Measurement and modeling of electron and anion kinetics in N2O discharges

Andreas Hösl, Juriy Pachin, Eda Egüz, Alise Chachereau, Christian M. Franck

ETH Zürich, Power Systems and High Voltage Laboratories, Physikstr. 3, 8092 Zurich, Switzerland
E-mail: cfranck@ethz.ch

Abstract. From Pulsed Townsend measurements in nitrous oxide (N2O) we obtain swarm parameters for various electron and in particular anion processes. We discuss various assumptions on the discharge model in literature, and motivate a suitable model. Our findings agree with modern sources on the electron swarm parameters. Contrary to many sources however we find evidence for electron detachment from O− with a coefficient of \( \approx 3.2 \times 10^{-20} \text{m}^2 \), and we suggest further changes to the commonly accepted discharge model. Based on the obtained swarm parameters, an electric strength dependent on pressure is estimated and compared to breakdown measurements.

1. Introduction

Nitrous oxide is a gaseous compound with various chemical, medical and physical applications. It is an important greenhouse gas and contributes significantly to climate change (global warming potential of 265 on 100 year horizon [1]), since it is emitted in large quantities from fertilized soil. \( \text{N}_2\text{O} \) has been considered as electrical insulation gas in high-voltage equipment, either pure or in mixtures, which is the main focus of this publication. The gas is a highly interesting candidate in the search for a replacement of \( \text{SF}_6 \) which is commonly used in high-voltage energy-transmission equipment, and has a global warming potential of 23,500 [1]. \( \text{N}_2\text{O} \) has a very low boiling point of \(-88.5^\circ\text{C}\) and would allow application at higher pressures than \( \text{SF}_6 \). It is further non-flammable and non-toxic. As an important characteristic of gases intended for gaseous electric insulation, the molecule readily captures electrons and dissociates to \( \text{O}^- \) and \( \text{N}_2 \) already at low electron energies with resonances at 0.55 and 2.4 eV [2, 3]. Despite its importance in various fields, the plasma discharge and electric insulation properties of \( \text{N}_2\text{O} \) are not yet fully understood. The reason for this is certainly the exceptionally complicated anion kinetics in \( \text{N}_2\text{O} \) discharges.

Swarm parameters of \( \text{N}_2\text{O} \) have been thoroughly investigated for almost a century, and are for the most part contradictory. The main path of the anion kinetics has been identified, but there is disagreement about the relevance of various processes. Estimated and calculated magnitudes of anion processes differ by several orders of magnitude, and measurements are sparse or lacking.

In the present work, we use a Pulsed Townsend experiment over a wide pressure range, from a few hundred pascal up to several tens of kilopascal, to investigate the ion kinetics of \( \text{N}_2\text{O} \) with the aim of estimating its electric strength. Having measured discharges at various pressures, electrode spacings and electric fields, we fit simulated currents with the measured current waveforms.

The structure of this publication is as follows: In section 2, the experiment and the data analysis are shortly presented. Subsequently in section 3 we present a thorough literature review of \( \text{N}_2\text{O} \), with focus on the discharge model. Since various assumptions in literature regarding the kinetics were later rejected and revised, and certain conclusions were taken based on false premises, it is helpful to do this in (mostly) chronological form, yet sorted by reacting species (electrons, \( \text{O}^- \), \( \text{NO}^- \)) where applicable.

We compare this to some experimental observations which are relevant for the kinetic model of \( \text{N}_2\text{O} \) in section 4. Then, in section 5, we motivate and discuss our choice of kinetic model.

We then present our results in section 6 and compare them to literature where available. In a next step, we estimate the breakdown strength of \( \text{N}_2\text{O} \) and compare to breakdown voltage measurements.

2. Methods

2.1. Pulsed Townsend experiment

We study electrical discharges in \( \text{N}_2\text{O} \) using the Pulsed Townsend experiment described in a previous publication [4], which is able to operate at relatively high pressure (up to 100 kPa) and correspondingly high voltages (up to 50 kV). Electrons are released from a photocathode with a pulsed UV laser (1.5 ns duration) and travel in a homogeneous field between two Rogowski-shape electrodes. The total displacement...
current of electrons and ions is recorded. We took multiple measurements at various fixed $E/N$ for different electrode spacing and different pressures, from 0.3 kPa up to 30 kPa.

The $\text{N}_2\text{O}$ was obtained from Carbagas, with a stated gas purity of 99.998%. The base pressure of the experimental vessel is $10^{-5}$ Pa. Due to leakage of the pipes, we estimate a maximum impurity in the order of 1 Pa. The gas was filled to maximum measurement pressure, and the pressure was then reduced in several steps for subsequent measurements.

2.2. Measurement analysis

The one-dimensional equations of motion for charged particles (electrons and ions) are given as

$$\frac{\partial}{\partial t} \vec{p}(x,t) + \frac{\partial}{\partial x}(\vec{w}_i \rho_i)(x,t) = M \vec{\rho}(x,t)$$

with $\vec{p}(x,t) = (\rho_e(x,t), \rho_{\text{N}_2\text{O}^+}(x,t), \rho_{\text{O}^-}(x,t), \ldots)$, and $\vec{w}_i$ the drift velocities of the respective species. The entries of matrix $M$ are the rates of conversion of electrons and anions, as defined by the chosen kinetic model. From there, the total current is given as

$$I(t) = \sum_i I_i(t) = q_0 \sum_i \frac{w_i}{d} \int_{x=0}^{d} \rho_i(x,t) \, dx, \quad (1)$$

where $q_0$ is the elementary charge, and $d$ the electrode spacing. In a next step, an optimization algorithm tries to find values for the rate coefficients which give an overlap between the simulated and the measured currents. The method was presented in a previous publication [5], where we applied it to dry air, and further developed when we extended our study to other $\text{N}_2/\text{O}_2$ mixtures [6].

2.3. Gas mixtures

Besides pure $\text{N}_2\text{O}$, we study also mixtures of 99.4% $\text{N}_2\text{O}$ with 0.6% $\text{H}_2$, and 98% $\text{N}_2\text{O}$ with 1% $\text{O}_2$ and 1% $\text{CO}_2$ for validating our kinetic model. This technique has been proposed and applied by various authors [7, 8]. Hydrogen will introduce a very efficient electron detachment process via

$$\text{O}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + e, \quad (2)$$

while oxygen very efficiently captures the electron from $\text{NO}^-$ via

$$\text{NO}^- + \text{O}_2 \rightarrow \text{NO} + \text{O}_2^- \quad (3)$$

$\text{CO}_2$ will then cluster with $\text{O}_2^-$ to prevent electron detachment from $\text{O}_2^-$. This enables us to specifically target certain anions and processes.

Figure 1: Kinetic model for $\text{N}_2\text{O}$ discharges, consisting of collisional processes with a rate depending linearly (single arrows) on pressure, or quadratically (double arrows) in the case of three-body processes. Bold arrows denote processes with high rate coefficients.

3. Literature review

3.1. $\text{O}^-$ system

3.1.1. Early findings

Bailey and Rudd [9], 1932, observed several unidentified anions in $\text{N}_2\text{O}$ discharges when applying a sufficiently strong electric field, and measured Townsend coefficient and mobility of electrons. Bradbury and Tatel [10], 1934, proposed dissociative attachment under formation of $\text{O}^-$ above 6 Td.

$$e + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}^- \quad (4)$$

They also found that $\text{N}_2\text{O}$ itself has no electron affinity. Nielsen and Bradbury [11], 1934, investigated anion mobilities in electronegative gases. They found a non-constant (evolving in time) mobility of the unidentified anion in $\text{N}_2\text{O}$, which they attributed to the conversion of $\text{O}^-$ in $\text{NO}^-$:

$$\text{O}^- + \text{N}_2\text{O} \rightarrow \text{NO} + \text{NO}^- \quad (5)$$

They were, two our knowledge, the first to propose this reaction.

3.1.2. Dissociative electron attachment to $\text{O}^-$

Burtt and Henis [12], 1964, measured resonances of the dissociative attachment cross section at 0.6 and 2.2 eV for the formation of $\text{O}^-$, equation (4).

One year later, Rapp and Briglia [2] measured besides $\text{N}_2\text{O}$ also various other gases. Their results peak at 2.2 eV, with an onset at 0.4 eV.
3.1.3. Conversion of $O^-$ in NO$^-$

The conversion of $O^-$ to NO$^-$, equation (5), was confirmed in 1959 when Rudolph, Melton and Bagon [15] used an isotope labeling technique and showed that an ion-molecule reaction leads to the formation of NO$^-$.

In 1964, Gorden and Ausloos [16] dissociated isotopic-labeled$N_2O$ with gamma-rays. They considered the reaction $\text{NO}^- + N_2O \rightarrow \text{NO} + N_2 + O^-$ which is opposite to reaction (5). However, the validity of the latter process was later disputed by Chantry [14].

In 1975, Lindering, Albritton, Fehsenfeld and Ferguson [17] measured the reaction of $O^-$ with various neutral molecules including $N_2O$. They obtained charge transfer rates to NO$^-$, reaction (5), in function of $O^-$ energy.

3.1.4. Three-body electron attachment to $N_2O^-$?

Phelps and Vorshall [18] considered three-body electron attachment to $N_2O$ for near-thermal electrons below 2 Td at a very low rate of $6 \cdot 10^{-45} \text{m}^6\text{s}^{-1}$

$$e + 2N_2O \rightarrow N_2O^- + N_2O.$$ (6)

However, Ferguson, Fehsenfeld and Schmeltekopf [19] argued that direct formation of $N_2O^-$ is implausible: the configuration of $N_2O^-$ is strongly bent, while $N_2O$ is a linear molecule. Therefore, the necessary strong change in the molecular structure suppresses the reaction.

Bardsley [20], 1969, agreed that only the bent configuration of $N_2O^-$ is an electronegative anion, and therefore judges direct three-body attachment to $N_2O^-$ as unlikely.

On the other hand, Chaney and Christophorou [21] claimed, for a mixture of $N_2$ with traces of $N_2O$, a three-body attachment reaction resulting in the formation of $N_2O^-$ that is strongly increasing with the electron energy, and reaching low values of $6 \cdot 10^{-13} \text{m}^6\text{s}^{-1}$ for a mean electron energy of 0.8 eV ($E/N \approx 20 \text{Td}$).

On the other hand, $N_2O^-$ was never observed in measurements at moderate pressures [8, 22].

3.1.5. Electron detachment from $O^-$?

Chaney and Christophorou [21] hinted at the possibility of an electron detachment process involving $O^-$ and $N_2O$ in order to explain observed pressure dependencies in their data. They suggested the reaction

$$O^- + N_2O \rightarrow N_2O_2 + e.$$ (7)

Similarly, Parkes [8] proposed the reaction

$$O^- + N_2O \rightarrow 2NO + e.$$ (8)

to explain discrepancies between experiments.

However, Lindering, Albritton, Fehsenfeld and Ferguson [17], who studied the reaction of $O^-$ with $N_2O$, considered $O^-$ detachment upon collision with $N_2O$ as unlikely or low.

Barlow and Bierbaum [23], 1990, used nitrogen and oxygen isotope labeling in order to study the reaction of $O^-$ with $N_2O$. Likewise, they concluded that the formation of NO$^-$ and NO, equation (5), is the only reaction that occurs. They see no evidence for electron detachment from $O^-$, citing the reaction

$$O^- + N_2O \rightarrow N_2 + O_2 + e.$$ (9)

Our own findings will show strong indication for the occurrence of $O^-$ detachment.

3.1.6. Formation of $O_2^-$

In 1964, Gorden and Ausloos [16] considered formation of $O_2^-$ via

$$O^- + N_2O \rightarrow O_2^- + N_2,$$ (10)

and the same year Burtt and Henis [12] observed, besides $O^-$ and NO$^-$ also $O_2^-$ and $NO_2^-$ in a study where electrons of defined energy above 2 eV were fired onto $N_2O$. Like Gorden and Ausloos, they propose that $O_2^-$ is formed via reaction (10).

Reaction (10) was confirmed in 1970 by Paulson [24], who showed that an $O^-$ energy of at least 2.5 eV is required.

In 1999, Date, Radouane, Despax, Yousfi, Caquineau and Heniad [25] conducted experiments with $N_2O$ in a radio-frequency discharge reactor, and derived cross sections for the reactions of $O^-$ and NO$^-$ with $N_2O$. In agreement with Paulson [24], their cross section for reaction (10) has an energetic barrier of a few eV.

It may seem like a contradiction to these findings at first, but in $N_2O$ discharges at a field strength below 200 Td the formation of $O_2^-$ does presumably not occur. The reason is the energetic barrier, which is unusual for an exothermic process [24]. Mean energies of $O^-$ at 100 Td was calculated to 0.21 eV [26], far below this threshold.
3.2. NO$^-$ system

3.2.1. Electron detachment from NO$^-$

Parkes and Sugden [27], 1972, determined the electron affinity of NO as 0.026 eV. This extremely low value suggests fast electron detachment from NO$^-$,

$$\text{NO}^- + \text{N}_2\text{O} \rightarrow \text{NO} + \text{N}_2\text{O} + e^- \quad (11)$$

and could even allow auto-detachment at thermal conditions.

McFarland, Dunkin, Fehsenfeld, Schmeltekopf and Ferguson [28], 1972, measured the detachment rate of NO$^-$. Letting NO$^-$ collide with various gases, they obtained values at different temperatures.

Warman, Fessenden and Bakale [14], 1972, also proposed strong electron detachment of NO$^-$. They investigated dissociative electron attachment to N$_2$O, in the absence of electric field and with controllable temperature. They studied pure N$_2$O, as well as mixtures of N$_2$O with N$_2$ and H$_2$. The mixtures served as a verification, because they enabled efficient electron detachment from O$^-$. They found a strong increase in the dissociative attachment with increasing temperature in accordance with Chantry [13]. Viggiano, Morris and Paulson [29] studied reactions of NO$^-$ with various gases and measured the corresponding reaction rate coefficients.

3.2.2. Formation of NO$_2^-$ and/or N$_2$O$^-$?

Besides reactions (5) and (10), Burtt and Henis [12], 1964, also proposed the formation of NO$_2^-$ via O$^- +$ N$_2$O$^- +$ N. This reaction was picked up again in a more recent publication [30], yet disputed by several earlier sources. Paulson, 1970, found no evidence for this process [24] and claims a low upper bound for the cross section. Also, our own measurements suggest that this process does not occur or only at low efficiency.

Rather, Moruzzi and Dakin [22] and Parkes and Sugden [8, 27] established (at moderate to high pressures) that the process for the formation of NO$_2^-$ is

$$\text{NO}^- + \text{N}_2\text{O} \rightarrow \text{NO}_2^- + \text{N}_2. \quad (12)$$

Smit and Fields [31], 1977, used negative ion mass spectroscopy to investigate N$_2$O in mixture with H$_2$ and CH$_4$. At their measurement pressure of 500 Pa, NO$_2^-$ is the most intense observed anion. They further observed NO$^-$, O$^-$, O$_2^-$, and N$_2$O$_2^-$. Besides evidence for NO$_2^-$, several measurements at lower pressures rather suggested a different anion. Chantry [32], 1969, having observed N$_2$O$^-$, proposed the reaction

$$\text{NO}^- + \text{N}_2\text{O} \rightarrow \text{N}_2\text{O}^- + \text{NO} \quad (13)$$

at pressures below 1 Pa, and found minimal occurrence of N$_2$O$_2^-$ and no N$_3$O$_2^-$. He disputed process (12), and claimed an upper bound for of $1 \cdot 10^{-20}$ m$^3$s$^{-1}$ for the rate coefficient (however, most references lie not much higher). He argued that traces of NO$_2$ impurities, commonly found in N$_2$O gas, would lead to spurious observation of NO$_2^-$ for experiments measuring at higher pressures.

Paulson [24], 1970, measured reactions of O$^-$ and NO$^-$ with N$_2$O at low pressures in dependence of the anion energy. He confirmed process (13), and dismissed process (12).

Knapp, Echt, Kreisle, Mërck and Recknagel [33], 1986, studied the formation of N$_2$O$^-$ via reaction (13) under the specific conditions of a cluster beam of N$_2$O. They predicted that N$_2$O$^-$ dissociates rapidly if excitation energies above 0.4 eV are available, which may be an explanation for the missing N$_2$O$^-$ anion in higher pressure measurements.

Morris, Viuggiano and Paulson [34], 1990, settled the decades-long discussion regarding N$_2$O$^-$ and NO$_2^-$, with a measurement using isotope labeling at very low temperatures: both (12) and (13) are found to occur, with roughly equal and low rates (upper bound at room temperature $4 \cdot 10^{-20}$ m$^3$s$^{-1}$).

3.3. Three-body formation of N$_2$O$_2^-$ and N$_3$O$_2^-$

Apart from two-body reactions at low pressures, pressure-dependent three-body reactions in both the O$^-$ and NO$^-$ system are important and even dominant for the modeling of discharges at elevated pressures.

In 1968, Moruzzi and Dakin [22] observed the anions NO$^-$, N$_2$O$^-$, NO$_2^-$ and N$_3$O$_2^-$ in a beam experiment in N$_2$O, at pressures up to 1 kPa and up to 30 Td. While O$_2^-$ was initially present, the signal vanished after removing air impurities from N$_2$O. They were the first to propose the formation of the clustered anions N$_2$O$_2^-$ and N$_3$O$_2^-$ (more accurately O$^-$(N$_2$O) and NO$^-$·(N$_2$O)), and accordingly the three-body reactions:

$$\text{O}^- + 2\text{N}_2\text{O} \rightarrow \text{N}_2\text{O}_2^- + \text{N}_2\text{O}, \quad (14)$$

$$\text{NO}^- + 2\text{N}_2\text{O} \rightarrow \text{N}_3\text{O}_2^- + \text{N}_2\text{O}. \quad (15)$$

The tiny electron affinity of NO$^-$ was only later discovered, and they did not consider electron detachment in their evaluation.

In measurements up to 100 Td in a drift tube experiment, Parkes [8], 1972, confirmed the identities of the anions proposed by Moruzzi and Dakin, and likewise dismissed the possibility of an N$_2$O$^-$ anion of substantial lifetime. He extended the model of Moruzzi and
In 1975, Dutton, Harris and Hughes [35] used a high-pressure steady-state Townsend experiment. They assumed that neither the formation of NO$_2^-$ nor N$_2$O$^-$ from NO$^-$, equations (12) and (13), are important at their elevated pressures above 6 kPa. The same model was also later used by Aleksandrov and Konchakov [36].

3.3.1. N$_2$O$_2^-$

Posey and Johnson [37], 1988, studied three different anionic species of N$_2$O$_2^-$ in N$_2$O. Foremost the anion termed O$^-$·N$_2$O is formed, with a large electron affinity of 2.3 eV. Agreeing with early work of Moruzzi and Dakin, they found a meta-stable intermediate for reaction (14).

In several studies combining photospectroscopy and quantum mechanical calculations, the N$_2$O$_2^-$ anion was analyzed and the energy levels of different isomers and dissociation products were determined [38–40].

3.3.2. N$_3$O$_2^-$

Coe et al. [41] studied photoelectron spectroscopy of N$_3$O$_2^-$ and N$_2$O$_3^-$.$^-$ They found that N$_3$O$_2^-$ dissociates into NO$^-$ and N$_2$O with a low dissociation threshold of only 0.26 eV

$$N_3O_2^- + N_2O \rightarrow NO^- + 2N_2O.$$ (16)

Hiraoka, Fujimaki and Aruga [42], 1994, studied and measured gas-phase clustering in N$_2$O. They considered triplet and singlet molecular clusters N$_3$O$_2^-$, and calculated a very weak bound for the triplet with a dissociation energy of just 0.22 eV, in agreement with Coe et al., and 2.2 eV for the singlet. Torchia, Sullivan and Sunderlin [43] studied N$_3$O$_2^-$ in an afterglow experiment, and derived a lower dissociation energy of 0.76 eV. They assumed that other workers may have studied different isomers, and therefore derived different values.

There is further works on N$_3$O$_2^-$, which is an anion of high theoretical interest. The publication of Alijah and Kryachko [44] elaborates on the puzzles still surrounding this cluster molecule, which seems to allow for at least four different isomers.

3.3.3. N$_4$O$_2^-$

Coe et al. [45] studied yet another cluster anion, N$_2$O·N$_2$O$^-$, which would also form in a three-body process. They discuss electron affinities of 0.4 eV for the cluster, and 0.2 eV for N$_2$O$^-$. The latter value agrees with calculations of Hopper et al. [46].

3.3.4. Later works

Yoshida, Sasaki, Ohuchi and Hasegawa [47], 1999, measured the ionization and dissociative attachment rate coefficients of pure N$_2$O over a large E/N range. Yousfi, Henmad and Benhenni [26] calculated cross sections, mean energies and mobilities for anions in N$_2$O. Also, mean energies of O$^-$ and NO$^-$ are estimated, which we use to convert units of several sources.

Dupljanin et al. [48] compiled a cross section set for N$_2$O, based on Pulsed Townsend measurements.

3.4. Electric strength and breakdown measurements

Raju and Hackam [49] reviewed breakdown and swarm measurements in N$_2$O, and considered N$_2$O in admixture with SF$_6$ as electrical insulation gas. They discussed the weakening effect of electron detachment on the electrical insulation performance of N$_2$O.

Biasiutti [50] found an increase in the electric strength of N$_2$O from 0.1 – 2 bar pressure, while Akbar and Malik [51], 1985, measured the breakdown of N$_2$O up to high pressures of 1 MPa. They found that at high pressures, the electric strength of N$_2$O is constant at 178 Td.

4. Observations

It is revealing to discuss two waveform measurements at different pressures, before sorting through the various processes.

Figure 2 shows the measured current in N$_2$O at E/N = 139.8 Td, for an electrode spacing of 27 mm, and at a pressure of 462 Pa. The same current is shown on two different timescales in the upper and lower plots.

4.1. First electron detachment feature

In the upper plot, the current is largely dominated by the electrons, and it can be seen that the typical drop in current due to the absorption of electrons at the anode at the electron crossing time $T_e = 175$ ns is “smeared out”. This suggests that there is fast electron detachment from an anion between 170 and 350 ns. The lifetime $\tau$ of this anion could be in the order of 100 ns. Thus, a very high detachment rate coefficient of roughly $k_d \approx 1/(\tau N) \approx 1.10^{-16}$ m$^3$s$^{-1}$ would explain the observed current shape.

4.2. Second electron detachment feature

A second feature appears later at 0.5 $\mu$s in the lower plot, where a small current maximum is measured.
Figure 2: Measured and fitted currents in N$_2$O at $E/N = 139.8$ Td, for an electrode spacing of 27 mm, and at a pressure of 462 Pa.

Figure 3: Measured and fitted currents in N$_2$O at $E/N = 140$ Td, for an electrode spacing of 21 mm, and at a pressure of 15430 Pa. The vertical lines indicate the crossing times of the respective ion species. The dashed line indicates the current if no back-conversion from N$_3$O$_2^-$, (16), occurred.
This detachment signature indicates a conversion process of few 100 ns duration, followed by anion detachment in the order of $10^{-17} \text{m}^3\text{s}^{-1}$.

Both detachment rate coefficients are very high, indicating weak anions. The magnitude of the "detachment current" is very strong for a measurement at this low pressure, and can hardly stem from any impurities. Both features appear as well in measurements at low $E/N$ (down to 19 Td) with very similar shape, indicating that these detachment processes are exothermic (or only very weakly endothermic).

Figure 3 shows the measured current in N$_2$O at $E/N = 140$ Td, for an electrode spacing of 21 mm, and at a comparably high pressure of 15430 Pa. In the upper plot, the electron-dominated initial current is fully obscured. This is due to the fact that at this high pressure electron attachment is very strong, and the current is so steeply decreasing that we are unable to capture it with our limited bandwidth. The peculiar current maximum around 1500 ns bears some resemblance with the maximum of the low pressure example of figure 2.

4.3. Third electron detachment feature

Furthermore, there appears to be yet another, slower electron detachment process taking effect in the very late ion current (lower plot). This feature can be explained by a very slow release of electrons in the order of $1 \cdot 10^{-20} \text{m}^3\text{s}^{-1}$, three to four orders of magnitude lower than the other two detachment processes. We observed similar signals in other gases with slowly detaching anions, as for instance in oxygen [6] or C$_4$F$_7$N [52]. Although it may look like it, but the current shape cannot be reproduced by assuming lower ion mobilities (which would also be in conflict with measurements at lower pressures, where the mobilities fit well).

5. Kinetic model

For the most part, we adopted the high-pressure model set up by Moruzzi and Dakin, and extended by Parkes, but we made some modifications based on other literature and our own experimental findings. The resulting model is shown in figure 1. The reasons that led us to this model are discussed in the following.

5.1. Ruling out O$_2^-$ formation

We think that the conclusion of Moruzzi and Dakin concerning the formation of O$_2^-$ are well founded: It is likely that observations of O$_2^-$ in pure N$_2$O in a few publications stem from oxygen impurities. Typical stated purities of N$_2$O decades ago contained as much as few percent of air, and the charge transfer

$$\text{NO}^- + \text{O}_2 \rightarrow \text{NO} + \text{O}_2^-$$

(17)

is known to be extremely efficient, with a rate coefficient of $5 \cdot 10^{-18} \text{m}^3\text{s}^{-1}$ [28]. O$_2^-$ was also found to form via reaction (10) in drift-tube experiments, requiring however O$^-$ energies of a few electronvolts. For slower O$^-$, the reaction does not occur and therefore it is not necessary to consider it in discharges at our conditions. Typical mean energies of O$^-$ are much lower than Yousfi et al. showed, who calculated 0.21 eV at 100 Td [26].

5.2. Ruling out reaction NO$_2^-$ formation from O$^-$

The hypothesis of Burtt and Henis [12] that NO$_2^-$ is directly formed from O$^-$, despite being refuted by Paulson [24] and others, was picked up again in some more recent publications with large rates. To test the relevance of this reaction, we try to add it to the model. Within the bounds from $10^{-21} - 10^{-17} \text{m}^3\text{s}^{-1}$, we obtained structureless values with a median value of $1 \cdot 10^{-19} \text{m}^3\text{s}^{-1}$ and mean of $4 \cdot 10^{-19} \text{m}^3\text{s}^{-1}$. Compared to the large conversion rate coefficient to NO$^-$, it appears this process is not necessary to explain the measured current.

We do consider however, the formation of NO$_2^-$ from NO$^-$ via reaction (12).

5.3. N$_2$O$^-$ formation

There are solid arguments against three-body attachment to N$_2$O$^-$. In addition, even if it would occur at a rate in the order of $6 \cdot 10^{-43} \text{m}^6\text{s}^{-1}$ claimed by Chaney and Christophorou, the process is by far exceeded by dissociative attachment to O$^-$, even at our highest measurement pressures of 30 kPa. Therefore, we do not consider N$_2$O$^-$ formation via reaction (6). However, N$_2$O$^-$ formation by charge transfer from NO$^-$ to N$_2$O$^-$ via reaction (13) presumably takes place.

5.4. Electron detachment

Our measurements show evidence for three distinct electron detachment processes, acting on different timescales. The only anion in N$_2$O for which electron detachment is commonly accepted is NO$^-$, with reaction (11). Therefore, we have to consider which of the other anions formed in N$_2$O discharges are likely to detach. For the fast electron detachment features one and two our considerations are:

- We observe two of these detachment processes at relatively low pressure, namely 462 Pa. At this pressure, N$_2$O$_2^-$ and N$_3$O$_2^-$ are not formed in
large numbers, because they require three-body processes for their formation. Reactions involving \( \text{N}_2\text{O}^-\) or \( \text{N}_3\text{O}_2^-\) could therefore not explain our observations.

- For the same reason, any three-body attachment to \( \text{N}_2\text{O} \) under formation of \( \text{N}_2\text{O}^- \) (this reaction is also highly disputed) followed by electron detachment from \( \text{N}_2\text{O}^- \) would be several orders of magnitude too small to explain the observed features.

- \( \text{NO}_2^- \), formed by charge transfer from \( \text{NO}^- \), has a high electron affinity and is therefore very unlikely to exhibit electron detachment.

- \( \text{N}_2\text{O}^- \), on the other hand, also formed from \( \text{NO}^- \), is a good candidate for fast electron detachment due to its extremely small electron affinity.

- Finally, although \( \text{O}^- \) has a high electron affinity of 1.5 eV, two exothermic processes for electron detachment from \( \text{O}^- \) were proposed (see section 3.1.5), namely reaction (7) suggested by Chaney and Christophorou [21], or reaction (8) proposed by Parkes [8]. These reactions were however explicitly disputed by some authors.

The (more speculative) third, slow electron detachment process is observed at high pressures at which three-body processes dominate. After few \( \mu \text{s} \) only anions which do not react further (or only comparably slowly), i.e. \( \text{N}_2\text{O}_2^- \), \( \text{NO}_2 \) or \( \text{N}_3\text{O}_2^- \) remain.

- The likely candidate for slow electron detachment is either direct electron detachment from \( \text{N}_3\text{O}_2^- \), or dissociation of \( \text{N}_3\text{O}_2^- \) in \( \text{NO}^- + \text{N}_2\text{O} \) via reaction (16), followed by electron detachment from \( \text{NO}^- \). This cluster decay was originally proposed by Parkes [8], at his lower field strength of up to \( \approx 50 \) Td. The proposed dissociation energies for reaction (16) are widely spread from 0.26 – 2.2 eV, which is presumably due to different measured isomers. If the value is in fact rather low, the reaction may well be possible.

- \( \text{N}_3\text{O}_2^- \) is the second dominating anion at high pressures, and could potentially also exhibit a slow anion decay rate. However, Posey and Johnson [37] suggested a rather high electron affinity of 2.2 eV for the isomer of \( \text{N}_2\text{O}_2^- \). Therefore, \( \text{N}_3\text{O}_2^- \) seems more likely.

- It is tempting to consider as a further possibility electron detachment from \( \text{O}_2^- \), because we observed in a previous publication [6] a detachment process just in the order of \( 1 \cdot 10^{-20} \) \( \text{m}^3\text{s}^{-1} \) for \( \text{O}_2 \) in \( \text{N}_2\text{O}_2 \) mixtures around 100 Td (which would fit with the rate of the presumed slow detachment). However, \( \text{O}_2^- \) would have to be formed in substantial numbers by unknown chemical processes, which contradicts several findings.

After trying out many different model variants it became evident that the first, fastest detachment feature is due to \( \text{O}^- \) detachment. Not only does a model assuming \( \text{O}^- \) detachment reproduce the current shape perfectly, in the result section we will provide further evidence from measurements in 99% \( \text{O}_2 \) and 1% \( \text{N}_2\text{O} \). Any alternative explanation would require a substantial amount of other anions than \( \text{O}^- \) to be present already very early on, within the first 200 ns. If it was \( \text{NO}^- \), a very rapid conversion from \( \text{O}^- \) to \( \text{NO}^- \) of at least \( 1 \cdot 10^{-15} \text{m}^3\text{s}^{-1} \) would be necessary, and subsequent fast \( \text{NO}^- \) detachment could in principle reproduce the measured first feature. However, this conversion is higher than what most sources agree on: \( \approx 2 \cdot 10^{-16} \text{m}^3\text{s}^{-1} \). Also, the second feature could not be brought to a match under this assumptions. It would further contradict the results in 99% oxygen.

The third feature fits well with a cluster-decay of \( \text{N}_2\text{O}_2^- \). Other mechanisms involving long-lived anions are conceivable, but cannot be cleared up further within this study.

This leaves \( \text{NO} \) and potentially \( \text{N}_2\text{O}^- \) as the responsible anion for the second feature. If we assume detachment from \( \text{NO}^- \), disregarding \( \text{N}_2\text{O}^- \), in a straight-forward way via

\[
e \rightarrow \text{O}^- \rightarrow \text{NO}^- \rightarrow e
\]

it turns out that the temporal characteristic of the second feature cannot be replicated. However, once a kind of “delay” in this sequence is introduced, the current with its complicated shape can be fitted. We consider both

\[
e \rightarrow \text{O}^- \rightarrow \text{NO}^- \rightarrow \text{N}_2\text{O}^- \rightarrow e,
\]

where at least part of \( \text{NO}^- \) is first converted to \( \text{N}_2\text{O}^- \) and then detaches, and

\[
e \rightarrow \text{O}^- \rightarrow \text{N}_2\text{O}_2^{-\ast} \rightarrow \text{NO}^- \rightarrow e
\]

\[
e \rightarrow \text{O}^- \rightarrow \text{NO}^- \rightarrow \text{N}_3\text{O}_2^{-\ast} \rightarrow e
\]

where a long-lived intermediate \( \text{N}_2\text{O}_2^{-\ast} \) (or potentially \( \text{N}_3\text{O}_2^{-\ast} \)) delays the conversion to and detachment from \( \text{NO}^- \). For both models we achieve perfect overlap of simulation and measurement for all measurements. Conversion of \( \text{NO}^- \) into \( \text{N}_2\text{O}^- \) has been claimed in literature, and the measured cross sections of Paulson [24] and Chantry [32] would match in magnitude. However, in high pressure mass spectrometer studies of Moruzzi et al. [22] or Parkes [8], \( \text{N}_2\text{O}^- \) was never observed (Moruzzi measured from \( \approx 50 - 1300 \text{Pa at 30 Td} \)). Most mass spectrometer have extraction times of at least micro-seconds, and the similarity in mass
with NO$_2^-$ certainly makes the distinction challenging.

The plausibility of a long-lived N$_2$O$_2$ or N$_3$O$_2^-$ in the order of 100 ns is unclear to us. In vacuum, this lifetime could well be realistic for this cluster with its high electron affinity. Such a long lifetime would suggest a large three-body conversion to a "stable N$_2$O$_2^-$", but that does not seem to be the case. On the other hand, long lifetimes have indeed been speculated about by Parkes [8] for N$_3$O$_2^-$ in order to explain discrepancies in his measurements. Barlow et al. [23] brought up the possibility of a long life-time of the N$_2$O$_2^-$ complex (without estimating a time-scale). Likewise, Moruzzi and Dawkin [22] proposed lifetimes of even 1 µs for N$_2$O$_2^-$. For simplicity, and since we cannot distinguish in between the variants, the conversion to N$_2$O$^-$ is introduced in the model (see figure 1), which inherently reproduces the delay of the second feature. Basically, regardless of the physical interpretation, the two additional fit parameters $k_c[NO^- \rightarrow N_2O^-]$ and $k_d[N_2O^-]$ add two degrees of freedom for the optimization routine to shape a temporal characteristic of the detachment signal.

6. Results

In the following section we present the fit results of almost 600 measurements, measured over a widespread range of pressure and electric field. The results present themselves as follows: with the model of figure 1, all waveforms can be fitted perfectly to the eye. While the complicated current shapes carry a lot of information, the number of fit parameters is very high, and not all can be obtained independently. For most processes, only a certain subset of measurements are sensitive (mostly dependent on pressure).

Rather than having the ion mobilities as fit parameters, we use the mobilities of O$^-$, NO$^-$ and N$_2$O$^+$ calculated by Yousfi, Hemad and Benhenni [26]. Our data fit better when we increase their value for N$_2$O$^+$ by roughly 20 – 30%, but our signal is quite weak. The measured current is entirely insensitive to the mobility of O$^-$ and NO$^-$.

Literature values for all other anions (N$_2$O$_2^-$, N$_3$O$_2^-$, NO$_2^-$) are not available. From the highest measured $E/N$ values above 120 Td and highest measured pressures above above 10 kPa we estimate that the mobility of these stable anions is roughly 20 – 30% higher than the one of the positive ion.

Reference values from dedicated measurements for electron mobility (Yoshida [47, 53]) and electron longitudinal diffusion (Nakamura [53, 54]) are found to agree well, and spread less than ours.

6.1. Electron system

6.1.1. Ionization of N$_2$O

Our values for the ionization rate coefficient are shown in figure 4. They are in good agreement with most references. There is overall little dispute about shape and magnitude of the ionization rate coefficient in N$_2$O, the only exception being values of Raju and Hackam [49], which are almost one order of magnitude higher than others. While the older cross section set of MAGBOLTZ (version 11.2) matches with the present results, the newer set (11.6) aligns with Raju and Hackam [49].

6.1.2. Dissociative electron attachment to O$^-$

In contrast to this, there is strong disagreement of almost two orders of magnitude between various sources on the dissociative attachment of N$_2$O, shown in figure 5. While most older references agree on values below $1 \cdot 10^{-17}$ m$^3$s$^{-1}$, the more recent measurements of Yoshida et al. [47], Dupljanin [48] and Teich [56]...
Figure 5: Dissociative attachment to $\text{N}_2\text{O}$, forming $\text{O}^-$. Our data is given in the bottom plot. References are taken from [9, 10, 18, 22, 25, 35, 47, 48, 55–57].
lie much higher. Parkes [8] explained this discrepancy: large errors are introduced in older evaluations since strong electron detachment processes were not known and not taken into account. Our results fit with all modern sources, but spread considerably (fit results such as ours should not be averaged over). Date’s calculation [25] agrees in magnitude, but not in shape with our measurements: the characteristic maximum of \( k_\text{O}^- \) at 100 Td is in their case shifted to 40 Td. Our data agree well with simulations of MAGBOLTZ [55] version 11.2. The newer set of version 11.6 received an update where the attachment cross section was scaled down by a factor of 10, presumably to take into account attachment effects. When this scaling is removed (as shown in the figure), the simulation with version 11.6 agrees with our data. The ionization and attachment rate coefficients of \( \text{N}_2\text{O} \) calculated with the solver Bolsig+ [58] with the cross section set of Dupljanin et al. [48] are as well in good agreement with our data.

### 6.2. \( \text{O}^- \) system

\[
\begin{align*}
\text{e}^- & \rightarrow \text{O}^- \\
\text{NO}^- & \rightarrow \text{N}_2\text{O}_2^-
\end{align*}
\]

#### 6.2.1. Electron detachment from \( \text{O}^- \)

We find that, at sufficiently high \( E/N \), a very substantial fraction of all \( \text{O}^- \) exhibits detachment (from 5 to 30%, depending on the pressure and on the electric field) instead of converting to \( \text{N}_2\text{O}_2^- \) or \( \text{NO}^- \). Similar findings have, to our knowledge, never been published (except for a careful suggestion of Chaney and Christopheron [21]) and it seemed at first highly unlikely that such an efficient process should have been missed in various studies. We cannot fully assess if \( \text{O}^- \) detachment is in direct contradiction to any findings, or whether it was just never directly observed. The process might be difficult to detect at thermal conditions, where our results suggest a rate of one tenth of the highly efficient \( k_\text{O}^- (\text{O}^- \rightarrow \text{NO}^-) \).

We therefore check this hypothesis in oxygen. In a recent publication [9], we added traces of hydrogen in oxygen and observed the increase in the electron detachment from \( \text{O}^- \) (which also occurs without \( \text{H}_2 \), at a lower rate), which is linear in the mole fraction of hydrogen, by

\[
\text{O}^- + \text{H}_2 \rightarrow \text{H}_2\text{O} + e.
\]

The process was measured for instance by Moruzzi [7], who gave a value of \( k = 7.5 \cdot 10^{-16} \text{m}^3\text{s}^{-1} \) (we obtained ourselves a slightly lower value of \( 5.1 \cdot 10^{-16} \text{m}^3\text{s}^{-1} \) in a previous work [6]). Instead of hydrogen, we now added 1% of \( \text{N}_2\text{O} \) in 99% of oxygen. The result in figure 6 confirms that \( \text{N}_2\text{O} \) has a similar effect as hydrogen, in that it enhances electron detachment from \( \text{O}^- \). While we measured a rate coefficient of \( 5.1 \cdot 10^{-16} \text{m}^3\text{s}^{-1} \) for process 18 (scaled to 100% \( \text{H}_2 \)), the efficiency of the corresponding process with \( \text{N}_2\text{O} \) is lower at \( 4 \cdot 10^{-17} \text{m}^3\text{s}^{-1} \) (scaled to 100% \( \text{N}_2\text{O} \)). The coefficient \( k = k_\text{O}^- / w_\text{O}^- \) in oxygen is \( 3.2 \cdot 10^{-20} \text{m}^2 \).

The detachment anion cannot be \( \text{NO}^- \), since charge transfer from \( \text{NO}^- \) to \( \text{O}_2 \) is highly efficient (5 \( \text{m}^3\text{s}^{-1} \) [28]) and would dominate, thus inhibiting detachment.

Another argument in favor of \( \text{O}^- \) detachment is that the proposed detachment reactions (7) and (8) of \( \text{O}^- \) with \( \text{N}_2\text{O} \) are both exothermic, and the cross section would therefore not depend much on \( E/N \). This fits well with the observation in section 4 that the detachment features are present over the whole \( E/N \) range.

The two plots of figure 7 give our obtained rate coefficient and spatial coefficient for electron detachment from \( \text{O}^- \) in \( \text{N}_2\text{O} \). Meaningful values for this process could only be obtained from measurements at pressures below 0.75 kPa. Within the spread, the coefficient (figure 7b) is found to be constant and high in value, implying an exothermic process. In addition
to pure N$_2$O, we measured N$_2$O with an addition of 0.6% hydrogen. The overall electron detachment rate coefficient of O$^-$ is expected to increase by $k \cdot 0.006 = 4.5 \cdot 10^{-18}$ m$^3$s$^{-1}$ due to process 18 (the expected increase is illustrated by the double arrow in the figure). If this increase is observed, this should confirm that there is indeed O$^-$ detachment. However, it turns out that this contribution is quite small compared to the unexpectedly strong electron detachment process in pure N$_2$O. The detachment rate coefficients for the admixture with H$_2$ are slightly higher on average, but the spread is considerable so this test is not very conclusive.

Comparing to the results in oxygen with traces of N$_2$O, where we obtained a coefficient of $4 \cdot 10^{-17}$ m$^3$s$^{-1}$ at 110 Td (scaled to 100% N$_2$O), this certainly fits quite well. Note that the value scales with the respective anion mobilities of O$^-$ in oxygen and N$_2$O, and thus the comparison in terms of the coefficient in units of m$^2$ is more accurate, as shown in figure 7b. The mobility of O$^-$ in N$_2$O is taken from the theoretical calculation of [26].

6.2.2. Conversion of O$^-$ in NO$^-$
6.2.3. Formation of stable anions

We are unable to directly obtain $k_c[O^{-} \rightarrow N_2O_2^{-}]$, $k_c[NO^{-} \rightarrow N_3O_2^{-}]$ and $k_c[NO^{-} \rightarrow NO_2^{-}]$ independently of each other. The current contains little information that would allow the fit routine to distinguish between these anions. For example, decreasing $k_c[O^{-} \rightarrow N_2O_2^{-}]$ can be compensated by increasing $k_c[NO^{-} \rightarrow N_3O_2^{-}]$, leaving the current mostly unchanged. Rather than the magnitude of the processes, we can better obtain the overall probability for an initially formed O$^-$ to “stabilize”, i.e. the formation of either N$_2$O$_2^-$, N$_3$O$_2^-$ or NO$_2^-$:

$$p[\text{stabilization}] = \frac{p[c \rightarrow \ldots \rightarrow N_2O_2^{-}]}{p[O^{-} \rightarrow \ldots \rightarrow N_3O_2^{-}/NO_2^{-}]}$$  \hspace{1cm} (19)$$

These probabilities are given as

$$p[O^{-} \rightarrow \ldots \rightarrow N_2O_2^{-}] = \frac{\nu_O^{-} \rightarrow N_2O_2^{-}}{\nu_O^{-} \rightarrow N_2O_2^{-} + \nu_O^{-} \rightarrow NO^{-} + \nu_O^{-} \rightarrow NO_2^{-}}$$  \hspace{1cm} (20)$$

and

$$p[O^{-} \rightarrow \ldots \rightarrow N_3O_2^{-}/NO_2^{-}] = \frac{\nu_O^{-} \rightarrow NO^{-}}{\nu_O^{-} \rightarrow N_2O_2^{-} + \nu_O^{-} \rightarrow NO^{-} + \nu_O^{-} \rightarrow NO_2^{-}}$$  \hspace{1cm} (21)$$

These lengthy expressions are simply the branching probabilities. The result is shown in figure 9. The stabilization probability decreases with increasing $E/N$, since endothermic electron detachment processes increase while exothermic stabilization processes remain constant or decrease. At higher pressures, more electrons are stabilized due to pressure-dependent three-body clustering processes. The results are independent of any assumption on O$^-$ detachment, but the spread is reduced for the higher pressures if the previously found rate coefficient is fixed.

The mixture with H$_2$ shows no deviation, while the admixture of traces of O$_2$ and CO$_2$ apparently has dramatic effects: the probability of stabilization is strongly increased. This is to be expected: The conversion from NO to O$_2^-$,

$$\text{NO}^{-} + \text{O}_2 \rightarrow \text{NO} + \text{O}_2^{-}$$  \hspace{1cm} (22)$$

is known to be fast and its value has been given as $5 \cdot 10^{-16} \text{m}^3 \text{s}^{-1}$ [28]. With 1% O$_2$ we expect an additional $5 \cdot 10^{-16} \text{m}^3 \text{s}^{-1}$ of stabilization of NO$^-$. We added some CO$_2$ in order to stabilize O$_2^-$, forming CO$_4^-$, which does not react further. The stabilizing effect of

$$\text{O}^{-} + \text{CO}_2(+M) \rightarrow \text{CO}_3^-(+M)$$  \hspace{1cm} (23)$$

is presumably less important (due to competition with the fast $k_c[O^{-} \rightarrow NO^{-}]$), but would also increase the
stabilization.

This probability is most relevant for estimating the critical field strength of N₂O. Since the electron detachment processes are fast, all other anions except for N₂O²⁻, N₃O²⁻ and potentially NO₂⁻ do not contribute to the electric strength. The “apparent” attachment rate coefficient is \( p[\text{stabilization}] \cdot k_a[O^-] \), and much lower than the real attachment rate coefficient. Presumably, this value is given in many older sources when electron detachment was not taken into account, and this explains the large scatter in figure 5. It further becomes clear why we are limited to \( E/N \) below \( \approx 160 \text{Td} \) due to impending breakdown, whereas the ionization rate coefficient is still a factor of two lower than the dissociative attachment (see figure 5).

References values for \( k_c[O^- \rightarrow N_2O_2^-] \), \( k_c[NO^- \rightarrow N_3O_2^-] \) and \( k_c[NO^- \rightarrow NO_2^-] \) are sparse. For \( k_c[O^- \rightarrow N_2O_2^-] \) and \( k_c[NO^- \rightarrow N_3O_2^-] \), Parkes \[8\] suggests the high values \( 4.2 \cdot 10^{-14} \text{m}^6\text{s}^{-1} \) and \( 8.5 \cdot 10^{-12} \text{m}^6\text{s}^{-1} \) for thermal conditions. Dutton \[35\] extrapolates Parkes results, combines with his own measurements, and calculates \( 4 \cdot 10^{-12} \text{m}^6\text{s}^{-1} \) and \( 2.5 \cdot 10^{-12} \text{m}^6\text{s}^{-1} \) at 160 Td. These values do not match our findings, and the observed pressure dependency of \( p[\text{stabilization}] \), which suggests roughly one order of magnitude lower values. For practical purposes, an effective three-body stabilization of O⁻ of \( \approx 3.5 \cdot 5 \cdot 10^{-41} \text{m}^6\text{s}^{-1} \cdot \exp(-E/N[\text{Td}]/100) \), while disregarding the stabilization of N₃O₂⁻ entirely, reproduces the measured \( p[\text{stabilization}] \) approximately.

6.3. NO⁻ system

\[
\begin{align*}
\text{N}_2\text{O}^- & \rightarrow e^- \\
\text{N}_3\text{O}_2^- & \rightarrow \text{NO}^- \\
\text{NO}_2^- & \rightarrow \text{N}_2\text{O}^- \\
\end{align*}
\]

While we are unable to separate the stabilization processes, we can still obtain detachment rate coefficients from NO⁻ and N₂O⁻. These detachment processes are responsible for the peculiar current peak (see figure 3) at few \( \mu \text{s} \), and this peak gives information about the lifetime and number of these anions.

In figure 10a the rate coefficient leading to electron detachment from NO⁻ is shown. The three fit parameters \( k_a[NO^-] \), \( k_c[NO^- \rightarrow N_2O^-] \) and \( k_c[N_2O^-] \), regardless of their physical interpretation, give the optimization routine a great flexibility in shaping a temporal detachment characteristic. The sum of \( k_a[NO^-] \) and \( k_c[NO^- \rightarrow N_2O^-] \) is the effective rate coefficient

![Figure 10a](image)

Figure 10a: The obtained electron detachment rate coefficient of NO⁻ (upper plot, (11)) and N₂O⁻ (lower plot). The assignment to these two anions is uncertain. References: Yousfi et al. \[26\]; a measurement of total NO⁻ reaction with N₂O (of which electron detachment is presumably dominant) is given by Viggiano \[29\], in terms of relative kinetic energy. Values at room temperature are roughly \( 0.5 - 3 \cdot 10^{-17} \text{m}^3\text{s}^{-1} \) for energies from 0.03 – 0.5 eV. The value of Dutton \[35\] uses and extrapolates results of Parkes \[8\]. Values of McFarland et al. \[28\] (corrected and interpolated for temperature), and Parkes/Sugden \[8\], are measurements at thermal conditions.
for detachment from NO$^-$, and shown in figure 10a. There is no apparent influence of the admixtures with H$_2$ or O$_2$, and none is expected (the competing stabilization by O$_2^-$ does not lower the detachment rate coefficient).

All references agree on slightly higher values: direct measurements are available for thermal NO$^-$ [8, 28]; the value of Yousfi [26] is calculated from cross section data; Dutton’s result [35] lies somewhat higher. The electron detachment rate coefficient of N$_2$O$^-$ is found with a clear pressure dependence, which requires interpretation. The size of this rate coefficient influences the timescale of the detachment process in the NO$^-$ system, but not its magnitude because N$_2$O$^-$ is certain to detach. The size of the rate coefficient for higher pressures appears to be too low for an anion that was never detected in measurements above 100 Pa. Our rate coefficients for $k_c[\text{NO}^- \rightarrow \text{N}_2\text{O}^-]$, reaction (13), scatter strongly in between $10^{-18} - 10^{-17}$ m$^3$s$^{-1}$. For comparison, the cross section measurements of Paulson [24] and Chantry [32] both find an efficiency of roughly one third of $k_c[\text{O}^- \rightarrow \text{NO}^-]$ for anion energies at few eV and below 1 eV. This would suggest values in the order of $5 \cdot 10^{-18}$ m$^3$s$^{-1}$ and would fit well with our results. Morris, Viggiano and Paulson [34], however, gave a thermal rate coefficient (upper bound) of only $4 \cdot 10^{-28}$m$^3$s$^{-1}$. They, however, mention the possibility of loss of N$_2$O$^-$ signal due to electron detachment over the drift time.

For the highest measured $E/N$ values, we require a slow electron detachment process to explain the huge late ion current (see figure 3, the dashed line indicates a simulation without this process). Breakup of the N$_3$O$_3^-$ cluster at a small rate coefficient, and subsequent detachment from NO is the most likely candidate, and explains the measurements. The result is given in figure 11. Due to the very small magnitude of this process, it only affects the waveforms at highest measured pressures.

7. Discussion

7.1. Kinetic model

On top of the dozen processes proposed in literature, we added two additional electron detachment processes from O$^-$ and N$_3$O$_2^-$ in order to explain our measurements. Having tried out a large number of model variants, most of which do not match with the measurements, we are confident that the model we chose comes close to the physical picture, although it certainly requires interpretation and correction in the NO$^-$ system.

7.2. Electron parameters

The ionization and attachment rate coefficients of figures 4 and 5 are well in line with reference values. The cross section set of Dupljanin et al. [48] appears to give matching results, as does the older version of MAGBOLTZ (11.2). The newer set has presumably a too high ionization cross section. The attachment cross section in this new set was adapted to fit with “apparent attachment” results, i.e. trying to take into account the severe electron detachment in N$_2$O, and was therefore down-scaled by a factor of 10.

7.3. O- system

Judging not only from the fit quality but also several references, it is likely that the rate coefficients of the O$^-$ system are correct in ratio and magnitude. The electron detachment from O$^-$, figure 7a was already discussed at length in section 6.2.1. The three-body clustering rate coefficient to N$_2$O$^-$ could not be obtained independently from the clustering rate forming N$_3$O$_2^-$, and from the conversion to NO$_2^-$ . The stabilization probability, however, could be obtained with a low spread. It indicates how dramatic the detachment processes are even at our relatively high pressures. The low stabilization further explains the extreme discrepancies, of more than one order of magnitude, in the attachment rate coefficient between newer and older results.

7.4. NO- system

The model assuming conversion to and detachment from N$_2$O$^-$ cannot be fully discarded, but our results
imply that there is a model deficiency, which we were not able to fully clear up. The effective detachment from NO\(^-\), figure 10a, that we obtain is slightly lower compared to several reference values. The detachment rate coefficient of N\(_2\)O\(^-\) shows a pressure dependence. This could be interpreted as a missing time-delay mechanism, which might involve N\(_2\)O or NO\(^-\) but could also stem from long-lived N\(_3\)O\(_2\)^{−}\(^-\) or N\(_3\)O\(_2\)^{-}\(^-\) meta-stables. While our relatively large conversion from NO\(^-\) to N\(_2\)O\(^-\) in the order of \(5 \cdot 10^{-14}\text{m}^3\text{s}^{-1}\) is not in contradiction to cross section data of Paulson and Chantry, other findings of Morris et al. suggest much lower thermal values.

### 7.5. Comparison to mass spectrometer studies

Parkes as well as Moruzzi and Dakin used mass spectrometers and measured anion ratios in dependence of the field strength and gas pressure. From this, they derive rate coefficients and in particular the three-body clustering processes \(k_c[O^- \rightarrow N_2O_2^-]\) and \(k_c[NO^- \rightarrow N_3O_2^-]\). Their values are very high and do not match our findings, since they suggest a very high stabilization (in the sense of capturing and converting to anions which do not exhibit electron detachment), which cannot be reconciled easily with our measurements. We require roughly one order of magnitude lower \(k_c[O^- \rightarrow N_2O_2^-]\) and \(k_c[NO^- \rightarrow N_3O_2^-]\) in order to match the stabilization probability of figure 9. Our \(p[\text{stabilization}]\) values are presumably reliable, since they are in a simple way connected to the critical field strength \((E/N)_{\text{crit}}\):

\[
k_i = k_a[O^-] \cdot p[\text{stabilization}] \tag{24}
\]

is the condition for an avalanche where effective attachment followed by stabilization equals the electron ionization. For instance, the measurement at 140 Td in figure 3 is visibly over-critical and growing in electron number (confirmed also by simulation, figure 12) at a pressure of 15 kPa, although the attachment rate coefficient is roughly 7 times (!) larger than the ionization rate coefficient (see figure 5). Our low stabilization \(p[\text{stabilization}]\) of only \(\approx 0.14\) explains this. The high \(k_c[O^- \rightarrow N_2O_2^-]\) and \(k_c[NO^- \rightarrow N_3O_2^-]\) of Dutton and Parkes, however, enforce at least 25\% stabilization even when we use their higher \(k_a[NO^-]\), several multiples above our levels, which lowers stabilization. Over the whole \(E/N\) range, their high three-body rate coefficients lead to at least 2 – 3 times higher stabilization than what we observe.

Moruzzi gave an example at 30 Td and geometric dimensions. In order to probe their values, we simulated his conditions using our obtained rate coefficients. We obtain an order of magnitude lower count of N\(_3\)O\(_2\)^{−}\(^-\) and N\(_3\)O\(_2\)^{-}\(^-\) (relative to O\(^-\) and NO\(^-\)), and thus our rate coefficients do not match with their measurements. Taking into account our observed detachment from O\(^-\) does not influence the anion count much, and does not explain the discrepancy. Using their higher values for \(k_c[O^- \rightarrow N_2O_2^-]\) and \(k_c[NO^- \rightarrow N_3O_2^-]\), however, reproduces their anion count quite well.

Could natural impurities have weakened our measurement gas, such that we obtain a too low stabilization \(p[\text{stabilization}]\)? We think not, since in terms of electric strength N\(_2\)O is highly resilient to H\(_2\) impurities, and virtually every other natural impurity would rather strengthen it. Therefore, the anion count is in conflict with our results.

It is difficult to judge whether there is a possibility that the count of NO\(^-\) and O\(^-\) was too low in their experiments for some reason. Potentially, what we model as O\(^-\) and NO\(^-\) could in fact exist part of the time as weakly clusters, or long-lived meta-stables N\(_2\)O\(_2\)^{−}\(^-\) and N\(_3\)O\(_2\)^{-}\(^-\), without stabilizing to what we term in the model N\(_2\)O\(_2\)^{-}\(^-\) and N\(_3\)O\(_2\)^{-}\(^-\). If the life-time is long enough, this could shift the measured anion ratio.

Another possibility is that N\(_3\)O\(_2\)^{−}\(^-\) is not stable, but exhibits substantial electron detachment or cluster decay already at the comparable low fields of 30 Td. For instance, collision-induced breakup into N\(_2\) + N\(_2\)O + e could be possible. In this case, we would attribute the detachment from N\(_3\)O\(_2\)^{−}\(^-\) falsely to NO\(^-\) or NO\(_2\)^{−}\(^-\), and obtain a pressure-dependent detachment characteristic. Fitting with this, the effective three-body stabilization that reproduces \(p[\text{stabilization}]\) fits quite well with the value for \(k_c[O^- \rightarrow N_2O_2^-]\) of Parkes, disregarding \(k_c[NO^- \rightarrow N_3O_2^-]\) entirely.

### 7.6. Electric strength of N\(_2\)O

Despite possible discrepancies in the model, the critical field strength of N\(_2\)O is certainly reliable, since is can be well confirmed with the measured waveforms. The critical field strength is simply defined by
whether the number of free electrons increases in an infinite gap. For a given set of rates, this can be determined from the eigenvalues of the model matrix (described in [52]). We use the Bolsig+ simulation and the cross section set of Dupljanin et al. [48], and the derived effective three-body stabilization. Figure 13 gives the presumed critical field strength compared to the high-pressure breakdown study of Akbar and Malik [51] and Biasiutti [50].

8. Conclusion

Our measurements confirm ionization and dissociative rate coefficients in N$_2$O and match with most modern sources. There is an additional efficient electron detachment process from O$^-$, confirmed by measurements not only in N$_2$O but also in 99% O$_2$ plus 1% N$_2$O. The simplest explanation is either O$^-+N_2O\rightarrow2NO+e^-$ or O$^-+N_2O\rightarrowN_2+O_2+e^-$. The comparison with mass spectrometer studies reveals discrepancies. In order to match our observed anion stabilization, lower three-body conversion rate coefficients are required than what was proposed in literature. Finally, an estimation of the electric strength of N$_2$O predicts a slowly increasing strength reaching 190 Td, or 47.5 kV/cm bar. Breakdown studies are planned in order to check these results, and derive design recommendations for gaseous insulated equipment.

9. Acknowledgement

This work is financially supported by GE Grid (Switzerland) GmbH, Pfiffner Technologie AG, ABB Switzerland Ltd and Siemens AG. We wish to express our gratitude to Prof. Nickolay Aleksandrov at MIPT for his input.

References


[29] AA Viggiano, Robert A Morris, and John F Paulson. “Kinetic energy and temperature dependences of the rate constants for electron detachment of oxonitrate (1-) by nitrogen oxide (N2O), carbon dioxide, nitrogen, methane, ethane, and propane”. In: Journal of Physical Chemistry 94.8 (1990), pp. 3286–3290.


[31] ALC Smit and FH Field. “Gaseous anion chemistry. Formation and reactions of hydroxide (1-) ion; reactions of anions with nitrous oxide; hydroxide (1-) ion negative chemical ionization”. In: Journal of the American Chemical Society 99.20 (1977), pp. 6471–6483.


[34] Robert A Morris, AA Viggiano, and John F Paulson. “Rate constants for reactions of NO- with N2O, 14N15NO, and 15NO2”. In: The Journal of Chemical physics 92.4 (1990), pp. 2342–2343.


