Associative electron detachment in sprites

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Abstract

The balance of processes affecting electron density drives the dynamics of upper-atmospheric electrical events, such as sprites. We examine the detachment of electrons from negatively charged atomic oxygen (O⁻) via collisions with neutral molecular nitrogen (N₂) leading to the formation of nitrous oxide (N₂O). Past research posited that this process, even without significant vibrational excitation of N₂, strongly impacts the dynamics of sprites. We introduce updated rate coefficients derived from recent experimental measurements which suggest a negligible influence of this reaction on sprite dynamics. Given that previous rates were incompatible with the observed persistence times of luminous features in sprites, our findings support that these features result from electron depletion in sprite columns.
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Key Points:

\begin{itemize}
  \item Associative detachment of electrons in sprites proceeds almost exclusively from vibrationally excited \( N_2 \).
  \item We provide updated rate coefficients for electron associative detachment.
  \item In models with the updated rates, sprite glows persist tens of milliseconds, in agreement with observations.
\end{itemize}

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Abstract
The balance of processes affecting electron density drives the dynamics of upper-atmospheric electrical events, such as sprites. We examine the detachment of electrons from negatively charged atomic oxygen (O\(^-\)) via collisions with neutral molecular nitrogen (N\(_2\)) leading to the formation of nitrous oxide (N\(_2\)O). Past research posited that this process, even without significant vibrational excitation of N\(_2\), strongly impacts the dynamics of sprites. We introduce updated rate coefficients derived from recent experimental measurements which suggest a negligible influence of this reaction on sprite dynamics. Given that previous rates were incompatible with the observed persistence times of luminous features in sprites, our findings support that these features result from electron depletion in sprite columns.

Plain Language Summary
Sprites are transient, filamentary luminous structures appearing between approximately 50 and 85 kilometers above Earth’s surface. While the primary sprite activity is ephemeral, lasting mere thousandths of a second, certain luminous features persist up to a hundred times longer. The key to understanding these enduring structures lies in the evolution of free electron populations that facilitate electrical conductivity. Here we show that a process that influences this population is slower than previously thought. This may explain why luminous structures can persist for so long.

1 Introduction
Sprites are high-altitude filamentary discharges occurring in the upper mesosphere following a strong cloud-to-ground lightning discharge in a thunderstorm (Pasko et al., 1997; Luque & Ebert, 2009; Liu et al., 2015). One notable benefit arising from the discovery of sprites (Franz et al., 1990) has been a renewed interest in the chemistry of the upper mesosphere, in particular on the reaction mechanisms induced by free, super-thermal electrons as present in sprites, where they are accelerated by intense electric fields. Several questions motivate this interest: for example there is the question of whether sprites have global, regional, or local effects on the composition of the atmosphere (Sentman et al., 2008; Arnone et al., 2008; Gordillo-Vázquez & Pérez-Invernón, 2021; Malagón-Romero et al., 2023). Understanding the spectra of sprites (Gordillo-Vázquez et al., 2012; Passas et al., 2016) is another motivation, particularly relevant in the context of space-based detection of sprites (Chanrion et al., 2019) and discrimination from other events such as Blue Luminous Events (BLUEs) in thundercloud tops (Chanrion et al., 2017; Soler et al., 2020).

Finally, understanding the chemistry of electrons and ions in the upper mesosphere is crucial for elucidating the fundamental physics of sprites. Conversely, investigations into sprites have highlighted previously overlooked reactions. A notable example is the reaction of detachment of electrons from O\(^-\) to form N\(_2\)O, which is the focus of the present work:

\[
O^- + N_2 \rightarrow N_2O + e. \tag{1}
\]

Luque and Gordillo-Vázquez (2012) pointed out that this reaction may strongly affect the dynamics of sprite inception and dynamics. That study questioned the assumption that when the electric field is below a certain, fixed threshold determined by competition between electron impact ionization and electron attachment, free electrons are removed and cease to efficiently transport charge. Detachment reactions such as (1) reverse this attachment and return electrons to their free state. At the time, the most recent laboratory measurements of reaction (1) where those by Rayment and Moruzzi (1978), who argued that the reaction is effective even when nitrogen is in its vibrational ground state. Subsequent studies took for granted the rates of Rayment and Moruzzi (1978) in different contexts. Pancheshnyi (2013) considered how, among others, reaction (1) influences an effective ionization rate whereas da Silva and Pasko (2013) applied them to their investigation of the streamer-to-leader transition.

Other investigations, such as (Luque et al., 2016) indicated potential inaccuracies in the reaction rate coefficients of Rayment and Moruzzi (1978). That study explained the appearance in sprites of
beads and glows, which are luminous structures that persist for up to 100 milliseconds even after
the main streamer activity has subsided (Stenbaek-Nielsen & McHarg, 2008). The model presented
by Luque et al. (2016) matched the observations but only as long as detachment reactions such as
(1) were disregarded. This was later confirmed by Malagón-Romero et al. (2020), where a similar
mechanism was proposed as the origin of upward branches in sprites which, if not always,
emerge from pre-existing glows.

A further step was taken in a careful literature analysis by Janalizadeh and Pasko (2021), where,
besides identifying several issues in the data reporting by Rayment and Moruzzi (1978), they pointed
that under atmospheric conditions electron detachment from O\(^{−}\) is not possible in collisions with
nitrogen in its ground state.

The controversy motivated Shuman et al. (2023) to carry out new measurements of the reaction
rate of (1). The rate coefficients of O\(^{−}\) + N\(_{2}\) were measured using a flow tube apparatus under ther-
mal conditions from 800 K–1200 K; at lower temperatures the rate coefficients were smaller than the
limit of the experiment. The results were inconsistent with the literature determination by Rayment
and Moruzzi (1978), but supported the results of Janalizadeh and Pasko (2021) indicating that re-
action with vibrational ground state N\(_{2}\) was negligible. The results were modeled and vibrationally
resolved rate constants for \(v \leq 2\) derived with extrapolation over the thermal range 300 K – 1400 K.

The objective of this study is to investigate the implications of an enhanced understanding of
reaction (1) on the chemistry of sprites and related high-atmosphere electrical phenomena. We hope
that this work will garner interest of the geophysical community into the updated knowledge of
electron detachment in the atmosphere.

2 Updated reaction rate

As described in detail elsewhere, the O\(^{−}\) + N\(_{2}\) associative detachment reaction must overcome
two kinetic bottlenecks. First, a large energetic barrier separates the weakly bound entrance complex
O\(^{−}\)(N\(_{2}\)) from the metastable, but longer-lived, N\(_{2}\)O\(^{−}\) intermediate. Second, the system must cross
from the N\(_{2}\)O\(^{−}\) anion potential surface to the N\(_{2}\)O neutral potential surface. It happens that both
the height of the energetic barrier and the location of the lowest-energy crossing geometry are very
similar, about 0.3 eV above the energy of the separated reactants. A simple model considering only
the vibrational state of N\(_{2}\) and the relative kinetic energy of the reactants reproduced the measured
thermal rate constants. Increased vibrational energy increased the probability of overcoming the
transition state to N\(_{2}\)O\(^{−}\) (both from the inherently higher energy and from increased overlap with
the geometry of the transition state, which lies at a larger N-N bond distance). Increased kinetic
energy also increased the probability of overcoming the transition state, but decreased the probability
of crossing to the neutral surface, such that increasing kinetic energy initially increases the rate
coefficient but at larger values decreases the rate coefficient.

The vibrationally-resolved thermal rate constants reported previously are converted to a func-
tion of \(E/n\) here under the assumption that rotational energy and translational energy affect the
reaction similarly (Viggiano & Morris, 1996; Viggiano & Williams, 2001):

\[
\frac{E}{n} = \frac{v_d(T_{ei}, T_0)}{\kappa_0 n_0}, \tag{2}
\]

where \(E/n\) is the electric field strength divided by neutral gas density, \(\kappa_0\) is the reduced ion mobility,
\(n_0\) is Loschmidt’s number, and \(v_d(T_{ei}, T_0)\) is the drift velocity at temperature \(T_0\) equivalent to the
thermal velocity at temperature \(T_{ei}\) related by

\[
v_d(T_{ei}, T_0) = \left[\frac{3k(T_{ei} - T_0)}{m_{N_2}}\right]^{1/2}, \tag{3}
\]

where \(k\) is the Boltzmann constant and \(m_{N_2}\) is the nitrogen mass. Here \(T_0\) is taken to be 200 K and
\(T_{ei}\) are the temperatures reported previously. The values of \(\kappa_0\) are interpolated from the compilation
of Viehland and Mason (1995) up to \(E/n = 100\) Td and extrapolated from that data up to 120 Td.
Table 1 contains the resulting reaction rate coefficients for reaction (1).
The dependence of the reaction rate coefficients on the effective temperature is well approximated by a modified Arrhenius expression of the form

\[ k = k_0 \left( \frac{T_{\text{eff}}}{300 \, \text{K}} \right)^d \exp \left( - \frac{T_A}{T_{\text{eff}}} \right). \]  

(4)

The best-fit parameters \( k_0, T_A \) and \( d \) for \( v = 0, 1, 2 \) are listed in table 2. Figure 1 shows the rate coefficients as well as the values from expression (4). Also, as a reasonable approximation that foregoes the use of interpolating tables for the ion mobility, we also show the results of (4) with a constant reduced ion mobility \( k_0 = 4.5 \times 10^{-4} \, \text{m}^2\text{V}^{-1}\text{s}^{-1} \). By further neglecting \( T_0 \) in (3), we reach this simple expression for the reaction rate coefficient:

\[ k = k_0 \left( \frac{E/n}{43 \, \text{Td}} \right)^{2d} \exp \left( - \left( \frac{E_A/n}{E/n} \right)^2 \right). \]  

(5)

with the values of reduced electric fields \( E_A/n \) listed in the last column of table 2.

We also plot in figure 1 the reaction rate coefficients by Rayment and Moruzzi (1978) as approximated by Pancheshnyi (2013) (labelled as RM78). For most of the studied range of reduced electric field, the updated rate coefficients for the vibrational ground state of \( \text{N}_2 \) \((v = 0)\) are several orders of magnitude below those from Rayment and Moruzzi (1978). Close to the classical breakdown field \( (E/n \approx 120) \), the updated rate is still about five times lower than RM78.

3 Implications

We now discuss some of the implications of the new rates on the physics of upper-atmospheric electrical discharges. Table S1 in the supplemental material details a simple chemical scheme that accounts for the main processes within a halo or sprite discharge and up to about 100 ms after its initiation. The rate coefficients for electron-molecule processes, which depend on the electron energy distribution function, are modelled by solving the steady-state Boltzmann equation with the Bolsig+ solver (Hagelaar & Pitchford, 2005) and the Phelps’ cross-section database (Phelps & Pitchford, 1985; Lawton & Phelps, 1978) as provided by LxCat (Pancheshnyi et al., 2012; Pitchford et al., 2017; Carbone et al., 2021). With these rates we follow the vibrational distribution of the electronic ground state of nitrogen, which induce associative detachment from \( \text{O}^- \) with the rates discussed in the previous section. We also consider detachment from \( \text{O}_3^- \) and negative ion conversion as modelled by Pancheshnyi (2013). Finally, for the sake of completeness, we include positive ion conversion as modelled by Aleksandrov and Bazelyan (1999) and electron-ion and ion-ion recombination as modelled by Kossyi et al. (1992).

To compare with previous models, we also consider a reaction scheme where the rate of (1) follows Rayment and Moruzzi (1978) as fitted by Pancheshnyi (2013) and regardless of the vibrational state of \( \text{N}_2 \). We name the two models “new” and “RM78”.

First we look at the chemical evolution under constant reduced electric field. Figure 2 shows the evolution of the main negatively-charged species in the wake of a streamer that leaves an electron density \( n_e = 10^{13} \, \text{m}^{-3} \) at an altitude of 80 km. The left column of the figure (labelled (a)) corresponds to the reaction rates of (1) presented here, whereas the right column (b) contains the densities predicted by the rates by Rayment and Moruzzi (1978). In both cases we simulate constant applied reduced electric fields of 70 Td and 90 Td.

There are clear differences between the two columns. Enhanced detachment rates of \( \text{O}^- \) in the right column result in elevated electron and \( \text{O}^- \) densities. Specifically, at an electric field strength of 70 Td with the updated rate coefficients, the electron density exhibits a two-order-of-magnitude reduction prior to stabilization. In contrast, according to the rate coefficients of Rayment and Moruzzi (1978), the electron density experiences only a marginal decrease before entering a growth regime.

Next we investigate the consequences of the updated reaction rate coefficient in a self-consistent 2D axisymmetric model of a sprite discharge. In this model, the electron density \( (n_e) \) under a local
Figure 1. Rate coefficients of $O^- + N_2(v) \rightarrow N_2O + e$ for $v = 0, 1, 2$. On the left panel we show the dependence of the rate coefficients on temperature assuming equilibrium conditions. The dots correspond to the values in table 1 whereas lines show the fits using (4) with the parameters listed in table 2. The right panel shows the rate dependence on the reduced electric field, following the conversion of equations (2) and (3) with $T_0 = 200$ K. The solid lines use the same fits as in the left panel and the ion mobilities from Viehland and Mason (1995). The dashed lines replace these mobilities by a field-independent reduced ion mobility $\kappa_0 = 4.5 \times 10^{-4}$ m$^2$V$^{-1}$s$^{-1}$.
Table 1. Reaction rate coefficients for the reaction $O^- + N_2(e) \rightarrow N_2O + e$ for different values of an effective collision temperature $T_{\text{eff}}$ and reduced electric field $E/n$. $K_0$ is the mobility of $O^-$ ions for the given electric field, at atmospheric pressure and 300 K. For drift velocities below $10^3$ ms$^{-1}$ (reduced electric fields below $E/n \approx 85$ Td) we use ion mobilities interpolated from Viehland and Mason (1995) for higher reduced electric fields we extrapolate as $K_0 = 1 \times 10^{-5}$ m$^2$ V$^{-1}$ s$^{-1} \times \ln(v_0(T_{\text{eff}})/10^2$ ms$^{-1}) - 7 \times 10^{-4}$ m$^2$ V$^{-1}$ s$^{-1}$.

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<th>$T_{\text{eff}}$ (K)</th>
<th>$E/n$ (Td)</th>
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<th>$v=0$</th>
<th>$k$ (m$^3$ s$^{-1}$)</th>
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Table 2. Fitting parameters for the reaction rate coefficients for the reaction $O^- + N_2(e) \rightarrow N_2O + e$ with $v = 0, 1, 2$ according to expression 4.

<table>
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<th>$v$</th>
<th>$k_0$ (m$^3$ s$^{-1}$)</th>
<th>$T_A$ (K)</th>
<th>$d$</th>
<th>$E_A/n$ (Td)</th>
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<td>186</td>
<td>-1.10</td>
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Figure 2. Evolution of the dominant negatively-charged species in our chemical models under a constant reduced electric field. Starting with an initial condition of an electron density of $10^{11}$ m$^{-3}$, which is representative of the state of a sprite column in the wake of a streamer at 80 km.
electric field $E$, evolves according to the conservation equation:

$$
\partial_t n_e = \nabla \cdot (\mu_e E + D_e \nabla n_e) + C_e,
$$

(6)

where $\mu_e$ and $D_e$ are the electron mobility and the diffusion coefficient, and $C_e$ is the chemical source term accounting for the chemical reactions listed in Table S1 in the supplemental material. Transport coefficients ($\mu_e$ and $D_e$) are assumed to be functions of the local electric field and are computed with Bolsig+ (Hagelaar & Pitchford, 2005) using as above the cross sections for electron impact with $N_2$ and $O_2$ provided in Phelps’ database retrieved from LxCat.

Neutral species and ions ($n_i$ with $i = 0, 1, \ldots$) are considered motionless and their time evolution obeys a simplified version of equation (6), namely,

$$
\partial_t n_i = C_i,
$$

(7)

where $C_i$ is the chemical source term determined by the reactions in Table S1 in the supplemental material.

The electric field $E$, is calculated as $E = -\nabla \phi$, where $\phi$ is the electrostatic potential obtained upon the solution of Poisson’s equation

$$
\nabla^2 \phi = \sum_s \frac{q_s R_s}{\varepsilon_0},
$$

(8)

where the sum extends over all charged species $s$, $q_s$ is the charge of the species $s$ and $\varepsilon_0$ is the vacuum permittivity.

The model is implemented in Afivo-streamer (Teunissen & Ebert, 2017) and is based on Afivo (Teunissen & Ebert, 2018), an octree-based adaptive mesh refinement framework, with OpenMP capabilities and a geometric multigrid solver for Poisson’s equation. Equations (6) and (7) are solved with an explicit second order time stepping and a flux-limited second order accurate spatial discretization.

In this study, we initiate our model with the exact same conditions discussed by Malagón-Romero et al. (2020), that consist in a neutral column of radius $a_0 = 400$ m with a truncated funnel attached to its lower part that roughly approximates the multiple branching events the parent streamer discharge undergoes as it propagates. The initial electron density is then computed as

$$
n_e(r, z) = n_{e,0}(z) a_0^2 \frac{a(z)}{a_0^2} \max \left(0, 1 - \frac{r^2}{a(z)^2} \right) + n_{c, bg}(z),
$$

(9)

where $n_{e,0}(z) = C n_{air}(z)$ is the electron density at the axis, $C = 3.33 \times 10^{-11}$, $n_{air}$ is the air density obtained by scaling the ground air density $n_{air,0} = 2.5 \times 10^{25}$ m$^{-3}$ as $n_{air}(z) = n_{air,0} \exp(-z/7.2$ km), and $a(z)$ is a piece-wise linear function that models the radius of the channel and the funnel, ensuring a smooth transition. The funnel has a radius of 5 km at the base $z_b = 50$ km with the upper vertex at $z_a = 60$ km and is calculated as

$$
a(z) = \max \left(a_0, \frac{z_a - z}{z_a - z_b} \times 5 \text{ km} \right).
$$

(10)

Finally, the background electron density follows the Wait-Spies profile estimated by Hu et al. (2007):

$$
n_{c, bg}(z) = 10^{-2}$ cm$^{-3}$ exp$\left(-\frac{z - 60 \text{ km}}{2.86 \text{ km}}\right).
$$

(11)

The computational domain is a 10 km radius and 40 km height cylinder with its base at 40 km altitude. The minimum grid spacing in our simulation has been 1.22 m. We apply homogeneous Neumann boundary conditions at all boundaries to solve equations (6) and (7). Poisson’s equation has been solved with homogeneous Neumann boundary conditions at the axis and outer boundaries. The bottom boundary is grounded while the top boundary is set to a fixed voltage of 2.9 MV. The
result is a constant background field of 72.38 V/m pointing downwards, setting a reduced electric field $E/n_{air}$ of approximately 120 Td at roughly 77 km.

The results are displayed in figure 3 where we show simulated light emissions (N$_2$ 1P) from the sprite column. With the detachment rate coefficients of Rayment and Moruzzi (1978) (RM78) a more elevated conductivity inside the column contributes to a fast screening of the electric field and light emissions that decay within a few milliseconds. On the other hand, with the updated rates of detachment (new), the attachment instability discussed e.g. by Luque et al. (2016) leads to a sharply defined, light-emitting segment which is consistent with observations (Stenback-Nielsen & McHarg, 2008; Bór, 2013).

A closer look at the light-emitting segment in figure 4 shows that the luminosity decays faster than exponentially within 5 ms when using the RM78 detachment rate coefficients. This contrasts with the results for the new detachment rate coefficients (table 1). In this case, the luminosity exhibits an exponential decay, consistent with observations (Luque et al., 2016), with a decay constant of approximately 1.7 ms. The exponential trend becomes evident after 6 ms, whereas observations show it almost from the very beginning. This discrepancy is likely attributed to the neutral charge conditions used to initiate the simulations.
Figure 4. Emissions from the first positive system of N$_2$ integrated in 400 m-radius and 1 km-tall cylinders centered at 71 km, 73 km and 75 km altitudes, considering the detachment rate coefficient from Rayment and Moruzzi (1978) (RM78) and the updated detachment rate coefficients from table 1 (new), showing faster than exponential and exponential decay respectively.
4 Conclusions

In this work we provide updated rate coefficients for the reaction of associative electron detachment and discuss its implications for the dynamics of sprites. For the vibrational ground state of N\textsubscript{2}, these rate are significantly smaller than previous estimates. We conclude that, given the low population of vibrationally excited N\textsubscript{2}, this reaction is too slow to play a significant role in sprites.

Future investigations of electrical phenomena in the upper atmosphere should consider the new understanding of electron associative detachment presented here. For relatively short timescales such as those of sprites the reaction process can be disregarded. The possibility that it is relevant for timescales beyond the tens of milliseconds deserves to be studied in the future.

Open Research Section

The code containing the simple sprite chemical model used to generate figure 2 is available in the repository https://github.com/aluque/spritechem (hash aceaced...). The output and source files for the generation of the results presented in figures 3 and 4 are openly available at https://doi.org/10.5281/zenodo.10219918.

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Supporting Information for “Associative electron detachment in sprites”
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1. Table S1: Chemical scheme.
Table S1. List of reaction and rate coefficients in our chemical model. In the rate coefficient expressions temperatures are expressed in K, reduced electric fields are expressed in Td and rate coefficients are expressed in m$^3$s$^{-1}$ for binary reactions and m$^6$s$^{-1}$ for ternary reactions. $T_{\text{eff}}$ is an effective temperature computed from the local electric field and gas temperature (200 K) as explained in the main text. The rate coefficients labelled as “Bolsig+” are electric-field-dependent rates obtained from the solution of the Boltzmann equation with the Bolsig+ solver using Phelp’s cross-section database.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate ((m^{3(n-1)}s^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(e + N_2 \rightarrow 2e + N_2^+) Bolsig+</td>
<td>(Lawton &amp; Phelps, 1978; Phelps &amp; Pitchford, 1985; Hagelaar &amp; Pitchford, 2005)</td>
</tr>
<tr>
<td>2</td>
<td>(e + O_2 \rightarrow 2e + O_2^+) Bolsig+</td>
<td>(Lawton &amp; Phelps, 1978; Phelps &amp; Pitchford, 1985; Hagelaar &amp; Pitchford, 2005)</td>
</tr>
<tr>
<td>3</td>
<td>(e + O_2 + O_2 \rightarrow O_2^- + O_2) Bolsig+</td>
<td>(Lawton &amp; Phelps, 1978; Phelps &amp; Pitchford, 1985; Hagelaar &amp; Pitchford, 2005)</td>
</tr>
<tr>
<td>4</td>
<td>(e + O_2 \rightarrow O + O^-) Bolsig+</td>
<td>(Lawton &amp; Phelps, 1978; Phelps &amp; Pitchford, 1985; Hagelaar &amp; Pitchford, 2005)</td>
</tr>
<tr>
<td>5</td>
<td>(M + O_2^- \rightarrow e + O_2 + M) (k_0e^{-\left(\frac{E_a}{kT}\right)^2}) (k_0 = 1.24 \times 10^{-17}, a = 179, b = 8.8)</td>
<td>(Pancheshnyi, 2013)</td>
</tr>
<tr>
<td>6</td>
<td>(O_2 + O^- \rightarrow O_2^- + O) (k_0e^{-\left(\frac{E_a}{kT}\right)^2}) (k_0 = 6.96 \times 10^{-17}, a = 198, b = 5.6)</td>
<td>(Pancheshnyi, 2013)</td>
</tr>
<tr>
<td>7</td>
<td>(N_2 + O^- \rightarrow e + N_2O) (4 \times 10^{-17} \times (T_{e\text{ff}}/300)^{-1.36} \exp(-5097/T_{e\text{ff}}))</td>
<td>(Shuman et al., 2023)</td>
</tr>
<tr>
<td>8</td>
<td>(N_2(v_1) + O^- \rightarrow e + N_2O) (9 \times 10^{-18} \times (T_{e\text{ff}}/300)^{-0.85} \exp(-674/T_{e\text{ff}}))</td>
<td>(Shuman et al., 2023)</td>
</tr>
<tr>
<td>9</td>
<td>(N_2(v_2) + O^- \rightarrow e + N_2O) (2.7 \times 10^{-17} \times (T_{e\text{ff}}/300)^{-1.10} \exp(-186/T_{e\text{ff}}))</td>
<td>(Shuman et al., 2023)</td>
</tr>
<tr>
<td>10</td>
<td>(O_2 + O^- + M \rightarrow O_3^- + M) (k_0e^{-\left(\frac{E_a}{a}\right)^2}) (k_0 = 1.1 \times 10^{-42}, a = 65)</td>
<td>(Pancheshnyi, 2013)</td>
</tr>
</tbody>
</table>
11 e + N₂ \rightarrow e + N₂(v₁) \quad \text{Bolsig+} \quad (\text{Lawton & Phelps, 1978; Phelps & Pitchford, 1985; Hagelaar & Pitchford, 2005})

12 e + N₂ \rightarrow e + N₂(v₂) \quad \text{Bolsig+} \quad (\text{Lawton & Phelps, 1978; Phelps & Pitchford, 1985; Hagelaar & Pitchford, 2005})

13 e + N₂ \rightarrow e + N₂(v₁) \quad \text{Bolsig+} \quad (\text{Lawton & Phelps, 1978; Phelps & Pitchford, 1985; Hagelaar & Pitchford, 2005})

14 N₂⁺ + N₂ + M \rightarrow N₄⁺ + M \quad 5 \times 10^{-41} \times (300/T)^3 \quad (\text{Aleksandrov & Bazelyan, 1999})

15 N₄⁺ + O₂ \rightarrow 2N₂ + O₂⁺ \quad 2.5 \times 10^{-16} \times (300/T)^3 \quad (\text{Aleksandrov & Bazelyan, 1999})

16 O₂⁺ + O₂ + M \rightarrow O₄⁺ + M \quad 2.4 \times 10^{-42} \times (300/T)^3 \quad (\text{Aleksandrov & Bazelyan, 1999})

17 e + O₄⁺ \rightarrow O₂ + O₂ \quad \text{Bolsig+} \quad (\text{Kossyi et al., 1992})

18 A⁺ + B⁻ \rightarrow 1 \times 10^{-13} \quad (\text{Kossyi et al., 1992})
References


