5$	
51.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y) + e \to \operatorname{CO} + \operatorname{O} + e$	[28]([28, 62]), [38]([38])
	$Y = {}^{3}\Sigma_{+}^{+}\epsilon = 7.4$	
52.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y) + e \to \operatorname{CO} + \operatorname{O} + e$	[43, 82–84]([16, 21, 40])
	$Y = {}^{3}\Sigma_{\mu}^{+}, {}^{3}\Pi_{a}, {}^{3}\Delta_{\mu}, {}^{3}\Sigma_{\mu}^{-}, {}^{1}\Pi_{a}, {}^{1}\Delta_{\mu}, \epsilon = 7.0$	
53.0	$\operatorname{CO}_2(00^00) + e \to \operatorname{CO}_2(Y) + e \to \operatorname{CO} + \operatorname{O} + e$	[35]([16, 21, 40]) [40]([16, 21, 40])
	$Y = {}^{3}\Sigma_{\mu}^{+}, {}^{1}\Pi_{\mu}, {}^{1}\Delta_{\mu}, \epsilon = 7.0, Y = {}^{1}\Sigma_{\mu}^{+}, \epsilon = 10.5$	
54.0	$CO_2(00^{0}0) + e \rightarrow CO_2(Y) + e \rightarrow CO + O + e$ $\varepsilon = 6.1$	[44]([44])
55.0	$CO_2(00^00) + e \rightarrow CO_2(Y) + e \rightarrow CO(^{1}\Sigma^{+}) + O(^{1}S) + e$ $\varepsilon = 12.0$	[45]([45]), [46]([46]), [14]([46, 85])
55.1	$CO_2(00^00) + e \rightarrow CO_2(Y) + e \rightarrow CO(a^3\Pi) + O(^3P) + e$ $\varepsilon = 12.0$	[45]([45])
56.0	$CO_2(00^{0}0) + e \to CO_2(Y) + e \to CO(Y_{\varepsilon}, Y_{\varepsilon}') + O(^{3}P) + e$ $\varepsilon = 7-9$	[9]([9])
56.1	$\operatorname{CO}(Y_{\varepsilon}) \to \operatorname{CO}(a^{3}\Pi) + hv$ $\varepsilon = 7-9$	[9]([9])
56.2	$CO(Y_{\varepsilon}') + M \rightarrow CO(a^{3}\Pi) + M$ $\varepsilon = 7-9$	[9]([9])

de-excitation of rotational levels of the molecule is simplified and can be carried out in the diffusion approximation [42].

Models that allow obtaining analytical solution to the kinetic equation governing the EEDF under the conditions of gas-discharge  $CO_2$  lasers were described in [23, 26]. They have limited application in studies of the electron component. A large number of physicochemical processes involving electrons and  $CO_2$  molecules have to be taken into account for correct description of EEDF behavior (see the Table 1). This kind of analysis can be done only be means of numerical methods. In the present work, we solved the equation governing the EEDF using the numerical method discussed in [12, 28].

The set of cross sections used when solving the equation governing the EEDF must describe principal moments of the latter obtained by the swarm measurement technique [50]. Such set of cross sections that includes cross sections of elastic and inelastic electron collisions with particles and electron collisions of the second kind with excited particles is referred to as the self-consistent set of cross sections. Usually, self-consistent set of cross sections is formed based on the EEDF obtained in the two-term approximation. In the present work, when solving the equation for the EEDF, we used self-consistent sets of cross section adapted from [41-43].

The method of forming the self-consistent set of cross sections is characterized by the following specific features. When finding unknown cross sections, it is necessary simultaneously taking into account the set of elastic and inelastic cross sections that are used in the model of calculation of the EEDF. Since many cross sections are not always known while the number of measured moments of the EEDF is smaller than the number of unknown cross sections, the problem of finding cross sections becomes indeterminate. This method does not yield a well-defined self-consistent set of cross sections [11]. The latter vary depending on the models used for calculating the EEDF [41-43]. They are found by means of successive iterations. At the first iteration, the dependence of initial cross sections on electron energy and their thresholds is defined. The initial cross sections for processes of excitation of molecular states can be estimated using expressions obtained in [101]. When defining the dependence of cross sections on electron energy and their thresholds, preference is given to the data obtained in experiments [13, 70, 91, 102]. The energy spectrum of electrons is determined from the solution to the equation governing the EEDF obtained using the initial cross sections. The principal moments of the EEDF are calculated taking into account the obtained EEDF and given initial cross sections. The results of the calculations are compared with the corresponding moments measured by the swarm technique [50], along with those obtained by the microwave method, electron spectroscopy, and mass spectrometry [13, 70, 91, 102]. Cross section is varied in the course of subsequent iterations until the best agreement between measured and calculated EEDF moments  $(V_{\rm dr}, D/\mu, \text{ and } \alpha_r/N)$  is achieved. When constructing the self-consistent set of cross sections, experimental and calculated values of  $v_{\rm dr}$  and  $D/\mu$ obtained by different authors agree with each other to within 5%, while the difference of calculated and measured values of  $\alpha_r/N$  can be as large a factor of two. In the present study, experimental data ( $V_{\rm dr}$ ,  $D/\mu$ , and  $\alpha_r/N$  were adapted from review articles and studies [103–127]. Importantly, the cross section of electronimpact dissociation of CO2 was not included in selfconsistent sets of cross sections used in models [41-43]. They represent the result of comparative analysis and compilation of data obtained in [9, 14, 28, 35, 44-46]. Cross sections of CO<sub>2</sub> dissociation were used as initial data for determining the rate constant of CO<sub>2</sub> decomposition.

The values of E/N, pressure p, and gas temperature T represent initial parameters for determining the rate constants of CO<sub>2</sub> dissociation, the EEDF, and its principal moments [41–43]. Translational gas temperature T in atmospheric-pressure gas discharges can be high ( $\leq$ 3000 K) [3, 88, 90, 99]. Preliminary calculations of the rate constants of electron-impact dissociation of CO<sub>2</sub> reveal that they weakly depend on temperature T. The rate constants of CO<sub>2</sub> dissociation were calculated at T = 300 K, p = 760 Torr, and E/N = 30, 40, 60, 80, and 100 Td. In the calculations, vibrational temperatures of symmetric ( $T_1$ ), deformation ( $T_2$ ), and asymmetric ( $T_3$ ) modes of CO<sub>2</sub> vibrations were set equal to T.

## 3. RESULTS AND DISCUSSION

Before performing calculations, let us analyze known models [6–9, 12, 15–38, 40–46] used upon calculation of EEDF and the data on parameters of electron component of plasma containing  $CO_2$ . First, it will give an idea on the current state of studies in this important field. Second, results of calculations presented henceforth are largely explained and determined by the logic of development of models [6–9, 12, 15–38, 40–46].

A model of calculation of the EEDF and its principal moments in a direct-current gas discharge in CO<sub>2</sub> in the range of E/N = 0.8-100 Td at T = 300 K was developed in [15]. The following processes and reactions (see the list in the Table) were assumed to play an important role in forming the EEDF in the gas discharge: collisions accompanied by momentum transfer from electrons to CO<sub>2</sub> molecules (process 1.0); dissociative electron attachment to CO<sub>2</sub> molecule (reaction 3.0); electron-impact vibrational excitation of CO<sub>2</sub> molecule characterized by cross sections with excitation thresholds of 0.083 eV (process 4.0), 0.29 eV (process 7.0), 0.5 eV (process 10.0), and 0.9 eV; electron-impact  $CO_2$  ionization (process 12.0); impact excitation of electronic states of  $CO_2$  (processes 16.0 and 18.0 described by cross sections with excitation thresholds of 3.85 and 7.0 eV, respectively).

Studies [12, 16, 18, 21, 32] dealt with improvement of model [15] by using initial cross sections obtained in experiments [50, 57]. In these models, the kinetic scheme describing electron-impact excitation of vibrational levels and electronic states of CO2 was expanded and given in detail. In order to obtain a better agreement between calculated and measured values of principal moments of the EEDF, a cross section with excitation threshold of 3.1 eV was proposed in model [16]. It was established in [128] that this cross section characterizes resonance impact excitation of CO<sub>2</sub> vibration (resonance component of the total excitation cross section of process (5.0)). The values of cross sections of processes (4.0) and (7.0) were refined in [18]. Calculations performed in [16, 21] revealed that taking into account in the model process (5.0) and further expansion of the kinetic scheme by including the process of electron-impact excitation of vibrational level  $(00^{\circ}2)$  [129, 130] weakly affect the results of formation of the self-consistent set of cross sections.

The scheme of electron-impact excited states of  $CO_2$  was revised in [16, 21]. Excitation of electronic states with thresholds of 7.0 and 10.5 eV (processes 18.0 and 30.0, respectively) were taken into account. It was assumed that dissociation of  $CO_2$  proceeds via formation of electronic states in reaction (50.0) [131]. The results of determining the self-consistent set of cross sections [16, 21] were summarized in [49, 132].

Self-consistent approaches alternative to models [15, 16, 21] that describe EEDF relaxation in gas discharges were described in [12, 32].

A model of the multicomponent plasma of a gasdischarge  $CO_2$  laser for investigation of relaxation of the EEDF and specific energies stored in vibrational modes of CO<sub>2</sub> molecule was proposed in [12]. The EEDF and its principal moments in different mixtures of gas-discharge CO<sub>2</sub> laser (CO<sub>2</sub> :  $N_2$  : He = 3 : 3 : 4, 16: 42: 42, and 1: 7: 12) for E/N values of up to 200 Td at atmospheric pressure and translational temperature of 300 K were analyzed. Results of numerical analysis of the influence of electron collisions of the second kind with vibrationally excited CO<sub>2</sub> molecules were presented. Model [12] took into account electron-electron collisions. Cross sections of elastic and inelastic electron collisions with CO<sub>2</sub> molecules were adapted from database [49, 132]. According to model [12] of EEDF calculation, the rate constants of electron-impact excitation of deformation and asymmetric vibrational modes of CO<sub>2</sub> molecule attain maximum values of  $\approx 10^{-9}$  cm<sup>3</sup>/s in the range of *E*/*N* from 50 to 200 Td in a  $CO_2 : N_2 : He = 3 : 3 : 4$  mixture. It

was established that, in the case of  $CO_2$ :  $N_2$ : He = 16:42:42 mixture, electron collisions of the second kind with vibrationally excited  $CO_2(00^01)$  molecules have substantial impact on the EEDF and its principal moments at E/N = 50 Td,  $T_3 = 4000$  K [133], and equilibrium values of population of all other excited levels of CO<sub>2</sub>, N<sub>2</sub>, and He. Characteristic relaxation time  $\tau_e$  of initial energy spectrum of electrons calculated at E/N = 50 Td to values of the EEDF corresponding to E/N = 20 Td in a CO<sub>2</sub> : N<sub>2</sub> : He = 1 : 7 : 12 mixture were on the order of several picoseconds  $(\sim 10^{-12} \text{ s})$ . Electron–electron collisions did not play an important role when determining the EEDF if the degree of ionization of the gas medium did not exceed  $10^{-7}$ . It follows from the results obtained in [12] that electron collisions of the second kind with  $CO_2(00^{0}1)$ molecules must be taken into account at high concentrations of CO<sub>2</sub> and vibrational temperature of  $T_3 \ge$ 4000 K.

Results obtained in [12, 15, 16, 21, 32] formed the foundation for further improvement of models [17, 19, 22] that were used for investigation of EEDF and its principal moments, power of the laser output radiation, the energy balance of electrons, and the rate constants of inelastic processes under the conditions of continuous-wave gas-discharge  $CO_2$  lasers in a  $CO_2$ : N<sub>2</sub>: He gas mixtures in the range of E/N = 10-50 Td and average energy of electrons  $\langle \epsilon \rangle$  between 1 and 3 eV.

It was established [17, 19, 22] that, among inelastic collisions of electrons with gas molecules, processes of excitation of vibrational levels and electronic states of  $CO_2$ ,  $N_2$ , and CO are dominant in formation of the energy spectrum of electrons. Calculations [22] revealed that variation of percent composition of gas mixtures (CO<sub>2</sub>:  $N_2$ : He) at fixed value of average electron energy  $\langle \varepsilon \rangle$  influences the rates of energy exchange between translational degrees of freedom of electrons and vibrational degree of freedom of  $N_2$ , along with the rate constants of excitation of vibrational levels of  $N_2$ . For a  $CO_2$ : He gas mixture, this conclusion is also valid for the electron drift velocity. The influence becomes weaker upon addition of N2 into the gas mixture. Taking into account electron collisions of the second kind with vibrationally excited CO<sub>2</sub> molecules has minor impact on the results of calculation of electron transport coefficients in gas-discharge CO<sub>2</sub> lasers at low values of level population of the asymmetric mode of CO<sub>2</sub> (at  $T_3 \leq 1500$  K).

Taking into account the data of [49, 132] and results obtained in [12, 15–17, 19, 21, 22, 32, 128–131], a set of initial cross sections, processes and reactions (see the Table 1) was formed in [40, 41] that is widely used in studies of kinetics of processes and reactions in gas discharges containing  $CO_2$ .

Models for studying EEDF relaxation and calculation of its principal moments were described in [24, 27, 28, 42, 54, 62, 78]. In the process, a self-consistent set of cross sections alternative to that obtained in [12, 15, 16, 21, 32, 41, 49, 132] was formed. The necessity of forming this self-consistent set of cross sections was dictated by extension of the range of E/N and detailed analysis of composition and kinetic scheme of processes with participation of electrons and CO<sub>2</sub>. The electron component was studied in a wider range of E/N (0.1–300 Td) than in [12, 15, 16, 21].

Results of analysis of relaxation of EEDF, energy balance,  $v_{dr}$ , and  $\alpha_r/N$  (in the presence of easily ionizable admixtures of benzene, toluene, xylene, etc.) in pure gases (N<sub>2</sub>, CO<sub>2</sub>) and in gas mixtures (N<sub>2</sub> : CO<sub>2</sub> = 1 : 1, along with N<sub>2</sub> : CO<sub>2</sub> : He = 1 : 1 : 8 and 3 : 3 : 4) in an electron-impact-ionization CO<sub>2</sub> laser in the range of E/N=9–45 V/(cm Torr) at p = 1000 Torr and ionization degree of 10<sup>-5</sup> were presented in [24]. Processes (1.0, 4.0, 5.0, 7.0, 18.0, and 30.0) and reactions (3.0 and 12.0) were taken into account upon solution of the equation governing the EEDF using cross sections adapted from [16, 60, 66, 128–130].

It was established that relaxation time  $\tau_e$  of the energy spectrum of electrons falls in the range of  $(0.5-4) \times 10^{-9}$  s and is shorter than the time of electron multiplication and recombination. The value of  $\langle \epsilon \rangle$ varies in direct proportion to the ratio of E/p. Specific energy W absorbed by plasma is used mainly for excitation of electronic states and vibrational level (10<sup>0</sup>0) of the symmetric mode of CO<sub>2</sub>. Electron attachment to CO<sub>2</sub> (reaction 3.0) limits creation of electrons and decreases W. Addition of admixtures (benzene, toluene, xylene, etc.) compensates a decrease in concentration of electrons and increases stability of the discharge along with power of the laser output radiation.

Specific features of relaxation of the EEDF and average electron energy  $\langle \varepsilon \rangle$  in an atmospheric-pressure pulsed volume discharge ( $n_e = 10^{12}-10^{13}$  cm<sup>-3</sup>, E/N =10-100 Td, pulse duration  $\tau_L = 10^{-6}$  s, the ionization degree of  $10^{-7}-10^{-6}$  s, T = 300 K) [134–137] in pure CO<sub>2</sub> and gas mixtures (CO<sub>2</sub> : N<sub>2</sub> : He) were studied in [27] by solving the equation governing an isotropic part of the EEDF. The model took into account processes (1.0, 4.0, 5.0, 6.0, 7.0, 11.0, 18.0, and 30.0) along with reactions (3.0 and 12.0).

Calculations show that the EEDF relaxation time in a discharge in CO<sub>2</sub> falls in the range of  $0.5 \times 10^{-10}$  s  $< \tau_e < 2 \times 10^{-10}$  s  $(\tau_L \gg \tau_e)$  and decreases with increase in *E/N*. The values of  $\tau_e$  agree with the results obtained in [24] to within an order of magnitude and are larger than the value of  $\tau_e$  calculated in [12]. Regardless of the value of *E/N*, variation of  $\langle \varepsilon \rangle$  with time is characterized by slow growth at the beginning of the process of relaxation of the energy spectrum of electrons (0  $< \tau_e < (0.05-0.32) \times 10^{-10}$  s), followed by considerably faster increase upon average energy of electrons reaching the value of  $\langle \epsilon \rangle = 0.07-0.1$  eV. The time dependence levels off when energy reaches a stationary value. Stationary values of  $\langle \epsilon \rangle$  increase with increase in E/N and coincide with the corresponding values obtained in [24]. The larger the value of E/N, the higher the relaxation rate of  $\langle \epsilon \rangle$  at the second stage. The latter starts decreasing upon average energy of electrons reaching the value of  $\langle \epsilon \rangle = 1.5-2.0$  eV. Specificity of relaxation of  $\langle \epsilon \rangle$  is explained by the fact that the time dependence of frequency of inelastic energy losses of electrons is nonmonotonic.

In contrast to models [12, 15–17, 19, 22, 24], models developed in [28, 62] take into account excitation of rotational energy levels of CO<sub>2</sub> molecule. Kinetic scheme of processes of excitation of vibrational and electronic states of CO<sub>2</sub> was expanded and analyzed in detail. Particular attention was paid to identification of states. Processes and reactions (1.0–12.0, 19.0. 22.0, 28.0, 32.0, and 40.0) were taken into account when solving the equation governing the EEDF (at p = 760Torr and T = 300 K). The value of excitation cross section of level (00<sup>0</sup>1) of the asymmetric mode of CO<sub>2</sub> in models [28, 62] was refined by forming a self-consistent set of cross sections using the results of measurements of the rate constant of electron-impact excitation adapted from [138].

It was assumed in the models proposed in [28, 62] that the dependence of excitation cross section of triplet state  ${}^{3}\Sigma_{u}^{+}$  of carbon-dioxide molecule (process 19.0) on electron energy is similar to the corresponding dependence for excitation cross section of metastable triplet state  $A^{3}\Sigma_{u}^{+}$  of nitrogen molecule. In contrast to [16, 21], electron-impact dissociation of CO<sub>2</sub> in [9, 28, 62] was assumed to take place via the discussed triplet state (reaction 51.0). The value of this cross section was determined by forming a self-consistent set of cross sections using the results of measurements of coefficients of dissociative electron attachment to CO<sub>2</sub> and electron-impact ionization of CO<sub>2</sub>. This value of cross section satisfactorily describes experimental results obtained while studying CO<sub>2</sub> dissociation in  $(CO_2 : CO: O_2 : O = 0.22 : 0.51 : 0.22 : 0.05)$  mixture in a direct-current discharge [9]. The dependence of cross sections on electron energy for states  ${}^{1}\Delta_{\mu}$ ,  ${}^{1}\Pi_{a}$ ,

and  ${}^{1}\Sigma_{u}^{+}$  (processes 22.0, 28.0, and 32.0) was approximated by the corresponding dependence established for allowed electric-dipole transitions.

Calculations of energy balance of electrons conducted in [28, 62] revealed that the fraction of specific energy transferred to rotational degrees of freedom of CO<sub>2</sub> (process 2.0) at  $E/N \sim 0.1$  Td is considerable and exceeds 0.5. At 0.1 Td  $\leq E/N \leq 1$  Td, a comparable fraction of specific energy of electrons is transferred to the deformation mode of CO<sub>2</sub> vibration: level (01<sup>1</sup>0) (process 4.0). At higher values of E/N > 1 Td, specific energy of electrons is used for excitation of the asymmetric mode of CO<sub>2</sub> vibration: level (00<sup>0</sup>1) and the sum of the remaining vibrational levels ( $\sum_{v_1>2} v_1 l^1 0$ ) (processes 7.0 and 11.0, respectively).

The results obtained in [28, 62] thus underscore an important role played by the process of excitation of rotational levels of  $CO_2$  molecule in balance of electron energy at high concentration of  $CO_2$  and low E/N values. The electronic state participating in electron-impact dissociation of  $CO_2$  was specified, and  $CO_2$  dissociation cross section was found. The self-consistent set of cross sections obtained in [28, 54, 62, 78] was refined in [29] and tested in [30, 35].

Study [29] aimed at experimental determination of the fraction of energy used for direct heating of  $(CO_2 : N_2 : He = X_c : 0.5 : 0.5, X_c = 0-0.04)$  gas mixture of a fast-axial-flow continuous-wave CO<sub>2</sub> laser (E/N = 6-20 Td, flow speed of gas mixture equal to 60 m/s) pumped by a combined discharge at p =45 Torr [139]. Possible channels of energy loss by electrons that lead to direct gas heating were analyzed in [29]. Specific energy absorbed by plasma is determined by the following processes (processes involving  $CO_2$  are listed according to the Table 1): elastic scattering of electrons from helium atoms He, along with  $N_2$  and  $CO_2$  molecules (process 1.0); electron scattering from  $N_2$  and  $CO_2$  accompanied by excitation of rotational levels (process 2.0); electron-impact excitation of vibrational levels of the deformation mode  $(01^{1}0)$  and symmetric mode  $(10^{0}0)$  of CO<sub>2</sub> vibration (processes 4.0 and 5.0, respectively); excitation of vibrational levels of  $N_2$  and the asymmetric mode of CO<sub>2</sub> in electron collisions (process 7.0); excitation of electronic states of N<sub>2</sub>, He, and CO<sub>2</sub> in electron collisions (processes 19.0, 22.0, 28.0, 32.0, and 40.0); electron-impact ionization of  $CO_2$  (reaction 12.0).

It was established that processes (1.0, 2.0, 4.0, and 5.0) result in direct gas heating under the conditions of experiment [29]. Relative contribution of these processes to direct heating of studied mixtures in the discharge was found by solving the equation governing the EEDF. In the process, the self-consistent set of cross sections adapted from [28, 62] was used, except excitation cross section of vibrational level  $(01^{1}0)$ . Calculations showed that heating of mixture was systematically underestimated relative to experimental results in the region of low E/N values when excitation cross section of level  $(01^{1}0)$  adapted from [28, 62] was used. This cross section was found in [62] using the energy dependence calculated in the Born approximation. It was noted in [29] that there is an arbitrariness in choosing the form of this cross section in the range of energies between the threshold and 3 eV that did not contradict experimental data available at that time. The value of excitation cross section of level  $(01^{1}0)$  was

found from comparison of calculated and experimentally obtained values of T,  $v_{dr}$ ,  $D/\mu$ , and  $\alpha_r/N$  [29].

The results obtained in [15, 16, 21, 28, 40, 41, 62] thus suggest that the method of formation of the selfconsistent set of cross sections yields an ambiguous definition of the EEDF (see the results of calculations below), the self-consistent set of cross sections for  $CO_2$  in [11], and the degree of completeness of the kinetic scheme of the model (see the Table 1). The self-consistent set of cross sections obtained in [28, 54, 62, 78] that was refined in [29] and supplemented by data obtained in [21, 47] represents databases presented in [38, 42]. Note that databases [38, 70] also include reactions of  $CO_2$  photoionization (13.1–13.4 and 15.0–15.3) with corresponding cross sections (see the Table 1).

The EEDFs for the conditions of a direct-current discharge (DCD) and a microwave discharge (MD) (at circular frequency of excitation equal to  $\omega = 1.5 \times$  $10^{10}$  s<sup>-1</sup>) in CO<sub>2</sub> at p = 1-2 Torr and specific energy absorbed by plasma  $W = (0.5-10) \times 10^{-12}$  W/el were compared in [30] on the basis of solution of the equation governing an isotropic part of the energy spectrum of electrons. Also studied was the influence of electron-electron collisions and electron collisions of the second kind with vibrationally excited CO2 molecules. The results of calculation of the EEDF were compared with experimental data [25]. Seemingly, the only available results of probe measurements of the EEDF in an MD in pure CO<sub>2</sub> at p = 1-2 Torr and  $\omega =$  $1.5 \times 10^{10}$  s<sup>-1</sup> were presented in the latter study. When solving the equation governing the EEDF in the quasistationary approximation,  $\omega^2 \gg (1/\tau_e)^2$ , composition of processes characterized by self-consistent set of cross sections from [28] was adapted without any changes.

Calculations performed in [30] revealed that the EEDF and its principal moments determined by its low-energy part for a DCD and an MD are close to each other. The high-energy part of the EEDF in an MD is substantially enriched by electrons relative to DCD. Measurements conducted up to electron energies of  $\varepsilon < 10 \times \langle \varepsilon \rangle$  showed that the EEDF in the case of MD is enriched by fast electrons ( $\varepsilon > 3 \times \langle \varepsilon \rangle$ ) relative to Maxwell EEDF for the same average energy  $\langle \varepsilon \rangle$ . The EEDF in the case of a DCD is depleted of fast electrons at comparable values of  $\langle \epsilon \rangle$ . The ratio of the EEDF calculated in [30] to the Maxwell one in  $CO_2$ for the conditions of [25] agrees with the ratio obtained experimentally within experimental error (20% at  $\langle \epsilon \rangle < \epsilon < 5 \times \langle \epsilon \rangle$ , 200–300% at  $\epsilon > 6 \times \langle \epsilon \rangle$ ). This fact corroborates the existence of the established effect. The difference between EEDFs for DCD and MD can be explained by the value of cross section accompanied by momentum transfer from electrons to  $CO_2$  molecules and its dependence on energy [25, 30]: if the cross section of the collision accompanied by momentum transfer from electrons to CO<sub>2</sub> molecules decreases slower than  $\epsilon^{-1/2}$ , and this is how this cross section behaves in pure CO<sub>2</sub>, the EEDF in an MD is enriched by fast electrons relative to that in a DCD at the same values of  $\langle \epsilon \rangle$ .

It was demonstrated in [30] that vibrational excitation (process 7.0) represents the main channel of electron-energy loss (90%) in both DCD and MD. At  $W = (0.5-10) \times 10^{-12}$  W/el (at E/N > 1 Td), level  $(00^{0}1)$  becomes excited with high efficiency, which agrees with the results obtained in [28]. Distribution of energy consumption for excitation of different modes (except the total energy flux used for excitation of states  $\sum_{v_1>2} v_1 l^1 0$  and their dependence on W are the same for the DCD and MD. For  $CO_2(\sum_{v_1>2} v_1 l^1 0,$ energy consumption in an MD is twice lower than that in a DCD. Energy consumption for excitation of electronic states of CO<sub>2</sub> in an MD exceeds the corresponding energy consumption in a DCD by more than an order of magnitude. Similar to DCD, electron collisions in an MD weakly affect the EEDF. At high degrees of ionization exceeding 10<sup>-3</sup>, electron-electron collisions tend to reshape the EEDF making it closer to Maxwellian. The obtained result is close to that obtained in [12]. The EEDF is influenced by electron collisions of the second kind with excited  $CO_2$ molecules at low magnitudes of electric field E. Collisions with vibrationally excited molecules lead to an increase in  $\langle \epsilon \rangle$ . Election collisions with CO<sub>2</sub> molecules occupying (00<sup>0</sup>1) and ( $\sum_{v_1>2} v_1 l^1 0$ ) levels influence the EEDF. The rest of the collisionally excited molecules

can be neglected. The role of collisions of the second kind diminishes with increase in *E* and low values of population of vibrational levels of the asymmetric mode of  $CO_2$  (at  $T_3 \le 1500$  K). This result agrees with the result obtained in [12, 22].

The EEDF for the conditions of a gas-discharge  $CO_2$  laser in (He : N<sub>2</sub> :  $CO_2$  : CO = 72 : 18 : 2.5 : 7.5) mixture at E/N=5-20 Td and T=500 K was studied in [34]. The main attention was paid to studying the influence of electron collisions of the second kind (superelastic collisions) with excited atoms and molecules on the EEDF and the rate constant of dissociation of  $CO_2$  molecule. The model included superelastic electron collisions with  $CO_2$  molecules excited to  $(01^{10}, 10^{00}, and 00^{01})$  levels, along with nitrogen molecules N<sub>2</sub> and helium atoms He excited to electronic

states  $A^{3}\Sigma_{u}^{+}$  and  ${}^{3}S$ , respectively. It was assumed that  $CO_{2}$  dissociation (reaction 52.0) occurs via excited states of  $CO_{2}$  molecule characterized by excitation threshold of 7.0 eV (processes 18.0). This point of view was adapted in [83], where the rate constant of dissociation of  $CO_{2}$  in an electric-discharge  $CO_{2}$  laser was measured. The results of the measurements agree with

the experimental results obtained in [44] and calculations [84].

In the model developed in [34], cross sections needed for solution of the equation governing the EEDF were adapted from [140]. We underscore that, in contrast to self-consistent model [12] of calculation of EEDF and concentrations in vibrational levels of  $CO_2$ , relative concentrations of molecules and atoms in excited states upon solution of the equation for the EEDF in the discussed model were specified in the form of parameters, similar to [22, 30]. Relative concentrations in levels  $(01^{1}0)$  and  $(10^{0}0)$  were calculated at corresponding temperatures  $T_2$  and  $T_1$  equal to 500 K. Temperature  $T_3$  for the asymmetric mode of vibrations of CO2 molecule was higher and was set equal to 1500 K. Note that the value of  $T_3$  used in model [34] was substantially lower than the value of  $T_3 = 4000$  K used in model [12]. Relative concentra-

tions  $[N_2(A^3\Sigma_u^+)]/[N_2]$  and  $[He(^3S)]/[He]$  in mixtures were varied in the calculations, reaching the values of  $10^{-4}$ . Calculations revealed that the rate constant of CO<sub>2</sub> dissociation weakly changed as a result of superelastic electron collisions with vibrationally excited CO<sub>2</sub> molecules at  $T_3 = 1500$  K. Superelastic electron collisions with  $N_2(A^3\Sigma_u^+)$  and  $He(^3S)$  considerably increase the CO<sub>2</sub> dissociation rate at E/N = 5-15 Td. The effect of superelastic collisions with excited molecules and atoms becomes weaker with increase in E/N, which agrees with the results obtained in [22, 30].

Results obtained in [12, 22, 30, 34] are thus indicative of the necessity of self-consistent determination of the EEDF and its principal moments, the rate constant of electron-impact dissociation of CO<sub>2</sub>, and concentrations of molecules at vibrational levels, along with electronically excited states of CO<sub>2</sub>, N<sub>2</sub>, and He in gas discharges (at moderate values of E/N) and afterglow in (He : N2: CO2: CO) mixtures. At low values of concentrations and relative populations of vibrational levels of asymmetric mode of CO<sub>2</sub> molecule (at  $T_3 \leq 1500$  K), the role of electron collisions of the second kind with molecules in formation of the EEDF decreases with increase in E/N (= 5–20 Td). Their role becomes noticeable upon increase in CO<sub>2</sub> concentration and vibrational temperature  $(T_3 \ge$ 4000 K) [12, 28, 133].

Degradation spectrum of electrons that appears upon action of an ionizing source in the form of flux of particles or quanta of electromagnetic radiation on  $CO_2$  [141–143] was studied in [20, 31, 35]. A model for calculation of the degradation spectrum of electrons in a plasma-beam discharge was constructed in [20]. Dissociative electron attachment to  $CO_2$  molecule (reaction 3.0) in the case of monoenergetic source of primary electrons with energy below 10 eV was studied in [31]. A plasma-beam discharge for monoenergetic source of primary electrons with energy of 1 keV and

power per single molecule of 1 eV  $s^{-1}$  was studied in [35].

Composition of plasma-chemical reactions corresponding to electron-impact ionization and dissociative ionization of  $CO_2$  was expanded in [35]. Reaction products and their quantum levels were analyzed in detail. The self-consistent set of cross sections used in [35] was close to that used in [144, 145] and differed from the one used in [21, 31]. The model constructed in [35] included processes and reactions (1.0–12.0, 12.1–12.4, 14.0–14.2, 19.0, 22.0, 28.0, 32.0, and 40.0) with cross sections adapted from [20, 28, 51, 53, 58, 59, 62, 66–68, 147]. Cross sections of Rydberg states (process 40.0) were extrapolated to the region of electron energies of up to 40 eV using the method developed in [146]. Calculations of energy balance of primary high-energy electrons showed that:

-54% of deposited energy were used for ionization of CO<sub>2</sub>, while 34\% were used for excitation of electronic states of CO<sub>2</sub>;

-12% were used for excitation of vibrational levels of CO<sub>2</sub> (most of energy was deposited to level (00<sup>0</sup>1));

-0.1% were used for inelastic collisions, excitation of rotational levels of CO<sub>2</sub>, and dissociative attachment of electron to CO<sub>2</sub>.

Calculated energy cost of formation of an electron—ion pair (ionization energy) satisfactorily agrees with the one measured in [148]. It was noted in [20, 35] that using cross sections from [16, 47] leads to overstated values of energy cost of ionization.

Electronic states of CO<sub>2</sub> involved in dissociation of CO<sub>2</sub> molecule were specified in detail in [35]. It was assumed that dissociation of CO<sub>2</sub> molecule into neutral products in the course of collisions with electrons occurs through excitation of all four electronic levels  ${}^{3}\Sigma_{u}^{+}$ ,  ${}^{1}\Delta_{u}$ ,  ${}^{1}\Pi_{g}$ , and  ${}^{1}\Sigma_{u}^{+}$  of CO<sub>2</sub> molecule (reactions 53.0). This assumption was based on the fact that calculated total excitation rate of electronic states in the discussed study was comparable with the ionization rate of CO<sub>2</sub> molecule. A similar relation between the rates of excitation of electronic states, dissociation, and ionization was established for  $N_2$  and  $O_2$  [148]. Carbon monoxide molecule CO in excited state  $a^3\Pi$ represents one of products of  $CO_2$  dissociation. This fact explains the appearance of the CO Cameron band emission  $(a^{3}\Pi \rightarrow X^{1}\Sigma^{+})$  in the upper layers of the Earth's atmosphere.

Partial cross section measured in [149] was used in [35] for determining the rate constant of formation of CO( $a^{3}\Pi$ ). Calculations carried out in [35] suggest that negative O<sup>-</sup> oxygen ion appears in a plasma– beam discharge as a result of dissociative attachment of electron to CO<sub>2</sub> (reaction 3.0).

Electronic states of  $CO_2$  participating in the mechanism of dissociation of this molecule in the course of collisions with electrons were thus specified in [35]. They differ from the states analyzed in models [16, 21, 28, 34].

Study [36] dealt with construction of a self-consistent model of a fast-axial-flow CO<sub>2</sub> laser operating in gas mixture (He :  $CO_2$ : N<sub>2</sub> = 28 : 1 : 11) in the range of E/N = 20-40 Td. Special attention was paid to development of numerical method of calculation of the EEDF that allows solving the set of equations [150] governing the EEDF, electrodynamics, processes of radiation transfer, concentrations of populations of energy levels of particles and chemical compounds of plasma-forming gas, thermal conductivity, etc., in a self-consistent formulation in the continuousmedium approximation. Contribution of collisional processes and reactions with participation of electrons and particles to formation of EEDF was studied in [36]. Processes and reactions that can be ignored when solving the equation governing the EEDF were determined. The model took into account processes (with participation of electrons and CO<sub>2</sub> molecules) and corresponding set of cross sections adapted from [21]. Note that electron-impact excitation of the asymmetric mode of CO<sub>2</sub> vibrations was described in the stepwise approximation. Values of populations of vibrational levels of the molecules were assumed to obey Boltzmann distribution. They served as model parameters. Level populations for symmetric and deformation modes of CO<sub>2</sub> were determined at temperatures of  $T_1 = 293$  K and  $T_2 = 350$  K, respectively. Temperature  $T_3$  of the asymmetric mode of  $CO_2$  molecule and vibrational temperature of  $N_2$  were set equal to 293, 2000, and 3000 K. Excitation of rotational levels of  $CO_2$  (process 2.0) with cross sections adapted from [32, 151] was taken into account in the model developed in [36]. It was assumed that rotational temperature was equal to gas temperature (T = 300 K). A finite-difference scheme analogous to that used for solution of the motion equation of a fluid was developed for solving the equation governing the EEDF [150]. The EEDFs calculated using models developed in [36] and [32] satisfactorily agree with each other. It was established that variation of temperatures  $T_1$  and  $T_2$  from 293 to 350 K had minor effect on the results of calculation of the EEDF. The influence of rotational excitation of CO<sub>2</sub> and N<sub>2</sub> molecules on the EEDF could also be neglected. On the contrary, superelastic electron collisions with vibrationally excited CO2 and  $N_2$  molecules played an important role in formation of the EEDF. Their influence was particularly strong at values of reduced electric field of about E/N = 20 Td. This result agrees with the results obtained in [12, 22, 30, 34].

A self-consistent model of an MD that is used in a CO<sub>2</sub> laser (He : N<sub>2</sub> : CO<sub>2</sub> = 75 : 15 : 10 and He : N<sub>2</sub> : CO<sub>2</sub> : CO : O<sub>2</sub> = 75 : 15 : 6 : 4 : 2 at p =22.5 Torr and excitation frequency of 2.45 GHz) [152] was developed in [37] to investigation how variation of gas-mixture composition influences the magnitude of E/N. Special attention was paid to the influence of  $CO_2$  dissociation on isotropic part of the EEDF, its principal moments, and electron energy balance. The MD was sustained at pressure in the range from 5 to 100 mbar (3.7–75 Torr) in (He :  $CO_2$  :  $N_2 = 75$  : 15 : 10) gas mixture. Specific power Wabsorbed by plasma was varied reaching the value of 100 W/ cm<sup>3</sup>. Cross sections adapted from [49, 132] and supplemented by the data from [153, 154] were used for description of electron collisions with CO<sub>2</sub> upon solution of the equation governing the EEDF. Numerical method developed in [155] was used for interpolation of cross sections. When determining the EEDF, electron collisions of the second kind with vibrationally excited CO<sub>2</sub> and N<sub>2</sub> molecules were neglected. According to the results obtained in studies [12, 22, 30, 34], such an approximation turns out to be valid. Temperatures corresponding to different vibrational modes of CO<sub>2</sub> and vibrations of N<sub>2</sub> molecules do not exceed 1500 K in an MD at  $E/N \ge 30$  Td [156]. When solving the equation governing the EEDF, relative concentrations of products (CO and O) of CO<sub>2</sub> dissociation in initial mixture were specified in the form of initial parameters similar to [12, 22, 30, 34]. The degree of dissociation  $\alpha_{CO_2}$ obtained from the mass-spectrometric data varied in the range from 20 to 70% for the studied conditions and was used as an initial parameter in the calculations of the EEDF. It was established that the fraction of the low-energy electrons in the EEDF (up to 2 eV) that are responsible for excitation of vibrational levels of CO<sub>2</sub> substantially decreased with increase in  $\alpha_{CO_2}$  and decrease in gas pumping speed. At the same time, the fraction of the high-energy electrons in the EEDF (from 2 to 12 eV) increased. In the calculation, the observed effect was accompanied by an increase in  $\langle \varepsilon \rangle$ from 1.49 to 2.16 eV and reduction in  $n_e$  from 1.27 ×  $10^{11}$  to  $3.9 \times 10^{10}$  cm<sup>-3</sup>. This behavior agrees with the results of studying the EEDF in an MD in pure CO<sub>2</sub> [25]. The results of self-consistent calculations of the EEDF and concentrations of gas components obtained in [37] are indicative of enrichment of the high-energy part of the EEDF due to increase in E/N. The value of E/N increases with increase in  $\alpha_{CO_2}$ . At large value of the latter, percent concentration of  $\tilde{O}_2$  in the discharge is higher than that of CO and  $CO_2$ . In this case, the creation and annihilation sources in the particle-balance equation become equal to each other at higher values of E/N. Energy transferred by electrons to  $(00^{0}1)$  energy level of the asymmetric mode of  $CO_2$  and vibrational levels (v = 1-8) of  $N_2$  molecules decrease with increase in  $\alpha_{\text{CO}_2}$  This behavior qualitatively agrees with the results of the experiment: the output power of a CO<sub>2</sub> laser drops; the discharge becomes contracted; the input microwave power has to be increased to sustain the gas discharge.

A model for determination of the EEDF and its principal moments that represents part of the selfconsistent collisional-radiative model of a pulsed glow discharge and afterglow was presented in [7]. The discharge was created in a discharge tube with a length of 23 cm and radius of 1 cm under the following conditions: E/N = 40-80 Td; electron temperature of 1– 2 eV; translational temperature of 680 K; pressure of 3–5 Torr; discharge duration of  $\tau_L = 5$  ms; current of 50 mA. A self-consistent set of cross sections different from the corresponding set of cross sections presented in [15, 16, 21, 28, 29, 38, 40–42, 62] was formed. The discussed self-consistent set of cross sections was formed on the ground of a wider range of E/N(= 0.01 - 1000 Td) and electron energies (up to 1000 eV) within which the equation governing the EEDF was solved. In contrast to [15, 16, 21, 28, 29, 38, 40-42, 62], attention in [7] was paid to the fact that electron collisions of the second kind with vibrationally excited molecules at the  $(01^{1}0)$  level of the deformation mode of CO<sub>2</sub> must be taken into account when forming the self-consistent set of cross sections. This conclusion was based on the fact that the energy difference between adjacent vibrational levels of the deformation mode of the molecule ( $\approx 0.08$  eV) is comparable (within an order of magnitude) with the energy of translational motion of molecules at T = 300 K. Population of  $(01^{1}0)$  level becomes sufficiently high for superelastic electron collisions with CO<sub>2</sub> molecules excited to  $(01^{1}0)$  level to start affecting the results of calculation of the EEDF at  $E/N \le 1$  Td. This finding formed the basis for extrapolation of the initial cross section of the collision accompanied by momentum transfer from electrons to CO<sub>2</sub> molecules obtained in [16, 21] to the range of electron energies  $\varepsilon \le 0.1$  eV. Detailed structure of vibrational levels of CO<sub>2</sub> was adapted for interpretation of results of time-resolved Fourier-spectroscopic analysis of kinetics of vibrational excitation of CO<sub>2</sub> molecules in a pulsed directcurrent glow discharge and an afterglow [157]. When forming the self-consistent set of cross sections, special attention was paid to estimation of cross section of electron-impact dissociation of CO<sub>2</sub>, along with detailed analysis of processes of excitation of vibrational levels and electronic states of CO<sub>2</sub>. The selfconsistent set of cross sections was determined using initial cross sections obtained in [1, 7, 14, 21, 64, 65] for processes (1.0, 3.0-5.0, 6.1, 7.0-9.0, 10.1, 10.2, 11.0, 12.0, 18.0, and 30.0). The cross section of superelastic electron collisions with CO2 molecules occupying the  $(01^{1}0)$  level was determined by means of the Klein-Rosseland relation [90]. The resulting selfconsistent set of cross sections forms database [43].

It was assumed that dissociation of  $CO_2$  occurs via excitation of electronic states ( $Y_{10.5}$  and  $Y_{7.0}$ ) of  $CO_2$ 

molecule (reactions 50.0 and 52.0, respectively). This assumption was based on the results of theoretical [9, 14, 16, 21, 34, 158] and experimental [44–46, 158] investigation of electron-impact dissociation of  $CO_2$  in gas discharges.

The rate constant of  $CO_2$  dissociation was measured experimentally and calculated using excitation cross sections of a group of electronic states  $Y_{7,0}$  (reaction 52.0) in [158]. The authors concluded that reaction (52.0) that is characterized by excitation cross section of a group of electronic states  $Y_{7,0}$  cannot be the only channel of  $CO_2$  dissociation.

The value of cross section of electron-impact dissociation was retrieved in [44] from the measured rate constant of  $CO_2$  dissociation by using Maxwell distribution for electrons. The obtained value of cross section of reaction (54.0) was characterized by the threshold of 6.1 eV.

The cross section of CO<sub>2</sub> dissociation was measured by means of electron spectroscopy in [45]. It was found that decomposition of CO<sub>2</sub> is characterized by higher threshold of the reaction (12.0 ± 0.8 eV) than was described in [44]. It was allowed for the possibility that the measured threshold of CO<sub>2</sub> dissociation corresponds to two reactions (55.0 and 55.1) in which O and CO are formed in excited states <sup>1</sup>S and  $a^{3}\Pi$ , respectively. The percent composition of products of CO<sub>2</sub> dissociation, oxygen atoms and carbon monoxide, in excited states <sup>1</sup>S and  $a^{3}\Pi$ , was found to be equal to 73 and 27%, respectively.

In study [14], it was recommended using the cross section of  $CO_2$  dissociation measured in [46] by means of electron spectroscopy. It was established that O in excited state <sup>1</sup>S (reaction 55.0) represents one of the products of  $CO_2$  dissociation. The presence of additional reactions that lead to formation of  $O(^1S)$  was also assumed [14].

A model of CO<sub>2</sub> dissociation in gas discharges that was different from those reported in [28, 35, 40, 44– 46] was proposed in [9]. The model takes into account dissociation reactions (56.0) accompanied by formation of carbon monoxide CO in metastable state  $(a^{3}\Pi)$ , radiative electronic states  $Y_{\varepsilon}$  characterized by excitation thresholds of 7-9 eV, and electronic states  $Y_{\epsilon}$  characterized by excitation thresholds of 7–9 eV for which electric dipole transitions to lower electronic states are forbidden. According to model [9], 40% of the total cross section of electron-impact dissociation of CO<sub>2</sub> correspond to cross section of the reaction that leads to formation of CO( $a^{3}\Pi$ ). The remaining 60% of the total cross section of electron-impact dissociation of CO<sub>2</sub> correspond to cross section of dissociative electron-impact excitation of CO2 accompanied by formation of CO in radiative triplet states  $Y_{\varepsilon}$  characterized by excitation thresholds in the range of 7-9 eV that lie higher on the energy scale than the  $a^3\Pi$  state.

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These states allow cascade population of  $a^3\Pi$  state as a result of electric dipole transitions (process 56.1). Excitation cross sections for these reactions can be determined using absorption spectra of CO molecule. Contribution of these reactions to formation of CO in

states  $Y_{\varepsilon}$ ' characterized by excitation thresholds of 7– 9 eV for which electron dipole optical transitions are forbidden turns out to be very small. State  $a^{3}\Pi$  can be populated from these states as a result of processes (56.2). They are ignored when determining the total cross section of dissociation.

A self-consistent set of cross sections and a kinetic scheme of processes (see the Table 1) different from those described in [15, 16, 21, 28, 35, 40, 41, 62] were thus formed in [7]. It was demonstrated that both the kinetics of the election-impact rotational excitation of  $CO_2$  [28, 42, 54, 62, 78] and kinetics of electron collisions of the second kind with  $CO_2$  molecules excited to (01<sup>1</sup>0) level must be taken into account for increasing the accuracy of determining the self-consistent set of cross sections at  $E/N \sim 0.1$  Td. Electronic states of  $CO_2$  in the mechanism of electron-impact dissociation of  $CO_2$  molecule were specified in detail.

Zero-dimensional collisional radiative models of multi-component plasma developed for investigation of the dissociation degree of  $CO_2$  and efficiency of discharge devices based on barrier discharge (BD) and pulsed MD were described in [6].

The barrier discharge was initiated in a CO<sub>2</sub> flow between two coaxial electrodes with a frequency of f = 35 kHz. The duration of an individual microscopic discharge was equal to  $\tau_{\rm R} = 30$  ns. The value of  $\tau_{\rm R}$ determines the time during which the energy of electromagnetic field is transferred to plasma electrons. In the course of effective period of  $T_{\rm eff}$ , microscopic discharges fill the volume equal to 5% of the total volume occupied by the BR. Effective pulse period  $T_{\rm eff}$  defined as  $T_{\rm eff} = (0.05 \times 2 \times f)^{-1}$  was equal to  $2.9 \times 10^{-4}$  s. Electron concentration  $n_e$  was equal to  $5 \times 10^{13}$  cm<sup>-3</sup>. Time  $\tau_{\rm L}$  that the gas spent in the discharge volume was in the range from 0.52 to 5.15 s. Specific power *W* absorbed by plasma was equal to 10.6 W cm<sup>-3</sup> at T = 300 K.

Pulsed MD was initiated in a discharge tube with a radius of 1 cm at p = 20 Torr and T = 300 K. The tube crossed a rectangular waveguide used for delivering microwave-radiation power in pulsed regime through an opening so that a 10-cm segment of the tube was inside the waveguide. The MD was sustained in a flow of CO<sub>2</sub> with volume gas consumption of 83.33 cm<sup>3</sup>/s. Time  $\tau_L$  coincided with the duration of the MD and was equal to 9.13 ms. It was assumed that *W* in MD was constant and fell in the range from 10 to 100 W cm<sup>-3</sup>.

Special attention was paid in model [6] to description of vibrational kinetics and relaxation involving excited  $CO_2$  molecules occupying vibrational energy



Fig. 1. Rate constant  $K_D$  of CO<sub>2</sub> dissociation as a function of E/N. Symbols correspond to the results of measurements of  $K_D$  in a direct-current discharge obtained in [44]. Curves show the values of  $K_D$  determined using the model of calculation of EEDF [42] with cross sections of CO<sub>2</sub> dissociation adapted from [9, 14, 28, 35, 40 (with thresholds of 7.0 and 10.5 eV), 44–46]. Vertical and horizontal lines define the boundaries of an array of  $K_D$  values adapted from [35, 40, 44] that correspond to E/N = 80-100 Td and were selected for determining the dependence of rate constant  $K_{Dm}$  of CO<sub>2</sub> decomposition on E/N.

levels up to the CO<sub>2</sub> dissociation limit (5.5 eV). The EEDF was determined as a function of E/N by using cross sections of electron collisions with CO<sub>2</sub> adapted from [21, 71]. When solving the equation governing the EEDF, processes and reactions with participation of CO<sub>2</sub> (1.0, 3.0–7.0, 8.1, 12.0, 14.0–14.3, 28.0, 29.0, and 61.0) were taken into account. Note that, in contrast to self-consistent models [7, 12, 36], multi-quantum transitions  $00^0v_3 \rightarrow 00^0w_3$  between vibrational lev-

els  $(00^0 v_3)$  and  $(00^0 w_3)$  of asymmetric mode of CO<sub>2</sub> were taken into account in model [6], similar to model [36].

It was established that dissociation of  $CO_2$  molecules in a BD is caused by direct electron impacts due to high value of E/N. Contribution of reactions with participation of  $CO_2$  and vibrationally excited molecules  $CO_2(00^0v_3)$  to the rate of  $CO_2$  dissociation in an MD can be comparable (or larger) to contribution of the reaction of electron-impact decomposition of the molecule. They represent the essence of the (secondary) mechanism of  $CO_2$  decomposition that is different from the electron-impact decomposition in an MD at atmospheric pressure. Secondary mechanisms of  $CO_2$  dissociation in an MD were studied in [8].

Let us illustrate the above consideration by calculations. The rate constant  $K_{Dm}$  of electron-impact dissociation of CO<sub>2</sub> is determined using the following procedure:

(1) Arrays of rate constants  $K_D$  of electron-impact dissociation of CO<sub>2</sub>, the EEDF, and its principal moments are calculated as a function of E/N using models [41–43] and the set of cross sections from [9, 14, 28, 35, 44–46].

(2) A comparative analysis of experimental and calculated rate constants  $K_D$  is conducted in order to determine the range of E/N within which the scatter of  $K_D$  values is the smallest.

(3) The values of  $K_D$  characterized by the smallest scatter are selected within established range of E/N.

(4) The fitting procedure consisting in finding a linear combination of given functions by the least squares method for selected values of  $K_D$  is used for determining the dependence of rate constant  $K_{Dm}$  on E/N. When choosing the linear combination of given functions, the form of functional dependence of calculated values of  $K_D$  on E/N is taken into account.

The results of calculations of the rate constants  $K_D$  of electron-impact dissociation of CO<sub>2</sub> at atmospheric pressure as a function of E/N in the range from 30 to 100 Td at T = 300 K are illustrated in Figs. 1–3. For comparison, also shown are the results of measurements of  $K_D$  in a direct-current discharge adapted from [44]. The values of  $K_D$  were determined taking into account the difference of processes and reactions that were included in models [41–43], corresponding self-consistent sets of cross sections (see the Table 1), and cross sections  $\sigma_D$  of CO<sub>2</sub> dissociation adapted from [9, 28, 35, 40, 44–46].

Figures 4a, 4b, and 5 illustrate the comparison of the EEDFs calculated using models [41–43] at different values of E/N (60 and 80 Td), along with the dependences of cross sections of CO<sub>2</sub> dissociation  $\sigma_D$  on electron energy  $\varepsilon$ , respectively.

The dependences of  $v_{dr}$ ,  $D/\mu$ , and  $\alpha_r/N$  on E/N measured in [103–127] and calculated using models [41–43] are compared in Figs. 6–8. It can be seen that



**Fig. 2.** Rate constant  $K_D$  of CO<sub>2</sub> dissociation as a function of E/N. Curves show the values of  $K_D$  determined using the model of calculation of EEDF [43] with cross sections of CO<sub>2</sub> dissociation adapted from [9, 14, 28, 35, 40 (with thresholds of 7.0 and 10.5 eV), 44–46]. Vertical and horizontal lines define the boundaries of an array of  $K_D$  values adapted from [9, 35, 40, 44] that correspond to E/N = 55-100 Td and were selected for determining the dependence of rate constant  $K_{Dm}$  of CO<sub>2</sub> decomposition on E/N.



**Fig. 3.** Rate constant  $K_D$  of CO<sub>2</sub> dissociation as a function of E/N. Curves show the values of  $K_D$  determined using the model of calculation of EEDF [41] with cross sections of CO<sub>2</sub> dissociation adapted from [9, 14, 28, 35, 40 (with thresholds of 7.0 and 10.5 eV), 44–46]. Vertical and horizontal lines define the boundaries of an array of  $K_D$  values adapted from [44] that correspond to E/N = 55-100 Td and were selected for determining the dependence of rate constant  $K_{Dm}$  of CO<sub>2</sub> decomposition on E/N.

the results are in reasonable agreement with each other.

Figure 9 represents the results of determining the dependence of rate constant  $K_{\text{Dm}}$  of CO<sub>2</sub> decomposition on E/N.

In can be seen in Figs. 1–3 that calculated values of electron-impact rate constants  $K_D$  of CO<sub>2</sub> dissociation linearly depend on E/N. They monotonically increase with increase in E/N and differ from those measured in [44]. The difference between the results of calculations and measurements is particularly large for models [42, 43]. The observed difference between calculated and experimentally obtained data within each

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particular model is explained by the difference in cross sections  $\sigma_D$  of CO<sub>2</sub> dissociation (Fig. 5).

The values of  $K_{\rm D}$  calculated using model [42] fall in the range of 0.2 × (10<sup>-16</sup>-10<sup>-12</sup>) cm<sup>3</sup> s<sup>-1</sup> at E/N =30 Td and 0.2 × 10<sup>-10</sup>-0.5 × 10<sup>-9</sup> cm<sup>3</sup> s<sup>-1</sup> at E/N =100 Td (Fig. 1). The smallest scatter of experimental and theoretical data is observed in a narrow range of E/N values (80–100 Td) when using cross sections  $\sigma_{\rm D}$ from [35, 40, 44]. These data were selected for determining the dependence of rate constant  $K_{\rm Dm}$  of CO<sub>2</sub> decomposition on E/N.



Fig. 4. EEDFs calculated at (a) E/N = 60 Td and (b) E/N = 80 Td by using models: I = [42], 2 = [41], 3 = [43].



Fig. 5. Cross sections  $\sigma_D$  of electron-impact dissociation of CO<sub>2</sub> as functions of electron energy  $\varepsilon$  adapted from [9, 14, 28, 35, 40 (with thresholds of 7.0 and 10.5 eV), 44–46]. Arrows mark cross sections that were selected for determining the dependence of rate constant  $K_{Dm}$  of CO<sub>2</sub> decomposition on E/N.

Rate constants  $K_{\rm D}$  obtained using model [43] attain higher values of  $0.4 \times 10^{-15}-0.14 \times 10^{-11}$  cm<sup>3</sup> s<sup>-1</sup> and  $0.4 \times 10^{-10}-0.7 \times 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup> than those calculated using model [42] at corresponding values of E/N =30 Td and E/N = 100 Td (Fig. 2). The  $K_{\rm D}$  data group with smallest scatter in a wider range of E/N =100 Td than in the case of model [42]. This result is valid for the set of cross sections  $\sigma_{\rm D}$  adapted from [9, 35, 40, 44]. The latter contains cross sections that are pulled out when using model [42]. These data were used for determining the dependence of  $K_{\rm Dm}$  on E/Nin the range from 55 to 100 Td.

When comparing with the results of calculations carried out using models [42, 43], the largest values of  $K_{\rm D}$  are obtained using model [41]: calculated values of  $K_{\rm D}$  fall in the range of  $0.1 \times 10^{-13}$ – $0.16 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup> at E/N = 30 Td and in the range of  $0.4 \times 10^{-10}$ – $0.1 \times 10^{-8}$  cm<sup>3</sup> s<sup>-1</sup> at E/N = 100 Td. It can be seen from

Fig. 3 that the smallest difference between measured and calculated values of  $K_D$  is obtained in the range of E/N between 55 and 100 Td with cross sections  $\sigma_D$ adapted from [44]. When using model [41], satisfactory agreement between the theory and the experiment is obtained in the same range of E/N values (55– 100 Td) with cross section  $\sigma_D$  adapted from [44] that is contained in the data obtained using models [42, 43]. Thus found values of  $K_D$  were used for plotting the dependence of  $K_{Dm}$  on E/N in the range from 55 to 100 Td.

The dependence of  $K_D$  values on specific model [41–43] is explained by the difference of EEDFs. Figures 4a and 4b demonstrate that the EEDFs calculated for the same values of E/N using different self-consistent sets of cross sections and compositions of processes and reactions from [41–43] (see the Table 1) differ from one another. The maximum value of the EEDF in the range of high values of  $\varepsilon$  is obtained using



**Fig. 6.** The total ionization coefficient  $\alpha_r/N$  for CO<sub>2</sub> as a function of E/N. Symbols and curves with symbols represent the results of measurements of  $\alpha_r/N$  adapted from database [122] and studies [103, 104, 109, 110, 115, 116, 126, 127]. Curves (without symbols) represent the results of calculation of  $\alpha_r/N$  using models [41–43].

model [41]. The smallest difference between the EEDFs is observed when using models [42, 43]. The difference between the EEDFs becomes particularly pronounced upon decrease in E/N in the range of high electron energies ( $\varepsilon \ge 4$  eV). This range of energies includes thresholds of processes of impact excitation of electronic states and reactions of impact dissociation and ionization of CO<sub>2</sub> molecule (Fig. 5 and the Table 1).

The scatter of values of  $K_{\rm D}$  (symbols) as a function of EEDF experimentally obtained in [44] and those calculated using models [41–43] is illustrated in Fig. 9. Curve 1 in Fig. 9 corresponds to the dependence of  $K_{\rm Dm}$  on E/N. This curve was plotted by choosing a linear combination of functions  $(E/N)^{-2}$  and  $(E/N)^{0.5}$ obtained using the least squares method for chosen values of  $K_{\rm D}$ :

$$K_{\rm Dm} = 4.5 \times 10^{-11} [(E/N)^{0.5} - 1.75 \times 10^4 (E/N)^{-2}].$$

Quantities  $K_{\rm Dm}$  and E/N in the above expression have the dimensions of cm<sup>3</sup>/s and Td, respectively. Note that the linear combination of functions was found from considerations that the dependence of  $K_{\rm Dm}$ on E/N in the range from 55 to 100 Td must be similar to those calculated using models [41–43] (Figs. 1–3). It can be seen from the diagram that these dependences differ from both quadratic (curve 2) and linear (curve 3) dependences.

It can thus be expected from comparison of  $K_D$  values measured in [44] and calculated using models [41–43] that the electron-impact dissociation of CO<sub>2</sub> molecule via excitation of its electronic states [3, 9]

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**Fig. 7.** Electron drift velocity  $v_{dr}$  as a function of *E/N*. Symbols and curves with symbols represent the results of measurements of  $v_{dr}$  adapted from databases [122–125] and studies [107, 108, 113, 115–121]. Curves (without symbols) represent the results of calculation of  $v_{dr}$  using models [41–43].

represents the dominant mechanism of CO<sub>2</sub> decomposition under stationary conditions of a gas discharge at E/N = 55-100 Td. The obtained value of  $K_{\text{Dm}}$  can be recommended for using in studies of CO<sub>2</sub> decomposition in a gas discharge at atmospheric pressure in the range of E/N = 55-100 Td.



**Fig. 8.** Ratio of coefficient *D* of transverse diffusion and mobility  $\mu$  (*D*/ $\mu$ ) as a function of *E*/*N*. Symbols and curves with symbols represent the results of measurements of *D*/ $\mu$  adapted from databases [122, 124] and studies [105, 106, 111, 112, 114–116, 119]. Curves (without symbols) represent the results of calculation of *D*/ $\mu$  using models [41–43].



**Fig. 9.** Approximation of the dependence of constants  $K_D$  of CO<sub>2</sub> dissociation (symbols) measured in [44] and calculated using models [41–43] on E/N by the least-squares method. The data obtained in [41–44] were processes using a linear combination of functions  $(E/N)^{-2}$  and  $(E/N)^{0.5}$  (curve *I*), a second-degree polynomial (quadratic function, curve *2*) and a first-degree polynomial (linear function, curve *I*).

It follows from calculations and comparison of  $K_D$  values (Figs. 1–3, 9), EEDFs, and their principal moments ( $v_{dr}$ ,  $D/\mu$ , and  $\alpha_r/N$ , Figs. 6–8) obtained using models [41–43] that the method of formation of the self-consistent set of cross sections leads to ambiguous determination of the self-consistent set of cross sections, composition and number of reactions and processes (see the Table 1). It should be underscored that the difference in  $K_D$  values (Figs. 1–3, 9) is caused not only by an uncertainty in determination of the EEDF when using models [41–43].

#### 4. CONCLUSIONS

In the present review, we analyzed available data on self-consistent sets of cross sections that are used for determining the isotropic part of the EEDF in gas discharges in CO<sub>2</sub> by solving the Boltzmann equation using the two-term spherical harmonics expansion of the electron energy distribution function at values of the reduced electric field  $E/N \le 100$  Td. The fitting procedure involving calculated and measured values of moments (the drift velocity, characteristic electron energy, and ionization coefficient) of the electron energy distribution function was used to form the set of cross sections. It was demonstrated that, despite similar approach to formation of a self-consistent set of cross sections, identical values of fitting parameters can be obtained using different sets of cross sections. This leads to ambiguity of calculated values of the rate constants of processes that take place upon electron collision.

Based on analysis of the literature, we compiled a table that contains spatial physicochemical processes with corresponding notations of quantum energy levels of initial reactants and final products of chemical reactions with participation of electrons, including elastic electron collisions with CO<sub>2</sub> molecules; electron-impact excitation of electronic states, rotational, and vibrational levels of CO<sub>2</sub> molecules; dissociative electron attachment to CO<sub>2</sub> molecules; dissociation and ionization of CO<sub>2</sub> molecules as a result of collisions with electrons; dissociative ionization of CO<sub>2</sub> molecules in collisions with electrons. The main inelastic processes are: electron-impact rotational excitation of CO<sub>2</sub> molecule, along with electron collisions of the first and second kind with CO<sub>2</sub> molecules in the ground state ( $00^{0}0$ ) and excited state ( $01^{1}0$ ) at  $E/N \sim 0.1$  Td; collisional excitation of vibrations of CO<sub>2</sub> molecule at the (01<sup>1</sup>0) level in the range of E/Nfrom 0.1 to 1 Td; excitation of vibrations of CO<sub>2</sub> mole-

cule at energy levels (00<sup>0</sup>1) and ( $\Sigma v_1 l^{10}$  for  $v_1 > 2$ ), electronic states, and ionization of CO<sub>2</sub> molecule at E/N > 1 Td.

The range of values of E/N = 55-100 Td in which  $CO_2$  dissociation via electron-impact excitation of electronic states represents the dominant mechanism of  $CO_2$  decomposition is established. An expression governing the rate constant of  $CO_2$  dissociation as a function of E/N is obtained for this range. Contribution of secondary reactions, e.g., those with participation of  $CO_2$  molecules and vibrationally excited mole-

cules  $CO_2(00^0v_3)$ , to direct-electron-impact dissociation of  $CO_2$  can become comparable at lower magnitudes of the reduced electron field (E/N < 40 Td).

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#### CONFLICT OF INTEREST

The authors declare no conflicts of interest.

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