Monte Carlo simulations of electron dynamics in N$_2$/CO$_2$ mixtures

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Abstract. Motivated by experimental investigations of electrical discharges in N$_2$/CO$_2$/H$_2$O, Monte Carlo (MC) electron dynamics simulations in atmospheric N$_2$/CO$_2$ mixtures were performed. The goal was to obtain electron energy distribution functions (EEDFs), mean free path, drift velocity, collision frequency and mean energy of electrons, rate coefficients of electron-impact reactions, ionisation and attachment coefficients, as functions of the reduced electric field strength ($E/N$) and of the concentration of individual gas components. The results obtained by MC simulations were fitted with polynomials of up to the 3rd order with reasonable accuracy for $E/N$ above 80 Td. The studied parameters below 80 Td were strongly non-linear as functions of $E/N$. This is mostly due to the influence of elastic collisions of electrons with CO$_2$ molecules prevailing in CO$_2$-dominant mixtures for $E/N < 40$ Td, and vibrational excitation collisions of N$_2$ species prevailing in N$_2$-dominant mixtures for $E/N$ from 40 to 90 Td. The effect of these electron-impact processes was specific for each of the studied parameters.

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Electrical properties (ionisation, breakdown, electron and ion mobility, etc.)

1 Introduction

Plasma, unlike gases that are usually chemically inert at standard conditions, possesses chemical activity due to electrons, excited particles, ions and radicals present. Chemical effects of plasmas generated by various types of electrical discharges operating in many gaseous mixtures have been extensively investigated during the last few decades [1,2]. Such plasmas can be applied for ozone generation, exhaust gas and waste water treatment, chemical utilisation, surface modifications, removal of hazardous compounds, bio-decontamination, etc. [3–6].

Chemistry induced by atmospheric pressure DC electrical discharges in N$_2$/CO$_2$/H$_2$O mixtures was studied recently [7–10]. This mixture represents a model prebiotic atmosphere of the Earth and a simplified flue gas from the stoichiometric combustion of the natural gas. The aim of these studies was the decomposition of CO$_2$, which is the dominant contributor to the enhanced greenhouse effect, and the formation of organic species, especially amino acids. Synthesis of some essential amino acids was detected by electrical discharges, which is very interesting from the viewpoint of the theory of origins of life. The mechanism of synthesis of amino acids from simple inorganic molecules is still not completely understood.

Generally, a detailed description of the reaction mechanisms in plasmas is a complicated task. However, it is well-known that high energy electrons accelerated in an electric field represent the key initiating factor in electrical discharges inducing low-temperature plasma chemistry. For this reason we show here calculations of the rate coefficients of electron-impact reactions in N$_2$/CO$_2$ mixtures. Next, we plan to study the influence of humidity on these rate coefficients in N$_2$/CO$_2$/H$_2$O mixtures.

The calculation of the rate coefficients for electron-impact reactions requires the knowledge of electron energy distribution functions (EEDFs). The EEDF, $f(\varepsilon)$, can be defined in such a way that the local fraction of electrons in the energy range ($\varepsilon, \varepsilon + d\varepsilon$) is given by $f(\varepsilon)\varepsilon^{1/2}d\varepsilon$. In cold plasmas, EEDFs may have strongly non-Maxwellian shape but they satisfy the Boltzmann equation. Thus, one way to obtain EEDFs is to solve numerically simplified versions of the Boltzmann equation. The second approach is to use Monte Carlo (MC) methods that are widely used for complex physical and mathematical problems.

The examples of the utilization of MC methods can be also found in the fields of both low and high temperature plasmas. The MC methods were used for example for the modelling of edge plasma and plasma surface interactions in fusion experiments [11–13], or for the simulation of low energy electrons and photons interactions [14]. The MC algorithms can be also used to compute a trajectory...
of electrons [15–19]. The so-called ‘zero-collision’ MC method, originally developed by Skullerud [20], is frequently used to compute plasma parameters, see [21, 22]. This algorithm, based on collisional frequencies of the electron, is currently mostly used for noble gases. The so-called particle-in-cell method has been applied to RF discharges by Birdsall [23] and Sommeren [24].

The similarity of results obtained by MC methods and the numerical solution of the Boltzmann equation was shown by Segur et al. [25], although the authors stressed the necessity of using more than the first four terms of the spherical harmonic expansion in the solution of the Boltzmann equation. We decided to use MC simulation of electron dynamics to calculate EEDFs in the studied gas mixtures. For this purpose, we developed an open source software named ‘Web-EEDF’ [26, 27], based on the algorithm presented by Tas et al. [28]. The reliability of our results was proved by their comparison with data found in literature [26, 29].

2 Algorithm

The EEDF is usually defined as the energy distribution of an assembly of \( n \) electrons at time \( t \). Our algorithm (Fig. 1) is based on the presumption, that the same EEDF is found when the energy of a single electron is sampled at \( n \) moments in time (ergodic theory). We follow a single electron as it moves in the studied gas mixture and we record its energy and several further characteristics in \( n \) computational cycles. The energy of the electron and the direction of its motion changes during the simulation, due to its acceleration by an electric field and due to its interaction with other species (atoms, molecules, background electrons). There are three types of electron interactions implemented:

1. elastic electron-molecule (atom) collisions,
2. inelastic electron-molecule (atom) collisions,
3. electron-electron interactions.

The composition of the gas, its pressure \( (p) \) and temperature \( (T_a) \), the reduced electric field strength \( (E/N) \), the initial temperature of electrons \( (T_e) \), the number of computational cycles \( (n) \), and the degree of ionisation \( (\xi) \) which is defined as the ratio of electron and neutral densities, are taken as initial parameters in our algorithm. The initial energy of the test electron is randomly chosen from the Maxwellian distribution given by \( T_e \). The direction of its motion relative to the electric field vector \( E \) is chosen randomly as well. Afterwards, the motion of the test electron is followed in a required number of computational cycles. Within one computational cycle, the electron is accelerated over a distance \( \Delta s \), which is equal to the average distance between molecules at the given \( p \) and \( T_a \), and its new energy and new direction of its motion are calculated. The direction is determined by the velocity vector \( v \), which has two components: parallel \( (v_\parallel) \) and perpendicular \( (v_\perp) \) to \( E \). This is the most important feature in our algorithm compared to the original algorithm of Tas et al. [28], where the electron movement was straightforward along \( E \), and its acceleration over \( \Delta s \) was approximated by a parametrisation.

During each cycle, after the electron changes its position by the distance \( \Delta s \), a random number determines the type of molecule with which the electron may interact. Another random number determines whether the electron will really interact with this molecule or not and the type of this interaction. The probability of each type of interaction depends on its cross section. We used the compilation of cross sections obtained from Joint Institute for Laboratory Astrophysics (JILA) [30], with the update for CO\(_2\) cross sections according to Itikawa [31].

If the interaction occurs, the energy of electron is decreased by \( \Delta \varepsilon \) and a new direction of its motion is chosen randomly. The value of \( \Delta \varepsilon \) depends on the type of this interaction. In case of the elastic scattering, \( \Delta \varepsilon \) is taken equal to average momentum transfer: \( \Delta \varepsilon = 2m_e\varepsilon/M \), where \( m_e \) and \( M \) are the masses of the electron and neutral species, respectively. The excitation of a molecule decreases the energy of the test electron by the amount of energy required to excite the molecule \( (\varepsilon_{\text{exc}}) \): \( \Delta \varepsilon = -\varepsilon_{\text{exc}} \). In case of ionization, electron loses the energy which is required to ionize the molecule \( (\varepsilon_{\text{ion}}) \), plus its remaining energy is shared randomly between itself and the second electron released by the ionized species. The released electron is not further considered in the calculations.

As we assumed an isotropic scattering, the orientation of the electron’s motion after each collision is random. However, the momentum transfer cross sections (\( q_{\text{m}} \))
that we use include some anisotropic effects. By definition, a large angle scattering contributes to \( q_a \) more than a small angle scattering. Moreover, the typical probability of the interaction of the test electron with neutrals during each cycle is around 1% at atmospheric pressure and room temperature in \( \text{N}_2/\text{CO}_2 \) mixture. It means that there is approximately 100 computational cycles with no collision per 1 cycle with a collision. Thus, we minimize the influence of the initial random direction of the electron motion after each collision on EEDF by a large number of ‘zero-collisional’ cycles between collisions.

If the interaction of the test electron with neutral species does not occur and \( \xi > 0 \), the possibility of interaction with a background electron is tested by another random number. The electron-electron interaction is described by so-called Coulomb cross section taken from Mitchner and Kruger [32], and the energy exchange between these electrons is approximated by the scheme of Weng and Kushner [21].

The energy of the electron, the direction of its motion, and the time since its last collision (\( \tau \)) are stored after each computational cycle, regardless an interaction occurs or not. At the end of the simulation, after \( n \) computational cycles, the obtained EEDF is normalised so that \( \int_0^{\infty} f(\varepsilon) \sqrt{\varepsilon} \mathrm{d} \varepsilon = 1 \). Final results include the electron drift velocity \( (v_d) \), the electron mean energy \( (\bar{\varepsilon}) \), the collision frequency of electrons with neutrals \( (\nu) \), the electron mean free path \( (\lambda) \), the electron mobility, the rate coefficients of electron-impact reactions and the branching of the electron energy towards various electron-impact processes. It is further possible to use these data to calculate additional parameters. For example, we present here the calculation of ionisation \( (\alpha) \) and attachment \( (\eta) \) coefficients that are defined as follows:

\[
\alpha = k_{\text{ion}} N / v_d \tag{1}
\]

\[
\eta = k_{\text{att}} N / v_d \tag{2}
\]

where \( k_{\text{ion}} \) is the rate coefficient for electron-impact ionisation, \( N \) is the density of neutrals in \( \text{cm}^{-3} \), \( k_{\text{att}} \) is the rate coefficient for electron attachment reactions. These coefficients reflect the increase or the decrease in electron density per centimetre resulting from ionisation and attachment, respectively. The ionization coefficient is also known as the first Townsend coefficient.

2.1 Computational conditions

The value of \( E/N \) varied from 10 to 400 Td (1 Td = \( 10^{-17} \text{ V cm}^2 \)) and the concentration of \( \text{CO}_2 \) varied from 0 to 100 vol.% during our simulations. Calculations were performed at normal conditions (pressure \( 10^5 \text{ Pa} \) and gas temperature 293 K). The initial electron temperature was also 293 K. The degree of ionisation was set to zero \( (\xi = 0) \), i.e. we neglected electron-electron interactions. According to our previous calculations [26], this simplification is correct for plasmas with \( \xi < 10^{-4} \), corresponding to the concentration of electrons \( (n_e) \) below \( 2.5 \times 10^{15} \text{ cm}^{-3} \) at normal conditions. At higher electron densities, the curves of the EEDF tends towards Maxwellian distribution due to the electron-electron interactions [28].

All simulations were performed with 20 million computational cycles. This number is a good compromise between the accuracy of the obtained data and the computational time [29]. In order to obtain accurate values of \( \varepsilon, v_d, \lambda \) and \( \nu \), even 5 million cycles would be enough, but the rate coefficients of reactions with a high threshold energy \( (\varepsilon_{\text{th}}) \) require at least 20 million computational cycles. The reason is in the statistics: parameters such as \( \varepsilon, v_d, \lambda \) and \( \nu \) were calculated from the whole EEDF, whereas rate coefficients were calculated only from its ‘tail’ above the \( \varepsilon_{\text{th}} \). The standard deviations of the mean values of the rate coefficients calculated in ten runs at 60, 100, and 140 Td showed that the accuracy decreases with the increasing \( \varepsilon_{\text{th}} \) and with the decreasing value of \( E/N \). At 60 Td, the deviation for processes with \( \varepsilon_{\text{th}} > 12 \text{ eV} \) was more than 50%. At 100 Td, only the rate coefficient for the ionisation of \( \text{N}_2 \), with \( \varepsilon_{\text{th}} = 15.6 \text{ eV} \), performed the deviation approaching 50%. Above 140 Td, all the rate coefficients had deviations below 10%. The deviations of \( \varepsilon, v_d, \lambda, \nu \) did not depend on \( E/N \) and they were below 1.5% [29].

3 Results and discussion

There are dozens of possible reactions that can result from the electron interaction with \( \text{N}_2 \) and \( \text{CO}_2 \) molecules. The elastic scattering of electrons and vibrational excitations of \( \text{N}_2 \) and \( \text{CO}_2 \) molecules are the fastest electron-impact processes, but they do not directly influence the plasma chemistry. Here, we present only the calculated rate coefficients of the electron-impact reactions, which we consider to be the most important for plasma chemistry and generation of electrical discharges in \( \text{N}_2/\text{CO}_2 \) mixture. Namely, the reactions leading to the dissociation of \( \text{N}_2 \) and \( \text{CO}_2 \) (Eqs. (7) and (4)), the production of metastable \( \text{N}_2(A^3\Sigma_u^+) \) species, (Eq. (5)), and the electron-impact ionisation and attachment (Eqs. (3), (9), and (10)).

The metastable \( \text{N}_2(A^3\Sigma_u^+) \) species may also be generated by the radiative de-excitation cascade from \( \text{N}_2(B^3\Pi_u) \) and \( \text{N}_2(C^3\Pi_u) \) species, produced primarily by electron-impact reactions (Eqs. (6) and (8)).

\[
e + \text{CO}_2 \rightarrow \text{CO} + \text{O}^- \quad \varepsilon_{\text{th}} = 3.9 \text{ eV} \tag{3}
\]

\[
e + \text{CO}_2 \rightarrow \text{CO}_2(a^3\pi) + e \quad \varepsilon_{\text{th}} = 6.1 \text{ eV} \tag{4}
\]

\[
e + \text{N}_2 \rightarrow \text{N}_2(A^3\Sigma_u^+) + e \quad \varepsilon_{\text{th}} = 6.17 \text{ eV} \tag{5}
\]

\[
e + \text{N}_2 \rightarrow \text{N}_2(B^3\Pi_u) + e \quad \varepsilon_{\text{th}} = 7.35 \text{ eV} \tag{6}
\]

\[
e + \text{N}_2 \rightarrow \text{N} + \text{N} + e \quad \varepsilon_{\text{th}} = 10.0 \text{ eV} \tag{7}
\]

\[
e + \text{N}_2 \rightarrow \text{N}_2(C^3\Pi_u) + e \quad \varepsilon_{\text{th}} = 11.03 \text{ eV} \tag{8}
\]

\[
e + \text{CO}_2 \rightarrow \text{CO}_2^+ + 2e \quad \varepsilon_{\text{th}} = 13.3 \text{ eV} \tag{9}
\]

\[
e + \text{N}_2 \rightarrow \text{N}_2^+ + 2e \quad \varepsilon_{\text{th}} = 15.6 \text{ eV} \tag{10}
\]

We refer to an individual rate coefficient by the number of the specific reaction, e.g. \( k_7 \) is the rate coefficient of the reaction (7). Besides these rate coefficients, we present \( \varepsilon, v_d, \nu, \lambda, \alpha, \) and \( \eta \).
3.1 Fitting of calculated parameters

The EEDF and the derived parameters depend on $E/N$ and the composition of the mixture, determined for example by the concentration of nitrogen ($\delta_{N_2}$). In order to describe the changes of the studied parameters as functions of $E/N$ and $\delta_{N_2}$, we fitted them. In the first step, we fitted them by polynomials of up to the 3rd order, as functions of $\delta_{N_2}$ at fixed values of $E/N$:

$$\Phi\left(\frac{E}{N}, \delta_{N_2}\right) = a_0 + a_1 \delta_{N_2} + a_2 (\delta_{N_2})^2 + a_3 (\delta_{N_2})^3. \quad (11)$$

Here, $\Phi$ represents any of presented parameters ($\lambda, \nu, \ldots$), Thus we obtained a set of fitting coefficients $a_i$, which were subsequently fitted by the polynomials of up to the 3rd order, as functions of $E/N$:

$$a_i\left(\frac{E}{N}\right) = b_{i0} + b_{i1} \left(\frac{E}{N}\right) + b_{i2} \left(\frac{E}{N}\right)^2 + b_{i3} \left(\frac{E}{N}\right)^3. \quad (12)$$

Finally, we obtained a set of fitting coefficients $b_{ij}$, which enable to calculate the value of each studied parameter by the following formula:

$$\Phi\left(\frac{E}{N}, \delta_{N_2}\right) = \left((\frac{E}{N})^1, \ldots, (\frac{E}{N})^{n-1}\right) B \phi \left((\delta_{N_2})^1, \ldots, (\delta_{N_2})^{n-1}\right) \quad (13)$$

where $B_{\phi}$ is a matrix of $m \times n$ type with fitting coefficients $b_{ij}$. If $m$ or $n$ are smaller than 4, it was not necessary to use polynomials of the 3rd order to fit the parameter $\Phi$. On the other hand, it was not possible to fit all coefficients $a_i$ with sufficient accuracy in the whole range of $E/N$ even with polynomials of the 3rd order.

The differences between the values of the studied parameters obtained by MC simulations ($\Phi_{MC}$) and their values calculated from the fitting coefficients ($\Phi_{fit}$) were also evaluated. The average differences between $\Phi_{MC}$ and $\Phi_{fit}$ defined as

$$\Delta = \frac{|\Phi_{MC} - \Phi_{fit}|}{\Phi_{MC}} \times 100 \text{ [%]} \quad (14)$$

for various values of $E/N$ are summarised in Table 1, where the corresponding range of $E/N$ for which the given fitting coefficients may be applied can be also found. The fitting coefficients themselves can be downloaded from http://enviro.fmph.uniba.sk/web-eedf.

3.2 Mean energy of electrons

For $E/N < 25$ Td, the electron mean energy $\varepsilon$ was determined mostly by the large momentum transfer cross section of CO$_2$. In stronger fields, the influence of cross sections for vibrational excitation of N$_2$ dominated. This influence was the strongest at around 40 Td, where even in the mixture with 50% of CO$_2$, the value of $\varepsilon$ was almost identical with the value in pure N$_2$ (Fig. 2). For $E/N \geq 40$ Td, the value of $\varepsilon$ grew monotonously with the deceasing $\delta_{N_2}$. For $E/N \geq 80$ Td, this growth was approximately linear and it was possible to fit $\varepsilon$ according to equations (11–13).

3.3 Drift velocity of electrons

The changes of $v_d$ due to the changes of $\delta_{N_2}$ were also non-linear for $E/N$ below 80 Td. Their character, however, was different compared to $\varepsilon$, since the maximum $v_d$ did not occur in pure gases but in the mixtures with certain values of $\delta_{N_2}$, depending on $E/N$ (Fig. 3). For $E/N \geq 80$ Td, $v_d$ changed linearly with the increasing $\delta_{N_2}$, and it was possible to fit it according to equations (11–13). For $E/N$ below 300 Td, $v_d$ decreased with the increasing $\delta_{N_2}$, though the slope of this decrease diminished with the increase of $E/N$.

\[\varepsilon\]
\[v_d\]
\[\lambda\]
\[k_3\]
\[k_4\]
\[k_5\]
\[k_6\]
\[k_7\]
\[k_8\]
\[k_9\]
\[k_{10}\]

Table 1. The range of applicability of obtained fitting coefficients and average differences between the results obtained by MC simulations and those obtained by using the fitting coefficients for different values of $E/N (\langle \Delta E/N \rangle)$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Applicability</th>
<th>80 Td</th>
<th>120 Td</th>
<th>200 Td</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\varepsilon$</td>
<td>80–400</td>
<td>3.1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>$v_d$</td>
<td>80–400</td>
<td>5.5</td>
<td>5.5</td>
<td>3.4</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>60–400</td>
<td>2.8</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>$k_3$</td>
<td>60–400</td>
<td>1.3</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>$k_4$</td>
<td>80–400</td>
<td>4.5</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>$k_5$</td>
<td>80–400</td>
<td>10.4</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>$k_6$</td>
<td>80–400</td>
<td>8.1</td>
<td>9.0</td>
<td>2.0</td>
</tr>
<tr>
<td>$k_7$</td>
<td>100–400</td>
<td>–</td>
<td>9.2</td>
<td>2.8</td>
</tr>
<tr>
<td>$k_8$</td>
<td>120–400</td>
<td>–</td>
<td>14</td>
<td>2.6</td>
</tr>
<tr>
<td>$k_9$</td>
<td>120–400</td>
<td>–</td>
<td>12</td>
<td>8.3</td>
</tr>
<tr>
<td>$k_{10}$</td>
<td>120–400</td>
<td>–</td>
<td>23</td>
<td>7.5</td>
</tr>
</tbody>
</table>

Fig. 2. Electron mean energy in N$_2$/CO$_2$ mixture for $E/N < 80$ Td.
At 300 Td, the value of $v_d$ was already almost constant in the whole range of $\delta N_2$. Above 300 Td, the value of $v_d$ started to grow linearly with the increasing $\delta N_2$ (Fig. 4).

### 3.4 Collision frequency of electrons with neutrals

For $E/N$ below 40 Td, the dependence of $\nu$ on $\delta N_2$ was strongly non-linear (Fig. 5), because low energy electrons were under the significant influence of the momentum transfer cross section of CO$_2$, i.e. they encountered a large number of elastic collisions. Therefore, in CO$_2$-dominant mixtures, the increase of $E/N$ from 10 to 40 Td lead to the decrease of $\nu$, since the number of elastic collisions decreased with the increasing energy of electrons. For $E/N > 40$ Td, $\nu$ grew again, but mainly due to the increasing number of inelastic collisions. The situation was different in N$_2$-dominant mixtures. Since the momentum transfer cross section for electron-impact collisions of electrons with N$_2$ is small for low energy electrons, $\nu$ grew monotonously with the increasing $E/N$.

### 3.5 Mean free path of electrons

The mean free path of electrons as a function of $\delta N_2$ was non-linear in the whole region of $E/N$ we dealt with. However, it was possible to fit $\lambda$ with polynomials of the 3rd order for $E/N > 60$ Td. For $E/N > 40$ Td, $\lambda$ decreased with increasing $\delta N_2$, but for $E/N < 40$ Td, the behaviour of $\lambda$ as a function of $\delta N_2$ was very complicated (Fig. 6). In mixtures with $\delta N_2 \geq 0.8$, $\lambda$ was almost constant, it lied between $3.2 \times 10^{-7}$ and $4.0 \times 10^{-7}$ m for $E/N$ ranging from 10 to 400 Td. With the increasing concentration of CO$_2$, $\lambda$ varied more significantly as a function of $E/N$, caused by a large momentum transfer cross section of CO$_2$. And,
The growth of rate coefficients with $E/N$ for $\lambda E/N > 1$ and $N E/N < 1$ and concentrations $\delta E/N < 1$ and $E/N \alpha E/N$ and $(\text{grew in the ground state to states } k \text{ mixtures as a function of } E/N = 0.5)$. For both $E/N = 120$ Td, $\delta E/N$ decreased exponentially with $\eta k$ and was logarithmic (Fig. 10). For both $E/N$ and $\eta$, the slope of these curves changed and was specific for every rate coefficient. For $E/N > 80$ Td, they usually decreased and was logarithmic (Fig. 4). For both $E/N$ and $\eta$, the slope of these curves changed and was specific for every rate coefficient.

### 3.6 Rate coefficients of electron-impact reactions

The rate coefficients of electron-impact reactions as functions of $E/N$ at constant $\delta N_2$ performed three typical features (Fig. 7). Some rate coefficients grew exponentially with increasing $E/N$, e.g. $k_9$ and $k_{10}$ for the ionisation of CO$_2$ and N$_2$, respectively. Other rate coefficients grew exponentially for $E/N < 80$ Td, and then almost linearly for higher $E/N$, e.g. $k_5$ and $k_8$ for the electron-impact excitations of N$_2$ in the ground state to states N$_2(A^3\Sigma_u^+)$ and N$_2(C^3\Pi_g)$, respectively. Finally, there are rate coefficients, which exhibited a logarithmic-like growth with the increasing $E/N$, with even a slight decrease for $E/N > 300$ Td, e.g. $k_4$ for the dissociative excitation of CO$_2$. However, the type of the growth of some rate coefficients changed with $\delta N_2$.

The influence of $\delta N_2$ dominated below 80 Td, where all studied rate coefficients decreased exponentially with increasing $\delta N_2$. For $E/N > 80$ Td, they usually decreased linearly with the increasing $\delta N_2$. The slope of these curves depended on $E/N$ and was specific for every rate coefficient. For $k_3$, $k_9$ and $k_{10}$, the slope even changed its sign for $E/N > 300$ Td, where these three rate coefficients increased linearly with the increasing $\delta N_2$, i.e. they exhibited behaviour similar to $\nu_d$ (Fig. 4).

Figure 8 shows the rate coefficients of the studied electron-impact reactions as functions of $\delta N_2$ at 120 Td. As can be seen, the dissociative excitation of CO$_2$ to the repulsive state CO$_2(a^3\pi)$ ($k_4$), and electronic excitations of N$_2$ ($k_5$, $k_6$, and $k_8$), were the fastest reactions. On the other hand, the dissociative attachment ($k_9$) and ionisation ($k_9$, $k_{10}$) were the slowest among these processes.

### 3.7 Ionisation and attachment coefficients

Despite the dissociative attachment and ionisation were the slowest reactions, they are very important for the development, properties and stability of electrical discharges. Therefore, it is necessary to know their values as functions of $E/N$ and $\delta N_2$. We found that the $\alpha$ and $\eta$ increased with $E/N$ for all $\delta N_2$ ranging from 0.05 to 1. The growth of $\alpha$ was exponential (Fig. 9), whereas the growth of $\eta$ was logarithmic (Fig. 10). For both $\alpha$ and $\eta$, the growth was steeper in the mixtures with higher concentration of CO$_2$. At the constant $E/N$, $\alpha$ and $\eta$ grew with the decreasing $\delta N_2$.

### 4 Conclusions

Motivated by the decomposition of CO$_2$ and the synthesis of amino acids in DC electrical discharges, we investigated the electron dynamics by Monte Carlo simulations in N$_2$/CO$_2$ gas mixtures. The results of the simulations
include electron mean energy, drift velocity, collision frequency of electrons with neutrals, mean free path of electrons, rate coefficients of selected electron-impact processes, and ionisation and attachment coefficients as functions of the reduced electric field strength and the composition of a gas mixture. The knowledge of these parameters is crucial for the understanding of plasma induced chemistry and behaviour of electrical discharges in such mixtures.

For $E/N$ below approximately 80 Td, the studied parameters were mostly non-linear functions of $N_2$ concentration ($\delta N_2$). Above 80 Td, these dependences were still often non-linear but they could be fitted by polynomials of up to the 3rd order. The fitting coefficients enabled the calculation of the studied parameters as functions of $E/N$ and $\delta N_2$ with high accuracy. The rate coefficients for electron-impact reactions with high $\varepsilon_{th}$, however, were fitted with high accuracy only for $E/N$ above 140 Td. It is due to the statistics, since these rate coefficients are calculated only from the ‘tail’ of the EEDF. The EEDFs and the derived parameters were mostly influenced by elastic collisions and vibrational excitations. The elastic collisions prevailed for $E/N$ below 40 Td in CO$_2$-dominant mixtures. For $E/N > 40$ Td, the influence of vibrational excitations of $N_2$ dominated. This influence was the strongest for $E/N$ from 40 to 60 Td, and it decreased with the increasing $E/N$ and with the decreasing concentration of $N_2$. The vibrational excitations also influenced the rate coefficients of electron-impact reactions, as they decreased with the increasing $\delta N_2$. However, the influence of the vibrational excitations on the rate coefficients weakened with the increasing $E/N$.

The applied computational method was proved useful for the calculation of steady-state EEDFs and derived parameters characterising electrons in homogeneous electric fields in various gaseous mixtures. However, we will warmly welcome any suggestions for its further development. Web-EEDF source code can be downloaded from http://enviro.fmph.uniba.sk/web-eedf.

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