Reaction chemistry in oxygen or hexamethyldisiloxane containing noble gas microplasma jets: a quantitative molecular beam mass spectrometry study

Dissertation

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1 Introduction and Motivation

Cold atmospheric plasmas exhibit many unique properties, which make them highly attractive for a broad field of applications. This kind of plasma combines the advantages of low pressure and atmospheric pressure plasmas without their respective disadvantages.

Low pressure plasmas are low temperature, non-equilibrium plasmas. They are used commonly in industry for e.g. thin film deposition or etching especially in semiconductor industries. However, a complicated vacuum system is needed to sustain the plasma. Atmospheric pressure plasmas, on the contrary, are operated at atmospheric pressure with no need for a vacuum system. These plasmas are used for several applications like ozone generation, activation and cleaning of surfaces in the case of cold non-equilibrium plasmas or plasma spraying and plasma welding in the case of hot thermal plasmas. The key advantage of atmospheric pressure plasmas is that they can be easily integrated in existing production lines. However, they tend to form thermal arcs and filaments, which restricts the field of applications.

Overall, cold atmospheric plasmas offer non-equilibrium chemistry at atmospheric pressure with high densities of reactive neutral and charged species and high fluxes of photons. Especially, treatment of temperature and vacuum sensitive materials is made possible. Prominent applications are e.g. treatment of polymers or living tissues and localized deposition of thin films.

However, considerable differences exist between cold atmospheric plasmas and low pressure plasmas. The short mean free path and the high collision rate due to the high pressure have a high impact on the plasma chemistry. Therefore, the plasma chemistry at atmospheric pressure is, in contrast to low pressure plasmas, only poorly understood.

This work focuses on microplasma jets, a special kind of cold atmospheric plasmas with a high gas flow through a micro-scaled discharge. The reactive species generated in the micro discharge are delivered by the gas flow to a surface to be treated. In recent years, many different sources have been developed and studied for a variety of applications.

A promising field of applications of microplasma jets that has to be highlighted is the relatively new field of plasma medicine. It has been observed that pathogens are
 deactivated under plasma exposure. Consequently, microplasma jets can be used for a localized treatment of living tissue and wounds to accelerate wound healing. However, since plasmas are complex systems consisting of electrons, ions, reactive species, and photons, it is challenging to reveal the precise bacteria deactivation mechanism. Reactive species, like atomic oxygen and ozone, are supposed to play a crucial role during the inactivation of bacteria. A synergism between the different plasma constituents is also likely.

The measurement of absolute densities of reactive species generated by a microplasma jet are of high interest in the study of these reaction mechanisms. However, it is a challenging task due to the high pressure and the small dimensions of the jet. Many of the standard diagnostics of low pressure plasma cannot be applied. A specially designed molecular beam mass spectrometer has therefore been developed within the scope of this work. This mass spectrometer is perfectly suited for analysis of atmospheric pressure plasmas due to its very high sensitivity.

In this thesis, the production of reactive oxygen species in a helium/oxygen microplasma jet is studied in detail by molecular beam mass spectrometry. The questions of particular interest are:

- What are the optimal conditions for generation of atomic oxygen and ozone?
- How do these densities behave with increasing distance from the nozzle of the plasma jet?

For reasons of simplicity, all prospective microplasma jet applications take place in air ambiance. The effect of admixing air into the effluent may severely affect the composition of the emerging species. The questions, which are to be solved are:

- How much air does admix into the effluent of the microplasma jet?
- Does the air admixture has a big influence on the atomic oxygen and ozone densities?
- Which are the important reactions in the effluent and does UV radiation play a crucial role?

Especially the last question can be solved by comparing the measured densities to results of a fluid model of the plasma effluent.

The developed molecular beam mass spectrometer is also capable to measure positive and negative ions.

- However, are ions still left in the effluent of the plasma jet?
- If so, how are they produced?

The gained knowledge can be used to optimize the process of surface treatment and, especially, bacteria deactivation.
Plasmas are also widely used for deposition of surface coatings, for example SiO$_2$-like films of good quality are desired in industry. Over the past years, the research focused on deposition of silicon oxide films at atmospheric pressure to achieve as good films as in low pressure plasmas. However, the studies are often limited to an analysis of the resulting silicon oxide film, such as measurements of the deposition rate and the elemental composition of the film. For a precise comprehension of the deposition mechanism of silicon oxide films, the plasma itself must be analyzed.

A He/O$_2$ microplasma jet with admixtures of hexamethyldisiloxane is used in combination with the molecular beam mass spectrometer to study the microplasma chemistry leading to depositions of SiO$_2$-like films. The questions of particularly interest are:

- Under which conditions is the hexamethyldisiloxane consumption maximized and how large is the consumption?
- Which reaction products are generated in the hexamethyldisiloxane plasma and what are their absolute densities?
- Do ions contribute to the film growth at atmospheric pressure?

The answers to these questions can contribute to a more precise understanding of the deposition mechanism at atmospheric pressure.

**Outline of the thesis**

The following chapter provides the necessary background knowledge regarding microplasmas, their applications, and the diagnostics used. The principle of mass spectrometry, and particularly molecular beam mass spectrometry and composition distortion are explained here in detail.

Chapter three introduces the experimental setup used in this work. The different versions of the microplasma jet and the design of the molecular beam mass spectrometer are described here.

A fluid model of the plasma effluent is defined in the next chapter. The fluid model has been developed for a better understanding of the reaction chemistry going on in the effluent.

The results of the measurements are presented and discussed in chapter five. First, the performance of the molecular beam mass spectrometer is demonstrated by means of several test measurements and the calibration procedure is explained. Then the measurements of oxygen and hexamethyldisiloxane microplasma jets are shown. The measurements of reactive oxygen species in the effluent are also compared to the results of the fluid model.

The final chapter summarizes the thesis and gives a brief outlook on prospective investigations.
2 Fundamentals

In this thesis, the plasma chemistry of a microplasma jet has been analyzed by means of mass spectrometry. The necessary fundamentals are provided in this chapter. First, an introduction into microplasmas is given. Their possible applications are explained in detail with the help of two examples, which are of particular interest for this work. The following section focuses on the principle of mass spectrometry. For the analysis of atmospheric pressure plasmas, molecular beam mass spectrometry needs to be applied and, therefore, is explained here. When absolute densities should be determined, one needs to understand the behavior of a molecular beam and its influence on the initial gas composition. These informations are provided here. The principle of two-photon absorption laser induced fluorescence spectroscopy is described as well.

2.1 Microplasma

»Except near the electrodes, where there are sheaths containing very few electrons, the ionized gas contains ions and electrons in about equal numbers so that the resultant space charge is very small. We shall use the name plasma to describe this region containing balanced charges of ions and electrons.«

By this quote, Irving Langmuir introduced the term plasma for the fourth state of matter in 1928 [1]. More precisely, a plasma is a quasineutral, (partially) ionized gas that exhibits collective behavior. It comprises many different species: neutrals, radicals, photons, and charged species. Especially the charged species, ions and electrons, are characteristic for a plasma. Technical plasmas used in industry usually are non-thermal, non-equilibrium low pressure plasmas. This means that heavy species (neutrals and ions) are close to room temperature, whereas the light electrons can be at temperatures above 10000 K. The advantage of this condition is that the gas stays cold and thus temperature sensitive materials can be treated. The electrons in turn are hot and initiate chemical reactions by collisions, which normally would require very high gas temperatures during equilibrium gas phase reactions. The energetic electrons in a plasma excite and dissociate the neutral gas producing reactive species and ions. The reactive species interact with the substrate and lead to the desired treatment.
The ignition of a glow discharge can be described by Paschen's law. The necessary breakdown voltage \( V_b \) for a glow discharge is a function of the product of the pressure \( p \) and the electrode distance \( d \): \( V_b = f(pd) \) [3]. As can be seen in figure 2.1, Paschen curves depend largely on the used gas, the electrode material plays only a minor role. The Paschen curves shown exhibit a minimum breakdown voltage around 1 cm · Torr. This results in a required pressure of about 10 Pa for a typical electrode distance of some centimeters for ignition of a glow discharge. Assuming Paschen’s law is valid for all possible \( p \) and \( d \), a glow discharge at atmospheric pressure can only be realized by reducing the electrode distance below one millimeter. The dimension of these so-called microplasmas is in the range of some tens of micrometers up to one millimeter. Investigations of the breakdown of microplasmas revealed a deviation of Paschen’s law [4, 5]. When using small electrode distances (< 20 µm), the breakdown voltage stays almost constant with decreasing \( p \cdot d \) and does not incline to infinity. This is possibly due to field induced electron emission.

A variety of microplasma sources has been developed in recent years. They are typically categorized in five different groups, classified by their excitation frequency and electrode geometry [6, 7]. A selection of microplasma sources grouped by their excitation frequency is shown in figure 2.2. Metal-insulator-metal microhollow cathodes (a) [8] and microtubes (b) [9] are typically operated with direct current. Dielectric barrier microdischarges with at least one electrode covered by a dielectric layer are usually excited by kHz frequencies. Well known examples of this type are inverted pyramid DBDs (c) [10] and capillary microdischarges (d) operating in the plasma bullet mode [11]. Capacitively coupled radio frequency microdischarges can, for example, be realized in a parallel plate (e) [12] or coaxial geometry (f) [13]. Furthermore, microplasmas can also be ignited by inductive coupling (g) [14] or microwaves (h) [15].
2.1 Microplasma

Figure 2.2: Schematic of different microplasma geometries (taken from [7]): DC (a and b), dielectric barrier (c and d), radio frequency (e and f), inductively coupled (g), and microwave (h) microdischarges.

However, atmospheric pressure microplasmas tend to form hot arcs due to thermal instabilities. The thermal instability can be described by the following closed chain [2]:

$$\delta n_e \uparrow \rightarrow \delta T_0 \uparrow \rightarrow \delta n_0 \downarrow \rightarrow \delta \left( \frac{E}{n_0} \right) \uparrow \rightarrow \delta n_e \uparrow.$$

Starting from a stochastic, local increase of the electron density, the gas will heat up by electron impact. At constant pressure $p = n_0 k_B T_0$, the gas density consequently decreases. A lower gas density in turn results in a higher reduced electric field. Finally, an increasing reduced electric field leads to a higher ionization rate and thus to an increase of electron density. This instability can be prevented by a sufficient cooling. On the one hand, the electrodes can be cooled e.g. by water. On the other hand, heating of the gas can be prevented by reducing the residence time of the gas in the discharge. This is effectively done by using a high gas flow through the microplasma. Furthermore, inert gases as working gas are preferred because they exhibit a sufficiently high ionization rate at relatively low reduced electric field strengths. Especially helium offers a high heat conductivity and a low collision cross section for electrons, which lower the appearance probability of thermal instabilities. This motivates the use of microplasma jets with a high gas flow of an inert gas. Typical geometries of microplasma jets are illustrated in figure 2.2 (d-g).

Besides the mentioned stability of microplasma jets, they offer another important advantage, namely fast transport of species. Reactive species generated in the discharge are delivered by the high gas flow to a treated surface. This, in combination with their portability and the low power consumption, makes microplasmas highly attractive for the treatment of substrates at atmospheric pressure.

In any case, the reaction processes of atmospheric pressure plasmas in general and of low pressure plasmas differ. The high pressure in itself has a huge influence on the chemistry. Due to the high collision rate and the short mean free path, three-
body reactions are much more likely than at low pressure. Ion-neutral reactions need to be considered at atmospheric pressure as well. Furthermore, a collisional plasma sheath exists at atmospheric pressure. Ions can thus not be accelerated effectively in the sheath and reach the surface at low kinetic energies. In addition, surface reactions are in microplasmas very important due to the large surface-to-volume ratio.

Due to these major differences between high and low pressure plasmas, the fundamental plasma physics and chemistry is, in contrast to the well-known plasma physics of low pressure plasmas, not very well understood, yet.

### 2.1.1 Applications

Due to their unique properties, microplasmas offer a broad spectrum of possible applications. They can be coupled with an emission spectrometer or a mass spectrometer and work in this way as analytical gas analyzer [8]. Atmospheric trace gases are excited and ionized in e.g. microhollow cathode discharges. The characteristic emission spectrum of the plasma can be used to determine its composition. Microhollow cathode discharges can also be employed as an ionization source for mass spectrometers because of their high ionization degree. Arrays of inverted pyramid DBDs are used for light generation in plasma display panels [16]. Localized treatment of thermo and vacuum sensitive materials with microplasma jets is a further popular research topic. Especially the localized treatment of living tissue is a promising application in plasma medicine [17, 18, 19, 20]. Besides the inactivation of pathogens, deposition of thin films [21, 22, 23], etching of surface material [24], and generation of nanoparticles [25] are in the research focus.

In the following, two possible applications are highlighted due to their particular interest for this work.

#### 2.1.1.1 Biomedical applications

Sterile surfaces are of great significance for many different technological domains. Surgical instruments must be free of any microorganisms to avoid nosocomial infection [26]. Food packaging must be sterilized to ensure fresh and nonperishable food [27]. Even disinfection of instruments and equipment for space missions need to be considered [28]. For all of these applications, different sterilization methods exist like autoclave or using toxic chemicals. However, these methods exhibit disadvantages. When high temperatures are needed for sterilization, only heat resistant materials can be treated. The toxic substances for the chemical sterilization must be safely disposed. Some of the toxics can even affect and alter the material [29]. Studies have shown that even the sterilization procedure used in hospitals leaves some remainders on the surface of instruments [30, 31, 32]. This remaining contamination is a potential risk for
the health of patients. Thus, novel sterilization methods are required.

In the recent past, especially non-equilibrium plasmas are studied for their ability to deactivate bacteria and biomolecules. Plasmas exhibit miscellaneous species, which are capable to deactivate biological material, like atoms, radicals, electrons, ions, and UV photons. The combination of these different species is very effective in killing bacteria [26]. But the exact deactivation mechanism is still the topic of current research.

The field of application for biomedical purposes is even broader if atmospheric pressure microplasma jets are used. Besides the advantage of a more economical treatment, microplasma jets allow another promising biomedical application: the treatment of tissues and wounds. Living human tissue cannot be exposed to vacuum; it would not survive. Thus, bacteria in wounds cannot be deactivated by low pressure plasmas. But by applying microplasma jets, a local plasma treatment is made possible. For instance, wound healing can be accelerated and caries of teeth can be cured. This promising field is studied by various researchers in recent years [17, 18, 19, 20].

Like in low pressure plasmas, the exact deactivation mechanism is only poorly identified. Topic of recent research is determination of the species which are responsible for sterilization. Especially reactive oxygen species (ROS) are believed to be responsible for deactivation of bacteria [20]. ROS correspond to reactive species containing oxygen. Radicals like atomic oxygen, stable molecules like ozone, and ions like negative oxygen ions belong to the group of ROS. For the optimization of bacteria deactivation, the behavior of the crucial species is needed: under which conditions is the production maximized and how high are their absolute densities?

### 2.1.1.2 Deposition of silicon dioxide film

Silicon dioxide, or quartz, is a mineral known for its hardness since the ancient world. The basic frame of silicon dioxide is a SiO$_4$ tetrahedral structure with a silicon atom in the center surrounded by four oxygen atoms. Each oxygen atom is shared by two silicon atoms of contiguous tetrahedra. This results in an overall chemical formula of SiO$_2$. In every day life, silicon dioxide can be found in many different fields. Glass windows, prisms, and lenses are often made up of silicon dioxide. Quartz powders are added frequently to paints, pharmaceuticals and cosmetic products and quartz crystals are used as piezoelectric crystals in watches. Apart from these applications, a further very important one is surface modification with thin silicon oxide coatings. Due to its chemical inertness, silicon oxide films are deposited for corrosion protection on metals. In the food packaging industry, silicon oxide is, for instance, used as permeation barrier coating on PET bottles [33]. Pores and holes are thus closed and permeation of atmospheric oxygen into the bottle as well as the permeation of carbon dioxide out of the bottle are reduced. As a result of its high transparency for visible
light and its hardness, quartz is widely used as scratch resistant coating on plastic glasses [34]. The dielectric properties of silicon oxide are used in the semiconductor industry for insulation.

A technique for producing thin silicon oxide layers on top of silicon wafers is thermal oxidation. A furnace with Si wafers inside is filled with O\textsubscript{2} gas or H\textsubscript{2}O vapor and heated up to ca. 1100 - 1500 K [35, 36]. The oxygen atoms from the molecules can diffuse into the silicon and react with Si to SiO\textsubscript{2}. However, this technique exhibits two essential disadvantages. On the one hand, only silicon dioxide layers on the surface of silicon substrates can be produced. Deposition on other materials than silicon is not possible with thermal oxidation. On the other hand, high temperatures are needed to make the oxidation reaction possible. No temperature sensitive substrates, like plastics, can be treated. In doped silicon, the dopants may diffuse due to the high temperature and change the electrical properties.

When silicon dioxide coatings are desired on other materials than silicon, the principle of low pressure chemical vapor deposition (LPCVD) can be used: During the low temperature oxide process, silane (SiH\textsubscript{4}) and molecular oxygen are pyrolyzed at a temperature of about 700 K and react to SiO\textsubscript{2}. Tetraethylorthosilicate (TEOS, Si(OC\textsubscript{2}H\textsubscript{5})\textsubscript{4}) is used during high temperature oxide processes. TEOS is pyrolyzed at ca. 1000 K and forms a SiO\textsubscript{2} layer on the substrate. For all of these methods, the substrate must be at high temperature to provide the necessary energy for the reactions. If a high temperature of the substrate is not allowed, the energy can be introduced directly to the gas. This is done by plasma enhanced chemical vapor deposition (PECVD). The energy for the chemical reactions is then provided by a plasma and not by the substrate temperature. Many different silicon containing precursors can be used for PECVD. Well-established precursors are silane or liquid monomers. Silane is a highly flammable and pyrophoric gas under standard conditions and thus rarely used. More popular are liquid monomers like TEOS or liquid monomers like HMDSO (hexamethyldisiloxane) because they can be handled in an easier way. For the evaporation of the liquid, a noble gas is directed through a bubbler filled with the precursor. HMDSO is often preferred because it exhibits a higher vapor pressure and has also been chosen for the silicon oxide film deposition presented in this thesis.

An HMDSO molecule, like shown in figure 2.3, consists of a Si-O-Si group with three methyl groups bound to each silicon atom. The bond between the silicon and carbon atom is the weakest one, whereas the Si-O and C-H bond strength are approximately equal [37] (cf. table 2.1).

The plasma and surface chemistry in low pressure PECVD leading to deposition of silicon oxide films has been extensively studied in the past years [38, 39]. However, LPCVD and PECVD require expensive and complex vacuum systems to establish the
2.1 Microplasma

![Chemical structure of an HMDSO molecule](image)

**Figure 2.3:** Chemical structure of an HMDSO molecule

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O</td>
<td>4.6 eV</td>
</tr>
<tr>
<td>Si-C</td>
<td>3.7 eV</td>
</tr>
<tr>
<td>C-H</td>
<td>4.5 eV</td>
</tr>
</tbody>
</table>

*Table 2.1: Bond energies of the different bondings of HMDSO [37]*

required low pressure condition. Consequently, these plasmas cannot be easily integrated in production lines; batch processing would be necessary. These problems can be overcome by applying atmospheric pressure plasmas. Due to the high pressure, atmospheric pressure plasmas do not exhibit high energetic electrons or ions. The excitation mechanism is thus not driven by energetic species but probably by Penning reactions with metastables [40]. Consequently, it is possible that the entire atmospheric pressure plasma chemistry leading to silicon oxide films differs from low pressure plasma chemistry of PECVD.

Sonnenfeld et al. [41] analyzed atmospheric pressure DBDs with HMDSO admixed in a gas mixture of a noble gas (He or Ar) and a molecular gas (O₂ or N₂). Different DBD configurations have been used, but the electrode distance was typically smaller than 2 mm and the excitation frequency in the order of kHz. By means of gas chromatography, x-ray photoelectron spectroscopy, fourier transform infrared spectroscopy, and scanning electron microscopy measurements, they proposed a reaction scheme leading to silicon oxide depositions. This reaction scheme is illustrated in figure 2.4.

The HMDSO molecule can be dissociated by a Si–C bond breaking leaving a Si₂OC₅H₁₅ and a methyl radical (path 1). In further reactions, pentamethyldisiloxane (PMDSO, Si₂OC₅H₁₆) and tetramethyldisiloxane (TMDSO, Si₂OC₄H₁₄) are formed. Another bond breaking can occur between the Si and the O atom (path 2). Then, two radicals are formed: SiC₅H₉ and SiOC₅H₉. The former radical can finally react to tetramethylsilane (TMS, SiC₄H₁₂) or trimethylsilane (TriMS, SiC₃H₁₀). All of the mentioned radicals are supposed to contribute to the film growth, but the reaction path 1 seems to dominate over path 2.
However, the used DBD is a filamentary discharge that may deposit inhomogeneous films. Furthermore, only flat substrates can be treated with a plate-to-plate geometry of the DBD. By using microplasma jets, a local deposition of homogeneous films is also possible on three dimensional substrates. It is possible that the plasma chemistry of a microplasma jet excited by radio frequency differs from the chemistry of a DBD excited with kHz frequencies. Therefore, it is worthwhile to study the microplasma chemistry leading to silicon oxide films.

### 2.2 Mass spectrometry for microplasma diagnostics

Mass spectrometry is a technique for gas analysis established in the early 20th century by Francis W. Aston. The first pioneers of mass spectrometry used self-made machines that provided only a few mass spectra per day. Fortunately, mass spectrometers improved in the following decades leading to an outstanding analytic diagnostic. Nowadays, even small and powerful mass spectrometers are commercially available offering an unequaled sensitivity, detection limit, and speed.

Mass spectrometry is used to identify the chemical composition of a gaseous sample. As the name implies, a mass spectrometer (MS) determines the mass (more precisely: mass-to-charge ratio) of the sampled particles. The basic principle of mass spectrometry is generating ions from the sample, separating them by the mass-to-charge ratio
and detecting these ions using a quantitative method. Therefore, an MS consists usually of (at least) three modules: an ion source, a mass analyzer, and a detector.

The mass analyzer can only handle charged particles. However, the sample consists usually of a neutral gas. Hence, an ion source is needed that produces ions from the sampled atoms and molecules. No ion source is needed when ions are measured. A variety of different ionization methods is known, like electron impact ionization, chemical ionization, thermal ionization, or electron attachment ionization. The classical most universal method of ionization is electron impact ionization (EI). In principle, high energy electrons interact with the neutral species in the ionizer during EI. It has to be taken into account that the gas sample needs to be highly diluted to ensure a long mean free path for the ions. Otherwise, the lifetime of the ions would be too short for subsequent analysis. The pressure is typically in the range of $10^{-4}$ Pa for EI.

The ion source, or ionizer, comprises a filament (cf. figure 2.5), which emits electrons by thermionic emission. These electrons are accelerated by an applied voltage (typically 70 V) to the desired electron energy (EE) and focused into the ionization volume filled with the neutral gas. When one energetic electron hits a neutral particle in the ionization volume, some of the EE is transferred to the neutral, which can lead to the ejection of one electron:

$$M + e^- \rightarrow M^+ + 2 e^-.$$  

The EE is usually 70 eV. This value is chosen because the electron impact ionization cross sections $\sigma_{EI}$ (a measure for the ionization probability) for almost all gases have their maximum near this energy. This can be seen in figure 2.6, which shows the cross section for different gases as a function of the EE [42]. A certain minimum energy (approx. 7-20 eV) is needed for the ionization of an atom or molecule. Below this ionization energy, or threshold energy, the cross section is zero and no ions are produced.
Depending on the EE, it is possible that not only one but two electrons are ejected during EI:

\[ M + e^- \rightarrow M^{2+} + 3e^- . \]

During the interpretation of mass spectra, one needs to take into account that double charged species \( M^{2+} \) appear at a mass-to-charge ratio of \( M/2 \) even when their mass do not differ from the species \( M^+ \).

Beside the ionization, several other processes are possible when molecules are to be detected, like dissociative ionization and dissociative rearrangement.

\[
\begin{align*}
\text{ABC} + e^- & \rightarrow \text{AB}^+ + \text{C} + 2e^- , \text{ dissociative ionization} \\
& \rightarrow \text{A}^+ + \text{BC} + 2e^- , \text{ dissociative ionization} \\
& \rightarrow \text{AC}^+ + \text{B} + 2e^- , \text{ dissociative rearrangement} \\
& \rightarrow \text{B}^+ + \text{AC} + 2e^- , \text{ dissociative rearrangement}
\end{align*}
\]

Dissociative ionization and dissociative rearrangement are of particularly importance for large molecules. This can be illustrated with the help of HMDSO as example. The generated HMDSO ions after EI are not stable due to a high amount of internal energy. The HMDSO ions will consequently dissociate leaving a multitude of different neutral and positive charged fragment molecules. A mass spectrum of HMDSO is shown in figure 2.7. As can be seen, no signal can be found at mass 162 amu, which is the molecular weight of HMDSO. The highest signal exhibits mass 147 amu. This fragment ion

**Figure 2.6:** Electron impact ionization cross section for different gases as a function of the electron energy [42]
2.2 Mass spectrometry for microplasma diagnostics

Figure 2.7: Mass spectrum of HMDSO (only masses with a signal higher than 0.2 % are shown) [43]

is generated by dissociative ionization of an HMDSO molecule resulting in a release of a methyl group CH$_3$. Besides this most probable fragment ion, many other ions can be produces. The shown mass spectrum is a characteristic "fingerprint" of HMDSO and can be used to identify unambiguously HMDSO.

As already mentioned before, no ionization of the species is necessary if ions and not neutrals are measured. In this case, it is of importance that electrostatic lenses are installed in front of the ionizer to focus the ions into the ionizer. However, absolute densities can only be determined for neutrals.

The ions leaving the ion source are deflected by an extraction electrode into the mass analyzer. The mass analyzer is responsible for the ion-separation by the mass-to-charge ration. Generally, one denotes an MS by the type of mass analyzer. There are several different types of mass analyzers known, like time-of-flight, electric or magnetic sector field, linear quadrupole, and ion trap. Despite their different ion-separation techniques, all of them have in common that they use (static and/or dynamic) electric and/or magnetic fields for ion-separation.

Linear quadrupole mass spectrometers (QMS) are usual chosen for the analysis of plasmas because they stand out in comparison to other techniques due to the low price, light weight, compact construction, and high scan speed. A minor drawback of QMS is the relatively low resolution (QMS: $\frac{M}{\Delta M} \approx 2000$, time-of-flight: up to $\frac{M}{\Delta M} \approx 20000$) and low sensitivity (QMS: 100 ppm, time-of-flight: 10 ppm).

A QMS is the linear version of the Nobel-prize awarded Paul-trap and has been described first by Paul and Steinwedel in 1953 [44]. As the name implies, a quadrupole consists of four cylindric or hyperbolic rod electrodes that are mounted in square con-
Figure 2.8: Cross section, electrical connection (a), and schematic (b) of a cylindrical quadrupole mass analyzer

configuration and are set highly parallel to each other (cf. figure 2.8). Each opposed electrode pair is connected to the same electrical potential, which is superposed by a DC component $U$ and an AC component $V \cos(\omega t)$. The resulting total potential $\Phi_0$ is then: $\Phi_0 = U + V \cos(\omega t)$. When a particle with the charge $q$ enters the quadrupole configuration in the x-y-plane traveling in z-direction, the Coulomb force exerts on the ion:

$$m \frac{d^2x}{dt^2} = -q \frac{d\Phi(x,y)}{dx}$$

$$m \frac{d^2y}{dt^2} = -q \frac{d\Phi(x,y)}{dy}$$

$$m \frac{d^2z}{dt^2} = 0.$$

The idealized potential distribution $\Phi(x,y)$ inside the quadrupole is given by $\Phi(x,y) = \Phi_0 \frac{x^2-y^2}{r_0^2}$, where $r_0$ is half of the distance between two opposed electrode rods. Thus, the further motion of the ion is given by the set of differential equations:

$$\frac{d^2x}{dt^2} + \frac{2q}{mr_0^2}[U + V \cos(\omega t)]x = 0$$

$$\frac{d^2y}{dt^2} - \frac{2q}{mr_0^2}[U + V \cos(\omega t)]y = 0$$

$$\frac{d^2z}{dt^2} = 0.$$

Inside the quadrupole, the ion will start to oscillate in the x-y-plane. The ion will pass the quadrupole when it follows a stable trajectory, this means that it does not hit one of the rods. This is the case when $x$ and $y$ never exceed $r_0$.

By introducing the dimensionless parameters
2.2 Mass spectrometry for microplasma diagnostics

Figure 2.9: First Mathieu stability region in the (a,b)-plane

\[ a_x = -a_y = \frac{8q}{m r_0 \omega^2} U, \quad b_x = -b_y = \frac{4q}{m r_0 \omega^2} V, \quad \tau = \frac{\omega t}{2}, \]

one can transform the equations of motion into Mathieu’s differential equations:

\[ \frac{d^2 x}{dt^2} + [a_x + 2b_x \cos(2\tau)]x = 0 \]
\[ \frac{d^2 y}{dt^2} - [a_y + 2b_y \cos(2\tau)]y = 0. \]

The Mathieu’s differential equation has two types of solution: i) a stable solution, where \( x \) and \( y \) are limited for \( \tau \to \infty \) and ii) an unstable solution, where the amplitudes in \( x \)- and \( y \)-direction increase exponentially for \( \tau \to \infty \).

By plotting the parameter \( a \) against parameter \( b \), one obtains a stability diagram. The so-called first Mathieu stability region is illustrated in figure 2.9. This diagram shows different regions for the stability of the \( x \)- and \( y \)-trajectories. However, only for the gray stability-triangle, a stable \( x \)- and \( y \)-trajectory exists. For every point inside this triangle, a set of \( (a,b) \) exists for which the \( x \)- and \( y \)-coordinate of the ion is less than \( r_0 \). Figure 2.10 shows a simulation of the \( x \)- and \( y \)-trajectory for an ion inside a quadrupole. One can recognize that the motion of the ion consists of a macro- and a micro-oscillation, but it never exceeds half the rod electrode distance (here: \( r_0 = 8.33 \text{ mm} \)).

For a quadrupole with given \( r_0 \) and fixed frequency \( \omega \), the remaining operation parameters are the voltages \( U \) and \( V \). The ratio \( \frac{a}{b} = \frac{2U}{V} \) is independent of the ratio \( \frac{m}{q} \) and stays constant during the operation of the MS. \( \frac{a}{b} \) is chosen in such a way that the \( \frac{a}{b} \)-line intersects the stability-triangle in at least one point (cf. figure 2.9). The interval \([b_1, b_2]\) denotes the stable region for that ions can pass the quadrupole. The mass filter is thus passable for ions in the mass-to-charge interval \([m_1, m_2]\) with
Figure 2.10: Simulation of the x- and y-trajectories of an ion traveling through a quadrupole (taken from [45])

\[
m_1 = \frac{4V}{r_0 \omega_a} b_1^{-1} \quad \text{and} \quad m_2 = \frac{4V}{r_0 \omega_a} b_2^{-1}.
\]

By scaling the ratio \( \frac{a}{b} \) (i.e. \( U \) in respect to \( V \)) up, the \( \frac{a}{b} \)-line becomes steeper and with it a higher resolution is achieved. Typically, the resolution for a specific \( m/q \) is chosen so that species with \( m/q \pm 0.5 \) can pass the mass filter.

Each \( m/q \) value has its own stability triangle. When \( U \) and \( V \) are varied while the \( \frac{a}{b} = \frac{2U}{V} \) ratio is kept constant, the stability triangle shifts along the \( \frac{a}{b} \)-line. In doing so, a mass scan can be performed.

It is important that collisions of ions with the background gas are prevented to ensure the proper operation of the mass analyzer. This requires a long mean free path of the ions and thus a good vacuum (\( p < 10^{-3} \text{Pa} \)).

After the ions have been separated by a \( m/q \) ratio, they need to be transformed into an evaluable signal. This is done by an ion detector. The simplest detector for ions is a Faraday cup. A Faraday cup consists, as the name implies, of a metal cup that collects all of the ions leaving the mass filter. The current flowing away from the Faraday cup is transformed by a resistor of high-impedance into a voltage. This voltage is proportional to the impinging ion current and is used for further analysis. The sensitivity of a Faraday cup is time constant and not dependent of the mass of the ions. However, the sensitivity is relatively low and the response time is slow.
The most common detector used in mass spectrometry is a secondary electron multiplier (SEM). A sketch of an SEM is shown in figure 2.11. An SEM contains a conversion dynode at a high potential whose polarity is opposed to the charge of the ions leaving the mass filter. The ions are hence accelerated towards this conversion dynode and impinge on it. This causes emission of several secondary electrons which are again accelerated towards the following dynode. The following electron multiplier consisting of several dynodes amplifies the secondary electron current in a cascade process with a gain of several magnitudes. Depending on the applied high voltage and the number of dynodes, an SEM can reach an amplification factor of $10^6 - 10^8$. The amplified electron current is collected by an electrode and then converted into a voltage signal that is proportional to the number of impinging ions.

The advantage of an SEM in contrast to a Faraday cup is the high amplification factor and the fast response time. However, the lifetime of an SEM is limited to a few years. The impact of ions on the dynodes leads to a contamination of their surface and hence to a decreasing amplification over the years. Furthermore, the gain of SEMs is dependent on the ion mass. Different ions of the same energy have due to their different mass also a different velocity. Thus, heavier ions produce, because of their lower velocity, less secondary electrons than lighter ions. Heavy ions are therefore discriminated against light ones.

### 2.2.1 Threshold ionization mass spectrometry

As mentioned above, the neutrals in the ionizer are produced by energetic electrons with an EE of typically 70 eV. This energy is higher than the typical binding energy of a molecule. Consequently, not only ionization of molecules occurs in the ionizer, but also dissociative ionization. That means that the molecule dissociates and fragment ions appear after the impact of the electron. This process is explained for the case of
molecular oxygen [43]:

\[
\begin{align*}
O_2 + e^- & \rightarrow O^+_2 + 2e^-, \text{ for } EE > 12.1 \text{ eV} \\
& \rightarrow O^+ + O + 2e^-, \text{ for } EE > 18.7 \text{ eV}.
\end{align*}
\]

The ionization energy of molecular oxygen is 12.1 eV. If the EE exceeds this threshold, 
\(O^+_2\) ions are generated. Dissociative ionization will additionally occur if the EE is further increased beyond 18.7 eV. An oxygen ion \(O^+\) and an oxygen atom O can then also be produced.

If one wants to determine the atomic oxygen density in an \(O_2\) plasma, the oxygen ions \(O^+\) produced by electron impact ionization of oxygen atoms must be distinguished from the oxygen ions generated in the dissociative ionization of \(O_2\). This can be done by lowering the EE below the threshold energy of dissociative ionization so that dissociative ionization is prevented. The ionization energy of atomic oxygen is 13.6 eV [43]:

\[
O + e^- \rightarrow O^+ + 2e^-, \text{ for } EE > 13.6 \text{ eV}.
\]

Oxygen atoms originating from the plasma, which are ionized in the ionizer, can be measured when one chooses an EE between the ionization energy of atomic oxygen and the dissociative ionization energy of molecular oxygen:

\[
13.6 \text{ eV} < EE < 18.7 \text{ eV}.
\]

This principle is called \textit{threshold ionization mass spectrometry} or TIMS. The disadvantage of TIMS is the fact that the electron impact ionization cross section decreases by lowering the EE, too. This results in significantly lower sensitivities.

### 2.2.2 Calibration of a mass spectrometer

A mass spectrometer is capable to measure absolute densities of neutral species when a proper calibration procedure has been carried out. The measured signal \(S_i\) of species \(i\) in counts per second is given by [46, 47]:

\[
S_i = n^{\text{ionizer}}_i \cdot \sigma_i(EE) \cdot \beta \cdot l_{\text{ionizer}} \cdot I_e \cdot T(m_i) \cdot \theta(m_i),
\]

where \(n^{\text{ionizer}}_i\) is the density of species \(i\) in the ionizer, \(\sigma_i(EE)\) is the electron energy dependent EI cross section, \(\beta\) is the ion extraction efficiency of the ionizer, \(l_{\text{ionizer}}\) is the length of the ionizer, \(I_e\) is the electron emission current in the ionizer, \(T(m_i)\) is mass-to-charge ratio dependent transmission function of the quadrupole, and \(\theta(m_i)\) is the mass-to-charge ratio dependent sensitivity of the detector.
Absolute densities can be obtained by measuring a calibration gas of known density $n_{\text{cal}}$. By taking the ratio of both signals, one gets:

$$n_{i, \text{ionizer}} = F(m_i, m_{\text{cal}}) \cdot \frac{S_i \cdot \sigma_{\text{cal}}(EE)}{S_{\text{cal}} \cdot \sigma_i(EE)} n_{i, \text{cal}},$$

with the mass dependent transmission function $F(m_i, m_{\text{cal}}) = T(m_{\text{cal}}) \cdot \theta(m_{\text{cal}}) / (T(m_i) \cdot \theta(m_i))$. Since $F(m_i, m_{\text{cal}})$ is a function of the mass-to-charge ratio, $F$ is equal to unity when species $i$ and calibration species $\text{cal}$ have the same mass. Otherwise, $F$ can be determined by measuring different gases of known densities.

It has to be kept in mind that the mass spectrometer measures always the species density inside the ionizer. This is not a problem when gases at high vacuum are measured. However, plasma processes are often operated at a pressure of a few pascal. This pressure is order of magnitudes higher than the maximum operation pressure of a typical MS. Then, the gas needs to be transferred from the plasma to the ionizer, which is usually done by a molecular beam. The densities in the molecular beam change so that the density in the ionizer differs from the density of the plasma.

### 2.2.3 Molecular beam mass spectrometry

As stated above, vacuum-based processes are often operated at a pressure of a few pascal. One needs, hence, to separate the MS from the process chamber by, for example, placing it in a separately pumped enclosed chamber. This chamber can be connected by a leak valve or a low conduction tube with the volume of interest. In this way, the MS operates as a residual gas analyzer. This means that no reactive species and ions can be detected because they are lost during collisions with the walls.

By using the technique of molecular beam mass spectrometry (MBMS), one can overcome this issue. The MS chamber is connected via a small orifice to the process chamber and the ionizer of the MS is installed in line-of-sight with the orifice. The particles entering this differential pumping system directly reach the ionizer without collisions with the wall. This allows the detection of reactive and charged species.

The number density $n_{\text{beam}}$ of the molecular beam on the center line is decreasing with increasing distance and can be calculated by [48, 47]

$$n_{\text{beam}}(x) = \frac{1}{4} n_0 \left( \frac{r}{x} \right)^2,$$

where $n_0$ denotes the undisturbed density at a wall without a sampling orifice, $r$ is the radius of the orifice, and $x (x \gg r)$ is the distance from the orifice. A density of $\frac{n_0}{4}$ is directly at the sampling orifice. The number density $n_{\text{beam}}(x)$ is independent from the
species characteristics (e.g. mass and adiabatic index) and only determined by geometric conditions.

The MS signal is superposed by two components: the line-of-sight (or beam) signal and the background signal. The beam signal is the signal of interest and can be used to determine the particle density in the process chamber. The particles accounting for the beam signal originate directly from the process chamber, whereas the background signal is determined by the background density (or pressure) in the MS chamber. Particles accounting for the background signal have undergone several collisions with the chamber walls. If reactive or charged species are measured, the background signal is consequently low and the measured MS signal is the beam signal. But if not very reactive neutrals are measured, the contribution of the background signal to the MS signal can exceed the beam signal. For an accurate determination of particle densities in the process chamber, the beam signal must be separated from the background signal. This is usually done by installing a mechanical chopper between the orifice and the ionizer of the MS. The chopper can be moved into the beam to block it. The detected signal by the MS is then consequently only the background signal. When the chopper is moved away, the full signal is measured again.

If a singly differentially pumped mass spectrometer is used (like shown in figure 2.12a), the diameter of the orifice is limited by the pressure in the MS chamber. Hence, the density in the beam is low while the background pressure is relatively high. An example measurement with an orifice diameter of 150 $\mu$m in the single differential pumping system of figure 2.12a is shown by the upper curve in figure 2.13. Note that the beam-to-background ratio for argon at a pressure of $p = 1.33$ Pa in the single differential pumping system is only 0.029.

To improve the signal-to-background ratio, differential pumping systems with multiple stages can be used. All of the stages are separately pumped and are connected with each other by orifices or skimmers. All orifices and skimmers are in line-of-sight with the ionizer of the MS, and a mechanical beam chopper is installed in the last stage in front of the ionizer (cf. figure 2.14). The overall gas flow into the MS stage is low, which allows enlargement of the orifice diameters. The density in the beam scales with the orifice diameters and is consequently high. A sketch of a triple differential pumping system with orifice diameters of 900 $\mu$m, 6 mm, and 10 mm is shown in figure 2.12b. The ionizer of the MS is now 2.6 times further away from the sampling orifice than before. This leads to a decrease of the beam signal. However, this is compensated by a six times larger cross section of the sampling orifice. The corresponding MS signal is the lower line in figure 2.13. It can be seen that the beam signal is now noticeable higher and the background signal is lower in contrast to single differential pumping. The beam-to-background ratio increased significantly and is equal to 1.2.
2.2 Mass spectrometry for microplasma diagnostics

(a) Single differential pumping system

(b) Triple differential pumping system

Figure 2.12: Schematics of the plasma reactor and the differentially pumped mass spectrometer by Singh et al. [49]

Figure 2.13: Mass spectrometer signal measured in a single and triple differential pumping system (gas: argon, pressure: 1.33 Pa)[49]
2.2.4 Molecular beam

A molecular beam (MB) is a directed beam of atoms or molecules without collisions among the particles in the beam. An MB is formed by letting a gas expand from a high-pressure region through a small sampling orifice into a low-pressure ambient background. There are two cases that are needed to distinguish according to the Knudsen number. The Knudsen number \( Kn \) is defined as the ratio of the mean free path \( \lambda \) to a characteristic length \( L \):

\[
Kn = \frac{\lambda}{L}
\]

Here, in the concrete scenario of MBMS, \( \lambda \) is the mean free path of the particles in the high-pressure region and the characteristic length \( L \) is the diameter of the orifice through which the gas expands into the low-pressure region.

In case of a large mean free path compared to the diameter of the orifice (i.e. \( Kn > 1 \)), a free molecular flow through the orifice is obtained. This means that no collisions occur in the vicinity of the orifice and the molecules do not "feel" the orifice. The molecules just hit the orifice in a stochastic manner (cf. figure 2.15a). The molecular flow often applies for sampling low-pressure plasmas, like illustrated with the example of Singh et al. (cf. figure 2.12b and [49]). The sampling orifice used by Singh et al. has a diameter of 0.9 mm, and the mean free path is in the range of several millimeters. The Knudsen number is consequently larger than one. The particle flow behind the sampling orifice

Figure 2.14: Sketch of a molecular beam mass spectrometer
is termed molecular beam because almost no collisions of beam particles with other beam particles or with the background gas occur behind the orifice.

As already mentioned in the previous section 2.2.3, the number density \( n^{\text{beam}} \) of the molecular beam on the center line is decreasing with increasing distance:

\[
n^{\text{beam}}(x) = \frac{1}{4} n_0 \left( \frac{r}{x} \right)^2.
\]

It should be emphasized that the beam density is in this case only a function of the geometry and independent of the properties of the gas. When a gas mixture is sampled, the ratios between the respective species do not change. The relative beam composition stays the same in the molecular beam at free molecular flow conditions and is equal to the relative composition of the high-pressure region in front of the orifice.

When a higher initial pressure and/or a larger sampling orifice is used, the Knudsen number gets much less than one \((Kn \ll 1)\), and the gas dynamic is determined by a continuum flow. The motion of particles is dominated by collisions and thus by diffusion. A pressure gradient toward the sampling orifice exists, which causes the gas molecules to flow through the orifice into the low-pressure region (cf. figure 2.15b).

The mean free path at atmospheric pressure is about 0.1 µm, which is much smaller than typical diameters of sampling orifices of 20 µm to 500 µm. Consequently, the Knudsen number is much less than one, and continuum flow conditions apply for sampling atmospheric pressure gases.

The equation of Hugoniot (1887) can be used to describe the behavior of continuum flow through the orifice [50]:

\[
\frac{dA}{A} + \frac{dv}{v}(1 - M^2) = 0,
\]

Figure 2.15: Illustration of kinetic gas dynamics at different Knudsen numbers
where $A$ denotes the cross-section area, $v$ denotes the flow velocity, and $M = \frac{v}{c}$ is the Mach number. In the initial stagnation state (i.e. high pressure region), the molecules velocity is lower than the speed of sound ($v < c$, $M < 1$). So the velocity of molecules increases with decreasing cross-section area. If the pressure gradient is sufficiently large, the molecules reach speed of sound ($M = 1$) at the minimum cross-section area ($dA = 0$) or throat. The cross-section area increases beyond the orifice again, and for $M > 1$ the flow velocity $v$ increases, too. Supersonic velocities are reached then.

The energy equation \[ h_1 + h_2 = \frac{1}{2}(v_2^2 - v_1^2) = c_p(T_1 - T_2) \]
reveals that the enthalpy $h$ decreases when the flow velocity $v$ increases. In other words, the molecules are accelerated by using the heat of the gas. This results in a change of gas temperature described by the right hand side of the energy equation. By using the energy equation, one can derive the maximum particle velocity:

$$v_{\text{max}} = c\sqrt{\frac{2}{\gamma - 1}\left[\left(\frac{P_0}{P_b}\right)^{(\gamma - 1)/\gamma} - 1\right]}.$$\[50\]

$\gamma = c_p/c_v$ is the adiabatic index, $P_0$ and $P_b$ are the initial stagnation pressure and background pressure, respectively. By inserting $v = c$, one obtains the critical pressure ratio $P_0/P_b$, which is needed to achieve sonic speed at the throat:

$$\frac{P_0}{P_b} \geq G = \left(\frac{\gamma + 1}{2}\right)^{\gamma/(\gamma - 1)}.$$\[50\]

The critical pressure ratio $G$ is less than 2.1 for all gases. If the pressure ratio is lower than the critical ratio $G$, (super)sonic speed is never obtained and the exit pressure at the orifice is the background pressure $P_b$. No further expansion of the gas appears then. However, if the pressure condition is fulfilled, sonic speed is reached at the throat and the exit pressure is equal to $P_0/G$. Since the exit pressure is higher than the background pressure, the gas flow is underexpanded and consequently has to expand into the low-pressure region. The structure of this free-jet expansion \[51\] is shown in figure 2.16. This type of expansion is called “free”-jet because, in contrast to nozzle jets, no diverging nozzle is used to confine the expansion.

The underexpanded gas expands behind the orifice, and the pressure in the free-jet decreases with increasing distance to the orifice. A supersonic flow is not able to “sense” downstream boundary conditions because boundary informations cannot propagate with a velocity faster than the speed of sound. Consequently, the free-jet continues to expand even when its pressure falls below the background pressure $P_b$. Then
the free-jet becomes overexpanded and is recompressed by a system of shock waves to adjust to the downstream boundary conditions. Shock waves are localized, isentropic zones of large density, pressure, temperature, and velocity gradients. The shock wave at the sides of the free-jet is called "barrel shock" and at the downstream end "Mach disk shock" (cf. figure 2.16). Due to the large density gradients inside a shock wave, they can be characterized by light-scattering methods \[52, 53\]. The thickness of a shock wave is of the order of the mean free path and the location of the Mach disk \[x_m\] (in units of the orifice diameter \[d\]) was found to be at

\[
\frac{x_m}{d} = 0.67 \sqrt{\frac{P_0}{P_b}}.
\]

The supersonic flow inside these shock waves does not sense any external conditions and is therefore isentropic and independent of the background pressure \[P_b\]. For this reason, the core region is called "zone of silence".

For the extraction of a molecular beam, one needs to place a cone-shaped skimmer into the free-jet. However, the exact positioning of the skimmer is crucial. The MB is necessarily extracted from a flow that has not been disturbed by any shock waves. This can be done by placing the skimmer upstream of the Mach disk, inside the zone of silence. In this case, the shape of the skimmer might even be very important to avoid detached shock waves in front of the skimmer. An aerodynamic skimmer design is necessary.

These considerations and challenges can be avoided if no shock waves occur during free-jet expansion. As previously stated, shock zones appear when the pressure in the expansion drops below the background pressure. Hence, no shock zones will appear if the free-jet expands into perfect vacuum. Since perfect vacuum can never be reached, the background pressure needs to be as low as possible to move the Mach disk shock
far downstream. For instance, if atmospheric gas is sampled into a vacuum of $10^{-2}$ Pa, the location of the Mach disk is $x_m \approx 2100$ or $x_m \approx 21$ cm with an orifice diameter of 0.1 mm. The thickness of the Mach disk is several decimeters, so a smooth transition from continuum flow to free molecular flow is observed.

The importance of a very good background pressure can be illustrated by means of a bad example of a commercially available MBMS system. The gas expands from atmosphere into a poor vacuum of about 100 Pa background pressure. The Mach disk is then located in a distance $x_m \approx 2.1$ mm of the sampling orifice ($\varnothing = 100$ µm). This means that the skimmer must be positioned within the first 2 mm directly behind the sampling orifice. Otherwise, the shock waves will significantly distort the molecular beam.

As an approximation, the free-jet expansion can be divided into two regions, a continuum flow region behind the sampling orifice followed by a free molecular flow [51]. The so-called quitting surface separates both regions. No collisions between the particles in the MB are assumed to take place downstream from the quitting surface. In reality, the quitting surface is not a sharp border but a smooth transition to a collisionless flow. The location $x_q$ of the quitting surface is approximately [51]

$$x_q \approx \left( \frac{M_{\infty}}{C_1} \right)^{1/(\gamma-1)},$$

where $d$ is the diameter of the sampling orifice, $M_{\infty}$ is the final Mach number, and $C_1$ is 3.2, 3.6, or 3.9 for an adiabatic index $\gamma$ of 5/3, 7/5, and 9/7, respectively.

In the case of atmospheric air sampled through an orifice of 100 µm diameter, the location of the quitting surface is approximately at $x_q = 2.1$ mm downstream of the sampling orifice.

### 2.2.5 Composition distortion

It should be noted that the relative beam composition in an MB originating from a free-jet expansion changes. Several effects account for this change in composition; they are known under the name of composition distortion [54]. By understanding the composition distortion in MBMS sampling, it is possible to minimize it or correct for it. The main contributions to composition distortion are summed up in the following:

**Radical recombination at external probe surfaces:** The density of radicals diminishes in the vicinity of a surface due to radical recombination [55]. This recombination also takes place at the MBMS sampling orifice and the surrounding surface. The radical recombination can probably be avoided by selecting nonreactive materials.
2.2 Mass spectrometry for microplasma diagnostics

**Acceleration into the probe orifice:** The density determined by MBMS is not the density at the surface without a sampling orifice. The acceleration through the orifice and the drop of the pressure in front of the orifice (cf. figure 2.15b) cause a distortion of the density profile in front of the surface. The MBMS measures a density at the sampling orifice that is equal to the undistorted density a certain distance $\delta$ in front of the wall. This shift of concentration is found to be [54]:

$$\frac{\delta}{d} = 0.19\sqrt{\text{ReSc}},$$

where $\text{ReSc}$ is the product of Reynolds and Schmidt number and $d$ is the diameter of the sampling orifice. In different experiments the concentration shift was measured and seems to be shifted about 2 up to 5 orifice diameters [54, 56, 57].

**Chemical relaxation in the free-jet:** The chemical relaxation is a shift in the chemical concentration of reactive species due to the falling temperature and pressure in the free-jet expansion. It depends on the ratio between the residence time in the sampling orifice and the relaxation time of the species. If the residence time is smaller than the relaxation time, this contribution to the composition distortion can be neglected. This is the case when an orifice with a maximum length of 0.3 mm is used for sampling from atmospheric pressure [57].

**Radial diffusion in the free-jet:** Strong radial pressure gradients exist in the free-jet expansion. Hence, pressure diffusion leads to a mass separation downstream from the orifice. It has been shown, that heavy species tend to stay on the central streamline, whereas light species diffuse outwards along the pressure gradients [58]. The enrichment factor $\alpha_p$ can be obtained by using Sherman’s formula [54, 59]:

$$\alpha_p = \frac{n_H}{n_L} = 1 + \frac{C}{(\text{ReSc})_0} \left( \frac{m_H - m_L}{m_0} \frac{\gamma}{\gamma - 1} - \alpha_0 \right) \cdot F(\gamma, x/d),$$

where $n$ is the number density, $\text{ReSc}$ is the product of Reynolds and Schmidt number, $C$ is the viscosity-temperature constant defined by $\frac{\mu}{\mu_0} = C \frac{T}{T_0}$, $m$ is the molecular weight, $\gamma$ is the adiabatic index, and $\alpha_0$ is the thermal diffusion factor. The indices $H, L$, and $0$ refer to heavy species, light species, and stagnation condition, respectively. $F(\gamma, x/d)$ is a function of the distance and reaches its final value of 13, 16, or 18 for $\gamma = 5/3, 7/5$, or 9/7 at a distance of $x/d = 3$, respectively.

**Skimmer interference:** Beam molecules are distorted by collisions with other molecules in the vicinity of the skimmer. Common reasons for the distortion are a close position of the skimmer orifice to shock waves, collisions of beam molecules with the inner surface of the skimmer, a blunt skimmer lip, or a large skimmer orifice. This leads to a decrease of the beam density, an increase of the velocity distribution width, a decrease
of the mean velocity, and a distortion of the beam composition. Skimmer interferences can be avoided by a carefully designed skimmer and a low background pressure.

*Mach-number focusing:* Mass separation due to differences in the velocity perpendicular to the beam direction is known as "Mach-number focusing" or, more precisely, "speed-ratio focusing". The perpendicular speed ratio $S$ is the quotient of beam velocity divided by the most-probable random speed perpendicular to the beam [50]:

$$S = \frac{v}{\sqrt{2k_B T_\perp/m}}.$$

Since all gas components in a sampled mixture have nearly the same velocity and temperature after the transition point from continuum to free molecular flow, light species have a lower speed ratio than heavy species. Therefore, light species spread laterally faster than heavy species and are discriminated against heavy ones at the skimmer orifice.

*Fragmentation during detection:* Since fragment patterns depend on the energy of the parent molecule, the initial temperature of the gas has also an influence on the fragment patterns. One obtains consequently different mass spectra for the same gas at different temperatures. However, this effect only plays a role during sampling high temperature gases, like combustion exhaust, and can be neglected for gases near room temperature.

When absolute densities should be obtained by MBMS measurements, composition distortion needs to be avoided or either theoretically or experimentally calibrated.
## 2.3 Laser induced fluorescence spectroscopy

Laser induced fluorescence spectroscopy (LIF) is a laser-based diagnostic with high sensitivity that provides spatially resolved densities. Since the densities determined by mass spectrometry are benchmarked with results of two-photon absorption laser induced fluorescence spectroscopy measurements, a direct comparison between both diagnostics is additionally given. A laser is focused into the plasma of interest like shown in figure 2.17. The wavelength of the laser is adjusted for exciting the ground state of one atom or molecule into one excited state [60, 61]. The excited species de-excite, not necessarily into the ground state, within micro- or nanoseconds and emit fluorescence light. The fluorescence light is focused with a lens, typically perpendicular to the laser beam, into a detector. The observed emission light is directly proportional to the ground state density in the plasma. Usually, the observed radiation has a longer wavelength than the laser beam. For this reason, the background signal is very low and the signal-to-noise ratio is very high.

A disadvantage of LIF is that for some excitations high energies and thus VUV lasers are necessary. Due to VUV absorption in air, complicated vacuum systems are required.

This disadvantages of LIF can be avoided by using two-photon absorption LIF (TALIF). This principle is based on the simultaneous absorption of two photons of same energy instead of one. The sum of both photons equals the energy needed for the transition $|i\rangle \rightarrow |k\rangle$ like shown in figure 2.18. One photon needs only to carry half of the energy in contrast to LIF. For high energetic transition a UV laser is sufficient in TALIF, whereas a VUV laser is necessary in LIF.

However, the TALIF signal is not directly proportional to the ground state density. This necessitates a sophisticated calibration process. During the interpretation of (TA)LIF data, quenching processes must be taken into account. Quenching leads to non radiative de-excitation of excited atoms or molecules by e.g. collisions.
Due to similar optical transitions of xenon in comparison to oxygen, it can be used for an absolute calibration of atomic oxygen. Measurements of atomic oxygen in the discharge core and in the effluent of a micro-scaled atmospheric pressure plasma jet demonstrated the potential of TALIF as microplasma diagnostic [62].

### 2.4 Comparison between MBMS and TALIF

Since the results of the MBMS measurements are benchmarked with TALIF measurements in this work, a brief comparison between both diagnostics is provided here.

With the TALIF system, the entire $\mu$-APPJ can be analyzed due to its good optical access. The laser beam can be focused into the effluent as well as into the plasma core. In this way, an undisturbed effluent can be analyzed because the laser beam has no influence on the gas flow. The disadvantage of the TALIF system is that with this system only one species can be detected. For other species, another laser with a specific wavelength is needed and, especially, a new adapted calibration routine needs to be applied. Due to an unknown effect of air on the collisional quenching, absolute densities can only be determined in a controlled helium atmosphere. No absolute calibration in air is possible.

In contrast to the TALIF system, the MBMS necessarily disturbs the effluent by the presence of the front plate with the sampling orifice. Consequently, a stagnation of the gas flow occurs and radicals may recombine at the surface. However, this is not necessarily a disadvantage of the MBMS concept because during all microplasma applications a surface, which should be treated, is placed in the effluent. Therefore, a MBMS is especially suited for microplasma measurements, because it determines densities at the vicinity of this surface. Another advantage of the MBMS diagnostic is that all (stable) atoms and molecules can be detected with the MS. But only the effluent of a microplasma jet can be analyzed due to the size of the MBMS system.

In summery, the MBMS can detect all species, but is limited to the effluent, whereas the TALIF diagnostic can only detect one single species, but works in the plasma core as well as in the effluent.
3 Experiment

The experimental setup is introduced. First, the different versions of the micro-scaled atmospheric pressure plasma jet are described. These microplasma jets have been analyzed by a molecular beam mass spectrometer whose configuration and design is specified afterwards.

3.1 Atmospheric pressure microplasma jet

Three modifications of the so-called micro-scaled atmospheric pressure plasma jet (\(\mu\)-APPJ) have been analyzed in this study. Similar to the microplasma configuration shown in figure 2.2 (e), the \(\mu\)-APPJ is a capacitively coupled plasma jet with parallel electrodes. Usually, the \(\mu\)-APPJ is operated with helium and a small addition of a molecular gas.

The standard \(\mu\)-APPJ consists of two stainless steel electrodes with a 1 mm gap in between (cf. figure 3.1a). The electrodes have a length of 30 mm and a thickness of 1 mm. The plasma is ignited in this gap filling a volume of 1 x 1 x 30 mm\(^3\). The plasma volume is confined on both sides by glass plates. In some of the previous versions of the \(\mu\)-APPJ by V. Schulz-von der Gathen et al. [63, 64, 65], the glass plates end 3 mm upstream from the \(\mu\)-APPJ’s nozzle, so that the plasma volume is not entirely confined by glass. In this study, the glass plates cover the entire electrode length (cf. figure 3.1a).

\[\text{Figure 3.1: Drawings of the two designs of the micro-scaled atmospheric pressure plasma jet}\]
One electrode is connected to a power supply (13.56 MHz, absorbed power <1 W) through a matching network, and the other one is grounded.

This plasma jet configuration is used in different modifications by several authors [66, 63, 64, 65, 67]. An advantage of this simple microplasma jet design is the good optical access. The entire plasma volume can be observed from two sides through the glass plates, which confine the plasma. Furthermore, the simple plane-parallel geometry is easy to model within simulations.

In this study, the 30 mm long µ-APPJ version has always been used for the study of helium/oxygen microplasmas. Then, the gas flow through the µ-APPJ is typically 1.4 slm helium with a small admixture of molecular oxygen (< 1.6%). Both, the helium flow and the O₂ flow, are controlled by mass flow controllers. A photograph of a µ-APPJ during operation can be found in figure 3.2.

The µ-APPJ has also been used for the deposition of thin SiO₂-like films. Then, HMDSO is admixed as precursor. However, the HMDSO plasma chemistry can lead to formation of dust particles when the residence time of the gas in the plasma is too long. The length of the electrodes has therefore been reduced to 10 mm (cf. figure 3.1b) and the gas flow has additionally been increased to 5 slm helium. Overall, the residence time of the gas was reduced down to a tenth, which makes the formation of dust unlikely.

When using the µ-APPJ for thin film deposition, liquid HMDSO is used as a precursor. The HMDSO is filled into a bubbler through which a helium flow is channeled. The absolute HMDSO amount in the helium flow can be calculated with the known vapor pressure of liquid HMDSO. The vapor pressure of HMDSO is 1333 Pa and 5599 Pa for 0 °C and 23 °C, respectively [43]. The HMDSO flow of typically less than 0.1 sccm is mixed with the 5 slm helium flow and injected into the gas inlet of the µ-APPJ. An additional molecular oxygen flow of maximum 10 sccm can be added to the He/HMDSO mixture.
The $\mu$-APPJ is not necessarily convenient for applications like the deposition of SiO$_2$-like films. The plasma containing the reactive gas is in contact with the electrodes, so a thin film is also deposited on the electrodes. The film on the electrodes leads to changing plasma properties, so that the $\mu$-APPJ has a limited life-time and needs to be replaced after a few hours of operation. But for fundamental research of microplasmas and the plasma chemistry, the $\mu$-APPJ is perfectly suited.

3.2 X-Jet

The so-called X-Jet is a modified version of the $\mu$-APPJ and allows the separation of heavy species from photons in the effluent downstream of the plasma [68]. This is done by extending the direct channel of the $\mu$-APPJ and adding a crossing side channel, as shown in figure 3.3. The side channel crosses the direct channel under an angle of 45° and has the same cross section of 1 mm$^2$. Additional to the standard helium flow of 1.4 slm through the direct channel, a helium flow of 2 slm is applied through the side channel. This crossing flow diverts the plasma effluent into the side channel, like illustrated in figure 3.3. In contrast to the heavy species, the radiation originating from the plasma propagates further on through the direct channel. Since the transport of the heavy species is dominated by convection because diffusion is very slow at atmospheric pressure, the entire plasma effluent can be diverted into the side channel. The heavy species are separated from the radiation in this way.

3.3 Molecular beam mass spectrometer

The microplasma jet described above has been analyzed by means of a molecular beam mass spectrometer. Especially, radical densities in the effluent of the plasma are of interest. But due to their reactivity, the radical density is expected to be very low. When using an MBMS with a differential pumping system like shown in chapter 2.2.3, it
3 Experiment

Figure 3.4: Sketch of the differential pumping system with the chopper in the first stage. The two insets at the top show the two different chopper designs: metal disk with conical hole (1) and with embedded skimmer (2).

is possible that the radical density is below the detection limit of the MBMS system. The sensitivity of the system can be improved by increasing the number of radicals in the ionizer. The number of radicals in the MB, in turn, can be increased by enlarging the diameter of the sampling orifice. On the one hand, this leads to an increased pressure in the last pumping stage with the mass spectrometer and therefore also to a high background signal and a low beam-to-background ratio. On the other hand, the pressure in the first pumping stage increases, too, which is undesired because shock zones may form at high pressure (cf. chapter 2.2.4). It would be beneficial to increase the density in the MB and to reduce the background density at the same time. This can be done by allowing only a pulsed gas flow into the pumping stages. The density in the gas pulse can be larger by selecting an enlarged sampling orifice. This does not increase the background pressure in the pumping stage with the MS when the pulses are on a short time scale. After the gas pulse, there is sufficient time for the pumps to establish a good vacuum. In this way, the overall gas flow into the pumping stages is effectively reduced resulting in a low background pressure, whereas the beam density is increased by a larger orifice. Overall, one can consequently obtain a significantly higher beam-to-background ratio than typical values around unity and therefore a higher sensitivity.

In this study, a molecular beam sampling system with a rotating skimmer in the first
stage has been used [69, 70]. The basic design of the used system is similar to standard designs as shown in figure 2.14 of chapter 2.2.3. A sketch and a technical drawing of the differential pumping system are shown in figure 3.4 and 3.5. The species of interest enter the first pumping stage via a sampling orifice with a diameter of 100 µm. The orifice to the second stage has a diameter of 5.2 mm and the skimmer to the third stage has an opening of 0.8 mm. In the last stage a Pfeiffer HiQuad quadrupole MS is installed. The three orifices are in line of sight with the ionizer of the MS. The vacuum in the first stage is established by a rotary oil pump, whereas the second and third stage are each pumped by a turbomolecular pump. The pressure during operation is usually around 40 Pa in the first stage, some $10^{-2}$ Pa in the second stage and some $10^{-5}$ Pa in the third stage.

The main difference to traditional sampling systems is that the chopper is installed within the first stage. The chopper consists of a stainless steel disk with a conical hole. Two different chopper designs have been tested, a design with a conical hole in a 2 mm thick metal disk (cf. (1) in figure 3.4) and a design with a 2 mm long conical skimmer embedded in a 1.5 mm thick metal disk (cf. (2) in figure 3.4). Both, the conical hole and the embedded skimmer exhibit an opening of about 1 mm on the narrow side and an opening of 5 mm on the wide side. The opening angle is 90°. The chopper is rotated by a stepper motor. When the chopper is in the opened position (like shown in figure 3.4), the gap between the conical hole or embedded skimmer and the sampling orifice is as small as possible. In this way a direct short cut from the atmosphere through the sampling orifice into the second stage is established. The free-jet forming downstream of the sampling orifice can directly expand into good vacuum of ca. $10^{-2}$ Pa; no shock waves occur at this pressure. The gap size can be adjusted by controlling the position of the front plate with four distance screws. A bigger O-ring (marked with green arrows in figure 3.5) provides a certain flexibility for adjusting the distance. When the chopper rotates a little further, the steel disk blocks the free-jet and the gas entering the first stage is pumped away by the rotary oil pump. The chopper disk is aligned in a way that the distance between the disk and the orifice to the second stage is as close as possible (approximately 100-200 µm). This ensures a very low conductivity of gas into the second stage when the chopper is closed.

Two facts need to be considered to properly choose the right chopper frequency. The opening time of the chopper orifice must be much smaller than the residence time of the gas in the pumping stage. The residence time of the gas is calculated to be approx. 50 ms (see later). Additionally, the opening time of the chopper has to be much larger in comparison to the formation time of the molecular beam. The estimated formation time is the time, which the species need to reach the quitting surface. The estimated location of the quitting surface is about 2.1 mm (cf. chapter 2.2). Assuming thermal
Figure 3.5: Technical drawing of the differential pumping system. PD represents the photodiode and M the stepper motor. The green arrows mark the bigger O-ring.
velocity, which is the lowest approximation here, the upper limit of the formation time is about \(7 \mu s\). In reality, the species need less time to reach the quitting surface because they are accelerated to supersonic velocities.

An opening time of the chopper of ca. \(250 \mu s\) has been chosen, which is well in between the calculated time limitations. This corresponds to a rotation frequency of \(14.3\) Hz. One rotation of the chopper takes about \(70\) ms. The duty cycle is consequently ca. \(0.4\)%. The signal measured during the time when the chopper is opened corresponds to the beam signal superimposed by the background signal. The background signal is measured when the chopper is closed. Time resolved measurements are required to discriminate between beam and background signal. A photodiode is therefore installed in the first pumping stage to measure the chopper position. The MS signal is synchronized with the chopper rotations by means of this photodiode and measured with a multichannel scaler PCI-card with a time resolution of \(1\mu s\). In practice, this is done by converting the raw ECL signal from every single detected ion to a TTL pulse and guiding it into the multichannel scaler card. The photodiode emits one TTL voltage pulse every chopper rotation at the same position. The photodiode signal is also connected to the multichannel scaler PCI-card. As soon as a signal from the photodiode is received, the converted TTL pulses from the MS are time resolved recorded. The measurement is stopped after ca. \(98\)% of one rotation. The multichannel scaler card waits for the next measurement until the next photodiode signal is received. Signal integration over many chopper rotations is possible in this way.

A disadvantage of this MBMS design with a rotation chopper is the low duty cycle and the longer measurement times. This has been improved by installing a chopper with four instead of one embedded skimmer. This increases the duty cycle and reduces the required measurement time by a factor of four.

Furthermore, an ultrahigh vacuum stepper motor is required for the chopper. The used UHV stepper motor is relatively expensive, but has a limited life time due to a bearing without lubricant. A problem for all sampling systems is that the sampling orifice is also coated during measurements with depositing plasmas. After a while, the orifice is clogged and no gas can get into the pumping system. Then, the sampling orifice needs to be replaced. For that purpose, the MBMS system must be vented and evacuated again. New measurements can then only be started as soon as the pressure is low enough, which can take up to few days.

Several further major changes have been considered during the construction of an improved version of the described MBMS system. A technical drawing of the improved sampling system can be found in figure 3.6. In this version, the chopper in the first stage is rotated by a stepper motor that is installed outside of the vacuum chamber. A ferrofluidic rotary feedthrough transfers the rotation of the motor from the atmo-
sphere into the vacuum chamber to the chopper. No expensive UHV stepper motor is hence needed. Another important development is a sealing cap that can be put on the skimmer to the third stage while the system is under vacuum. The second stage can thereby be separated from third stage. The first two stages can then be vented while the third pumping stage is still pumped by the turbomolecular pump. This allows replacement of the sampling orifice without venting the mass spectrometer. The replacement of the sampling orifice is even easier than before. The orifice is not fixed in the front plate of the pumping system, but is fixed mechanically or with glue to a small sampling orifice cartridge. This cartridge can easily be exchanged with a backup cartridge. The cartridge is inserted in a supporting table in the first pumping stage, whose elevation can be adjusted by screws also from the atmospheric side. The gap between sampling orifice and chopper can be adjusted and minimized in this way.

The improved MBMS system has been employed with a HIDEN PSM mass spectrometer. This MS is not only suited for measurement of neutrals but also for positive and negative ions. It should be noted that the MBMS system has been designed for the measurement of neutral species and is not perfectly suited for ion measurements. For ion measurements it is important to have an adequate ion optic inside the pumping stages. Due to the electrostatic repulsion force between equally charged ions, the ion beam will widen and many ions are consequently lost. This can be avoided with electrostatic lenses, which focus the ion beam.

To improve the MS signal during ion measurements, the skimmer has been replaced by an insulated one. The insulated skimmer acts as an ion lens when it is biased to a few hundred volts and helps to focus more ions into the ion optics of the MS. Most of the measurements in this study are done with a grounded skimmer resulting in a relatively low ion signal.

The background signal of ions is zero due to the high reactivity of ions at surfaces. Therefore, no chopper is needed for ion measurements. For the ion measurements in the He/O$_2$ plasma, the chopper has been removed allowing continuous gas sampling and measuring. A sampling orifice with a diameter of 20 µm is used instead of an 100 µm one. However, the 20 µm sampling orifice would clog too fast during ion measurements in the He/O$_2$/HMDSO plasma. Here, an 100 µm sampling orifice in combination with the installed chopper is used, like in the case of neutral species measurements.

As shown in the figures 3.5 and 3.6, the sampling orifice of the improved MBMS system is horizontally orientated in contrast to the previous MBMS system. Thus, the µ-APPJ is oriented in the first case horizontally and in the second case vertically. This has an impact on the buoyancy force exerting on the helium effluent in ambient air.
Figure 3.6: Technical drawing of the improved differential pumping system. The adjustment bracket of the sealing cap and the flange to the pump of the first stage is, due to the sectional drawing, not visible.
4 Fluid model of the plasma effluent

Absolute atomic oxygen and ozone densities in the effluent of the $\mu$-APPJ obtained by MBMS can be used to reveal possible reaction pathways leading to their formation. The densities of ROS in the effluent of similar plasmas have already been measured and the chemical kinetics of these species have been modeled in the past [67, 71]. The reaction pathways proposed in their works are used here as a starting reaction scheme in a 2D axially symmetric fluid model of the $\mu$-APPJ. The model is based on the model already described by Schneider et al. [68], however, the effect of ambient air is added now and the measured absolute densities of O and O$_3$ are used to validate the model results. A 2D axially symmetric geometry is used to be able to model the diffusion of air into the gas stream emanating from the plasma jet and to take the diffusion of ROS into account. The fluid model combines the solution of the Navier-Stokes equations for the gas flow in the gas mixture of He and air with the model of chemical kinetics of ROS. The model is solved using the commercial COMSOL 3.5 software.

4.1 Model of the gas flow

First, the gas flow through the jet and in the effluent is solved. Only He and air (represented by N$_2$, see below) are considered in the model of the gas flow because the concentrations of O$_2$, which is injected into the plasma, and all other plasma products are less than 1 % and can be neglected. The gas flow is described by incompressible momentum conservation and continuity equations:

$$\rho \frac{\partial \mathbf{u}}{\partial t} - \nabla \cdot (\eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T)) + \rho (\mathbf{u} \cdot \nabla) \mathbf{u} + \nabla p = 0$$

$$\nabla \cdot \mathbf{u} = 0$$

with $\rho$ being gas density, $\mathbf{u}$ gas flow velocity, $\eta$ dynamic viscosity and $p$ the pressure (101325 Pa). No volume force is assumed to work on the gas.

The transport of He through the ambient air is simulated as a diffusion-convection transport:

$$\frac{\partial c}{\partial t} + \nabla \cdot (-D_{He} \nabla c) = -\mathbf{u} \nabla c$$
with \( c \) being the He concentration in the gas mixture (\( c \in [0,1] \)) and \( D_{He} \) being the diffusion coefficient of He in the gas mixture. The gas density, dynamic viscosity, and also the diffusion coefficient are a function of the He concentration, which varies in space due to air diffusion from the sides into the effluent. The viscosity, density and diffusion coefficients of \( N_2 \) instead of air are used in the flow simulation for simplicity.

The density of the He-\( N_2 \) gas mixture is calculated as:

\[
\rho_{\text{mixture}} = \rho_{\text{He}} \cdot c + \rho_{\text{N}_2} \cdot (1 - c),
\]

where \( c \) is the He concentration, \( \rho_{\text{He}} = 0.164 \text{ kg/m}^3 \) and \( \rho_{\text{N}_2} = 1.146 \text{ kg/m}^3 \). The viscosity of the He-\( N_2 \) mixture measured at 303.15 K is taken from the literature [72] and fitted with following function:

\[
\eta(c) = -7.912 \times 10^{-6} \cdot c^4 + 1.154 \times 10^{-5} \cdot c^3 - 4.906 \times 10^{-6} \cdot c^2 + 3.355 \times 10^{-6} \cdot c + 1.8 \times 10^{-5}.
\]

The diffusion coefficients of He in the He-\( N_2 \) gas mixture is calculated using:

\[
\frac{1}{D_{\text{He in mixture}}} = \frac{c}{D_{\text{He in He}}} + \frac{1 - c}{D_{\text{He in N}_2}}.
\]

A self diffusion coefficient of He in He \( D_{\text{He in He}} = 1.7513 \times 10^{-4} \text{ m}^2 \text{s}^{-1} \) and a diffusion coefficient of He in \( N_2 \) \( D_{\text{He in N}_2} = 0.7337 \times 10^{-4} \text{ m}^2 \text{s}^{-1} \) is used [73, 74].

The jet and its effluent is modeled as two cylinders representing plasma channel and the effluent region as indicated in figure 4.1. The upper cylinder corresponds to the last 10 mm of the plasma channel and has a radius \( r=0.564 \text{ mm} \) (1 mm\(^2\) cross-section area). The top base serves as a gas inlet, where a parabolic velocity profile through a cylindrical tube calculated from the gas flow of 1.4 slm through 1 mm\(^2\) area (average velocity \( \sim 25.6 \text{ m/s} \)) and He concentration equal one are used as boundary conditions. The bottom base serves as a gas outlet from the plasma channel into the effluent. No slip for the gas flow and insulation/symmetry for the He transport are selected as a boundary conditions for the outer wall of this cylinder.

The effluent is modeled as a second cylinder with 3 mm radius and length of 50 mm. The bottom base and the outer part of the top base of this cylinder are assumed to be solid with no slip boundary condition. The outer wall is divided into two parts. The lower half of its length is defined as a gas outlet (boundary condition: convective flux, constant pressure \( p = 101325 \text{ Pa} \)) and the upper part is defined as a gas inlet with constant gas velocity of 0.2 m/s (corresponding to a constant flow of 56 sccm). He \( (c=1) \) or \( N_2 \ (c=0) \) are introduced into the effluent region through this boundary and allow to simulate different ambient atmospheres. The inflow of ambient gas represents
the "infinitely" larger reservoir of ambient air in our laboratory compared to the small volume of the plasma jet. Additionally, the flow field in the effluent region is stabilized by this inflow without formation of any vortexes in the numerical solution, which is a necessary condition to obtain a converging solution. This additional gas inflow into the effluent region could potentially influence the model results, but it has been verified that selecting other gas velocities (4 time lower or higher) do not affect the model results presented later.

The gas flow streamlines and a color map of the He concentration $c$ for the case of air ($N_2$) as ambient gas are also shown in figure 4.1. It can be seen that air diffuses into the helium effluent as the distance from the nozzle of the $\mu$-APPJ is increased. Additionally, the results show that back diffusion of air into the plasma channel can be neglected in this modeled ideal case.

4.2 Model of chemical kinetics

When the gas flow and He concentration simulation is finished, the reactions and transport of ROS can be simulated.

Again, the transport of given species $i$ ($i = O, O_3, O_2(1 \Delta_g)$, or vibrationally excited oxygen $O_2(v)$) is simulated as a diffusion-convection transport:

$$\frac{\partial n_i}{\partial t} + \nabla \cdot (-D \nabla n_i) = R_i - u \nabla n_i$$
with $D_i$ and $R_i$ being diffusion coefficient and production/loss term of a given particle due to gas phase reactions, respectively. Diffusion coefficients of O and O$_3$ in He are $D_{O\text{ in He}} = 1.29 \times 10^{-4}$ m$^2$s$^{-1}$ and $D_{O_3 \text{ in He}} = 0.713 \times 10^{-4}$ m$^2$s$^{-1}$ [75]. $D_{O_3 \text{ in N}_2} = 0.137 \times 10^{-4}$ m$^2$s$^{-1}$ is the diffusion coefficient for O$_3$ in N$_2$ and has been averaged over the two stated values by Massman [76]. Since no diffusion coefficient for O in N$_2$ could be found in literature, the diffusion coefficient for Ne in N$_2$ has been calculated using the results of Chapman and Enskog [74]. The masses of Ne and O are similar and both are atoms. This supports the assumption that both atoms exhibit a similar diffusion coefficient. A diffusion coefficient for Ne in N$_2$ of $D_{\text{Ne in N}_2} = 0.338 \times 10^{-4}$ m$^2$s$^{-1}$ has been derived and used for the diffusion of O in N$_2$. A gas temperature of 300 K is assumed in the model. The values of the diffusion coefficients of O$_2$ in He ($D_{O_2 \text{ in He}} = 5.51 \times 10^{-5}$ m$^2$s$^{-1}$) and in N$_2$ ($D_{O_2 \text{ in N}_2} = 2.32 \times 10^{-5}$ m$^2$s$^{-1}$) are used for O$_2$($^1\Delta_g$) and vibrationally excited oxygen O$_2$(v). The dependence of $D_i$ on the He concentration $c$ is calculated in the same way as described in the previous section using

$$\frac{1}{D_{i\text{ in mixture}}} = \frac{c}{D_{i \text{ in He}}} + \frac{1-c}{D_{i \text{ in N}_2}}.$$  

The dissociation degree of O$_2$ molecules in the plasma is less than 5% under our experimental conditions. Therefore, the O$_2$ density is not calculated in the model, but it is assumed to be constant (concentration of 0.6%) in the case of He as ambient gas and is calculated as $n_{O_2} = 0.006 + (1 - c) \times 0.2 \times n_0$ with $n_0 = 2.45 \times 10^{25}$ m$^{-3}$ in the case of air as ambient gas.

The boundary conditions are selected as follows. The boundary condition at any wall is different for stable O$_3$ (insulation/symmetry) and reactive or excited species (O, O$_2$($^1\Delta_g$), O$_2$(v)). Oxygen atoms and O$_2$(v) can recombine or be deexcited at the surface, which has to be considered in the model. The Neumann’s boundary condition considering the surface loss is therefore used [68, 77]. A surface loss probability of $\beta = 10^{-3}$ has been chosen for atomic oxygen and for O$_2$(v). Due to the long lifetime of O$_2$($^1\Delta_g$) [78], it has been assumed to be unreactive at the walls. Particles are introduced into the model by setting their density at the gas inlet into the plasma channel. They leave the volume through the convection losses at the gas outlet in the effluent region.

Table 4.1 contains the gas phase reactions, which are implemented in the model. These reactions have been proposed by Jeong et al. [71] and are used here in the simulation called Model 1. No reactions with ions or electrons are assumed because their densities in the effluent are negligible [75]. Additionally, the reactions shown in table 4.2 have been added to explain our measurements with air as ambient atmosphere. The reactions $R_9$ - $R_{10}$ of Model 2 are motivated and explained later in the chapter Results.
4.2 Model of chemical kinetics

Table 4.1: Reactions of Model 1 with rate constants. (⊛ No literature values for three body reactions with N\textsubscript{2} have been found. Instead, the reaction rate of the corresponding reaction with O\textsubscript{2} as collision partner has been chosen, cf. [79].)

<table>
<thead>
<tr>
<th>reactions</th>
<th>rate constants</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>R\textsubscript{1} O + O\textsubscript{2} + He → O\textsubscript{3} + He</td>
<td>$3.4 \times 10^{-46} \left(300/T_g\right)^{1.2}$ m\textsuperscript{6}s\textsuperscript{-1}</td>
<td>[79]</td>
</tr>
<tr>
<td>R\textsubscript{2} O + O\textsubscript{2} + O\textsubscript{2} → O\textsubscript{3} + O\textsubscript{2}</td>
<td>$6 \times 10^{-46} \left(300/T_g\right)^{2.8}$ m\textsuperscript{6}s\textsuperscript{-1}</td>
<td>[79]</td>
</tr>
<tr>
<td>R\textsubscript{3} O + O\textsubscript{2} + N\textsubscript{2} → O\textsubscript{3} + N\textsubscript{2}</td>
<td>$6 \times 10^{-46} \left(300/T_g\right)^{2.8}$ m\textsuperscript{6}s\textsuperscript{-1}</td>
<td>est. ⊛</td>
</tr>
<tr>
<td>R\textsubscript{4} O + O + He → O\textsubscript{2} + He</td>
<td>$1 \times 10^{-45}$ m\textsuperscript{6}s\textsuperscript{-1}</td>
<td>[79]</td>
</tr>
<tr>
<td>R\textsubscript{5} O + O + O\textsubscript{2} → O\textsubscript{3} + O\textsubscript{2}</td>
<td>$2.56 \times 10^{-46} \left(300/T_g\right)^{0.63}$ m\textsuperscript{6}s\textsuperscript{-1}</td>
<td>[79]</td>
</tr>
<tr>
<td>R\textsubscript{6} O + O + N\textsubscript{2} → O\textsubscript{2} + N\textsubscript{2}</td>
<td>$2.56 \times 10^{-46} \left(300/T_g\right)^{0.63}$ m\textsuperscript{6}s\textsuperscript{-1}</td>
<td>est. ⊛</td>
</tr>
<tr>
<td>R\textsubscript{7} O + O\textsubscript{3} → O\textsubscript{2} + O\textsubscript{2}</td>
<td>$1.5 \times 10^{-17} \exp\left(-2250/T_g\right)$ m\textsuperscript{3}s\textsuperscript{-1}</td>
<td>[71]</td>
</tr>
<tr>
<td>R\textsubscript{8} O\textsubscript{2}(^1\Delta\textsubscript{u}) + O\textsubscript{3} → O + 2 O\textsubscript{2}</td>
<td>$6.01 \times 10^{-17} \exp\left(-2853/T_g\right)$ m\textsuperscript{3}s\textsuperscript{-1}</td>
<td>[71]</td>
</tr>
</tbody>
</table>

Table 4.2: Additional reactions of Model 2. Rate and time constants have been used as fitting parameters.

<table>
<thead>
<tr>
<th>reactions</th>
<th>rate or time constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>R\textsubscript{9} O\textsubscript{2}(v) + O\textsubscript{2} → O\textsubscript{3} + O</td>
<td>$2 \times 10^{-21}$ m\textsuperscript{3}s\textsuperscript{-1}</td>
</tr>
<tr>
<td>R\textsubscript{10} O\textsubscript{2}(v) → O\textsubscript{2}</td>
<td>$5 \times 10^{-4}$ s</td>
</tr>
</tbody>
</table>

The model with the complete set of reactions from table 4.1 and 4.2 is called Model 2.

The volume is again divided into two parts: the plasma channel, where a steady state situation with constant densities of all species is assumed, and the effluent, where the reactive species can recombine. This assumption is supported by two-photon absorption laser-induced fluorescence measurements [63], which show a constant O atom density in the plasma channel and a decaying density in the effluent. Therefore, no reactions are assumed in the plasma channel (the ROS densities are introduced into the model via boundary condition). The reactions from table 4.1 and 4.2 are considered only in the effluent region.

Table 4.3 shows the boundary conditions and parameters of both models. The shown initial densities are introduced at the gas inlet of the plasma channel.
### 4 Fluid model of the plasma effluent

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial He density</td>
<td>$2.48 \times 10^{25} \text{ m}^{-3}$</td>
<td>He at 101325 Pa</td>
</tr>
<tr>
<td>initial $O_2$ density</td>
<td>$1.49 \times 10^{23} \text{ m}^{-3}$</td>
<td>0.6% of He density</td>
</tr>
<tr>
<td>$O_2$ content in He/air mixture</td>
<td>$0.2 \cdot (1-c)$</td>
<td>20% $O_2$ in air</td>
</tr>
<tr>
<td>initial O density</td>
<td>$8.5 \times 10^{20} \text{ m}^{-3}$</td>
<td>extrapolated value from [80]</td>
</tr>
<tr>
<td>initial $O_3$ density</td>
<td>$3.5 \times 10^{20} \text{ m}^{-3}$</td>
<td>extrapolated value from [80]</td>
</tr>
<tr>
<td>initial $O_2(\nu)$ density</td>
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<td>fitting parameter</td>
</tr>
<tr>
<td>initial $O_2(1\Delta_g)$ density</td>
<td>$7 \times 10^{20} \text{ m}^{-3}$</td>
<td>evaluated using [71] and [80]</td>
</tr>
<tr>
<td>gas temperature $T_g$</td>
<td>300 K</td>
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</tr>
</tbody>
</table>

**Table 4.3:** Used parameters in the model
5 Results

In this chapter, all of the obtained results are presented and discussed. First, the performance of the molecular beam mass spectrometer is demonstrated by means of several test measurements. These test measurements enabled a significant improvement of the system. Then, the calibration procedure needed for the measurements of absolute densities is explained. Finally, the results of the plasma measurements are shown and discussed. In principle, two different plasma chemistries have been analyzed, an oxygen containing and a hexamethyldisiloxane containing helium microplasma. In each case, measurements of neutral species and of positive ions are shown. Additionally, the results of the fluid model are compared to the absolute densities of the ROS in the helium/oxygen microplasma jet to understand the generation mechanism of reactive oxygen species.

5.1 Performance of the molecular beam mass spectrometer

During the first measurements, it turned out that the specific chopper design has a huge influence on the measured signal. The shape of the conical hole has been improved leading to a significantly improved signal quality. The performance of the molecular beam mass spectrometer is demonstrated by means of measurements of atmospheric air. Furthermore, the influence of the species mass on the signal and the gas flow rate through the sampling orifice has been evaluated.

5.1.1 Influence of the chopper design on the signal

As already stated above, different chopper designs have been tested. The first chopper contained one conical hole in a 2 mm thick metal disk with a sharp opening of 1.3 mm.

Figure 5.1: Cross section of the chopper with the conical chopper hole
Figure 5.2: Time resolved MBMS signal of atmospheric N\textsubscript{2} (28 amu, measured with EE \(\approx 26\) eV)

(cf. figure 5.1). A time resolved measurement of molecular nitrogen (28 amu) sampled from atmosphere is shown in figure 5.2. An electron impact energy in the ionizer of 26 eV has been chosen. The detected MS signal is normalized to the number of chopper rotations. Two sharp peaks can be recognized in figure 5.2, they correspond to the beam signal measured during the time when the chopper is open. The peak repeatedly appears every 69.9 ms, which matches the used rotation frequency of 14.3 Hz of the chopper. The background signal measured during the time when the chopper is closed decreases relatively slowly. By fitting an exponential function \(S = S_0 + Ae^{-t/\tau}\) to the time interval between 8 ms and 69 ms, one obtains a residence time of the gas in the third stage of \(\tau = 51.5\) ms. This value corresponds to the theoretical residence time, determined by the volume of the third stage \(V\) and the pumping speed \(S\) of the turbomolecular pump, \(\frac{V}{S} = \frac{21}{401/\text{s}} = 50\) ms.

By taking a closer look at the signal shape in the vicinity of the peak (cf. figure 5.3), one can recognize the peak of the beam signal approximately in a time period between 1.91 ms and 2.13 ms. However, this indicates not the time when the chopper is open. The chopper is approximately open in the time period between 1.73 ms and 1.95 ms. Due to the time of flight of the particles in the molecular beam, the peak is a little bit shifted. The extent of the time of flight shift depends on the sampled species. As is shown later, the velocity of the particles is a function of the mass. Light species are faster than heavier one.

Furthermore, figure 5.3 shows that the peak has a more complex structure and is not a sharp peak. Two rises of the signal can be found just before the peak appears, the first one at a time of 0.76 ms (position 1) and the second one at 1.65 ms (position 2). At a time of 0.76 ms the chopper is in the position shown in figure 5.4(a). Here, an
5.1 Performance of the molecular beam mass spectrometer

Figure 5.3: Detail view of the signal shape

Figure 5.4: Position of the chopper during the rise of signal

overlapping of the 5 mm wide conical opening with the orifice to the second stage exists for the first time. Two possible explanations for the first rise of the signal are conceivable. On the one hand, the gas in the volume of the conical chopper hole can drain into the second stage as soon as the overlapping is established. On the other hand, it is possible that the gas entering the first stage via the sampling orifice can flow through the chopper hole into the second stage. Both effects would lead to a rising background pressure of the third stage and thus to an increase in MS signal.

During the time when the chopper is opened, ca. 1640 N\textsubscript{2} molecules are detected per revolution. An average signal of 310 N\textsubscript{2} molecules are detected during an equal long time interval of the background. This results in an overall beam-to-background ratio of about 4.3, which is significantly higher than beam-to-background ratios obtained with continual gas sampling systems as described in chapter 2.2.3.
5 Results

During measurements with rotating chopper, the pressure in the first stage is about 47 Pa. By the following experiment the origin of the rise of signal at position 1 can be found: the sampling orifice was closed and gas was injected by means of a needle valve into the first stage through a flange at the side until a constant pressure of 47 Pa is established. If the gas volume in the conical hole is the origin of the rise of signal, the structure before the peak would exist in both cases, with opened and closed sampling orifice. The corresponding measurements are shown in figure 5.5.\(^1\) Substantially, the pressure in the first stage has no influence on the signal shape. An almost constant background signal is only measured when the sampling orifice is closed and the first stage is filled with 47 Pa air. This is evidence that the gas volume in the conical chopper hole cannot explain the rise of the signal at position 1. This means that a gas flow from the sampling orifice through the chopper hole into the second stage exists at chopper position 1. The rise of the signal at position 2 can be explained by the fact that the sampling orifice is not on the same plane as the surrounding material, but protrudes a little bit (like shown in figure 5.4). The gap between sampling orifice and chopper is very small and the volume in between cannot be pumped very efficiently. This leads to a local high pressure region, which can be recognized in the rise of signal at position 2.

As described in chapter 3.3, the position of the front plate and thus the distance between sampling orifice and chopper can be adjusted by distance screws. The distance between sampling orifice and chopper has been varied to determine the influence of

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\(^1\)The sharp peak is missing in the measurement with opened sampling orifice. This is probably due to a locally too high pressure behind the sampling orifice. As can be seen later, the distance between sampling orifice and chopper needs to be increased.
the distance on the signal shape. Measurements of atmospheric nitrogen for three different distances are shown in figure 5.6. The difference between the minimum and maximum distance is about 0.9 mm. With decreasing distance, the beam signal increases linearly as well as the background signal. The structures before the peak at position 1 and 2 increase in a similar manner. This supports the hypothesis that a small gap between sampling orifice and chopper leads to a local region of high pressure. This effect gets more severe by reducing the gap size as can be seen in figure 5.6. Furthermore, the sharp peak disappears when the distance is too low. This is probably due to the local region of high pressure, which disturbs the formation of the free jet. Essentially, this needs to be prevented, otherwise problems will occur e.g. for measurements of reactive species.

As stated above, it would be beneficial to increase the gap between sampling orifice and chopper because the volume in between could be better pumped. But when the chopper is opened, the distance must be very small to ensure that the MB can directly expand into the good vacuum of the second stage without being disturbed by the relative high pressure of the first stage. The chopper hole must act as a direct short cut to the second stage. This contradiction can be solved by embedding a small skimmer into a thinner chopper disk, like shown in figure 5.7. A small skimmer with an opening of ca. 0.8 mm has been glued in the metal disk with a thickness of 1.6 mm. Thus, the chopper looks like a ”rotating skimmer”. This concept has the advantage that there is always a gap of 0.6 mm between sampling orifice and chopper when the chopper is closed. This distance is sufficient large enough to allow a good pumped vicinity of the sampling orifice. When the chopper is opened, a direct short cut between atmosphere and second stage is established.
A comparison of the time resolved MBMS signals obtained with the conical chopper hole and with the rotating skimmer measured at the same conditions is shown in figure 5.8. A noticeable difference is that the background signal decreases by a factor of approx. 4 while the beam signal is about 2.5 times lower when the rotating skimmer is used. A decrease of the beam signal has been expected because the diameter of the embedded skimmer is smaller than before. However, the beam-to-background ratio increases to ca. 14. Furthermore, the rise of signal at position 1 disappeared and the rise of signal at position 2 became insignificantly small.

It should be noted that the MBMS system is qualified to analyze atmospheric pressure plasmas only with this improved chopper. The problem with local regions of high pressure is solved by the chopper with an embedded skimmer. It has been shown that the emerging free jet is not disturbed by the chopper or a high pressure region.

A further improvement has been made by using four embedded skimmers in the chopper instead of one. The comparison of both cases can be found in figure 5.9. It can be seen that the background signal stays almost the same even though more gas enters the third stage. The beam-to-background ratio only decreases slightly and the overall measurement time can be reduced by a factor of four by using four embedded skimmers.
5.1 Performance of the molecular beam mass spectrometer

Figure 5.9: Comparison of time resolved MBMS signals of atmospheric N$_2$ obtained with one and four embedded skimmers (28 amu, measured with EE $\approx$ 66 eV)

5.1.2 Analysis of air

A first performance test of the MBMS system has been performed by analyzing the air atmosphere. Normal air has been chosen because it contains several kinds of gases with different, known concentrations. Besides the major components N$_2$ (28 amu) and O$_2$ (32 amu) also the trace gases He (4 amu), $^{36}$Ar (36 amu), $^{38}$Ar (38 amu), $^{40}$Ar (40 amu), CO$_2$ (44 amu), and Kr (84 amu) could be detected. The experimentally determined composition is shown in table 5.1 and compared with the values from the literature [81]. The different ionization cross sections at 66 eV have been taken into account as well as the mass dependent transmission function of the MS. It is demonstrated that even $^{84}$Kr atoms with a concentration of only 0.65 ppm can be detected in air, showing the sensitivity limit of the MBMS system. The $^{84}$Kr signal integrated over 10007 chopper revolutions is shown in figure 5.10. Even if the signal is very low, one can clearly see that more particles are detected in the beam than in the background. 21 counts are registered during the time when the chopper is open in contrast to 6 counts of the background signal. Consequently, even $^{84}$Kr could be measured with a relatively high beam-to-background ratio of 2.5.

However, the measured and literature values don’t correspond perfectly to each other. This is due to the composition distortion, which has not been taken into consideration during the analysis. The composition distortion can be seen with lighter species being more discriminated than heavier species.
5 Results

<table>
<thead>
<tr>
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<th>literature</th>
</tr>
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<tr>
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</tr>
<tr>
<td>N₂</td>
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<td>78.08 %</td>
</tr>
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<td>O₂</td>
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<td>6 ppm</td>
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</tr>
<tr>
<td>40Ar</td>
<td>1.10 %</td>
<td>0.93 %</td>
</tr>
<tr>
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<td>730 ppm</td>
<td>380 ppm</td>
</tr>
<tr>
<td>84Kr</td>
<td>1.62 ppm</td>
<td>0.65 ppm</td>
</tr>
</tbody>
</table>

**Table 5.1**: Measured composition of air with literature values

![Figure 5.10: 84Kr signal integrated over 10007 chopper revolutions (measured with EE ≈ 66 eV)](image)

**Figure 5.10**: $^{84}$Kr signal integrated over 10007 chopper revolutions (measured with EE ≈ 66 eV)

![Figure 5.11: Comparison of normalized signals of atmospheric N₂ (28 amu), O₂ (32 amu), and Ar (40 amu)](image)

**Figure 5.11**: Comparison of normalized signals of atmospheric N₂ (28 amu), O₂ (32 amu), and Ar (40 amu)
5.1 Performance of the molecular beam mass spectrometer

Figure 5.12: Comparison of normalized signals of pure He (4 amu), Ne (20 amu), Ar (40 amu), and Kr (84 amu)

5.1.3 Mass dependence of the peak shape

To check the influence of the mass of the species on the shape of the peak, the obtained MBMS signals of atmospheric nitrogen, oxygen and argon have been normalized and plotted in figure 5.11. The peak shape is almost the same for the three depicted gases and thus independent of the mass of the species. The peaks of light particles seem to appear slightly earlier than the peaks of heavier particles. This indicates that light particles possess a higher velocity than heavy particles.

The peak positions of several pure atomic and molecular gases have been compared for a further analysis. Now, no gas mixtures have been used, only pure gases. The peak shapes of some rare gases are shown exemplarily in figure 5.12. One can recognize a clear trend that light species posses a higher velocity than heavier species. This is due to the fact that the species are accelerated in the free-jet expansion, where the terminal velocity $v_\infty$ depends on the weight $m$ of the species [51]:

$$v_\infty = \sqrt{\frac{2R}{m} \left( \frac{\gamma}{\gamma - 1} \right) T_0},$$

with $R$ being the universal gas constant, $\gamma$ the adiabatic index, and $T_0$ the initial gas temperature. Light species are therefore accelerated to a higher velocity than heavy species (theoretical values e.g. $v_\infty = 1770$ m/s for He, $v_\infty = 776$ m/s for dry air and $v_\infty = 560$ m/s for Ar).
5 Results

![Graph showing time of flight of different atoms and molecules as function of mass.](Image)

Figure 5.13: Time of flight of different atoms and molecules as function of the mass

The necessary flight time to reach the ionizer after opening of the chopper is shown for different species as function of the atomic or molecular mass in figure 5.13. Two fits for atoms and molecules using the above formula for the terminal velocity $v_\infty$ have been additionally plotted in the graph. An adiabatic index of $\gamma = 1.66$ has been used for atoms and $\gamma = 1.4$ for molecules. Both fits reproduce the measurements quite well.

As soon as a gas mixture is used, the different species of the mixture adapt their velocity by collisions. Heavy species are accelerated by diluting them in a light gas and light species are slowed down by diluting them in a heavy gas [51]. That is why all peaks of the air measurement in figure 5.11 overlap and the species travel with the same velocity.

5.1.4 Gas flow rate into the MBMS system

As soon as a microplasma jet is analyzed by means of the MBMS system, it is important to ensure that the MBMS doesn’t disturb the plasma jet. When the gas flow rate through the sampling orifice into the MBMS is too high in comparison to the gas flow rate of the microplasma jet, no stagnation of the flow will occur in front of the sampling orifice and the effluent of the plasma jet is distorted.

The maximum mass rate $G_{\text{max}}$ through an orifice is calculated by the equation [50]

$$G_{\text{max}} = p_0 A_{\text{min}} \left( \frac{2}{\gamma + 1} \right)^{\frac{\gamma + 1}{\gamma - 1}} \sqrt{\gamma \frac{m}{RT_0}}.$$ 

$p_0$ is the initial pressure, $A_{\text{min}}$ is the minimal cross section area of the orifice, $\gamma$ denotes the adiabatic index, $M$ is the mass of the atoms/molecules, $R$ is the universal gas
constant and $T_0$ is the initial gas temperature. For helium, one gets a maximum gas flow rate of about 0.25 slm and for air ca. 0.08 slm through a sampling orifice with a diameter of 100 $\mu$m. These values are well below the gas flow rates of the microplasma jets. The plasma jets are operated at a gas flow with at least 1.4 slm. A stagnation of the gas flow is thus ensured.

## 5.2 Calibration of the MBMS system

An MBMS can provide absolute densities of measured neutral species. However, several different things need to be carefully considered during the calibration procedure. As already mentioned in chapter 2.2.2, the different electron impact ionization cross sections for different gases need to be taken into account. The SEM of the MS possesses a mass-dependent transmission function, which leads to a discrimination of heavy against light ions. The mass-dependent transmission function has been determined by measuring known densities of different gases [82]. These effects have to be considered during any MBMS measurements [46, 47].

Moreover, further effects must be taken into account during collisional gas sampling, when gas is sampled from atmosphere to low pressure. The composition of the MB is, however, different from the original composition of the gas mixture in front of the sampling orifice. This is due to the earlier mentioned composition distortion in MBMS sampling (cf. chapter 2.2.5). Probably, one of the most important effects is radial diffusion in the supersonic free jet. Huge radial pressure gradients exist inside of this expansion which result in larger diffusion fluxes in the radial direction. The extent of this diffusion is different for different species, depending mainly on their mass, collision cross section, and main collisional partner. It has been shown that heavy species tend to remain on the central streamline because their diffusion is slow, whereas light species diffuse faster outwards along the pressure gradients. This effect leads to discrimination of light species against heavy ones in the composition of the MB. The effect of composition distortion was demonstrated by measurements of air (cf. table 5.1).

Since many different effects account for the composition distortion, it is difficult or even impossible to determine the influence of composition distortion theoretically. But, the observed changes in the signal can be measured and used to compensate for the composition distortion experimentally.

In general, the calibration procedure for composition distortion is for every species the same. A known density of the species of interest is measured by the MBMS. Due to the composition distortion, the measured species density in the ionizer of the MS differs from the known species density in front of the sampling orifice. The ratio of both densities is the calibration factor for composition distortion.
This calibration procedure can only be used when the species of interest is a stable, non-reactive atom or molecule because one needs a known quantitative source of the species. Since absolute densities of radicals are of particular interest, one needs to use a gas for the calibration that behaves similar to the radical. The mass of both species should be similar as well as the adiabatic index. Therefore, neon has been chosen for the calibration of atomic oxygen and argon or nitrous oxide is used for ozone calibration. Calibration factors of 2.2 and 2.9 have been determined for atomic oxygen and ozone, respectively, when diluted in helium. These factors are used for calibrating the helium effluent of the μ-APPJ in an ambient helium atmosphere.

As already mentioned early, the extent of composition distortion depends on the main collisional partner. The influence of composition distortion thus changes when the main collisional partner changes. This has to be considered when the plasma jet is not operated in a controlled atmosphere of a gas equal to the plasma forming gas.

The μ-APPJ has also been analyzed in ambient air. Under this condition, air will diffuse into the helium effluent and change continuously its composition with increasing distance between the μ-APPJ nozzle and the sampling orifice. The change of the composition is demonstrated in figure 5.14. The μ-APPJ was just operated at a gas flow of 1.4 slm He without any addition of oxygen and without igniting a plasma. The distance between the nozzle of the plasma jet and the sampling orifice was varied between 1 and 52 mm while recording the He, N$_2$ and O$_2$ signal. The sum of the N$_2$ and O$_2$ signal determines the air signal. The results below have been corrected for the composition distortion by measurements of different known He/air mixtures.
5.2 Calibration of the MBMS system

Up to a distance of 4 mm almost no air admixes into the helium effluent. Beyond this point, air diffuses into the effluent changing continuously its composition. The calculated composition on the symmetry axis from the fluid model is shown in figure 5.14 as well. The results of the fluid model are in very good agreement with the measurements, substantiating the accuracy of the used model and corroborating that the MBMS can determine very well the composition of the gas mixture.

The results show that the composition of the effluent, and consequently also the main collisional partner, is a sensitive function of the distance from the nozzle. The extend of composition distortion changes thus with the distance from the nozzle, too. This effect can be demonstrated by a "simulated distance variation". A He/air mixture with a constant addition of Ne(1 %) and N$_2$O(0.5 %) has been used. The He/air mixture has been varied between pure He (light atoms with small collision cross section as main collision partner) and pure air (heavy diatomic molecules with larger collision cross section) whereas the Ne and N$_2$O amount was always kept constant. Ne is in pure He the heavier species and will enrich on the center line of the MB. While changing the He/air ratio towards pure air, Ne becomes the lighter species compared to the mean molecular mass of the mixture and will consequently diffuse faster out of the MB. Figure 5.15 shows the relative Ne signal measured by the MBMS as function of the air content in the He/air mixture. The Ne signal decreases by a factor of four during the He/air variation. The N$_2$O signal exhibits surprisingly a very similar behavior, even though it is more as twice as heavy than Ne and heavier than N$_2$ and O$_2$ molecules in air. The difference between the masses of Ne, N$_2$O, and air is probably not significant and the effect is dominated by their difference to He.

These measurements clearly show that the composition distortion has to be taken into account. The amount of air in the effluent and the effect of composition distortion will strongly depend on the distance from the jet nozzle. The following procedure is adopted to take this effect into account in the signal calibration.

First, the amount of air in the effluent at a given distance from the jet is determined by measuring the He and N$_2$/O$_2$ signals. These signals are compared to measurements with known He/air mixtures. The local air content in the effluent can be determined in this way (cf. figure 5.14). This air content, together with the data in figure 5.15, is used to determine the necessary correction factors to compensate for the difference in the composition distortion in pure He and in He/air mixtures. The O and O$_3$ signals are hence scaled to the values that would be obtained in pure He.
Figure 5.15: Measurement of the Ne and N$_2$O signal of different He/air mixtures with constant addition of Ne(1%) and N$_2$O(0.5%)

The universal calibration procedure is summarized in the following list. The signal of a reactive species $x$ (here: O or O$_3$) is measured in the carrier gas (here: He). Absolute densities are to be calculated.

**Background correction:** When the chopper is open, the measured signal is composed of the beam signal and the background signal. Always, the background signal must be subtracted from this measured signal to correct for the background signal and to obtain the pure beam signal.

**Compensation for mass dependences:** The measured signal $S_x$ of species $x$ is given by:

$$S_x = n_x \cdot \sigma_x(EE) \cdot G \cdot F(m_x) \cdot CD(m_x, \gamma_x, M, \gamma_M),$$

where $n_x$ is the density of species $x$, $F(m_x)$ is the mass-dependent MS function without composition distortion, $G$ includes all mass-independent factors (like geometry of the ionizer, extraction efficiency, and emission current; cf. chapter 2.2.2), and $CD$ is an expression describing the composition distortion. This expression is a function of the mass $m_x$ and the adiabatic index $\gamma$ of species $x$. Furthermore, it depends on the properties (mass $M$ and adiabatic index $\gamma_M$) of the main collision partner (gas of the effluent). Calibration of an MS is always done by measuring a known density $n_{cal}$ of a calibration gas $cal$ and comparing the signals:

$$n_x = n_{cal} \cdot \frac{S_x}{S_{cal}} \cdot \frac{\sigma_{cal}}{\sigma_x} \cdot \frac{F(m_{cal})}{F(m_x)} \cdot \frac{CD(m_{cal}, \gamma_{cal}, M, \gamma_M)}{CD(m_x, \gamma_x, M, \gamma_M)}.$$
The easiest way to calibrate the measured signal $S_x$ of species $x$ is to measure a known density of the same species under identical conditions (i.e. equal main collision partner). This is done in the following sections for the calibration of the reaction products in the HMDSO plasma. Since these reaction products are stable, liquids of them are available. The calibration is then simplified to:

$$n_x = n_{\text{cal}} \cdot \frac{S_x}{S_{\text{cal}}}.$$

When the species of interest $x$ is unstable, like in the case of atomic oxygen and ozone, then no known density of them is available and can be measured. An atom or molecule with similar properties (i.e. mass $m$ and adiabatic index $\gamma$) should be used for simplicity. As already described, Ne is used instead of atomic oxygen and N$_2$O instead of O$_3$.

This calibration procedure is used to obtain absolute densities of the species $x$ in the helium effluent when the ambient atmosphere is also helium.

*Calibration in ambient air:* If the ambiance is air, then the calibration should be repeated each time the composition of the effluent (i.e. main collision partner) changes. Here, this is separated into three steps. First, the signals are calibrated for the case of an ambient helium atmosphere like described above.

Then, these signals have to be corrected for the change in main collision partner due to admixing air. A known concentration of the calibration gas is admixed into different He/air mixtures while the concentration of the calibration gas stays constant. The signal change of the calibration gas is observed during a variation of the He-air ratio of the mixture. In this way, a lookup table is created for the calibration gas that contains for every He/air mixture a correction factor for the changed composition distortion due to air entrainment.

After that, the exact gas composition of the effluent needs to be determined. This is done by measuring the He and N$_2$/O$_2$ signals of the He effluent in ambient air. The absolute air content in the effluent can be obtained then by comparing known air densities in helium with their respective measured signals. The effect of the changing composition distortion due to the changing main collision partner can be found for each He/air ratio in the created lookup table.
5 Results

5.3 Production of reactive oxygen species

In this chapter, the measurements of reactive oxygen species in the effluent of a He/O₂ micro-scaled atmospheric pressure plasma jet are shown and discussed. First, the results of neutral species obtained in an ambient helium atmosphere are presented. Afterwards, the jet has been operated in ambient air to determine the influence of air admixture on the ROS densities.

5.3.1 Measurement of neutral species

Atomic oxygen and ozone densities in the effluent of the \( \mu \)-APPJ have been measured. The O and O₃ densities were observed for a variation of the O₂ admixture, of the applied electrode voltage, and of the distance between the nozzle of the jet and the sampling orifice. The plasma jet was placed in a helium atmosphere, so no reactions between ROS and air molecules can take place. Additionally, the depletion of molecular oxygen was measured by MBMS.

Atomic oxygen has been measured with an electron energy in the ionizer of about 15 eV to prevent dissociative ionization of molecular oxygen. Ozone has been measured with an electron energy of 70 eV because the signal does not overlap with dissociative ionization of other species.

A typical time resolved signal of atomic oxygen in the effluent of the \( \mu \)-APPJ is shown in figure 5.16. The oxygen atom measurement has been integrated over 3147 chopper revolutions. For comparison, the corresponding helium signal is additionally shown in the figure. The He signal has been scaled down by a factor of 500 and was integrated over 1038 revolutions. It can be seen that both signal shapes are very similar. The background signal of atomic oxygen is very low, on average just slightly above zero, resulting in a beam-to-background ratio higher than seven.

O₂ depletion

The signal of molecular oxygen has been measured while the plasma was turned on and off. The difference between both signals corresponds to O₂ depletion in the plasma. The O₂ depletion has been determined as a function of the applied electrode voltage and of the amount of admixed oxygen.

The relative O₂ depletion decreases slightly from ca. 5% to 3% while changing the O₂ admixture between 0% and 1% (cf. figure 5.17). The plasma was operated at a voltage of 230 V\textsubscript{RMS} and with a distance of 2 mm between \( \mu \)-APPJ and sampling orifice.

A variation of the electrode voltage at a distance of 2 mm and an O₂ admixture of 0.6% reveals a linear correlation between the voltage and O₂ depletion (cf. figure 5.18). At
5.3 Production of reactive oxygen species

![Graph showing production of reactive oxygen species](image)

**Figure 5.16:** He (26 eV EE, 1038 revolutions) and O (15 eV EE, 3147 revolutions) signals as measured from a He/O$_2$ μ-APPJ. Time resolution of the x-axis is 20 μs.

![Graph showing O$_2$ depletion](image)

**Figure 5.17:** O$_2$ depletion depending on the admixed O$_2$ content. (1.4 slm He flow, 2 mm distance, 230 V$_{RMS}$ electrode voltage)

an applied voltage of about 190 V$_{RMS}$, where the plasma ignites, the O$_2$ consumption is below 1%. At a voltage of 340 V$_{RMS}$, just before the μ-APPJ starts to arc, the consumption reaches its maximum value of 10%.

N. Knake et al. reported a maximum dissociation degree of molecular oxygen up to 20% in the discharge core of the μ-APPJ [63]. This value corresponds approximately to the value determined by MBMS in the effluent. The O$_2$ depletion is probably lower in the effluent due to recombination of oxygen atoms leading again to formation of molecular oxygen.
Variation of the $\text{O}_2$ admixture

The atomic oxygen and ozone signals were recorded while varying the admixture of molecular oxygen at a constant helium flow of 1.4 slm, an applied voltage of 230 V$_{RMS}$, and a distance of 3 mm. The corresponding densities are shown in figure 5.19 together with the O density determined by TALIF spectroscopy [80]. The atomic oxygen density increases with raising $\text{O}_2$ admixture peaking at about 0.6 %. Beyond this point, the O density decreases again until the plasma extinguishes at a high $\text{O}_2$ admixture. The MBMS measurements could only be performed up to an $\text{O}_2$ admixture of 1 %. With higher admixtures, the plasma could not be ignited anymore. Both, MBMS and TALIF, yield an almost identical dependence of the O density on the $\text{O}_2$ flow. However, the absolute O density measured by MBMS is about 3.7 time smaller than the value determined by TALIF. The maximum O density measured by MBMS and TALIF is about $8.5 \times 10^{14}$ cm$^{-3}$ and $3.2 \times 10^{15}$ cm$^{-3}$, respectively.

Considering errors of available ionization cross sections (typically 5-10 %), inaccuracy of calibration of the mass-dependent transmission function of the MS, drifts in the electronics, and aging of the detector, the MBMS should provide absolute densities with systematic errors within a factor of two. An additional systematic error can arise due to different composition distortions for the measured and calibrated gas. As already shown, this error is probably small. The overall reliability of the TALIF measurements is stated to be 50 %. Consequently, the MBMS and TALIF measurements are in very good agreement, especially because both measurements are performed under different conditions (undisturbed effluent vs. stagnation of the flow, cf. chapter 2.4).

In contrast to the O density, the $\text{O}_3$ density does not show a maximum. It increases until the plasma extinguishes at high $\text{O}_2$ admixtures. A maximum value of about $1 \times 10^{15}$ cm$^{-3}$ was found at an admixture of 1 % $\text{O}_2$. 

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**Figure 5.18:** Influence of the applied electrode voltage on the $\text{O}_2$ depletion. (1.4 slm He flow with 0.6 % $\text{O}_2$, 2 mm distance)
5.3 Production of reactive oxygen species

A possible explanation for the observed trends is given in the following. Assuming that atomic oxygen is produced in the plasma core via the reaction \( e^- + O_2 \rightarrow 2O + e^- \), the O density increases with increasing O\(_2\) admixture, but is limited by the plasma (i.e. electron density). A competing process is the three body reaction \( O + O_2 + M \rightarrow O_3 + M \) consuming oxygen atoms and producing ozone. The ozone production and therefore the O consumption gets more effective at higher O\(_2\) concentrations, thus the O\(_3\) density increases and the O density decreases. Additionally, the electron density decreases with rising O\(_2\) concentration due to the electronegativity of the O\(_2\) molecule [83]. Furthermore, the electron temperature \( T_e \) changes due to vibrational and rotational excitation of molecular oxygen. This leads to a lower number of high energetic electrons at high oxygen admixtures. Overall, the dissociation rate of O\(_2\) and therefore the atomic oxygen density decreases at high O\(_2\) concentrations, too.

**Variation of the electrode voltage**

The atomic oxygen and ozone density were measured at a distance of 3 mm in front of the \( \mu \)-APPJ’s nozzle while varying the electrode voltage between the point of plasma ignition and arcing, corresponding to 185 V\(_{RMS}\) and 315 V\(_{RMS}\), respectively. The helium flow through the jet was 1.4 slm with an admixture of 0.6 % O\(_2\). Because of technical reasons, it was not possible to measure the electrode voltage during the TALIF measurements. Instead, the rf-transceiver power was recorded. Since it is difficult to compare voltage and power explicitly, the quantitative behavior of the MBMS and TALIF densities is shown in the interval from ignition to arcing (cf. figure 5.20). This corresponds to a power from 2 W to 11 W. At the ignition point, an atomic oxygen density of \( 4.6 \times 10^{14} \text{ cm}^{-3} \) and \( 1.3 \times 10^{15} \text{ cm}^{-3} \) can be measured by MBMS and TALIF,

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**Figure 5.19:** Influence of the O\(_2\) admixture on the atomic oxygen and ozone density. The O density obtained by TALIF is scaled by a factor of 0.27. (1.4 slm He flow, 3 mm distance, 230 V\(_{RMS}\) electrode voltage)
respectively. By increasing the applied electrode voltage, the atomic oxygen production also increases linearly. At the highest possible power, before arcing, a density of $2.0 \times 10^{15} \text{ cm}^{-3}$ (MBMS) or $4.7 \times 10^{15} \text{ cm}^{-3}$ (TALIF) is reached, respectively. It is not possible to strictly compare the electrode voltage with the applied power. Therefore it is not surprising that the qualitative behaviors of both signals are not in perfect agreement with each other. However, both diagnostics show the same trend in the O density.

The ozone density is about $3.4 \times 10^{14} \text{ cm}^{-3}$ at the ignition point and increases to $4.5 \times 10^{14} \text{ cm}^{-3}$ at a voltage of 200 $V_{\text{RMS}}$. Beyond this maximum, the $O_3$ density decreases slightly to a value of $3.0 \times 10^{14} \text{ cm}^{-3}$ at the highest voltage of 315 $V_{\text{RMS}}$.

By applying higher voltages to the electrode, the $O_2$ dissociation degree increases (cf. figure 5.18), possibly due to an increasing electron density [83]. Therefore, it is reasonable that the atomic oxygen density increases in the same manner. The ozone density behaves differently. As will be shown later, ozone molecules are mainly produced in the effluent. This explains the nearly unaffected ozone signal while increasing the applied voltage. Only a slight increase can be observed first, because more atomic oxygen is available to produce ozone molecules. But with higher powers, the dissociation rate of the ozone molecules increases, too, and hence the ozone density decreases.
5.3 Production of reactive oxygen species

![Graph showing atomic oxygen and ozone density as a function of distance from the jet.](image)

**Figure 5.21:** Atomic oxygen and ozone density as a function of the distance from the jet. The O density obtained by TALIF is scaled by a factor of 0.27. The lines reflect the results obtained by Model 1. (1.4 slm He flow with 0.6 % O\textsubscript{2} admixture, 230 V\textsubscript{RMS} electrode voltage)

**Variation of the distance**

The distance between the $\mu$-APPJ and the sampling orifice was varied to monitor a spatial variation of the densities while the $\mu$-APPJ was operated in an ambient helium atmosphere. Figure 5.21 shows the spatial O and O\textsubscript{3} density distribution in the effluent of the jet. The jet was operated with a helium flow of 1.4 slm and an addition of 0.6 % O\textsubscript{2} at an electrode voltage of 230 V\textsubscript{RMS}. The atomic oxygen density decreases monotonically with increasing distance from the jet and can still be detected in a distance of 30 mm. Again, the absolute atomic oxygen density measured by MBMS is 0.27 times the density measured by TALIF. The highest O density obtained by TALIF spectroscopy is about $3.2 \times 10^{15}$ cm\textsuperscript{-3} in contrast to $7.0 \times 10^{14}$ cm\textsuperscript{-3} obtained by MBMS. A detection limit of the MBMS system of about 6 ppm can be estimated by the lowest detectable atomic oxygen signal at high distances.

In contrast to the atomic oxygen production, the ozone production mainly takes place in the effluent: direct at the nozzle, the ozone density ($3.7 \times 10^{14}$ cm\textsuperscript{-3}) is lower than the atomic oxygen density. But with increasing distance, the ozone density grows till it saturates beyond a distance of 40 mm at a density of about $1.4 \times 10^{15}$ cm\textsuperscript{-3}.

These measurements provide absolute densities in the effluent of the $\mu$-APPJ. A comparison of these results with the fluid model described in chapter 4 can be used to understand the chemistry in the effluent. The simulated O and O\textsubscript{3} densities are shown as lines in figure 5.21, too.
The atomic oxygen density simulated by the fluid model (Model 1) matches perfectly with the MBMS and TALIF measurements. In contrast, the simulated ozone density profile (“Model 1 without filling effect” in figure 5.21) doesn’t correspond to the measurements. The modeled density exhibits a maximum at a distance of 21 mm and decreases beyond. In this case, the plasma effluent has been simulated in an infinitely large volume filled with He. This has been realized in the model by an additional injection of helium through the gas inlet at the side (cf. figure 4.1 in chapter 4). However, the µ-APPJ is located during the MBMS measurements in a chamber for the controlled He atmosphere with a volume of 1.1 dm³. This chamber fills continuously with ozone during the time the plasma is operated and the ozone diffuses back into the plasma effluent and causes an artificially higher ozone signal. To take this filling of the chamber with ozone into account, we assume that all O recombines into O₃ (neglecting O losses due to reactions R₄-R₈, cf. table 4.1) and that an O₃ density of \( n_{\text{O,init}} + n_{\text{O,init}} \) is recycled through the gas inlet in the effluent region (boundary condition at the gas inlet). This assumption is reasonable because tests showed the effect of the reactions R₄-R₈ on the model results under our experimental conditions. The change of the densities is less than 5% when reaction R₄-R₈ are included. The gas phase chemistry is dominated by the O recombination with O₂ forming O₃ (R₁-R₃). The result of the simulation with this recirculation of ozone is represented by the solid line in figure 5.21. Now, the modeled data reproduce the trend of the measurement very well, even if the absolute values do not match perfectly. The profile of the O density is the same for both cases.

Concerning the reactions stated above,

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (\text{M} = \text{He, N}_2, \text{and O}_2),
\]

one expects that every oxygen atom finally transforms into an ozone molecule. This implies that the ozone density cannot exceed the initial atomic oxygen density plus the initial ozone density in an opened system. Like shown in figure 5.21, the O₃ density can only exceed this maximum value in a closed system which is continuously filled with O₃.

In summary, one sees that Model 1 and the measurements are in reasonable agreement and that the proposed chemistry can very well describe the O and O₃ densities in the effluent.

5.3.2 Effluent chemistry in ambient air

The MBMS measurements of the plasma effluent are now repeated with air as ambient gas to determine the influence of admixing air into the helium effluent. As
5.3 Production of reactive oxygen species

Figure 5.22: Atomic oxygen and ozone density as a function of the distance from the jet in ambient air. The lines reflect the results obtained by Model 1. (1.4 slm He flow with 0.6% O\textsubscript{2} admixture, 230 V\textsubscript{RMS} electrode voltage shown above, the composition of the effluent changes rapidly with increasing distance from the nozzle of the jet because atmospheric air diffuses into the effluent (cf. figure 5.14). The plasma jet was operated with the same parameters described in the previous section. The obtained densities are shown, together with the densities calculated by Model 1, in figure 5.22.

The measured atomic oxygen density is about $8 \times 10^{14}$ cm$^{-3}$ at the nozzle of the µ-APPJ and declines with increasing distance almost linearly. In a distance of 15 mm oxygen atoms are still present in the effluent (ca. $1.5 \times 10^{14}$ cm$^{-3}$). The atomic oxygen trends in ambient air and helium are very similar. No TALIF measurements of O density are available for comparison because the TALIF signal is influenced by additional non radiative quenching of the excited states by air.

There is no difference between the ozone densities as measured in He and air atmosphere up to a distance of 4 mm. This is an expected result because the air starts to admix into the effluent only beyond this distance (cf. figure 5.14). At larger distances, the ozone density in ambient air significantly increases in contrast to the density in ambient helium. A maximum O\textsubscript{3} density of $3.4 \times 10^{15}$ cm$^{-3}$ is reached in a distance of 20 mm. Afterwards, the O\textsubscript{3} density decreases to a value of $0.7 \times 10^{15}$ cm$^{-3}$ at a distance of 48 mm. The steep decline of the O\textsubscript{3} density in ambient air beyond a distance of 20 mm can be explained by the effect of buoyancy force. Absorption spectroscopy measurements of ozone by H. Bahre et al. [84] have shown that the helium effluent (including the small concentration of ozone molecules) starts to ascend in a surrounding air atmosphere beyond a distance of ca. 20 mm. The origin of buoyancy can be the
lighter density of helium in contrast to air combined with the slightly higher temperature of the plasma effluent. Later measurements of ozone with the modified MBMS setup does not show such a distinct shape due to a different configuration: the jet is mounted vertically and the front plate with the sampling orifice is oriented horizontally at the modified MBMS setup (cf. figure 3.6 in chapter 3.3).

We have seen in the previous case, that the conversion of all O into O$_3$ leads to an ozone density of about 1.2 to 1.4 \times 10^{15} \text{ cm}^{-3}. This means that more ozone is produced due to admixture of air into the effluent than due to atomic oxygen emanating from the plasma. However, there is no reaction in the proposed scheme of Jeong et al., which could explain the additional production of ozone. This can be clearly seen, when the measured densities are compared to the results of Model 1, also plotted in figure 5.22.

The Model 1 predicts a faster decrease of the atomic oxygen density due to a faster reaction rate of reactions $R_1$, $R_2$, $R_3$, $R_5$, and $R_6$. This is caused by additional O$_2$ and N$_2$ in the effluent because of the air entrainment. Correspondingly, ozone is produced faster compared to the case in ambient He. However, its maximal density predicted by Model 1 is still limited by the limited amount of oxygen atoms from the plasma and cannot exceed the limit given by the sum of initial O and O$_3$ densities. Both O and O$_3$ densities simulated by Model 1 do not reproduce the measured data (cf. figure 5.22). The atomic oxygen density does not decrease as fast as expected by the model, but stays relatively high even at a larger distance from the jet and, as already mentioned, much more ozone is produced. These results indicate that some reactions, which generate additional O atoms and O$_3$ molecules, are missing in the simulation Model 1.

**On the origin of the additional ozone and atomic oxygen**

The additional production of O atoms has already been observed by other authors. S. Reuter et al. [67] have observed that oxygen atoms could be detected by TALIF even at the distance of 10 cm from a similar, but larger, planar jet operated in He with 0.5% O$_2$ gas mixture and in He as ambient atmosphere. They concluded that electrons and ions as well as metastable helium atoms can be excluded as an origin for an energy transport into the effluent because their respective densities rapidly decrease, as soon as electric excitation ceases. Additionally, they have detected energetic vacuum ultraviolet (VUV) radiation by OES and have shown that (V)UV radiation originating from the discharge region reaches far into the effluent. Therefore, they have concluded that "(V)UV radiation produces atomic oxygen in the effluent by dissociation of ozone or molecular oxygen." [67] This conclusion has been corroborated in their following work, where the plasma emitted photons have been blocked, which resulted in a decrease of O densities in the effluent [85]. (V)UV radiation as a source of reactive species
in the effluent of the µ-APPJ has also been observed indirectly during the inactivation of bacteria by the effluent of the X-Jet [68, 86]. With the help of the absolutely calibrated data, additional MBMS measurements, and adjustment of the fluid model, more details about a possible O and O₃ generation scheme in the plasma effluent can be revealed.

The possible effect of air back diffusion
As already discussed, the results in the literature indicate that plasma generated (V)UV photons can initiate photodissociation reactions leading to the formation of additional O and subsequently O₃. Before we discuss the possible photodissociation reactions, we need to check for the possible effect of air back diffusion into the plasma channel. The gas flow simulation has shown, that air back diffusion is almost negligible. But the model represents an ideal case without effects due to actual design and realization of the plasma jet such as diffusion along the corner edge of the square geometry. Additionally, the simulation shows that even in the ideal case the air can come into direct contact with the active plasma zone. Point A in figure 4.1 marks the edge of the plasma channel, where it takes place. The electron driven dissociation of atmospheric O₂ followed by the diffusion of the products towards the jet axis could also be a source of additional O and O₃. To exclude this effect, a modified µ-APPJ with an elongated gas channel has been built. This gas channel is made from glass plates, starts directly at the electrodes, has a length of 3 mm, and a $1 \times 1 \text{mm}^2$ cross section. The plasma effluent is therefore confined within the first 3 mm after the plasma region and a direct interaction between atmospheric air and the plasma is prevented. Figure 5.23 shows the comparison of the ozone signals obtained with the standard µ-APPJ without extension and the extended µ-APPJ. Only relative data are shown, no absolute calibration and compensation for the changing composition distortion have been performed. No significant difference can be found between both measurements. One can, therefore, conclude that diffusion of air into the plasma cannot explain the increased ozone (and also atomic oxygen) production.

During these measurements, the newer MBMS setup with horizontally oriented front plate has been used. Therefore, the influence of the helium buoyancy is different and the shape of the measured ozone signal differs a little bit from the previous measurement (cf. figure 5.22).

Photodissociation as the source of additional O and O₃
Photodissociation of oxygen molecules or ozone has been suggested as a possible source of additional O and consequently also O₃. The quantitative and space resolved MBMS measurements of O₃ allows now the quantitative estimation of the necessary
Figure 5.23: Relative MS signal at mass 48 amu (ozone) as function of the distance to the nozzle for the standard $\mu$-APPJ and extended $\mu$-APPJ under same conditions (in ambient air, applied electrode voltage: 230 $V_{\text{RMS}}$, gas flow: 1.4 slm He with 0.6 % $O_2$).

O$_3$ production rate needed to explain the rise of its density as observed in figure 5.22. This estimated production rate can be used to estimated the necessary photon flux, if photodissociation is the main source of this ozone. The O$_3$ density rises from $0.5 \times 10^{15}$ to $3.0 \times 10^{15}$ cm$^{-3}$ on a distance of 13 mm (starting at 6 mm from the jet nozzle). The fluid model predicts an average gas velocity on the axis of about 25 m/s resulting in a transport time of t=0.013/25 s = 0.52 ms. The averaged ozone production rate in the effluent can therefore be estimated as:

$$\frac{\partial n_{O_3}}{\partial t} = 2.5 \times 10^{15} \text{cm}^{-3}/5.2 \times 10^{-4} \text{s} = 4.8 \times 10^{18} \text{cm}^{-3}\text{s}^{-1} \sim 2 \cdot \Gamma \cdot \sigma_{ph} \cdot n_{source}.$$  

The right hand side of this equation is the estimated production rate of ozone due to photodissociation of some source molecule (e.g. O$_2$ or O$_3$) with a density $n_{source}$. The $\sigma_{ph}$ is the photodissociation cross section, $\Gamma$ is the photon flux from the plasma per unit area and second, and the factor 2 takes into account that two O$_3$ molecules can be produced in each reaction. The possible reactions could be the direct dissociation of O$_2$ into 2 O atoms, which than quickly react with O$_2$ from the air into O$_3$ or the photodissociation of O$_3$ into O and highly vibrationally excited O$_2(v)$, which can again react with O$_2$ producing O$_3$ and O in this case. The two O atoms will, as in the previous case, react to O$_3$ providing again a net production of two new O$_3$ molecules.

The typical maximum of the photodissociation cross sections of O$_2$ or O$_3$ molecules ($\sigma_{ph} \sim 10^{-17}$ cm$^2$) [87, 88] can be used to estimate the lowest necessary photon flux in the ideal case, in which each photon is absorbed with maximum probability. With $n_{O_2} \sim 10^{24}$ m$^{-3}$ and $n_{O_3} \sim 2 \times 10^{21}$ m$^{-3}$, photon fluxes of at least $\Gamma_{O_2} \sim 2.5 \times 10^{21} \text{m}^{-2}\text{s}^{-1}$ and $\Gamma_{O_3} \sim 1.2 \times 10^{24} \text{m}^{-2}\text{s}^{-1}$ are necessary for the ozone production via
5.3 Production of reactive oxygen species

Figure 5.24: Sketch of the X-Jet measurement

photodissociation of O\(_2\) or O\(_3\), respectively. With the 1 mm\(^2\) cross-section area of the jet and a chosen photon energy of 5 eV, a necessary energy flux of at least 2 mW in the case of dissociation of O\(_2\) and 1 W in the case of photodissociation of O\(_3\) is obtained. The latter reaction can be directly excluded, because the power absorbed by the plasma is for sure lower than 1 W and the plasma cannot generate so many photons. Even in the case of photodissociation of O\(_2\), the power of the photon flux seems too high, considering the crude simplifications in the estimation of the photon flux. However, it could still contribute to the production of O and ozone in the effluent.

Luckily, the photodissociation reaction of O\(_2\) by plasma generated photons can directly be tested by the X-Jet modification of the \(\mu\)-APPJ (cf. chapter 3.2). For this experiment, the additional He flow with different concentrations of O\(_2\) is directed through the side channel of the X-Jet, whereas the plasma is ignited in the standard mixture of He with 0.6% of O\(_2\) in the direct channel between the electrodes. The additional flow diverts the plasma effluent from the direct channel into the side channel after the crossing of both channels and fills at the same time the part of the direct channel after the crossing with a He/O\(_2\) gas mixture as shown in figure 5.24. The plasma generated photons, which are propagating through the direct channel of the X-Jet, overlap spatially with the He/O\(_2\) gas. The possible flow of O and O\(_3\) from the direct channel, generated now by photodissociation reactions, can be measured by the MBMS system. O\(_2\) concentrations of up to 20% and different distances between the nozzle of the direct channel and the sampling orifice of the MBMS were tested to allow the photons traveling different lengths through the He/O\(_2\) mixture and also to allow air to diffuse into the gas flow.

Ozone has never been detected in these measurements. These X-Jet experiments revealed that molecular oxygen is not dissociated by radiation.

Additionally, the normal \(\mu\)-APPJ operated in pure He gas, without the addition of O\(_2\) gas, has been operated in an ambient air atmosphere and the production of ozone in
the effluent at different distances from the jet has been measured. Even more VUV radiation is expected to be produced in this case due to slower quenching of excited states and higher densities of helium excimers. The ozone density was also in this case below the detection limit of the MS. This is in agreement with the important finding that photodissociation of O$_2$ does not play a role in the effluent of the $\mu$-APPJ.

All these measurements are evidence that photodissociation of ground state O$_2$ molecules can very probably be excluded as the source of additional O and O$_3$ in the effluent. It seems, that photodissociation reactions are not the source of additional O atoms and ozone molecules under our experimental conditions and some other oxygen containing species generated in the plasma have to be involved in this process. These observations are inconsistent with the results of S. Reuter et al. [85]. However, no quantification of the necessary photon flux has been done by them. Absolute measurements of the photon flux could probably support or disprove their assumption that photodissociation of O$_2$ is a source of the additional O signal.

Summarizing, the following conditions have to be fulfilled in the involved reaction mechanism: (i) the VUV radiation can probably be excluded as a source of additional O and O$_3$; (ii) molecular ground state oxygen from air is required because the additional ozone signal only appears when air diffuses into the effluent; (iii) atomic oxygen is produced in this reaction because the O densities are at larger distances from the jet higher as predicted by Model 1 (cf. figure 5.22); (iv) some reactive oxygen species from the plasma have to be involved in the reaction because the interaction of the effluent of pure He plasma with ambient air does not lead to formation of O and O$_3$; and (v) the reaction has to be somehow limited by the O$_2$ density because the effect is weak with 0.6% of O$_2$ in the mixture (the measurements with He as ambient atmosphere) but becomes significant at higher O$_2$ densities when air admixes into the effluent.

The reaction of highly vibrationally excited O$_2(v)$ molecules, which are generated in the plasma and have a limited life time, with ground state O$_2$ is proposed here as a possible reaction mechanism. The vibrationally excited oxygen molecules can directly react with ground state oxygen molecules (reaction R$_9$, cf. table 4.2) producing an oxygen atom and an ozone molecule. Two O$_3$ are therefore effectively formed per reaction. The reactions of highly excited O$_2(v>26)$ molecules have been for example discussed in the literature and were proposed to solve the ozone deficit problem in the atmosphere [89, 90]. Additionally, the O$_2(v)$ decay to its ground state (reaction R$_{10}$) is proposed to explain the small amount of additional O$_3$ observed in the experiments in ambient He. This reaction scheme has been included to the simulation (Model 2, cf. chapter 4). Since some of the needed parameters are unknown, they have been adjusted until Model 2 fits reasonably well the measured densities. The fitting parameters are reaction rate of reaction R$_9$ and the lifetime and the initial density of the
vibrationally excited oxygen molecules. The used values of the fitting parameters are shown in the tables 4.2 and 4.3. The results of the Model 2 are shown in figure 5.25 for the case of ambient helium and in figure 5.26 for the case of ambient air. Model 2 is in very good agreement with the measurements for both cases, ambient helium and ambient air.

![Graph showing atomic oxygen and ozone density as a function of distance from the jet in ambient helium. The lines reflect the results obtained by Model 2.](image)

**Figure 5.25:** Atomic oxygen and ozone density as a function of the distance from the jet in ambient helium. The lines reflect the results obtained by Model 2 (applied electrode voltage: 230 V\textsubscript{RMS}, gas flow: 1.4 slm He with 0.6 % O\textsubscript{2}).

![Graph showing atomic oxygen and ozone density as a function of distance from the jet in ambient air.](image)

**Figure 5.26:** Atomic oxygen and ozone density as a function of the distance from the jet in ambient air. The lines reflect the results obtained by Model 2 (applied electrode voltage: 230 V\textsubscript{RMS}, gas flow: 1.4 slm He with 0.6 % O\textsubscript{2}).
This result corroborates that a reasonable reaction mechanism without involvement of photons can explain under our experimental conditions the observed results. It should be stressed here, that it is just a hypothesis. A validation by possible measurements of $O_2(v)$ and by comparison of fitted rates and relaxation times with measured rates and relaxation times, if they exist, should be performed before accepting this reaction mechanism. Additionally, it should be checked whether this proposed reaction mechanism can explain the observations, which have lead to the conclusion that VUV and UV photons are involved in the effluent chemistry.

### 5.3.3 Measurement of ions

Charged species are, besides of neutral ROS, another important component of a plasma. The densities of positive and negative charged species in a cold atmospheric He/$O_2$ plasma has been simulated in a global model by Liu et al. [91]. $O_2^+$ and $O_4^+$ ions dominate the positive ion spectrum for oxygen admixtures between 0.1 and 1 %, their density is around $10^{11}$ cm$^{-3}$. The main negative ions are $O_3^-$, $O^-$, and $O_2^-$ with densities of about $10^{10}$ - $10^{11}$ cm$^{-3}$.

The spatial distribution of charged species in the effluent of the $\mu$-APPJ has been simulated in a two-dimensional numerical model by T. Hemke et al. [92]. Positive oxygen ions $O^+$ are only present in the discharge core and not in the effluent. The $O^-$ and $O_2^-$ densities decay exponentially with increasing distance from the nozzle and vanish beyond a distance of 4 mm. The densities of $O_2^+$ and $O_3^-$ ions extend further in the effluent, but their densities drop by a factor of about 30 within the first 4 mm to about $10^9$ cm$^{-3}$.

To prove or disprove these simulations, mass spectra of positive ions have been recorded while varying the oxygen admixture into the helium plasma, the distance between the nozzle of the $\mu$-APPJ and the sampling orifice, the applied electrode voltage, and helium flow. Two mass spectra of positive ions are shown for two different distances in figure 5.27.

It is remarkable that almost only water cluster ions could be detected during these measurements. Only a weak signal of $O_2^+$ at the mass 32 amu can be found when the distance between $\mu$-APPJ nozzle and sampling orifice is below 1 mm. In contrast to the models of Liu et al. and Hemke et al., no other ions like $O_2^+$ and $O_4^+$ could be found. Furthermore, no negative ions could be detected in the effluent of the $\mu$-APPJ.

Water cluster ions have the chemical formula $H^+(H_2O)_n$, $n>1$. These ions are growing step-by-step around an ion core by association of water molecules [93]:

$$H^+(H_2O)_{n-1} + H_2O \rightarrow H^+(H_2O)_n.$$
5.3 Production of reactive oxygen species

Two different possible ion cores are known, the Eigen core $\text{H}_2\text{O}^+$ and the Zundel core $(\text{H}_2\text{O})_n^+$ [94]. The geometrical structure of different water cluster ions can be found in figure 5.28. Water cluster ions can be generated by electron or photon impact ionization of water vapor [95].

The behavior of the water cluster ions with $n=4, 5, \text{ and } 6$ during an O$_2$ admixture variation is shown in figure 5.29. The distance between the nozzle of the $\mu$-APPJ and the sampling orifice is 3 mm. These water cluster ions do not show an uniform behavior. The $\text{H}^+(\text{H}_2\text{O})_4$ ion density decreases with increasing oxygen admixture while the $\text{H}^+(\text{H}_2\text{O})_5$ ion density slightly increases. On the $\text{H}^+(\text{H}_2\text{O})_5$ ion, the O$_2$ content even seems to have no influence.

The applied electrode voltage seems to have almost no influence on the densities of the water cluster ions. The signals stay constant within the noise of signal (not shown here).

A variation of the distance between the nozzle of the $\mu$-APPJ and the sampling orifice revealed that the densities of the water cluster ions decrease very steeply within the first 3 mm. Beyond this point, the density of the three ions stays constant. Even in a distance of 1 cm, ions can be detected. However, the expected life time of an ion in air is low due to the high collision frequency. The simulations of T. Hemke et al. showed a very steep decrease of the ion densities [92]. The measurements point out that the water cluster ions are not (only) produced in the plasma but also in the effluent. Ions could be produced via photoionization by (V)UV radiation originating from the plasma.
5 Results

Figure 5.28: Calculated geometries of water cluster ions (taken from Headrick et al. [94])

Figure 5.29: Measurement of positive ions during a variation of the O₂ admixture (1.4 slm He flow, 3 mm distance, 230 \( V_{RMS} \) electrode voltage)
5.3 Production of reactive oxygen species

The photoionization threshold of a water molecule is around 12.6 eV [43], thus radiation with 100 nm or shorter is needed. Assuming that the radiation with \( \lambda < 100 \text{ nm} \) is only adsorbed by oxygen molecules, the range of the radiation can be estimated. The photoionization cross section \( \sigma \) of O\(_2\) by photons with at least 12.6 eV is around \( 1 \times 10^{-17} \text{ cm}^2 - 2 \times 10^{-17} \text{ cm}^2 \) [96]. With an oxygen density of \( n_{O_2} = 1.49 \times 10^{23} \text{ m}^{-3} \), one can calculate the distance \( d_{1/e} \) on which the radiation intensity drops by 1/e:

\[
d_{1/e} = (n \cdot \sigma)^{-1}.
\]

Depending on the exact cross section, an effective range \( d_{1/e} \) between 3 and 6 mm can be estimated. Consequently, the radiation could reach far enough into the effluent to ionize water molecules. Unfortunately, no radiation intensity with \( \lambda < 115 \text{ nm} \) generated by the \( \mu\)-APPJ could be measured by S. Schneider et al. due to the cutting wavelength of the used MgF\(_2\) window [86].

Furthermore, one may assume by inspecting figure 5.30 that the positive ion signal is composed of two different ion signals. The steeply decaying ion density within the first 3 mm is probably generated in the plasma and are transported by the gas flow with a velocity of about 25 m/s outwards. An ion lifetime of ca. 30 \( \mu s \) can be estimated by fitting an exponential curve to the first 3 mm. The constant ion signal beyond 3 mm is then generated in the effluent by photoionization.

The hypothesis of photoionization has been tested by measurements with the X-Jet, which has been described in chapter 3.2. The X-Jet has been operated in two different modes while the direct channel has been analyzed by the MBMS. On the one hand, there was only a gas flow of 1.4 slm He through the direct plasma channel and no gas flow through the side channel. At this condition, ions are detected that are produced in the discharge and in the effluent by (V)UV radiation. On the other hand, an additional side flow of 2 slm He was switched on (like illustrated in figure 3.3). Now, the

![Figure 5.30: Variation of the distance between \( \mu\)-APPJ and sampling orifice (gas flow: 1.4 slm He + 0.6 % O\(_2\), 230 V\(_{\text{RMS}}\) electrode voltage)](image-url)
Figure 5.31: Measurement of the direct channel of the X-Jet with gas flow through the side channel. Only ions generated in the effluent by photons are detected in this way (gas flow through direct plasma channel: 1.4 slm He, gas flow through side channel 2 slm He with and without O$_2$, 200 V$_{RMS}$ electrode voltage, 4 mm distance).

plasma effluent is diverted into the side channel and only the radiation travels further along the direct channel. Only ions generated by radiation are detected under these circumstances. The plasma was operated with a voltage of 200 V$_{RMS}$ in both cases. The distance between the nozzle of the X-Jet and the sampling orifice was 4 mm. However, the plasma in the X-Jet ends about 7 mm upstream from the nozzle. The distance between plasma and sampling orifice is consequently ca. 11 mm and not 4 mm like in the case with the $\mu$-APPJ.

Under both conditions, the signal of the water cluster ion with n=4 is very similar in intensity. The signal of the ion with n=5 decreases by a factor of about three when the side channel is turned on. These results let one conclude that the water cluster ions are produced in the discharge volume as well as in the effluent by photoionization. The majority even seems to be generated in the effluent and not in the plasma.

In a next step, different oxygen flows were admixed to the side channel of the X-Jet. The X-Jet has been operated with a gas flow through the direct channel (1.4 slm He) and through the side channel (2 slm He with and without O$_2$). The influence of the oxygen amount on the ion signals can be tested in this way. Like in the previous
5.3 Production of reactive oxygen species

measurements, the side flow is turned on to divert the plasma effluent into the side channel. Then, only reaction products of radiation with the He/O\textsubscript{2} mixture are measured. Figure 5.31 shows mass spectra of the positive ion measurements with different O\textsubscript{2} admixtures to the side flow.

It can be seen that addition of oxygen to the side flow leads, in general, to an increase of the ion signals (apart from the pos. ions 108-110 amu). The ion signal is again lower with an O\textsubscript{2} admixture of 4.2 %. This could be due to a decrease over time of the water concentration in the system (see below). It should be noted again that these measured ions are generated in the effluent by photoionization and do not originate from the plasma.

These ion measurements with the X-Jet are done, in contrast to previous measurements, with a biased skimmer. The skimmer connecting the second and third pumping stage is biased to -200 V. This leads to an increase of the ion signals by a factor of ca. 100 in comparison with a grounded skimmer and explains the appearance of other positive ions in addition to the water cluster ions with the masses 73, 91, and 109 amu. The other ions are probably water cluster ions with more or less hydrogen atoms.

The helium flow through the normal \textit{µ}-APPJ has been varied between 1 and 6 slm within a further study. As shown in figure 5.32, the signal of the water cluster ion increases almost linearly with the helium flow. This observation can easily be explained. With increasing gas flow, the water cluster ions are transported faster and further into the effluent. The gas velocity increases up to 150 m/s by increasing the gas flow by a factor of six. With the estimated ion lifetime of 30 \(\mu\)s, the water cluster ions reach now 4.5 mm into the effluent. The measurements shown in figure 5.32 are performed in a distance of 3 mm, so ions generated in the discharge core are detected, too.
The experiments revealed that the water cluster ion signal decreases exponentially with time. Figure 5.33 shows the signal of two water cluster ions as a function of time. After 50 minutes, their signals has dropped by two orders of magnitude. This indicates that the origin of the necessary water for the water cluster ions is the helium feed gas and not the humidity from the ambient gas. Probably, water molecules that are adsorbed at the inner surfaces of the helium gas line are carried with the helium flow.

Other ions than the water cluster ions with n=4, 5, or 6 could sometimes be detected when the distance between $\mu$-APPJ nozzle and the sampling orifice is smaller than 1 mm. At small distances, the microplasma can be disturbed by the metal surface of the orifice and an additional plasma appears between the powered electrode and the metal orifice. Then, also low signals of $O_2^+$ and water cluster ions with n=1, 2, 3, and 7 are detected. These ions disappear as soon as the distance is increased and the additional plasma vanishes.

A global model of a low-temperature He/H$_2$O plasma has been implemented by Liu et al. [97]. Water impurities between 1 ppm and 0.3 % in helium have been simulated. For small concentrations of water, He$^+$, He$_2^+$, OH$^+$, and H$_2$O$^+$ are the main positive ions with a density of ca. $10^{10}$ - $10^{11}$ cm$^{-3}$. This changes when the water concentration increases. Then, OH$^+$, H$_2$O$^+$, and water cluster ions with n=4, 5, and 6 dominate the ion spectrum. Their densities are also in the range of $10^{10}$ - $10^{11}$ cm$^{-3}$. 

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**Figure 5.33**: Signal of two water cluster ions as a function of time. Measurement of the direct channel of the X-Jet with gas flow through the side channel (gas flow through direct plasma channel: 1.4 slm He, gas flow through side channel 2 slm He with 0.8 % O$_2$, 200 V$_{RMS}$ electrode voltage, 4 mm distance)
A direct comparison between the simulated densities of Liu et al. [91, 97] with the MBMS measurements is difficult due to different conditions. Positive ions have been simulated in a He/O₂ and a He/H₂O plasma, whereas the measurements were performed at a He/O₂ plasma with impurities of water. A combined model of an He/O₂/H₂O plasma would be necessary for a proper comparison. The measurements shown here indicate that an important ion production mechanism is photoionization. This mechanism is not included in the model. Additionally, the ion measurements are performed in the effluent of the plasma jet, whereas the model simulates the densities in the discharge core. Furthermore, the amount of water impurities in the μ-APPJ is unknown. The water concentration is assumed to be somewhere between the amount of the water impurity of the helium bottle (∼3 ppm) and the ambient humidity (<1.5%), but the exact concentration needs to be determined.

In summary, it was shown that impurities of water have a huge influence on the ion spectrum. Negative ions could never be detected. The reason is still not clear. On the one hand, it is possible that no negative ions exist in the effluent. On the other hand, the MBMS system has been designed for measurements of neutral species and is perhaps not perfectly suited for ion measurements. The MBMS system can be improved to lower the sensitivity limit for ion measurements by installing a suited ion optic.
5.4 Analysis of hexamethyldisiloxane containing microplasmas

HMDSO and HMDSO/O\textsubscript{2} plasmas at atmospheric pressure are commonly used by many researchers and in industry for the deposition of SiO\textsubscript{2}-like films. However, the exact deposition mechanism and the plasma chemistry is only barely understood. The He $\mu$-APPJ used for generation of ROS is also used here as a model system for the HMDSO and HMDSO/O\textsubscript{2} chemistry. The same He/O\textsubscript{2}/HMDSO jet is also applied to deposit thin silicon oxide films at atmospheric pressure [98, 99]. But, almost no knowledge about the reaction chemistry is gained by the analysis of the deposited films. A combination of these measurements with an analysis of the plasma chemistry can help to gain an insight into the deposition mechanism of SiO\textsubscript{2}-like films at atmospheric pressure.

In this study, the gas phase of the He $\mu$-APPJ with admixtures of O\textsubscript{2} and HMDSO has been analyzed by the MBMS system. For reasons described in chapter 3.1, a shorter version of the $\mu$-APPJ is applied for the analysis.

First, measurements of positive ions in the effluent of the $\mu$-APPJ are shown and then the results of neutral species are presented. If not stated otherwise, the $\mu$-APPJ was operated with an applied electrode voltage of 230 V\textsubscript{RMS} and a gas flow of 5 slm He without admixture of molecular oxygen. A distance of 4 mm between $\mu$-APPJ and sampling orifice was set.

5.4.1 Measurement of positive ions

Ions play an important role during the deposition of thin films by means of low pressure plasmas. The film quality improves due to ion bombardment. At atmospheric pressure, this is not expected because of the high collision rate in the plasma sheath. However, ions may also have an influence on the film growth at atmospheric pressure.

Previous studies of V. Raballand et al. showed that good film qualities can be obtained by means of HMDSO containing plasmas even without addition of O\textsubscript{2} [23]. This surprising behavior has not been observed by other authors. An ion driven polymerization has been proposed as a possible deposition mechanism for the used coaxial microplasma jet operated in argon. Later measurements of surface reactions have shown that carbon free films are probably obtained by Ar-metastable or Ar-ion induced surface reaction. However, the possible role of ion driven polymerization has not been excluded. Additionally, ion driven polymerization reactions of HMDSO are observed in experiments with ion traps [100]. Due to the attractive polarization force, these reactions are in general faster than reactions of neutral species. Therefore, it is necessary
5.4 Analysis of hexamethyldisiloxane containing microplasmas

Figure 5.34: Mass spectrum of positive ions in a HMDSO plasma (gas flow 5 slm He with 1.3 ppm HMDSO, 2 mm distance, 230 V\textsubscript{RMS} electrode voltage)

to study the possible role of these reactions in atmospheric pressure plasma. Measurements of plasma generated ions are necessary.

First, mass spectra of positive ions have been recorded. An example is shown in figure 5.34. Again, the main constituents are water cluster ions. Basically, these are the water cluster ions with \(n=4\) and 5, but also a weak signal can be found at \(n=1\) and 3. Besides the water cluster ions, also positive ions with a mass of 163 amu and 181 amu have been detected.\(^2\) These ions are very probably build in the plasma effluent in proton (H\(^+\)) transfer or ligand (H\(_3\)O\(^+\)) switching reactions of HMDSO molecules with H\(^+(H_2O)_n\) clusters \([101]\). This leads to formation of an H\(^+:\)HMDSO or H\(_3\)O\(^+:\)HMDSO ion, respectively. A weak signal could also be found at mass 201 amu. It is still not clear what ions this is.

A study of positive ions during a variation of the HMDSO admixture is shown in figure 5.35. The maximum density of the water cluster ions is reached at a very low HMDSO admixture of about 0.26 ppm. By increasing the HMDSO content in the plasma, the ion signals decrease very steeply again. No ions are detected anymore beyond an admixture of 5 ppm. Signals of other water cluster ions were too low during these measurements.

The signals of the HMDSO ions (H\(^+:\)HMDSO and H\(_3\)O\(^+:\)HMDSO) behave similar to the signals of the water cluster ions. First, the signal increase with the HMDSO admixture. The maximum HMDSO ion signals are reached at a slightly higher HMDSO admixture.

\(^2\)Figure 5.34 shows only a signal at mass 163 amu near the statistic noise. However, further measurements confirmed a positive ion signal at this mass.
admixture (1.3 ppm) in comparison to the water cluster ion signals. Beyond an admixture of 1.3 ppm, the signals of the HMDSO ions decrease again and are (almost) zero at an admixture of 10 ppm or higher.

For a further study of the behavior of positive ions in the effluent of the HMDSO plasma, a distance variation has been performed. An HMDSO content of 1.3 ppm has been chosen because the ion signal is here at its maximum value. The trends of the four different detected water cluster ions (n=3, 4, 5, and 6) are shown in figure 5.36. While the signal of the ions with n=3 and 6 is very low and decreases with the distance, the signal of the ions with n=4 and 5 is much higher and exhibits a maximum. The maximum signal of these water cluster ions is reached at a distance of 5 mm and 3 mm, respectively, and decreases beyond. But still in a distance of 19 mm, positive ions exist in the effluent.

A similar trend can be found for the positive HMDSO ions. Both ions, H⁺:HMDSO and H₃O⁺:HMDSO, exhibit a maximum signal at a distance between 5 mm and 8 mm. The signal decreases slowly beyond this point.

The behavior of the ions in the effluent can again be explained by the fact that the ions are produced by photoionization of water molecules and H⁺ or H₃O⁺ transfer reactions. That is why the ion signals decline relative slowly and positive ions are still remaining in the effluent.
5.4 Analysis of hexamethyldisiloxane containing microplasmas

In summary, no indications could be found that polymerized HMDSO ions originating from the plasma are present in the plasma effluent. Their contribution to the film growth is therefore in a He microplasma negligible. Furthermore, no positive ions are anymore remaining in the effluent at the used standard conditions for film deposition (i.e. 20 ppm HMDSO content and 4 mm distance). Consequently, positive ions do not play a role for the deposition of silicon dioxide films at atmospheric pressure.

5.4.2 Measurement of neutral species

As a first step for understanding the film deposition process, one needs to identify the reaction products produced in the HMDSO microplasma to find possible growth precursors for SiO$_x$ films. Thereby, it is essential to remember that besides ionization also dissociative ionization of molecules takes place in the ionizer of the MS (cf. chapter 2.2). This is especially important for large molecules.

It should be emphasized that the analysis of the HMDSO microplasma is a very challenging task. This can be easily understood by a comparison between the already discussed He/O$_2$ and the He/HMDSO microplasma.

An amount up to 1% O$_2$ was used for the He/O$_2$ microplasma. Maximum atomic oxygen densities around $10^{15}$ cm$^{-3}$ (= 40 ppm) could be detected in the effluent.

The standard HMDSO admixture for deposition of thin SiO$_2$-like films is 20 ppm. This means that the precursor admixture is in the order of magnitude of the radical density in the He/O$_2$ plasma. The reaction products generated in the He/HMDSO plasma

![Figure 5.36: Positive ions as a function of the distance from the nozzle (gas flow 5 slm He with 1.3 ppm HMDSO admixture without O$_2$, 230 V$_{RMS}$ electrode voltage)
are then most likely much lower than these densities, probably around or below the sensitivity limit of the MBMS system. The sensitivity limit has been estimated to be around 0.65 ppm (cf. chapter 5.1.2). This illustrates the expected challenges during the analysis of the He/HMDSO microplasma jet.

A mass spectrum of HMDSO measured with an electron energy of 70 eV in the ionizer is shown in figure 5.37. Positive HMDSO ions generated in the ionizer will dissociate immediately because they are unstable (cf. chapter 2.2). Thus, (almost) no signal can be found at the mass of HMDSO (162 amu), but therefore many different fragment ions are appearing. The highest signal appears at a mass of 147 amu. This fragment ion is generated during the dissociation of an HMDSO molecule by release of a methyl group CH$_3$.

This measured mass spectrum of HMDSO is in good agreement with the reference mass spectrum from the literature shown in figure 2.7 of chapter 2.2. The dominant peaks are found in both cases at 45 amu, 52 amu, 59 amu, 66 amu, 73 amu, and 147 amu. The ratios between the different peaks differ a little bit, probably because the measured mass spectrum has not been corrected for the mass dependent transmission function of the MS.

For an unambiguous identification, reaction products of the plasma have to be distinguished from products generated in the ionizer by dissociative ionization of HMDSO molecules. This can be done by lowering the electron energy in the ionizer below the threshold of dissociative ionization (TIMS, cf. chapter 2.2.1). This threshold is about 15 eV [102]. However, no reaction products can be detected anymore when the electron energy is so low because their expected densities are near the detection limit of the MBMS system.
5.4 Analysis of hexamethyldisiloxane containing microplasmas

Figure 5.38: Partial electron impact ionization cross section for dissociative ionization of HMDSO and TMS producing Si(CH$_3$)$_3^+$ (73 amu). Data taken from [102, 103].

A solution can be demonstrated by an example of tetramethylsilane (TMS). TMS has a mass of 88 amu, but during ionization in the ionizer it releases a methyl group. The generated Si(CH$_3$)$_3^+$ ion is the largest among the fragment ions and has a mass of 75 amu. If one wants to measure TMS as reaction product of an HMDSO plasma, one needs to consider that the signal of TMS at mass 75 amu overlaps with fragment ions of HMDSO at mass 75 amu (cf. figure 5.37). Fortunately, the partial electron impact ionization cross sections of HMDSO and TMS producing Si(CH$_3$)$_3^+$ differ. Figure 5.38 shows both partial electron impact ionization cross sections. The partial cross section of TMS increases steeply within the first 10 eV above the threshold and stays almost constant beyond an electron energy of 20 eV. In contrast, the partial cross section of HMDSO increases gently above the threshold.

In general, one can state that the partial cross section producing the largest fragment ion increases more steeply than the partial cross section producing smaller fragment ions. Therefore, an electron energy of 20 eV has been chosen within this study because the partial cross sections of the largest fragment ions have almost reached their maximum, whereas dissociative ionization of HMDSO is minimized.

Analysis of the HMDSO and oxygen consumption

As a first step, the consumption of HMDSO in the plasma has been determined by the MBMS. The dominant fragment ion of HMDSO at a mass 147 amu has been measured with an electron energy of 20 eV during the plasma was turned on and off. The difference between both signals determines the HMDSO depletion.

The relative HMDSO depletion as a function of the HMDSO admixture is shown in figure 5.39. The HMDSO depletion decreases by admixing more HMDSO into the
Figure 5.39: Relative HMDSO depletion as a function of the HMDSO admixture (5 slm He, 4 mm distance, 230 $V_{RMS}$ electrode voltage, 20 eV electron energy).

Microplasma jet. For admixtures higher than 20 ppm, the HMDSO depletion seems to stay constant at ca. 2%. The HMDSO consumption increases up to ca. 8% by lowering the HMDSO admixture. However, the error bars are huge due to the low difference between the plasma on and plasma off signals. Overall, the HMDSO consumption in the microplasma is very low, most of the HMDSO is not affected by the plasma. This lets conclude that the microplasma is a very weak one.

Oxygen admixtures to the He/HMDSO plasma lead to an improvement of the deposited film [99]. Therefore, the influence of $O_2$ on the plasma chemistry is studied here, too.

Figure 5.40 shows the HMDSO depletion as a function of the $O_2$ admixture. The HMDSO depletion seems to be constant for low oxygen admixtures. For an $O_2$ addition between 0 and 0.02%, a consumption of about 4% can be obtained. When the $O_2$ content is further increased to 0.4%, the HMDSO consumption rises up to ca. 12%.

The film deposition rate exhibits a very similar behavior during an $O_2$ variation. R. Reuter et al. measured the thickness of films deposited during equal times at various $O_2$ admixtures [99]. It has been revealed that the deposition rate stays constant for oxygen admixtures below 1 sccm (= 0.02%) and increases for higher admixtures by a factor larger than two (cf. figure 5.41). The very good agreement between HMDSO depletion and deposition rate indicates a very close connection between both.
5.4 Analysis of hexamethyldisiloxane containing microplasmas

**Figure 5.40:** HMDSO depletion as a function of the $O_2$ admixture (gas flow 5 slm He with 20 ppm HMDSO, 4 mm distance, $230V_{RMS}$ electrode voltage)

**Figure 5.41:** Carbon content in the deposited film and film thickness under variation of the oxygen flow. Taken from [99]. (gas flow 5 slm He with 20 ppm HMDSO)
5 Results

Figure 5.42: Comparison between signals during plasma off and plasma on phase. The signals of 207 and 221 amu have been multiplied by a factor of 5.

The depletion of molecular oxygen has also been determined during the variation of O₂ admixture. However, no distinct trend could be observed due to statistic fluctuations and large error bars. The O₂ consumption seems to be very low, it was never higher than 4%. This observation confirms that the used microplasma is only very weak.

Analysis of reaction products

By taking a look at the mass spectrum shown in figure 5.37, one can see that many different fragment ions appear in the HMDSO mass spectrum even without igniting a plasma. When a plasma is ignited, reaction products will be produced that may overlap with the dissociation products. Therefore, an electron energy of 20 eV has been used for reasons described above. The signals from fragment ions from HMDSO are not negligible in this case. Therefore, reaction products of the HMDSO plasma have been determined by comparing the signals while the plasma is switched off and on. A reaction product generated in the plasma is found when the signal increases by switching the plasma on.

Several masses have been tested with this method, namely 2, 14, 15, 16, 28, 30, 43, 45, 47, 59, 73, 75, 84, 119, 131, 132, 133, 134, 147, 148, 149, 150, 151, 163, 164, 207, and 221 amu. Most of the signals at these masses do not show a significant change, a change can only be found at the masses 75, 131, 133, 147, 207, and 221 amu. The comparison between the signals during plasma off and plasma on phase is shown in figure 5.42.

Again, an HMDSO consumption of ca. 6% can be determined from the decrease of the 147 amu signal.
Furthermore, the measurements show that reaction products with a mass of 75, 131, 133, 207, and 221 amu are generated in the HMDSO plasma. The corresponding error bars are relatively large because the signals are near the detection limit of the MBMS system. However, these measurements are reproducible, supporting the assumption that these products are generated in the plasma.

Reaction products with the masses of 75, 131, 133, 207, and 221 amu could be identified by means of MBMS measurements. But, the exact molecules corresponding to the masses cannot be determined by MS. It is assumed that these molecules release also a methyl group during ionization in the ionizer. Therefore, molecules with the masses 90, 146, 148, 222, and 236 amu are suggested as reaction products. The NIST Chemistry WebBook database [43] has been used to identify possible molecules at these masses. However, many different molecules can be found at the same mass. Example molecules with a mass of 148 amu are shown in figure 5.43. It is not possible to determine the exact structure by means of MBMS measurements.

We assume that the reaction products are the simplest products that can be formed from HMDSO in minimum number of reaction steps. Thus, the five identified reaction products are probably trimethylsilanol (mass 90 amu, measured at 75 amu), hexamethyldisilane (mass 146 amu, measured at 131 amu), pentamethyldisiloxane (mass 148 amu, measured at 133 amu), heptamethyltrisiloxane (mass 222 amu, measured at 207 amu), and octamethyltrisiloxane (mass 236 amu, measured at 221 amu). The molecule structure is illustrated in figure 5.44. Like in the case of the ionization of HMDSO, these reaction products will also dissociate after the electron impact ionization and will release a methyl group. Therefore, the MS measures a signal at a mass reduced by 15 amu (example of trimethylsilanol: molecular mass = 90 amu, release of one methyl group: 90 amu - 15 amu = 75 amu, MS measures signal at a mass of 75 amu).

Still, it cannot be excluded that several different molecules with equal masses contribute to the signal at 75, 131, 133, 207, and 221 amu. Furthermore, isomers with different molecular configurations do probably exist.
Figure 5.44: Possible chemical structures of the identified reaction products in comparison with HMDSO.
5.4 Analysis of hexamethyldisiloxane containing microplasmas

As already mentioned, various measurements showed that the film quality and the deposition rate improve by admixing oxygen into the He/HMDSO microplasma [98]. Therefore, it is well worth to study the behavior of the reaction products under oxygen admixture to get an insight into the microplasma chemistry. The influence of admixed O\textsubscript{2} on the HMDSO consumption and on the five reaction products is shown in figures 5.45 and 5.46. With an admixture of 0.2 % O\textsubscript{2}, the HMDSO depletion is about twice as high (ca. 15 %) as without oxygen. This is consistent with deposition measurements, which revealed that the deposition rate approximately doubles when oxygen is admixed [99]. The production of trimethylsilanol (75 amu), pentamethyldisiloxane (133 amu), heptamethyltrisiloxane (207 amu), and octamethyltrisiloxane (221 amu) increases significantly, too. But, no hexamethyldisilane (131 amu) seems to be produced anymore. The behavior of these products can be understood by inspecting the reactions taking place in the plasma.

The proposed reaction scheme, which could explain the measurements, is similar to the scheme proposed by Sonnenfeld et al. [41] (cf. chapter 2.1.1.2) and is illustrated in figure 5.47. Different bond breakings of HMDSO molecules are possible in the plasma. In the case of a bond breaking between the Si and O molecule caused by electron impact, an SiOC\textsubscript{3}H\textsubscript{9} and an SiC\textsubscript{3}H\textsubscript{9} radical is produced. The former radical, SiOC\textsubscript{3}H\textsubscript{9}, can react with a hydrogen atom and form a trimethylsilanol molecule. Two of the latter radicals, SiC\textsubscript{3}H\textsubscript{9}, can combine and result in a hexamethyldisilane molecule. The situation changes when molecular oxygen is included in the reaction scheme. On the one hand, an oxygen atom can probably break the Si-O bond and react directly with
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Figure 5.46: Influence of admixed oxygen on the 147, 207, and 221 amu signals (gas flow 5 slm He with 20 ppm HMDSO with and without 0.2 % O₂, 4 mm distance, 230 V_RMS electrode voltage)

the silicon atom. Two SiOC₃H₉ radicals are formed in this case. On the other hand, the SiC₃H₉ radicals can react with oxygen atoms leading also to SiOC₃H₉ radicals. In both cases, no hexamethyldisilane is produced anymore when O₂ is admixed because the needed SiC₃H₉ radical is missing. Consequently, more amount of trimethylsilanol is produced.

Another bond breaking is possible between the Si atom and the methyl group. This results in an Si₂OC₅H₁₅ and a methyl radical. The Si₂OC₅H₁₅ radical can saturate with a hydrogen radical and become finally a pentamethyldisiloxane molecule. When oxygen is admixed into the plasma, the produced atomic oxygen can probably react directly with the methyl group and form formaldehyde (CH₂O) leaving a pentamethyldisiloxane molecule, too.

Heptamethyltrisiloxane and octamethyltrisiloxane are possibly build via a reaction of an SiOC₃H₉ radical with pentamethyldisiloxane and HMDSO, respectively.

However, it is not yet fully understood if the admixed oxygen has a direct influence on the reactions, like described above, by reacting with the Si or C of the HMDSO molecule, or if the admixed oxygen changes the electron density and electron energy distribution function in a way that the plasma is more effective.

It has been shown that admixed nitrogen has a similar influence on the reaction chemistry like oxygen. The influence of N₂ admixture on the reaction products is shown in figure 5.48. As in the case of admixed oxygen, the HMDSO depletion significantly increases to ca. 14 % when N₂ is admixed. The hexamethyldisilane and pentamethyl-
5.4 Analysis of hexamethyldisiloxane containing microplasmas

\[
\begin{align*}
\text{(I)} & \quad \text{Hexamethyldisilane} \\
\text{H}_3\text{Si-SiO-Si-CH}_3 & \quad \text{H}_3\text{Si-SiO-Si-CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{Si-SiO-Si-CH}_3 + \cdot \text{O}^+ & \quad \text{Trimethylsilanol} \\
\text{H}_3\text{Si-SiO-Si-CH}_3 + \cdot \text{O}^+ & \quad \text{H}_3\text{Si-SiO-Si-CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{(II)} & \quad \text{Pentamethyldisiloxane} \\
\text{H}_3\text{Si-SiO-Si-CH}_3 & \quad \text{H}_3\text{Si-SiO-Si-CH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{Si-SiO-Si-CH}_3 + \cdot \text{O}^+ & \quad \text{Pentamethyldisiloxane} \\
\text{H}_3\text{Si-SiO-Si-CH}_3 + \cdot \text{O}^+ & \quad \text{H}_3\text{Si-SiO-Si-CH}_3 \\
\end{align*}
\]

**Figure 5.47:** Proposed reaction scheme
Figure 5.48: Influence of admixed N$_2$ on the reaction products (gas flow 5 slm He with 20 ppm HMDSO with and without 0.14 % N$_2$, 4 mm distance, 230 V$_{RMS}$ electrode voltage)

Disiloxane signals increase as well, but the trimethylsilanol signals stays constant under addition of N$_2$. However, further informations are missing to find a conclusive explanation for the observed behavior. It is possible that the trimethylsilanol density stays constant because atomic oxygen is missing to react with SiC$_3$H$_9$ radicals. Therefore, enough of the SiC$_3$H$_9$ radicals are left to form hexamethyldisilane. Assuming the admixed nitrogen changes the electron density and the electron energy distribution function, the increase of HMDSO depletion and of the pentamethyldisiloxane density can be due to a more effective plasma.

The differential signals (plasma off and on) of trimethylsilanol and pentamethyldisiloxane have also been recorded as a function of the amount of admixed oxygen, as shown in figures 5.49 and 5.50. Even if the error bars are large, one can recognize a distinct trend. Both of the signals increase almost linearly with the oxygen content.

A calibration for absolute densities has also been performed for these two reaction products. Helium was directed through a bubbler filled with pure liquid trimethylsilanol and pentamethyldisiloxane, respectively. When the vapor pressures of these liquids are known, the absolute concentration of these molecules in helium can be calculated. A vapor pressure of about 50 mbar has been used in the case of trimethylsilanol at 0°C [43]. No vapor pressure could be found in the literature for pentamethyldisiloxane. Since pentamethyldisiloxane and HMDSO have a very similar structure, the vapor pressure of HMDSO (13.3 mbar) has been used instead [43]. By comparing the known concentration in helium with the measured signals, a calibration factor can be found.

A maximum density of trimethylsilanol of about $5 \times 10^{12}$ cm$^{-3}$ can thus be found in the He/O$_2$/HMDSO plasma. The maximum pentamethyldisiloxane density is with
5.4 Analysis of hexamethyldisiloxane containing microplasmas

Figure 5.49: Measurement of trimethylsilanol (75 amu) during a variation of the O$_2$ admixture (gas flow 5 slm He with 20 ppm HMDSO, 4 mm distance, 230 V$_{\text{RMS}}$ electrode voltage)

Figure 5.50: Measurement of pentamethyldisiloxane (133 amu) during a variation of the O$_2$ admixture (gas flow 5 slm He with 20 ppm HMDSO, 4 mm distance, 230 V$_{\text{RMS}}$ electrode voltage)

cia. 2×10$^{12}$ cm$^{-3}$ a little bit lower. This is consistent with the HMDSO depletion shown above. An HMDSO amount of ca. 4.8×10$^{14}$ cm$^{-3}$ (= 20 ppm) is typically admixed to the helium flow. An absolute consumption of ca. 5.8×10$^{13}$ cm$^{-3}$ HMDSO molecules in the plasma can be calculated with the maximum HMDSO depletion of 12%. Consequently, about 9% and 3% of the consumed HMDSO molecules become finally trimethylsilanol and pentamethyldisiloxane.

The large error bars in figures 5.49 and 5.50 can be explained by the fact that the reaction products have a density (<0.2 ppm) near the detection limit of the MBMS system.
5 Results

In summary, 88% of the admixed HMDSO is not affected by the plasma and only 12% are consumed. 12% of the reaction products of the consumed HMDSO molecules could be identified. It can be assumed that these stable reaction products do not contribute to the SiO$_x$ film deposition. R. Reuter et al. estimated that approximately 33% of the consumed HMDSO ends up in the deposited film [99]. Then, the stable reaction products of 55% of the consumed HMDSO molecules are still unknown. These are possibly larger molecules (like heptamethyltrisiloxane and octamethyltrisiloxane). But these molecules are difficult to quantify because of the discriminating transmission function of the mass spectrometer.

The main species in the HMDSO microplasma could be identified by the MBMS, but almost no information about growth precursors and the film deposition process in detail can be obtained only by the MBMS. A comparison with analyses of the stoichiometric composition of deposited films can probably help to gain more knowledge about the deposition process.
6 Conclusion and Outlook

Within the scope of this work, the reaction chemistry of oxygen or hexamethyldisiloxane (HMDSO) containing microplasma jets has been analyzed by means of molecular beam mass spectrometry (MBMS). A special gas sampling system has been developed, tested and improved for this purpose. The used MBMS system yields significantly higher beam-to-background ratios in comparison to common systems. Only a pulsed gas flow with a duty cycle of about 2% is allowed into the gas sampling system by placing a special beam chopper into the first stage. In this way, a very low pressure can be reached in the last stage where the mass spectrometer is mounted. At the same time, the beam signal can be very high because of an enlarged sampling orifice. It has been shown that atmospheric concentrations below 1 ppm can be measured due to the high beam signal.

It turned out that special care has to be taken during the calibration procedure to obtain absolute densities. The composition distortion in the free-jet expansion downstream of the sampling orifice changes significantly the relative composition in the molecular beam by discriminating light species against heavy species. The composition distortion has been taken into account by measuring different gas mixtures with known densities.

It has been shown that the developed MBMS system is qualified to analyze the plasma chemistry of atmospheric pressure microplasma jets. A micro-scaled atmospheric pressure plasma jet (µ-APPJ) operated with helium/oxygen mixtures in an ambient helium atmosphere has been studied in detail. The atomic oxygen and ozone production has been measured in the effluent as a function of the oxygen admixture, the applied electrode voltage, and the distance from the nozzle of the µ-APPJ. A maximum atomic oxygen density of around $10^{15}$ cm$^{-3}$ was found at an admixture of 0.6% molecular oxygen. It increases linearly with the applied electrode voltage and decreases almost linearly as the distance from the jet increases. However, oxygen atoms are also detectable even in a distance of 30 mm from the jet. In contrast to the atomic oxygen density, the ozone density continuously increases with the oxygen admixture and by increasing the distance from the jet. The influence of the applied electrode voltage on the ozone density is small, the density stays almost constant. Overall, a maximum ozone density of about $10^{15}$ cm$^{-3}$ was found. Additionally, the depletion of the admixed molecular oxygen has been determined. Only a slight decrease of the
relative oxygen depletion could be observed by increasing the oxygen admixture. The oxygen depletion increases linearly with the applied electrode voltage reaching a maximum of about 10%.

The MBMS measurements of atomic oxygen have been benchmarked with two-photon absorption laser induced fluorescence (TALIF) spectroscopy measurements. The relative trends measured by both diagnostics are in very good agreement with each other. However, the absolute densities obtained by TALIF are slightly higher than the values measured by MBMS. This is probably due to the different measuring conditions and unavoidable systematic errors.

Surprising results have been revealed when the $\mu$-APPJ is operated in ambient air. The atomic oxygen density decreases almost as slowly as in a helium atmosphere with increasing distance. This is inconsistent with the expected faster consumption of oxygen atoms due to fast recombination reactions with $O_2$ from air. Also the ozone density exhibits a surprising result: it exhibits a maximum value about three times higher than expected.

To understand this behavior and to get a better insight into the reaction chemistry of the effluent, a 2D axially symmetric fluid model of the gas flow with reaction kinetics has been developed. It turned out that besides the recombination reactions $O + O_2 + M \rightarrow O_3 + M$ also a reaction mechanism producing oxygen atoms and ozone molecules in the effluent is needed to explain the measurements. It has been shown that (V)UV radiation and photochemistry reactions suggested in the literature are not responsible for the observed $O$ and $O_3$ production in the effluent. A reaction is suggested that produces an oxygen atom and an ozone molecule by a reaction of a highly vibrationally excited oxygen molecule with a ground state oxygen molecule. The vibrationally excited oxygen molecule is produced in the plasma and has a limited life-time. By including this reaction into the model, the measured and calculated densities of atomic oxygen and ozone agree very well with each other.

But, further measurements and simulations are needed to verify this reaction. It is also possible that another reaction with similar involved species is responsible for the additional oxygen atom and ozone production in ambient air.

Besides neutral species, also positive ions have been measured in the effluent of the $\mu$-APPJ. Against one’s expectations, no oxygen ions could be detected, only water cluster ions are present in the effluent. The oxygen admixture and the applied electrode voltage have almost no influence on the signal of the water cluster ions. With increasing distance, their signal decreases but stays constant beyond a distance of 4 mm. It has been shown that ions are not only produced in the plasma core but also in the effluent via photo ionization. The necessary water source for the cluster ions are adsorbed water molecules on the surface of the helium gas line.
The analysis of hexamethyldisiloxane (HMDSO) containing microplasma jets was another major topic of this work. First, positive ions in the effluent have been analyzed. Two kinds of positive ions could be found in the HMDSO plasma, namely water cluster ions and HMDSO molecules attached with an $\text{H}^+$ or $\text{H}_3\text{O}^+$ ion. However, it has been shown that ions do not play a role during the deposition process of silicon oxide films by means of atmospheric pressure microplasma jets. This is due to the decrease in ion signal when the HMDSO concentration in the plasma increases.

Second, the neutral species have been analyzed. A maximum HMDSO consumption of ca. 12% has been detected. This indicates that the $\mu$-APPJ is a very weak plasma since most of the HMDSO is not affected by the plasma. The HMDSO consumption as a function of oxygen admixture showed a very similar behavior like the deposition rate. Additionally, different reaction products of the HMDSO plasma (trimethylsilanol, hexamethyldisilane, pentamethyldisiloxane, heptamethyltrisiloxane, and octamethyltrisiloxane) could be identified by the MBMS. Since only a very low HMDSO admixture of about 20 ppm is used, measurements of reaction products are really challenging. A maximum absolute density of trimethylsilanol and pentamethyldisiloxane of about $5 \times 10^{12} \text{ cm}^{-3}$ and $2 \times 10^{12} \text{ cm}^{-3}$ could be found, respectively. These densities are at the detection limit of the MBMS system.

The high density of trimethylsilanol in contrast to pentamethyldisiloxane indicates that the Si–O bond of HMDSO is preferentially broken in the microplasma.

These absolute densities and relative signals are a significant contribution to understand the HMDSO microplasma chemistry at atmospheric pressure and can be used for future analyses of film growth precursors.

In summary, the present work provides the first quantitative measurements of reaction products generated by a micro-scaled atmospheric pressure plasma jet with admixtures of oxygen or hexamethyldisiloxane. These results can be used to optimize e.g. the process of bacteria deactivation and thin film deposition. Prospective models of microplasmas can be validated on the basis of the presented results.
Bibliography


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