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Plasma-chemical and plasma-catalytic processes associated with low-temperature plasma generated by electrical discharges in gas, liquid, and gas–liquid environments have recently generated considerable interest. Nonthermal plasmas offer a unique way to initiate chemical reactions in the gas phase as well as in liquids, which have potential for practical utilization in different environmental, biological, or medical applications, and also in energy topics or molecular synthesis. Since plasma-chemical processes are rather nonselective, combination with catalysis can provide improved selectivity, by steering the reactions in the desired direction. Catalyst activation by plasma is different from that in case of conventional heating, and therefore the knowledge of plasma-catalyst interaction represents a key issue both from the fundamental point of view, for the understanding of reaction mechanisms involved in the plasma-catalytic process, and obviously, from the point of view of applications. Promising results have been obtained in environmental applications, where it was found that nonequilibrium plasma generated in electrical discharges at atmospheric pressure and room temperature can be successful in destroying a wide range of air pollutants. Serious attention is also directed to plasma-catalytic applications for hydrogen production, which plays a key role in fuel cell technology, as well as for the conversion of natural gas into syngas or into higher hydrocarbons, which can be used as fuel for transportation and raw material in chemical industry. In this direction, the control of catalyst properties by preparation or treatment techniques, as well as their modifications during plasma-catalytic reactions, catalyst stability, and regeneration processes, are important issues. Another vital issue for environmental research is water pollution. During the past 20 years, promising results have been obtained for the degradation of water pollutants and inactivation of various microorganisms using nonequilibrium plasma generated by electrical discharges in liquids and gas–liquid environments. These discharges have been shown to initiate various chemical and physical processes that have potential for practical utilization in different environmental, biological, or medical applications. For example, electrical discharges were successfully applied to degrade and inactivate a number of organic compounds and microorganisms in water. There are also first successful biomedical applications of discharge plasma in liquids.
This book provides an overview of the basic principles of plasma-chemical and plasma-catalytic processes generated by electrical discharges in gas, liquid, and gas–liquid environments, which is addressed by experts in the fields of plasma physics, plasma chemistry, and plasma catalysis. The book is divided into four major sections containing altogether nine chapters that cover the state of the art of this topic in both fundamental and applied aspects.

The first section contains two introductory chapters (Chapters 1 and 2). The first chapter provides an introduction to the fundamental aspects of nonthermal plasma generated by various types of electrical discharges operating in gas at atmospheric pressure and its properties. Chapter 2 focuses on the analysis of the intrinsic characteristics of the catalysts used in plasma-catalytic processes. The control of catalyst properties by preparation and treatment techniques and factors controlling the catalyst stability and regeneration processes represent other issues analyzed in this chapter. All these aspects are important criteria for the selection of appropriate catalysts for the desired applications.

The Chapters 3–5 give an extensive overview of the plasma-catalytic processes associated with low-temperature electrical discharge plasma in gases and their application for air pollution abatement. Chapter 3 is devoted to nitrogen oxides remediation (deNH₃) by plasma-assisted catalysis. Chapters 4 and 5 are dedicated to the decomposition of volatile organic compounds (VOCs) in air using plasma-catalytic systems. Results obtained in different plasma-catalytic systems are discussed, and the interactions between plasma and catalysts as well as the mechanisms responsible for NOₓ and VOC remediation are addressed.

The Chapters 6–8 present the state-of-art fundamental and applied knowledge on plasma-chemical processes associated with nonequilibrium plasma generated by electrical discharges in liquids and gas–liquid environments. In these chapters, for the first time, a comprehensive overview of the elementary chemical and physical phenomena in low-temperature plasma in liquid and gas–liquid environments is provided, including fundamental mechanisms of plasma generation by electrical discharges in water and gas–liquid environments, chemistry and reaction kinetics of primary and secondary species generated by plasma in water and gas–liquid interfaces, mechanisms of interaction of plasma with chemical and biological content in water, plasma-catalytic processes in water and gas-liquid environments, and environmental and biomedical applications of plasma in water and gas–liquid environments.

Chapter 9 focuses on applications of nonthermal plasma and plasma-catalytic processes in energy conversion. An overview of the current state of hydrogen and syngas production, applications, and technical requirements is presented. Detailed discussions are provided with respect to steam reforming, partial oxidation, and carbon dioxide dry reforming, including coupling to higher hydrocarbons and plasma pyrolysis, as well as combined processes, highlighting the key issues to determine practical and economic viability.

This book is equally addressed to scientists and engineers with research interests in the fields of plasma, chemistry, catalysis, pollution abatement, synthesis of new
materials, or energy conversion techniques. It may also be a very good support for students and Ph.D. students performing research in one of these fields.

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1
An Introduction to Nonequilibrium Plasmas
at Atmospheric Pressure

Sander Nijdam, Eddie van Veldhuizen, Peter Bruggeman, and Ute Ebert

1.1
Introduction

1.1.1
Nonthermal Plasmas and Electron Energy Distributions

Plasmas are increasingly used for chemical processing of gases such as air, combustion exhaust, or biofuel; for treatment of water and surfaces; as well as for sterilization, plasma deposition, plasma medicine, plasma synthesis and conversion, cleaning, and so on. These plasmas are never in thermal equilibrium – actually, we know of no exemption – and this fact has two main reasons.

1) It is easier to apply electromagnetic fields than to uniformly heat and confine a plasma. However, electromagnetic fields naturally transport charged species whose concentrations and energies therefore naturally vary in space, particularly, close to the walls of the container. Generically, the species in such a plasma are not in thermal equilibrium.

2) It is energy efficient to not feed energy equally into all degrees of freedom within a gas or plasma, such as into the thermal displacement, rotation, and vibration of neutral molecules, but only into those degrees of freedom that can efficiently create the desired final reaction products for the particular application. Therefore it is frequently preferable to accelerate only electrons to high velocities and let them excite and ionize molecules by impact while keeping the gas cold. If the electron energy distribution is appropriate, some reactions can be triggered very specifically.

In this manner, the nonthermal nature of the plasmas that are created electromagnetically is made into an asset. By varying gas composition, electrode and wall configuration, and circuit characteristics more energy can be channeled into specific excitations and reactions. Recent examples include the optimization of the
pulsed power source for ozone generation in streamer corona reactors [1], or dual frequency RF-generated plasmas [2].

To elaborate the physical understanding further, Mark Kushner has proposed a workshop at the Gaseous Electronics Conference (GEC) 2011 on how the electron energy distribution within a discharge can be tailored for a specific application. A joint approach to this question by theory and experiment now seems within reach because of the large progress of theory in recent years.

1.1.2
Barrier and Corona Streamer Discharges – Discharges at Atmospheric Pressure

The past has mainly seen an experimental approach by trial and error, also guided by some physical understanding. Within the limited space available here, we will review some setups and their physical mode of operation. A common theme is the avoidance of plasma thermalization in the form of arcs and sparks. Variations over two basic approaches are used very commonly and will make the main theme of this review: the corona discharge and the barrier discharge. In a barrier discharge, large currents are suppressed by dielectric barriers on the electrodes. Basically, the discharge evolves only up to the moment when so much charge is deposited on the insulator surfaces that the field over the gas is screened. In a corona discharge, the discharge expands from a needle or wire electrode into outer space where the electric field decreases and finally does not support a discharge anymore. The discharge then has to feed its current into the high-ohmic region of the nonionized gas, which limits the current as well. These two basic principles have seen many variations in the past years and decades. For example, in corona discharges, short and highly ramped voltage pulses create much more efficient streamers that do not cease due to the spatial decrease of the electric field away from the curved electrode but due to the final duration of the voltage pulse.

Both discharge types can (but need not) operate at atmospheric pressure. This poses an advantage as well as a challenge. The advantage lies in the fact that no expensive and complex vacuum systems are required. This makes the design of any reactor a lot simpler, not only when the operating gas is air but also when other gases (such as argon or helium) are used. The challenge consists of the observation that characteristic length scales within the discharge can be much smaller than the discharge vessel and that the discharge can therefore form complex structures, rather than a more or less uniform plasma. These structures have to be understood and used appropriately. For instance, the initial evolution of streamer discharges follows similarity laws [3]: when the gas density is changed, the same voltage will create essentially the same type of streamer, but on different length and timescales. Therefore, streamer fingers and trees grow in a similar manner at 10 μbar as at 1000 mbar, but 10 μbar corresponds to an atmospheric altitude of 83 km where the so-called sprite streamers have a diameter of at least ∼10 m, while at 1000 mbar, the minimal streamer diameter is ∼100 μm and conveniently fits into typical experiments.
1.1.3 Other Nonthermal Discharge Types

There is a large variety of nonthermal plasmas. They can be classified into different discharge types, although definitions used by different authors vary significantly. The plasmas or discharges can be classified according to their time dependence (transient or stationary), importance of space charge effects or of heating of the neutral gas species, and presence of a surface close to the discharge. The most important nonthermal plasmas along with their energization method and typical applications are listed in Table 1.1.

This table is intended to give a general idea, but it is far from complete. A further complication is that definitions are used in different ways. For example, in Ref. 8, Braun et al. use what they call a microdischarge for ozone generation, whereas the microdischarges as intended in Table 1.1 are much smaller. The microwave discharge made by Hrycak et al. [28] qualifies much more for the term plasmajet than for microdischarge. More information on the different types of microdischarges is given in [29]; some examples of the use of microdischarges are given in Section 1.4.4.

In many transient discharges, the different discharge types can occur after each other. For example, a discharge can start as an avalanche and then become a streamer, which can develop into a glow and finally into an arc discharge. When applying a DC field between two metal electrodes, a discharge at high pressure will become a thermal arc if the power supply can deliver the current. Nonthermal discharges are, by definition, almost always transient.

Table 1.1 Overview of nonthermal discharge types and their most common applications.

<table>
<thead>
<tr>
<th>Type of discharge</th>
<th>Gap (mm)</th>
<th>Plasma</th>
<th>Energization</th>
<th>Typical application</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corona</td>
<td>10–300</td>
<td>Filaments</td>
<td>Pulsed/DC</td>
<td>Gas cleaning/dust precipitation</td>
<td>[4, 5]</td>
</tr>
<tr>
<td>Corona with barrier</td>
<td>10–30</td>
<td>Filaments</td>
<td>Pulsed</td>
<td>Gas and water cleaning</td>
<td>[6, 7]</td>
</tr>
<tr>
<td>Plates/cylinders</td>
<td>1–5</td>
<td>Filaments</td>
<td>AC</td>
<td>Ozone generation/ large surface treatment/ excimer lamps</td>
<td>[8–12]</td>
</tr>
<tr>
<td>with barrier</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barrier with packed</td>
<td>3–10</td>
<td>Filaments</td>
<td>AC</td>
<td>Chemicals conversion</td>
<td>[13–15]</td>
</tr>
<tr>
<td>bed</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plates with barrier</td>
<td>1–5</td>
<td>Diffuse</td>
<td>AC</td>
<td>Surface treatment/deposition</td>
<td>[16, 17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface discharge</td>
<td>1–5</td>
<td>Filaments</td>
<td>AC</td>
<td>Surface treatment/deposition</td>
<td>[18, 19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface barrier</td>
<td>1–5</td>
<td>Filaments</td>
<td>Pulsed</td>
<td>Aerodynamic control</td>
<td>[20–22]</td>
</tr>
<tr>
<td>Plasma jets</td>
<td>0.5–10</td>
<td>Diffuse</td>
<td>AC/RF</td>
<td>Local surface</td>
<td>[18, 23–25]</td>
</tr>
<tr>
<td>Microdischarge</td>
<td>0.1–1</td>
<td>Diffuse</td>
<td>AC/RF</td>
<td>Chemicals conversion/ light generation</td>
<td>[26, 27]</td>
</tr>
</tbody>
</table>
An essential feature of a cold nonthermal discharge is its short duration. Therefore, the largely varying timescales of the processes inside the discharge must be considered. The excitation timescales, which often range from picoseconds to a few microseconds, are clearly not the timescale necessary for preventing thermalization as thermalization occurs in millisecond-order timescales. The critical timescale is basically the characteristic time of the glow-to-spark transition. This transition time can highly depend on conditions such as voltage amplitude and gas composition but is often in the order of a (few) hundred nanoseconds [30]. Dielectric barrier discharges (DBDs) are a well-known example of how (dielectric) barriers can reduce current density and $n_e$ to keep the gas temperature of the discharge low.

Like streamer and avalanche discharges, Townsend and glow discharges are cold discharges. They usually occur as a stationary discharge but have to be preceded by another discharge such as a streamer or avalanche discharge to ignite. In Townsend and glow discharges, electrons are emitted from the electrode and are then multiplied in the gap. In the case of a Townsend discharge, the electron multiplication takes place in the whole gap, while in a glow discharge, space charge concentrates the multiplication in the cathode sheath region. Electrons are freed from the cathode by the temperature of the cathode itself or by secondary emission either due to the impact of energetic positive ions or due to photons or heavy neutrals.

Several cold atmospheric pressure discharges operate in helium. This is not a coincidence as He has a thermal heat conductivity that is about 10 times larger than that of most other gases, which renders heat removal from the discharge to be more efficient. Other methods for efficient heat removal include strongly forced convection cooling in flow stabilized discharges and creation of discharge with a large area-to-volume ratio (microplasmas, see also further) to make the heat losses to the walls more efficient.

1.1.3.1 Transition to Sparks, Arcs, or Leaders
Avalanches, Townsend, streamer, and glow discharges are examples of cold discharges. This means that the heavy particle temperature is not much above room temperature and definitely far below the electron temperature ($T_e \gg T_i \approx T_n$ where e, i, and n stand for electron, ion, and neutral, respectively). At even higher currents, at higher pressures, or with longer pulse durations, these discharges can transform into spark, arc, or leader discharges. These are hot discharges, the heavy particle temperature is close to the electron temperature and can reach thousands of Kelvin ($T_e \gtrsim T_i \approx T_n$). In applications, heating of the gas is often unwanted, and therefore, cold discharges are preferred in many plasma treatment applications.

1.1.4 Microscopic Discharge Mechanisms

1.1.4.1 Bulk Ionization Mechanisms
The main ionization mechanism in electric discharges is impact ionization; in attaching gases such as air, impact ionization is counteracted by electron attachment.
Other mechanisms that create free electrons such as photoionization or electron detachment from negative ions are discussed in Section 1.2.4.1. Impact ionization occurs when electrons are accelerated in a high local electric field. At a certain kinetic energy, they can ionize background gas atoms or molecules and create more electrons. In air, this occurs by the following reactions:

\[
\begin{align*}
O_2 + e & \longrightarrow O_2^+ + 2e \quad (1.1) \\
N_2 + e & \longrightarrow N_2^+ + 2e \quad (1.2)
\end{align*}
\]

In the so-called local field approximation (i.e., when the reaction rate is approximated as depending on the local electron density and local electric field only) [31, 32], the number of electrons generated per unit length per electron is called the Townsend impact ionization coefficient \( \alpha_i(|E|) = \sigma_i(|E|) n_0 \). Here \( E \) is the electric field, \( \sigma_i \) the cross section for electron impact ionization, and \( n_0 \) is the background gas density. An old and much used approximation is

\[
\alpha_i(|E|) = \alpha_0 \exp\left(-\frac{E_0}{|E|}\right) \quad (1.3)
\]

This notation illustrates that the Townsend coefficient is characterized by two parameters: \( E_0 \) characterizes the electric field where impact ionization is important; this electric field is proportional to the gas density \( n_0 \). \( \alpha_0 \) characterizes the inverse of the ionization length at these fields. More precisely, \( 1/\alpha_i(|E|) \) is the mean length that an electron drifts in the field \( E \) before it creates an electron–ion pair by impact. Therefore, in geometries smaller than this length, no gas discharge can occur. Both the electron mean free path, between any collision, and the ionization length scale with inverse gas density.

The electron loss rate due to electron attachment on attaching gas components has a similar functional dependence as the impact ionization rate, but different parameters. One needs to distinguish between dissociative attachment

\[
e + O_2 \longrightarrow O + O^- \quad \text{(in air)} \quad (1.4)
\]

and three-body attachment

\[
e + O_2 + M \longrightarrow O_2^- + M \quad \text{(in air)} \quad (1.5)
\]

where \( M \) is an arbitrary third-body collider, for example, \( N_2 \) or \( O_2 \). As a third body is required here to conserve energy and momentum, the importance of three-body attachment relative to dissociative attachment increases with density. Dissociative attachment scales with gas density in the same manner as the impact ionization reaction, while three-body attachment is favored at higher gas density. On the other hand, dissociative attachment becomes more important at higher electric fields, even at standard temperature and pressure. For detailed discussions of the derivation of these reaction coefficients, we refer to [33–36].

The breakdown field is defined as the field where impact ionization and electron attachment precisely balance; at higher electric fields, an ionization reaction sets in. The spatial and temporal evolution of the discharge depends on the distribution of electrons and electric fields; this is discussed in more detail below.
1.1.4.2 **Surface Ionization Mechanisms**

Next to the bulk gas, the presence of a dielectric or metallic surface can also affect the discharge significantly. It will modify the electric field configuration, and it is able to provide electrons. Dielectrics can also store surface charges [37] and prevent charge carrier flow through the surface.

Electrons can be freed from a surface by high fields or by secondary emission on impact of ions [38], fast neutrals, or (UV) photons [39]. Photons can be generated in the bulk of the discharge and then free an electron from the surface. Electron emission can be enhanced by the local electric field at the surface or by higher surface temperatures. The freed electrons can form the start of an avalanche, which enables the discharge to initiate or propagate (over the surface). See Section 1.4.3 for a more elaborate discussion on this topic.

1.1.5 **Chemical Activity**

The main advantage of nonthermal plasmas is their high chemical efficiency. As little or no heat is produced, nearly all input energy is converted to energetic electrons. This is in contrast to thermal plasmas in which the heating itself leads to higher thermal losses and thereby can be a waste of energy, which reduces the chemical efficiency of these hot plasmas [40] and can damage walls and other nearby surfaces (such as the substrate in a surface processing application).

Furthermore, higher gas temperatures will change the reaction kinetics which, amongst others, may lead to breakdown of ozone and increased formation of \( \text{NO}_x \). Of course, the different reaction kinetics of higher gas temperatures can also be beneficial for some chemical reactions such as destruction of hydrocarbons.

The fast electrons produced in a nonthermal plasma can have energies of the order 10 eV or even higher and can therefore trigger many different chemical processes. Besides fast electrons, energetic photons can also play a role in the reactions in a nonthermal plasma. One important example of such a reaction is photoionization in air, which is discussed in detail in Section 1.2.4.1. However, the primary source of all reactions is electron impact on the bulk gas molecules, which leads to many reactive species that can than further react with more stable species. Examples of the reactive species are OH, O, and N radicals; excited N\(_2\) molecules; and atomic and molecular ions (e.g., \( \text{O}^+ \), \( \text{O}_2^+ \)).

One of the main paths of chemical activity in nonthermal plasmas in air is ozone production. This is generally believed to be a two-step process as described by Chang *et al.* [41] and Ono and Oda [42].

1) First, free oxygen radicals are produced by inelastic electron impact.

\[
\begin{align*}
\text{O}_2 + e & \rightarrow \text{O}^+ + \text{O} + 2e \\
\text{O}_2 + e & \rightarrow \text{O} + \text{O} + e \\
\text{O}_2 + e & \rightarrow \text{O}^- + \text{O}
\end{align*}
\]
2) Then, ozone is created by reactions of these free radicals.

\[
O + O_2 + M \rightarrow O_3 + M \quad M = O_2 \text{ or } N_2 \tag{1.9}
\]

Ozone can be produced with a wide range of electrode and discharge topologies, many of which are treated below; the most popular are dielectric barrier discharges. An early example is the ozone generator of Siemens made in 1857. The most important application of this device was ozone production for disinfection of water. Even now, this device is used, with only minor modifications [43]. But corona discharges can create O radicals (and thereby ozone) with very high energy efficiency as well [1], as will be discussed in more detail further below. In commercial ionizers, pure oxygen is often used as the starting gas because the nitrogen that is present in air can lead to the formation of NO\(_x\) (a general term used for NO and NO\(_2\) and sometimes other nitrogen–oxygen compounds) with the following reactions [44]:

\[
N + O_2 \rightarrow NO + O \tag{1.10}
\]

\[
O + N_2 \rightarrow NO + N \tag{1.11}
\]

where the O radicals come from Eqs. (1.6–1.8) and the N radicals are produced by [45]

\[
N_2 + e \rightarrow N + N + e \tag{1.12}
\]

The produced NO can further react with NO\(_2\) as described in [45, 46]

\[
O + NO + M \rightarrow NO_2 + M \tag{1.13}
\]

\[
2NO + O_2 \rightarrow 2NO_2 \tag{1.14}
\]

\[
2NO + O_2 \rightarrow NO_2 + N + O_2 \tag{1.15}
\]

However, nonthermal plasmas can also remove NO from gas streams. The main path for the removal of NO from air at low NO concentrations is (Eq. (1.12)) followed by [47]

\[
N + NO \rightarrow N_2 + O \tag{1.16}
\]

A second type of radical that is important in nonthermal plasmas is OH. This is produced in moist gases (e.g., moist air) by the following reaction [48]:

\[
H_2O + e \rightarrow H + OH + e \tag{1.17}
\]

Note that apart from electron-induced dissociation, dissociative electron recombination of water containing ions can also efficiently produce OH.

\[
H_3O^+ + e \rightarrow OH + H_2 \tag{1.18}
\]

The rate of this reaction for nonthermal discharges with \(T_e\) in the range 1–2 eV is sometimes even faster than electron dissociation [49]. Several secondary reactions are also believed to play an important role in the production of OH

\[
H_2O + O(^1D) \rightarrow 2OH \tag{1.19}
\]

\[
H_2O + N_2(A) \rightarrow OH + H + N_2(X) \tag{1.20}
\]
where $O(^1D)$ is an excited state of atomic oxygen, $N_2(A)$ is a metastable nitrogen molecule and $N_2(X)$ is a nitrogen molecule in the ground state. It is clear that Eq. (1.17) occurs only in the ionizing phase, while Eqs. (1.18–1.20) also occur in the recombining phase when the electron temperature is equal to the gas temperature.

Which reactions dominate depends on the electron energy (which is dependent on topology, voltage shape, and amplitude, etc.) and the composition of the gas. In general, thermal discharges mostly produce NO\textsubscript{x}, while nonthermal discharges produce ozone instead and can remove NO\textsubscript{x} when concentrations are high. At low NO\textsubscript{x} concentrations also, nonthermal discharges can lead to the net production of NO\textsubscript{x}. A comparison of NO\textsubscript{x} production by sparks and corona discharges was performed by Rehbein and Cooray [50]. They found that sparks produce about 2 orders of magnitude more NO\textsubscript{x} per Joule than corona discharges. Overviews of different reactive species and the conditions in which they are important are given by Eliasson and Kogelschatz [51] and Kim [43].

Besides NO\textsubscript{x} removal, which was discussed above, a host of other species can be removed from gas streams by nonthermal plasmas. Examples are volatile organic compounds (VOCs), chlorofluorocarbons (CFCs), SO\textsubscript{2}, odors, and living cells (in disinfection or sterilization).

Most charges in a nonthermal discharge in air are initially produced by the direct impact ionization of nitrogen

$$N_2 + e \rightarrow N_2^+ + e + e$$

(1.21)

with a threshold ionization energy of 15.58 eV or of oxygen (Eq. (1.1)) with a threshold ionization energy of 12.07 eV. According to Aleksandrov and Bazelyan [52], $N_2^+$ and $O_2^+$ will quickly change to other species according to the following scheme (for dry air under standard conditions):

$$N_2^+ \rightarrow N_4^+ \rightarrow O_2^+ \rightarrow O_4^+$$

(1.22)

After some tens of nanoseconds, the positive ions are dominated by $O_4^+$. Electrons are quickly attached to molecular oxygen by reactions given in Eqs. (1.4) and (1.5).

1.1.6 Diagnostics

In all nonthermal plasmas, fast electrons excite species. Many of the excited species can fall back to lower excited levels or the ground level and thereby emit a photon. These photon emissions are by far the most important property of cold discharges that are studied experimentally. They are used for imaging and for optical emission spectroscopy. Spectra of cold discharges in air are dominated by the emissions of the second positive systems of $N_2$ (SPSs, upper states $B^1\Pi_g$ and $C^3\Pi_u$). The SPS is often used to obtain the rotational temperature, which is mostly a good indication of the gas temperature [53].

For strongly pulsed and high field discharges and also in discharges in, for example, helium with air impurities, the first negative system of $N_2^+$ (FNS, upper state $B^2\Sigma^+_u$) readily occurs. Relative intensity comparisons of the SPS and this FNS have
been performed by many authors and are used to determine the electric field in nitrogen-containing discharges. This method is employed, for example, by Kozlov et al. [54] for laboratory scale discharges and by Liu et al. [55] for sprites.

There are many other rotational bands of different molecules that can be used to obtain rotational temperatures, which are mostly a good indication of the gas temperature. Especially popular is the UV emission band of OH(A–X) around 309 nm [53]. However, it has recently been found that the rotational population distribution is not always in equilibrium with the gas temperature and sometimes leads to overestimates [56].

Electron densities above $10^{20}$ m$^{-3}$ can be determined by measuring the Stark broadening of the hydrogen Balmer lines. Especially the Balmer $\beta$ line is very popular. It is important to note that it is necessary to carefully take into account all broadening mechanisms including van der Waals broadening, which can become quite important for low-temperature atmospheric pressure plasmas. A detailed description can be found in [53].

Besides (passive) optical emission spectroscopy, there are many other techniques to study nonthermal plasmas. Apart from standard voltage and current waveform measurements, several electrical probes exist, especially developed for low pressure plasmas, although it is often difficult and very complicated to apply them on atmospheric pressure plasmas. The active laser spectroscopy techniques have developed into a wide field. The techniques most commonly applied to atmospheric pressure plasmas include laser-induced fluorescence (LIF) and two-photon-absorption laser-induced fluorescence (TALIF), which are good ways to obtain information on the chemical composition of radicals. With proper calibration, even absolute densities can be obtained [57, 58]. Other well-known laser-based techniques are based on scattering of photons. Thomson scattering can give direct information on the electron density and temperature [59, 60]. Rayleigh and Raman scattering provide information on gas density and temperatures. The conceptually simplest active technique is absorption spectroscopy (often also performed with lasers). This technique is used to determine absolute densities of certain species, often in the ground state (e.g., OH). Radical density fluxes can also be obtained by appearance potential mass spectrometry [61]. Mass spectrometry also gives the possibility to measure the ion flux of one of the electrodes directly and determine the ion composition of the plasma [62].

1.2
Coronas and Streamers

1.2.1
Occurrence and Applications

Streamers are the earliest stage of electric breakdown of large nonionized regions. They precede sparks and create the path for lightning leaders; they also occur as
enormous sprite discharges, far above thunderclouds. Streamers and the subsequent electric breakdown are a threat to most high-voltage technology.

However, streamers are also used in a variety of applications and are appreciated for their energy-efficient plasma processing. The following is an (incomplete) application list:

- Gas and water cleaning: The chemical active species that are produced by streamers can break up unwanted molecules in industrially polluted gas and water streams. Contaminants that can be removed include organic compounds (including odors), NO\textsubscript{x}, SO\textsubscript{2}, and tar [3, 6, 63, 64].
- Ozone generation: By simply applying a streamer discharge in air, first O\textsuperscript{*} radicals and then ozone is created. The low temperature in a streamer discharge limits the destruction of the produced ozone. The ozone can be used for different purposes such as disinfection of medical equipment, sanitizing of swimming pools, manufacturing of chemical compounds, and more [4].
- Particle charging: A negative DC corona discharge can charge dust particles in a gas flow. These charged dust particles can now be extracted from the gas by electrostatic attraction. Such a system is called an electrostatic precipitator (ESP) and is used in the utility, iron/steel, paper manufacturing, and cement and ore-processing industries. Similar charging methods are used in copying machines and laser printers [4, 65].

A corona discharge is (an often DC-driven) discharge in which many streamers are initiated from one electrode and, depending on the conditions, may or may not reach another electrode. The name corona comes from the crownlike appearance of the many streamer channels around the primary (driven) electrode.

Traditionally, DC corona discharges are classified in several different forms depending on the field polarity and electrode configuration [41]. In case of a positive point-plane discharge, one can recognize the burst pulse corona, streamer corona, glow corona, and spark for an increase in applied voltage. In a negative point-plane corona, this is replaced by a Trichel pulse corona, a pulseless corona, and again, a spark.

Since the 1980s, corona discharges are separated into two different categories: continuous and pulsed. Continuous corona discharges occur at DC or low-frequency AC voltages. If the circuit providing the voltage can support high currents, these will transform into a stationary glow or spark discharge. Therefore, continuous corona discharges can only occur if the current is limited. One example is a continuous corona discharge around high-voltage power lines, where the large gap to the ground limits the current. A recent example of work on DC-excited corona discharges is by Eichwald \textit{et al.} [66].

The current of a continuously excited corona is often spiked because the discharge is not really continuous but is self-repetitive in nature. In such a self-repetitive corona, the discharge stops itself due to the buildup of space charge near the electrode tip. Only after this space charge has disappeared by diffusion and drift will a new discharge occur [67].