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Vibrational excitation in a nitrogen plasma, generated by a dielectric-barrier discharge exploring the possibilities of optical emission spectroscopy and current-voltage measurements

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Award date:
2013

Link to publication
Vibrational excitation in a nitrogen plasma, generated by a dielectric-barrier discharge
Exploring the possibilities of optical emission spectroscopy and current-voltage measurements

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July 2013

PMP 13-06

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Abstract

In the past decades, the use of plasmas in chemical processes has increased significantly. Especially in non thermal plasmas, chemical processes can be run with high reactivity (i.e. high reaction rate coefficients), without spending much energy on (translational) heating of the gas. For this reason, plasma chemistry can offer an energy efficient option for inducing or assisting chemical reactions. The dielectric-barrier discharge (DBD) is a plasma chemical reactor configuration which is widely used, since it offers a convenient and cost-effective way for creating a non thermal plasma.

Vibrational excitation and gas temperature (translational excitation) have a large influence on rate coefficients and the energy efficiency of plasma chemical reactions. Therefore, vibrational excitation and gas temperature of a nitrogen plasma, generated in a DBD reactor, are investigated in a wide range of the available process variables, namely applied voltage amplitude, pressure and residence time. Also the specific energy input and the reduced electric field, two other relevant plasma parameters in a DBD reactor, are determined as a function of these process variables in order to find possible correlations with vibrational excitation.

Optical emission spectroscopy (OES) is used to determine vibrational excitation and gas temperature (translational temperature) of nitrogen molecules in the plasma and to estimate the reduced electric field in the plasma, an important parameter for all gas discharges. Current-voltage (I-U) measurements are performed to determine the specific energy coupled into the plasma, an important parameter regarding the energy efficiency of a chemical process, and to obtain a second estimate for the reduced electric field. The latter diagnostic is also used for a thorough electrical characterization of the gas discharge. From this characterization, the capacitances of the dielectric barriers and the discharge gap are determined, together with the voltage across the discharge gap, both averaged over the discharge phase and as a function of time.

The capacitances of the dielectric barriers and the discharge gap correspond to theoretically calculated values. Contrary to a common assumption, the voltage across the discharge gap is not found to be constant during the discharge phase. From the same analysis, the effect of residual charge in a nitrogen DBD is observed. By comparing two methods for determining the voltage across the discharge gap, the possible effect of charge accumulation in a discharge filament is observed. Both methods for determining the reduced electric field yield similar values, though the trends are not identical. Under all conditions, vibrational excitation is found to be in Boltzmann equilibrium, making it possible to assign a vibrational temperature to each operating condition, ranging 2100-3200 K. Gas temperatures are found in the range of 340-650 K. The vibrational temperature is found to be positively correlated with the specific energy input (ranging 0.24-64 kJ per standard liter) and negatively correlated with the reduced electric field (340-530 Td, OES based values) which suggests that a high specific energy input and a low reduced electric field are beneficial for rate coefficients and the energy efficiency of a plasma chemical process in a nitrogen DBD. No conclusive scaling parameter for vibrational temperature is found in this work. For a pure nitrogen plasma, generated in a DBD reactor, the highest rate coefficients may be expected for high values of the applied voltage amplitude and medium values for the residence time, while the highest energy efficiency may be expected at low pressures.
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Chapter 1  Introduction

In the past decades, the use of plasmas [1] in chemical processes has increased significantly. Some examples are plasma chemical processes for the removal of volatile organic compounds (VOCs) out of air or surface modification [2]. The reason for this increasing popularity of plasma chemical processes can be found in the many merits that plasma technology can offer within the field of chemistry. Particularly non thermal plasmas have properties that make them very suitable for inducing or assisting chemical reactions [1]. In non thermal plasmas, also known as non equilibrium plasmas, the energy coupled into the plasma is not evenly distributed over all particle species (e.g. molecules, atoms, radicals, ions and free electrons) and all degrees of freedom (e.g. translational, rotational, vibrational and electronic). Typically, most of the energy is converted into kinetic energy of free electrons (i.e. the translational degree of freedom for free electrons), since free electrons initially receive most of the energy put into the plasma (via the electric field). The free electrons then redistribute the energy input over all other particle species and degrees of freedom by elastic or non elastic collisions. Some particle species and some degrees of freedom, also known as channels of excitation, contribute much more to inducing chemical reactions than others. Especially vibrational excitation of molecules, and particle species like free electrons and radicals are known to be very beneficial for inducing or assisting chemical reactions [1, 3, 4]. In a non thermal plasma, most of the energy coupled into the plasma can be directed into these beneficial routes, which makes it possible to achieve a high reactivity without ‘losing’ too much energy into channels of excitation that contribute less to the chemical process, like heating of the gas (i.e. translational excitation of atoms or molecules). Conventional chemical routes, like wet chemical processing, do not have the advantages that accompany non thermal behaviour. For this reason, plasma chemical processes can potentially yield high energy efficiencies for running a chemical process, compared to other chemical processes.

Despite this promising prospect, the quest for obtaining high energy efficiencies does not end with simply using non thermal plasmas for chemical processes. The distribution of the energy, coupled into the plasma, over the different particle species and channels of excitation depends strongly on the type of reactor that is being used, but also on the process variables of the plasma chemical process (e.g. pressure) [1]. For this reason, possibilities exist for optimizing energy efficiencies of plasma chemical processes, which is needed in order for them to compete with other chemical processes and become economically viable. Since optimal windows of operation are reactor dependent, finding optimal process variables for running a plasma chemical process is not sufficient. Before industrial upscaling can occur, it is also necessary to understand the underlying physics that explains why certain values of the process variables yield a high energy efficiency. Only then, optimal operating conditions can be extrapolated to bigger reactors.

In the following sections, first a short introduction is set forth into the plasma chemical reactor which is used in this work. Subsequently, the influence of vibrational excitation and translational excitation (‘classical’ heating) of molecules on plasma chemical processes is treated. After that, an overview is given of all other relevant physical parameters that are measured in this work, along with a short description of their relevance for a plasma chemical process. This chapter will conclude by stating the outline for the research and its goals.
1.1 Plasma chemical reactors

Plasma chemical reactors have been in use for over a century. During their history, main applications have been ozone generation and the removal of volatile organic compounds (VOC) out of air [2, 5]. The type of plasma chemical reactor that is used in this work is a dielectric-barrier discharge (DBD) reactor. This type of reactor was invented by Werner von Siemens in the mid 19th century for the purpose of ozone generation [2]. In a DBD, ozone was generated by creating a gas discharge (i.e. an electrical discharge in a gas) in air or oxygen, after which the ozone was used for purification of water. This would remain the main application of DBD reactors until the end of the 20th century [2]. During this period, the amount of research on the DBD increased, along with corresponding industrial applications. In the 1930s and 1940s, solid progress was made by Buss and Manley regarding the nature of the DBD and its electrical characterization [2, 5]. In the last decades, DBD reactors have increasingly been used for other applications beside ozone generation, like surface modification and pollution control [2]. Some of these new applications have now even outgrown the original use of ozone generation [2].

The dielectric-barrier discharge offers an accessible and very convenient option for creating a non thermal plasma [2]. Because of its long history of industrial and scientific applications, the technology and physical understanding of the DBD is well established, which makes this type of reactor suitable for industrial upscaling [2]. Furthermore, construction and operation of a DBD reactor are relatively straightforward. Another distinct advantage is that a DBD can be operated at or near atmospheric pressures, which enables a DBD reactor to run with a high throughput and without the need for expensive pumps [2, 5]. This makes DBD reactors very cost-effective. For these reasons, the DBD is a very appropriate first choice for generating a non thermal plasma.

Figure 1.1 shows a photograph of a small, ‘homemade’ DBD reactor, very similar to the one used in this work. Between two electrodes, of which one is usually grounded, a gas discharge is created, turning the gas into a plasma. In this work, a pure nitrogen plasma is investigated. The difference between a DBD and other similar plasma sources is that at least one dielectric layer is present between the electrodes, hence the name dielectric-barrier discharge [2, 5]. Several configurations can be seen in figure 1.2. Because of the presence of the dielectric barrier(s), a DBD can only be operated with alternating voltage (AC, RF or pulsed DC). Furthermore, the dielectric barrier(s) also serve(s) to prevent the plasma from becoming thermal. Both statements will be clarified further in chapter 2.

Figure 1.1: Photograph of a ‘homemade’ dielectric-barrier discharge plasma reactor in operation
1.2 Vibrational and translational excitation in a plasma chemical process

As mentioned before, high energy efficiencies for plasma chemical processes can be achieved by directing the energy, coupled into the plasma, into the vibrational channel of excitation and by limiting the amount of energy that is directed into translational excitation of molecules. In this section, more information is provided on vibrational and translational excitation of molecules and their effect on rate coefficients and energy efficiencies in a plasma chemical process.

1.2.1 Vibrational excitation

Vibrational excitation of molecules expresses the motion of atoms in a molecule, relative to each other. This form of excitation is discretized, which means that it can only increase in discrete steps, often called levels or states, as can be seen from figure 1.3. Each vibrational level corresponds to a certain vibrational energy. The vibrational levels follow from solving Schrödinger’s equation for the anharmonic potential well of a molecule (see Appendix A).
The anharmonicity of the potential well of a real molecule is mainly represented by the asymptote corresponding to the dissociation energy. Because of this anharmonicity, the spacing between the vibrational levels decreases for higher vibrational energies, contrary to the case of a harmonic oscillator in which the vibrational levels are equally spaced. More information on the potential well of a real molecule is provided in subsection 2.2.2. The vibrational distribution function (VDF) for a collection of molecules (e.g. a volume of gas) expresses what the relative population of each vibrational state is with respect to the vibrational ground state or, in other words, how many molecules are present with a certain level of vibrational excitation. A type of VDF that is worth mentioning, is the Boltzmann distribution function, in which the relative population of a vibrationally excited state $\nu$ decreases exponentially with its corresponding vibrational energy $E_\nu$:

$$
\frac{n_\nu}{n_0} = e^{-\frac{(E_\nu - E_0)}{kT_{vib}}} \tag{1.1}
$$

In this expression, $n_\nu$ is the particle density of molecules that have a vibrational level of $\nu$, $n_0$ is the particle density of molecules that are in the vibrational ground state, $E_0$ is the vibrational energy corresponding to the vibrational ground state, $k$ is the Boltzmann constant and $T_{vib}$ is the vibrational temperature. Thus, the vibrational temperature determines the relative populations of vibrational levels. At high vibrational temperatures, particle densities of vibrationally excited molecules are relatively higher than at low vibrational temperatures. A defined vibrational temperature only exists when the distribution over the vibrational levels is a Boltzmann distribution. In that case, the vibrational excitation is said to be in Boltzmann equilibrium. In solids, liquids and gasses this is usually the case. However, since this work is concerned with non equilibrium (non thermal) plasmas, it cannot be assumed a priori that the vibrational excitation in a plasma is in Boltzmann equilibrium, which means that a plasma may not have a defined vibrational temperature at all. For ease of reading however, the term vibrational temperature is often used in the remainder of this work when no specific vibrational distribution is addressed. In other words, vibrational temperature can always be replaced by vibrational excitation (or distribution).

### 1.2.2 Translational excitation

Translational excitation of molecules expresses the random and undirected movement of molecules due to their thermal motion. This form of excitation corresponds to the classical concept of heat. Contrary to vibrational excitation, translational excitation is not discretized. The kinetic energy corresponding to thermal movement of molecules can increase with any amount, not only in discrete steps. In a collection of molecules (e.g. a volume of gas), some molecules are moving faster than average while others are moving slower. The distribution function for the kinetic energy due to thermal movement expresses how many molecules are present with a certain thermal kinetic energy, compared to other kinetic energies. In almost all cases, a Maxwell-Boltzmann distribution function for translational excitation of molecules holds. The distribution function for thermal kinetic energies $E_k$ can then be expressed as:

$$
f(E_k) = \frac{1}{\sqrt{\pi}} \frac{E_k}{T_{trans}^3} \cdot e^{-\frac{E_k}{kT_{trans}}} \tag{1.2}
$$

In this expression, $k$ is again the Boltzmann constant and $T_{trans}$ is the translational temperature. Figure 1.4 graphically depicts the Maxwell-Boltzmann distribution of thermal kinetic energies
for a collection of molecules at translational temperatures of 300 and 600 K. For higher translational temperatures, the most probable thermal kinetic energy is higher, as can be seen from the maximum of both distribution functions. Furthermore, at higher translational temperatures more molecules with a high thermal kinetic energy are present. Since the total amount of molecules remains the same, less molecules with a low thermal kinetic energy are then present. This makes the Maxwell-Boltzmann distribution function, if normalized, a probability density function in which the area under the curve represents the probability that a molecule has a thermal kinetic energy within that domain. A defined translational temperature only exists when translational excitation is in Maxwell-Boltzmann equilibrium (i.e. obeying the Maxwell-Boltzmann distribution). This is usually the case, even in non equilibrium systems like the non thermal plasmas in this work. The average kinetic energy of a molecule due to thermal movement is then directly related to the translational temperature as follows:

\[ \bar{E}_K = \frac{3}{2}kT_{\text{trans}} \]  

(1.3)

![Figure 1.4: Maxwell-Boltzmann distribution of kinetic energies for translational temperatures of 300 K (blue) and 600 K (red)]

The translational temperature corresponds to the classical concept of temperature. For this reason, it is usually called ‘the gas temperature’ \( T_{\text{gas}} \) (or \( T_0 \)) or just ‘the temperature’ in plasma physics:

\[ T_{\text{trans}} \equiv T_{\text{gas}} \equiv T_0 \]  

(1.4)

In the remainder of this work, it will most often be referred to as gas temperature.

### 1.2.3 Thermal and non thermal plasmas

Even in the case of non thermal plasmas with defined temperatures (i.e. excitation in equilibrium), one difference between thermal and non thermal plasmas always remains. In thermal plasmas, all temperatures are equal, making the vibrational temperature of molecules equal to, for instance, the rotational temperature \( T_{\text{rot}} \) or translational temperature \( T_{\text{trans}} \) [1]:

\[ T_{\text{vib}} = T_{\text{rot}} = T_{\text{trans}} \equiv T \]  

(1.5)
For rotational excitation, something similar holds as for vibrational excitation: rotational excitation is also discretized and if it is in Boltzmann equilibrium, a defined rotational temperature exists which describes the relative populations of rotational levels.

As can be seen from equation 1.5, a thermal plasma has only one temperature $T$ which describes all channels of excitation for all particles, just like in the case of a ‘normal’ gas. For non thermal plasmas however, this is not the case. This follows from the fact that, in non thermal plasmas, the energy coupled into the plasma is not evenly distributed over all particle species and channels of excitation. The non thermal plasma in this work falls within the category of high pressure, low temperature (i.e. low gas temperature) plasmas. For this category of plasmas, the following relation holds [1], provided that vibrational excitation, rotational excitation and translational excitation of molecules are each in equilibrium (i.e. a defined temperature exists):

$$T_{vib} > T_{rot} \approx T_{trans}$$

(1.6)

Amongst these three channels of excitation for a molecule, most of the energy coupled into the plasma is going into vibrational excitation, while less is going into rotational and translational excitation. The two latter channels of excitation approximately have the same temperature. Especially for nitrogen plasmas, like the one in this work, the rotational temperature and gas temperature can be assumed to be equal [8-12].

1.2.4 Rate coefficients and energy efficiency

As mentioned before, especially vibrational excitation of molecules can greatly assist in running a chemical process. The underlying reason is that vibrational excitation reduces the threshold energy for dissociation of a molecule, as can be seen from figure 1.5. Since every chemical reaction is initiated by breaking of molecular bonds (i.e. dissociation) after which the available atoms are rearranged into new molecules, vibrational excitation reduces the activation energy for chemical reactions in general.

1\hspace{1em}5

Figure 1.5: Lowering the threshold energy for dissociation with vibrational excitation
The fact that vibrational excitation of molecules reduces the activation energy $E_a$, needed for inducing a chemical reaction, is reflected by the expression of the rate coefficient $k_R$ for elementary reactions [1, 4, 13]:

$$k_R(E_v, T_{\text{gas}}) = k_{R0} \cdot e^{-\left(\frac{E_a - \alpha E_v}{T_{\text{gas}}}\right)} \quad (1.7)$$

In this expression, $k_{R0}$ is the rate coefficient in case the activation energy would be zero and $\alpha$ is a coefficient, with a value between 0 and 1, that expresses how efficient vibrational excitation is in overcoming the activation barrier. Both depend on what specific reaction is looked at.

Equation 1.7 only holds when the effective activation energy $E_a - \alpha E_v \geq 0$. From this equation, it becomes clear that the rate coefficient for elementary reactions increases exponentially with the vibrational excitation of a molecule, as expected. Since the average vibrational energy is proportional to the vibrational temperature ($\bar{E}_v \propto T_{\text{vib}}$), the rate coefficient also increases exponentially with vibrational temperature. Equation 1.7 also predicts that the rate coefficient of elementary reactions increases with gas temperature. The reason is that at higher gas temperatures the molecules, present before the reaction, collide more often and with higher kinetic energies. The latter means that there is more (translational) energy available for overcoming the effective activation energy.

Regarding energy efficiency of a plasma chemical process, the increase of the rate coefficient for increasing temperatures (vibrational or translational) appears to be very promising. It is known, though, that high gas temperatures have a detrimental effect on the energy efficiency of a plasma chemical process, contrary to vibrational excitation, which is known to have a positive effect on energy efficiency [1, 4]. A possible explanation is that, for higher gas temperatures, the increase in rate coefficient is outweighed by the increase in loss of heat energy to the surroundings.

Since vibrational temperature and gas temperature play such an important role in plasma chemical processes, these two parameters have been investigated in this work.

### 1.3 Physical parameters

Besides vibrational temperature and gas temperature, also other physical parameters that are relevant to a dielectric-barrier discharge are investigated in this work, namely the rotational temperature, the reduced electric field, the specific energy input and the gap voltage.

Determining the rotational temperature of nitrogen molecules in a nitrogen plasma is by itself not crucial for this work. However, as mentioned before, in a high pressure, low (gas) temperature nitrogen plasma, the gas temperature can be assumed to be equal to the rotational temperature. Given the diagnostics, which will be treated later, measuring the gas temperature directly is not possible, while the rotational temperature can be determined directly relatively easy. Therefore, in this work the rotational temperature provides a credible value for the gas temperature. From this value of the gas temperature, a reliable estimate can be made for the neutral particle density in the nitrogen plasma, using the ideal gas law ($p = n k T_{\text{gas}}$). This estimate is necessary for determining the reduced electric field. This makes the rotational temperature (i.e. gas temperature) a crucial parameter in this work.

The reduced electric field is an important parameter for gas discharges in general, so also for the dielectric-barrier discharge. It is usually defined as the strength of the electric field,
divided by the neutral particle density \((\frac{E}{n})\). This is also the definition which is used for this work. In some literature however, the pressure is used in this definition instead of the neutral particle density \((\frac{E}{p})\). The reduced electric field determines whether breakdown of a gas occurs in a plasma and it determines the shape of the electron energy distribution function (EEDF). Since electronic, vibrational and rotational excited states of molecules in a plasma can be (and often mainly are) populated by electron impact, the fractions of the total power input, directed into these different channels of excitation, is determined by the reduced electric field \([1, 14, 15]\). Furthermore, also the fraction of power directed into ionization processes and the ionization degree is directly influenced by the reduced electric field \([14-16]\).

The specific energy input expresses how much energy is coupled into the plasma per (standard) liter of gas flowing through the reactor \((1 \text{ standard liter} = \text{one liter at standard pressure and temperature, containing approximately } 2.7 \cdot 10^{22} \text{ molecules})\). Thus, this parameter also determines the average energy a molecule absorbs during the time it spends in the reactor, which makes it an important physical parameter to know when investigating plasma chemical reactions.

The gap voltage is the electric potential difference across the discharge gap. It determines the acceleration of free electrons in the plasma and is therefore necessary for the electrical characterization of the gas discharge.

### 1.4 Research outline and aims

This work aims to shed light on three issues, namely optimization of rate coefficients and energy efficiencies for running a plasma chemical process in general \((1)\), understanding the physics behind the optimization process \((2)\) and exploring the possibilities of the diagnostics that have been used in this work, namely optical emission spectroscopy (OES) and current-voltage \((I-U)\) measurements \((3)\). Regarding the possibilities of the two diagnostics, a nitrogen plasma is used as a test bed in this work. Since no plasma chemical reactions of our interest take place in a pure nitrogen plasma, no specific plasma chemical reaction is addressed. In the remainder of this section, the three aims are explained further.

1) Since it is known that vibrational excitation and gas temperature influence rate coefficients and energy efficiencies of plasma chemical reactions, controlling these two parameters is important in order to find optimal windows of operation for running a plasma chemical process in a DBD reactor. Therefore, vibrational excitation and gas temperature are investigated as a function of several process variables in order to find operating conditions at which high rate coefficients and/or high energy efficiencies for running a plasma chemical process may be expected. Since no plasma chemical reaction of our interest takes place in a pure nitrogen plasma, the effect of vibrational excitation and gas temperature is considered for a hypothetical elementary reaction in a pure nitrogen plasma, using equation 1.7.
2) Optimal windows of operation for running a plasma chemical process are always reactor specific. In order to extrapolate optimal operating conditions to bigger reactors, which is necessary for industrial upscaling, a thorough understanding of the involved physics is required. In other words, it is necessary to understand why certain values of the process variables yield vibrational and gas temperatures that are beneficial for running a plasma chemical process at high rate coefficients or with high energy efficiencies. In order to achieve a better physical understanding, other relevant physical parameters for running a plasma chemical process in a DBD reactor, namely reduced electric field and specific energy input, have been investigated in order to observe their influence on, or at least correlation with, vibrational excitation. This information can be used to control vibrational excitation by tuning these physical parameters.

3) As mentioned before, optical emission spectroscopy (OES) and current-voltage ($I$-$U$) measurements have been used in this work for investigating a pure nitrogen plasma. Both diagnostics are relatively inexpensive, readily available and easy to implement. For this reason, it is interesting to explore the possibilities of OES and $I$-$U$ measurements in order to see what can be done with these two diagnostics before one would have to resort to more expensive or more complicated diagnostics. Especially when investigating a nitrogen plasma, OES and $I$-$U$ measurements can provide much information on physical parameters concerning the plasma or the discharge characteristics. Several reasons are that a nitrogen plasma has bright emission lines in or near the optical spectral range and that much is already known about nitrogen plasmas, making it easier, or even possible at all, to determine crucial physical parameters like gas temperature or the reduced electric field. By achieving aim (1) and (2), already many possibilities of OES and $I$-$U$ measurements are featured. Beside these possibilities, $I$-$U$ measurements have also been used to conduct a thorough (electrical) characterization of the gas discharge. From this characterization, two different methods for determining the gap voltage are compared. Furthermore, a method for determining the reduced electric field with OES is compared with a method using $I$-$U$ measurements.

The three aims above conclude the introduction into this work. In the next chapter, more information is provided on the plasma chemical reactor which is used in this work, the dielectric-barrier discharge. The two diagnostics that are used for investigating the nitrogen plasma, optical emission spectroscopy and current-voltage measurements, are also treated into more detail. Chapter 3 starts with research questions concerning the characterization of a nitrogen DBD, being part of issue (3), after which corresponding results and their interpretation are treated. Chapter 4 deals likewise with issues (1) and (2). This work will conclude with a short summary, recommendations and an outlook onto possible future research in chapter 5.
Chapter 2  Experimental setup

In this chapter, details concerning the experimental setup are provided. The first section describes the plasma reactor which is used for this work, a dielectric-barrier discharge (DBD), along with extra information on its operation and extra theory on DBDs that are relevant for this work. The second and third section treat the two diagnostics which are used in this work, optical emission spectroscopy and current-voltage measurements, respectively. In each section, first the experimental configuration of the diagnostics is described, along with relevant details on the data acquisition. After this description, both sections end with basic theory behind these two diagnostics, which is necessary for interpreting the acquired data.

2.1  The dielectric-barrier discharge

The dielectric-barrier discharge (DBD) is a special type of a capacitively coupled discharge, which means that the discharge cell acts as a capacitive load within the electrical circuit (matching network) that is used for applying a voltage to the discharge cell. In capacitively coupled discharges, a plasma is usually created by applying a large voltage over a gas which flows between two electrodes, of which one is often grounded. A plasma is a partially ionized gas, thus containing not only neutral particles (molecules and/or atoms), but also ions, free electrons, radicals and various energetic excited species [1].

Mainly because of cosmic radiation and radioactive elements in nearby building materials (e.g. K-40 in walls), a small amount of free electrons is always present in a gas. This phenomenon is called background ionization [17]. Due to background ionization, breakdown of a gas can occur when the voltage over the gas, and thus the (reduced) electric field, is above a certain level. This level is called the breakdown voltage. During breakdown, the initially present free electrons collide with neutral particles, causing these neutral particles (atoms or molecules) to be ionized. Since every ionization yields one more free electron, an electron avalanche is initiated [1]. This electron avalanche is the beginning of a gas discharge, which will spread very quickly through the whole region in which the (reduced) electric field is above breakdown level, thus transforming the gas into a plasma. This event is often called ignition of the plasma.

What distinguishes a DBD from other capacitively coupled discharges, is that one or two dielectric layers are present between the electrodes. Several configurations are treated in reference [5]. In this work, a symmetrical DBD configuration is used in which both parallel plated electrodes (7.88±0.05 cm² area, roughly 4 times longer than wide), of which one is grounded, are covered with a dielectric layer (2.00±0.05 mm thickness), made of quartz, as can be seen in figure 2.1. Conveniently, the quartz barriers are part of the quartz flow tube, which is cooled during operation by a cooling fan, mainly to avoid excessive heating of electrical connections. Between the dielectric barriers, a discharge gap (0.90±0.05 mm width) exists. In this discharge gap, the nitrogen plasma is created with its characteristic violet glow. The discharge cell in this work is driven by a sinusoidal voltage, applied to the high voltage (HV) electrode, which means that figure 2.1 only depicts the situation during the half cycle in which the high voltage electrode is positively charged and the ground electrode negatively charged. This situation is the starting point for all calculations and expressions that follow, but these are also valid for the opposite situation. The amplitude of the applied voltage is varied in the range of 2-20 kV pk-pk (peak to peak amplitude), determined by the minimal value at which the plasma can be sustained (at lowest operating pressure) and the maximal value necessary to avoid
parasitic discharges to other parts of the setup, or anomalous behaviour of a DBD (e.g. plasma expansion into the exhaust or inlet tube). The operating frequency cannot be varied, at least not independently, since it must always be very close to the resonance frequency of the matching network, which is around 130 kHz (see Appendix B). Only when operating at resonance frequency, the used power source (ENI Power Systems inc., Plasmaloc 1-HF) can deliver the required power in order to achieve the applied voltage amplitude that is necessary to sustain the plasma. However, the resonance frequency depends slightly on the amplitude of the applied voltage, since the amplitude determines the heating up of several electrical components in the matching network. Therefore, the resonance frequency, and thus also the operating frequency, is in the range of 124-141 kHz, increasing with the amplitude of the applied voltage. Even though amplitude and frequency cannot be varied independently, the assumption in this work is that changing the amplitude of the applied voltage by a factor of ten has a more significant influence on the parameters of interest in this work (e.g. vibrational temperature) than changing the operating frequency by less than 20%. For this reason, the applied voltage amplitude is regarded as one of the independent process variables that can be controlled in this work, while the operating frequency is regarded as a process variable that cannot be controlled and that is roughly constant. The applied voltage is measured via a voltage divider (see Appendix B) by a voltage probe (TESTEC, 100:1, 2500 Vp) that is connected to an oscilloscope (Agilent DSO5034A, 300 MHz bandwidth, 1 MΩ input impedance).

![Discharge cell schematic](image)

*Figure 2.1: Schematic representation of the discharge cell, used for this work*

Other independent process variables that are controlled in this work are the flow rate of nitrogen flowing through the discharge cell, ranging 0.010-3.000 standard liters per minute (sl/m), and the pressure in the reactor, ranging 20-600 mbar. The flow rate is controlled by a mass flow controller (MFC, Bronkhorst High-Tech, 0.020-3.000 sl/m or 0-100 scc/m, 5 bar, 20° C calibrated), while the pressure can be set by controlling the amount to which the variable valve of the exhaust pump (Pfeiffer vacuum, DUO10, 10 m³/h, nitrogen calibrated) is opened or closed (0-1250 mbar l/s), in conjunction with the chosen flow rate. The pressure is measured in the exhaust of the reactor by a pressure sensor (MKS instruments inc., Baratron, 1 mV/mbar, 0-10 bar, offset around -20 mV), connected to a multimeter (TENMA 72-7770).
2.1.1 Charge accumulation

After a gas discharge in a DBD reactor is initiated, the electric field between the electrodes $E_{el}$ forces the free electrons to move towards the anode. However, since both electrodes are covered by a quartz dielectric barrier, the free electrons accumulate at the surface of the anode barrier [2, 18, 19], creating a negatively charged region in which more electrons than ions are present, as can be seen in figure 2.2. At the surface of the cathode barrier, a positively charged region is created where less electrons than ions are present (this does not necessarily mean that ions are actively moving towards the cathode barrier, though [19]). This phenomenon, often called charge accumulation [2], has a large influence on the development of the gas discharge and it accounts for most differences between a dielectric-barrier discharge and similar discharges that do not include dielectric barriers.

The separation of charge within the plasma, caused by charge accumulation, generates an additional electric field $E_{acc}$, counteracting the ‘external’ field $E_{el}$, which reduces the effective electric field (superposition of $E_{el}$ and $E_{acc}$) compared to the case without dielectric barriers [2, 18, 20]. Thus, the discharge current limits itself (negative feedback), often called ‘choking’ [2, 18], which prevents the glow discharge [1] of a DBD from evolving into an arc discharge [1, 20]. Since arc discharges yield thermal plasmas at near atmospheric pressures [1], which are less suitable for inducing or assisting plasma chemical reactions [1], the presence of dielectric barriers in conjunction with the phenomenon of charge accumulation is crucial for the purpose of this work.

![Diagram of charge accumulation in a DBD discharge](image)

*Figure 2.2: Charge accumulation in a symmetric dielectric-barrier discharge (exaggerated width of discharge gap relative to thickness of quartz barriers)*

The description above of charge accumulation in a DBD and the schematic representation in figure 2.2 are both rather crude. A more refined description will be provided later, when needed.

2.1.2 Simplest equivalent circuit

Since Manley in 1943 [21], much work has been done on the electrical characterization of the dielectric-barrier discharge. This has led to a better understanding of the electrical properties of the discharge cell. As mentioned before, the discharge cell of a DBD reactor acts as a capacitive load within the bigger electrical circuit that is used. This description can be refined, however, as
can be seen in figure 2.3 on the left, which depicts the simplest equivalent circuit for a dielectric barrier discharge [22, 23]. The charge of the HV and grounded electrode are also indicated.

\[ C_{\text{quartz}} = \frac{\varepsilon_{\text{quartz}} A}{d_{\text{quartz}}} \]  

(2.1)

The discharge gap can be represented by two parallel branches: one branch containing an ideal capacitor which represents the capacitance \( C_{\text{gap}} \) of the nitrogen in the discharge gap, the other branch containing an ideal resistor which represents the resistance \( R \) that the discharge current encounters during the gas discharge. No simple expression exists for this resistance and it is not constant in time. An expression for the capacitance of the discharge gap, henceforth referred to as the gap capacitance, can be found analogous to that of the quartz barriers, using instead the dielectric constant of nitrogen \( \varepsilon_{\text{nitrogen}} \) and the width of the discharge gap \( d_{\text{gap}} \):

\[ C_{\text{gap}} = \frac{\varepsilon_{\text{nitrogen}} A}{d_{\text{gap}}} \]  

(2.2)

The switch represents the fact that there is not always a discharge current flowing through the plasma, even after ignition of the plasma, when the DBD is in operation. During every half cycle of the applied sinusoidal voltage, a so called discharge phase and dark phase occur, which will be explained into more detail later in subsections 2.1.3 and 2.3.2. For convenience, the capacitances of the quartz barriers \( C_{\text{quartz}} \), henceforth referred to as the quartz capacitance, are often combined into one total capacitance \( C_{\text{die}} \) for the dielectric barriers (see figure 2.3 on the right), henceforth referred to as the dielectric capacitance, following the rules for combining capacitances that are connected in series:

\[ \frac{1}{C_{\text{die}}} = \frac{1}{C_{\text{quartz}}} + \frac{1}{C_{\text{quartz}}} = \frac{2}{C_{\text{quartz}}} \]  

(2.3)

\[ C_{\text{die}} = \frac{C_{\text{quartz}}}{2} \]  

(2.4)
Regarding the simplest equivalent circuit for a DBD, depicted in figure 2.3, the applied voltage $U$ is divided over the equal quartz barriers and the discharge gap:

$$U = U_{\text{quartz}} + U_{\text{gap}} + U_{\text{quartz}}$$  \hspace{1cm} (2.5)

$$U = U_{\text{diel}} + U_{\text{gap}}$$  \hspace{1cm} (2.6)

$U_{\text{diel}}$ represents the total voltage across both quartz barriers:

$$U_{\text{diel}} = 2 \cdot U_{\text{quartz}}$$  \hspace{1cm} (2.7)

The voltage across the quartz barriers $U_{\text{quartz}}$ and the charge $Q$ on the electrodes are related as follows:

$$Q = C_{\text{quartz}} \cdot U_{\text{quartz}}$$  \hspace{1cm} (2.8)

An analogous expression holds for the total voltage across both quartz barriers $U_{\text{diel}}$:

$$Q = C_{\text{diel}} \cdot U_{\text{diel}}$$  \hspace{1cm} (2.9)

For the voltage across the discharge gap, henceforth called the gap voltage, such a relation with the charge on the electrodes does not exist. It can only be calculated from equation 2.5 or 2.6, when the (total) voltage across the quartz barriers is known.

### 2.1.3 Gap voltage

The evolution over time of the gap voltage in a DBD, during one half cycle of the sinusoidal applied voltage, is often depicted as in figure 2.4. According to this depiction, before breakdown, during the so called dark phase, the value of the gap voltage is equal to that of the applied voltage. At first breakdown, a sudden transfer of charge occurs within the discharge gap, leading to charge accumulation at the dielectric barriers. This causes the gap voltage to decrease suddenly, deviating from the applied voltage. After first breakdown, the gap voltage oscillates around a certain value, slightly lower than the breakdown voltage of the gas, until the so called discharge phase ends, usually when the applied voltage reaches its maximal value [2]. The value around which the gap voltage oscillates, can be regarded as the average gap voltage during the discharge phase ($U_{\text{gap discharge}}$). The oscillation can be explained from the following consideration: after the initial decrease of the gap voltage, due to the initial breakdown of the gas, the discharge current is choked because of charge accumulation [24]. Since the external voltage (i.e. the applied voltage) is still increasing, the gap voltage will also increase until the breakdown voltage of the gas is reached again. This scenario repeats itself until the maximal value of the applied voltage is reached. From that moment on, the discharge phase ends since the applied voltage cannot push the gap voltage above breakdown value anymore. Because of this mechanism, interestingly, it is the ‘swing’ (or rise rate [25]) of the applied voltage, not the magnitude, that determines the intensity of the gas discharge. In this work, the ‘swing’ of the applied voltage $U$ is defined as its time derivative:

$$U(t) = U_{\max} \sin(\omega t)$$  \hspace{1cm} (2.10)

$$\frac{du}{dt} = U_{\max} \omega \cos(\omega t)$$  \hspace{1cm} (2.11)
In this expression, $U_{\text{max}}$ is the amplitude and $\omega$ is the angular frequency of the applied voltage. Thus, both amplitude and frequency influence the rise rate of the applied voltage. The magnitude of the applied voltage is only important during the dark phase, in order for the gap voltage to reach breakdown value in the first place. However, once the discharge phase has started, only the rise rate of the applied voltage is of relevance.

The oscillation of the gap voltage during the discharge phase is usually too small to be observed. Therefore, according to classical electrical theory for sinusoidal driven ozonizers [22, 23], the gap voltage during the discharge phase can be assumed to be equal to the breakdown voltage $U_{BD}$ of the gas: $(U_{\text{gap}})_{\text{discharge}} = U_{BD}$

![Breakdown voltage](image)

*Figure 2.4: Common depiction of gap voltage as a function of time (red) during one half cycle of the applied voltage (black) [24]*

2.1.4 Process variables revised
As mentioned earlier in this section, three independent process variables are controlled in this work, namely applied voltage amplitude (2-20 kV_{pk-pk}), pressure (20-600 mbar) and flow rate (0.010-3.000 sl/m). The parameters of interest in this work (e.g. vibrational temperature or reduced electric field) have been investigated as a function of these three process variables. In the measurement series, performed for this work, two of these process variables are kept constant while only one is varied during the series. In this work, a measurement series is named after the process variable that is changing. For instance, a measurement series in which pressure and flow rate are kept constant while the applied voltage amplitude is changed, is called an amplitude series (or applied voltage amplitude series).

In the remainder of this work, however, the process variable flow rate is replaced by the physically more relevant process variable residence time, which is in the range of 1-1000 ms:

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Process variables</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplitude applied voltage</td>
<td>Amplitude applied voltage</td>
</tr>
<tr>
<td>Pressure</td>
<td>Pressure</td>
</tr>
<tr>
<td>Flow rate</td>
<td>Residence time</td>
</tr>
</tbody>
</table>

The residence time $\tau_{\text{res}}$ expresses the period of time a molecule on average spends in the active volume between the electrodes. It can be calculated by dividing the active volume $V_{\text{act}}$ (0.71±0.05 cm$^3$) by the flow rate $\phi$. However, since the flow rate is usually given for standard conditions ($\phi_0$), standard liter per minute in this work, it needs to be corrected for the fact that
standard pressure $p_0$ (1013 mbar) and (gas) temperature $T_{gas0}$ (293.15 K) do not necessarily apply in the active volume:

$$\tau_{res} = \frac{V_{act} \cdot p \cdot \tau_{gas0}}{\phi_0 \cdot p_0 \cdot \tau_{gas}}$$

(2.12)

In this work, especially the reactor pressure can be far away from standard pressure, at most a factor of 50 smaller. The gas temperature in the active volume, on the other hand, is usually relatively close to standard temperature, but always higher, at most a factor of 2.4. The residence time is kept constant during a pressure or applied voltage amplitude series by keeping the ratio between pressure $p$ and (standard) flow rate $\phi_0$ constant. The effect of gas temperature on the residence time is ignored beforehand, since it is only measured afterwards in this work. After data analysis, the residence time is corrected for the fact that the gas temperature also changes during a pressure or applied voltage amplitude series, by filling in the determined values of the gas temperature into equation 2.12. Following this procedure means that the residence time is not perfectly constant during a pressure or applied voltage amplitude series, which might cause residence time to have a parasitic effect on the physical parameters of interest (e.g. vibrational temperature or reduced electric field) during both series. However, the gas temperature, and thus residence time, is changing only by approximately 20% during the applied voltage amplitude series and approximately 70% during the pressure series (see section 4.1), while these process variables themselves change by a factor of 10 and 30, respectively, as a function of these process variables. Therefore, the parasitic effect of residence time is assumed to be negligible compared to the effect of both process variables themselves. In chapter 4, further justification for this assumption is provided, based on the determined values for all physical parameters of interest in this work.

The choice for residence time as a third process variable, instead of flow rate, is mainly motivated by the interpretation of results from a pressure series. With the original set of process variables, changing the pressure by a factor of 30, while keeping the flow rate constant, causes the residence time to also change significantly (see equation 2.12). This would be undesirable in this work, since two relevant physical parameters, pressure and residence time, would both be changing strongly during the pressure series. In that case, the effect of pressure and the effect of residence time on the physical parameters of interest (e.g. vibrational temperature or reduced electric field) can never be disentangled. In other words, during a pressure series one has to choose whether to keep flow rate or residence time constant (see equation 2.12). In this work, residence time is considered to be a more relevant physical parameter than flow rate. The latter is considered more as a system parameter.

### 2.2 Optical emission spectroscopy

Optical emission spectroscopy (OES) measures radiation from the visible part of the electromagnetic spectrum (i.e. visible light), caused by electronic transitions. In this work, the emission accompanying electronic relaxation of the nitrogen molecule and molecular ion is measured. The collected spectra contain information about, amongst others, vibrational excitation, rotational excitation and the reduced electric field, as will be explained later in this section. Thus, OES is used in this work for determining these physical parameters of interest.
2.2.1 Experimental configuration and data acquisition

An optical system with two positive lenses is used for collecting the light from the nitrogen plasma and for focusing it onto an optical fiber, as can be seen in the schematic representation in figure 2.5 (compare with figure 1.1 in section 1.1). The first lens the light encounters has a focal length of 180 mm, equal to the distance from the plasma, leading to a parallel beam of light in between the two lenses that are 35 mm apart (all dimensions are approximate). The second lens has a focal length of 49 mm, equal to the distance from the entrance of the optical fiber, so the beam of light is optimally focused on the optical fiber. The optical fiber transfers the light to a spectrograph (Avantes, 0.1-0.3 nm FHWM) which processes the light into an optical spectrum. Via a USB connection, the spectral information is transferred to a computer with Avantes software (Avasoft). This software shows the real-time measured spectrum of the light coming from the plasma and enables saving the spectral information.

For each operating condition, one spectrum at low integration time (22-800 ms, depending on the operating condition) and one spectrum at high integration time (400-20000 ms, also depending on the operating condition) is collected. The spectrum at low integration time is collected in order to determine the gas temperature while the spectrum at high integration time is collected in order to determine the vibrational temperature and reduced electric field. The integration time is chosen such that the emission peaks of interest (see Appendix C), necessary for determining the mentioned parameters, have a high spectrographic intensity, but do not yet saturate the detector.

![Figure 2.5: The optical system and data transfer, used for collecting and processing the optical emission from the nitrogen plasma](image-url)

The measured spectra, obtained by the spectrographic software, are wavelength calibrated. A relative intensity calibration is also performed (see Appendix I), which corrects for wavelength dependent transmission of light through the optical system and for wavelength dependent response of the spectrograph. The corresponding calibration function is used for processing the measured spectra, though this is not crucial for this work, since the emission peaks, necessary for determining a physical parameter of interest (e.g. vibrational temperature), are always close to each other. No absolute intensity calibration is performed, since it is not necessary for the purpose of this work.
2.2.2 Optical emission

Most optical emission in the nitrogen plasma under investigation originates from electronic transitions in the N$_2$ molecule or molecular ion (N$_2^+$). Therefore, in order to interpret an optical spectrum, it is helpful to have a look at the electronic potential energy scheme of the nitrogen molecule and molecular ion. This scheme is depicted in figure 2.6, which shows the electronic potential energy of several discrete electronic states of the molecule and molecular ion as a function of the distance between the two nitrogen nuclei. These potential curves show a minimum at a certain internuclear distance. For that reason, they are often called potential wells. Closely around the minimum, the potential well somewhat resembles a harmonic oscillator (parabola shaped potential well). However, at shorter internuclear distances, the Coulombic repulsion amongst the electrons increases exponentially. At longer internuclear distances, the potential well behaves asymptotic. This asymptote corresponds to the dissociation energy of a molecule in that particular electronic state. When the electronic potential energy is equal to the dissociation energy, the internuclear distance will become infinite (i.e. the molecule or molecular ion will dissociate). Because of their shape, these potential wells are called anharmonic oscillators. The simplest approximation of the potential well of a real molecule (e.g. nitrogen) is the Morse potential energy function [27, 28], which can be written in the following form:

$$V(r) = D_e \left(1 - e^{-a(r-r_e)}\right)^2$$  \hspace{1cm} (2.13)

In this expression, $V$ is the electronic potential energy, having the minimum of the potential well as a reference level, $r$ is the internuclear distance, $r_e$ is the equilibrium internuclear distance (minimal potential energy) and $a$ is a parameter that determines how broad or narrow the potential well is. The potential wells for all molecules are anharmonic oscillators, so nitrogen is in that sense no special case.

![Figure 2.6: The energy scheme of the nitrogen molecule and molecular ion [26]](image-url)
In this work, all observable optical emission from the N\textsubscript{2} molecule originates from the transition of the third to second excited electronic state of the molecule, also respectively known as the C-state and the B-state. The corresponding configurations of the molecular orbitals are \textsuperscript{3}Π\texttextsubscript{u} and \textsuperscript{3}Π\texttextsubscript{g}, respectively. Even though this is just one electronic transition, a typical optical spectrum of a nitrogen plasma, like the one in figure 2.7, shows multiple emission peaks that originate from the N\textsubscript{2} molecule. This multitude of peaks can be explained from the energy scheme of the nitrogen molecule: on top of the electronic states, which are widely spaced in potential energy, also discrete vibrational states exist. This substructure of vibrational levels, which are more narrowly spaced in potential energy, is indicated by horizontal stripes. The potential energies of the different vibrational states follow from solving the Schrödinger wave equation for the given potential well (see Appendix A). Vibrational states are expressed with their corresponding vibrational quantum number \( \nu \) (Greek small letter ‘upsilon’). Thus, \( \nu = 0 \) represents the vibrational ground state, \( \nu = 1 \) represents the first excited vibrational state, etc. On top of the electronic structure and vibrational substructure, an even more narrowly spaced sub-substructure of rotational states exists. These are not indicated in figure 2.6 since their spacing is too small to show. If a Boltzmann distribution over the excited vibrational and rotational levels can be assumed, the vibrational and rotational temperature determine the relative populations of these levels. Because of these vibrational and rotational (sub-)substructures, multiple transitions are possible that belong to the same electronic transition (C-state to B-state). The large collection of emission peaks above 290 nm (approximately) almost all originate from the earlier mentioned transition from the third to second excited electronic state of the N\textsubscript{2} molecule, differing only in their initial and final vibrational state. An overview of several of the bigger peaks in the spectrum and the corresponding transitions is given in table 2.1. These peaks all correspond to a different change in vibrational quantum number \( \Delta \nu \). In this work, \( \Delta \nu \) is defined as the quantum number of the final vibrational state minus the quantum number of the initial vibrational state:

\[
\Delta \nu = \nu_f - \nu_i
\]  

(2.14)

\[\text{Figure 2.7: A typical optical spectrum of the nitrogen plasma under investigation}\]
Table 2.1: Responsible transitions for several emission peaks [29]

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Corresponding transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>337.13</td>
<td>( \text{N}_2 (C^3 \Pi_u ; \nu=0 \rightarrow B^3 \Pi_g ; \nu=0) )</td>
</tr>
<tr>
<td>357.69</td>
<td>( \text{N}_2 (C^3 \Pi_u ; \nu=0 \rightarrow B^3 \Pi_g ; \nu=1) )</td>
</tr>
<tr>
<td>380.49</td>
<td>( \text{N}_2 (C^3 \Pi_u ; \nu=0 \rightarrow B^3 \Pi_g ; \nu=2) )</td>
</tr>
<tr>
<td>405.94</td>
<td>( \text{N}_2 (C^3 \Pi_u ; \nu=0 \rightarrow B^3 \Pi_g ; \nu=3) )</td>
</tr>
<tr>
<td>434.36</td>
<td>( \text{N}_2 (C^3 \Pi_u ; \nu=0 \rightarrow B^3 \Pi_g ; \nu=4) )</td>
</tr>
<tr>
<td>315.93</td>
<td>( \text{N}_2 (C^3 \Pi_u ; \nu=1 \rightarrow B^3 \Pi_g ; \nu=0) )</td>
</tr>
<tr>
<td>297.68</td>
<td>( \text{N}_2 (C^3 \Pi_u ; \nu=2 \rightarrow B^3 \Pi_g ; \nu=0) )</td>
</tr>
</tbody>
</table>

Besides these bigger peaks, one can also see smaller peaks left of them (at lower wavelengths). The optical spectrum seems to be built up out of a sequence of peak sets, each peak set containing bigger and smaller peaks. Zooming in on one of these sets leads to the zoomed in view of figure 2.8. The emission peaks, belonging to one set, have in common that they originate from transitions with the same change in vibrational quantum number, as can be seen from table 2.2. In this case, \( \Delta \nu=3 \). If the potential wells of the C-state and B-state of the \( \text{N}_2 \) molecule would be identical, these peaks would all be at the same wavelength. Since this is not the case, these transitions are separately visible in the spectrum, which makes the vibrational temperature analysis much more convenient.

The peak at 391.44 nm is not mentioned in table 2.2, since it does not belong to the \( \Delta \nu=3 \) peak set. It does not originate from emission of the \( \text{N}_2 \) molecule at all, but from the \( \text{N}_2^+ \) molecular ion. To be more precise, the transition from the vibrational ground state in the second excited electronic state to the vibrational ground state in the electronic ground state (X-state):

\[ \text{N}_2^+ (B^2 \Sigma_u^+ ; \nu=0 \rightarrow X^2 \Sigma_g^+ ; \nu=0) \] [29]. This transition causes the most dominant \( \text{N}_2^+ \) emission peak. Contrary to other \( \text{N}_2^+ \) emission peaks, it is always clearly visible in the spectrum, regardless of the process variables. It is the only \( \text{N}_2^+ \) peak which is used for the data analysis in this work.

![Figure 2.8: A zoomed in part of the optical spectrum of the nitrogen plasma, showing one set of peaks](image)
Table 2.2: Responsible transitions for emission peaks in the \( \Delta \nu=3 \) peak set [29]

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Corresponding transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>405.94</td>
<td>( \text{N}_2(\text{C}^3\Pi_u; \nu=0 \rightarrow \text{B}^3\Pi_g; \nu=3) )</td>
</tr>
<tr>
<td>399.84</td>
<td>( \text{N}_2(\text{C}^3\Pi_u; \nu=1 \rightarrow \text{B}^3\Pi_g; \nu=4) )</td>
</tr>
<tr>
<td>394.30</td>
<td>( \text{N}_2(\text{C}^3\Pi_u; \nu=2 \rightarrow \text{B}^3\Pi_g; \nu=5) )</td>
</tr>
<tr>
<td>389.46</td>
<td>( \text{N}_2(\text{C}^3\Pi_u; \nu=3 \rightarrow \text{B}^3\Pi_g; \nu=6) )</td>
</tr>
<tr>
<td>385.79</td>
<td>( \text{N}_2(\text{C}^3\Pi_u; \nu=4 \rightarrow \text{B}^3\Pi_g; \nu=7) )</td>
</tr>
</tbody>
</table>

Since the discrete rotational levels are so narrowly spaced, the rotational sub-substructure does not lead to more distinguishable emission peaks because of broadening of emission lines (e.g. thermal Doppler broadening) in combination with a limited resolution of the detector. Rotational excitation does influence the shape of an emission peak however. This phenomenon is used for the rotational temperature analysis.

As mentioned before, OES is used to determine the rotational temperature (gas temperature), the vibrational temperature and the reduced electric field. More details on the data analysis concerning these three plasma parameters are given in Appendix C.

2.3 Current-voltage measurements

In this work, current-voltage \((I-U)\) measurements are performed in order to determine the specific energy input, the reduced electric field, the dielectric capacitance, the gap capacitance, the average gap voltage during the discharge phase and the gap voltage as a function of time during one or more AC cycles.

2.3.1 Experimental configuration and data acquisition

The sinusoidal voltage \(U\), applied to the high voltage (HV) electrode, and the current \(I\) from the discharge cell to the ground are measured, as can be seen in figure 2.9. Since most voltage probes, including the one used in this work, cannot cope with voltages as high as the voltage on the HV electrode, the applied voltage is measured via a voltage divider, as mentioned before. Therefore, figure 2.9 only provides a simplified picture of the \(I-U\) measurement. The current is measured as depicted, though. A full electrical circuit, including matching network and voltage divider can be found in Appendix B.

Both the voltage probe (TESTEC, 100:1, 2500 V\(_p\)) and the current probe (Pearson current monitor, Rogowski coil type, model 4100, 1 V/A) are connected to the same oscilloscope (Agilent DSO5034A, 300 MHz bandwidth, respectively 1 M\(\Omega\) and 50 \(\Omega\) input impedance) which is able to save both signals.
2.3.2 Applied voltage and current

As mentioned before, a plasma generated with a dielectric-barrier discharge setup can only be operated with an alternating voltage (AC, RF or pulsed DC), unlike similar discharges without dielectric barriers, of which some can also be DC operated. This can be explained from the fact that, because of the dielectric barriers, free electrons cannot be transferred from cathode to plasma and from plasma to anode, but accumulate at the surface of the dielectric barriers (see subsection 2.1.1). Since one cannot extract free electrons from a plasma indefinitely, a DC discharge cannot be sustained in a DBD. Despite of this very hard limit, another mechanism extinguishes a DC discharge in a DBD long before charge depletion would do so. As mentioned in subsection 2.1.3, after charge accumulation has quenched the initial discharge, a ‘swing’ in the applied voltage is necessary to push the gap voltage above its breakdown value again. When the DBD is DC operated, there is no ‘swing’ in the applied voltage, so the discharge would extinguish immediately after first breakdown.

In this work, the DBD setup is AC operated. As mentioned before, the applied voltage alternates in time as a sinusoidal function with a frequency of approximately 130 kHz, as depicted in figure 2.10. The applied voltage is distributed over the quartz dielectric barriers and the discharge gap, which contains nitrogen (see subsection 2.1.2). When the gap voltage is above breakdown value, breakdown of the nitrogen occurs. The breakdown voltage depends on the gas (nitrogen), the width of the discharge gap (0.90±0.05 mm) and the pressure in the reactor (20-600 mbar) [1, 5]. The voltage over the quartz barriers is never high enough to cause breakdown in the quartz.

After ignition of the plasma, the current in series with the discharge cell typically looks like the one in figure 2.10 for operation at near atmospheric pressures. One can easily recognize the sinusoidal displacement current, phase shifted by a quarter of a period with respect to the applied voltage.
voltage, that is characteristic to an ideal capacitor. However, a discharge cell is not an ideal capacitor. In every half cycle, a discharge phase can be identified in which discharge events, often called microdischarges [40-45], can be seen as spikes on the signal. Every spike represents either a single microdischarge or a set of microdischarges occurring at the same time, but at different locations in the reactor. Peculiar is that most microdischarges occur during two ‘bursts’ every half cycle, since regular AC operation of a DBD usually assumes only one discharge phase (one burst) every half cycle [2]. The first burst occurs right after the initial breakdown. After this first burst, the intensity of the discharges diminishes and the discharge phase seems to be interrupted until a second burst occurs. This second burst is less intense, because the ‘swing’ of the applied voltage is smaller (see subsection 2.1.3). Further investigation into the origin of this double burst behaviour is required as our research group has found it to be a more general phenomenon, occurring for various operating conditions and for several gasses, both atomic and molecular.

![Figure 2.10](image)

**Figure 2.10:** Applied voltage and current from discharge cell to ground as a function of time at $2U_{max}=18.5\pm0.2 \text{ kV}_{pk-pk}$, $p=600\pm5 \text{ mbar}$ and $\tau_{res}=36\pm3 \text{ ms}$

At lower pressures, typically below 100 mbar, the discharge current becomes more homogeneous, as can be seen from figure 2.11. The microdischarges have decreased in intensity, but the amount of microdischarges per time increased, so they cannot be identified separately anymore. Furthermore, the ‘double burst’ pattern within one discharge phase is not visible anymore. This may be explained from the fact that the breakdown voltage is lower [1, 5] at lower pressures, which means that the discharge phase is not as easily interrupted like for higher pressures.
In order to process voltage and current signals, like the ones depicted above, into quantities like specific energy input and reduced electric field, it is helpful to convert these signals into Lissajous figures. A Lissajous figure is a graph which contains the applied voltage on the X-axis and the charge of the electrodes on the Y-axis (see figure 2.12) [18], which is why it is also often called a charge-voltage plot (Q-V or Q-U plot) [22]. Every point on the Lissajous figure represents a moment in time. Thus, a Lissajous figure describes the evolution of charge and applied voltage during one or more AC cycles. The direction is always counterclockwise [18, 23].
According to classical electrical theory for sinusoidal driven ozonizers [22, 23], henceforth named CETSDO, a Lissajous figure looks like a perfect parallelogram. The two steeper parts represent the two discharge phases during an AC cycle, while the two less steep parts represent the two so-called ‘dark phases’. The difference in steepness arises from the fact that the capacitive load of the discharge cell differs between the dark phase and the discharge phase (see Appendix J). In large scale or industrial setups using air or nitrogen, the Lissajous figures usually closely resemble a parallelogram. In small scale setups using air or nitrogen, like the one in this work, the Lissajous figure only closely resembles a parallelogram when operating at low pressures.

Besides from being helpful tools in determining quantities like specific energy input or gap voltage, Lissajous figures are also very insightful in their own right. They can reveal information that the raw voltage and current signals cannot reveal, or at least not as easily. Amongst others, the shape of the Lissajous figure reveals information on the length and steadiness of the discharge phase, its similarity to CETSDO and the stability of the plasma. Figure 2.12, for instance, represents a stable plasma (strong overlap between successive cycles) which obeys CETSDO very well (parallelogram shape). The discharge phase is long and steady. Figure 2.13 on the other hand, shows the Lissajous figure of a plasma which is also stable, but agrees less with CETSDO and has a shorter discharge phase. Furthermore, the steep parts, representing the discharge phase, bend twice. One time outward, becoming less steep, and one time inward, becoming steeper. This corresponds with the double burst behaviour during the discharge phase, already observed in figure 2.10. The first bend reflects the diminishing of the first burst and the second bend reflects the beginning of the second burst. Figure 2.14 represents a plasma which is not stable at all (successive cycles overlap poorly) and has an even shorter discharge phase. The discharge phase is strong in the beginning, but diminishes rapidly until the steepness is almost equal to that of the dark phase. This discharge agrees poorly with CETSDO and is often seen in this work when close to the extinguishing point of the plasma, when the amplitude of the applied voltage is too low to sustain a stable discharge at a certain pressure. In Appendix J, more details are provided on how Lissajous figures are constructed from the raw data (i.e. the current-voltage measurement).

As mentioned before, current-voltage measurements are used to determine the specific energy input, the reduced electric field, the dielectric capacitance, the gap capacitance, the average gap voltage during the discharge phase and the gap voltage as a function of time. More information on the data analysis concerning these (plasma) parameters is also provided in Appendix J.
Figure 2.13: Lissajous figure (13 full cycles) 
at $2U_{\text{max}}=18.5\pm0.2$ kV$_{\text{pk-pk}}$, $p=600\pm5$ mbar and $\tau_{\text{res}}=36\pm3$ ms

Figure 2.14: Lissajous figure (12 full cycles) 
at $2U_{\text{max}}=3.1\pm0.2$ kV$_{\text{pk-pk}}$, $p=20\pm2$ mbar and $\tau_{\text{res}}=32\pm2$ ms
Chapter 3  Characterization of a nitrogen DBD

As mentioned in the introduction, this work is concerned with three issues:

1) Optimization of rate coefficients and energy efficiencies for running a plasma chemical process in general
2) Understanding the physics behind the optimization process
3) Exploring the possibilities of the diagnostics that have been used in this work

This chapter is concerned with the last issue, while chapter 4 mainly takes a closer look at issues (1) and (2). Recapitulating from the introduction: the two diagnostics that have been used in this work, optical emission spectroscopy (OES) and current-voltage (I-U) measurements, are relatively inexpensive, readily available and easy to implement. Therefore, it is interesting to see how much information these diagnostics can provide, before considering more expensive or complicated diagnostics. Especially I-U measurements can be used for much more than is necessary in order to treat issues (1) and (2). This chapter aims to provide an overview of the results of all proceedings concerning the (electrical) characterization of the nitrogen dielectric-barrier discharge (DBD).

In the first section, a comparison is made between theoretically calculated values of the dielectric capacitance and the gap capacitance on one hand, and corresponding values determined from the electrical characterization (based on the I-U measurements) on the other hand. The second section compares two different methods, both based on I-U measurements, for determining the gap voltage. One method provides the average gap voltage during the discharge phase, while the other method provides the gap voltage as a function of time. In the third section, the behaviour of the gap voltage as a function of the process variables is characterized. The fourth section compares two methods for obtaining the reduced electric field, one method based on OES and another based on I-U measurements. To conclude the introduction into this chapter, an overview of the research questions concerning this chapter is provided:

- How well do the values for the dielectric capacitance and gap capacitance, determined from the electrical characterization, agree with the theoretically calculated values from equations 2.1, 2.2 and 2.4 in subsection 2.1.2? Which values are more credible or more relevant? (section 3.1)
- Does the gap voltage as a function of time correspond with the theoretical prediction from subsection 2.1.3? Is there any agreement between the average gap voltage during the discharge phase and the gap voltage as a function of time? Which method yields more credible or more relevant values? (section 3.2)
- How is the gap voltage influenced by process variables? (section 3.3)
- Is there any agreement between the two methods for determining the reduced electric field? Which method is more credible or more relevant? (section 3.4)

3.1 Dielectric capacitance and gap capacitance

From the electrical characterization of the discharge cell, based on the I-U measurements, the dielectric capacitance \( C_{\text{dielectric}} \) and the gap capacitance \( C_{\text{gap}} \) can be determined (see Appendix J for details). In this section, these values are compared with theoretically calculated values, based on equations 2.1, 2.2 and 2.4 (see subsection 2.1.2). Also the cell capacitance \( C_{\text{cell}} \) is considered for
both methods. The cell capacitance is defined as the total capacitance of the dielectric barriers and discharge gap, connected in series (see figure 2.3 in subsection 2.1.2):

\[
\frac{1}{C_{cell}} = \frac{1}{C_{diel}} + \frac{1}{C_{gap}}
\]  

(3.1)

Despite its name, the cell capacitance is not by definition always equal to the capacitive load of the discharge cell. During the dark phase, when no discharge current runs through the plasma, this equality holds. During the discharge phase however, the capacitive load of the discharge cell is higher, equal to the dielectric capacitance (see Appendix J for more information).

In table 3.1, all determined capacitance values are shown for both methods, along with a short remark on the agreement between the methods. The values that are bold and blue, are not determined with the corresponding method directly, but are calculated from the two other capacitances, using equation 3.1. The poorest agreement between both methods is for the value of the dielectric capacitance. These two values deviate approximately by 45%. A possible explanation can be found in the layer of glue that fixes both electrodes to the quartz flow tube. This layer forms another capacitive load in series with the quartz barriers, thus effectively reducing the total dielectric capacitance. For the gap capacitance, both methods yield similar values, approximately deviating only 15%. This agreement is remarkable, since the theoretical value for the gap capacitance is calculated with the dielectric constant of nitrogen (almost equal to that of air or vacuum), ignoring the effect of background ionization. Even during the dark phase, the nitrogen gas has an ionization degree that is higher than in a ‘normal’ gas. The largest contributors to this elevated level of background ionization are leftover electrons and ions from the previous discharge phase, so called residual charge [1, 11, 19, 22, 45, 46]. It is known that repetitive discharges in nitrogen, like the one in this work, are influenced by background ionization due to residual charge, even at low frequency of the applied voltage (down to 1 Hz) [17]. The elevated level of background ionization raises questions on using the dielectric constant of nitrogen (under normal conditions) for calculating the gap capacitance. Nevertheless, the values for both methods show a reasonable agreement. A possible explanation is that even a small amount of residual charge significantly influences the gas discharge (e.g. lower breakdown voltage, see section 3.2), while a much larger amount is necessary to significantly influence the dielectric constant of the gas.

<table>
<thead>
<tr>
<th></th>
<th>I-U meas.</th>
<th>Theoretical</th>
<th>Agreement</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{diel}) (pF)</td>
<td>4.47±0.02</td>
<td>6.5±0.4</td>
<td>Poor, possibly due to glue</td>
</tr>
<tr>
<td>(C_{gap})  (pF)</td>
<td>9±1</td>
<td>7.8±0.5</td>
<td>Reasonable, despite background ionization</td>
</tr>
<tr>
<td>(C_{cell}) (pF)</td>
<td>3.0±0.1</td>
<td>3.5±0.2</td>
<td>Good</td>
</tr>
</tbody>
</table>

The dielectric capacitance is necessary for determining the gap voltage as a function of time (see section 3.2 or Appendix J). Since the values for both methods deviate, the value resulting from the I-U measurement is used for further analysis, because this value corresponds better to the real situation than the theoretical value. Both methods for determining the gap capacitance and cell capacitance agree better and are not used for further analysis. Nevertheless, it can be expected that also for these capacitances the I-U measurement yields a more reliable value than the theoretical calculation.
3.2 Gap voltage, a comparison of two I-U methods

Based on the current-voltage measurements, two independent methods exist for determining the gap voltage. One method is based on the simplest equivalent circuit of the discharge cell (see figure 2.3 in subsection 2.1.2) by combining equation 2.6 and 2.9:

\[ U_{\text{gap}} = U - \frac{Q}{C_{\text{dielectric}}} \]  

(3.2)

The applied voltage \( U \) is measured as a function of time. If the charge \( Q \) on the electrodes is also known as a function of time (see Appendix J), equation 3.2 can be used to calculate the gap voltage as a function of time. Henceforth, this method will be referred to as method I. The second method, henceforth referred to as method II, is based on the definition of voltage:

\[ \langle U_{\text{gap}} \rangle_{\text{discharge}} = \frac{[E_{\text{plasma}}]_{\text{cycle}}}{2 \cdot \Delta Q_{\text{d}}} \]  

(3.3)

Thus, the average gap voltage during the discharge phase can be calculated if the energy that is dissipated in the plasma during one cycle, \([E_{\text{plasma}}]_{\text{cycle}}\), is known and if the charge that is discharged through the plasma during one cycle is known (i.e. twice the discharged charge during one discharge phase \( \Delta Q_{\text{d}} \), see Appendix J). More details on the data analysis concerning both methods can be found in Appendix J. This section is mainly concerned with comparing methods I and II.

In figure 3.1, the applied and gap voltages are shown as a function of time for low pressure and large applied voltage amplitude, based on method I. In the top graph, both voltage signals are shown on the same scale. In the bottom graph, the scale for the gap voltage is altered in order to provide a more in-depth view on its behaviour. Even without further analysis, it can be seen that the behaviour of the gap voltage is unlike the depiction that was shown in subsection 2.1.3 on two points: the gap voltage is not equal to the applied voltage just before breakdown, nor is it approximately constant during the discharge phase. After the first breakdown in a half cycle has occurred, the gap voltage first decreases sharply as predicted, but then increases significantly to almost twice the breakdown value, instead of remaining approximately constant during the discharge phase. Only near the end of the discharge phase, when the rise rate of the applied voltage (see subsection 2.1.3) has become much smaller and charge accumulation (see section 2.1.1) may have grown large enough, the gap voltage starts to flatten out and eventually decrease again. From the gap voltage behaviour, the breakdown voltage under these conditions can be determined to be approximately 240 V.

The procedure above is also performed for an I-U measurement at high pressure (and large applied voltage amplitude), leading to the graphs of figure 3.2. These graphs also contradict the depiction of figure 2.4 in subsection 2.1.3. Since the pressure is higher, the breakdown voltage is also higher, approximately 1200 V. The double burst behaviour at high pressures, as observed in subsection 2.3.2, is also reflected by the behaviour of the gap voltage as a function of time. In most half cycles shown in figure 3.2, a sudden decrease in the gap voltage occurs not only at the beginning of the discharge phase, but also towards the end of the discharge phase, just before the applied voltage reaches its extreme value. This is caused by the second burst, which causes the gap voltage to decrease through charge accumulation.
Figure 3.1: Applied voltage (black) and gap voltage (red) as a function of time on equal voltage scale (top) and different voltage scale (bottom) at $2U_{\text{max}}=18.5\pm0.2$ kV$_{\text{pk-pk}}$, $p=20\pm2$ mbar and $\tau_{\text{res}}=60\pm1$ ms.

In order to make a comparison between method I, described above, and method II, which inherently provides only the average gap voltage during the discharge phase, the gap voltage signals above must be time averaged over their discharge phase. The comparison is given in table 3.2, along with the earlier mentioned values for the breakdown voltage. The third column contains the time averaged values of method I and the fourth column contains the values for method II, which is already intrinsically averaged. There is a good agreement between both methods, especially at low pressures. At high pressures, a small discrepancy of about 12% between both methods exists.
Figure 3.2: Applied voltage (black) and gap voltage (red) as a function of time on equal voltage scale (top) and different voltage scale (bottom) at $2U_{\text{max}} = 18.5 \pm 0.2 \text{ kV}_{\text{pk-pk}}$, $p = 600 \pm 5 \text{ mbar}$ and $\tau_{\text{res}} = 36 \pm 1 \text{ ms}$

Table 3.2: Breakdown voltage and average gap voltage during the discharge phase (for both methods) at high and low pressure (at $2U_{\text{max}} = 18.5 \pm 0.2 \text{ kV}_{\text{pk-pk}}$ and $\tau_{\text{res}} = 50 \pm 17 \text{ ms}$)

<table>
<thead>
<tr>
<th>Pressure (mbar)</th>
<th>Breakdown voltage (V) (Method I)</th>
<th>$&lt;U_{\text{gap}(t)}&gt;_{\text{discharge}}$ (V) (Method I)</th>
<th>$&lt;U_{\text{gap}}&gt;_{\text{discharge}}$ (V) (Method II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>240±20</td>
<td>350±20</td>
<td>340±7</td>
</tr>
<tr>
<td>600</td>
<td>1200±20</td>
<td>1390±20</td>
<td>1240±40</td>
</tr>
</tbody>
</table>

Before continuing with the discussion in order to answer the research questions for this section, one additional aspect concerning the gap voltage is worth mentioning. Especially for high pressures, the determined values for the breakdown voltage are significantly lower than the values predicted by the Paschen curve for nitrogen (see figure 3.3). Paschen curves express the
relation between breakdown voltage $U_{BD}$, pressure $p$ and the width of the gas gap $d_{gap}$ for a certain gas and are usually of the form [1, 5]:

$$U_{BD} = \frac{A pd_{gap}}{\ln(Bpd_{gap})}$$

(3.4)

The coefficients A and B have gas specific values. Thus, the product of pressure and gap width determines the breakdown voltage for a certain gas. Given that the discharge gap is roughly 0.90 mm wide, this product of pressure and gap width is 0.18 kPa·cm at 20 mbar pressure and 5.4 kPa·cm at 600 mbar pressure. According to the Paschen curve in figure 3.3, the breakdown voltage for these values should be approximately 300 V at 20 mbar and at least 3 kV at 600 mbar. However, the measured values are lower, especially at high pressure. The reason for this lowering of the breakdown voltage can be found in the background ionization due to residual charge from the previous discharge phase. It is known that the breakdown voltage of a gas can be significantly reduced by residual charge [22]. This effect enables running a DBD at low gap voltages. Only for ignition and the first few discharge phases, a high gap voltage is required, corresponding to the Paschen value. Once ignition is achieved, the required gap voltage for breakdown decreases, along with the discharge current density. At some point, a stable situation is reached in which consecutive discharge phases are roughly similar [20].

![Paschen curves for several gases over a wide range of p·d values](image)

**Figure 3.3: Paschen curves for several gases over a wide range of p·d values [47]**

**Discussion**

From the results of this section, it can be concluded that the common prediction of a constant gap voltage during the discharge phase [24], supported by classical electrical theory for sinusoidal driven ozonizers (CETSDO) [22, 23], does not apply to a nitrogen DBD at the present conditions. Apparently, the increase in gap voltage due to the rise rate of the applied voltage is stronger than the decrease due to charge accumulation. Only towards the end of the discharge phase, when the rise rate of the applied voltage has become smaller and the charge separation has grown large enough, the gap voltage first flattens out and then starts to decrease again. The non-constant gap voltage during the discharge phase appears to be a more general phenomenon, as
our research group has encountered it at several reactors, for various operating conditions (e.g. rise rate of the applied voltage) and for several gasses, both atomic and molecular.

Regarding the comparison between the two methods for determining the gap voltage, the results demonstrate that there is a good correspondence between both methods. Only for higher pressures, the two methods yield slightly deviating results. A tentative explanation for this deviation at high pressures may be found by refining the rather crude depiction of the gas discharge that was provided in subsection 2.1.1. A nitrogen dielectric-barrier discharge at near atmospheric pressures, like the one in this work, is usually not perfectly homogeneous, as depicted in figure 3.4 on the left, but contains discharge filaments as depicted on the right [1, 2, 5, 19, 20, 40, 41, 46, 48]. From a layman’s perspective, these discharge filaments (or microdischarges) can be visualized best as small lighting strikes. Discharge filaments contain an ionized plasma channel through which charge can flow [2, 19]. During the discharge phase, discharge current can only flow through these plasma channels [2, 19]. The filamentary character of the discharge has an effect on charge accumulation, as can be seen in figure 3.4 on the right. The charge accumulation is not evenly distributed over the surface area of the dielectric barriers, but is concentrated near the location of a discharge filament [2, 19]. Method I for calculating the gap voltage, represented by equation 3.2, is based on the simplest equivalent circuit of a DBD (see subsection 2.1.2), which regards the gas gap as one entity. Thus, even though this method does take charge accumulation into account, it does not include the effect that the filamentary character of the discharge has on charge accumulation. Therefore, this method determines a value for the gap voltage (as a function of time) that is averaged over the cross-sectional area of the active volume, which corresponds with the depiction on the left of figure 3.4. Method II however, represented by equation 3.3, does take into account the effect that the filamentary character of the discharge has on charge accumulation. Since the charge, discharged through the plasma during one discharge phase ($\Delta Q_d$) is only flowing through discharge filaments, this method determines the gap voltage at the locations of discharge filaments. Because charge accumulation is concentrated near these locations, this value for the gap voltage can be expected to be lower than the value that is averaged over the cross-sectional area of the active volume. The gap voltage in between the discharge filaments is thus higher than the cross-sectional averaged value. Concluding, method II can be expected to yield a lower value for the gap voltage than method I, as is the case in this work. It is known that a discharge is less diffuse (stronger filamentary character) at higher pressures [1], which may explain why the difference between both methods is largest at high pressure.

![Figure 3.4: A simplified depiction of charge accumulation in a nitrogen DBD (left) and a depiction that takes the filamentary character of the discharge into account (right)](image)
Even though both methods for determining the gap voltage (averaged over the discharge phase) yield similar results, method II is used for the characterization of the gap voltage (see section 3.3) and for one method of determining the reduced electric field (see section 3.4). This choice is motivated by the fact that the gap voltage over a discharge filament is more relevant than the average of the gap voltage over the cross-sectional area of the active volume, since vibrational excitation occurs mainly in discharge filaments.

### 3.3 Gap voltage characterization

Since the gap voltage over a discharge filament is relevant within the main theme of this work (i.e. vibrational excitation), the corresponding values (method II) are characterized as a function of all three process variables. Appendix J provides more information on how these values are obtained.

Figure 3.5 depicts the gap voltage values that have been determined as a function of the applied voltage amplitude. The data point at lowest applied voltage amplitude cannot be viewed as part of the trend, since it is determined close to the extinguishing point of the plasma, when the applied voltage amplitude is too low to sustain a stable plasma. According to these measurements, the gap voltage increases as a function of the applied voltage amplitude. The explanation for this increasing trend can be found in the rise rate of the applied voltage. For a higher applied voltage amplitude, and thus higher applied voltage rise rate, the bulge on top of the breakdown voltage level (see figure 3.1 in section 3.2) is higher, which leads to a higher value for the gap voltage, averaged over the discharge phase.

![Figure 3.5: Gap voltage as a function of applied voltage amplitude at $p=20\pm2$ mbar and $\tau_{res}=31\pm5$ ms](image)

In figure 3.6, the trend of the gap voltage as a function of the pressure is displayed. As mentioned briefly before, this increasing trend can be explained by considering that the breakdown voltage, and thus the average gap voltage during the discharge phase, increases with pressure. Figure 3.7 shows the dependence of the gap voltage on residence time (or flow rate). The graph suggests the existence of a minimum in gap voltage around a residence time of 70 ms.
The first part, in which the gap voltage decreases as a function of residence time, may be explained as follows. Residual charge in the reactor is concentrated near the locations where discharge filaments were present during the previous discharge phase. For a higher flow rate, and thus a lower residence time, the residual charge from a previous discharge phase is dispersed more quickly, which causes the breakdown voltage to be higher. When the breakdown voltage is higher, the average gap voltage during the discharge phase can also be expected to be higher, analogous to the pressure dependence. Further investigation into the dependence of gap voltage on residence time is needed in order to explain the second part, which seems to suggest an increasing trend.

Figure 3.6: Gap voltage as a function of pressure at $2U_{max}=18.5\pm0.2$ kV<sub>pk-pk</sub> and $\tau_{res}=50\pm17$ ms

Figure 3.7: Gap voltage as a function of residence time at $2U_{max}=18.5\pm0.2$ kV<sub>pk-pk</sub> and $p=150\pm5$ mbar
3.4 Reduced electric field: comparing OES and I-U measurements

In this work, two different methods are used to determine the reduced electric field, one being based on optical emission spectroscopy (OES) and the other on current-voltage (I-U) measurements. The OES based method determines the reduced electric field from the ratio between emission from a specific transition of the N$_2^+$ molecular ion and a specific transition of the N$_2$ molecule. The I-U based method determines the reduced electric field from the average gap voltage during the discharge phase that follows from the electrical characterization:

$$\frac{E}{n} = \frac{(U_{gap \text{ discharge}})}{d_{gap}} = \frac{(U_{gap \text{ discharge}})k_BT_{\text{gas}}}{p'd_{gap}}$$

Even though the second method includes the gas temperature, determined by OES, it will consistently be referred to as the I-U based method. More details on the data analysis concerning the reduced electric field can be found in Appendix C and J. In figure 3.8, the trends for the reduced electric field as a function of the applied voltage amplitude are given. Both methods yield values in the same order of magnitude, though the I-U based values are roughly a factor of two higher. Furthermore, the trend in the I-U based values is stronger. Peculiar is that both trends are opposite since the OES based trend is decreasing (which can be seen more clearly from figure 4.9 in section 4.3).

![Figure 3.8: Reduced electric field, based on OES (solid triangles) and I-U measurements (open triangles), as a function of applied voltage amplitude at p=20±2 mbar and $\tau_{\text{res}}=31±5$ ms](image)

Figure 3.9 shows the trends for both methods as a function of pressure. Also in this case, both methods yield values for the reduced electric field in the same order of magnitude. Furthermore, the trend in the I-U based values is again stronger than the trend in the OES based values. However, the pressure dependence shows a similar trend for both methods, contrary to the dependence on applied voltage amplitude. At pressures above approximately 70 mbar, the OES based values for the reduced electric field are consistently higher, while I-U based values are higher below 70 mbar.
Figure 3.9: Reduced electric field, based on OES (solid triangles) and I-U measurements (open triangles), as a function of pressure at $2U_{\text{max}} = 18.5 \pm 0.2 \text{kV}_{\text{pk-pk}}$ and $\tau_{\text{res}} = 50 \pm 17 \text{ ms}$

Figure 3.10 depicts the residence time (or flow rate) series for both methods of determining the reduced electric field. Values for both methods are again in the same order of magnitude. However, in this case the OES based values show a larger trend, contrary to the pressure and applied voltage amplitude series. The trends for both methods show some similarity, but are not identical.

Figure 3.10: Reduced electric field, based on OES (solid triangles) and I-U measurements (open triangles), as a function of residence time at $2U_{\text{max}} = 18.5 \pm 0.2 \text{kV}_{\text{pk-pk}}$ and $P = 150 \pm 5 \text{ mbar}$
Discussion
The results of this section indicate that there is an order of magnitude agreement between both methods for determining the reduced electric field, although values can deviate up to a factor of three under some conditions. The trends for both methods as a function of process variables are found to be not necessarily similar. Furthermore, the I-U based values show a stronger dependence on applied voltage amplitude and pressure, compared to the OES based values. The latter values, on the other hand, depend more strongly on residence time (or flow rate), compared to the I-U based values.

In order to provide a possible explanation for the differences between the two methods, both in absolute values and trends, it is necessary to first have a closer look at a few physical details behind both methods. Regarding the I-U based method, represented by equation 3.5, the neutral particle density is calculated by filling in the determined values for reactor pressure and gas temperature into the ideal gas law. It is doubtful whether the ideal gas law, and mostly the reactor pressure, hold in a discharge filament. Consequently, this procedure yields values for the reduced electric field that probably reflect an average over the entire active volume, but not necessarily apply to the plasma regions in the discharge (see figure 3.4 in section 3.2). The OES based values, on the other hand, are based on optical emission coming from these plasma regions, meaning that these values probably reflect the reduced electric field in those regions. This physical interpretation for both values can provide a tentative explanation for some of the differences between both methods.

Especially the pressure dependence seems to support the physical interpretation of both methods. In the plasma regions of the discharge, the ionization degree is significantly higher than at other locations in the active volume. Therefore, the neutral particle density can be assumed to be lower in the plasma regions. Since the OES based method takes this lower value for the neutral particle density in a plasma region into account, contrary to the I-U based method, it yields a higher value for the reduced electric field (equation 3.5). In figure 3.9, it can be seen that the OES based value is indeed higher than the I-U based value for most pressures. For lower pressures, the discharge becomes more diffuse (more microdischarges per time and cross-sectional area), decreasing the difference between the value holding in the plasma regions (OES based) and the value averaged over the active volume (I-U based). It remains unclear, however, why the I-U based method yields higher values than the OES based method for the lowest pressures.

Given the main theme of this work, vibrational excitation and its influence on plasma chemical reactions, OES based values for the reduced electric field are consistently used in chapter 4, since vibrational excitation mainly occurs in discharge filaments, which are part of the plasma region. Only in this section, I-U based values are shown.

3.5 Conclusions
Looking back at the research questions that have been posed at the start of this chapter, the following conclusions can be drawn.

Theoretical values for dielectric capacitance, gap capacitance and cell capacitance agree relatively well with the values that are based on the electrical characterization, following from the current-voltage measurements. The largest deviation between the two values is for the dielectric capacitance (approximately 45%), which may be explained from the glue that fixes the electrodes to the flow tube. Despite background ionization due to residual charge, the theoretical
value for the gap capacitance deviates only roughly 15% from the experimentally determined value. The values, following from the $I$-$U$ measurement are considered to be more reliable.

Contrary to the common depiction in subsection 2.1.3, the gap voltage is not found to be constant during the discharge phase. A possible explanation is that the effect of the rise rate of the applied voltage is stronger than the effect of charge accumulation. Furthermore, the breakdown voltage for nitrogen in this work is found to be significantly lower than the value predicted by the Paschen curve, which is due to residual charge from the previous discharge phase. A good agreement exists between the two methods for determining the gap voltage. Only for higher pressures, both methods deviate somewhat (roughly 12%), which may be explained from the effect that the filamentary character of the discharge has on charge accumulation. The method that intrinsically yields a time averaged value is considered to be more relevant for vibrational excitation.

The average gap voltage during the discharge phase is characterized, though further investigation is needed in order to provide a conclusive explanation regarding its behaviour as a function of residence time (or flow rate).

In this work, both methods for determining the reduced electric field agree within an order of magnitude, although the trends need not be similar. The $I$-$U$ based value is probably an average of the reduced electric field over the active volume, while the OES based value is expected to reflect the value in the plasma regions. Since vibrational excitation mainly occurs in discharge filaments, which are part of the plasma region, the OES based value is considered to be more relevant for vibrational excitation. Differences between the two values can be explained best by considering the neutral particle density in the plasma regions, which is expected to be significantly lower than at other locations in the reactor.
Chapter 4  Vibrational excitation in an N2 DBD

As mentioned in the introduction, this work is concerned with three issues:

1) Optimization of rate coefficients and energy efficiencies for running a plasma chemical process in general
2) Understanding the physics behind the optimization process
3) Exploring the possibilities of the diagnostics that have been used in this work (3).

This chapter is mainly concerned with issues (1) and (2). In the first part of this chapter, the results concerning issue (1) are treated. Recapitulating from the introduction: since vibrational excitation and gas temperature influence rate coefficients and energy efficiencies of plasma chemical reactions, a control over these two parameters is desired in order to find optimal windows of operation for running a plasma chemical process in a DBD plasma reactor. Controlling vibrational excitation and gas temperature can be achieved by means of the process variables involved. For this reason, both parameters are investigated in this work as a function of the applied voltage amplitude, pressure and residence time in order to find windows of operation for which high rate coefficients and energy efficiencies can be expected (see figure 4.1). To summarize, the first section aims to answer the following research questions:

- How do pressure, applied voltage amplitude and residence time influence vibrational excitation and gas temperature?
- Can optimal windows of operation, yielding high rate coefficients or energy efficiency, be identified from the previous?

![Figure 4.1: Schematic depiction of the parameters of interest concerning the optimization of rate coefficients and energy efficiency (issue (1))](image)

Sections 4.2-4.4 treat the results concerning issue (2), the physical understanding behind the optimization process. Since optimal windows of operation for running a plasma chemical process are reactor specific, it is required to understand why certain values of process variables yield vibrational temperatures and gas temperatures that are beneficial for plasma chemical processes. Only then can optimal windows of operation be extrapolated to other reactors, necessary for industrial upscaling. In order to achieve this aim, other relevant physical parameters for running a plasma chemical process in a DBD reactor are investigated, namely the reduced electric field (OES based value) and the specific energy input. These parameters have an influence on vibrational temperature and gas temperature that is less reactor specific than the influence of most process variables. From the results, the influence of process variables on reduced electric field and specific energy input is determined, although the main focus is on the correlation between these two parameters and vibrational temperature (see figure 4.2). This correlation can be used for controlling vibrational excitation by tuning the reduced electric field and the specific
energy input. In this work, pressure is assumed to be the only process variable having also a direct influence on vibrational excitation, besides the indirect influence via reduced electric field and specific energy input (see figure 4.2). Applied voltage amplitude and residence time are assumed to have only an indirect influence on vibrational temperature. To summarize, sections 4.2-4.4 aim to answer the following research questions:

- How do pressure, applied voltage amplitude and residence time influence the specific energy input? Can a consistent correlation be found between specific energy input and vibrational temperature? (section 4.2)
- How do pressure, applied voltage amplitude and residence time influence the reduced electric field? Can a consistent correlation be found between the reduced electric field and vibrational temperature? (section 4.3)
- Is the vibrational temperature determined by merely one physical parameter? In other words: can a physical parameter be identified whose value alone determines the vibrational temperature, regardless of the values of other physical parameters? If this is not the case, can a mathematical combination of parameters be found that alone determines the vibrational temperature? Such a parameter is often called a scaling parameter. (section 4.4)

<table>
<thead>
<tr>
<th>Process variables</th>
<th>Physical parameters</th>
<th>Target parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>Pressure</td>
<td></td>
</tr>
<tr>
<td>Amplitude applied voltage</td>
<td>Reduced electric field</td>
<td>Vibrational temperature</td>
</tr>
<tr>
<td>Residence time / Flow rate</td>
<td>Specific energy input</td>
<td></td>
</tr>
</tbody>
</table>

*Figure 4.2: Schematic depiction of the parameters of interest concerning the understanding of the physics behind the optimization process (issue (2))*

### 4.1 Rate coefficients and energy efficiency

Under all conditions in this work, vibrational excitation is found to be in Boltzmann equilibrium. Vibrational temperatures are found in the range of 2100-3200 K, while gas temperatures are found in the range of 340-650 K.

Figure 4.3 shows the obtained values of vibrational temperature and gas temperature as a function of applied voltage amplitude. Both temperatures demonstrate a clear increasing trend, which can best be explained from the increase of the average gap voltage during the discharge phase as a function of the applied voltage amplitude (see figure 3.5 in section 3.3). A higher gap voltage causes more energy to be dissipated in the plasma. The peculiarly high gas temperature around 3 kV_{pk-pk} is disregarded since it represents an unstable condition, close to the extinguishing point of the plasma.

In figure 4.4, values for both temperatures are shown as a function of pressure. The vibrational temperature decreases as a function of pressure while the gas temperature increases. The most likely explanation can be found by considering energy transfer between colliding molecules. During a collision between molecules, of which at least one is vibrationally excited, vibrational energy can be converted into translational energy, thus decreasing the total vibrational energy of the involved molecules, while increasing the total translational energy. This phenomenon is often called vibrational-translational relaxation (VT-relaxation) [1, 3]. Since the collisional frequency increases with pressure, the vibrational temperature and gas temperature
can be expected to respectively decrease and increase as a function of pressure due to VT-relaxation. A more global point of view, corresponding to the explanation above, is that a higher pressure leads to more interactions in the plasma, bringing it closer to thermal equilibrium. Thus, the vibrational temperature and gas temperature will tend to similar values and therefore must decrease and increase, respectively.

Figure 4.3: Vibrational temperature (black squares) and gas temperature (purple circles) as a function of applied voltage amplitude at $p=20\pm 2$ mbar and $\tau_{res}=31\pm 5$ ms

Figure 4.4: Vibrational temperature (black squares) and gas temperature (purple circles) as a function of pressure at $2U_{max}=18.5\pm 0.2$ kV$_{pk-pk}$ and $\tau_{res}=50\pm 17$ ms

Figure 4.5 depicts the determined trends for vibrational temperature and gas temperature as a function of residence time. The vibrational temperature clearly shows a maximum at residence
times around 50 ms. The trend of the gas temperature is less clear. It can be continuously increasing as a function of residence time, have a maximum around 50 ms too, or most likely, flatten out above 50 ms after an initial increase. This ambiguous trend is most probably caused by the fact that the change in gas temperature is relatively small compared to the margin of error, in conjunction with the procedure of data analysis (see Appendix C). The initial increase in gas temperature can be explained by considering that the nitrogen molecules spend more time in the active volume and therefore experience more microdischarges. The flattening out of the gas temperature at higher residence times is not that easily explained. A possible explanation is that, above a certain residence time, the increase in temperature is cancelled out by the increase of heat loss to the surroundings. Regarding the vibrational temperature, the initial increase may also be tentatively explained as a residence time effect: for longer residence times, and thus lower flow rates, a nitrogen molecule spends more time in (the vicinity of) a discharge filament, which leads to an increase in energetic excitation of the molecule. At least some of that increase in energetic excitation will be in the form of vibrational excitation. For the decreasing trend at residence times above 50 ms, an obvious explanation does not exist. A possible explanation is provided in section 4.3.

![Figure 4.5: Vibrational temperature (black squares) and gas temperature (purple circles) as a function of residence time at $2U_{\text{max}}=18.5\pm0.2$ kV$_{pk-pk}$ and $p=150\pm5$ mbar](image)

**Discussion**

From equation 1.7 in subsection 1.2.4, it is known that both vibrational temperature and gas temperature have a positive effect on rate coefficients for elementary reactions. From this point of view, the results in figure 4.3 and 4.5 indicate that high rate coefficients for chemical reactions in a nitrogen DBD may be achieved by operating at high applied voltage amplitudes and medium residence times (or medium flow rates). The effect of pressure on rate coefficients cannot be identified since both temperatures have an opposite trend as a function of pressure (see figure 4.4). Equation 1.7 can only be used to identify the effect that an opposite trend has on the rate coefficient of a plasma chemical reaction if the activation energy and the coefficient $\alpha$ are known. In other words, if there is a specific chemical reaction of interest. In that case, an
opposite trend in vibrational temperature and gas temperature is especially interesting, since it harbors the possibility of having an optimum for the rate coefficient in the operational range of the reactor. If this optimum exists, its approximate location can be determined with equation 1.7.

The energy efficiency for running a plasma chemical process is also positively influenced by the vibrational temperature, as is discussed in subsection 1.2.4. A high gas temperature, on the contrary, is known to have a detrimental effect on energy efficiency. From this perspective, the results indicate that a high energy efficiency for chemical reactions in a nitrogen DBD can be achieved by operating at low pressures. The effect of applied voltage amplitude and residence time (or flow rate) on energy efficiency cannot be identified, since both temperatures show a similar trend as a function of these process variables. However, using an analogous reasoning as for rate coefficients, a similar trend in vibrational temperature and gas temperature harbors the possibility of having an optimum for energy efficiency in the operational range.

In subsection 2.1.4, a possible parasitic effect of residence time on the measured physical parameters (e.g. vibrational temperature) was identified, based on the fact that the residence time is not perfectly constant during the applied voltage amplitude series and pressure series. An argument was put forward to support the assumption that this will not significantly influence the measured trends for these series. Based on the results, shown in this section, this assumption can be supported further: looking at figure 4.5, it becomes clear that the residence time only has a weak effect on vibrational temperature and gas temperature. A significant change in these temperatures is only achieved by varying the residence time over one or two orders of magnitude. Taking the margin of error in residence time for the applied voltage amplitude series (31±5 ms) and pressure series (50±17 ms) into account, already including the possible parasitic effect, it can be concluded that the parasitic effect could not have had a significant influence on the trends of both temperatures as a function of applied voltage amplitude and pressure.

4.2 Influence of specific energy input
As mentioned shortly in section 1.3, the specific energy input expresses how much energy is coupled into the plasma per (standard) liter of gas flowing through the reactor or, in other words, the average energy a molecule absorbs during the time it spends in the active volume. Values for the specific energy input in this work have been found in the range 0.24-64 kJ/ sl (1 sl = 1 standard liter, containing approximately 2.7·10^{22} molecules), corresponding to 0.056-15 eV per molecule.

In figure 4.6, the measured trend for the specific energy input as a function of applied voltage amplitude is depicted, together with the trend of the vibrational temperature that has already been shown. The increase in specific energy input as a function of applied voltage amplitude supports the explanation that is given in the previous section for the increase in vibrational temperature and gas temperature, since the both trends can be explained similarly, namely from the increase in the average gap voltage during the discharge phase.

Figure 4.7 depicts the determined values for the specific energy input as a function of pressure. The decreasing trend seems surprising, since the average gap voltage during the discharge phase (and thus also the power input) increases as a function of pressure (see figure 3.6 in section 3.3). However, because a pressure series is performed at constant residence time, the flow rate is increased along with pressure (see equation 2.12). Since the increase in flow rate is larger than the increase in power input, the specific energy decreases as a function of pressure (see equation J.14 in Appendix J).
Figure 4.6: Vibrational temperature (black squares) and specific energy input (green triangles) as a function of applied voltage amplitude at $p=20\pm2$ mbar and $\tau_{res}=31\pm5$ ms

Figure 4.7: Vibrational temperature (black squares) and specific energy input (green triangles) as a function of pressure at $2U_{max}=18.5\pm0.2$ kV$_{pk-pk}$ and $\tau_{res}=50\pm17$ ms

Figure 4.8 shows the values that have been determined in this work for the specific energy input as a function of residence time. The clear, increasing trend supports the explanation, given in section 4.1, for the initial increase in vibrational and gas temperatures as a function of residence time, since the same explanation can be used for both trends, namely an increase in dissipated energy going into the translational and vibrational channel of excitation due to a residence time effect.
Figure 4.8: Vibrational temperature (black squares) and specific energy input (green triangles) as a function of residence time at $2U_{\text{max}} = 18.5 \pm 0.2$ kV$\text{pk-pk}$ and $p = 150 \pm 5$ mbar

Discussion
When trying to find a correlation between vibrational temperature and specific energy input, the pressure series must be discarded, since pressure is expected to have a large direct influence on vibrational temperature anyway, besides the indirect influence via specific energy input (see figure 4.2). From the applied voltage amplitude series and residence time series, a positive correlation can be found (i.e. similar trends), which is not surprising. When the input of energy per molecule increases, at least some of that extra energy will be directed into vibrational excitation. The only exception for this positive correlation is the decrease in vibrational temperature as a function of residence time above 50 ms, which does not agree with the increase in specific energy input. Thus, the maximum in vibrational temperature as a function of residence time cannot be explained from the specific energy input. For residence times above 50 ms, an additional explanation is still required.

Regarding the possible parasitic effect that residence time may have in the applied voltage amplitude series and pressure series: analogous to the reasoning in the previous section, by looking at the numbers it can be concluded that the undesired effect of residence time is not large enough to significantly influence the applied voltage amplitude series and pressure series.

4.3 Influence of reduced electric field
As mentioned briefly before (see section 1.3), the reduced electric field is an important parameter in gas discharges. It is defined as the strength of the electric field in the plasma, divided by the neutral particle density ($\frac{E}{n}$). In this work, values for the reduced electric field have been found in the range 340-530 Td (1 Td = one Townsend = $10^{-21}$ Vm$^2$).

In figure 4.9, the measured trend for the reduced electric field as a function of applied voltage amplitude is displayed, along with the values for the vibrational temperature that have been shown before in section 4.1. The downward trend in the reduced electric field as a function of the applied voltage amplitude is unexpected, especially since the average gap voltage during
the discharge phase shows an increasing trend as a function of the applied voltage amplitude (see figure 3.5 in section 3.3). Further investigation on the dependence of the reduced electric field on the applied voltage amplitude is required in order to provide a satisfactory explanation for this behaviour.

Figure 4.9: Vibrational temperature (black squares) and reduced electric field (red triangles) as a function of applied voltage amplitude at \( p=20\pm2 \text{ mbar} \) and \( \tau_{res}=31\pm5 \text{ ms} \)

Figure 4.10 shows the values that have been determined for the reduced electric field as a function of pressure. The downward trend can be explained best by first working out the definition of the reduced electric field, using the ideal gas law:

\[
E = \frac{U_{\text{gap discharge}}}{n d_{\text{gap}}} = \frac{U_{\text{gap discharge}} k_B T_{\text{gas}}}{p d_{\text{gap}}} \tag{4.1}
\]

The average gap voltage during the discharge phase and the gas temperature both increase as a function of pressure (see section 3.3 and 4.1, respectively). However, since the increase of pressure itself is larger than the combined increase of gap voltage and gas temperature, the reduced electric field decreases as a function of pressure.

In figure 4.11, the determined values for the reduced electric field as a function of residence time are displayed. The first noteworthy aspect of this trend is that the dependence on residence time is significant, even equally large as the dependence on pressure, which is not trivial. Furthermore, the trend suggests the existence of a minimum in the reduced electric field around 15-20 ms residence time. The decreasing part can be explained best from equation 4.1 by considering that the decrease in gap voltage as a function of residence time (see figure 3.7 in subsection 3.3) is larger than the increase in gas temperature (see figure 4.5 in section 4.1). The increasing part may also be explained from equation 4.1 by considering a combination of an increase in gas temperature until roughly 70 ms, and an increase in gap voltage above roughly 70 ms.
Figure 4.10: Vibrational temperature (black squares) and reduced electric field (red triangles) as a function of pressure at $2U_{\text{max}}=18.5\pm0.2 \text{ kV}_{\text{pk-pk}}$ and $\tau_{\text{res}}=50\pm17 \text{ ms}$

Figure 4.11: Vibrational temperature (black squares) and reduced electric field (red triangles) as a function of residence time at $2U_{\text{max}}=18.5\pm0.2 \text{ kV}_{\text{pk-pk}}$ and $p=150\pm5 \text{ mbar}$

Discussion
For the same reason as in the previous section, the pressure series is ignored when looking for a correlation between vibrational temperature and the reduced electric field. The applied voltage amplitude series and residence time (or flow rate) series suggest that the reduced electric field is negatively correlated with vibrational temperature (i.e. opposite trends). A possible explanation can be found in the fact that the reduced electric field determines the fraction of the power input directed into the vibrational channel of excitation. The physical background behind this phenomenon is that vibrational excitation of molecules in a nitrogen plasma, generated by a
DBD, is mainly achieved by collisions with free electrons. In these collisions, part of the kinetic energy of the free electron is converted into vibrational energy of the molecule. This process is often called vibrational pumping [3]. The probability of a nitrogen molecule being vibrationally excited in a collision with a free electron depends on the kinetic energy of the electron, as can be seen in figure 4.12. This probability, often expressed by means of a collisional cross section, has a maximum roughly between 1-5 eV when the kinetic energy of the electron is somewhat higher than the transition energies corresponding to vibrational excitation from the vibrational ground state (lowest being 0.29 eV). At lower energies, the electrons mainly populate rotationally excited states of the nitrogen molecule, corresponding to lower transition energies. At higher electron energies, the probability is highest for electronic excitation or even ionization of nitrogen molecules.

![Cross sections for excitation of the nitrogen molecule by collisions with free electrons from several works [14, 15, 49]](image)

Figure 4.12: Cross sections for excitation of the nitrogen molecule by collisions with free electrons from several works [14, 15, 49]

When the reduced electric field in the nitrogen plasma is higher (i.e. higher electric field or lower neutral particle density), free electrons gain more energy from the electric field before they collide with a neutral (e.g. a nitrogen molecule). This phenomenon, combined with the energy
dependent collisional cross sections for excitation of the nitrogen molecule, causes the fractional power input into the possible channels of excitation (e.g. vibrational excitation) to be dependent on the reduced electric field, as can be seen from figure 4.13. When the reduced electric field is roughly below 1 Td (1·10^{-17} Vcm^2), most of the power coupled into the plasma is directed into the rotational channel of excitation. Approximately between 1-80 Td (1·10^{-17}-8·10^{-16} Vcm^2), most of the power input is directed into vibrational excitation, with a maximum around 10 Td (1·10^{-16} Vcm^2). Roughly between 80-600 Td (8·10^{-16}-6·10^{-15} Vcm^2), most of the energy coupled into the plasma is directed into electronic excitation of the nitrogen molecule, with a maximum around 300 Td (3·10^{-15} Vcm^2). Above 600 Td (6·10^{-15} Vcm^2), approximately, most of the power coupled into the plasma is directed into ionization processes. In this work, all determined values for the reduced electric field, both by OES and I-U measurements, are above 200 Td. Thus, most energy is directed into electronic excitation or even ionization, not into vibrational excitation. Relatively high (reduced) electric fields are inherent to dielectric-barrier discharges, which means that DBDs are not ideal for optimizing vibrational excitation. This is actually one of the few disadvantages of using DBDs for inducing plasma chemical reactions. Since the values for the reduced electric field in this work are too high for optimal vibrational excitation, a decrease in the reduced electric field may lead to an increase in vibrational temperature, which can serve as an explanation for the negative correlation between these two parameters. This negative correlation may explain why the vibrational temperature decreases as a function of residence time above 50 ms.

Figure 4.13: Fractional power input into several channels of excitation of the nitrogen molecule as a function of reduced electric field, from several works [14, 15]

Analogous to the previous two sections, also for the reduced electric field it can be concluded that the possible parasitic effect of residence time is not large enough to significantly influence the measured trends as a function of applied voltage amplitude and pressure.
4.4 Scaling parameter

As depicted in figure 4.2, three parameters in this work are assumed to have a direct influence on vibrational excitation, namely pressure, specific energy input and reduced electric field. In this section, all determined values for these three parameters in this work are considered, along with corresponding values for the vibrational temperature in order to possibly identify a scaling parameter that alone determines the vibrational temperature. In that case, vibrational temperature would be a unique function of this scaling parameter. From figure 4.3 and 4.5 in section 4.1, it can be concluded that pressure alone does not determine the vibrational temperature, since almost equal values for the pressure can yield strongly different values for the vibrational temperature.

In order to check if the specific energy input alone determines the vibrational temperature, all determined values for both parameters in this work are depicted in figure 4.14. From this overview, it becomes clear that also specific energy input alone does not determine the vibrational temperature, since strongly deviating vibrational temperatures can exist for the same specific energy input, especially at higher values for the specific energy input.

In order to check if the reduced electric field alone determines the vibrational temperature, all determined values for this parameter in this work are depicted in figure 4.15. Obviously, also the reduced electric field does not determine the vibrational temperature only by itself.

Figure 4.14: All determined values for vibrational temperature and corresponding specific energy input in this work

Figure 4.15 is created by applying an analogous procedure for the reduced electric field, in order to check if the vibrational temperature is merely determined by this parameter. Obviously, also the reduced electric field does not determine the vibrational temperature only by itself.
From the analysis above, it can be concluded that the vibrational temperature is not determined by only one of the three physical parameters pressure, specific energy input ($E_{\text{spec}}$) or reduced electric field, but rather from a combination of all three (or at least two). Therefore, a tentative scaling parameter is used, consisting of all three physical parameters, to investigate whether the vibrational temperature is determined by this scaling parameter alone. Since the specific energy input $E_{\text{spec}}$ is positively correlated with vibrational temperature, while pressure and reduced electric field are negatively correlated with vibrational temperature, this tentative scaling parameter is of the form:

$$\text{Scaling parameter } I = \frac{E_{\text{spec}}}{p} \left( \frac{E}{\pi} \right)$$ (4.2)

Figure 4.15 shows all values for vibrational temperature in this work as a function of the corresponding reduced electric field in this work. Although this combination of parameters gives a better result in predicting the vibrational temperature than each of the three parameters separately, the values for the vibrational temperature still deviate strongly, especially for higher values of the scaling parameter. Fine tuning of this scaling parameter is necessary in order to find a unique function for the vibrational temperature, provided that it exists at all.

A more practical scaling parameter would be one that consists of the process variables, since those can be directly controlled. Since the vibrational temperature increases as a function of the applied voltage amplitude, decreases as a function of pressure and mainly increases as a function of residence time, this scaling parameter (also tentative) is of the form:

$$\text{Scaling parameter } II = \frac{(2b_{\text{max}}) \tau_{\text{res}}}{p}$$ (4.3)
Figure 4.16: All determined values for vibrational temperature and corresponding scaling parameter I in this work.

Figure 4.17 shows all values for the vibrational temperature in this work as a function of the corresponding values for scaling parameter II. Again, the values for the vibrational temperature deviate strongly for higher values of the scaling parameter, although they converge rather well for lower values. Also for this more practical scaling parameter, fine tuning if necessary in order to possibly find a unique function for the vibrational temperature.

Figure 4.17: All determined values for vibrational temperature and corresponding scaling parameter II in this work.
4.5 Conclusions

Looking back at the research questions that have been posed at the start of this chapter, the following conclusions can be drawn.

In most cases, clear trends in vibrational temperature (2100-3200 K) and gas temperature (340-650 K) have been determined as a function of applied voltage amplitude, pressure and residence time. Tentative explanations for these trends can mostly be found by considering the influence of the average gap voltage during the discharge phase, vibrational-translational relaxation or residence time effects. Especially the existence of a maximum in vibrational temperature as a function of residence time (or flow rate) is interesting within the framework of this research, which may be explained from the combination of a residence time effect and the influence of the reduced electric field. The measured trends for vibrational temperature and gas temperature in this work suggest that high rate coefficients for a plasma chemical reaction in a nitrogen plasma can be achieved for high values of the applied voltage amplitude and medium values of the residence time (or flow rate), while a high energy efficiency can be expected at low pressures. Possibly, an optimum in the rate coefficient as a function of pressure exists. Energy efficiency may also have such an optimum as a function of applied voltage amplitude and residence time (or flow rate).

Also for the specific energy input (0.056-15 eV per molecule), clear trends as a function of the process variables have been determined. Again, tentative explanations can be found in the effect of the average gap voltage during the discharge phase and residence time effects (or flow rate effects). By comparing the trends of vibrational temperature and specific energy input, a positive correlation between these two parameters is found, which is not surprising and can easily be explained from basic considerations.

The measured trends of the reduced electric field (340-530 Td) as a function of process variables are also clear. It is worth noting that residence time (or flow rate) has a significant effect on the reduced electric field and that this trend appears to have a minimum. Most trends can be explained, at least tentatively, by considering the neutral particle density or the combined effects of gas temperature and the average gap voltage during the discharge phase. Further investigation is required in order to explain the dependence of the reduced electric field on the applied voltage amplitude. The comparison between the trends of vibrational temperature and reduced electric field suggests a negative correlation between these two parameters. This correlation may be explained from the fact that cross sections for (vibrational) excitation by collisions with free electrons are strongly dependent on the (mean) free electron energy and therefore also on the reduced electric field. This phenomenon is reflected by the influence that the reduced electric field has on the fractional power input into several channels of excitation (e.g. vibrational). A dielectric-barrier discharge inherently harbors a reduced electric field that is ideal for electronic excitation or even ionization, but too large for efficient vibrational excitation. A decrease in the reduced electric field may thus yield higher vibrational temperatures.

In this work, three parameters are assumed to have a direct influence on vibrational excitation, namely pressure, reduced electric field and specific energy input (see figure 4.2). None of these parameters is found to be a scaling parameter that alone determines the vibrational temperature, regardless of the values for the other two parameters. Two tentative scaling parameters are defined by combining several parameters. One scaling parameter consists of physical parameters, while the other consists of process variables. Vibrational temperature is not found to be a unique function of these scaling parameters. Further investigation is needed in order to find a more conclusive scaling parameter.
Chapter 5  General conclusion

In this work, an investigation into vibrational excitation is performed, from the point of view that high rate coefficients and/or energy efficiencies for running a plasma chemical reaction are desired. A nitrogen dielectric-barrier discharge (DBD) is used as test bed for future measurements on plasmas that are more relevant within the field of plasma chemistry. By investigating a nitrogen plasma, many interesting physical parameters can be investigated with the relatively straightforward and inexpensive diagnostics that are used in this work, namely optical emission spectroscopy (OES) and current-voltage (I-U) measurements. The dielectric-barrier discharge is of special interest to the field of plasma chemistry, since it offers a convenient and cost effective route for generating a non-thermal plasma at (near) atmospheric pressures. Besides the main theme of vibrational excitation and plasma chemical reactions, this work also attempts to provide an overview of at least some of the possibilities of OES and I-U measurements, in particular when investigating a nitrogen plasma.

In this work, many physical parameters have been determined over a broad range of the available process variables, which are pressure, residence time (or flow rate) and the amplitude of the applied voltage. The next section contains concluding remarks on these physical parameters, based on the obtained results and their interpretation. In section 5.2, recommendations are provided for researchers who intend to start working with a dielectric-barrier discharge (especially nitrogen DBD) or either of the diagnostics featured in this work, but who are still inexperienced in this field. Section 5.3 provides an outlook onto possible future research that may follow from this work.

5.1  Conclusion

Vibrational temperatures and gas temperatures have been determined by OES in order to get a perspective on possible rate coefficients and energy efficiencies for running a plasma chemical process in a nitrogen DBD. From this perspective, the maximum in vibrational temperature as a function of residence time, located around 50 ms, appears promising, though further investigation is required in order to provide a conclusive explanation. In this work, only a tentative explanation is provided, based on the combined effects of residence time (increasing part) and reduced electric field (decreasing part). Furthermore, the obtained values for both temperatures suggest that high rate coefficients in a nitrogen plasma can be achieved by operating at high values for the applied voltage and medium residence times (or flow rates). High energy efficiencies, on the other hand, may be achieved by operating at low pressures. The results on both temperatures, in combination with the expression for the rate coefficient (equation 1.7), indicate the possibility of having an optimum in rate coefficients as a function of pressure. An optimum in energy efficiency as a function of applied voltage amplitude and residence time may also exist, given the similar trends of both temperatures as a function of these process variables. Future research may focus on finding these optima for plasmas that are more relevant to plasma chemistry.

A positive correlation is found between vibrational temperature and specific energy input, the latter being determined by I-U measurements. When the input of energy per molecule increases, at least some of that extra energy is directed into vibrational excitation. The only exception for this positive correlation is the decrease in vibrational temperature as a function of residence time above 50 ms, which may be explained by the trend in the reduced electric field.
The results on the reduced electric field, determined by OES, suggest a negative correlation between vibrational temperature and reduced electric field, which may be explained by considering that the reduced electric field in a DBD, at least in this work, is too high for efficient vibrational excitation. A decrease in reduced electric field may thus lead to an increase in vibrational temperature. This negative correlation may be used to explain the decreasing part in the trend of the vibrational temperature as a function of residence time. It is worth noting that the reduced electric field depends on residence time (or flow rate) roughly as much as it depends on pressure, which is not trivial. Further investigation is required in order to provide a conclusive explanation for the observed trend in the reduced electric field as a function of the applied voltage amplitude.

No simple scaling parameter concerning vibrational temperature is found. Pressure, specific energy input and reduced electric field all appear to have an independent influence on vibrational excitation. Further investigation is needed in order to find a more conclusive scaling parameter, provided it exists at all.

Besides the investigation into vibrational excitation in a nitrogen DBD that is described above, also a thorough (electrical) characterization of the nitrogen DBD has been performed. The values for the dielectric, gap and cell capacitances that follow from this characterization agree well with calculated theoretical values.

Contrary to the common prediction for DBDs, the gap voltage does not remain roughly equal during the discharge phase, which is tentatively explained by considering the effect of the rise rate of the applied voltage to be stronger than the effect of charge accumulation, at least in this work. Further investigation may reveal how the behaviour of the gap voltage during the discharge phase depends on operating conditions. From the same analysis, the breakdown voltage of nitrogen is found to be significantly lower than the Paschen curve prediction, which can be explained by considering residual charge from the previous discharge phases. The two methods for determining the gap voltage, both determined from the \(I-U\) measurements, show a good agreement. The effect that the filamentary character of the discharge has on charge accumulation may explain why the values for both methods deviate slightly at higher pressures.

Values for the average gap voltage during the discharge phase have been characterized as a function of process variables. Further investigation is required into its dependence on residence time (or flow rate).

Both methods for determining the reduced electric field, one based on OES and one based on \(I-U\) measurements, yield values in the same order of magnitude. However, trends as a function of process variables do not always agree. The \(I-U\) based value for the reduced electric field is expected to represent an average over the entire active volume, whereas the OES based value more probably reflects the reduced electric field in the plasma regions. Different values for both methods can then be explained best by considering the neutral particle density. However, further investigation is needed in order to explain why the \(I-U\) based value is higher than the OES based value at pressures roughly below 70 mbar.

### 5.2 Recommendations

When planning a measurement campaign on a setup with similar process variables as the ones in this work, it is worth considering whether flow rate or residence time should remain constant during a pressure series. This may depend on what is most relevant to the research. When characterizing a setup, it may be easier to keep the flow rate constant. However, if the effects of
pressure and residence time should be disentangled, like was the case in this work, a more proper approach is to attempt to keep the residence time constant. Furthermore, when doing measurements on a dielectric-barrier discharge, it is advisable not to measure close to the extinguishing point of the plasma if this is possible within the research. Under such conditions, determined values for physical parameters are erratic and several assumptions, necessary for the data analysis, do not apply anymore.

When using optical emission spectroscopy, consider which channel of the spectrograph is best suited for the investigation, since it determines the wavelength range and the resolution of the measured spectrum. Therefore, it is important to have an overview of the emission peaks that are relevant to the investigation and how high the resolution for these emission peaks should be. In this work, for instance, only emission peaks in the relatively small range of 330-440 nm have effectively been used for determining physical parameters. For most of these parameters, a low resolution would have sufficed. However, for the rotational temperature analysis (yielding the gas temperature) a high resolution was very convenient, if not crucial (see Appendix C).

Choosing the right integration time for the spectrograph is also important for optimizing the acquired spectra. At the right integration time, the spectrographic intensity of an emission peak of interest is high, though not that high that the corresponding pixels of the spectrograph are saturated. Choosing the right integration time is important since it influences the signal to noise ratio of a spectrum. Naturally, the signal $S$ is proportional to the integration time $t_{int}$ ($S \propto t_{int}$). The noise level $N$ also increases with integration time, but only proportional to its square root, since it can be viewed as a statistical deviation from a mean value ($N \propto \sqrt{t_{int}}$). Thus, the signal to noise ratio increases with the square root of the integration time ($S/N \propto \sqrt{t_{int}}$). In this analogy with statistics, the population is formed by the amount of collected photons, which is proportional to the integration time. In this work, for instance, two spectra at two different integration times were collected for each condition. The spectrum at low integration time was optimized for the brightest emission peak in the spectrum, used for the rotational temperature analysis, while the spectrum at high integration time was optimized for smaller emission peaks that were used for determining other parameters. In the process of optimizing the integration time for smaller emission peaks, larger emission peaks in the vicinity of these peaks of interest may saturate. In principle this should not be a problem, though it must be ensured that the emission peaks of interest are not influenced by the saturation of neighboring emission peaks.

In this work, values for the reduced electric field have been determined by using the ratio between emission from the N$_2^+$ molecular ion and the N$_2$ molecule. In the corresponding literature, the brightest emission peak of N$_2^+$ at 391.44 nm is always used. However, two different emission peaks of the N$_2$ molecule can be used, namely the brightest emission peak at 337.13 nm or a smaller emission peak at 394.30 nm. For reasons mentioned in Appendix C, the latter emission peak should preferably be used. Nevertheless, both ratios have been tried by the author, with the latter ratio indeed yielding more credible results.

When performing (optical emission) spectroscopy, it may be worth spending time on automating the data analysis, especially if many spectra have been collected.

In this work, charge-voltage plots (Lissajous figures) have been used in order to process the collected data from the $I-U$ measurements. Since this method makes use of the integrated current (i.e. charge) for the power analysis, instead of the current signal itself, it is not necessary to resolve individual discharge current peaks in the current signal. This lowers the demands on the
current probe, but also on the used oscilloscope, especially regarding its bandwidth and sample rate. Furthermore, when integrating the current signal, the noise level is intrinsically suppressed. When intending to perform \( I-U \) measurements, it is worth to consider the use of a Lissajous capacitor, which has not been used in this work. A Lissajous capacitor is an auxiliary capacitor in series with the discharge cell [50], having a significantly larger capacitance value \( (C_{\text{Liss}}) \). In that case, only a small portion of the total applied voltage stands across the Lissajous capacitor \( (U_{\text{Liss}}) \), from which the charge \( Q_{\text{Liss}} \) on the electrodes of this auxiliary capacitor can be calculated \( (Q_{\text{Liss}} = C_{\text{Liss}} \cdot U_{\text{Liss}}) \). The charge on the electrodes of the Lissajous capacitor is equal to the charge on the electrodes of the discharge cell \( (Q = Q_{\text{Liss}}) \). By doing so, the charge on the electrodes can be determined more directly, without the necessary corrections that accompany the integration of the current signal (see Appendix J). After the charge-voltage plot has been made, it is advisable to use a numerical method in order to determine the area of the Lissajous figure (i.e. energy input during one AC cycle), especially when many measurements have been performed. In this work, for instance, cumulative integration is used in order to calculate the (specific) energy input.

It is important to emphasize that both methods for measuring the reduced electric field (OES based and \( I-U \) based) not necessarily determine its value at the same location in the reactor. Since the reduced electric field may have significantly different values at different locations, one must always take into account how relevant the used method is within the framework of the intended research. In this work, for instance, the OES based value for the reduced electric field proved to be more relevant than the \( I-U \) based value, given the main theme of vibrational excitation.

### 5.3 Outlook

Several concrete suggestions for future research have already been provided in section 5.1, mainly based on finding explanations for unexpected behaviour of the physical parameters involved in this work. An additional issue that may be addressed by future research can be found in the double burst behaviour that has been observed in this work, but also in a broader context within our research group.

In this work, a nitrogen plasma has been used, mainly motivated by the extensive possibilities that OES and \( I-U \) measurements have when investigating a nitrogen plasma, even though no plasma chemical reaction of our interest occurs in a pure nitrogen plasma. Future research may therefore use this work as a blueprint for a similar investigation into a plasma which is more interesting within the field of plasma chemistry, with the only difference being the use of other diagnostics that are more suited for investigating the relevant physical parameters in that particular plasma. By measuring vibrational excitation and gas temperature as a function of process variables, equation 1.7 may then be used to find optimal windows of operation for running that particular plasma chemical reaction, even in the case of opposite trends. By finding correlations between these temperatures on one hand and other relevant physical parameters (e.g. reduced electric field) on the other hand, physical insights can be gained that are not just reactor specific. Perhaps, even scaling parameters or ratios for controlling vibrational excitation and gas temperature can be found. These insights may then be used for controlling vibrational excitation and gas temperature, and thus rate coefficients and energy efficiency, in industrial scale reactors by tuning the relevant physical parameters involved.
Acknowledgements

A graduation project is never performed without any help. By means of these acknowledgements, I would like to express my gratitude to several members of the research group of Plasma and Materials Processing (PMP) within the department of Applied Physics at the Eindhoven University of Technology.

Floran Peeters is thanked for his help in interpreting the different methods for determining the gap voltage and the reduced electric field.

I would like to thank Twan Haenen for the nice conversations and discussions we had in the PMP student room, but especially for sharing with me his extensive hands-on experience and knowhow concerning spectroscopic calibration and for his assistance during the calibration procedure.

José Palomares Linares is thanked for taking the time to review this thesis, even though he was not one of my supervisors. Beside reviewing, he has given recommendations for the spectroscopic data analysis and provided ideas for the interpretation of several results, based on his extensive experience and knowledge within the field of gas discharge physics.

Many thanks go out to Florian Brehmer for the information and recommendations he provided regarding the data analysis in general, but in particular that of current-voltage measurements. Furthermore, he practically fulfilled the role of technician for the ‘homemade’ DBD reactors in our research group, beside performing his own PhD research.

I would like to thank all my fellow football players of the Plasma Enhanced Soccer Team (PEST) for the good times we had playing our almost weekly football matches. Thanks to PEST, I also experienced excitation and relaxation beyond the scope of molecular vibrations.

Also many thanks to all the students in the PMP student room for their sociability and the fun conversations we had. Our little dart competition makes the student room a place where you can also relax and clear your thoughts, beside the hard work that is obviously being performed there.

I thank Richard Engeln for enabling me to perform my graduation project in his subgroup and for being my chief supervisor, after he already supervised my bachelor project a couple of years ago. He monitored the overall progress of my graduation project and reviewed this thesis. Furthermore, I would like to thank him for providing ideas regarding the spectroscopic data analysis.

My gratitude also goes out to Stefan Welzel, my co supervisor (let us call it that), for monitoring the progress of my research and adjusting course if necessary. Besides that, I thank him for always being available to answer the many questions I had and for thinking along with me, sometimes even on a very detailed level. Furthermore, I want to thank him for providing ideas concerning the interpretation of results and for reviewing this thesis.

The last person I would like to thank, but certainly not the least, is my daily supervisor Srinath Ponduri. I will not even try to give a full overview of all things I can thank him for, since most of the above also applies to him. Certainly worth mentioning is that he inspired me to join his investigation into vibrational excitation. I also thank him for showing me how to operate our DBD setup and its diagnostics. Furthermore, I am grateful for all the time he has spent and all the patience he has shown while supervising me.
In general, I would like to thank the entire PMP research group for enabling this graduation project. Also many thanks for the great group atmosphere and all the nice group activities that have been organized in the past year.
Bibliography


[37] M.A. Khakoo, P.V. Johnson, I. Ozkay, P. Yan, S. Trajmar and I. Kanik, “Differential cross sections for the electron impact excitation of the A 3Σ_u^+, B 3Π_g, W 3Δ_u, B' 3Σ_u^−, a' 1Σ_u^−, a' 1Π_g, w' 1Δ_u, and C' 3Π_u states of N₂”, Physical Review A: Atomic, Molecular, and Optical Physics, 71 (6), 062703 (2005)


Appendix A  Quantum mechanical wavefunctions in an anharmonic potential well

This appendix serves to provide an intuitive picture on the origin of the discrete vibrational levels, or states, of molecules consisting of two (or more) atoms. For a more thorough physical and mathematical treatment of this matter, the reader is referred to more general literature, textbooks or lecture notes regarding quantum mechanics or molecular physics.

In quantum physics, a (quantum) state in a potential well can only exist if it is represented by a solution for the Schrödinger wave equation:

\[
\frac{i\hbar}{\partial t} \psi(\mathbf{r}, t) = \hat{H}(\mathbf{r}, t) \psi(\mathbf{r}, t)
\]  

(A.1)

In this general expression, \(i\) is the imaginary unit, \(\hbar\) is the reduced Planck constant, \(\psi(\mathbf{r}, t)\) is the time dependent quantum mechanical wave function and \(\hat{H}(\mathbf{r}, t)\) is the time dependent Hamiltonian operator, which contains all information on the potential well. Since the potential well of a molecule is not changing in time, the Hamiltonian operator is time independent. In that case, stationary states exist, defined by the so called time independent Schrödinger wave equation:

\[
E \cdot \psi(\mathbf{r}) = \hat{H}(\mathbf{r}) \psi(\mathbf{r})
\]  

(A.2)

In this expression, \(E\) is the total energy (potential plus kinetic) of the considered system. By solving this equation for the potential well of the given molecule, a multitude of solutions for the wave function can be found, each corresponding to different total energies. Thus, discrete levels of (total) energy are found, corresponding to the vibrational states of a molecule. In figure A.1, the probability functions (square of the absolute value of a wave function) of these vibrational states are shown. The most probable internuclear distance for a molecule in the vibrational ground state is the equilibrium distance. For a molecule in the first excited vibrational state, the most probable internuclear distances are higher and lower than the equilibrium distance. For the states with highest total energy, the most probable internuclear distance is quite large. This observation makes the comparison with classical physics tempting, but in no way complete.

Figure A.1: Quantum mechanical probability functions in the anharmonic potential well of a molecule [7]
Appendix B  Full electrical circuit of the experimental setup

Figure B.1 depicts the full electrical circuit that is used for this work. One can easily recognize this circuit as an LC resonance circuit with which high voltages can be applied to the discharge cell by choosing the right frequency (i.e. resonance frequency). The power source applies a sinusoidal voltage to the total circuit, which is divided over a matching inductance $L_{\text{match}}$ (4 mH) and the total capacitive load of the circuit, $C_{\text{tot}}$ (see figure B.2). The voltage over the latter is consistently called the applied voltage $U$ in this work. The main part of the total capacitive load is a matching capacitance $C_{\text{match}}$ (376 pF) which is cooled during operation by a cooling fan. Furthermore, smaller capacitances that contribute to the total capacitive load are the discharge cell $C_{\text{cell}}$ (3.0 pF) and the voltage divider $C_{\text{div}}$. The voltage divider is used in order to measure the applied voltage with a regular voltage probe instead of a high voltage (HV) probe, as can be seen in figure B.1. Since the voltage divider consists of two capacitances in series ($C_{\text{div1}}$ and $C_{\text{div2}}$, respectively 18 pF and 496 pF), its total capacitance can be calculated with the following expression, analogous to resistances connected in parallel:

$$\frac{1}{C_{\text{div}}} = \frac{1}{C_{\text{div1}}} + \frac{1}{C_{\text{div2}}} \quad (B.1)$$

$$C_{\text{div}} = \frac{C_{\text{div1}}C_{\text{div2}}}{C_{\text{div1}}+C_{\text{div2}}} = 17.4 \text{ pF} \quad (B.2)$$

Since the capacitance $C_{\text{div2}}$ is a factor of 28.6 times larger than the total capacitance of the voltage divider, the measured voltage is expected to be a factor of 28.6 times smaller than the applied voltage, making it possible to use a regular voltage probe. However, the voltage divider has been calibrated under operation (high voltage at resonance frequency) with a HV probe, yielding a multiplication factor of 30.86. This difference can be explained by considering that the measured capacitances are not perfectly constant, but depend on temperature, applied voltage and frequency.

In this work, the current from the discharge cell to the ground is measured by a Rogowski coil type current monitor.

![Full electrical circuit of the experimental setup](image)

*Figure B.1: Full electrical circuit of the experimental setup, containing matching components, the discharge cell, a voltage divider, a voltage probe and a current monitor*
Figure B.2: Simplified electrical circuit of the experimental setup, used for resonance frequency calculation

The total capacitive load can be calculated from the three parallel capacitances as follows:

\[ C_{\text{tot}} = C_{\text{match}} + C_{\text{cell}} + C_{\text{div}} = 396 \text{ pF} \]  \hspace{1cm} (B.3)

Thus, the electrical circuit can be reduced to its simplest form, an LC resonance network (see figure B.2). The voltage, delivered by the power source, has amplitude \( U_{ps0} \) and angular frequency \( \omega \). From the simplified electrical circuit, the resonance frequency for the applied voltage can be calculated. To this aim, the complex impedances of the matching inductance \( Z_L \) and the total capacitive load \( Z_C \) must first be considered:

\[ Z_L = i \omega L_{\text{match}} \]  \hspace{1cm} (B.4)

\[ Z_C = \frac{1}{i \omega C_{\text{tot}}} \]  \hspace{1cm} (B.5)

In these expressions, \( i \) is the imaginary unit. The total complex impedance \( Z \) of the LC network can then be expressed as:

\[ Z = Z_L + Z_C = i \left( \frac{\omega^2 L_{\text{match}} C_{\text{tot}} - 1}{\omega C_{\text{tot}}} \right) \]  \hspace{1cm} (B.6)

The total current in the circuit \( I_{\text{tot}} \) can then be calculated as a vector in the complex plane:

\[ I_{\text{tot}} = \frac{U_{ps0}}{Z} = i \left( \frac{\omega C_{\text{tot}} U_{ps0}}{1 - \omega^2 L_{\text{match}} C_{\text{tot}}} \right) \]  \hspace{1cm} (B.7)

From this equation, it can be concluded that, depending on the numerator, the total current is phase shifted a quarter of a period ahead or behind the voltage delivered by the power source. The applied voltage can then also be calculated as a vector in the complex plane:

\[ U = I_{\text{tot}} Z_C = \frac{U_{ps0}}{1 - \omega^2 L_{\text{match}} C_{\text{tot}}} \]  \hspace{1cm} (B.8)

Thus, the resonance frequency \( \omega_{\text{res}} \) can be calculated:

\[ 1 - \omega_{\text{res}}^2 L_{\text{match}} C_{\text{tot}} = 0 \]  \hspace{1cm} (B.9)
During the discharge phase, the total capacitive load of the discharge cell is slightly higher than during the dark phase, having no observable influence on the resonance frequency. In this work, the resonance frequencies, and thus operating frequencies, are in the range 124-141 kHz, mainly depending on the applied voltage amplitude. The difference with the calculated value can again be explained by considering that some components in the electrical circuit are not perfectly constant, but depend on temperature, applied voltage and frequency. This is especially the case for the capacitances.

From equation B.8, it can be deduced that the applied voltage is in phase with the power source voltage for operating frequencies below the resonance frequency. For very low frequencies, the applied voltage and power source voltage are even equal, since the inductor practically acts like a wire under this condition. For operating frequencies above the resonance frequency, the applied voltage is in antiphase with the power source voltage. At very high frequencies, the applied voltage is practically 0 V. In that case, the voltage across the inductance is equal to the power source voltage, since the total capacitive load practically acts like a wire under this condition.

\[
\omega_{res} = \left[\frac{1}{L_{match}C_{tot}}\right]^{-1} \tag{B.10}
\]

\[
f_{res} = \frac{\omega_{res}}{2\pi} = \left[\frac{1}{2\pi L_{match}C_{tot}}\right] = 126 \text{ kHz} \tag{B.11}
\]
Appendix C  Data analysis of optical emission spectroscopy

Rotational temperature (gas temperature)
Zooming in on the biggest emission peak in the spectrum, caused by the transition $N_2(C^3\Pi_u; \nu=0 \rightarrow B^3\Pi_g; \nu=0)$, leads to the view of figure C.1. In theory, this transition would not yield just one peak, but a multitude of peaks. All these peaks would result from the same vibronic transition (i.e. an electronic transition in which also vibrational states are involved), but differ in their corresponding initial and/or final rotational state. However, due to broadening of emission lines (e.g. Doppler broadening caused by thermal movement of molecules) and a limited resolving power of the detector, this series of emission lines cannot be identified as separate peaks, but appears as a big peak with a rotational shoulder/tail at lower wavelengths. In literature, this collection of peak and tail is often called a rotational band \([2, 11, 30]\). The rotational band looks roughly similar for all vibronic transitions, so it is not special for the vibronic transition $N_2(C^3\Pi_u; \nu=0 \rightarrow B^3\Pi_g; \nu=0)$. However, since the emission peak resulting from this transition is brightest, it is used for the rotational temperature analysis.

![Figure C.1: A zoomed in part of the optical spectrum, showing the emission peak at 337.13 nm](image)

The rotational temperature analysis is performed by comparing the shape of the rotational tail of the 337.13 nm peak in a measured spectrum with a calculated version by ‘Specair’ software \([31]\). ‘Specair’ is often used for calculating spectra and it is well known by people who use optical emission spectroscopy intensively. The shape of the rotational tail depends on the rotational excitation of nitrogen molecules in the vibrational ground state of the third excited electronic state (C-state). At high rotational temperatures, the higher excited rotational states are more heavily populated. This will lead to slightly higher transition energies and thus to a longer rotational tail, as can be seen in figure C.2. By trying out different rotational temperatures, the ‘best match’ can be found by eye. A good example is given in figure C.3. The rotational temperature at which the best match is found, is assumed to be the real rotational temperature, which describes the rotational distribution of C-state nitrogen molecules that are in the vibrational ground state. This rotational temperature is also assumed to be the same for C-state
nitrogen molecules that are not in the vibrational ground state and even for molecules in different electronic states, like X-state nitrogen molecules (electronic ground state). In high pressure, low temperature nitrogen plasmas, it is also justified to assume that this rotational temperature is equal to the gas temperature [8-12]. A good estimate of the gas temperature is necessary in order to determine the reduced electric field, either with OES or I-U measurements. More information on how ‘Specair’ is used, can be found in Appendix D.

**Figure C.2:** A zoomed in part of the optical spectrum, showing a calculated spectrum at 300 K (blue) and 500 K (red)

**Figure C.3:** A zoomed in part of the optical spectrum, showing a measured spectrum at $2U_{\text{max}}=18.5\pm0.2$ kV_{pk-pk}, $p=20\pm2$ mbar and $\tau_{\text{res}}=29\pm2$ ms (black) and a calculated spectrum at 395 K (red)
Reduced electric field

As mentioned in subsection 2.2.1, an optical spectrum at long integration time is collected for the reduced electric field analysis. A typical appearance of such a spectrum is presented in figure C.4. Obviously, a lot of the bigger peaks are severely saturated, but these are not needed for the reduced electric field analysis. The emission below 290 nm is not N₂ or N₂⁺ emission, but nitrogen oxide emission, mainly from the NO gamma transition system [29]. It is always present, even in a pure N₂ plasma and it is not caused by an air leak into the system. On the contrary, it is known that a significant amount of air leaking into the system causes this NO emission to decrease significantly. No consensus exists on the origin of the oxygen atoms, necessary to create the nitrogen oxide, though a possible explanation is that they originate from the quartz flow tube, which is in direct contact with the plasma.

![Spectrum](image)

Figure C.4: A typical optical spectrum of the nitrogen plasma under investigation, collected with a long integration time at $2U_{\text{max}}=18.5\pm0.2$ kV$_{\text{pk-pk}}$, $p=150\pm5$ mbar and $\tau_{\text{res}}=400\pm50$ ms

For the reduced electric field analysis, the emission peaks at 391.44 and 394.30 nm are important. These peaks correspond to the transitions N₂⁺(B $^2\Sigma_u^+ ; \nu=0 \rightarrow X ^2\Sigma_g^+ ; \nu=0$) and N₂(C $^3\Pi_u ; \nu=2 \rightarrow B ^3\Pi_g ; \nu=5$), respectively [29]. A zoomed in view of the spectrum around these two peaks is given in figure C.5. From literature [30], an empirical relation is known that gives the reduced electric field as a function of the ratio of these two emission intensities. This empirical relation is used for calculating the reduced electric field out of the measured peak ratio. In this calculation, the gas density must also be known, which is calculated by assuming the ideal gas law and filling in gas temperature and pressure.

In principle, the ratio between any N₂⁺ emission peak and any N₂ peak is a function of the reduced electric field. The intuitive reasoning behind this is that a higher electric field or lower particle density will cause an electron to gain more kinetic energy from the electric field before it collides with an N₂ molecule. This increases the chance of ionization (i.e. creation of N₂⁺) and...
thus increases the amount of $\text{N}_2^+$ emission. However, an empirical relation is only known for the ratio of the emission peaks at 391.44 nm and 337.13 nm and the emission peaks at 391.44 nm and 394.30 nm [30]. The latter ratio is more useful, since these two emission peaks are close together, both in wavelength and relative intensity. Being close in wavelength means that a relative intensity calibration of the optical system is not crucial, while being close in relative intensity makes it possible to chose the integration time of the detector such that both emission peaks have a high spectrographic intensity and thus a good signal to noise ratio. When using the ratio of the emission peaks at 391.44 nm and 337.13 nm, on the contrary, one is comparing a rather small peak, having a poor signal to noise ratio, with a very large peak. This yields poorer results.

![Graph showing spectral data with emission peaks at 391.44 and 394.30 nm]

Figure C.5: A zoomed in part of the optical spectrum, showing, amongst others, the emission peaks at 391.44 and 394.30 nm

**Vibrational temperature**

The vibrational temperature determines the relative populations of excited vibrational states with respect to the vibrational ground state. Also for the vibrational temperature analysis, the spectrum collected at long integration time is used. In figure C.6, a zoomed in part of this spectrum is depicted. This spectral part contains the $\Delta \nu=4$ peak set, which is used for the vibrational temperature analysis. In table C.1, the wavelengths of the emission peaks in this peak set are given, together with their corresponding vibronic transitions. The remaining emission peaks at 423.65, 427.81 and 435.50 nm that are visible in figure C.6, but not mentioned in table C.1, are either the result of $\text{N}_2^+$ emission or $\text{N}_2$ $\Delta \nu=5$ emission.

In order to determine a vibrational temperature, the relative populations of the vibrational states must be known. The population of a vibrational state is proportional to the intensity of the emission peak that corresponds to the vibronic transition which has that particular vibrational state as its initial state:

$$n_{v_i} \propto I_{v_i \rightarrow v_f}$$  \hspace{1cm} (C.1)
For instance, looking at table C.1, the population of the vibrational ground state is proportional to the intensity of the emission peak at 434.36 nm, the population of the first excited vibrational state is proportional to the emission peak at 426.97 nm, etc.

Table C.1: Responsible transitions for emission peaks in the $\Delta \nu=4$ peak set [29]

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Corresponding transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>434.36</td>
<td>$^2\Pi_u; \nu=0 \rightarrow ^2\Pi_g; \nu=4$</td>
</tr>
<tr>
<td>426.97</td>
<td>$^2\Pi_u; \nu=1 \rightarrow ^2\Pi_g; \nu=5$</td>
</tr>
<tr>
<td>420.05</td>
<td>$^2\Pi_u; \nu=2 \rightarrow ^2\Pi_g; \nu=6$</td>
</tr>
<tr>
<td>414.18</td>
<td>$^2\Pi_u; \nu=3 \rightarrow ^2\Pi_g; \nu=7$</td>
</tr>
<tr>
<td>409.48</td>
<td>$^2\Pi_u; \nu=4 \rightarrow ^2\Pi_g; \nu=8$</td>
</tr>
</tbody>
</table>

This is not the whole story, however. The emission intensity of a vibronic transition is not only dependent on the population of the initial state, but also on the transition probability. The transition probability is given by the Einstein A coefficient for spontaneous emission, which is proportional to the wavenumber $\nu$ (Greek small letter ‘nu’) of the transition and the Franck-Condon factor $q$ as follows:

$$A_{\nu_i \rightarrow \nu_f} \propto \nu_{\nu_i \rightarrow \nu_f}^3 \cdot q_{\nu_i \rightarrow \nu_f}$$  \hspace{1cm} (C.2)

The wavenumber is defined as the reciprocal of the wavelength of the emission resulting from that transition and it is proportional to the transition energy (i.e. photon energy). The Franck-Condon factor is the square of the overlap integral of the quantum mechanical vibrational wavefunctions belonging to the initial and final vibronic state (i.e. a combined electronic and vibrational state). The greater the overlap between the vibrational wavefunctions of initial state and possible final state, the greater the chance that this transition will occur. This principle is called the Franck-Condon principle. For nitrogen, the Franck-Condon factors for most vibronic transitions are known [33]. A higher transition probability is the reason why, looking back at
figure C.6, the emission peak at 426.97 nm is more intense than the one at 434.36 nm, even though the vibrational ground state is more heavily populated. Other quantities that determine the Einstein A coefficient are either physical constants or are dependent only on the electronic transition, which is always the same in the vibrational temperature analysis in this work (C-state to B-state). The wavenumber and Franck-Condon factor are the only quantities that depend on the vibrational transition and are therefore the only ones mentioned. More information on the Franck-Condon principle and the validity of equation C.2 are given in Appendix E and F, respectively. Taking into account the transition probability, equation C.1 can be refined:

\[ n_{\nu l} \propto \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} \]  

(C.3)

With this equation, the relative populations of the vibrational states can be calculated. In order to determine a vibrational temperature, a Boltzmann distribution over the vibrational states must be assumed:

\[ \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} = a \cdot n_{\nu l} \]  

(C.4)

\[ \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} = a \cdot n_0 \frac{g_0 e^{-\frac{E_{\nu_l}-E_0}{kT_{vib}}}}{g_{\nu_l}} \]  

(C.5)

In the equations above, \( a \) is a proportionality constant, \( n_0 \) is the population of the vibrational ground state, \( g_0 \) is the degeneracy of the vibrational ground state, \( g_{\nu_l} \) is the degeneracy of the initial vibrational state, \( E_{\nu_l} \) is the vibrational energy of the initial vibrational state, \( E_0 \) is the vibrational energy of the vibrational ground state, \( k \) is the Boltzmann constant and \( T_{vib} \) is the vibrational temperature. Since vibrational levels in \( \text{N}_2 \) are non-degenerate, the following holds:

\[ \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} = a \cdot n_0 e^{-\frac{E_{\nu_l}-E_0}{kT_{vib}}} \]  

(C.6)

Further mathematical manipulation yields:

\[ \ln \left( \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} \right) = \ln \left( a \cdot n_0 e^{-\frac{E_{\nu_l}-E_0}{kT_{vib}}} \right) \]  

(C.7)

\[ \ln \left( \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} \right) = \ln(a \cdot n_0) + \ln \left( e^{-\frac{E_{\nu_l}-E_0}{kT_{vib}}} \right) \]  

(C.8)

\[ \ln \left( \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} \right) = \ln(a \cdot n_0) - \frac{E_{\nu_l}-E_0}{kT_{vib}} \]  

(C.9)

\[ \ln \left( \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} \right) = \ln(a \cdot n_0) + \frac{E_0}{kT_{vib}} - \frac{E_{\nu_l}}{kT_{vib}} \]  

(C.10)

\[ \ln \left( \frac{I_{\nu_l \rightarrow \nu_f}}{\nu_{\nu_l}^3 \nu_{\nu_l}^3} \right) = b - \frac{E_{\nu_l}}{kT_{vib}} \]  

(C.11)
The constant $b$ contains the first two terms on the right hand side of equation C.10. Equation C.11 can be used to construct a Boltzmann plot. A Boltzmann plot is a graph, containing the natural logarithm of the ‘corrected intensity’ (or the ‘corrected intensity’ on a logarithmic scale) on the Y-axis and the vibrational energy of the initial vibrational state on the X-axis. Thus, a Boltzmann plot depicts the vibrational distribution over the excited vibrational states. An example of a Boltzmann plot is depicted in figure C.7. Processing a measured optical spectrum into a Boltzmann plot goes as follows. The measured intensities of the emission peaks in the $\Delta \nu=4$ peak set (see figure C.6 and table C.1) are collected, together with their corresponding wavenumbers, the Franck-Condon factors of the corresponding transitions and the vibrational energies belonging to the initial vibrational states of the corresponding transitions. The wavenumbers can either be looked up in a database [29] or in the measured spectrum itself. The Franck-Condon factors are looked up in a database [33] and the vibrational energies of the initial states are calculated (see Appendix G). By filling in these numbers in equation C.11, every emission peak is represented by one data point in the Boltzmann plot. In figure C.7, for instance, the first data point corresponds to the 434.36 nm emission peak, the second data point corresponds to the 426.97 nm emission peak, etc.

![Boltzmann plot example](image)

*Figure C.7: Typical appearance of a Boltzmann plot and its linear fit (red), based on the $\Delta \nu=4$ peak set*

If the relative population of the vibrational states obeys a Boltzmann distribution, the Boltzmann plot will show descending linear behaviour (see linear fit in figure C.7). In that case, the constant $b$ corresponds to the intersection point between the linear fit and the Y-axis. From the negative slope of the Boltzmann plot, the vibrational temperature can then easily be calculated with equation C.11. This vibrational temperature determines the vibrational distribution of the C-state nitrogen molecules (third excited electronic state). In this work, it is assumed that the same vibrational temperature (or distribution in general) also holds for X-state molecules (electronic ground state). This assumption can be justified by considering the fact that the potential wells of the X-state and C-state align very well (see figure 2.6 in subsection 2.2.2), in combination with
the Franck-Condon principle (see Appendix E). This makes transitions having (almost) equal initial and final vibrational states more likely [36, 37], which means that the vibrational distributions of both electronic states can be expected to be similar. Furthermore, it is common use to determine the vibrational temperature of a nitrogen plasma from optical emission resulting from the C-state to B-state transition [9].

If the relative population of the vibrational states does not obey a Boltzmann distribution, the Boltzmann plot will show non-linear descending behaviour. In that case, the vibrational temperature is not defined and one can only make statements about the appearance of the distribution. In Appendix H, more information is given on why peak sets are analyzed separately and why specifically the Δν=4 peak set is chosen for vibrational temperature analysis.

In the analysis above, the spectral intensity is defined as photon intensity. Often, a spectrum is measured not in photon intensity, but in spectral radiance (‘energy intensity’). In that case, the photon intensity at a certain wavelength must be weighted with the corresponding photon energy at that wavelength:

\[ I_{\text{radiation}} \propto E_{\text{photon}} \cdot I_{\text{photon}} \]  

(C.12)

Since the wavenumber is proportional to the photon energy, the wavenumber can also be used as a weight factor:

\[ I_{\text{radiation}} \propto \nu \cdot I_{\text{photon}} \]  

(C.13)

Thus, working with spectral radiance instead of photon intensity changes little in the analysis above. The only difference is that an extra ν\(_{\nu_i \rightarrow \nu_f}\) is present in all numerators: ν\(_{\nu_i \rightarrow \nu_f}^4\) instead of ν\(_{\nu_i \rightarrow \nu_f}^3\).
Appendix D Using ‘Specair’ software

With ‘Specair’ software [31], a measured optical spectrum can be compared to an optical spectrum that is calculated by the program. Figure D.1 shows the general appearance of the program, along with a calculated spectrum that is typical for the nitrogen plasma in this work. A measured spectrum (space delimited format) can be imported into the program using the ‘File’ tab. The calculated spectrum is based on a list of calculation options, shown in figure D.2, and a slit function that is defined by the user. The slit function is related to the resolving power of the detector and depends on the dispersion of light, caused by the entrance slit of the spectrograph. Even when perfectly monochromatic light falls onto the detector, it is not registered by the spectrograph as having only one wavelength. The slit function can be defined via the ‘Settings’ tab. Defining a slit function that corresponds to the resolving power of the spectrograph is especially important when one is interested in the shape of an emission peak, like is the case for the rotational temperature analysis in this work. A triangular slit function is used in this work, having a base of 0.40 nm and a height of 1.

![Figure D.1: Typical optical spectrum of a nitrogen plasma in this work, calculated by ‘Specair’](image)

Looking at some of the calculation options, listed in figure D.2: the electronic temperature determines the relative populations (or densities) of electronic excited states with respect to the electronic ground state and should therefore not be confused with the electron temperature, which only applies to free electrons. It is only relevant when an absolute intensity calibration of the optical system has been performed or when one is interested in relative intensities of transitions with different initial electronic states. Both are not the case in this work. However, for a good calculation, the electronic temperature must always be chosen to be higher than the other temperatures.
The rotational temperature determines the relative populations of rotational states with respect to the rotational ground state. Therefore, it influences the shape of the rotational tail of emission peaks, which has been used for the rotational (or gas) temperature analysis in this work (see Appendix C).

The translational temperature determines the kinetic energy distribution of neutral species. Therefore, it has an influence on thermal Doppler broadening of emission lines. In this work, the translational temperature can be assumed to be equal to the rotational temperature [8-12].

The vibrational temperature determines the relative populations of vibrational states with respect to the vibrational ground state. Thus, it influences the intensities of emission peaks that originate from the same electronic transition, but with different initial (and final) vibrational states, which is used for the vibrational temperature analysis in this work (see Appendix C).

Under the category ‘Calculation Settings’, absorption of optical emission in the plasma slab can be accounted for. The width of the slab must be entered in centimeters. One can also choose whether to apply a slit function or not.

In the remaining categories, mole fractions of the emitting species can be entered, several radiative transitions can be considered (1) or ignored (0) and absorption of light in the air path between plasma and optical fiber can be accounted for. Since ‘Specair’ is only used to investigate the rotational temperature in this work, only N₂ emission from the C-state to B-state
transition is considered (also called the second positive system, 2+). Absorption of light in between the plasma and the optical fiber is not accounted for.

After a spectrum has been imported or calculated, different colors can be assigned to it. Using the ‘Data’ tab, spectra can be normalized for better comparison. The ‘Data’ tab also enables performing simple mathematical operations on the spectrum (e.g. wavelength shift of spectral data).

In order to avoid frustration, it is worth noting that ‘Specair’ can be quite sensitive to the format in which a value is entered into the program. For instance, the base of the triangular slit function has to be entered in the format 40E-2 or 4E-1. Simply typing 0.40 is interpreted differently than the user intends (i.e. wrong). Unfortunately, ‘Specair’ suffers from more, similar bugs, depending on which version is used. Nevertheless, it is certainly worth to consider using this program. For further details on the use of ‘Specair’, the reader is referred to the manual, which can be found on the ‘Specair’ website [32].
Appendix E  The Franck-Condon principle

This appendix serves to provide an intuitive understanding of the Franck-Condon principle. For a more thorough physical and mathematical treatment of the matter, the reader is referred to more general literature, textbooks or lecture notes regarding molecular spectroscopy.

According to the Einstein A coefficient, the transition probability for spontaneous emission increases with the transition energy (see Appendix F). However, the similarity between the quantum mechanical wavefunctions of the initial and final state also determine the transition probability. A stronger similarity leads to a higher transition probability.

For the case of vibronic transitions in molecules in general, not only spontaneous emission, this effect is described by the Frank-Condon principle and it can be interpreted as follows. Vibronic transitions occur on a very small timescale (i.e. virtually instantaneous) with respect to (inter)nuclear motions. Therefore, such a transition can be represented by a ‘vertical leap’ in the potential energy diagram of a molecule, as can be seen in figure E.1. Considering that vibronic states are represented by quantum mechanical wavefunctions, the transition probability is highest when the wavefunctions, corresponding to the initial and final vibronic state, have a strong overlap. For a given electronic transition, this usually means that the extreme values of the involved vibrational wavefunctions should align more or less (see figure E.1). The amount of overlap is quantified by the overlap integral between the vibrational wavefunctions $\psi_v^{\text{init}}$ and $\psi_v^{\text{final}}$, respectively belonging to the initial and final vibrational state. The Franck-Condon factor $q$ is defined as the square of this overlap integral:

$$q_{v\rightarrow v'} = \left[ \int \psi_v^{\text{init}} \psi_v^{\text{final}} \, dr \right]^2$$

(E.1)

Figure E.1: Schematic depiction of the Franck-Condon principle [35]
Appendix F  The Einstein A coefficient

The Einstein A coefficient for spontaneous emission, due to a transition from initial state \( n \) to final state \( m \), can in general be expressed as [34]:

\[
A_{nm} = \frac{64\pi^4v_{nm}^3}{3\hbar} |R_{nm}|^2
\]  

(F.1)

In this expression, \( v_{nm} \) is the wavenumber corresponding to the observed transition, \( \hbar \) is the Planck constant and the matrix element \( R_{nm} \) is the corresponding transition moment. The transition moment is defined as follows, regardless of which state is the initial or final state [34] :

\[
R_{nm} = \int \psi^m \ast \psi^n dV
\]  

(F.2)

\( \psi^n \) is the total quantum mechanical wave function representing one state, either initial or final, \( \psi^m \ast \) is the complex conjugate of the other state and \( dV \) is an infinitesimal volume element. The vector \( M \) is the electric moment.

Regarding vibronic transitions in molecules, the total quantum mechanical wave function \( \psi \) of any molecular state can be considered as a combination of an electronic \( \psi_e \) and a nuclear \( \psi_n \) wave function (Born-Oppenheimer approximation):

\[
\psi = \psi_e \psi_n
\]  

(F.3)

By ignoring rotation of molecules, the nuclear wave function can be considered to be equal to the vibrational wave function \( \psi_v \) [34] :

\[
\psi = \psi_e \psi_v
\]  

(F.4)

Furthermore, the electric moment can be split up similarly into a part \( M_e \), depending on the electrons, and a part \( M_n \), depending on the nuclei:

\[
M = M_e + M_n
\]  

(F.5)

By combining equations F.2, F.4 and F.5, the transition moment can eventually be written into the following form [34] :

\[
R_{nm} = \int \psi^m_v \psi^n_v dr \int M_e \psi^m_e \ast \psi^n_e dV
\]  

(F.6)

The first integral accounts for the overlap between the vibrational wave functions of the initial and final state, which is why it is often called the overlap integral. Its square is equal to the Franck-Condon factor \( q_{nm} \) (see Appendix E). The second integral is called the electronic transition moment \( R_e \). Since the electronic wavefunctions of the initial and final state depend slightly on the internuclear distance \( r \), \( R_e \) not only depends on the electronic transition, but also on the initial and final vibrational state. However, the dependence of \( R_e \) on \( r \) is assumed to be weak [34]. Therefore, for a given electronic transition it may be replaced by an average electronic transition moment \( \bar{R}_e \), independent of the vibrational transition [34] :

\[
R_{nm} = \bar{R}^{nm}_e \int \psi^m_v \psi^n_v dr
\]  

(F.7)
For the vibrational temperature analysis in this work, this given electronic transition is the transition from the third to second excited electronic state of the nitrogen molecule (C-state to B-state). Substituting equation F.7 into F.1 yields:

\[
A_{nm} = \frac{64\pi^4 v_{\text{nm}}^4}{3\hbar} \left( \overline{\langle n_m | R_e | n \rangle} \right)^2 \left[ \int \psi_{\nu}^m \psi_{\nu}^n \, dr \right]^2 \quad (F.8)
\]

Since the square of the overlap integral is equal to the Franck-Condon factor \( q_{nm} \) (see Appendix E), the Einstein A coefficient can also be expressed as:

\[
A_{nm} = \frac{64\pi^4 v_{\text{nm}}^4}{3\hbar} \left( \overline{\langle n_m | R_e | n \rangle} \right)^2 q_{nm} \quad (F.9)
\]

Within the context of the vibrational temperature analysis in this work, this general expression can be written in a more appropriate form:

\[
A_{\nu_l \rightarrow \nu_f} = \frac{64\pi^4 v_{\text{nm}}^4}{3\hbar} \left( \overline{\langle n_m | R_e | n \rangle} \right)^2 q_{\nu_l \rightarrow \nu_f} \quad (F.10)
\]
Appendix G  Vibrational energies of C-state molecules

All of the emission peaks that are used for the vibrational temperature analysis in this work originate from transitions from the third two second excited electronic state (C-state to B-state). Thus, the vibrational energies of the initial (vibrational) states must be calculated for the third excited electronic state of the nitrogen molecule. The following expression exists for calculating vibrational energies in an anharmonic potential well:

\[ E_v = \Delta E^{\text{H}}_v \left[ \left( v + \frac{1}{2} \right) - x \left( v + \frac{1}{2} \right)^2 + y \left( v + \frac{1}{2} \right)^3 - z \left( v + \frac{1}{2} \right)^4 + \ldots \right] \]  

(G.1)

In this expression, \( \Delta E^{\text{H}}_v \) is the constant energy spacing between the vibrational levels that would exist for a harmonic potential well that approximates the bottom of the real potential well of the molecule (see figure 1.3). For the third excited electronic state of the nitrogen molecule, \( \Delta E^{\text{H}}_v = 0.2525 \text{ eV} \). The coefficients \( x, y \) and \( z \) in the higher order terms correct for the fact that the potential well is not harmonic. In this work, it suffices to only include the first higher order term, since only transitions from lower vibrational states \( (v \leq 4) \) are used for the vibrational temperature analysis. For the third electronic excited state of the nitrogen molecule, \( x=8.4 \cdot 10^{-3} \).
Appendix H  Peak sets in vibrational temperature analysis

For the vibrational temperature analysis in this work, only the $\Delta v=4$ peak set is used. When performing OES in order to determine the vibrational temperature of a nitrogen plasma, or a plasma mixture containing nitrogen, it is common use to analyze peak sets separately. Especially the $\Delta v=4$ and $\Delta v=5$ peak sets are often used [9]. In this work, the $\Delta v=4$ peak set is chosen over the $\Delta v=5$ peak set, since one of the more important emission peaks in the latter peak set falls outside the measured spectral range.

Beside that it is common use, there are also good practical reasons for analyzing peak sets separately and analyzing the $\Delta v=4$ peak set in particular. First, the calibration function (or correction function) that corrects for wavelength dependent transmission of light through the optical system (see figure I.1 in Appendix I) is not valid for the entire measured spectral range. Therefore, it is incorrect to include many different peak sets in the same Boltzmann plot. Furthermore, the $\Delta v=4$ peak set consists of emission peaks with similar relative intensities, as can be seen in figure C.6 in Appendix C. Having emission peaks with similar relative intensities is beneficial for the vibrational temperature analysis (actually any analysis for that matter), since it enables choosing the integration of the detector such that all relevant emission peaks have a high spectrographic intensity and thus a good signal to noise ratio.
Appendix I  Relative intensity calibration

In order to correct for the wavelength dependent transmission of light through the optical system and the wavelength dependent response of the spectrograph, a relative intensity calibration is performed. By comparing the measured optical spectrum of a tungsten ribbon lamp with a theoretical counterpart, which is known to be correct, a calibration function can be calculated (see figure I.1). The calibration function can be obtained as follows:

\[ K(\lambda) = \frac{I_{\text{real}}(\lambda)}{I_{\text{meas}}(\lambda)} \]  

(I.1)

In this expression, \( \lambda \) is the wavelength of the (optical) emission, \( I_{\text{real}} \) is the real wavelength dependent spectral intensity (i.e. real spectrum) of the tungsten ribbon lamp, \( I_{\text{meas}} \) is the corresponding measured wavelength dependent spectral intensity (i.e. measured spectrum) and \( K \) is the wavelength dependent correction factor (i.e. calibration function). Once the calibration function is determined, the calibrated spectrum (i.e. real spectrum) of a plasma can be obtained by multiplying the measured spectrum with the calibration function. Naturally, the correction factor has no unit. Its value only has relevance if an absolute intensity calibration is performed, which is not the case in this work. The procedure for obtaining the known spectrum of the tungsten ribbon lamp is less trivial as may seem from the above and has been described rigorously before, for instance in references [38, 39].

Looking at the calibration function in figure I.1: for higher wavelengths (visible light), the correction factor is roughly constant, increasing only slightly for lower wavelengths. Below wavelengths of approximately 390 nm, the correction factor starts to increase strongly. This represents the fact that the optical system is much less transparent for UV light than for visible light. Below wavelengths of 350 nm the increase in correction factor flattens out until the correction factor decreases again for even lower wavelengths. However, this behaviour at
wavelengths below 350 nm is not real, but an artifact of the calibration measurements. At increasingly lower wavelengths, both the theoretical and measured spectral intensity of the tungsten ribbon lamp approach zero. In the measured spectrum, a constant noise level always remains, however. Therefore, the denominator in equation I.1 continues to decrease for lower wavelengths while the numerator continuous to hold a certain value, causing the correction factor to decrease. In reality, the correction factor should continue to increase for increasingly lower wavelengths. For this reason, the calibration function can only be trusted for wavelengths above 350 nm. Only by using a UV source (e.g. deuterium lamp), the real behaviour of the optical system for wavelengths below 350 nm can be accounted for. Such a calibration is also performed for this work (see figure I.2), although it is not used for any data analysis. The calibration with the deuterium lamp is performed in a similar way as the calibration with the tungsten ribbon lamp, described above.

Figure I.2: The calibration function for the optical setup in this work, using the deuterium lamp

For the rotational temperature and reduced electric field analysis, only a small wavelength domain is used, less than 5 nm wide (see Appendix C). Therefore, a calibration function is not necessary for determining these physical parameters. However, for the vibrational temperature analysis, several emission peaks in the range of 405-435 nm have been used. To avoid possible faulty results, the calibration function based on the tungsten ribbon lamp is applied for this analysis.
Appendix J Data analysis of current-voltage measurements

Lissajous figures
In order to create Lissajous figures from the signals of the applied voltage and the current (see figure 2.10 in subsection 2.3.2), the following steps are taken.

Step 1 Fitting and smoothing
The applied voltage signal is fitted as a sinusoidal function of time, which includes an offset, amplitude, frequency and phase shift. Smoothing of the applied voltage signal is also possible. The fit function, or the smoothed version, is used for creating the Lissajous figure. This is necessary in order to remove the noise from the signal. Using the raw applied voltage signal yields an unclear Lissajous figure, which makes further analysis more difficult, if not impossible.

Optionally, the current signal can also be smoothed (of course not fitted). This is not crucial however, since the current signal will be integrated anyway (step 3), which already leads to suppression of the noise level.

Step 2 Offset correction
Voltage and current probes always have a certain offset. These offsets must be corrected for by subtracting them from the corresponding signals:

\[
U(t) = U_{probe}(t) - U_{offset}
\]

\[
I(t) = I_{probe}(t) - I_{offset}
\]

Offset correction is especially crucial for the current probe, since the signal of a current probe is often relatively small compared to its offset. Furthermore, since the current signal will be integrated (step 3), an offset would be very inconvenient, as will be clarified later.

The offset in the applied voltage signal is given either by the offset in the fit function or by the average value over an integer number of AC cycles of its smoothed version. The offset in the current signal is given by the average value over an integer number of AC cycles, either in the smoothed or unsmoothed version.

Step 3 Integration
The offset corrected current signal is integrated over time in order obtain the charge as a function of time on the grounded electrode (see figure 2.9 in subsection 2.3.1 for plus or minus signs):

\[
-Q(t) = -Q(t_0) - \int_{t_0}^{t} [I_{probe}(t) - I_{offset}] dt
\]

The charge on the high voltage electrode can then be expresses as:

\[
Q(t) = Q(t_0) + \int_{t_0}^{t} [I_{probe}(t) - I_{offset}] dt
\]

The integration constant \(Q(t_0)\) is a priori unknown. However, from the pragmatic consideration that the charge fluctuation should be symmetric around \(Q=0\), it can easily be deduced. The integration constant is only important for the analysis concerning gap voltage as a function time. A typical example of the charge signal (charge as a function of time) is given in figure J.1. The charge signal closely resembles the voltage signal, since they are in phase and have roughly the same shape. However, because of the discharge phases the charge signal is not a perfect
sinusoidal function, but a slightly deformed one. To stress the importance of the offset correction in the current signal, figure J.2 depicts how the charge signal looks when this correction has not been done (properly). On top of the charge fluctuation, a linear term is also present because the integration also included a constant (the offset value), which is negative in this case. This would mean that there is a continuous build up of charge on the electrodes, which cannot be true.

Figure J.1: Charge on the HV electrode as a function of time at $2U_{\text{max}}=18.5\pm0.2$ kV_{pk-pk}, $p=600\pm5$ mbar and $\tau_{\text{res}}=36\pm3$ ms

Figure J.2: Charge on the HV electrode as a function of time without offset correction at $2U_{\text{max}}=18.5\pm0.2$ kV_{pk-pk}, $p=600\pm5$ mbar and $\tau_{\text{res}}=36\pm3$ ms
**Step 4  Q-U plot**
After making sure that the applied voltage signal and the charge signal have the same amount of data points per unit of time, the charge can be plotted as a function of applied voltage for one or more cycles (see figure J.3). Tracing the Lissajous figure counterclockwise corresponds to going forward in time. The Lissajous figure is now ready for further analysis. Again, if the offset correction of the current probe is not performed, the Lissajous figure will spiral upward or downward, as can be seen from figure J.4.

**Figure J.3:** Lissajous figure (almost 14 full cycles) at $2U_{\text{max}}=18.5\pm0.2\ kV_{\text{pk-pk}}$, $p=600\pm5\ mbar$ and $\tau_{\text{res}}=36\pm3\ ms$

**Figure J.4:** Lissajous figure (almost 14 full cycles) without offset correction at $2U_{\text{max}}=18.5\pm0.2\ kV_{\text{pk-pk}}$, $p=600\pm5\ mbar$ and $\tau_{\text{res}}=36\pm3\ ms$
Specific energy input

From literature [18, 22], it is known that the area, enclosed by a Lissajous figure, is equal to the amount of dissipated energy in the discharge cell during one AC cycle. Since no energy is dissipated in the dielectric barriers [23], this amount is equal to the consumed energy by the plasma during one AC cycle. The enclosed area of a Lissajous figure, and thus the energy consumption, can be determined in several ways. Although visual estimation is possible, it is much more convenient to use cumulative integration. In figure J.5, the same Lissajous figure as in figure J.3 is depicted. The Lissajous figure as a whole is shifted upward so that all charges are positive. This procedure makes it easier to visualize integrals as areas, though it is not strictly necessary. The directionality forward in time is indicated by arrows and the transitions between dark and discharge phases are indicated by the numbers 1-4.

![Figure J.5: A closer look on the Lissajous figure](image)

The somewhat smaller area I, indicated by red horizontal stripes, can be expressed as:

\[
\text{Area I} = \left[ \int_{1}^{3} Q(U) \, dU \right]_{\text{via } 2} \tag{J.5}
\]

The somewhat bigger area II, indicated by the blue vertical stripes, can be expressed as:

\[
\text{Area II} = \left[ \int_{1}^{3} Q(U) \, dU \right]_{\text{via } 4} \tag{J.6}
\]

The Lissajous area, or the dissipated energy in the plasma during one cycle \([E_{\text{plasma}}]_{\text{cycle}}\), is the difference between these two areas:

\[
[E_{\text{plasma}}]_{\text{cycle}} = \left[ \int_{1}^{3} Q(U) \, dU \right]_{\text{via } 4} - \left[ \int_{1}^{3} Q(U) \, dU \right]_{\text{via } 2} \tag{J.7}
\]

\[
[E_{\text{plasma}}]_{\text{cycle}} = - \left[ \int_{3}^{1} Q(U) \, dU \right]_{\text{via } 4} - \left[ \int_{1}^{3} Q(U) \, dU \right]_{\text{via } 2} \tag{J.8}
\]
The latter notation is more useful, since the applied voltage data and charge data are automatically sorted forward in time, not backward. This also simplifies the final expression, as can be seen from the following:

\[
[E_{\text{plasma}}]_{\text{cycle}} = -\left[ \int_{3}^{1} Q(U) \, dU \right]_{\text{via} \ 4} - \left[ \int_{1}^{3} Q(U) \, dU \right]_{\text{via} \ 2} \quad (J.9)
\]

\[
[E_{\text{plasma}}]_{\text{cycle}} = -\left\{ \left[ \int_{3}^{1} Q(U) \, dU \right]_{\text{via} \ 4} + \left[ \int_{1}^{3} Q(U) \, dU \right]_{\text{via} \ 2} \right\} \quad (J.10)
\]

\[
[E_{\text{plasma}}]_{\text{cycle}} = -\int_{\text{cycle}} Q(U) \, dU \quad (J.11)
\]

Using cumulative integration, one can simply integrate forward in time, over any integer number of cycles \(n\), through the applied voltage and charge data sets in order to obtain the power input \(P\) into the plasma:

\[
P = \frac{[E_{\text{plasma}}]_{\text{n,cycles}}}{n \cdot T} = \frac{f \cdot [E_{\text{plasma}}]_{\text{n,cycles}}}{n} \quad (J.12)
\]

\[
P = -\frac{\int_{\text{n,cycles}} Q(U) \, dU}{n \cdot T} = -\frac{f \cdot \int_{\text{n,cycles}} Q(U) \, dU}{n} \quad (J.13)
\]

In the formulas above, \(T\) is the period and \(f\) is the frequency of the applied voltage signal. The specific energy input is defined as the amount of energy consumed by the plasma per standard liter of gas flowing through the reactor, which is equal to the power input per flow rate (expressed for standard conditions):

\[
E_{\text{spec}} = \frac{E_{\text{plasma}}}{v_0} = \frac{P \cdot t}{\phi_0 \cdot t} = \frac{P}{\phi_0} \quad (J.14)
\]

**Gap voltage and reduced electric field**

In order to calculate the reduced electric field by means of \(I-U\) measurements, the gap voltage during the discharge phase must first be determined. The gap voltage during the dark phase is not relevant, since (vibrational) excitation of molecules only occurs during the discharge phase. It is known from literature [18, 22, 23] that, if classical electrical theory for sinusoidal driven ozonizers (CETSDO) can be assumed, the Lissajous figure looks like a perfect parallelogram. Furthermore, in that case the width of the Lissajous figure is twice the average gap voltage during the discharge phase (see figure J.6). The gap voltage can then also be assumed to remain rather constant around the breakdown voltage of the gas, as depicted in figure 2.4 in subsection 2.1.3.

In this work, however, Lissajous figures do not always look like perfect parallelograms, which means that CETSDO cannot be assumed in those cases and that determining the average gap voltage during the discharge phase \((U_{\text{gap}})_{\text{discharge}}\) as half the width of the Lissajous figure is not justified anymore. It can still be used as an approximation however. Another approximation is to draw straight lines between the four corner points (see figure J.5) of the Lissajous figure and assume half the width of the thus constructed parallelogram to be equal to the average gap voltage during the discharge phase.
A better approximation, and the one used for determining the reduced electric field, is based on an intuitive reasoning that can be found in literature [18]: the amount of energy, consumed by the plasma during one cycle, is dissipated there by a discharge current running through the plasma. Since the physical quantity voltage expresses how much energy is dissipated per unit of charge (1 V = 1 J/C) and since there are two discharge phases during one cycle, the following relation must hold for the charge $\Delta Q_d$, discharged through the plasma in a half cycle, the amount of energy dissipated during one cycle, and the average gap voltage during the discharge phase:

$$\langle U_{gap}\rangle_{\text{discharge}} = \frac{[E\text{\_plasma}]_{\text{cycle}}}{2 \cdot \Delta Q_d}$$  \hspace{1cm} (J.15)

The amount of energy, deposited in the plasma during one cycle, is already known from the enclosed area of the Lissajous figure (see figure J.5) and the charge, discharged through the plasma during one half cycle, can be determined easily from the Lissajous figure (see figure J.6). The advantage of this approximation, besides that it is supported by solid reasoning, is that one uses two values, $[E\text{\_plasma}]_{\text{cycle}}$ and $\Delta Q_d$, that can both be determined accurately.

The three different approximations roughly give the same result when the Lissajous figure closely resembles a parallelogram, in this work usually at low pressures. At medium pressures, around 300 mbar, they differ the most. The first approximation, simply using the width of the Lissajous figure, is very sensitive to the shape of the two discharge slopes in the Lissajous figure, while the recommended approximation only depends on the locations of the four corner points. These locations can always be easily identified, whereas the discharge slopes can look quite erratic. The second approximation, using the four corner points to construct a perfect parallelogram, has the big disadvantage that one is approximating the real Lissajous figure with a parallelogram that has a different (often bigger) enclosed area and thus represents a different energy input. This raises questions about comparability. For these reasons, the approximation represented by equation J.15 can be considered best.

**Figure J.6: Lissajous figure according to CETSDO [18]**

![Lissajous figure diagram](image)
Once the average gap voltage during the discharge phase is calculated with equation J.15, the average reduced electric field during the discharge phase can be calculated as follows:

$$E = \left( \frac{U_{\text{gap}} \text{discharge}}{d_{\text{gap}}} \right) = \frac{p \cdot d_{\text{gap}}}{k_B T_{\text{gas}}}$$  \hspace{1cm} (J.16)

$d_{\text{gap}}$ represents the width of the discharge gap. In this work, the neutral particle density $n$ is estimated from the reactor pressure and the translational temperature of the gas (i.e. gas temperature) by assuming the ideal gas law ($p = n k_B T_{\text{gas}}$).

**Dielectric capacitance and gap capacitance**

When a voltage is applied to a capacitor, the following relation holds for its capacitance $C$, the charge $Q$ on its electrodes and the applied voltage $U$:

$$Q = C \cdot U$$  \hspace{1cm} (J.17)

In case of alternating voltages, the change in charge is related similarly to the change in voltage:

$$dQ = C \cdot dU$$  \hspace{1cm} (J.18)

$$C = \frac{dQ}{dU}$$  \hspace{1cm} (J.19)

This relation is used in CETSDO [18, 22, 23] in order to determine the dielectric capacitance and cell capacitance from the slopes in the Lissajous figure, corresponding to the discharge phase and the dark phase, respectively (see figure J.6). Looking back at figure 2.3 in subsection 2.1.2, which depicts the simplest equivalent circuit of the discharge cell: during the discharge phase, most (displacement) current runs through the branch containing the resistive load of the discharge gap $R$ instead of the branch containing the capacitive load of the discharge gap $C_{\text{gap}}$. Therefore, the total capacitance during the discharge phase, and thus the corresponding slope, can be assumed to be equal to only that of the dielectric barriers ($C_{\text{diel}}$):

$$C_{\text{discharge}} = C_{\text{diel}}$$  \hspace{1cm} (J.20)

During the dark phase, however, all (displacement) current runs through the branch containing the capacitive load $C_{\text{gap}}$. Therefore, the total capacitance during the dark phase, and thus the corresponding slope, is equal to that of both the dielectric barriers and the discharge gap, connected in series, which is also called the total cell capacitance $C_{\text{cell}}$:

$$\frac{1}{C_{\text{dark}}} = \frac{1}{C_{\text{diel}}} + \frac{1}{C_{\text{gap}}} \equiv \frac{1}{C_{\text{cell}}}$$  \hspace{1cm} (J.21)

$$C_{\text{dark}} = C_{\text{diel}} \cdot C_{\text{gap}} \equiv C_{\text{cell}}$$  \hspace{1cm} (J.22)

Even though the dielectric capacitance can ideally be determined from the discharge slope in the Lissajous figure, this proves to be difficult when the discharge slope is not as straight as in the case of CETSDO. In literature [22], an alternative method is suggested for determining the dielectric capacitance, even when CETSDO cannot be assumed (i.e. discharge slope is not straight). In this method, Lissajous figures taken at different amplitudes of the applied voltage
are compared. More precisely, the points of maximal charge $Q_{\text{max}}$ and corresponding applied voltage $U_{\text{max}}$ (top right corner) at different amplitudes are compared, as can be seen in figure J.7. Since equations J.19 and J.20 hold, the slope of the linear fit through these points is equal to the dielectric capacitance. In this work, this method is used to determine the dielectric capacitance.

Since the dark slope is not as erratic as the discharge slope, the cell capacitance can be determined in the same way as in the ideal case of CETSDO:

$$C_{\text{cell}} = C_{\text{dark}}$$  \hspace{1cm} (J.23)

The gap capacitance $C_{\text{gap}}$ can then be determined by using equation J.21:

$$\frac{1}{C_{\text{gap}}} = \frac{1}{C_{\text{cell}}} - \frac{1}{C_{\text{det}}}$$  \hspace{1cm} (J.24)

$$C_{\text{gap}} = \frac{C_{\text{cell}}C_{\text{det}}}{C_{\text{cell}} - C_{\text{det}}}$$  \hspace{1cm} (J.25)

![Figure J.7: Maximal charge on the electrodes during an AC cycle as a function of the corresponding value of the applied voltage](image)

**Gap voltage as a function of time**

The voltage over the discharge gap is a priori unknown. However, now the charge on the electrodes and the dielectric capacitance have been determined, equation 2.9 in subsection 2.1.2 can be used to calculate the voltage across the dielectric barriers:

$$Q = C_{\text{det}} \cdot U_{\text{det}}$$  \hspace{1cm} (J.27)

$$U_{\text{det}} = \frac{q}{C_{\text{det}}}$$  \hspace{1cm} (J.28)

The voltage over the discharge gap can then be expressed as:

$$U_{\text{gap}} = U - U_{\text{det}}$$  \hspace{1cm} (J.29)
\[ U_{\text{gap}} = U - \frac{Q}{c_{\text{die}}} \]  \hspace{1cm} \text{(J.30)}

By filling in the datasets of the measured applied voltage \( U \) and the earlier calculated charge \( Q \) on the electrodes into equation J.30, the gap voltage as a function of time can be calculated.